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Radical chain reactions: novel examples of S[subscript RN]1 processes and the mechanism of substitution reactions for vinyl mercurials

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RADICAL CHAIN REACTIONS: NOVEL EXAMPLES OF S(RN)1 PROCESSES AND THE MECHANISM OF SUBSTITUTION REACTIONS FOR VINYL MERCURIALS

Iowa State University PH.D. 1981

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Radical chain reactions: Novel examples of $S_{RN}1$ processes and the mechanism of substitution reactions for vinyl mercurials

by

James William Hershberger

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INTRODUCTION

As an organizational convenience, this thesis has been formated in two parts. Two examples of $S_{RN}1$ processes, the coupling of dialkyl phosphite ions with α-substituted nitroalkanes and the coupling of nitronate salts with alkylmercury halides, are presented in Part I. Substitution reactions of vinylmercury compounds are presented in Part II.

Although a separate experimental section follows each presentation of results and discussion, descriptions of techniques and sources of starting materials are mentioned only once to avoid repetitions. Most items utilized in subsequent sections are to be located at the beginning of the experimental section under the heading of "General considerations."

PART I. $S_{RN}1$ COUPLING REACTIONS

I. INTRODUCTION TO $S_{RN}1$ CHEMISTRY

The mechanistic description of a generalized $S_{RN}1$ reaction is provided by Scheme 1. Although the net reaction resulting from such a process (Eq. 1) has the appearance of a familiar S_N2, S_N1, or S_NAr

Scheme 1

Step 1: Initiation

$$RX + A^- \xrightarrow{ET} RX^{\dot{-}} + A\cdot$$

Step 2: Propagation

$$RX^{\dot{-}} \longrightarrow R\cdot + X^-$$

Step 3: Propagation

$$R\cdot + A^- \longrightarrow RA^{\dot{-}}$$

Step 4: Propagation

$$RA^{\dot{-}} + RX \xrightarrow{ET} RA + RX^{\dot{-}}$$

R = alkyl, aryl
A^- = anion
X = leaving group

$$RX + A^- \longrightarrow RA + X^- \qquad (1)$$

process, the $S_{RN}1$ reaction is a chain process involving free radical intermediates. The chain initiating step 1 is an electron transfer (ET) reduction of RX to form an unstable radical anion which decomposes to lose the leaving group as X^- in propagation step 2. The radical ($R\cdot$) thus formed adds to anion (A^-) to form a new radical anion (propagation step 3). $RA^{\dot{-}}$ is a powerful reducing agent and thus transfers an electron to RX in propagation step 4. Since step 4 regenerates the reactive intermediate $RX^{\dot{-}}$ as well as product RA, a chain process continuing with step 2 may proceed. Step 1 need occur only at a rate required to offset chain terminating processes.

Often, initiation step 1 is too endothermic to occur thermally at reaction temperatures and light is required. Presumably, either A^- or a charge transfer complex between A^- and RX is the light absorbing species.

Other initiation processes have been employed such as reduction of RX at an electrode and reduction of RX by solvated electron. Still other initiation processes can be imagined such as the introduction of small amounts of a radical ($R'^{\cdot}$) capable of adding to A^- to form the strong reducing agent $R'A^{\dot{-}}$.

Early work centered on the aliphatic $S_{RN}1$ reaction of substrates such as 2-chloro-2-nitropropane and p-nitrobenzylchloride [1,2,3]. With these substrates, electron transfer reduction occurs at a saturated carbon atom. The anions employed for these reactions were "soft nucleophiles" such as the anions of secondary nitroalkanes and enolates of certain 1,3-dicarbonyl compounds. Subsequently, numerous leaving groups, such as $(CH_3)_2S$, NO_2^-, $ArSO_2^-$, Br^-, I^-, and R_3N, were employed [4] as well as a variety of nucleophiles such as azide, sulfinates, and enolates [4,5].

Some generalizations can be made regarding the feasibility of an $S_{RN}1$ process involving electron transfer to a saturated carbon. First, light is usually required to initiate the chain process, although examples of thermal initiation are known [4,5]. Second, the substrate RX usually bears a nitro group such that the radical ion $RX^{\dot{-}}$ is made energetically accessible by the low-lying antibonding pi-orbital of the nitro moiety. Third, even though NO_2^- might be the leaving group, the radical anion $RA^{\dot{-}}$ still bears a nitro group for stabilization. Examples in which neither $RX^{\overset{\bullet}{-}}$ nor $RA^{\overset{\bullet}{-}}$ possess a nitro substituent have been reported recently [6].

Several diagnostic tests are frequently applied to the $S_{RN}1$ reaction. Inhibition by traces of radical scavengers such as molecular oxygen or di-t-butyl nitroxide is characteristic of radical chain reactions. Inhibition by powerful one-electron acceptors such as m-dinitrobenzene is characterized by a reaction proceeding through radical anions [4].

Since 1970, numerous examples of aromatic $S_{RN}1$ reactions (*i.e.*, RX = ArX) have been reported. In fact, the designation "$S_{RN}1$" was first used to describe the reaction of aryl halides with amide in liquid ammonia [7,8]. Aromatic $S_{RN}1$ reactions have been reported for a wide variety of nucleophiles and leaving groups [9]. These reactions have been initiated thermally, by light. by solvated electron, and by electrochemical reduction [9]. The antibonding pi-orbitals of the aromatic ring are sufficiently low lying to allow the intermediacy of $RA^{\overset{\bullet}{-}}$. Thus, unlike the aliphatic counterpart, stabilization by substituents such as nitro are not required in aromatic $S_{RN}1$. In fact, no aromatic $S_{RN}1$ reaction in which one of the reactants bears a nitro substituent is known [9].

II. REACTIONS OF DIALKYL PHOSPHITE ANION WITH α-NITROALKYL CHLORIDES AND α-NITROALKYL SULFONES

A. Introduction

The anion of diethyl phosphite (1) is known to undergo facile photostimulated $S_{RN}1$ reactions with aryl halides to produce arylphosphonate esters [9]. However, phosphite ion has not been reported to participate

$$(EtO)_2PO^-$$

1

in aliphatic $S_{RN}1$ processes. Consequently, we selected three types of α-substituted nitro compounds for study as $S_{RN}1$ participants with dialkyl phosphite ion.

Compound 2, an α-nitroalkyl chloride, loses chloride ion [1] in

$(O_2N)C(R^1)(R^2)Cl$

2

$O_2NC(R^1)(R^2)O_2SC_6H_5Me$-P

3

$(O_2N)_2CR^1R^2$

4

$S_{RN}1$ processes, while 3 and 4 lose sulfinate [10,11] and nitrite [12] ions, respectively. With dialkyl phosphite anion as the $S_{RN}1$ nucleophile, the anticipated product is an α-nitroalkylphosphonate dialkyl ester such as 5 in all three cases. Compound 5 represents a

$$(O_2N)C(R^1)(R^2)P(O)(OR^3)_2$$

5

nearly unknown class of compounds. One example, α-nitroisopropylphosphonate diethyl ester, has been reported by the permanganate oxidation of the corresponding amine [13].

B. Results and Discussion

1. Reaction of phosphite ion with α-nitroalkyl chlorides

The potassium salts of dialkyl phosphites (generated by the action of potassium t-butoxide on the dialkyl phosphite) were found to react rapidly with α-nitroalkyl chlorides such as 2-chloro-2-nitropropane to produce α-nitroalkylphosphonates [14]. The reaction was so rapid, in fact, that careful cooling was required to prevent thermal runaway and drastic yield reduction. Yields of about 70% could be achieved when the reactions were run at -45°C with tetrahydrofuran (THF) as solvent (Eq. 2). Examples and yields are listed in Table I.

$$(O_2N)C(R^1)_2Cl + (R^2O)_2PO^- \xrightarrow[-45°C]{THF} (O_2N)C(R^1)_2P(O)(OR^2)_2 + Cl^- \qquad (2)$$

Unlike many aliphatic $S_{RN}1$ reactions, light was not required. Reactions run in aluminum foil-wrapped flasks to exclude light produced the same yield as those run in sunlamp-irradiated flasks. Furthermore, chain character was not demonstrated for this reaction as a trace (3 mole %) of di-t-butyl nitroxide had no effect on either yield or induction time. (These reactions initiated instantaneously as judged by the precipitation of potassium chloride.)

The α-nitroalkylphosphonates were shown to arise from radical intermediates. No product was observed when the reaction was run either

Table I. Synthesis of α-nitroalkylphosphonates from α-nitroalkyl chlorides and sulfones

$$(O_2N)C(R^1)_2X + (R^2O)_2PO^- \longrightarrow (O_2N)C(R^1)_2P(O)(OR^2)_2$$

R^1	R^2	X	% Yield (N.M.R.)	% Yield (distilled)
Me	Me	Cl	---	60
Me	Et	Cl	75	63
$(CH_2)_4$	Et	Cl	80	---
Me	Et	$MeC_6H_4SO_2$-P	92	---
$(CH_2)_4$	Et	$MeC_6H_4SO_2$-P	75	62

in the presence of an equivalent of di-t-butyl nitroxide or oxygen-saturated THF. It should be noted that phosphite ion was shown to be reasonably stable to oxygen (see Experimental Section).

2. Reaction of dialkyl phosphite ion with α-nitro sulfones

Sulfinate anion is displaced from α-nitro sulfones by dialkyl phosphite ion to produce α-nitroalkyl phosphonates (Eq. 3) [14]. When

$$KOP(OR^3)_2 + (O_2N)C(R^1)(R^2)O_2SC_6H_4Me\text{-}p \xrightarrow[0\text{-}5^\circ C]{THF}$$
$$(O_2N)C(R^1)(R^2)P(O)(OR^3)_2 + KO_2SC_6H_4Me\text{-}p \qquad (3)$$

THF was used as solvent at 0-5°C, the reaction is complete is approximately one hour in good yield (see Table I). Unlike the reaction of dialkyl phosphite ions with α-nitroalkyl chlorides, the reaction did not initiate instantly. Induction times up to about five minutes were observed (as judged by the precipitation of THF-insoluble potassium p-toluenesulfinate). Reproducible induction times were only observed when pure α-nitro sulfones were employed. If the sulfone was not carefully recrystallized long, quite variable induction periods occurred making diagnostic radical inhibition tests uninterpretable.

As in the case of the α-nitroalkyl chlorides, reaction of phosphite ion with α-nitro sulfones was not affected by the presence or absence of light (see Experimental Section). However, chain inhibition was observed when radical scavengers were present. Thus, the addition of 3 mole % di-t-butyl nitroxide to the reaction of diethyl phosphite ion with 6 ($R^1=R^2=Me$) delayed the appearance of potassium p-toluenesulfinate for 45 minutes at 0-5°C. Likewise, when the reaction solution was saturated with oxygen, no product formation occurred and nearly all of the starting α-nitro sulfone was recovered.

3. Reaction of phosphite ion with 2,2-dinitropropane

Expecting the formation of diethyl α-nitroisopropylphosphonate, diethyl phosphite ion and 2,2-dinitropropane were allowed to react in THF at reduced temperature. None of the expected compound was observed. Instead, a good yield (based on N.M.R. integration for the methyl group) of an unidentified compound was isolated. No structure entirely consistent with available data (see Experimental Section) could be proposed at the time this thesis was prepared.

4. Reaction of dialkyl phosphite ion with α-nitro sulfones bearing acidic hydrogens

Hydrogens bonded to the carbon bearing the nitro and sulfonyl moieties, such as in $(O_2N)CH_2SO_2C_6H_4Me\text{-}p$, are quite acidic. They are removed, for instance, by aqueous carbonate. Since phosphite ion is a strong base, it seemed likely that any attempt to prepare an α-nitroalkylphosphonate bearing acidic hydrogens would fail due to the undesirable proton exchange reaction between phosphite ion and the starting sulfone. Such an exchange (Eq. 4) was observed (see

$$(O_2N)(p\text{-}MeC_6H_5SO_2)CH_2 \xrightarrow{K^{+}\,{}^{-}OP(OEt)_2} (O_2N)(p\text{-}MeC_6H_4SO_2)CH^{-}K^{+} \qquad (4)$$

Experimental Section). Even with dimethyl sulfoxide as the solvent, a solvent in which all of the salts were soluble, little or no desired product was formed.

5. Attempts to react nitronate and dialkyl phosphite ions with α-nitroalkylphosphonates

Considering the number of α-nitroalkyl compounds which undergo $S_{RN}1$ substitution, it seemed likely that α-nitroalkylphosphonates themselves might react with good $S_{RN}1$ nucleophiles. Consequently, reactions of diethyl α-nitroisopropylphosphonate with the anions of 2-nitropropane and diethyl phosphite were attempted in dimethyl sulfoxide and THF, respectively (nitronate salts are insoluble in THF). Even with extensive sunlamp irradiation in both cases, the only identifiable isolate was the starting phosphonate ester.

6. Mechanistic considerations for the formation of α-nitroalkylphosphonates

The reaction between phosphite ion and α-nitro sulfones is clearly explained well by the $S_{RN}1$ mechanism. With the radical chain character of the reaction established, only mechanisms involving unreasonable processes such as Equation 5 remain as an alternative. The absence of

$$(O_2N)C(Me)_2O_2SC_6H_4Me\text{-}p + \cdot OP(OEt)_2 \longrightarrow \qquad (5)$$

$$(O_2N)C(Me)_2P(O)(OEt)_2 + \cdot O_2SC_6H_4Me\text{-}p$$

$$\cdot O_2SC_6H_4Me\text{-}p + {}^{-}OP(OEt)_2 \xrightarrow{Et} {}^{-}O_2SC_6H_4Me\text{-}p + \cdot OP(OEt)_2 \qquad (6)$$

a light effect and the observation of a 45 minute induction period with 3 mole percent di-t-butyl nitroxide present imply a reasonably rapid thermal initiation.

Unfortunately, chain character was not demonstrated for the reaction of phosphite ion with α-nitroalkyl chlorides. Although the intermediacy of radicals was established by experiments with oxygen saturation and stoichiometric amounts of di-t-butyl nitroxide, a nonchain mechanism may be proposed as an alternative to $S_{RN}1$. Scheme 2 describes the

Scheme 2

$$(EtO)_2PO^{-} + (O_2N)C(Me)_2Cl \xrightarrow{Et} (EtO)_2PO\cdot + [(O_2N)C(Me)_2Cl]^{\dot{-}}$$

$$[(O_2N)C(Me)_2Cl]^{\dot{-}} \longrightarrow (O_2N)\dot{C}(Me)_2 + Cl^{-}$$

$$(O_2N)\dot{C}(Me)_2 + (EtO)_2P\cdot \longrightarrow (O_2N)C(Me)_2P(O)(OEt)_2$$

reaction as occurring via rapid electron transfer from the dialkyl phosphite ion to the organic chloride. The radicals thus formed selectively cross-couple to give the α-nitroalkylphosphonate.

It seems unlikely that the mechanism of Scheme 2 is operative to a large extent. The highly selective cross-coupling of α-nitroalkyl and phosphite radicals is difficult to explain. Notably, the yields of α-nitroalkylphosphonates were significantly improved by running the reaction at lower temperature. The $S_{RN}1$ mechanism suggests that lower temperatures should give improved product yields. Only low concentrations of reactive species (i.e., radicals) are required to produce product by the chain mechanism. Higher temperatures lead to high thermal initiation rates which, in turn, lead to high chain termination rates. Consequently, an $S_{RN}1$ process driven by an extremely facile thermal initiation seems the best explanation of the observed phenomena.

C. Conclusion

A general synthesis of α-nitroalkylphosphonate esters, a previously unexplored class of compounds, has been described. These compounds are produced in good yield by the reaction of phosphite ion with α-nitroalkyl chlorides or sulfones. Evidence has been presented that the reactions proceed via the $S_{RN}1$ pathway.

D. Experimental Section

1. General considerations

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Analytical gas chromatography (G.L.C.) was performed on a Beckman GC 72-5 instrument. Preparative G.L.C. was performed on an Aerograph model A-90-P gas chromatograph. High resolution mass spectra (M.S.) were recorded on an AEI MS 902 mass spectrometer. G.C. mass spectra (G.C.M.S.) were recorded on a Finnegan 4000 instrument. ^{1}H N.M.R. (60 MHz) were recorded on a Varian A-60, a Varian EM360, or a Hitachi-Perkin Elmer R-20B instrument. Infrared spectra (I.R.) were recorded on a Beckman 4250 spectrophotometer. ^{13}C N.M.R. (22.6 MHz) were recorded on a JEOL FX-90Q spectrometer. ^{31}P N.M.R. (36.4 MHz) were recorded on a Bruker HX-90.

2-Nitropropane, diethyl phosphite, dimethyl phosphite, and potassium t-butoxide were purchased from Aldrich. Sodium p-toluenesulfinate dihydrate was purchased from Aldrich or Eastman Organic. Solvents were purchased from Fisher, Baker, or Malinkrodt.

Dimethyl sulfoxide (DMSO) was distilled from calcium hydride before use and stored over 4A molecular sieves under nitrogen. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use and stored over 4A molecular sieves under nitrogen. Other solvents were purchased reagent grade, if available, and used without purification.

^{1}H N.M.R. yields were determined by integration comparison with a known amount of an appropriate reference (usually CH_2Cl_2, $CHCl_3$, or DMSO).

2-Chloro-2-nitropropane was prepared by the addition of chlorine to an ice-cold aqueous solution of 2-nitropropane and sodium hydroxide. The liquid product was collected from the bottom of the flask, washed with aqueous thiosulfate, dried, and distilled (b.p. 133-134°C/760 torr).

2,2-Dinitropropane [15], 2-(p-tolylsulfonyl)-2-nitropropane [10,16], p-tolylsulfonyl nitromethane [10], the lithium salt of 2-nitropropane [11], and di-t-butyl nitroxide [17] were prepared by literature procedures.

1-Chloro-1-nitrocyclopentane was prepared by the addition of aqueous hypochlorite to an ice-cold aqueous solution of nitrocyclopentane [18] and sodium hydroxide. The product was extracted with ether, and the extract washed with aqueous thiosulfate, dried, and concentrated. Distillation (b.p. 70-73°C/16 torr) provided pure 1-chloro-1-nitrocyclopentane in 37% yield. This compound has been prepared by a different method and characterized [19].

1-(p-Tolylsulfonyl)-1-nitrocyclopentane was prepared by the general procedure of Zielstra and Engberts [10] from the potassium salt of nitrocyclopentane, sodium p-toluenesulfinate, and iodine in N,N-dimethyl formamide and recrystallized from ethanol/water in 64% overall yield (m.p. 111.5-112.5°C). ^{1}H N.M.R. (δ, $CDCl_3$) 4H (m) 7.56, 4H (m) 2.5-2.9, 3H (s) 2.48, 4H (m) 1.55-2.0. I.R. (KBr pellet, cm^{-1}) 1600 (s), 1550 (vs), 1455 (m), 1330 (vs), 1150 (vs). Elemental analysis.

Calculated for $C_{12}H_{16}NO_4S$: C, 53.52; H, 5.61; N, 5.20; O, 23.76; S, 11.90. Found: C, 53.68; H, 5.76.

2. Preparation of $(O_2N)C(Me)_2P(O)(OEt)_2$ by the reaction of diethyl phosphite ion with 2-chloro-2-nitropropane

2-Chloro-2-nitropropane (1.1 g, 9 mmol) was added to a solution of potassium *t*-butoxide (1.0 g, 9 mmol) and diethyl phosphite (1.4 g, 10 mmol) in 30 ml dry THF at -45°C under nitrogen. After the addition, potassium chloride started to precipitate. After stirring 30 minutes, the reaction mixture was warmed to -20°C for 30 minutes and finally to 0°C for 30 minutes. The THF was removed under vacuum and the residue extracted from brine with ether. The extract was dried ($MgSO_4$) and concentrated to yield 1.7 g crude product shown to contain 75% yield diethyl α-nitroisopropylphosphonate and 6% recovered 2-chloro-2-nitropropane by ^1H N.M.R.

In a scaled-up reaction (135 mmol) using the same procedure, the crude product was distilled (94-95°C/0.2 torr) through a short distillation head to obtain 19.1 g (63%) pure product. This compound has been prepared by another method [13].

^1H N.M.R. (δ, $CDCl_3$) 4H (m) 4.0-4.48, 6H (d) 1.75 (J_{P-H} = 16 Hz), 6H (t) 1.38 (J_H = 6 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 2950 (m), 1550 (vs), 1470 (w), 1400 (m), 1370 (m), 1340 (w), 1260 (s), 1160 (w), 1045 (vs, broad), 1015 (vs, broad), 970 (s, broad), 855 (s), 770 (w).

In the M.S. of the α-nitroalkylphosphonates, the parent ion was not observed. This is typical of aliphatic nitro compounds. The P-46 ion (loss of NO_2) was measured. Calculated for $C_7H_{16}O_3P$: 179.0837. Measured: 179.08295. Error = -4.2 ppm.

Elemental analysis. Calculated for $C_7H_{16}NO_5P$: C, 37.34; H, 7.16; N, 6.22; P, 13.75; O, 35.52. Found: C, 37.62; H, 7.27.

^{13}C N.M.R. (proton decoupled, $CDCl_3$, reported in ppm from TMS) $(O_2N)\underline{C}(Me)_2P$- (d) 85.6 ppm ($J_{C-P}$ = 150 Hz), $(O_2N)C(\underline{C}H_3)_2P$- (d) 15.67 ($J_{C-P}$ = 4.9 Hz), $-P(O)(O\underline{C}H_2CH_3)_2$ (d) 63.45 (J_{C-P} = 7.3 Hz), $-P(O)(OCH_2\underline{C}H_3)$ (s) 22.12.

^{31}P N.M.R. (proton decoupled, $CDCl_3$, reported in ppm from H_3PO_4) one singlet 17.20.

3. Preparation of $(O_2N)C(Me)_2P(O)(OEt)_2$ by the reaction of diethyl phosphite ion with 2-(p-tolylsulfonyl)-2-nitropropane

Solid 2-(p-tolylsulfonyl)-2-nitropropane (2.2 g, 9 mmol) was added to an ice-cold solution of potassium *t*-butoxide (2.0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) in 30 ml dry THF under nitrogen. After stirring a few minutes, the precipitation of potassium p-toluenesulfinate was observed. (Induction times were minimized by use of pure nitro sulfone and by purging the THF with nitrogen before addition of the nitro sulfone.) The reaction was stirred at 0-5°C for 1 hour and at room temperature for 30 minutes. The THF was removed under vacuum and the residue extracted from brine with either. The extract was dried ($MgSO_4$) and concentrated, yielding 1.9 g crude product.

^{1}H-N.M.R. showed the isolate to be nearly pure and contain 92% of the expected phosphonate. The crude isolate contained no starting nitro sulfone. The N.M.R. spectrum was identical to that of the product prepared from 2-chloro-2-nitropropane.

4. Preparation of $(O_2N)C(Me)_2P(O)(OMe)_2$ by the reaction of dimethyl phosphite ion with 2-chloro-2-nitropropane

2-Chloro-2-nitropropane (8.7 g, 72 mmol) was added to a solution of potassium *t*-butoxide (7.9 g, 70 mmol) and dimethyl phosphite (7.7 g, 70 mmol) in 150 ml dry THF at -45°C under nitrogen. The reaction was stirred 20 minutes at -45°C, 30 minutes at -20°C, and then allowed to warm to room temperature. The THF was removed under vacuum. Since the product was found to be somewhat water soluble, extraction procedures were avoided and the product distilled directly from the residue using a short distillation head (80-90°C/0.1 torr) to obtain 8.3 g colorless product (60% yield, purity ∿95%). A portion of the product was redistilled for analysis (80-81°C/0.1 torr).

^{1}H N.M.R. (δ, $CDCl_3$) 6H (d) 3.86 (J_{P-H} = 10 Hz), 6H (d) 1.72 (J_{P-H} = 14 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 2690 (m), 1550 (s), 1460 (m), 1400 (m), 1340 (m), 1270 (s), 1190 (m), 1040 (vs), 850 (m), 830 (m), 780 (m).

M.S. (P-46 peak measured). Calculated for $C_5H_{12}O_3P$: 151.0524. Measured: 151.0520. Error = -2.7 ppm.

Elemental analysis. Calculated for $C_5H_{12}NO_5P$: C, 30.46; H, 6.14; N, 7.10; O, 40.58; P, 15.71. Found: C, 30.61; H, 6.30; N, 7.05.

5. Preparation of $(O_2N)C(CH_2)_4P(O)(OEt)_2$ by the reaction of diethyl phosphite ion with 1-(p-tolylsulfonyl)-1-nitrocyclopentane

Solid 1-(p-tolylsulfonyl)-1-nitrocyclopentane (2.4 g, 9 mmol) was reacted with diethyl phosphite ion (18 mmol) according to the procedure given for the reaction of diethyl phosphite ion with 2-(p-tolylsulfonyl)-2-nitropropane. After workup, the crude isolate (1.95 g, ∿95% pure, 75% N.M.R. yield) was purified for analysis by Kugelrohr distillation (95°C/0.4 torr) to yield 1.35 g pure colorless product. This nitro phosphonate discolored after a few days stored in a vial at room temperature.

^{1}H N.M.R. (δ, $CDCl_3$) 4H (m) 3.9-4.4, 8H (broad m) 1.5-3.0, 6H (t) 1.35 (J_H = 7 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 2980 (s), 1545 (vs), 1445 (m), 1395 (w), 1345 (w), 1260 (s), 1160 (m), 1050 (broad, s), 1020 (broad, s), 970 (broad, s), 850 (w), 790 (w).

M.S. (P-46 peak measured). Calculated for $C_9H_{18}O_3P$: 205.09936. Measured: 205.09943. Error = 0.34 ppm.

Elemental analysis. Calculated for $C_9H_{18}NO_5P$: C, 43.03; H, 7.22; N, 5.58; O, 31.84; P, 12.33. Found: C, 43.03; H, 7.37.

6. Preparation of $(O_2N)C(CH_2)_4P(O)(OEt)_2$ by the reaction of diethyl phosphite ion with 1-chloro-1-nitrocyclopentane

1-Chloro-1-nitrocyclopentane (1.3 g, 9 mmol) was reacted with the anion of diethyl phosphite (9 mmol) according to the procedure for the reaction of diethyl phosphite ion with 2-chloro-2-nitropropane. After workup, the crude isolate (1.9 g) was analyzed to contain an 80% yield of the desired product of approximately 95% purity. The ^1H N.M.R. spectrum was identical to that of the product prepared by the reaction of 1-(p-tolylsulfonyl)-1-nitrocyclopentane with diethyl phosphite ion.

7. Effect of light on the reaction of diethyl phosphite ion with 2-chloro-2-nitropropane

2-Chloro-2-nitropropane (1.1 g, 9 mmol) was added via syringe through a foil-covered septum to a solution containing potassium *t*-butoxide (1.0 g, 9 mmol) and diethyl phosphite (1.29 g, 9.3 mmol) in 30 ml dry THF under nitrogen at 0-5°C in a flask wrapped tightly with several layers of aluminum foil to exclude light. After stirring 30 minutes, the reaction was quenched by injection of 50 mmol acetic acid in 5 ml water. After removal of the THF under vacuum, the residue was extracted from brine with ether. The extract was washed with aqueous bicarbonate and dried ($MgSO_4$). Concentration of the extract yielded 1.0 g liquid shown by N.M.R. to contain 50% yield of α-nitroisopropylphosphonate diethyl ester.

The reaction was performed again under the same conditions, except that the Pyrex reaction flask was irradiated with a 275 watt sunlamp. A 44% yield of product was obtained.

8. Effect of di-t-butyl nitroxide on the reaction of diethyl phosphite ion with 2-chloro-2-nitropropane

Potassium _t_-butoxide (2.0 g, 18 mmol), diethyl phosphite (2.8 g, 20 mmol), and di-t-butyl nitroxide (1.3 g, 9 mmol) were dissolved in 20 ml dry THF at 0-5°C under nitrogen. 2-Chloro-2-nitropropane (1.1 g, 9 mmol) in 10 ml dry THF was added over a period of 10 minutes. The reaction was warmed to room temperature and the THF removed under vacuum. The residue was extracted from brine with ether and the extract was dried ($MgSO_4$) and concentrated. The crude isolate (2.65 g) had sufficient paramagnetic material to broaden the ^{1}H N.M.R. spectrum severely. Most of this paramagnetic material was removed by warming the isolate to 45°C at 0.4 torr. ^{1}H-N.M.R. indicated little or no α-nitroisopropylphosphonate. The residue was distilled (Kugelrohr) to obtain 0.95 g material which was found to contain no α-nitroisopropylphosphonate by N.M.R.

When the same reaction was performed utilizing only 3 mole % (0.27 mmole) di-t-butyl nitroxide, quenching with aqueous acetic acid and workup afforded a 49% yield of diethyl α-nitroisopropylphosphonate.

9. Stability of diethyl phosphite ion to molecular oxygen

By means of a glass frit, oxygen was vigorously foamed through a solution containing potassium _t_-butoxide (2.0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) in 20 ml dry THF at 0-5°C for 30 minutes. The solution was then purged with nitrogen and 2-chloro-2-nitropropane (1.1 g, 9 mmol) added. The solution was warmed to room temperature, the THF removed under vacuum, and the residue extracted from brine with ether. Concentration of the dried extract afforded 1.7 g of liquid material which was found to contain a 45% yield (N.M.R.) of diethyl α-nitroisopropylphosphonate. The 2-chloro-2-nitropropane had been completely consumed.

The same reaction performed without treating the phosphite anion solution with oxygen afforded a 44% yield of the nitro phosphonate.

10. Effect of oxygen on the reaction of diethyl phosphite ion with 2-chloro-2-nitroprane

Potassium t-butoxide (2.0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) were dissolved in 20 ml dry THF at 0-5°C under nitrogen. The nitrogen sweep was removed and the solution was saturated with oxygen by vigorous foaming through a glass frit placed near the bottom of the reaction flask. 2-Chloro-2-nitropropane (1.1 g, 9 mmol) in 30 ml dry THF, also saturated with oxygen by means of a glass frit, was added over a 30 minute period. The reaction was then warmed to room temperature and worked up as previously described to yield 1.7 g of a liquid. N.M.R. analysis showed that no nitrophosphonate had been formed and all of the 2-chloro-2-nitropropane had been consumed.

11. Effect of light on the reaction of diethyl phosphite ion with 2-(p-polylsulfonyl)-2-nitropropane

Solid 2-(p-tolylsulfonyl)-2-nitropropane (2.2 g, 9 mmol) was added to a solution of potassium *t*-butoxide (2.0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) in 20 ml dry THF at 0-5°C in a flask tightly wrapped with several layers of aluminum foil to exclude light. The reaction was stirred 45 minutes before quenching with 50 mmol acetic acid in 5 ml water. The usual workup afforded 1.36 g of liquid found to contain diethyl α-nitroisopropylphosphonate (52%) and starting sulfone (2.3% recovered). The low yield of nitro phosphonate was probably due to storing the acid-quenched reaction mixture about 10 hours before workup and allowing some hydrolysis of product to occur.

The reaction was repeated, except the flask (Pyrex) was irradiated with a 275 watt sunlamp. Immediate workup afforded a 66% yield of nitro phosphonate and a 10% recovery of starting nitro sulfone.

12. Effect of oxygen on the reaction of diethyl phosphite ion with 2-(p-tolylsulfonyl)-2-nitropropane

Solid 2-(p-tolylsulfonyl)-2-nitropropane (2.2 g, 9 mmol) was added to an oxygen-saturated solution of potassium *t*-butoxide (2.0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) in 30 ml dry THF at 0-5°C. After stirring 45 minutes, the reaction was quenched with 50 mmol acetic acid in 5 ml water. Workup afforded 1.95 g of solid material. ^{1}H-N.M.R. analysis showed this material to be practically pure starting α-nitro sulfone (87% recovery).

The same reaction performed under a nitrogen atmosphere and quenched after 45 minutes yielded 66% nitro phosphonate and 10% recovered nitro sulfone.

13. Effect of di-*t*-butyl nitroxide on the reaction of diethyl phosphite ion with 2-(p-tolylsulfonyl)-2-nitropropane

Small amounts of di-*t*-butyl nitroxide were found to delay the initiation of reaction as indicated by the precipitation of potassium p-toluenesulfinate. Thus, when solid 2-(p-tolylsulfonyl)-2-nitropropane (2.2 g, 9 mmol) was added to a solution of potassium t-butoxide (2.0 g, 18 mmol), diethyl phosphite (2.8 g, 20 mmol), and di-t-butylnitroxide (40 μl, 0.039 g, 0.27 mmol) in 30 ml dry THF under nitrogen at 0-5°C, the appearance of precipitate occurred after an induction period of 45 minutes without added nitroxide, appearance times were from 2 to 5 minutes.

14. Reaction of 2,2-dinitropropane with diethyl phosphite ion

2,2-Dinitropropane (2.4 g, 18 mmol) in 10 ml dry THF was added over a 10 minute period to a solution of potassium *t*-butoxide (4.0 g, 36 mmol) and diethyl phosphite (5.6 g, 40 mmol) in 30 ml dry THF at -78°C under nitrogen. The solution became cloudy, presumably due to the precipitation of potassium nitrite. After stirring 1 hour, the reaction was warmed to room temperature and the THF removed under vacuum. The residue was extracted from brine with ether. The extract was washed with brine, dried ($MgSO_4$), and concentrated to yield 4.0 g of a colorless liquid. Assuming the singlet at δ 2.0 was due to gem dimethyl groups, the ^1H N.M.R. yield was determined to be 78%. A careful distillation through a 5 inch vacuum jacketed Vigreaux column (97°C/0.3 torr) resulted in considerable decomposition, but afforded 1.4 g colorless liquid which appeared to be a pure compound.

^1H N.M.R. (δ, $CDCl_3$) 4H (m) 3.95-4.45, 6H (s) 2.0, 6H (t) 1.37 (J_H = 7 Hz). The assigned integrations must only be taken as relative, as the identity of the compound is not known.

I.R. (neat, NaCl plates, cm^{-1}) 2990 (s), 1650 (w), 1570 (w), 1550 (m), 1450 (m), 1395 (m), 1370 (s), 1270 (broad, vs), 1170 (s), 1030 (broad, vs), 975 (broad, vs), 920 (broad, vs), 855 (s), 820 (s), 750 (w).

M.S. The molecular ion was not observed. The highest mass fragment was measured. Calculated for $C_7H_{16}O_3P$: 179.0837. Measured: 179.08446. Error = +4.7 ppm.

Elemental analysis. Found: C, 39.24; H, 7.90; Cl, 0.00; N, 6.73; P, 14.33.

15. Attempted preparation of $O_2NCH_2P(O)(OEt)_2$ by reaction of diethyl phosphite ion with (p-tolylsulfonyl)nitromethane

When (p-tolylsulfonyl)nitromethane was added to an ice-cold THF solution containing diethyl phosphite anion, a white solid precipitated from solution which, upon workup, proved to be the potassium salt of the nitro sulfone. It was hoped the desired reaction might occur if the solvent was chosen to allow homogeneous conditions. Consequently, (p-tolylsulfonyl)nitromethane (1.9 g, 9 mmol) was added to a solution containing potassium t-butoxide (2 0 g, 18 mmol) and diethyl phosphite (2.8 g, 20 mmol) in 20 ml dry dimethyl sulfoxide at room temperature under nitrogen. After stirring 4 hours, the reaction solution was brine acidified with acetic acid and extracted with ether. The extract was washed with aqueous bicarbonate, dried ($MgSO_4$), and concentrated to yield 1.2 g of residue which ^1H N.M.R. showed to contain starting sulfone and other unidentified compounds. G.C.M.S. analysis of the three volatile components revealed that only a trace of the desired product might have been produced (P-46 = 151 observed). The major components were not identified.

16. Reaction of $(O_2N)C(Me)_2P(O)(OEt)_2$ with the lithium and potassium salts of 2-nitropropane

The nitro phosphonate (2.0 g, 9 mmol) was added to a solution of lithium salt of 2-nitropropane (1.4 g, 15 mmol) in 50 ml dry DMSO under nitrogen. The Pyrex reaction flask was irradiated for 13 hours at ambient temperatures from an 8 inch distance with a 275 watt sunlamp during which time the solution turned light yellow. The reaction mixture was extracted from brine with ether. The extract was washed with brine, dried, and concentrated to yield 1.42 g colorless liquid. ^1H N.M.R. revealed the isolate to be nearly pure starting nitro phosphonate.

A similar reaction employing the sparingly-soluble potassium salt of 2-nitropropane (generated from equimolar amounts of 2-nitropropane and potassium t-butoxide) was performed. Again, starting nitro phosphonate was isolated.

17. Reaction of $(O_2N)C(Me)_2P(O)(OEt)_2$ with diethyl phosphite ion

The nitro phosphonate (2.0 g, 9 mmol) was added to a solution of potassium *t*-butoxide (1.1 g, 10 mmol) and diethyl phosphite (1.4 g, 10 mmol) in 20 ml dry THF under nitrogen. After 18 hours of sunlamp irradiation, the THF was removed under vacuum and the residue worked up by ether extraction from brine. ^1H N.M.R. analysis of the 1.4 g light yellow liquid isolate revealed 47% of the starting nitro phosphonate had been recovered. There was no evidence of products such as $(EtO)_2P(O)C(Me)_2P(O)(OEt)_2$ or $(EtO)_2P(O)C(Me)_2C(Me)_2P(O)(OEt)_2$.

III. REACTION OF NITRONATE IONS WITH ALKYLMERCURY HALIDES: SYNTHESIS OF TERTIARY NITRO COMPOUNDS

A. Introduction

In nearly all known examples of aliphatic $S_{RN}1$ reactions, the molecule undergoing reduction bears one or more nitro groups (in the only reported exception a cyano-substituted benzyl group sufficed [6]). This is reasonable in light of the low-lying pi-antibonding orbital of the nitro moiety available to stabilize the radical anion ($RX^{\overset{\bullet}{-}}$ in Scheme 1). A metal bonded to the carbon undergoing reduction might also serve to facilitate electron transfer.

Mercury was selected for study. Organomercurials were readily available [20,21] and appeared capable of the processes required for the $S_{RN}1$ reaction. Organomercury halides have been electrochemically reduced in liquid ammonia at low temperatures to produce organomercury radicals (or organomercury radical dimers) which, upon warming, decompose to diorganomercury(II) compounds and mercury metal [22,23] (Eq. 7). Room

$$\mathrm{RHgCl} + e^- \longrightarrow \underset{(\frac{1}{2}\,\mathrm{RHgHgR})}{\mathrm{RHg}\cdot} + \mathrm{Cl}^- \xrightarrow{\Delta} \frac{1}{2}\,\mathrm{R_2Hg} + \frac{1}{2}\,\mathrm{Hg} \qquad (7)$$

temperature polarographic reduction of organomercuric salts has also been found to produce organomercury radicals [24,25]. The $E_{1/2}$ for the polarographic wave corresponding to (irreversible) one-electron reduction of phenylmercury chloride has been measured as -0.1 to -0.2 volts depending on the nature of the solvent and electrolyte [24].

Organomercury salts undergo reduction with sodium borohydride via a free radical chain process [26-29]. Scheme 3 details the generally accepted mechanism for this reaction. A key feature is the dissociation of an organomercury radical into elemental mercury and an organic radical (step 3), a process estimated to have an activation energy as low as 6 kcal mol^{-1} [30].

Scheme 3

Step 1 $\quad$ RHgX + NaBH4 ⟶ RHgR + NaX + BH_3

Step 2 $\quad$ RHgH ⟶ RHg• + H•

Step 3 $\quad$ RHg• ⟶ R• + Hg^{o}

Step 4 $\quad$ R• + RHgH ⟶ RH + RHg•

then step 3, 4, 3, etc.

We supposed that an organic radical, mercury metal, and halide ion would result from homogeneous reduction of an organomercury halide. In the presence of a suitable anion, such as a nitronate ion, a stable radical anion might form (i.e., the radical anion of a nitro compound) and propagate a reaction chain by transferring an electron to an organomercury halide molecule. Such a process seemed reasonable since the (reversible) oxidation potential of t-nitroalkane radical anions is approximately +1.6 - 1.8 volts in glyme [31].

The proposed reaction, a modified $S_{RN}1$ process, is summarized in Scheme 4. Displacement of halide ion and mercury metal ("reductive substitution") from carbon by an anion (Eq. 8) other than "hydride" is

Scheme 4

$$R^1HgX + R^2R^3C{=}NO_2^- \xrightarrow{\text{initiation}} R^1\cdot + Hg^0 + X^- + R^2R^3\dot{C} - NO_2$$

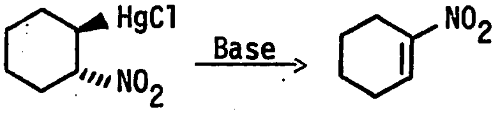
$$R^1\cdot + R^2R^3C{=}NO_2^- \longrightarrow [R^1R^2R^3CNO_2]^{\dot{-}}$$

$$[R^1R^2R^3CNO_2]^{\dot{-}} + R^1HgX \longrightarrow R^1R^2R^3CNO_2 + R^1\cdot + Hg^0 + X^-$$

without literature precedent. A vaguely related reaction, the elimination of mercury metal and chloride ion from the salts of

$$RHgX + A^- \longrightarrow RA + Hg^0 + X^- \qquad (8)$$

β-chloromercury nitro compounds, has recently been reported [32] (Eq. 9).



$+ Hg^0 + Cl^-$ (9)

The scope and mechanism of the reaction of nitronate salts with alkylmercury halides is discussed in parts 1-7 of the following section. Part 8 treats an entirely different reaction between nitronate salts and vinyl- or arylmercury halides. Parts 9-11 deal with the reactions of alkylmercury halides with several anions other than nitronates.

B. Results and Discussion

1. β-Nitro ketones from 2-halomercurycyclohexanones

Initial experiments were conducted by Karen Owens [33] on the 2-halomercurycyclohexanones. It was hoped that initial reduction of the mercurial and formation of radical anion adduct (Scheme 4) would be facilitated by the carbonyl group.

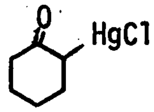
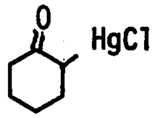
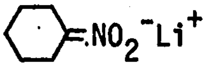
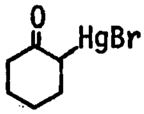
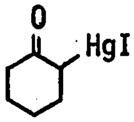
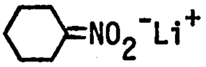
Results, some of which have been published in preliminary form [34], are tabulated in Table II. Although 2-iodomercurycyclohexanone failed to yield the expected coupled product (a thermally unstable iodine-containing residue was obtained), the bromo- and chloro- analogues afforded β-nitro ketones with the lithium salts of 2-nitropropane or nitrocyclohexane in 56-68% isolated yield. The isolated ketones were nearly pure. The product with 2-nitropropane anion was particularly sensitive to loss of the elements of nitrous acid under the influence of heat or base. The resulting α-isopropylidene cyclohexanone was conveniently characterized as the 2,4-DNP derivative. β-Nitro ketones and α-alkylidene ketones have been prepared by the more general $S_{RN}1$ reaction of lithium enolates with α-halo nitro compounds [5].

In a normal reaction, mercury metal was observed to precipitate from DMF or DMSO solutions after one or two minutes of sunlamp irradiation when nitrogen purged solutions were employed. When the solvent was not deoxygenated prior to dissolution of reagents and sunlamp irradiation, longer induction periods were observed. Complete reaction at ambient temperatures (25-40°C) required one to two hours.

When sunlamp irradiation was not employed and all light omitted from the reaction flask with an aluminum foil wrapping, essentially no mercury metal or nitro ketone was observed after acid quenching and workup. Furthermore, the reaction of 2-chloromercurycyclohexanone with the lithium salt of 2-nitropropane was completely inhibited for 30

Table II. Reaction of organomercury halides with nitronate salts to form nitro compounds

$$R^1HgX + R^2R^3C{=}NO_2^-M^+ \xrightarrow{light} R^1R^2R^3CNO_2 + Hg^0 + MX$$

R^1HgX	$R^2R^3C{=}NO_2^-M^+$	Solvent	Time[a]	% Yield Nitro Compound
	$Me_2C{=}NO_2^-Li^+$	DMSO	1 h	56
		DMSO	2 h	60
	$Me_2C{=}NO_2^-Li^+$	DMF	1 h	68
	$Me_2C{=}NO_2^-Li^+$	DMF	1 h	0
$PhCH_2HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	2 h	100
$PhCH_2HgCl$		DMSO	2 h	87
$PhCH_2HgCl$	$MeCH{=}NO_2^{=}Li^+$	DMSO	2 h	_ca_. 5[b]

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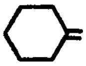
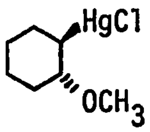
[a] All reactions were performed in nitrogen-purged solvents at ambient temperatures (25-45°C) with irradiation from a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel.

[b] The major product (_ca_. 40%) was 2-methyl-2-nitro-1,3-diphenylpropane.

Table II. (Continued)

R^1HgX	$R^2R^3C{=}NO_2^-M^+$	Solvent	Time[a]	% Yield Nitro Compound
n-$C_6H_{13}HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	37 h	90
n-$C_6H_{13}HgBr$	$Me_2C{=}NO_2^-Li^+$	DMSO	70 h	50
n-$C_6H_{13}HgI$	$Me_2C{=}NO_2^-Li^+$	DMSO	70 h	80
<u>cyclo</u>-$C_6H_{17}HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	34 h	76
<u>cyclo</u>-$C_6H_{17}HgCl$	 $=NO_2^-Li^+$	DMSO	60 h	84
$Me_2CHHgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	17 h	63
$CH_2{=}CHCH_2HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	24 h	50
	$Me_2C{=}NO_2^-Li^+$	DMSO	47 h	14.5[c]
<u>cyclo</u>-$C_5H_9CH_2HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	41 h	35
<u>cyclo</u>-$C_5H_9CH_2HgCl$	$Me_2C{=}NO_2^-K^+$	DMSO	40 h	47

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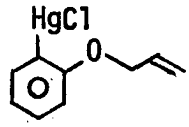
[c] Trans and cis isomers are formed. Trans:cis = 8:1.

Table II. (Continued)

R^1HgX	$R^2R^3C{=}NO_2^-M^+$	Solvent	Time[a]	% Yield Nitro Compound
$CH_2{=}CH(CH_2)_4HgCl$	$Me_2C{=}NO_2^-K^+$	DMSO	21 h	48[d]
$CH_2{=}CH(CH_2)_4HgCl$	$Me_2C{=}NO_2^-Li^+$	DMSO	48 h	35[d]
MeHgCl	$Me_2C{=}NO_2^-Li^+$	DMSO	40 h	*ca.* 2[e]
Me_3CHgCl	$Me_2C{=}NO_2^-Li^+$	DMSO	4 h	0
Me_3CCH_2HgCl	$Me_2C{=}NO_2^-Li^+$	DMSO	21 h	*ca.* 2-5[f]
PhHgCl	$Me_2C{=}NO_2^-Li^+$	DMSO	15 h	0[e]
(*E*)-Me_3CCH-CHHgCl	$Me_2C{=}NO_2^-Li^+$	DMSO	16 h	0[g]
	$Me_2C{=}NO_2^-Li^+$	DMSO	23 h	0[h]

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[d] The cyclized products, 1-cyclopentyl-2-methyl-2-nitropropane and 2-cyclohexyl-2-nitropropane, are formed in a 25:1 ratio. The indicated yield is the sum of these products.

[e] A trace of 2,3-dimethyl-2,3-dinitrobutane was isolated.

[f] Irradiation was provided by a Rayonet RPR-100 reactor equipped with 16 "350 nm" bulbs. Evidence for the formation of bis[neopentyl]mercury was obtained.

[g] Bis[(*E*)-3,3-dimethyl-1-butenyl]mercury (82%) and 2,3-dimethyl-2,3-dinitrobutane (52%) were isolated.

[h] Bis[*o*-allyloxyphenyl]mercury (17%) and 2 3-dimethyl-2,3-dinitrobutane (39%) were isolated.

minutes by the addition of 3 mole % (relative to organomercurial) di-t-butyl nitroxide, an efficient radical scavenger. A 30 minute reaction period produced a 41% yield of nitro ketone in a control experiment. These observations are consistent with the $S_{RN}1$ mechanism of Scheme 4.

2. Reactions of benzylmercury chloride with nitronate salts

The carbonyl moiety proved to be unnecessary for the coupling of organomercurials with nitronate anions. Benzylmercury chloride reacted with the lithium salts of 2-nitropropane and nitrocyclohexane to afford the corresponding tertiary nitro compounds in high yield (Table II). As noted in the case of 2-halomercurycyclohexanones, light was required to initiate the reaction and the reaction was completely inhibited by the addition of 5 mole % di-t-butyl nitroxide. No reaction occurred when the solvent (DMSO) was kept saturated with oxygen. Oxygen inhibition, as well as light initiation and nitroxide inhibition, is consistent with the $S_{RN}1$ mechanism.

A reaction was performed between benzylmercury chloride and the lithium salt of nitroethane (Table II). The first-formed product, 2-nitro-1-phenylpropane, proved to be sufficiently acidic to lose a proton to the anion of 2-nitropropane and suffer a second benzylation (Scheme 5). Although not investigated, the use of a radical-inert base

Scheme 5

$$PhCH_2CH(NO_2)Me + MeCH{=}NO_2^- \longrightarrow PhCH_2C(Me){=}NO_2^- + MeCH_2NO_2$$

$$PhCH_2C(Me){=}NO_2^- + PhCH_2HgCl \longrightarrow (PhCH_2)_2C(NO_2)Me + Hg^0 + Cl^-$$

such as "Proton Sponge" might have afforded enhanced yields of disubstitution products.

3. Reactions of simple alkylmercury halides with nitronate salts

A number of simple alkylmercury halides were found to couple with nitronate salts to give nitroaliphatic products (Table II), although the reactions required considerably longer irradiation times and often afforded lower yields than reactions of α-keto or benzylmercury halides.

To demonstrate radical chain character for reactions of simple alkylmercury halides, the reaction between 2-chloromercurypropane and the lithium salt of 2-nitropropane was performed in the presence of 5 mole % di-*t*-butyl nitroxide. A 17 hour irradiation period and subsequent workup afforded only 8% 2,3-dimethyl-2-nitrobutane. A control reaction with no added inhibitor yielded 63% coupled product.

The successful coupling of n-hexylmercury iodide with nitronate (Table II) demonstrated that the failure of 2-iodomercurycyclohexanone to couple is not general for iodo mercurials.

Steric effects clearly play an important role in the reactivity of alkylmercurials toward nitronate ion. n-Hexylmercury chloride coupled with the lithium salt of 2-nitropropane in 90% yield. Neopentylmercury chloride, also a primary alkylmercury chloride, was unreactive towards the nitronate under simple sunlamp irradiation. Extended irradiation in an RPR-100 Rayonet photochemical reactor (sixteen "350 nm" bulbs) yielded only a trace of the expected product as detected by G.C.M.S. The somewhat hindered *trans*-1-chloromercury-2-methoxycyclohexane afforded only a 14.5% yield of trans and cis coupled products in a ratio of 8:1.

Allylmercury chloride might be expected to demonstrate the same enhanced reactivity as benzylmercury chloride. The yield of coupled product with the lithium salt of 2-nitropropane was only 50%, but resinous material discarded during workup suggested that polymerization was a competing process.

It has already been observed that electronic effects (*i.e.*, benzylmercury chloride versus n-hexylmercury chloride) influence the reactivity of alkyl mercurials towards coupling. Electronic stabilization of the intermediate alkyl radical appears to favor reaction rate and yield. Methylmercury chloride might be expected to react more sluggishly with lithium 2-nitropropane-ate than n-hexylmercury chloride. In fact, after 40 hours of sunlamp irradiation, only about 2% of the expected *t*-nitrobutane was detected by G.L.C.

t-Butylmercury chloride, one of the few characterized tertiary alkylmercury halides, failed to couple with the anion of 2-nitropropane. Although significant amounts of metallic mercury were observed to precipitate from the reaction solution, only unreacted mercurial was isolated.

4. Mechanistic possibilities: alternatives to Scheme 4

Thus far, the application of an $S_{RN}1$ mechanism (Scheme 4) has been presumed correct in discussions of the reductive coupling of nitronate salts with alkylmercury halides. The repeated demonstration of radical chain behavior in these reactions is consistent with this view, but as we shall see at least three other distinct radical chain mechanisms predicting the observed coupled products may be proposed. In each case, the bulk stoichiometry of Equation 10 is expected.

$$R^1HgCl + R^2R^3C{=}NO_2^- \xrightarrow{\text{light}} R^1R^2R^3CNO_2 + Hg^0 + Cl^- \qquad (10)$$

In Scheme 6, ligand exchange on mercury of nitronate for halide is assumed to precede an $S_{RN}1$ process.

Scheme 6

$$\text{exchange} \quad R^1HgX + R^2R^3C{=}NO_2^- \longrightarrow R^1Hg(R^2R^3C{=}NO_2) + X^-$$

$$\text{initiation} \quad R^1Hg(R^2R^3C{=}NO_2) + R^2R^3C{=}NO_2^- \xrightarrow{\text{light}} [R^1Hg(R^2R^3C{=}NO_2)]^{\dot{-}} + R^2R^3\dot{C}-NO_2$$

$$\text{chain}\left\{\begin{array}{l} [R^1Hg(R^2R^3C{=}NO_2)]^{\dot{-}} \longrightarrow R^1\cdot + Hg^0 + R^2R^3C{=}NO_2^- \\ R^1\cdot + R^2R^3C{=}NO_2^- \longrightarrow [R^1R^2R^3CNO_2]^{\dot{-}} \\ [R^1R^2R^3CNO_2]^{\dot{-}} + R^1Hg(R^2R^3C{=}NO_2) \longrightarrow R^1R^2R^3CNO_2 \\ \qquad\qquad + [R^1Hg(R^2R^3C{=}NO_2)]^{\dot{-}} \end{array}\right.$$

Scheme 7 and Scheme 8 are radical chain reactions involving homolytic substitution instead of radical anions.

Scheme 7

$$\text{initiation} \quad R^2R^3C{=}NO_2^- \xrightarrow{[OX]} R^2R^3\dot{C}-NO_2$$

Scheme 7 (Continued)

$$\text{chain}\left\{\begin{array}{l} R^2R^3\dot{C}\text{-}NO_2 + R^1HgX \longrightarrow R^1R^2R^3CNO_2 + \cdot HgX \\ \cdot HgX + R^2R^3C{=}NO_2^- \longrightarrow Hg\cdot + X^- + R^2R^3\dot{C}\text{-}NO_2 \end{array}\right.$$

Scheme 8

$$\text{exchange} \quad R^1HgX + R^2R^3C{=}NO_2^- \longrightarrow R^1Hg(R^2R^3C{=}NO_2) + X^-$$

$$\text{initiation} \quad ? \longrightarrow R^1\cdot$$

$$\text{chain}\left\{\begin{array}{r} R^1\cdot + R^1Hg(R^2R^3C{=}NO_2) \longrightarrow R^1Hg\cdot + R^1R^2R^3CNO_2 \\ R^1Hg\cdot \longrightarrow R^1\cdot + Hg\cdot \end{array}\right.$$

Schemes 4, 6, 7, and 8 differ in the nature of the reactive intermediates and/or the nature of the reacting mercury(II) species. The observations of light initiation and inhibition by radical scavengers alone do not allow a firm distinction, however, of the operative mechanism. The resolution of this conundrum is discussed in parts 5 and 6 of this section.

5. Nature of the reacting mercury(II) species in the coupling reactions of alkylmercury halides with nitronate salts

Schemes 6 and 8 require ligand exchange at mercury (nitronate for halide). Accordingly, the reaction between benzylmercury chloride and the lithium salt of 2-nitropropane in d_6-DMSO was monitored by ^1H N.M.R. The spectrum recorded prior to sunlamp irradiation showed only the starting mercurial and nitronate salt. The sample was exposed to short periods of sunlamp irradiation (resulting in the precipitation of mercury metal). N.M.R. spectra showed only the starting materials and the coupled product (2-methyl-2-nitro-1-phenylpropane).

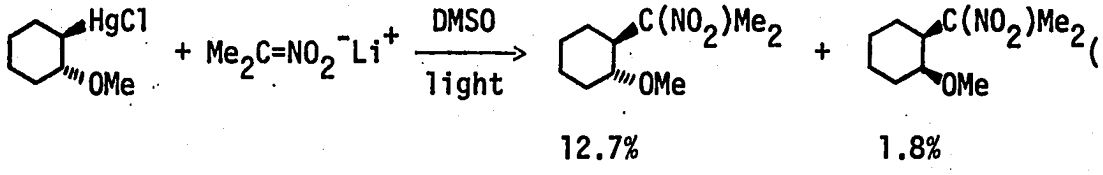
It is conceivable that benzylmercury 2-nitropropane-ate might have the same spectrum as a mixture of benzylmercury chloride and the lithium salt of 2-nitropropane. Consequently, reaction solutions were prepared and worked up at different states of reaction completion. When the solution was worked up with no sunlamp irradiation, only benzylmercury chloride was recovered, nearly quantitatively. When the reaction solution was irradiated for short periods of time and worked up, mixtures of benzylmercury chloride and 2-methyl-2-nitro-1-phenylpropane were isolated with good material balance in benzyl groups.

Mechanistic Schemes 6 and 8 are thus disfavored due to evidence that the proposed bulk reagent, alkylmercury nitronate, is not present (at least) in the model reaction between benzylmercury chloride and lithium 2-nitropropanate.

6. Nature of the intermediate radical: the 5-hexen-1-yl rearrangement

A major distinction between mechanistic Schemes 4 and 7 is the nature of the intermediate radical. Scheme 4 ($S_{RN}1$ mechanism) invokes the intermediacy of the alkyl radical derived from cleavage of the carbon-mercury bond of the alkylmercury halide, whereas the carbon radical in Scheme 7 is derived from one-electron oxidation of the nitronate ion. The use of an organomercury substrate leading to a radical known to rapidly rearrange or stereochemically equilibrate was dictated.

The previously mentioned reaction between trans-1-chloromercury-2-methoxycyclohexane and the anion of 2-nitropropane afforded the expected coupled product as an 8:1 trans:cis mixture (Eq. 11). This apparent



(11)

manifestation of the 2-methoxycyclohexyl radical (consistent with Scheme 4) is somewhat obscured by the 14.5% overall reaction yield, possibly due to unfavorable steric effects. Thus, the yield of cis product is only about 2% from a reaction that afforded a very complex product mixture (roughly a dozen volatile components were observed by G.L.C.). The cis product could have (arguably) arisen from secondary processes while the trans was produced by the main pathway, Scheme 7.

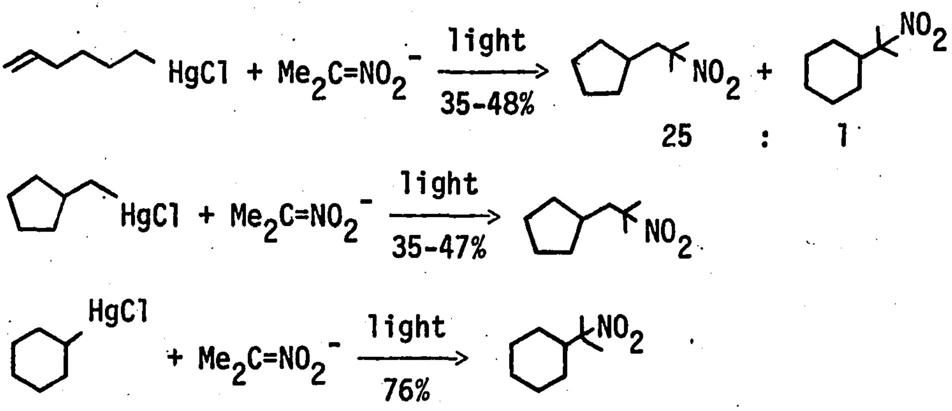
Firm evidence that coupled product is the offspring of the organomercury-derived radical was provided by the 5-hexen-1-yl rearrangement, a probe which has found extensive application in mechanistic studies [35]. The radical rearrangement from 5-hexen-1-yl to cyclopentylmethyl (Eq. 12) is diagnostic for the free radical, as the anion does not


(12)

cyclize [36] and the cation closes exclusively to the six-membered ring [37]. The unimolecular rate constant for cyclization of the radical has been measured to be 10^5 sec^{-1} [38,39].

Scheme 9 illustrates data extracted from Table II. 6-Chloromercury-1-hexene reacted photochemically with the lithium and potassium salts of 2-nitropropane to produce a 25:1 ratio of cyclopentylmethyl and cyclohexyl products. No uncyclized (olefinic) products were detected by ^{1}H N.M.R. or G.C.M.S. The structure of the observed products were verified by comparison of spectral and chromatographic data with authentic samples prepared by coupling 2-nitropropane-ate salts with cyclopentylmethyl- and cyclohexylmercury chlorides.

Scheme 9



Mechanistic Scheme 7 is apparently not operative in these coupling reactions since neither stereochemical equilibration nor rearrangement is allowed for in the organometal-derived alkyl moiety. The $S_{RN}1$ mechanism of Scheme 4 most reasonably explains the available data.

7. The nature of photochemical initiation

In all the reactions of nitronate salts with alkylmercury halides, no precipitation of mercury metal was observed in the absence of light.

Slow reaction was induced by roomlight in the cases of the most active mercurials (benzyl and α-keto mercury halides) while significant rates for simple alkylmercury halide required the use of a sunlamp. Unfortunately, little can be concluded regarding the mode of photochemical initiation.

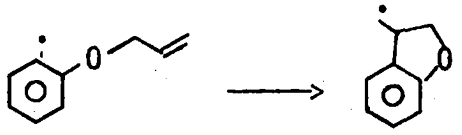
Light more energetic than 320 nm may be disregarded since all reactions were performed in Pyrex vessels. The lithium salt of 2-nitropropane exhibits an absorption maximum at 352 nm in DMSO corresponding to the $n \rightarrow \pi^*$ transition. This absorption tails into the visible spectrum giving these solutions a faint yellow tint. The absorption spectrum of a solution containing the lithium salt of 2-nitropropane and benzylmercury chloride appears to be the sum of the spectra of the pure compounds, benzylmercury chloride exhibiting the tail of the strong $\pi \rightarrow \pi^*$ absorption from approximately 340 nm to the DMSO cutoff at 300 nm. Since a charge-transfer complex present in low equilibrium concentration cannot be ruled out distinction between two likely modes of initiation, photon absorption by a nitronate-mercurial charge-transfer complex versus electron transfer from a photochemically excited nitronate ion, cannot be made.

Direct photolysis of the alkylmercury halide is not generally responsible for free radical initiation. Mercurials bearing saturated alkyl substituents absorb no radiation above 310 nm.

8. Reactions of nitronate ion with aryl- and vinylmercury halides

Phenylmercury chloride proved unreactive towards the anion of 2-nitropropane. Extensive sunlamp irradiation resulted in only a trace of mercury metal. Workup revealed a trace of 2,3-dimethyl-2,3-dinitrobutane and starting mercurial. In a similar experiment, a dilute DMSO solution of sodium borohydride was slowly added to the reaction to generate phenyl radicals. Again, a trace of 2,3-dimethyl-2,3-dinitrobutane was isolated. None of the desired cross-coupled product, 2-nitro-2-phenylpropane, was detected. Nitronate salts are not known to participate in aryl $S_{RN}1$ reactions [9], although adducts of phenyl radicals with nitronate ions have been observed by E.S.R. [40].

On the assumption that aryl radicals were failing to add efficiently to the nitronate ion, an attempt was made to utilize the rearrangement of **6** to **7**. Somewhat analogous to the 5-hexen-1-yl case, this rearrangement



6 **7**

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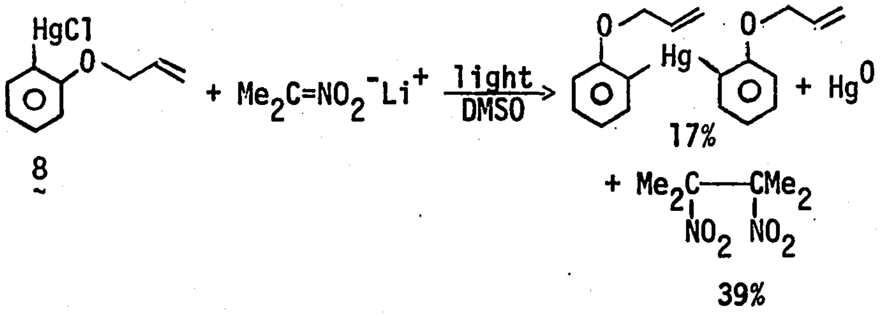
has been employed to detect aryl radical intermediates in the lithium aluminum hydride reduction of aryl halides [41]. When mercurial **8** was

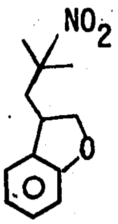


8

(14)

reacted with the lithium salt of 2-nitropropane for 23 hours, mercury metal was observed to precipitate. None of the expected coupled product

9 was produced. ^{1}H N.M.R. clearly revealed the symmetrized mercurial in

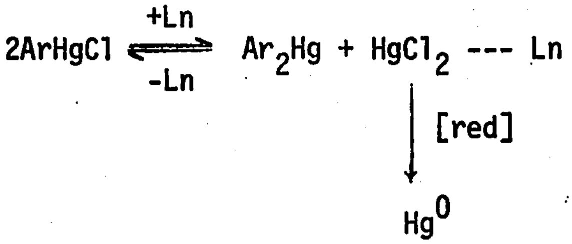


9

17% yield and 2,3-dimethyl-2,3-dinitrobutane in 39% yield. Lack of rearrangement suggests (but does not prove) that the symmetrization did not proceed via the phenyl radical.

Similar "reductive symmetrizations" of alkyl mercurials have been thought to proceed through free radicals [42,43]. The symmetrization equilibrium in Scheme 10 for aryl mercurials is known to be exceptionally sensitive to ligands which serve to complex mercuric chloride [44,45].

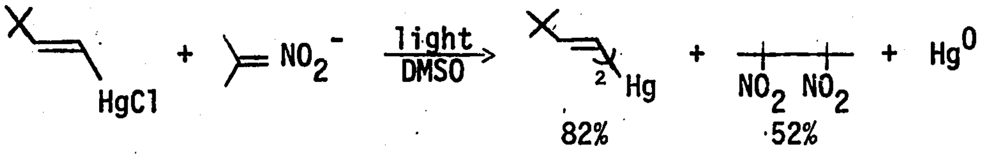
Scheme 10



$$2ArHgCl \underset{-Ln}{\overset{+Ln}{\rightleftharpoons}} Ar_2Hg + \underset{Hg^0}{\underset{\downarrow\,[red]}{HgCl_2}} \text{ --- } Ln$$

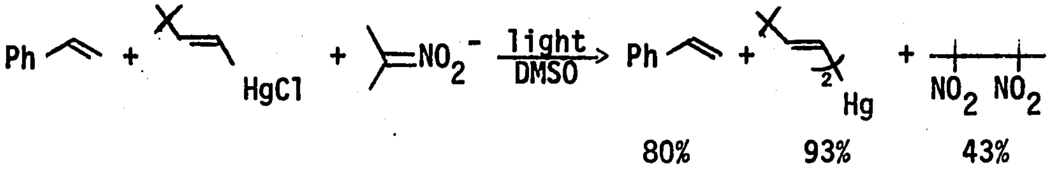
Notably, mercuric chloride is reduced by lithium 2-nitropropane-ate in DMSO to yield mercury metal and a moderate (35%) quantity of 2,3-dimethyl-2,3-dinitropropane. Thus, photochemical reductive symmetrization of 8 may well proceed via trapping of the ionic equilibrium (Scheme 10) by mercuric chloride reduction. Light may be required because of the less favorable reduction potential of ligated mercury chloride. (Nitronate ion only slowly reduces mercuric chloride in the presence of diethyl phosphite ion, a strong complexing agent for mercury chloride as discussed later.)

The lithium salt of 2-nitropropane efficiently symmetrized (E)-3,3-dimethyl-1-butenylmercury chloride in DMSO under sunlamp irradiation (Table II and Eq. 15). When light is omitted from the reaction flask by



(15)

means of an aluminum foil wrapping, no reaction occurs. Symmetrization does occur without polymerizing styrene (Eq. 16) and occurs even in the presence of 150 mole % di-t-butyl nitroxide (Eq. 17). 2,3-Dimethyl-2,3-



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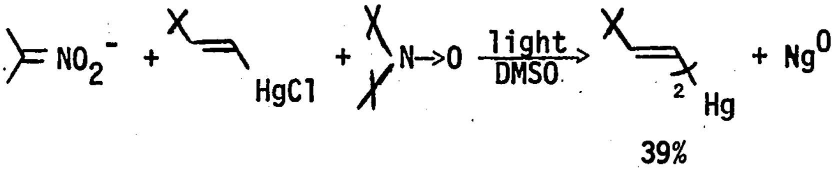


(17)

dinitrobutane did not appear in the presence of nitroxide. This is not surprising since the 2-nitropropyl radical must be an intermediate in dimer formation.

The mechanism of Scheme 10 is probably operative both in the nitronate-induced symmetrization of arylmercury halides and the

(E)-3,3-dimethyl-1-butenylmercury chloride. ^{1}H N.M.R. experiments in d_6-DMSO showed that prior to irradiation the vinylmercury chloride exists (predominently) in the unsymmetrized form. Likewise, (E)-3,3-dimethyl-1-butenylmercury chloride could be nearly quantitatively recovered from non-irradiated DMSO solutions containing the nitronate salt. The equilibrium reaction of Scheme 10 must lie ≥ 95% in favor of the unsymmetrized form.

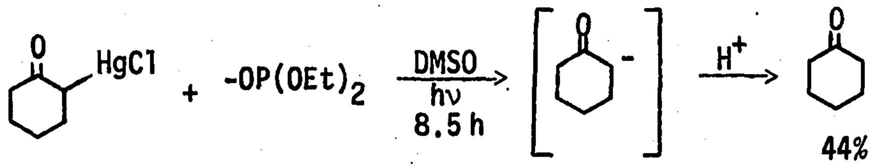
9. Reaction of diethyl phosphite ion with alkylmercury halides

Potassium diethyl phosphite in DMSO under sunlamp illumination efficiently converted benzylmercury chloride into bibenzyl (Eq. 18). The

$$PhCH_2HgCl + K^{+-}OP(OEt) \xrightarrow[\text{light}]{\text{DMSO}} \underset{84\%}{PhCH_2CH_2Ph} + Hg^0 + ? \qquad (18)$$

precipitation of mercury metal was slow, an irradiation period of 39.5 h being employed. The fate of phosphorous compounds was not determined. All phosphorous compounds were lost during the extractive workup from brine (see Experimental Section).

"Reductive dimerization" of alkylmercury halides by phosphite ion is not general. Cyclohexylmercury chloride and n-hexylmercury chloride failed to produce G.L.C.-detectable amounts of dicyclohexyl or n-dodecane, respectively. 2-Chloromercurycyclohexanone reacted with rapid precipitation of mercury metal to afford, after workup, cyclohexanone (Eq. 19). The first-formed product was probably cyclohexanone



(19)

potassium enolate produced by two one-electron reductions of the starting mercurial followed by protonation during workup.

The formation of bibenzyl appears to be a radical nonchain process: 1) No bibenzyl formation or mercury precipitation occurred in the absence of light. 2) Mercury precipitation occurred normally when oxygen-saturated DMSO was employed, but only a trace (1.8%) bibenzyl was formed. Instead benzyl alcohol, benzaldehyde and benzoic acid were obtained (Eq. 20). 3) Addition of varying quantities of di-t-butyl nitroxide only reduced the yield of bibenzyl stoichiometrically (see Table III).

$$PhCH_2HgCl + {}^-OP(OEt)_2 \xrightarrow[\text{light}]{\text{DMSO}} PhCH_2OH + PhCHO + PhCOOH + Hg^0 \quad (20)$$
$$O_2$$

Table III. Effect of added di-t-butyl nitroxide on the yield of bibenzyl

Time[a]	Mole % di-t-butyl nitroxide	% Yield bibenzyl[b]
4 h	0	10
4 h	10	0
8 h	0	21
8 h	10	12.5

[a] Duration of 275 watt sunlamp irradiation with bulb placed 7 inches from the reaction flask.

[b] Yield determined by quantitative ^1H N.M.R. of worked-up reaction products.

Although there is no evidence for a chain reaction, the scavenging experiments prove benzyl radical is an intermediate in bibenzyl formation. Bibenzyl may simply arise from the coupling of benzyl radicals (Eq. 21), although homolytic attack of benzyl radical on benzylmercury(II) species may also be envisioned.

$$PhCH_2\cdot + PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph \qquad (21)$$

The mode of benzyl radical generation is not entirely clear. ^1H N.M.R. experiments in d_6-DMSO revealed that benzylmercury chloride is immediately symmetrized to bis[benzyl]mercury by diethyl phosphite ion $\geq$ 95%. Bis[benzyl]mercury can be isolated in quantitative yield by workup of nonirradiated solutions of benzylmercury chloride and diethyl phosphite ion in DMSO.

This symmetrization is not a redox process (Eq. 22), because

$$2PhCH_2HgCl \overset{^{-}OP(OEt)_2}{\rightleftarrows} (PhCH_2)_2Hg + HgCl_2 \qquad (22)$$

mercury metal is only formed upon irradiation of the reaction mixture (with concomitant formation of bibenzyl). Bibenzyl does not result from irradiation of DMSO solutions of bis[benzylmercury] alone or with diethyl phosphite ion added. Not surprisingly, bibenzyl <u>does</u> result from irradiation of a solution containing bis[benzyl]mercury, diethyl phosphite anion, and an equivalent of mercuric chloride (Scheme 11).

Scheme 11

$$[PhCH_2]_2Hg \xrightarrow{light} \text{no reaction}$$

Scheme 11 (Continued)

$$[PhCH_2]_2Hg \xrightarrow[K^{+-}OP(OEt)_2]{\text{light}} \text{no reaction}$$

$$[PhCH_2]_2Hg \xrightarrow[\substack{K^{+-}OP(OEt)_2 \\ HgCl_2}]{\text{light}} \underset{92\%}{PhCH_2CH_2Ph} + Hg^0$$

In view of the lack of data concerning phosphorous-containing products, the origin of benzyl radicals, and the exact nature of bibenzyl formation, it is presently impossible to formulate a detailed mechanism for this reaction. A significant conclusion, however, is that benzyl radical was not trapped by diethyl phosphite ion.

10. Reactions of benzylmercury chloride with other anions

Diethyl phosphite ion participates readily in aryl $S_{RN}1$ reactions [9] and aliphatic $S_{RN}1$ reactions in which the intermediate radical ion is stabilized by a nitro group [14]. Failure to react similarly with alkyl mercury halides might be due to lack of an available low-lying pi-antibonding orbital to stabilize the radical ion. Butyl phenylphosphinite ion, known to participate in aryl $S_{RN}1$ reactions [46], also failed to couple with benzyl radical (Table IV) inducing only the formation of bibenzyl instead. This was surprising since **10**, the anticipated radical ion, might have enjoyed stability similar to **11**, the radical ion resulting from addition of an aryl radical to diethyl phosphite ion.

Table IV. Reactions of benzylmercury chloride with several anions

$$PhCH_2HgCl + M^+A^- \xrightarrow{light} products$$

A^-	M^+	Time[a]	Solvent	Products (% yield)
$PhP(OBu)O^-$[b]	K^+	28.5 h	DMSO	bibenzyl (88%)
P-$MePhSO_2^-$	Na^+	17.5 h	DMSO	bibenzyl (18%)
N_3^-	Na^+	21 h	$DMSO/H_2O$	bibenzyl (42%)
$PhC(Me)_2O^-$[c]	K^+	18.5 h	DMSO	---[d]
Me_3Si^-[e]	K^+	---[f]	HMPA	bibenzyl (0%), benzyl trimethylsilane (0%)
NO_2^-	Na	19 h	DMSO	bibenzyl (36%)

[a] Irradiation period (275 watt sunlamp).

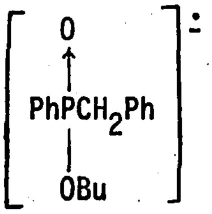
[b] Generated from equivalent amounts of n-butyl phenylphosphinite and potassium t-butoxide in DMSO.

[c] Generated from equivalent amounts of isobutyrophenone and potassium t-butoxide in DMSO.

[d] No metallic mercury was observed.

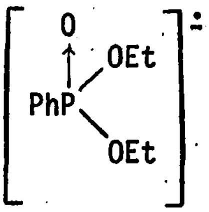
[e] Generated from equivalent amounts of potassium t-butoxide and hexamethyl disilane in HMPA.

[f] No irradiation was required. Instantaneous exothermic reaction with precipitation of metallic mercury occurred.



$$\left[\overset{\displaystyle O}{\overset{\uparrow}{\underset{\underset{\displaystyle OBu}{|}}{\mathrm{PhPCH_2Ph}}}}\right]^{\cdot-}$$

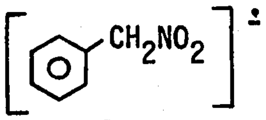
10



11

Sulfinate [10,11] and azide [4] ions are known to participate in some aliphatic $S_{RN}1$ reactions. Their failure with benzylmercury chloride (Table IV) can be rationalized in terms of the energetic accessibility of the intermediate radical ion. Primary enolates react with aryl halides [9] and α-nitro halides [5] in $S_{RN}1$ fashion. Isobutyrophenone enolate failed to reduce benzylmercury chloride, however (Table IV). The failure of trimethylsilyl anion to produce coupled products with benzylmercury halide is not surprising. Silyl anions couple with aryl halides in what has been presumed, perhaps incorrectly [47], to be an $S_{RN}1$ process [48].

Nitrite ion reacts with alkyl $S_{RN}1$ substrates [49] and is capable of trapping phenyl radical [40]. However, nitrite apparently failed to trap benzyl radical (Table IV) and only bibenzyl was produced. This is particularly difficult to reconcile since the proposed radical ion intermediate, 12, is quite similar to that produced when benzyl radical



12

is trapped by nitronate ion. Unfortunately, the available data afford little insight. Either 12 is not formed at a significant rate, or else 12 is formed reversibly under circumstances in which oxidation (i.e., electron transfer from 12 to benzylmercury chloride) is slow. Benzylmercury chloride is not simply a special case. Nitrite failed to produce either 1-nitrohexane or n-dodecane with n-hexylmercury chloride.

11. Reaction of the anion of 2-nitropropane with benzylmercury chloride in the presence of other anions

As further evidence that known $S_{RN}1$ nucleophiles fail to propagate a chain reaction in the presence of benzyl radicals, the normal coupling reaction between the anion of 2-nitropropane and benzylmercury chloride was observed in the presence of added diethyl phosphite, nitrite, or sulfinate salt (Table V). 2-Methyl-2-nitro-1-phenylpropane

Table V. Coupling the anion of 2-nitropropane in the presence of a second anion

$$Me_2C{=}NO_2^- + PhCH_2HgCl + A^- \xrightarrow[DMSO]{light}$$

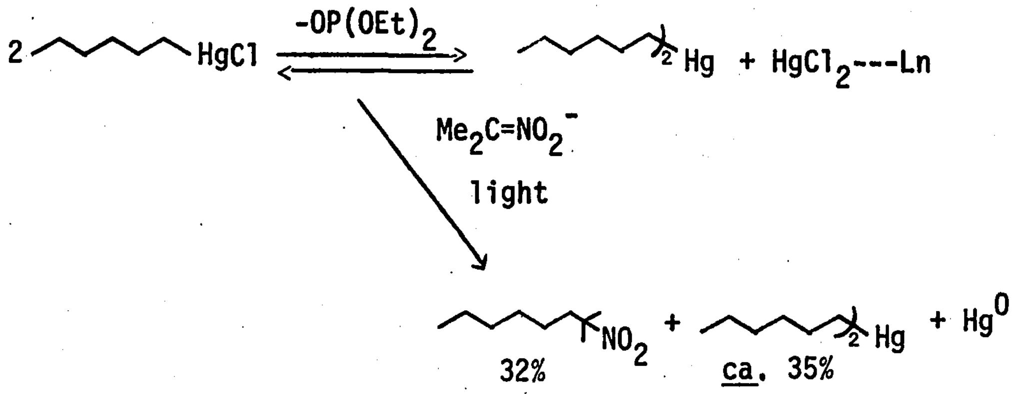
A^-	Time[a]	Product (% yield)
$^-OP(OEt)_2$[b]	14.5 h	$PhCH_2C(Me)_2NO_2$ (61%)
NO_2^-	20 h	$PhCH_2C(Me)_2NO_2$ (91%)
$^-O_2SPhMe$-p	17 h	$PhCH_2C(Me)_2NO_2$ (90%)

[a] Irradiation time (275 watt sunlamp).

[b] Generated from equivalent amounts of lithium t-butoxide and diethyl phosphite in DMSO.

was formed in each case. No bibenzyl was detected nor any 2,3-dimethyl-2,3-dinitrobutane. The successful coupling in the presence of diethyl phosphite ion is noteworthy, since it has been shown that the mercurial is symmetrized in this medium (part 9, this section). When the coupling of nitronate ion with n-hexylmercury chloride was performed with diethyl phosphite ion present, mercury precipitation ended after 15 hours sunlamp irradiation with the production of only 32% yield nitro compound. G.C.M.S. revealed at least as high a yield of bis[n-hexyl]-mercury (Scheme 12).

Scheme 12



C. Conclusion

Salts of secondary aliphatic nitro compounds couple with alkylmercury halides to yield tertiary nitro compounds, mercury metal, and halide salt. The observations that 1) the reactions are light-initiated radical chain processes, 2) the reacting mercury(II) species is alkylmercury halide since nitronate ion does not exchange with halide on mercury or induce symmetrization, and 3) the intermediate free radical is derived from the alkyl mercurial are strong evidence for the $S_{RN}1$ mechanism of Scheme 4 and disfavor several alternative mechanistic formulations (Schemes 6, 7, and 8).

Steric and electronic factors strongly affect the reactivity of alkylmercury halides. The highly hindered neopentylmercury chloride is essentially unreactive towards the anion of 2-nitropropane while unhindered primary and secondary alkyl mercurials afford moderate yields of nitro compounds. Benzyl and α-keto mercurials were especially reactive towards nitronate coupling.

Aryl and vinyl mercurials do not couple with nitronate ion, and are unreactive or afford symmetrization products. This light-induced reductive symmetrization appears not to involve aryl or vinyl radicals.

A number of anions other than nitronate were found not to couple with alkyl mercurials despite their known $S_{RN}1$ activity with certain substrates. Some of these anions photochemically reduce benzylmercury chloride to bibenzyl. In the case of diethyl phosphite ion, bibenzyl production was shown to involve benzyl radicals in a nonchain process.

D. Experimental Section

1. General considerations

Nitroethane and nitrocyclohexane were purchased from Aldrich. The lithium salt of nitrocyclohexane was prepared by the literature method [11]. The lithium salt of nitroethane was prepared by the method described for the 2-nitropropane salt [11].

2,3-Dimethyl-2,3-dinitrobutane was purchased from Aldrich as was phenylmercury chloride.

Preparative reactions of nitronate salts with alkylmercury halides were usually performed in DMSO or DMF used as received. Yields and product distributions were insensitive to water content of the solvent. When dry solvents were required, DMSO, DMF, and HMPA were distilled from calcium hydride and stored in septum-sealed bottles over 4A molecular sieves.

The reactions of nitronate salts with 2-halomercurycyclohexanones were investigated by Karen Owens [33].

Aqueous sodium thiosulfate was often employed in the workup procedure as a convenient method for removing organomercury salts from the organic medium. In trial extractions, the following mercurials were found to be effectively removed from ether solution:n-hexyl mercury chloride, neopentylmercury chloride, benzylmercury chloride, phenylmercury chloride. However, (<u>E</u>)-3,3-dimethyl-1-butenylmercury chloride or bromide was partially symmetrized (<u>ca.</u> 50% bis[vinyl] mercurial isolated) and so the thiosulfate wash seems to be inappropriate for work-up of reactions involving vinyl mercurials.

2. Preparation of organomercurials

The following general procedure was found convenient for the synthesis of several alkylmercury halides: to the Grignard reagent in THF was added one equivalent of mercuric halide dissolved in the minimum amount of THF. The reaction mixture was warmed to reflux for 1 hour, then cooled to room temperature and poured into cold 2% acetic acid containing several equivalents of sodium halide. The solid product was collected and dried. Inorganic salts were then removed by dissolving the product in excess chloroform, filtering, and concentrating the solution under vacuum. Generally, a pure substance resulted. If desirable, the product was recrystallized once from hot ethanol. Thus prepared were n-hexylmercury chloride (82%, m.p. 120-121°C, lit. [50] 125°C), 2-chloromercury propane (74%, m.p. 93.5-94.5°C, lit. [51] 94.5-95.5°C), cyclopentylmethylmercury chloride (84%, m.p. 53-54°C, lit. [52] 57-58°C), and 6-chloromercury-1-hexene (86%, m.p. 100.5-101.5°C, lit. [52] 100-101°C).

Samples of cyclohexylmercury chloride [53], n-hexylmercury bromide [50], and n-hexylmercury iodide [50] were kindly supplied by the group of Professor R. C. Larock.

Literature procedures were employed for the preparations of benzylmercury chloride [54], 2-chloromercury-1-methoxycyclohexane [55], methylmercury chloride [56], allylmercury chloride [57], neopentylmercury chloride [58], (E)-3,3-dimethyl-1-butenylmercury chloride [59], 2-iodomercurycyclohexanone [60], and t-butylmercury chloride [61]. The elemental analysis for t-butylmercury chloride was obtained as it has not been reported in the literature. Calculated for C_4H_9ClHg: C, 16.39; H, 3.09; Cl, 12.09; Hg, 68.42. Found: C, 16.41; H, 3.01; Cl, 11.97; Hg, 68.73.

(E)-3,3-dimethyl-1-butenylmercury bromide was prepared in a manner analogous to the preparation of (E)-3,3-dimethyl-1-butenylmercury chloride [59]. Recrystallization from hot ethanol afforded pure mercurial (m.p. 81-82°C). Elemental analysis. Calculated for $C_6H_{11}BrHg$: C, 19.82; H, 3.05; Br, 21.97; Hg, 55.16. Found: C, 19.93; H, 3.05.

2-Chloromercurycyclohexanone (m.p. 140-140.5°C, lit. [62] 134-135°C) and 2-bromomercurycyclohexanone [63] (m.p. 130-131°C) were prepared by the method described for 2-iodomercurycyclohexanone [60], except that mercuric chloride and mercuric bromide were used instead of mercuric iodide. The elemental analysis of 2-bromomercurycyclohexanone was obtained since it has not been reported. Calculated for C_6H_9BrHgO: C, 19.08; H, 2.41; Br. 21.26; Hg, 53.12. Found: C, 19.36; H, 2.54; Br, 20.87; Hg, 53.54.

Bis[benzyl]mercury was prepared by the action of 0.5 equivalents of mercuric chloride on the Grignard reagent in ethyl ether (m.p. 110-111°C, lit. [64] 111°C).

Bis[(E)-3,3-dimethyl-1-butenyl]mercury was prepared by the addition of solid (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) to a solution containing potassium t-butoxide (0.6 g, 5.4 mmol) and diethyl phosphite (1.1 g, 7.8 mmol) in 25 ml dry DMSO under nitrogen. After stirring 5 minutes, the solution was poured into brine and the product extracted with ether. The ether extract was washed with water, dried ($MgSO_4$) and concentrated under vacuum to afford 0.6 g (100% yield) of the bis[vinyl] mercurial (>95% pure by N.M.R.). Kugelrohr distillation (75°C/0.1 torr) afforded analytically pure product. ^1H N.M.R. ($CDCl_3$, δ) 1H (d, J_H = 16 Hz) 6.09, 1H (d, J_H = 16 Hz) 5.70, 9H (s) 1.03. I.R. (neat, NaCl plates, cm^{-1}) 2940 (s), 1590 (s), 1460 (s), 1360 (s), 1256 (s), 990 (s). Elemental analysis. Calculated for $C_{12}H_{22}Hg$: C, 39.28; H, 6.04; Hg, 54.67. Found: C, 39.40; H, 6.12.

Bis[o-allyloxyphenyl]mercury was prepared by slow addition of a THF solution (40 ml) of mercuric chloride (12 g, 0.044 mol) to o-allyloxyphenylmagnesium bromide (0.094 mol) in 60 ml THF under nitrogen. The solution was refluxed 12 hours, cooled, and poured into 1500 ml 5% NH_4Cl. The solid product was collected and recrystallized from ethanol/water. The yield of pure bis[o-allyloxyphenyl]mercury was 16 g (73% yield based on Grignard, m.p. 69.5-70.5°C). ^1H N.M.R. ($CDCl_3$, δ) 8H (m) 6.8-7.5, 2H (m) 5.75-6.4, 4H (m) 5.05-5.6, 4H (m) 4 4-4.6. Elemental analysis. Calculated for $C_{18}H_{18}HgO$: C, 46.30; H, 3.89; Hg, 42.96; O, 6.85. Found: C, 46.32; H, 3.96.

o-Allyloxyphenylmercury chloride was prepared by the slow addition of a THF (10 ml) solution of mercuric chloride (1.2 g, 4.4 mmol) to bis[o-allyloxyphenyl]mercury (2.0 g, 4.3 mmol) in 25 ml THF. The solution was warmed to reflux for 30 minutes, cooled, and poured into 250 ml 2% sodium chloride. The white solid was collected, air-dried, and dissolved in 125 ml chloroform. Gravity filtration (to remove inorganic mercury salts) followed by chloroform removal under vacuum afforded 2.5 g (79% yield) of pure white o-allyloxymercury chloride (m.p. 93.5-95°C). ^1H N.M.R. ($CDCl_3$, δ) 4H (m) 6.7-7.4, 1H (m) 5.7-6.3, 2H (m) 5.1-5.5, 2H (m) 4.4-4.6. Elemental analysis. Calculated for C_9H_9ClHgO: C, 29.28; H, 2.46; Cl, 9.60; Hg. 54.33; O, 4.33. Found: C, 29.30; H, 2.44.

3. Reactions of 2-halomercurycyclohexanones with the lithium salt of 2-nitropropane

2-Chloromercurycyclohexanone (0.51 g, 1.5 mmol) was dissolved in a nitrogen-purged solution of the lithium nitronate (0.18 g, 1.9 mmol) in 30 ml DMSO. The reaction solution was irradiated for 1 hour with a 275 watt sunlamp placed approximately 8 inches from the Pyrex flask during which time metallic mercury was observed to precipitate. The reaction was quenched with dilute hydrochloric acid and the solution diluted with water (filtration through a cake of "Celite" was sometimes required to remove the mercury metal). Product was extracted with ether. The extract was washed with aqueous bicarbonate and dried ($MgSO_4$). Concentration under vacuum afforded 170 mg (56% yield) of 2-(α-nitroisopropyl)cyclohexanone as a crystalline solid (m.p. 44-50°C) which appeared N.M.R. pure. Such high purity suggests that the rather poor isolated yield was due to the solubility of the product in water.

^1H N.M.R. ($CDCl_3$, δ) 1H (m) 3.5, 9H (broad) 1.8-3.7, 3H (s) 1.7, 3H (s) 1.6. Note the methyl groups, which are diastereotopic, exhibit individual ^1H N.M.R. signals.

I.R. (melt, NaCl plates, cm^{-1}) 1705 (s), 1585 (vs), 1340 (s).

This β-nitro ketone, somewhat unstable towards loss of HNO_2, was conveniently characterized as the 2,4-dinitrophenylhydrazone derivative of β-isopropylidene cyclohexanone (m.p. 172-174°C, lit. [65] 181.5-182.5°C). Elemental analysis. Calculated for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.75; H, 5.83; N, 17.78. M.S.

Calculated for $C_{15}H_{18}N_4O_4$: 318.13281. Measured: 318.13279. Error = 0.06 ppm.

The reaction of the lithium salt of 2-nitropropane with 2-bromomercurycyclohexanone was performed similarly on a 5.7 mmol scale in 30 ml DMF. The β-nitro ketone was isolated in 68% yield.

2-Iodomercurycyclohexanone reacted with the lithium salt of 2-nitropropane with the precipitation of mercury metal. The usual workup afforded a brown liquid which began to decompose upon concentration of the ethereal extract. A qualitative test (sodium fusion/silver nitrite) indicated the presence of iodine. ^1H N.M.R. and I.R. showed the isolate to contain no nitro group.

4. Reaction of 2-chloromercurycyclohexane with the lithium salt of nitrocyclohexane

2-Chloromercurycyclohexanone (2.25 mmol) and the lithium salt of nitrocyclohexane (3 mmol) in 30 ml nitrogen-purged DMSO were irradiated for 2 hours with a sunlamp. The usual workup afforded 2-(α-nitrocyclohexyl)cyclohexanone (0.3 g, 60% yield) as a solid. An analytical sample was obtained by recrystallization from pentane (m.p. 66-68°C).

^1H N.M.R. ($CDCl_3$, δ) 1H (broad) 4.4, 18H (broad) 1.0-3.3.

I.R. (melt, NaCl plates, cm^{-1}) 2940 (s), 1715 (s), 1540 (s), 1450 (m), 1350 (m), 850 (m).

M.S. Calculated for $C_{12}H_{18}O$ (loss of NO_2): 179.14359. Measured: 179.14305. Error = -3.0 ppm.

5. Effect of light on the reaction of 2-chloromercurycyclohexanone with the lithium salt of 2-nitropropane

2-Chloromercurycyclohexanone (2.1 g, 6 mmol) was dissolved in a solution of the nitronate salt (0.78 g, 7 mmol) in 30 ml nitrogen-purged DMF in a flask tightly wrapped with aluminum foil to omit light. After stirring for 30 minutes, the reaction was quenched with dilute hydrochloric acid and the foil removed. A trace of mercury metal was observed. The usual workup afforded a small amount (<5% yield) of 2-(α-nitroisopropyl)cyclohexanone.

A control reaction performed without the foil wrapping for a 30 minute sunlamp-irradiation period afforded a 41% yield of product.

6. Effect of di-*t*-butyl nitroxide on the reaction of 2-chloromercurycyclohexanone with the lithium salt of 2-nitropropane

A solution of 2-chloromercurycyclohexanone (2.1 g, 6 mmol) and the nitronate salt (0.7 g, 7 mmol) in 30 ml nitrogen-purged DMF with 27 mg (0.18 mmol, 3 mole %) di-*t*-butyl nitroxide added released only a trace of mercury metal after 30 minutes of sunlamp irradiation. The usual workup afforded no detectable 2-(α-nitroisopropyl)cyclohexanone.

For comparison, the uninhibited reaction yielded 41% β-nitro ketone after 30 minutes sunlamp irradiation and the usual workup.

7. Reaction of benzylmercury chloride with the lithium salt of 2-nitropropane

The following procedure serves as a model for most of the ensuing compling reactions of nitronate salts with alkylmercury halides.

Benzylmercury chloride (1.0 g, 3 mmol) was added to a nitrogen-purged solution of the lithium salt of 2-nitropropane (0.35 g, 3.7 mmol) in 50 ml DMSO. The gently stirred solution was maintained under nitrogen atmosphere. The Pyrex reaction flask was irradiated with a 275 watt sunlamp, placed about 8 inches distant, without external cooling. Ambient reaction temperature was 28-30°C, although in coupling reactions of other organomercurials requiring longer irradiation times temperatures as high at 40°C were noted. After 2 to 3 minutes, mercury metal began to precipitate. The reaction was irradiated a total of 2 hours, although precipitation of mercury appeared complete after 60 minutes. Beads of mercury formed at the bottom of the flask, so the DMSO solution was merely decanted into brine (filtration of the DMSO solution through a Celite cake was at other times necessary). The brine was extracted repeatedly with ether. The combined ether extract was washed with brine and dried ($MgSO_4$). Concentration under vacuum afforded 0.44 g (100%) of pale green liquid which ^1H N.M.R. revealed to be pure 2-methyl-2-nitro-1-phenylpropane. An analytical sample was obtained by crystallization from ethanol/water (m.p. 25°C).

^1H N.M.R. ($CDCl_3$, δ) 5H (m) 6.9-7.3, 2H (s) 3.1, 6H (s) 1.5.

I.R. (neat, NaCl plates, cm^{-1}) 3040 (w), 1540 (vs), 1495 (m), 1450 (w), 1350 (m), 740 (s), 720 (s), 695 (s).

M.S. Calculated for $C_{10}H_{13}NO_2$ (observable at 20 eV): 179.09463. Measured: 179.09415. Error = -3.7 ppm.

Elemental analysis. Calculated for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82; O, 17.85. Found: C, 67.21; H, 7.43; N, 7.61.

8. Reaction of benzylmercury chloride with the lithium salt of nitrocyclohexane

Benzylmercury chloride (4.0 g, 12 mmol) and the lithium salt of nitrocyclohexane (1.8 g, 13 mmol) were reacted in 160 ml DMSO in the usual manner employing a 2 hour irradiation period. Workup afforded 2.4 g (87%) colorless oil which solidified on standing. ^{1}H N.M.R. showed the isolate to be essentially pure. Recrystallization from pentane afforded white needles (m.p. 68.5-69°C).

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 6.9-7.3, 2H (s) 3.07, 2H (m, broad) 2.25-2.6, 8H (m, broad) 1.2-1.8.

I.R. (melt, NaCl plates, cm^{-1}) 3030 (w), 2940 (s), 2860 (m), 1585 (vs), 1500 (m), 1450 (s), 1350 (m), 715 (s), 695 (s).

M.S. Calculated for $C_{13}H_{16}$ (loss of HNO_2): 172.12520. Measured: 172.12503. Error: -1.0 ppm.

Elemental analysis. Calculated for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39; O, 14.59. Found: C, 71.02; H, 7.90; N, 6.31.

9. Reaction of benzylmercury chloride with the lithium salt of nitroethane

Benzylmercury chloride (1.0 g, 3 mmol) and the lithium salt of nitroethane (0.5 g, 6 mmol) were reacted in the usual manner in 75 ml DMSO employing a 2 hour irradiation period. Workup afforded 0.45 g liquid found to be a mixture of 4 volatile components by G.L.C. (1/8" x 5', 5% SE-30, 90°C). G.C.M.S. analysis revealed a minor component (*ca.* 5% overall yield) to be the desired

2-nitro-1-phenylpropane. The major component (ca. 40% overall yield) was the doubly-benzylated product, 2-methyl-2-nitro-1,3-diphenylpropane.

10. Effect of light on the reaction of benzylmercury chloride with the lithium salt of 2-nitropropane

The mercurial (2.0 g, 6 mmol) in 25 ml nitrogen-purged DMSO was introduced through a septum inlet into an aluminum foil-wrapped flask containing the nitronate salt (0.95 g. 10 mmol) in 75 ml nitrogen-purged DMSO. After stirring for 1 hour under a nitrogen atmosphere, the solution was acidified by injection of dilute aqueous hydrochloric acid. No metallic mercury was observed upon removal of the foil wrapping. The usual workup afforded benzylmercury chloride (95%) and some 2-nitropropane. No 2-methyl-2-nitro-1-phenylpropane could be detected in the isolate by ^{1}H N.M.R.

A control reaction (performed with sunlamp illumination on the uncovered reaction flask) afforded a 60% yield of coupled product after 1 hour.

11. Effect of di-*t*-butyl nitroxide on the reaction of benzylmercury chloride with the lithium salt of 2-nitropropane

The mercurial (2.0 g, 6 mmol), nitronate salt (0.95 g, 10 mmol) and di-*t*-butyl nitroxide (0.043 g, 0.3 mmol, 5 mole %) were dissolved in 100 ml nitrogen purged DMSO and the solution irradiated for 1 hour with a sunlamp. Only a trace of mercury metal was observed to precipitate. The usual workup afforded only starting mercurial. No coupled product was observed by ^{1}H N.M.R. of the isolate.

A control reaction (no added nitroxide) afforded a 60% yield of coupled product after 1 hour.

12. Effect of oxygen on the reaction of benzylmercury chloride with the lithium salt of 2-nitropropane

Benzylmercury chloride (1.09 g, 3 mmol) and the lithium salt of 2-nitropropane (0.7 g, 7 mmol) were dissolved in 50 ml DMSO. The solution was kept saturated with oxygen by foaming the gas through a glass frit placed at the bottom of the reaction flask. After 2 hours of sunlamp irradiation, no metallic mercury was observed. The solution was acidified with dilute aqueous hydrochloric acid and worked up in the usual manner. Benzylmercury chloride (90%) was recovered. No coupled product was detected by ^{1}H N.M.R. of the isolate.

13. Nature of the reacting mercury(II) species in the reaction of benzylmercury chloride with the lithium salt of 2-nitropropane

Benzylmercury chloride (50 mg, 0.1 mmol) and the lithium salt of 2-nitropropane (12 mg, 0.1 mmol) were dissolved in 0.5 ml d_6-DMSO in an N.M.R. tube in subdued roomlight. The ^{1}H N.M.R. spectrum exhibited only pure benzylmercury chloride (7.0-7.2 ppm, 5H; 2.97 ppm, 2H) and pure lithium nitronate (1.85 ppm).

The N.M.R. tube was irradiated for five-minute periods and the N.M.R. spectrum recorded after each period. Decreasing intensity of starting material signals and the formation of 2-methyl-2-nitro-1-phenylpropane were observed. No intermediate species were detected.

In a complementary experiment, benzylmercury chloride (1.0 g, 3 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) were dissolved in 40 ml DMSO in subdued roomlight. After stirring 10 minutes, the solution was poured into brine and worked up in the usual manner to afford 0.95 g N.M.R. pure benzylmercury chloride.

14. Reaction of n-hexylmercury halides with the lithium salt of 2-nitropropane

n-Hexylmercury chloride (0.2 g, 0.6 mmol) and the lithium salt of 2-nitropropane (0.3 g, 3.1 mmol) in 20 ml DMSO were reacted in the usual manner employing a 37 hour irradiation period. Workup afforded 0.1 g liquid found to contain a 90% yield of 2-methyl-2-nitrooctane by quantitative ^{1}H N.M.R. An analytical sample was obtained by preparative G.L.C. (1/4" x 5'; 20% DEGS; 140°C).

^{1}H N.M.R. ($CDCl_3$, δ) 6H (s) 1.57, 13H (m, broad) 0.85-2.1.

I.R. (neat, NaCl plates, cm^{-1}) 2920 (s), 1540 (s), 1470 (m), 1395 (m), 1370 (w), 1345 (w), 850 (m).

M.S. Calculated for C_9H_{19} (loss of NO_2): 127.14067. Measured: 127.14035. Error: 2.2 ppm.

Elemental analysis. Calculated for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.08. Found: C, 62.42; H, 10.91; N, 8.18.

n-Hexylmercury bromide (1.1 g, 3 mmol) and the lithium salt of 2-nitropropane (0.6 g, 6 mmol) in 25 ml DMSO were reacted in the usual manner employing a 70 hour irradiation period. The usual workup, including a washing of the ethereal extract with aqueous thiosulfate to remove remaining mercurials, afforded 0.32 g crude product determined by quantitative ^{1}H N.M.R. to contain a 50% yield of coupled product. A reaction with n-hexylmercury iodide on the same scale afforded 0.39 g crude isolate found to contain an 80% yield of product. The crude isolate was essentially pure 2-methyl-2-nitrooctane.

15. Reaction of cyclohexylmercury chloride with the lithium salt of 2-nitropropane

Cyclohexylmercury chloride (1.0 g, 3 mmol) and the lithium salt of 2-nitropropane (0.75 g, 8 mmol) dissolved in 30 ml DMSO were reacted in the usual manner employing a 34 hour irradiation period. The usual work-up included a thiosulfate wash to the ethereal extract to remove unreacted mercurial. Concentration of the extract afforded 0.45 g oil determined by quantitative ^{1}H N.M.R. to contain a 76% yield of 2-cyclohexyl-2-nitropropane. An analytical sample was obtained either by preparative G.L.C. (1/4" x 6'; 20% DEGS; 180°C) or by Kugelrohr distillation (55°C/0.1 torr) followed by recrystallization from pentane (large white needles, m.p. 46-47°C).

^{1}H N.M.R. ($CDCl_3$, δ) 6H (s) 1.55, 11H (m, broad) 0.6-2.4.

I.R. (KBr pellet, cm^{-1}) 2920 (s), 2840 (m), 1535 (s), 1450 (m), 1400 (m), 1375 (m), 1350 (m), 1340 (m), 840 (m).

M.S. Calculated for C_9H_{17} (loss of NO_2): 125.13303. Measured: 125.13251. Error: 4.2 ppm.

Elemental analysis. Calculated for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18; O, 18.69. Found: C, 62.85; H, 9.71; N, 8.08.

16. Reaction of cyclohexylmercury chloride with the lithium and potassium salts of nitrocyclohexane

Cyclohexylmercury chloride (0.25 g, 0.8 mmol) and the lithium salt of nitrocyclohexane (0.5 g, 4 mmol) in 60 ml DMSO were reacted in the usual manner employing a 60 hour irradiation period. The usual workup, including a thiosulfate wash of the ether extract, afforded 0.2 g oil. Quantitative G.L.C. analysis (1/8" x 5'; 5% SE-30; 170°C) using diphenylmethane as an internal standard (molar response of product/ standard = 0.89) showed the isolate to contain an 84% yield of 1-cyclohexyl-1-nitrocyclohexane.

Preparative scale reactions performed with the lithium nitronate suffered drastic reductions in yield. Improved results were obtained using the potassium salt. Thus, cyclohexylmercury chloride (6 mmol) and the potassium salt of nitrocyclohexane (prepared by dissolution of 10 mmol potassium _t_-butoxide and 10 mmol nitrocyclohexane in DMSO) were reacted in the usual manner in 60 ml DMSO employing a 100 hour irradiation period. The usual workup, including an aqueous thiosulfate wash of the ether extract, afforded 1.2 g crude product. Careful Kugelrohr distillation (90°C/0.4 torr) yielded 0.5 g of essentially pure white solid (38% yield). For analysis, a sample was recrystallized from pentane (m.p. 56-57°C).

^{1}H N.M.R. ($CDCl_3$, δ) 3H (broad) 2.2-2.6, 18H (broad) 0.85-2.0.

I.R. (nujol mull, NaCl plates, cm^{-1}) 1538 (vs), 1345 (m).

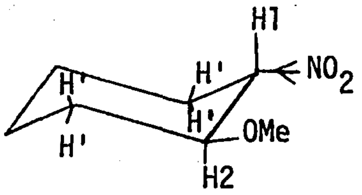
M.S. Calculated for $C_{12}H_{20}$ (loss of HNO_2): 164.15591. Measured: 164.15568. Error: 4.3 ppm.

Elemental analysis. Calculated for $C_{12}H_{21}NO_2$: C, 68.21; N, 10.02; N, 6.63; O, 15.14. Found: C, 67.97; H, 10.17.

17. Reaction of trans-1-chloromercury-2-methoxycyclohexane with the lithium salt of 2-nitropropane

trans-1-Chloromercury-2-methoxycyclohexane (1.0 g, 3 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) were reacted in the usual manner in 50 ml DMSO employing a 47 hour irradiation period. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.13 g crude material ground to contain a 14.5% yield of cis- and trans-2-methoxy-1-(α-nitroisopropyl)cyclohexane by quantitative ^1H N.M.R. The G.L.C. trace (1/8" x 5'; Carbowax 6000; 150°C) exhibited, among numerous impurities, two peaks in a ratio of 8:1 exhibiting highest mass fragments at m/e = 155 (loss of NO_2) and nearly identical fragmentation patterns. These were taken to be the cis and trans product isomers. The major (and first eluting) isomer was isolated by preparative G.L.C. (1/4" x 6'; 20% DEGS; 180°C).

^1H N.M.R. ($CDCl_3$, δ) 3H (s) 3.3, 1H (m) 2.8-3.15, 1H (m) 2.4-2.7, 4H (broad, m) 1.5-2.3, 4H (broad) 1.1-1.4, 3H (s) 1.6, 3H (s) 1.5. Note that the diastereotopic methyl groups exhibit distinct signals. The ^1H N.M.R. spectrum recorded at 100 MHz (on a Varian HA-100 instrument) allowed the assignment of trans stereochemistry to be made.



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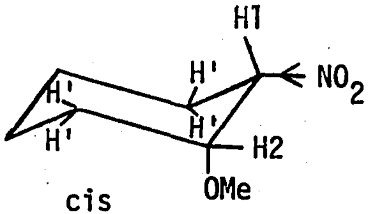


cis

Although the protons labeled H' exhibit an undefined signal ranging from 1.5-2.3 ppm, the H2 multiplet was fortuitously reduced to a 1:2:1 triplet ($J_H \sim 6.5$ Hz) by RF irradiation at 2.15 ppm. The triplet implies coupling to two trans protons. Such a condition only exists in the trans product.

I.R. ($CHCl_3$ solution, NaCl cells. cm^{-1}) 2940 (s), 2820 (s), 1540 (s), 1455 (m), 1380 (m), 1350 (m), 1115 (s), 1095 (s), 980 (m), 870 (m), 860 (m).

M.S. Calculated for $C_{10}H_{19}O$ (loss of NO_2): 155.14359. Measured: 155.14371. Error: 0.8 ppm.

18. Reaction between 2-chloromercurypropane and the lithium salt of 2-nitropropane

2-Chloromercurypropane (2.0 g, 7 mmol) and the lithium salt of 2-nitropropane (1.0 g, 10 mmol) were reacted in the usual manner in 40 ml DMSO employing a 17 hour irradiation period. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.59 g colorless liquid (63% yield) found by ^1H N.M.R. to be essentially pure 2,3-dimethyl-2-nitrobutane.

^1H N.M.R. ($CDCl_3$, δ) 1H (heptet, $J_H = 7$ Hz) 2.36, 6H (s) 1.51, 6H (d, $J_H = 7$ Hz) 0.93.

I.R. (neat, NaCl plates, cm^{-1}) 2980 (m), 1540 (s), 1460 (m), 1400 (m), 1390 (m), 1375 (m), 1350 (m), 1150 (w), 1080 (w), 855 (m).

M.S. Calculated for C_6H_{12} (loss of HNO_2): 84.093895. Measured: 84.09375. Error: 1.7 ppm.

2,3-Dimethyl-2-nitrobutane has been previously prepared and characterized by permanganate oxidation of the tertiary amine [66].

19. Effect of di-t-butyl nitroxide on the reaction of 2-chloromercurypropane and the lithium salt of 2-nitropropane

2-Chloromercurypropane (2.0 g, 7 mmol), the lithium salt of 2-nitropropane (1.0 g, 10 mmol), and 0.052 g (0.36 mmol, 5 mole %) di-t-butyl nitroxide in 40 ml DMSO were reacted as above for 17 hours. Workup afforded 0.14 g oil which proved to contain an 8% yield of 2,3-dimethyl-2-nitrobutane by quantitative ^{1}H N.M.R.

20. Reaction of allylmercury chloride with the lithium salt of 2-nitropropane

Allylmercury chloride (2.0 g, 7 mmol) and the lithium salt of 2-nitropropane (2.0 g, 21 mmol) in 60 ml DMSO were reacted in the usual fashion employing a 24 hour irradiation period. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.46 g (50% yield) of 4-methyl-4-nitro-1-pentene which proved to be ca. 95% pure by ^{1}H N.M.R. An analytical sample was obtained by preparative G.L.C. (1/4" x 6'; 20% DEGS; 120°C).

^{1}H N.M.R. ($CDCl_3$, δ) 3H (complex) 4.6-6.2, 2H (d, J_H = 6 Hz) 2.68, 6H (s) 1.62.

I.R. (neat, NaCl plates, cm^{-1}) 3100 (w), 3000 (m), 2960 (w), 1650 (w), 1550 (vs), 1475 (m), 1400 (m), 1380 (m), 1350 (s), 1000 (m), 930 (m), 860 (m).

M.S. Calculated for C_6H_{11} (loss of NO_2): 83.08608. Measured: 83.08592. Error: -1.9 ppm.

Elemental analysis. Calculated for $C_6H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84; O, 24.77. Found: C, 55,56; H, 8.71; N, 10.65.

21. Reaction of 6-chloromercury-1-hexene with the lithium and potassium salts of 2-nitropropane

6-Chloromercury-1-hexene (1.0 g, 3 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) in 30 ml DMSO were reacted in the usual manner employing a 48 hour irradiation period The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.2 g liquid. The crude isolate proved to contain a 35% yield of 1-cyclopentyl-2-methyl-2-nitropropane by quantitative ^{1}H N.M.R. and was 90% pure (by weight). No olefinic protons were observed in the spectrum. G.L.C. retention time matching (1/4" x 6'; 20 DEGS; 140°C) with an authentic sample as well as the G.C.M.S. fragmentation pattern identified a late-eluting peak to be 2-cyclohexyl-2-nitropropane (1.4% yield). An analytical sample of 1-cyclopentyl-2-methyl-2-nitropropane was obtained by preparative G.L.C. (1/4" x 6'; 20% DEGS; 140°C).

^{1}H N.M.R. ($CDCl_3$, δ) 6H (s) 1.59, 11H (broad, m) 0.68-2.18.

I.R. (neat, NaCl plates, cm^{-1}) 2960 (s), 2880 (m), 1540 (vs), 1475 (w), 1410 (w), 1400 (m), 1378 (m), 1352 (m), 860 (w).

The mass spectrum did not exhibit the parent ion. Measurement of the P-46 or P-47 ions was rendered impossible by incompletely resolved double peaks (<u>i</u>.<u>e</u>., C_9H_{16} and $C_8H_{14}N$ at 124, C_9H_{17} and $C_8H_{15}N$ at 125).

Elemental analysis. Calculated for $C_9H_{17}NO_2$: C, 63.13, H, 10.01; N, 8.18; O, 18.69. Found: C, 63.39; H, 10.16; N, 8.16.

A systematic effort was made to improve the yield of this reaction (Table VI). The reaction with lithium nitronate was not improved by variation of solvents. The sparingly-soluble potassium salt of 2-nitropropane in DMSO did afford an improved yield of 48% coupled product.

Table VI. Effect of solvent and counterion on the reaction of 6-chloromercury-1-hexene with the anion of 2-nitropropane

$$CH_2{=}CH(CH_2)_4HgCl + M^+O_2^-NCMe_2 \xrightarrow{\text{Solvent}} \underline{\text{cyclo}}\text{-}C_5H_9CH_2C(NO_2)Me_2$$

Solvent	M^+	Time[a]	% Yield (N.M.R.)
DMSO	Li^+	48 h	35
DMSO (dry)	Li^+	45 h	35
THF (dry)[b]	Li^+	17.5 h	0.0
DMF (dry)	Li^+	19.5 h	9
HMPA (dry)	Li^+	19.5 h	16
DMSO (dry)	K^{+c}	21 h	48

[a] Irradiation period with 275 watt sunlamp placed ca. 8 inches from the Pyrex reaction flask.

[b] The lithium nitronate appeared insoluble

[c] Generated from equivalent amounts of potassium-t-butoxide and 2-nitropropane.

22. Reaction of cyclopentylmethylmercury chloride with the lithium and potassium salts of 2-nitropropane

Cyclopentylmethylmercury chloride (1.0 g, 3 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) in 30 ml DMSO were reacted in the usual manner employing a 41 hour irradiation period. The usual workup, including an aqueous thiosulfate wash of the ether extract, afforded 0.2 g of crude isolate found to contain a 35% yield of 1-cyclopentyl-2-methyl-2-nitropropane. This compound exhibited the same ^{1}H N.M.R., I.R., and G.C.M.S. spectral features as the cyclopentyl product derived from 6-chloromercury-1-hexene. G.L.C. retention times were also found to be identical on 5% OV-3 and 5% Carbowax 20M columns.

The yield of 1-cyclopentyl-2-methyl-2-nitropropane was improved to 47% by the use of potassium as the counterion (potassium nitronate was prepared *in situ* by dissolving equivalent amounts of potassium-*t*-butoxide and 2-nitropropane in dry DMSO).

23. Reaction of methylmercury chloride with the lithium salt of 2-nitropropane

Methylmercury chloride (1.0 g, 4 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) in 15 ml DMSO were reacted in the usual manner for a 40 hour irradiation period. During the reaction, formation of *t*-nitrobutane was monitored by G.L.C. (1/4" x 12'; 15% OV-3; 80°C). After 40 hours, only a 2.1% yield of *t*-nitrobutane was detected. Only a small amount of mercury metal precipitated during the reaction. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 70 mg (17% yield based on methylmercury chloride) of 2,3-dimethyl-2,3-dinitrobutane.

24. Reaction of *t*-butylmercury chloride with the lithium salt of 2-nitropropane

t-Butylmercury chloride (1.0 g, 3.4 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) in 30 ml DMSO were reacted in the usual manner employing a 4 hour irradiation period. Mercury metal began to precipitate soon after sunlamp irradiation was applied. The usual workup afforded only 0.75 g (75% recovery) of pure *t*-butylmercury chloride. Thus, any products of the reaction were either volatile or water soluble. 2,3,3-Trimethyl-2-nitrobutane was evidently not formed.

25. Reaction of neopentylmercury chloride with the lithium salt of 2-nitropropane

No reaction occurred between the sterically hindered mercurial and the anion of 2-nitropropane with sunlamp initiation. Thus, neopentylmercury chloride (2.0 g, 6.4 mmol) and the lithium salt of 2-nitropropane (1.0 g, 10.6 mmol) in 100 ml nitrogen-purged DMSO were irradiated in a Rayonet RPR-100 photochemical reactor equipped with 16 "350 nm" bulbs at ambient reactor temperature for 21 hours. A small amount of mercury metal precipitated. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.29 g orange oil. G.C.M.S. analysis of the crude isolate revealed the major component to be bis[neopentylmercury] (parent ion observed at m/e = 342). A trace

(2-5% overall yield) of the expected product, 2,4,4-trimethyl-2-nitropentane (m/e = 113, loss of NO_2) was also observed.

26. Reaction of phenylmercury chloride with the lithium salt of 2-nitropropane

Phenylmercury chloride (2.0 g, 6 mmol) and the nitronate salt (0.95 g, 10 mmol) in 20 ml DMSO were irradiated in the usual manner for 15 hours during which time a trace of mercury metal was observed to precipitate. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 100 mg of 2,3-dimethyl-2,3-dinitrobutane. No 2-nitro-2-propane was observed.

In an attempt to stimulate coupling with phenyl radicals generated by addition of sodium borohydride, sodium borohydride (0.018 g, 0.5 mmol) dissolved in 25 mmol nitrogen-purged dry DMSO was added dropwise to a stirred solution of phenylmercury chloride (3.0 g, 9.6 mmol) and the lithium salt of 2-nitropropane (1.8 g, 19 mmol) in 125 ml nitrogen-purged DMSO. The time for sodium borohydride addition was 30 minutes. During the addition, the reaction flask was irradiated with a 275 watt sunlamp. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 200 mg solid which proved by quantitative ^1H N.M.R. to contain 180 mg 2,3-dimethyl-2,3-dinitrobutane. No 2-nitro-2-phenylpropane was observed.

27. Reaction of *o*-allyloxyphenylmercury chloride with the lithium salt of 2-nitropropane

o-Allyloxyphenylmercury chloride (1.0 g, 2.7 mmol) and the lithium salt of 2-nitropropane (0.5 g, 5 mmol) in 30 ml DMSO were reacted in the usual manner employing a 23.5 hour irradiation period. Mercury metal was observed to precipitate after about 10 minutes of sunlamp irradiation. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.38 g solid. Quantitative ^{1}H N.M.R. determined the crude isolate to consist largely of bis[*o*-allyloxyphenyl]mercury (17% yield) and 2,3-dimethyl-2,3-dinitrobutane (39% yield based on mercurial). The identification of the bis[organo]mercury was certain as the authentic compound had been synthesized. Some polymeric material was noted during this workup and discarded.

28. Reaction of (*E*)-3.3-dimethyl-1-butenylmercury chloride with the lithium salt of 2-nitropropane

The mercurial (1.0 g, 3 1 mmol) and the lithium salt of 2-nitropropane (1.0 g, 10 mmol) in 40 ml DMSO were reacted in the usual manner employing a 16 hour irradiation period during which time mercury metal precipitated. The usual workup (thiosulfate *was* *not* employed as it symmetrizes vinyl mercurial halides) afforded 0.62 g crude isolate determined by ^{1}H N.M.R. to contain 2,3-dimethyl-2,3-dinitrobutane (52%) and bis[(*E*)-3,3-dimethyl-1-butenyl]mercury (82%). The G.C.M.S. of the mercurial exhibited the parent ion at m/e = 366. Identity of the mercurial was further verified by spectral comparison with the authentic compound prepared independently.

Symmetrization was found not to occur immediately upon mixing. When the mercury halide (33 mg, 0.1 mmol) and nitronate salt (14 mg, 0.15 mmol) were dissolved in 0.5 ml d_6-DMSO, the ^{1}H N.M.R. spectrum showed the starting (E)-3,3-dimethyl-1-butenylmercury halide to be present, not the symmetrized mercurial.

This symmetrization process was found to require light. When the 3.1 mmol-scale reaction was performed without sunlamp illumination in an aluminum foil-wrapped flask, workup after 18 hours afforded only 0.95 g (95% recovery) of pure (E)-3,3-dimethyl-1-butenyl mercury.

29, Effect of styrene on the reductive symmetrization of (E)-3,3-dimethyl-1-butenylmercury chloride by nitronate ion

The mercurial (1.0 g, 3 mmol), the lithium salt of 2-nitropropane (0.6 g, 6 mmol), and freshly distilled styrene (0.42 g, 4 mmol) were dissolved in 40 ml dry, nitrogen-purged DMSO and the solution irradiated with a 275 watt sunlamp for 17 hours. After the first few minutes, mercury metal was observed. The usual workup afforded 1.4 g liquid determined by ^{1}H N.M.R. to contain styrene (80% recovery), 2,3-dimethyl, 2,3-dinitrobutane (43% yield based on mercurial) and bis[(E)-3,3-dimethyl-1-butenyl]mercury (93%).

30. Effect of di-t-butylnitroxide on the nitronate-induced reductive symmetrization of (E)-3,3-dimethyl-1-butenylmercury bromide

The mercurial (1.1 g, 3 mmol) and lithium salt of 2-nitropropane (0.5 g, 5 mmol) were dissolved in 25 ml dry, nitrogen-purged DMSO containing di-t-butylnitroxide (0.72 g, 5 mmol) and the solution irradiated 40 hours, during which time mercury metal was observed to precipitate. The usual workup afforded an oil containing a large amount of the nitroxide, rendering N.M.R. analysis impossible due to paramagnetic line broadening. Quantitative G.L.C. determined the yield of bis[(E)-3,3-dimethyl-1-butenyl]mercury to be 39% (dibenzyl ether was employed as internal standard, molar response of product:ether = 1.15). Pure (E)-3,3-dimethyl-1-butenylmercury bromide in acetone was not symmetrized on the column employed (1/8" x 5'; 5% OV-3), but the possibility exists that symmetrization did occur in the medium of the crude isolate upon G.L.C. injection.

31. Reaction of mercuric chloride with the lithium salt of 2-nitropropane

Mercuric chloride (1.4 g, 5.3 mmol) was added to 40 ml nitrogen-purged DMSO containing the lithium salt of 2-nitropropane (1.5 g, 16 mmol). A rapid exothermic reaction occurred with the precipitation of metallic mercury. Extraction of product from brine afforded 0.3 g (32% yield) of essentially pure 2,3-dimethyl-2,3-dinitrobutane.

32. Reaction of benzylmercury chloride with diethyl phosphite ion

The mercurial (1.0 g, 3 mmol) was added to a solution containing potassium t-butoxide (0.4 g, 3,6 mmol) and diethyl phosphite (0.55 g, 4 mmol) in 30 ml dry, nitrogen-purged DMSO. The reaction mixture was irradiated 39.5 hours with a 275 watt sunlamp during which time mercury metal slowly precipitated. The usual workup, including an aqueous thiosulfate was of the ethereal extract afforded 0.23 g (84% yield) of essentially pure bibenzyl identified by comparison with an authentic sample of ^{1}H N.M.R. and I.R. spectra as well as G.L C. retention times.

The same reaction performed in the absence of light after 39.5 hours resulted in the isolation of a 51% yield of bis[benzyl]mercury identified by spectral comparison with the authentic compound. No bibenzyl was isolated. It was subsequently found that a quantitative yield of bis[benzyl]mercury could be obtained by working up the reaction mixture after a few minutes of stirring.

The same reaction performed in DMSO that was kept saturated with oxygen still precipitated mercury metal. The usual workup afforded a liquid found by ^{1}H N.M.R. to be a mixture of benzoic acid, benzaldehyde, and benzyl alcohol (acidic, aldehydic and alcoholic protons were observed). A trace (1.7% overall yield) of bibenzyl also was observed.

Traces of di-t-butyl nitroxide were found to reduce bibenzyl yields stoichiometrically. The results are tabulated in Table III.

Bis[benzyl]mercury is not decomposed to bibenzyl by diethyl phosphite ion. When bis[benzyl]mercury (0.5 g, 1.3 mmol) and diethyl phosphite potassium salt (2.7 mmol, from the action of potassium t-butoxide on diethyl phosphite) in 25 ml dry, nitrogen-purged DMSO were irradiated 19 hours, extensive precipitation of mercury metal occurred. The usual workup afforded a 41% recovery of bis[benzyl]mercury. No bibenzyl was isolated.

Irradiation for 46 hours of a solution containing diethyl phosphite potassium salt (5.3 mmol), mercuric chloride (2.6 mmol) and bis[benzyl]mercury (1.3 mmol) added in listed sequence to 40 ml dry, nitrogen-purged DMSO resulted in the isolation of a 92% yield of bibenzyl.

33. Reaction of *n*-hexylmercury chloride with diethyl phosphite ion

Hexylmercury chloride (1.0 g, 3.1 mmol) and potassium diethyl phosphite (from 4.0 mmol diethyl phosphite and 3.6 mmol potassium *t*-butoxide) in 30 ml dry, nitrogen-purged DMSO was subjected to 39.5 hours of sunlamp irradiation during which time mercury metal slowly precipitated from solution. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.12 g oil. Comparison with an authentic sample by G.L.C. retention times revealed the isolate to be a complex mixture containing no (<1%) n-dodecane.

34. Reaction of cyclohexylmercury chloride with diethyl phosphite ion

Cyclohexylmercury chloride (1.0 g, 3.1 mmol) and potassium diethyl phosphite (from potassium *t*-butoxide (3.6 mmol) and diethyl phosphite (4.0 mmol) in 30 ml dry, nitrogen-purged DMSO was subjected to 70 hours of sunlamp irradiation during which time a trace of mercury precipitated. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.1 g crude oil. G.C.M.S revealed no dicyclohexyl in the complex mixture.

35. Reaction of 2-chloromercurycyclohexanone with diethyl phosphite ion

2-Chloromercurycyclohexanone (1.0 g, 3 mmol) and potassium diethyl phosphite (from potassium *t*-butoxide (3.6 mmol)) and diethyl phosphite

(4.0 mmol) in 20 ml dry, nitrogen-purged DMSO was subjected to 8.5 hours of sunlamp irradiation during which time mercury metal precipitated rapidly. The usual workup, including an aqueous thiosulfate wash of the ethereal extract, afforded 0.13 g light yellow liquid which proved to be nearly pure cyclohexanone (44% yield). Identification was made based on N.M.R., I.R., G.L.C., and G.C.M.S. comparisons with authentic cyclohexanone. The yield of cyclohexanone was undoubtedly lowered by loss during removal of the ethyl ether at 20 torr during workup.

IV. CONCLUSION TO PART I

Two quite different examples of the $S_{RN}1$ process have been described. The coupling of dialkyl phosphite ions with α-nitro halides and sulfones produces α-nitroalkylphosphenate esters. The reaction, which initiates via a remarkably facile thermal process, is the first general route to this virtually unexplored class of compounds. Anions of secondary aliphatic nitro compounds couple with alkylmercury halides to form tertiary nitroparafins. This photochemically initiated process is the first recognized organometallic $S_{RN}1$ reaction. Several $S_{RN}1$-type nucleophiles fail to couple with alkyl mercurials, although some anions reduce benzylmercury chloride to bibenzyl. Aryl- and vinylmercury halides undergo photo-symmetrization with nitronate ion instead of substitution.

PART II: SUBSTITUTION REACTIONS OF VINYL MERCURIALS

I. INTRODUCTION TO SUBSTITUTION REACTIONS OF VINYL MERCURIALS

The carbon-mercury bond of alkyl, aryl, and vinyl mercurials is subject to cleavage by strong electrophilic reagents. Acidolysis, halogenolysis, and related reactions common to organomercurials have been extensively studied and reviewed [20,21,67]. Recently, transformations of aryl and alkyl mercurials have been achieved by the mediation of transition metal complexes [68].

Two electrophilic cleavage reactions have been reported in which the carbon-carbon double bond exhibits special participation. Brominolysis of vinylmercury bromides in carbon disulfide solvent results in vinyl bromides of reversed stereochemistry [69]. The investigators proposed an initial anti addition of bromine across the double bond followed by anti elimination of mercuric bromide. The Lewis acid catalyzed acylation of vinyl mercurials was found to proceed via addition of an "acyl cation" to the $\underline{\alpha}$-carbon of the double bond and subsequent elimination of mercury salt from the intermediate $\underline{\beta}$-mercury cation [70].

Foster and Tobler found that a number of weak Brönsted acids react thermally with bis[ethenyl]mercury to produce ethylene, mercury metal, and a substituted ethylene (Eq. 23) [71,72,73] where X = SR, SC(=O)CH,

$$(CH_2{=}CH)_2Hg + HX \xrightarrow{\Delta} CH_2{=}CH_2 + CH_2{=}CHX + Hg^\circ \qquad (23)$$

OPh, O_2CR, and O_2SPhMe-p. The pyrolyses were generally performed without solvent at 100-200°C. In certain cases, the reaction could be stopped at partial completion and good yields of an intermediate species,

CH_2=CHHgX, isolated. The vinylmercury salts CH_2=CHHgSR, CH_2CHHgO_2CR, R'CH=CR'HgO_2CR, and CH_2=CHHgSCN were decomposed with loss of mercury metal at 100-200°C to CH_2=CHSR, CH_2=CHO_2CR, R'CH=CR'O_2CR, and CH_2CHSCN and CH_2C=CHNCS. Studies with substituted vinylmercury acetates revealed the reductive elimination of mercury metal to proceed with loss of stereochemistry. Russian workers have extended the reaction of Equation 23 to include $X^-=(EtO)_2P(=O)O^-$, $MeP(=O)(OR)O^-$, $(RO)_2P(=S)S^-$, $C_nF_{2n+1}CO_2^-$, and $(CF_3)_2C=NO^-$ [74,75]. The reactions of bis[ethenyl]-mercury with fluorocarbon carboxylic acids were performed at 180°C with added hydroquinone.

The following chapters describe a set of substitution reactions peculiar to vinyl mercurials. These transformations have the appearance of common carbon-metal bond cleavage reactions (reductive elimination, electrophilic cleavage, reductive coupling), but the vinyl moiety is essential in each case. A general mechanism describing the special activation of vinylmetallics is proposed.

II. REACTION OF MERCAPTIDE ION WITH VINYLMERCURY SALTS TO FORM VINYL SULFIDES: PHOTOCHEMICAL ELIMINATION OF MERCURY METAL FROM VINYLMERCURY MERCAPTIDES

A. Introduction

Mercaptide ions or mercaptans react readily with organomercury halides to give organomercury mercaptides (Eq. 24) [76,77]. Similarly,

$$R^1HgX + R^2S^-(R^2SH) \longrightarrow R^1HgSR^2 + X^-(HX) \qquad (24)$$

diorgano mercurials react with mercaptans upon heating to afford organomercury mercaptides and the reduced organic fragment (Eq. 25) [71,72,78].

$$R^1_2Hg + R^2SH \xrightarrow{\Delta} R^1HgSR^2 + R^1H \qquad (25)$$

Mercaptan derivatives of aryl and alkyl mercurials are stable, well-characterized compounds. Although Foster and Tobler [71,72] found that vinylmercury mercaptides could be pyrolyzed to vinyl sulfides and mercury metal, we were startled to discover the transformation to occur at room temperature in dilute solution under irradiation from an ordinary sunlamp (Eq. 26). The reaction was rapid (several hours) and generally

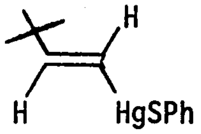
$$R^1HgSR^2 \xrightarrow{\text{light}} R^1SR^2 + Hg^\circ \qquad (26)$$

quantitative. The scope and mechanistic detail of this photochemical reductive elimination are presented in the following section.

B. Results and Discussion

1. Preparation of vinylmercury mercaptides

The sodium salt of thiophenol and (*E*)-3,3-dimethyl-1-butenyl mercury chloride in DMSO reacted upon mixing. The usual workup (extraction of organic products from brine/DMSO with ethyl ether) was accompanied by noticeable precipitation of mercury metal. The crude gray oil obtained by concentration of the ethereal extract was determined by ^{1}H N.M.R. to contain two organic compounds, (*E*)-3,3-dimethyl-1-butenylmercury thiophenoxide (13) and (*E*)-3,3-dimethyl-1-butenyl phenyl sulfide (14). The ratio of 14 to 13 increased during storage in roomlight. Conversion of 13 to 14 was accelerated by sunlamp irradiation and did not occur in the dark.



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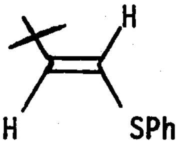

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Pure vinylmercury mercaptides (Table VII) were prepared by addition of a small amount (*ca.* 0.5 mole % based on mercury) of di-*t*-butyl nitroxide to the DMSO solvent prior to the introduction of vinylmercury halide and mercaptide ion. Workups were performed in subdued roomlight. Those vinylmercury mercaptides which were solids were recrystallized from hexane or hexane/benzene in the dark. Oils were evacuated for one or two hours at 0.1 torr to remove traces of the volatile nitroxide and were carefully protected from light.

Table VII. Preparation of vinylmercury mercaptides

$$R^1HgX + R^2S^- \xrightarrow{DMSO^a} R^1HgSR^2 + X^-$$

R^1HgX	R^2S^{-b}	% Yield[c]	m.p./°C
(E)-$Me_3CCH{=}CHHgCl$	PhS^-	97 (83)	55-55.5
(E)-$Me_3CCH{=}CHHgCl$	n-$C_4H_9S^-$	100	44.5-46
(E)-n-$C_3H_5CH{=}CHHgCl$	PhS^-	94	oil
(E)-$PhCH{=}CHHgCl$	PhS^-	100 (86)	103-105 (dec.)
$Ph_2C{=}CHHgBr$	PhS^-	96	oil
$Ph_2C{=}C(Me)HgBr$	PhS^-	91 (81)	129-130
$CH_2{=}C(HgBr)CH_2$(cyclo-C_6H_{11})	PhS^-	98	oil

[a] Solvent contains *ca.* 0.5 mole % (based on mercurial) of di-*t*-butyl nitroxide.

[b] Prepared *in situ* from equimolar quantities of potassium *t*-butoxide and the mercaptan.

[c] Crude yield. Recrystallized yield in parentheses.

Solid vinylmercury mercaptides are generally light-stable. Compound 13 was stored in an ordinary vial exposed to air and roomlight for six months without graying. The solid (E)-2-phenyl-1-ethenylmercury thiophenoxide, on the other hand, grayed perceptibly after a few days. Oils and solutions of vinylmercury mercaptides began to precipitate mercury metal after a few minutes of exposure to roomlight unless a "stabilizer" such as di-t-butyl nitroxide was added.

Attempts to prepare vinylmercury selenides failed. Alkenylmercury halides were symmetrized by phenyl selenide ion; the diorgano mercurial and mercury(II) phenyl selenide were isolated (Eq. 27). Likewise,

$$2R^1MgX + 2PhSe^- \xrightarrow{DMSO} R^1_2Hg + PhSeHgSePh \qquad (27)$$

efforts to prepare alkynylmercury mercaptides were unsuccessful. Addition of thiophenoxide ion to a DMSO solution containing bis[phenylethynyl]mercury and mercuric chloride afforded bis[phenylethynyl]mercury and mercury(II) thiophenoxide. Heating bis[phenylethynyl]mercury and thiophenol also produced mercury(II) thiophenoxide.

2. Photochemical decomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide (13)

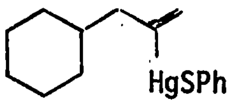
Pure 13 in deoxygenated DMSO was completely decomposed to 14 and mercury metal by four hours of sunlamp irradiation (Table VIII). The alkenyl sulfide was isolated as a light-yellow oil in 98% yield. The crude isolate was pure by N.M.R. and G.L.C. Quantitative short-path distillation effectively removed the yellow tinge to afford the colorless alkenyl sulfide. Only the E isomer was observed in the ^{1}H N.M.R. spectrum.

When volatile solvents were employed, the isolation of vinyl sulfides was greatly facilitated. (E)-3,3-dimethyl-1-butenylmercury thiophenoxide (13) was thus converted essentially quantitatively to 14 in ethyl ether and benzene under sunlamp irradiation. The workup consisted of decanting the reaction solution from the beads of mercury, rinsing the mercury with portions of solvent, and concentrating the combined solution under vacuum. Benzene was selected as the solvent of choice. Ether afforded a crude isolate containing approximately two percent impurity by ^{1}H N.M.R. and G.L.C.

3. Photochemical decomposition of other vinylmercury mercaptides

Results of the photochemical decomposition of a variety of vinylmercury mercaptides are summarized in Table VIII. In general, the conversion to the organosulfide was quantitative. The three exceptions bear discussion.

1-(Cyclohexylmethyl)-1-ethenylmercury thiophenoxide (15) failed to



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decompose significantly under ordinary sunlamp irradiation. Exposure for 5.5 hours to fourteen "350 nm" bulbs in a Rayonet RPR-100 photoreactor induced complete precipitation of mercury metal. The crude isolate was found to contain approximately 80% of the expected alkenyl

Table VIII. Photochemical decomposition of vinylmercury mercaptides to vinyl sulfides and mercury metal

$$R^1HgSR^2 \xrightarrow{\text{light}} R^1SR^2 + Hg^\circ$$

R^1HgSR^2	Solvent	Time[a]	% Yield (stereochemistry)[b]
(*E*)-Me_3CH=CHHgSPh	DMSO	4 h	98 (>98% *E*)
(*E*)-Me_3CH=CHHgSPh	Et_2O	15.5 h	98 (>98% *E*)
(*E*)-Me_3CH=CHHgSPh	PhH	3 h	100 (>98% *E*)
(*E*)-PhCH=CHHgSPh	PhH	6 h	100 (*E*:*Z* = 91:9)
(*E*)-*n*-C_3H_5CH=CHHgSPh	PhH	4 h	100[c]
Ph_2C=CHHgSPh	PhH	15.5 h	100
Ph_2C=C(Me)HgSPh	PhH	10 h	100
(*E*)-Me_3CCH=CHHgS-*n*-C_4H_9	PhH	6 h	100 (>98% *E*)
CH_2=C(HgSPh)CH_2(*cyclo*-C_6H_{11})	PhH	---[d]	80[d]
PhHgSPh	PhH	---[e]	2[e]
PhCH_2HgSPh	PhH	15.5 h	2[f]

[a] Irradiation period with 275 watt sunlamp placed 6-10 inches from the Pyrex reaction vessel. All reactions were performed under nitrogen at ambient temperature (25-40°C).

[b] Isolated yield of pure material. Stereochemistry by ^1H N.M.R.

[c] Unidentified stereoisomers produced in a ratio of 46:54 (glass capillary G.L.C.).

[d] Irradiated with sunlamp for 2 hours and Rayonet RPR-100 (equipped with fourteen (350 nm" bulbs) for 5.5 hours. Approximate yield of impure product based on G.C.M.S.

[e] Irradiated with sunlamp 15 hours and Rayonet RPR-100 (equipped with fourteen "350 nm" bulbs) for 9 hours. Yield determined by quantitative G.L.C. of crude isolate.

[f] Yield by quantitative ^1H N.M.R. of the crude isolate.

sulfide and 20% of an unidentified impurity by G.C.M.S. Compound **15** is distinguished by the bulky alkyl substituent *α* to mercury. The photodecomposition reaction appears insensitive to substitution in the *β* position.

Included in Table VIII for comparison are the photodecompositions of phenyl- and benzylmercury thiophenoxide. The Rayonet reactor was required to decompose the aryl mercurial. Quantitative G.L.C. of the crude isolate indicated that diphenyl sulfide was generated in 2% yield (at most). The benzyl mercurial decomposed appreciably under sunlamp illumination, but also afforded at most 2% of the expected benzyl phenyl sulfide. The photochemical reductive elimination of mercury from organomercury mercaptides appears limited to alkenyl mercurials.

The mercaptide derivatives of (*E*)-3,3-dimethyl-1-butenylmercury decomposed stereoselectively to the (*E*)-alkenyl sulfides (Table VIII). In contrast, (*E*)-2-phenyl-1-ethenylmercury thiophenoxide afforded (*E*)- and (*Z*)-alkenyl sulfides, identifiable by ^{1}H N.M.R. vinyl proton absorptions and separable by glass capillary G.L.C., in a ratio of 91:9. (*E*)-1-pentenylmercury thiophenoxide afforded two isomers similarly separable by G.L.C. in a 54:46 ratio, but isomer assignments were precluded by the complexity of the ^{1}H N.M.R. spectrum. These examples serve to illustrate that the reaction is only completely stereoselective for (*E*)-1-alkenylmercury mercaptides when a sufficiently bulky *β*-substituent favors the formation of the (*E*)-1-alkenyl sulfide. Any mechanism proposed for this reaction must account for stereochemical interconversion of the double bond.

4. In situ generation and photochemical decomposition of vinylmercury mercaptides

(E)-3,3-dimethyl-1-butenylmercury acetate was observed to react spontaneously with thiophenol to produce 13 and acetic acid in d_6-benzene monitored by ^1H N.M.R. (Eq. 28). Sunlamp irradiation induced

$$(E)\text{-Me}_3\text{CCH=CHHgOAc} + \text{PhSH} \xrightarrow{d_6\text{-benzene}} (E)\text{-Me}_3\text{CCH=CHHgSPh} + \text{HOAc} \qquad (28)$$

precipitation of mercury metal and the vinylmercury mercaptide was quantitatively converted to the vinyl sulfide 14. The reaction proceeded equally well on the millimole scale (Table IX).

The analogous reaction of mercaptan with vinylmercury halides releases hydrogen halide. The mineral acid was found to be scavenged conveniently by solid sodium bicarbonate suspended in the benzene solvent. Thus, the addition of a mercaptan to a suspension (magnetic stirring) of sodium bicarbonate in a benzene solution containing the vinylmercury halide resulted in the gentle evolution of carbon dioxide over a period of about 5 minutes. Mercury metal precipitated under sunlamp illumination. The benzene solution was decanted from the residue of mercury metal and inorganic salts. The residue was washed with benzene and the combined solution concentrated under vacuum. (Excess mercaptan was generally removed by vacuum. When insufficiently volatile, mercaptans were conveniently removed from benzene solution by aqueous carbonate extraction.) In some cases, the workup afforded a trace of solid mercuric mercaptide salt along with the vinyl sulfide. This was apparently due to the use of mercaptans contaminated with the

Table IX. Preparation of vinyl sulfides by photochemical decomposition of vinylmercury mercaptide generated *in situ*

$$R^1HgX + R^2SH \xrightarrow[NaHCO_3]{light/PhH} R^1HgSR^2 + Hg^\circ$$

R^1HgX	R^2SH	Time[a]	% Yield (stereochemistry)[b]
(*E*)-$Me_3CCH{=}CHHgOAc$[c]	PhSH	3 h	100 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	PhSH	17 h	99 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgOAc$[c]	$PhCH_2SH$	18 h	97 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	$PhCH_2SH$	5 h	64 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	Me_3CSH	15 h	100 (>98% *E*)
(*E*)-$PhCH{=}CHHgCl$	*n*-C_4H_9SH	3 h	100 (>95% *E*)
$CH_2{=}CHHgCl$	PhSH	3 h	100
(*E*)-$EtC(OAc){=}CHHgCl$	PhSH	11 h	92[d]
(*E*)-$HOCH_2C(Cl){=}CHHgCl$	PhSH	5.25 h	61[d]
(*E*)-$Me_3CCH{=}CHHgCl$	$CH_3C({=}O)SH$	17 h	43[e]
(*E*)-$Me_3CCH{=}CHHgCl$	$HSCH_2COOH$	7 h	0[f]

[a] Irradiation period with a 275 watt sunlamp placed 6-10 inches from the Pyrex reaction vessel. Reactions were performed in benzene under nitrogen at ambient temperature (25-40°C) with a 2-3-fold molar excess of solid sodium bicarbonate present

[b] Yield of pure sulfide. Stereochemistry by ^1H N.M.R.

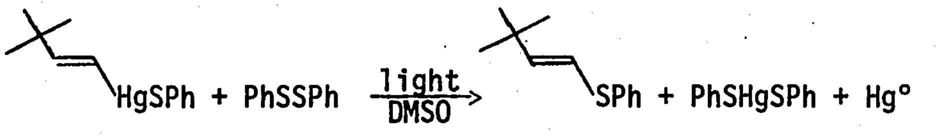
[c] No sodium bicarbonate was employed.

[d] Stereochemistry not determined.

[e] Black precipitate (HgS) observed instead of mercury metal.

[f] No mercury metal observed. White precipitate formed upon mixing.

disulfide. Compound **13** in the presence of diphenyl disulfide afforded **14** in good yield, but most of the mercury was recovered as mercury(II) thiophenoxide (Eq. 29). The reactions of disulfides with vinylmercury



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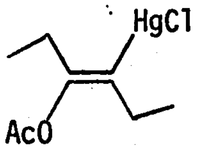
13 **14** (trace)

salts is discussed in detail in Chapter III, Part II of this thesis. Mercuric mercaptide salts were readily separated from vinyl sulfides by simply taking the organic sulfide into hexane. The mercury salt was then removed by filtration.

Some interesting vinyl sulfides were prepared by the in situ method (Table IX). Ethenylmercury chloride vinylated thiophenol quantitatively, although the product is sensitive to radical and cationic polymerization. (The isolated ethenyl phenyl sulfide did in fact polymerize after storage for several days at room temperature.) (E)-2-(acetyloxy)-1-ethyl-1-butenylmercury chloride (**16**) reacted with



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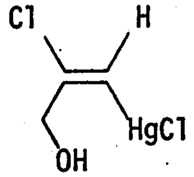

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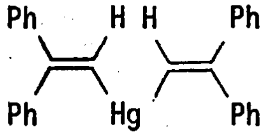
thiophenol to afford a high yield (92%) of the vinyl sulfide purified by Kugelrohr distillation. The highly functionalized (E)-2-chloro-3-hydroxy-1-propenylmercury chloride (**17**) reacted with thiophenol to afford, after distillation, the pure vinyl sulfide as a colorless oil in 61% yield. The modest yield was due to thermal decomposition during distillation. This vinyl sulfide decomposed at room temperature within a few days to a red-brown tar.

Attempts to prepare vinyl ethers by reactions similar to those employed for vinyl sulfides were unsuccessful. Phenol did not react photochemically with (*E*)-3,3-dimethyl-1-butenylmercury acetate in benzene. Neither did sodium phenoxide react with (*E*)-3,3-dimethyl-1-butenylmercury chloride in DMSO under the influence of "350 nm" Rayonet radiation to precipitate metallic mercury.

5. Attempted photochemical decomposition of other vinylmercury compounds

The sensitivity of vinylmercury mercaptides to light is not characteristic of vinylmercury compounds in general. Bis[2,2-dimethylethenyl]mercury (**18**) in benzene, 2,2-diphenylethenylmercury bromide (**19**) in benzene, (*E*)-3,3-dimethyl-1-butenyl mercury acetate (**20**) in benzene, and (*E*)-3,3-dimethyl-1-butenylmercury chloride (**21**) in DMSO were stable towards prolonged irradiation in a Rayonet reactor at 350 nm.



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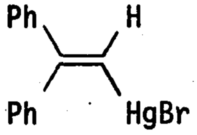

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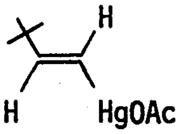

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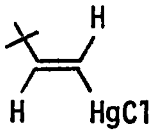

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Although this survey is far from exhaustive, the stability of 20 suggests only a limited correlation between the photochemical and thermal [71-75] reductive elimination reactions of vinyl mercurials.

6. Inhibition of the photodecomposition of (*E*)-3,3-dimethyl-1-butenylmercury thiophenoxide (13)

Table X summarizes a series of experiments performed to determine the effect of a series of additives on the photodecomposition of 13 in DMSO. The standard reaction conditions included the use of a water cooled Pyrex reaction vessel thermostated at 25°C and a 30 minute irradiation period in a Rayonet RPR-100 photoreactor equipped with fourteen "350 nm" bulbs. It was found that after irradiation, the solutions could be stabilized towards further reaction by the addition of a small amount of di-*t*-butyl nitroxide.

Of particular interest is the powerful inhibitory effect of 5 mole percent di-*t*-butyl nitroxide and 25 mole percent sodium thiophenoxide. Regardless of their mode of operation, these inhibitors apparently do not function in a stoichiometric fashion. That is, the photochemical reductive elimination reaction is a chain process. Oxygen, an effective scavenger for many free radicals, essentially prevented photodecomposition. A series of salts, potassium diethyl phosphite, sodium p-toluenesulfinate, and lithium 2-nitropropanate, were found to slow the reaction. The most effective of these was the nitronate salt which essentially stopped the photodecomposition completely.

Table X. Effect of additives on the photochemical decomposition of (*E*)-3,3-dimethyl-1-butenylmercury thiophenoxide in DMSO[a]

$$(\underline{E})\text{-Me}_3\text{CCH=CHHgSPh} + \text{additive} \xrightarrow[\text{light}]{\text{DMSO}}$$

Additive (mmol)	% Yield Sulfide	% Recovered starting material
None	75[b]	19[b]
PhS^-Na^+ (0.76)	1	80
PhS^-Na^+ (3.03)	6	80
$(EtO)_2PO^-K^+$ (4.5)[c]	10	73
p-$MePhSO_2{}^-Na^+$ (3.1)	12	85
$Me_2C{=}NO_2{}^-Li^+$ (3.0)	2	98
di-*t*-butyl nitroxide (0.15)	0	92
oxygen (saturated solution)	5	92

---

[a] All reactions were performed with 3.06 mmol mercurial in 50 ml dry, nitrogen purged DMSO in a water-cooled Pyrex reaction vessel. The light source was a Rayonet RPR-100 reactor (equipped with fourteen "350 nm" bulbs). Each solution was irradiated 30 minutes at 25°C and then quenched with di-*t*-butyl nitroxide.

[b] Average of four trials. Standard deviation of product yield is ±11%; standard deviation of mercurial recovery is ±13%.

[c] Prepared *in situ* from equimolar amounts of potassium *t*-butoxide and diethyl phosphite.

7. Failure of thiophenol to affect the photodecomposition of vinylmercury mercaptides

Some radical scavengers such as di-*t*-butyl nitroxide, galvinoxyl, and oxygen generally inhibit radical chain process by coupling with reactive radical intermediates to produce relatively inert species (Eq. 30). Hydrogen transfer agents, however, intercept radicals by

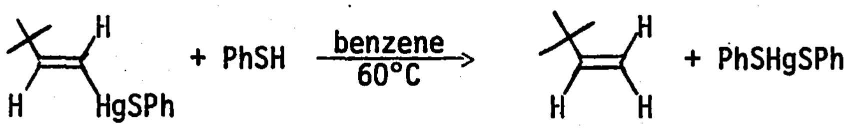
$$R\cdot + \text{Scavenger} \longrightarrow \text{R-Scavenger} \qquad (30)$$

donating a hydrogen atom generating a diamagnetic species and a relatively inert paramagnetic residue. Mercaptans are efficient hydrogen transfer agents (Eq. 31). Thiophenol traps phenyl radical in

$$R\cdot + R^1SH \longrightarrow RH + R^1S\cdot \qquad (31)$$

carbon tetrachloride at a rate of $1.9 \times 10^9\ M^{-1}\ s^{-1}$ [79]. This rate is within a factor of 10 of the diffusion controlled limit. If vinyl-type radicals are involved in the photodecomposition of vinylmercury mercaptides, similarly effective radical scavenging by thiophenol would be expected.

Interestingly, the presence of excess mercaptan from the *in situ* generation of vinylmercury mercaptides did not prevent subsequent facile photodecomposition (Table IX). In fact, thiophenol present in over 100 mole percent (based on mercurial) had no effect on the decomposition of **13** in benzene or DMSO at room temperature (see Experimental Section). Quantitative yields of **14** were obtained, initiation appeared normal (1 or 2 minute induction period), and the thiophenol survived the complete reaction intact (as followed by ^{1}H N.M.R.). When a solution of **13** and thiophenol in d$_6$-benzene containing di-*t*-butyl nitroxide was heated in the dark at 60°C, the thiophenol reacted with the mercurial (protonolysis) to afford 3,3-dimethyl-1-butene (Eq. 32).



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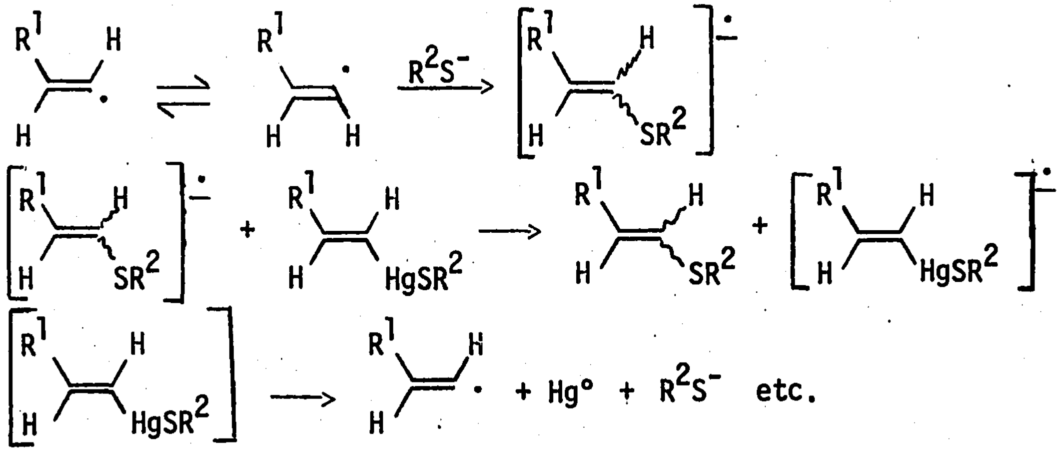
8. Mechanistic possibilities: chain propagating processes

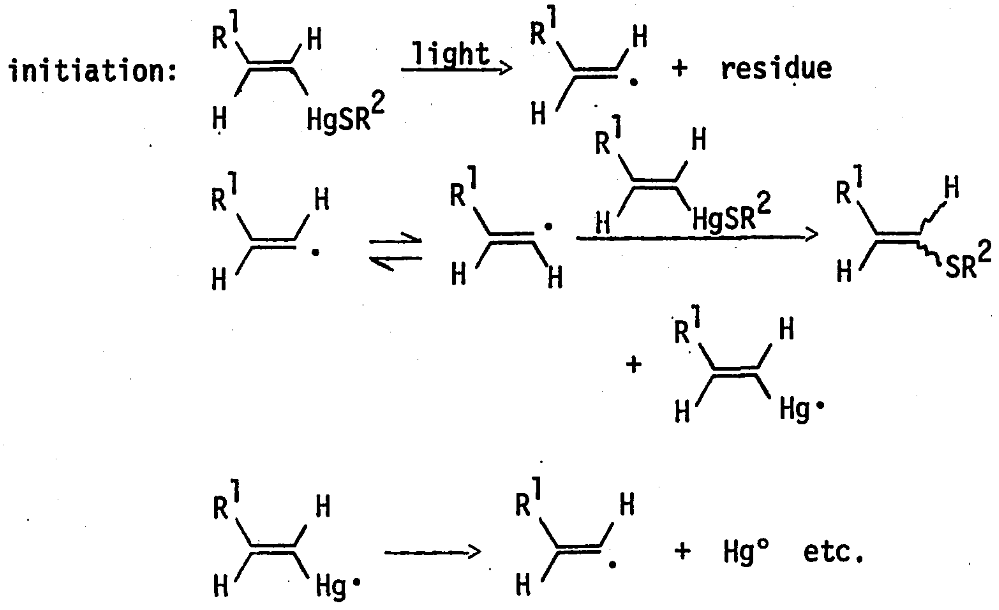
Nonchain mechanisms are discounted out of hand. The inhibition results of Table X, particularly the effect of added di-*t*-butyl nitroxide, unambiguously establish the photodecomposition as a chain process.

Scheme 13 is a modified S$_{RN}$1 mechanism predicted to be catalytic in mercaptide ion. Schemes 14 and 15 are radical chain mechanisms not involving radical ions.

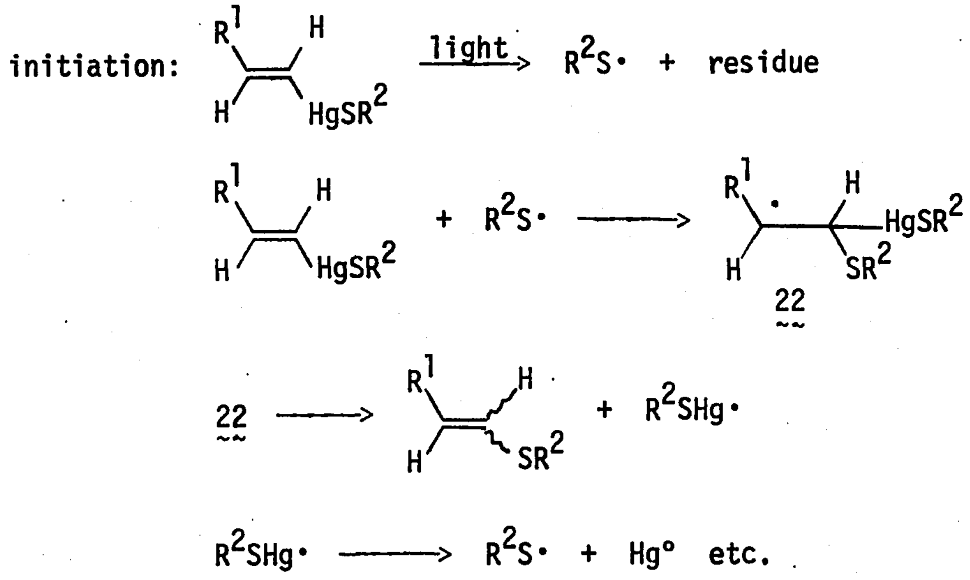
Scheme 13



Scheme 14

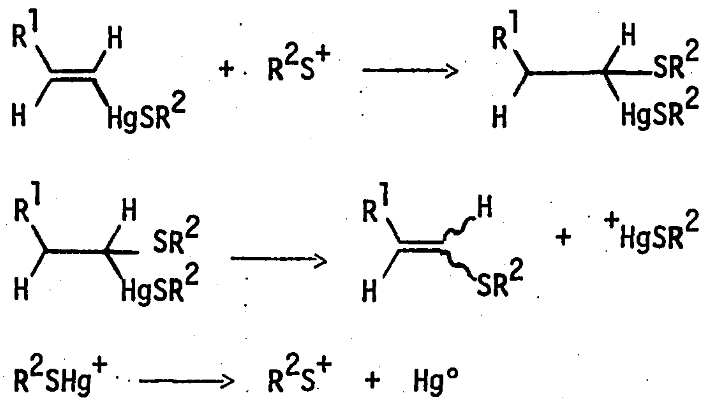


Scheme 15



Scheme 16, the cationic analogue of Scheme 15, might also bear consideration.

Scheme 16



Scheme 13 may be discounted by the observation of inhibition by mercaptide ion (Table X) and the lack of inhibition by thiophenol. The lack of thiophenol inhibition, likewise, eliminates the mechanism of Scheme 14. Even if chain propagation via vinyl-type radicals occurred at a rate approaching the diffusion limit hydrogen atom transfer from thiophenol would be expected to observably slow the chain reaction based on the reactivity of phenyl radical [79]. Scheme 16 also appears unreasonable. Oxygen would not be expected to inhibit the process. Solvents such as DMSO and benzene should serve as scavengers for such cationic species, as should the product alkenyl sulfides. The carbo-cation analogue of Scheme 16 is similarly discounted.

Scheme 15 provides a mechanistic description consistent with all available experimental observations. First, the limitation of the photochemical reductive elimination to alkenylmercury mercaptides

(Table VIII) is clearly explained. Intermediate 22 is not possible for alkylmercury mercaptides and requires loss of aromaticity for arylmercury mercaptides. The intermediacy of a thiyl radical (as opposed to vinyl) also appears more consistent with the tolerance of the photodecomposition for functional groups such as hydroxy, acetyloxy, and chloro (Table IX).

The observation that decomposition of 13 is unaffected by the presence of thiophenol is explainable in terms of Scheme 15. Obviously, only degenerate hydrogen exchange can occur between thiophenol and the phenylthiyl radical. The thiophenoxymercury(I) radical intermediate might be expected to be unreactive hydrogen atom donors since mercury hydrides are notoriously unstable [26-29]. The product of such a transfer is a chain-propagating thiyl radical anyway, and the thiophenoxymercury hydride would be expected to rapidly decompose to mercury metal and thiophenol by analogy with alkylmercury hydrides [26-29]. Intermediate 22 is presumably too short-lived to be trapped by mercaptan. Although 22 may exist long enough for rotation about the new carbon-carbon single bond, hydrogen transfer from mercaptans to alkyl radicals is much slower than the rate of diffusion. The bimolecular rate constant for such a transfer is on the order of 10^6 M^{-1} s^{-1} [80,81]. Intermediate 22 may enjoy special stabilization resulting in even lower reactivity towards mercaptan.

Inhibition by oxygen and di-*t*-butyl nitroxide is characteristic of radical chain reactions. It is not clear which species of radical is scavenged, however. Thiyl, mercaptomercury(I), and intermediate 22 are candidates for trapping by paramagnetic agents.

The observed inhibitory activity of certain salts (Table X) may be rationalized in terms of Scheme 15. Thiophenoxide ion must trap a paramagnetic species to form a relatively inert radical ion. Two likely candidates are thiyl (Eq. 33) and thiophenoxymercury(I) (Eq. 34). Other

$$\mathrm{PhS^{-} + PhS\cdot \longrightarrow [PhSSPh]^{\overset{\bullet}{-}}} \qquad (33)$$

$$\mathrm{PhSHg\cdot + PhS^{-} \longrightarrow [PhSHgSPh]^{\overset{\bullet}{-}}} \qquad (34)$$

salts may inhibit reaction either by coupling with a radical to produce a stable radical anion or by reducing a paramagnetic species to produce a new anion and an unreactive radical (Eq. 35). In Equation 35, A^- is

$$\mathrm{A^{-} + R\cdot \longrightarrow A\cdot + R^{-}} \qquad (35)$$

the added anion and R• represents a normal chain-propagating paramagnetic species.

Finally, the observation was made that the decomposition of 13 in the presence of diphenyl disulfide with DMSO solvent produces mostly mercuric thiophenoxide instead of metallic mercury. The reaction was found not to occur in the dark and is therefore not a thermal electrophilic cleavage reaction (Eq. 36). The observed mercury salt

$$(\underline{E})\text{-}\mathrm{Me_3CCH{=}CHHgSPh + PhSSPh \overset{\Delta}{\not\longrightarrow} (\underline{E})\text{-}Me_3CCH{=}CHSPh + (PhS)_2Hg} \qquad (36)$$

formation may be explained either by reaction of the disulfide with thiophenoxymercury(I) (Eq. 37) or with the (presumably) highly reactive mercury atom (or polyatomic mercury cluster) (Eq. 38). Neither process

$$\mathrm{PhSHg\cdot} + \mathrm{PhSSPh} \longrightarrow \mathrm{PhSHgSPh} + \mathrm{PhS\cdot} \qquad (37)$$

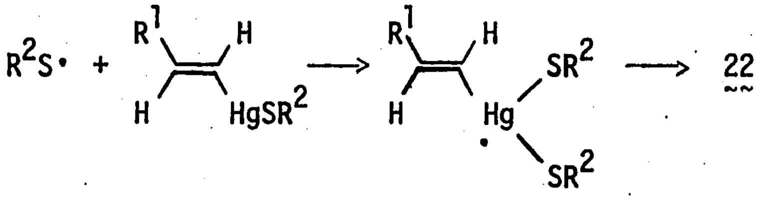
$$\mathrm{Hg^{\circ}} + \mathrm{PhSSPh} \longrightarrow \mathrm{PhSHgSPh} \qquad (38)$$

involves the net removal of chain-propagating thiyl radicals and thus the formation of alkenyl sulfide product is not inhibited.

9. Nature of the reactive intermediates in Scheme 15

The rapid loss of mercury metal from the mercaptomercury(I) radical appears an entirely reasonable process in light of the behavior of alkylmercury(I) radicals [26-29,34]. The resulting thiyl radical is a frequently observed chain-carrying species in free-radical sulfur chemistry. The addition of thiyl to olefins has been studied extensively [82]. Intermediate 22, however, has no direct literature precedent. _β_-Substituted carbon radicals represent an intriguing class of reactive intermediates.

The high regiospecifity demonstrated by the attack of thiyl radical on the vinylmercury mercaptide may be partly due to precomplexation of thiyl with mercury (Eq. 39). Mercury(III) intermediates have



(39)

been invoked to explain the free radical-induced racemization of alkylmercury salts and dialkyl mercurials containing a chiral carbon bonded to mercury [42,83].

Mercury is known to stabilize β-carbon cations (i.e., the removal of β-hydride [84] from dialkyl mercurials or the addition of mercury(II) to olefins [85]). It has been proposed that similar stabilization may be provided β-mercurio carbon radicals. Nugent and Kochi found hydrogens on carbons with a β-mercury substituent to be as much as 600 times more reactive towards abstraction by trichloromethyl radical than hydrogens of simple hydrocarbons [86]. The same investigators found dialkyl mercurials to react by a radical chain mechanism with carbon tetrachloride to afford an olefin, alkyl halide, chloroform, and mercury metal (Scheme 17) [86]. The elimination of an

Scheme 17

$$RCH_2CH_2HgCH_2CH_2R + \cdot CCl_3 \longrightarrow R\underset{\bullet}{C}HCH_2HgCH_2CH_2R + CHCl_3$$

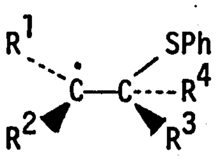
$$R\underset{\bullet}{C}HCH_2HgCH_2CH_2R \longrightarrow RCH{=}CH_2 + \cdot HgCH_2CH_2R$$

$$\cdot HgCH_2CH_2R \longrightarrow Hg^\circ + \cdot CH_2CH_2R$$

$$\cdot CH_2CH_2R + CCl_4 \longrightarrow ClCH_2CH_2R + \cdot CCl_3$$

organomercury(I) radical from the β-mercurio radical is analogous to the proposed decomposition pathway for intermediate **22**. Thus, the formation of **22** may well be influenced by special stabilization of the β-mercurio radical and the proposed decomposition of **22** to an alkenyl sulfide and a mercaptomercury(I) radical is supported by literature precedent.

The possibility of stereochemical interconversion via rotation about the single bond between the *α* and *β* carbons in **22** has been noted. Unfortunately, due to the relative inaccessibility of the appropriate (*Z*)-1-alkenylmercury salts, the extent of stereochemical randomization via **22** has not been investigated. It is not necessarily true that such radical intermediates achieve rotational equilibrium. The β-sulfur radicals **23**, **24**, and **25** were generated by the abstraction of bromine by tri-*n*-butylstannyl radical from the *erythro* or *threo* β-sulfur bromides [87-89]. Radicals **23** and **25** eliminated thiyl and sulfonyl radicals at a sufficiently slow rate to allow complete loss of stereochemistry. Radical **24**, however, afforded olefins stereospecifically.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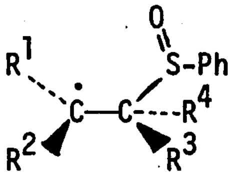
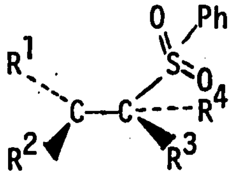
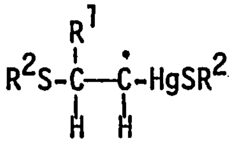

24


25

Thiyl radicals are known to add reversibly to carbon-carbon double bonds [82]. In cases where β-attack is not sterically disfavored, the reversible formation of **26** appears plausible. Likewise, reversible additions to the product vinyl sulfides may occur. These reversible


$$R^2S\text{-}\overset{R^1}{\underset{H}{C}}\text{—}\underset{H}{\dot{C}}\text{-}HgSR^2$$

26

additions may be responsible for all or part of the observed stereochemical equilibration in the decomposition of vinylmercury mercaptides with small β-substituents.

10. Relationship between the photochemical and thermal decomposition of vinylmercury salts

Some of the vinylmercury salts found to reductively eliminate mercury metal thermally [71-75] may well decompose by a process similar to Scheme 15. The vinylmercury carboxylates, however, probably do not decompose via carboxyl radicals. Acetyloxy radical decomposes to methyl radical and carbon dioxide with a unimolecular rate constant of 1.6×10^9 sec^{-1} at 60°C [90], a rate approaching the diffusion limit for bimolecular chain-carrying processes. Since reactions of vinylmercury carboxylates were generally performed without solvent and yields were often only moderate, it is difficult to categorically exclude the mechanism of Scheme 15, although it is noteworthy that some decompositions were performed in the presence of hydroquinone, a free radical scavenger [75].

C. Conclusion

The photochemical reductive elimination of mercury metal from vinylmercury mercaptides is a mechanistically fascinating reaction. Strong evidence has been presented for a radical chain mechanism involving neutral species (Scheme 15). A novel S_H2 process, the transfer of a vinyl group from mercaptomercury(I) to thiyl, has been proposed to proceed via quasi-stable intermediate **22**, a carbon radical stabilized by a *β*-mercurio substituent.

Synthetically, the described reaction complements existing methods. The Hörner-Wittig reaction of thioalkoxymethylphosphonate esters with aldehydes is general for 2-substituted-1-ethenyl alkyl sulfides [91], although yields are modest. The addition of mercaptans to acetylenes has been applied to few examples [92]. The elimination of hydrogen chloride from *β*-chloroalkyl phenyl sulfides [93] is limited by the availability of the starting material. Recently, the coupling of mercaptide ion with vinyl bromides mediated by catalytic palladium(0) catalyst has been described [94]. None of the reported methods has demonstrated functional group tolerance. The present method affords good to quantitative yields of vinyl phenyl and vinyl alkyl sulfides under neutral conditions at room temperature with demonstrated tolerance for vinyl halide, hydroxyl, and carbonyl functionality. The primary limitation of the method is the availability of vinylmercury salts [20].

Vinyl sulfides are useful synthetic intermediates. Mercury salt-assisted hydrolysis affords the corresponding carbonyl compound [95, 96]. The versatile vinyl sulfones are available via peroxide oxidation [97]. Vinyl sulfides are also terminal acetylene equivalents [98]. Vinyl phenyl sulfides are readily metalated at the vinylic *α*-position and elaborated with suitable electrophiles (*i.e.*, aldehydes, ketones, and primary alkyl halides) [99,100,101].

D. Experimental Section

1. General considerations

Glass capillary gas chromatography was performed on a Varian 3700 instrument. UV-VIS absorption spectra were recorded on a Perkin-Elmer 320 spectrophotometer. Ethenylmercury chloride was purchased from Orgmet, Inc. Thiophenol, *n*-butane thiol, and *t*-butyl mercaptan were purchased from Eastman Organic. Benzyl mercaptan, thiolacetic acid, mercaptoacetic acid, and authentic samples of benzyl phenyl sulfide, diphenyl sulfide, and 3,3-dimethyl-1-butene were purchased from Aldrich. Phenyl selenol was purchased from Orgmet, Inc.

The sodium salt of thiophenol was prepared from sodium methoxide (0.1 mol) and thiophenol (0.11 mol) in 500 ml methanol under nitrogen. The methanol was removed under vacuum and the white powder stored under nitrogen until used.

(*E*)-1-Pentenylmercury chloride [59], (*E*)-2-phenyl-1-ethenylmercury chloride [59], and bis[phenylethynyl]mercury [102] were prepared by literature methods. Samples of (*E*)-2-(acetyloxy)-1-ethyl-1-butenylmercury chloride [103] and (*E*)-2-chloro-3-hydroxy-1-propenylmercury chloride [104] were donated by the group of R. C. Larock.

2. Preparation of 2,2-diphenylethenylmercury bromide

The method employed was a variation of that reported by Schlenk [105]. To the Grignard reagent prepared from 1,1-diphenyl-1-bromoethene (27 g, 103 mmol) and magnesium turnings (2.5 g, 103 mmol) in 100 ml dry THF under nitrogen was slowly added a solution of mercuric chloride (13.6 g, 50 mmol) in 40 ml THF. The resulting mixture was refluxed overnight, allowed to cool to room temperature, and poured into 1500 ml ice-cold 5% aqueous ammonium chloride. The solid product was collected and air dried. Recrystallization from hot ethanol/chloroform afforded 22.3 g (78% yield) of light yellow needles of the previously reported bis[2,2-diphenylethenyl]mercury (m.p. 139-139.5°C, lit. [105] 140.5°C). ^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.2-7.3, 1H (s) 6.63.

Mercuric bromide (7.5 g, 21 mmol) in 25 ml THF was slowly added to bis[2,2-diphenylethenyl]mercury (11.2 g, 20 mmol) in 50 ml THF. The solution was stirred overnight at room temperature and poured into 1200 ml 2% aqueous sodium bromide. The solid product was collected and air dried. Inorganic salts were removed by dissolving the product in 600 ml chloroform and filtering insoluble materials. Removal of the solvent under vacuum afforded 16.1 g (86% yield) of 2,2-diphenylethenylmercury bromide (m.p. 155-156°C, lit. [105] 158-159°C). ^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.2-7.4, 1H (s) 6.43.

3. Preparation of 2,2-diphenyl-1-methylethenylmercury bromide

To the Grignard reagent prepared from 1,1-diphenyl-2-bromopropene (13.6 g, 50 mmol) and magnesium turnings (1.2 g, 50 mmol) in 50 ml dry THF under nitrogen was slowly added a solution of mercuric bromide (18.5 g, 51 mmol) in 40 ml dry THF. The resulting mixture was refluxed overnight, cooled to room temperature, and poured into 1500 ml ice-cold 1% aqueous sodium bromide. The solid product was collected and air dried. The product was dissolved in 250 ml chloroform and filtered to remove inorganic salts. Removal of the chloroform under vacuum and recrystallization from hot ethanol afforded 14.0 g (59% yield) of the pure mercurial as yellow needles (m.p. 163.5-164.5).

^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.3, 3H (s) 2.15.

Elemental analysis. Calculated for $C_{15}H_{13}BrHg$: C, 38.03; H, 2.77; Br, 16.87; Hg, 42.34. Found: C, 38.12; H, 2.92.

4. Preparation of 1-(cyclohexylmethyl)-1-ethenylmercury bromide

To the Grignard reagent prepared from 3-cyclohexyl-2-bromopropene [106] (10.1 g, 50 mmol) and magnesium turnings (1.21 g, 50 mmol) in 40 ml dry THF under nitrogen was slowly added a solution of mercuric bromide (18.4 g, 51 mmol) in 40 ml dry THF. The resulting mixture was refluxed for 30 minutes, cooled to room temperature, and poured into 1500 ml ice-cold 5% aqueous sodium bromide. The solid product was collected, air-dried, and dissolved in 200 ml chloroform. The chloroform solution was filtered to remove inorganic salts and concentrated under vacuum. Recrystallization from hot ethanol afforded 12.5 g (62% yield) of the pure mercurial (m.p. 95-96°C).

^{1}H N.M.R. ($CDCl_3$, δ) 1H (t) 5.57 (J_H = 1 Hz), 1H (s) 5.0, 2H (d, broad) 2.3 (J_H = 6 Hz), 11H (m, broad) 0.8-2.0.

Elemental analysis. Calculated for $C_9H_{15}BrHg$: C, 27.78; H, 3.74; Br, 19.79; Hg, 49.69. Found: C, 26.71; H, 3.70.

5. Preparation of (*E*)-3,3-dimethyl-1-butenylmercury acetate

(*E*)-3,3-Dimethyl-1-butenylmercury chloride (2.0 g, 6.3 mmol) and silver acetate (1.08 g, 6.5 mmol) were stirred in 100 ml methanol at room temperature for 20 hours in an aluminum foil-covered flask. The silver chloride was removed by filtration ("Celite" filter aid was employed) and the clear filtrate concentrated under vacuum. Recrystallization of the resulting solid from warm methanol/water afforded 1.5 g (70% yield) of the pure mercurial as large white plates (m.p. 95.5-96°C).

^{1}H N.M.R. ($CDCl_3$, δ) 1H (d) 6.01 (J_H = 17 Hz), 1H (d) 5.67 (J_H = 17 Hz), 3H (s) 2.05, 9H (s) 1.07.

I.R. (KBr pellet, cm^{-1}) 2950 (w), 1570 (vs, broad), 1400 (s), 1250 (s), 1140 (w), 1010 (w), 975 (s), 910 (m), 760 (w), 745 (w).

Elemental analysis. Calculated for $C_8H_{14}HgO_2$: C, 28.03; H, 4.12; Hg, 58.52; O, 9.33. Found: C, 27.98; H, 4.20.

6. Preparation of phenylmercury thiophenoxide

Phenylmercury chloride (6.3 g, 20 mmol) was added to a solution of sodium thiophenoxide (3.0 g, 22 mmol) in 180 ml nitrogen-purged DMSO with gentle stirring. After 10 minutes, the solution was poured into 500 ml aqueous 10% potassium carbonate and the product extracted with ethyl ether. The ethereal extract was washed with aqueous carbonate, dried ($MgSO_4$), and concentrated under vacuum to afford 6.8 g (88% yield) of light yellow powdery solid (m.p. 98-99°C, lit. [76] 105-106°C). Three recrystallizations (once from acetone/hexane, twice from ethanol/benzene) failed to raise the melting point. Elemental analysis. Calculated for $C_{12}H_{10}HgS$: C, 37.26; H, 2.60; Hg, 51.85; S, 8.29. Found: C, 37.10; H, 2.76.

7. Preparation of benzylmercury thiophenoxide

Benzylmercury chloride (3.0 g, 9.2 mmol) was added to a gently stirred solution containing potassium *t*-butoxide (1.3 g, 11.6 mmol) and thiophenol (1.29 g, 11.7 mmol) in 30 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured into 250 ml aqueous 10% potassium carbonate and the product extracted with benzene. The extract was washed with aqueous carbonate, dried ($MgSO_4$), and concentrated under vacuum to afford 3.6 g crude product. Recrystallization from ethanol/benzene yielded 3.1 g (84%) pure benzylmercury thiophenoxide (m.p. 83.0-83.5°C, lit. [76] 87°C).

^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.0-7.45, 2H (s) 2.92.

8. Preparation of (*E*)-3,3-dimethyl-1-butenylmercury thiophenoxide

In subdued roomlight, (*E*)-3,3-dimethyl-1-butenylmercury chloride (7.5 g, 23.5 mmol) was added to a solution containing potassium *t*-butoxide (3.4 g, 30.3 mmol), thiophenol (3.34 g, 30.3 mmol) and di-*t*-butyl nitroxide (7 mcl, 6.8 mg, 0.047 mmol) in 180 ml nitrogen-purged DMSO with gentle stirring. After 5 minutes, the solution was poured into 500 ml water containing 80 g potassium carbonate and 20 g sodium chloride. The product was extracted with three 100 ml portions of ethyl ether. The combined ethereal extract was washed with aqueous carbonate, dried ($MgSO_4$) and concentrated under vacuum to afford 9.0 g solid product. Recrystallization from hexane yielded 7.6 g (83%) pure white (*E*)-3,3-dimethyl-1-butenylmercury thiophenoxide. The white needles were treated with a 0.1 torr vacuum for 1 hour to remove traces of the nitroxide (m.p. 55.0-55.5°C).

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m, broad) 7.08-7.53, 2H (s) 5.90, 9H (s) 1.0. Note the magnetic equivalence of the vinyl protons.

I.R. (KBr pellet, cm^{-1}) 2960 (m), 1580 (s), 1480 (s), 1440 (m), 1360 (m), 1255 (m), 1023 (s), 980 (s), 735 (vs), 690 (vs).

Elemental analysis. Calculated for $C_{12}H_{16}HgS$: C, 36.68; H, 4.10; Hg, 51.05; S, 8.16. Found: C, 36.71; H, 4.16; S, 8.12.

UV-VIS (hexane) λ_{max} = 248,232 nm. Tail apparent to 380 nm.

The product vinylmercury mercaptide was found to be indefinitely stable to room light in the solid state. In solution or in the melt, however, rapid mercury metal precipitation accompanied exposure to sun or room light. Thus, when it was necessary to handle these compounds in solution (i.e., during isolation, purification) the room was nearly darkened and a trace of di-t-butyl nitroxide added as a stabilizer.

Vinylmercury mercaptides cannot be analyzed by G.L.C. When (E)-3,3-dimethyl-1-butenylmercury thiophenoxide in acetone was injected (injector temp. 250°C) on 5% OV-3/Chromosorb W at 120°C, only (E)-3,3-dimethyl-1-butenyl phenyl sulfide (ca. 30%) was eluted (identified by retention time).

9. Preparation of (E)-1-pentenylmercury thiophenoxide

In subdued light (E)-1-pentenylmercury chloride (0.5 g, 1.64 mmol) was added to a stirred solution containing potassium t-butoxide (0.2 g, 1.78 mmol), thiophenol (0.2 g, 1.85 mmol), and di-t-butyl nitroxide (2 mcl, 1.9 mg, 0.093 mmol) in 10 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured into 100 ml water containing 10 g potassium carbonate and 5 g sodium chloride. The product was extracted with ether, the extract washed with aqueous carbonate, dried ($MgSO_4$) and concentrated under aspirator vacuum, and the resulting oil maintained for 1 hour under an oil-pump vacuum to remove traces of di-_t_-butyl nitroxide. This oil (0.58 g, 94% crude yield) was found to precipitate mercury metal with brief exposure to light. An acceptable elemental analysis was obtained by shipping the oil in an aluminum foil-wrapped ampoule.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.5-7.9, 2H (m) 5.8-5.9, 2H (m) 1.9-2.3, 2H (m) 1.1-1.7, 3H (t) 0.9 (J_H = 6.5 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 3070 (w), 2960 (vs), 2930 (vs), 2880 (s), 1600 (w), 1580 (vs), 1480 (vs), 1465 (m), 1440 (s), 1380 (w), 1340 (w), 1300 (w), 1275 (w), 1190 (m), 1080 (s), 1065 (w), 1025 (s), 980 (s), 890 (w), 735 (vs), 690 (vs).

Elemental analysis. Calculated for $C_{11}H_{14}HgS$: C, 34.87; H, 3.72; Hg, 52.94; S, 8.46. Found: C, 34.70; H, 3.91.

10. <u>Preparation of (_E_)-2-phenyl-1-ethenylmercury thiophenoxide</u>

In subdued light (_E_)-2-phenyl-1-ethenylmercury chloride (0.5 g, 1.47 mmol) was added to a stirred solution containing potassium _t_-butoxide (0.2 g, 1.78 mmol), thiophenol (0.2 g, 1.8 mmol), and di-_t_-butyl nitroxide (2 mcl, 1.9 mg, 0.013 mmol) in 10 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured into 100 ml water containing 10 g potassium carbonate and 5 g sodium chloride, and the product extracted with ethyl ether. The ethereal extract was washed with aqueous carbonate, dried ($MgSO_4$), and evaporated under vacuum to afford

0.61 g (100% yield) of the crude product. The crude solid was recrystallized from warm hexane/benzene containing 3 mol di-t-butyl nitroxide as stabilizer and the resulting needles placed under vacuum at 0.05 torr for one hour to remove traces of the nitroxide. The pure white crystals (0.52 g, 86% yield) did not demonstrate a melting point (dec. 103-105°C) and were somewhat sensitive to room light (the crystals turned gray over a period of 3-5 days).

^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.0-7.6, 2H (s) 6.77. Note the magnetic equivalence of the vinyl protons.

I.R. (KBr pellet, cm^{-1}) 3070 (w), 3020 (w), 1600 (w), 1580 (m), 1570 (m), 1500 (m), 1480 (s), 1450 (w), 1445 (s), 1300 (w), 1290 (w), 1215 (w), 1190 (w), 1180 (m), 1090 (m), 1075 (m), 1030 (s), 990 (s), 980 (m), 905 (w), 740 (vs), 730 (vs), 690 (vs), 480 (m).

Elemental analysis. Calculated for $C_{14}H_{12}HgS$: C, 40.72; H, 2.93; Hg, 48.58; S, 7.77. Found: C, 40.56; H, 2.84.

11. Preparation of 1-(cyclohexylmethyl)-1-ethenylmercury thiophenoxide

In subdued light, 1-(cyclohexylmethyl)-1-ethenylmercury bromide (2.0 g, 5.0 mmol) was added with stirring to a solution of potassium-t-butoxide (0.6 g, 5.3 mmol), thiophenol (0.6 g, 5.5 mmol), and di-t-butyl nitroxide (5 mcl, 4.8 mg, 0.034 mmol) in 25 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured in 200 ml of water containing 20 g potassium carbonate and 10 g sodium chloride and then the product was extracted with ethyl ether. The ethereal extract was washed with aqueous carbonate, dried ($MgSO_4$) and concentrated to afford an oil (2.05 g, 98% yield). Evacuation at 0.05 torr for 1 hour removed traces of the nitroxide. The resulting oil was not particularly light sensitive, presumably due to the steric hindrance deactivating the reactive sites of molecules.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.1-7.7, 1H (m) 5.63, 1H (m) 5.02, 2H (m, broad) 2.32, 11H (m) 0.6-2.0.

I.R. (neat, NaCl plates, cm^{-1}) 3070 (w), 2915 (vs), 2855 (s), 1585 (s), 1480 (s), 1452 (m), 1440 (m), 1210 (w), 1085 (m), 1025 (m), 905 (m), 735 (s), 690 (s).

Elemental analysis. Calculated for $C_{15}H_{20}HgS$: C, 41.61; H, 4.66; S, 7.40; Hg, 46.33. Found: C, 41.68; H, 4.67; S, 7.65.

12. Preparation of 2,2-diphenylethenylmercury thiophenoxide

In subdued light, 2,2-diphenylethenylmercury bromide (0.5 g, 1.1 mmol) was dissolved in a stirred solution containing potassium *t*-butoxide (0.2 g, 1.78 mmol), thiophenol (0.2 g, 1.85 mmol), and di-*t*-butyl nitroxide (2 mcl, 1.9 mg, 0.013 mmol) in 10 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured into 100 ml water containing 10 g potassium carbonate and 5 g sodium chloride, and then the product was extracted with benzene. The extract was washed with aqueous carbonate, dried ($MgSO_4$) and concentrated to afford 0.52 g (96% yield) of 2,2-diphenylethenylmercury thiophenoxide as a light yellow oil. Evacuation for 1 hour at 0.05 torr removed traces of nitroxide. The oil was light sensitive and was stored in aluminum foil-covered ampoules.

^{1}H N.M.R. ($CDCl_3$, δ) 15H (m) 7.0-7.35, 1H (s) 6.45.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (m), 3200 (m), 1585 (s), 1500 (s), 1480 (s), 1445 (s), 1220 (w), 1200 (w), 1090 (m), 1030 (m), 925 (w), 900 (w), 825 (w), 760 (vs, 3 peaks), 700 (vs, 2 peaks).

Elemental analysis. Calculated for $C_{20}H_{16}HgS$: C, 49.12; H, 3.30; Hg, 41.02; S, 6.56. Found: C, 49.09; H, 3.46; S. 6.36.

13. Preparation of 2,2-diphenyl-1-methylethenylmercury thiophenoxide

In subdued light, 2,2-diphenyl-1-methylethenylmercury bromide (0.5 g, 1.05 mmol) was added to a stirred solution containing potassium t-butoxide (0.2 g, 1.78 mmol), thiophenol (0.2 g, 1.8 mmol), and di-t-butyl nitroxide (2 mcl, 1.9 mg, 0.013 mmol) in 10 ml of nitrogen-purged DMSO. After 5 minutes, the solution was poured into 100 ml water containing 10 g potassium carbonate and 5 g sodium chloride, and then the product was extracted with benzene. The extract was washed with aqueous carbonate, dried ($MgSO_4$), and concentrated to afford 0.51 g (91% yield) of a white solid. Recrystallization from warm hexane/benzene afforded 0.43 g (81% yield) of the pure 2,2-diphenyl-1-methylethenylmercury thiophenoxide as white needles (m.p. 129-130°C).

^1H N.M.R. ($CDCl_3$, δ) 15H (m) 7.0-7.4, 3H (s) 2.12.

I.R. (KBr pellet, cm^{-1}) 3080 (w), 3060 (w), 3020 (w), 2940 (w), 2900 (w), 1600 (w), 1580 (m), 1490 (m), 1475 (m), 1440 (s), 1385 (w), 1110 (m), 1085 (m), 1025 (m), 1000 (w), 918 (m), 780 (s), 750 (m), 740 (vs), 700 (vs), 690 (s), 590 (m), 500 (m), 480 (m).

Elemental analysis. Calculated for $C_{21}H_{18}HgS$: C, 50.14; H, 3.61; Hg, 39.88; S, 6.37. Found: C, 50.03; H, 3.58.

14. Preparation of (E)-3,3-dimethyl-1-butenylmercury n-thiobutoxide

In subdued light, (E)-3,3-dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) was added to a stirred solution of potassium-t-butoxide (0.2 g, 1.78 mmol), n-butyl mercaptan (0.175 g, 1.9 mmol), and di-t-butyl nitroxide (2 mcl, 1.9 mg, 0.013 mmol) in 10 ml of nitrogen-purged DMSO. After 5 minutes, the solution was poured into 100 ml of water containing 10 g potassium carbonate and 5 g sodium chloride, and then the organic product was extracted with ethyl ether. The ethereal extract was washed with aqueous carbonate, dried ($MgSO_4$), and concentrated under vacuum to afford 0.59 g (100% yield) of the product as a colorless solid (m.p. 44.5-46°C).

^{1}H N.M.R. ($CDCl_3$, δ) 2H (s) 5.94, 2H (t) 3.03 (J_H = 5.5 Hz), 7H (m) 0.7-1.8, 9H (s) 1.07. Note the magnetic equivalence of the vinyl protons.

I.R. (melt, NaCl plates, cm^{-1}) 3000 (w), 2970 (vs), 2870 (m), 1600 (w), 1515 (m), 1365 (m), 1260 (w), 1225 (w), 990 (m), 910 (w).

Elemental analysis. Calculated for $C_{10}H_{20}HgS$: C, 32.21; H, 5.41; Hg, 53.79; S, 8.60. Found: C, 32.33; H, 5.51.

15. Attempted preparation of (E)-3,3-dimethyl-1-butenylmercury phenyl selenide

(E)-3,3-dimethyl-1-butenylmercury chloride (2.0 g, 6.27 mmol) was added with stirring to a solution containing potassium t-butoxide (0.8 g, 7.1 mmol), phenyl selenol (1.2 g, 7.6 mmol), and di-t-butyl nitroxide (5 mcl) in 25 ml DMSO (nitrogen-purged). After 10 minutes, the solution was poured into 250 ml aqueous 10% potassium carbonate and the organic products extracted with benzene. The extract was washed with aqueous carbonate, dried ($MgSO_4$), and concentrated to afford a mixture of an oil and a yellow solid. The oil and solid were separated by stirring the crude isolate with 75 ml of warm hexane and filtering the insoluble yellow solid. The hexane was evaporated to afford 1.3 g liquid determined by ^{1}H N.M.R. to be bis[(E)-3,3-dimethyl-1-butenyl]mercury. The solid (1.2 g yellow plates) demonstrated only aromatic hydrogens in the ^{1}H N.M.R. (7.0-7.6 ppm in $CDCl_3$). A sample was recrystallized from warm benzene (m.p. 148.5-149°C, lit. [107] 152-153°C). The elemental analysis was consistent with mercuric phenylselenide (PhSeHgSePh).

I.R. (KBr pellet, cm^{-1}) 3060 (w), 1570 (w), 1470 (w), 1435 (m), 1300 (w), 1060 (w), 1015 (w), 995 (w), 900 (w), 730 (s), 685 (s), 465 (m).

Elemental analysis. Calculated for $C_{12}H_{10}HgSe_2$: C, 28.11; H, 1.97; Hg, 39.12; Se, 30.80. Found: C, 27.92; H, 2.00; Se, 30.59.

16. Attempted preparation of phenylethynylmercury thiophenoxide

Potassium t-butoxide (0.6 g, 5.35 mmol) and thiophenol (0.66 g, 5.97 mmol) in 15 ml of nitrogen-purged DMSO was added to a stirred solution of bis[phenylethynyl]mercury (1.0 g, 2.48 mmol) and mercuric chloride (0.7 g, 2.58 mmol) in 50 ml nitrogen-purged DMSO. After 5 minutes, the solution was poured into 250 ml of 10% aqueous potassium carbonate and the suspension shaken with ethyl ether. A portion of suspended material was not ether soluble and was removed by filtration.

The solid (1.0 g) proved to be mercuric thiophenoxide, PhSHgSPh (m.p. 150-153°C, lit. [71] 150-151°C). The ethereal extract contained the bis[alkynyl]mercury compound and some PhSHgSPh.

An attempt was made to generate the alkynylmercury mercaptide by the electrophilic attack of thiophenol on the bis[alkynyl] mercurial. Bis[phenylethynyl]mercury (2.0 g, 4.97 mmol) and thiophenol (0.55 g, 5.0 mmol) were dissolved in 25 ml of benzene and the solution was refluxed for one hour under nitrogen. The solution was cooled and ethyl ether added, inducing the precipitation of PhSHgSPh (ca. 1 g).

17. Photochemical decomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide: a model procedure

(E)-3,3-Dimethyl-1-butenylmercury thiophenoxide (1.0 g, 2.55 mmol) was dissolved in 10 ml nitrogen-purged DMSO. The solution was stable in subdued light, but rapidly precipitated metallic mercury under the influence of 275 watt sunlamp illumination after an induction period of 1 or 2 minutes. The sunlamp was generally placed 6-10 inches from the Pyrex reaction flask. External cooling was not employed. Ambient reaction temperatures were within the range of 26-45°C. Precipitation of mercury appeared complete in the present reaction after 2 hours, but irradiation was continued for a total of 4 hours. The solution was decanted from the mercury beads into 50 ml brine and the product extracted with ethyl ether. The ethereal extract was washed with brine dried ($MgSO_4$), and concentrated under vacuum to afford 0.48 g (98% yield) of (E)-3,3-dimethyl-1-butenyl phenyl sulfide as a straw-colored liquid, purity >98% by ^{1}H N.M.R. and G.L.C. (1/8" x 5'; 5% OV-3/Chromosorb W; 145 °C). The spectral properties agreed with the literature report [108].

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.0-7.4, 2H (s) 6.02, 9H (s) 1.08. Note the magnetic equivalence of the vinyl protons.

I.R. (neat, NaCl plates, cm^{-1}) 2960 (s), 1590 (m), 1480 (m), 1440 (m), 1360 (m), 1265 (w), 1090 (w), 1030 (m), 955 (m, broad), 834 (w), 737 (s), 990 (m).

M.S. The present ion, m/e = 192, was observed.

The conversion of alkenylmercury mercaptides to alkenyl sulfides also proceeded well in volatile solvents more amenable to simple workup procedures. Thus, (_E_)-3,3-dimethyl-1-butenylmercury thiophenoxide (1.2 g, 3.06 mmol) in 50 ml ethyl ether under nitrogen decomposed with 15.5 hours of sunlamp irradiation. The ether solution was decanted from the mercury bead and the mercury rinsed with a little ether. Concentration of the combined ether portions afforded 0.58 g (98% yield) of the desired vinyl phenyl sulfide as a yellow oil. G.L.C. and ^{1}H N.M.R. revealed a small impurity (_ca._ 2%).

Benzene proved to be superior to ether as a reaction solvent. (_E_)-3,3-dimethyl-1-butenylmercury thiophenoxide (1.0 g, 2.55 mmol) in 20 ml benzene under nitrogen was decomposed by 3 hours of sunlamp irradiation. Workup afforded 0.49 g (100% yield) of the desired sulfide as a light yellow oil (purity >98%). The yellow tinge was removed by essentially quantitative Kugelrohr shortpath distillation (47-50°C/ 0.02 torr/0.48 g pure colorless product recovered).

18. Photodecomposition of 2.2-diphenylethenylmercury thiophenoxide

2,2-Diphenylethenylmercury thiophenoxide (2.0 g, 4.2 mmol) was dissolved in 35 ml of nitrogen-purged benzene and was gently stirred while being irradiated by a 275 watt sunlamp for 15.5 hours. Workup afforded 1.2 g (100% yield) of 2,2-diphenylethenyl phenyl sulfide (purity >98%) as a straw-colored liquid. This compound has been reported previously [109].

^{1}H N.M.R. ($CDCl_3$, δ) 15H (m) 7.15-7.5, 1H (s) 6.88.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (m), 3020 (w), 1580 (m), 1490 (m), 1480 (m), 1440 (s), 1080 (w), 1070 (w), 1020 (m), 930 (w), 900 (w), 810 (w), 760 (s), 750 (s), 735 (s), 715 (m), 690 (vs).

M.S. Calculated for $C_{20}H_{16}S$: 288.09728. Measured: 288.09633. Error: 3.3 ppm.

19. Photodecomposition of 2,2-diphenyl-1-methylethenyl thiophenoxide

2,2-Diphenyl-1-methylethenyl thiophenoxide (0.92 g, 1.83 mmol) in 20 ml nitrogen-purged benzene was decomposed by 10 hours of sunlamp irradiation. Workup afforded 0.56 g (100% yield) of the expected 2,2-diphenyl-1-methylethenylphenyl sulfide (purity >98%) as an oil. This compound has been previously reported [109].

^{1}H N.M.R. ($CDCl_3$, δ) 15H (m) 7.1-7.5, 3H (s) 1.98.

I.R. (neat, NaCl plates, cm^{-1}) 3080 (w), 3060 (m), 3020 (w), 1600 (w), 1575 (m), 1490 (m), 1475 (s), 1440 (s), 1120 (w), 1075 (w), 1020 (m), 1005 (m), 905 (m), 740 (vs), 700 (vs).

M.S. Calculated for $C_{21}H_{18}S$: 302.11293. Measured: 302.11423. Error: 4.3 ppm.

20. Photodecomposition of (E)-3,3-dimethyl-1-butenylmercury n-thiobutoxide

(E)-3,3-Dimethyl-1-butenylmercury n-thiobutoxide (1.1 g, 2.95 mmol) in 25 ml of nitrogen-purged benzene was decomposed by 6 hours of sunlamp irradiation. Workup afforded 0.51 g (100% yield) of the desired (E)-3,3-dimethyl-1-butenyl phenyl sulfide (purity >98%) as an oil. This compound has been reported in the literature [110].

^{1}H N.M.R. ($CDCl_3$, δ) 1H (d) 5.84 (J_H = 15.5 Hz), 1H (d) 5.63 (J_H = 15.5 Hz), 2H (t, broad) 2.64 (J_H = 6.5 Hz), 7H (m, broad) 0.7-1.75, 9H (s) 1.02.

I.R. (neat, NaCl plates, cm^{-1}) 2970 (vs), 2880 (m), 1610 (w), 1520 (m), 1370 (m), 1270 (m), 950 (m), 920 (w), 840 (w), 740 (w).

M.S. Calculated for $C_{10}H_{20}S$: 172.12858. Measured: 172.12790. Error: -3.9 ppm.

21. Photodecomposition of (E)-2-phenyl-1-ethenylmercury thiophenoxide

(E)-2-Phenyl-1-ethenylmercury thiophenoxide (1.1 g, 2.67 mmol) in 20 ml nitrogen-purged benzene was decomposed by 6 hours of sunlamp irradiation. Workup provided the desired 2-phenyl-1-ethenyl phenyl sulfide (0.57 g oil, 100% yield) as a mixture of E and Z isomers (purity >98%). Both isomers were apparent in the 100 M Hz ^{1}H N.M.R. by their distinctive vinyl hydrogens. Integration of the vinyl region indicated a ratio of 91 E:9 Z. Separation of the isomers was achieved on a 30 meter glass capillary G.L.C. column loaded with SE-30 at 214°C. The Z isomer eluted first. By peak integration the isomer ratio was 91 E:9 Z.

^{1}H N.M.R. (100 M Hz, $CDCl_3$, δ) E + Z isomers:10H (m) 7.1-7.55.

E isomer: 1H (d) 6.83 (J_H = 15 Hz), 1H (d) 6.70 (J_H = 15 Hz).

Z isomer: 1H (d) 6.55 (J_H = 10 Hz), 1H (d) 6.46 (J_H = 10 Hz).

I.R. (E + Z isomers, neat, NaCl plates, cm^{-1}) 3070 (w), 3035 (w), 1600 (m), 1590 (m), 1575 (w), 1500 (w), 1480 (s), 1450 (m), 1442 (m), 1090 (w), 1070 (w), 1025 (w), 945 (s), 740 (vs), 690 (vs).

M.S. Calculated for $C_{14}H_{12}S$: 212.06597. Measured: 212.06535. Error: -2.9 ppm.

The isomeric mixture was distilled (Kugelrohr, 97°C/0.02 torr) to afford 0.563 g colorless liquid (99% yield). 2-Phenyl-1-thenylphenyl sulfide has been reported in the literature [92].

22. Photodecomposition of (E)-1-pentenylmercury thiophenoxide

(E)-1-Pentenylmercury thiophenoxide (3.2 g, 8.45 mmol) in 50 ml nitrogen-purged benzene was decomposed with 4 hours of sunlamp irradiation. Workup afforded 1.5 g (100% yield) of the 1-pentenyl phenyl sulfide as a light yellow oil (purity >98%). G.L.C. on a 30 meter glass capillary column loaded with SE-30 at 145°C revealed two isomers in a 46:54 ratio (the lower abundance isomer eluted first). Unfortunately, the ^{1}H N.M.R. was complex and the isomers were not assigned.

^{1}H N.M.R. (mixture of E and Z isomers, $CDCl_3$, δ) 5H (m) 7.0-7.4, 2H (m) 5.5-6.25, 2H (m) 1.9-2.4, 2H (m) 1.1-1.7, 3H (m) 0.7-1.05.

I.R. (mixture of E and Z isomers, neat, NaCl plates, cm^{-1}) 3070 (w, 2 peaks), 3050 (w), 2960 (s), 2880 (m), 1590 (m), 1480 (s), 1440 (s), 1090 (m), 1026 (m), 950 (m), 735 (s), 688 (s).

M.S. Calculated for $C_{11}H_{14}S$: 178.08163. Measured: 178.08130. Error: -1.5 ppm.

1-Pentenyl phenyl sulfide has been reported in the literature [111].

23. Photodecomposition of 1-(cyclohexylmethyl)-1-ethenylmercury thiophenoxide

1-(Cyclohexylmethyl)-1-ethenylmercury thiophenoxide (1.5 g, 3.47 mmol) in 20 ml nitrogen-purged benzene was irradiated for 2 hours by a 275 watt sunlamp placed 4 inches from the Pyrex reaction vessel. A negligible amount of mercury precipitated. The reaction was subsequently irradiated for 5.5 hours in a Rayonet RPR-100 photoreactor equipped with fourteen "350 nm" bulbs. Under these conditions, mercury precipitated rapidly. Workup afforded 0.8 g of yellow oil determined by G.C.M.S. to contain ca. 80% of the desired 1-(cyclohexylmethyl)-1-ethenyl phenyl sulfide and ca. 20% of an unidentified component, m/e = 248 = parent ion. The desired product was not purified since the mixture was not easily resolved by G.L.C. or T.L.C.

^1H N.M.R. (mixture of compounds, $CDCl_3$, δ) 5H (m) 7.33, 1H (s) 5.06, 1H (s, broad) 4.83, 13H (m) 0.5-2.3.

I.R. (mixture of compounds, neat, NaCl plates, cm^{-1}) 3080 (w), 2940 (vs), 2860 (s), 1615 (w), 1590 (w), 1480 (m), 1440 (m), 1450 (m), 1025 (w), 745 (m), 690 (s).

24. Photodecomposition of phenylmercury thiophenoxide

Phenylmercury thiophenoxide (1.0 g, 2.59 mmol) was dissolved in 20 ml nitrogen-purged benzene and irradiated for 15 hours with a sunlamp placed 10 inches from the Pyrex reaction vessel. Only a trace of mercury precipitated. Irradiation in a Rayonet RPR-100 reactor (equipped with fourteen "350 nm" bulbs) for 9 hours induced what appeared to be complete mercury precipitation. The solution was decanted from the mercury and concentrated to afford 0.66 g of orange oil. Quantitative G.L.C. (1/8" x 5'; 5% OV-3 on Chromosorb W; 160°C) revealed 2% yield (maximum limit) of diphenyl sulfide (biphenyl was employed as an integration standard; molar response ratio = 1.0). The identification of the presumed diphenyl sulfide was based on retention matching on 5% OV-3 and 5% FFAP columns at several temperatures.

A similar experiment employing 25 ml DMSO (nitrogen-purged) as solvent and a 25 hour Rayonet irradiation period afforded 0.68 g crude orange oil found to contain no diphenyl sulfide by G.L.C.

25. Photodecomposition of benzylmercury thiophenoxide

Benzylmercury thiophenoxide (1.0 g, 2.5 mmol) in 20 ml nitrogen-purged benzene was irradiated for 15.5 hours with a sunlamp placed 10 inches from the reaction vessel. Some precipitation of mercury metal was observed. Workup afforded 0.88 g of white solid. Quantitative ^1H N.M.R. revealed a complex mixture including the starting thiophenoxide (66%) and benzyl phenyl sulfide (2% maximum). The benzyl phenyl sulfide was identified by the methylene absorption (4.12 ppm in $CDCl_3$) which corresponds to that of the authentic compound.

26. Effect of di-t-butylnitroxide on the photodecomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide

(E)-3,3-Dimethyl-1-butenylmercury thiophenoxide (1.2 g, 3.06 mmol) was dissolved in 50 ml dry nitrogen-purged DMSO containing di-t-butylnitroxide (22 mg, 0.15 mmol) in a Pyrex flask equipped with water cooling from an internal cold finger and a magnetic stir bar. The reaction vessel was placed at the center of a Rayonet RPR-100 photoreactor equipped with fourteen "350 nm" bulbs. The reaction flask was cooled with 25°C circulating water, although thermal lag allowed reaction solutions to warm to about 27-28°C. A 30 minute irradiation period induced no precipitation of mercury metal. The solution was poured into brine and 1.1 g (92%) of the unreacted alkenylmercury mercaptide recovered by ether extraction. No (E)-3,3-dimethyl-1-butenyl phenyl sulfide was isolated.

Four control reactions were performed (no inhibitor was added). In each case after the 30 minute irradiation period, 3 mcl of di-t-butylnitroxide was added to quench any reaction and allow the organic residues to be extracted from brine with ethyl ether. The yield distributions were (product:starting mercurial) 87:13, 80:10, 63:26, 70:25.

27. Effect of oxygen on the photodecomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide

(E)-3,3-Dimethyl-1-butenylmercury thiophenoxide (1.2 g, 3.06 mmol) in 50 ml oxygen-saturated DMSO (oxygen saturation was maintained by the rapid discharge of an oxygen stream from a glass frit placed at the bottom of the reaction vessel) was irradiated for 30 minutes in the apparatus described above (part 26, this section). The usual workup afforded a mixture of the starting mercurial (92%) and (E)-3,3-dimethyl-1-butenyl phenyl sulfide (5%) as determined by quantitative N.M.R. Control reactions described previously (part 26, this section) resulted in an average 75% yield product and 19% yield starting mercurial.

28. Effects of added salts on the photodecomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide

The (E)-3,3-dimethyl-1-butenylmercury thiophenoxide (1.2 g, 3.06 mmol) and the salt (consult Table X) were dissolved in 50 ml dry nitrogen-purged DMSO and the solution irradiated for 30 minutes in the apparatus described above (part 26, this section). When the irradiation period was over, the reaction was quenched with 3 mol di-*t*-butylnitroxide and the solution poured into brine. The products were extracted with ether and the extract washed with brine, dried ($MgSO_4$) and concentrated to afford a mixture containing only the starting mercurial and (E)-3,3-dimethyl-1-butenyl phenyl sulfide in yields determined by quantitative ^1H N.M.R. (see Table X). Comparison with control experiments (part 26 this section and Table X) revealed that the photodecomposition is strongly inhibited by mercaptide ion and lithium 2-nitropropanate. The potassium salt of diethyl phosphite and the sodium salt of *p*-toluenesulfinic acid also inhibit the reaction significantly.

29. Effect of added thiophenol on the photodecomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide

(E)-3,3-Dimethyl-1-butenylmercury thiophenoxide (1.2 g, 3.06 mmol) and thiophenol (0.38 g, 3.4 mmol) were dissolved in 15 ml nitrogen-purged benzene and the solution irradiated for 1.5 hours with a 275 watt sunlamp placed 8 inches from the Pyrex reaction vessel. Rapid precipitation of metallic mercury commenced after 1 minute. When irradiation was complete, the solution was decanted from the mercury beads and concentrated (0.05 torr, 30 minutes) to afford 0.59 g (100% yield) of the pure (E)-3,3-dimethyl-1-butenyl phenyl sulfide.

Similarly, the alkenylmercury thiophenoxide (80 mg, 0.02 mmol) and thiophenol (43 mg, 0.039 mmol) in 0.5 ml d_6-DMSO reacted under the influence of light in a Pyrex N.M.R. tube to cleanly afford the vinyl phenyl sulfide and unchanged thiophenol (the acidic proton is observed before and after irradiation). No 3,3-dimethyl-1-butene was formed. If 1 mol di-t-butyl nitroxide was added to the unreacted reagents in the N.M.R. tube and the tube heated to 60°C in an oil bath in subdued light, an appreciable amount (32% yield after 30 minutes) of 3,3-dimethyl-1-butene could be observed.

30. Effect of added phenyl disulfide on the photodecomposition of (E)-3,3-dimethyl-1-butenylmercury thiophenoxide

Phenyl disulfide (0.8 g, 3.7 mmol), (E)-3,3-dimethyl-1-butenylmercury chloride (1.1 g, 3.4 mmol), and sodium thiophenoxide (0.4 g, 3.0 mmol) were dissolved in 20 ml nitrogen-purged DMSO. This solution of phenyl disulfide and in situ-generated alkenylmercury thiophenoxide was irradiated for 2 hours in a Rayonet reactor (fourteen "350 nm" bulbs). Only a trace of mercury metal precipitated. The solution was poured into brine and organic products extracted with ethyl ether. A quantity (ca. 1 g) of ether-insoluble precipitate was collected by filtration and proved to be PhSHgSPh. The ether-soluble material was determined by quantitative ^{1}H N.M.R. to contain an 88% yield of (E)-3,3-dimethyl-1-butenyl phenyl sulfide. No alkenylmercury thiophenoxide was detected.

31. Photostability of some vinyl mercurials

The following vinyl mercurials (1.0 g) were found to be photostable in a Rayonet reactor (350 nm light) dissolved in 20 ml nitrogen-purged solvent: (E)-3,3-dimethyl-1-butenylmercury acetate (in benzene) for 6 hours, (E)-3,3-dimethyl-1-butenylmercury chloride (in DMSO) for 3 hours, bis[2,2-diphenylethenyl]mercury (in benzene) for 20 hours, and 2,2-diphenylethenylmercury bromide (in benzene) for 12 hours.

32. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury acetate with thiophenol

(E)-3,3-Dimethyl-1-butenylmercury acetate (0.5 g, 1.46 mmol) and thiophenol (0.183 g, 1.66 mmol) were dissolved in 20 ml of nitrogen-purged benzene and irradiated with a 275 watt sunlamp placed approximately 8 inches from the Pyrex reaction vessel for 3 hours. After the first minute of irradiation, mercury metal began to precipitate. The solution was decanted from the mercury beads and concentrated.

Evacuation at 0.1 torr (25°C) for 1 hour to remove traces of acetic acid and thiophenol afforded 0.28 g (100% yield) of ^{1}H N.M.R.-pure (E)-3,3-dimethyl-1-butenyl phenyl sulfide.

In an N.M.R. tube (E)-3,3-dimethyl-1-butenylmercury acetate (0.13 g, 0.38 mmol), thiophenol (0.041 ml, 0.4 mmol), and di-t-butyl nitroxide (0.1 mcl added as a stabilizer) were dissolved in 0.5 ml d_6-benzene. The ^{1}H N.M.R. spectrum revealed a quantitative conversion to (E)-3,3-dimethyl-1-butenylmercury thiophenoxide and acetic acid (1H, 11.93 ppm; 3H, 1.62 ppm).

33. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with thiophenol

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and thiophenol (0.44 g, 4 mmol) were dissolved in 25 ml of nitrogen-purged benzene containing 0.8 g of sodium bicarbonate suspended by the action of gently stirring. Bubbles of carbon dioxide were observed for several minutes. The slurry was irradiated for 17 hours with a 275 watt sunlamp placed 8 inches from the Pyrex reaction flask. After the first few minutes of irradiation, mercury metal was observed to precipitate. The solution was decanted from the salt/mercury metal residue. The residue was rinsed once with benzene. The combined benzene solution was concentrated under vacuum (0.1 torr/25°C for 1 hour to remove excess thiophenol) to afford 0.59 g (99% yield) of (E)-3,3-dimethyl-1-butenyl phenyl sulfide (^{1}H N.M.R.-pure) as a light yellow oil.

34. Photoreaction of benzyl mercaptan with (E)-3,3-dimethyl-1-butenylmercury acetate or chloride

(E)-3,3-Dimethyl-1-butenylmercury acetate (0.5 g, 1.46 mmol) and benzyl mercaptan (0.19 g, 1.54 mmol) were dissolved in 20 ml nitrogen-purged benzene and the solution irradiated for 18 hours with a sunlamp. Workup afforded a mixture of an oil and a solid (PhSHgSPh). The solid was removed by taking the mixture up in warm hexane and filtering. The hexane solution was concentrated under vacuum to afford 0.29 g (97% yield) of N.M.R.-pure (E)-3,3-dimethyl-1-butenyl benzyl sulfide as a light yellow oil. The yellow color was removed by Kugelrohr distillation (58-60°C/0.015 torr) to obtain 0.28 g (93% yield) colorless liquid.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.33, 1H (d) 5.88 (J_H = 16 Hz), 1H (d) 5.75 (J_H = 16 Hz), 2H (s) 3.73, 9H (s) 0.96.

I.R. (neat, NaCl plates, cm^{-1}) 3040 (m), 2960 (vs), 2900 (m), 2870 (m), 1600 (w), 1500 (m), 1450 (m), 1360 (m), 1250 (m), 1070 (w), 1025 (w), 945 (m), 820 (w), 760 (w), 650 (s).

M.S. Calculated for $C_{13}H_{18}S$: 206.11293. Measured: 206.11321. Error: 1.4 ppm.

Elemental analysis. Calculated for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54. Found: C, 75.51; H, 8.61.

The alkenyl benzyl sulfide was also prepared by the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) with benzyl mercaptan (0.5 g, 4 mmol) in 25 ml nitrogen-purged benzene in which 1.5 g of sodium bicarbonate was suspended by gentle stirring. After 5 hours of sunlamp irradiation, the solution was decanted into 100 ml of 10% aqueous potassium carbonate (to remove excess mercaptan) and the product extracted with ether. The ether extract afforded, after Kugelrohr distillation (60-62°C/0.02 torr), 0.41 g (64% yield) of the pure (E)-3,3-dimethyl-1-butenyl benzyl sulfide.

35. Photoreaction of n-butyl mercaptan and (E)-2-phenyl-1-ethenylmercury chloride

(E)-2-Phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) was dissolved in 25 ml of nitrogen-purged benzene containing n-butane thiol (0.28 g, 3.1 mmol) and 1.0 g of sodium bicarbonate suspended by gentle stirring. The mixture was irradiated with a sunlamp for 3 hours. The solution was then decanted from the residue and the residue rinsed with a little benzene. Concentration of the combined benzene solution under vacuum afforded 0.57 g (100% yield) of N.M.R.-pure (E)-2-phenyl-1-ethenyl n-butyl sulfide as a light yellow liquid. This sulfide has been reported in the literature [112].

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.15-7.6, 1H (d) 6.68 (J_H = 15 Hz), 1H (d) 6.42 (J_H = 15 Hz), 2H (m) 2.65-3.2, 7H (m) 0.7-2.0.

I.R. (neat, NaCl plates, cm^{-1}) 3020 (w), 2960 (s), 2930 (s), 2870 (m), 1590 (w), 935 (s), 910 (w), 730 (vs), 690 (s).

M.S. Calculated for $C_{12}H_{16}S$: 192.09728. Measured: 192.09799. Error: 3.7 ppm.

36. Photoreaction of t-butyl mercaptan and (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) was dissolved in 25 ml of nitrogen-purged benzene containing t-butyl mercaptan (0.32 g, 3.5 mmol) and 1.0 g of sodium bicarbonate suspended with gentle stirring. The mixture was irradiated with a sunlamp for 15 hours. Workup afforded a mixture of an oil and a solid ($(t\text{-Bu})_2Hg$) which was resolved by taking up the oil in warm hexane and filtering off the solid mercury salt. Concentration of the hexane solution afforded 0.53 g (100% yield) of N.M.R.-pure (E)-3,3-dimethyl-1-butenyl t-butyl sulfide as a light yellow liquid. This sulfide has been reported in the literature [113].

^{1}H N.M.R. ($CDCl_3$, δ) 2H (s) 5.96, 9H (s) 1.30, 9H (s) 1.03. Note the magnetic equivalence of the vinyl protons.

I.R. (neat, NaCl plates, cm^{-1}) 3020 (w), 2960 (vs), 2900 (s), 2860 (s), 1465 (m), 1450 (s), 1360 (s), 1155 (s), 950 (m).

M.S. Calculated for $C_{10}H_{20}S$: 172.12858. Measured: 172.12857. Error: -0.1 ppm.

37. Photoreaction of thiophenol and (E)-2-(acetyloxy)-1-ethyl-1-butenylmercury chloride

(E)-2-(Acetyloxy)-1-ethyl-1-butenylmercury chloride (1.0 g, 2.65 mmol) was dissolved in 25 ml of nitrogen-purged benzene containing thiophenol (0.32 g, 2.9 mmol) and 1.0 g of sodium bicarbonate suspended with gentle stirring. The mixture was irradiated with a sunlamp for

11 hours. Workup afforded 0.72 g of a crude yellow oil determined to contain a 98% yield of the anticipated alkenyl sulfide by quantitative ^{1}H N.M.R. Kugelrohr distillation (78-80°C/0.015 torr) yielded 0.61 g (92% yield) of the pure 2-(acetyloxy)-1-ethyl-1-butenyl phenyl sulfide as a colorless oil. The stereochemistry of the product was not determined.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.0-7.5, 2H (quartet) 2.66 (J_H = 7 Hz), 2H (quartet) 2.14 (J_H = 7 Hz), 3H (s) 2.18, 3H (t) 1.02 (J_H = 7 Hz), 3H (t) 0.99 (J_H = 7 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 3060 (w), 2980 (m), 2940 (w), 2880 (w), 1750 (vs), 1640 (w), 1580 (w), 1470 (m), 1450 (w), 1430 (m), 1365 (m), 1220 (vs), 1170 (vs), 1105 (s), 1030 (m), 1005 (w), 900 (w), 730 (s), 680 (m).

M.S. Calculated for $C_{14}H_{18}O_2S$: 250.10276. Measured: 250.10309. Error: 1.3 ppm.

Elemental analysis. Calculated for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; O, 12.78; S, 12.81. Found: C, 67.40; H, 7.41.

38. Photoreaction of (E)-2-chloro-3-hydroxy-1-propenylmercury chloride with thiophenol

(E)-2-Chloro-3-hydroxy-1-propenylmercury chloride (1.0 g, 3.05 mmol) was dissolved in 25 ml of nitrogen-purged benzene containing thiophenol (0.33 g, 3 mmol) and 1.0 g of solid sodium bicarbonate suspended with gentle stirring. The mixture was irradiated for 5.25 hours with a sunlamp. Workup afforded 0.77 g crude yellow oil. Kugelrohr distillation (100-103°C/0.01 torr) yielded 0.375 g (61%) pure 2-chloro-3-hydroxy-1-propenyl phenyl sulfide as a colorless oil. The stereochemistry of the product was not determined. Significant yield reduction was due to thermal decomposition during distillation. The compound was rather thermally unstable even at room temperature (after a few days, the oil had decomposed to a red-brown tar), so a satisfactory elemental analysis could not be obtained.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (s) 7.27, 1H (s) 6.40, 2H (s) 4.42, 1H (s, broad) 3.05 (variable).

I.R. (neat, NaCl plates, cm^{-1}) 3350 (s, broad), 3050 (w), 2920 (w), 2860 (w), 1575 (m), 1470 (s), 1430 (s), 1055 (s), 1020 (s), 810 (m), 730 (s), 680 (s).

M.S. Calculated for $C_9H_9ClOS\cdot$ 200.00727. Measured: 200.0058. Error: -2.2 ppm.

39. Photoreaction of ethenylmercury chloride and thiophenol

Ethenylmercury chloride (1.0 g, 3.8 mmol) was dissolved in 25 ml of nitrogen-purged benzene containing thiophenol (0.44 g, 4.0 mmol) and 1.0 g of solid sodium bicarbonate suspended with gentle stirring. The mixture was irradiated for 3 hours. Workup afforded 0.52 g (100% yield) of N.M.R.-pure ethenyl phenyl sulfide as a light yellow oil. This sulfide has been reported in the literature [114].

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.1-7.5, 1H (doublet of doublets) 6.52 ($J_{H,trans}$ = 17 Hz, $J_{H,cis}$ = 7 Hz), 1H (d) 5.30 (J_H = 7 Hz), 1H (d) 5.30 (J_H = 17 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 3050 (w), 1575 (w), 1020 (w), 950 (w), 900 (w), 730 (s), 675 (w).

M.S. Calculated for C_8H_8S: 136.03467. Measured: 136.03450. Error: -1.2 ppm.

40. Photoreaction of $CH_3C(=O)SH$ and (E)-3,3-dimethyl-1-butenylmercury acetate

(E)-3,3-Dimethyl-1-butenylmercury acetate (0.5 g, 1.46 mmol) and thiolacetic acid (0.16 g, 2.1 mmol) were dissolved in 20 ml nitrogen-purged benzene and irradiated with a sunlamp for 17 hours. Black precipitate (presumably HgS) appeared, but no metallic mercury was observed. The resulting black suspension was filtered to afford a colorless solution which, upon concentration, afforded 0.22 g of slush containing white solid and colorless liquid. Kugelrohr distillation (115°C/30 torr) afforded 0.1 g (43% yield) of a colorless liquid determined to be (ca. 95% purity) (E)-3,3-dimethyl-1-butenyl acetyl sulfide.

^1H N.M.R. ($CDCl_3$, δ) 1H (d) 6.42 (J_H = 16 Hz), 1H (d) 5.92 (J_H = 16 Hz), 3H (s) 2.33, 9H (s) 1.07.

I.R. (neat, NaCl plates, cm^{-1}) 3050 (w), 2960 (vs), 2900 (m), 2860 (m), 1700 (vs), 1460 (m), 1360 (s), 1260 (w), 1110 (vs), 950 (vs), 915 (m), 830 (m).

M.S. Calculated for $C_8H_{14}OS$: 158.07654. Measured: 158.07658. Error: 0.3 ppm.

When a three-fold excess of thioacetic acid was employed, none of the expected alkenyl thioacetate was formed, although the appearance of the reaction was the same as described above. Evaporation of the benzene solvent afforded only a chloroform-insoluble white solid.

41. Photoreaction of $HSCH_2COOH$ and (E)-3,3-dimethyl-1-butenylmercury acetate

(E)-3,3-Dimethyl-1-butenylmercury acetate (0.5 g, 1.46 mmol) and mercaptoacetic acid (0.15 g, 1.6 mmol) were dissolved in 20 ml of nitrogen-purged benzene. Immediately, a white precipitate formed. After 7 hours of sunlamp irradiation, no mercury metal had precipitated and the white precipitate remained intact.

42. Attempted preparation of 1-alkenyl phenyl ethers from 1-alkenylmercury salts

(E)-3,3-Dimethyl-1-butenylmercury acetate (0.5 g, 1.46 mmol) and phenol (0.2 g, 2.1 mmol) were dissolved in 20 ml of nitrogen-purged benzene and the solution irradiated with a sunlamp for 1 hour. Since no mercury metal was observed to precipitate, the reaction vessel was placed in a Rayonet RPR-100 reactor (fourteen "350 nm" bulbs) and the solution was irradiated for 21 hours. The solution yellowed slightly, but only a trace of mercury precipitated.

In another experiment, (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.0 mmol) was added to a solution containing potassium t-butoxide (0.34 g, 3.0 mmol) and phenol (0.3 g, 3.2 mmol) in 50 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 5 hours in Rayonet reactor (fourteen "350 nm" bulbs). The solution gradually blackened, but only a trace of metallic mercury was observed.

III. PHOTOCHEMICAL REACTIONS OF DISULFIDES, PHENYL DISELENIDE, AND PHENYL DITELLURIDE WITH VINYLMERCURY HALIDES TO FORM VINYL SULFIDES, SELENIDES AND TELLURIDES

A. Introduction

Organomercury salts are generally unreactive towards electrophilic cleavage by reagents such as disulfides [67]. This low reactivity is readily understood in terms of the weak electron donating ability of organomercury salts coupled with the weak electrophilicity of the disulfide [115]. We have found that vinylmercury halides are activated towards photo-induced "electrophilic" substitution reactions with disulfides, phenyl diselenide, and phenyl ditelluride.

B. Results and Discussion

1. Reaction of disulfides with vinylmercury halides

No reaction occurred between phenyl disulfide and (E)-3,3-dimethyl-1-butenylmercury chloride upon prolonged heating (50°C) in benzene solution in the dark. Reaction (Eq 40) occurred quantitatively within

$$R^1HgX + R^2YYR^2 \xrightarrow[PhH]{light} R^1YR^2 + R^2YHgX \tag{40}$$

R^1 = vinyl　　X = halogen (Br, Cl)

Y = S, Se, Te

a few hours to afford chloromercury thiophenoxide as a white salt, nearly benzene-insoluble, and (E)-3,3-dimethyl-1-butenyl phenyl sulfide (100% yield, see Table XI) under the influence of radiation from an

Table XI. Photoreaction of vinylmercury halides with disulfides, phenyl diselenide, and phenyl ditelluride

$$R^1HgX + R^2YYR^2 \xrightarrow[PhH]{light} R^1YR^2 + R^2YHgX$$

R^1HgX	R^2YYR^2	Time[a]	% Yield[b] R^1YR^2 (stereochemistry)
(*E*)-$Me_3CCH{=}CHHgCl$	PhSSPh	6 h	100 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	*n*-BuSSBu-*n*	17 h	100 (>98% *E*)
(*E*)-PhCH=CHHgCl	PhSSPh	2 h	91 (*E*:*Z* = 89:11)
$(Ph)_2C{=}CHHgBr$	MeSSMe	8 h	100
$(Ph)_2C{=}CHHgBr$	*i*-PrSSPr-*i*	24 h	98
$CH_2{=}C(HgBr)$(*cyclo*-C_6H_{11})	MeSSMe	67 h	---[c]
(*E*)-$Me_3CCH{=}CHHgCl$	$CH_3C(=O)SSC(=O)Me$	14 h	*ca*. 5[d] (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	PhSeSePh	2 h	95 (>98% *E*)
$CH_2{=}CH_2HgCl$	PhSeSePh	2.5 h	91
(*E*)-PhCH=CHHgCl	PhSeSePh	2 h	90 (>98% *E*)
(*E*)-$Me_3CCH{=}CHHgCl$	PhTeTePh	18 h	89 (>98% *E*)[e]

---

[a] Irradiation provided by a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel. Reactions were performed at ambient temperatures (25-40°C).

[b] Yield of N.M.R.-pure product. Stereochemistry determined by ^1H N.M.R.

[c] Complex product mixture was obtained.

[d] Some (*E*)-$Me_3CCH{=}CHHgCl$ and acetyl disulfide were recovered.

[e] The product decomposed rapidly when exposed to room light and air.

ordinary 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel. After the sunlamp was turned on the precipitation of the halomercury mercaptide began within 5 minutes. Workup consisted of filtering off the precipitate and removing the benzene to afford a mixture of the alkenyl sulfide (generally an oil) and a trace of the halomercury mercaptide. The mercury salt was easily separated from the sulfide owing to the total insolubility of the salt in hexane. The crude sulfide was light yellow in color, although N.M.R.-pure. G.L.C. revealed the presence of ca. 3% phenyl disulfide. Further purification was achieved by a simple Kugelrohr distillation.

The effects of possible inhibitors were surveyed. The addition of 5-7 mole % di-t-butyl nitroxide to the reaction of (E)-3,3-dimethyl-1-butenylmercury chloride and phenyl disulfide significantly delayed initiation (see Experimental Section). Galvinoxyl (5 mole %), a stable paramagnetic species and known free radical scavenger, completely inhibited the reaction for at least 5 hours. 2,6-Di-t-butyl phenol, a hydrogen transfer agent, had a slight retarding effect on the reaction rate, but did not prevent the clean conversion of starting materials to products even when present in 100 mole %. Oxygen failed to completely inhibit the reaction, although the rate was somewhat retarded. The complete description of these experiments is given in the Experimental Section.

Alkyl disulfides were found to react cleanly with vinylmercury halides. Thus, (E)-3,3-dimethyl-1-butenylmercury chloride and n-butyl disulfide afforded a quantitative yield of (E)-3,3-dimethyl-1-butenyl n-butyl sulfide (Table XI). Methyl disulfide and isopropyl disulfide, likewise, reacted with 2,2-diphenylethenylmercury bromide in high yields. Acetyl disulfide failed to react cleanly, however, and prolonged sunlamp irradiation resulted in a very low yield (ca. 5%) of (E)-3,3-dimethyl-1-butenyl acetyl sulfide along with recovered acetyl disulfide and starting mercurial.

(E)-2-Phenyl-1-ethenylmercury chloride reacted with phenyl disulfide to give a mixture of E and Z products in an 89:11 ratio (Table XI). This is essentially the same product distribution obtained by the photochemical decomposition of (E)-2-phenyl-1-ethenylmercury thiophenoxide described in the previous chapter (see Table VIII).

The reaction between phenyl disulfide and 1-(cyclohexylmethyl)-1-ethenylmercury bromide demonstrated the dramatic effect of steric hindrance at the α-vinyllic position (Table XI). An irradiation time of 67 hours was required for complete precipitation of the bromomercury thiophenoxide salt. Workup afforded a complex mixture containing five major components by G.L.C. and the crude isolate was not further analyzed.

2. Reactions of vinylmercury halides with phenyl diselenide and phenyl ditelluride

Phenyl diselenide did not react with (E)-3,3-dimethyl-1-butenylmercury chloride in benzene solution at 50°C in the dark, but under sunlamp irradiation (E)-3,3-dimethyl-1-butenyl phenyl selenide was formed in high yield (Table XI). The reaction was slowed by the presence of one equivalent of 2,6-di-t-butyl phenol, but the vinyl selenide and starting vinyl mercurial were recovered after partial reaction completion in quantities corresponding to complete mass balance (i.e., no 3,3-dimethyl-1-butene was formed) with respect to the starting vinylmercury halide. Other vinylmercury halides, ethenylmercury chloride and (E)-2-phenyl-1-ethenylmercury chloride, also reacted photochemically to afford the corresponding selenides in high yield (Table XI).

The reaction method was extended in one example to the preparation of an alkenyl telluride, representative of a virtually unexplored class of compounds. Thus, (E)-3,3-dimethyl-1-butenylmercury chloride reacted with phenyl ditelluride in benzene with sunlamp irradiation to afford (after a shortpath distillation) an 89% yield of pure (E)-3.3-dimethyl-1-butenyl phenyl telluride (Table XI). Quite unlike the analogous sulfides and selenides, this product decomposed within a few days of storage exposed to air and room light with the precipitation of an insoluble white solid. A survey of recent literature reveals that organotellurides of the general form RTePh are known to be sensitive to photo-oxidation and that such compounds are best handled in a photographic darkroom illuminated by a red light [116].

3. Reactions of nonvinylic organomercury halides with phenyl disulfide

Allylmercury chloride reacted in benzene with phenyl disulfide over an 18 hour irradiation period with a sunlamp, afforded a 32% yield of allyl phenyl sulfide (determined by ^{1}H N.M.R. analysis of the crude reaction isolate). Benzylmercury chloride and phenyl disulfide in benzene with 18.25 hours of irradiation in a Rayonet RPR-100 reactor ("350 nm" light) afforded a crude isolate containing only a 3% yield of benzyl phenyl sulfide (determined by ^{1}H N.M.R.). A benzene solution of cyclopropylmercury bromide and phenyl disulfide failed to precipitate any bromomercury thiophenoxide even after 19 hours of Rayonet irradiation. Phenylmercury chloride and phenyl disulfide in DMSO (the mercurial is only slightly soluble in benzene) afforded no diphenyl sulfide (determined by G.L.C.) after 22 hours of sunlamp and 3 hours of Rayonet irradiation. These examples serve to illustrate that vinylmercury halides enjoy a special activation towards substitution reactions by disulfides.

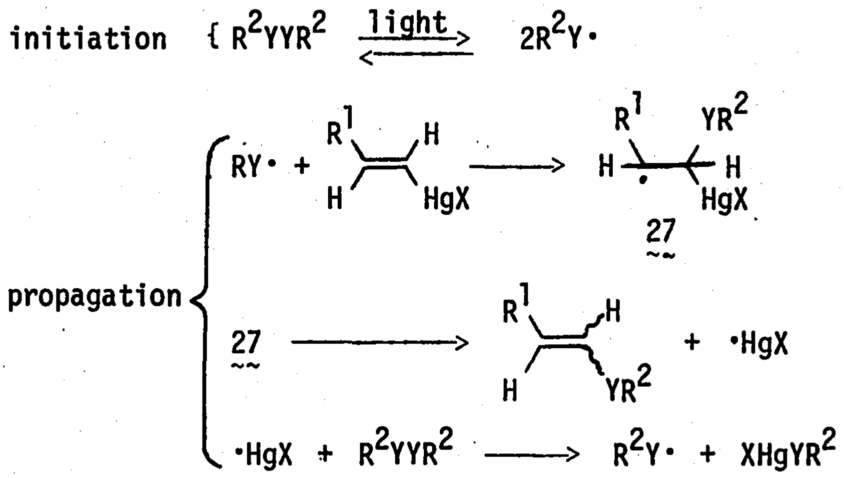
4. Mechanistic considerations

The data allow a selection of the basic operative mechanism. Scheme 17 outlines a radical chain mechanism employing the basic features of Scheme 15, the mechanism for photodecomposition of vinylmercury mercaptides. The mercury(I) paramagnetic species, instead of decomposing to a mercury atom and a radical as in Scheme 15, attacks R^2YYR^2 (S_H2 displacement) to generate the chain-carrying radical, $R^2Y\cdot$, and the observed mercury(II) salt.

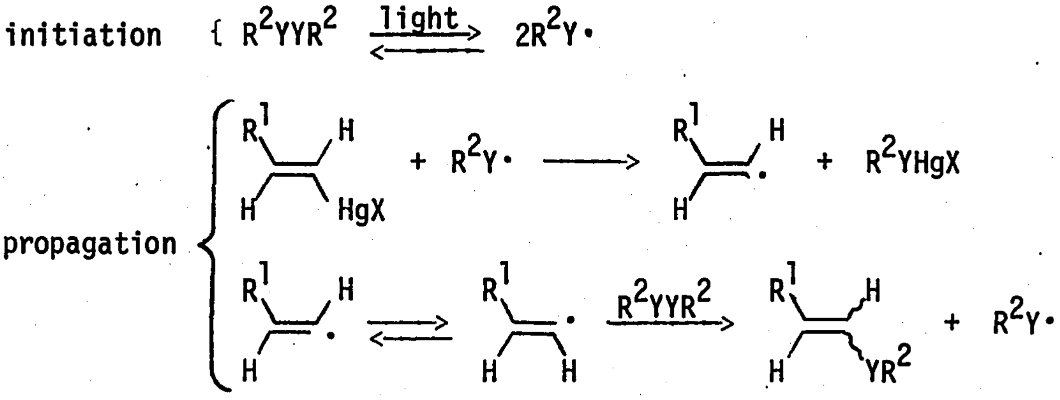
Scheme 19 depicts a mechanism in which a vinyl radical replaces halomercury(I) as a chain-carrying species and thiyl attacks mercury(II) in S_H2 fashion.

Scheme 18

X = halogen Y = S, Se, Te



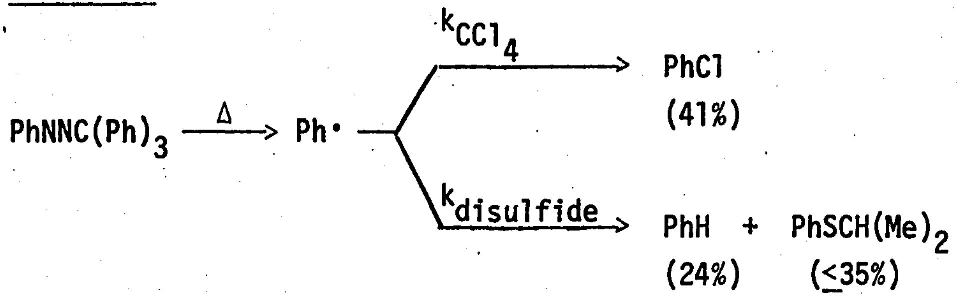
Scheme 19



Both mechanisms involve radical chains, supported by inhibition by free radical scavengers and observed photo-initiation. The proposed initiation process, the photo-fragmentation of R^2YYR^2, is reasonable since disulfides are well known the homolyticaly photo-dissociate [82]. Production of free radicals by the fragmentation of the vinylmercury halide cannot be ruled out.

Distinction between the mechanisms of Schemes 18 and 19 rests upon the differences between the proposed vinyl and halomercury(I) radicals. Since vinylic radicals would be expected to readily abstract a hydrogen atom from 2,6-di-_t_-butyl phenol, the lack of a powerful inhibitory effect on reactions by this hydrogen transfer agent favors the intermediates of Scheme 18. Thiyl radicals would not be expected to readily abstract hydrogen from the phenolic oxygen (the bond formed is weaker than the bond broken). Likewise, the halomercury radical is a poor hydrogen atom acceptor [26-29]. Scheme 17 is also favored by the observation that vinylmercury halides cleanly react with alkyl disulfides. It is known that when phenyl radicals are formed by the decomposition of phenyl azotriphenylmethane at 60°C in a solvent composed of equimolar amounts of carbon tetrachloride and isopropyl disulfide, the product distribution includes chlorobenzene (41%) and benzene (24%) for a phenyl radical balance of 65% [117]. Thus, the maximum possible yield of isopropyl phenyl sulfide produced is 35% (Scheme 20) and the maximum ratio of phenyl attack on sulfur to phenyl attack on hydrogen is 1.46. However, the reaction between 2,2-diphenylethenylmercury bromide and

Scheme 20



isopropyl disulfide (Table XI) afforded a 98% yield of 2,2-diphenylethenyl isopropyl sulfide. No 2,2-diphenylethene was observed. It seems unreasonable that the 2,2-diphenylethenyl radical should demonstrate a completely different reactivity towards isopropyl disulfide than phenyl radical. Again, the intermediacy of the halomercury(I) radical (Scheme 18) is favored.

The decomposition of intermediate **27** to a mercury(I) radical and a vinyl sulfide molecule is analogous to the decomposition of **22** discussed in the previous chapter. The halomercury(I) species thus produced would not be expected to readily dissociate to form a mercury atom and a halogen atom in contrast to the documented instability of alkylmercury(I) radicals [26-29]. The dissociation energy for Cl-Hg• has been measured at 24±2 kcal mol^{-1} and that of Br-Hg• at 17±2 kcal mol^{-1} [118-120]. These values are considerably higher than 7 kcal mol^{-1} for Me-Hg• [30].

The proposed reaction of halomercury(I) radicals with disulfides is analogous to the well-studied reaction of disulfides with the tributyl tin radical (Eq. 41). For R = phenyl, $k_s = 4.5 \times 10^6\ M^{-1}\ sec^{-1}$, while

$$(\underline{n}\text{-Bu})_3\text{Sn}\cdot + \text{RSSR} \xrightarrow{2\ k_s} (\underline{n}\text{-Bu})_3\text{SnSR} + \text{RS}\cdot \qquad (41)$$

for R = butyl, $k_s = 5.5 \times 10^5\ M^{-1}\ sec^{-1}$ [121]. Thus, the proposed reactivity of the halomercury(I) species appears reasonable.

Interestingly, alkyl phenyl selenides and tellurides are reported to be the products of the (thermal) reaction between dialkyl mercurials and phenyl diselenide or phenyl ditelluride (Eq. 42) [107]. The

$$R_2Hg + PhYYPh \xrightarrow[\text{reflux}]{\text{dioxane}} 2RYPh + Hg^\circ \qquad (42)$$

$$Y = Se,\ Te$$

reaction proceeds at room temperature with excess PhYYPh to yield two equivalents of alkyl phenyl selenide (telluride) and one equivalent of mercury(II) selenide (telluride) salt (Eq. 43). The authors

$$R_2Hg + 2PhYYPh \xrightarrow[25^\circ C]{\text{dioxane}} 2RYPh + PhYHgYPh \qquad (43)$$

demonstrated the thermal instability of the mercury selenide and telluride salts (Eq. 44), thus clarifying somewhat the transformation

$$PhYHgYPh \xrightarrow[\text{reflux}]{\text{dioxane}} PhYYPh + Hg^\circ \qquad (44)$$

of Equation 42 [107]. The mercury(II) salt, PhYHgYPh, is formed either by disproportionation of alkylmercury selenide (telluride) (Eq. 45) or

$$2PhYHgR \rightleftharpoons R_2Hg + PhYHgYPh \qquad (45)$$

$$RHgYPh + PhYYPh \longrightarrow RYPh + PhYHgYPh \qquad (46)$$

by the electrophilic cleavage of the alkylmercury selenide (telluride) by PhYYPh (Eq. 46). The authors did not address the question of whether or not reaction might be occurring via a radical chain mechanism [107] analogous to that operating in the free radical halogenolysis of alkylmetals [67] (Scheme 21).

Scheme 21

R = alkyl Y = Se, Te

$$R_2Hg + PhY\cdot \longrightarrow R\cdot + RHgYPh$$

$$R\cdot + PhYYPh \longrightarrow RYPh + PhY\cdot$$

No thermal (dark) reaction was detected between phenyl diselenide and (E)-3,3-dimethyl-1-butenylmercury chloride. Since the light-initiated reaction was not completely inhibited nor product formation diverted by the presence of 100 mole % 2,6-di-t-butyl phenol (the rate is markedly attenuated, however), the reaction probably does not proceed via the vinyl radical nor by the concerted S_E2 process. Thus, substitution does not occur by the pathway operative in Equation 42.

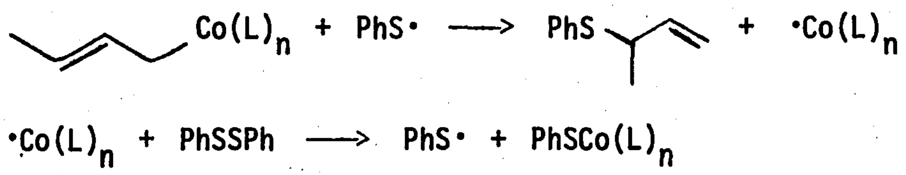
The weak inhibition by oxygen of the reaction between vinylmercury halide and disulfide was unexpected in light of the strong inhibitory effect exhibited in the photodecomposition of vinylmercury mercaptides. Thiyl radicals are probably not readily trapped by oxygen as illustrated by the oxygen-initiated exchange reaction between thiols and disulfides, known to proceed via thiyl radicals (Eq. 47) [122].

$$PhSH + PhS^{*}\text{-}SPh \rightleftharpoons PhS^{*}H + PhSSPh \tag{47}$$

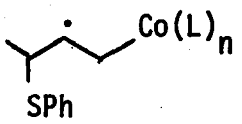
Apparently, the other paramagnetic intermediates of Scheme 18, the mercury(I) radical and 27, are either unreactive towards oxygen or are too short-lives to be efficiently trapped.

Allylcobaloximes (bis(dimethylslyoximato)allylpyridine-cobalt(III)) react with phenyl disulfide or phenyl diselenide by a radical chain mechanism [123] (Scheme 22). As indicated in the Scheme,

Scheme 22



complete allylic transposition occurs. The S_H2 displacement on allyl may be concerted or may involve a β-cobalt radical (28). A similar



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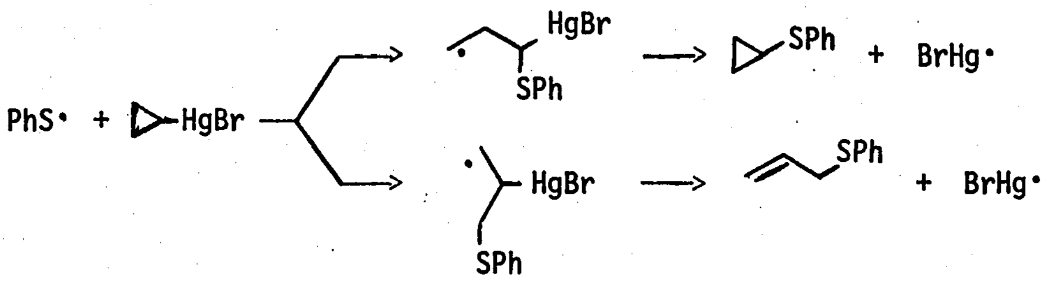
mechanism can be written for the reaction between allylmercury chloride and phenyl disulfide. Unfortunately, only a 32% yield of allyl phenyl sulfide was produced. Similarly, a radical chain substitution by thiyl of cyclopropylmercury bromide involving attack on the ring and ring opening (Scheme 23) may be imagined, but the mercurial was unreactive towards phenyl disulfide.

Scheme 23



As predicted by the mechanism of Scheme 18, benzylmercury chloride and phenylmercury chloride do not react with phenyl disulfide to give benzyl phenyl sulfide and diphenyl sulfide, respectively. The non-reactivity of aryl and alkyl mercurials is not easily accommodated by the alternative mechanism of Scheme 19.

C. Conclusion

Although alkyl- and arylmercury halides are not cleaved by disulfides even with photo-initiation, vinylmercury halides rapidly react under the influence of ordinary sunlamp irradiation to provide halomercury mercaptide salts and vinyl sulfides in high yield. The exceptional reactivity of vinyl mercurials towards cleavage is attributed to the special activation afforded these compounds via the mechanism of Scheme 18. Thus, the photochemical reductive elimination of vinylmercury mercaptides (Chapter II, Part II of this thesis) and the cleavage of vinylmercury halides by disulfides are shown to be linked mechanistically by the intermediacy of β-mercury radicals (22 and 27) which decompose to form the observed vinyl sulfide product and a chain-carrying mercury(I) species.

The photo-initiated cleavage of vinylmercury halides was extended to include phenyl diselenide and phenyl ditelluride. Vinyl selenides are generally prepared by the elimination of HX from β-halo selenides [124]. One selenide, (E)-2-phenyl-1-ethenyl phenyl selenide, has been reportedly prepared by the reaction of phenylselenyl chloride with (E)-2-phenyl-1-ethenylmercury chloride [124]. (We have been unable to obtain the desired product in greater than 25% yield using the literature procedure, however.) Vinyl tellurides appear to be an unexplored class of compounds. The instability of many diorganotellurium(II) compounds may be responsible for the lack of literature in this area. Owing to the simple workup procedure, the present method appears to be a satisfactory approach to many of these compounds.

D. Experimental Section

1. General considerations

Phenyl disulfide was purchased from Columbia and recrystallized before use from ethanol. Methyl disulfide n-butyl disulfide, isopropyl disulfide, and phenyl diselenide were purchased from Aldrich. 2,6-Di-t-butyl phenol was purchased from K and L Laboratories and galvinoxyl was purchased from Aldrich. Phenyl ditelluride was obtained from the group of R. J. Angelici and is available from the air oxidation of phenyl telluryl anion [107]. An authentic sample of allyl phenyl sulfide was prepared by the literature method [125]. Cyclopropylmercury bromide was prepared by James Tanko by the addition of mercuric bromide to cyclopropylmagnesium bromide in THF (m.p. 192-193, lit. [126] 196.5-197.5). Acetyl disulfide was prepared by a literature procedure [127].

2. Photochemical reaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and phenyl disulfide (0.7 g, 3.2 mmol) were dissolved in 30 ml of nitrogen-purged benzene in a Pyrex flask equipped with a magnetic stir bar. Refluxing for 45 minutes induced no apparent change in the solution, but white precipitate rapidly formed when the flask was irradiated with a sunlamp placed 6 inches from the reaction vessel. After 3 hours of irradiation, the solution was cooled and filtered. The precipitate was washed with a little benzene and the combined benzene solution concentrated under vacuum to afford a light yellow oil containing a little of the white solid chloromercury thiophenoxide salt. The oil was (E)-3,3-dimethyl-1-butenyl phenyl sulfide (100% yield by quantitative ^{1}H N.M.R.). The solid contaminant was removed by taking the oil up in warm hexane and filtering. Removal of the hexane followed by a Kugelrohr distillation (47°C/0.02 torr) afforded the vinyl sulfide as a colorless oil in 96% yield.

The use of reflux conditions was found to be unnecessary. The light-induced reaction (6 hours) at ambient temperature afforded a nearly quantitative yield of the vinyl sulfide.

3. Effect of dark on the reaction between (E)-3,3-dimethyl-1-butenylmercury chloride and phenyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl disulfide (0.9 g, 4.1 mmol) were dissolved in 20 ml of nitrogen-purged DMSO in a flask tightly wrapped in aluminum foil to omit light. The flask was immersed in a 25°C water bath and stirred for 15 hours. Galvinoxyl (2 mg) was then added to prevent light-promoted reactions and the solution was poured into 100 ml brine. Ether extraction afforded a mixture of phenyl disulfide and (E)-3,3-dimethyl-1-butenylmercury chloride (94% recovery by quantitative ^{1}H N.M.R.). No (E)-3,3-dimethyl-1-butenyl phenyl sulfide was detected.

In a control experiment, 1.5 hours of sunlamp irradiation with the reaction solution maintained at 25°C by a water bath afforded an 88:12 ratio of the product vinyl sulfide by the starting mercurial.

The reaction in benzene was found not to occur even with prolonged heating. (E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl disulfide (0.35 g, 1.6 mmol) in 10 ml benzene did not react detectably after stirring for 18 hours in an aluminum foil-wrapped flask immersed in a 50°C oil bath.

4. Effect of oxygen on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl disulfide (0.9 g, 4.1 mmol) were dissolved in 20 ml of DMSO saturated with oxygen rapidly foamed through the solution via a glass frit placed near the bottom of the reaction flask. The reaction temperature was maintained at 25°C by a water bath as the solution was irradiated for 1.5 hours with a sunlamp placed 4 inches from the Pyrex reaction vessel. The solution was then stabilized by the addition of galvinoxyl (2 mg) and poured into 100 ml brine. Ether extraction afforded a mixture of (E)-3,3-dimethyl-1-butenyl phenyl sulfide and starting mercurial in a 30:70 ratio. A control experiment performed under nitrogen afforded a product:starting material ratio of 88:12.

5. Effect of galvinoxyl on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol), phenyl disulfide (0.4 g, 1.8 mmol), and galvinoxyl (33 mg, 0.078 mmol) were dissolved in 10 ml of nitrogen-purged benzene and the solution was irradiated for 5 hours with a sunlamp placed 8 inches from the reaction vessel. The reaction temperature was maintained at 25°C with water cooling. Only a trace of precipitate was observed. The solvent was removed under vacuum and the residue analyzed by quantitative ^{1}H N.M.R. The spectrum revealed a nearly quantitative recovery of (E)-3,3-dimethyl-1-butenylmercury chloride. Quantitative G.L.C. (1/8" x 5'; 5% OV-3; internal standard = biphenyl; correction factor = 1.0) revealed a small peak of the correct reaction time for (E)-3,3-dimethyl-1-butenyl phenyl sulfide corresponding to a 3% yield.

6. Effect of di-t-butyl nitroxide on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl disulfide

In 0.5 ml of d_6-benzene in an N.M.R. tube was dissolved (E)-3,3-dimethyl-1-butenylmercury chloride (0.1 mmol), phenyl disulfide (0.12 mmol) and di-t-butyl nitroxide (0.007 mmol). A control experiment was similarly prepared, but without the nitroxide. Both tubes were exposed to irradiation from a sunlamp placed 6 inches distant. After each irradiation period, the contents of both tubes were analyzed by ^1H N.M.R. The results are summarized in Table XII.

Table XII. Effect of nitroxide on the photoreaction of phenyl disulfide with (E)-3,3-dimethyl-1-butenylmercury chloride

$$(E)\text{-}Me_3CCH{=}CHHgCl + PhSSPh \xrightarrow{light} (E)\text{-}Me_3CCH{=}CHSPh$$

Irradiation Time	mmol Vinyl Mercurial[a]	mmol Vinyl Sulfide[a]
0 minutes	0.100 (0.10)	0.000 (0.000)
5	0.100 (0.096)	0.000 (0.004)
10	0.100 (0.087)	0.000 (0.013)
25	0.100 (0.068)	0.000 (0.032)
40	0.100 (0.053)	0.000 (0.047)
60	0.094 (0.038)	0.006 (0.062)

[a] Amount given for the reaction inhibited with 7 mole % di-t-butyl nitroxide. Amounts in parentheses are for the control reaction.

Similar results were obtained with a larger reaction scale. (E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol), phenyl disulfide (0.5 g, 2.3 mmol), and di-t-butyl nitroxide (12 mcl, 11 mg, 0.078 mmol) were dissolved in 15 ml of nitrogen-purged benzene in a Pyrex flask equipped with a magnetic stir bar. The reaction flask was immersed in a 25°C water bath and irradiated with a 275 watt sunlamp positioned 4 inches from the reaction vessel. After about 40 minutes, the first trace of chloromercury thiophenoxide was observed to precipitate. After 1 hour of irradiation, 2 mg of galvinoxyl was added and the solvent removed under vacuum. Quantitative ^{1}H N.M.R. analysis of the residue revealed (E)-3,3-dimethyl-1-butenyl phenyl sulfide (11.4% yield) and the starting vinyl mercurial (86% recovery). In a control experiment, the yield of product vinyl sulfide was 86% and 11% of the starting mercurial was recovered.

7. Effect of 2,6-di-t-butyl phenol on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl disulfide (0.8 g, 3.7 mmol) were dissolved in 10 ml of nitrogen-purged benzene containing 2,6-di-t-butyl phenol (0.3 g, 1.53 mmol). The Pyrex reaction flask was immersed in a 25°C water bath and stirred gently as the solution was irradiated for 2 hours with a sunlamp. The solvent was removed under vacuum in subdued light to afford (E)-3,3-dimethyl-1-butenyl phenyl sulfide (84%) and starting vinyl mercurial (16%) by quantitative ^{1}H N.M.R. A control experiment afforded complete conversion to the product vinyl sulfide (100% yield).

8. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with n-butyl disulfide

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and n-butyl disulfide (0.563 g, 3.16 mmol) were dissolved in 20 ml of nitrogen-purged benzene and the solution was irradiated for 17 hours with a sunlamp. The benzene was removed under vacuum to afford a mixture of the vinyl sulfide (an oil) and the halomercury mercaptide salt (a solid). The oil was taken up in warm hexane and the solid removed by filtration. Removal of the hexane afforded N.M.R.-pure (E)-3,3-dimethyl-1-butenyl n-butyl sulfide as a light yellow liquid (0.55 g, 100% yield) containing a trace of n-butyl disulfide by G.L.C. The spectral properties of the product matched those of the compound prepared from n-butyl mercaptan and the alkenylmercury halide.

9. Photoreaction of (E)-2-phenyl-1-ethenylmercury chloride with phenyl disulfide

(E)-2-Phenyl-1-ethenylmercury chloride (0.5 g, 1.47 mmol) and phenyl disulfide (0.33 g, 1.5 mmol) were dissolved in 15 ml of nitrogen-purged benzene and irradiated for 2 hours with a sunlamp. The resulting precipitate was removed by filtration. Removal of the benzene under vacuum afforded 0.29 g of yellow liquid found to contain 2-phenyl-1-ethenyl phenyl sulfide (91% yield by ^{1}H N.M.R.) and a trace of phenyl disulfide. The ^{1}H N.M.R. spectrum at 100 MHz revealed an 89:11 ratio of E and Z isomers by integration of the vinyl proton absorptions.

10. Photoreaction of 2,2-diphenylethenylmercury bromide with methyl disulfide

2,2-Diphenylethenylmercury bromide (1.0 g, 2.18 mmol) and methyl disulfide (0.42 g, 4.5 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated with a sunlamp for 8 hours with gentle stirring. The accumulated bromomercury methyl mercaptide salt was removed by filtration and the benzene solution removed under vacuum to afford 0.5 g (100% yield) of ^{1}H N.M.R.-pure 2,2-diphenylethenyl methyl sulfide, a previously reported compound [128].

^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.22-7.33, 1H (s) 6.53, 3H (s) 2.33.

I.R. (melt, NaCl plates, cm^{-1}) 3060 (w), 3020 (w), 2820 (w), 1590 (w), 1500 (s), 1446 (s), 1320 (w), 1080 (m), 1034 (w), 812 (s), 775 (s), 760 (vs), 700 (vs).

M.S. Calculated for $C_{15}H_{14}S$: 226.08163. Measured: 226.08183. Error: 0.9 ppm.

Recrystallization from pentane afforded long white needles (m.p. 72-73°C, lit. [128] 74-74.5°C).

11. Photoreaction of 2,2-diphenylethenylmercury bromide with isopropyl disulfide

2,2-Diphenylethenylmercury bromide (1.0 g, 2.18 mmol) and isopropyl disulfide (3.3 g, 22 mmol) were dissolved in 15 ml of nitrogen-purged benzene and the solution was irradiated with a sunlamp for 24 hours. The precipitate of bromomercury isopropyl mercaptide was removed by filtration and the benzene solution concentrated under vacuum.

Kugelrohr distillation (110°C/0.01 torr) afforded 0.54 g (98% yield) of the pure 2,2-diphenylethenyl isopropyl sulfide as a colorless oil.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (s) 7.28, 5H (s) 7.18, 1H (s) 6.63, 1H (septet) 3.16 (J_H = 7 Hz), 6H (d) 1.33 (J_H = 7 Hz).

I.R. (neat, NaCl plates. cm^{-1}) 3060 (w), 3030 (w), 2970 (m), 2930 (w), 2870 (w), 1600 (w), 1585 (w), 1495 (m), 1445 (m), 1385 (w), 1365 (w), 1245 (m), 1155 (m), 1170 (w), 1130 (w), 940 (w), 815 (m), 770 (s), 750 (s), 695 (vs).

M.S. Calculated for $C_{17}H_{18}S$: 254.11293. Measured: 254.11309. Error: 0.45 ppm.

Elemental analysis. Calculated for $C_{17}H_{18}S$: C, 80.26; H, 7.13; S, 12.60. Found: C, 80.17; H, 7.12.

12. Photoreaction of 1-(cyclohexylmethyl)-1-ethenylmercury bromide with methyl disulfide

1-(Cyclohexylmethyl)-1-ethenylmercury bromide (1.0 g, 2.48 mmol) and methyl disulfide (0.42 g, 4.45 mmol) were dissolved in 20 ml of nitrogen-purged benzene and the solution was irradiated with a sunlamp for 22 hours. Workup afforded a 30% recovery of the starting mercurial. The reaction was subsequently repeated with 5.3 g (56 mmol) of methyl disulfide and a 67 hour irradiation period. Filtration and removal of the solvent under vacuum afforded 0.52 g of a yellow oil. The crude isolate contained 5 major volatile components by G.L.C. (5' x 1/8"; 5% OV-3) and was not analyzed further.

13. Photoreaction of (*E*)-3 3-dimethyl-1-butenylmercury chloride with acetyl disulfide

(*E*)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and acetyl disulfide (0.5 g, 3.3 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 14 hours with a sunlamp. The resulting dark brown slurry was filtered and concentrated under vacuum to afford a colorless oil which solidified upon standing. ^{1}H N.M.R. revealed mostly acetyl disulfide and the starting vinylmercury chloride along with a low yield (*ca*. 5%) of (*E*)-3,3-dimethyl-1-butenyl acetyl sulfide, previously prepared by the photoreaction of (*E*)-3,3-dimethyl-1-butenylmercury acetate and thiolacetic acid (Chapter II, Part II of this thesis).

14. Photoreaction of allylmercury chloride with phenyl disulfide

Allylmercury chloride (0.5 g, 1.8 mmol) and phenyl disulfide (0.4 g, 1.83 mmol) were dissolved in 15 ml of nitrogen-purged benzene and the solution was irradiated for 17 hours with a sunlamp. Yellow precipitate was noted after 30 minutes. Filtration and concentration of the solution under vacuum afforded a mixture of an oil and a solid found to contain a 32% yield of allyl phenyl sulfide by quantitative ^{1}H N.M.R. The presence of allyl phenyl sulfide was verified by G.L.C. (5' x 1/8"; 5% OV-3, 120°C) retention matching with the authentic compound.

15. Photoreaction of cyclopropylmercury bromide with phenyl disulfide

Cyclopropylmercury bromide (0.5 g, 1.56 mmol) and phenyl disulfide (0.4 g, 1.8 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 2.5 hours with a sunlamp. No precipitate of bromomercury thiophenoxide was observed. A 19 hour irradiation period in a Rayonet RPR-100 photoreactor ("350 nm" light) also failed to induce formation of the precipitate. The reaction was not investigated further.

16. Photoreaction of benzylmercury chloride with phenyl disulfide

Benzylmercury chloride (1.0 g, 3.1 mmol) and phenyl disulfide (0.7 g, 3.2 mmol) were dissolved in 15 ml of nitrogen-purged benzene in a Pyrex flask and the solution irradiated for 18.25 hours in a Rayonet RPR-100 reactor (fifteen "350 nm" bulbs were employed). Filtration of the yellow precipitate and concentration of the resulting clear solution afforded 0.53 g of a yellow oil determined to contain a 3.0% yield of benzyl phenyl sulfide by quantitative ^{1}H N.M.R. A compound exhibiting a methylene singlet corresponding to benzylmercury thiophenoxide (31% yield) was also detected. The presence of benzyl phenyl sulfide was verified by G.L.C. retention matching with an authentic sample (5' x 1/4"; 5% OV-3; 170°C).

17. Photoreaction of phenylmercury chloride with phenyl disulfide

Phenylmercury chloride (1.0 g, 3.2 mmol) and phenyl disulfide (0.8 g, 3.7 mmol) were dissolved in 20 ml of nitrogen-purged DMSO (since phenylmercury chloride is essentially insoluble in benzene) and the solution was irradiated with a sunlamp for 22 hours. Since no apparent reaction had occurred, the solution was further irradiated for 3 hours in a Rayonet RPR-100 reactor equipped with "350 nm" light. The clear solution was then poured into 100 ml of 50%-saturated brine containing ca. 10 g of sodium thiosulfate (to remove unreacted phenylmercury chloride) and organic products extracted with ethyl ether. The ether extract was dried over $MgSO_4$ and concentrated under vacuum to afford an oil found by G L.C. (5' x 1/4"; 5% OV-3; 170°C) to contain only phenyl disulfide. No diphenyl sulfide was detected.

18. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl diselenide

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and phenyl diselenide (1.0 g, 3.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the orange solution was irradiated for 2 hours with a sunlamp. Rapid formation of a precipitate (chloromercury phenyl selenide) was observed. Removal of the precipitate by filtration and concentration of the clear solution under vacuum afforded 0.71 g of a yellow oil determined to be (E)-3,3-dimethyl-1-butenyl phenyl selenide (95% yield). The N.M.R.-pure material was found to be contaminated with ca. 3% phenyl diselenide by G.L.C. (5' x 1/4"; 5% OV-3; 220°C). The impurity was removed by careful Kugelrohr distillation (60°C/0.03 torr) to afford the pure product as a faintly yellow oil. This compound has been reported in the literature [124].

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.15-7.6, 1H (d) 6.37 (J_H = 15 Hz), 1H (d) 6.18 (J_H = 15 Hz), 9H (s) 1.05.

I.R. (neat, NaCl plates, cm^{-1}) 3070 (w), 2960 (vs), 2900 (w), 2860 (w), 1580 (m), 1480 (s), 1440 (m), 1360 (m), 1260 (m), 1070 (w), 1020 (w), 950 (w), 728 (s), 680 (m).

M.S. Calculated for $C_{12}H_{16}Se$: 240.0417. Measured: 240.0409. Error: -3.5 ppm.

19. Effect of dark on the reaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl diselenide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl diselenide (0.6 g, 1.9 mmol) were dissolved in 15 ml of nitrogen-purged benzene in a flask that was tightly wrapped with aluminum foil to exclude light. The reaction flask was immersed in a 50°C oil bath and gently stirred for two hours. The solution was then removed under vacuum to afford only the starting vinylmercury halide and phenyl diselenide by ^{1}H N.M.R.

20. Effect of 2,6-di-t-butyl phenol on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl diselenide

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.57 mmol) and phenyl diselenide (0.6 g, 1.9 mmol) were dissolved in 15 ml of nitrogen-purged benzene containing 2,6-di-t-butyl phenol (0.4 g, 1.9 mmol) and the solution was irradiated for 6.5 hours with a sunlamp. Chloromercury phenyl selenide was observed to precipitate. The benzene was removed under vacuum and the residue found to contain the starting mercurial

(44% recovery) and (E)-3,3-dimethyl-1-butenyl phenyl selenide (56%) by quantitative ^{1}H N.M.R. No 3,3-dimethyl-1-butene was formed.

21. Photoreaction of ethenylmercury chloride with phenyl diselenide

Ethenylmercury chloride (1.0 g, 3.8 mmol) and phenyl diselenide (1.2 g, 3.85 mmol) were dissolved in 30 ml of nitrogen-purged benzene and the solution was irradiated for 2.5 hours with a sunlamp. The resulting precipitate was removed by filtration and the solution concentrated under vacuum. Kugelrohr distillation (95°C/20 torr) of the resulting oil afforded 0.63 g (91% yield) of ethenyl phenyl selenide as a colorless oil. This compound has been reported in the literature [129].

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.1-7.6, 1H (doublet of doublets) 6.81 ($J_{H\text{-trans}}$ = 17 Hz, $J_{H\text{-cis}}$ = 8 Hz), 1H (d) 5.71 (J_H = 8 Hz), 1H (d) 5.46 (J_H = 17 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 3080 (w), 3060 (w), 1580 (vs), 1480 (vs), 1440 (vs), 1375 (m), 1250 (s), 1070 (m), 1020 (s), 995 (m), 950 (s), 880 (m), 730 (vs), 685 (vs).

M.S. Calculated for C_8H_8Se: 183.9791. Measured: 183.9783. Error: -4.0 ppm.

22. Photoreaction of (E)-2-phenyl-1-ethenylmercury chloride with phenyl diselenide

(E)-2-Phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) and phenyl diselenide (0.93 g, 2.98 mmol) were dissolved in 35 ml of nitrogen-purged benzene and the solution was irradiated with a sunlamp for 2 hours. The precipitate was removed by filtration and the solution concentrated under vacuum to afford the crude product. Kugelrohr distillation (110°C/0.05 torr) yielded the ^{1}H-N.M.R.-pure (E)-2-phenyl-1-ethenyl phenyl sulfide (0.68 g, 90% yield) as a light yellow liquid. None of the Z isomer was observed by N.M.R. The compound has been previously reported [124].

^{1}H N.M.R. ($CDCl_3$, δ) 10H (m) 7.1-7.6, 1H (d) 7.13 (J_H = 17 Hz), 1H (d) 6.75 (J_H = 17 Hz).

I.R. (neat, NaCl plates, cm^{-1}) 3060 (w), 3025 (w), 1600 (m), 1580 (m), 1500 (m), 1480 (s), 1440 (s), 1070 (m), 1020 (m), 1000 (w), 950 (s), 730 (s), 685 (s).

M.S. Calculated for $C_{14}H_{12}Se$: 260.0104. Measured: 260.0097. Error: -2.7 ppm.

23. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with phenyl ditelluride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and phenyl ditelluride (1.31 g, 3.2 mmol) were dissolved in 20 ml of nitrogen-purged benzene and the solution was irradiated for 18 hours with a sunlamp. A yellow precipitate formed. Filtration followed by concentration of the solution under vacuum afforded a brown oil containing a little of the starting mercurial and an 89% yield of (E)-3,3-dimethyl-1-butenyl phenyl telluride. Kugelrohr distillation (60-63°C/0.015 torr) yielded the pure vinyl telluride as a light yellow liquid. Upon storage (exposed to air and light), an insoluble white solid precipitated over a period of several days. Due to the instability of the product, a satisfactory elemental analysis was not obtained.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.1-7.7, 1H (d) 6.66 (J_H = 16 Hz), 1H (d) 6.40 (J_H = 16 Hz), 9H (s) 1.04.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (m), 2955 (vs), 2900 (m), 2860 (m), 1570 (m), 1470 (s), 1450 (m), 1430 (s), 1355 (s), 1250 (s), 1010 (m), 995 (w), 960 (m), 720 (s), 680 (s).

M.S. Calculated for $C_{12}H_{16}Te$: 288.02990. Measured: 288.02845. Error: -5.0 ppm.

IV. PHOTOCHEMICAL REACTION OF PHENYL DISULFIDE WITH BIS[VINYL]MERCURY COMPOUNDS TO FORM VINYL SULFIDES

A. Introduction

In the course of our investigation of the reactivity of vinyl mercurials in cleavage reactions with disulfides, we found bis[vinyl]-mercury compounds to react with phenyl disulfide according to Equation 48. The transformation may be formally represented as sequential

$$R_2Hg + PhSSPh \xrightarrow{\text{light}} 2RSPh + Hg^\circ \qquad (48)$$

$$R = \text{vinyl}$$

electrophilic substitution (to form a molecule of vinyl sulfide and vinylmercury thiophenoxide) and reductive elimination. The delineation of the mechanism for this reaction is the subject of the following section.

B. Results and Discussion

1. The reaction of phenyl disulfide with bis[vinyl]mercury compounds

Bis[2,2-diphenylethenyl]mercury and phenyl disulfide in benzene reacted under the influence of sunlamp irradiation to precipitate mercury metal and yield 2,2-diphenylethenyl phenyl sulfide (99%) according to the stoichiometry of Equation 48 (see Table XIII). Analogous reactions with bis[(E)-3,3-dimethyl-1-butenyl]mercury and bis[(E)-2-phenyl-1-ethenyl]mercury afforded the corresponding vinyl phenyl

Table XIII. Reaction of phenyl disulfide with bis[organo]mercury compounds

$$R_2Hg + PhSSPh \xrightarrow[PhH]{light} 2RSPh + Hg^{\circ}$$

R_2Hg	Time[a]	% Yield RSPh (stereochemistry)[b]
$[(Ph)_2C{=}CH]_2Hg$	3 h	99
$[(\underline{E})\text{-}Me_3CCH{=}CH]_2Hg$	2 h	100 (>98% E)
$[(\underline{E})\text{-}PhCH{=}CH]_2Hg$	2 h	99 (E:Z = 89:11)
$[Ph]_2Hg$	---[c]	6[c]
$[PhCH_2]_2Hg$	19 h	11.4

[a] Irradiation period with a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel.

[b] Yield of sulfide determined by quantitative ^1H N.M.R. Stereochemistry determined by ^1H N.M.R.

[c] Irradiated for 18 hours with a sunlamp and for 4 hours in a Rayonet RPR-100 reactor ("350 nm" light). Yield determined by quantitative G.L.C. (5' x 1/4"; 5% OV-3, internal reference = biphenyl).

sulfides in 100% and 99% yields, respectively. Only (E)-3,3-dimethyl-1-butnyl phenyl sulfide was produced, while the (E)-2-phenyl-1-ethenyl mercurial afforded an 89:11 ratio of E and Z isomers, essentially the same product distribution observed from the photo-decomposition of the vinylmercury thiophenoxide (Chapter II, Part II, this thesis) and from the photochemical reaction of phenyl disulfide with the vinylmercury halide (Chapter III, Part II, this thesis).

Phenyl disulfide did not react cleanly with diphenyl- or dibenzylmercury. Low yields of the expected sulfides were detected in complex product mixtures (Table XIII). These results parallel those obtained for the photo-decomposition of organomercury mercaptides and the photochemical reactions of organomercury halides with disulfides (see Chapters II and III, Part II, this thesis).

Interestingly, nonaryl disulfides (*i.e.*, methyl, *n*-butyl, and benzyl) failed to react with bis[2,2-diphenylethenyl]mercury even with extended irradiation periods (see Experimental Section).

2. Reaction between thiophenol and bis[2,2-diphenylethenyl]mercury

Thiophenol reacted with bis[2,2-diphenylethenyl]mercury in benzene under the influence of sunlamp irradiation to afford 2,2-diphenylethenyl phenyl sulfide (65% yield) and 2,2-diphenylethene (92% yield) along with mercury metal (Eq. 49). When the reaction was performed at 25°C in

$$\mathrm{PhSH} + [(\mathrm{Ph})_2\mathrm{C{=}CH}]_2\mathrm{Hg} \xrightarrow[\text{light}]{\text{PhH}} \underset{92\%}{(\mathrm{Ph})_2\mathrm{C{=}CH_2}} + \underset{65\%}{(\mathrm{Ph})_2\mathrm{C{=}CHSPh}} + \mathrm{Hg}^{\circ} \qquad (49)$$

a flask tightly wrapped with aluminum foil to exclude light, no 2,2-diphenylethenyl phenyl sulfide was formed. Instead, 2,2-diphenylethene (93% yield) and 2,2-diphenylethenylmercury thiophenoxide (62% yield) were observed (Eq. 50).

$$\mathrm{PhSH} + [(\mathrm{Ph})_2\mathrm{C{=}CH}]_2\mathrm{Hg} \xrightarrow[\text{dark}]{\text{PhH}} \underset{93\%}{(\mathrm{Ph})_2\mathrm{C{=}CH_2}} + \underset{62\%}{(\mathrm{Ph})_2\mathrm{C{=}CHHgSPh}} \qquad (50)$$

$$25°\mathrm{C}$$

3. Effect of darkness and chemical inhibitors on the reaction between phenyl disulfide and bis[2,2-diphenylethenyl]mercury

The reaction phenyl disulfide and bis[2,2-diphenylethenyl]mercury was performed in benzene at 50°C in a flask tightly wrapped with aluminum foil to exclude light (Table XIV). After 21 hours, no reaction had taken place and the starting mercurial was recovered nearly quantitatively.

The requirement of sunlamp irradiation for any reaction to occur suggested that radical chain processes, not concerted S_E2-type processes, were responsible for the transformation. Consequently, a series of potential chemical inhibitors were introduced to the reaction medium and their effects tabulated (Table XIV). Molecular oxygen (1 atm), galvinoxyl (5 mole %) and di-t-butyl nitroxide (5 mole %) all strongly inhibited formation of 2,2-diphenylethenyl phenyl sulfide although the reaction times employed were sufficient for complete conversion in the absence of inhibitor. Thiophenol (100 mole %) did not significantly slow the reaction and 2,2-diphenylethenyl phenyl sulfide was formed quantitatively when the reaction was performed at 0°C.

4. Mechanism of the reaction of bis[vinyl]mercury compounds with phenyl disulfide

The concerted S_E2-type reaction between phenyl disulfide and the bis[vinyl]mercury compound (Eq. 51) was clearly shown not to occur in

$$R_2Hg + PhSSPh \xrightarrow[S_E2]{\Delta} RSPh + RHgSPh \qquad (51)$$

$$R = \text{vinyl}$$

Table XIV. Effect of darkness and chemical inhibitors on the reaction of bis[2,2-diphenylethenyl]mercury with phenyl disulfide

$$[(Ph)_2C{=}CH]_2Hg + PhSSPh + X \xrightarrow[PhH]{light^a} products^b$$

(0.895 mmol) (excess)

X (mmol)	Time	$[(Ph)_2C{=}CH]_2Hg$ (mmol)	$(Ph)_2C{=}CHHgSPh$ (mmol)	$(Ph)_2C{=}CHSPh$ (mmol)	Temp (°C)
None	1 h	0.00	0.00	1.75	25°
None	21 h[c]	0.87	0.00	0.00	50°
Galvinoxyl (0.045)	3 h	0.58	0.00	0.12	25°
di-t-butyl nitroxide (0.045)	1 h	0.80	0.00	0.00	25°
O_2 (1 atm)[d]	1 h	0.68	0.10	0.00	25°
PhSH (0.90)[e]	3.5 h	0.00	0.00	1.80	0°

[a] Irradiation period with a 275 watt sunlamp directed at the Pyrex reaction vessel immersed in a constant-temperature water bath.

[b] Yields determined by quantitative ^1H N.M.R.

[c] No light employed. The aluminum foil-wrapped reaction vessel was immersed in a 50°C oil bath.

[d] The solvent was 2:1 DMSO:benzene.

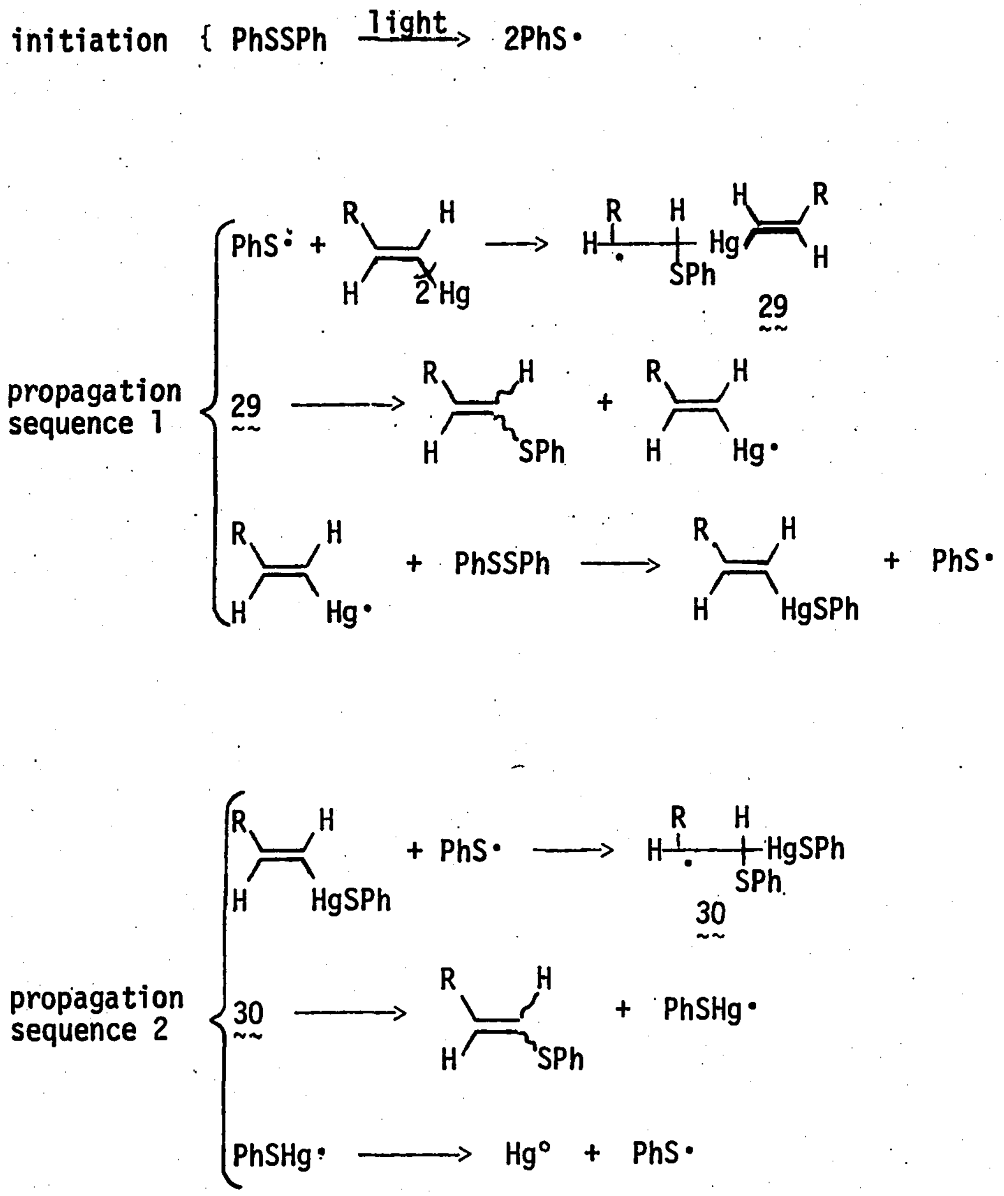
[e] The solvent was 5:1 benzene:hexane.

the temperature range of this study by the absence of a dark reaction and the effects of free radical chain inhibitors. Thiophenol was found to react thermally with bis[2,2-diphenylethenyl]mercury in benzene at room temperature, but at 0°C this process was sufficiently slow that the course of the reaction between the mercurial and phenyl disulfide was unaltered. Thus, the reaction between the mercurial and phenyl disulfide does not involve vinyl radicals since these intermediates are expected to be intercepted by thiophenol (hydrogen atom transfer) at nearly the diffusion controlled rate [79] (see the mechanistic discussion of Chapter II, Part II of this thesis). Furthermore, the proposed mechanism should accommodate the observations that alkyl disulfides do not participate in the reaction and that diphenyl- and dibenzylmercury only reacted to produce low yields of the expected sulfides.

Scheme 24 outlines a free radical chain process incorporating the features of Schemes 15 and 18. Propagation sequence 2 is identical to Scheme 15 (**30** is equivalent to **22** for $R^2 = SPh$). Propagation sequence 1 most importantly differs from Scheme 18 in the nature of the mercury(I) radical. Most organomercury(I) species rapidly dissociate to form the organic radical and mercury metal [26-29] (see Chapter III, Part I of this thesis). Here a vinylmercury(I) radical is proposed to propagate the chain reaction by attacking phenyl disulfide.

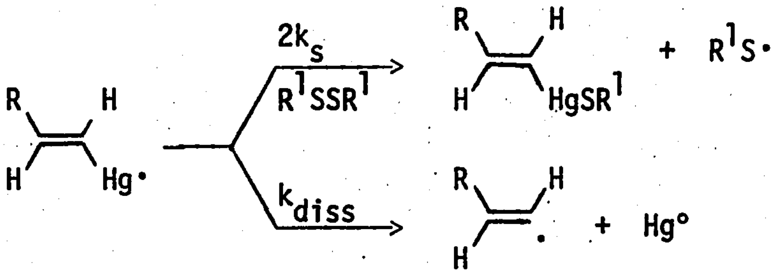
The proposed intermediacy of the vinylmercury(I) species is not unreasonable. The dissociation energy for the carbon-mercury bond of ethenylmercury radical is estimated to be 19±6 kcal $mole^{-1}$ [30,118].

Scheme 24


initiation
PhSSPh
light
2PhS•
propagation sequence 1
PhS• +
R
H
H
2 Hg
29
Hg•
+ PhSSPh
HgSPh
+ PhS•
SPh
propagation sequence 2
+ PhS•
30
+ PhSHg•
PhSHg•
Hg°
+ PhS•

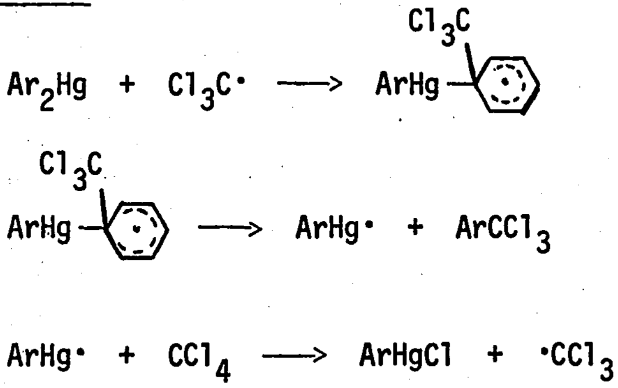
Thus, the fragmentation of the vinylmercury(I) species to give the vinyl radical and mercury metal does not compete with the rate of attack on phenyl disulfide (Scheme 25, R^1 = Ph). There is apparent literature

Scheme 25



precedent for the intermediacy of a related species, the phenylmercury radical (Scheme 26). Diphenylmercury reacts with carbon tetrachloride

Scheme 26



(under the influence of peroxide initiation) to afford trichloromethylbenzene and phenylmercury chloride [130]. Dialkylmercury compounds also react with carbon tetrachloride via a chain process, but the trichloromethyl radical abstracts the β-mercury hydrogen of the dialkylmercury resulting in the formation of an olefin and chloroform instead of the trichloromethylated alkyl compound [86, 130]. In light of the present work, the ability of trichlorimethyl to attack the aryl carbon in an S_H2 fashion (but not alkyl carbons) is nicely explained by the addition-elimination mechanism of Scheme 26.

Phenyl disulfide failed to react with bis[aryl]- or bis[alkyl]-mercury compounds. In terms of Scheme 24, S_H2 at saturated carbon clearly cannot occur by the addition-elimination pathway and presumably does not readily occur. The addition of thiyl to the aromatic ring with concomitant loss of aromaticity must be too energetically unfavorable to permit the facile reaction of phenyl disulfide with diphenylmercury. In contrast, trichloromethyl radical will add to the aromatic ring (Scheme 26) and diphenylmercury thus is subject to attack from this more reactive species [130].

Scheme 25 offers an explanation for the observed unreactivity of alkyl disulfides towards bis[2,2-diphenylethenyl]mercury. The rate constant k_s is dependent on the nature of the disulfide. For R^1 = alkyl, $2k_s$ is sufficiently small compared with k_{diss} so that decomposition of the vinylmercury(I) species competes with chain propagation. Hydrogen abstraction (chain transfer) is expected to be an important process in the reaction of vinylic radicals with alkyl disulfides (see Chapter III, Part II of this thesis). In agreement with the proposed reactivity trend, the ratio of k_2 ($R^1 = Ph$) to k_s ($R^1 = \underline{n}\text{-Bu}$) for the analogous reaction of disulfides with tributyltin radicals is approximately 8 [121].

C. Conclusion

Phenyl disulfide reacts with bis[vinyl]mercury compounds via a photo-initiated chain process to afford vinyl phenyl sulfides and mercury metal. The reaction was shown to proceed via thiyl, vinylmercury(I), and thiophenoxymercury(I) paramagnetic intermediates (Scheme 24) by inhibition studies with oxygen, galvinoxyl, and di-t-butyl nitroxide. The intermediacy of vinylic radicals was ruled out by the lack of effect of thiophenol on the course of the reaction at 0°C. Thiophenol was found to react thermally with the bis[vinyl]mercury compound to afford the olefin and a vinylmercury thiophenoxide. Alkyl disulfides were unreactive towards the bis[vinyl]mercury compounds, possibly because the disulfides were insufficiently reactive towards S_H2 attack by the intermediate vinylmercury radical which is subject to decomposition. In accordance with the proposed mechanism, bis[aryl]- and bis[alkyl]mercury compounds failed to react with phenyl disulfide to give substantial amounts of the corresponding sulfides.

D. Experimental Section

1. General considerations

Benzyl disulfide was purchased from Aldrich and recrystallized from ethanol before use. Diphenylmercury was a product of Eastman Organic.

Bis[(E)-2-phenyl-1-ethenyl]mercury [131] was prepared in the following manner: (E)-2-phenyl-1-ethenylmercury chloride (10 g, 29.5 mmol) was added to a solution containing potassium t-butoxide (6.8 g, 60.6 mmol) and diethyl phosphite (9.65 g, 69.9 mmol) in 150 ml of dry DMSO under nitrogen. After 5 minutes of stirring, the solution was poured into 500 ml of 50%-saturated brine and the product extracted with benzene. The benzene extract was washed with water, then brine, and then dried over $MgSO_4$. Concentration under vacuum afforded 5 g (83% yield) of the crude bis[(E)-2-phenyl-1-ethenyl]mercury as a yellow solid. Recrystallization from ethanol/chloroform gave the pure product (4.5 g, 75% yield overall) as small light-yellow crystals (m.p. 140.5-141.5°C). ^{1}H N.M.R. ($CDCl_3$, δ) 10H (broad) 7.3, 1H (d) 7.1 (J_H = 17 Hz), 1H (d) 6.7 (J_H = 17 Hz).

2. Photoreaction of bis[2,2-diphenylethenyl]mercury with phenyl disulfide

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol) and phenyl disulfide (0.2 g, 0.92 mmol) were dissolved in 10 ml of nitrogen-purged benzene and the solution was irradiated for 3 hours with a 275 watt sunlamp positioned 4 inches from the Pyrex reaction vessel. After the first 5 minutes of irradiation, mercury metal was observed. When the reaction was complete, the solution was decanted from the mercury beads and concentrated under vacuum. The crude isolate, 0.52 g of light-yellow oil, was found by quantitative ^{1}H N.M.R. to contain 1.77 mmol (99% yield) of 2,2-diphenylethenyl phenyl sulfide. A trace of unreacted phenyl disulfide, the reagent in excess, also remained. The identity of the vinyl sulfide was verified by comparison of the ^{1}H N.M.R. and I.R.

spectra with those of the authentic pure compound prepared by the photo-decomposition of 2,2-diphenylethenylmercury thiophenoxide (Chapter II, Part II of this thesis).

3. Photoreaction of bis[(E)-2-phenyl-1-ethenyl]mercury with phenyl disulfide

Bis[(E)-2-phenyl-1-ethenyl]mercury (0.5 g, 1.23 mmol) and phenyl disulfide (0.3 g, 1.38 mmol) were dissolved in 15 ml of nitrogen-purged benzene and the solution was irradiated for 2 hours with a sunlamp positioned 5 inches from the Pyrex reaction vessel during which time mercury metal was observed to precipitate. The solution was decanted from the beads of mercury and concentrated under vacuum to afford a 99% yield of 2-phenyl-1-ethenyl phenyl sulfide as well as left-over phenyl disulfide. Integration of the vinylic proton signal in the 100 MHz N.M.R. spectrum determined the E:Z isomer ratio to be 89:11.

4. Photoreaction of bis[(E)-3,3-dimethyl-1-butenyl]mercury with phenyl disulfide

Bis[(E)-3,3-dimethyl-1-butenyl]mercury (0.5 g, 1.36 mmol) and phenyl disulfide (0.3 g, 1.38 mmol) were dissolved in 10 ml of nitrogen-purged benzene and the solution was irradiated for 2 hours during which time mercury metal was observed to precipitate. The solution was decanted from the mercury beads and concentrated under vacuum to afford 0.53 g of light-yellow liquid determined to contain a 100% yield of (E)-3,3-dimethyl-1-butenyl phenyl sulfide by quantitative ^{1}H N.M.R.

5. Photoreaction of phenyl disulfide with dibenzylmercury

Dibenzylmercury (0.5 g, 1.31 mmol) and phenyl disulfide (0.3 g, 1.38 mmol) were dissolved in 10 ml of nitrogen-purged benzene and the solution was irradiated for 19 hours with a 275 watt sunlamp positioned 8 inches from the Pyrex reaction vessel during which time mercury metal was observed to precipitate. The solution was decanted from the mercury beads and concentrated under vacuum to afford a yellow oil determined to contain an 11.4% yield (0.296 mmol) of benzyl phenyl sulfide by quantitative ^{1}H N.M.R. The presence of the sulfide was confirmed by retention matching in the G.L.C. (5' x 1/4"; 5% OV-3; 200°C) with the authentic compound as well as G.C.M.S. (m/e = 200 observed for parent ion).

6. Photoreaction of diphenylmercury with phenyl disulfide

Diphenylmercury (1.0 g, 2.82 mmol) and phenyl disulfide (0.7 g, 3.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 18 hours with a sunlamp positioned 8 inches from the Pyrex reaction vessel. Since only a trace of metallic mercury was observed, the solution was subsequently irradiated for 4 hours in a Rayonet RPR-100 reactor equipped with thirteen "350 nm" bulbs. The solution was then decanted from the small mercury bead and concentrated under vacuum. Quantitative G.L.C. (5' x 1/4"; 5% OV-3; internal standard = biphenyl; molar response factor biphenyl/phenyl disulfide = 0.95) revealed the isolate to contain a 6.0% yield of diphenyl sulfide. The identity of the diphenyl sulfide was verified by G.C.M.S. (m/e = 186 observed for the parent ion).

7. Photoreaction of bis[2,2-diphenylethenyl]mercury with methyl disulfide

Bis[2,2-diphenylethenyl]mercury (1.0 g, 1.79 mmol) and methyl disulfide (0.21 g, 2.3 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 1.25 hours with a sunlamp. Since no mercury metal was observed, irradiation was continued for 12 hours in a Rayonet RPR-100 reactor equipped with thirteen "350 nm" bulbs. Still, no mercury was observed.

8. Photoreaction of bis[2,2-diphenylethenyl]mercury with *n*-butyl disulfide

Bis[2,2-diphenylethenyl]mercury (1.0 g, 1.79 mmol) and *n*-butyl disulfide (0.28 g, 1.9 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 13 hours with a sunlamp positioned 8 inches from the Pyrex reaction vessel. No mercury metal precipitated.

9. Photoreaction of bis[2,2-diphenylethenyl]mercury with benzyl disulfide

Bis[2,2-diphenylethenyl]mercury (1.0 g, 1.79 mmol) and benzyl disulfide (0.45 g, 1.8 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 3 hours with a sunlamp positioned 4 inches from the Pyrex reaction vessel. Since no mercury was observed, irradiation was continued for 3 hours in a Rayonet RPR-100 reactor equipped with thirteen "350 nm" bulbs. Still no mercury precipitated.

10. Photoreaction of bis[2,2-diphenylethenyl]mercury with thiophenol

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol) and thiophenol (0.108 g, 0.98 mmol) were dissolved in 10 ml of nitrogen-purged benzene and the solution was irradiated for 2.5 hours with a sunlamp during which time mercury metal precipitated (ambient reaction temperature increased from 25°C to 35°C during the irradiation period). The solution was decanted from the mercury beads and concentrated under vacuum to afford 2,2-diphenylethene (92% yield, 0.82 mmol) and 2,2-diphenylethenyl phenyl sulfide (65% yield, 0.58 mmol) as determined by quantitative ^{1}H N.M.R. The components were identified both by the chemical shifts of their protons compared with those of authentic samples and by retention matching in the G.L.C. (5' x 1/4"; 5% OV-3).

11. Effect of darkness on the reaction of thiophenol with bis[2,2-diphenylethenyl]mercury

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol) and thiophenol (0.108 g, 0.98 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a flask wrapped tightly with aluminum foil to exclude light. The solution was stirred for 14 hours at 25°C and the foil removed in subdued roomlight. No mercury metal was observed. Concentration of the solution under vacuum and analysis by quantitative ^{1}H N.M.R. determined the presence of 2,2-diphenylethene (93% yield, 0.832 mmol) and 2,2-diphenylethenylmercury thiophenoxide (62% yield, 0.55 mmol). No starting mercurial or 2,2-diphenylethenyl phenyl sulfide was detected. Product identification was based on the vinyl proton chemical shifts compared with those of the authentic compounds.

12. Effect of darkness on the reaction of phenyl disulfide with bis[2,2-diphenylethenyl]mercury

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol) and phenyl disulfide (0.2 g, 0.92 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a flask completely covered with aluminum foil to exclude light. The flask was immersed in a 50°C oil bath and gently stirred for 21 hours. After the solution was cooled, the foil was removed and the solvent removed under vacuum in subdued roomlight. No metallic mercury was observed. Quantitative ^{1}H N.M.R. determined the isolate to contain a 97% recovery of the starting mercurial. No 2,2-diphenylethenylmercury thiophenoxide or 2,2-diphenylethenyl phenyl sulfide was detected.

13. Effect of galvinoxyl on the photoreaction of phenyl disulfide with bis[2,2-diphenylethenyl]mercury

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol), phenyl disulfide (0.2 g, 0.92 mmol), and galvinoxyl (19 mg, 0.045 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a Pyrex flask immersed in a 25°C water bath and irradiated for 3 hours with a sunlamp positioned 8 inches from the reaction vessel. No mercury metal was observed. The solution was concentrated under vacuum. The isolate was found to contain the starting mercurial (65% recovery) along with 2,2-diphenylethenyl phenyl sulfide (7% yield, 0.12 mmol) by quantitative ^{1}H N.M.R. No 2,2-diphenylethenylmercury thiophenoxide was detected. The identity of the alkenyl sulfide was verified by G.L.C. retention matching with the authentic compound (5' x 1/4"; 5% OV-3).

A control experiment (performed identically, but without galvinoxyl) afforded a 92% yield of 2,2-diphenylethenyl phenyl sulfide. The starting mercurial was completely consumed.

14. Effect of di-*t*-butyl nitroxide on the photoreaction of phenyl disulfide with bis[2,2-diphenylethenyl]mercury

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol), phenyl disulfide (0.4 g, 1.8 mmol), and di-*t*-butyl nitroxide (6.4 mg, 0.045 mmol) were dissolved in 15 ml of nitrogen-purged benzene in a Pyrex flask immersed in a 25°C water bath and the solution was irradiated for 1 hour with a sunlamp placed 4 inches from the reaction vessel. No mercury metal was precipitated. The solution was stabilized by the addition of 2 mg of galvinoxyl and concentrated under vacuum. Quantitative ^{1}H N.M.R. revealed a 90% recovery of starting mercurial. No 2,2-diphenylethenyl phenyl sulfide or 2,2-diphenylethenylmercury thiophenoxide was detected.

In a control experiment (performed identically, but without di-*t*-butyl nitroxide), the starting mercurial was completely consumed and a 98% yield of 2,2-diphenylethenyl phenyl sulfide obtained.

15. Effect of oxygen on the photoreaction of bis[2,2-diphenylethenyl]mercury with phenyl disulfide

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol) and phenyl disulfide (0.4 g, 1.83 mmol) were dissolved in a mixture of DMSO (20 ml) and benzene (10 ml). The benzene was required to solublize the mercurial. The solution was saturated with oxygen by means of foaming the gas from a glass frit placed near the bottom of the Pyrex flask. DMSO was the solvent of choice in this experiment since local evaporation at the glass frit (with concomitant clogging) is not a problem with a high-boiling solvent. The reaction vessel was immersed in a 25°C water bath and irradiated for 1 hour with a sunlamp placed 4 inches from the flask. No metallic mercury was observed. The solution was stabilized by the addition of 2 mg of galvinoxyl and then concentrated under vacuum. Quantitative ^{1}H N.M.R. revealed the residue to contain a 76% recovery of the starting mercurial and an 11% yield of 2,2-diphenylethenylmercury thiophenoxide. No 2,2-diphenylethenyl phenyl sulfide was observed.

In a control experiment (performed identically, but under nitrogen), the expected alkenyl phenyl sulfide was obtained in a 98% yield.

16. Effect of thiophenol on the photoreaction of bis[2,2-diphenylethenyl]mercury with phenyl disulfide

Bis[2,2-diphenylethenyl]mercury (0.5 g, 0.895 mmol), phenyl disulfide (0.2 g, 0.92 mmol), and thiophenol (0.099 g, 0.90 mmol) were dissolved in a mixture of benzene (10 ml) and hexane (2 ml) under nitrogen in a flask immersed in a 0°C water bath. (The function of the hexane was to prevent freezing of the solvent.) The solution was irradiated for 3.5 hours with a sunlamp positioned 8 inches from the Pyrex reaction vessel during which time mercury metal was observed to precipitate. The solution was decanted from the mercury beads and concentrated under vacuum. Quantitative ^{1}H N.M.R. revealed the residue to contain a 101% yield of 2,2-diphenylethenyl phenyl sulfide (1.8 mmol). No 2,2-diphenylethene, 2,2-diphenylethenylmercury thiophenoxide, or starting mercurial was observed.

V. PHOTOCHEMICAL COUPLING OF HALO COMPOUNDS WITH VINYL MERCURIALS

A. Introduction

Organomercury compounds are not known to be reactive towards substitution reactions with organic halides [67]. Nevertheless, vinylmercury halides undergo photostimulated coupling reactions with certain halo compounds, particularly organosulfonyl halides (Eq. 52) to form the

$$R^1HgX^1 + R^2X^2 \xrightarrow{\text{light}} R^1\text{-}R^2 + HgX^1X^2 \qquad (52)$$

R^1 = vinyl

X = halogen

mercuric halide salt and the coupled organic species. The mechanism and scope of this transformation, formally an electrophilic substitution reaction, is the topic of the following section.

B. Results and Discussion

1. Reaction of organosulfonyl chlorides with organomercury halides

Benzenesulfonyl chloride reacted with (E)-3,3-dimethyl-1-butenylmercury chloride in benzene solution under 350 nm radiation to form (E)-3,3-dimethyl-1-butenyl phenyl sulfone in high yield (see Table XV). The mercurial also reacted with p-toluenesulfonyl chloride to afford the corresponding vinyl sulfone in 75% yield. The analogous reaction with methanesulfonyl chloride only afforded (E)-3,3-dimethyl-1-butenyl methyl sulfone in 32% yield after an extended reaction period.

Table XV. Reactions of halo compounds with organomercury halides

$$R^1HgX^1 + R^2X^2 \xrightarrow[\text{PhH}]{\text{light}} R^1R^2 + HgX^1X^2$$

R^1HgX^1	R^2X^2	Time[a]	% Yield R^1R^2 (stereochemistry)[b]
($\underline{E}$)-Me$_3$CCH=CHHgCl	PhSO$_2$Cl	3 h	99% (>98% $\underline{E}$)
PhCH$_2$HgCl	PhSO$_2$Cl	3 h	0%
PhHgCl	PhSO$_2$Cl	22 h	0 %
($\underline{E}$)-Me$_3$CCH=CHHgCl	$\underline{p}$-MePhSO$_2$Cl	2.5 h	75% (>98% $\underline{E}$)
($\underline{E}$)-Me$_3$CCH=CHHgCl	MeSO$_2$Cl	22 h	32% (>98% $\underline{E}$)
($\underline{E}$)-Me$_3$CCH=CHHgCl	Cl$_3$CSO$_2$Cl	19 h	0%[c]
($\underline{E}$)-Me$_3$CCH=CHHgCl	PhCH$_2$SO$_2$Cl	40 h	0%
($\underline{E}$)-Me$_3$CCH=CHHgCl	$\underline{N}$-bromosuccinimide	1.5 h	<10%
($\underline{E}$)-Me$_3$CCH=CHHgCl	(EtO)$_2$P(=O)Cl	17 h	<5%
($\underline{E}$)-Me$_3$CCH=CHHgCl	PhCOCl	17 h	0%
($\underline{E}$)-Me$_3$CCH=CHHgCl	(Me)$_2$C(NO$_2$)Br	55 h	0%

---

[a] Period of irradiation in a Rayonet RPR-100 reactor equipped with "350 nm" bulbs. Pyrex reaction vessels were employed.

[b] Yields and stereochemistry by quantitative ^{1}H N.M.R. of the crude reaction isolate.

[c] G.C.M.S. evidence suggests the formation of Me$_3$CCH=CHCCl$_3$ in low yield.

Table XV. (Continued)

R^1HgX^1	R^2X^2	Time[a]	% Yield R^1R^2 (stereochemistry)[b]
(E)-PhCH=CH_2HgCl	PhSeCl[d]	10 min[e]	24% (E)
(E)-Me_3CH=CHHgCl	2,4-$(O_2N)_2$PhSCl	4.5 h[f]	0%
$(Ph)_2$C=CHHgBr	$(Me)_2$CHI	2 h	50%[g]
$(Ph)_2$C=CHHgBr	MeI	30 h	36%[h]
$(Ph)_2$C=CHHgBr	$PhCH_2Br$	28 h	0%

[d] The solvent was methylene chloride.

[e] No irradiation was employed.

[f] A 275 watt sunlamp was employed as the irradiation source.

[g] 2-Bromo-1,1-diphenylethene (ca. 8%) and 2-iodo-1,1-diphenylethene (ca. 5%) detected.

[h] 2-Bromo-1,1-diphenylethene (ca. 36%) and 2-iodo-1,1-diphenylethene (ca. 18%) detected.

Trichloromethylsulfonyl chloride and α-toluenesulfonyl chloride failed to couple with the vinyl mercurial.

Photostimulation is required for these coupling reactions. No reaction occurred between (E)-3,3-dimethyl-1-butenylmercury chloride and benzenesulfonyl chloride in benzene solution in the dark even after stirring for 12 hours at 50°C. In a control experiment employing a water-cooled flask, a 1.5 hour irradiation period at 25°C in a Rayonet reactor (350 nm light) induced nearly quantitative formation of the vinyl sulfone (see Experimental Section).

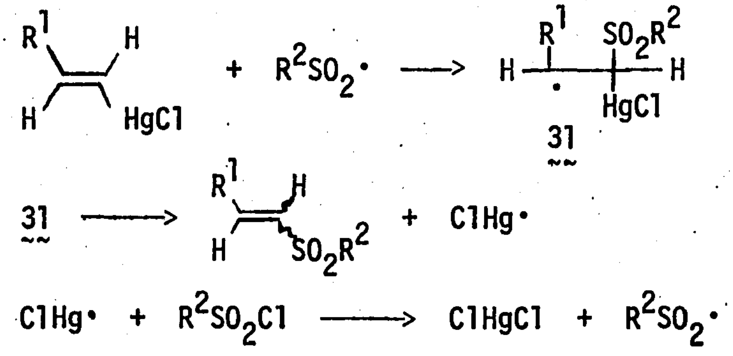
The photostimulated reaction between benzenesulfonyl chloride and (*E*)-3,3-dimethyl-1-butenylmercury chloride in benzene at 25°C was completely inhibited for 1.5 hours by the addition of 10 mole % di-*t*-butyl nitroxide, a free radical scavenger. Molecular oxygen (1 atmosphere) also completely inhibited the reaction (see Experimental Section).

The vinyl moiety appears necessary for the coupling of organomercury halides with organosulfonyl halides. Phenylmercury chloride and benzylmercury chloride both failed to react with benzenesulfonyl chloride to give detectable amounts of the expected diphenyl and phenyl benzyl sulfones.

2. Mechanism of the reaction between organosulfonyl chlorides and (*E*)-3,3-dimethyl-1-butenylmercury chloride

The data are accommodated by the mechanism of Scheme 27 which is nearly identical to Scheme 18. The halomercury(I) radical propagates

Scheme 27



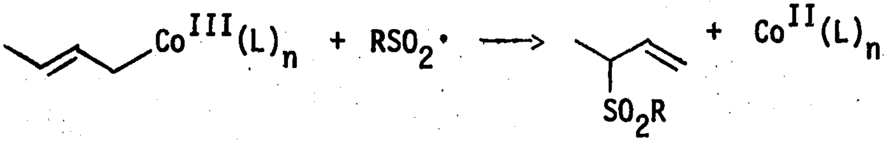
the chain reaction by abstracting a halogen atom from the organosulfonyl halide. The mechanism is consistent with the observed reaction inhibitions by a trace of di-t-butyl nitroxide and molecular oxygen. The addition of a sulfonyl radical to the olefinic bond nicely explains the nonreactivity (towards sulfone formation) of aryl- and alkylmercury halides. Perhaps less obvious is the poor reaction between methanesulfonyl chloride and (E)-3,3-dimethyl-1-butenylmercury chloride. One explanation is that dissociation of the alkylsulfonyl radical (Eq. 53)

$$RSO_2\cdot \xrightarrow{k_{diss}} R\cdot + SO_2\cdot \qquad (53)$$

competes with attack of the sulfonyl radical on the vinyl mercurial. However, alkylsulfonyl radicals are possible intermediates in the related reaction between vinylmercury halides and alkylsulfinate ions (Chapter VI, Part II of this thesis). An alternative explanation is that halomercury radicals do not readily dehalogenate alkylsulfonyl halides.

Precedent for the reactivity of mercury(I) radicals towards halogen abstraction is provided by the reaction between diphenylmercury and carbon tetrachloride (see Scheme 26) [130]. Sulfonyl radicals have been found to displace cobalt(II) species from allylcobaloximes [132] (Scheme 28). The paramagnetic cobalt(II) propagates a radical chain

Scheme 28

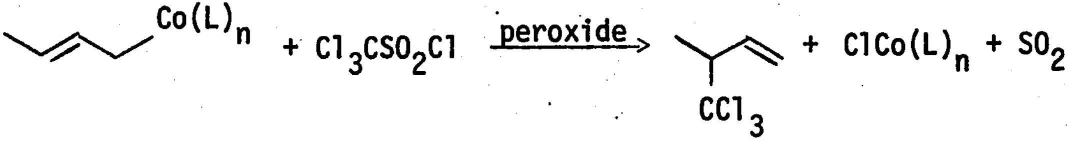


Scheme 28 (Continued)

$$Co^{II}(L)_n + RSO_2Cl \longrightarrow ClCo^{III}(L)_n + RSO_2\cdot$$

R = alkyl, aryl

process by abstracting a chlorine from the organosulfonyl chloride. For the special case where R = Cl_3C (Scheme 28), the intermediate trichloromethylsulfonyl radical rapidly decomposes with loss of sulfur dioxide (Eq. 53) and the product of trichloromethyl radical attack on the



(54)

allylcobaloxime was isolated (Eq. 54) [132].

Notably, trichloromethylsulfonyl chloride failed to yield the vinyl sulfone upon reaction with (E)-3,3-dimethyl-1-butenylmercury chloride (Table XV), although the yield of trichloromethylation product was apparently low. The failure of α-toluenesulfonyl chloride to react at all with (E)-3,3-dimethyl-1-butenylmercury chloride may also be attributed to the instability of the intermediate sulfonyl radical. This instability (Eq. 53) is supported by the observations that α-toluenesulfonyl iodide rapidly decomposes (presumably via a chain process) to benzyl iodide and sulfur dioxide (Eq. 55) [133] and that the sodium salt of α-toluenesulfinic acid rapidly evolves sulfur dioxide upon exposure to air (Eq. 56) [133]. In the reaction between the

$$PhSO_2I \xrightarrow{\text{light}} PhCH_2I + SO_2 \qquad (55)$$

$$PhCH_2SO_2\cdot \xrightarrow{O_2} [PhCH_2SO_2\cdot] \longrightarrow SO_2 + \text{other products} \qquad (56)$$

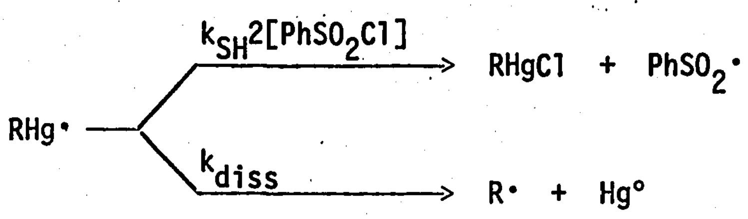
vinylmercury halide and α-toluenesulfonyl chloride, the intermediate benzyl radical apparently failed to propagate a radical chain by adding to the vinyl mercurial. Consequently, most of the starting vinylmercury chloride was recovered after a 40 hour irradiation period (see the Experimental Section).

An interesting prediction from mechanistic Scheme 27 is that bis[vinyl]mercury compounds should react with two equivalents of an organosulfonyl chloride to form two equivalents of the vinyl sulfone and mercuric chloride (by analogy with Scheme 24). Bis[(E)-3,3-dimethyl-1-butenyl]mercury did in fact react with excess benzenesulfonyl chloride under the influence of 350 nm light to afford, after 3.5 hours, a mixture of products (Eq. 57). The starting mercurial was completely consumed. The poor mass balance (0.42 mmol of R-groups were lost) and the apparent reluctance of the reaction to proceed to completion suggest that the alkenylmercury(I) intermediate is unstable towards competitive dissociation (Scheme 29). Some mercury metal was actually observed in the reaction flask (see Experimental Section).

$$\underset{(0.8\ \text{mmol})}{R_2Hg} + \underset{(\text{excess})}{PhSO_2Cl} \xrightarrow[\text{3.5 hours}]{\text{light}} \underset{(0.67\ \text{mmol})}{RHgCl} + \underset{(0.51\ \text{mmol})}{RSO_2Ph} \qquad (57)$$

R = (E)-3,3-dimethyl-1-butenyl

Scheme 29



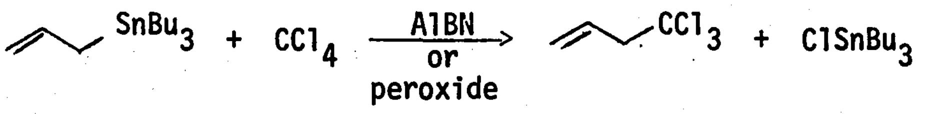
R = (E)-3,3-dimethyl-1-butenyl

3. Reaction of other halo compounds with vinyl mercurials

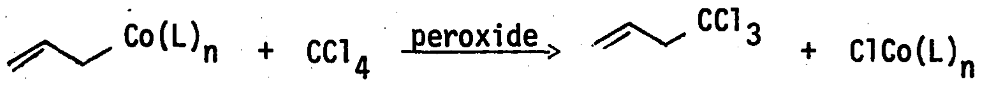
Attempts to photo-induce coupling reactions between (E)-3,3-dimethyl-1-butenylmercury chloride and N-bromosuccinimide, benzoyl chloride, diethyl chlorophosphonate, 2-bromo-2-nitropropane, and 2,4-dinitrobenzenesulfenyl chloride all failed (see Table XV). An attempted thermal coupling between (E)-2-phenyl-1-ethenylmercury chloride and phenylselenyl chloride in methylene chloride (reported to proceed in 80% yield [124]) afforded a complex product mixture containing only a 24% yield of the expected alkenyl selenide, presumably due to side reactions involving the addition of the selenyl halide across olefinic bonds.

Isopropyl iodide, reacted with 2,2-diphenylethenylmercury bromide in benzene solution to afford a 50% yield of the expected 3-methyl-1,1-diphenyl-1-butene along with approximately 8% of the 2-bromo-1,1-diphenylethene and 5% of the 2-iodo-1,1-diphenylethene (Table XV). Methyl iodide reacted only sluggishly to give a 36% yield of 1,1-diphenylpropene along with approximately 36% of the 2-bromo-1,1-diphenylethene and 18% of 2-iodo-1,1-diphenylethene. Benzyl bromide failed to react with 2,2-diphenylethenylmercury bromide even after 28 hours of irradiation at 350 nm.

The mechanism of alkyl iodide coupling with vinylmercury halides may well be similar to that of the coupling reactions between the mercurials and organosulfonyl chlorides (Scheme 27). The picture is clouded, however, by low coupling yields and rather complex product mixtures. The isolation of vinylic halide products indicates that part of the reaction proceeds via vinylic radicals or free halogen. There are literature examples of allylmetals reacting with alkyl halides by a free radical chain mechanism analogous to that of Scheme 28. Allyltin compounds react with carbon tetrachloride in the presence of a free radical initiator [134] (Eq. 58) as do allylcobaloximes [135] (Eq. 59).



(58)



(59)

C. Conclusion

Certain organic halo compounds, particularly arylsulfonyl chlorides, photoreact with vinyl mercurials in benzene solution via the free radical chain mechanism of Scheme 27. Support for the proposed mechanism includes inhibition by radical scavengers, the lack of a thermal (dark) reaction, and the unique reactivity of the vinyl moiety. Alkyl iodides only afforded coupled products in poor yield. A number of other halo compounds in which the halogen was bonded to carbon, nitrogen, or sulfur failed to yield coupled products.

D. Experimental Section

1. General considerations

N-bromosuccinimide was purchased from Fisher Scientific Co. and recrystallized from water before use. Diethyl chlorophosphonate was purchased from Aldrich and distilled before use. Benzoyl chloride was a product of Malinkrodt and was distilled prior to use Benzyl bromide, 2,4-dinitrobenzenesulfenyl chloride, α-toluenesulfonyl chloride, and methanesulfonyl chloride were purchased from Aldrich. The methanesulfonyl chloride was distilled before use. Isopropyl iodide, trichloromethanesulfonyl chloride, benzenesulfonyl chloride, and p-toluenesulfonyl chloride were obtained from Eastman. Phenylselenyl chloride was purchased from Orgmet, methyl iodide from Fisher Scientific, and diphenyl sulfone from K and K Laboratories. Benzyl phenyl sulfone [136] and 2-bromo-2-nitropropane [137] were prepared according to literature procedures.

2. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with benzenesulfonyl chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and benzenesulfonyl chloride (1.1 g, 6.3 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 3 hours in a Rayonet RPR-100 reactor (equipped with fifteen "350 nm" bulbs) at ambient temperature (40-45°C). Mercuric chloride precipitate was observed. The precipitate was removed by filtration and the solution concentrated under vacuum to afford a liquid found to contain (E)-3,3-dimethyl-1-butenyl phenyl sulfone (99% yield by quantitative ^{1}H N.M.R.) and left over benzenesulfonyl chloride.

The crude isolate was dissolved in 50 ml of chloroform and the solution stirred for 4 hours with 100 ml of aqueous bicarbonate to remove the benzenesulfonyl chloride. The chloroform solution was collected, dried over $MgSO_4$, and concentrated to afford 0.61 g of colorless liquid found to contain an 88% yield of the nearly pure vinyl sulfone by ^{1}H N.M.R. The product was not further purified as this sulfone is readily prepared by the reaction of the vinylmercury halide and the sodium salt of benzenesulfinic acid (Chapter VI, Part II of this thesis) and has been fully characterized via that procedure (see the Experimental Section of Chapter VI, Part II). In addition to ^{1}H N.M.R., the identity of the crude sulfone was verified by G.C.M.S. (m/e = 224 for the parent ion) and found to be identical to the product of the coupling between the vinylmercury halide and the sulfinate salt.

3. Effect of darkness on the reaction of benzenesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (0.5 g, 1.55 mmol) and benzenesulfonyl chloride (0.55 g, 3.1 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a flask tightly wrapped with aluminum foil to omit light. The flask was immersed in a 50°C oil bath and the solution gently stirred for 12 hours. Upon cooling of the solution and removal of the foil, no mercuric chloride was observed. The solvent was removed under vacuum to afford an oil containing a 97% recovery of the starting mercurial (by quantitative ^{1}H N.M.R.). No (E)-3,3-dimethyl-1-butenyl phenyl sulfone was detected.

4. Effect of di-t-butyl nitroxide on the photoreaction of benzenesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol), benzenesulfonyl chloride (1.1 g, 6.2 mmol) and di-t-butyl nitroxide (45 mg, 0.31 mmol) were dissolved in 25 ml of nitrogen-purged benzene in an externally water-jacketed quartz reaction flask. The solution was irradiated for 1.5 hours at 25°C in a Rayonet RPR-100 reactor equipped with fifteen "350 nm" bulbs. No precipitate of mercuric chloride was observed. Removal of the solvent under vacuum yielded an 85% removery of the starting mercurial (as determined by quantitative ^{1}H N.M.R.). No (E)-3,3-dimethyl-1-butenyl phenyl sulfone was detected.

In a control experiment (performed without di-t-butyl nitroxide), the same irradiation period afforded a 100% yield of the vinyl sulfone.

5. Effect of oxygen on the photoreaction of benzenesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and benzenesulfonyl chloride (1.1 g, 6.2 mmol) were dissolved in 25 ml of benzene in an externally water-jacketed quartz reaction flask. The solution was maintained saturated with oxygen by means of a stream of oxygen gas from a syringe needle. The solution was irradiated for 1.5

hours at 25°C in a Rayonet RPR-100 reactor equipped with fifteen "350 nm" bulbs during which time no mercuric chloride precipitate was observed. The solvent was removed under vacuum and the isolate determined to contain 95% of the original mercurial by quantitative ^{1}H N.M.R. No vinyl sulfone was detected. The control experiment (performed under nitrogen) afforded the vinyl sulfone in 100% yield.

6. Photoreaction between benzenesulfonyl chloride and benzylmercury chloride

Benzylmercury chloride (1.0 g, 3.06 mmol) and benzenesulfonyl chloride (0.94 g, 5.3 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex reaction flask. The solution was irradiated for 3 hours in a Rayonet reactor (equipped with "350 nm" bulbs) during which time a white precipitate was observed. The solution was concentrated under vacuum and analyzed by ^{1}H N.M.R. An authentic sample of benzyl phenyl sulfone exhibits the methylene absorption at 4.3 ppm. This absorption was not observed in the crude reaction isolate.

7. Photoreaction of benzenesulfonyl chloride with phenylmercury chloride

Phenylmercury chloride (0.5 g, 1.6 mmol) and benzenesulfonyl chloride (0.4 g, 2.3 mmol) were dissolved in 30 ml of nitrogen-purged benzene (the mercurial only partially dissolved) in a Pyrex reaction vessel. The solution was irradiated for 22 hours in a Rayonet reactor equipped with thirteen "350 nm" bulbs during which time the mercurial completely dissolved and a new white precipitate formed. The solvent was removed under vacuum and the residue analyzed by G.L.C. (5' x 1/4"; 5% OV-3; 220°C) for the presence of diphenyl sulfone by retention matching with the authentic compound. No diphenyl sulfone was detected.

8. Photoreaction of p-toluenesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and p-toluenesulfonyl chloride (0.8 g, 4.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 2.5 hours in a Rayonet RPR-100 reactor (350 nm light) during which time mercury chloride was observed to precipitate. The solution was poured directly onto 50 ml of aqueous bicarbonate and stirred for 4 hours. The organic layer was extracted with ether. The extract was dried ($MgSO_4$) and concentrated under vacuum to afford 0.61 g of colorless oil found to contain a 75% yield of (E)-3,3-dimethyl-1-butenyl p-tolyl sulfone by quantitative ^1H N.M.R. Identification of the sulfone was based on spectral comparison with the authentic compound conveniently prepared in pure form via the reaction of the sulfinate salt with (E)-3,3-dimethyl-1-butenylmercury chloride (see Chapter VI, Part II of this thesis).

9. Photoreaction of methanesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

Methanesulfonyl chloride (0.74 g, 6.5 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 22 hours in a Rayonet reactor ("350 nm" bulbs). Precipitation of mercuric chloride was observed. The solution was poured onto 100 ml of aqueous bicarbonate and the mixture stirred for 4 hours. The organic layer was collected, dried ($MgSO_4$) and concentrated under vacuum to afford an oil containing the starting mercurial (12% recovery) and (presumably) the (E)-3,3-dimethyl-1-butenyl methyl sulfone (36% yield by quantitative ^1H N.M.R.). The ^1H N.M.R. of the impure sulfone follows: ($CDCl_3$, δ) 1H (d) 6.94 (J_H = 15.5 cps), 1H (d) 6.29 (J_H = 15.5 cps), 3H (s) 2.94, 9H (s) 1.12.

The reactions of vinyl mercurials with simple alkyl sulfonyl chlorides were not investigated further. The alkenyl alkyl sulfones are readily available by the coupling of alkylsulfinate salts with vinylmercury halides (see Chapter VI, Part II of this thesis).

10. Photoreaction of trichloromethanesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and trichloromethanesulfonyl chloride (1.0 g, 4.6 mmol) were dissolved in 20 ml of nitrogen-purged benzene in a Pyrex flask. A 19 hour irradiation period in a Rayonet RPR-100 reactor ("350 nm" bulbs) resulted in the formation of a brown, sticky precipitate. Filtration and concentration of the solution under vacuum afforded a brown oil. ^1H N.M.R. analysis proved unhelpful as the vinylic region of the spectrum was poorly resolved. G.C.M.S. demonstrated the presence of a volatile compound with the formula $C_7H_{11}Cl_3$ (m/e observed for the parent ion along with isotope peaks characteristic of three chlorines). This compound is probably 1,1,1-trichloro-4,4-dimethyl-2-pentene. None of the eight volatile components of the crude isolate was 3,3-dimethyl-1-butenyl trichloromethyl sulfone.

11. Photoreaction of α-toluenesulfonyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and α-toluenesulfonyl chloride (0.6 g, 3.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 40 hours during which time only a trace of brown precipitate was observed. Removal of the solvent afforded a 90% recovery of the starting mercurial of ^{1}H N.M.R. and no evidence of (E)-3,3-dimethyl-1-butenyl benzyl sulfone or 1-phenyl-4 4-dimethyl-2-pentene.

12. Photoreaction of benzenesulfonyl chloride with bis[(E)-3,3-dimethyl-1-butenyl]mercury

Bis[(E)-3,3-dimethyl-1-butenyl]mercury (0.3 g, 0.8 mmol) and benzenesulfonyl chloride (0.29 g, 1.6 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 3.5 hours in a Rayonet reactor (fourteen "350 nm" bulbs) during which time a little mercury metal precipitated. The solution was decanted from the mercury bead and concentrated under vacuum. Quantitative ^{1}H N.M.R. analysis of the residue revealed 0.51 mmol of (E)-3,3-dimethyl-1-butenyl phenyl sulfone and 0.67 mmol of

(E)-3,3-dimethyl-1-butenylmercury chloride. None of the starting bis[alkenyl]mercury compound was recovered.

13. Photoreaction of N-bromosuccinimide with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and NBS (0.57 g, 3.2 mmol) were dissolved in 25 ml of CH_2Cl_2 in a Pyrex flask. The solution was irradiated in a Rayonet reactor (equipped with fifteen "350 nm" bulbs) for 1.5 hours during which time a white solid precipitated. The solution was filtered and concentrated under vacuum to afford a complex mixture containing at least 9 volatile components by G.L.C. (5' x 1/4"; 5% OV-3; 150°C). The ^1H N.M.R. demonstrated a complex vinylic region. The reaction was not investigated further.

14. Photoreaction of diethyl chlorophosphonate with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and diethyl chlorophosphonate (0.84 g, 4.8 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 17 hours in a Rayonet RPR-100 reactor (fifteen "350 nm" bulbs) during which time a white precipitate formed. Filtration and concentration of the solution under vacuum afforded a 70% recovery of the starting mercurial by quantitative ^1H N.M.R. The crude isolate contained little or none (<5% yield) of the expected diethyl (E)-3,3-dimethyl-1-butenylphosphonate, a compound which is easily prepared by the coupling of diethyl phosphite ion with the vinyl mercurial (Chapter VI, Part II of this thesis).

15. Photoreaction of benzoyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and benzoyl chloride (0.73 g, 5.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene and the solution was irradiated for 17 hours in a Rayonet reactor (fifteen "350 nm" bulbs). A small quantity of brown precipitate was observed. Filtration and concentration under vacuum of the solution afforded a greenish liquid residue. The ^{1}H N.M.R. spectrum was uninformative due to the low resolution of the vinyl region. No 3,3-dimethyl-1-butenyl phenyl ketone was detected by G.C.M.S.

16. Photoreaction of 2-bromo-2-nitropropane with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and 2-bromo-2-nitropropane (0.9 g, 5.4 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 55 hours in a Rayonet RPR-100 reactor (thirteen "350 nm" lamps). A small amount of white precipitate formed. Filtration and concentration under vacuum of the solution afforded a crude oil. No components were eluted by G.L.C. (5' x 1/4"; 5% FFAP; 100-200°C) and the ^{1}H N.M.R. was complex.

17. Reaction of phenylselenyl chloride with (E)-2-phenyl-1-ethenylmercury chloride

The following procedure was taken from Raucher and coworkers [124].

(E)-2-Phenyl-1-ethenylmercury chloride (1.06 g, 3.1 mmol) was suspended in 15 ml of methylene chloride at 0°C. A cold (0°C) solution of phenylselenyl chloride (0.6 g, 3.1 mmol) in 15 ml of methylene chloride was added to the suspension of the mercurial. After stirring for 10 minutes, the mixture was poured onto 100 ml of brine layered with ethyl ether. The ethereal extract was dried over $MgSO_4$ and concentrated under vacuum to afford 0.78 g of oil. The crude isolate was a complex mixture found to contain a 24% yield of the expected (E)-2-phenyl-1-ethenyl phenyl selenide by quantitative ^1H N.M.R. (the authentic compound described in Chapter III, Part II of this thesis was employed for spectral comparison).

The yield of vinyl selenide from this procedure is reported to be 80% [124].

18. Photoreaction of 2,4-dinitrobenzenesulfenyl chloride with (E)-3,3-dimethyl-1-butenylmercury chloride

(E)-3,3-Dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and 2,4-dinitrobenzenesulfenyl chloride (0.8 g, 3.4 mmol) were dissolved in 30 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 4.5 hours with a 275 watt sunlamp positioned 6 inches from the reaction vessel. A brown precipitate formed. Filtration and concentration of the solution under vacuum afforded 1.8 g of a dark brown solid. ^{1}H N.M.R. revealed the isolate to contain starting materials (85% of the starting mercurial was recovered) and unidentified impurities exhibiting broad absorptions.

19. Photoreaction of isopropyl iodide with 2,2-diphenylethenylmercury bromide

2,2-Diphenylethenylmercury bromide (1.0 g, 2.18 mmol) and isopropyl iodide (3.4 g, 20 mmol) were dissolved in 30 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 2 hours in a Rayonet RPR-100 reactor (fifteen "350 nm" bulbs). After the first hour, a yellow precipitate was noted, although after the second hour, the precipitate was bright red. The colorless solution was decanted from the precipitate and concentrated under vacuum to afford 0.55 g of a mixture of a white solid and a colorless oil. Quantitative ^{1}H N.M.R. revealed the isolate to contain a 50% yield of the expected 3-methyl-1,1-diphenyl-1-butene and a 5% recovery of the starting mercurial along with other unidentified compounds. The ^{1}H N.M.R. spectrum of the impure (known) 3-methyl-1,1-diphenyl-1-butene follows: ($CDCl_3$, δ) 10H (m) 7.2-7.5, 1H (d) 5.87 (J_H = 12 Hz), 1H (m) 2.5, 6H (d) 1.0 (J_H = 7 Hz). The G.C.M.S. analysis demonstrated the presence of the product olefin (m/e = 222 was observed for the parent ion) as well as 2-bromo-1,1-diphenylethene (ca. 8% yield) and 2-iodo-1,1-diphenylethene (ca. 5% yield).

20. Photoreaction of methyl iodide with 2,2-diphenylethenylmercury bromide

2,2-Diphenylethenylmercury bromide (0.5 g, 1.1 mmol) and methyl iodide (5 g, 35 mmol) were dissolved in 10 ml of nitrogen-purged benzene in a Pyrex reaction flask. The solution was irradiated for 30 hours in a Rayonet RPR-100 reactor (equipped with thirteen "350 nm" bulbs). Only after approximately 20 hours was (red) precipitate observed. The solution was decanted and concentrated under vacuum. Quantitative ^1H N.M.R. revealed a 36% yield of the expected 1,1-diphenyl-1-propene. The starting mercury compound had been entirely consumed. G.C.M.S. analysis revealed, in addition to the propene derivative, 2-bromo-1,1-diphenylethene (ca. 36% yield), 2-iodo-1,1-diphenylethene (ca. 18% yield), and what may be 2-methyl-1,1-diphenyl-1-propene (ca. 10% yield, m/e = 208 observed for the parent ion).

21. Photoreaction between benzyl bromide and 2,2-diphenylethenylmercury bromide

2,2-Diphenylethenylmercury bromide (1.0 g, 2.18 mmol) and benzyl bromide (0.72 g, 4.2 mmol) were dissolved in 25 ml of nitrogen-purged benzene in a Pyrex flask. The solution was irradiated for 28 hours in a Rayonet RPR-100 reactor (fifteen "350 nm" bulbs) during which time only a trace of white precipitate was observed. Removal of the solvent under vacuum afforded a mixture containing benzyl bromide, an 85% recovery of the starting mercurial, and small quantities of unidentified compounds (determined by ^1H N.M.R.).

VI. PHOTOCHEMICAL REACTIONS OF DIALKYL PHOSPHITE AND SULFINATE ANIONS WITH VINYLMERCURY HALIDES TO FORM VINYLPHOSPHONATE ESTERS AND VINYL SULFONES

A. Introduction

The anions of alkyl and aryl sulfinic acids and diethyl phosphite couple with vinylmercury halides by a light-induced process (Eq. 60).

$$R^1HgX + A^- \xrightarrow{\text{light}} R^1A + Hg^\circ + X^- \qquad (60)$$

$$R^1 = \text{vinyl} \qquad X = Br, Cl \qquad A^- = R^2SO_2^-, (EtO)_2PO^-$$

Superficially similar to the coupling of nitronate ions with alkylmercury halides (see Chapter III, Part I of this thesis), reaction 60 appears not to proceed by the $S_{RN}1$ mechanism. The scope of the reaction and probable mechanism are two topics of the following section.

B. Results and Discussion

1. Photochemical coupling of vinylmercury halides with diethyl phosphite ion

Photoreaction of benzylmercury chloride with diethyl phosphite ion affords bibenzyl and mercury metal, apparently by a nonchain free radical route (Chapter III, Part II of this thesis). Substituted vinylmercury halides, however, afford diethyl alkenylphosphonate esters in moderate yields (Table XVI). (*E*)-3,3-Dimethyl-1-butenylmercury halides gave the best yields of phosphonate esters due either to the steric barrier to olefin polymerization or to the lack of allylic hydrogens.

The attempted coupling of ethenylmercury chloride was a notable failure. Resinous, presumably polymeric material, was discarded during the work-up. Phenylmercury chloride did couple with diethyl phosphite ion in low yield. Symmetrization of the mercurial was a competing process (Table XVI). Vinyl mercurials bearing the bulky *trans*-*t*-butyl substituent gave only the (*E*)-alkenylphosphonate. The less bulky *n*-propyl and *n*-octyl substituted mercurials afforded mixtures of *E* and *Z* isomers in the ratio of approximately 10:1.

The coupling reaction between (*E*)-3,3-dimethyl-1-butenylmercury bromide and diethyl phosphite ion in DMSO at 25°C under sunlamp irradiation was completely inhibited for 2.25 hours by the addition of 10 mole % of di-*t*-butyl nitroxide. A control reaction afforded a 47% yield of (*E*)-3,3-dimethyl-1-butenylphosphonate ester in the same period of irradiation. The coupling reaction failed to proceed at all at 25°C in darkness even after 20 hours (see the Experimental Section).

Vinylmercury halides appear to be symmetrized by diethyl phosphite ion in DMSO (Scheme 30). This reaction is presumably due to mercury(II)

Scheme 30

$$\begin{tikzcd}
(\underline{E})\text{-}Me_3CCH{=}CHHgCl + n(EtO)_2PO^- \arrow[r, shift left, "DMSO"] & {[(\underline{E})\text{-}Me_3CCH{=}CH]_2Hg} \arrow[l, shift left] \\
& + \\
& HgCl_2 \text{ --- } n(OEt)_2PO^- \arrow[dl, "light"] \\
2\ (\underline{E})\text{-}Me_3CCH{=}CHP({=}O)(OEt)_2 + 2\,Hg^\circ + 2\,Cl^- &
\end{tikzcd}$$

Table XVI. Photoreaction between vinylmercury halides and diethyl phosphite ion

$$R^1HgX + (EtO)_2PO^{-a} \xrightarrow[DMSO]{light} R^1P(=O)(OEt)_2 + Hg^\circ + X^-$$

R^1HgX	Time[b]	Yield of $R^1P(=O)(OEt)_2$ (stereochemistry)[c]
(E)-$Me_3CCH=CHHgCl$	20.5 h	69% (>95% E)
(E)-$Me_3CCH=CHHgBr$	29 h	76% (>95% E)
(E)-n-$PrCH=CHHgCl$	27 h	56% (10:1 E:Z)
n-$C_8H_{17}CH=CHHgCl$	16.5 h	53% (9:1 E:Z)
$CH_2=CHHgCl$	30 h	0%
PhHgCl	25 h[d]	22%[d]

[a] Generated from equimolar amounts of potassium t-butoxide and diethyl phosphite in dry DMSO.

[b] Irradiation period with a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel. All reactions were performed under nitrogen.

[c] Yield of purified (>95%) vinylphosphonate ester. Stereochemistry determined by N.M.R., I.R., and G.L.C.

[d] Irradiation provided by a Rayonet RPR-100 reactor at 350 nm. A 26% yield of diphenylmercury was isolated along with diethyl phenylphosphonate.

halide complexation with the dialkyl phosphite ions [20,21,67]. Thus, (E)-3,3-dimethyl-1-butenylmercury chloride dissolved in d_6-DMSO containing excess diethyl phosphite ion exhibited the ^{1}H N.M.R. spectrum of bis[(E)-3,3-dimethyl-1-butenyl]mercury. Nonirradiated DMSO solutions containing vinylmercury halides and diethyl phosphite ion yielded the symmetrized mercurials nearly quantitatively upon aqueous dilution and ether extraction. These results parallel the observed nonreductive symmetrization of benzylmercury chloride by diethyl phosphite ion (Chapter III, Part II of this thesis).

2. Photochemical coupling of vinylmercury halides with organosulfinate ions

The sodium salt of p-toluenesulfinic acid reacted sluggishly with benzylmercury chloride under sunlamp irradiation to afford bibenzyl (Chapter III, Part I of this thesis) and was unreactive towards phenylmercury chloride (Table XVII). With prolonged irradiation at 350 nm in a Rayonet RPR-100 reactor, phenylmercury iodide and sodium p-toluenesulfinate reacted in DMSO to produce a low yield of phenyl p-tolyl sulfone (Table XVII) contaminated with di-p-tolyl sulfone. In contrast, vinylmercury halides reacted with alkyl and aryl sulfinate salts with irradiation from a 275 watt sunlamp to give the corresponding vinyl sulfones in good yields (Table XVII) [138] according to Equation 61.

$$R^1HgX + R^2SO_2Na \xrightarrow{\text{light}} R^1SO_2R^2 + Hg^\circ + NaX \qquad (61)$$

$$R^1 = \text{vinyl} \qquad X = Br, Cl \qquad R^2 = \text{alkyl, aryl}$$

Table XVII. Photoreaction of organosulfinate ions with vinylmercury halides

$$R^1HgX + R^2SO_2Na \xrightarrow{light} R^1SO_2R^2 + Hg^\circ + NaX$$

R^1HgX	R^2	Solvent	Time[a]	% Sulfone (stereochemistry)[b]
(E)-$Me_3CCH{=}CHHgCl$	Ph	t-C_4H_9OH/H_2O	23.75 h	85 (88) (>95% E)
(E)-$Me_3CCH{=}CHHgCl$	p-MePh	t-C_4H_9OH/H_2O	21 h	68 (81) (>95% E)
(E)-n-$PrCH{=}CHHgCl$	p-MePh	t-$C_4H_9OH/H_2O/DMSO$	22 h	63 (71) (E:Z = 8.6:1.4)
n-$C_8H_{17}CH{=}CHHgCl$	p-MePh	t-$C_4H_9OH/H_2O/DMSO$	15 h	55 (74) (E:Z = 8.9:1.1)
$MeCH{=}C(HgBr)Me$	p-MePh	t-$C_4H_9OH/H_2O/DMSO$	24 h	67[c]
$Ph_2C{=}CHHgBr$	p-MePh	DMSO/t-C_4H_9OH	42 h	61 (80)
(E)-$PhCH{=}CHHgCl$	p-MePh	DMSO/t-C_4H_9OH	19 h	81 (>95% E)
$Ph_2C{=}C(HgBr)Me$	p-MePh	DMSO/t-C_4H_9OH/H_2O	69 h[d]	31 (66)

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[a] Irradiation period with a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel. Reactions were performed under nitrogen at ambient temperatures (35-45°C).

[b] Yield of pure sulfone (^1H N.M.R. crude yield in parentheses). Stereochemistry was determined by ^1H N.M.R., I.R., and G.L.C.

[c] Stereochemistry not determined.

[d] Irradiation provided by a Rayonet RPR-100 reactor (350 nm light).

Table XVII. (Continued)

R^1HgX	R^2	Solvent	Time[a]	% Sulfone (stereochemistry)[b]
$CH_2{=}C(HgBr)(CH_2C_6H_{11}\text{-}\underline{c})$	$\underline{p}$-MePh	DMSO/$\underline{t}$-C_4H_9OH/H_2O	51 h[d]	(<10)
$CH_2{=}CHHgCl$	$\underline{p}$-MePh	DMSO/$\underline{t}$-C_4H_9OH	27 h	0
PhHgCl	$\underline{p}$-MePh	DMSO	21 h	0 (no reaction)
PhHgI	$\underline{p}$-MePh	DMSO	46 h[d]	(40)
($\underline{E}$)-$Me_3CCH{=}CHHgCl$	$\underline{c}$-C_6H_{11}	DMSO/$\underline{t}$-C_4H_9OH/H_2O	18 h	66 (71) (>95% $\underline{E}$)
($\underline{E}$)-PhCH=CHHgCl	$\underline{c}$-C_6H_{11}	DMSO/$\underline{t}$-C_4H_9OH/H_2O	25 h	65 (68) (>95% $\underline{E}$)
($\underline{E}$)-PhCH=CHHgCl	$\underline{t}$-C_4H_9	DMSO/$\underline{t}$-C_4H_9OH	24 h	55 (56) (>95% $\underline{E}$)
($\underline{E}$)-$Me_3CCH{=}CHHgCl$	$\underline{n}$-C_3H_7	$\underline{t}$-C_4H_9OH/DMSO/H_2O	30 h	69 (75) (>95% $\underline{E}$)
($\underline{E}$)-$Me_3CCH{=}CHHgCl$	Cl_3C	DMSO	43 h[d]	0 (no reaction)
($\underline{E}$)-$Me_3CCH{=}CHHgCl$	$PhCH_2$	$\underline{t}$-C_4H_9OH/H_2O	19 h	0 (no reaction)

The coupling reactions were performed generally in mixed solvent systems selected primarily to accommodate the solubilities of the reagents. Pure DMSO was avoided since partial symmetrization of (E)-3,3-dimethyl-1-butenylmercury chloride by sodium p-toluenesulfinate was observed in this solvent (see the Experimental Section). The use of t-butyl alcohol and/or water as cosolvents often resulted in a simple workup procedure since the metallic mercury tended to form beads instead of dispersions. Simple Kugelrohr distillation or recrystallization of the crude product generally afforded sulfones of high purity.

Exclusively (E)-alkenyl sulfones resulted from coupling reactions with vinylmercury halides bearing bulky trans-substituents. Mercurials such as (E)-1-pentenylmercury chloride afforded mixtures of E and Z isomers.

Mercurials substituted at the α-vinylic carbon reacted sluggishly with sulfinate ions compared with less highly substituted analogues. Thus, 1-methyl-2,2-diphenylethenylmercury bromide coupled with sodium p-toluenesulfinate very slowly under the influence of sunlamp irradiation and a Rayonet reactor equipped with "350 nm" bulbs was employed to induce formation of a reasonable yield of the expected sulfone. By comparison, 2,2-diphenylethenylmercury bromide coupled with sodium p-toluenesulfinate under ordinary sunlamp irradiation to afford a higher yield of sulfone in less time (Table XVII). The highly hindered 1-(methylcyclohexyl)-1-ethenylmercury bromide only gave a trace of alkenyl sulfone with sodium p-toluenesulfinate detectable by G.C.M.S. of the complex crude reaction isolate. Ethenylmercury chloride failed to couple with sodium p-toluenesulfinate, but appeared to polymerize.

No coupling occurred between vinylmercury halides and sulfinate salts in the dark. Thus (E)-2-phenyl-1-ethenylmercury chloride and sodium p-toluenesulfinate did not react after 16 hours at 23°C. The same coupling reaction was completely inhibited by the presence of 10 mole % of di-t-butyl nitroxide for 4.5 hours of sunlamp irradiation at 25°C. In the control experiment, 4.5 hours of sunlamp irradiation at 25°C afforded a 38% yield of (E)-2-phenyl-1-ethenyl p-tolyl sulfone (see the Experimental Section).

Although vinylmercury halides are symmetrized by the action of diethyl phosphite ion (Scheme 30), organosulfinate ions do not have a similar effect (i.e., the equilibrium in Scheme 31 is balanced >95% in favor of the unsymmetrized mercurial). Thus, the ^{1}H N.M.R. spectrum of (E)-3,3-dimethyl-1-butenylmercury chloride in d_6-DMSO was not affected by the addition of sodium benzenesulfinate and sunlamp irradiation resulted in essentially quantitative formation of the vinyl sulfone with no evidence for the presence of an intermediate vinylmercury compound. Furthermore, (E)-3,3-dimethyl-1-butenylmercury chloride was recovered intact in 95% yield from a t-butyl alcohol/water solution containing sodium benzenesulfinate (see the Experimental Section).

Sodium trichloromethanesulfinate and α-toluenesulfinate failed to couple with (E)-3,3-dimethyl-1-butenylmercury chloride even with prolonged irradiation (Table XVII). A mixture of the trichloromethanesulfinate and benzenesulfinate salts reacted with the vinyl mercurial to give only the alkenyl phenyl sulfone (Eq. 62). The crude sulfone

$$(\underline{E})\text{-}Me_3CCH{=}CHHgCl + \left\{\begin{matrix} PhSO_2Na \\ + \\ Cl_3CSO_2Na \end{matrix}\right\} \xrightarrow{\text{light}} \underset{(85\%)}{(\underline{E})\text{-}Me_3CC{=}CHSO_2Ph} \quad (62)$$

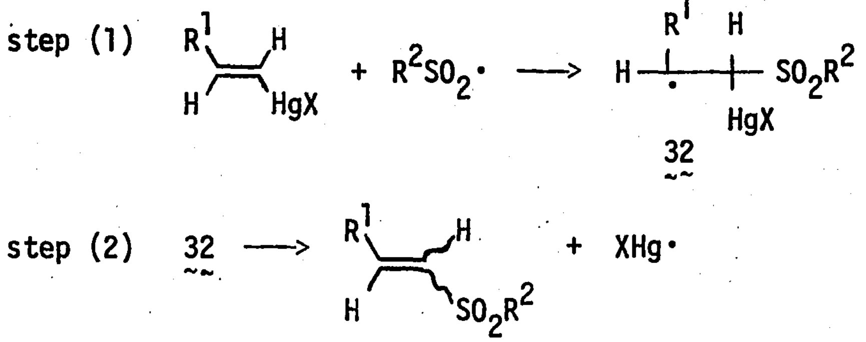
was pure except for a trace of the unreacted vinylmercury halide.

3. Mechanism of the coupling reaction between vinylmercury halides and organosulfinate ions

The mechanism detailed in Scheme 31 is consistent with the available data. The first two proposed propagation steps, the addition of a sulfonyl radical to the α-carbon of the double bond and subsequent elimination of a halomercury(I) radical, are borrowed directly from the proposed mechanism for the coupling of vinylmercury halides with

Scheme 31

propagation:



step (3) $XHg\bullet + R^2SO_2^- \longrightarrow Hg^\circ + X^- + RSO_2\bullet$

arylsulfonyl halides (Chapter V, Part II of this thesis). Similar processes have been proposed for the reactions of thiyl radicals with vinylmercury mercaptides and bis[vinyl]mercury compounds as well as the reactions of thiyl, selenyl, and telluryl radicals with vinylmercury halides (Chapters II-IV, Part II of this thesis). Propagation step (3), the reduction of the halomercury(I) species by a sulfinate ion, is apparently unprecedented. No distinction between direct (outer sphere) electron transfer and sequential displacement of halide followed by dissociation of the mercury(I) sulfinate species (Eq. 63) is intended.

$$XHg\cdot + R^2SO_2^- \longrightarrow R^2SO_2Hg\cdot + X^- \longrightarrow R^2SO_2\cdot + Hg^\circ + X^- \quad (63)$$

Scheme 31 accommodates the apparent photo-induced radical chain character of the reactions, the observed product stereochemistries, and the unreactivity of alkyl and aryl mercurials. An alternate mechanism, the $S_{RN}1$ process, is difficult to exclude (see Chapters I and III, Part I of this thesis for discussion concerning the $S_{RN}1$ mechanism).

The lack of reaction between phenylmercury chloride and sodium p-toluenesulfinate appears inconsistent with an $S_{RN}1$ mechanism. Vinyl halide $S_{RN}1$ reactions, if authentic, are far less facile than analogous reactions of aryl halides [139]. Notably, attempts to stimulate coupling between phenyl iodide and p-toluenesulfinate ion with ultraviolet radiation or solvated ammonia failed (see the Experimental Section) and there are no examples in the literature of aryl $S_{RN}1$ reactions with sulfinate ions. Finally, the $S_{RN}1$ mechanism does not explain the behavior of sodium α-toluenesulfinate and sodium trichloromethanesulfinate towards vinylmercury halides. Radical anion 33 is potentially unstable towards loss of chloride ion and may not propagate an $S_{RN}1$ chain

$[(\underline{E})\text{-}Me_3CCH{=}CHSO_2CCl_3]^{\dot{-}}$ 33

$[(\underline{E})\text{-}Me_3CCH{=}CHSO_2CH_2Ph]^{\dot{-}}$ 34

reaction, but the presence of trichloromethanesulfinate ion would still be expected to interfere with the normal coupling between a vinylmercury halide and benzenesulfinate ion (Eq. 62) which it does not. Radical anion 34 would be expected to be a viable intermediate if the $S_{RN}1$ mechanism were operative, yet the $\underline{\alpha}$-toluenesulfinate ion did not react with (E)-3,3-dimethyl-1-butenylmercury chloride.

Clearly, a key distinction between Scheme 31 and the $S_{RN}1$ process lies in the identity of the chain-carrying radicals. The original motivation for the attempted coupling of a vinylmercury halide and sodium trichloromethanesulfinate was the hope that an intermediate trichloromethanesulfonyl radical would decompose rapidly with loss of sulfur dioxide (Eq. 53) [132] giving rise to trichloromethylated products not containing the sulfonyl moiety. The unreactivity of the trichloromethanesulfinate ion is accommodated by Scheme 31 on account of the undoubtedly lower oxidation potential of the ion compared with alkyl and aryl sulfinates (i.e., step (3) fails). The unreactivity of the $\underline{\alpha}$-toluenesulfinate ion is explained by assuming a rapid loss of sulfur dioxide from the intermediate sulfonyl radical (Eq. 53) [133] to give a benzyl radical which fails to propagate a chain process.

4. Mechanism of the coupling reaction between vinylmercury halides and diethyl phosphite ion

Any mechanistic approach to the photo-induced coupling of diethyl phosphite ion and vinylmercury halides is complicated by initial non-reductive symmetrization of the mercurial (Scheme 30). One may reasonably argue that the low equilibrium concentration of the vinylmercury halide renders an $S_{RN}1$ mechanism improbable. A key $S_{RN}1$ chain propagating process, the oxidation of an alkenylphosphonate radical anion by a molecule of vinylmercury halide, seems less likely than the non-propagating oxidation of the radical anion by mercuric halide, the oxidizing agent present in high concentration (Scheme 32). (Chapters I and III in Part I of this thesis contain detailed discussions of the $S_{RN}1$ process).

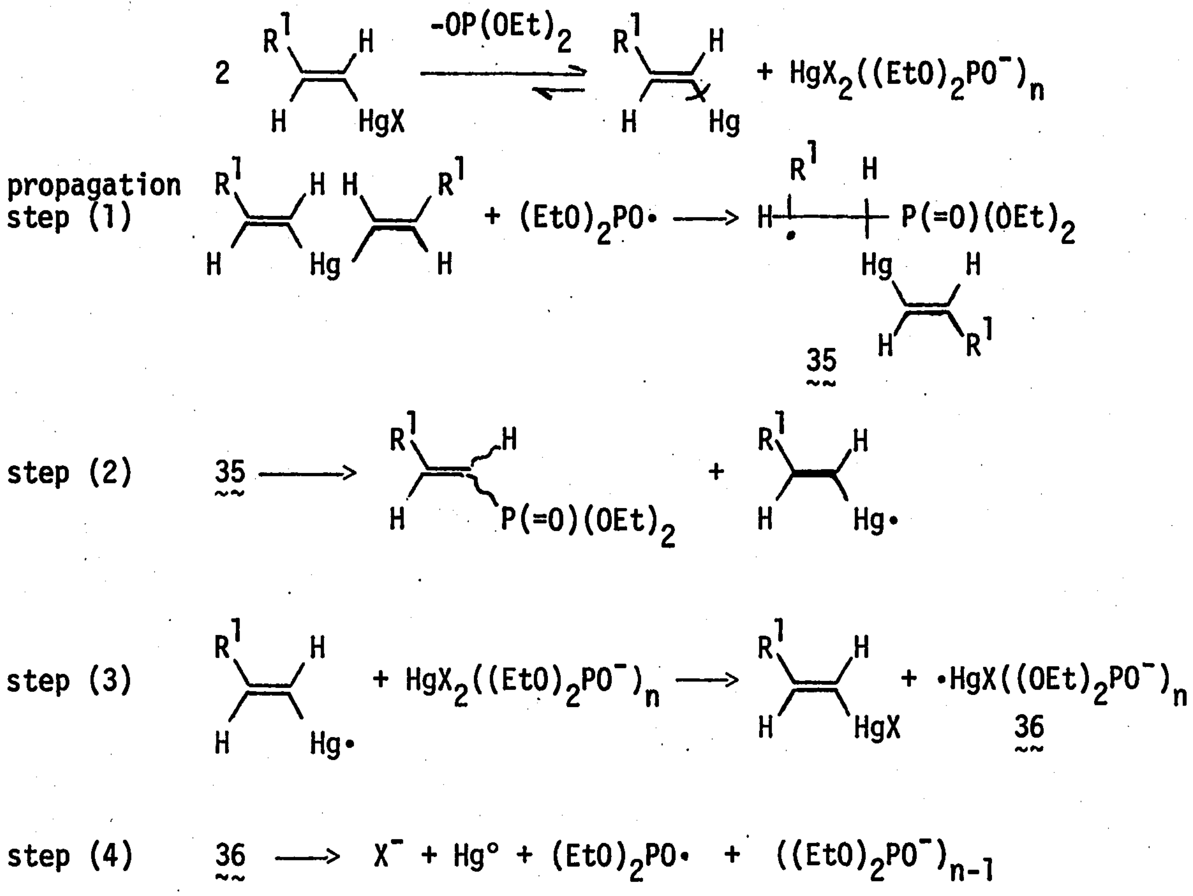
Scheme 32

R^1 = vinyl

$$\begin{tikzcd}
{[R^1P(=O)(OEt)_2]^{\cdot-}} \arrow[r, "R^1HgX"] \arrow[d, "HgX_2"] & R^1P(=O)(OEt) + [R^1HgX]^{\cdot-} \arrow[d] \\
R^1P(=O)(OEt) + X^- + XHg\cdot \arrow[d] & S_{RN}1 \\
\text{no } S_{RN}1 \text{ process} &
\end{tikzcd}$$

A plausible, albeit highly speculative, mechanism is outlined in Scheme 33. The apparent radical chain character of the reaction and the inability of organomercurials in which the metal atom is bonded to a saturated (sp^3 hybridized) carbon (for example, benzylmercury chloride and n-hexylmercury chloride) to couple with diethyl phosphite ion are clearly accommodated. Each of the proposed steps in Scheme 33 is

Scheme 33



closely related to processes invoked to explain other substitution reactions of vinyl mercurials: the addition of a diethyl phosphite radical to the bis[vinyl]mercury compound to form 35 is analogous to the addition of sulfonyl, thiyl, selenyl, and telluryl radicals to vinyl mercurials (Chapters II-V, Part II of this thesis). A vinylmercury radical, formed by the decomposition of 35, is proposed to abstract a halogen atom from complexed mercuric halide in step (3). Phenylthiyl abstraction from phenyl disulfide by vinylmercury radicals (Chapter IV, Part II of this thesis) and chlorine abstraction from organosulfonyl chlorides by halomercury radicals (Chapter V, Part II of this thesis) have been established. In step (4), the resulting (complexed) halomercury(I) radical is subsequently (or possibly concomitantly) reduced by a diethyl phosphite ion. A similar process was invoked to explain the reaction between vinylmercury halides and organosulfinate ions (Scheme 31). The vinylmercury halide generated in step (3) presumably re-enters the reaction chain after symmetrization by diethyl phosphite ion.

5. Reactions of other nucleophiles with (E)-3,3-dimethyl-1-butenylmercury chloride

Some of the attempted coupling reactions between (E)-3,3-dimethyl-1-butenylmercury chloride and nucleophiles other than organosulfinate and diethyl phosphite ions are summarized in Table XVIII. The photosymmetrization of (E)-3,3-dimethyl-1-butenylmercury chloride by the anion of 2-nitropropane was discussed previously in Chapter III, Part II of this thesis. Of the nucleophiles tested, only nitrite ion and n-butyl phenylphosphonite ion gave coupling product. Neither reaction was studied in detail, although both required sunlamp irradiation. Both reactions are presumed to proceed by mechanisms such as described in Scheme 31 or Scheme 33.

Table XVIII. Photoreaction of nucleophiles with (E)-3,3-dimethyl-1-butenylmercury chloride

$$(E)\text{-}Me_3CCH{=}CHHgCl + M^+A^- \xrightarrow{\text{light}} (E)\text{-}Me_3CCH{=}CHA + Hg^\circ + M^+Cl^-$$

M^+A^-	Time[a]	Solvent	% Yield Coupled Product
$NaNO_2$	68 h	DMSO	56 (>95% E)[b]
NaN_3	38 h	HMPA	0
$PhC(O^-)=CMe_2K^+$[c]	18 h	DMSO	0
$(EtO_2C)_2MeCK$[c]	18 h	DMSO	0
$PhP(O^-)(OBu)K^+$[c]	3.5 h	DMSO	84 (>95% E)
Ph_2PLi[d]	13.5 h	THF	0
$Ph_3PCHCOCH_3$	19 h	THF	0
Ph_3P	100 h	THF	0
Me_3SiK[c]	0.5 h[e]	HMPA	0

[a] Irradiation period with a 275 watt sunlamp positioned 4-8 inches from the Pyrex reaction vessel.

[b] Tentatively identified by G.C.M.S. (P-46 ion observed) and by ^1H N.M.R. A 36% yield of bis[(E)-3,3-dimethyl-1-butenyl]mercury was also formed.

[c] Formed from equimolar amounts of the conjugate acid and potassium t-butoxide in dry DMSO or HMPA.

[d] Formed from equimolar quantities of diphenylphosphine and n-butyl lithium in dry THF.

[e] Spontaneous exothermic reaction including the precipitation of mercury metal occurred without irradiation.

6. Competitive coupling between a vinylmercury halide and two anions

Several preliminary experiments (summarized in Table XIX) were carried out in an attempt to establish relative anion reactivities towards coupling with vinylmercury halides. The anion of 2-nitropropane was utilized in two experiments in an attempt to induce coupling to form homoallylic nitro compounds as opposed to the reductive symmetrization observed when the anion of 2-nitropropane alone is reacted with a vinylmercury halide (this symmetrization is discussed in Chapter III, Part II of this thesis).

Table XIX. Competitive coupling of a vinylmercury halide with two anions

$$R^1HgX + A_1^- + A_2^- \xrightarrow{light^a} R^1A_1 + R^2A_2 (+Hg^\circ + X^-)$$

R^1HgX	A_1^-	A_2^-	Solvent	% Yield R^1A_1	% Yield R^1A_2
(*E*)-$Me_3CCH=CHHgCl$	$(EtO)_2PO^-$	$Me_2C=NO_2^-$	DMSO	0[b,c]	0[b,c]
(*E*)-$Me_3CCH=CHHgCl$	$(EtO)_2PO^-$	NO_2^-	DMSO	0[b]	0[b]
(*E*)-$Me_3CCH=CHHgCl$	$(EtO)_2PO^-$	*p*-$MePhSO_2^-$	DMSO	15[b]	0[b]
(*E*)-$Me_3CCH=CHHgCl$	*p*-$MePhSO_2^-$	NO_2^-	DMSO/*t*-C_4H_9OH	76	0
(*E*)-PhCH-CHHgCl	*p*-$MePhSO_2^-$	$Me_2C=NO_2^-$	DMSO	14[b,c]	0[b,c]

---

[a] Irradiation for 10-20 hours with a 275 watt sunlamp positioned 6 inches from the Pyrex reaction vessel. All reactions were performed under nitrogen.

[b] Extensive formation of $(R^1)_2Hg$.

[c] Formation of 2,3-dimethyl-2,3-dinitrobutane.

Unfortunately, in reactions employing diethyl phosphite ion and/or the anion of 2-nitropropane, the major process was symmetrization of the vinylmercury halide to give the bis[vinyl]mercury compound, halide ion, and mercury metal. Reductive symmetrization is the normal photo-induced reaction between a nitronate ion and a vinylmercury halide. In reactions involving diethyl phosphite ion, the mercurial is nonreductively symmetrized to yield the mercuric halide and bis[vinyl]mercury compound in a rapid thermal process and the second anion (sulfinate, nitrite, or nitronate) acts to reduce the mercuric halide.

The qualitative conclusions drawn from Table XIX are that towards coupling with vinylmercury halides, arylsulfinate ion is more reactive than nitrite ion and diethyl phosphite ion is more reactive than arylsulfinate. The coupling of a nitronate ion with a vinylmercury halide was not accomplished by introducing a second anionic species into the reaction.

C. Conclusion

Organosulfinate ions and vinylmercury halides undergo light-induced coupling to give vinyl sulfones, mercury metal, and halide ion by a radical chain process. In the proposed mechanism, halomercury(I) radical is displaced from the vinylmercury halide by an organosulfonyl radical. Electron transfer from an organosulfinate ion to the halomercury(I) species regenerates the chain carrying organosulfonyl radical along with mercury metal and halide ion.

Diethyl phosphite ion and vinylmercury halides similarly are coupled by a light-initiated radical chain reaction to produce a diethyl vinylphosphonate, mercury metal, and halide ion. Vinylmercury halides are induced by diethyl phosphite ion to disproportionate to the bis[vinyl]-mercury compound and the mercuric halide. The proposed mechanism involves displacement of a vinylmercury radical from the bis[vinyl]-mercury compound by a diethyl phosphite radical yielding a molecule of the observed vinylphosphonate ester. The vinylmercury radical subsequently abstracts a halogen atom from the mercuric halide salt regenerating the starting mercurial. Diethyl phosphite ion is oxidized by the halomercury radical to regenerate the chain carrying diethyl phosphite radical, mercury metal, and halide ion.

Vinyl sulfones are versatile synthetic intermediates [140] serving as electrophiles for Michael additions of organometallic reagents [141, 142,143] and potent dienophiles for Diels-Alder reactions [140,144]. Vinyl sulfones bearing an α-vinylic proton can be lithiated and subsequently elaborated with electrophiles such as carbonyl compounds and alkyl halides [145]. Reduction of the sulfone to a vinyl sulfide can be accomplished with diisobutylaluminum hydride [146], while sodium amalgam reduces the sulfone to the unsaturated hydrocarbon (reductive desulfonylation) [147]. Vinyl sulfones are synthetic olefin equivalents when the Diels-Alder reaction is combined with reductive desulfonylation [147], and are synthetic ketene equivalents when the Diels-Alder reaction is followed by oxidative desulfonylation (α-carbanion formation with lithium diisopropyl amide followed by oxidation with MoO_5•Py•HMPA) [148].

Vinyl sulfones are traditionally prepared by the Hörner-Wittig reaction [142,149,150,151], the oxidation of vinyl sulfides [97], or the dehydrohalogenation of β-halo sulfones prepared by oxidation of β-halo sulfides [93] or addition of organosulfonyl halides to olefins [152-155].

Traditional synthetic approaches to the less studied vinylphosphonic acids and esters include the pyrolysis of β-halo alkylphosphonic acids [156] and the addition of phosphorous pentachloride to an olefin followed by hydrolysis [157]. The Arbuzov-type reaction of vinyl halides with trialkyl phosphites to form vinylphosphonate esters is catalyzed by nickel(II) chloride [158] and by palladium(0) [159]. The palladium catalyzed reaction appears presently the most general synthetic route and is stereospecific with retention of the configuration of the starting vinyl halide [159].

D. Experimental Section

1. General considerations

Sodium benzenesulfinate was purchased from Aldrich. Sodium p-toluenesulfinate (a product of Eastman) was employed as the dihydrate unless otherwise specified. Iodobenzene was purchased from Baker. Phenyl p-tolyl sulfone [160], 1-decenylmercury chloride (a mixture of cis and trans isomers) [104], diethyl phenylphosphonate [161,162] and n-butyl phenylphosphonite (PhP(OH)(OBu)) [163] were prepared according to the literature. Phenylmercury iodide was prepared by the addition of a THF solution of mercuric iodide to a refluxing THF solution containing diphenylmercury. The product (a THF-insoluble precipitate) was collected and repeatedly washed with THF (m.p. 270-271°C, lit. [164] 269°C). Sodium trichloromethanesulfinate and α-toluenesulfinate were prepared according to the literature [133,165]. The sodium salts of t-butyl [166], cyclohexyl [167], and n-propyl sulfinic [168] acids were prepared by the method of Houlton and Tartar. 1-Methyl-1-propenylmercury [69] bromide (a mixture of cis and trans isomers) was prepared by addition of mercuric bromide to the alkenylmagnesium bromide in THF.

2. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with diethyl phosphite ion

Solid (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) was added to a solution containing diethyl phosphite (0.55 g, 4.0 mmol) and potassium t-butoxide (0.4 g, 3.6 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 20.5 hours with a 275 watt sunlamp placed 8 inches from the Pyrex flask. The ambient reaction temperature rose to approximately 40°C. Mercury metal was observed to precipitate after the first 20 minutes of irradiation. After the reaction was complete, the DMSO solution was decanted from the mercury beads into brine layered with ethyl ether. The ether extract was washed with water and brine, then dried over anhydrous $MgSO_4$ and concentrated under vacuum to afford 0.47 g of a colorless liquid. The crude isolate was determined to be diethyl (E)-3,3-dimethyl-1-butenylphosphonate (>98% pure).

^1H N.M.R. ($CDCl_3$, δ) 1H (doublet of doublets) 6.78 (J_H = 17.5 Hz, J_P = 23 Hz), 1H (doublet of doublets) 5.43 (J_H = 17.5 Hz, J_P = 20 Hz), 4H (m) 4.08, 6H (t) 1.32 (J_H = 7 Hz), 9H (s) 1.05.

I.R. (neat, NaCl plates, cm^{-1}) 2960 (s), 1625 (m), 1475 (m), 1460 (m), 1440 (w), 1390 (m), 1365 (m), 1250 (s), 1160 (m), 1050 (s), 1025 (s), 985 (m), 950 (s), 845 (m), 815 (m), 780 (m), 760 (m), 725 (w).

M.S. Calculated for $C_{10}H_{21}O_3P$: 220.12284. Measured: 220.1229. Error: 0.29 ppm.

A small amount of material was purified by preparative G.L.C. for elemental analysis (6' x 1/4"; 20% Carbowax 20M; 170°C).

Elemental analysis. Calculated for $C_{10}H_{21}O_3P$: C, 54.53; H, 9.61; O, 21.79; P, 14.06. Found: C, 54.21; H, 9.74; P, 13.91.

3. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury bromide with diethyl phosphite ion

Solid (E)-3,3-dimethyl-1-butenylmercury bromide (1.1 g, 3.0 mmol) was added to a solution containing diethyl phosphite (0.55 g, 4.0 mmol) and potassium t-butoxide (0.4 g, 3.6 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 29 hours with a sunlamp during which time metallic mercury precipitated. The product was extracted from brine with ethyl ether to afford 0.50 g of a colorless liquid determined to be diethyl (E)-3,3-dimethyl-1-butenylphosphonate (>95% pure). The spectral characteristics of the product were identical to those of the compound prepared from diethyl phosphite ion and (E)-3,3-dimethyl-1-butenylmercury chloride.

4. Photoreaction of (E)-1-pentenylmercury chloride with diethyl phosphite ion

Solid (E)-1-pentenylmercury chloride (0.8 g, 2.6 mmol) was added to a solution containing diethyl phosphite (0.55 g, 4.0 mmol) and potassium t-butoxide (0.4 g, 3.6 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 27 hours during which time mercury metal precipitated. The product was extracted from brine with ethyl ether to afford 0.37 g of diethyl 1-pentenylphosphonate (92-95% pure). The G.L.C. trace exhibited two peaks in a ratio of 10:1 (5' x 1/8"; 5% FFAP; 150°C) both demonstrating parent ions at m/e = 206 in the G.C.M.S. The major (and later eluting) component was isolated by preparative G.L.C. and determined to be the (E)-alkenyl phosphonate. The smaller component was presumed the Z isomer.

^{1}H N.M.R. for the E isomer ($CDCl_3$, δ) 1H (m) 6.4-7.5, 1H (m) 5.35-6.15, 4H (m) 4.13, 2H (m) 2.24, 2H (m) 1.63, 6H (t) 1.34 (J_H = 8 Hz), 3H (t) 0.94 (J_H = 6.5 Hz).

I.R. for the E isomer (neat, NaCl plates, cm^{-1}) 2980 (s), 2960 (s), 2920 (s), 2900 (s), 2880 (m), 1635 (s), 1455 (m), 1440 (m), 1390 (s), 1245 (vs, broad), 1160 (s), 1100 (s), 1050 (vs, broad), 950 (vs, broad), 825 (s), 790 (s), 745 (m).

M.S. for the E isomer. Calculated for $C_9H_{18}O_3P$: (P-1 ion was measured) 205.09931. Measured: 205.09910. Error: 1.0 ppm.

A satisfactory elemental analysis was not obtained, presumably due to contamination by a trace of a mercury containing species.

5. Photoreaction of 1-decenylmercury chloride with diethyl phosphite ion

Solid 1-decenylmercury chloride (1.0 g, 2.7 mmol) was added to a solution containing diethyl phosphite (0.55 g, 4.0 mmol) and potassium t-butoxide (0.4 g, 3.6 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated with a sunlamp for 16.5 hours during which time mercury metal precipitated. The mercury metal was removed by filtration of the DMSO solution through "Celite" filter aid. The product was extracted from brine with ethyl ether to afford 0.49 g of colorless liquid determined by ^{1}H N.M.R. to contain a 53% yield of diethyl-1-decenylphosphonate. The G.C.M.S. showed two components (9:1 ratio) to have the same molecular ion (m/e = 276) and nearly identical fragmentation patterns. The major component (later eluting) was isolated by preparative G.L.C. and identified as the (E)-alkenyl phosphonate (6' x 1/4"; 20% FFAP; 210°C). The minor component was assumed to be the Z isomer.

^{1}H N.M.R. for the E isomer ($CDCl_3$, δ) 2H (complex) 5.2-7.2, 4H (m) 4.1, 23 H (complex) 0.6-2.6.

I.R. for the E isomer (neat, NaCl plate, cm^{-1}) 2980 (s), 2960 (vs), 2930 (vs), 2860 (vs), 1635 (m), 1470 (m), 1390 (m), 1250 (vs, broad), 1160 (m), 1095 (m), 1055 (vs, broad), 955 (vs, broad), 830 (m), 790 (m).

M.S. for the E isomer. Calculated for $C_{14}H_{29}O_3P$: 276.18544. Measured: 276.18557. Error: 0.5 ppm.

Elemental analysis for the E isomer. Calculated for $C_{14}H_{29}O_3P$: C, 60.85; H, 10.58; O, 17.37; P, 11.21. Found: C, 60.64, H, 10.45.

6. Photoreaction of phenylmercury chloride with diethyl phosphite ion

Solid phenylmercury chloride (2.0 g, 6.4 mmol) was added to a solution containing diethyl phosphite (0.98 g, 7.1 mmol) and potassium *t*-butoxide (0.75 g, 6.7 mmol) in 60 ml of dry, nitrogen-purged DMSO in a Pyrex flask. The solution was irradiated for 25 hours in a Rayonet RPR-100 reactor equipped with sixteen "350 nm" bulbs during which time mercury metal precipitated. The solution was decanted into brine and the organic products extracted with ethyl ether. The extract was washed with sodium thiosulfate solution to remove unreacted phenylmercury chloride, dried over anhydrous Na_2SO_4, and concentrated under vacuum to afford 0.6 g of yellow oil. The yield of diethyl phenylphosphonate by ^1H N.M.R. (and verified by G.L.C.) was 22%. The only other volatile material detected by G.L.C. (5' x 1/4"; 5% OV-3; 200°C) was diphenylmercury (26% yield, 0.85 mmol). The identity of both products was verified by G.L.C. retention matching with the authentic substances and by G.C.M.S.

7. Photoreaction of ethenylmercury chloride with diethyl phosphite ion

Solid ethenylmercury chloride (1.0 g, 3.8 mmol) was added to a solution containing diethyl phosphite (0.7 g, 5.1 mmol) and potassium *t*-butoxide (0.5 g, 4.5 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 30 hours with a sunlamp during which time mercury metal precipitated. The solution was poured into brine and the suspension was extracted with ethyl ether. Insoluble resinous matter was discarded. Concentration of the ether extract afforded 0.05 g of yellow oil found to contain no diethyl ethenylphosphonate by ^1H N.M.R.

8. Effect of darkness on the reaction of (E)-3,3-dimethyl-1-butenylmercury bromide with diethyl phosphite ion

Solid (E)-3,3-dimethyl-1-butenylmercury bromide (1.1 g, 3.0 mmol) was added to a nitrogen-purged solution containing diethyl phosphite (0.55 g, 4.0 mmol) and potassium *t*-butoxide (0.4 g, 3.6 mmol) in 30 ml of dry DMSO in a flask wrapped a flask wrapped with aluminum foil to exclude light. The solution was stirred for 20 hours at room temperature and then acidified with aqueous acetic acid. No mercury metal was observed when the foil was removed. The usual workup afforded no diethyl (E)-3,3-dimethyl-1-butenylphosphonate by ^{1}H N.M.R.

9. Effect of di-*t*-butyl nitroxide on the photoreaction of (E)-3,3-dimethyl-1-butenylmercury bromide with diethyl phosphite ion

Solid (E)-3,3-dimethyl-1-butenylmercury bromide (1.1 g, 3.0 mmol) was added to a nitrogen-purged solution containing diethyl phosphite (0.55 g, 4.0 mmol), potassium *t*-butoxide (0.4 g, 3.6 mmol), and di-*t*-butyl nitroxide (45 mcl, 0.3 mmol) in 30 ml of dry DMSO in a Pyrex flask. The reaction vessel was immersed in a 25°C water bath and irradiated for 2.25 hours with a sunlamp positioned 8 inches distant. No mercury metal was observed. The usual workup afforded 0.11 g of orange oil containing <2% of the expected diethyl (E)-3,3-dimethyl-1-butenyl phosphonate. In a control experiment (performed without the added nitroxide), the same irradiation period induced the formation of a 47% yield of the vinylphosphonate.

10. Action of diethyl phosphite ion on (E)-3,3-dimethyl-1-butenylmercury chloride

Solid (E)-3,3-dimethyl-1-butenylmercury chloride (0.033g, 0.1 mmol) was added to a solution containing diethyl phosphite (0.055 g) and potassium t-butoxide (0.039 g) in 1 ml of d_6-DMSO in an N.M.R. tube. The ^{1}H N.M.R. spectrum of the vinyl region matched that of bis[(E)-3,3-dimethyl-1-butenyl]mercury (described in Chapter III, Part I of this thesis). Interestingly, apparently quantitative conversion of diethyl (E)-3,3-dimethyl-1-butenylphosphonate occurred with sunlamp irradiation.

Bis[(E)-3,3-dimethyl-1-butenyl]mercury was isolated in 98% yield from a solution containing (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) and diethyl phosphite ion (from diethyl phosphite (1.07 g, 7.8 mmol) and potassium t-butoxide (0.6 g, 5.4 mmol)) in 25 ml of dry DMSO by pouring the solution into brine and extracting the bis[vinyl]mercury compound with ethyl ether.

Bis[vinyl]mercury compounds do not couple with diethyl phosphite ion to yield vinylphosphonates. Thus, bis[(E)-3,3-dimethyl-1-butenyl]-mercury (0.6 g, 1.6 mmol) was added to a nitrogen-purged solution containing diethyl phosphite (0.858 g, 6.2 mmol) and potassium t-butoxide (0.6 g, 5.3 mmol) in 50 ml of dry DMSO. The solution was irradiated for 23 hours with a sunlamp during which time a little mercury metal precipitated. The solution was decanted into brine and worked-up in the usual manner to afford 0.4 g of a foul-odored yellow oil. ^{1}H N.M.R. showed the isolate to contain no diethyl (E)-3,3-dimethyl-1-butenylphosphonate.

11. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with sodium benzenesulfinate - a general procedure for coupling sulfinate ions with vinylmercury halides

Many details of the following reaction and particularly the workup procedure are general for coupling reactions between sulfinate ions and vinylmercury halides.

Sodium benzenesulfinate (1.0 g, 6 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml) and water (10 ml) in a Pyrex vessel. The solution was irradiated by a 275 watt sunlamp positioned 6 inches distant and ambient temperature (25-45°C) for 23.75 hours during which time mercury metal precipitated. The solution was decanted away from the mercury beads (in some reaction systems the mercury metal remained finely suspended in the solvent and filtration through "Celite" filter aid was required) and most of the solvent removed under vacuum. The residue was poured into brine and the product extracted with three portions of ethyl ether. The ethereal extract was washed with portions of water, aqueous sodium thiosulfate, and brine. Dehydration over $MgSO_4$ and concentration under vacuum afforded 0.61 g (88% yield) of the crude (E)-3,3-dimethyl-1-butenyl phenyl sulfone as a colorless liquid. A Kugelrohr distillation (97-99°C/0.03 torr) provided the analytically pure sulfone in 85% overall yield. When the reaction was performed on a 10 mmol (or starting mercurial) scale, the yield of the distilled product was 76%.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.4-7.9, 1H (d) 6.87 (J_H = 16 Hz), 1H (d) 6.11 (J_H = 16 Hz), 9H (s) 1.09.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (m), 2960 (s), 1670 (w), 1620 (s), 1480 (s), 1465 (m), 1450 (s), 1370 (m), 1320 (vs), 1300 (vs), 1290 (vs), 1143 (vs), 1085 (vs), 975 (m), 830 (s), 805 (m), 760 (s), 750 (s), 710 (s), 685 (s), 590 (s), 550 (s).

M.S. Calculated for $C_{12}H_{16}O_2S$: 224.08711. Measured: 224.08722. Error: 0.5 ppm.

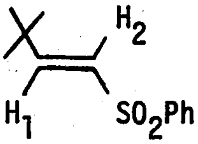
Elemental analysis. Calculated for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; O, 14.26; S, 14.29. Found: C, 64.01; H, 7.16.

An interesting characteristic of many of the vinyl sulfones described in this chapter is the strong dependence upon substrate concentration and the solvent of the vinylic proton N.M.R. chemical shifts. The high field proton ($\underline{\beta}$ to the sulfonyl moiety) is particularly affected. For example, 10 mg of (E)-3,3-dimethyl-1-butenyl phenyl sulfone in 0.5 ml HMPA exhibits magnetically equivalent vinylic protons at 6.85 ppm! The proton chemical shifts are compiled for various solvents in Table XX.

12. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (2.0 g, 9.3 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml) and water (5 ml). The solution was irradiated for 21 hours with a 275 watt sunlamp positioned 6 inches from the Pyrex reaction vessel during which time mercury metal

Table XX. Vinylic proton chemical shifts for (E)-3,3-dimethyl-1-butenyl phenyl sulfone in various solvents



Solvent[a]	H_2 (ppm)[b]	H_1 (ppm)[b]
Carbon tetrachloride	6.83	6.07
Ethyl acetate	6.88	6.32
Ethyl alcohol	6.93	6.35
Acetonitrile	6.94	6.36
DMSO	6.88	6.65
HMPA	6.84	6.84
Nitromethane	6.96	6.33
Ethylene chloride	6.90	6.19
n-Butyl alcohol	6.88	6.26
Methyl alcohol	6.91	6.40
Isopropyl alcohol	6.90	6.26
t-Butyl alcohol	6.81	6.24
80:20 Ethanol/water	6.93	6.36
80:20 Acetone/water	6.86	6.47
Acetone	6.78	6.44
Ethyl ether	6.87	6.23

[a] An R20-B Hitachi/Perkin-Elmer 60 MHz spectrometer was employed for these measurements. The concentration in each case was 10 mg of sulfone in 0.5 ml solvent with 0.5 ml of TMS vapor added via a septum cap on the N.M.R. tube.

[b] The vinyl proton coupling constant was always 15.5 ± 0.5 Hz.

precipitated. The usual workup afforded 0.5 g (81% yield) of (essentially pure) (E)-3,3-dimethyl-1-butenyl p-tolyl sulfone as a colorless liquid. A Kugelrohr distillation (105°C/0.15 torr) afforded the analytically pure sulfone in 68% overall yield as a viscous liquid which solidified upon prolonged storage.

^{1}H N.M.R. ($CDCl_3$, δ) 4H (m) 7.20-7.80, 1H (d) 6.88 (J_H = 15 Hz), 1H (d) 6.16 (J_H = 15 Hz), 3H (s) 2.42, 9H (s) 1.09.

I.R. (neat, NaCl plates, cm^{-1}) 3065 (w), 2975 (s), 1630 (m), 1610 (m), 1330 (s), 1305 (s), 1150 (vs), 1095 (s), 980 (m), 845 (s), 810 (s), 763 (s), 665 (s).

M.S. Calculated for $C_{13}H_{18}O_2S$: 238.10276. Measured: 238.10282. Error: 0.3 ppm.

Elemental analysis. Calculated for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61, O, 13.42; S, 13.45. Found: C, 65.75; H, 7.63.

When the coupling reaction between sodium p-toluenesulfinate and (E)-3,3-dimethyl-1-butenylmercury chloride was performed in pure DMSO, a mixture of the expected vinyl sulfone (44% yield) and bis[3,3-dimethyl-1-butenyl]mercury (16% yield) was isolated.

13. Photoreaction of (E)-1-pentenylmercury chloride with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.5 g, 7.0 mmol) and (E)-1-pentenylmercury chloride (1.0 g, 3.28 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml), DMSO (25 ml) and water (10 ml) in a Pyrex flask. The solution was irradiated with a sunlamp for 22 hours during which time mercury metal precipitated. The usual workup afforded 0.52 g (71% yield) of the 1-pentenyl p-tolyl sulfone (>95% pure) as a colorless oil. A Kugelrohr distillation (120-122°C/0.1 torr) afforded the pure sulfone in 63% overall yield as a colorless oil. The E and Z product isomers were separable by G.L.C. (6' x 1/4"; 15% OV-3; 195°C) and determined to occur in a ratio of 8.6:1.4. Both components exhibited the parent ion at m/e 224 and showed similar fragmentation patterns in the G.C.M.S. The major (and later eluting) isomer was assigned the E configuration based primarily on the I.R. spectrum of the mixture.

^{1}H N.M.R. for the mixture of E and Z isomers. ($CDCl_3$, δ) 4H (m) 7.2-7.8, 2H (complex) 6.1-7.2, 2H (m) 1.95-2.4, 3H (s) 2.4, 2H (m) 1.15-1.8, 3H (t) 0.88 (J_H = 6.5 Hz).

I.R. for the E,Z mixture. (Neat, NaCl plates, cm^{-1}) 2960 (m), 2930 (m), 2875 (w), 1633 (w), 1600 (m), 1455 (w), 1315 (s), 1300 (s), 1285 (s), 1145 (vs), 1085 (s), 965 (w), 810 (s), 785 (m), 653 (s).

M.S. for the E,Z mixture. Calculated for $C_{12}H_{16}O_2S$: 224.087106. Measured: 224.08724. Error: 0.6 ppm.

Elemental analysis for the E,Z mixture. Calculated for $C_{12}H_{16}O_2S$: C, 64.25; H, 64.25; H, 7.19; O, 14.26; S, 14.29. Found: C, 64.00; H, 7.22.

14. Photoreaction of 1-decenylmercury chloride with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.0 g, 4.7 mmol) and 1-decenylmercury chloride (1.0 g, 2.67 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml), DMSO (20 ml), and water (10 ml). The solution was irradiated for 15 hours with a sunlamp during which time mercury metal precipitated. The usual workup provided 0.6 g of yellow oil containing a 74% crude yield (by ^{1}H N.M.R.) of the expected 1-decenyl p-tolyl sulfone. A Kugelrohr distillation (150-155°C/0.15 torr) afforded 0.43 g (55% overall yield) of the pure sulfone. The E and Z isomers were barely separable by G.L.C. (5' x 1/8"; 5% OV-3; 200°C). The supposed Z isomer eluted first. The ratio (by G.L.C. integration) of E:Z was 8.9:1.1. Both isomers exhibited parent ions at m/e = 294 and nearly identical fragmentation patterns in the G.C.M.S.

^{1}H N.M.R. for the E,Z mixture ($CDCl_3$, δ) 4H (m), 7.2-7.8, 2H (complex) 6.1-7.1, 2H (m) 2.0-2.4, 3H (s) 2.4, 15H (m) 0.7-1.7.

I.R. for the E,Z mixture (neat, NaCl plates, cm^{-1}) 2940 (vs), 2860 (s), 1600 (w), 1340 (s), 1150 (vs), 1090 (s), 970 (w), 810 (m), 660 (s).

M.S. for the E,Z mixture. Calculated for $C_{17}H_{26}O_2S$: 294.16536. Measured: 294.16560. Error: 0.8 ppm.

Elemental analysis. Calculated for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90; O, 10.87; S, 10.89. Found: C, 69.00; H, 9.07.

15. Photoreaction of 1-methyl-1-propenylmercury bromide with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.3 g, 6.1 mmol) and 1-methyl-1-propenylmercury bromide (1.0 g, 3.0 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml), DMSO (10 ml), and water (5 ml). The solution was irradiated for 24 hours with a sunlamp during which time mercury metal precipitated. The usual workup afforded 0.45 g of colorless oil found to contain a 72% yield of 1-methyl-1-propenyl p-tolyl sulfone by ^{1}H N.M.R. Kugelrohr distillation (115°C/0.15 torr) afforded the pure sulfone (stereochemistry not determined) in 67% overall yield. This sulfone has been reported in the literature [169].

^{1}H N.M.R. ($CDCl_3$, δ) 4H (m) 7.2-7.75, 9H (m) 6.7-7.1, 3H (s) 2.4, 6H (m) 1.7-2.1.

I.R. (neat, NaCl plates, cm^{-1}) 2920 (w), 1650 (m), 1600 (m), 1130 (vs), 1085 (s), 815 (s), 710 (vs), 700 (s), 650 (s).

M.S. Calculated for $C_{11}H_{14}O_2S$: 210.07146. Measured: 210.07126. Error: -0.9 ppm.

16. Photoreaction of 2,2-diphenylethenylmercury bromide with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.3 g, 6 mmol) and 2,2-diphenylethenylmercury bromide (1.4 g, 3.05 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml) and t-butyl alcohol (25 ml). The solution was irradiated for 42 hours with a sunlamp positioned 6 inches from the Pyrex reaction vessel during which time mercury metal precipitated. The usual workup afforded 0.8 g of a light yellow solid determined to be nearly pure 2,2-diphenylethenyl p-tolyl sulfone by ^{1}H N.M.R. The pure sulfone was obtained in 61% overall yield (0.61 g of long white needles) by recrystallization from ether/hexane (m.p. 101.5-103°C).

^{1}H N.M.R. ($CDCl_3$, δ) 14H (m) 7.0-7.6, 1H (s) 6.97, 3H (s) 2.38.

I.R. (KBr pellet, cm^{-1}) 3020 (w), 1610 (w), 1600 (w), 1580 (w), 1495 (m), 1445 (m), 1300 (s), 1140 (s), 1090 (s), 910 (m), 850 (m), 840 (m), 810 (m), 800 (m), 790 (w), 770 (m), 760 (s), 730 (s), 700 (s), 655 (m), 580 (m), 540 (s).

M.S. Calculated for $C_{21}H_{18}O_2S$: 334.10275. Measured: 334.10407. Error: 3.9 ppm.

Elemental analysis. Calculated for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42; O, 9.57; S, 9.59. Found: C, 75.47; H, 5.48.

17. Photoreaction of (E)-2-phenyl-1-ethenylmercury chloride with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.0 g, 4.7 mmol) and (E)-2-phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) were dissolved in a nitrogen-purged mixture containing DMSO (30 ml) and t-butyl alcohol (25 ml). The solution was irradiated for 19 hours with a sunlamp during which time mercury metal precipitated. The usual workup afforded 0.59 g of a light yellow solid determined to be nearly pure (E)-2-phenyl-1-ethenyl p-tolyl sulfone (81% yield) by ^{1}H N.M.R. This compound has been reported in the literature [97].

^{1}H N.M.R. ($CDCl_3$, δ) 9H (m) 7.2-7.8, 1H (d, partially obscured) 7.63 (J_H = 15 Hz), 1H (d) 6.82 (J_H = 15 Hz), 3H (s) 2.39.

M.S. Calculated for $C_{15}H_{14}O_2S$: 258.07145. Measured: 248.07139. Error: -0.24 ppm.

18. Photoreaction of 1-methyl-2,2-diphenylethenylmercury bromide with sodium p-toluenesulfinate

Sodium *p*-toluenesulfinate dihydrate (2.0 g, 11 mmol) and 1-methyl-2,2-diphenylethenylmercury bromide (1.5 g, 3.17 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml), *t*-butyl alcohol (20 ml), and water (2 ml) in a Pyrex reaction vessel. Only a trace of mercury metal precipitated when the solution was irradiated 12 hours with a sunlamp. The reaction occurred faster when the solution was irradiated in a Rayonet RPR-100 reactor equipped with sixteen "350 nm" bulbs. After 69 hours in the Rayonet reactor, the solution was worked-up in the usual manner to afford 0.83 g of a light yellow solid found to contain 1-methyl-2,2-diphenylethenyl *p*-tolyl sulfone (66% yield) and 1,1-diphenylpropene (14% yield) by quantitative ^{1}H N.M.R. The 1,1-diphenylpropene was removed by evaporative distillation (120°C/ 0.1 torr). Recrystallization of the residue from ether/hexane gave the pure sulfone in 31% overall yield (m.p. 158.5-160°C).

^{1}H N.M.R. ($CDCl_3$, δ) 14H (m) 6.9-7.6, 3H (s) 2.33, 3H (s) 2.13.

I.R. (KBr pellet, cm^{-1}) 3055 (w), 1627 (m), 1600 (s), 1490 (s), 1445 (s), 1312 (vs), 1305 (vs), 1290 (s), 1187 (m), 1155 (vs), 1120 (s), 1077 (vs), 1004 (s), 930 (m), 917 (m), 842 (w), 813 (vs), 800 (s), 789 (vs), 750 (vs), 700 (vs), 695 (vs), 688 (s), 678 (vs), 645 (s), 578 (vs), 545 (vs), 512 (s), 480 (m), 466 (m).

M.S. Calculated for $C_{22}H_{22}O_2S$: 348.11841. Measured: 348.11877. Error: 1.0 ppm.

Elemental analysis. Calculated for $C_{22}H_{22}O_2S$: C, 75.83; H, 5.78; O, 9.18; S, 9.20. Found: C, 75.66; H, 5.90.

19. Photoreaction of 1-(cyclohexylmethyl)-1-ethenylmercury bromide

Sodium p-toluenesulfinate dihydrate (1.5 g, 8.4 mmol) and 1-(cyclohexylmethyl)-1-ethenylmercury bromide (1.5 g, 3.7 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml), t-butyl alcohol (25 ml), and water (5 ml) in a Pyrex reaction vessel. Sunlamp irradiation induced no observable reaction, but irradiation in a Rayonet RPR-100 reactor equipped with sixteen "350 nm" bulbs resulted in the slow precipitation of mercury metal. The irradiation was stopped after 51 hours and the solution worked-up in the usual manner to afford 0.27 g of orange oil. The maximum possible yield of the expected 1-(cyclohexylmethyl)-1-ethenyl p-tolyl sulfone by quantitative ^{1}H N.M.R. was 10% based on the integration of the methyl signal at 2.4 ppm.

20. Photoreaction of ethenylmercury chloride with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.5 g, 7 mmol) and ethenylmercury chloride (1.0 g, 3.8 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml) and t-butyl alcohol (25 ml) in a Pyrex reaction vessel. The solution was irradiated for 27 hours with a sunlamp during which time a little mercury metal precipitated and the solution turned brown. During the usual workup, a quantity of ether-insoluble brown resinous material was discarded. A yellow gum (0.43 g) was isolated but determined by ^{1}H N.M.R. to contain no ethenyl p-tolyl sulfone (no vinylic protons were observed).

21. Photoreactions of phenylmercury chloride and phenylmercury iodide with sodium p-toluenesulfinate

Sodium p-toluenesulfinate dihydrate (1.5 g, 7.0 mmol) and phenylmercury chloride (1.0 g, 3.2 mmol) were dissolved in 50 ml of nitrogen-purged DMSO and the solution was irradiated for 21 hours with a sunlamp positioned 3 inches from the Pyrex flask. No mercury metal precipitated.

When the same reaction was performed with phenylmercury iodide (1.5 g, 3.7 mmol), a 46 hour irradiation period followed by the usual workup afforded 0.45 g of yellow solid. ^{1}H N.M.R. and G.L.C. analysis (aided by comparison with the authentic compounds and the G.C.M.S.) determined the crude isolate to be a binary mixture containing the expected phenyl p-tolyl sulfone (40% yield) and di-p-tolyl sulfone (0.45 mmol, 12% yield based on the starting mercurial).

22. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with sodium cyclohexyl sulfinate

Sodium cyclohexyl sulfinate (1.1 g, 6.5 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture containing t-butyl alcohol (40 ml) and water (10 ml) in a Pyrex flask. The solution was irradiated for 18 hours with a 275 watt sunlamp positioned 4 inches from the reaction vessel during which time mercury metal precipitated. The usual workup afforded 0.49 g of a yellow oil determined to contain a 71% yield of nearly pure

(E)-3,3-dimethyl-1-butenyl cyclohexyl sulfone by ^1H N.M.R. The pure sulfone was obtained in 66% overall yield by a Kugelrohr distillation (105°C/0.15 torr). The colorless oil solidified upon prolonged storage.

^1H N.M.R. ($CDCl_3$, δ) 1H (d) 6.83 (J_H = 15.5 Hz), 1H (d) 6.07 (J_H = 15.5 Hz), 11H (complex) 0.9-3.0, 9H (s) 1.14.

I.R. (neat, NaCl plates, cm^{-1}) 2950 (vs), 2940 (vs), 2860 (s), 1640 (m), 1455 (s), 1370 (m), 1310 (vs), 1300 (vs), 1270 (vs), 1130 (vs), 1110 (s), 925 (m), 830 (s), 605 (s).

M.S. Calculated for $C_{12}H_{22}O_2S$: 230.13406. Measured: 230.13406. Error: 0.1 ppm.

Elemental analysis. Calculated for $C_{12}H_{22}O_2S$: C, 62.56; H, 9.63; O, 13.89; S, 13.92. Found: C, 62.78; H, 9.45.

23. Photoreaction of (E)-2-phenyl-1-ethenylmercury chloride with sodium cyclohexyl sulfinate

Sodium cyclohexyl sulfinate (0.7 g, 4.1 mmol) and (E)-2-phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml), t-butyl alcohol (25 ml), and water (1 ml). The solution was irradiated for 25 hours with a sunlamp during which time the precipitation of mercury metal was observed. The usual workup afforded 0.49 g of a yellow oil containing a 68% yield of the expected (E)-2-phenyl-1-ethenyl cyclohexyl sulfone (determined by quantitative ^1H N.M.R.). The pure sulfone was obtained by Kugelrohr distillation (150-155°C/0.15 torr) in 65% yield overall as a light yellow oil which solidified after prolonged storage.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.2-7.6, 1H (d, partially obscured) 7.60 (J_H = 15.5 Hz), 1H (d) 6.80 (J_H = 15.5 Hz), 11H (complex) 1.0-3.2.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (w), 2940 (s), 2860 (m), 1620 (m), 1450 (m), 1300 (s), 1130 (s).

M.S. Calculated for $C_{14}H_{18}O_2S$: 250.102757. Measured: 250.102738. Error: -0.1 ppm.

Elemental analysis. Calculated for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; O, 12.78; S, 12.81. Found: C, 67.28; H, 7.22.

24. Photoreaction of (E)-2-phenyl-1-ethenylmercury chloride with sodium t-butyl sulfinate

Sodium t-butyl sulfinate (1.0 g, 6.9 mmol) and (E)-2-phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml) and t-butyl alcohol (25 ml). The solution was irradiated for 24 hours with a sunlamp during which time mercury metal precipitated. The usual workup afforded 0.4 g of yellow oil determined to contain a 56% yield of the expected (E)-2-phenyl-1-ethenyl t-butyl sulfone by quantitative ^{1}H N.M.R. A Kugelrohr distillation (120°C/0.1 torr) gave the pure sulfone as a colorless oil which solidified after prolonged storage.

^{1}H N.M.R. ($CDCl_3$, δ) 5H (m) 7.1-7.6, 1H (d, partially obscured) 7.6 (J_H = 16 Hz), 1H (d) 6.8 (J_H = 16 Hz), 9H (s) 1.40.

I.R. (neat, NaCl plates, cm^{-1}) 1610 (m), 1290 (s), 1280 (s), 1110 (vs), 980 (s), 850 (m), 825 (m), 725 (s), 685 (m), 650 (m), 525 (m), 475 (m).

M.S. Calculated for $C_{12}H_{16}O_2S$: 224.08711. Measured: 224.08715. Error: 0.2 ppm.

Elemental analysis. Calculated for $C_{12}H_{16}O_2S$. C, 64.25; H, 7.19; O, 14.26; S, 14.29. Found: C, 64.56; H, 7.55.

25. Photoreaction of (*E*)-3,3-dimethyl-1-butenylmercury chloride with sodium *n*-propyl sulfinate

Sodium *n*-propyl sulfinate (0.8 g, 6.2 mmol) and (*E*)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture of *t*-butyl alcohol (40 ml), water (10 ml), and DMSO (10 ml). The solution was irradiated for 30 hours during which time mercury metal precipitated. Thus, usual workup afforded 0.53 g of colorless oil determined to contain a 75% yield of the expected (*E*)-3,3-dimethyl-1-butenyl *n*-propyl sulfone by quantitative ^{1}H N.M.R. A Kugelrohr distillation (80-85°C/0.08 torr) gave the pure sulfone in 69% overall yield. This sulfone has previously been reported in the literature [110].

^{1}H N.M.R. ($CDCl_3$, δ) 1H (d) 6.88 (J_H = 15.5 Hz), 1H (d) 6.23 (J_H = 15.5 Hz), 2H (m) 2.85-3.12, 2H (m) 1.55-1.95, 12H (broad, coincident *t*-butyl and terminal methyl signals).

I.R. (neat, NaCl plates, cm^{-1}) 3060 (m), 2960 (s), 2878 (m), 1637 (m), 1470 (m), 1375 (m), 1280 (3 peaks, vs), 1250 (s), 1130 (vs), 1100 (w), 1062 (m), 990 (m), 872 (m), 830 (m), 810 (m), 780 (m).

M.S. Calculated for $C_9H_{18}O_2S$: 190.10276. Measured: 190.10252. Error: -1.2 ppm.

26. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with sodium trichloromethanesulfinate

Sodium trichloromethanesulfinate (1.0 g, 4.9 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in 20 ml of dry, nitrogen-purged DMSO in a Pyrex reaction vessel. A 20 hour irradiation period with a sunlamp caused no change in the appearance of the solution and no mercury metal precipitated. The solution was subsequently irradiated for 23 hours in a Rayonet RPR-100 reactor (thirteen "350 nm" bulbs), but still no mercury precipitated.

27. Competitive photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with a mixture of sodium benzenesulfinate and sodium trichloromethanesulfinate

Sodium trichloromethanesulfinate (0.8 g, 3.9 mmol), sodium benzenesulfinate (0.7 g, 4.3 mmol), and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture of t-butyl alcohol (40 ml) and water (10 ml) in a Pyrex flask. The solution was irradiated for 23 hours with a sunlamp during which time mercury metal precipitated. The usual workup afforded an 85% yield of (E)-3,3-dimethyl-1-butenyl phenyl sulfone, a trace of the starting mercurial, and absolutely no 3,3-dimethyl-1-butenyl trichloromethyl sulfone or 1,1,1-trichloro-4,4-dimethyl-2-pentene (determined by quantitative ^{1}H N.M.R.).

28. Photoreaction of (*E*)-3,3-dimethyl-1-butenylmercury chloride with sodium *α*-toluenesulfinate

Freshly prepared sodium *α*-toluenesulfinate (1.78 g, 10 mmol) and (*E*)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in a nitrogen-purged mixture containing *t*-butyl alcohol (40 ml) and water (10 ml) in a Pyrex reaction vessel. The solution was irradiated for 19 hours with a sunlamp. No mercury metal was observed. The solution was poured into brine. Extraction with ethyl ether recovered 0.78 g of the starting mercurial (>98% pure) and no coupled product.

29. Effect of darkness on the reaction of (*E*)-2-phenyl-1-ethenylmercury chloride with sodium *p*-toluenesulfinate

Sodium *p*-toluenesulfinate dihydrate (1.0 g, 4.7 mmol) and (*E*)-2-phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml) and *t*-butyl alcohol (25 ml) in a flask wrapped with aluminum foil to exclude light. The solution was irradiated for 16 hours at 23°C. No mercury metal was observed upon removal of the foil and the usual workup afforded none of the (*E*)-2-phenyl-1-ethenyl *p*-tolyl sulfone.

30. Effect of di-t-butyl nitroxide on the photoreaction between (*E*)-2-phenyl-1-ethenylmercury chloride and sodium *p*-toluenesulfinate

Sodium *p*-toluenesulfinate dihydrate (1.0 g, 4.7 mmol), (*E*)-2-phenyl-1-ethenylmercury chloride (1.0 g, 2.95 mmol), and di-*t*-butyl nitroxide (21 mg, 0.15 mmol) were dissolved in a nitrogen-purged mixture of DMSO (30 ml) and t-butyl alcohol (25 ml) in a Pyrex flask immersed in a 25°C water bath. The solution was irradiated for 4.5 hours with a 275 watt sunlamp positioned 10 inches from the reaction vessel. No mercury metal was observed. The usual workup afforded absolutely no (E)-2-phenyl-1-ethenyl p-tolyl sulfone.

A control reaction (performed identically except without added di-t-butyl nitroxide) afforded a 38% yield of the sulfone after the same irradiation period.

31. Nature of the reacting mercury species: the photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with sodium benzenesulfinate

Sodium benzenesulfinate (20 mg, 0.12 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (33 mg, 0.1 mmol) in 0.5 ml of d_6-DMSO gave the ^{1}H N.M.R. spectrum corresponding to the sum of the spectra of the individual compounds. That is, the vinylmercury halide was not detectably symmetrized. No spectral change occurred when the solution was warmed in an oil bath to 100°C for 30 minutes. Two minutes of sunlamp irradiation, however, induced the precipitation of metallic mercury and the ^{1}H N.M.R. spectrum revealed a mixture of starting materials and (E)-3,3-dimethyl-1-butenyl phenyl sulfone. Continued sunlamp irradiation resulted in the apparently quantitative conversion of the starting mercurial into vinyl sulfone.

Sodium benzenesulfinate (1.0 g, 6 1 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmole) were dissolved in a mixture of t-butyl alcohol (40 ml) and water (10 ml). After 10 minutes of stirring, the solution was concentrated to a slurry under vacuum and the residue taken up in brine layered with ethyl ether. The ethereal extract was concentrated to afford 0.95 g (95% recovery) of the starting (E)-3,3-dimethyl-1-butenylmercury chloride.

32. Attempted coupling of phenyl iodide with sodium p-toluenesulfinate

Phenyl iodide (2.2 g, 11 mmol) and sodium p-toluenesulfinate dihydrate (3.0 g, 14 mmol) were dissolved in 50 ml of nitrogen-purged DMSO in a Pyrex flask. The solution was irradiated at ambient temperature for 12.5 hours in a Rayonet RPR-100 reactor equipped with sixteen "350 nm bulbs". The solution was then poured into 300 ml brine and the organic products were extracted with ethyl ether. The ethereal extract afforded only recovered phenyl iodide. No phenyl p-tolyl sulfone was detected by ^{1}H N.M.R. When the reaction was repeated and a 22 hour irradiation period employed, a trace of the expected sulfone ($\leq$ 4% yield) was detected by quantitative ^{1}H N.M.R. and G.L.C. The identity of the sulfone was established by comparison with the authentic compound.

Anhydrous sodium p-toluenesulfinate (7.1 g, 40 mmol, prepared by warming the dihydrate salt to 140°C for 4 hours at 0.005 torr) was dissolved in 150 ml of liquid qmmonia. Phenyl iodide (4.1 g, 20 mmol) was added and the ammonia allowed to reflux. Potassium metal (1.0 g, 25 mmol) was added to the solution in small pieces over a period of 45 minutes. Ammonium chloride (2.0 g) was then added and the solvent allowed to evaporate. The residue was taken up in brine layered with ethyl ether. The ethereal extract gave 1.0 g of a brown liquid containing no phenyl p-tolyl sulfone.

33. Photoreaction of (E)-3,3-dimethyl-1-butenylmercury chloride with n-butyl phenylphosphonite ion

Solid (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) was added to a solution containing n-butyl phenylphosphonite (1.18 g, 5.9 mmol) and potassium t-butoxide (0.6 g, 5.3 mmol) in 30 ml of dry, nitrogen-purged DMSO. The solution was irradiated for 3.5 hours with a sunlamp positioned 3 inches from the Pyrex reaction vessel during which time mercury metal precipitated. The solution was decanted from the mercury beads into brine and the product extracted from diethyl ether. The extract was washed repeatedly with water, dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 0.75 g of colorless oil found to contain an 84% yield of n-butyl (E)-3,3-dimethyl-1-butenyl phenylphosphinate by quantitative ^1H N.M.R. The major impurity was a little n-butyl phenylphosphonite identified by G.L.C. (5' x 1/8"; 5% OV-3; 200°C).

^1H N.M.R. ($CDCl_3$, δ) 5H (m) 7.45-8.03; 1H (doublet of doublets) 6.86 (J_H = 17 Hz, J_P = 21 Hz), 1H (doublet of doublets) 5.83 (J_H = 17 Hz, J_P = 22.5 Hz), 2H (m) 3.78-4.23, 7H (m) 0.75-1.84, 9H (s) 1.05.

I.R. (neat, NaCl plates, cm^{-1}) 3060 (w), 2960 (vs), 2870 (m), 1620 (m), 1470 (m), 1440 (m), 1370 (m), 1225 (vs), 1125 (s), 1060 (m), 1025 (s), 990 (s), 970 (s), 890 (w), 840 (m), 750 (m), 695 (m).

M.S. Calculated for $C_{16}H_{25}O_2P$: 280.15922. Measured: 280.15990. Error: 2.4 ppm.

34. Photoreaction of nitrite ion with (E)-3,3-dimethyl-1-butenylmercury chloride

Sodium nitrite (0.5 g, 7.2 mmol) and (E)-3,3-dimethyl-1-butenylmercury chloride (1.0 g, 3.1 mmol) were dissolved in 25 ml of dry, nitrogen-purged DMSO. The solution was irradiated with a 275 watt sunlamp positioned 4 inches from the Pyrex reaction vessel for 68 hours during which time mercury metal slowly precipitated. The solution was then poured into brine and the organic products extracted with ethyl ether. The ethereal extract afforded 0.48 g of yellow oil. Quantitative ^{1}H N.M.R. determined the isolate to be a binary mixture of (presumed) (E)-3,3-dimethyl-1-nitro-1-butene (56% yield) and bis[(E)-3,3-dimethyl-1-butenyl]mercury (36% yield). The G.C.M.S. confirmed the bis[vinyl]-mercury compound (m/e = 366 observed for parent ion) and was consistent with the nitro olefin (m/e = 83 was observed for the highest mass fragment which corresponds to the loss of NO_2 from the molecular ion).

^{1}H N.M.R. of the nitro olefin contaminated with bis[(E)-3,3-dimethyl-1-butenyl]mercury ($CDCl_3$, δ) 1H (d) 6.92 (J_H = 15 Hz), 1H (d) 6.28 (J_H = 15 Hz), 9H (s) 1.13.

Notably, the G.C.M.S. is not consistent with the presence of an organic nitrite ester (as opposed to an organic nitro compound) as these compounds readily lose NO from the parent ion and thus exhibit a pronounced P-30 peak [170].

No reaction occurred when the reaction was performed in DMSO/water. Also, no reaction occurred when sunlamp irradiation was not employed (i.e., the reaction solution was stirred in darkness at 50°C). ^{1}H N.M.R.

experiments showed that the vinylmercury halide was not symmetrized by nitrite ion prior to irradiation. Similarly, (E)-3,3-dimethyl-1-butenylmercury chloride was recovered from a DMSO solution containing sodium in 90% recovered yield by pouring the solution into brine and extraction with ethyl ether.

VII. CONCLUSION TO PART II

Vinylmercury mercaptides are sensitive to light-promoted elimination of mercury metal to form vinyl sulfides in high yield. These are radical chain reactions established to proceed via displacement of a mercury(I) mercaptide radical from the vinylmercury mercaptide by a thiyl radical. The mercury(I) mercaptide radical undergoes facile thermal dissociation to give mercury metal and a chain-carrying thiyl radical.

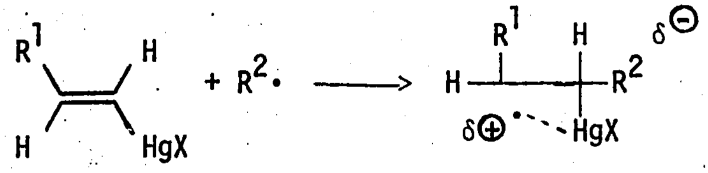
Vinylmercury halides undergo photo-initiated reactions with disulfides, phenyl diselenide, phenyl ditelluride, arylsulfonyl chlorides, and organosulfinate ions to form vinyl sulfides, selenides, tellurides, and sulfones along with mercury(II) salts or mercury metal. These are radical chain reactions, the unifying mechanistic feature being the displacement of a halomercury(I) radical from the vinylmercury halide by a thiyl, selenyl, telluryl, or sulfonyl radical. The halomercury(I) radical reacts by abstracting a thiyl, selenyl, or telluryl moiety (from disulfides phenyl diselenide, or phenyl ditelluride), by abstraction of a chlorine atom (from arylsulfonyl chlorides), or by oxidizing an organosulfinate ion. In each case, the chain-carrying thiyl, selenyl, telluryl, or sulfonyl radical is regenerated.

Vinylmercury halides and diethyl phosphite ion undergo a photo-induced radical chain coupling reaction to yield vinyl phosphonate esters, halide ion, and mercury metal. The reaction mechanism is presumed to be similar to that detailed for the coupling reaction of vinylmercury halides and organosulfinate ions, but is complicated by the observation that diethyl phosphite ion promotes the disproportionation of vinylmercury halides to form bis[vinyl]mercury compounds and the mercuric halide salt.

Bis[vinyl]mercury compounds react with phenyl disulfide by a light-promoted radical chain process to give two equivalents of the vinyl phenyl sulfide and mercury metal. The mechanism has been shown to consist of two reaction chains. In the first chain, phenyl thiyl radical displaces a vinylmercury(I) radical from the bis[vinyl]mercury compound. The vinylmercury(I) radical then abstracts phenyl thiyl from phenyl disulfide to give a vinylmercury mercaptide and a phenylthiyl radical. The second chain consists of the light-promoted decomposition of the vinylmercury mercaptide to the vinyl sulfide and mercury metal.

All of the above reactions require the vinyl moiety and are not stereospecific. Consistent with these observations is the view that mercury(I) radicals are displaced from vinyl mercurials by the sequential addition of an incoming radical to the $\underline{\alpha}$-vinylic carbon to form a $\underline{\beta}$-mercury radical (possibly a mercury bridged species) followed by expulsion of a mercury(I) radical.

As a step towards predicting which radicals will react with vinyl mercurials by the addition-elimination mechanism, at least two characteristics concerning the radicals found to react thus far may be noted. First, all of the radicals are known or expected to be capable of reversible additions to carbon-carbon double bonds. Therefore, attack at the $\underline{\beta}$-vinylic carbon of a vinyl mercurial, which cannot lead to product formation, is reversible. Second, the radicals are all electrophilic (*i.e.*, capable of accepting negative charge). Attack at the *α*-vinylic carbon of a vinyl mercurial might proceed via a species having electronic character similar to a *β*-mercury carbenium ion (Eq. 64).



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