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FREE-RADICAL SUBSTITUTION REACTIONS INVOLVING ORGANOMERCURIALS

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Free-radical chain substitution reactions involving organomercurials

by

Preecha Ngoviwatchai

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TABLE OF CONTENTS

INTRODUCTION

This dissertation has been divided into four parts. Reactions of 1-alkenyl derivatives with organomercurials are presented in Part I; whereas, reaction of allyl and alkynyl derivatives with mercurials are in Part II. Part III considers the relative reactivities of alkenyl and alkynyl derivatives towards both cyclohexyl and thiophenoxy radicals. The determination of the initial kinetic chain length of the reactions of 2,2-diphenylethenyl iodide and tri-*n*-butyl-(*E*)-2-phenylethenylstannane with *t*-butylmercury chloride are also included in Part III. Part IV presents the reactions of mercuric carboxylates.

Following each presentation of results and discussion is a separate experimental section. Descriptions of techniques and sources of starting materials, however, are mentioned only once to avoid repetition. Most of the instrumentation employed is mentioned in the experimental section in Part I.

PART I. FREE RADICAL CHAIN REACTIONS OF VINYL DERIVATIVES WITH ORGANOMERCURIALS

I. INTRODUCTION TO ORGANOMERCURIALS

Organomercurials have been known for over a century, but their organic synthetic potential has only been appreciated in recent years [1]. The first organomercury compound, methylmercuric iodide (CH_3HgI), was reported by Edward Frankland in 1852 [2]. Since that time, many organomercurials have been prepared. Today hundreds, perhaps thousands, of these compounds are known.

The slow development of the chemistry of organomercurials in the early years may be due to their toxicity, especially of the highly volatile dialkylorganomercurials (R_2Hg). However, the vast majority of organomercury compounds are high melting crystalline solids. They are generally easily-handled, stable to elevated temperatures, air, dilute acids and bases, and protic solvents. These compounds are easily obtained by a number of different synthetic procedures [1,3].

The most commonly used organomercurials are of the type RHgX which are less volatile than the diorganomercury compounds, R_2Hg. A large number of alkyl-, alkenyl-, alkynyl-, and carboalkoxymercurials are also known.

Organomercury compounds undergo a variety of reactions. They can undergo transmetalation reaction with many metals. This is one of the most important applications of organomercurials that makes organomercury compounds valuable intermediates in organic synthesis [4,5].

The direct use of organomercury compounds as synthetic reagents in organic synthesis is limited because they are unreactive towards many important organic functional groups. However, the oxymercuration-

demercuration of olefins is very well-known and is very valuable in organic synthesis [6,7]. This reaction has been extended to acetylenes [8]. A number of heterocyclic compounds have been synthesized by solvomercuration of aryl acetylenes with mercuric acetate [9].

Electrophilic substitution reactions of organomercurials have been well-studied [10-13]. On the contrary, homolytic substitution reactions of these compounds have been studied to a lesser extent. The cleavage of alkylmercury halides by iodine and bromine in a non-polar solvent has been recognized to involve a free radical mechanism [14,15]. Dialkylmercurials, RHgR', have also been found to react with polyhalomethanes by radical process [16-20].

In recent years, radical reactions have been increasingly employed in organic synthesis [21,22]. Many new methods for the generation of radicals have been developed. Organomercurials, particularly of the type RHgX, have been found to undergo homolytic substitution reactions to give the corresponding radical, R•. The reduction of alkylmercury halides by metal hydrides has been proved to be a radical reaction [23-26]. Alkylmercury hydride, RHgH, is proposed to be involved in this reaction. The mechanism is outlined in Scheme 1.

The alkyl radicals generated by this method can be trapped by electron deficient olefins [27]. Giese and co-workers have extensively studied the formation of carbon-carbon bonds by addition of free radicals, generated by alkylmercury halides and sodium borohydride, to electron poor alkenes [28-31].

Recently, Russell et al. have reported the reaction of alkylmercury

halides with various anions which proceeds by an $S_{RN}1$ process as shown

Scheme 1

$$RHgX \xrightarrow{BH_4^-} RHgH$$

$$RHgH \longrightarrow R\bullet + Hg^0 + H\bullet$$

$$R\bullet + RHgH \longrightarrow RH + RHg\bullet$$

$$RHg\bullet \longrightarrow R\bullet + Hg^0$$

$$RHgX \xrightarrow{BH_4^-} RH + Hg^0 + X^-$$

in Scheme 2 [32,33]. The reduction of alkylmercury halides by $LiAlH_4$

Scheme 2

$$R\bullet + A^- \longrightarrow RA^{\bullet-}$$

$$RA^{\bullet-} + RHgX \longrightarrow RA + RHgX^{\bullet-}$$

$$RHgX^{\bullet-} \longrightarrow R\bullet + Hg^0 + X^-$$

$$RHgX + A^- \longrightarrow RA + Hg^0 + X^-$$

has also been suggested to proceed by an electron transfer chain mechanism of the $S_{RN}1$-type [34]. Alkylmercurials can react with phenyl disulfide, phenyl diselenide, phenyl ditelluride, arylsulfonyl

phenyl selenide, and benzenesulfonyl chloride (Eq. 1) by the radical chain mechanism as shown in Scheme 3 [35].

$$RHgX + Q\text{-}Y \xrightarrow{h\nu} RY + QHgX \qquad (1)$$

Q = PhS, PhSe, PhTe, $PhSO_2$, $p\text{-}CH_3C_6H_4SO_2$, CCl_3

Y = PhS, PhSe, PhTe, Cl, Br

Scheme 3

$$RHgX + Q\bullet \longrightarrow R\bullet + QHgX$$

$$R\bullet + Q\text{-}Y \longrightarrow RY + Q\bullet$$

1-Alkenylmercury halides undergo photostimulated reactions with sulfinate anions, alkyl or aryl disulfide, phenyl diselenide, and phenyl ditelluride to give substitution products [36,37]. Unlike the reactions of alkylmercury halides, these reactions do not involve vinyl radicals but proceed by a free radical addition elimination mechanism which will be discussed in more detail in the next section.

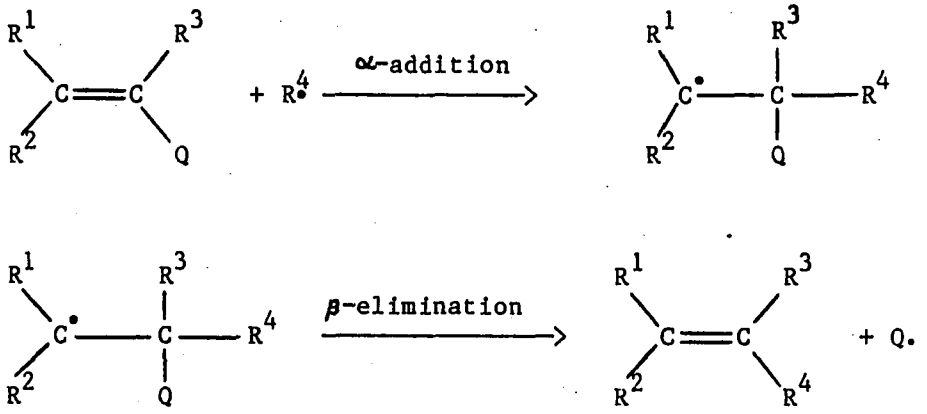
It is evident that organomercurials have been receiving more attention in recent years, particularly in the field of radical chemistry. Some properties of radical reactions which are important in synthesis have been reviewed [38]. The use of organomercury compounds in organic synthesis has interested many synthetic chemists. The synthetic potential and application of organomercurials in organic synthesis will undoubtedly increase in the near future.

II. SUBSTITUTION REACTIONS OF ALKENYL DERIVATIVES

A. Introduction

The addition of a radical to an unsaturated system is a well-known reaction [39]. When a radical adds to a multiple bond, the resulting new radical can undergo many different reactions depending on the type of the radical and the conditions. One of the reactions is a β-elimination which will form an unsaturated product. This reaction would be expected to occur if the radical has a good potential leaving group at the β-position. The addition-elimination reaction for an alkenyl system is outlined in Scheme 4.

Scheme 4



Q = good leaving group

Homolytic substitution reactions of alkenyl derivatives are known and several examples have appeared in the literature. It has been reported that β-styrylmercury halides undergo electrophilic

substitution reactions with bromine and iodine in a polar solvent to give β-bromostyrene and β-iodostyrene with retention of configuration [40,41]. In contrast, loss of stereochemistry was observed for the reactions in non-polar solvents. This result has been interpreted as an indication that the reactions in non-polar solvents involved radical intermediates.

Russian workers have reported the isomerization of alkenyltin derivatives under radical conditions [42]. They studied alkenyltin compounds of the type $R_3SnCH=CHR'$ (R = Me, Et; R' = Me, Ph, COOMe, CN). The cis isomers were converted to the trans isomers in the presence of a trialkylstannane and an initiator for radical processes, such as azobisisobutyronitrile (AIBN) or UV radiation. The isomerization also occurred thermally above 100 °C [43]. The mechanism involves the attack of the stannyl radical at the α-position, followed by rotation of the carbon—carbon single bond and subsequent β-elimination to give the trans isomer (Eq. 2).

$$\underset{\text{cis}}{R_3SnCH=CHR'} + R_3Sn\bullet \rightleftharpoons \begin{matrix} R_3Sn \\ | \\ CH-\!\!-\dot{C}HR' \\ | \\ R_3Sn \end{matrix} \rightleftharpoons \underset{\text{trans}}{R_3SnCH=CHR'} + R_3Rn\bullet \qquad (2)$$

Thiyl radicals have been reported to add to vinyltin derivatives [44]. The addition occurred at both α- and β-positions depending on the sizes of the alkyl groups attached to Sn and S and also depending on the electrophilicity of the thiyl radical. With large alkyl groups,

the thiyl radical can only attack the double bond at the β-position because of steric hindrance. Thus, the reaction of tri-n-butylvinylstannane with isopropylmercaptan gave only 2-(tri-n-butylstannyl)ethyl isopropyl sulfide (Eq. 3).

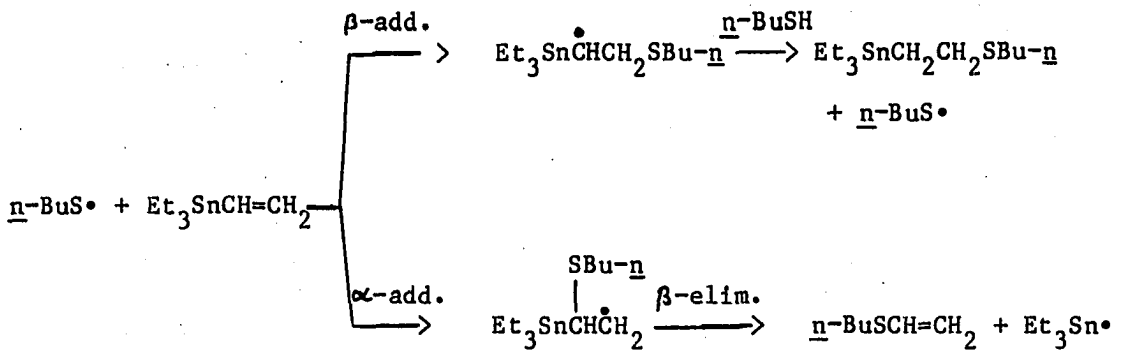
$$\underline{n}\text{-}Bu_3SnCH{=}CH_2 + \underline{i}\text{-}PrSH \longrightarrow \underline{n}\text{-}Bu_3SnCH_2CH_2S\underline{i}\text{-}Pr \qquad (3)$$

With smaller alkyl groups and higher electrophilicity of the thiyl radical, attack at the α-position would also be expected to occur. Thus, the reaction of triethylvinylstannane with n-butylmercaptan under UV irradiation gave bis(triethylstannyl)ethane and bis(n-butylthio)ethane as byproducts (Eq. 4). These byproducts resulted

$$Et_3SnCH{=}CH_2 + \underline{n}\text{-}BuSH \longrightarrow Et_3SnCH_2CH_2S\underline{n}\text{-}Bu + Et_3SnCH_2CH_2SnEt_3 + \underline{n}\text{-}BuSCH_2CH_2S\underline{n}\text{-}Bu \qquad (4)$$

from α-addition of the thiyl radical to triethylvinylstannane and β-decomposition of the resulting radical to give n-butyl vinyl sulfide and triethylstannyl radical (Scheme 5). The triethylstannyl radical then added to triethylvinylstannane with subsequence abstraction of the hydrogen atom from the mercaptan to give bis(triethylstannyl)ethane. The bis(n-butylthio)ethane was formed from the addition of the thiyl radical to n-butyl vinyl sulfide followed by hydrogen atom abstraction. The formation of the stannyl radical intermediate was indicated by the formation of benzene and triethyltin bromide when bromobenzene was the reaction medium (Eq. 5) [45].

Scheme 5



$$Et_3Sn\bullet + Et_3SnCH{=}CH_2 \longrightarrow Et_3SnCHCH_2SnEt_3 \xrightarrow{\underline{n}\text{-BuSH}} Et_3SnCH_2CH_2SnEt_3 + \underline{n}\text{-BuS}\bullet$$

$$\underline{n}\text{-BuS}\bullet + BuSCH{=}CH_2 \longrightarrow \underline{n}\text{-BuSCHCH}_2\text{SBu-}\underline{n} \xrightarrow{\underline{n}\text{-BuSH}} \underline{n}\text{-BuSCH}_2CH_2\text{SBu-}\underline{n} + \underline{n}\text{-BuS}\bullet$$

$$Et_3Sn\bullet + PhBr \xrightarrow{\text{H donor}} Et_3SnBr + PhH \qquad (5)$$

Miyamoto et al. have reported the reaction of styryl sulfoxides and sulfones with organoboranes which gave β-alkylated styrenes in preparative yields (Eq. 6) [46].

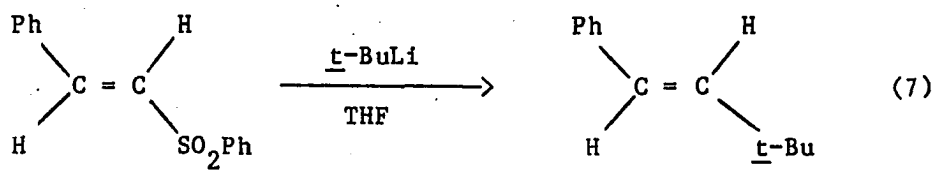
(6)

n = 1,2

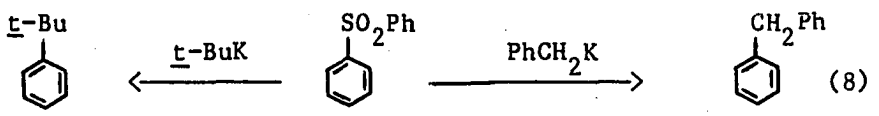
The authors suggested that the reaction involved vinyl radical intermediates, but it is more likely to involve the addition-elimination

mechanism as outlined in Scheme 4.

The substitution reactions of β-styryl sulfone with t-butyllithium and diphenylsulfone with t-butylpotassium or benzylpotassium were reported to involve alkyl radicals formed by an electron transfer process (Eqs. 7,8) [47].

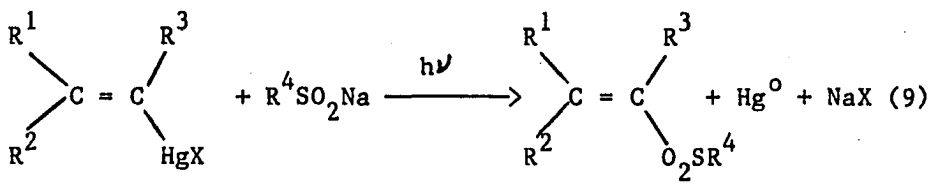


(7)



(8)

Recently, Hershberger and Russell have reported that α,β-unsaturated sulfones can be conveniently prepared by a photostimulated coupling of 1-alkenylmercury halides with sodium salts of alkane- or arenesulfinic acids (Eq. 9) [36].



(9)

1-Alkenylmercury halides have also been reported to readily undergo photostimulated free-radical chain substitution reactions with a variety of reagents (Eqs. 10-12) [37]. Scheme 6 outlines the mechanism of

$$RCH{=}CHHgX + R'Y{-}YR' \xrightarrow{h\nu} RCH{=}CHYR' + XHgYR' \qquad (10)$$

Y = S, R′ = alkyl or aryl;

Y = Se, Te, R^1 = phenyl

$$RCH{=}CHHgX + Z{-}Q \xrightarrow{h\nu} RCH{=}CHZ + XHgQ \qquad (11)$$

Z = $PhSO_2$, Q = Cl; Z = i-Pr, Q = I

$$RCH{=}CHHgX + A^- \xrightarrow{h\nu} RCH{=}CHA + Hg^o + X^- \qquad (12)$$

A^- = $(RO)_2PO^-$, $PhP(OBu)O^-$, $AlkSO_2^-$, $ArSO_2^-$, $AlkS^-$, ArS^-

these reactions. The mechanism involves attack of the radical at the

Scheme 6

$$RCH{=}CHHgX + R'Y\bullet(Z\bullet \text{ or } A\bullet) \longrightarrow R\dot{C}H{-}\overset{\displaystyle YR'(Z \text{ or } A)}{\overset{|}{C}}HHgX$$

$$R\dot{C}H{-}\overset{\displaystyle YR'(Z \text{ or } A)}{\overset{|}{C}}HHgX \longrightarrow RCH{=}CHYR'(Z \text{ or } A) + HgX$$

$$HgX + R'Y{-}YR' \longrightarrow XHgYR' + R'Y\bullet$$

or $HgX + Z{-}Q \longrightarrow XHgQ + Z\bullet$

or $HgX + A^- \longrightarrow Hg^o + X^- + A\bullet$

α-position followed by β-elimination to give the products. Besides the vinylmercurials, tri-n-butylvinylstannane was also mentioned as undergoing a similar reaction with phenyl disulfide to give phenyl

vinyl sulfide in excellent yield [37].

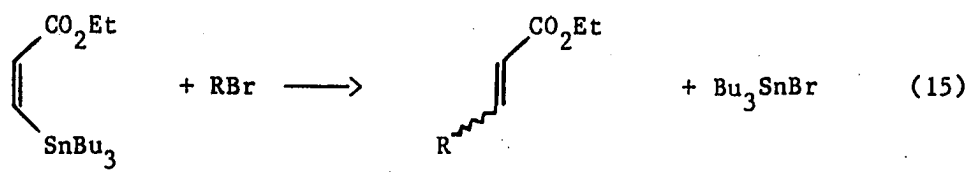
Vinyl organostannanes have been reported to react with acid chlorides and anhydrides in the presence of aluminum chloride to give α,β-unsaturated ketones (Eq. 13) [48]. These alkenylstannanes

$$Bu_3SnCH{=}CR^1R^2 + R^3COCl \xrightarrow[CH_2Cl_2,\ -10\ ^\circ C]{AlCl_3} R^3COCH{=}CR^1R^2 + Bu_3SnCl \qquad (13)$$

failed to give substitution products with alkyl halides under any conditions. However, upon heating, they reacted with haloesters to give low to moderate yields of α,β-unsaturated esters (Eq. 14). No mechanism was given for this reaction.

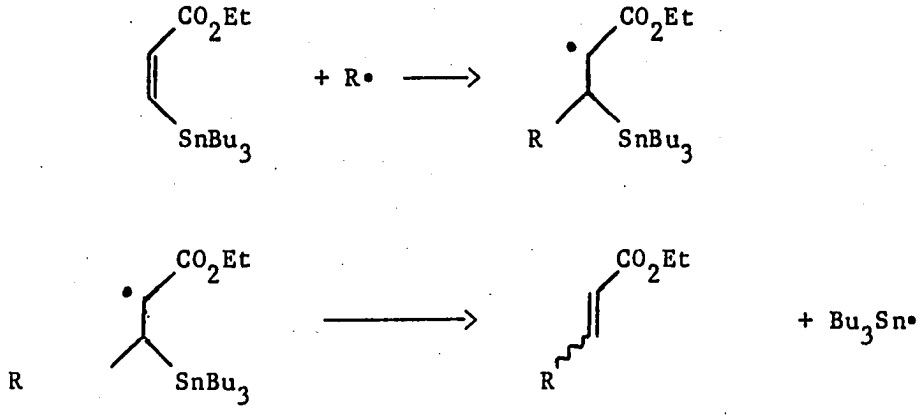
$$Bu_3SnCH{=}CR^1R^2 + XCH_2COOEt \xrightarrow[120\text{-}150^\circ C]{} R^1R^2C{=}CHCH_2COOEt + Bu_3SnX \qquad (14)$$

Baldwin et al. have reported the reaction of β-stannyl acrylates with alkyl bromides (Eq. 15) [49,50]. The reaction gave substitution products in good yields. Scheme 7 outlines the mechanism which involves alkyl radicals.



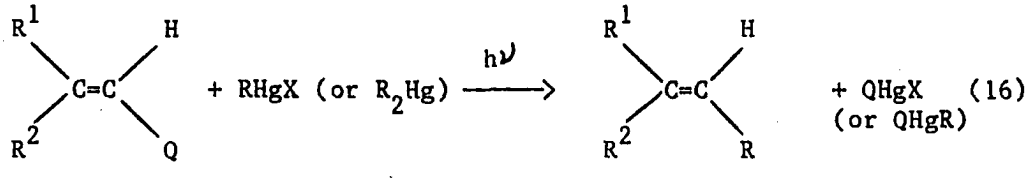
(15)

Scheme 7



They used this reaction in a synthesis of fungal dienyl isonitrile antibiotic [49].

In the course of our studies, we have found that a number of alkenyl derivatives undergo photostimulated substitution reactions with many organomercurials by the radical chain addition-elimination process (Eq. 16).



(16)

Q = HgX, I, Br, SPh, S(O)Ph, SO_2Ph, $SnBu_3$

R = alkyl, PhS, $PhSO_2$, $(EtO)_2PO$, PhSe, etc.

The following sections will present the scope and mechanism of the above reaction. The main source of the adding radicals will be

organomercury compounds. However, some other possible sources of radicals will also be considered.

B. Results and Discussion

1. Reactions of 1-alkenyl iodides with alkylmercury chlorides

2,2-Diphenylethenyl iodide was allowed to react with isopropylmercury chloride in dimethyl sulfoxide (DMSO) under UV irradiation. The reaction was found to proceed according to Eq. (17). After the workup, the reaction afforded a substitution product in high

$$R_2C{=}CHI + R'HgCl \xrightarrow{h\nu} R_2C{=}CHR' + IHgCl \qquad (17)$$

yield as a colorless liquid which appeared to be pure by GLC and ^1H NMR. The reaction gave a higher yield with an excess of isopropylmercury chloride than with a stoichiometric amount of the alkylmercurial as shown in Table 1.

DMSO was used as the solvent because the reaction seemed to proceed well and all the starting materials and products were readily dissolved. After the reaction, DMSO and the mercury(II) salt were easily removed by washing the reaction mixture with water while the organic product was extracted with ether or benzene. The extract was then washed with an aqueous solution of sodium thiosulfate to remove the remaining alkylmercury chloride. The mixture was then concentrated and analyzed by GLC, GCMS, and ^1H NMR. The yield was determined by quantitative ^1H NMR using dibromomethane as an internal standard.

Table 1. Photoreaction of 1-alkenyl iodides with alkylmercury chlorides

$$R_2C{=}CHI + R'HgCl \xrightarrow{h\nu} R_2C{=}CHR' + IHgCl$$

R	R′	equiv R′HgCl	Conditions[a]	% Yield[b] $R_2C{=}CHR'$
Ph	n-Bu	5	DMSO, 14 h	38
Ph	i-Pr	5	DMSO, 8 h	89
Ph	i-Pr	5	PhH, 14 h	54
Ph	i-Pr	5	DMSO, 1 h	73
Ph	i-Pr	5	DMSO, Dark, 24 h	0
Ph	i-Pr	5	DMSO, DTBN, 1 h	0[c]
Ph	i-Pr	2	DMSO, 20 h	84
Ph	i-Pr	1	DMSO, 20 h	55
Ph	c-C_6H_{11}	5	DMSO, 14 h	95
Ph	t-Bu	5	DMSO, 14 h	86
Me	c-C_6H_{11}	2	DMSO, 6 h	< 10
H	c-C_6H_{11}	2	DMSO, 16 h	0
Ph	$(PhCOCH_2)_2Hg$	1	DMSO, 13 h	64

[a]Typical conditions $R_2C{=}CHI$ (0.1 mmol) and R′HgCl in 10 mL of nitrogen-purged solvent were irradiated in a 350 nm Rayonet Photoreactor.

[b]Yields were determined by ^1H NMR.

[c]DTBN = 5 mol % di-tert-butyl nitroxide.

Benzene was also employed as the reaction medium, but it was found that the reaction in this medium occurred sluggishly and the yield was low. When benzene was used, a white solid (presumably IHgCl) precipitated during the reaction. Solubility of alkylmercurials was also the problem as some alkylmercury halides, cyclohexylmercury chloride in particular, have a low solubility in benezene.

Table 1 summarizes the results of the reactions between 1-alkenyl iodides and alkylmercury chlorides. In most cases, a 5-fold excess of the alkylmercurial was employed and the reactions were carried out in DMSO under UV irradiation. The reactions were irradiated for a period of time, but no attempt was made to determine the exact time needed to complete the reactions. All the products appeared to be stable under the reaction conditions.

The substitution reaction (Eq. 17) appears to proceed by a radical chain process since the reaction required an initiator (light) and no reaction was observed in the dark. Furthermore, the reaction was completely inhibited by di-tert-butyl nitroxide (DTBN), a radical chain inhibitor. We believe that the mechanism involves radical addition-elimination as outlined in Scheme 8.

Scheme 8

Initiation

$$R_2C{=}CHI \xrightarrow{h\nu} R_2C{=}\dot{C}H + I\bullet$$

or

$$R'HgCl \xrightarrow{h\nu} R'\bullet + Hg^{o} + Cl\bullet \text{ or } R'\bullet + HgCl$$

Propagation

$$R_2C{=}CHI + R'\bullet \xrightarrow{\alpha\text{-add.}} R_2\dot{C}-\underset{1}{\overset{R'}{\underset{|}{CHI}}}$$

$$1 \xrightarrow{\beta\text{-elim.}} R_2C{=}CHR' + I\bullet$$

$$R'HgCl + I\bullet \longrightarrow R'\bullet + IHgCl$$

The initiation step may be the homolytic cleavage of the alkenyl iodide to give the alkenyl radical and iodine atom. Evidence for this homolytic scission is that the colorless solution of an alkenyl iodide in DMSO or benzene changed slowly to yellow or pink presumably due to the formation of iodine. The photolysis of vinyl halides to give vinyl radicals is a well-known process [51]. The initiation may also arise from the photolysis of the alkylmercurial since a solution of an alkylmercury halide, particularly t-BuHgCl, slowly decomposed to give mercury metal.

In the propagation step, the alkyl radical regioselectively adds to the double bond at the α-position to give 1. The resulting radical 1 undergoes β-elimination to give the substitution product and iodine atom. The iodine atom then reacts with the alkylmercury chloride to give IHgCl and the alkyl radical which continues the chain. The reaction between iodine atom and RHgCl may occur in a concerted manner and it will be discussed in Section B.13 of this part of this thesis.

Vinyl iodide was also allowed to react with cyclohexylmercury

chloride in DMSO under UV irradiation (Eq. 18), but it failed

$$H_2C{=}CHI + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow[\text{DMSO}]{h\nu} \underset{0\%}{H_2C{=}CHC_6H_{11}\text{-}\underline{c}} + IHgCl \qquad (18)$$

to give the substitution product. One possible explanation is that the cyclohexyl radical attacks the double bond at the less hindered β-position to give **2** (Scheme 9).

Scheme 9

$$H_2C{=}CHI + \underline{c}\text{-}C_6H_{11}\bullet \xrightarrow{\beta\text{-add.}} \underset{\mathbf{2}}{\underline{c}\text{-}C_6H_{11}CH_2\text{-}\dot{C}HI}$$

$$\mathbf{2} \xrightarrow{\underline{c}\text{-}C_6H_{11}HgCl} \underset{\mathbf{3}}{\underline{c}\text{-}C_6H_{11}CH_2\text{-}\underset{HgCl}{CHI}} + \underline{c}\text{-}C_6H_{11}\bullet$$

The radical **2** is trapped by cyclohexylmercury chloride to give **3** and cyclohexyl radical and the chain continues.

Russell and Jiang have found that alkyl radicals, $\underline{t}$-Bu•, $\underline{c}$-C_6H_{11}•, and $\underline{n}$-Bu•, add at the β-position of substituted vinyl compounds and the resulting radical is trapped by RHgX (Eq. 19) [52]. The β-addition is

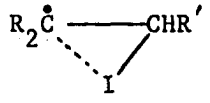
$$R\bullet + H_2C{=}CHQ \longrightarrow RCH_2\text{-}\dot{C}HQ \xrightarrow{RHgX} RCH_2\text{-}\overset{HgX}{\overset{|}{C}}HQ + R\bullet \qquad (19)$$

$$Q = (EtO)_2PO,\ SO_2Ph,\ COOR,\ SiMe_3$$

apparently due to less steric hindrance as the yield decreased with a

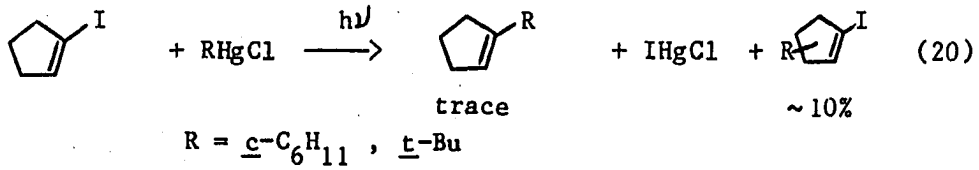
substituent at the β-position of the vinyl compounds. The reaction between ethyl β-phenylacrylate and t-butylmercury chloride gave only the product derived from the attack of t-Bu• at the α-position [52]. The steric effects in the addition of alkyl radicals to alkenes have been studied by Giese and Lachhein [53].

The failure of vinyl iodide, $H_2C=CHI$, to give the substitution product with RHgX (Eq. 18) suggests that the regioselective α-addition of an alkyl radical to the double bonds of the 1-alkenyl iodides, $R_2C=CHI$ where $R \neq H$, is apparently due to a steric effect and, more importantly, the stabilization of the resulting radical by the adjacent substituent at the β-position. Therefore, good yields were observed with 2,2-diphenylethenyl iodide; whereas, 2,2-dimethylethenyl iodide gave a poor yield and vinyl iodide failed to give the coupling product. It also suggests that the stabilization of the radical by iodine bridging as in 4, which could induce α-attack, is not important.



4

1-Iodocyclopentene also failed to give the substitution product with alkylmercury chlorides (Eq. 20). The reaction gave only a trace amount of the coupling product.



(20)

$R = \underline{c}\text{-}C_6H_{11}$, $\underline{t}$-Bu

The main reason for the failure of 2,2-dimethylethenyl iodide and 1-iodocyclopentene to react with alkylmercury halides is the low reactivities of these alkenes towards alkyl radicals. These systems are electron-rich olefins, but alkyl radicals such as $\underline{t}$-butyl, cyclohexyl and $\underline{n}$-butyl radicals have nucleophilic character and are trapped more effectively by electron-deficient than by electron-rich olefins. Giese and co-workers have successfully trapped these alkyl radicals by electron-poor alkenes to form new carbon-carbon bonds [27-31].

The presence of allylic hydrogens, although of less importance, may also be a problem. An alkyl radical can abstract an allylic hydrogen atom to form the corresponding allylic radical which does not continue the chain.

The mechanism of a radical-induced (E_H) elimination reaction has been studied by Stark et al. [54]. They found that the β-elimination occurred preferentially by anti elimination (to the C-H bond being attacked) which confirmed the earlier report by Strunk et al. [55]. This may also explain why 1-iodocyclopentene failed to undergo the photostimulated substitution reaction. It is apparent that the carbon-carbon single bonds of the cyclopentyl radical cannot rotate to give an absolutely co-planar conformation for β-elimination.

2. Reactions of 1-alkenylmercury halides with alkylmercury chlorides

1-Alkenylmercury halides have been reported to undergo photostimulated reactions with many reagents to give substitution products (Eqs. 9-12) [36,37]. These reactions involve free radical addition-elimination as outlined in Scheme 6. We have found that 1-alkenylmercury halides can also react with alkylmercury halides under photostimulation.

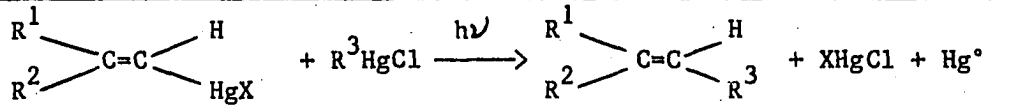
2,2-Diphenylethenylmercury bromide and t-butylmercury chloride were dissolved in DMSO and the mixture was photolyzed in a Rayonet Photoreactor. The reaction was irradiated for 12 h during which time mercury metal precipitated. After workup, GLC indicated that the reaction mixture consisted of only the coupling product in quantitative yield (Eq. 21).

$$Ph_2C{=}CHHgBr + t\text{-}BuHgCl \xrightarrow[DMSO]{h\nu} \underset{100\%}{Ph_2C{=}CH\text{-}Bu\text{-}t} + Hg^0 + BrHgCl \qquad (21)$$

Other 1-alkenylmercury halides and alkylmercury chlorides were also employed and were found to give good yields of the coupling products. Results are summarized in Table 2. In general, the reactions gave high yields with 3°-alkyl- and 2°-alkylmercury chlorides and low yields with 1°-alkylmercury chlorides. We can see from Table 2 that the reactions with i-PrHgCl, c-C_6H_{11}HgCl and t-BuHgCl gave almost quantitative yield of the coupling products; whereas, n-BuHgCl gave only 20-30% of the expected substitution products.

These reactions failed to occur in the dark and were retarded by

Table 2. Photoreaction of 1-alkenylmercury halides with alkylmercury chlorides



R^1	R^2	X	R^3HgCl(equiv)[a]		% Yield[b] $R^1R^2C=CHR^3$
Ph	Ph	Br	neo-$C_5H_{11}HgCl$	(5)	30
Ph	Ph	Br	$PhCH_2HgCl$	(5)	56[c]
Ph	Ph	Br	$PhCH_2HgCl$	(1.5)	30[d]
Ph	Ph	Br	i-PrHgCl	(5)	96
Ph	Ph	Br	c-$C_6H_{11}HgCl$	(5)	97
Ph	Ph	Br	t-BuHgCl	(5)	100
Ph	H	Cl	neo-$C_5H_{11}HgCl$	(5)	23[e]
Ph	H	Cl	$PhCH_2HgCl$	(5)	31[e,f]
Ph	H	Cl	i-PrHgCl	(5)	83[e]
Ph	H	Cl	c-$C_6H_{11}HgCl$	(5)	78[e] (E/Z = 6.4)
Me	Me	Br	c-$C_6H_{11}HgCl$	(5)	< 10
t-Bu	H	Br	c-$C_6H_{11}HgCl$	(5)	10[e]
Ph	Ph	Br	$(PhCOCH_2)_2Hg$	(1)	21

[a] A mixture of $R^1R^2C=CHHgX$ (0.1 mmol) and R^3HgCl in 10 mL of DMSO was irradiated under N_2 in a 350 nm Rayonet Photoreactor for 12 h.

[b] Yields were determined by ^1H NMR.

[c] $PhCH_2CH_2Ph$ was formed in 60% yield (based upon $PhCH_2HgCl$).

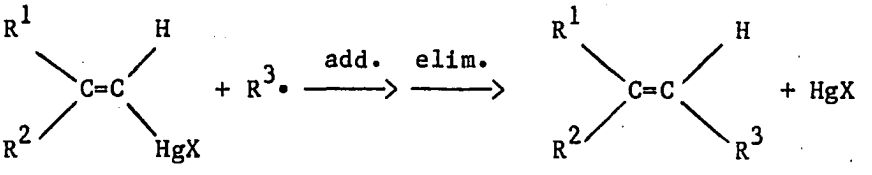
[d] $PhCH_2CH_2Ph$ was formed in 20% yield (based upon $PhCH_2HgCl$).

[e] Mixtures of (E) and (Z) isomers.

[f] $PhCH_2CH_2Ph$ was formed in 70% yield (based upon $PhCH_2HgCl$).

di-tert-butyl nitroxide (DTBN). This suggests that these reactions are radical chain reactions. The proposed mechanism is similar to that of 1-alkenyl iodides with alkylmercurials outlined in Scheme 8. In these reactions, monomeric HgX is the leaving group as shown in Scheme 9.

Scheme 9



$$HgX + R^3HgX \longrightarrow R^3\bullet + HgX_2 + Hg^o$$

One of the key steps for this mechanism is the reaction of HgX with R^3HgX to form the alkyl radical, HgX_2 and Hg^o. We believe that this important step involves electron transfer in which HgX can either accept or donate an electron and it occurs in a concerted manner. This will be discussed in more detail in Section B.13.

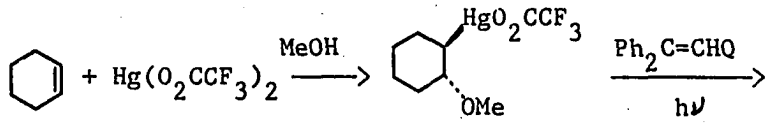
3,3-Dimethyl-1-butenylmercury bromide reacted with cyclohexylmercury chloride to afford only 10% of the coupling product; whereas, 2 2-dimethyl-1-ethenylmercury bromide gave less than 10% of the substitution product (see Table 2). The former does not have allylic hydrogens but still gave the coupling product in low yield. This confirms the earlier discussion in Section 1 that low reactivity of the alkenes towards alkyl radicals is primarily responsible for the low yields of products.

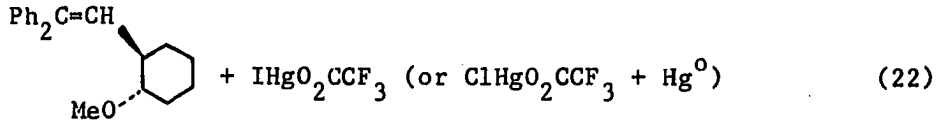
When benzylmercury chloride was employed, a large amount of

bibenzyl was formed. The formation of bibenzyl is also a radical process since an initiator (light) is necessary to induce the reaction. The formation of bibenzyl, however, is not a chain process. The initial kinetic chain length was found to be about zero which suggests that bibenzyl was formed from the coupling of two benzyl radicals [56].

3. Reactions of 2,2-diphenylethenyl iodide and 2,2-diphenylethenylmercury chloride with 2-methoxycyclohexylmercury trifluoroacetate generated in situ

Solvomercuration is a well-known reaction which has been used to prepare organomercurials from alkenes and mercury (II) salts [6,7]. We have found that trans-2-methoxycyclohexylmercury trifluoroacetate, generated in situ by a solvomercuration reaction, underwent photostimulated reaction with 2,2-diphenylethenyl iodide and 2,2-diphenylethenylmercury chloride to give substitution product in high yields (Eq. 22). GLC analysis indicated only one isomer which is presumed to be the trans-cyclohexane 5.





(22)

5

Thus, cyclohexene and mercuric trifluoroacetate were allowed to

react in MeOH at room temperature. After stirring for 10-15 min, 2,2-diphenylethenyl iodide or 2,2-diphenylethenylmercury chloride was added and the mixture was irradiated in a Rayonet Photoreactor for 24 h to give 5 in good yields. Styrene was also used instead of cyclohexene and the reactions were carried out the same way (Eq. 23). These reactions

$$PhCH{=}CH_2 + Hg(O_2CCF_3)_2 \xrightarrow{MeOH} PhCH(OMe)CH_2HgO_2CCF_3 \xrightarrow[h\nu]{Ph_2C{=}CHQ}$$

$$Ph_2C{=}CHCH_2CH(OMe)Ph + IHgO_2CCF_3 \text{ (or } ClHgO_2CCF_3 + Hg^o) \qquad (23)$$

6

afforded product 6 in good yields. Results are summarized in Table 3.

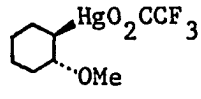
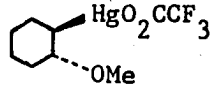
4. Reactions of 1-alkenyl phenyl sulfides, sulfoxide and sulfone with alkylmercury chlorides

2,2-Diphenylethenyl phenyl sulfone was found to react with alkylmercury chlorides to give good yields of the substitution products under photostimulation. The corresponding sulfoxide and sulfides were also found to give the analogous products under the same conditions, however, the yields were low and the reactions appeared to proceed slowly. Equation (24) represents the reaction and the results are summarized in Table 4.

These reactions did not occur in the dark. The photostimulated reactions were strongly retarded by 10 mol% di-tert-butyl nitroxide

Table 3. Reaction of 2,2-diphenylethenyl iodide and 2,2-diphenylethenylmercury chloride with alkylmercury trifluoroacetates generated *in situ*

$$Ph_2C{=}CHQ + RHgO_2CCF_3 \xrightarrow{h\nu} Ph_2C{=}CHR + IHgO_2CCF_3 \text{ (or } ClHgO_2CCF_3 + Hg^o)$$

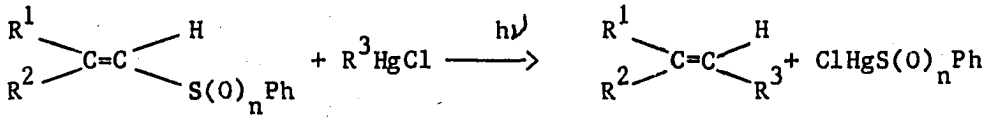
Q	$RHgO_2CCF_3$ (equiv)	% Yield[a] $Ph_2C = CHR$
I		(1 or 5)[b] 75
I	OMe $PhCHCH_2HgO_2CCF_3$	(1)[b] 63
HgCl		(5)[c] 69
HgCl	OMe $PhCHCH_2HgO_2CCF_3$	(5)[c] 69

[a]Yields were determined by ^1H NMR.

[b]$Ph_2C{=}CHI$ (0.2 mmol) and $RHgO_2CCF_3$ in MeOH (10 mL) in a Pyrex vessel were irradiated in a 350 nm Rayonet Photoreactor for 24 h.

[c]DMSO (2 mL) was added to the reaction mixture to dissolve $Ph_2C{=}CHHgCl$.

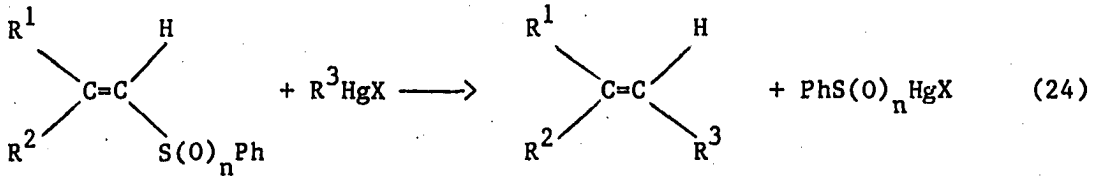
Table 4. Photoreaction of 1-alkenyl phenyl sulfides, sulfoxide and sulfone with alkylmercury chlorides



R^1	R^2	n	R^3HgCl (equiv)	Time (h)[a]	% Yield[b] $R^1R^2C=CHR^3$
Ph	Ph	0	i-PrHgCl (5)	96	55
Ph	Ph	0	c-C_6H_{11}HgCl (5)	96	58
Me	Me	0	n-BuHgCl (5)	18	0
Ph	H	1	i-PrHgCl (5)	24	20
Ph	H	1	t-BuHgCl (5)	24	32
Ph	Ph	2	i-PrHgCl (5)	20	87
Ph	Ph	2	i-PrHgCl (2)	20	62
Ph	Ph	2	i-PrHgCl (1)	22	32
Ph	Ph	2	c-C_6H_{11}HgCl (5)	20	91
Ph	Ph	2	t-C_6H_{11}HgCl (5)	20	88

[a]Mixtures of $R^1R^2C=CHS(O)_nPh$ (0.1 mmol) and R^3HgCl in DMSO (10 mL) in Pyrex reaction vessels were irradiated under N_2 in a 350 nm Rayonet Photoreactor.

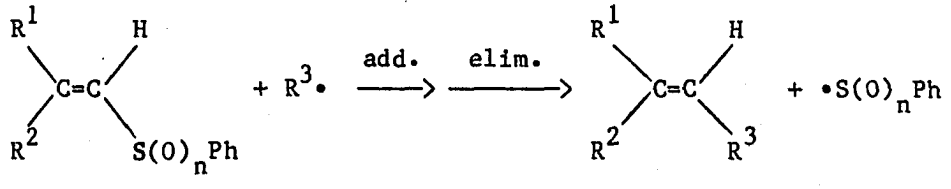
[b]GLC yields.

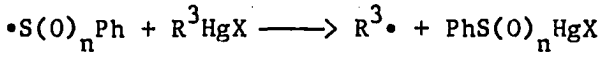


$n = 0,1,2$

(DTBN). This evidence suggests that the reactions proceed by a radical chain process. The mechanism is proposed to involve free radical addition-elimination as outlined in Scheme 10.

Scheme 10



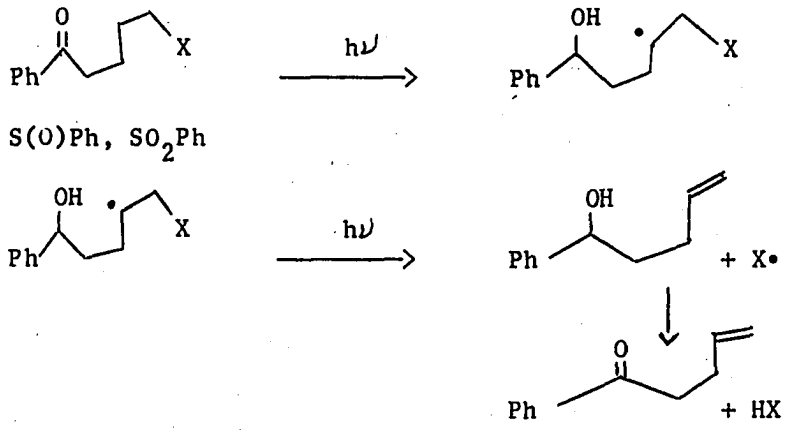


This mechanism is essentially the same as those proposed earlier, except that the leaving groups for this mechanism are SPh, S(O)Ph. and SO_2Ph. The reactions between sulfur-centered radicals and alkylmercury chlorides have been reported in the literature [35]. Results obtained in our research group suggest that this step does not involve tricovalent mercury of the type $RH\dot{g}(X)S(O)_nPh$. It is likely to occur by a S_H2 or an electron transfer process in a concerted manner (see Section B.13).

It has been established that relative rates for loss of sulfur radicals are: $PhSO > PhS > PhSO_2$ [57,58]. This result was obtained by the photoelimination of HX as shown in Scheme 11.

Our results show that yields increase in the order PhSO < PhS < $PhSO_2$ and that the reaction with the sulfide was very slow (Table 4). The results may not reflect the actual leaving ability of the leaving groups and other factors have to be considered. The reactivities of

Scheme 11



the alkenyl phenyl sulfide, sulfoxide, and sulfone towards the attacking alkyl radical may control the overall reaction. Our results indicate that 2,2-diphenylethenyl phenyl sulfone is more reactive than (E)-2-phenylethenyl phenyl sulfoxide which is more reactive than 2,2-diphenylethenyl phenyl sulfide. This has been confirmed by the indirect competition between 2,2-diphenylethenyl phenyl sulfone and 2,2-diphenylethenyl phenyl sulfide which indicates that 2,2-diphenylethenyl phenyl sulfone is about 1.5 times more reactive than 2,2-diphenylethenyl phenyl sulfide towards cyclohexyl radical (see Part III).

5. Reactions of 1-alkenyl compounds with mercuric phenylmercaptide, mercuric phenylselenide, mercuric benzenesulfinate

1-Alkenylmercury halides have been reported to undergo photostimulated reactions with the sodium salt of mercaptans and with alkyl or aryl disulfides to give the substituted 1-alkenyl alkyl or aryl sulfide [36,37]. Benzenesulfonyl chloride, the sodium salt of benzenesulfinic acid and phenyl diselenide also react with 1-alkenylmercury halides to give the corresponding substitution products.

We have found that $Hg(SPh)_2$, $Hg(SePh)_2$, and $Hg(SO_2Ph)_2$ reacted with alkenyl compounds, $R^1R^2C{=}CHQ$ (Q = I, HgX, SO_2Ph, $SnBu_3$), to give the substitution products. Therefore, the alkenyl compounds and mercuric phenylmercaptide were allowed to react in DMSO under UV irradiation for 20-24 h to give the coupling products in good to quantitative yields (Eq. 25). Table 5 presents the results of these reactions.

$$R^1R^2C{=}CHQ + Hg(SPh)_2 \xrightarrow{h\nu} R^1R^2C{=}CHSPh + QHgSPh \quad (25)$$

Q = I, HgX, SO_2Ph, $SnBu_3$

or $PhSHgX + Hg^o$

or $PhSSnBu_3 + Hg^o$

The photoreactions of the alkenyl compounds with mercuric phenylselenide were carried out under the same conditions to give the alkenyl phenyl selenide in moderate to good yields (Eq. 26). The

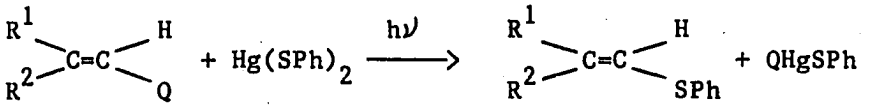
$$R^1R^2C{=}CHQ + Hg(SePh)_2 \xrightarrow{h\nu} R^1R^2C{=}CHSePh + PhSeHgQ \quad (26)$$

Q = I, HgX, SO_2Ph, $SnBu_3$

or $PhSeHgX + Hg^o$

or $PhSeSnBu_3 + Hg^o$

Table 5. Reaction of alkenyl compounds with mercuric phenylmercaptide



R^1	R^2	Q	Time (h)[a]	% Yield[b] $R^1R^2C{=}CHSPh$	($\underline{E}/\underline{Z}$)
Ph	Ph	I	20	100[c]	
Ph	Ph	HgBr	20	100[c]	
Ph	Ph	$SnBu_3$	20	66[c]	
Ph	Ph	$PhSO_2$	24	100[c]	
Ph	H	I	20	97[c]	(> 50)
Ph	H	HgCl	20	97[c]	(> 50)
Me	Me	HgBr	20	39[c]	
Me	Me	$SnBu_3$	20	56[c]	
$\underline{t}$-Bu	H	HgBr	20	91[c]	(> 50)
H	H	HgCl	20	46[c]	
H	H	$SnBu_3$	20	45[c]	
Ph	H	$PhSO_2$	24	50[c,d]	(> 50)

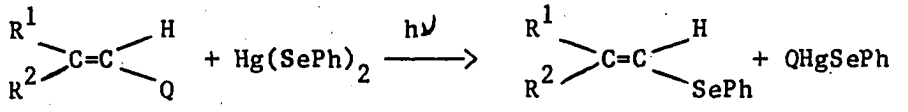
[a]Substrates (0.1 mmol of each) in DMSO (10 mL) in Pyrex vessels under N_2 were irradiated in a 350 nm Rayonet Photoreactor.

[b]Yields were determined by GLC.

[c]PhSSPh was also formed in about 5% yield.

[d]$PhCH{=}CHSO_2Ph$ was recovered in 42% yield.

Table 6. Reaction of alkenyl compounds with mercuric phenylselenide



R^1	R^2	Q[a]	% Yield[b] (E/Z) $R^1R^2C{=}CHSePh$
Ph	Ph	I	78
Ph	Ph	HgBr	80
Ph	Ph	SO_2Ph	12[c]
Ph	Ph	$SnBu_3$	92
Ph	H	HgCl	27 (1.3)
Ph	H	I	34 (1.1)
Me	Me	HgBr	38
t-Bu	H	HgBr	35 (> 50)
H	H	HgCl	39[d]
H	H	$SnBu_3$	64

[a]Equimolar amounts of substrates (0.1 mmol each) in nitrogen-purged DMSO (10 mL) in Pyrex vessels were irradiated in a 350 nm Rayonet Photoreactor for 20 h.

[b]Yields were determined by ^1H NMR.

[c]PhSeSePh was also formed in 11% yield (based upon $Hg(SePh)_2$).

[d]PhSeSePh was also detected (1%).

yields, however, are lower than in reactions with mercuric phenylmercaptide (see Table 6). Phenyl diselenide was also formed in low yields in the reactions with Q = SO_2Ph, HgCl.

Reactions of the alkenyl compounds with mercuric benzenesulfinate were found to give good yields of the coupling products (Table 7). The reactions were complete in about 12 h and Eq. (27) represents these reactions. In most cases, the reaction mixtures consisted mainly of the alkenyl phenyl sulfones. They were, however, accompanied by some

$$R^1R^2C{=}CHQ + Hg(SO_2Ph)_2 \xrightarrow{h\nu} R^1R^2C{=}CHSO_2Ph + \begin{matrix} PhSO_2HgI \\ PhSO_2HgX + Hg^o \\ PhSO_2SnBu_3 + Hg^o \end{matrix} \qquad (27)$$

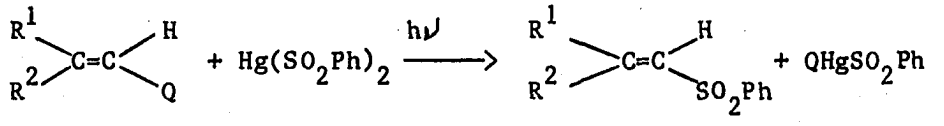
Q = I, HgX, $SnBu_3$

byproducts which are given in Table 7. These side products apparently resulted from the use of an excess of mercuric benzenesulfinate. It suggests that excess mercuric benzenesulfinate should be avoided. Prolonged irradiation may also result in lower yield due to the formation of alkenyl phenyl sulfides.

6. Reactions of 1-alkenyl compounds with diethoxyphosphinylmercury chloride and bis(diethoxyphosphinyl)mercury

Potassium diethyl phosphite was reported to react with 1-alkenylmercury halides under photostimulated reactions to give the substitution products [32]. The key step is the reaction between monomeric HgCl and diethyl phosphite anion to form diethyl phosphite radical by an electron transfer process (Eq. 28).

Table 7. Reaction of alkenyl compounds with mercuric benzenesulfinate



R^1	R^2	Q	Conditions[a]	% Yield[b] $R^1R^2C{=}CHSO_2Ph$	Byproduct (%)
Ph	Ph	I	R, 12 h	86	$Ph_2C{=}CHSPh$(12) $PhSO_2Ph$[c](6)
Ph	Ph	I	R, 12 h	93[d]	$Ph_2C{=}CHSPh$(6)
Ph	Ph	HgBr	R, 12 h	100	-
Ph	Ph	$SnBu_3$	SL, 4 h	63	-
Ph	H	I	R, 12 h	88	$PhSO_2Ph$(15), $PhSPh$[c](2)
Ph	H	HgCl	R, 12 h	74	$PhSO_2Ph$(9), $PhSPh$(8) $PhCH{=}CHSPh$(5)
t-Bu	H	HgBr	R, 12 h	42	$PhSO_2Ph$(6), $PhSPh$(2)
Me	Me	HgBr	R, 12 h	38	$PhSO_2Ph$(11), $PhSPh$(2)
Me	Me	$SnBu_3$	SL, 4 h	38	-
H	H	HgCl	R, 12 h	43	$PhSO_2Ph$(10), $PhSPh$(2)
H	H	$SnBu_3$	SL, 4 h	trace	-

[a]Substrates (5 equiv of $Hg(SO_2Ph)_2$) in DMSO (10 mL) were irradiated under N_2. R = 350 nm Rayonet Photoreactor; SL = sunlamp.

[b]Yields were determined by GLC.

[c]Based upon $Hg(SO_2Ph)_2$.

[d]$Hg(SO_2Ph)_2$ (1 equiv) was employed.

$$HgCl + (EtO)_2PO^- \xrightarrow{E.T.} (EtO)_2PO\bullet + Hg^o + Cl^- \qquad (28)$$

Diethoxyphosphinylmercury chloride was also found to react with 1-alkenyl compounds to give the substitution products in good yields (Eq. 29). Results are summarized in Table 8.

$$R^1R^2C{=}CHQ + (EtO)_2\overset{O}{\overset{\|}{P}}HgCl \xrightarrow{h\nu} R^1R^2C{=}CH\overset{O}{\overset{\|}{P}}(OEt)_2 + QHgCl \qquad (29)$$

$Q = I, HgX, SO_2Ph, SnBu_3$ or $XHgCl + Hg^o$ or $Bu_3SnCl + Hg^o$

The reactions gave good yields when Q = I, HgX and $SnBu_3$, but gave a low yield with Q = SO_2Ph and only a trace amount of the coupling product was observed with Q = SPh. This may indicate that 2,2-diphenylethenyl phenyl sulfone and 2,2-diphenylethenyl phenyl sulfide are not reactive towards diethoxyphosphinyl radical.

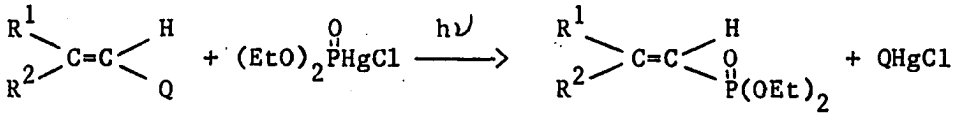
The results in Table 8 suggest that prolonged irradiation should be avoided since polysubstitution can occur resulting in lower yields of the expected products. The reactions, at least with Q = HgX, seem to proceed as well when stoichiometric amounts of the reagents were used.

The reactions of the alkenyl compounds with bis(diethoxyphosphinyl)mercury (Eq. 30) also gave good yields of the substitution products (Table 9).

$$R^1R^2C{=}CHQ + [(EtO)_2\overset{O}{\overset{\|}{P}}]_2Hg \xrightarrow{h\nu} R^1R^2C{=}CH\overset{O}{\overset{\|}{P}}(OEt)_2 + (EtO)_2\overset{O}{\overset{\|}{P}}HgQ \qquad (30)$$

$Q = I, HgX, SO_2Ph, SnBu_3$ or $(EtO)_2\overset{O}{\overset{\|}{P}}SnBu_3 + Hg^o$ or $(EtO)_2\overset{O}{\overset{\|}{P}}HgX + Hg^o$

Table 8. Reaction of alkenyl compounds with diethoxyphosphinylmercury chloride



R^1	R^2	Q	Conditions[a]	% Yield[b] $R^1R^2C{=}CH\overset{O}{\overset{\|}{P}}(OEt)_2$
Ph	Ph	I	1:1, SL, 1 h	20[c]
Ph	Ph	I	1:1, SL, DTBN, 1 h	0[d]
Ph	Ph	I	1:3, R, 12 h	84
Ph	Ph	I	1:3, R, 24 h	77[e]
Ph	Ph	HgBr	1:3, R, 2 h	59
Ph	PH	HgBr	1:3, R, DTBN, 2 h	0
Ph	Ph	HgBr	1:3, R, 4 h	85
Ph	Ph	HgBr	1:1, R, 12 h	85
Ph	Ph	HgBr	1:3, R, 24 h	79[f]
Ph	Ph	$SnBu_3$	1:3, R, 24 h	65

[a]Substrates (0.1 mmol of $R^1R^2C{=}CHQ$) in nitrogen-purged DMSO (10 mL) were irradiated by sunlamp (SL) or in a 250 nm Rayonet Photoreactor (R).

[b]GLC yields or ^1H NMR yields.

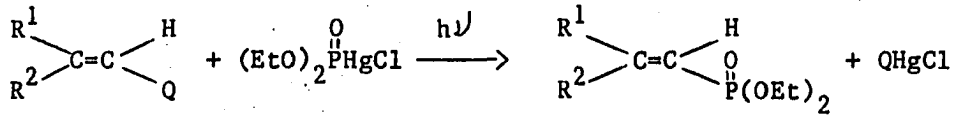
[c]$Ph_2C{=}CHI$ (60%) was recovered.

[d]$Ph_2C{=}CHI$ (95%) was recovered. DTBN = 10 mol% di-tert-butyl nitroxide.

[e]Disubstituted product (~ 19%) was also formed.

[f]Disubstituted product (~4%) was detected.

Table 8. (continued)



R^1	R^2	Q	Conditions[a]	% Yield[b] $R^1R^2C{=}CHP(O)(OEt)_2$
Ph	Ph	SO_2Ph	1:3, R, 24 h	26[g]
Ph	Ph	SPh	1:3, R, 24 h	trace[g]
Ph	H	I	1:3, R, 4 h	88[h]
Ph	H	HgCl	1:3, R, 4 h	57[h]
t-Bu	H	HgBr	1:1, R, 24 h	67[h]
t-Bu	H	HgSPh	1:1, R, 12 h	31,[h,i]
Me	Me	HgBr	1:1, R, 24 h	31[h]
Me	Me	$SnBu_3$	1:1, R. 24 h	36
H	H	HgCl	1:1, R, 24 h	trace

[g]Starting material was recovered.

[h]Only (E) isomer.

[i](E)-t-BuCH=CHSPh was also formed in 68%.

When a large excess of bis(diethoxyphosphinyl)mercury was employed or if the reaction was irradiated for a long time, the product underwent further reaction to give polysubstitution products. The reactions with Q = SO_2Ph and SPh failed to give the substitution products and the starting materials were recovered from the reactions.

The reactions (Eqs. 29,30) are believed to proceed by a free radical chain addition-elimination process. Evidence for this process included the failure of the reactions to occur in the dark or in the presence of di-tert-butyl nitroxide. The proposed mechanism is outlined in Scheme 12.

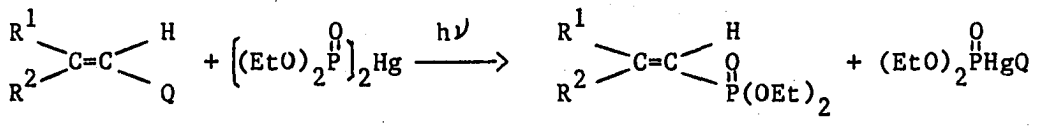
Scheme 12

$$R^1R^2C{=}CHQ + (EtO)_2\overset{O}{\overset{\|}{P}}\bullet \xrightarrow{\text{add.}} \xrightarrow{\text{elim}} R^1R^2C{=}CH\overset{O}{\overset{\|}{P}}(OEt)_2 + Q\bullet$$

$$Q\bullet + (EtO)_2\overset{O}{\overset{\|}{P}}HgCl \begin{cases} \xrightarrow{Q = I,\ SO_2Ph,\ SPh} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + QHgCl \\ \xrightarrow{Q = HgX} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + Hg^o + XHgCl \\ \xrightarrow{Q = SnBu_3} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + Hg^o + Bu_3SnCl \end{cases}$$

$$Q\bullet + [(EtO)_2\overset{O}{\overset{\|}{P}}]_2Hg \begin{cases} \xrightarrow{Q = I,\ Br} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + (EtO)_2\overset{O}{\overset{\|}{P}}HgQ \\ \xrightarrow{Q = HgX} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + (EtO)_2\overset{O}{\overset{\|}{P}}HgX + Hg^o \\ \xrightarrow{Q = SnBu_3} (EtO)_2\overset{O}{\overset{\|}{P}}\bullet + Hg^o + (EtO)_2\overset{O}{\overset{\|}{P}}SnBu_3 \end{cases}$$

Table 9. Reaction of alkenyl compounds with bis(diethoxyphosphinyl)-mercury



R^1	R^2	Q	Conditions[a]	% Yield[b] (E/Z) $R^1R^2C{=}CHP(O)(OEt)_2$
Ph	Ph	I	1:1, Dark, 24 h	0[c]
Ph	Ph	I	1:1, R, 24 h	86
Ph	Ph	I	1:5, R, 20 h	49[d]
Ph	Ph	I	1:5, R, 96 h	0[d]
Ph	Ph	Br	1:1, R, 24 h	23[e]
Ph	Ph	HgBr	1:1, R, 24 h	86
Ph	Ph	$SnBu_3$	1:1, R, 20 h	14[f]
Ph	Ph	SO_2Ph	1 1, R, 20 h	0[c]
Ph	Ph	SPh	1:1, R, 20 h	0[c]
Ph	H	I	1:1, R, 8 h	78 (E only)
Ph	H	HgCl	1:1, R, 8 h	68 (10.3)

[a]An alkenyl compound (0.1 mmol) and bis(diethoxyphosphinyl)-mercury in DMSO (10 mL) under N_2 were irradiated in a 350 nm Rayonet Photoreactor (R).

[b]Yields were determined by ^1H NMR or GLC.

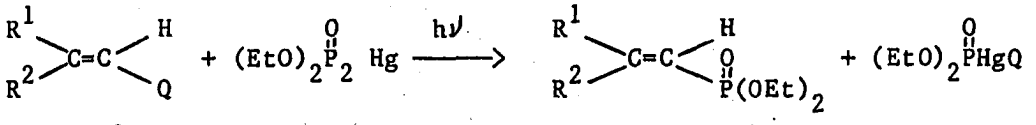
[c]Starting material was recovered.

[d]Disubstituted product was formed in a large amount.

[e]$Ph_2C{=}CHBr$ (68%) was recovered.

[f]$Ph_2C{=}CHSnBu_3$ (72%) was recovered.

Table 9. (continued)



R^1	R^2	Q	Conditions[a]	% Yield[b] (E/Z) $R^1R^2C{=}CHP(O)(OEt)_2$
Ph	H	SO_2Ph	1:1, R, 20 h	0[c]
Ph	H	SPh	1:1, R, 20 h	0[c]
Me	Me	HgBr	1:1, R, 15 h	trace
t-Bu	H	HgBr	1:1, R, 15 h	86 (E only)

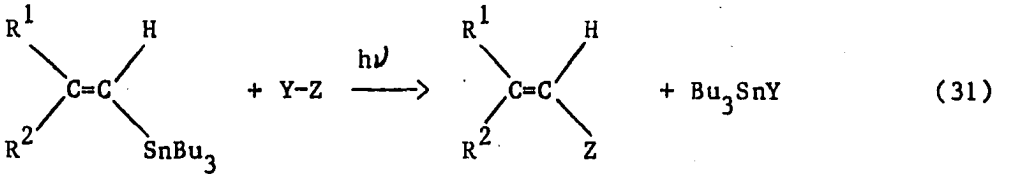
Tri-n-butyl-2,2-diphenylethenylstannane gave a higher yield with diethoxyphosphinylmercury chloride than with bis(diethoxyphosphinyl)-mercury. This may suggest that the reactions occur by a different mechanism. With diethoxyphosphinylmercury chloride, tri-n-butylstannyl radical may abstract a chlorine atom from the mercurial to form tri-n-butyltin chloride and diethoxyphosphinylmercury radical which decomposes to give diethoxyphosphinyl radical and Hg^0. However, electron transfer from tri-n-butylstannyl radical to the mercurial is more likely to occur. If the latter process operates, it suggests that electron transfer occurs more readily with diethoxyphosphinyl-mercury chloride than with bis(diethoxyphosphinyl)mercury.

7. Substitution reactions of tri-n-butyl-1-alkenylstannanes with disulfides and various reagents

Tri-n-butyl-2,2-dimethylethenylstannane was allowed to react with diphenyl disulfide in benzene under sunlamp irradiation. The reaction occurred rapidly to afford 2,2-dimethylethenyl phenyl sulfide in almost quantitative yield. The thermal reaction in the dark in the presence of 10 mol% azobisisobutyronitrile (AIBN) at 80 °C also gave the same yield of the substitution product. Without AIBN, no reaction occurred under the same conditions. The reaction under sunlamp was completely inhibited by 5 mol% di-tert-butyl nitroxide (DTBN). These facts indicate that the reaction involves a free radical chain addition-elimination mechanism.

Benzyl disulfide and benzene sulfonyl chloride were also found to react with the alkenylstannane to give the corresponding substitution products in excellent yields. Results are presented in Table 10.

Equation (31) represents the overall reaction and the mechanism is



(31)

$R^1 = R^2$ = Me, Ph

Y = PhS, $PhCH_2S$, Cl

Z = PhS, $PhCH_2S$, $PhSO_2$

outlined in Scheme 13. This mechanism has been discussed in ref 59.

Diphenyl diselenide has been reported to undergo photostimulated

Table 10. Reaction of tri-n-butyl-1-alkenylstannanes with phenyl disulfide, benzyl disulfide, phenyl diselenide and benzenesulfonyl chloride

$$R_2C{=}CHSnBu_3 + Z\text{-}Y \xrightarrow[\text{or } \Delta]{h\nu} R_2C{=}CHZ + Bu_3SnY$$

R	Z-Y	Conditions[a]	% Yield[b] (isolated) $R_2C{=}CHZ$
Me	PhSSPh	SL, 2 h	97 (74)
Me	PhSSPh	80 °C, AIBN, 2 h	97[c]
Me	PhSSPh	SL, DTBN, 1 h	0[d]
Me	PhSSPh	80 °C, Dark, 2 h	0
Me	$PhCH_2SSCH_2Ph$	SL, 8 h	84
Me	$PhSO_2Cl$	SL, 4 h	90
Me	PhSeSePh	SL, 4 h	0[e]
Ph	PhSSPh	SL, 2 h	93
Ph	$PhSO_2Cl$	SL, 4 h	76

[a]Reaction mixtures in benzene were irradiated with a 275 W sunlamp approximately 15 cm from the Pyrex reaction vessels at ambient temperature.

[b]^1H NMR yields.

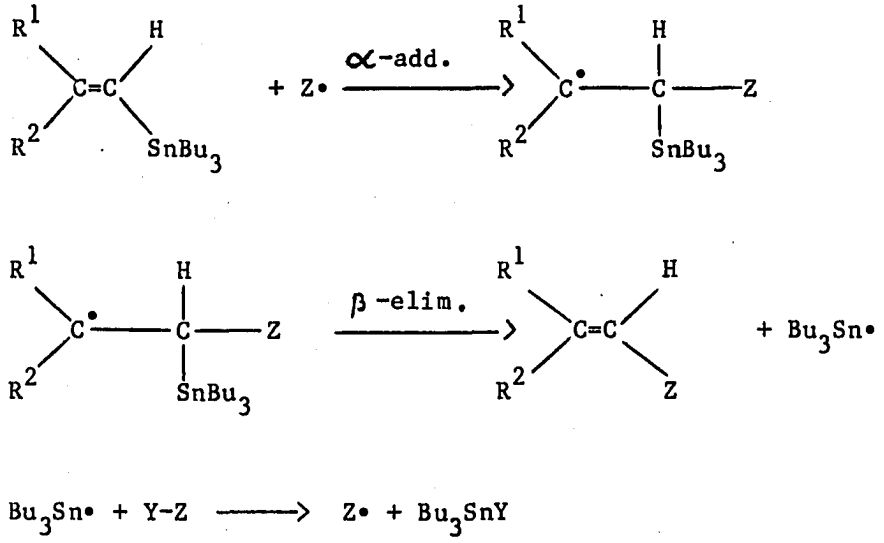
[c]AIBN = 10 mol% azobisisobutyronitrile.

[d]DTBN = 5 mol% di-tert-butyl nitroxide.

[e]All starting materials were recovered. Reaction was performed in an NMR tube.

reactions with 1-alkenylmercury halides to give excellent yields of the coupling products [37]. In contrast, it failed to react with 1-alkenylstannanes. The reaction between tri-n-butyl-2,2-dimethyl-

Scheme 13



ethenylstannane and phenyl diselenide was carried out in benzene under sunlamp irradiation. After 4 h, all the starting materials were recovered unchanged. Diphenyl diselenide also failed to react with tri-n-butylvinylstannane and tri-n-butyl-2-phenylethenylstannane as reported previously [59].

We found that tri-n-butyl-1-alkenylstannanes underwent facile photostimulated reactions with mercuric phenylselenide to give high yields of the substitution products (Table 6). Therefore, the failure of phenyl diselenide to react with 1-alkenylstannanes is not because

the 1-alkenylstannanes do not trap the selenyl radical. A possible explanation for the failure of the reaction is that $Bu_3Sn\bullet$ does not react with the diselenide by either a S_H2 or an electron transfer process to give the selenyl radical (Eq. 32). This is puzzling because

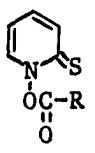
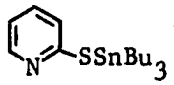
$$Bu_3Sn\bullet + PhSeSePh \not\longrightarrow Bu_3SnSePh + PhSe\bullet \qquad (32)$$

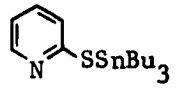
pheny diselenide is considerably more reactive than phenyl disulfide towards 5-hexenyl radical [35].

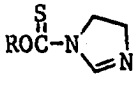
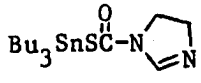
Organostannanes have been used extensively in organic synthesis in the past few decades [28]. Many alkyl radicals have been generated from triorganostannyl radicals. Substrates which react with tri-n-butylstannyl radical to give the corresponding alkyl radicals are illustrated in the following Eqs. (33-38).

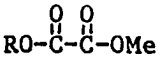
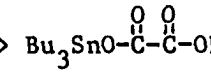
$Bu_3Sn\bullet +$

RX $\longrightarrow$ $Bu_3SnX + R\bullet$ (33) [60]

 $\longrightarrow$  $+ CO_2 + R\bullet$ (34) [61,62]

 $\longrightarrow$  $+ R\bullet$ (35) [62]

 $\longrightarrow$ Bu_3Sn  $+ R\bullet$ (36) [63]

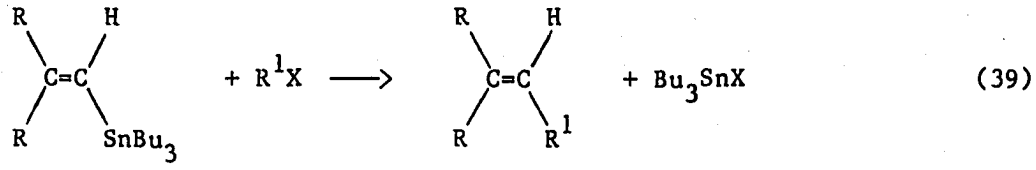
 $\longrightarrow$ Bu_3Sn  $+ R\bullet$ (37) [64]

(R = 2^o, 3^o-alkyl)

RNO_2 $\longrightarrow$ $Bu_3SnNO_2 + R\bullet$ (38) [65,66]

(R = 2^o, 3^o-alkyl)

We have carried out reactions of tri-n-butyl-1-alkenylstannanes with alkyl halides under UV irradiation (Eq. 39). The progress of the reactions were monitored by ^{1}H NMR. Only small amounts of the coupling products were observed after irradiation for 24 h.



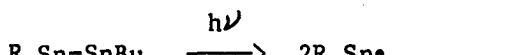
(39)

< 10%

R = Me, Ph R^1 = 2°, 3°-alkyl

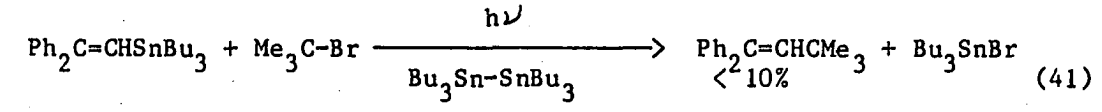
X = Cl, Br, I

Organoditins have been used as an initiator for radical reactions [49, 67,68]. They undergo homolytic cleavage under irradiation to give triorganostannyl radicals (Eq. 40). We also used hexabutylditin as an



(40)

initiator in this reaction (Eq. 41). Unfortunately, the reaction again



(41)

to give a good yield of the coupling product.

The reactions between tri-n-butyl-2-phenylethenylatannane and alkyl halides were reported earlier by Tashtoush [59]. Surprisingly, only n-butyl iodide gave an appreciable yield (64%) of the coupling product. Secondary and tertiary alkyl halides which were expected to

react better gave only small amounts of the expected products.

Recently, tri-n-butyl-2-phenylethenylstannane has been reported to undergo radical chain addition-elimination reactions with alkyl bromides (Eq. 42) [50]. The reaction was carried out using toluene as the

$$(E)\text{-PhCH=CHSnBu}_3 + \text{RBr} \xrightarrow[\text{AIBN, 86 °C}]{\text{Toluene}} \text{PhCH=CHR} + \text{Bu}_3\text{SnBr} \qquad (42)$$

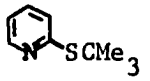
solvent at 86 °C with azobisisobutyronitrile as an initiator. A large amount of the initiator (16 mol% every 12 h) was added and the reactions were carried out for 24-36 h. The yields obtained were 22-82%.

N-(Trimethylacetoxy)pyridine-2-thione, 7, was allowed to react with tri-n-butyl-2,2-diphenylethenylstannane in benzene under sunlamp irradiation. The reaction was expected to occur according to Eq. (43). However, the reaction mixture afforded only a small amount of the coupling product

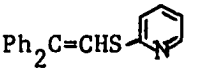
$$\text{Ph}_2\text{C=CHSnBu}_3 + \text{7} \longrightarrow \text{Ph}_2\text{C=CHCMe}_3 + \text{CO}_2 + \text{N, SSnBu}_3 \qquad (43)$$

7

and some minor unidentified products. The major products were t-butyl 2-pyridyl sulfide, 8, and 2,2-diphenylethenyl 2-pyridyl sulfide, 9.



8



9

The formation of 8 was not surprising since 7 has been reported to undergo rearrangement to give the sulfide 8 as shown in Scheme 14 [62].

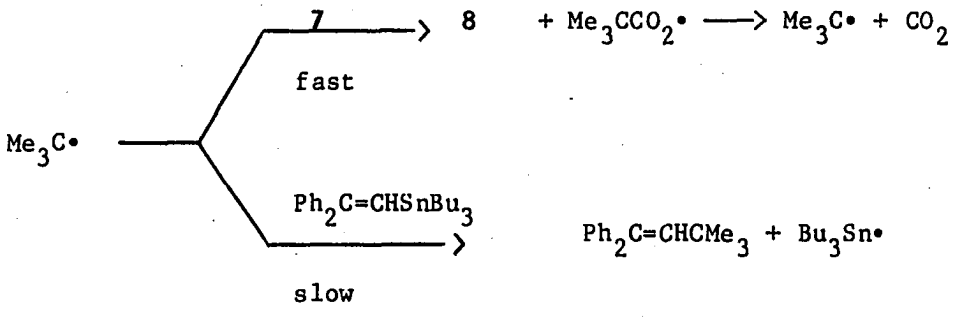
Scheme 14

$$7 + Me_3C\bullet \longrightarrow 8 + Me_3CCOO\bullet$$

$$Me_3CCOO\bullet \longrightarrow Me_3C\bullet + CO_2$$

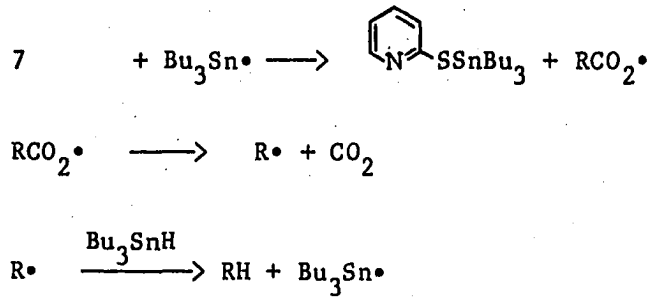
The proposed mechanism involves the attack of the alkyl radical at the sulfur atom with the expulsion of the carboalkoxy radical. Loss of CO_2 gives t-butyl radical which continues the chain. It is apparent that 7 traps the alkyl radical more effective than does the 1-alkenylstannane (Scheme 15).

Scheme 15



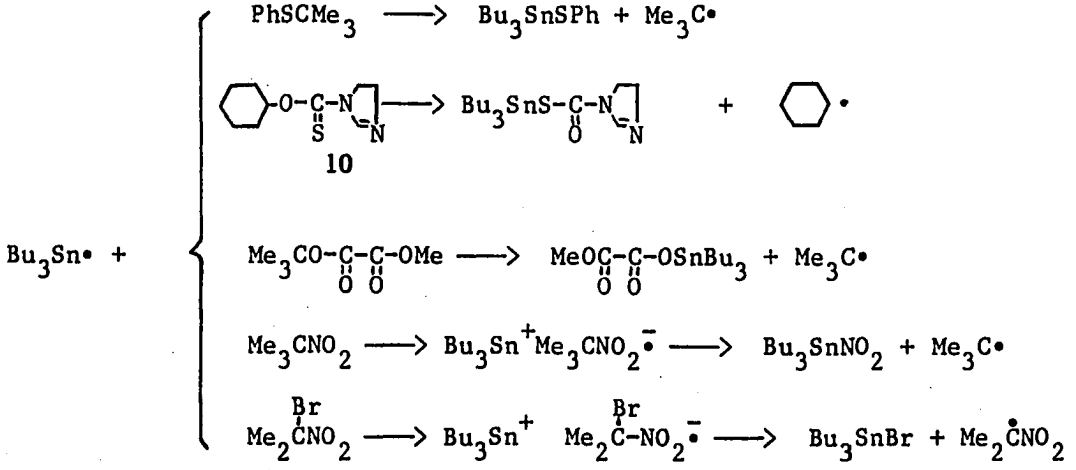
The formation of 9 was not expected. This product was not formed in the dark. A mixture of tri-n-butyl-2,2-diphenylethenylstannane and 7 in benzene when heated at 80 °C for 2 h in the dark, gave the rearranged product as the major product and only a small amount of 9. The reaction leading to 9 is unlikely to involve the sulfur-centered radical,  , since it has been reported that the ester of N-hydroxypyridine 2-thione was reduced by tri-n-butyltin hydride to give the nor-alkane as shown in Scheme 16. Thus the formation of 9 most

Scheme 16



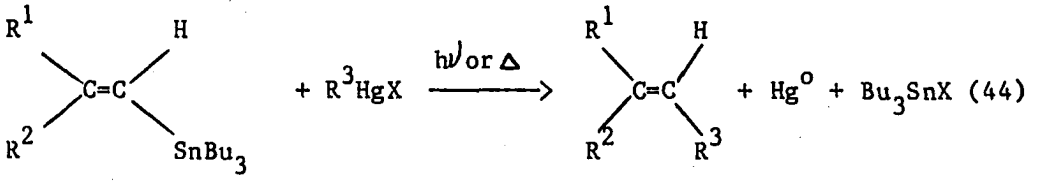
likely involves a process in which $Ph_2C{=}CH\bullet$ is formed as an intermediate, perhaps by direct photolysis of tri-n-butyl-2,2-diphenylethenylstannane.

Other substrates, t-butyl phenyl sulfide, N-(cyclohexyloxythiocarbonyl)imidazole,(10), t-butyl methyl oxalate, 2-methyl-2-nitropropane and 2-bromo-2-nitropropane were allowed to react with tri-n-butyl-2,2-diphenylethenylstannane under photo or thermal conditions (see Experimental Section). In most cases, all the starting materials were recovered even through it was expected that $Bu_3Sn\bullet$ would propagate a chain reaction by the following reactions:



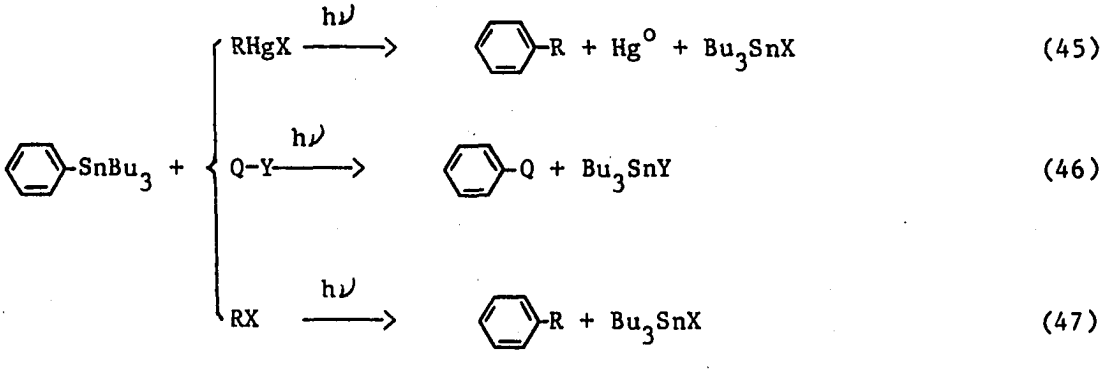
8. Reactions of tri-n-butylphenylstannane with organomercurials

Tri-n-butyl-1-alkenylstannanes were found to react with alkylmercury halides to give good yields of the coupling products (Eq. 44) [59]. The mechanism which has been discussed in ref 59 is



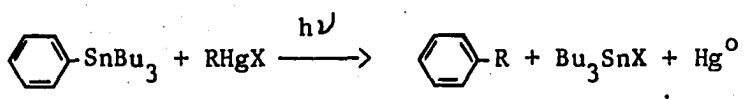
believed to involve a free radical addition-elimination process.

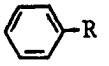
We have extended this reaction to a substituted aromatic system, tri-n-butylphenylstannane. The reaction was carried out with various organomercurials (Eq. 45), phenyl disulfide (Eq. 46), benzenesulfonyl chloride, and alkyl halides (Eq. 47) under UV irradiation for 26-30 h. The reactions afforded low yields of the substitution products as summarized in Table 11.



The mechanism, similar to that of the alkenyl systems, is believed to involve radical addition-elimination as shown in Scheme 17.

Table 11. Substitution reaction of tri-n-butylphenylstannane with organomercurials, phenyl disulfide benzenesulfonyl chloride and alkyl iodides



RHgX (equiv)	Conditions[a]	% Yield[b] 	% Bu_3SnX[b]
n-BuHgCl (5)	PhH/DMSO, R	7[c]	60
c-C_6H_{11}HgCl (5)	PhH/DMSO, R	13	30
i-PrHgCl (5)	PhH/DMSO, R	13	94
t-BuHgCl (5)	PhH, R	3	76
$(EtO)_2\overset{O}{\overset{\|}{P}}HgCl$ (5)	PhH/DMSO, R	16	28
$(PhS)_2Hg$ (1.5)	PhH/DMSO, R	3[d]	50
PhSSPh (1.5)	PhH, R	5[e]	14
$(PhSO_2)_2Hg$ (1.5)	PhH/DMSO, R	7	?
$PhSO_2Cl$ (1.5)	PhH, R	31[f]	58
i-PrI (5)	PhH, R	14	71
n-BuI (5)	PhH, R	19	85

[a]Reactants in nitrogen-purged solvents were irradiated in a 350 nm Rayonet Photoreactor (R) for 26 h.

[b]Yields were determined by GLC.

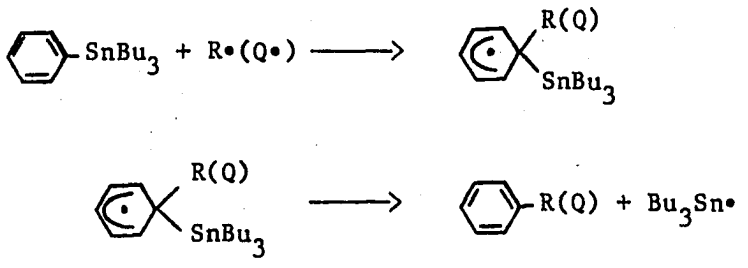
[c]$PhSnBu_3$ (6%) was recovered.

[d]$PhSnBu_3$ (12%) was recovered.

[e]$PhSnBu_3$ (61%) was recovered.

[f]$PhSnBu_3$ (22%) was recovered.

Scheme 17



$$Bu_3Sn\bullet + RX \longrightarrow R\bullet + Bu_3SnX$$

or $$Bu_3Sn\bullet + RHgX \longrightarrow R\bullet + Bu_3SnX + Hg^{o}$$

or $$Bu_3Sn\bullet + Q\text{-}Y \longrightarrow Q\bullet + Bu_3SnY$$

9. Reactions of 1-alkenyl derivatives with trialkylboranes

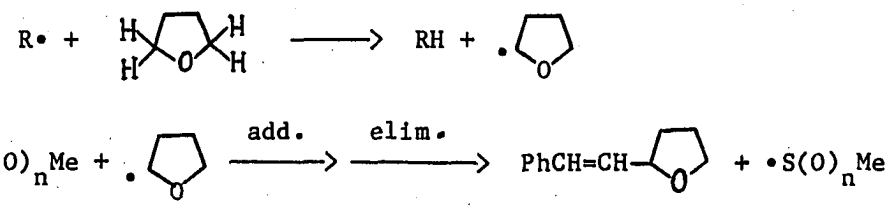
β-Styryl sulfoxide and sulfone have been reported to react with trialkylboranes to give preparative yields of the coupling products (Eq. 48) [46]. Because of the formation of β-(2-tetrahydrofuryl)styrene

$$(\underline{Z})\text{-PhCH=CHS(O)}_n\text{Me} + R_3B \xrightarrow[h\nu]{THF} PhCH=CHR + PhCH=CH\text{-}\langle O \rangle \qquad (48)$$

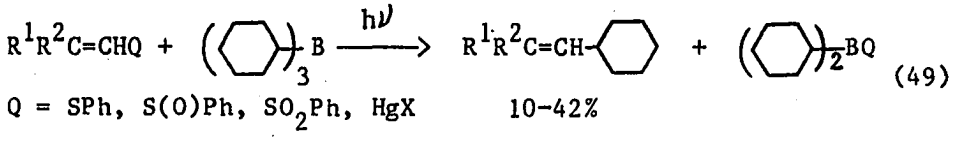
n = 1, 2 11

(11), the authors suggested that the mechanism involves a β-styryl radical intermediate. It is more likely that the reaction proceeds by a radical addition-elimination process. The formation of 11 can arise by the abstraction of a hydrogen atom of the solvent to give the corresponding radical which then adds to the double bond followed by β-elimination (Scheme 18).

Scheme 18



We have found that alkenyl derivatives of the type $R^1R^2C{=}CHQ$ (Q = S(O)Ph, SO_2Ph, HgX) undergo photostimulated reactions with tricyclohexylborane to give moderate yields of the coupling products (Eq. 49). The reaction between triethylborane and 2,2-diphenylethenyl phenyl sulfone or 2,2-diphenylethenyl iodide failed to occur under the same conditions. Results are presented in Table 12.



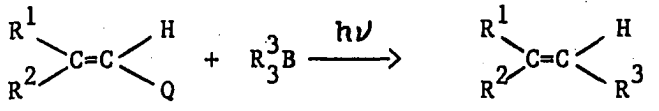
(49)

10. Reactions of 1-alkenyl compounds with triisopropylaluminum

2,2-Diphenylethenyl phenyl sulfone was found to react with triisopropylaluminum in benzene under UV irradiation to give a 54% yield of the coupling product which was analyzed by GLC and ^1H NMR. 2,2-Diphenylethenylmercury chloride also reacted with triisopropylaluminum to give the substitution product in 33% yield. Analysis by GLC showed that other unidentified products were formed in small amounts.

Other 1-alkenyl compounds failed to react with the organoaluminum compound under the same conditions. Results are summarized in Table 13.

Table 12. Photoreaction of alkenyl compounds with trialkylboranes



R^1	R^2	Q	R^3	Conditions[a]	% Yield[b] (E/Z) $R^1R^2C{=}CHR^3$
Ph	Ph	HgBr	c-C_6H_{11}	SL, 1 h	42
Ph	Ph	HgBr	c-C_6H_{11}	R, 2 h	37
Ph	Ph	SO_2Ph	c-C_6H_{11}	R, 24 h	23
Ph	Ph	I	c-C_6H_{11}	SL, 47 h	0
Ph	H	S(O)Ph	c-C_6H_{11}	R, 24 h	33
Ph	H	SO_2Ph	c-C_6H_{11}	R, 24 h	14
Ph	H	SPh	c-C_6H_{11}	SL, 47 h	10
Ph	H	HgCl	c-C_6H_{11}	R, 2 h	22
Ph	Ph	SO_2Ph	C_2H_5	R, 7 h	0

[a]Reactants (5 equiv of R^3_3B) in nitrogen-purged benzene were irradiated with a sunlamp (SL) or in a 350 nm Rayonet Photoreactor (R).

[b]Yields were determined by ^1H NMR.

Table 13. Reaction of alkenyl compounds with triisopropylaluminum

$$Ph_2C{=}CHQ + (Me_2CH)_3Al \xrightarrow{h\nu} Ph_2C{=}CHCHMe_2$$

Q	Conditions[a]	% Yield[b] $Ph_2C{=}CHCHMe_2$
SO_2Ph	PhH, R 24 h	54
HgBr	PhH, R 24 h	33
I	PhH, R 24 h	0[c]
SPh	PhH, R 24 h	0[c]
$SnBu_3$	PhH, R 24 h	0[c]

[a]An alkenyl compound (0.1 mmol) and triisopropylaluminum (0.5 mmol) in benzene (10 mL) were irradiated under N_2 in a Rayonet Photoreactor (R).

[b]Yields were determined by ^1H NMR.

[c]Starting material was recovered.

11. Reaction of 2,2-diphenylethenylmercury chloride with isopropylmagnesium iodide

2,2-Diphenylethenylmercury chloride was allowed to react with isopropylmagnesium iodide in DMSO under UV irradiation for 24 h. The reaction afforded a 35% yield of the substitution product (Eq. 50) together with a 26% yield of 1,1-diphenylethylene. No substitution product was observed in the dark.

$$Me_2CHMgI + Ph_2C{=}CHHgCl \xrightarrow{h\nu} \underset{35\%}{Ph_2C{=}CHCHMe_2} + \underset{26\%}{Ph_2C{=}CH_2} + Hg^{o} + IMgCl \qquad (50)$$

Grignard reagents and mercury(II) salts are known to react to give organomercury salts or diorganomercurials depending on the ratio of the reactants [1,3]. It is possible that the organomercury chloride reacted with isopropylmagnesium iodide to give 12 (Eq. 51). The diorgano-mercurial 12 may have decomposed under photolysis to give the

$$Ph_2C{=}CHHgCl + Me_2CHMgI \longrightarrow \underset{12}{Ph_2C{=}CHHgCHMe_2} + ClMgI \qquad (51)$$

substitution product. Scheme 19 outlines a possible mechanism.

Scheme 19

$$Ph_2C{=}CHHgCHMe_2 + {\bullet}CHMe_2 \xrightarrow{\text{add.}} \xrightarrow{\text{elim.}} Ph_2C{=}CHCHMe_2 + HgCHMe_2$$

$$HgCHMe_2 \longrightarrow Hg^{o} + {\bullet}CHMe_2$$

12. Competition reactions between alkylmercury chlorides with a deficient amount of (E)-2-phenylethenylmercury chloride or tri-n-butyl-(E)-2-phenylethenylstannane

Competition reactions between alkylmercury chlorides with nitronate anion, phenyl disulfide, or phenyl diselenide have been obtained in our research group. The relative reactivities are in the order alkyl = 3° > 2° > 1°. It was also of interest to determine the relative reactivities of alkylmercury chlorides with a deficient amount of an alkenyl compound since the relative reactivities may explain the mechanism for formation of the alkyl radical from an alkylmercurial.

The relative reactivities were determined by performing the following reactions. A ten fold excess of each of the alkylmercury

$$(\underline{E})\text{-PhCH=CHHgCl} + \underline{n}\text{-BuHgCl} + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow{h\nu} \underset{0.01}{PhCH=CHBu\text{-}\underline{n}} : \underset{1.0}{PhCH=CHC_6H_{11}\text{-}\underline{c}}$$

$$(\underline{E})\text{-PhCH=CHHgCl} + \underline{t}\text{-BuHgCl} + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow{h\nu} \underset{90}{PhCH=CHBu\text{-}\underline{n}} : \underset{1.0}{PhCH=CHC_6H_{11}\text{-}\underline{c}}$$

$$(\underline{E})\text{-PhCH=CHSnBu}_3 + \underline{n}\text{-BuHgCl} + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow{h\nu} \underset{0.2}{PhCH=CHBu\text{-}\underline{n}} : \underset{1.0}{PhCH=CHC_6H_{11}\text{-}\underline{c}}$$

$$(\underline{E})\text{-PhCH=CHSnBu}_3 + \underline{t}\text{-BuHgCl} + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow{h\nu} \underset{90}{PhCH=CHBu\text{-}\underline{n}} : \underset{1.0}{PhCH=CHC_6H_{11}\text{-}\underline{c}}$$

chlorides was employed. The observed relative ratios of the products are indicated in each reaction. The relative reactivities are obtained from the relative ratios of the substitution products. Therefore, the relative reactivities are:

(E)-PhCH=CHHgCl; alkyl = t-Bu:c-C_6H_{11}:n-Bu = 1.0:0.011:0.0001

(E)-PhCH=CHSnBu_3; alkyl = t-Bu:c-C_6H_{11}:n-Bu = 1.0:0.025:0.005

The results demonstrate that in the reaction of RHgCl with either HgCl or $Bu_3Sn\bullet$ that there is an appreciable preference for attack at the t-alkymercurial. The reactivity order of t-BuHgCl > c-C_6H_{11}HgCl > n-BuHgCl indicates that the rate of the reactions leading to alkyl radicals are controlled by the stability of the radical being formed. This suggests that attack of HgCl upon RHgCl (to give R•, $HgCl_2$ and Hg^o) or of n-$Bu_3Sn\bullet$ upon RHgCl (to give R•, Hg^o, Bu_3SnCl) are one-step reactions with an appreciable formation of the incipient alkyl radical in the transition state.

13. Mechanistic considerations

We believe that most of the reactions that we have carried out involve radical chain addition-elimination. The evidence includes the need for a radical initiator (light or azobisisobutyronitrile), the failure of the reactions to occur in the dark, and the strong retardation by di-tert-butyl nitroxide, a radical chain inhibitor.

The mechanism, except for the last step in the propagation, has already been discussed in each section. This section will consider the generation of the alkyl radical by the chain carrier Q• as shown in Eqs. (52-54). Parts of the discussion and some results are taken from ref 69.

$$Q\bullet + RHgX \longrightarrow R\bullet + QHgX;\ Q = I,\ Br,\ SPh,\ S(O)Ph,\ SO_2Ph \qquad (52)$$

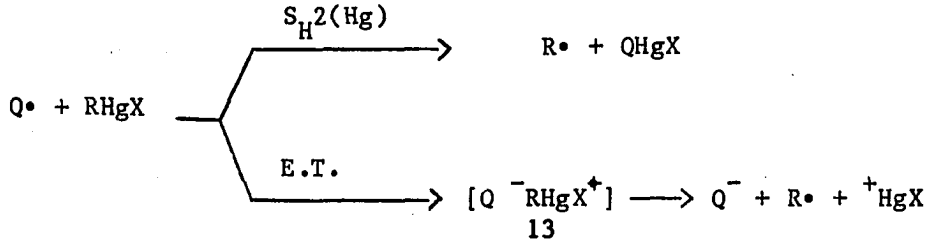
$$Q\bullet + RHgX \longrightarrow R\bullet + Hg^{o} + QX;\ Q = SnBu_3 \qquad (53)$$

$$Q\bullet + RHgX \longrightarrow R\bullet + Hg^{o} + HgX_2;\ Q = HgX \qquad (54)$$

Recently alkylmercury halides have been recognized to participate in many radical chain reactions. They can react with electron donor radicals or radical anions and electron acceptor radicals [32, 70-73].

With Q = I, Br, SPh, S(O)Ph, and SO_2Ph, Q• reacts with alkylmercury halides by either a S_H2 process at Hg or an electron transfer process as shown in Scheme 20. In the electron transfer process, Q• reacts as an

Scheme 20



electron acceptor via transition state 13.

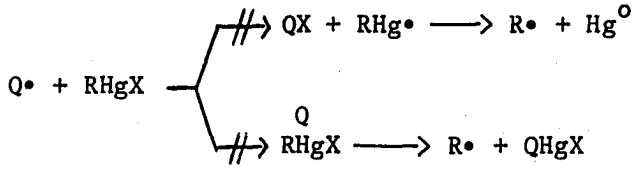
With Q = Bu_3Sn, we believe that Q• reacts with RHgX by an electron transfer process in which Q• is an electron donor and RHgX is an acceptor as shown in Eq. (55). HgX in Eq. (54) can be either a donor or an acceptor.

$$Q\bullet + RHgX \longrightarrow [Q^{+}\cdots RHgX^{-}\bullet] \longrightarrow Q^{+} + R\bullet + Hg^{o} + X^{-} \qquad (55)$$

The abstraction of the halogen atom from RHgX by Q• (Q = $SnBu_3$ or HgX) or the formation of Hg(III), $R\dot{H}gX(Q)$, intermediate as shown in

Scheme 21 are excluded. This is based on the observation that with few

Scheme 21



exceptions, the rates are faster and the product yields are higher according to the sequence R = t-butyl > 2°-alkyl > 1°-alkyl. We believe that this is a result of the incipient radical stability in the transition state of Reactions 52-54 which apparently do not involve Hg(I) or Hg(III) intermediates such as $RHgX^{\bullet-}$, RHg•, or $R\dot{H}gX(Q)$.

In competitive experiments between R^1HgCl and R^2HgCl and a deficiency of the reagent $Me_2C{=}NO_2^-$ (Eq. 56), Y-A (Y-A = PhS-SPh, PhSe-SePh) (Eq. 57), (E)-PhCH=CHHgCl (Eq. 58), and (E)-PhCH=CHSnBu$_3$ (Eq. 59), we have found the following relative reactivities:

$$R^1HgCl + R^2HgCl + Me_2C{=}NO_2^- \longrightarrow R^1Me_2CNO_2 + R^2Me_2CNO_2 + Hg^o + Cl^- \quad (56)$$

$$R^1HgCl + R^2HgCl + Y\text{-}A \longrightarrow R^1Y + R^2Y + AHgCl \quad (57)$$

$$R^1HgCl + R^2HgCl + (E)\text{-}PhCH{=}CHHgCl \longrightarrow PhCH{=}CHR^1 + PhCH{=}CHR^2 + HgCl_2 + Hg^o \quad (58)$$

$$R^1HgCl + R^2HgCl + (E)\text{-}PhCH{=}CHSnBu_3 \longrightarrow PhCH{=}CHR^1 + PhCH{=}CHR^2 + Bu_3SnCl + Hg^o \quad (59)$$

$Me_2{=}NO_2^-$; R = $PhCH_2$: t-Bu : i-Pr : n-Bu = 4.7:1.0:0.07:0.005

Y-A = PhS-SPh; R = t-Bu : i-Pr : n-Bu = 1.0:0.08: < 0.003

Y-A = PhSe-SePh; R = t-Bu : i-Pr : n-Bu = 1.0:0.3: < 0.004

(E)-PhCH=CHHgCl; R = t-Bu : c-C_6H_{11} : n-Bu = 1.0:0.011:0.0001

(E)PhCH=CHSnBu_3; R = t-Bu : c-C_6H_{11} : n-Bu = 1.0:0.025:0.005

Explanations of the observed relative reactivities based on equilibria involving R•, RHg•, $RHgCl^{\bullet-}$, or $R\dot{H}gCl(Q)$ have been excluded in specific cases. The equilibrium (Eq. 60) can be excluded in Eq. (57)

$$R^1\bullet + R^2HgCl \rightleftharpoons R^1HgCl + R^2\bullet \qquad (60)$$

since the concentration of PhSeSePh has no effect on the observed relative reactivities.

Reversible formation of $RHgCl^{\bullet-}$ as shown in Eq. (61) can be

$$RMe_2CNO_2^{\bullet-} + RHgCl \rightleftharpoons RMe_2CNO_2 + RHgCl^{\bullet-} \qquad (61)$$

eliminated since RMe_2CNO_2 fails to retard the rate of substitution in Eq. (56). Reversible formation of RHgCl(SPh) as shown in Eq. (62) seems unlikely since a strong mercury-sulfur bond is being broken more rapidly than the weaker carbon-mercury bond.

$$RHgX + PhS\bullet \rightleftharpoons R\dot{H}gX(SPh) \qquad (62)$$

If the formation of $RHgX^{\bullet-}$ or RHgX(SPh)• are not formed in a reversible manner; and, if the following equilibrium (Eqs. 63-65) were involved, the presence of an unreactive RHgX (e.g., n-BuHgCl) should

$$R^1HgCl^{\bullet-} + R^2HgCl \rightleftharpoons R^1HgCl + R^2HgCl^{\bullet-} \qquad (63)$$

$$R^1Hg\bullet + R^2HgCl \rightleftharpoons R^1HgCl + R^2Hg\bullet \quad (64)$$

$$R^1\dot{H}gCl(SPh) + R^2HgCl \rightleftharpoons R^1HgCl + R^2\dot{H}gCl(SPh) \quad (65)$$

retard the rate of reaction of a reactive RHgX (e.g., t-BuHgCl).

We have found that n-BuHgCl does not reduce the kinetic chain length of the photostimulated reaction of t-BuHgCl with $Me_2C{=}NO_2^-$, PhSSPh, and PhSeSePh, the reaction product being nearly exclusively t-$BuMe_2CNO_2$, t-BuSPh, and t-BuSePh. We conclude that the photoinitiation involves mainly t-BuHgCl and that reactions (Eqs. 52, 53) occur in a concerted fashion. Equation (54) is also believed to occur in the same concerted manner.

Because of the concerted nature of the reactions (Eqs. 52-54), the reactions between 1-alkenyl compounds with alkylmercury halides are particularly effective with 3°-alkylmercury halides. The following scheme (Scheme 22) summarizes the mechanism of the reactions presented in this part.

Scheme 22

$$R^1R^2C{=}CHQ + R^3HgX \xrightarrow{h\nu} R^1R^2C{=}CHR^3 + QHgX$$

Initiation

$$R^3HgX \xrightarrow{h\nu} R^3\bullet + HgX \ (Hg^\circ + X\bullet)$$

or $R^1R^2C{=}CHQ \xrightarrow{h\nu} R^1R^2C{=}CH\bullet + Q\bullet$

Propagation

$$R^1R^2C{=}CHQ + R^3\bullet \xrightarrow{\alpha\text{-add.}} R^1R^2\dot{C}\text{-}CHQ(R^3)$$

$$R^1R^2\dot{C}\text{-}CHQ(R^3) \xrightarrow{\beta\text{-elim}} R^1R^2C{=}CHR^3 + Q\bullet$$

$$Q\bullet + R^3HgX \xrightarrow{S_H2 \text{ or } E.T.} R^3\bullet + QHgX$$

(Q = I, Br, SPh, S(O)Ph, SO_2Ph)

or $$Q\bullet + R^3HgX \xrightarrow{E.T.} R^3\bullet + QX + Hg^o$$

(Q = $SnBu_3$, HgX)

C. Conclusion

Substituted 1-alkenyl compounds of the type $R^1R^2C{=}CHQ$ (Q = I, Br, HgX, SPh, S(O)Ph, SO_2Ph, $SnBu_3$) react with organomercurials, RHgX and R_2Hg, to afford substitution products. The yields are usually high with R^1 or R^2 = Ph due to the stabilization of the resulting radical intermediates. Stabilities of the adding radicals also play an important role in determining the yields of the substitution products which, in general, increase in the order 1°-alkyl- < 2°-alkyl- < 3°-alkylmercury halide.

The reactions are believed to occur via a free-radical addition-elimination process. The regioselective α-addition of radicals is influenced by the substituents (R^1,R^2) at the β-position. The stabilization of the adduct radical by Q, which could also influence the regiochemistry of the α attack, seems unimportant at least in the case

where Q = I.

Alkylmercury halides and diorganomercurials react with Q• by either a S_H2 or an electron transfer process in which the organomercurials accept or donate an electron. In the electron transfer process, the reaction is believed to occur in a concerted manner. Mercury(I) and (III) intermediates such as RHg• and RHg(X)Q• are not believed to be involved in these reactions.

Heteroatom-centered radicals, PhS•, PhSe•, $PhSO_2$•, and $(EtO)_2PO$•, can be generated from $Hg(SPh)_2$, $Hg(SePh)_2$, $Hg(SO_2Ph)_2$ and $(EtO)_2\overset{O}{\overset{\|}{P}}HgCl$ or $[(EtO)_2\overset{O}{\overset{\|}{P}}]_2Hg$, respectively. These heteroatom-centered radicals add effectively to the double bonds of the 1-alkenyl system ($R^1R^2C{=}CHQ$) to give the substitution products.

Other substrates which react with 1-alkenyl compounds to give the coupling products include triisopropylaluminum, tricyclohexylborane, and RMgX. The reactions, however, afford low yields and appear to be limited to Q = $PhSO_2$ or HgX.

Tri-<u>n</u>-butyl-1-alkenylstannanes react with phenyl disulfide, benzyl disulfide and benzenesulfonyl chloride to give excellent yields of the substitution products. The reaction with phenyl diselenide, on the other hand, failed to proceed under the same conditions. It appears that tri-<u>n</u>-butystannyl radical does not react readily with phenyldiselenide by the S_H2 process which occurs readily with phenyl disulfide.

Tri-<u>n</u>-butyl-1-alkenylstannanes failed to react with certain substrates with which a reasonable chain mechanism could be postulated.

These substrates include esters of N-hydroxypyridine-2-thione (7), t-butyl phenyl sulfide, N-(cyclohexyloxythiocarbonyl)imidazole (10), 2-methyl-2-nitropropane and 2-bromo-2-nitropropane.

A photostimulated reaction of tri-n-butylphenylstannane with alkyl halides, organomercurials, phenyl disulfide, and benzenesulfonyl chloride was observed. Unfortunately, the reactions afforded only low yields of substitution products.

D. Experimental Section

1. Instrumentation and techniques

Analytical gas chromatography (GLC) was performed on a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. Preparative GLC was performed on an Aerograph Model 700 gas chromatograph. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. G.C. mass spectra (GCMS) were recorded on a Finnegan 4000 spectrometer. High resolution mass spectra (MS) were recorded on an AEI MS 902 mass spectrometer. ^{1}H NMR (60 MHz) were recorded on a Varian EM 360A or EM 360L spectrometer. High resolution ^{1}H NMR (300 MHz) were recorded on a Nicolet NT 300 spectrometer.

GLC yields were determined by using an internal standard (naphthalene or biphenyl) and, in most cases, were corrected with predetermined response factors. ^{1}H NMR yields were determined by integration with a known amount of an internal standard (usually dibromomethane).

2. Solvents and chemical reagents

Solvents were purchased from Fisher or Baker. Dimethyl sulfoxide (DMSO) was distilled from calcium hydride and stored over 4A Molecular Sieves under nitrogen. Benzene and tetrahydrofuran (THF) were distilled from lithium aluminum hydride (LAH) and stored over 4A Molecular Sieves under nitrogen. Diethyl ether and other solvents were purchased and used without purification.

Chemical reagents in high purity grades were purchased mostly from Aldrich. In most cases the reagents were used without further purification.

3. Preparation of organomercurials

Most of the alkylmercury halides were prepared by literature procedures [3]. They were usually prepared from Grignard reagents and mercury salts (1:1 equiv) in THF. Thus prepared were n-butylmercury chloride (lit. [74] mp 127.5 °C), neopentylmercury chloride (lit. [75] mp 117-118 °C), benzylmercury chloride (lit. [76] mp 104 °C), isopropylmercury chloride (lit. [77] mp 94.5-95.5 °C), cyclohexylmercurychloride (lit. [78] mp 163-164 °C), and t-butylmercury chloride (mp 110-113 °C lit. [79] mp 123 °C). The preparation of t-butylmercury chloride in refluxing THF in the usual manner afforded a low yield (20-30%) of the product because of the instability of the mercurial. The yield, however, could be improved to over 50% yield by performing the reaction at a low temperature. Thus a solution of t-butylmagnesium chloride prepared from t-butyl chloride and Mg in THF under a nitrogen atmosphere was cooled in an ice bath while an

equimolar amount of mercuric chloride in THF was added dropwise with stirring. After the addition, the mixture was stirred overnight in the ice bath. The reaction mixture was then poured into 2% acetic acid in ice water containing several equivalents of sodium chloride. The white precipitate of t-butylmercury chloride was filtered and dissolved in chloroform and filtered again to remove the remaining mercuric chloride. Chloroform was then removed under vacuum to give a white solid of t-butylmercury chloride. All of the alkylmercury chlorides were recrystallized from 95% ethanol. t-Butylmercury chloride, unlike other alkylmercury chlorides, slowly decomposed to give mercury metal when stored on a lab bench. Therefore, it was kept in a closed container in a refrigerator.

α-Mercurybisacetophenone (lit. [80] mp 171-172.5 °C), mercuric phenylmercaptide (mp 149-150 °C lit. [81] mp 150 °C), mercuric phenylselenide (mp 148.5-149 °C lit. [82] mp 152-153 °C), mercuric benzenesulfinate (lit. [83] mp 130 °C (dec.)), bis(diethoxyphosphinyl)mercury (lit. [84] mp 56.8-58.2 °C), diethoxyphosphinylmercury chloride (lit. [84] mp 103-104 °C), and mercuric trifluoroacetate (lit. [85] mp 164-168 °C) were synthesized by the methods described in the literature.

4. Preparation of alkenyl derivatives

1,1-Diphenylethylene was a precursor of many alkenyl derivatives employed in this study. The method for the preparation of 1-(m-tolyl)-1-phenylethylene [86] was modified to synthesize 1,1-diphenylethylene. Thus methyl iodide (1 mol) and magnesium turnings (1

mol) were allowed to react in 1 L of diethyl ether in a round bottom flask equipped with a dry-ice condenser. The reaction occurred vigorously; and, therefore, the flask was immersed in an ice bath. After completion, benzophenone (0.7 mol) in 250 mL of diethyl ether was added slowly and the mixture was heated to reflux for 2 h. The reaction mixture was then poured into 1.4 L of 6 N aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the product was distilled in the presence of a few crystals of iodine at 7 mmHg. Dehydration occurred during the distillation and the product was collected at 120-130 °C. The pale orange distillate was dilute with either and washed with 10% aqueous sodium thiosulfate to remove the iodine. After the removal of ether, the product was fractionally distilled to give 80 g of a colorless liquid product (bp 100 °C at 1 mmHg).

2,2-Diphenylethenyl bromide was prepared by bromination of 1,1-diphenylethylene. Thus bromine (0.3 mol) was slowly added to a solution of 1,1-diphenylethylene (0.3 mol) in 100 mL of carbon tetrachloride with stirring. After the addition, the mixture was stirred for an additional 0.5 h. The solvent was removed in vacuo and the product was distilled at reduced pressure. Dehydrobromination occurred during the distillation and the product obtained was the ethenyl bromide. The product was redistilled again by fractional distillation to give a pale yellow liquid (bp 135 °C at 1.5 mmHg) which solidified upon storing at room temperature.

^{1}H NMR ($CDCl_3$) δ 7.28(s,5H), 7.18(s,5H), 6.68(s,1H).

Tri-n-butyl-2,2-diphenylethenylstannane was prepared from the Grignard reagent and tri-n-butyltin chloride [87]. The Grignard reagent was prepared from 2,2-diphenylethenyl bromide (0.05 mol) and magnesium turnings (0.05 mol) in 30 mL dry THF. The mixture was heated until the reaction started. Once the reaction had started, 70 mL of THF was added and the reaction mixture was heated to reflux for 2 h. After completion of the reaction, the Grignard reagent solution was transferred to another flask under an atmosphere of nitrogen. A solution of tri-n-butyltin chloride (0.04 mol) in THF (50 mL) was added slowly and the mixture was refluxed for 72 h. The reaction mixture was then poured into 200 mL of saturated aqueous ammonium chloride solution. The organic products were extracted with ether, washed with water and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give yellow liquid product. The product was purified by distillation at reduced pressure (bp 162-164 °C at 0.35 mmHg). The distillation, however, yielded only ca. 50% of the alkenyltin as the remaining material polymerized in the flask. Column chromatography with hexane as the eluent was found to be a better method to purify the alkenyltin product: ^{1}H NMR ($CDCl_3$) δ 7.4-7.1(m,10H), 6.65(s,1H), 1.55-0.5(m,27H).

Tri-n-butyl-2,2-dimethylethenyltstannane was also prepared by similar procedure from the reaction of 2,2-dimethylethenylmagnesium bromide and tri-n-butyltin chloride in THF. The reaction was heated at reflux for only 19 h. The same workup afforded a product which

was fractionally distilled to give the colorless ethenylstannane (bp 84-85 °C at 0.07 mmHg). ^{1}H NMR ($CDCl_3$) δ 5.35(br,S,1H), 2.0-0.65(m,33H).

2,2-Dimethylethenylmercury bromide was synthesized from the Grignard reagent and mercuric bromide as follows. 2,2-Dimethylethenyl bromide (0.1 mol) from the dehydrobromination of 1,2-dibromo-2-methylpropane [88,89] was allowed to react with magnesium (0.1 mol) in 10 mL of dry THF. The mixture was heated to initiate the reaction. An additional 40 mL of THF was added after the reaction had started and the reaction was heated at reflux for 1 h. The mixture was filtered through glass wool into another flask. Mercuric bromide (0.1 mol) was added slowly and the reaction stirred at reflux overnight. The mixture was then poured into ice water containing several equivalents of sodium bromide. The product was extracted with chloroform, washed with water and dried over sodium sulfate. The solvent was removed in vacuo to give a pale yellow solid which was recrystallized from 95% ethanol (mp > 200 °C. ^{1}H NMR ($CDCl_3$) δ 5.55(br,s,1H), 1.95(s,3H), 1.9(s,3H).

2,2-Dimethylethenyl iodide was prepared from reaction of 2,2-dimethylethenyl mercury bromide (10 mmol) and iodine (10 mmol) in 100 mL of chloroform. The reaction was stirred at room temperature for 2 h and the solid was filtered off. The filtrate was washed with 10% aqueous sodium thiosulfate solution and dried over sodium sulfate. The solvent was removed under vacuum to give a liquid product which was indicated to be pure by ^{1}H NMR. ^{1}H NMR ($CDCl_3$) δ 5.8(br,s,1H),

1.89(s,3H), 1.84(s,3H).

Literature procedures were employed for the preparation of 2,2-diphenylethenylmercury chloride (mp 141-142 °C lit. [90] mp 143 °C) and bromide (mp 156-157 °C lit [90] mp 157 °C), 2,2-diphenylethenyl iodide (mp 40-40.5 °C lit. [90] mp 40-41 °C), 2,2-diphenylethenyl phenyl sulfone (mp 113-114 °C lit. [91] mp 114-115 °C), 2,2-diphenylethenyl phenyl sulfide [37], (E)-2-phenylethenylmercury chloride (lit. [92] mp 216-217 °C), (E)-3,3-dimethyl-1-butenylmercury bromide (lit. [92] mp 81-82 °C), (E)-2-phenylethenyl phenyl sulfoxide [46], 1-iodocyclopentene [93], vinyl iodide [94], (E)-2-phenylethenyl iodide [95], (E)-2-phenylethenyl phenyl sulfide [96], (E)-2-phenylethenyl phenyl sulfone (lit. [96] mp 74-75 °C), tri-n-butylvinylstannane [87], tri-n-butylphenylstannane [97].

5. Preparation of triisopropylaluminum

Triisopropylaluminum was prepared by the same method reported for the synthesis of triisopentylaluminum [98]. Thus isopropyl bromide (0.3 mole) and magnesium (0.3 mol) were allowed to react in 100 mL of diethyl ether. After completion, the Grignard reagent was added dropwise to well-stirred, boiling toluene and the ether was boiled off. The suspension of Grignard reagent was cooled to room temperature and anhydrous aluminum chloride (0.05 mole) was added slowly with vigorous stirring. The mixture was stirred at room temperature overnight and the precipitate was centrifuged off. The triisopropylaluminum was isolated by vacuum distillation (bp 44-46

°C at 2 mmHg). This compound is sensitive to air and, therefore, was handled under a nitrogen atmosphere. ^{1}H NMR ($CDCl_3$) δ 1.55-0.9 (m).

6. Photoreactions of 2,2-diphenylethenyl iodide with alkylmercurials

2,2-Diphenylethenyl iodide (0.1 mmol) and the alkylmercurial were dissolved in a solvent (10 mL) in a Pyrex tube equipped with a rubber septum. After a nitrogen-purge for 5 min, the mixture was irradiated at 350 nm in a Rayonet Photoreactor for a period of time (see Table 1). The reaction mixture was clear, but in some cases contained a small amount of mercury metal.

After completion of the reaction, benzene (20 mL) was added to the reaction mixture and the mixture was washed once with water and twice with 20 mL of 10% aqueous sodium thiosulfate solution to remove the remaining alkylmercurial. The mixture was then dried over anhydrous sodium sulfate and the solvent was removed under vacuum to give a pale yellow or colorless oily residue. GLC analysis indicated the presence of only one compound which was identified by ^{1}H NMR and GCMS to be the substitution product. Yield of the product was determined by ^{1}H NMR by adding a known amount of dibromomethane. Yields of the substitution products from the reaction of 1-alkenyliodide and alkylmercurials are summarized in Table 1.

Identification of the substitution products, in many cases, was confirmed by comparison of their ^{1}H NMR and GCMS data with those of the authentic compounds synthesized by known literature methods or by comparison of their ^{1}H NMR data with those of the compounds reported in the literature. ^{1}H NMR and GCMS data of the substitution products are

given in Table 14.

7. Reaction of 2,2-diphenylethenyl iodide with isopropylmercury chloride in the dark

2,2-Diphenylethenyl iodide (0.1 mmol) and isopropylmercury chloride (0.5 mmol) were dissolved in 10 mL of nitrogen-purged DMSO in a Pyrex tube. The tube was wrapped with aluminum foil to exclude light and placed in a Rayonet Photoreactor at 40-45 °C. After 24 h, the usual workup afforded only the iodide starting material. None of the substitution product was observed.

8. Photoreaction of 2,2-diphenylethenyl iodide with isopropylmercury chloride in the presence of di-tert-butyl nitroxide (DTBN)

2,2-Diphenylethenyl iodide (0.1 mmol), isopropylmercury chloride (0.5 mmol) and DTBN (0.005 mmol) in 10 mL of nitrogen-purged DMSO in a Pyrex tube were irradiated in a Rayonet Photoreactor for 1 h. The usual workup gave a product which was identified to be the unchanged iodide starting material. No substitution product was observed. The control reaction (in the absence of DTBN) carried out exactly under the same conditions afforded the substitution product in 73% yield.

9. Photoreactions of 1-alkenylmercury halides with alkylmercurials

A general procedure involved 0.1 mmol of 1-alkenylmercury halide and 0.5 mmol of the alkylmercurial dissolved in 10 mL of DMSO in a Pyrex tube equipped with a rubber septum. After a 5-min nitrogen purge, the mixture was irradiated in a Rayonet Photoreactor at 40-45 °C for 12 h during which time mercury metal precipitated as mercury

Table 14. ^{1}H NMR and GCMS data for the substitution products from the reactions of alkenyl iodides with organomercurials

Compound	GCMS[a] m/e (relative intensity)	^{1}H NMR[b] (ppm, δ)
$Ph_2C{=}CHCH_2CH_2CH_2CH_3$	238(0.5), 236(30,M^+), 193(94), 115(100), 91(43)	7.6-6.9(m,10H), 6.05(t,1H), 2.3-0.7(m,9H)
$Ph_2C{=}CHCH(CH_3)_2$	224(0.8), 222(50,M^+), 207(92), 129(100), 91(44)	7.45-7.05(m,10H), 5.9(d,1H), 2.8-2.1(m,1H), 1.02(d,6H)
$Ph_2C{=}CHC_6H_{11}$-c	264(0.6), 262(32,M^+), 180(100, 91(60)	7.45-6.9(m,10H), 5.9(d,1H), 2.35-0.8(m,11H)
$Ph_2C{=}CHC(CH_3)_3$	238(1), 236(62,M^+), 221(100), 143(72), 91(37)	7.5-6.9(m,10H), 6.05(s,1H), 0.98(s,9H)
$(CH_3)_2C{=}CHC_6H_{11}$-c	138(28,M^+), 123(29), 95(61), 81(65), 67(100), 55(71)	---
$Ph_2C{=}CHCH_2\overset{O}{\overset{\|}{C}}Ph$	298(2,M^+), 193(25), 105(100)	8.2-6.9(m,15H) 6.41(t,1H), 3.8(d,2H)

[a]Only M+2, M^+ and major fragments are given.

[b]60 MHz; in $CDCl_3$.

beads.

After completion, the reaction mixture was decanted from the mercury beads into water and extracted with benzene (20 mL). The extract was washed twice with 20 mL of 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. Benzene was then removed in vacuo to afford a liquid product which was analyzed by GLC, ^{1}H NMR and GCMS. Yields of the substitution products were determined by ^{1}H NMR by the procedure described earlier and the results are presented in Table 2. Identification of the products was confirmed by comparison of their GLC retention times, ^{1}H NMR and GCMS data with those of the products obtained previously.

In addition to the data in Table 14, the following ^{1}H NMR and GCMS data were obtained for the following compounds.

4,4-Dimethyl-1,1-diphenyl-1-pentene:

GCMS, m/e (relative intensity) 252(0.14), 250(10,M^+), 193(89), 115(100), 91(40), 57(56).

1,1,3-Triphenylpropene:

GCMS, m/e (relative intensity) 272(0.38), 270(19,M^+), 192(100), 179(49), 178(49), 115(65), 91(71).

4,4-Dimethyl-1-phenyl-1-pentene:

GCMS, m/e (relative intensity) 174(10,M^+), 159(3), 118(31), 117(35), 91(12), 57(100).

1,3-Diphenylpropene:

GCMS, m/e (relative intensity) 196(0.72), 194(79,M^+), 115(100), 91(50).

3-Methyl-1-phenyl-1-butene:

^{1}H NMR ($CDCl_3$) δ 7.32-7.05(m,5H), 6.32-6.2(m,2H), 2.7-2.2(m,1H), 1.05(d,6H, J=6.5 Hz).

GCMS, m/e (relative intensity) 146(31,M^+), 131(100), 91(50).

(2-Phenylethenyl)cyclohexane:

^{1}H NMR ($CDCl_3$) δ 7.5-7.0(m,5H), 6.38-6.2(m,2H), 2.6-0.7(m,11H).

GCMS, m/e (relative intensity) 188(0.2), 186(17,M^+), 104(100), 91(17).

(3,3-Dimethyl-1-butenyl)cyclohexane:

GCMS, m/e (relative intensity) 166(12,M^+), 83(39), 82(100), 67(47), 55(70).

10. Photoreactions of 2,2-diphenylethenyl iodide and 2-methoxy-(2,2-diphenyethenyl)cyclohexane with alkylmercury trifluoroacetate generated in situ

Mercuric trifluoroacetate (1 mmol) and freshly distilled cyclohexene (1 mmol) were dissolved in 10 mL of methanol in a Pyrex flask. The mixture was stirred at room temperature for 10 min to give 2-methoxycyclohexylmercury trifluoroacetate. This mercurial was used without isolation. Thus 2,2-diphenylethenyl iodide (1 mmol or 0.2 mmol) was added to the reaction mixture in methanol and a stream of nitrogen was passed through the mixture for 5 min. The mixture was then irradiated in a Rayonet Photoreactor for 24 h. After the irradiation, the mixture was poured into water and extracted with benzene (20 mL). The extract was washed with 2 x 20 mL of 10% aqueous sodium thiosulfate and dried over anhydrous sodium sulfate. The oily

residue, after the removal of the solvent, was analyzed by GLC, ^{1}H NMR and GCMS which indicated the presence of the substitution product (2,2-diphenylethenyl(2-methoxy)cyclohexane,5) in 75% yield, 1,1-diphenylethylene (7% yield) and small amounts of unidentified products.

Reaction of 2,2-diphenylethenylmercury chloride and 2-methoxycyclohexylmercury trifluoroacetate was also carried out by the same procedure under the same conditions. DMSO 2 mL was added to help dissolve the alkenylmercurial. The reaction afforded 2-methoxy-(2,2-diphenylethenyl)cyclohexane(5) in 69% yield and a small amount of an unidentified product.

The substitution product 2-methoxy-(2,2-diphenylethenyl)-cyclohexane) obtained from both reactions had the following ^{1}H NMR and GCMS data:

^{1}H NMR ($CDCl_3$) δ 7.3(s,5H),7.22(s,5H), 5.98(d,1H), 3.52-2.8(m,4H), 2.5-0.8(m,9H).

GCMS, m/e (relative intensity) 292(55,M^+), 260(40), 217(51), 205(78), 112(100), 91(75).

2-Methoxy-2-phenylethylmercury trifluoroacetate generated in situ from the reaction of mercuric trifluoroacetate and styrene in methanol was allowed to react with 2,2-diphenylethenyl iodide and 2,2-diphenylethenylmercury chloride. The reactions were carried out by a procedure similar to the reactions with 2-methoxycyclohexylmercury trifluoroacetate described above. The reactions afforded 4-methoxy-1,1,4-triphenyl-1-butene (6). The substitution product (4-methoxy-

1,1,4-triphenyl-1-butene, 6) had the following ^{1}H NMR and GCMS data:

^{1}H NMR ($CDCl_3$) δ 7.5-6.9 (m,15H), 6.12(t,1H), 4.18(t,1H), 3.2(s,3H), 2.55(m,2H).

GCMS, m/e (relative intensity) 314(0.14,M^+), 121(100), 91(16), 77(16).

11. Photoreactions of 1-alkenyl phenyl sulfides, sulfoxide and sulfone with alkylmercury chlorides

The alkenyl compound (0.1 mmol) and the alkylmercury chloride (see Table 14) were dissolved in 10 mL of nitrogen-purged DMSO. The mixture was irradiated in a Rayonet Photoreactor. After completion of the reaction, the mixture was poured into water and extracted with benzene (20 mL). The extract was washed twice with 20 mL of 10% aqueous sodium thiosulfate solution, dried and concentrated in vacuo. The resulting product was analyzed by GLC to contain the substitution product. Identity of the product was confirmed by comparison of its GLC retention time, ^{1}H NMR and GCMS data with those of the product obtained previously. Results are summarized in Table 14.

12. Photoreactions of alkenyl compounds with mercuric phenylmercaptide, mercuric phenylselenide and mercuric benzenesulfinate

The alkenyl derivative, $R^1R^2C{=}CHQ$ (Q = I, HgX, $SnBu_3$, SO_2Ph), (0.1 mmol) and mercuric phenylmercaptide (0.1 mmol) were dissolved in 10 mL of nitrogen-purged DMSO in a Pyrex tube equipped with a rubber septum. The mixture was irradiated in a Rayonet Photoreactor for 20-

24 h (see Table 5). The usual workup gave a liquid product which was identified by GLC, ^{1}H NMR and GCMS to be the substitution product. Identity of the product was further confirmed by comparison of its GLC retention time, ^{1}H NMR and GCMS to those of the authentic compound. All the results are presented in Table 5.

Reactions with mercuric phenylselenide and mercuric benzenesulfinate were also carried out by the same procedure. All the products were confirmed by comparison of their GLC retention times, ^{1}H NMR and GCMS data with those of the authentic compounds. Results and experimental conditions are summarized in Tables 6 and 7.

2-Phenylethenyl phenyl selenide [99,100], 2-methyl-1-propenyl phenyl selenide [101], 3,3-dimethyl-1-butenyl phenyl selenide [99,100] and phenyl vinyl selenide [100,102] have been reported in the literature.

The following data were obtained for the substitution products.

2,2-Diphenylethenyl phenyl selenide:

^{1}H NMR ($CDCl_3$) δ 7.7-7.2(m,15H), 7.1(s,1H).

GCMS, m/e (relative intensity) 336(47,M^+), 256(22), 255(25), 179(34), 178(100), 169(23), 167(29), 77(29), 51(32).

(E)-2-Phenylethenyl phenyl selenide:

GCMS, m/e (relative intensity) 260(46,M^+), 258(24), 180(71), 179(70), 178(39), 169(26), 165(26), 103(30), 102(37), 78(36), 77(100), 51(71).

(Z)-2-Phenylethenyl phenyl selenide:

GCMS, m/e (relative intensity) 260(39,M^+), 258(19), 180(63),

179(62), 178(33), 169(23), 165(23), 103(29), 102(34), 78(35), 77(100), 51(68).

2-Methyl-1-propenyl phenyl selenide:

^{1}H NMR ($CDCl_3$) δ 7.5-7.1(m,5H), 6.12(br,s,1H), 1.9(s,3H), 1.85(s,3H).

GCMS, m/e (relative intensity) 212(48,M^+), 210(24), 132(29), 131(79), 117(50), 116(33), 115(27), 105(28), 91(89), 78(66), 77(62), 55(87), 53(100), 51(82), 50(30).

(E)-3,3-Dimethyl-1-butenyl phenyl selenide:

GCME, m/e (relative intensity) 240(22,M^+), 145(27), 83(100), 55(72).

Phenyl vinyl selenide:

GCMS, m/e (relative intensity) 184(98,M^+), 183(79), 182(56), 181(53), 180(35), 104(90), 103(56), 91(40), 78(100), 77(98), 51(89), 50(39).

13. Photoreactions of 1-alkenyl compounds with diethoxyphosphinylmercury chloride and bis(diethoxyphosphinyl)mercury

The 1-alkenyl compound (0.1 mmol) and diethoxyphosphinylmercury chloride in 5 mL of nitrogen-purged DMSO in a Pyrex tube were irradiated at 350 nm in a Rayonet Photoreactor. After completion, the mixture was poured into water and extracted with benzene. The extract was washed with 10% aqueous sodium thiosulfate solution (two times) and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting liquid product was analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated the presence of the substitution

product. The yield of the product was determined by either GLC or ^{1}H NMR. All of the results are summarized in Table 8.

Reactions of 1-alkenyl derivatives with bis(diethoxyphosphinyl)mercury were also performed under similar conditions. Results are presented in Table 9. Table 15 presents ^{1}H NMR and GCMS data of the substitution products.

14. Photoreactions of 2,2-diphenylethenyl iodide and 2,2-diphenylethenylmercury bromide with diethoxyphosphinylmercury chloride in the presence of di-t-butyl nitroxide (DTBN)

A mixture of 2,2-diphenylethenyl iodide (0.1 mmol), diethoxyphosphinylmercury chloride (0.1 mmol) and DTBN (0.01 mmol) in 10 mL of nitrogen-purged DMSO was irradiated with a 275 W sunlamp placed about 15-20 cm from the reaction vessel. After irradiation for 1 h, the usual workup afforded no substitution product. Only the unreacted ethenyl iodide was recovered in 95% yield. The control reaction without DTBN, carried out under the same conditions, on the other hand, gave a 20% yield of the substitution product.

The reaction of 2,2-diphenylethenylmercury bromide (0.1 mmol) and diethoxyphosphinylmercury chloride (0.3 mmol) in 10 mL of DMSO was irradiated at 350 nm in a Rayonet Photoreactor. The reaction afforded a 59% yield of the substitution product. In contrast, the reaction in the presence of 10 mol% of DTBN which was performed at the same time and under the same conditions failed to react to give any of the substitution product.

Table 15. ^{1}H NMR and GCMS data of substituted vinylphosphonates

Compound	GCMS[a] (m/e) (relative reactivity)	^{1}H NMR[b] (ppm, δ)
$Ph_2C{=}CHP(O)(OEt)_2$	316(5,M^+), 207(40), 180(36), 178(100)	7.5-7.15(m,10H), 6.15(d, 1H, J_P=16.8 Hz), 3.85(m, 4H), 1.10(t, 6H,J_H=7 Hz)
(E)-$PhCH{=}CHP(O)(OEt)_2$[c]	240(12,M^+), 131(100)	7.9-7.15(m,5+1H), 6.6-5.7(m,1H), 4.12(m,4H), 1.34 (t,6H,J_H=7 Hz)
(E)-$Me_3CCH{=}CHP(O)(OEt)_2$	220(8,M^+), 149(29), 138(32), 111(49), 83(100)	6.78(dd,1H,J_H=17.5 Hz, J_P=23 Hz), 5.43(dd, 1H, J_H=17.5 Hz, J_P=20 Hz), 4.08 (m,4H), 1.32(t,6H, J_H=7 Hz)
$Me_2C{=}CHP(O)(OEt)_2$	192(12,M^+), 136(92), 121(35), 83(100)	---

[a] Only M^+ and major fragments are given.

[b] 60 MHz; in $CDCl_3$.

[c] Vinyl proton signals have been reported in ref 103. ^{1}H NMR of the (Z)-isomer has been reported in ref 104.

15. Reaction of 2,2-diphenylethenyl iodide and bis(diethoxyphosphinyl)mercury in the dark

2,2-Diphenylethenyl iodide (0.1 mmol) and bis(diethoxyphosphinyl)-mercury (0.1 mmol) were dissolved in 10 mL of DMSO in a Pyrex flask. The mixture was degassed for 5 min and the flask was wrapped with aluminum foil to exclude light. The flask was placed in a Rayonet Photoreactor at 40-45 °C for 24 h. The reaction mixture was poured into water and extracted with benzene by the usual workup. GLC analysis indicated no substitution product and only the iodide starting material was present in the mixture.

16. Photoreaction of tri-n-butyl-2,2-dimethylethenylstannane with phenyl disulfide

Tri-n-butyl-2,2-dimethylethenylstannane (3 mmol) and phenyl disulfide (3.6 mmol) were dissolved in 10 mL of benzene in a Pyrex flask equipped with a rubber septum. The mixture was degassed for 5 min and irradiated with a 275-W sunlamp placed 15 cm from the reaction flask. The progress of the reaction was followed by GLC which indicated that all the alkenylstannane starting material had been consumed when irradiated for 1 h. The reaction, however, was irradiated for 2 h. Benzene was then removed under vacuum to give an oily residue which was found to contain the substitution product in 97% yield. The substitution product, 2-methyl-1-propenyl phenyl sulfide, was isolated by vacuum distillation. The product thus obtained was a colorless liquid which had bp 40-53 °C at 0.007 mmHg. The product was identified by ^{1}H NMR and GCMS. The ^{1}H NMR of 2-methyl-1-propenyl phenyl sulfide

has been reported in the literature [105].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.09(m,5H), 5.91(s,1H), 1.93(s,3H), 1.87(s,3H).

GCMS, m/e (relative intensity) 166(5), 164(100,M^+), 149(31), 55(46).

17. Photoreaction of tri-n-butyl-2,2-dimethylethenylstannane with phenyl disulfide in the presence of di-tert-butyl nitroxide (DTBN)

Tri-n-butyl-2,2-dimethylethenylstannane (3 mmol), phenyl disulfide (3.6 mmol) and DTBN (0.15 mmol) were dissolved in 10 mL of benzene in a Pyrex flask. After a nitrogen purge, the mixture was irradiated with a 275-W sunlamp placed about 15 cm from the reaction flask for 1 h. The mixture was concentrated and analyzed by GLC and ^{1}H NMR. No substitution product was observed. The mixture consisted of only the unreacted starting materials in quantitative yields.

18. Reaction of tri-n-butyl-2,2-dimethylethenylstannane with phenyl disulfide in the dark

Tri-n-butyl-2,2-dimethylethenylstannane (3 mmol) and phenyl disulfide (3.6 mmol) were dissolved in 10 mL of nitrogen-purged benzene in a round-bottom flask. The flask was wrapped with aluminum foil to exclude light and was heated at 80 °C in an oil bath. After 2 h, the mixture was concentrated and analyzed by GLC and ^{1}H NMR which indicated the presence of the unreacted starting materials. No substitution product was observed.

19. Thermal reaction of tri-n-butyl-2,2-dimethylethenylstannane with phenyl disulfide

The mixture of tri-n-butyl-2,2-dimethylethenylstannane (3 mmol), phenyl disulfide (3.6 mmol) and azobisisobutyronitrile (AIBN) (0.3 mmol) in 10 mL of benzene was heated at 80 °C in an oil bath for 2 h. The reaction mixture was then concentrated and analyzed by ^{1}H NMR which indicated the presence of the substitution product, 2-methyl-1-propenyl phenyl sulfide, in 97% yield.

20. Photoreaction of tri-n-butyl-2,2-dimethylethenylstannane with benzyl disulfide

Reaction of tri-n-butyl-2,2-dimethylethenystanne (3 mmol) and benzyl disulfide (3.6 mmol) in 10 mL of nitrogen-purged benzene was irradiated with a 275-W sunlamp placed about 15 cm from the reaction flask. GLC indicated that the reaction required 8 h to consume all of the ethenystannane. After completion of the reaction, benzene was removed in vacuo to give a colorless oil which had a very unpleasant smell. The mixture was analyzed by ^{1}H NMR and GCMS which indicated the presence of the substitution product, 2-methyl-1-propenyl benzyl sulfide, in 84% yield. The ^{1}H NMR of this compound has been reported in ref 105.

^{1}H NMR ($CDCl_3$) δ 7.22(s,5H), 5.56(br,s,1H), 3.73(s,2H), 1.67(s,6H).

GCMS, m/e (relative intensity) 180(1), 178(23,M^+), 91(100), 65(22).

21. Photoreaction of tri-n-butyl-2,2-dimethylethenylstannane and benzenesulfonyl chloride

A mixture of tri-n-butyl-2,2-dimethylethenylstannane (3 mmol) and benzenesulfonyl chloride (3.6 mmol) in 10 mL of nitrogen-purged benzene was irradiated with a 275-W sunlamp placed about 15 cm from the reaction flask. The reaction was shown by GLC to be complete when irradiated for 4 h. After completion of the reaction, benzene was distilled off to yield an oily residue. ^{1}H NMR analysis indicated the presence of the substitution product, 2-methyl-1-propenyl phenyl sulfone, in 90% yield. The product was isolated by removing tri-n-butylstannane chloride and the remaining benzenesulfonyl chloride under reduced pressure. The substitution product remaining in the flask soon solidified. The solid was recrystallized from ethanol to give a white crystal 2-methyl-1-propenyl phenyl sulfone in 53% yield (mp 47.5° - 48.5 °C. The isolated yield was low because of loss of the product during the distillation.

^{1}H NMR (300 MHz, $DCDl_3$) δ 7.89-7.80(m,2H), 7.59-7.44(m,3H), 6.19(s,1H), 2.15(s,3H), 1.89(s,3H).

MS calculated for $C_{10}H_{12}O_2S$:196.05581. Measured: 196.05617. Error: 1.8 ppm.

22. Photoreaction of tri-n-butyl-2,2-dimethylethenylstannane with phenyl diselenide

Tri-n-butyl-2,2-dimethylethenylstannane (0.3 mmol) and phenyl diselenide (0.35 mmol) were dissolved in C_6D_6 (1 mL) in a NMR tube. The mixture was irradiated with a 275-W sunlamp placed about 15 cm

from the tube. After 4 h, the mixture was analyzed by ^{1}H NMR which indicated no reaction had occurred. Only the starting materials were observed even at a longer irradiation period.

23. Photoreactions of tri-n-butyl-2,2-diphenylethenylstannane with phenyl disulfide and benzenesulfonyl chloride

Tri-n-butyl-2,2-diphenylethenylstannane (3 mmol) and phenyl disulfide (3.5 mmol) were dissolved in 10 mL of benzene in a Pyrex flask equipped with a rubber septum. The mixture was degassed for 5 min and irradiated with a sunlamp for 2 h. The mixture was concentrated and analyzed by ^{1}H NMR and GCMS. The analysis indicated the presence of the substitution product, 2,2-diphenylethenyl phenyl sulfide, in 93% yield. Identity of the product was confirmed by comparison of its ^{1}H NMR and GCMS with those of the authentic compound.

Reaction of the alkenylstannane and benzenesulfonyl chloride was also performed under the same conditions. The reaction afforded 2,2-diphenylethenyl phenyl sulfone in 76% yield.

24. Photoreaction of tri-n-butyl-2,2-diphenylethenylstannane and N-(trimethylacetoxy)pyridine-2-thione(7)

N-(trimethylacetoxy)pyridine-2-thione was generated by the literature procedure [62] and used without isolation. Thus sodium salt of 2-mercaptopyridine-N-oxide (0.22 mmol) and trimethylacetyl chloride (0.22 mmol) and a catalytic amount of 4-dimethylaminopyridine (0.02 mmol) were mixed in benzene (3 mL). The mixture was heated to

reflux for 10 min to give a greenish yellow solution with some precipitate. Tri-n-butyl-2,2-diphenylethenylstannane (0.2 mmol) in 2 mL of benzene was added. The mixture was degassed and irradiated with a 275-W sunlamp while the mixture was stirred with a magnetic stirrer. The greenish-yellow solution changed to pale yellow after being irradiated for 10 min. The reaction was irradiated overnight, cooled and poured into water. The organic products were extracted with benzene. The extract was washed twice with water, dried over anhydrous sodium sulfate. The concentrated mixture was analyzed by GLC and GCMS. The mixture was found to contain t-butyl 2-pyridyl sulfide (**8**) (0.06 mmol), 2,2-diphenylethenyl 2-pyridyl sulfide (**9**) (0.1 mmol), the alkenylstannane starting material (0.06 mmol) and an unidentified product (0.04 mmol) which had GCMS similar to that of benzophenone.

The following GCMS data were obtained:

t-Butyl 2-pyridyl sulfide (**8**):

GCMS, m/e (relative intensity) 169(0.3), 167(6,M^+), 111(100).

2,2-Diphenylethenyl-2-pyridyl sulfide (**9**):

GCMS, m/e (relative intensity) 291(1.1), 289(16,M^+), 212(100), 111(66).

25. Reaction of tri-n-butyl-2,2-diphenylethenylstannane and t-butyl phenyl sulfide

Tri-n-butyl-2,2-diphenylethenylstannane (0.2 mmol) and t-butyl phenyl sulfide (0.4 mmol) and azobisisobutyronitrile (0.02 mmol) were dissolved in 2 mL of benzene. After a nitrogen purge, the mixture was

heated at 80 °C in an oil bath for 2 h. The mixture was concentrated and analyzed by GLC and ^{1}H NMR which indicated only the unreacted starting materials. No substitution product was formed.

The reaction was also carried out under photoconditions. Thus the alkenylstannane (0.1 mmol), the sulfide (0.2 mmol) and hexabutyldistannane (0.01 mmol) in 2 mL of nitrogen-purged benzene was irradiated in a Rayonet Photoreactor for 24 h. The concentrated reaction mixture was analyzed by GLC and ^{1}H NMR. No substitution product was observed. Only the starting materials were recovered.

26. Reaction of tri-n-butyl-2,2-diphenylethenylstannane and N-(cyclohexyloxythiocarbonyl)imidazole (10)

Tri-n-butyl-2,2-diphenylethenylstannane (0.5 mmol) and 10 (1 mmol) in 5 mL of chlorobenzene were heated to reflux for 24 h. The solvent was then removed under vacuum to give an oily residue. The mixture was analyzed by GLC which indicated that **10** had decomposed. The alkenylstannane starting material, however, was recovered unchanged in a quantitative yield.

27. Reaction of tri-n-butyl-2,2-diphenylethenylstannane and t-butyl methyl oxalate

The alkenylstannane (1 mmol) and t-butyl methyl oxalate (2 mmol) in 10 mL of toluene were heated to reflux. Azobisisobutyronitrile (0.1 mmol) was added in several batches every 15 min over a period of 5 h. After completion, the mixture was concentrated and analyzed by GLC. The analysis indicated the presence of the unreacted starting

materials without any other products.

28. Photoreactions of tri-n-butyl-2,2-diphenylethenylstannane with 2-methyl-2-nitropropane and 2-bromo-2-nitropropane

Tri-n-butyl-2,2-diphenylethenylstannane (0.5 mmol) and 2-methyl-2-nitropropane (0.51 mmol) were dissolved in benzene (2 mL). The mixture was degassed and irradiated in a Rayonet Photoreactor for 24 h. The concentrated reaction mixture was analyzed by GLC. No substitution product was observed. The mixture was found to contain only the starting materials.

Reaction of the alkenylstannane (0.1 mmol) in 5 mL of benzene was also performed by the same procedure. The reaction gave only a trace amount of the substitution product. The starting materials were recovered in almost quantitative yields.

29. Photoreactions of tri-n-butylphenylstannane with organomercurials

Tri-n-butylphenylstannane (1 mmol) and the organomercurial (see Table 11) were dissolved in a nitrogen-purged solvent in a Pyrex tube. The mixture was irradiated in a Rayonet Photoreactor for 26 h. During the irradiation, a small amount of mercury metal and, in many cases, a gray precipitate were also formed. After the irradiation, the mixture was washed twice with 10% aqueous sodium thiosulfate solution to remove the remaining organomercurial and dried over anhydrous sodium sulfate. The concentrated mixture was analyzed by GLC and GCMS. The substitution products were further confirmed by the GLC retention time of the authentic compound. Results are presented in Table 11.

30. Photoreactions of alkenyl derivatives with trialkylboranes

The alkenyl compound, $R^1R^2C{=}CHQ$ (Q = I, HgX, SO_2Ph), (0.1 mmol) and the trialkylborane (0.5 mmol) in 10 mL of nitrogen-purged benzene were irradiated either with a 275-W sunlamp or in a Rayonet Photoreactor (see Table 12). After completion of the reaction, the mixture was washed with water and twice with aqueous sodium thiosulfate solution for Q = HgX and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the mixture was analyzed by GLC, ^1H NMR and GCMS. The product was confirmed by comparison of its GLC retention time, ^1H NMR and GCMS with those of the product obtained previously. Results are summarized in Table 12.

31. Reactions of alkenyl derivatives and triisopropylaluminum

Triisopropylaluminum is sensitive to either air or moisture and, therefore, was transferred and weighed under a nitrogen atmosphere.

The alkenyl compound, $R^1R^2C{=}CHQ$ (Q = SO_2Ph, HgX, I, SPh, $SnBu_3$), (0.1 mmol) and triisopropylaluminum (0.5 mmol) were dissolved in 10 ml of benzene in a Pyrex flask. The mixture was degassed and irradiated in a Rayonet Photoreactor for 24 h. The usual workup afforded a concentrated mixture of reaction products which was analyzed by GLC and ^1H NMR. Results are presented in Table 13.

32. Competition reactions between alkylmercury chlorides with (E)-2-phenylethenylmercury chloride or tri-n-butyl-(E)-2-phenylethenylstannane

A competition reaction between two alkylmercury chlorides with an alkenyl compound was performed as follow. (E)-2-Phenylethenylmercury chloride (0.1 mmol), n-butylmercury chloride (1 mmol) and cyclohexylmercury chloride (1 mmol) were dissolved in 5 mL of DMSO in a Pyrex tube. The mixture was degassed for 5 min and irradiated with a 275-W sunlamp for 16 h. The mixture was then poured into water and extracted with benzene. The extract was washed three times with 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The mixture was concentrated and analyzed by GLC. The ratio of the substitution products corrected with the GLC response factors was then obtained.

The competition reaction between t-butylmercury chloride and cyclohexylmercury chloride with (E)-2-phenylethenylmercury chloride was carried out exactly under the same conditions. When tri-n-butyl-(E)-2-phenylethenylstannane was employed instead of the alkenylmercurial, the reactions were performed under the same conditions except that 2 mL of benzene was added to the mixture to solubilize the alkenylstannane.

III. STEREOSPECIFIC SUBSTITUTION REACTIONS OF 1,2-DISUBSTITUTED ETHYLENES

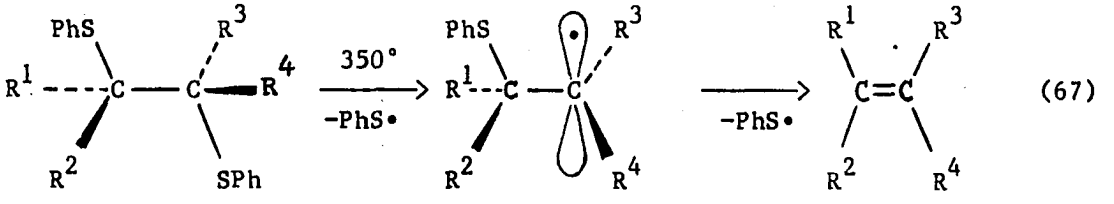
A. Introduction

Recently much attention has been given to the applications of radical reaction for the formation of new carbon-carbon bonds and radical chemistry has increased importance in organic synthesis.

The stereochemistry of free-radical eliminations (Eq. 66) of β-phenylthio radicals (Z = SPh) [106], β-phenylsulfinyl radicals (Z =

$$\underline{n}\text{-Bu}_3\text{Sn}\bullet + \text{MeCH(Br)-CH(Z)Me} \longrightarrow \underline{n}\text{-Bu}_3\text{SnBr} + \text{MeCH=CHMe} + \text{Z}\bullet \qquad (66)$$

S(O)Ph)[107] and β-phenylsulfonyl radicals [108] has been reported by Boothe et al. Only the elimination of β-phenylsulfinyl radical occurred in a stereospecific manner. Formation of alkenes in the pyrolysis of 1,2-bis(phenylthio)ethanes as shown in Eq. (67) had been reported



(67)

earlier [109]. The reaction was shown to be stereospecific, proceeding via a trans elimination. Free-radical dehalogenation of vicinal dibromides by tri-n-butyltin hydride (Eq. 66, where Z = Br) also occurred in a sterospecific manner [110].

We have found that vinylic free radical substitution proceeding by an addition-elimination mechanism (Scheme 23) can proceed in a

Scheme 23

$$XCH{=}CHZ + Q\bullet \xrightarrow{\text{add.}} X\dot{C}H{-}CHZ(Q)$$

$$X\dot{C}H{-}CHZ(Q) \xrightarrow{\text{elim.}} XCH{=}CHQ + Z\bullet$$

stereospecific manner. The following section will discuss the substitution reaction of 1,2-disubstituted ethylenes with organomercurials, phenyl disulfide and benzenesulfonyl chloride as shown in Eq. (68).

$$XCH{=}CHZ + Q{-}Y \xrightarrow{h\nu} XCH{=}CHQ + Z{-}Y \qquad (68)$$

$X = CO_2Me$; $Z = \underline{n}\text{-}Bu_3Sn$. I, Cl

X = Cl ; Z = Cl, I, SPh, HgCl

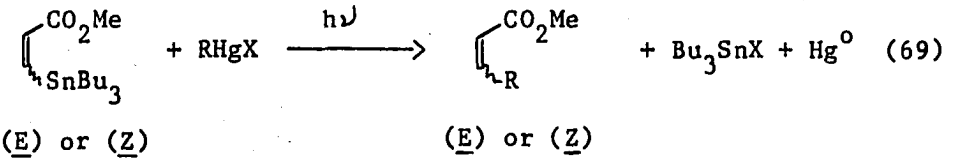
X = I ; Z = I

$Q{-}Y = R{-}HgX$, $(PhS)_2Hg$, $(PhSO_2)_2Hg$, $PhSO_2{-}Cl$

B. Results and Discussion

1. Reactions of methyl -tri-n-butylstannylacrylate with organomercurials, phenyl disulfide and benzenesulfonyl chloride

Methyl -tri-n-butylstannylacrylate and alkylmercury chlorides were allowed to react in benzene and dimethyl sulfoxide. The reactions were irradiated with either a 275-W sunlamp or a 350 nm Rayonet Photoreactor. Moderate to good yields of the coupling products were obtained (Eq. 69)



(E) or (Z) (E) or (Z)

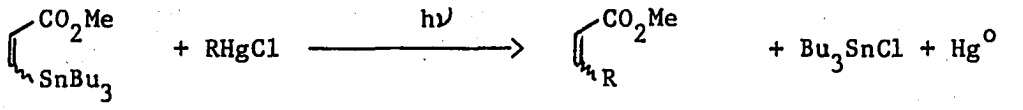
and results are summarized in Table 16. These reactions were found to give better yields with the methyl (Z)-β-tri-n-butylstannylacrylate than with the (E) isomer.

The stereochemistry of the substitution products determined by GLC indicates that (E)-and (Z)-β-tri-n-butylstannylacrylates reacted with cyclohexylmercury chloride to give different product compositions. A high (E)/(Z) ratio was observed with (E)-β-tri-n-butylstannylacrylate; whereas, the (Z)-isomer afforded a low (E)/(Z) ratio. The ratio of the product isomers changed during the course of the reaction. The reaction of methyl (E)-β-tri-n-butylstannylacrylate with cyclohexylmercury chloride gave the substitution product with (E)/(Z) = 36 when irradiated for 2 h with a sunlamp. The recovered starting material isomerized under the reaction conditions to give both isomers with (E)/(Z) = 10 (91%(E)). The same reaction gave a lower (E)/(Z) ratio (23) when it was performed to completion under UV irradiation in a Rayonet Photoreactor.

Reaction of methyl (Z)-β-tri-n-butylstannylacrylate and cyclohexylmercury chloride, on the other hand, gave (E)/(Z) ratios of 2.5 (sunlamp, 2 h) and 2.1 (UV, 5 h). The recovered starting material also isomerized to give both (E)-and (Z)-isomers which had (E)/(Z) = 0.1 (91%(Z)).

Reactions of (E)-and (Z)-β-tri-n-butylstannylacrylates with t-

Table 16. Reaction of methyl β-tri-n-butylstannylacrylate with alkylmercury chlorides



Reactant	RHgCl (equiv)	Conditions[a]	% Product[b]	(E)/(Z)[c]
(E)	c-C_6H_{11}HgCl(5)	PhH, SL 2 h	20	36[d]
(Z)	c-C_6H_{11}HgCl(5)	PhH, SL 2 h	34	2.5[e]
(E)	c-C_6H_{11}HgCl(1.5)	PhH/DMSO, UV 5 h	66	23
(Z)	c-C_6H_{11}HgCl(1.5)	PhH/DMSO, UV 5 h	70	2.1
(E)	t-BuHgCl(1.6)	PhH, UV 5 h	36	> 50
(Z)	t-BuHgCl(1.6)	PhH, UV 5 h	49	> 50

[a] β-Stannylacrylate (0.3 mmol) and RHgCl in 10 mL of solvent were irradiated under N_2 in a Pyrex tube; SL = 275-W sunlamp ca. 20 cm from reaction flask; UV^2 = 350 nm Rayonet reactor.

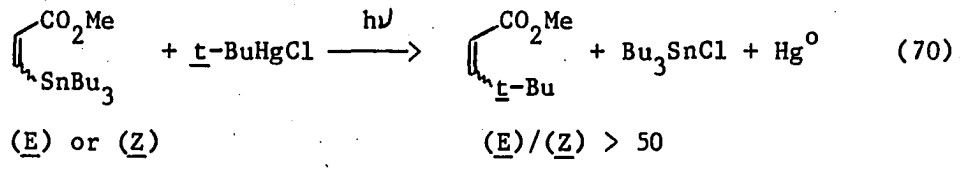
[b] Yields were determined by ^1H NMR.

[c] (E)/(Z) ratios were determined by GLC.

[d] Recovered starting material (75%) had (E)/(Z) = 10.

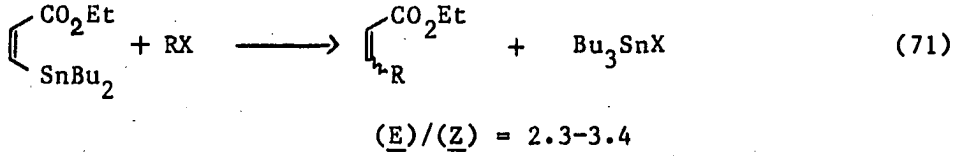
[e] Recovered starting material (47%) had (E)/(Z) = 0.1.

butylmercury chloride under UV irradiation gave substitution products which had the same isomer ratios. In both cases, the reactions afforded methyl (E)-4,4-dimethyl-2-pentenoate as the exclusive product.



Our results clearly indicate that reaction of methyl β-tri-n-butylstannylacrylate and cyclohexylmercury chloride is stereospecific. The (E)-and (Z)-β-tri-n-butylstannylacrylates gave significant different (E)/(Z) ratios of the substitution products especially at the beginning of the reaction. The lower (E)/(Z) ratio upon longer irradiation is apparently due to isomerization of the starting materials.

Baldwin et al. have reported the reactions between ethyl (Z)-β-tri-n-butylstannylacrylate and alkyl halides which underwent substitution reactions by a radical addition-elimination process [49,50]. The reactions were carried out in toluene at 86 °C with hexabutylditin as an initiator as shown in Eq. (71). The reactions afforded both (E)- and

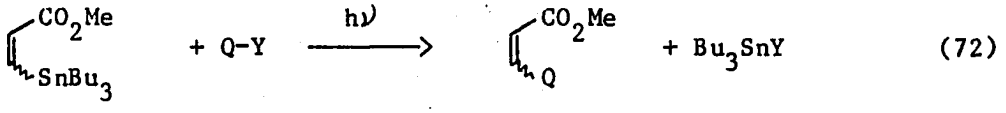


(Z)-β-alkylsubstituted acrylates in moderate to good yields. They, however, did not perform the reaction with ethyl (E)-β-tri-n-butylstannylacrylate and, therefore, no comments in regard to

stereospecificity can be made on the basis of their results. The (E)/(Z) ratios of their substitution products agree with our results in which the (E)-isomer was the major product.

The reaction of methyl β-tri-n-butylstannylacrylate and t-butylmercury chloride does not show any stereospecificity. Both (E)- and (Z)-β-tri-n-butylstannylacrylates gave methyl (E)-4,4-dimethyl-2-pentenoate as the exclusive product. This suggests that the elimination of tri-n-butylstannyl radical occurred from the more stable conformation which led to the (E)-product. Mechanistic detail of this elimination will be discussed later in Section III.B.9 of this part.

Tri-n-butyl-1-alkenylstannanes are known to react with phenyl disulfide, alkyl disulfides and benzenesulfonyl chloride to give good yields of the substitution products as shown in Table 10 and in ref 59. We have found that (E)- and (Z)-β-tri-n-butylstannylacrylate reacted with phenyl disulfide and with benzenesulfonyl chloride according to Eq. (72). Results are presented in Table 17.

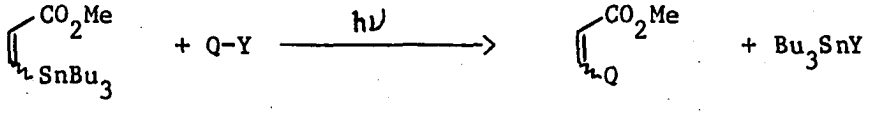


(72)

(E) or (Z) Q-Y = PhS-SPh, $PhSO_2$-Cl

Both (E)- and (Z)-β-tri-n-butylstannylacrylates reacted with phenyl disulfide to give the substitution product which had the same (E)/(Z) ratios after the reaction mixture was irradiated in a Rayonet Photoreactor for 8 h.

Table 17. Reaction of methyl β-tri-n-butylstannylacrylate with phenyl disulfide and benzenesulfonyl chloride



Reactant	Q-Y	Conditions[a]	% Product[b]	(E)/(Z)[c]
(E)	PhSSPh	PhH, UV 8 h	79	3.8(8 h) 8.9(5 min)
(Z)	PhSSPh	PhH, UV 8 h	91	3.7
(E)	$PhSO_2Cl$	PhH, UV 10 h	68	(E) only
(Z)	$PhSO_2Cl$	PhH, UV 10 h	76	(E) only

[a] β-Stannylacrylate (0.3 mmol) and Q-Y (0.5 mmol) in 10 mL of nitrogen-purged benzene were irradiated in a 350 nm Rayonet reactor.

[b] Yields were determined by ^1H NMR.

[c] (E)/(Z) ratios were determined by GLC.

To examine the (E)/(Z) ratios of the reaction products, reactions of (E)- and (Z)-β-tri-n-butylstannylacrylates with phenyl disulfide were carried out under sunlamp or UV irradiation. Small amounts of the reaction mixtures were withdrawn at different periods of time by a syringe and analyzed directly by GLC. The (E)/(Z) ratios of the product are given in Table 18. We can see that both (E)- and (Z)-β-tri-n-butylstannylacrylates gave the substitution product with high (E)/(Z) ratios at the beginning of the reaction. The ratios gradually decreased during the course of the irradiation. The changing of the ratios occurred more rapidly at 350 nm. The isomers, however, appeared to reach an equilibrium when the (E)/(Z) ratio was about 3.7.

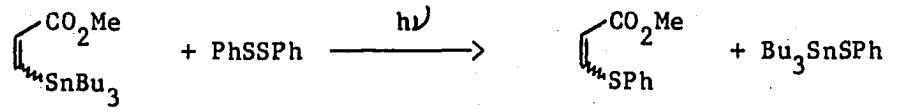
We believe that the elimination of tri-n-butylstannyl radical occurred from the more stable conformation which resulted in the formation of the (E)-product. The low (E)/(Z) ratios observed thus resulted from the isomerization of the products.

Benzenesulfonyl chloride also reacted with methyl β-tri-n-butylstannylacrylate to give the substitution product in high yield (Table 17). Once again, both (E) and (Z)-reactants gave the same reaction product mixtures which consisted of only the (E)-isomer. In this case, methyl (E)-β-benzenesulfonylacrylate appears to be the more stable of the two isomers. Therefore, it did not isomerize to give any methyl (Z)-β-benzenesulfonylacrylate.

2. Reactions of methyl β-haloacrylates with alkylmercurials

Methyl β-iodoacrylate and alkylmercury chlorides were allowed to react under sunlamp irradiation. The reactions proceeded to give the

Table 18. Ratio of product isomers (E/Z) occurring during the irradiation of (E) or (Z)-β-tri-n-butylstannylacrylate with phenyl disulfide



(E) or (Z) (E) or (Z)

Time (min)[a]	(E)/(Z)[b]		
	from (Z)[c]	from (Z)[d]	from (E)[d]
5		7.4	8.9
10	5.3	6.9	7.7
15		6.8	6.9
30	4.3	5.8	6.5
60	4.0	4.6	5.4
480	3.7	3.7	3.8

[a]Irradiation period. Reactions were performed with β-tri-n-butylstannylacrylate (0.3 mmol) and phenyl disulfide (0.5 mmol) in benzene (1 mL) in Pyrex tubes.

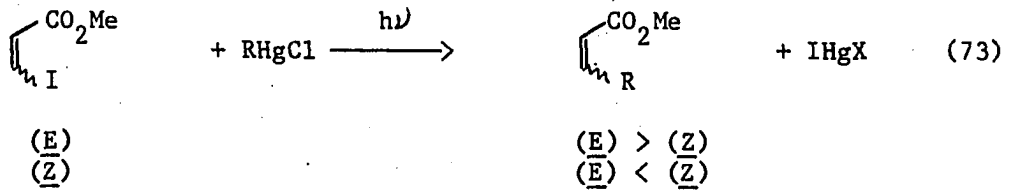
[b]Ratios were determined by GLC.

[c]Irradiated at 350 nm in a Rayonet Photoreactor.

[d]Irradiated with 275-W sunlamp ca. 20 cm from the reaction vessel.

substitution products in moderate yields as shown in Table 19. With methyl (E)-β-iodoacrylate, the substitution products had high (E)/(Z) ratios. When it reacted with t-butylmercury chloride, methyl (E)-4,4-dimethyl-2-pentenoate was formed exclusively and only a trace amount of the (Z)-isomer was detected. When cyclohexylmercury chloride was employed, the substitution product had a high (E)/(Z) ratio at the beginning but it decreased during the course of the reaction.

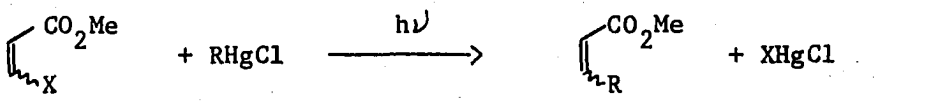
Methyl (Z)-β-iodoacrylate, on the other hand, reacted with alkylmercury chlorides to give the substitution products which had (E)/(Z) < 1 even with t-butylmercury chloride. The reactions can be summarized as in Eq. (73).



The results clearly show that methyl β-iodoacrylate reacted with alkylmercury chlorides in a stereospecific manner. The (E)- and (Z)-β-iodoacrylates gave the substitution products with significantly different (E)/(Z) ratios. The reaction of (Z)-β-iodoacrylate with t-butylmercury chloride gave the product with (E)/(Z) = 0.1. This indicates that the elimination of the iodine atom occurred faster than the rotation of the carbon-carbon single bond of the radical adduct. More mechanistic detail will be discussed in Section III.B.9.

In Section II.B. we found that 2,2-diphenylethenyl bromide was much less reactive than 2,2-diphenylethenyl iodide towards alkyl

Table 19. Reaction of methyl β-haloacrylates with alkylmercury chlorides



Isomer	X	RHgCl (equiv)	Conditions[a]	% Product[b]	(E)/(Z)[c]
(E)	I	i-PrHgCl(1.6)	PhH, SL 4 h	36	30
(Z)	I	i-PrHgCl(1.6)	PhH, SL 6 h	35	0.5
(Z)	I	i-PrHgCl(1.6)	PhH, UV 23 h	45	0.5
(E)	I	c-C_6H_{11}HgCl(5)	PhH/DMSO, SL 0.5 h	11	33[d]
(Z)	I	c-C_6H_{11}HgCl(5)	PhH/DMSO, SL 0.5 h	13	0.2[e]
(E)	I	c-C_6H_{11}HgCl(5)	PhH/DMSO, SL 6 h	34	20
(Z)	I	c-C_6H_{11}HgCl(5)	PhH/DMSO, SL 6 h	45	0.9
(E)	I	t-BuHgCl(5)	PhH, SL 6 h	43	> 50
(Z)	I	t-BuHgCl(5)	PhH, SL 6 h	41	0.1
(Z)	Cl	c-C_6H_{11}HgCl(1.5)	DMSO, SL 24 h	34	0.3
(Z)	Cl	t-BuHgCl(1.5)	DMSO, SL 24 h	49	> 50

[a]The substrates (0.3 mmol of β-haloacrylate) in 10 mL of solvent were irradiated under N_2 in a Pyrex tube; SL = sunlamp; UV = 350 nm Rayonet Photoreactor.

[b]^1H NMR yield.

[c]Stereochemistry was determined by GLC.

[d]Recovered starting material had (E)/(Z) = 28.5 (96.6% (E)).

[e]Recovered starting material had (E)/(Z) = 0.1 (90%(Z)).

radicals. The corresponding 1-alkenyl chloride is expected to be very unreactive towards alkyl radicals due to nucleophilicities of the attacking radicals. However, reactivity of an 1-alkenyl chloride can be increased by an electron withdrawing group attached directly to the double bond. Therefore, methyl β-chloroacrylate was found to react with cyclohexylmercury chloride and t-butylmercury chloride under sunlamp irradiation to give the substitution products in appreciable yields (Table 19). The reactions, however, proceeded slower than the corresponding β-iodoacrylate. The reaction of methyl (Z)-β-chloroacrylate and cyclohexylmercury chloride afforded the substitution product with (E)/(Z) = 0.3. On the other hand, the reaction with t-butylmercury chloride gave only methyl (E)-4.4-dimethyl-2-pentenoate. The result is consistent with the chlorine atom being a poor leaving group so that rotation of the carbon-carbon single bond in the adduct radical occurred faster than elimination of the chlorine atom (see Section III.B.9).

Methyl β-iodoacrylate also reacted with mercuric phenylmercaptide under photostimulation. The reaction was carried out under sunlamp irradiation and in a Rayonet Photoreactor to afford the substitution products which are presented in Table 20. The reaction proceeded according to Eq. (74).

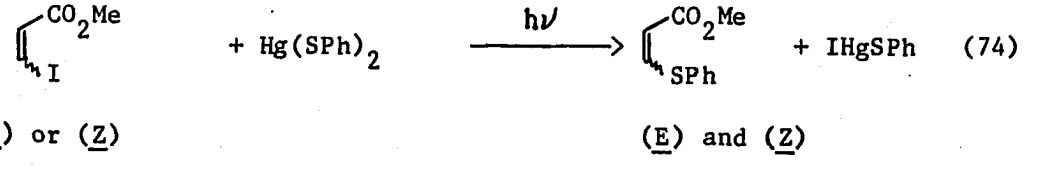
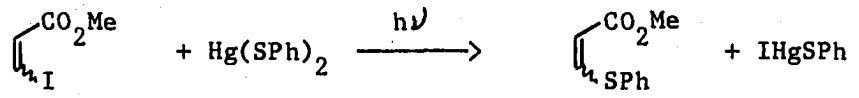


Table 20. Reaction of methyl β-iodoacrylate with mercuric phenylmercaptide



Reactant	Conditions[a]	% Product[b]	(E)/(Z)[c]
(E)	PhH/DMSO, SL 1h	19	4.8[d]
(E)	PhH/DMSO, UV 6h	60	3.5
(Z)	PhH/DMSO, SL 1h	10	1.9[e]
(Z)	PhH/DMSO, UV 6h	69	3.6

[a] β-Iodoacrylate (0.3 mmol) and $Hg(SPh)_2$ (0.5 mmol) in solvent (10 mL) were irradiated under N_2 in a Pyrex tube; SL = 275-W sunlamp ca. 20 cm from reaciton flask; UV ≅ 350 nm Rayonet Photoreactor.

[b] ^1H NMR yield.

[c] Stereochemistry was determined by GLC.

[d] Recovered iodoacrylate had (E)/(Z) = 66 (98.5% (E)).

[e] Recovered starting material had (E)/(Z) = 0.2 (83% (Z)).

When the reactions were carried out under sunlamp irradiation for 1 h, the reactions gave the substitution products with (E)/(Z) = 4.8 (from (E)-β-iodoacrylate) and (E)/(Z) = 1.9 (from (Z)-β-iodoacrylate). The unreacted starting materials were found to have isomerized with the (Z)-β-iodoacrylate isomerizing more rapidly. The same (E)/(Z) ratios were obtained when the reactions were carried out for 6 h in a Rayonet Photoreactor. This clearly indicates that the reaction of methyl β-iodoacrylate and mercuric phenylmercaptide proceeded in a stereospecific manner. Loss of stereochemistry is due to isomerization of the products and the starting materials.

3. Reactions of β-chlorovinylmercury chloride with organomercurials and phenyl disulfide

β-Chlorovinylmercury chloride reacted with cyclohexylmercury chloride and t-butylmercury chloride to give the substitution products which are summarized in Table 21. Reactions were carried out with 1.2 equiv of the alkylmercurials and the reactions are represented by Eq. (75).

$$\underset{\text{(E) or (Z)}}{\text{ClCH=CHHgCl}} + \text{RHgX} \xrightarrow{h\nu} \underset{\text{(E) and (Z)}}{\text{ClCH=CHR}} + \text{ClHgX} + \text{Hg}^{\text{o}} \qquad (75)$$

It is interesting to note that vinylmercury chloride, Section II.B.1, did not react with cyclohexylmercury chloride to give the substitution product when these reagents were irradiated in a Rayonet Photoreactor (Table 1). The vinylmercurial with a chlorine at the β-position, in contrast, underwent substitution with cyclohexylmercury

Table 21. Reaction of β-chlorovinylmercury chloride with organomercurials and phenyl disulfide

$$ClCH{=}CHHgCl + RHgX \xrightarrow{h\nu} ClCH{=}CHR + RCH{=}CHR + ClHgX + Hg^{0}$$

Reactant (1 mmol)	RHgX or PhSSPh (equiv)	Conditions[a]	% Product[b] ClCH=CHR (E)/(Z)	% Product[b] RCH=CHR (E)/(Z)
(E)	c-C_6H_{11}HgCl(1.2)	UV 10 h	28(4.3)	0
(Z)[c]	c-C_6H_{11}HgCl(1.2)	UV 10 h	38(0.7)	0
(E)	t-BuHgCl(1.2)	UV 10 h	33(5.6)	0
(Z)[c]	t-BuHgCl(1.2)	UV 10 h	44 (2.7)	0
(E)	PhSSPh(1.2)	SL 0.5 h	14(3.4)	56(0.9)
(E)	PhSSPh(0.5)	UV 6 h	20(2.5)	40(0.6)
(Z)[c]	PhSSPh(0.5)	UV 6 h	16(0.9)	32(0.7)
(E)	PhSSPh(1.2)	UV 6 h	0	81(0.7)
(Z)[c]	PhSSPh(1.2)	UV 6 h	0	81(0.8)

[a]Substrates in 5 mL of DMSO under N_2 in a Pyrex tube were irradiated; UV = Rayonet Photoreactor, SL = 275-W sunlamp ca. 20 cm from reaction flask.

[b]Yields and stereochemistry were determined by GLC.

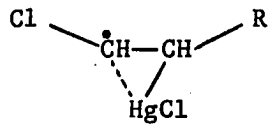
[c]Starting material had (Z):(E) = 3:1.

chloride. The addition of the alkyl radicals was regioselective since the alkyl radicals only attack at the α position of the vinylmercurial. No disubstitution product was observed with either cyclohexylmercury chloride or t-butylmercury chloride.

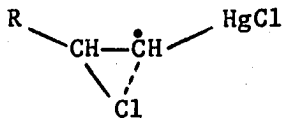
Reactions of (E)- and (Z)-β-chlorovinylmercury chlorides with cyclohexylmercury chloride gave different major products. The (E)-β-chlorovinylmercury chloride gave (E)-2-chloroethenylcyclohexane, whereas the (Z)-alkenylmercurial gave (Z)-2-chloroethenylcyclohexane as the major product. When t-butylmercury chloride was allowed to react with (E)- and (Z)-β-chlorovinylmercury chlorides, (E)-1-chloro-3,3-dimethyl-1-butene was obtained as the major product. However, the reactions afforded the substitution products with different (E)/(Z) ratios.

It should be noted that the starting material, (Z)-β-chlorovinylmercury chloride, was not isomerically pure. It consisted of both (E)- and (Z)-isomers with (E):(Z) = 1:3. Therefore, with pure (Z)-β-chlorovinylmercury chloride, the (E)/(Z) ratio of the substitution product would be expected to be lower than reported in Table 21. However, the results shown in Table 21 still indicate that the reactions occurred in a stereospecific manner.

The reaction also occurred regioselectively. No product derived from attack at the β-position of the vinylmercurial was observed. The observed regioselectivity may be due to better stabilization of the radical center by chlorine than by mercury. Furthermore, stabilization of the β-radical by HgCl as shown in 14 may also induce attack of



14



15

the alkyl radical at the carbon attached to HgCl. The stabilization by chlorine as shown in **15** is apparently not effective.

1-Alkenylmercury chlorides have been reported to react with phenyl disulfide to give excellent yields of the coupling products [37]. We have found that phenyl disulfide can also react with β-chlorovinylmercury chloride under photostimulation. Reactions of both (E)- and (Z)-β-chlorovinylmercury chlorides with phenyl disulfide gave an 81% yield of the disubstitution product with about the same (E)/(Z) ratios (Eq. 76). The results in Table 21 indicate that the thiophenoxy

$$\underset{\text{(E) or (Z)}}{\text{ClCH=CHHgCl}} + \text{PhSSPh} \xrightarrow{h\nu} \underset{\text{(E)/(Z)} \sim 0.7}{\text{PhSCH=CHSPh}} + \text{HgCl}_2 \qquad (76)$$

radical attacked the vinylmercurial at the ∝-position. The resulting radical then decomposed to give β-chlorovinyl phenyl sulfide (ClCH=CHSPh) and HgCl (Scheme 24).

Scheme 24

$$\text{ClCH=CHHgCl} + \text{PhS}\bullet \xrightarrow{\text{add.}} \xrightarrow{\text{elim.}} \text{ClCH=CHSPh} + \text{HgCl}$$

$$\text{HgCl} + \text{PhSSPh} \longrightarrow \text{ClHgSPh} + \text{PhS}\bullet$$

The product, β-chlorovinyl phenyl sulfide, is apparently quite reactive towards thiophenoxy radical. Therefore, it underwent substitution reaction with ClHgSPh to give 1,2-bis(phenythio)ethene as outlined in Scheme 25. At short reaction periods, β-chlorovinyl

Scheme 25

$$ClCH{=}CHSPh + PhS\bullet \xrightarrow{\text{add.}} \xrightarrow{\text{elim.}} PhSCH{=}CHSPh + Cl\bullet$$

$$Cl\bullet + ClHgSPh \longrightarrow PhS\bullet + HgCl_2$$

phenyl sulfide was formed in low yield with 1,2-bis(phenylthio)ethene as the major reaction product.

The (E)/(Z) ratios of β-chlorovinyl phenyl sulfide (see Table 21) suggest that the reaction of β-chlorovinylmercury chloride and phenyl disulfide occurred stereospecifically, since the (E)- and (Z)-vinylmercurials gave the substitution product with different (E)/(Z) ratios. The disubstitution product, in contrast, does not indicate any stereospecificity since both the (E)- and (Z)-vinylmercurials afforded a product which had about the same (E)/(Z) ratio. We believe that the reversible addition of thiophenoxy radical to the double bonds (which leads to isomerization of both the starting material and the product) is responsible for the observed stereochemistry.

4. Reaction of 1,2-dichloroethylene with organomercurials

Alkenyl chlorides of the type ClCH=CHX where X = alkyl are not reactive towards alkyl radicals due to the nucleophilic character of alkyl radicals. In contrast, with X = an electron withdrawing group

such as COOR, the alkene can trap alkyl radicals and undergo the substitution reaction. Therefore, methyl β-chloroacrylate reacted with alkylmercury chlorides to give moderate yields of the substitution products as presented in Table 19.

1,2-Dichloroethylene was also found to react with alkylmercurials under photostimulation to give the substitution products in preparative yields (Table 22). The reactions gave only monosubstitution products (Eq. 77) even when an excess amount of an

$$ClCH{=}CHCl + RHgCl \xrightarrow{h\nu} ClCH{=}CHR + HgCl_2 \qquad (77)$$

alkylmercurial was employed. The (E)- and (Z)-1,2-dichloroethylenes reacted with n-butylmercury chloride to give the 1-chloro-1-hexenes with the same (E)/(Z) ratios. Stereospecificity was also not observed when cyclohexylmercury chloride was employed. Both reactions gave the (Z)-isomer as the major product. When t-butylmercury chloride was allowed to react with (E)- or (Z)-1,2-dichloroethylene, the reactions afforded (E)-1-chloro-3,3-dimethyl-1-butene as the exclusive product.

The lack of stereospecificity observed is consistent with chlorine atom being a poor leaving group. Therefore, rotation of the carbon-carbon single bond in the adduct radical occurred faster than the elimination of the chlorine atom. This will be discussed in more detail later in this part.

Mercuric phenylmercaptide can also react with 1,2-dichloroethylene under UV irradiation. The reaction was carried out

Table 22. Reaction of 1,2-dichloroethylene with organomercurials

$$ClCH{=}CHCl + RHgX \xrightarrow{h\nu} ClCH{=}CHR + RCH{=}CHR + ClHgX$$

Reactant (equiv)	Mercurial	Conditions[a]	% Product[b]	
			ClCH=CHR (E)/(Z)	RCH=CHR (E)/(Z)
(Z)(2)	n-BuHgCl	UV 21 h	41(0.5)	0
(E)(2)	n-BuHgCl	UV 20 h	59(0.5)	0
(Z)(1)	c-C_6H_{11}HgCl	UV 21 h	45(0.7)	0
(Z)(2)	c-C_6H_{11}HgCl	UV 21 h	70(0.8)	0
(E)(3)	cC_6H_{11}HgCl	UV 20 h	63(0.7)	0
(Z)(1)	t-BuHgCl	UV 21 h	42(> 50)	0
(Z)(2)	t-BuHgCl	UV 21 h	63(41)	0
(E)(3)	t-BuHgCl	UV 20 h	75(> 50)	0
(Z)(1)	$(PhS)_2Hg$	UV 20 h	0	43(0.5)
(Z)(1)	$(PhS)_2Hg$	Dark 20 h	0	0
(Z)(5)	$(PhS)_2Hg$	UV 21 h	5[d](0.4)	81[e](0.5)
(E)(5)	$(PhS)_2Hg$	UV 20 h	14[d](0.4)	84[e](0.5)
(Z)(1)	$(PhSO_2)_2Hg$	UV 20 h	0	0

[a]Mercurial (1 mmol) and 1,2-dichloroethylene in 5 mL of DMSO in a Pyrex tube were irradiated under N_2 in a 350 nm Rayonet Photoreactor.

[b]Yields were determined by GLC.

[c]Stereochemistry was determined by GLC.

[d]Based on 1 mmol of $Hg(SPh)_2$ for 2 mmol of product.

[e]Based on 1 mmol of $Hg(SPh)_2$ for 1 mmol of product.

in a Rayonet Photoreactor for ca. 20 h to give high yields of 1,2-bis(phenylthio)ethene (Table 22). When stoichiometric amounts of the reactants were employed, only 1,2-bis(phenylthio)ethene was obtained in 43% yield. In contrast, an excellent yield of the disubstitution product and a low yield of β-chlorovinyl phenyl sulfide were observed when a 5 fold excess of mercuric phenylmercaptide was employed. This indicates that β-chlorovinyl phenyl sulfide is more reactive than 1,2-dichloroethylene. It is consistent with chlorine being a stronger electron withdrawing group than sulfur which makes 1,2-dichloroethylene less reactive than β-chlorovinyl phenyl sulfide towards thiophenoxy radical. The proposed mechanism is outlined in Scheme 26.

Scheme 26

$$ClCH{=}CHCl + PhS\bullet \xrightarrow{\text{add.}} \xrightarrow{\text{elim.}} ClCH{=}CHSPh + Cl\bullet$$

$$Cl\bullet + Hg(SPh)_2 \longrightarrow PhS\bullet + ClHgSPh$$

$$ClCH{=}CHSPh + PhS\bullet \xrightarrow{\text{add.}} \xrightarrow{\text{elim.}} PhSCH{=}CHSPh + Cl\bullet$$

Free-radical substitution reactions of vinyl chloride derivatives and alkyl or aryl thiols, even though rarely observed, have been reported in the literature [111,112]. The reaction of trichloroethylene with benzenethiol (Eq. 78) was found to afford the substitution product in excellent yield [111].

$$ClCH{=}CCl_2 + PhSH \xrightarrow[\text{benzoyl peroxide}]{} PhSCH{=}CCl_2 \quad (78)$$

92%

1,2-Dichloroethylene was also found to react with thiols to give, among other products, the substitution product as shown in Eq. (79) [112]. The reaction, however, was complicated because of addition of the thiol with α,β-chlorotropic rearrangement.

$$\text{RSH} + \text{ClCH=CHCl} \xrightarrow{h\nu} \text{RSCH}_2\text{CHCl}_2 + \text{RSSR} + \underset{(\underline{E}) \text{ and } (\underline{Z})}{\text{RSCH=CHCl}} + \underset{(\underline{E}) \text{ and } (\underline{Z})}{\text{RSCH=CHSR}} \qquad (79)$$

Mercuric benzenesulfinate failed to react with 1,2-dichloroethylene. No reaction was observed when they were irradiated in a Rayonet Photoreactor for 20 h; only the starting materials were recovered. The failure of the reaction suggests that the chlorine atom is a much poorer leaving group than benzenesulfonyl radical or that benzenesulfonyl radical does not add to the double bonds of 1,2-dichloroethylene at all.

5. Reactions of β-chlorovinyl phenyl sulfide with organomercurials

($\underline{E}$)-β-Chlorovinyl phenyl sulfide and an alkylmercury chloride in dimethyl sulfoxide were irradiated in a Rayonet Photoreactor. The reaction proceeded slowly to give the substitution product according to Eq. (80).

$$\underset{(\underline{E})}{\text{ClCH=CHSPh}} + \text{RHgX} \longrightarrow \underset{\substack{\text{Major} \\ (\underline{E})/(\underline{Z}) > 1}}{\text{RCH=CHSPh}} + \underset{\text{minor}}{\text{ClCH=CHR}} + \text{ClHgX (PhSHgX)} \qquad (80)$$

After 30 h of irradiation in a Rayonet Photoreactor, the reaction with $\underline{t}$-butylmercury chloride gave 56% of ($\underline{E}$)-3,3-dimethyl-1-butenyl

phenyl sulfide and 4% of (E)-1-chloro-3,3-dimethyl-1-butene (no starting material remained). On the other hand, the reactions with n-butylmercury chloride and with cyclohexylmercury chloride gave lower yields of the substitution products and a lot of starting materials still remained. In all cases, the (E)/(Z) ratios of the products are larger than 1 as shown in Table 23. The reactions afforded only monosubstitution products. The attack of the alkyl radicals is regioselective since the radicals preferred to attack at the carbon attached to chlorine.

Trichloromethyl and diethoxyphosphinyl radicals have electrophilic character and are not reactive towards electron deficient double bonds. Therefore, trichloromethylmercury chloride and diethoxyphosphinylmercury chloride failed to react with β-chlorovinyl phenyl sulfide under UV irradiation. The reactions gave only trace amounts of the substitution products.

β-Chlorovinyl phenyl sulfide appears to trap thiophenoxy radical effectively as mentioned in the preceding section. This has been confirmed by the finding that β-chlorovinyl phenyl sulfide reacted with mercuric phenylmercaptide under UV irradiation to give 1,2-bis(phenylthio)ethene with (E)/(Z) = 0.7 in 70% yield.

Mercuric benzenesulfinate, on the other hand, failed to react with β-chlorovinyl phenyl sulfide. This suggests that the alkene is not reactive towards benzenesulfonyl radical or the sulfonyl radical is a much better leaving group than chlorine atom or thiophenoxy radical and only the elimination of the sulfonyl radical occurred as

Table 23. Reaction of β-chlorovinylphenyl sulfide with organomercurials

$$\underset{(E)}{ClCH{=}CHSPh} + RHgX \xrightarrow{h\nu} RCH{=}CHSPh + ClCH{=}CHR + \underset{(PhSHgX)}{ClHgX}$$

Mercurial (equiv)	Conditions[a]	% Product[b]		% Starting material[b]
		RCH=CHSPh (E)/(Z)	ClCH=CHR (E)/(Z)	(E)/(Z)
n-BuHgCl(1)	UV 30 h	11(2.8)[c]	0	71(4.4)
c-C_6H_{11}HgCl(1)	UV 30 h	49(2.6)[d]	8(2.1)	26(4.3)
t-BuHgCl(1)	UV 30 h	56(> 50)[e]	4(E)	0
CCl_3HgCl(1)	UV 30 h	trace	0	56(5.1)
$(EtO)_2\overset{O}{\overset{\|}{P}}HgCl$(1)	UV 30 h	trace[f]	0	83(10.7)
$(PhS)_2Hg$(0.5)	UV 10 h	70(0.7)	0	0
$(PhSO_2)_2Hg$(0.5)	UV 10 h	0	0	95(5.4)

[a] β-Chlorovinyl phenyl sulfide (1 mmol) and an mercurial in DMSO (5 ml) were irradiated under N_2 in a 350 nm Rayonet Photoreactor.

[b] Yields and stereochemistry were determined by GLC.

[c] 1,2-Bis(phenylthio)ethene was found (0.07 mmol, (E)/(Z) = 0.6).

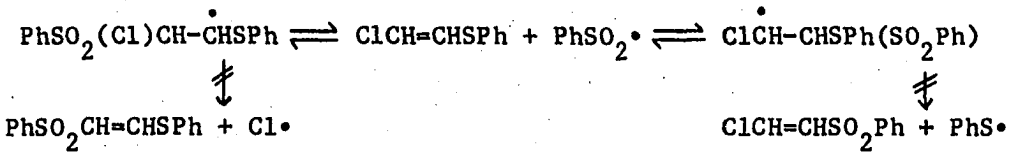
[d] 1,2-Bis(phenylthio)ethene (0.01 mmol, (E)/(Z) = 0.6) and cyclohexyl phenyl sulfide (0.09 mmol) were also formed.

[e] 1,2-Bis(phenylthio)ethene (0.11 mmol, (E)/(Z) = 0.5) and t-butyl phenyl sulfide (0.03 mmol) were detected.

[f] 1,2-Bis(phenylthio)ethene (0.03 mmol, (E)/(Z) = 0.5).

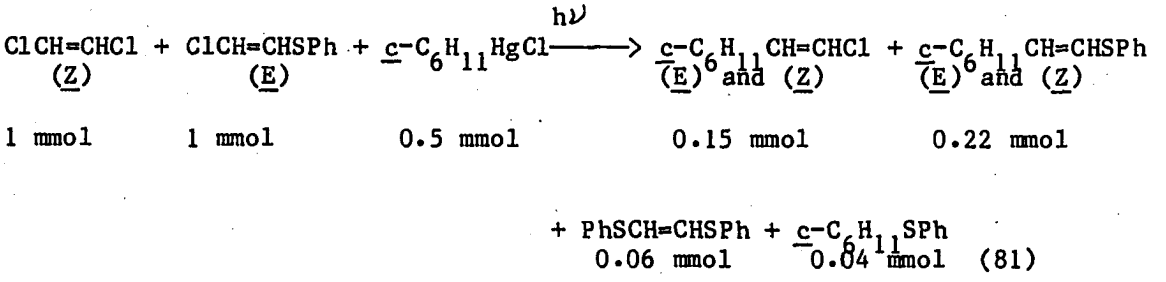
shown in Scheme 27.

Scheme 27



6. Competition reaction between 1,2-dichloroethylene and β-chlorovinyl phenyl sulfide towards cyclohexyl radical

To determine the relative reactivity between (Z)-1,2-dichloroethylene and β-chlorovinyl phenyl sulfide towards cyclohexyl radical, equimolar amounts of both alkenes in dimethyl sulfoxide were allowed to react with a deficient amount of cyclohexylmercury chloride (0.5 equiv) in a Rayonet Photoreactor. After irradiation for 10 h, the reaction mixture afforded the substitution products as shown in Eq. (81).



The relative reactivity of the two alkenes can be determined from the ratio of (2-phenylthioethenyl)cyclohexane to (2-chloroethenyl)-cyclohexane. The result indicates that β-chlorovinyl phenyl sulfide is at least 1.5 times more reactive than (Z)-1,2-dichloroethylene.

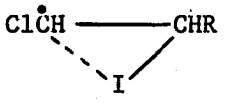
7. Reactions of (E)-1-chloro-2-iodoethylene with organomercurials

(E)-1-Chloro-2-iodoethylene was allowed to react with alkylmercury chlorides under UV irradiation to give monosubstitution products in good yields (Table 24). In this reaction, the iodine atom is the leaving group and only 2-alkyl substituted vinyl chlorides were observed as shown in Eq. (82). The (E)/(Z) ratio of the product is

$$\underset{(E)}{ClCH{=}CHI} + RHgCl \xrightarrow{h\nu} ClCH{=}CHR + IHgCl \qquad (82)$$

very high with t-butylmercury chloride, but low with either n-butylmercury chloride or cyclohexylmercury chloride.

The addition of the alkyl radicals is regioselective in that the radicals attacked at the carbon attached to the iodide. The regioselectivity may result from better stabilization of the resulting radical center by chloride than by iodide. In addition, iodide can stabilize a β-radical by forming a bridged radical as shown in 16; whereas, the chloride is not effective in forming such a radical.



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1-Chloro-2-iodoethylene did not react with diethoxyphosphinylmercury chloride, but it reacted with mercuric phenylmercaptide to give an excellent yield of 1,2-bis(phenylthio)ethene and a low yield of β-chlorovinyl phenyl sulfide.

Table 24. Reaction of 1-chloro-2-iodoethylene with mercurials

$$ClCH{=}CHI + RHgX \xrightarrow{h\nu} ClCH{=}CHR + RCH{=}CHR + IHgX(ClHgX)$$

(E) Mercurial (equiv)	Conditions[a]	% Product[b] ClCH=CHR (E)/(Z)	% Product[b] RCH=CHR (E)/(Z)	% S.M. ClCH=CHI
n-BuHgCl(1.5)	SL 10 h	60(1.7)	0	0
c-C_6H_{11}HgCl(1)	SL 6 h	49(2.4)	0	5
c-C_6H_{11}HgCl(1.5)	SL 10 h	63(2.3)	0	0
t-BuHgCl(1.5)	SL 10 h	60(> 30)	0	0
$(EtO)_2\overset{O}{\overset{\|}{P}}HgCl$(1.5)	SL 10 h	0	0	20
$(PhS)_2Hg$(0.25)	SL 6 h	14[c]	70[c]	43
$(PhS)_2Hg$(0.5)	SL 12 h	4	86[c](0.5)	33
$(PhSO_2)_2Hg$(0.5)	SL 12 h	80[d](47)	0	0

[a] 1-Chloro-2-iodoethylene (1 mmol) and mercurial in DMSO were irradiated under N_2 with a 275-W sunlamp placed ca. 20 cm from the reaction vessel.

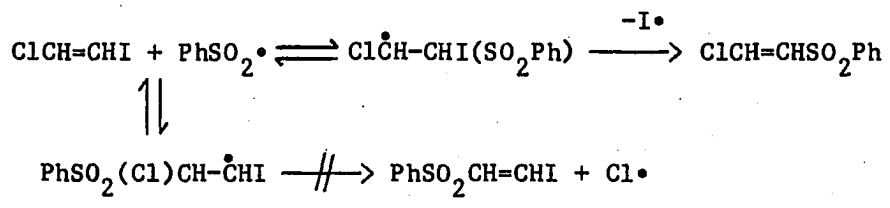
[b] Yield and stereochemistry were determined by GLC.

[c] Based on $(PhS)_2Hg$ as the limiting reagent; 1 mmol of $(PhS)_2Hg$ for 2 mmol of CHCl=CHSPh or 1 mmol of PhSCH=CHSPh.

[d] Based on 1 mmol of $(PhSO_2)_2Hg$ for 2 mmol of $ClCH{=}CHSO_2Ph$.

It also reacted with mercuric benzenesulfinate to give a high yield of the substitution product. The reaction gave only the monosubstitution product, β-chlorovinyl phenyl sulfone, in 80% yield. No product derived from the substitution of the chlorine atom was observed. This is consistent with the poor leaving ability of a chlorine atom and the reversible addition of the sulfonyl radical as shown in Scheme 27.

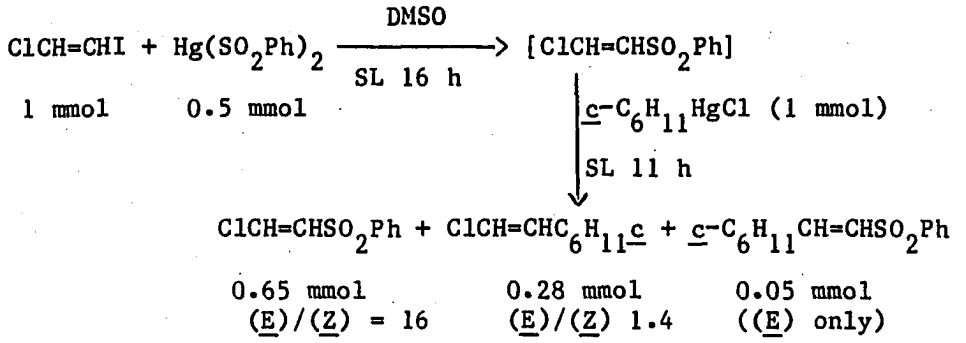
Scheme 27



β-Chlorovinyl phenyl sulfone is expected to react with alkylmercury chlorides to give the substitution product as does 2-chloro-2-iodoethylene. Therefore, 1,2-dichloroethylene was allowed to react with mercuric benzenesulfinate (0.5 equiv) in dimethyl sulfoxide. The reaction was irradiated under a sunlamp for 16 h to give β-chlorovinyl phenyl sulfone in high yield. The product, without isolation, was allowed to react with cyclohexylmercury chloride under sunlamp irradiation for 11 h. After workup, the reaction mixture was found to consist of three products as shown in Scheme 28.

The result confirms that β-chlorovinyl phenyl sulfone can react with an alkylmercury chloride under photostimulation. The reaction, however, afforded a somewhat lower yield than did 1-chloro-2-iodoethylene. In addition, a small amount of the product derived from substitution of the chlorine atom was also observed.

Scheme 28



8. Reactions of (E)-1,2-diiodoethylene with organomercurials

1,2-Diiodoethylene was found to react with alkylmercury chlorides to give the substitution products. Surprisingly, the reactions afforded an appreciable yield only with t-butylmercury chloride (Table 25). With n-butylmercury chloride and cyclohexylmercury chloride, the yields were low. Equation (83) represents the reaction.

$$\underset{(E)}{ICH=CHI} + RHgX \xrightarrow{h\nu} RCH=CHI + RCH=CHR + IHgX \quad (83)$$
$$(E) \text{ and } (Z) \text{ trace}$$

The (E)/(Z) ratios of the substitution products are higher than those obtained earlier from other 1,2-disubstituted ethylenes. The monosubstitution product, (2-iodoethenyl)cyclohexane, is apparently not reactive towards the cyclohexyl radical. Therefore, the reaction of 1,2-diiodoethylene with an excess amount of cyclohexylmercury chloride afforded only a small amount of 1,2-dicyclohexylethylene. When t-butylmercury chloride was employed, (E)-3,3-dimethyl-1-iodo-1-butene was the only organic product obtained from the reaction.

Table 25. Reaction of 1,2-diiodoethylene with organomercurials

$$\underset{(E)}{ICH{=}CHI} + RHgX \xrightarrow{h\nu} RCH{=}CHI + RCH{=}CHR + IHgCl$$

Mercurial (equiv)	Conditions[a]	% Product[b]	
		RCH=CHI (E)/(Z)	RCH=CHR (E)/(Z)
n-BuHgCl(1)	SL 7 h	14(3.8)	0
c-C_6H_{11}HgCl(1)	SL 7 h	15(8.4)	0
c-C_6H_{11}HgCl(5)	SL 20 h	15(7.5)	2[c]
c-C_6H_{11}HgCl(2)	UV 6 h	12(6.2)	trace
t-BuHgCl(1)	SL 7 h	48(> 50)	0
$(PhS)_2Hg$(1)	UV 6 h	0	60[d](0.5)
$(PhS)_2Hg$(1)	SL 6.5 h	0	76[d](0.5)
$(PhSO_2)_2Hg$(1)	UV 6 h	69(>50)	0
$(PhSO_2)_2Hg$(1)	SL 6.5 h	82(29)	0

[a]Reactions were performed with 1 mmol of ICH=CHI and mercurial in 5 mL of nitrogen-purged DMSO; SL = 275 W-sunlamp irradiation.

[b]Yields and stereochemistry were determined by GLC.

[c]Products from the decomposition of c-C_6H_{11}HgCl were also formed.

[d]Phenyl disulfide was also detected.

The photostimulated reaction of 1,2-diiodoethylene and mercuric phenylmercaptide gave 1,2-bis(phenylthio)ethene in good yield (Eq. 84). The reaction with mercuric benzenesulfinate, on the other hand,

$$\underset{(\underline{E})}{ICH=CHI} + Hg(SPh)_2 \xrightarrow{h\nu} \underset{(\underline{E})/(\underline{Z}) = 0.5}{PhSCH=CHSPh} + HgI_2 \qquad (84)$$

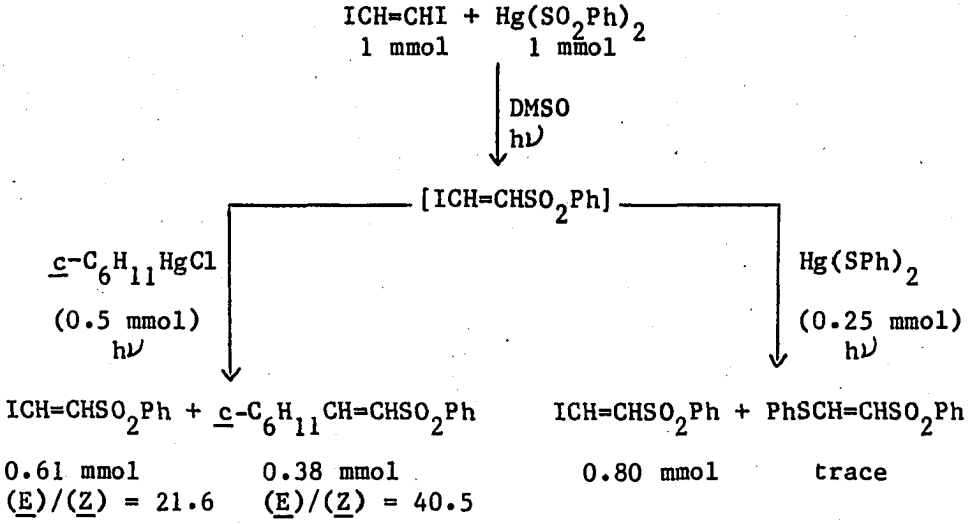
afforded only a monosubstitution product, β-iodovinyl phenyl sulfone, exclusively as the (E)-isomer (Eq. 85). This suggests that β-iodovinyl phenyl sulfone is not reactive towards benzenesulfonyl radical.

$$\underset{(\underline{E})}{ICH=CHI} + Hg(SO_2Ph)_2 \xrightarrow{h\nu} PhSO_2CH=CHI + IHgSO_2Ph \qquad (85)$$

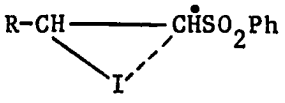
We observed that β-iodovinyl phenyl sulfone is reactive towards cyclohexyl radical. Therefore, β-iodovinyl phenyl sulfone, generated *in situ* from the reaction of 1,2-diiodoethylene and mercuric benzenesulfinate as described in Eq. (85), was allowed to react with cyclohexylmercury chloride or with mercuric phenylmercaptide under sunlamp irradiation. The results are summarized in Scheme 29.

We can see that the reaction with mercuric phenylmercaptide afforded only a trace amount of phenyl 2-(phenylthio)vinyl sulfone. This indicates that thiophenoxy radical was not trapped effectively. Otherwise, the reaction would give a higher yield of the substitution product.

Scheme 29

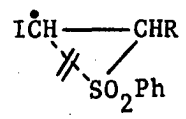


The reaction with cyclohexylmercury chloride, on the other hand, afforded 2-cyclohexylethenyl phenyl sulfone in high yield (76% yield if calculated from the mercurial). It is interesting to note that only the iodine was substituted by cyclohexyl radical which means that the alkyl radical regioselectively attacked the double bond at the carbon atom attached to iodine. This may be explained by structure 17 in which the iodine can stabilize the resulting radical by forming a bridged



17

radical. It is apparent that the sulfone sulfur cannot stabilize the resulting radical by forming a bridge if the adding radical attacks at the other end as shown in 18.



18

The regioselectivity of $\underline{c}$-$C_6H_{11}\bullet$ attack on $XCH{=}CHSO_2Ph$ is nearly exclusively on XCH= for X = I, but nearly exclusive on $=CHSO_2Ph$ for X = Cl. Apparently, the structure of X and not the $PhSO_2$ group controls the regioselectivity.

Professor Gary Keck has informed Professor Glen Russell that the addition of alkyl radicals to $\underline{n}$-$Bu_3SnCH{=}CHSO_2Ph$ occurs with regioselective attack at the stannyl-substituted carbon atom.

9. Mechanistic considerations

The reactions presented in this section are believed to occur by an addition-elimination mechanism as outlined in Scheme 30. The chain reactions have already been discussed in Section II.B. and will not be repeated here. We will consider the elimination process and factors which control and lead to the observed stereochemisty of the reaction products.

We have shown that methyl β-tri-$\underline{n}$-butylstannylacrylate, methyl β-iodoacrylate and β-chlorovinylmercury chloride reacted with cyclohexylmercury chloride in a stereospecific manner. The stereospecificity is higher for Z = I and HgCl than for Z = $\underline{n}$-Bu_3Sn.

Reaction of methyl β-tri-$\underline{n}$-butylstannylacrylate and $\underline{t}$-butylmercury chloride was not stereospecific. Both the ($\underline{E}$)- and ($\underline{Z}$)-reactants afforded methyl ($\underline{E}$)-4,4-dimethyl-2-pentenoate as the exclusive product.

Scheme 30

$$Q\bullet + XHC{=}CHZ \xrightarrow{\text{add.}} X\dot{C}H\text{-}CHZ(Q)$$

$$X\dot{C}H\text{-}CHZ(Q) \xrightarrow{\text{elim.}} XCH{=}CHQ + Z\bullet$$

$$Z\bullet + Q\text{-}Y \longrightarrow Z\text{-}Y + Q\bullet$$

$\underline{Z = n\text{-}Bu_3Sn}$

$$Z\bullet + RHgCl \longrightarrow Z\text{-}Cl + Hg^{o} + R\bullet$$

$$Z\bullet + PhSSPh \longrightarrow Z\text{-}SPh + PhS\bullet$$

$$Z\bullet + PhSO_2Cl \longrightarrow Z\text{-}Cl + PhSO_2\bullet$$

$\underline{Z = HgCl}$

$$Z\bullet + RHgCl \longrightarrow ZCl + Hg^{o} + R\bullet$$

$$Z\bullet + PhSSPh \longrightarrow ZSPh + PhS\bullet$$

$\underline{Z = I,\ Cl}$

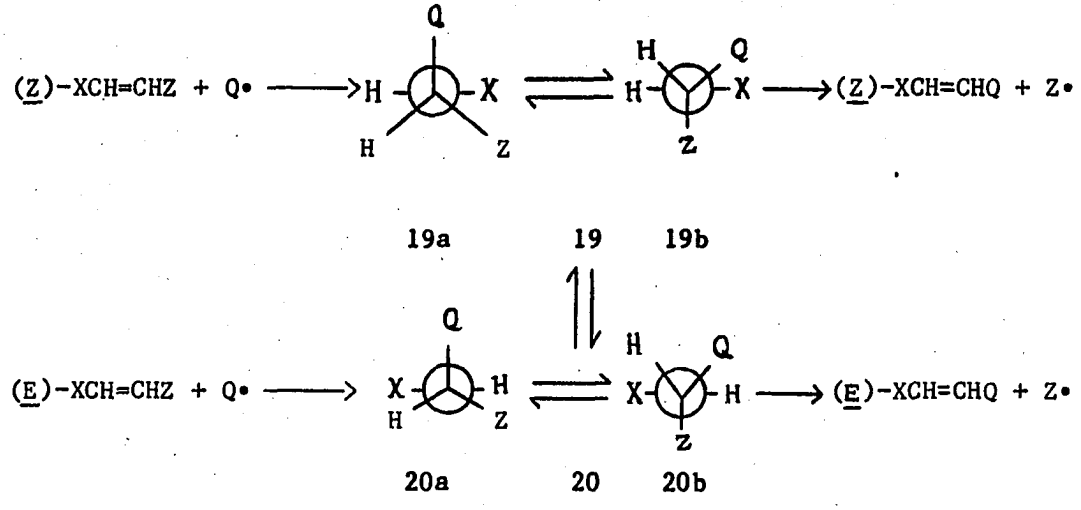
$$Z\bullet + RHgCl \longrightarrow ZHgCl + R\bullet$$

$$Z\bullet + Hg(SPh)_2 \longrightarrow ZHgSPh + PhS\bullet$$

Methyl β-iodoacrylate and β-chlorovinylmercury chloride, on the other hand, reacted with t-butylmercury chloride stereospecifically. This indicates that the elimination of Z• in Scheme 30 is apparently faster for Z = I or HgCl than for Z = $n\text{-}Bu_3Sn$.

Scheme 31 shows the conformations of the radical adducts for

Scheme 31



both (E)- and (Z)-reactants. With Q = 2° alkyl, elimination of Z = I, HgCl, Bu_3Sn must be faster than the equilibrium between **19** and **20**. With a bulky group, t-butyl, the **19** and **20** interconversion was also slower than the β-elimination of Z = I, HgCl. Therefore, the reactions were stereospecific. However, the case where Z = n-Bu_3Sn, a poorer leaving group, the interconversion from **19** to **20** with Q = t-butyl occurred faster than the elimination of n-Bu_3Sn•. This allowed the intermediate **19** to converted to the more stable conformation **20** which led to the formation of (E) substituted product.

With Q = SPh, stereospecificity was observed at the beginning of the reaction for the reactant with Z = I, HgCl. When reactions were carried out to completion, no stereospecificity was observed for the reactant with Z = I. Both (E)- and (Z)-reactants yielded the product with same (E)/(Z) ratios. The isomerization of the product was

responsible for the loss of the stereochemistry.

Methyl β-tri-n-butylstannylacrylate reacted with phenyl disulfide, benzenesulfonyl chloride, and t-butylmercury chloride in a non-stereospecific manner. With a bulky Q group (PhS, $PhSO_2$ t-Bu), conformation **19b** is apparently bypassed because of steric considerations and elimination only occurred from the more stable **20b**.

C. Conclusion

We have demonstrated that methyl β-iodoacrylate and β-chlorovinylmercury chloride can react with alkylmercurials by a free-radical chain addition-elimination process in a stereospecific manner with retention of stereochemistry. However, a lower stereospecificity was always observed under prolonged irradiation. The isomerization of the reactants, particularly the (Z)-reactants, as well as the isomerization of the resulting vinyl sulfides under the reaction conditions was a contributing factor to the stereochemistry observed.

Methyl β-tri-n-butylstannylacrylate also reacted with cyclohexylmercury chloride in a stereospecific manner, but reactions with t-butylmercury chloride, phenyl disulfide and benzenesulfonyl chloride were non-stereospecific. The reactions, however, were stereoselective in that the (E)-β-substituted acrylates were the major products. Indeed, only the (E)-products were observed for the reaction with t-butylmercury chloride and benzenesulfonyl chloride. Loss of stereochemistry for the reactions with phenyl disulfide is obviously the result of the isomerization of both the reactants and the products. Our results indicate that I• and HgCl are

better leaving groups than $\underline{n}$-$Bu_3Sn\bullet$.

1,2-Dichloroethylene can react with alkylmercurials, but in a non-stereospecific manner. This is due to the poor leaving ability of chlorine atom which allows the interconversion of the radical intermediates to the more stable conformation, or an equilibrated mixture of conformations, before the elimination of the chlorine atom.

We have also found that other 1,2-disubstituted ethylenes, β-chlorovinyl phenyl sulfide, β-iodovinyl phenyl sulfone, 1-chloro-2-iodoethylene and 1,2-diiodoethylene, can react with alkylmercurials to give the substitution products in reasonable yields.

1,2-Dichloroethylene, 1,2-diiodoethylene and 1-chloro-2-iodoethylene reacted with mercuric phenylmercaptide to give β-halovinyl phenyl sulfide. The vinyl sulfides was quite reactive towards thiophenoxy radical and underwent further reaction to give the disubstituted ethylene, 1,2-bis(phenylthio)ethene, in excellent yield.

For synthetic applications in which the stereochemistry is controlled in the substitution reaction with RHgX, vinyl iodides with electronegative β-substitutents (e.g., MeO_2C) are greatly preferred to vinylstannanes, vinyl chlorides, or vinyl sulfides. Vinylmercury halides lead to stereospecific substitutions, but the pure ($\underline{Z}$) isomers of β-substituted vinylmercurials are not readily available.

D. Experimental Section

1. General considerations

^{13}C NMR (22.6 MHz) were recorded on a JEOL FX-90Q spectrometer. Infrared spectra (IR) were recorded on a Beckman 4250 spectrophotometer. Melting points were determined on a Thomas-Hoover capillary melting-point apparatus and are uncorrected.

Solvents were purchased and dried as described previously. Commercially available compounds were purchased in high purity grades mostly from Aldrich and used without further purification. Most of the alkylmercurials were prepared by the literature procedures as mentioned before.

Trichloromethylmercury chloride was prepared from the reaction of mercuric chloride with sodium salt of trichloroacetic acid in refluxing monoglyme as described in the literature [113]. The trichloromethylmercury chloride prepared had mp 195-196 °C (lit. [113] mp 193-194 °C).

2. Preparation of 1,2-disubstituted ethylenes

Methyl (E)-β-iodoacrylate was prepared from the reaction of methyl propiolate and hydriodic acid (HI) at 0 °C [114]. Thus propiolic acid (from Aldrich) (0.1 mmol) and sulfuric acid (2 mL) were dissolved in 50 mL of methanol. The mixture was heated on a steam bath for 1 h. The mixture was cooled to room temperature and then poured into 100 mL of water. The product (methyl propiolate) was extract by 2 x 50 mL of chloroform ($CHCl_3$). The extract was

dried over anhydrous sodium sulfate and the solvent was then removed under vacuum. The crude product of methyl propiolate was slowly added into 100 mL of hydriodic acid (from Aldrich) while the mixture temperature was kept at 0 °C. After the addition, the mixture was stirred overnight in an ice bath. Water was added into the reaction mixture and the product was extracted by 3 x 30 mL of chloroform. The extract was dried (Na_2SO_4) and concentrated in vacuo. Distillation gave 4.5 g of methyl (E)-β-iodoacrylate (bp 115 °C/70 mmHg) ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1 H, J=15 Hz), 6.90 (d, 1H, J=15 Hz), 3.80 (s,3H).

Methyl (Z)-β-iodoacrylate was also prepared by the method described in the same literature [114]. Thus propiolic acid (0.2 mol) was added into 200 mL of 47% hydriodic acid. The mixture was heated on a steam bath for about 1.5 h during which time a white precipitate had formed. Water was added to the cooled reaction mixture and the product was extracted by ether. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated under vacuum. The white solid was recrystallized from chloroform to give 28 g of (E)-β-iodoacrylic acid ^{1}H NMR ($CDCl_3$) δ 11.32(br,s,1H), 8.12(d, 1H, J=14.5 Hz), 6.90(d, 1H, J=14.5 Hz). The β-iodoacrylic acid (22.5 g) and sulfuric acid (4 mL) were dissolved in 100 mL of methonol and the mixture was heated on a steam bath for 1 h. The mixture was cooled, poured into water and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4) and the solvent was removed in vacuo to give 24 g of methyl (E)-β-iodoacrylate as a pale yellow solid (mp 43-44 °C). ^{1}H NMR ($CDCl_3$) δ 7.95(d, 1H, J=15 Hz), 6.90(d, 1H. J=15 Hz), 3.80(s,3H).

Methyl (Z)-β-chloroacrylate was prepared by the literature procedure [115]. The acrylate prepared had bp 79-81 °C/78 mmHg (lit. [112] bp 79-83 °C/78 mmHg). ^{1}H NMR ($CDCl_3$) δ 6.78(d, 1H, J=8 Hz), 6.24(d, 1H, J=8 Hz), 2.80(s,3H). Methyl (E)-β-chloroacrylate was also prepared by the method described in the same literature [115] (lit. [115] bp 74-75 °C/131 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.35(d, 1H, J=14 Hz), 6.22(d, 1H, J=14), 3.75(s,3H).

Methyl (E)-β-tri-n-butylstannylacrylate was prepared by following the literature procedure [116]; ^{1}H NMR ($CDCl_3$) δ 7.72(d, 1H, J=19.5 Hz), 6.22(d, 1H, J=19.5 Hz), 3.70(s,3H), 1.8-0.7(m,27H). Methyl (Z)-β-tri-n-butylstannylacrylate was synthesized by the same procedure (bp 120-125 °C/1.5 mmHg or 70-80 °C/0.35 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.18(d, 1H, J=13 Hz), 6.70(d, 1H, J=13 Hz), 3.78(s,3H), 1.8-0.6(m,27H).

(E)-β-Chlorovinylmercury chloride was prepared from the reaction of mercuric chloride and acetylene in hydrochloric acid [3]. A stream of acetylene gas was passed into the mixture of mercuric chloride (100 g) in concentrated hydrochloric acid (75 mL) which was cooled in an ice bath. Unfortunately, no product formed unless a gas dispersion tube was used. With the gas dispersion tube, the white precipitate of β-chlorovinyl mercury chloride formed slowly. The precipitate started to form after passing the acetylene gas into the mixture for more than 0.5 h. The formation of the precipitate around or inside the dispersion tube blocked the stream of acetylene gas and, therefore, the tube needed to be cleaned or replaced occasionally. The precipitate was filtered

using sintered glass, washed with water, and air dried. Recrystallization from benzene gave a white solid of (E)-β-chlorovinylmercury chloride which had mp 115-123 °C (lit. [3] mp 123-124 °C). ^{1}H NMR ($CDCl_3$) δ 6.22(s,2H).

(Z)-β-Chlorovinylmercury chloride was prepared by the literature procedure [3]. Unfortunately, the mercurial was obtained in low yield and it was a mixture of (Z)- and (E)-β-chlorovinylmercury chloride in a 3:1 ratio (by ^{1}H NMR). Attempts were made but failed to improve the yield and the purity of the (Z)-isomer; ^{1}H NMR ($CDCl_3$) δ 6.98(d, 1H, J=7.2 Hz), 6.22(d, 1H, J=7.2 Hz).

(E)-β-Chlorovinyl phenyl sulfide was synthesized by following the literature procedure [117]. The sulfide was prepared by adding (dropwise) benzenesulfenyl chloride [118] (25 g) to ethyl acetate (100 mL) saturated with acetylene gas while the mixture was stirred in an ice bath. The acetylene gas was passed through the mixture by means of a gas dispersion tube during the addition of the benzenesulfenyl chloride. After the addition, acetylene was passed through the mixture for an additional 6 h. Ethyl acetate was removed under vacuum and the product was distilled (bp 90 °C/2.1 mmHg, lit. [117] bp 118 °C/15 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.32(s,5H), 6.61(d, 1H, J=13 Hz), 6.23(d, 1H, J=13 Hz); ^{13}C NMR (proton decoupled, $CDCl_3$, reported in ppm from TMS) δ 133.9, 129.4, 129.1, 127.1, 125.5, 120.1; GCMS, m/e (relative intensity) 172(26), 170(71,M^+), 135(100), 91(59).

(E)-1-Chloro-2-iodoethylene was prepared from the cleavage of (E)-β-chlorovinylmercury chloride by iodine. Thus (E)-β-

chlorovinylmercury chloride (40 mmol) was dissolved in diethyl ether (200 mL). Iodine (40 mmol) was added and the mixture was stirred for 3 days. The precipitate was removed by filtration. The filtrate was washed with 10% aqueous sodium thiosulfate solution to remove the remaining iodine and dried over anhydrous sodium sulfate. Ether was removed under vacuum to afford 2.3 g of a liquid product which was shown to be pure (E)-1-chloro-2-iodoethylene by GLC and ^{1}H NMR; ^{1}H NMR ($CDCl_3$) δ 6.82(d, 1H, J=14 Hz), 6.52(d, 1H, J=14 Hz).

(E)-1,2-Diiodoethylene was synthesized by the literature procedure [119]. Thus 45 g of iodine was dissolved in 200 mL of absolute ethanol in a round-bottom flask equipped with a magnetic stirrer. Acetylene was purified by passing through water and concentrated sulfuric acid before it was bubbled into the mixture. A white precipitate started to form after a few days and the reaction was carried out for about ten days. A small amount of 10% aqueous sodium thiosulfate solution was added to remove the red color of iodine. The solid was filtered and recrystallized form ethanol to give white crystal line 1,2-diiodoethylene (mp 71.5-72 °C, lit. [119] mp 73 °C).

^{1}H NMR ($CDCl_3$) δ 7.10(s,2H).

GCMS, m/e (relative intensity) 280(100, M^+), 254(38), 153(55), 127(41).

(E)-1,2-Dichloroethylene and (Z)-1,2-dichloroethylene were purchased from Aldrich. They were shown to be in high purity by GLC and were used without further purification.

3. General procedure for the photoreaction of methyl β-tri-n-butylstannylacrylate with alkylmercury chlorides

Methyl β-tri-n-butylstannylacrylate (0.3 mmol) and the alkylmercurial (see Table 16) were dissolved in 10 mL of benzene or a mixture of benzene and dimethyl sulfoxide (8:2). The mixture was degassed with a stream of nitrogen for 5 min and irradiated in a Rayonet Photoreactor or with a 275-W sunlamp placed about 15 cm from the reaction vessel. After the irradiation, the reaction mixture was washed with water and twice with 10% aqueous sodium thiosulfate solution. The mixture was dried over anhydrous sodium sulfate and concentrated in vacuo. The oily residue was analyzed by GLC, ^{1}H NMR and GCMS which indicated the presence of the substitution product. Yield of the substitution product was determined by ^{1}H NMR using dibromomethane as an internal standard. The (E)/(Z) ratio was determined by GLC. Identity of the substitution product was confirmed by comparison of its ^{1}H NMR with that of the authentic compound or with the ^{1}H NMR reported in the literature. The ^{1}H NMR of methyl (E)-3-cyclohexylpropenoate [120] and methyl (E)-4,4-dimethyl-2-pentenoate [121] have been reported in the literature.

The following ^{1}H NMR and GCMS data were obtained:

Methyl (E)-3-cyclohexylpropenoate:

^{1}H NMR ($CDCl_3$) δ 6.95(dd, 1H, J_{trans} = 16.8 Hz, $J_{1,2}$ = 6 Hz), 5.75(dd, 1H, J_{trans} = 16.8 Hz, $J_{1,3}$ = 1.5 Hz), 3.7(s,3H), 2.9-0.8(m,11H).

GCMS, m/e (relative intensity) (Z)-isomer:170(0.5), 168(53,M^+),

94(54), 87(78), 79(57), 67(98), 55(100). (E)-isomer:170(0.2), 168(31, M^+), 94(45), 87(82), 79(61), 67(99), 55(100).

Methyl (E)-4,4-dimethyl-2-pentenoate:

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98(d, 1H, J=15.9 Hz), 5.74(d,1H, J=15.9 Hz), 3.78(s,3H), 1.08(s,9H).

GCMS, m/e (relative intensity) 142(20,M^+), 127(55), 111(41), 95(56), 83(100), 67(56), 55(67), 41(71).

4. Photoreaction of methyβ-tri-n-butylstannylacrylate with phenyl disulfide

Methyl (E)-β-tri-n-butylstannylacrylate (0.3 mmol) and phenyl disulfide (0.5 mmol) in 10 mL of nitrogen-purged benzene in a Pyrex tube were irradiated at 350 nm in a Rayonet Photoreactor. After irradiation for 8 h, the reaction mixture was concentrated under vacuum to yield an oily residue. Analysis by GLC, ^{1}H NMR and GCMS indicated the presence of (E)- and (Z)-β-phenylthioacrylate in 79% yield. The (E)/(Z) ratio was determined by GLC to be 3.8. The substitution product, methyl β-phenylthioacrylate was further confirmed by comparison of its ^{1}H NMR with that reported in the literature [122].

The reaction of methyl (Z)-β-tri-n-butylstannylacrylate with phenyl disulfide was also carried out by the same procedure. The reaction afforded methyl β-phenylthioacrylate in 91% yield. The substitution product had (E/(Z) = 3.7.

Methyl (E)-β-phenylthioacrylate:

^{1}H NMR ($CDCl_3$) δ 7.82(d, 1H, J=15.6 Hz), 7.35(m,5H), 5.68(d, 1H,

J=15.6 Hz), 3.67(s,3H).

GCMS, m/e (relative intensity) 196(1), 194(48, M^+), 163(46), 135(100), 109(77), 91(67), 65(73), 51(80).

Methyl (Z)-β-phenylthioacrylate

^{1}H NMR ($CDCl_3$) δ 7.7-7.2(m, 1+5H), 5.9(d, 1H, J=10 Hz), 3.7(s,3H).

GCMS, m/e (relative intensity) 196(0.6), 194(77,M^+), 163(53), 135(100), 109(56), 91(41), 65(46), 51(50).

5. Determination of (E)/(Z) ratio of the substitution product occurring during the irradiation of β-tri-n-butylstannylacrylate with phenyl disulfide

Methyl (E)-β-tri-n-butylstannylacrylate or methyl (Z)-β-tri-n-butylstannylacrylate (0.3 mmol) and phenyl disulfide (0.5 mmol) were dissolved in 1 mL of nitrogen-purged benzene in a Pyrex tube. The mixture was irradiated in a Rayonet Photoreactor or with a 275-W sunlamp placed about 20 cm from the reaction vessel. Small amounts of the reaction mixture were withdrawn at different periods of time by a syringe and analyzed directly by GLC. The (E)/(Z) ratios are summarized in Table 18.

6. Photoreaction of methyl β-tri-n-butylstannylacrylate with benzenesulfonyl chloride

Methyl β-tri-n-butylstannylacrylate (0.3 mmol) and benzene sulfonyl chloride (0.5 mmol) were dissolved in 10 mL of benzene in a Pyrex tube. After a nitrogen purge, the mixture was irradiated in a Rayonet Photoreactor for 10 h. The reaction mixture was concentrated

in vacuo and analyzed by GLC, ^{1}H NMR and GCMS. The mixture was found to consist of methyl β-benzenesulfonylacrylate, tri-n-butyltin chloride and the remaining benzenesulfonyl chloride. Yields of the substitution product are presented in Table 17. The substitution product, methyl β-benzenesulfonylacrylate, was shown by ^{1}H NMR to be the pure (E)-isomer from the large coupling constant of the vinyl proton (J=16.2 Hz). The ^{1}H NMR of methyl (E)-β-benzenesulfonylacrylate has been reported in the literature [123].

^{1}H NMR ($CDCl_3$) δ 8.2-7.7(m,2H), 7.78-7.3(m,3H), 7.4(d, 1H, J=16.2 Hz), 6.82(d, 2H, J=16.2 Hz), 3.8(s,3H).

GCMS, m/e (relative intensity) 226(1.3,M^+), 125(100), 77(77), 51(88).

7. General procedure for the photoreactions of methyl β-haloacrylates with alkylmercury chlorides

The general procedure involved the reaction of methyl β-haloacrylate (0.3 mmol) and the alkylmercury chloride (see Table 19) in 10 mL of nitrogen-purged benzene in a Pyrex tube. The mixture was irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel or in a Rayonet Photoreactor for a period of time as indicated in Table 19. After the irradiation, 10 mL of benzene was added to the reaction mixture. The mixture was washed with 3 x 20 mL of 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The benzene was removed under vacuum and the oily residue was analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated the presence of the substitution product. All the yields were obtained

from ^{1}H NMR whereas the (E)/(Z) ratios were determined by GLC (Table 19). The ^{1}H NMR and GCMS data for methyl 3-cyclohexylpropenoate and methyl (E)-4,4-dimethyl-2-pentenoate were identical to those obtained previously. The ^{1}H NMR of methyl 4-methyl-2-pentenoate has been reported in the literature [120,124]. The following ^{1}H NMR and GCMS data were obtained for methyl (E)-4-methyl-2-pentenoate.

^{1}H NMR ($CDCl_3$) δ 6.9(dd, 1H, J_{trans} = 16 Hz, $J_{1,2}$ = 6.2 Hz), 5.75(dd, 1H, J_{trans} = 16 Hz, $J_{1,3}$ = 1.5 Hz), 3.65(s,3H).

GCMS, m/e (relative intensity) 130(0.8), 128(57,M^+), 113(27), 97(67), 81(32), 73(64), 69(100).

8. Photoreaction of methyl β-iodoacrylate with mercuric phenylmercaptide

Methyl β-iodoacrylate (0.3 mmol) and mercuric phenylmercaptide (0.5 mmol) were dissolved in 10 mL of a mixture of benzene and DMSO (8:2) in a Pyrex tube. The mixture was degassed for 5 min with a stream of nitrogen and irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel or in a Rayonet Photoreactor. After irradiation for a period of time (see Table 20), the mixture was poured into water. The organic products were extracted with benzene, washed with 2 x 20 mL aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The concentrated product mixture was analyzed by GLC, ^{1}H NMR and GCMS which revealed the presence of methyl β-phenylthioacrylate. Yields of the products were determined by ^{1}H NMR and the (E)/(Z) ratios were obtained from the GLC. Results are presented in Table 20.

9. Photoreaction of β-chlorovinylmercury chloride with organomercurials

β-Chlorovinylmercury chloride (1 mmol) and the alkylmercury chloride (1.2 mmol) were dissolved in a nitrogen-purged DMSO in a Pyrex tube. The mixture was irradiated in a Rayonet Photoreactor for 10 h. During the irradiation, mercury metal had precipitated. The mixture was decanted into water and the organic products were extracted with benzene. The extract was washed with 2 x 20 mL of 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. the solvent was then removed under vacuum to give a colorless liquid which was analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated the presence of the substitution products, the alkenyl chlorides. Yields and stereochemistry of the alkenyl chlorides were determined by GLC and are summarized in Table 21. The substitution product, (2-chloroethenyl)cyclohexane was isolated by preparative GLC. All the products were confirmed by comparing their ^{1}H NMR and IR to those reported in the literature [125]. The following data were obtained for the substitution products.

(E)-(2-Chloroethenyl)cyclohexane:

^{1}H NMR ($CDCl_3$) δ 6.25-5.4 (m,2H), 2.7-0.5(m, 11H).

IR (neat, NaCl plates, cm^{-1}) 2920(vs), 2850(vs), 1620(m), 1442(s), 930(s), 812(s), 728(s).

GCMS, m/e (relative intensity) 146(5), 144(15,M^+), 109(26), 82(64), 67(100).

(Z)-(2-Chloroethenyl)cyclohexane:

^{1}H NMR($CDCl_3$) δ 6.01-5.42(m,2H), 2.8-0.7(m,11H).

IR (neat, NaCl plates, cm^{-1}) 2940 (vs), 2870(s), 1637(m), 1458(s), 1345(m), 962(m), 893(m), 810(w), 743(s), 715(s).

GCMS, m/e (relative intensity) 146(5), 144(15,M^+), 109(31), 82(74), 67(100).

(E)-1-Chloro-3,3-dimethyl-1-butene:

^{1}H NMR ($CDCl_3$) δ 5.9(s,2H), 1.05(s,9H).

GCMS, m/e (relative intensity) 120(3), 118(10,M^+), 103(44), 83(100), 67(52).

10. Photoreaction of β-chlorovinylmercury chloride with phenyl disulfide

The mixture of β-chlorovinylmercury chloride (1 mmol) and phenyl disulfide (see Table 21) in 10 mL of nitrogen-purged DMSO in a Pyrex tube was irradiated in a Rayonet Photoreactor or with a sunlamp. After the irradiation, the usual workup afforded an oily residue. Analysis by GLC, ^{1}H NMR and GCMS indicated the presence of the substitution products as shown in Table 21. The identity of the substitution products was confirmed by comparison of their GLC retention times and ^{1}H NMR with those of the authentic compounds. 1,2-Bis(phenylthio)ethene was synthesized by the literature procedure [126].

(Z)-β-Chlorovinyl phenyl sulfide:

GCMS, m/e (relative intensity) 172(26), 170(74,M^+), 135(100). 91(61).

(Z)-Bis(phenylthio)ethene:
^{1}H NMR ($CDCl_3$) δ 7.7-7.0(m, 10H), 6.5(s,2H).

GCMS, m/e (relative intensity) 246(8), 244(82,M^+), 135(100), 134(75), 91(69).

(E)-Bis(phenylthio)ethene:

GCMS, m/e (relative intensity) 246(10), 244(95), 135(100), 134(77), 91(61).

11. Photoreaction of 1,2-dichloroethylene with organomercurials

The mercurial (1 mmol) and 1,2-dichloroethylene were dissolved in 5 mL of DMSO in a Pyrex tube equipped with a rubber septum. After a nitrogen purge, the mixture was irradiated in a Rayonet Photoreactor for 20-21 h (see Table 22). The mixture was poured into water and the organic products were extracted with 30 mL of benzene. The extract was washed with 2 x 20 mL of 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The mixture was then concentrated and analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated that the reaction mixture consisted of only the (E)- and (Z)-isomers of the substitution product. The results are summarized in Table 22.

1-Chloro-1-hexene:

GCMS, m/e (relative intensity) 120(6), 118(20,M^+), 56(100).

12. Photoreaction of 1,2-dichloroethylene with mercuric phenylmercaptide and mercuric benzenesulfinate

Mercuric phenylmercaptide (1 mmol) and 1,2-dichloroethylene (see Table 22) were dissolved in 5 mL of nitrogen-purged DMSO in a Pyrex

flask. The mixture was irradiated in a Rayonet Photoreactor for 20-21 h. The usual workup afforded the substitution products in good yields as shown in Table 22.

The same procedure was also applied for the reaction of (Z)-1,2-dichloroethylene with mercuric benzenesulfinate. Unfortunately, the reaction did not occur and no substitution product was observed.

13. Reaction of (Z)-1,2-dichloroethylene with mercuric phenylmercaptide in the dark

The reaction involved 1 mmol of (Z)-1,2-dichloroethylene and 1 mmol of mercuric phenylmercaptide dissolving in 5 mL of nitrogen-purged DMSO in a Pyrex flask. The flask was wrapped with aluminum foil to exclude light and placed in a Rayonet Photoreactor at 40-45 ° C. After 20 h, the usual workup gave no substitution product.

14. Photoreaction of (E)-β-chlorovinyl phenyl sulfide with organomercurials

(E)-β-Chlorovinyl phenyl sulfide (1 mmol) and the mercurial (see Table 23) were dissolved in 5 mL of DMSO in a Pyrex tube equipped with a rubber septum. After a nitrogen purge, the mixture was irradiated at 350 nm in a Rayonet Photoreactor. After irradiation, the mixture was poured into water. The organic products were extracted with 20 mL of benzene. The extract was washed with 2 x 20 ml of 10% aqueous sodium thiosulfate solution, dried over sodium sulfate and concentrated in vacuo. The concentrated mixture was analyzed by GLC, ^{1}H NMR and GCMS as usual. The analysis revealed the presence of the

substitution products. Yields and stereochemistry of the substitution products were determined by GLC and the results are given in Table 23. 1-Hexenyl phenyl sulfide [127] and 3,3-dimethyl-1-butenyl phenyl sulfide [100] have been reported in the literature.

The following data were obtained for the substitution products.

(E)-2-Cyclohexylethenyl phenyl sulfide:

GCMS, m/e (relative intensity) 220(5), 218(100,M^+), 109(57), 67(86).

(Z)-2-Cyclohexylethenyl phenyl sulfide:

GCMS, m/e (relative intensity) 220(5), 218(99,M^+), 109(95), 67(100).

(E)-3,3-Dimethyl-1-butenyl phenyl sulfide:

^{1}H NMR ($CDCl_3$) δ 7.0-7.4(m,5H), 6.05(s,2H), 1.08(s,9H).

GCMS, m/e (relative intensity0 194(2), 192(46,M^+), 177(92), 83(100), 65(62), 55(82).

15. Competition reaction of (Z)-1,2-dichloroethylene and (E)-β-chlorovinyl phenyl sulfide with cyclohexylmercury chloride

(Z)-1,2-Dichloroethylene (1 mmol), (E)-β-chlorovinyl phenyl sulfide (1 mmol) and cyclohexylmercury chloride (0.5 mmol) were dissolved in 5 mL of DMSO in a Pyrex tube. After a nitrogen purge, the mixture was irradiated in a Rayonet Photoreactor for 10 h. The usual workup afforded a product mixture which was analyzed by GLC. The analysis revealed the presence of (E)- and (Z)-(2-chloroethenyl)cyclohexanes (0.15 mmol) and (E)- and (Z)-(2-phenylthioethenyl)cyclohexane (0.22 mmol). 1,2-Bis(phenylthio)ethene

(0.06 mol), and cyclohexyl phenyl sulfide (0.04 mmol) were also observed. The results are summarized in Eq. (90).

16. Photoreaction of (E)-1-chloro-2-iodoethylene with organomercurials

(E)-1-Chloro-2-iodoethylene (1 mmol) and the mercurial (see Table 24) were dissolved in 5 mL of DMSO in a Pyrex flask. After a nitrogen purge, the mixture was irradiated with a 275-W sunlamp placed ca. 20 cm from the reaction vessel. After the irradiation, the usual workup afforded the concentrated product mixture which was analyzed by GLC and GCMS. The product mixture was found to consist of the substitution product in moderate to good yield. Yield and stereochemistry of the substitution product were determined by GLC and the results are summarized in Table 24.

The reaction of (E)-1-chloro-2-iodoethylene (1 mmol) with mercuric benzenesulfinate (0.5 mmol) was also carried out by the same procedure. The reaction afforded only the monosubstitution product, 2-chloroethenyl phenyl sulfone, exclusively as (E)-isomer in 80% yield. This substitution product was identified based on the ^{1}H NMR and GCMS data.

The following data were obtained for (E)-2-chloroethenyl phenyl sulfone.

^{1}H NMR ($CDCl_3$) δ 8.1-7.1(m,5+1H), 6.7(d, 1H, J=14 Hz).

GCMS, m/e (relative intensity) 204(5), 202(15,M^+), 125(100), 77(76), 51(52).

17. Photoreaction of cyclohexylmercury chloride with 2-chloroethenyl phenyl sulfone generated in situ

(E)-1-Chloro-2-iodoethylene (1 mmol) and mercuric benzenesulfinate (0.5 mmol) were dissolved in 5 mL of nitrogen-purged DMSO in a Pyrex flask. The mixture was irradiated with a 275-W sunlamp placed about 20 cm from the reaction flask. After the irradiation for 16 h, cyclohexylmercury chloride (1 mmol) was added to the reaction mixture and the irradiation continued for an additional 11 h. Workup as described before afforded a mixture which was analyzed by GLC and GCMS. The analysis indicated the presence of 2-chloroethenyl phenyl sulfone (0.65 mmol, (E)/(Z)=16), (2-chloroethenyl)cyclohexane (0.28 mmol, (E)/(Z)=1.4) and 2-cyclohexylethenyl phenyl sulfone (0.05 mmol, (E) only). 2-Cyclohexylethenyl phenyl sulfone had the following GCMS.

GCMS, m/e (relative intensity) 250 (1.6, M^+), 109(100), 67(62).

18. Photoreaction of (E)-1,2-diiodoethylene with organomercurials

The mixture of (E)-1,2-diiodoethylene (1 mmol) and the organomercurial (see Table 25) in 5 mL of nitrogen-purged DMSO in a Pyrex tube was irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel. After the irradiation, the mixture was poured into water and the organic products were extracted with benzene. The extract was washed with aqueous sodium thiosulfate and dried over anhydrous sodium sulfate. After the removal of benzene, the product mixture was analyzed by GLC, ^1H NMR and GCMS. The analysis indicated the presence of the substitution product and the results are

summarized in Table 24.

The following data were obtained for the substitution products.

(E)-1-Iodo-1-hexene:

GCMS, m/e (relative intensity) 210(65,M^+), 167(21), 154(41), 83(16), 55(100).

(Z)-1-Iodo-1-hexene:

GCME, m/e (relative intensity) 210(77.M^+), 167(18), 154(48), 83(35), 55(100).

(E)-(2-Iodoethenyl)cyclohexane:

GCMS, m/e (relative intensity) 236(21,M^+), 109(45), 67(100), 55(28).

(Z)-(2-Iodoethenyl)cyclohexane:

GCMS, m/e (relative intensity) 236(34,M^+), 109(48), 67(100), 55(28).

(E)-3,3-Dimethyl-1-iodo-1-butene:

^{1}H NMR ($CDCl_3$) δ 6.65(d, 1H, J=14.5 Hz), 5.98(d, 1H, J=14.5 Hz), 1.05(s, 9H).

GCMS, m/e (relative intensity) 210(18,M^+), 83(72), 68(53), 67(41), 55(100).

(E)-2-Iodoethenyl phenyl sulfone:

^{1}H NMR ($CDCl_3$) δ 8.02(d, 1H, J=14.4 Hz), 8.0-7.75(m,2H), 7.75-7.5(m,3H), 7.3(d, 1H, J=14.4 Hz).

GCMS, m/e (relative intensity) 294(11,M^+), 125(85), 77(100).

19. In situ photoreaction of β-iodovinyl phenyl sulfone with mercuric phenylmercaptide

(E)-1,2-Diiodoethylene (1 mmol) and mercuric benzenesulfinate (1 mmol) were dissolved in 5 mL of DMSO in a Pyrex flask. After a nitrogen purge, the mixture was irradiated for 7 h with a 275-W sunlamp placed about 20 cm from the reaction vessel. mercuric phenylmercaptide (0.25 mmol) was added into the reaction mixture and the irradiation was continued for an additional 10 h. The mixture was poured into water and the products were extracted with benzene. The extract was washed with aqueous sodium thiosulfate and dried over sodium sulfate. After the removal of the benzene, the residue was analyzed by GLC and GCMS which revealed the presence of β-iodovinyl phenyl sulfone (0.80 mmol, 80% yield) and a trace amount of phenyl 2-(phenylthio)vinyl sulfone.

20. In situ photoreaction of β-iodovinyl phenyl sulfone with cyclohexylmercury chloride

The mixture of 1,2-diiodoethylene (1 mmol) and mercuric benzenesulfinate (1 mmol) in 5 mL of nitrogen-purged DMSO was irradiated for 7 h with a 275-W sunlamp placed about 20 cm from the reaction vessel. Cyclohexylmercury chloride (0.5 mmol) was added in the reaction mixture and the irradiation was continued for an additional 10 h. The usual workup afforded the residue which was analyzed by GLC. The analysis indicated the presence of β-iodovinyl phenyl sulfone (0.61 mmol, (E)/(Z) = 21.6) and β-cyclohexylethenyl phenyl sulfone (0.38 mmol, (E)/(Z) = 40.5). The presence of the

products were verified by GLC retention time matching with the products obtained previously.

PART II. FREE RADICAL CHAIN REACTIONS OF ALLYL AND ALKYNYL DERIVATIVES WITH ORGANOMERCURIALS

I. SUBSTITUTION REACTIONS OF ALLYL DERIVATIVES

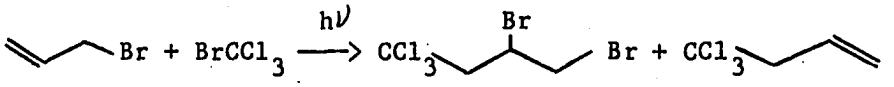
A. Introduction

Heterolytic substitution reactions of substituted allylic systems with migration of the double bonds are known and several reports have been appeared in the literature. Thus, Gendreau et al. [128], Barsanti et al. [129], Okamura and Takei [130], and Julia et al. [131] and their respective co-workers found independently that allylic sulfides, sulfones, and sulfonium salts undergo substitution with Grignard reagents in the presence of a copier(I) salt or a nickel-phosphine complex to give carbon-carbon bond formation. Trost and co-workers reported that regio- and stereoselective nucleophilic displacement of allylic sulfones with stabilized carbanions such as malonate occurred under the influence of palladium(0) catalysis [132]. Palladium-catalysed asymmetric carbon-carbon bond formation utilizing chiral allylic sulfinates by way of intermediate allylic sulfones has been reported by Hiroi et al. [133].

Lithium dialkylcuprates can also react with allylic sulfoxides and sulfones to give substitution products [134]. The reactions have been reported to occur in a regio- and stereoselective manner.

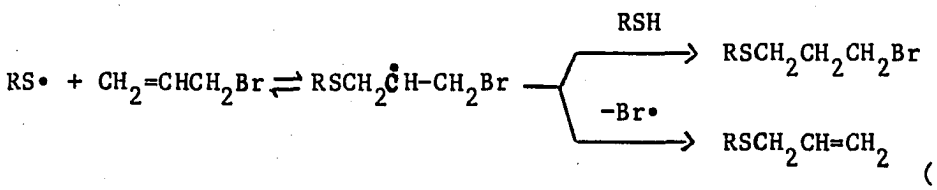
Homolytic substitution reactions of allylic systems by carbon-centered and heteroatom-centered radicals have been studied extensively and a number of reports have appeared in the literature. In 1949, Kharasch and Sage observed the formation of 4,4,4-trichloro-1-butene as a byproduct in the radical addition of bromotrichloro-methane to allyl bromide (Eq. 86) [135]. Since that time many similar

reactions have been reported. The reaction of allyl bromide with thiyl



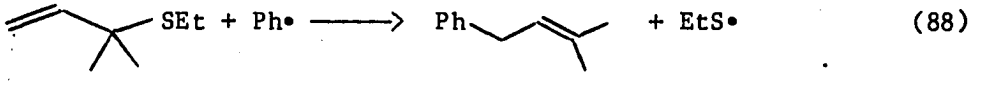
(86)

radicals which leads to the formation of allyl sulfides (Eq. 87) has been observed by Hall [136].



(87)

Reactions of allyl sulfides and halides with phenyl radical formed from thermal decomposition of phenylazotriphenylmethane have been reported to proceed by either a stepwise addition-elimination or a S_H2' process [137]. Reaction of α,α-dimethylallyl ethyl sulfide produced 2-methyl-4-phenyl-2-butene as shown in Eq. (88).



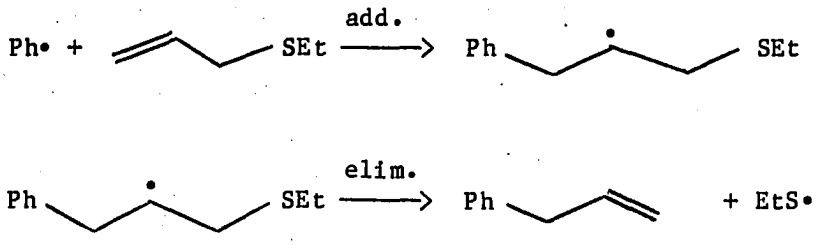
(88)

This apparent substitution reaction involves attack of a phenyl radical on the terminal unsaturated carbon atom of the allyl sulfide with subsequent elimination of the thiyl radical. The reaction can proceed by either a stepwise or a concerted process as shown in Scheme 32.

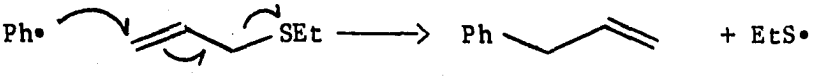
Organotin hydrides are useful intermediates for the reduction of organic compounds such as halides, aldehydes, ketones, isocyanates, and isothiocyanates [60]. They also find use in the synthesis of other organotin compou]nds because they add to carbon-carbon double

Scheme 32

Stepwise

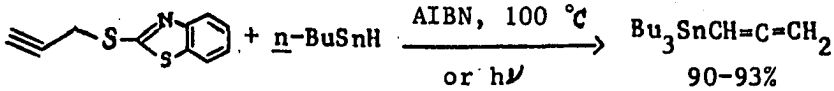


Concerted

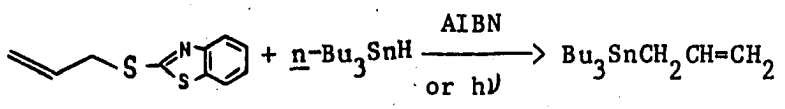


and triple bonds. Certain of these reactions can proceed by free-radical mechanisms in which organic radicals are intermediates. Hydrogen atom transfer from organotin hydrides to these radicals is a very fast process.

Tri-n-butylstannyl radical is known to add to multiple bonds reversibly [138]. Uneo and Okawara have reported the desulfurizative stannylation of allylic or propargylic sulfides via S_H' processes [139]. Thus, tri-n-butylstannyl radical generated from azobisisobutyronitile and tri-n-butyltin hydride reacted with 2-(propargylthio)benzothiazole or allylthiobenzothiazole to give tri-n-butylstannylallene or allyltri-n-butylstannane in high yield as shown in Eqs. (89) and (90).



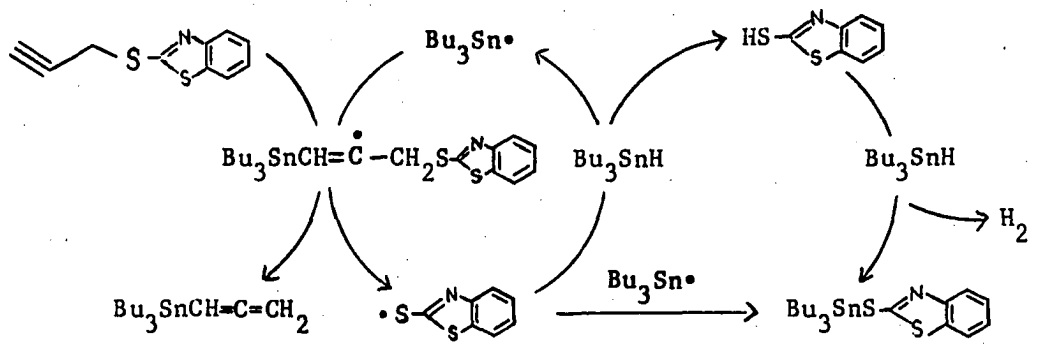
(89)



(90)

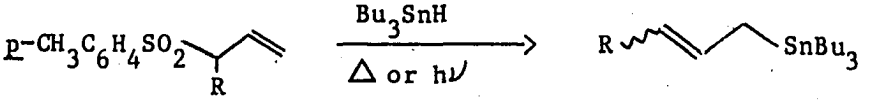
The mechanism as shown in Scheme 33 involves the addition of tri-n-butylstannyl radical at the terminal carbon atom of the multiple

Scheme 33



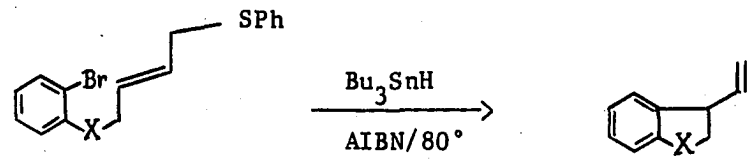
bond. The resulting radical then eliminates benzothiazoylthio radical to form the allene product. The thiyl radical abstracts hydrogen atom from the tin hydride to give the thiol and tri-n-butylstannyl radical which continues the chain.

Allylic sulfones can also undergo similar reactions. Reactions of allyl sulfones with tri-n-butyltin hydride in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) in refluxing benzene afforded allylstannanes in good yields (Eq. 91) [140]. The same stannylated products were also obtained by a photochemical procedure at room temperature.



(91)

Ueno et al. have also reported the first intramolecular cyclization involving radical desulfurization of an allylic sulfide [141]. The allylic sulfide 21 reacted with twice the molar amount of tri-n-butyltin hydride to give product 22 in high yield (Eq. 92).



(92)

21 22

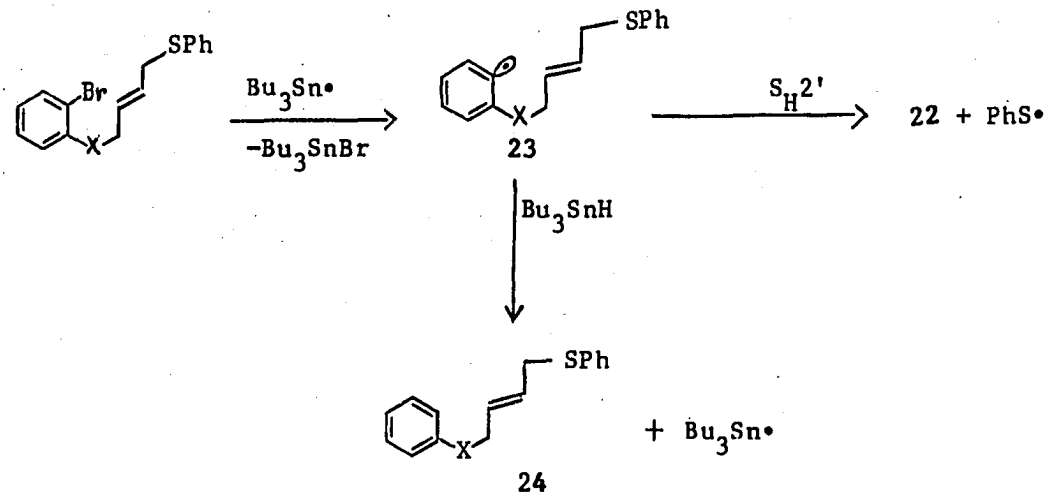
X = NH 96%

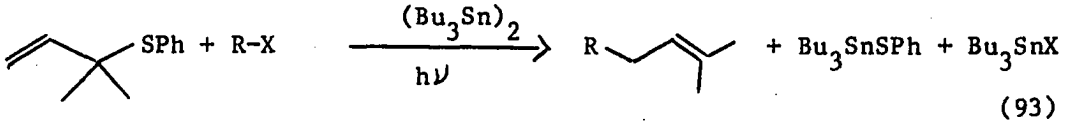
= O 75%

When the reaction was carried out in the presence of higher concentrations of tri-n-butyltin hydride, the simple reduction product 23 was also obtained in addition to 18. The data are consistent with the mechanism outlined in Scheme 34. It involves the abstraction of the bromine atom by tri-n-butylstannyl radical to give the aryl radical 23. The radical 23 then undergoes intramolecular addition to the double bonds with elimination of benzenethiyl radical to give 22. The formation of 22 apparently occurred by a concerted S_H2' process. With high concentrations of the tin hydride, 23 is trapped to give product 24.

Certain allylic phenyl sulfides react with alkyl halides or selenides upon irradiation in the presence of hexabutylditin to give formal S_H2' substitution products as shown in Eq. (93) [68]. The process was successful for the introduction of groups such as prenyl,

Scheme 34

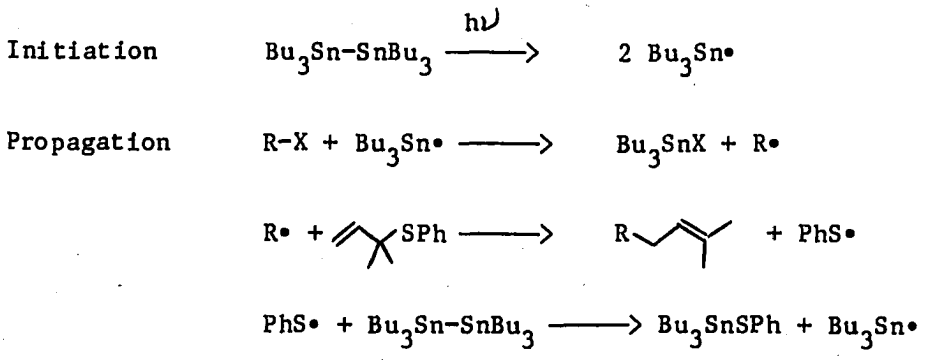




(93)

process was successful for the introduction of groups such as prenyl, which cannot be accomplished by using an allylstannane. The mechanism is outlined in Scheme 35.

Scheme 35



Allylstannanes are recognized to undergo S_H2' substitution with a variety of alkyl halides (Eq. 94,95). The first report of this

$$R\bullet + CH_2{=}CHCH_2SnR'_3 \xrightarrow{S_H2'} RCH_2CH{=}CH_2 + R_3'Sn\bullet \qquad (94)$$

$$R_3'Sn\bullet + R{-}X \longrightarrow R_3'SnX + R\bullet \qquad (95)$$

reaction by Kosugi et al. appeared in 1973 [142]. They investigated reactions of allyltrimethylstannane with alkyl halides (Eq. 96) under various conditions. The reaction was promoted by benzoyl peroxide

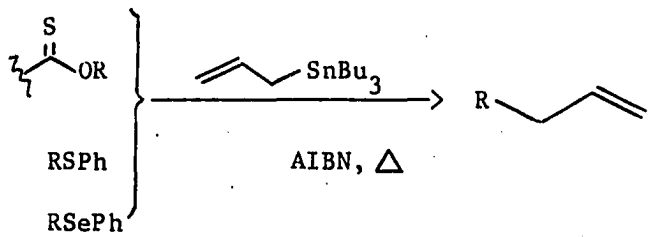
$$CH_2{=}CHCH_2SnMe_3 + R{-}X \xrightarrow[80\ ^\circ C]{BPO} RCH_2CH{=}CH_2 + Me_3SnX \qquad (96)$$

(BPO) and retarded by p-benzoquinone which supports the free-radical chain mechanism.

In 1975, Grignon et al. reported the reaction of allylic organotin compounds with numerous organic halides by a substitution pathway with complete allylic shift [143]. The reactions were carried out at high temperatures or under UV irradiation to give substitution products in moderate to good yields.

The synthetic utility of allylstannanes has been developed by Keck [144-147], Webb and Danishefsky [148], and Baldwin et al. [149] who applied Reaction 105 to natural product synthesis. The reactions of allylstannanes and alkyl halides have been studied in detail by Keck et al. [150]. They found that the reactions have the advantages

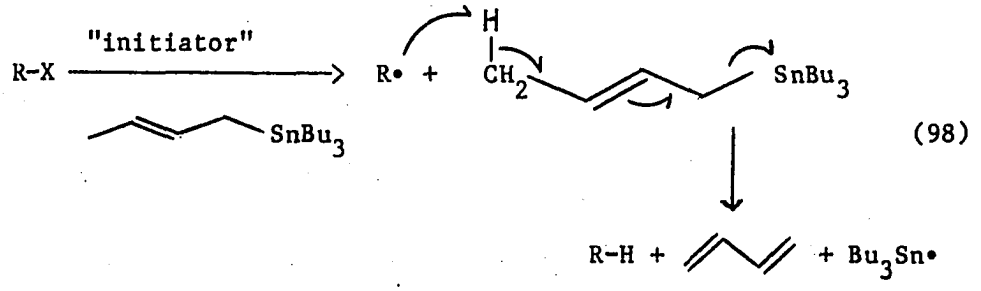
of tolerating quite complex functionality in the substrates, are nearly stoichiometric with regard to reagents, and do not require extensive experimentation for application to new substrates. Besides alkyl halides, other substrates such as thioacyl derivatives and alkyl phenyl sulfides or selenides, have been successfully employed in the reaction (Eq.).



(97)

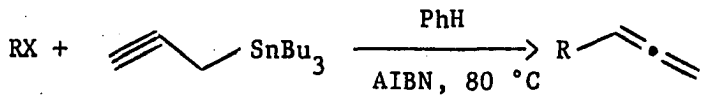
[150]

The reaction, unfortunately, has been limited to only the parent allyltri-n-butylstannane or derivatives with substitution in the 2 or 3 position of the allyl unit. With substitution in the 1 position of the allyl unit, such as crotyltri-n-butylstannane, the reaction only occurs at more forcing conditions, e.g., xylene or chlorobenzene at reflux, using di-tert-butyl peroxide as an initiator [146]. However, the observed products were not those expected for the allyl transfer process, but instead correspond to elimination as shown in Eq. (98).



(98)

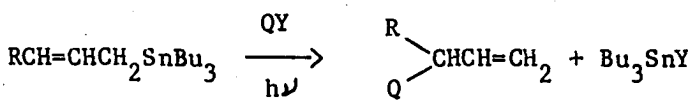
Baldwin et al. have extended the substitution reaction to propargyl systems [149]. They carried out the reaction of triphenylprop-2-ynylstannane and alkyl halides to provide terminal allenes in moderate yields (Eq. 99). The reaction has been applied



(99)

to a simple and sterospecific synthesis of the naturally occurring allenic amino acid, (S)-2-aminohexa-4,5-dienoic acid.

Recently, Russell and Herold have found that allyltri-n-butylstannane can undergo free-radical substitution reactions leading to allylic rearrangement with the various reagents shown in Eq. (100) [151]. They have also extended the reaction to include proparagyl-

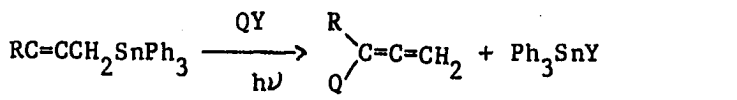


(100)

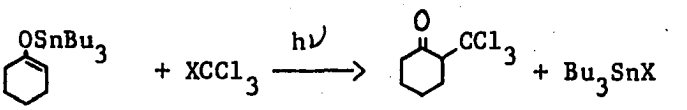
R = H, CH_3

QY = PhSSPh, $PhCH_2SSCH_2Ph$, PhSeSePh, $PhSO_2Cl$, n-$PrSO_2Cl$, CCl_3SO_2Cl.

and alkenyloxystannanes (Eqs. 101-103). Reaction 103 gave



(101)



(102)

$$Me_2C{=}CHOSnBu_3 + CHBr_3 \xrightarrow{h\nu} \underset{\displaystyle CHBr_2}{Me_2C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH} + Me_2C\!\!<\!\!\overset{O}{\diagup\diagdown}\!\!>\!\!CHCHBr_2 \qquad (103)$$

25 26

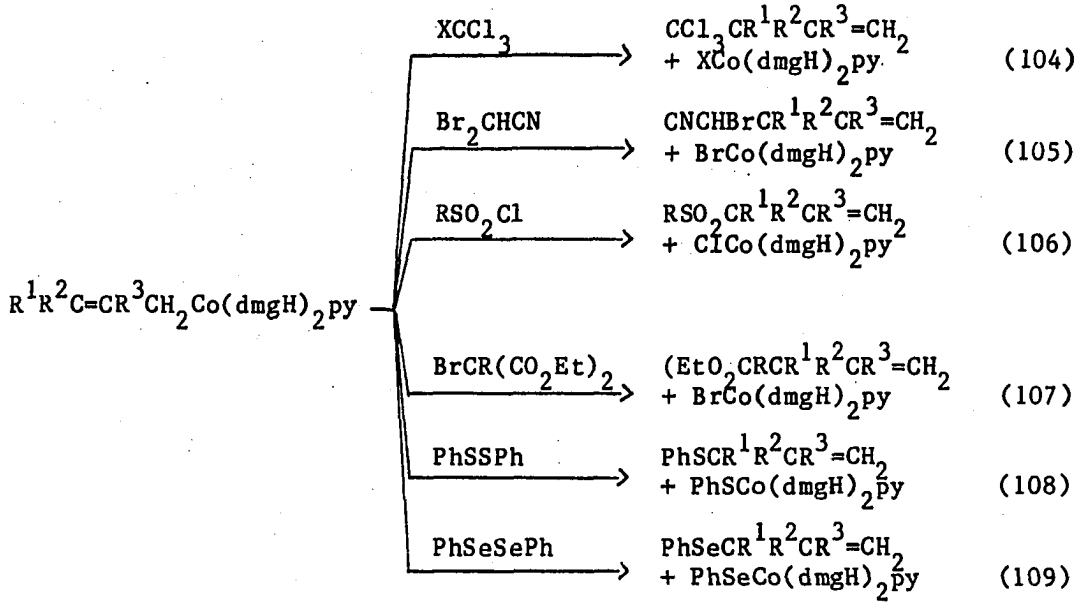
not only the expected 25 but also the epoxide 26 in a 3:1 ratio. Formation of the epoxide 26 most likely involves α-addition of $Br_2CH\bullet$ followed by an internal (S_Hi) displacement of $Bu_3Sn\bullet$ as shown in Scheme 36.

Scheme 36

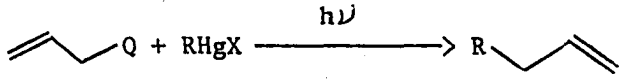
$$Me_2C{=}CHOSnBu_3 + Br_2CH\bullet \begin{cases} \xrightarrow[\beta\text{-add.}]{} Br_2CHCMe_2\dot{C}HOSnBu_3 \xrightarrow{\beta\text{-elim.}} 25 \\ \xrightarrow[\alpha\text{-add.}]{} Me_2\dot{C}\underset{\displaystyle CHBr_2}{C}HOSnBu_3 \xrightarrow{S_Hi} 26 \end{cases}$$

Allyl or propadienyl derivatives of Co can also undergo S_H2' substitution with both carbon-centered and heteroatom-centered radicals [152-159]. These reactions have been investigated extensively by Johnson and co-workers and the reactions are summarized in Eqs. (104) to (109). The bimolecular homolytic displacement of Co(III) complexes from carbon has been reviewed by Johnson [160].

All of these reactions are interpreted in terms of free-radical chain processes. The reactions are regiospecific and the substitutions occur with total rearrangement of the allyl group. The similar reactions of allyl or propadienyl derivatives of Rh and Ir with polyhalomethanes have also been reported [161].



In the course of our studies, we have found that allylic iodides, bromides, sulfides sulfones, and stannanes can undergo substitution reactions with organomercurials to give substitution products. The following section will present and discuss reactions of the allyl derivatives with organomercurials as shown in Eq. (110).



(110)

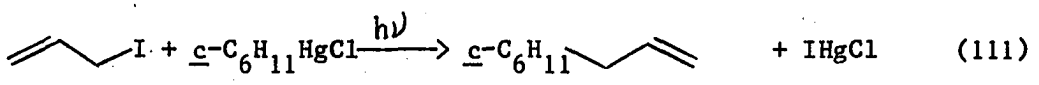
Q = I, Br, SPh, SO_2Ph, $SnBu_3$

B. Results and Discussion

1. Reactions of allyl iodide and organomercurials

Allyl iodide and cyclohexylmercury chloride were allowed to react in DMSO under photostimulation for 24 h. The reaction, after workup

with either aqueous sodium thiosulfate or sodium borohydride, afforded the substitution product in a moderate yield according to Eq. (111).



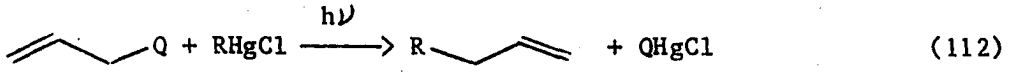
$$\text{allyl-I} + \underline{c}\text{-}C_6H_{11}HgCl \xrightarrow{h\nu} \underline{c}\text{-}C_6H_{11}\text{-allyl} + IHgCl \qquad (111)$$

A higher yield was observed with an excess amount of the mercurial (Table 26). The reactions carried out by either sunlamp or UV irradiation gave a similar yield of the product.

When mercuric phenylmercaptide or mercuric benzenesulfinate was allowed to react with allyl iodide under the same conditions, allyl phenyl sulfide or sulfone was obtained, respectively. A higher yield was observed with sunlamp irradiation.

2. Reactions of allyl bromide, sulfide, sulfone, and stannane with cyclohexylmercury chloride

Allyl bromide, sulfide or sulfone reacted with cyclohexylmercury chloride to give allylcyclohexane in moderate yields as shown in Table 27. The reaction is represented by Eq. (112). In all cases, mercury



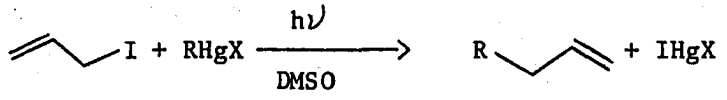
$$\text{allyl-Q} + RHgCl \xrightarrow{h\nu} \text{allyl-R} + QHgCl \qquad (112)$$

$$Q = Br,\ SPh,\ SO_2Ph,\ SnBu_3;\ R = \underline{c}\text{-}C_6H_{11}$$

metal was also observed. Allyl phenyl sulfide and sulfone reacted with the mercurial slowly and large amounts of the starting materials were recovered after the reaction was photolyzed for 24 h.

Reaction of allyl bromide with cyclohexylmercury chloride

Table 26. Photoreaction of allyl iodide and organomercurials



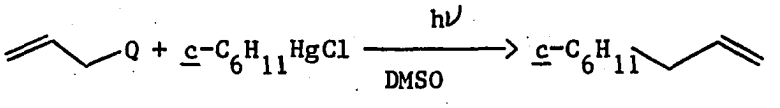
Mercurial (equiv)	Conditions[a]	% $RCH_2CH=CH_2$[b]
c-$C_6H_{11}HgCl$(1)	SL	31 (GC)
c-$C_6H_{11}HgCl$(1)	UV	31 (NMR)
c-$C_6H_{11}HgCl$(2)	SL	49 (GC)[c]
$(PhS)_2)_2Hg$(1)	UV	40 (NMR)
$(PhS)_2Hg$(1)	SL	75 (GC)
$(PhSO_2)_2Hg$(1)	UV	48 (GC)
$(PhSO_2)_2Hg$(1)	SL	51 (GC)

[a]Allyl iodide (1 mmol) and an organomercurial in 10 mL of nitrogen-purged DMSO were irradiated for 24 h; SL = 275-W sunlamp, UV = 350 nm Rayonet Photoreactor.

[b]Yields were determined by either GLC or ^1H NMR.

[c]Small amounts of unidentified products were also detected.

Table 27. Photoreactions of allyl bromide, sulfide, sulfone and stannane with cyclohexylmercury chloride



Q (mmol)	mmol of c-$C_6H_{11}HgCl$	Conditions[a]	% Product[b]	Byproduct[c] (mmol)
Br(1)	1	SL, 18 h	35	c-C_6H_{11}Br(0.05)
Br(1)	2	SL, 24 h	40	c-C_6H_{11}Br(0.14)
SPh(1)	1	SL, 18 h	30[d]	c-C_6H_{11}SPh(0.25)
SPh(1)	2	SL,24 h	51[e]	c-C_6H_{11}SPh(0.5)
SPh(0.5)	2.5	SL,24 h	57[f]	c-C_6H_{11}SPh(0.5)
SO_2Ph(1)	1	SL,48 h	24[g]	
SO_2Ph(1)	2	SL,24 h	42g	
SO_2Ph(0.5)	2.5	SL,24 h	57[h]	
$SnBu_3$(0.5)	2.5	DMSO/PhH,UV,23 h	12[i]	

[a]Reactants in 10 mL of nitrogen-purged solvent were irradiated; SL = 275-W sunlamp ca. 20cm from reaction flask, UV = 350nm Rayonet Photonreactor.

[b]Yields were determined by GLC.

[c]Mercury metal was observed in all reactions.

[d]Allyl phenyl sulfide (45%) was recovered.

[e]Allyl phenyl sulfide (15%) was recovered.

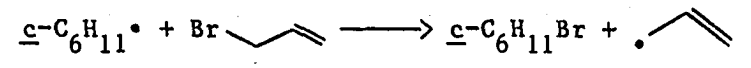
[f]Allyl phenyl sulfide (6%) was recovered.

[g]Allyl phenyl sulfone (~25%) was recovered.

[h]Small amounts of unidentified products were also observed.

[i]Bu_3SnCl 47% was formed together with small amounts of unidentified products.

afforded a small amount of cyclohexyl bromide as a byproduct. This byproduct could be formed from the abstraction of bromine atom by cyclohexyl radical as shown in Eq. (113).



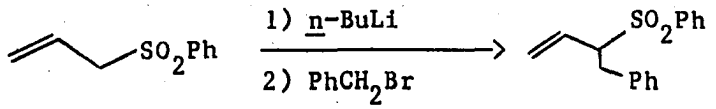
(113)

Allyl phenyl sulfide was found to react with cyclohexylmercury chloride and a higher yield of the substitution product was observed with an excess amount of the mercurial. In addition to the substitution product, cyclohexyl phenyl sulfide was also obtained in high yield. The yield of the sulfide byproduct increased with an increase in the amount of the mercurial employed. It is likely that the cyclohexyl phenyl sulfide was formed from the reaction between phenylthiomercury chloride and cyclohexylmercury chloride (Eq. 114).

$$\underline{c}\text{-}C_6H_{11}HgCl + PhSHgCl \xrightarrow{h\nu} \underline{c}\text{-}C_6H_{11}SPh + HgCl_2 + Hg^{o} \qquad (114)$$

Allyltri-n-butylstannane also reacted with cyclohexylmercury chloride but afforded a low yield of the expected product. Tri-n-butyltin chloride was formed as the other product in 47% yield.

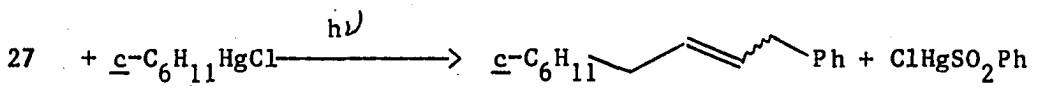
To determine the regiochemistry of the substitution product, a substituted allyl phenyl sulfone, 3-benzylallyl phenyl sulfone (27), was employed. This sulfone can easily be synthesized by treating allyl phenyl sulfone with n-butyllithium followed by addition of benzyl bromide as shown in Eq. (115) (see experimental section). The sulfone 27 was allowed to react with cyclohexylmercury chloride under sunlamp irradiation. The reaction was found to proceed slowly to



(115)

27

give (4-phenyl-2-butenyl)cyclohexane as the only substitution product (Eq. 116). The substitution product was identified by its GCMS



(E) + (Z) (116)

and by ^{1}H NMR. The ^{1}H NMR showed the vinyl proton signal at 5.50 ppm (multiplet) and the integration indicated two protons. This clearly indicates that the product has an internal not a terminal double bond. The spectrum (see experimental section) is consistent with the assigned structure, (4-phenyl-2-butenyl)cyclohexane. The GLC analysis indicated two isomers with a ratio of 4.6:1. The isomeric structures cannot be assigned based on the ^{1}H NMR due to its complexity. However, it is not unreasonable to assume that the major product is the (E)-(4-phenyl-2-butenyl)cyclohexane and the minor product is the (Z)-isomer.

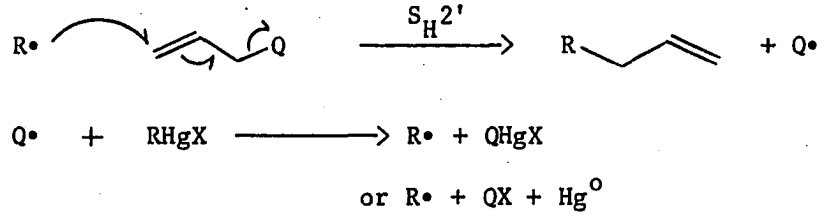
3. Mechanistic consideration

Reactions of allyl iodide, bromide, sulfide, sulfone, and stannane with organomercurials presented in this section are believed to involve free-radical reactions. This is based on the finding that the reactions only proceeded when irradiated. The mechanism could be either a concerted S_H2' or a stepwise addition-elimination process. However, based on the known examples in the literature, the former is

believed to operate in these reactions.

The reaction of 3-benzylallyl phenyl sulfone (27) and cyclohexylmercury chloride (Eq. 125) gave only (4-phenyl-2-butenyl)cyclohexane. This clearly suggests that the addition of cyclohexyl radical is regiospecific in that attack occurs only at the terminal carbon atom of the double bond. The mechanism is consistent with the one proposed in Scheme 37.

Scheme 37



Reaction between Q• and RHgX has already been discussed in Part I and will not be repeated here.

C. Conclusion

We have shown that allyl iodide, bromide, sulfide, sulfone, and stannane can react with organomercurials to give substitution products in moderate yields under photostimulation. The reactions are believed to occur via an S_H2' process. The substitution proceeds in a regiospecific manner with complete rearrangement of the allylic double bonds.

D. Experimental Section

1. General considerations

All the instrumentation and techniques employed in these experiments have already been described previously and, therefore, will not be repeated here. All the commercially available compounds were purchased from Aldrich and used without further purification.

2. Preparation of allylic compounds

Allyl iodide (98% pure) and allyl bromide (99% pure) were purchased from Aldrich and used without purification.

Allyl phenyl sulfide was prepared from the reaction of allyl bromide and sodium thiophenoxide by the procedure described in the literature [162]. The sulfide had bp 73 °C/3.5 mmHg (lit. [162] bp 104-106 °C/25 mmHg or 215-218 °C/750 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.55-7.0(m,5H), 6.25-5.45(m,1H), 5.3-4.8(m,2H), 3.52(d,2H).

Allyl phenyl sulfone was synthesized by the literature procedure [163]. The sulfone had bp 105-110 °C/0.25 mmHg; ^{1}H NMR ($CDCl_3$) δ 8.02-7.8(m,2H), 7.8-7.4(m,3H), 6.3-4.95(m,3H), 3.88(d,2H).

Allyltri-n-butylstannane was prepared by the procedure described in ref 164.

3. Photoreaction of allyl iodide and cyclohexylmercury chloride

Allyl iodide (1 mmol) and cyclohexylmercury chloride (1 mmol) were dissolved in 10 mL of DMSO in a Pyrex tube equipped with a rubber septum. The mixture was degassed for 5 min with a stream of nitrogen and irradiated with a 275-W sunlamp or in a Rayonet Photoreactor for

24 h. After the irradiation, the mixture was poured into water and extracted with benzene. The extract was washed with 2 x 30 mL of 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The benzene was removed to afford a colorless liquid which was analyzed by GLC, ^{1}H NMR and GCMS. The analysis revealed the presence of allylcyclohexane in 31% yield. When the reaction was carried out with 2 equiv of cyclohexylmercury chloride and irradiated with a sunlamp under the same conditions, the reaction afforded a 49% yield of allylcyclohexane.

^{1}H NMR ($CDCl_3$) δ 6.2-5.3(m,1H), 5.2-4.75(m,2H), 2.3-0.5(m,13H).

GCMS, m/e (relative intensity) 124(5,M^+), 83(78), 82(61), 67(21), 55(100).

4. Photoreaction of allyl iodide with mercuric phenylmercaptide and mercuric benzenesulfinate

Allyl iodide (1 mmol) and mercuric phenylmercaptide (1 mmol) were dissolved in 10 mL of nitrogen-purged DMSO in a Pyrex tube. The mixture was irradiated with a 275-W sunlamp placed about 15-20 cm from the reaction vessel or in a Rayonet Photoreactor. After 24 h of irradiation, the usual workup afforded an oily residue which was analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated the presence of allyl phenyl sulfide. Identity of the product was confirmed by comparison of its GLC retention time, ^{1}H NMR and GCMS with those of the authentic allyl phenyl sulfide. The reaction irradiated in a Rayonet Photoreactor afforded a 40% yield; whereas, the reaction irradiated with a sunlamp afforded a 75% yield of allyl phenyl sulfide.

The same procedure was also applied for the reaction of allyl iodide with mercuric benzenesulfinate. The reaction irradiated in a Rayonet Photoreactor afforded 48% yield; whereas, the reaction irradiated with a sunlamp gave 51% yield of allyl phenyl sulfone.

All the above results are presented in Table 26.

5. Photoreaction of allyl bromide with cyclohexylmercury chloride

The mixture of allyl bromide (1 mmol) and cyclohexylmercury chloride (1 or 2 mmol, see Table 27) in 10 mL of nitrogen-purged DMSO in a Pyrex tube was irradiated with a 275-W sunlamp. After the irradiation, the mixture was poured into water, extracted with benzene and dried (Na_2SO_4). The extract was concentrated and analyzed by GLC. The analysis revealed the presence of allylcyclohexane in 35-40% yield and another product which was identified by GCMS to be cyclohexyl bromide. The cyclohexyl bromide had the following GCMS.

GCMS, m/e (relative intensity) 164(3), 162(3,M^+), 83(100), 55(64).

6. Photoreaction of allyl phenyl sulfide with cyclohexylmercury chloride

Allyl phenyl sulfide and cyclohexylmercury chloride (see Table 27) were dissolved in 10 mL of nitrogen-purged DMSO in a Pyrex tube. The mixture was irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel. After the irradiation, the usual workup afforded a liquid mixture which was shown by GLC to consist of three products. The products were identified by GCMS to be the

substitution product (allylcyclohexane), cyclohexyl phenyl sulfide and the starting material (allyl phenyl sulfide). All the yields are given in Table 27. Identity of the byproduct (cyclohexyl phenyl sulfide) was confirmed by comparison of its GLC retention time, and GCMS with those of the authentic compound.

7. Photoreaction of allyl phenyl sulfone with cyclohexylmercury chloride

Reaction of allyl phenyl sulfone with cyclohexylmercury chloride was carried out as described before. The conditions and yield of the substitution product (allylcyclohexane) are given in Table 27.

8. Photoreaction of allyltri-n-butylstannane with cyclohexylmercury chloride

The mixture of allytri-n-butylstannane (0.5 mmol) and cyclohexylmercury chloride (2.5 mmol) in 15 mL of nitrogen-purged benzene-DMSO mixture (10:5) in a Pyrex tube was irradiated in a Rayonet Photoreaactor. After 23 h of irradiation, the mixture was poured into water and extracted with benzene. The extract was washed with aqueous sodium thiosulfate, dried (Na_2SO_4) and concentrated. Analysis indicated the presence of the substitution product, allylcyclohexane, in 12% yield, tri-n-butyltin chloride in 47% yield and small amounts of unidentified products.

9. Preparation and photoreaction of 3-benzylallyl phenyl sulfone with cyclohexylmercury chloride

3-Benzylallyl phenyl sulfone (27) was synthesized by following the literature method [165]. Thus allyl phenyl sulfone (20 mmol) and tetramethylethylenediamine (20 mmol), were dissolved in 50 mL of dry THF (under a nitrogen atmosphere) in a three-necked round-bottom flask, equipped with a magnetic stirrer and a dropping funnel. The mixture was cooled to -60 °C and n-butyllithium (2M in hexane; 10 mL, 20 mmol) was added dropwise with stirring over a 15 min period. After 1 h, benzyl bromide (20 mmol) was added and stirring continued at -60 °C for 3 h. The mixture temperature was raised to 0 °C and poured into ice-water. The product was extracted with ether, washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated to give a pale yellow oil which consisted of 3-benzylallyl phenyl sulfide and the remaining starting materials. The product was isolated from the mixture by column chromatography on silica gel using benzene as the eluent. The isolated product was recrystallized from hexane-benzene to give a white crystal 3-benzylallyl phenyl sulfone, mp 86 °C (lit. [165] mp 85 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85(d,2H), 7.7-7.5(m,3H), 7.3-7.1(m,5H), 5.72-5.55(m,1H), 5.17-4.70(m,2H), 3.80-2.80(m,3H).

3-Benzylallyl phenyl sulfone (5 mmol) and cyclohexylmercury chloride (25 mmol) were dissolved in 70 mL of a mixture of benzene and DMSO (50:20) in a Pyrex flask. The mixture was degassed with a stream of nitrogen for 10 min and irradiated with a 275-W sunlamp placed

about 20 cm from the flask. After 60 h of irradiation, the usual workup afforded an oily residue which consisted of the substitution product and the remaining starting material. The substitution product was separated by preparative GLC. The oily pale yellow product isolated was a mixture of two isomers with a ratio of 4.6:1. The isomers could not be identified based on the ^{1}H NMR due to the complexity of the vinyl proton signals. However, the major product was tentatively assigned to be the (E)-(4-phenyl-2-butenyl)cyclohexane and the minor product was assigned to be the (Z)-isomer.

The mixture of (4-phenyl-2-butenyl)cyclohexane had the following ^{1}H NMR and GCMS data.

^{1}H NMR ($CDCl_3$) δ 7.18(s,5H), 5.3-5.65(m,2H), 3.2-3.5(m,2H), 2.2-0.5(m,13H).

GCMS m/e (relative intensity), major isomer; 216(0.2), 214(23,M^+), 118(46), 117(36), 104(82), 91(51), 83(48), 55(100).

GCMS, m/e (relative intensity), minor isomer; 216(0.05), 214(16,M^+), 118(39), 117(30), 104(80), 91(45), 83(45), 55(100).

II. SUBSTITUTION REACTIONS OF ALKYNYL DERIVATIVES

A. Introduction

Recently, several reports of free-radical reaction of phenylacetylene derivatives have appeared in the literature. Nozaki and co-workers, in 1974, reported the reaction of methyl phenylethynyl sulfone and trialkylboranes [46]. The reaction (Eq. 117) was carried out in refluxing THF under a nitrogen atmosphere to give substitution products in good yield.

$$PhC{\equiv}CSO_2Me + R_3B \xrightarrow[N_2,\,\Delta]{THF} PhC{\equiv}CR + PhC{\equiv}C\text{-}\langle\text{O}\rangle + PhC{\equiv}CH \qquad (117)$$

70-73% 8.4-10% 3.2-6.3%

More recently, Eisch and Behrooz have found that phenyl phenylethynyl sulfone reacted with organolithiums or Grignard reagents to give substitution products in good yield (Eq. 118) [47]. They have

$$PhC{\equiv}CSO_2Ph + RM \longrightarrow PhC{\equiv}CR + PhSO_2M \qquad (118)$$

M = Li, MgX

shown that the reactions involved free-radical intermediates (R•) from a reaction of phenyl phenylethynyl sulfone and 5-hexenylmagnesium chloride. The reaction (Eq. 119) afforded cyclopentylmethyl phenyl-

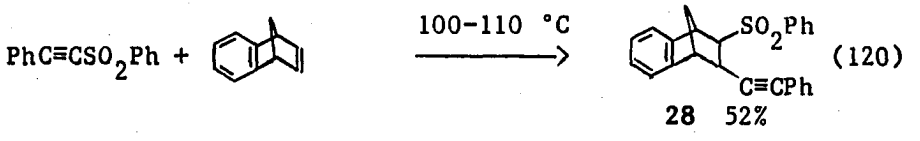
$$PhC{\equiv}CSO_2Ph + \text{/\!/}\wedge\wedge\wedge MgCl \longrightarrow PhC{\equiv}C\text{-}\langle\text{5-ring}\rangle + PhC{\equiv}C\wedge\wedge\wedge= \qquad (119)$$

acetylene and 5-hexenyl phenylacetylene in a 2:1 ratio. The reactions were interpreted in terms of an electron-transfer process as shown in Scheme 38.

Scheme 38

$$PhC{\equiv}CSO_2Ph + RM \longrightarrow [Ph\dot{C}{=}\bar{C}SO_2Ph]M^+ + R\bullet$$
$$\downarrow$$
$$PhC{\equiv}CR + PhSO_2M$$

Phenyl phenylethynyl sulfone has been found to react with olefins to give addition products which were derived form homolytic cleavage of the carbon-sulfur bond [166]. Thus, a mixture of phenyl phenylethynyl sulfone and benzonorbornadiene (heated at 100-110 °C under argon in a sealed tube for 2-3 h) gave the adduct **28** in 52% yield (Eq. 120). The reaction was suggested to proceed by either a charge-transfer or an electron-transfer process.



(120)

28 52%

Based on the well-established addition-elimination mechanism, it is more likely that Reactions 117-119 involve a free-radical addition-elimination process. Similar to the alkenyl system (Part I), we have found that phenylacetylene derivatives undergo photostimulated reactions with organomercurials to give substitution products. The following section will be concerned with the reaction of a series of β-substituted phenylacetylenes with organomercurials as shown in Eq.

(121).

$$PhC{\equiv}CQ + RHgX \xrightarrow{h\nu} PhC{\equiv}CR + QHgX \quad (\text{or } QX + Hg^{o}) \qquad (121)$$

Q = I, SO_2Ph, SPh, $SnBu_3$

R = alkyl, $(EtO)_2P(O)$, SPh

B. Results and Discussion

1. Reactions of phenylethynyl iodide with organomercurials

Phenylethynyl iodide did not react with t-butylmercury chloride in the dark and only the unchanged starting materials were recovered. In contrast, a smooth reaction occurred when the mixture was irradiated with a sunlamp to give the substitution product in quantitative yield within 7 h. The yield was drastically decreased when di-tert-butyl nitroxide was added. Thus the reaction with 10 mol% of di-tert-butyl nitroxide afforded less than 5% of the substitution product when photolyzed with a sunlamp for 0.75 h. Whereas, the control experiment without di-tert-butyl nitroxide gave a 25% yield under the same conditions.

Cyclohexyl- and n-butylmercury chloride were also employed and the reactions were carried out under similar conditions. The reaction with cyclohexylmercury chloride gave an excellent yield of the product, but the reaction with n-butylmercury chloride afforded only a 47% yield. The reactions proceeded according to Eq. (122) and the results are summarized in Table 28.

Table 28. Photoreaction of phenylethynyl iodide with organomercurials

$$PhC{\equiv}CI + RHgX \xrightarrow[DMSO]{h\nu} PhC{\equiv}CR + IHgX$$

RHgX (equiv)	Conditions[a]	% PhC≡CR[b]
t-BuHgCl(1.5)	SL, 7 h	100
t-BuHgCl(1.2)	SL, 0.75 h	25[c]
t-BuHgCl(1.2)	10 mol% DTBN, SL, 0.75 h	< 5[c]
t-BuHgCl(1.2)	Dark, 7 h	0[c]
c-C_6H_{11}HgCl(1.5)	SL, 7 h	93
n-BuHgCl(1.5)	SL, 7 h	48
$(EtO)_2\overset{O}{\overset{\|}{P}}HgCl$(1.1)	UV, 24 h	32[d]

[a]Reactions were performed on a 0.1 mmol scale of phenylethynyl iodide in 5 mL of DMSO at 35-40 °C with irradiation from a 275-W sunlamp (SL) or at 350 nm in a Rayonet Photoreactor (UV).

[b]Yields were determined by GLC.

[c]Unreacted starting materials were recovered.

[d]Yield was determined by ^{1}H NMR.

$$PhC{\equiv}CI + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + IHgCl \qquad (122)$$

Diethoxyphosphinylmercury chloride was also found to react with phenylethynyl iodide under photostimulation. The reaction was irradiated in a Rayonet Photoreactor for 24 h to give the substitution product in 32% yield.

2. Reactions of phenyl phenylethynyl sulfone and sulfide with alkylmercury chloride

Phenyl phenylethynyl sulfone and organomercurials were allowed to react in a nitrogen-purged solvent in a Rayonet Photoreactor. The reactions afforded moderate yields of the substitution products (Eq. 123) after irradiation for 24 h; the results are presented in Table 29.

$$PhC{\equiv}CSO_2Ph + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + PhSO_2HgCl \qquad (123)$$

The reactions may not need 24 h to proceed to completion as it was shown that cyclohexylmercury chloride and phenyl phenylethynyl sulfone in DMSO when irradiated by a sunlamp for 7 h gave a 66% yield of the substitution product.

Phenyl phenylethynyl sulfide was also found to react with organomercurials to give substitution products as shown in Eq. (124). The reaction using DMSO as the solvent were carried out in a Rayonet

$$PhC{\equiv}CSPh + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + PhSHgCl \qquad (124)$$

Photoreactor for 24 h. When benzene was employed as the reaction medium, the reactions proceeded sluggishly and a white precipitate,

Table 29. Reaction of phenyl phenylethynyl sulfone with organomercurials

$$PhC{\equiv}CSO_2Ph + RHgCl \xrightarrow[DMSO]{h\nu} PhC{\equiv}CR + PhSO_2HgCl$$

RHgCl (equiv)	Conditions[a]	% PhC≡CR[b]
i-C_3H_7HgCl(5)	PhH, UV 24 h	44[c]
c-$C_6H_{11}HgCl$(5)	PhH, UV 24 h	67[c,d]
c-$C_6H_{11}HgCl$(1.5)	DMSO, SL 7 h	66[d]
t-C_4H_9HgCl(5)	PhH, UV 24 h	55[e]
t-C_4H_9HgCl(5)	DMSO, UV 24 h	57
$(EtO)_2P(O)HgCl$(5)	PhH, UV 24 h	30

[a]The sulfone (0.1 mmol) and RHgX in 10 mL solvent were irradiated under a nitrogen atmosphere in a Pyrex tube; UV = 350 nm Rayonet Photoreactor, SL = 275-W sunlamp ca. 20 cm from the reaction vessel.

[b]Yields were determined by GLC.

[c]Some unidentified products were also formed.

[d]A product whose GCMS was identical to that of $Ph_2C{=}CHC_6H_{11}$-c was detected in about 20% yield.

[e]A product whose GCMS was identical to that of $Ph_2C{=}CHC_4H_9$-t was formed in ~ 40 % yield.

presumably phenylthiomercury chloride, was also formed. Results are summarized in Table 30.

Reactions of phenyl phenylethynyl sulfide and alkylmercury chlorides were complicated by a formation of a byproduct, the alkyl phenyl sulfide. The sulfide byproduct can be avoided by using an excess amount of the phenyl phenylethynyl sulfide. Thus, the reactions with 0.2 equiv of alkylmercury chlorides afforded exclusively the substitution products and only trace amounts of the byproducts. The formation of byproducts arises from the reaction of phenylthiomercury chloride and the alkylmercury chlorides as shown in Eq. (125).

$$PhSHgCl + RHgCl \xrightarrow{h\nu} PhSR + HgCl_2 + Hg^o \qquad (125)$$

3. Reactions of tri-n-butyl(phenylethynyl)stannane and bis(phenylethynyl)mercury with alkylmercury chlorides

Tri-n-butyl(phenylethynyl)stannane underwent photostimulated reactions with alkylmercury chlorides to give substitution products (Eq. 126). Results are summarized in Table 31. Yields of the

$$PhC{\equiv}CSnBu_3 + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + Bu_3SnCl + Hg^o \qquad (126)$$

substitution products increased in the order R = 1° < 2° < 3° . Tri-n-butyltin chloride was formed in good yield in this reaction.

Bis(phenylethynyl)mercury and organomercurials in DMSO were allowed to react in a Rayonet Photoreactor to give substitution products as

Table 30. Reaction of phenyl phenylethynyl sulfide with alkylmercury chlorides

$$PhC{\equiv}CSPh + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + PhSHgCl$$

R(equiv)	Conditions[a]	% Yield[b] (PhC≡CR)	% Byproduct[b] (PhSR)
i-C_3H_7(5)	DMSO, UV 24 h	25	38
i-C_3H_7(0.2)	DMSO, UV 24 h	42	trace
i-C_3H_7(5)	PhH, UV 24 h	37[c]	20
c-C_6H_{11}(5)	DMSO, UV 24 h	35	43
c-C_6H_{11}(0.2)	DMSO, UV 24 h	46	trace
t-C_4H_9(5)	PhH, UV 48 h	39[c]	-
t-C_4H_9(0.2)	DMSO, UV 24 h	44	-

[a]Phenyl phenylethynyl sulfide (0.1 mmol) and RHgCl in a nitrogen-purged solvent (10 mL) were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Yields were determined by GLC.

[c]Only 60% conversion of PhC≡CSPh.

Table 31. Photoreaction of (tri-n-butyl)phenylethynylstannane with alkylmercury chlorides

$$PhC{\equiv}CSnBu_3 + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR + Bu_3SnCl + Hg^0$$

R(equiv)	Conditions[a]	5 Yield[b] (PhC≡CR)	% Yield[b] (Bu_3SnCl)
n-C_4H_9(5)	PhH, UV 24 h	13	70
c-C_6H_{11}(5)	PhH, UV 24 h	43	80
t-C_4H_9(5)	PhH, UV 24 h	61	70

[a]Reactants (1 mmol of $PhC{\equiv}CSnBu_3$) in 10 mL of nitrogen-purged benzene were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Yields were determined by GLC.

summarized in Table 32. The reactions occurred according to Eq. (127 The percentage yields of the substitution products based on the

$$(PhC{\equiv}C)_2Hg + 2RHgCl \xrightarrow{h\nu} 2PhC{\equiv}CR + HgCl_2 + Hg^{\circ} \qquad (127$$

stoichiometry shown in Eq. (127) were not high. Only the reaction with diethoxyphosphinylmercury chloride gave an appreciable yield of the substitution product.

4. Reactions of phenylacetylene derivatives with mercuric phenylmercaptide and phenyl disulfide

Thiophenoxy radical has been shown to add to double bonds effectively (see Part I). We have also found that it can add to triple bonds as well. Thus, phenylacetylene derivatives and mercury phenylmercaptide or phenyl disulfide reacted at 350 nm in a Rayonet Photoreactor to give good yields of the substitution product as summarized in Table 33. The reactions proceeded as shown in the following equations (Eqs. 128-132).

$$PhC{\equiv}CI + Hg(SPh)_2 \xrightarrow{h\nu} PhC{\equiv}CSPh + IHgSPh \qquad (128)$$

$$(PhC{\equiv}C)_2Hg + Hg(SPh)_2 \xrightarrow{h\nu} 2PhC{\equiv}CSPh + 2Hg^{\circ} \qquad (129)$$

$$(PhC{\equiv}C)_2Hg + PhSSPh \xrightarrow{h\nu} 2PhC{\equiv}CSPh + Hg^{\circ} \qquad (130)$$

$$PhC{\equiv}CSnBu_3 + Hg(SPh)_2 \xrightarrow{h\nu} PhC{\equiv}CSPh + Bu_3SnSPh + Hg^{\circ} \qquad (131)$$

Table 32. Photoreaction of bis(phenylethynyl)mercury with organomercurials

$$(PhC{\equiv}C)_2Hg + 2RHgCl \xrightarrow{h\nu} 2PhC{\equiv}CR + HgCl_2 + Hg^0$$

R(equiv)	Conditions[a]	% Yield PhC≡CR[b]
n-C_4H_9(5)	DMSO, 24 h	9[c] (0.18 mmol)
c-C_6H_{11}(5)	DMSO, 24 h	26[c] (0.52 mmol)
t-C_4H_9(5)	DMSO, 24 h	34[c] (0.68 mmol)
$(EtO)_2P(O)$(5)	DMSO, 24 h	61[d] (1.22 mmol)

[a]Bis(phenylethynyl)mercury (0.1 mmol) and RHgX (0.5 mmol) in nitrogen-purged DMSO (10 ml) in a Pyrex tube were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Yields were based on 2 mmol of PhC-CR/mmol of $(PhC{\equiv}C)_2Hg$.

[c]Determined by GLC.

[d]Determined by ^1H NMR.

Table 33. Photoreaction of phenylacetylene derivatives with mercuric phenylmercaptide and phenyl disulfide

$$PhC{\equiv}CQ + R\text{-}Z \xrightarrow{h\nu} PhC{\equiv}CR + \mathbf{29} + \mathbf{30} + \mathbf{31} + \mathbf{32} + \mathbf{33}$$

Q (equiv)	R-Z 0.1 mmol	Condition[a]	PhC≡CR[b] (equiv)	Byproducts[b] (equiv)
I(1)	$(PhS)_2Hg$	DMSO, 4 h	0.32	**29**(0.25), **30-33**[c](0.41) PhSSPh(0.22)
I(1)	$(PhS)_2Hg$	DMSO, 24 h	< 0.10	**29**(0.30), **30-31**[d] (0.55), PhSSPh(0.05)
I(2)	$(PhS)_2Hg$	DMSO, 4 h	0.90	**29**(0.70), **30-31**[d](0.20)
I(10)	$(PhS)_2Hg$	DMSO, 4 h	1.70	**29**(0.04),**30-31**[d](0.05)
$PhSO_2$(10)	$(PhS)_2Hg$	DMSO, 4 h	1.60	--
PhC≡CHg(5)	$(PhS)_2Hg$	DMSO, 24 h	0.86	**29**(0.04),**30-31**[d](0.26)
PhC≡CHg(5)	PhSSPh	DMSO, 24 h	0.50	**29**(0.16),**30-31**[d](0.26)
Bu_3Sn(5)	$(PhS)_2Hg$	DMSO/PhH, 24 h	0.37	**29**(?), **30-33**[c](0.26)
Bu_3Sn(5)	PhSSPh	PhH, 12 h	0.60	**29**(?)[e], **30-33**[c](0.16)

[a]Substrates in 10 mL of a nitrogen-purged solvent in a Pyrex flask were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Determined by GLC.

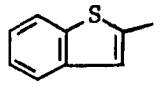
[c]Mixture of **30**, **31**, **32**, and **33**.

[d]Mixture of **30** and **31**.

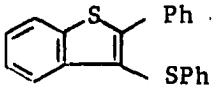
[e]$PhC{\equiv}CSnBu_3$ and **29** were not separated by GLC.

$$PhC{\equiv}CSnBu_3 + PhSSPh \xrightarrow{h\nu} PhC{\equiv}CSPh + Bu_3SnSPh \qquad (132)$$

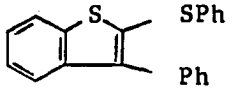
The reactions were complicated because the product phenyl phenylethynyl sulfide, underwent further photochemical reactions to give benzo[b]thiophenes **29**, **30**, and **31** and the alkenes **32** and **33**. Reaction



29



30



31

PhC(SPh)=CHSPh
(E) and (Z)
32

$PhCH=C(SPh)_2$
33

of phenylethynyl iodide with an equimolar amount of mercuric phenylmercaptide gave a 32% yield (0.32 equiv) of phenyl phenylethynyl sulfide and large amounts of byproducts **29**, **30**, **31**, **32**, and **33** after photolysis for 4 h. When the reaction was carried out for 24 h, the substitution product decreased to less than 10% (0.10 equiv); whereas, the yields of the byproducts increased to a total of 85% (0.85 equiv). This clearly indicates that byproducts **29**, **30**, **31**, **32**, and **33** are formed from phenyl phenylethynyl sulfide. This was confirmed by irradiation of phenyl phenylethynyl sulfide in DMSO at 350 nm in a Rayonet Photoreactor for 24 h where small amounts of **29**, **30**, and **31** were observed. In contrast, in the presence of mercuric phenylmercaptide, the reaction gave good yields of **29**, **30**, **31**, **32**, and **33** as shown in Eq. (133).

$$\underset{0.1\ \text{mmol}}{PHC{\equiv}CSPh} + \underset{0.1\ \text{mmol}}{Hg(SPh)_2} \xrightarrow[DMSO]{h\nu,\,24h} \underset{0.037\ \text{mmol}}{29} + \underbrace{\underset{0.037\ \text{mmol}}{30} + \underset{0.009\ \text{mmol}}{31}} + \underset{0.01\ \text{mmol}}{32} + 33 \qquad (133)$$

Reaction of phenylethynyl iodide and mercuric phenylmercaptide, however, gave a higher yield of the substitution product, phenyl phenylethynyl sulfide, when an excess amount of phenylethynyl iodide was employed. Therefore, the reaction with 2 equiv of the iodide afforded a 45% yield (0.90 equiv) of phenyl phenylethynyl sulfide and byproducts (29 + 30 + 31) in 55% yield (0.90 equiv). When 10 equiv of phenylethynyl iodide was used, phenyl phenylethynyl sulfide was formed as the exclusive product (85% yield, 1.70 equiv); whereas, the byproducts were formed in less than 10% (0.09 equiv).

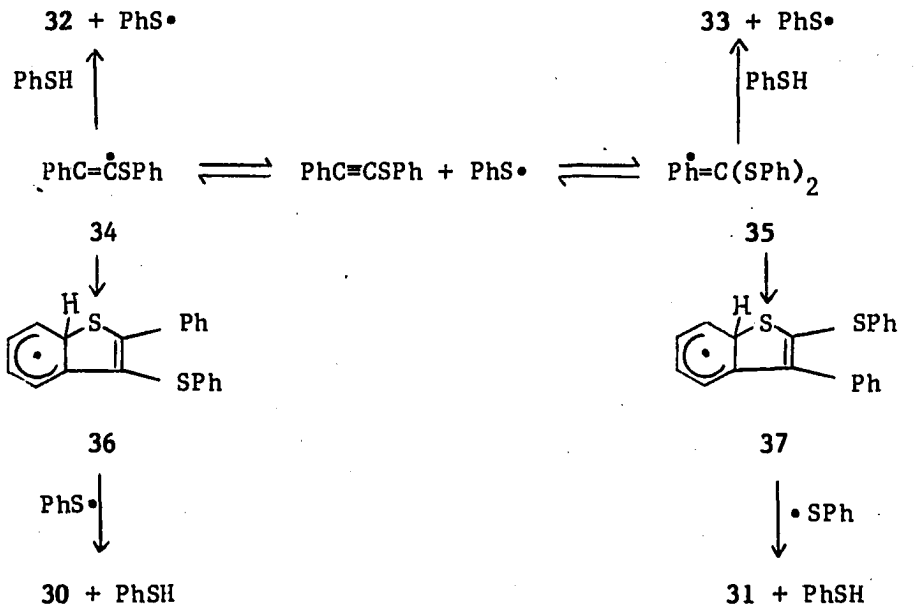
Undoubtedly phenyl phenylethynyl sulfide was formed as the primary product as shown in Eq. (128). Evidently, thiophenoxy radical added to the triple bond of the product as well as to that of the starting material. The formation of byproducts 30, 31, 32, and 33 may be explained by the mechanism outlined in Scheme 39.

Thiophenoxy radical apparently adds to the triple bond of phenyl phenylethynyl sulfide at either position to give 34 and 35 which may undergo intramolecular cyclization to give the cyclohexadienyl radicals 36 and 37. The hydrogen atom of the cyclohexadienyl radical 36 and 37 is easily abstracted by thiophenoxy radical to give products 30 and 31 and thiophenol. Thiophenol is known to be a good hydrogen atom donor. Therefore, when the concentration of the thiophenol increases, the radical intermediates 34 and 35 can abstract the

hydrogen atom from thiophenol to give 32 and 33 and thiophenoxy radical which will continue the chain.

The structure of 2-phenylbenzo[b]thiophene 29 was assigned based on its IR, ^{1}H NMR and GCMS. The structure has also been confirmed by comparison of the spectroscopic data and its GLC retention time with those of the authentic compound. The mechanism for the formation of 29 is not known. However, we have found that photolysis of a mixture of 30 and 31 in DMSO gave rise to 29.

Scheme 39



5. Mechanistic consideration

Reactions of phenylacetylene derivatives with organomercurials or phenyl disulfide presented in this section most likely involve a free-radical addition-elimination process. A possible mechanism is

depicted in Scheme 40. The process involves regiospecific addition of

Scheme 40

Initiation

$$RHgX \longrightarrow R\bullet + HgX$$

Propagation

$$PhC{\equiv}CQ + R\bullet \xrightarrow{\text{add.}} Ph\dot{C}{=}C(R)Q$$

$$Ph\dot{C}{=}C(R)Q \xrightarrow{\text{elim.}} PhC{\equiv}CR + Q$$

$$Q\bullet + RHgX \longrightarrow R\bullet + QHgX \quad (\text{or } QX + Hg^{o})$$

R• to the triple bonds at the carbon attached to Q. The observed regiochemistry may result from a better stabilization of the vinyl radical by the phenyl group than by Q. Of course, reversibility of the addition step may be important for the thiophenoxy radical. The reaction between Q• and organomercurials has been discussed in Part I.

C. Conclusion

Phenylacetylene derivatives, PhC≡CQ where Q = I, SO_2Ph, SPh, $SnBu_3$, and HgC=CPh, can undergo photostimulated reaction with organomercurials to give substitution products in moderate to good yields. The reactions are believed to involve a free-radical addition-elimination mechanism. Evidence for a free-radical process which has been demonstrated with phenylethynyl iodide includes the need for an initiator (light), the failure of the reaction to occur in

the dark and the retardation by 10 mol% di-tert-butyl nitroxide.

The substitution reaction proceeded best with Q = I in that the reaction gave the highest yield of the substitution products and no complication by any byproduct. Furthermore, the reaction was complete with 7 h of sunlamp irradiation. Reaction of the corresponding sulfone, although it gave reasonable yields of the substitution products, was sometimes accompanied by some byproducts. Phenyl phenylethynyl sulfide reacted with alkylmercury chlorides sluggishly especially when benzene was used as the reaction medium. In addition, the reaction was complicated by formation of alkyl phenyl sulfides which have GLC retention times close to those of the substitution products. However, the sulfide byproducts can be suppressed by using a large excess of phenyl phenylethynyl sulfide. Tri-n-butyl(phenylethynyl)stannane reacted with alkylmercury chlorides to give low yield of the substitution products, but the reactions gave good yield of tri-n-butyltin chloride as the other product.

The phenylacetylene derivatives can also react with mercuric phenylmercaptide or phenyl disulfide to give good yields of the substitution product, phenyl phenylethynyl sulfide. The reactions, however, were complicated because the substitution product is reactive towards the thiophenoxy radical. Therefore, the substitution product underwent further reaction to give other byproducts which resulted in a lower yield of the expected substitution product, phenyl phenylethynyl sulfide. This problem, however, can be overcome by using a large excess of the phenylacetylenes.

D. Experimental Section

1. Preparation of phenylacetylene derivatives

Phenylethynyl iodide was prepared form the reaction of phenylethynylmagnesium bromide [167] and iodine. Thus a solution of iodine (0.05 mole) in 25 mL of dry THF was added dropwise to the solution of the Grignard reagent (0.05 mole) in 100 mL of THF with vigorous stirring at room temperature. The reaction was exothermic and the color of iodine disappeared immediately at the beginning of the reaction with a formation of a white precipitate. After the addition, the mixture was stirred overnight at room temperature. The reaction mixture was then poured into a saturated aqueous ammonium chloride solution. The product was extracted with benzene, washed with 2% aqueous sodium thiosulfate solution and washed again with water. The extract was then dried over anhydrous sodium sulfate and concentrated under vacuum. The product was fractionally distilled at reduced pressure to afford a pale yellow liquid, bp 74 °C/1.6 mmHg (lit. [168], bp 83.5 °C/2.5 mmHg).

Phenyl phenylethynyl sulfide was synthesized by the procedure described in the literature [169]. The sulfide had bp 127 °C/0.6 mmHg (lit. [169] bp 146-147 °C/1 mmHg).

Phenyl phenylethynyl sulfone was also prepared by the same literature procedure [169]. The compound had mp 73.0-74.0 °C [169].

Tri-n-butyl(phenylethynyl)stannane was prepared by the literature procedure [170]. Thus, phenylacetylene (50 mmol) was added dropwise to a solution of 2.6 M n-butyllithium (50 mmol) in pentane at -78 °C with

stirring. After the addition, the temperature was raised to room temperature. Tri-n-butyltin chloride was added dropwise and the mixture was stirred at room temperature for 1 h. The mixture was then poured into water and the organic layer was separated. The organic fraction was washed again with water, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product mixture was found to consist of tri-n-butyl(phenylethynyl)stannane, phenylacetylene and tri-n-butyltin chloride. Phenylacetylene and tri-n-butyltin chloride were distilled off at reduced pressure to leave an oily residue in the flask. The product in the flask was purified by passing through a silica gel column using a mixture of hexane-ethyl acetate (90:10) as the eluent. The product, tri-n-butyl (phenylethynyl)stannane, was a pale yellow liquid.

Bis(phenylethynyl)mercury was synthesized by the method described in the literature [171]. The compound had mp 122.5-123 °C (lit. [171] mp 124.5-125 °C).

2. Photoreactions of phenylethynyl iodide with organomercurials

Phenylethynyl iodide (0.1 mmol) and the organomercurial (see Table 28) were dissolved in 5 mL of DMSO in a Pyrex tube equipped with a rubber septum. The mixture was degassed for 5 min and irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel for a period of time. After the irradiation, the mixture was poured into water and extracted with 20 mL of benzene. The extract was washed with 2 x 30 mL of 10% aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate and concentrated in vacuo. The crude mixture

was analyzed by GLC, ^{1}H NMR and GCMS which revealed the presence of the substitution product. The substitution products, (phenylethynyl)cyclohexane and 3,3-dimethyl-1-phenyl-1-butyne, were isolated by column chromatography using hexane as the eluent. All the results are summarized in Table 28.

The following ^{1}H NMR and GCMS data were obtained for the substitution products.

1-Phenyl-1-hexyne:

^{1}H NMR ($CDCl_3$) δ 7.6-7.1(m,5H), 2.65-0.6(m,9H).

GCMS, m/e (relative intensity) 158(41,M^+), 143(58), 129(69), 128(47), 115(100).

(Phenylethynyl)cyclohexane:

^{1}H NMR (300 MHz,$CDCl_3$) δ 7.70-7.05(m,5H), 1.76-0.80(m,11H).

GCMS, m/e (relative intensity) 184(69,M^+), 156(29), 155(59), 142(42), 141(100), 130(35), 129(28), 128(50), 115(47), 102(31).

3,3-Dimethyl-1-phenyl-1-butyne:

^{1}H NMR (300 MHz, $DCDl_3$) δ 7.40-7.33(m,2H), 7.28-7.21(m,3H), 1.31(s,9H).

GCMS, m/e (relative intensity) 158(38,M^+), 143(100), 128(42).

Diethyl phenylethynylphosphonate:

^{1}H NMR ($CDCl_3$) δ 7.7-7.1(m,5H), 4.2(m,4H), 1.4(t,6H).

GCMS, m/e (relative intensity) 238(11,M^+), 210(16), 195(15), 165(21), 129(24), 128(29), 102(100).

3. Photoreaction of phenylethynyl iodide with t-butylmercury chloride in the presence of di-tert-butyl nitroxide (DTBN)

Phenylethynyl iodide (0.1 mmol), t-butylmercury chloride (0.12 mmol) and DTBN (0.01 mmol) were dissolved in 10 mL of DMSO in a Pyrex tube equipped with a rubber septum. After a nitrogen purge, the mixture was irradiated with a 275-W sunlamp placed about 20 cm from the reaction vessel. The reaction was stopped after 45 min of irradiation. The usual workup afforded a crude reaction mixture which was analyzed by GLC. The analysis indicated the presence of the substitution product, 3,3-dimethyl-1-phenyl-1-butyne, in less than 5% yield and the unreacted phenylethynyl iodide (90% field). The control reaction in the absence of DTBN which was carried out at the same time afforded a 25% yield of the substitution product.

4. Dark reaction of phenylethynyl iodide with t-butylmercury chloride

The mixture of phenylethynyl iodide (0.1 mmol) and t-butylmercury chloride (0.12 mmol) in 10 mL of nitrogen-purged DMSO in a Pyrex tube was wrapped with aluminum foil to exclude light. The mixture was placed in a Rayonet Photoreact (at 40-45 °C) for 7 h. The usual workup gave only the unreacted starting material, phenylethynyl iodide, in almost quantitative yield. No substitution product was observed.

5. Photoreactions of phenyl phenylethynyl sulfone with organomericurials

Phenyl phenylethynyl sulfone (0.1 mmol) and the mercurial (0.5 mmol) were dissolved in 10 mL of the solvent (see Table 29). The mixture was irradiated at 350 nm in a Rayonet Photoreactor for 24 h. The usual workup afforded the crude product mixture which was analyzed as described previously. The reaction gave the substitution product in moderate yield.

The reaction of phenyl phenylethynyl sulfone (0.1 mmol) and cyclohexylmercury chloride (0.15 mmol) in DMSO irradiated with a sunlamp for 7 h also afforded the substitution product in 66% yield.

The reaction of phenyl phenylethynyl sulfone with cyclohexylmercury chloride gave a byproduct whose GCMS was identical to that of (2,2-diphenylethenyl)cyclohexane. Similarly, the reaction of phenyl phenylethynyl sulfone with t-butylmercury chloride also gave a byproduct whose GCMS was identical to that of 3,3-dimethyl-1,1-diphenyl-1-butene. However, the formation of the byproducts was not investigated further.

The results of the reactions are presented in Table 29.

3-Methyl-1-phenyl-1-butyne:

GCMS, m/e (relative intensity) 144(43,M^+), 129(100), 128(63), 127(24).

6. Photoreactions of phenyl phenylethynyl sulfide with alkylmercury chlorides

Phenyl phenylethynyl sulfide (0.1 mmol) and the alkylmercury chloride (see Table 30) were dissolved in 10 mL of nitrogen-purged DMSO in a Pyrex tube. The mixture was irradiated and worked up as described previously. Analysis of the crude product mixture revealed the presence of the substitution product. When a deficient amount (0.2 equiv) of the alkylmercury chloride was employed, the reaciton afforded only the substitution product and the unreacted phenyl phenylethynyl sulfide. In contrast, if an excess amount (5 equiv) of the alkylmercury chloride was employed, the reaction also gave a by-product, alkyl phenyl sulfide, together with the substitution product.

When benzene was employed as the solvent, the reaction proceeded slowly and a white precipitate, presumably phenylthiomercury chloride, was also formed.

The results are summarized in Table 30.

7. Photoreactions of tri-n-butyl(phenylethynyl)stannane with alkylmercury chlorides

The mixture of tri-n-butyl(phenylethynyl)stannane (1 mmol) and the alkylmercury chloride (5 mmol) in 10 mL of nitrogen-purged benzene in a Pyrex tube was irradiated in a Rayonet Photoreactor. The mixture was worked up as usual after 24 h of irradiation. The crude product was analyzed by GLC which indicated the presence of the substitution product in low to moderate yield and tri-n-butyltin chloride in good yield. Identities of the products were confirmed by

comparison of their GLC retention times with those of the products obtained previously. The results are presented in Table 31.

8. Photoreaction of bis(phenylethynyl)mercury with organomercurials

Bis(phenylethynyl)mercury (0.1 mmol) and the mercurial (0.5 mmol) were dissolved in 10 mL of DMSO in a Pyrex tube. After a nitrogen purge, the mixture was irradiated at 350 mm in a Rayonet Photoreactor for 24 h. The usual workup afforded a crude mixture which was analyzed by GLC. Analysis indicated the presence of the substitution product. All the yields were calculated based on 2 mol of product/1 mol of bis(phenylethynyl)mercury and were given in %. To avoid confusion, the yields were also given in mmol as shown in Table 32.

9. General procedure for the photoreactions of phenylacetylene derivatives with mercuric phenylmercaptide and phenyl disulfide

The general procedure involved the phenylacetylene compound (see Table 33 for the amount employed) and mercuric phenylmercaptide or phenyl disulfide (0.1 mmol). The substrates were dissolved in 10 mL of a nitrogen-purged solvent in a Pyrex flask and irradiated at 350 nm in a Rayonet Photoreactor for a period of time as indicated in Table 33. After the irradiation, the usual workup afforded an oily residue which was analyzed by GLC and GCMS. The analysis revealed the presence of phenyl phenylethynyl sulfide and the byproducts which are summarized in Table 33. Identification of the substitution product, phenyl phenylethynyl sulfide was confirmed by comparison of its GLC retention time and GCMS with those of the authentic compound.

Isolation and identification of the byproducts will be presented in the next section.

10. Isolation and identification of 2-phenylbenzo[b]thiophene (29), 2-phenyl-3-(phenylthio)benzo[b]thiophene (30) and 3-phenyl-2-(phenylthio)benzo[b]thiophene (31) from the reaction of phenylethynyl iodide with mercuric phenylmercaptide

With our GLC conditions (packed column; 7% OV-3, 1/8" x 10'), the GLC trace of a mixture of 2-phenyl-3-(phenylthio)benzo[b]thiophene (**30**, 3-phenyl-2-(phenylthio)benzo[b]thiophene (**31**), 1,2-bis(phenylthio)phenylethene (**32**) and 2,2-bis(phenylthio)-1-phenylethene (**33**) showed only 2 separated peaks. The first peak consisted of **33** and one isomer of **32**. The second peak consisted of **30**, **31** and the other isomer of **32**. Therefore, the products could not be isolated by the preparative GLC. Fortunately, we found that the photoreaction of a very dilute mixture of phenylethynyl iodide and mercuric phenylmercaptide (2:1 equiv) in DMSO afforded only phenyl phenylethynyl sulfide, 2-phenylbenzo[b]thiophene (**29**), 2-phenyl-3-(phenylthio)benzo[b]thiophene (**30**) and 3-phenyl-2-(phenylthio)benzothiophene (**31**). These products can be easily separated by either a preparative GLC or by column chomatography. Compound **30** and **31**, however, were isolated as a mixture.

Thus the mixture of phenylethynyl iodide (2 mmol) and mercuric phenylmercaptide (1 mmol) in 100 mL of nitrogen-purged DMSO in a Pyrex flask was irradiated in a Rayonet Photoreactor for 24 h. The usual workup gave an oily residue which consisted of phenyl phenylethynyl

sulfide, 2-phenylbenzo[b]thiophene (**29**), 2-phenyl-3-(phenylthio)benzo[b]thiophene (**30**) and 3-phenyl-2-(phenylthio)benzo[b]thiophene (**31**) in a ratio of phenyl phenylethynyl sulfide:**29**:(**30** + **31**) = 2.5:1.0:2.1. The crude mixture was divided into two portions. The products in the first portion were isolated by preparative GLC (7% OV-3, 1/4" x 7'). The substitution product, phenyl phenylethynyl sulfide, was isolated as a colorless liquid. 2-Phenylbenzo[b]thiophene (**29**) was collected as white feathers (mp 168-169 °C lit. [172] mp 171-173 °C). The mixture of **30** and **31** was isolated as a pale yellow viscous oil.

The products in the other portion of the crude reaction mixture were isolated by silica gel chromatography using hexane as the eluent. Phenyl phenylethynyl sulfide and 2-phenylbenzo[b]thiophene (**29**) were eluted together. The mixture was concentrated and cooled in an ice bath, where upon 2-phenylbenzo[b]thiophene precipitated as a white solid. The precipitate was filtered and recrystallized from hexane to give white feathers of 2-phenylbenzo[b]thiophene whose ^{1}H NMR was identical to that of the product isolated by preparative GLC.

The products, **30** and **31**, remaining on the column were eluted with benzene. The pale yellow viscous liquid obtained after removal of the solvent had a ^{1}H NMR which was identical to that of the mixture isolated by preparative GLC.

Identity of 2-phenylbenzo[b]thiophene was confirmed by comparison of its GLC retention time and ^{1}H NMR with those of the authentic compound synthesized by the literature procedure [172]. The mass

spectrum of 2-phenylbenzo[b]thiophene has been reported and discussed in the literature [173].

The following data were obtained for the isolated products.

2-Phenylbenzo[b]thiophene (29):

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.66(m,4H), 7.40(s,1H), 7.46-7.22(m,5H).

GCMS, m/e (relative intensity) 212(5), 210(100,M^+), 178(12), 165(25), 105(32,M^{++}), 104(14), 92(15), 79(7).

2-Phenyl-3-(phenylthio)benzo[b]thiophene (30) and 3-phenyl-2-(phenylthio)benzol[b]thiophene (31) (mixture):

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.0 (m).

GCMS, m/e (relative intensity) 320(11), 318(100,M^+), 285(20), 284(25), 241(36), 240(67), 208(29), 165(25), 142(22), 77(24), 51(30).

IR (neat, NaCl plates, cm^{-1}) 3043(s), 1593(w), 1576(s), 1470(s), 1448(s), 1433(s), 1422(s), 1075(m), 1063(m), 1015(s), 740(s), 680(s).

11. Preparation, isolation and identification of 1,2-bis(phenylthio)phenylethene (32) and 2,2-bis(phenylthio)-1-phenylethene (33) from the reaction of phenylphenylethynyl sulfide with thiophenol

Phenyl phenylethynyl sulfide (2.5 mmol) and thiophenol (2.5 mmol) were dissolved in 10 mL of benzene in a Pyrex flask. After a nitrogen purge, the mixture was irradiated at 350 nm in a Rayonet Photoreactor for 25 h. The solvent was removed under vacuum to yield an oily residue which was analyzed by GLC. The GLC trace indicated two separated peaks for the products. The products were isolated on a

silica gel column using hexane as the eluent. The first product was analyzed by ^{1}H NMR, GCMS and IR to be 2,2-bis(phenylthio)-1-phenylethene (33) and the second product was identified to be a mixture of (E) and (Z)-1,2-bis(phenylthio)phenylethene (32).

The isolated compounds, 32, and 33, were shown to be identical to the products obtained from the reaction of phenylethynyl iodide with mercuric phenylmercaptide by comparison of their GLC retention times and GCMS. The ^{1}H NMR and IR of 32 [174] and 33 [175,176] have been reported in the literaure. The following data were obtained.

1,2-Bis(phenylthio)phenylethene (32):

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.10(m).

GCMS, m/e (relative intensity) 322(5), 320(45,M^+), 211(96), 210(40), 179(23), 178(100), 167(83), 165(43), 134(68), 121(26), 109(58), 77(52), 65(59), 51(40).

IR (neat, NaCl plates, cm^{-1}) 3067(m), 1587(s), 1545(m), 1485(s), 1445(s), 1030(m), 740(s), 680(s).

2,2-Bis(phenylthio)-1-phenylethene (33):

^{1}H NMR ($CDCl_3$) (300 MHz, $CDCl_3$) δ 7.61(m), 7.4-7.1(m), 6.89(s).

GCMS, m/e (relative intensity) 322(5), 320(45,M^+), 211(97), 209(40), 179(23), 178(100), 167(83), 165(43), 134(68), 121(26), 109(58), 77(52), 65(59), 51(40).

IR (neat, NaCl plates, cm^{-1}) 3062(w), 1582(m), 1479(s), 1440(s), 1025(m), 738(s), 688(s).

PART III. RELATIVE REACTIVITY AND KINETIC CHAIN LENGTH

I. RELATIVE REACTIVITIES OF ALKENYL AND ALKYNYL DERIVATIVES TOWARDS CYCLOHEXYL AND THIOPHENOXY RADICALS

A. Introduction

The cyclohexyl radical is a nucleophilic radical and, therefore, adds to electron deficient olefins effectively. The nucleophilicity of cyclohexyl radical has been studied by Giese and Meister [31].

Thiophenoxy radical, in contrast, has an electrophilic character. It is known to add to a carbon-carbon multiple bond in a reversible manner [39]. Because of its electrophilic nature, thiophenoxy radical would be expected to add readily to electron-rich multiple bond systems.

In Part I and Part II, we have demonstrated that both cyclohexyl and thiophenoxy radicals react regioselectively with the carbon-carbon multiple bonds of alkenyl and alkynyl derivatives. The addition followed by elimination leads to the substitution products.

The following section will determine the relative reactivities of alkenyl and alkynyl derivatives towards both cyclohexyl and thiophenoxy radicals.

B. Results and Discussion

1. Relative reactivities towards cyclohexyl radical

In order to determine the relative reactivity towards cyclohexyl radical, a pair of substrates and a deficient amount of cyclohexylmercury chloride in DMSO were irradiated in a Rayonet Photoreactor under an atmosphere of nitrogen. To maintain a constant

ratio of the substrates, a 10-fold excess of the substrates was was employed. 2,2-Diphenylethenyl iodide was chosen as a standard and, in most cases, relative reactivities were obtained from a direct competition reaction between an alkene or alkyne and 2,2-diphenylethenyl iodide. When 2,2-diphenylethenyl iodide could not be used because the substrates and the iodide give the same product, the reactivities were measured by relative competition with phenylethynyl iodide.

In a typical reaction, equimolar amounts of substrates and 0.1 equiv of cyclohexylmercury chloride in DMSO were irradiated in a Rayonet Photoreactor for a period of time. After workup, the reaction mixture was analyzed by GLC and the ratio of the substitution products after correction by the predetermined GLC-response factor was then obtained. Results are summarized in Table 34.

Since the two competing substrates in the competition reactions were employed in equal molar amounts, the relative reactivities can be simply obtained from the ratios of the substitution products as shown in Eq. (134). Table 35 shows the adjusted relative reactivities of

$$\text{Relative reactivity} = \text{Ratio of Products} \qquad (134)$$

the unsaturated compounds towards cyclohexyl radical obtained from the data in Table 34.

From Table 35, one can see that in each series the sulfone is the most reactive towards cyclohexyl radical. Phenyl phenylethynyl sulfone displays a very high relative reactivity and it is the most

Table 34. Competition reactions with cyclohexylmercury chloride

Compound	Conditions[a]	Ratio of Products[b]	
		I[c]	II[d]
CH_2=$CHCH_2SnBu_3$	PhH, 24 h	<< 0.1	-
CH_2=$CHSnBu_3$	PhH, 24 h	< 0.1	-
Me_2C=$CHSnBu_3$	PhH, 24 h	0.1	-
(E)-PhCH=$CHSnBu_3$	PhH, 24 h	0.7	-
(E)-PhCH=CHI	PhH, 24 h	0.7	-
(E)-PhCH=CHSPh	PhH, 24 h	1.1	-
(E)-PhCH=CHHgCl	DMSO/PhH, 24 h	1.5	-
(E)-PhCH=$CHSO_2Ph$	PhH, 24 h	3.3	-
Ph_2C=$CHSnBu_3$	PhH, 5 h	-	0.2
Ph_2C=CHI	PhH, 6 h	1.0	0.26
Ph_2C=CHHgCl	PhH, 6 h	-	0.5
Ph_2C=CHSPh	PhH, 6 h	-	1.1

[a]Substrates (1 mmol each) and cyclohexylmercury chloride (0.1 mmol) in 10 ml of nitrogen-purged solvent were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Determined by GLC.

[c]In competition with 2,2-diphenylethenyl iodide.

[d]In competition with phenylethynyl iodide.

Table 34. (continued)

Compound	Conditions[a]	Ratio of Products[b]	
		I[c]	II[d]
$Ph_2C{=}CHSO_2Ph$	PhH, 6 h	-	1.7
$PhC{\equiv}SnBu_3$	PhH, 20 h	0.2	-
$(PhC{\equiv}C)_2Hg$	DMSO, 24 h	0.2	-
$PhC{\equiv}CSPh$	PhH, 20 h	0.8	-
$PhC{\equiv}CI$	PhH, 6 h	3.8	1.0
$PhC{\equiv}CSO_2Ph$	PhH, 20 h	12.1	-
PhSSPh	PhH, 4 h	36	-

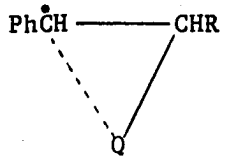
Table 35. Relative reactivities towards cyclohexyl radical

Compound	Relative Reactivity
CH_2=$CHCH_2SnBu_3$	<< 1
CH_2=$CHSnBu_3$	< 1
Me_2C=$CHSnBu_3$	1
(E)-PhCH=$CHSnBu_3$	7
(E)-PhCH=CHI	7
(E)-PhCH=CHSPh	11
(E)-PhCH=CHHgCl	15
(E)-PhCH=$CHSO_2Ph$	33
Ph_2C=$CHSnBu_3$	8
Ph_2C=CHI	10
Ph_2C=CHHgCl	19
Ph_2C=CHSPh	42
Ph_2C=$CHSO_2Ph$	65
PhC≡$CSnBu_3$	2
$(PhC≡C)_2Hg$	2
PhC≡CSPh	8
PhC≡CI	38
PhC≡CSO_2Ph	121
PhSSPh	360

reactive among the unsaturated compounds towards the addition of cyclohexyl radical.

In the series of phenylacetylene derivatives, the reactivity decreases in the order $PhSO_2$ > I > PhS > $SnBu_3$ ~ PhC≡CHg. The order is in agreement with the order of decreasing electronegativity of these substituents. With its nucleophilic character, cyclohexyl radical would be expected to add better to phenylacetylene derivatives with stronger electron withdrawing group. This is exactly what was observed. Therefore, it appears that reactivity of phenylacetylene derivatives towards the addition of cyclohexyl radical depends on the electronegativity of the substitutent.

In the alkenyl system, on the other hand, the relative reactivities are puzzling. However, the sulfones are still the most reactive towards cyclohexyl radical. In this system, the stabilization of the transition states leading to $Ph\dot{C}H$-CH(R)Q or Ph_2C-$\dot{C}$H(R)Q by hyperconjugation or bridging (34) together with the



34

inductive effect of Q may contribute to the observed reactivities.

The relative reactivity of phenyl disulfide and 2,2-diphenylethenyl iodide towards cyclohexyl radical has also been determined. Phenyl disulfide was found to be 36 times more reactive

than the iodide and to be more reactive towards cyclohexyl radical than any of the unsaturated systems studied.

2. Relative reactivities towards thiophenoxy radical

Relative reactivities of alkenyl, alkynyl, and allyl derivatives towards thiophenoxy radical have been determined in a manner similar to that employed for cyclohexyl radical in the preceding section. The competition reactions were carried out with mercuric phenylmercaptide as the source of thiophenoxy radical. Product ratios of the competition reactions are summarized in Table 36.

The reversibility of the addition of thiophenoxy radical to multiple bonds causes the competition to be more complicated as shown in Scheme 41. Reactivity would depend on $\underline{k}_1$, $\underline{k}_{-1}$, and $\underline{k}_2$ as shown in Eq. (135).

Scheme 41

$$\text{PhS}\bullet + \begin{cases} \text{PhCH=CHQ} \underset{\underline{k}_{-1}}{\overset{\underline{k}_1}{\rightleftharpoons}} \text{PhCH-CH(SPh)Q} \xrightarrow{\underline{k}_2} \text{PhCH=CHSPh} \\ \text{Ph}_2\text{C=CHQ} \underset{\underline{k}'_{-1}}{\overset{\underline{k}'_1}{\rightleftharpoons}} \text{Ph}_2\dot{\text{C}}\text{-CH(SPh)Q} \xrightarrow{\underline{k}'_2} \text{Ph}_2\text{C=CHSPh} \end{cases} + \text{Q}\bullet$$

$$\text{Reactivity} = \frac{\underline{k}_1 \cdot \underline{k}_2}{\underline{k}_{-1} + \underline{k}_2} \qquad (135)$$

If $\underline{k}_2 >>> \underline{k}_{-1}$ and $\underline{k}'_2 >>> \underline{k}'_{-1}$, reactivity will depend only upon $\underline{k}_1$ and $\underline{k}'_1$ and the relative reactivity may be simply written as

Table 36. Competition reactions with mercuric phenylmercaptide

Compound	Conditions[a]	Ratio of Products[b]		
		I[c]	II[d]	III[e]
CH_2=CHSnBu_3	DMSO/PhH, 20 h	0.05	-	1.00
CH_2=CHCH_2SnBu_3	DMSO/PhH, 20 h	0.13	-	-
Me_2C=CHSnBu_3	DMSO, 20 h	0.60	-	-
(E)-PhCH=CHSO_2Ph	DMSO, 24 h	0.01	-	-
(E)-PhCH=CHI	DMSO, 24 h	0.37	-	-
(E)-PhCH=CHSnBu_3	DMSO/PhH, 24 h	2.39	-	-
(E)-PhCH=CHHgCl	DMSO, 20 h	5.20	-	-
Ph_2C=CHSO_2Ph	DMSO, 20 h	-	1.48	-
Ph_2C=CHI	DMSO/PhH, 24 h	1.00	4.35	-
Ph_2C=CHSnBu_3	DMSO/PhH, 24 h	-	23.07	-
Ph_2C=CHHgCl	DMSO, 20 h	-	30.29	-
PhC≡CSnBu_3	DMSO/PhH, 20 h	-	-	0.16
PhC≡CI	DMSO, 20 h	0.23	1.00	-
PhC≡CSO_2Ph	DMSO, 24 h	1.18	-	-

[a]Substrates (1 mmol each) and mercuric thiophenoxide (0.1 mmol) in 10 ml of nitrogen-purged solvent were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Determined by GLC.

[c]In competition with 2,2-diphenylethenyl iodide.

[d]In competition with phenylethynyl iodide.

[e]In competition with tri-n-butyl vinylstannane.

Eq. (136).

$$\text{Relative reactivity} = \frac{k_1}{k'_1} = \text{Ratio of Products} \qquad (136)$$

Table 37 shows the adjusted relative reactivities of the unsaturated systems towards the thiophenoxy radical as obtained form the data from Table 36. Relative reactivities of phenylacetylene derivatives towards thiophenoxy radical are in the order $PhSO_2$ > I > $SnBu_3$; a reactivity series similar to that observed with cyclohexyl radical. Since the same relative reactivity order was found with both the nucleophilic cyclohexyl radical and the electrophilic thiophenoxy radical, the relative reactivities apparently reflect the intrinsic reactivities of the alkynes.

In the alkenyl system, the mercury and tin derivatives display high relative reactivities. 2,2-Diphenylethenylmercury chloride has the highest reactivity; whereas, tri-n-butyl-2,2-diphenylethenylstannane and (E)-2-phenylethenylmercury chloride have about the same reactivity.

The high reactivity of phenyl phenylethynyl sulfone relative to 2,2-diphenylethenyl phenyl sulfone or 2-phenylethenyl phenyl sulfone and the low reactivity of tri-n-butyl-2-phenylethynylstannane relative to tri-n-butyl-2,2-diphenylethenylstanne or tri-n-butyl-2-phenylethenylstannane are also puzzling. Perhaps the groups Q = $SnBu_3$ or HgX can stabilize the transition states leading to $PhC^{\bullet}H\text{-}CH(R)Q$, but not to $Ph\dot{C}\text{=}C(R)Q$, by hyperconjugation or bridging, particularly when the attacking radical is electrophilic in nature.

Table 37. Relative reactivities towards thiophenoxy radical

Compound	Relative Reactivity
CH_2=CHSnBu_3	1
CH_2=CHCH_2SnBu_3	3
Me_2C=CHSnBu_3	12
(E)-PhCH=CHSO_2Ph	0.2
(E)-PhCH=CHI	7
(E)-PhCH=CHSnBu_3	48
(E)-PhCH=CHHgCl	104
Ph_2C=CHSO_2Ph	7
Ph_2C=CHI	20
Ph_2C=CHSnBu_3	106
Ph_2C=CHHgCl	139
PhC≡CSnBu_3	0.16
PhC≡CI	5
PhC≡CSO_2Ph	24

C. Conclusion

Relative reactivities of alkenyl and alkynyl derivatives containing iodo, sulfide, sulfone, mercury, and stannane substituents towards the nucleophilic cyclohexyl radical and the electrophilic thiophenoxy radical have been determined. With cyclohexyl radical, the sulfone derivatives have the highest reactivity in each series.

In the phenylacetylene system, the order of reactivity towards both cyclohexyl and thiophenoxy radicals are in the order $PhSO_2$ > I > $SnBu_3$. This apparently indicates that the relative reactivities reflect the intrinsic reactivities of the alkynes.

The relative reactivities towards cyclohexyl and thiophenoxy radicals are puzzling for the alkenyl system. The stabilization of the transition states, by the substituent Q, by hyperconjugation or bridging may contribute to the observed relative reactivities.

The observed relative reactivities towards the addition of cyclohexyl radical are believed to be the true reactivities since no evidence for the reversible addition was observed. The relative reactivities towards thiophenoxy radical may be complicated by the reversible addition of the thiophenoxy radical.

Our results indicate that the preferred group for free radical substitution by an addition-elimination mechanism depends on the nature of the attacking radical with $PhSO_2$ being the preferred group in alkynes but often Bu_3Sn or HgX in the alkenes. However, when stereospecificity is desired, the iodo substituent seems to be the preferred leaving group (see Section III, Part I).

D. Experimental Section

1. General procedure for the competition reaction of two unsaturated compounds with cyclohexylmercury chloride

2,2-Diphenylethenyl iodide or phenylethynyl iodide (1 mmol), the alkenyl or alkynyl compound (1 mmol) and cyclohexylmercury chloride were dissolved in 10 mL of a nitrogen-purged solvent in a Pyrex tube equipped with a rubber septum. The mixture was irradiated at 350 nm in a Rayonet Photoreactor for a period of time (see Table 34 for the solvent and irradiation time). The reaction mixture was then poured into water and extracted with benzene. The extract was washed twice with 30 mL of 10% aqueous sodium thiosulfate solution, dried over anhydrous sodium thiosulfate and concentrated. The oily residue was then treated with hexane and the precipitate formed was filtered off. The mixture was concentrated and analyzed by GLC. The identities of all the substitution products were confirmed by comparison of their GLC retention times with those of the products obtained in Part I and Part II. The relative ratio of the products was obtained from GLC and was corrected by the predetermined GLC response factors. The results are summarized in Table 34.

The competition reaction of 2,2-diphenylethenyl iodide and phenyl disulfide with cyclohexylmercury chloride was also carried out by the same procedure. The crude product mixture was analyzed by GLC which indicated the presence of the substitution products, (2,2-diphenylethenyl)cyclohexane (minor) and cyclohexyl phenyl sulfide (major), and the remaining starting materials. 2,2-Diphenylethenyl

phenyl sulfide was also formed in considerable yield. The ratio of the substitution products is included in Table 34.

2. General procedure for the competition reaction of two unsaturated compounds with mercuric phenylmercaptide

The mixture of 2,2-diphenylethenyl iodide or 2-phenylethynyl iodide (1 mmol), the alkenyl or alkynyl compound (1 mmol) and mercuric phenylmercaptide in 10 mL of a nitrogen-purged solvent was irradiated in a Rayonet Photoreactor for 20-24 h (see Table 36). After the irradiation, the mixture was worked up as described previously to afford an oily residue. The ratio of the products was obtained from the GLC analysis and corrected with the predetermined GLC response factors. All the products were confirmed by comparison of their GLC retention times with those of the authentic compounds or the products obtained previously. The results are presented in Table 36.

II. KINETIC CHAIN LENGTH

A. Introduction

Reactions of alkenyl derivatives with organomercurials have been shown to be radical processes (Part I and II). The reactions are generally believed to involve a free-radical chain addition-elimination mechanism. The real proof for the chain process, however, has not yet been presented. The only way to prove if the reaction is a chain process is to measure its kinetic chain length.

The following section will determine the initial kinetic chain lengths of the reactions of 2,2-diphenylethenyl iodide and tri-n-butyl-(E)-2-phenylethenylstannane with t-butylmercury chloride.

B. Results and Discussion

1. Determination of kinetic chain length of the reaction between 2,2-diphenylethenyl iodide and t-butylmercury chloride

An initial kinetic chain length of a reaction can be expressed as shown in Eq. (137). Both the initial rate and rate of initiation can

$$\text{Kinetic Chain Length} = \frac{\text{Initial Rate}}{\text{Rate of Initiation}} \qquad (137)$$

be measured experimentally by following either rate of consumption of the substrate or rate of formation of the substitution product. The progress of the reaction is conveniently monitored by ^{1}H NMR.

In a typical reaction, 0.1 M of 2,2-diphenylethenyl iodide, 0.3 M of t-butylmercury chloride and 0.1 M of methylene chloride

(internal standard) in deuterated DMSO were placed in a NMR tube. The mixture was irradiated with a 275-W sunlamp at 30-35 °C and was checked at different periods of time by ^{1}H NMR. The formation of the product was determined by following the increase of the vinylic proton signal of $Ph_2C{=}CHCMe_3$ which appears at about 5.6 ppm. Yield of the product was obtained from the integration and the results are presented in Table 38. The table also includes the results from the reaction in the presence of di-tert-butyl nitroxide (DTBN) which was carried out under the same conditions. The plot of yields of the substitution product vs. time is shown in Figure 1.

The initial rate of the reaction is then obtained from the slope of the curve at the beginning of the reaction (determined by use of a tangent meter) as shown in the figure. The rate of initiation is calculated form the concentration of DTBN and the time needed to consume all of the DTBN which can also be determined from Figure 1.

From Figure 1

$$\text{Initial Rate} = 2.50 \times 10^{-2}\ \underline{M}/\text{min}$$

$$\text{Rate of Initiation} = 1.74 \times 10^{-2}\ \underline{M}/70\ \text{min}$$

$$\text{Kinetic Chain Length} = \frac{2.50 \times 10^{-2}\ \underline{M}/\text{min}}{1.74 \times 10^{-2}\ \underline{M}/70\ \text{min}} = 100$$

With a kinetic chain length of 100, reaction of 2,2-diphenylethenyl iodide and t-butylmercury chloride is definitely a chain process. The measured kinetic chain length, however, is based on the consumption of DTBN only by t-butyl radical but not by the

Table 38. Reaction of 2,2-diphenylethenyl iodide and t-butylmercury chloride

$$\underset{0.1\ M}{Ph_2C{=}CHI} + \underset{0.3\ M}{t\text{-}BuHgCl} \xrightarrow{h\nu} Ph_2C{=}CHBu\text{-}t + IHgCl$$

Time[a] (min)	% $Ph_2C{=}CHBu\text{-}t$[b]	
	without DTBN	with DTBN (1.74×10^{-2} M)
5	0	0
10	0	0
20	16	0
30	22	0
40	36	0
60	45	0
90		4
120	50	15
150		31
240	72	50

[a]Mixture in DMSO-d_6 in NMR tube was irradiated at 30-35 °C with a 275-W sunlamp ca. 20 cm^6 from the tube.

[b]Determined by ^1H NMR using CH_2Cl_2 as internal standard.

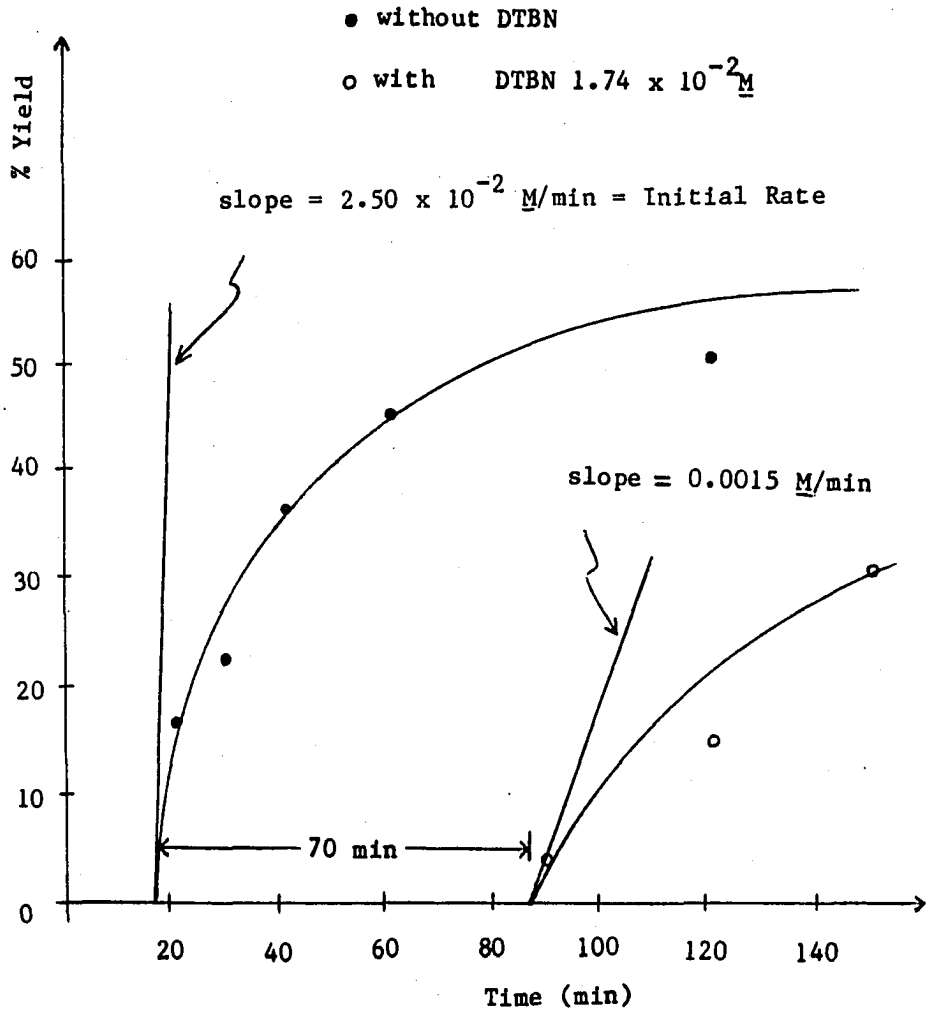


Figure 1. Formation of product vs. time for the reaction of 2,2-diphenylethenyl iodide and t-butylmercury chloride

monomeric HgCl. If, in fact, the DTBN was trapped by both t-butyl radical and HgCl, and if HgCl cannot initiate the chain, the initial kinetic chain length would be 100 x 2. Actually, it is believed that HgCl can initiate the chain by forming t-Bu• in the Reaction 138 (see Part I) and the trapping or lack of trapping of teh HgCl by DTBN will have no effect on the calculation of the kinetic chain length.

$$\text{t-BuHgCl} + \text{HgCl} \longrightarrow \text{t-Bu}\bullet + \text{Hg}^{\circ} + \text{HgCl}_2 \qquad (138)$$

2. Determination of the kinetic chain length of the reaction of tri-n-butyl-(E)-2-phenylethenylstannane and t-butylmercury chloride

The experimental conditions used to determine kinetic chain length of tri-n-butyl-(E)-2-phenylethenylstannane and t-butylmercury chloride are similar to those of the reaction with 2,2-diphenylethenyl iodide except for the solvent and the internal standard. Thus, 0.1 M of the stannane, 0.1 M of the mercurial and 0.1 M of DMSO (internal standard) in a nitrogen-purged deuterated benzene solution in a NMR tube were irradiated with a 275-W sunlamp at 30-35 °C. The reaction was monitored periodically by ^{1}H NMR. The yield of the substitution product was obtained by integration the signal of the vinylic protons compared with that of the internal standard. The results of the reactions with and without DTBN are given in Table 39. Figure 2 shows the plot of product vs. time.

From Figure 2:

Initial Rate = 2.00×10^{-2} M/min.

Rate of Initiation = 1.60×10^{-2} M/57 min.

$$\text{Kinetic Chain Length} = \frac{2.00 \times 10^{-2}\ \underline{M}/\text{min.}}{1.60 \times 10^{-2}\underline{M}/57\ \text{min.}} = 71$$

The result indicates that reaction of tri-n-butyl-(E)-2-phenylethenylstannane and t-butylmercury chloride is a radical chain process with an initial kinetic chain length of 71. If both t-butyl radical and HgCl are trapped by the DTBN, the measured kinetic chain length would be 71 x 2 provided HgCl is ineffective in initiating chains.

The reaction of the stannane and t-butylmercury chloride had a long induction period even with a nitrogen-purged solvent. This may indicate that the substrate stannane contained some inhibitor. The alkenyl stannane gradually decomposed to give a white gelatinous precipitate when stored. The stannane, however, was filtered through a silica gel column before being employed in the reaction.

It is apparent from Figures 1 and 2 that rates of the formation of the products decrease as the reaction proceeds which indicates a shorter kinetic chain length as the reaction proceeds towards completion. Both figures show lower initial rates for the reactions with DTBN. Perhaps the presence of HgCl from the decomposition of the mercurial retards the reaction by trapping the radical adduct before the elimination can occur.

C. Conclusion

The initial kinetic chain lengths of the reactions of 2,2-diphenylethenyl iodide and tri-n-butyl-(E)-2-phenylethenylstannane

Table 39. Reaction of tri-n-butyl-(E)-2-phenylethenylstannane and t-butylmercury chloride

$$\underset{0.1\ M}{(E)\text{-PhC=CHSnBu}_3} + \underset{0.3\ M}{t\text{-BuHgCl}} \xrightarrow{h\nu} \text{PhCH=CHBu} + \text{Bu}_3\text{SnCl} + \text{Hg}^{\circ}$$

Time[a] (min)	% PhCH=CHBu[b]	
	without DTBN	with DTBN (1.74×10^{-2} M)
30	0	0
60	0	0
80	0	0
95	19	0
110	29	0
140	57	0
150		5
180		27
200	70	
240		60

[a]Mixture in C_6D_6 in NMR tube was irradiated at 30-35 °C with a 275-W sunlamp ca. 20 cm from the tube.

[b]Determined by ^{1}H NMR using DMSO as internal standard.

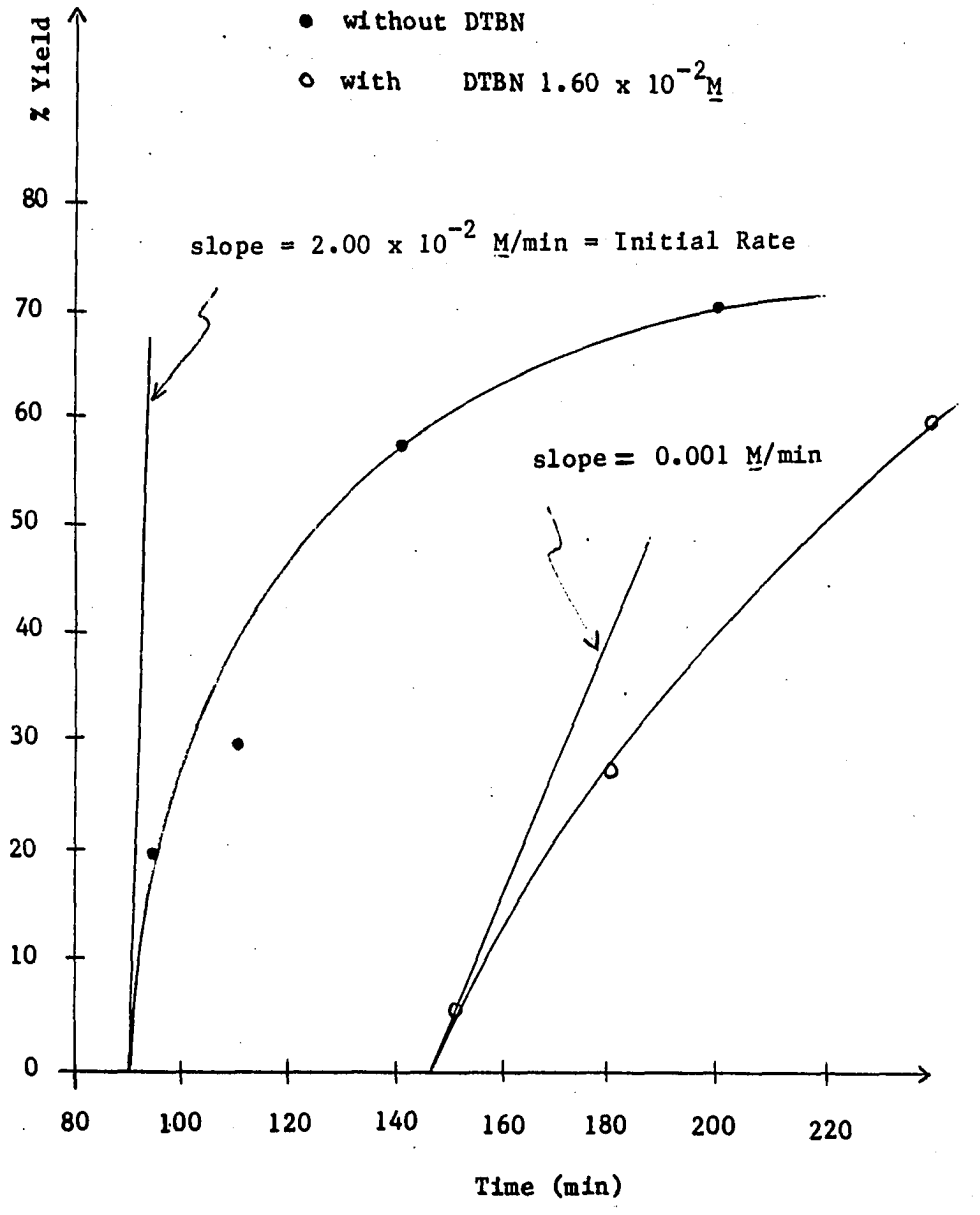


Figure 2. Formation of product vs. time for the reaction of tri-n-butyl-(E)-2-phenylethenylstannane and t-butylmercury chloride

with t-butylmercury chloride were determined. The measured initial kinetic chain lengths are 100 (or 100 x 2) and 71 (or 71 x 2), respectively. The results indicate that the reactions are definitely radical chain processes and most of the substitution products must be formed in the propagation steps.

D. Experimental Section

1. Determmination of initial kinetic chain length of the reaction of 2,2-diphenylethenyl iodide with t-butylmercury chloride

2,2-Diphenylethenyl iodide (0.1 mmol), t-butylmercury chloride (0.3 mmol) and methylene chloride (0.1 mmol) were dissolved in 1 mL of nitrogen-purged deuterated DMSO in a NMR tube equipped with a rubber septum. After a 300 MHz ^{1}H NMR spectrum was obtained, the mixture was irradiated at 30-35 °C with a 275-W sunlamp placed about 20 cm from the reaction tube. The progress of the reaction was monitored by 300 MHz ^{1}H NMR and the yield of the substitution product, 3,3-dimethyl-1,1-diphenyl-1-butene, was obtained from the integration of the vinylic protron signal (at 5.6 ppm). The yields of the substitution product at different periods of time are presented in Table 38.

We observed that a gray flocculent precipitate formed if the irradiation was continued after the reaction was complete. The yield of the substitution product, however, was not affected.

The reaction of 2,2-diphenylethenyl iodide with t-butylmercury chloride in the presence of DTBN was also carried out under the same conditions. Thus 0.1 mmol of the iodide, 0.3 mmol of the mercurial, 0.1

mmol of methylene chloride and 1.74×10^{-2} mmol of DTBN were dissolved in 1 mL of nitrogen-purged DMSO in a NMR tube. After a ^{1}H NMR spectrum was obtained, the mixture was irradiated with a sunlamp under exactly the same conditions described above. The progress of the reaction was followed by 300 MHz ^{1}H NMR and the yields of the substitution product obtained at different periods of time are presented in Table 38.

2. Determination of initial kinetic chain length of the reaction of tri-n-butyl-(E)-2-phenylethenylstannane with t-butylmercury chloride

Tri-n-butyl-(E)-2-phenylethenylstannane (0.1 mmol), t-butylmercury chloride (0.1 mmol) and DMSO (0.1 mmol) were dissolved in 1 mL of nitrogen-purged deuterated benzene in a NMR tube equipped with a rubber septum. After a 300 MHz ^{1}H NMR spectrum was obtained, the mixture was irradiated at 30-25 °C with a 275-W sunlamp placed about 20 cm from the reaction tube. The progress of the reaction was monitored periodically by 300 MHz ^{1}H NMR. The yield of the product was obtained from the integration of the vinylic proton signal (at 6.32 ppm) by comparison with that of the internal standard (DMSO). The results are summarized in Table 39.

We observed that a small bead of mercury metal formed during the irradiation. After completion of the reaction, a gray precipitate started to form but it had no effect on the yield of the substitution product.

The reaction of tri-n-butyl-(E)-2-phenylethenylstannane with t-butylmercury chloride in the presence of DTBN (1.60×10^{-2}M) was also

carried out under the same conditions. The results are also given in Table 39.

PART VI. RADICAL REACTIONS OF MERCURIC CARBOXYLATES

I. RADICAL REACTIONS OF MERCURIC CARBOXYLATES WITH ALKENYL AND ALKYNYL DERIVATIVES

A. Introduction

Mercuric carboxylates are easily prepared by a reaction between a carboxylic acid or its salt and mercuric oxide or mercuric nitrate. They have been used as precursors for preparing other mercury derivatives (ref 3, chapter 10). Thus alkyl and aryl mercury derivatives have been synthesized from mercury salts of carboxylic acids as shown in Eq. (139). The reaction offers a possibility of

$$(RCOO)_2Hg \xrightarrow{h\nu} RCOOHgR + CO_2 \qquad (139)$$

obtaining compounds of the type RHgX from easily available materials.

The reaction of mercuric carboxylates to form alkylmercury carboxylates is believed to involve a free-radical chain reaction. The reaction was initiated by an acyl peroxide or ultra-violet light. The mechanism is outlined in Scheme 42.

Scheme 42

Initiation

$$(RCOO)_2 \longrightarrow 2RCOO\bullet$$

$$\text{or } (RCOO)_2Hg \xrightarrow{h\nu} RCOOHg\bullet + RCOO\bullet$$

Propagation

$$RCOO\bullet \longrightarrow R\bullet + CO_2$$

$$(RCOO)_2Hg + R\bullet \longrightarrow RCOOHgR + RCOO\bullet$$

In Part I - Part III, we have shown that carbon-centered radicals generated from alkylmercury halides underwent substitution reactions with various alkenyl, alkynyl, and allyl derivatives. Furthermore, mercury compounds of the type R_2Hg where R = PhS, $PhSO_2$, $(EtO)_2P(O)$ or alkyl have been shown to undergo facile photostimulated substitution reactions with these unsaturated systems. Therefore, mercuric carboxylates appeared to be good candidates for a new radical source for this substitution reaction. Indeed, we have found that mercuric dimethylacetate and 2,2-diphenylethenyl iodide underwent a substitution reaction under UV irradiation to give the substitution product in good yield.

The following section will present the photostimulated reactions of mercuric carboxylates and alkenyl derivatives as shown in Eq. (140).

$$Ph_2C{=}CHQ + (RCOO)_2Hg \xrightarrow{h\nu} Ph_2C{=}CHR + RCOOHgQ + CO_2 \quad (140)$$

Q = I, HgX, SO_2Ph, $SnBu_3$

B. Results and Discussion

1. Reactions of mercuric carboxylates and 1-alkenyl derivatives

Mercuric dimethylacetate and 2,2-diphenylethenyl iodide in a 1: 1 mol ratio were allowed to react in benzene in a Rayonet Photoreactor. The reaction gave 0.78 equiv of 3-methyl-1,1-diphenyl-1-butene as shown in Eq. (141). When 2 equiv of the alkenyl iodide was employed, the yield of the substitution product increased to a maximum of 0.95

$$Ph_2C{=}CHI + (Me_2CHCOO)_2Hg \xrightarrow{h\nu} Ph_2C{=}CHCHMe_2 + CO_2 + Me_2CHCOOHgI \quad (141)$$

equiv and did not exceed 1 even at very long irradiation periods (Table 40). This indicates that only one carboxyl group underwent decarboxylation to give the radical, R•, which subsequently added to the double bond to give the substitution product. Apparently, iodomercury dimethylacetate does not react with the alkenyl iodide (Eq. 142).

$$Ph_2C{=}CHI + Me_2CHCOOHgI \not\longrightarrow Ph_2C{=}CHCHMe_2 + CO_2 + HgI_2 \quad (142)$$

The decomposition of mercuric carboxylates under the initiation by an acyl peroxide or ultra-violet light gave only alkylmercury carboxylate, RCOOHgR. At higher temperature, however, mercury salts can be converted to diorganomercurial (Eq. 143) [177]. This is one of the methods that have been used to synthesize diorganomercury compounds.

$$(RCOO)_2Hg \xrightarrow{\text{high T}} RHgR + CO_2 \quad (143)$$

Mercuric trimethylacetate which is expected to give a better yield of the substitution product was also employed. The decomposition of this mercury salt should give the t-butyl radical which is known to add to a carbon-carbon double bond effectively. However, it has been reported that irradiation of mercuric trimethylacetate in benzene did not lead to the formation of an organomercury compound but

Table 40. Photoreactions of mercuric carboxylates with alkenyl derivatives

$$Ph_2C{=}CHQ + (RCO_2)_2Hg \xrightarrow{h\nu} Ph_2C{=}CHR + RCO_2HgQ + CO_2$$

Q(equiv)	R	Conditions[a]	$Ph_2C{=}CHR$ (equiv)[b]
I (1)	i-Pr	24 h	0.78
I (2)	i-Pr	24 h	0.95[c]
I (2)	i-Pr	49 h	0.81[d]
I (1)	t-Bu	25 h	0.28[e]
I (1)	Et	24 h	0.48
HgCl (1)	i-Pr	24 h	0.27
HgCl (1)	i-Pr	72 h	0.55
HgBr (1)	i-Pr	24 h	0.34
HgBr (1)	i-Pr	67 h	0.74
HgBr (1)	t-Bu	36 h	0.15
$PhSO_2$ (1)	i-Pr	67 h	0.21
Bu_3Sn (1)	i-Pr	48 h	0

[a]Substrates (1 mmol of mercurial) in 25 mL of nitrogen-purged benzene were irradiated at 350 nm in a Rayonet Photoreactor.

[b]Determined by ^1H NMR.

[c]$Ph_2C{=}CH_2$ (0.11 equiv) was detected. $Ph_2C{=}CHI$ (0.43 equiv) was recovered.

[d]$Ph_2C{=}CH_2$ (0.20 equiv) was formed. $Ph_2C{=}CHI$ (0.43 equiv) was recovered.

[e]$Ph_2C{=}CHO_2CCMe_3$ (0.15 equiv) was detected.

benzene did not lead to the formation of an organomercury compound but led to only the separation of metallic mercury (ref 3, p. 281). Therefore, it is not surprising that photolysis of a mixture of mercuric trimethylacetate and 2,2-diphenylethenyl iodide in benzene in a Rayonet Photoreactor for 25 h afforded only 0.28 equiv of the substitution product (Eq. 144).

$$\underset{1\ \text{equiv}}{Ph_2C{=}CHI} + \underset{1\ \text{equiv}}{(Me_3CCOO)_2Hg} \xrightarrow{h\nu} \underset{0.28\ \text{equiv}}{Ph_2C{=}CHCMe_3} + CO_2 + Me_3CCOOHgI \qquad (144)$$

Irradiation of mercuric propionate in propionic acid or in benzene resulted in up to 70% yield of ethylmercury propionate. We have found that irradiation of mercuric propionate in the presence of 2,2-diphenylethenyl iodide in benzene gave a moderate yield (0.48 equiv) of 1,1-diphenyl-1-butene (Eq. 145).

$$\underset{1\ \text{equiv}}{Ph_2C{=}CHI} + \underset{1\ \text{equiv}}{(C_2H_5COO)_2Hg} \xrightarrow{h\nu} \underset{0.48\ \text{equiv}}{Ph_2C{=}CHC_2H_5} + CO_2 + C_2H_5COOHgI \qquad (145)$$

1-Alkenyl mercurials, sulfones and stannanes were also employed and the results are included in Table 40. Reactions of 2,2-diphenylethenylmercury chloride or bromide with mercuric dimethylacetate proceeded slowly under irradiation at 350 nm in a Rayonet Photoreactor. When irradiated for 24 h, the reactions gave only 0.3 equiv of the substitution product but the yield increased with a longer irradiation period. Mercuric trimethylacetate also reacted with the alkenylmercury bromide (but to give only a low yield of the

expected product).

Reaction of 2,2-diphenylethenyl phenyl sulfone with mercuric dimethylacetate proceeded sluggishly under the same conditions. The reaction gave only 0.21 equiv of the substitution product when irradiated for 67 h. On the other hand, the corresponding alkenylstannane failed to react at all with mercuric dimethylacetate and only the substrate was recovered.

Reactions of alkenyl derivatives and mercuric carboxylates are represented by Eqs. (146) and (147).

$$Ph_2C{=}CHQ + (RCOO)_2Hg \xrightarrow{h\nu} Ph_2C{=}CHR + CO_2 + RCOOHgQ \qquad (146)$$

$Q = I, PhSO_2$

$$Ph_2C{=}CHQ + (RCOO)_2Hg \xrightarrow{h\nu} Ph_2C{=}CHR + CO_2 + RCOOHgX + Hg^{\circ} \qquad (147)$$

$Q = HgX$

A possible mechanism for the formation of the substitution products is outlined in Scheme 43. The initiation is the

Scheme 43

Initiation

$$(RCOO)_2Hg \xrightarrow{h\nu} RCOOHg\bullet + RCOO\bullet$$

Propagation

$$RCOO\bullet \longrightarrow R\bullet + CO_2$$

$$Ph_2C{=}CHQ + R\bullet \longrightarrow Ph_2\dot{C}{-}CH(R)Q$$

$$Ph_2\overset{\bullet}{C}\text{-}CH(R)Q \longrightarrow Ph_2C{=}CHR + Q\bullet$$

$$Q\bullet + (RCOO)_2Hg \longrightarrow RCOOHgQ + RCOO\bullet$$

or $$HgX + (RCOO)_2Hg \longrightarrow RCOOHgX + RCOO\bullet + Hg^{o}$$

decomposition of the mercuric carboxylates under the irradiation conditions followed by decarboxylation to give carbon dioxide and the radical, R•. The radical adds regioselectively to the double bond followed by β-elimination of Q•. Q• will then react with mercuric carboxylate by a process similar to those described previously in Section I to give the carboalkoxy radical, RCOO•, which continues the chain by decarboxylation.

The failure of tri-n-butyl-2,2-diphenylethenylstannane to react with mercuric dimethylacetate seems to result from the inability of the stannyl radical to react with the mercuric salt to regenerate the alkyl radical as shown in Eq. (148). Another possible explanation is

$$Bu_3Sn\bullet + (RCOO)_2Hg \not\longrightarrow RCO_2SnBu_3 + CO_2 + R\bullet + Hg^{o} \qquad (148)$$

that the alkenylstannane is not reactive enough to compete with the mercuric carboxylate in trapping the alkyl radical.

2. Reaction of mercuric dimethylacetate with phenylethynyl iodide

We have attempted to extend the reaction to the alkynyl system. Thus a mixture of phenylethynyl iodide and mercuric dimethylacetate in benzene was irradiated in a Rayonet Photoreactor for 24 h. Unfortunately, the reaction failed to give any of the substitution product.

C. Conclusion

Mercuric carboxylates have been shown to undergo photostimulated reactions with 2,2-diphenylethenyl derivatives includeing the iodide, mercury halide, and sulfone but failed to react with the tri-n-butylstannane derivative. The reactions afforded a good yield of the substitution product with mercuric dimethylacetate, a moderate yield with mercuric propionate and a low yield with trimethylacetate.

Although reaction of mercuric dimethylacetate with 2,2-diphenylethenyl iodide gave a good yield of the substitution product, only one of the carboalkoxy groups underwent decarboxylation by the Hunsdiecker type reaction to give the substitution product. This is a drawback of employing mercuric carboxylates in this reaction, since half of the carboxylic acid is wasted.

D. Experimental Section

1. Preparation of mercuric carboxylates

Mercuric dimethylacetate was prepared from the reaction of isobutyric acid and mercuric oxide. Thus mercuric oxide (yellow) 21.6 g (0.1 mol) was slowly added to 30 mL of isobutyric acid with stirring. After the addition, 10 mL of an additional isobutyric acid was added and the mixture was heated on a steam bath until all of the mercury oxide dissolved. The mixture was allowed to cool to room temperature. The product was crystallized upon cooling in an ice bath. The white solid crystal was filtered and dried under vacuum to give 22.5 g (60% yield) of mercuric dimethylacetate which had mp 102-105 °C.

Mercuric propionate was also prepared by the same procedure from mercuric oxide (yellow) (21.6 g) and propionic acid (30 mL). The reaction was exothermic and heat was evolved. After the evolution of heat, the mixture was heated on a steam bath until all of the mercury oxide dissolved. The mixture was then cooled in an ice bath and a white solid product formed. The solid was filtered and recrystallized in chloroform to give 31 g (90% yield) of a white crystal of mercuric propionate, mp 108-112 °C.

Mercuric trimethylacetate was prepared by the literature procedure from the reaction of mercuric nitrate with sodium salt of trimethylacetic acid [177]. The product prepared had mp > 240 °C (lit. [177] mp 235 °C).

2. Photoreactions of mercuric carboxylates with alkenyl derivatives

2,2-diphenylethenyl iodide (1 mmol) and mercuric dimethylacetate (1 mmol) were dissolved in 25 mL of dry benzene in a Pyrex flask equipped with a rubber septum. After a nitrogen purge, the mixture was irradiated at 350 nm in a Rayonet Photoreactor for 24 h. The reaction mixture was poured into water and extracted with benzene. The extract was washed twice with 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. After the removal of the benzene, the crude mixture was analyzed by GLC, ^{1}H NMR and GCMS. The analysis indicated the presence of 0.78 mmol of the substitution product, 1,1-diphenyl-3-methyl-1-butene. Reactions of 2,2-diphenylethenyl iodide (1 mmol) and mercuric dimethylacetate (2 mmol) carried out under the UV irradiation for 24 h and 49 h afforded the

substitution product in yields of 0.95 mmol and 0.81 mmol, respectively.

Mercuric trimethylacetate and mercuric propionate were also allowed to react with 2,2-diphenylethenyl iodide in a 1:1 mol ratio under the same conditions. The reactions gave the substitution products in 0.28 mmol and 0.48 mmol, respectively. Besides the substitution product, reaction of mercuric trimethylacetate with 2,2-diphenylethenyl iodide also gave a byproduct (0.15 mmol) which had a molecular weight of 280. The following GCMS was obtained for the byproduct. GCMS, m/e (relative intensity) 280 (15,M^+), 197(14), 196(95), 167(24), 165(23), 57(100). Based on the GCMS data, this byproduct was tentatively assigned as 2,2-diphenylethenyl trimethylacetate.

The above procedure was also used for the reactions of the other alkenyl compounds with the mercuric carboxylates. All the results are summarized in Table 40.

Identities of all the products were confirmed by comparison of their GLC retention times, ^{1}H NMR and GCMS data with those of the products obtained previously (Part I). 1,1-Diphenyl-1-butene which was not reported in the previous sections has the following ^{1}H NMR:

^{1}H NMR ($CDCl_3$) δ 7.3(m,10H), 6.08(t,1H), 2.12(m,2H), 0.99(t,3H).

II. RADICAL REACTIONS OF MERCURIC CARBOXYLATES WITH PHENYL DISULFIDE, PHENYL DISELENIDE, N-(PHENYLTHIO)PHATHALIMIDE AND TRI-n-BUTYLTIN HYDRIDE

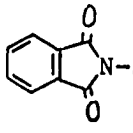
A. Introduction

Alkylmercury halides react with phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide to give alkyl phenyl sulfide or selenide in good yields [35]. The reactions have heen shown to be a radical chain reaction which involves the attack of the alkyl radicals at S or Se atom.

Mercuric carboxylates can provide alkyl radicals from the decarboxylation of carboalkoxy radicals as mentioned previously. This suggests that mercuric carboxylates should react with phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide under appropriate conditions to give the substitution products.

The following sections present the photoreactions of mercuric carboxylates with phenyl disulfide, phenyl diselenide, N-(phenylthio)phathalimide and tri-n-butyltin hydride as shown in Eq. 149.

$$(RCOO)_2Hg + Y\text{-}Z \xrightarrow{h\nu} R\text{-}Z + RCOOHgY + CO_2 \qquad (149)$$

Y-Z = PhS-SPh, PhSe-SePh,  , Bu_3Sn-H

B. Results and Discussion

1. Photoreactions of mercuric carboxylates with phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide

Mercuric trimethylacetate and phenyl disulfide or diselenide were allowed to react under UV irradiation. The reactions, surprisingly, gave a good yield of t-butyl phenyl sulfide, but only a moderate yield of t-butyl phenyl selenide was obtained (Table 41).

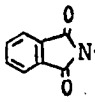
Reactions of mercuric dimethylacetate with phenyl disulfide, phenyl diselenide or N-(phenylthio)phathalimide gave moderate yields of the sulfide or selenide under the same conditions. In contrast, mercuric propionate and acetate failed to react with phenyl disulfide even at elevated temperatures.

A good yield of methylmercury acetate was obtained from the irradiation of mercuric acetate at reflux in glacial acetic acid [178]. Methylmercury iodide was obtained in 71% yield as the product after the reaction mixture was treated with aqueous sodium iodide solution. We carried out the reaction of mercuric acetate with phenyl disulfide in glacial acetic acid. The reaction was irradiated with a 275-W sunlamp at 100 °C for 10 h. The reaction, however, failed to afford any of the substitution product, methyl phenyl sulfide.

The reactions of mercuric carboxylates with phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide which afforded the substitution products are believed to involve free-radicals. A possible mechanism which involves a chain reaction is outlined in

Table 41. Photoreactions of mercuric carboxylates and phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide

$$(RCO_2)_2Hg + Y\text{-}Z \xrightarrow{h\nu} R\text{-}Z + RCO_2HgY + CO_2$$

R	Y-Z (equiv)	Conditions[a]	R-Z (equiv)[b]
t-Bu	PhS-SPh (2)	PhH, UV, 24 h	0.85
t-Bu	PhSe-SePh (2)	PhH, UV, 24 h	0.47
i-Pr	PhS-SPh (1)	PhH, UV, 20 h	0.35
i-Pr	PhS-SPh (2)	PhH, UV, 20 h	0.35
i-Pr	PhS-SPh (1)	PhH, UV, 68 h	0.43
i-Pr	PhSe-SePh (1)	PhH, UV, 52 h	0.41
i-Pr	 (1)	PhH, UV, 52 h	0.27
Et	PhS-SPh (2)	PhH, UV, 24 h	0
Et	PhSe-SePh (2)	PhH, UV, 24 h	0.1
Me	PhS-SPh (1)	PhH, 80 °, SL, 10 h	0
Me	PhS-SPh (1)	HoAc, 100 °, SL, 10 h	0

[a]Substrates (1 mmol of mercurial) in 10 mL of nitrogen-purged benzene were irradiated; UV = 350 nm Rayonet Photoreactor, SL = 275-W sunlamp ca. 20 cm from reaction vessel.

[b]Determined by ^1H NMR.

Scheme 44.

Scheme 44

$$RCOO\bullet \longrightarrow R\bullet + CO_2$$

$$R\bullet + Y\text{-}Z \longrightarrow R\text{-}Z + Y\bullet$$

$$Y\bullet + (RCOO)_2Hg \longrightarrow RCOOHgY + RCOO\bullet$$

$$(RCOO)_2Hg + Y\text{-}Z \xrightarrow{h\nu} RCOOHgY + R\text{-}Z + CO_2$$

The initiation is the decomposition of the mercuric carboxylates as described before. The mechanism involves the attack of R• at S or Se atom to give the alkyl phenyl sulfide or selenide and Y•. The radical, Y•, reacts with the mercuric carboxylates to give RCOOHgY and RCOO• which undergoes decarboxylation to give CO_2 and R•.

2. Reaction of mercuric diphenylacetate with tri-n-butyltin hydride

Mercuric carboxylates can also react with tri-n-butyltin hydride in benzene. When mercuric diphenylacetate and tri-n-butyltin hydride in a 1:2 mol ratio were mixed in benzene, a black precipitate of mercury formed immediately. After stirring for 10 min, the reaction mixture afforded diphenylacetic acid, mercury metal and a liquid product which appeared to be hexabutylditin (Eq. 150). It appears

$$\underset{\text{1 equiv}}{(Ph_2CHCOO)_2Hg} + \underset{\text{2 equiv}}{Bu_3SnH} \xrightarrow{PhH} \underset{71\%}{2Ph_2CHCOOH} + Bu_3SnSnBu_3 + \underset{91\%}{Hg^0} \qquad (150)$$

that the presence of tri-n-butyltin hydride facilitates the

decomposition of mercuric diphenylacetate. Apparently, the radical abstracted the hydrogen atom from the tin hydride faster than it underwent decarboxylation. Therefore, the reaction gave only the acid and tri-n-butylstannyl radical. The stannyl radical did not react with the mercuric carboxylate but instead coupled with another stannyl radical to give the ditin compound. The reaction of diethylmercury with triethyltin hydride in the absence of solvent at 100 °C has been reported to give ethane, hexaethylditin and mercury metal as shown in Eq. 151 (ref 3, p. 395).

$$(C_2H_5)Hg + 2Et_3SnH \xrightarrow{100\ ^\circ C} 2C_2H_6 + Et_3SnSnEt_3 + Hg^0 \qquad (151)$$

C. Conclusion

Mercuric carboxylates and phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide have been demonstrated to undergo photostimulated reactions to give the alkyl phenyl sulfides and selenides. Unlike the reactions of mercuric carboxylates with 1-alkenyl compounds (Part IV.I), the reactions afforded better yields of the substitution products with mercuric trimethylacetate than with mercuric dimethylacetate. Reactions of mercuric propionate and mercuric acetate with phenyl disulfide failed to give the substitution products.

Both mercuric trimethylacetate and mercuric dimethylacetate reacted with phenyl diselenide to give moderate yields of the alkyl phenyl selenides; whereas, the reaction of mercuric propionate with phenyl diselenide afforded only a low yield of the substitution product. No product was observed from the reaction of mercuric

acetate with phenyl diselenide.

Reaction of mercuric diphenylacetate with tri-n-butyltin hydride did not give the expected product, diphenylmethane, but instead afforded diphenylacetic acid, hexabutylditin, and mercury metal.

D. Experimental Section

1. Preparation of starting materials

Tri-n-butyltin hydride was prepared from the reaction of tri-n-butyltin chloride with lithium aluminum hydride [179]. The product was fractionally distilled at 74 °C/0.35-0.40 mmHg or 66 °C/0.2 mmHg (lit. [179] bp 68-74 °C/0.3 mmHg).

N-(phenylthio)phathalimide was synthesized by Dr. Hasan Tashtoush by following the literature procedure [180].

2. Photoreaction of mercuric carboxylates with phenyl sidulfide, phenyl diselenide and N-(phenylthio)phathalimide

The mercuric carboxylate (1 mmol) and phenyl disulfide (see Table 41 for equiv) were dissolved in 10 mL of benzene in a Pyrex tube equipped with a rubber septum. The mixture was degassed for 5 min and irradiated at 350 nm in a Rayonet Photoreactor for a period of time. After the irradiation, the reaction mixture was worked up and analyzed by the usual procedure. Identities of all of the products were confirmed by comparison of their GLC retentions with those of the authentic compounds synthesized by the literature procedure [35] or comparing their ^{1}H NMR and GCMS data with those reported in ref 59.

The following data were obtained for the substitution products.

t-Butyl phenyl sulfide:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.51(m,2H), 7.38-7.29(m,3H), 1.28(s,9H).

GCMS, m/e (relative intensity) 168(0.42), 166(8,M^+), 110(100), 57(65).

t-Butyl phenyl selenide:

^{1}H NMR ($CDCl_3$) δ 7.8-7.0(m,4H), 1.40(s,9H).

Ethyl phenyl selenide:

^{1}H NMR ($CDCl_3$) δ 7.8-7.0(m,5H), 2.85(q,2H), 1.38(t,3H).

SUMMARY

Part I of this dissertation presents the reactions of alkenyl derivatives of the type $R^1R^2C{=}CHQ$ (Q = I, Br, HgX, SPh, S(O)Ph, SO_2Ph, $SnBu_3$) with organomercurials (RHgX and R_2Hg). The reactions are believed to involve a radical chain reaction. Support for the mechanism includes the need for a radical initiator (light or azobisisobutyronitrile), the failure of the reaction to proceed in the dark and the strong retardation by di-tert-butyl nitroxide. The generation of the alkyl radical (R•) from the mercurial (RHgX or R_2Hg) by reaction with the chain carrier (Q•) occurs by either a S_H2 or an electron transfer process in which the organomercurials accepts or donates an electron. In the electron transfer process, the reaction is believed to occur in a concerted manner.

Heteroatom-centered radical (PhS•, PhSe•, $PhSO_2$•, $(EtO)_2PO$•), generated from the mercurials, add effeciently to the double bonds of the alkenyl compounds followed by a β-elimination of Q• to afford the substitution products in high yields. The alkenyl stannanes also react with phenyl disulfide, benzyl disulfide and benzenesulfonyl chloride to give excellent yields of the alkenyl sulfides and sulfone.

Other substrates which react with 1-alkenyl derivatives to give the substitution products include triisopropylaluminum, tricyclohexylborane and isopropylmagnesium iodide. The reactions, however, afford low yields of the coupling products and appear to be limited to the 1-alkenyl sulfones and mecurials.

Reactions of certain 1-alkenyl derivatives with organomercurials

and phenyl disulfide have been shown to occur stereospecifically. The stereospecificity has been demonstrated by the reactions of (E)- and (Z)-1,2-disubstituted ethylenes of the type XCH=CHZ (X = CO_2Me, Cl; Z = I, Cl, $SnBu_3$, HgCl) with the mercurials and phenyl disulfide.

The reactions have been extended to include allyl and alkynyl systems which are presented in Part II. Allyl and alkynyl iodides, bromides, sulfides, sulfones, mercurials, and stannanes undergo photostimulated reaction with organomercurials to give moderate to excellent yields of the substitution products.

In Part III, the relative reactivities of alkenyl and alkynyl derivatives towards cyclohexyl and thiophenoxy radicals are determined. With cyclohexyl radicals, the sulfone derivatives show a surprisingly high reactivity especially in the alkynyl system. The relative reactivities are in the order $PhSO_2$ > I > Bu_3Sn for the alkynyl system and $PhSO_2$ > PhS > HgCl > I > Bu_3Sn for the alkenyl system.

The relative reactivities towards thiophenoxy radical may be complicated by the reversible addition of the thiyl radical. The observed relative reactivities are in the order $PhSO_2$ > I > Bu_3Sn for the alkynyl system and HgCl > Bu_3Sn > I > $PhSO_2$ for the alkenyl system.

The determination of the initial kinetic chain length of the reactions of 2,2-diphenylethenyl iodide and tri-n-butyl-(E)-2-phenylethenylstannane with t-butylmercury chloride is also presented in Part III. The initial kinetic chain length obtained are 100 and 71,

respectively. This confirms that the reactions of 2,2-diphenylethenyl iodide or tri-*n*-butyl-(*E*)-2-phenylethenylstannane with *t*-butylmercury chloride are radical chain reactions as proposed in Part I.

Mercuric carboxylates are shown to be a source of alkyl radicals (Part IV). They can undergo photostimulated reaction with 1-alkenyl derivatives, phenyl disulfide, phenyl diselenide and N-(phenylthio)phathalimide. The reactions, however, afford good yields of the substitution products with only a limited number of substrates.

BIBLIOGRAPHY

1. Larock, R. C. "Organomercury Compounds in Organic Synthesis"; Springer-Verlag: Berlin, 1985.

2. Frankland, E. Phil. Trans. R. Soc. 1852, 142, 417.

3. Makarova, L. G.; Nesmeyanov, A. N. "Methods of Elemento Organic Chemistry," Vol. 4. North Holland Publishing Co.: Amsterdam, 1967.

4. Larock, R. C.; Takagi, K. J. Org. Chem. 1984, 49, 2701.

5. Larock, R. C.; Varaprath, S. J. Org. Chem. 1984, 49, 3432.

6. Larock, R. C. "Oxymercuration Demercuration"; Springer-Verlag: Berlin, 1986.

7. Kitching, W. Organomet. Chem. Rev. 1968, 3, 61.

8. Larock, R. C.; Liu, C. J. Org. Chem. 1983, 48, 2151.

9. Larock, R. C.; Harrison, L. W. J. Am. Chem. Soc. 1984, 106, 4218.

10. Reutov, O. A. Pure Appl. Chem. 1968, 17, 79.

11. Kitching, W. Rev. Pure Appl. Chem. 1969, 19, 1.

12. Makarova, L. G. In "Organometallic Reactions," Vol. I; Becker, E. I. and Tsutsui, M. Ed.; Wiley-Interscience: New York, 1970, pp. 325-348.

13. Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials," McGraw-Hill: New York, 1968.

14. Winstein, S.; Traylor, T. G. J. Am. Chem. Soc. 1956, 78, 2597.

15. Jensen, F. R.; Gale, L. H. J. Am. Chem. Soc. 1960, 82, 148.

16. Jensen, F. R.; Gurad, H. E. J. Am. Chem. Soc. 1968, 90, 3250.

17. Nugent, W. A.; Kochi, J. K. J. Am. Chem. Soc. 1976, 98, 5405.

18. Nugent, W. A.; Kochi, J. K. J. Organomet. Chem. 1977, 124, 327.

19. Nugent, W. A.; Kochi, J. K.; J. Organomet. Chem. 1977, 124, 349.

20. Nugent, W. A.; Kochi, J. K.; J. Organomet. Chem. 1977, 124, 371.

21. Minisci, F.; Citterio, A. Adv. Free Radical Chem. 1980, 6, 65.

22. Hart, D. J. Science (Washington, D.C.) 1984, 223, 883.

23. Pasto, D. J.; Gontarz, J. A. J. Am. Chem. Soc. 1969, 91, 719.

24. Gray, G. A.; Jackson, W. R. J. Am. Chem. Soc. 1969, 91, 6205.

25. Whitesides, G. M.; Filippo, J. S., Jr., J. Am. Chem. Soc. 1970, 92, 6611.

26. Hill, C. L.; Whitesides, G. M. J. Am. Chem. Soc., 1974, 96, 870.

27. Giese, B. Angew, Chem. Int. Ed. Engl 1983, 22, 753.

28. Giese, B. Angew. Chem. Int. Ed. Engl. 1985, 24, 553.

29. Giese, B.; Horler, H.; Zwick, W. Tetrahedron Lett. 1982, 23, 931.

30. Giese, B.; Kretzschmar, G. Angew. Chem. Int. Ed. Engl. 1981, 20, 965.

31. Giese, B.; Meister, J. Angew. Chem. Int. Ed. Engl. 1977, 16, 178.

32. Russell, G. A.; Hershberger, J.; Owens, K. J. Am. Chem. Soc. 1979, 101, 1312.

33. Russell, G. A.; Khanna, R. Tetrahedron 1985, 41, 4133.

34. Singh, P. R.; Khanna, R. K. Tetrahedron Lett. 1983, 24, 1411.

35. Russell, G. A.; Tashtoush, M. J. Am. Chem. Soc. 1983, 105, 1398.

36. Hershberger, J.; Russell, G. A. Synthesis 1980, 475.

37. Russell, G. A.; Hershberger, J. J. Am. Chem. Soc. 1980, 102, 7603.

38. Walling, C. Tetrahedron 1985, 41 (19), 3887.

39. Abell, P. I. In "Free Radicals," Vol. II. Kochi, J. R., Ed.; Wiley-Interscience: New York, 1973; Chapter 13.

40. Beletskaya, I. P.; Karpov, V. I.; Reutor, O. A. Izv. Akad. Nauk SSSR Ser. Khim. 1964, 1707. Bull. Acad. Sci. USSR, Div. Chem. Sci. 1964, 1615.

41. Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh, D. M. J. Chem. Soc. Perkin II 1976, 1261.

42. Leusink, A. J.; Budding, H. A.; Drenth, W. J. Organomet. Chem. 1968, 11, 541.

43. Leusink, A. J.; Budding, H. A.; Drenth, W. J. Gen. Chem. USSR 1977, 47, 1650.

44. Voronkov, M. G.; Mirskov, R. G.; Rakhlin, V. I. Dokl. Chem. Proc. Acad. Sci. USSR 1973, 209, 261.

45. Voronkov, M. G.; Rakhlin, V. I.; Mirskov, R. G. Bull. Acad. Sci. USSR, Div. Chem. Sci. 1978, 1454.

46. Miyamoto, N.; Fukuoka, D.; Utimoto, K.; Nozaki, H. Bull. Chem. Soc. Jap. 1974, 47, 503.

47. Eisch, J. J.; Behrooz, M.; Galle, J. E. Tetrahedron Lett. 1984, 25 (43), 4851.

48. Saihai, M. L.; Pereyre, M. Bull. Soc. Chem. Fr. 1977, 1251.

49. Baldwin, J. E.; Kelley, D. R.; Ziegler, C. B. J. Chem. Soc. Chem. Commun. 1984, 133.

50. Baldwin, J. E.; Kelly, D. R. J. Chem. Soc. Chem. Commun. 1985, 682.

51. Sammes, P. G. "Chemistry of the Carbon-Halogen Bond," Patai, S., Ed.; Wiley: New York, 1973: Chapter 11.

52. Russell, G. A.; Jiang, W. Unpublished results. Chem. Dept., Iowa State University, Ames, Iowa.

53. Giese, B.; Lachhein, S. Angew. Chem. Int. Ed. Engl. 1981, 20, 967.

54. Stark, T. J.; Nelson, N. T.; Jensen, F. R. J. Org. Chem. 1980, 45, 420.

55. Strunk, R. J.; DiGiacomo, P. M.; Aso, K.; Kuivila, H. G. J. Am. Chem. Soc. 1970, 92, 2849.

56. Russell, G. A.; Tashtoush, H. Unpublished results. Chem. Dept., Iowa State University, Ames, Iowa.

57. Wagner, P. J., Sedon, J. H.; Lindstrom, M. J. J. Am. Chem. Soc. 1978, 100, 2579.

58. Wagner, P. J.; Lindstrom, M. J. Abs. of Papers Am. Chem. Soc. 1984, 187, PETR 83.

59. Tashtoush, H. I. Ph. D. Dissertation, Iowa State University, Ames, Iowa, 1984.

60. Kuivila, H. G. Synthesis 1970, 499.

61. Barton, D. H. R.; Crich, D.; Motherwell, W. B. J. Chem. Soc. Chem. Commun., 1983, 939.

62. Barton, D. H. R.; Crich, D.; Motherwell, W. B. Tetrahedron 1985, 41, 3901.

63. Barton, D. H. R.; McCombie, S. W. J. Chem. Soc. Perkin I 1975, 1574.

64. Dolan, S. C.; MacWillan, J. J. Chem. Soc. Chem. Commun. 1985, 1588.

65. Dupuis, J.; Giese, B.; Hartung, J.; Leising, M. J. Am. Chem. Soc. 1985, 107, 4332.

66. Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. J. Am. Chem. Soc. 1981, 103, 1557.

67. Stork, G.; Sher, P. M. J. Am. Chem. Soc. 1983, 105, 6765.

68. Keck, G. E.; Byers, J. H. J. Org. Chem. 1985, 50, 5442.

69. Russell, G. A. Preprints of Papers, Division of Petroleum Chemistry, 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept. 1986, 31, 891.

70. Russell, G. A.; Khanna, R. K.; Guo, D. J. Chem. Soc. Chem. Commun. 1986, 632.

71. Russell, G. A.; Guo, D.; Khanna, R. K. J. Org. Chem. 1985, 50, 3423.

72. Russell, G. A.; Hershberger, J.; Owens, K. J. Organomet. Chem. 1982, 224, 43.

73. Kurosawa, H.; Okada, H.; Hattori, T. Tetrahedron Lett. 1981, 22, 4495.

74. Marvel, C. S.; Gauerke, C. G.; Hill, E. L. J. Am. Chem. Soc. 1925, 47, 3009.

75. Whitemore, F. C.; Whittle, E. L.; Harriman, B. R. J. Am. Chem. Soc. 1939, 61, 1585.

76. Hilpert, S.; Grüttner, G. Chem. Ber. 1915, 48, 906.

77. Robson, I. H.; Wright, G. F. Can. J. Chem. 1960, 38, 21.

78. Grüttner, G. Chem. Ber. 1914, 47, 1651.

79. Kharasch, M. S.; Swartz, S. J. Org. Chem. 1938, 3, 405.

80. House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. J. Org. Chem. 1973, 38(3), 514.

81. Canty, A. J.; Kishimoto, R. Inorg. Chim. Aeta. 1977, 24(2), 109.

82. Okamoto, Y.; Yano, T. J. Organomet. Chem. 1971, 29, 99.

83. Deacon, G. B. Aust. J. Chem. 1967, 20, 1367.

84. Venezky, D. L.; Fox, R. B. J. Am. Chem. Soc. 1956, 78, 1664.

85. Shearer, D. A.; Wright, G. F. Can. J. Chem. 1955, 3, 1002.

86. Dubois, J. E.; Hegarty, A. F.; Bergmann, E. D. J. Org. Chem. 1972, 37, 2220.

87. Seyferth, D.; Stone, F. G. A. J. Am. Chem. Soc. 1957, 79, 515.

88. Evers, W. L.; Rothrock, H. S.; Woodburn, H. M.; Stahly, E. E.; Whitmore, F. C. J. Am. Chem. Soc. 1933, 55, 1137.

89. Dieck, H. A.; Heck, R. F. J. Am. Chem. Soc. 1974, 96, 1133.

90. Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. J. Organomet. Chem. 1978, 162, 271.

91. Truce, W. E.; Goralski, C. T. J. Org. Chem. 1970, 35, 4220.

92. Larock, R. C.; Brown, H. C. J. Organomet. Chem. 1972, 36, 1.

93. Pross, A.; Sternhell, S. Aust. J. Chem. 1970, 23, 989.

94. Spence, J. J. Am. Chem. Soc. 1933, 55, 1290.

95. Brown, H. C.; Hamoka, T.; Ravindran, N. J. Am. Chem. Soc. 1973, 95, 5786.

96. Smith, L. I.; Davis, H. R., Fr. J. Org. Chem. 1950, 15, 824.

97. Gielen, M.; DePoorter, D. Rev. Silicon, Germanium, Tin, Lead Compd. 1977 3, 9.

98. Nesmeyanov, A. N.; Kocheshkov, K. A. "Methods of Elemento Organic Chemistry," Vol. 1: North Holland Publishing Co.: Amsterdam, 1967, pp. 387.

99. Raucher, S.; Hansen, M. R.; Cotter, M. A. J. Org. Chem. 1978, 43, 4885.

100. Hershberger, J. W. Ph.D. Dissertation. Iowa State University, Ames, Iowa, 1981.

101. Reich, H. J.; Willis, W. w., Jr.; Clark, P. D. J. Org. Chem. 1981, 46, 2775.

102. Okamoto, Y.; Homsany, R.; Yano, T. Tetrahedron Lett. 1972, 2529.

103. Tavs, T.; Weitkamp, H. Tetrahedron 1970, 26, 5529.

104. Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. Tetrahedron Lett. 1980, 21, 3595.

105. Aida, T.; Harpp, D.; Chan, T. H. Tetrahedron Lett. 1980, 21, 3247.

106. Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. J. Am. Chem. Soc. 1976, 98, 951.

107. Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B.; Willcott, M. R., III; Inners, Cornelis, A. J. Am. Chem. Soc. 1978, 100, 3874.

108. Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. J. Org. Chem. 1980, 45, 794.

109. Shevlin, P. B.; Greene, J. L., Jr. J. Am. Chem. Soc. 1972, 94, 8447.

110. Strunk, R. J.; DiGiacomo, P. M.; Aso, K.; Kuivila, H. G. J. Am. Chem. Soc. 1970, 92, 2849.

111. Cristol, S. J.; Jarvis, B. B. J. Am. Chem. Soc. 1966, 88, 3095.

112. Mirskova, A. N.; Martynov, A. V.; Kalikhman, I. D.; Keiko, V. V.; Vitkovskii, V. Y.; Voronkov, M. G. J. Org. Chem. USSR 1979, 1652.

113. Logan, T. J. J. Org. Chem. 1963, 28, 1129.

114. Biougne, J.; Théon, F. C. R. Acad. Science 1971, 272, 858.

115. Kurtz, A. N.; Billups, W. E.; Greenlee, R. B.; Hamil, H. F.; Pace, W. T. J. Org. Chem. 1965, 30, 3141.

116. Seitz, D. E.; Lee, S. H. Tetrahedron Lett. 1981, 22, 4909.

117. Montanari, F. Gazzetta, 1956, 86.

118. Garratt, D. G. Can. J. Chem. 1980, 58(22), 2329.

119. Kaufman, H. P. Chem. Ber. 1922, 55B, 249.

120. Wada, F.; Matsuda, T. Bull. Chem. Soc. Jpn. 1973, 46(2), 510.

121. Tantwijk, F. V.; Bekkum, H. V. J. Mol. Catal. 1976, 1(5), 383.

122. Shelton, J. R.; Davis, K. E. Int. J. Sulfur Chem. 1973, 8, 205.

123. Berdnikov, E. A.; Mukhitova, F. K.; Tantasheva, F. R.; Katave, E. G. J. Org. Chem. USSR 1977, 13, 1302.

124. McGreer, D. E.; Chiu, N. W. K. Can. J. Chem. 1968, 46, 2225.

125. Miller, R. B.; McGarvey, G. J. Org. Chem. 1978, 43, 4424.

126. Truce, W. E.; McManimie, R. J. J. Am. Chem. Soc. 1954, 76, 5745.

127. Neumann, H.; Seebach, D. Chem. Ber. 1978, 111(8), 2785.

128. Gendreau, Y.; Normant, J. F.; Villieras, J. J. Organomet. Chem. 1977, 142, 1.

129. Barsanti, P.; Calo, V.; Lopez, L.; Marchese, G.; Naso, F.; Gesce, G. J. Chem. Soc. Chem. Commun. 1978, 1085.

130. Okamura, H.; Takei, H. Tetrahedron Lett. 1979, 3425.

131. Julia, M.; Righini, A.; Verpeaux, J. Tetrahedron Lett. 1979, 2393.

132. Trost, B. M.; Schmuff, N. R.; Miller, M. J. J. Am. Chem. Soc. 1981, 102, 5979.

133. Hiroi, K.; Kitayama, R.; Sato, S. Chem. Lett. 1984, 929.

134. Masaki, Y.; Sakuma, K.; Kaji, K. J. Chem. Soc. Perkin Trans I 1985, 1171.

135. Kharasch, M. S.; Sage, M. J. Org. Chem. 1949, 14, 537.

136. Hall, D. J. Org. Chem. 1967, 32, 2982.

137. Migita, T.; Kosuki, M.; Takayama, K.; Kakagawa, Y. Tetrahedron 1973, 29, 51.

138. Kuivila, H. G.; Sommer, R. J. Am. Chem. Soc. 1967, 89, 5616.

139. Ueno, Y.; Okawara, M. J. Am. Chem. Soc. 1979, 101, 1893.

140. Ueno, Y.; Aoki, S.; Okawara, M. J. Am. Chem. Soc. 1979, 101, 5414.

141. Ueno, Y.; Chino, K.; Okawara, M. Tetrahedron Lett. 1982, 23, 2575.

142. Kosugi, M.; Kurino, K.; Takayama, K.; Migita, T. J. Organomet. Chem. 1973, 56, C11.

143. Grignon, J.; Servens, C.; Pereyre, M. J. Organomet. Chem. 1975, 96, 225.

144. Keck, G. E.; Yates, J. B. J. Am. Chem. Soc. 1982, 104, 5829.

145. Keck, G. E.; Yates, J. B. J. Org. Chem. 1982, 47, 3591.

146. Keck, G. E.; Yates, J. B. J. Organomet. Chem. 1983, 248, C21.

147. Keck, G. E.; Enholm, E. J.; Kachensky, D. E. Tetrahedron Lett. 1984, 25, 1867.

148. Webb, R. R.; Danishefsky, S. Tetrahedron Lett. 1983, 24, 1357.

149. Baldwin, J. E.; Adlington, R. M.; Basak, A. J. Chem. Soc. Chem. Commun. 1984, 1284.

150. Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. Tetrahedron 1985, 41, 4079.

151. Russell, G. A.; Herold, L. L. J. Org. Chem. 1985, 50, 1037.

152. Gupta, B. D.; Funabiki, T.; Johnson, M. D. J. Am. Chem. Soc. 1976, 98, 6697.

153. Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Bialkowska, E.; Duong, K. N. V.; Guademer, A. J. Chem. Soc. Perkin I, 1979, 2611.

154. Veber, M.; Duong, K. N. V.; Gaudemer, F.; Gaudemer, A. J. Organomet. Chem. 1979, 177, 231.

155. Bury, A.; Cooksey, C. J.; Funakibi, T.; Gupta, B. D.; Johnson, M. D. J. Chem. Soc. Perkin II 1979, (8), 1050.

156. Veber, M.; Doung, K. N. V.; Gaudemer, A. J. Organomet. Chem. 1981, 209, 393.

157. Bury, A.; Johnson, M. D. J. Chem. Soc. Chem. Commun. 1980, 498.

158. Bury, A.; Corker, S. T.; Johnson, M. D. J. Chem. Soc. Perkin Trans 1 1982, 645.

159. Deniau, J.; Doung, K. N. V., Gaudemer, A.; Bougeard, P.; Johnson, M. D. J. Chem. Soc. Perkin II 1981, 393.

160. Johnson, M. D. Acc. Chem. Res. 1983, 16, 343.

161. Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Moorhouse, S. J. Chem. Soc. Dalton 1978, 1821.

162. Hurd, C. D.; Greengard, H. J. Am. Chem.Soc. 1930, 52, 3356.

163. Thyagarajan, B. S.; Majumdar, K. C.; Bates, D. K. Phosphorus Sulfur 1976, 1(1), 67.

164. Herold, L. L. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1983.

165. Savoia, D.; Trombini, C.; Umani-Ronchi, A. J. Chem. Soc. Perkin I 1977, 123.

166. De Lucchi, O.; Licini, G.; Pasquato, L.; Senta, M. J. Chem. Soc. Chem. Commun. 1985, 1597.

167. Cohen, M. J.; McNelis, E. J. Org. Chem. 1984, 49, 515.

168. Cohen, M. J.; McNelis, E. J. Org. Chem. 1984, 49, 515.

169. Truce, W. E.; Hill, H. E.; Boudakian, M. M. J. Am. Chem. Soc. 1956, 78, 2760.

170. Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. J. Chem. Soc. Dalton Trans. 1973, 1202.

171. Johnson, J. R.; McEwen, W. L. J. Am. Chem. Soc. 1926, 48, 469.

172. Chow, A. W.; Hall, N. M.; Hoover, J. R. E.; Dolan, M. M.; Ferlauto, R. J. J. Med. Chem. 1966, 9, 551.

173. Porter, Q. N. Aust. J. Chem. 1967, 20, 103.

174. Oki, M.; Kobayashi, K. Bull. Chem. Soc. Jpn. 1973, 46(2), 687.

175. Murahashi, S.; Yamamura, M.; Yanagisava, K.; Mita, N.; Kondo, K. J. Org. Chem. 1979, 44, 2408.

176. Veenstra, G. E.; Zwanenburg, B. Tetrahedron 1978, 34(10), 1585.

177. Kharasch, M. S.; Stavelev, F. W. J. Am. Chem. Soc. 1923, 45, 2961.

178. Razuvaev, G. A.; Ol'dekop, Y. A. Dokl. Akad. Nauk SSSR 1955, 105, 738.

179. Kuivila, H. G.: Beumel, O. F., Jr. J. Am. Chem. Soc. 1961, 83, 1246.

180. Behforouz, M.; Kerwood, J. E. J. Org. Chem. 1969, 34, 51.

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