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Free radical and ionic reactions of (Benzoylmethyl)mercurials

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Iowa State University, 1991

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Free radical and ionic reactions of (Benzoylmethyl)mercurials

by

Shekhar V. Kulkarni

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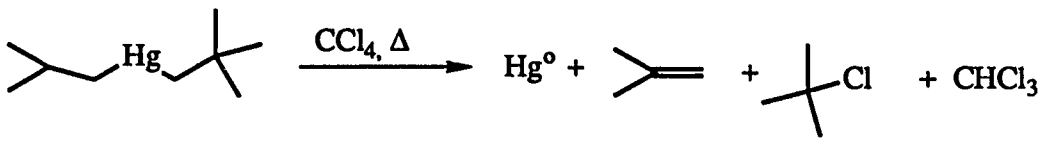
GENERAL INTRODUCTION

Organic synthesis with radicals began in 1937 when Hey and Waters[1] described the phenylation of aromatic compounds by benzoyl peroxide as a radical reaction. In the same year pioneering work by Kharasch[2], Mayo, Walling and Lewis[3] set the foundation for use of radicals in organic synthesis. In recent years increasing use has been made of free radical reactions in the synthesis of organic compounds.[4]

Organomercury compounds have been known since the middle of the past century, and they were one of the first types of organometallic compounds studied. For a long time they were not used in organic synthesis due to low reactivity of the mercury-carbon bond. However in the past 20 years, organomercury compounds have again acquired interest in organic synthesis, in relation mainly to the solvomercuration reaction,[5] which permits the preparation of functionalized organomercurials with high selectivity.

Radicals can be produced from organomercurials by a number of methods such as thermal, photochemical, reduction by hydrides, electrochemical, halodemercuration etc. In the thermal decomposition of dialkyl mercurials in the presence of carbon tetrachloride as solvent, olefins and alkylchlorides are obtained as reaction products through a chain mechanism (reaction 1).[6]

Organomercury halides have been electrochemically reduced in liquid ammonia at low temperatures to produce organomercury radicals which upon warming, decompose to diorganomercury(II) compounds and mercury metal[7] (reaction 2).



(1)

$$RHgCl + e^- \longrightarrow RHg^{\cdot} + Cl^- \xrightarrow{\Delta} 1/2\, R_2Hg + 1/2\, Hg^{o} \quad (2)$$

One of the most widely studied chain reactions of organomercurials has been the alkaline $NaBH_4$ reduction of alkylmercury halides or carboxylates to the alkane[8] or products derived from alkyl radical attack upon a suitable coreactant.[4b] Both the pyrolysis of R_2Hg and the alkaline $NaBH_4$ reduction of RHgCl are reactions that involve unstable mercury(I) intermediates. An alkylmercury hydride, RHgH, is proposed to be involved in the $NaBH_4$ reduction as shown in Scheme I.

Scheme I

Initiation :

$$RHgX + BH_4^- \longrightarrow RHgH$$
$$RHgH \longrightarrow R^{\cdot} + Hg^{o} + H^{\cdot}$$

Propogation :

$$R^{\cdot} + RHgH \longrightarrow RH + RHg^{\cdot}$$
$$RHg^{\cdot} \longrightarrow R^{\cdot} + Hg^{o}$$

The alkyl radicals generated by this method can be trapped by electron deficient olefins (Scheme II).

During the past several years Russell[9-30] has used the photochemical method for the generation of alkyl radicals from alkylmercurials to perform radical alkylations in which RHgX or R_2Hg participates in the propogation step of a chain process that does not usually involve RHg as an intermediate other than in the initiation step. The

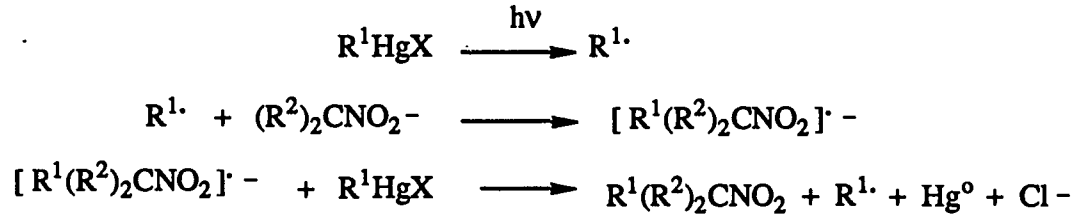
Scheme II

X = Ph, CO_2Me, CN

Y = Ph, CO_2Me, CN, CF_3, SePh, H

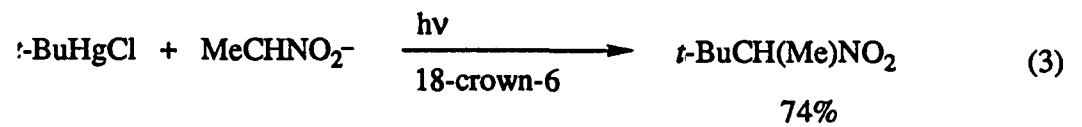
photochemically induced reaction of different primary or secondary alkylmercury chlorides or bromides with several anions derived from nitroalkanes leads to corresponding coupling products through the $S_{RN}1$ type mechanism (Scheme III).[9,12]

Scheme III



X = Cl, Br, R^1 = primary or secondary alkyl

This reaction does not work when vinyl or arylmercury chloride is used. In the case of *tert*-butyl mercury halides the reaction is facilitated by the presence of a stoichiometric amount of 18-crown-6 (reaction 3).[16,17]



(3)

A number of other nucleophiles such as Ph_2CCN^-, fluorene anion, $PhC(CO_2Et)_2^-$, $PhCOCHPh^-$ etc. also give this reaction with *t*-BuHgCl in presence of 18-crown-6.

The $S_{RN}1$ reaction can also be obtained with neutral substrates (Scheme IV).[20] In all these reactions the addition of the radical from the alkylmercurials to the substrate (anion or neutral) generates a donor radical (D·), which transfers an electron to the alkylmercury halide to generate another alkyl radical and continues the chain.

Scheme IV

$$t\text{-BuHgCl} \longrightarrow t\text{-Bu}^{\cdot}$$

$$t\text{-Bu}^{\cdot} + CH_2{=}C(p\text{-MeOC}_6H_4)_2 \longrightarrow t\text{-BuCH}_2{-}\dot{C}(p\text{-MeOC}_6H_4)_2$$

$$t\text{-BuCH}_2{-}\dot{C}(p\text{-MeOC}_6H_4)_2 + t\text{-BuHgCl} \longrightarrow t\text{-Bu}^{\cdot} + t\text{-BuCH}_2{-}\overset{+}{C}(p\text{-MeOC}_6H_4)_2 + Hg^{o} + Cl^{-}$$

$$t\text{-BuCH}_2{-}\overset{+}{C}(p\text{-MeOC}_6H_4)_2 \xrightarrow{-H^+} t\text{-BuCH}{=}C(p\text{-MeOC}_6H_4)_2$$

Chain reactions can also be achieved by attack of an acceptor radical (A·) upon the mercury atom of the alkylmercurial (reaction 4).[13,28]

$$RHgX + A^{\cdot} \longrightarrow AHgX + R^{\cdot} \qquad (4)$$

The acceptor radical can be formed by further reactions of an alkyl radical which itself is not strong donor or acceptor species. Some examples of reactions which provide such radicals are given below (reaction types A and B).

(A) S_H2 reactions of R·[22,28,31]

$$R\cdot + Y{-}A \longrightarrow R{-}Y + A\cdot$$

Y-A = dichalcogenides, H-SPh, H-$SnBu_3$, PhSe-SO_2Ph,
Cl-SO_2Ph, *N*-alkyl-1,4-dihydropyridines

(B) R—$\dot{\Pi}$ is an acceptor[22]

$$R\cdot + \Pi \longrightarrow R{-}\dot{\Pi}$$
$$R{-}\dot{\Pi} + RHgX \longrightarrow R{-}\Pi{-}HgX + R\cdot$$

Π = CH_2=CHP(O)$(OEt)_2$, CH_2=$CHSO_2$Ph, CH_2=$CHCH_2$OTs,
CH_2=$CHCH_2$OP(O)$(OEt)_2$, HC≡CPh, HC≡CCO_2Et,
HC≡CCOPh, HC≡CCH_2OTs, HC≡CCH_2OP(O)$(OEt)_2$

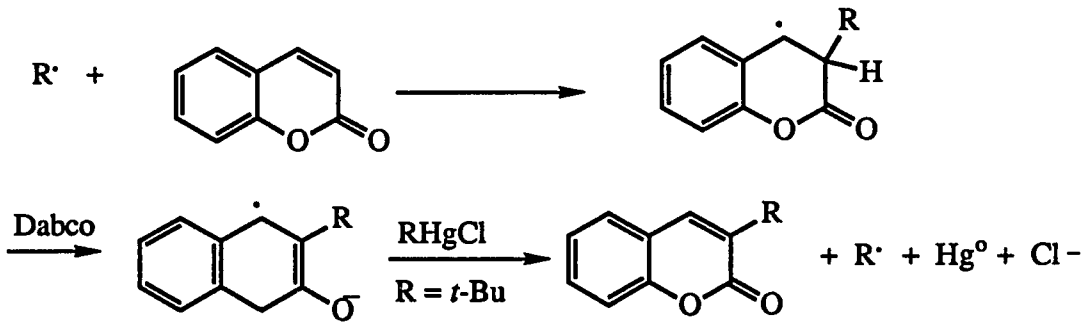
Another method by which chain reactions can be achieved with alkylmercurials is by an addition elimination reactions (reaction 5).[14,19,21,26,28]

$$R\cdot + \Pi{-}Q \longrightarrow R{-}\dot{\Pi}{-}Q \longrightarrow R{-}\Pi + Q\cdot \qquad (5)$$

Π−Q = PhCH=CHQ or PhC≡CQ (with Q = Cl, Br, I, $PhSO_2$, PhS, HgCl
$SnBu_3$); PhCOCH=CHCl; $PhSO_2$CH=CHSnBu_3; MeO_2CCH=CHI
CH_2=$CHCH_2$Cl (Br,I), HC≡CCH_2Cl

Radical chain alkylations of the S_{RN}-type have been developed which involve abstraction of a proton from intermediate adduct radicals to form radical anions capable of chain propogation by electron transfer to alkylmercury halides (Scheme V).[32]

Scheme V



Alkylmercury halides such as *t*-BuHgCl fail to undergo chain reactions with electron-rich alkenes, phosphines and phosphites. In many cases such substrates have a low reactivity toward nucleophilic alkyl radicals because of the polar effect in radical addition reactions.[33] However, to form an easily oxidized adduct radical capable of transferring an electron to RHgCl, an electron-rich substrate is required.

In the hope of extending the scope of S_{RN}-type substitutions using organomercurials as the radical source, we decided to investigate the photostimulated radical reactions of the (benzoylmethyl)mercurials since benzoylmethyl radical ($PhCOCH_2$·) is an electrophilic radical[34] and should add readily to electron rich substrates. For example, the rate of addition of the electrophilic radical ·$CH(CO_2Et)_2$ to a-substituted styrenes CH_2=C(X)Ph increases by a factor of 34 on going from X = COPh to X = NEt_2 at 110 °C.[34]

The electrophilic nature of these radicals arises due to the electron-withdrawing substituents at the radical center. These radicals have SOMO energies so low that the predominant interaction is between the SOMO of the radical and HOMO of the alkene (Figure 1).[4b]

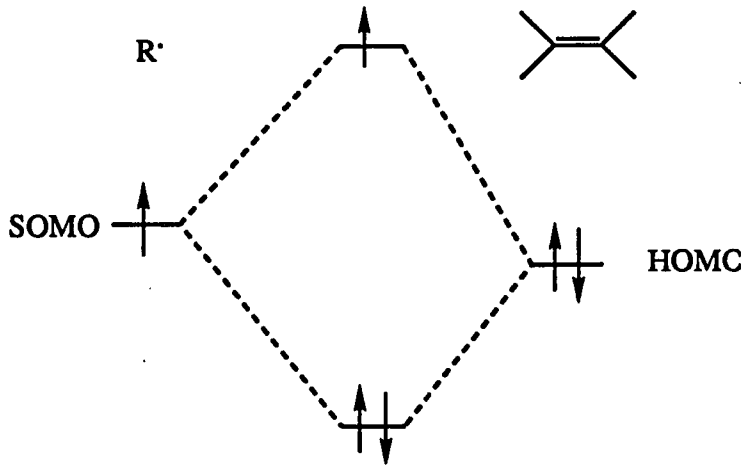


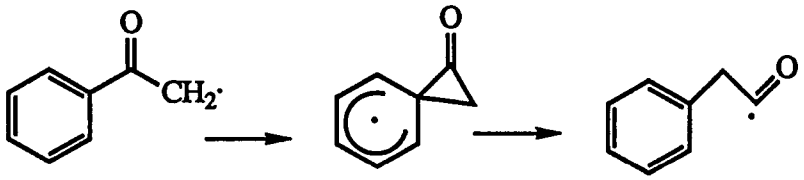
Figure 1. Orbital interaction between electrophilic radical and electron-rich alkene

The benzoylmethyl radical can be conveniently generated by photolysis of $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ or by electron transfer to either $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ (reaction 6).

$$\begin{array}{ccccc} & & PhCOCH_2HgCl & & \\ PhCOCH_2\cdot + Hg^{o} & \xleftarrow{e^-} & or & \xrightarrow{h\nu} & PhCOCH_2\cdot \\ + Cl^- & & (PhCOCH_2)_2Hg & & \end{array} \qquad (6)$$

The radical center in $PhCOCH_2\cdot$ is stabilized by the adjacent carbonyl group as evidenced by the BDE of $PhCOCH_2$-H and CH_3-H of 93 and 105 kcal/mol respectively.[35] The $PhCOCH_2\cdot$ radical is known to undergo a neophyl like rearrangement[36] with a rate of 10 $M^{-1}s^{-1}$ (reaction 7).

The (benzoylmethyl)mercurials $PhCOCH_2HgCl$ and $(PhCOCH_2)_2Hg$ can be readily prepared from the corresponding enol silyl ethers. From the IR, UV, and NMR



$$\longrightarrow PhCH_2^{\cdot} + CO \qquad (7)$$

spectra, these mercury(II) salts of ketones were found to exist as α-metalated ketones with a covalent carbon-mercury bond.[37] The (benzoylmethyl)mercurials undergo electrophilic attack by a proton readily[38] to form acetophenone making them unsuitable for acidic conditions. This is probably due to polarization $PhCOCH_2^{\delta-}Hg^{\delta+}X$ in the molecule. These are also readily attacked at the mercury atom by nucleophiles such as I^-, $(EtO)_2PO^-$ or $CH_2{=}NO_2^-$ to generate acetophenone and mercury salt.[23] The benzoylmethyl radicals generated by photolysis of the mercurials can be trapped by anions such as $Me_2C{=}NO_2^-$, $RC(CO_2Et)_2^-$ or $RC(O^-){=}CH_2$ to yield adduct radicals which transfer an electron to the mercurial to yield the coupling products (Scheme VI).[39]

Scheme VI

$$PhCOCH_2^{\cdot} + A^- \longrightarrow PhCOCH_2A^{\cdot -}$$

$$PhCOCH_2A^{\cdot -} + PhCOCH_2HgCl \longrightarrow PhCOCH_2A + PhCOCH_2HgCl^{\cdot -}$$

$$PhCOCH_2HgCl^{\cdot -} \longrightarrow PhCOCH_2^{\cdot} + Hg^{o} + Cl^-$$

$$A^- = Me_2C{=}NO_2^-, PhC(O^-){=}CH_2$$

Easily oxidized anions such as $PhCOCPh_2^-$ or $PhC(CH_3){=}NO_2^-$ react with $PhCOCH_2^{\cdot}$ by electron transfer to yield the dimer derived from the anion (Scheme VII).[39]

Scheme VII

$$PhCOCH_2^{\cdot} + A^- \longrightarrow PhCOCH_2^- + A^{\cdot}$$

$$A^{\cdot} + A^- \longrightarrow A\text{-}A^{\cdot -}$$

$$A\text{-}A^{\cdot -} + PhCOCH_2HgCl \longrightarrow A\text{-}A + PhCOCH_2^{\cdot} + Hg^{\circ} + Cl^-$$

$$A^- = PhC(O^-)=CPh_2,\ PhCH=NO_2^-,\ Ph_2P^-$$

Explanation of the dissertation format

This dissertation is written in an alternate format as described in the Iowa State University Thesis Manual. It consists of four papers (Part I, II, III and IV) written according to the American Chemical Society style. Part of the results described in Parts I, II and III has been published in The Journal of Organic Chemistry (ref. 39) and as a communication to the editor of The Journal of Organic Chemistry (ref. 32). The references cited in the General Introduction are listed after the General Summary.

PART I. REACTION OF (BENZOYLMETHYL)MERCURIALS WITH TRIALKYL PHOSPHITES

Reaction of (Benzoylmethyl)mercurials with trialkyl phosphites

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INTRODUCTION

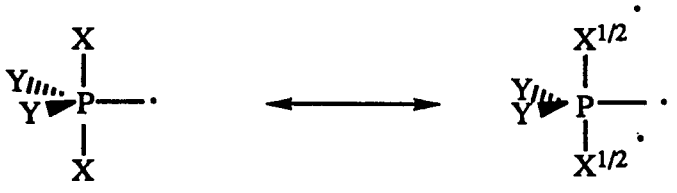
Trialkyl phosphites undergo numerous reactions because of the availability of the lone pair and the tendency of the phosphorus atom to expand its valence shell.

The attack of radicals on phosphites to form an intermediate phosphoranyl radical $R_4P\cdot$ was proposed as early as 1959[1] in the reactions of *t*-BuO· and RS· with phosphites (reaction 1).

$$t\text{-BuO}\cdot + P(OEt)_3 \longrightarrow t\text{-BuO}\dot{P}(OEt)_3 \xrightarrow{\beta\text{-scission}} t\text{-Bu}\cdot + OP(OEt)_3 \qquad (1)$$

Since that time the hypervalent free radical $R_4P\cdot$ has been the subject of a number of chemical and spectroscopic investigations.[2] Bentrude[3] has studied the factors determining the reactivity of a given radical Z· towards PX_3 to form $ZX_3P\cdot$ as well as the strucural features which influence the relative ease of subsequent α- or β- scission steps.

The structure of the phosphoranyl radical is generally written in terms of a trigonal bipyramid structure with the odd electron in an equatorial orbital and a high proportion of the spin density delocalized onto the apical substituents[3] (structures A and B).



A B

The potential reactions of radical Z· with PX_3 has been roughly divided into three cases. In case 1, addition takes place irreversibly and exothermally and at a near diffusion controlled rate. Some of these radicals include Ph·, Me_3SiO·, BzO·, and $(EtO)_2P(O)O$·. The second order rate constants ($M^{-1}s^{-1}$) for RO· reaction with Ph_3P and $(EtO)_3P$ has been found to be in the range of 8.1×10^8 to 5.1×10^9 at room temperature. The reaction of Ph· with $(MeO)_3P$, which is exothermic by about 10-15 kcal/mol, takes place at a rate of 3.5×10^8 $M^{-1}s^{-1}$ at 45 °C (reaction 2).[4] This reaction is a free radical version of the well known Arbuzov reaction.[5]

$$Ph\cdot + P(OMe)_3 \longrightarrow Ph-\overset{\overset{O}{\|}}{P}(OMe)_2 \quad (2)$$

96 - 99 %

Those reaction systems in which Z· adds to PX_3 reversibly comprise case 2. Net reaction requires a rapid subsequent α- or β- scission to trap the intermediate phosphoranyl radical. Et·, Me·, and Me_2N· give no net reaction with $P(OEt)_3$ even though $MeP^{\bullet}(OEt)_3$ was observed by ESR.[6] However addition of these radicals to $PhCH_2OP(OEt)_2$ yields a net substitution due to a rapid β-scission[6] (reaction 3).

$$Me_2N^{\bullet} + PhCH_2OP(OEt)_2 \longrightarrow \begin{matrix} Me_2N \\ \diagdown \\ \cdot P(OEt)_2 \\ \diagup \\ PhCH_2O \end{matrix}$$

$$\longrightarrow Me_2NP(O)(OEt)_2 + PhCH_2^{\bullet} \quad (3)$$

The major difference between cases 1 and 2 have been explained in terms of the relative strengths of the PZ bond in the phosphoranyl radical.

In case 3, radicals such as $PhCH_2$·, *t*-Bu·, which form very weak bonds to phosphorus , do not add even reversibly unless PX_3 is phenyl substituted. Thus *i*-Pr· and *t*-Bu· both give radical Arbuzov products with $ROPPh_2$ but not with $(EtO)_3P$ or even $PhP(OEt)_2$.[7]

Steric effects also affect the overall reactivity of these reactions. Steric crowding has been proposed[8] to account for the instability of $(CF_3)_3P^{\bullet}OR$. Only a very small uncorrelated effects of X on the reactivity of *t*-BuO· towards $XC_6H_4P(OMe)_2$ (X=*p*-H, *p*-MeO, *p*-Cl, and *m*-F) were found.[9] Large polar effects are thought to be involved with less reactive radicals.

Anions of dialkyl phosphites ($(RO)_2PO^-$) have also been shown to participate in radical reactions. Bunnett[10] has shown that dialkyl phophites participate as nucleophiles in aromatic $S_{RN}1$ reactions. Anions of dialkyl phosphites and thiophosphites also undergo aliphatic $S_{RN}1$ reactions with α-chloro, α-(*p*-tolylsulfonyl), α-nitro derivatives of 2-nitropropanes as well as with *p*-nitrobenzyl chloride and α,α-dimethyl-*p*-nitrobenzyl chlorides as substrates.[11] The mechanism of the reaction with 2-nitropropane derivatives is shown in Scheme I.

Scheme I

$$R_2C(X)NO_2^{\bullet -} \longrightarrow R_2\dot{C}NO_2 + X^-$$

$$R_2\dot{C}NO_2 + (R^1O)_2PO^- \longrightarrow (R^1O)_2P(O)CR_2NO_2^{\bullet -}$$

$$(R^1O)_2P(O)CR_2NO_2^{\bullet -} + R_2C(X)NO_2 \longrightarrow R_2C(X)NO_2^{\bullet -} + (R^1O)_2P(O)CR_2NO_2$$

RESULTS AND DISCUSSION

Photostimulated S_{RN} reaction of (benzoylmethyl)mercury chloride with trialkyl phosphites occurred efficiently (Scheme II) presumably because of a favorable polar effect in the addition step (reaction 4) in which the electrophilic $PhCOCH_2\cdot$ radical attacks an electron rich trialkyl phosphite and also due to a more favorable driving force for the electron transfer of reaction 5.

Scheme II

$$R\cdot + (MeO)_3P \longrightarrow \dot{R}P(OMe)_3 \quad (4)$$

$$\dot{R}P(OMe)_3 + RHgCl \longrightarrow RP(OMe)_3^+ + RHgCl\cdot^- \quad (5)$$

$$RHgCl\cdot^- \longrightarrow R\cdot + Hg^o + Cl^- \quad (6)$$

$$Cl^- + RP(OMe)_3^+ \longrightarrow MeCl + RP(O)(OMe)_2 \quad (7)$$

$R = PhCOCH_2$

It is known that phenacyl halides react with $(RO)_3P$ or $(RO)_2PO^-$ to yield enol phosphates (Perkow reaction) by what is formally a nucleophilic attack upon the carbonyl oxygen (reaction 8),[5,12] although in some cases with $(RO)_3P$ the ketophosphonate is a significant product. However the ketophosphonate and the enol phosphate are not easily separated.[13]

$$PhCOCH_2X + (RO)_3P \longrightarrow PhC(=CH_2)OP(O)(OR)_2 + RX \quad (8)$$

In an effort to get better yields of the ketophosphonate, a number of different solvents were tried. A typical photostimulated reaction between $PhCOCH_2HgCl$ and $P(OMe)_3$ in aprotic solvents such as PhH, Me_2SO, DMF forms acetophenone (1), 1,4-diphenyl-1,4-butanedione (2), and trimethyl phosphate (3) along with the ketophosphonate (4) (reaction 9).

$$PhCOCH_2HgCl + P(OMe)_3 \xrightarrow{h\nu} \underset{(1)}{PhCOCH_3} + \underset{(4)}{PhCOCH_2P(O)(OMe)_2} + \underset{(2)}{PhCOCH_2CH_2COPh} + \underset{(3)}{P(O)(OMe)_3} \quad (9)$$

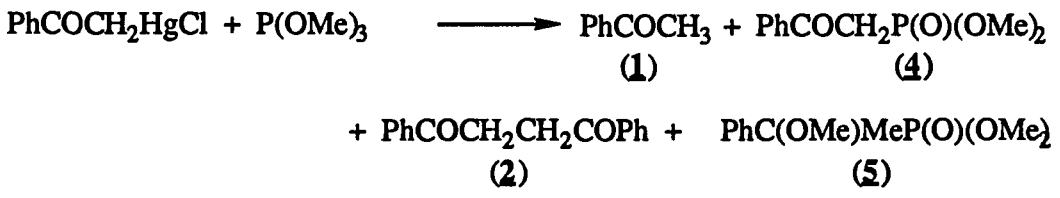
Upon irradiation in protic solvents such as methanol (MeOH), the ionic reaction predominates to give the phosphonate $PhC(OMe)(Me)P(O)(OMe)_2$ (5) along with acetophenone and phosphate (3).

The yields of these products in different solvents are summarized in Table 1. Reaction in Me_2SO gives the best yield of the ketophosphonate (4) and the lowest yield of unwanted acetophenone. Thus further studies of this photostimulated reaction were performed in Me_2SO as solvent.

Trimethyl phosphite is known to deoxygenate sulfoxides to produce trimethyl phosphate and dimethyl sulphide via an ionic reaction.[14] However the slow rate of this reaction under the reaction conditions and the excess of $P(OMe)_3$ employed ensured that loss of $P(OMe)_3$ via this route was negligible enough as to not to interfere in our present study.

The ratio of 2/4 was quite insensitive to the concentration of $(MeO)_3P$ (entries 2-4,6,7 of Table 2) at constant $[PhCOCH_2HgCl]_0$. On the other hand the ratio increased with

Table 1. Photostimulated reaction of $PhCOCH_2HgCl$ with $P(OMe)_3$ in different solvents[a]



Solvent	% Yield[b]			
	(1)	(2)	(4)	(5)
Me_2SO	tr	33	32	0
PhH	8	37	15	0
DME	5	45	3	0
MeOH	45	0	0	42
PhH/Me_2SO (5/1)	5	42	6	0
Me_2SO/MeOH (1/1)	21	21	8	0

[a]Photolysis of 0.5 mmol. of $PhCOCH_2HgCl$ with 5 equiv. of $P(OMe)_3$ in 5 mL solvent for 8 h in a 350-nm Rayonet photoreactor at around 40 °C.

[b]GC yield with biphenyl as internal standard.

the initial concentration of $PhCOCH_2HgCl$. However a doubling of $[PhCOCH_2HgCl]_o$ caused the ratio to increase (entries 3,5,6 of Table 2) by only about 1.3 (i.e. about $2^{1/2}$). Such a kinetic behavior is consistent with the steady state concentration of $PhCOCH_2\cdot$ being determined by an initiation process first order in $PhCOCH_2HgCl$ and a termination reaction second order in $PhCOCH_2\cdot$. However the data would be consistent with Scheme II only if the steady state $[PhCOCH_2\cdot]$ was proportional to $[PhCOCH_2HgCl]^{1/2}[(MeO)_3P]$.

Table 2. Photostimulated reactions of alkylmercurials with $(MeO)_3P$[a]

$$\text{Mercurial} + (MeO)_3P \xrightarrow[Me_2SO]{h\nu} RP(O)(OMe)_2 + (PhCOCH_2)_2 \quad (2)$$

Mercurial	mmol of $(MeO)_3P$	$RP(O)(OMe)_2$ % yield[b]	(2) %	Ratio (2)/(4)
t- BuHgCl(0.5)	2.5	tr	-	-
$PhCOCH_2HgCl$(0.5)	0.5	30	33	1.10
$PhCOCH_2HgCl$(0.5)	2.5	32	33	1.03
$PhCOCH_2HgCl$(0.5)	10.0	37	30	0.81
$PhCOCH_2HgCl$(0.25)	1.25	40	29	0.73
$PhCOCH_2HgCl$(0.125)	0.625	44	25	0.57
$PhCOCH_2HgCl$(0.125)	2.5	42	25	0.60
$PhCOCH_2HgCl$(0.5)	2.5[c]	33[c]	32[c]	0.97[c]
$(PhCOCH_2)_2Hg$(0.5)	2.5	48	70	1.46

[a]Photolysis for 8 h in a 350-nm Rayonet photoreactor in 5 mL Me_2SO.

[b]GC yield, mmol of $RP(O)(OMe)_2$/mol of mercurial.

[c]$(EtO)_3P$ yielding $PhCOCH_2P(O)(OEt)_2$.

This unusual behavior suggests an initiation reaction where rate is proportional to $[PhCOCH_2HgCl][P(OMe)_3]^2$. This in turn suggests the formation of complexes of the type $PhCOCH_2Hg[P(OMe)_3]^+Cl^-$ and $PhCOCH_2Hg[P(OMe)_3]_2^+Cl^-$ with the latter being the main source of $PhCOCH_2\cdot$ upon photolysis. Further evidence for the complexes of this

type became evident from the study of the dark (ionic) reactions of $PhCOCH_2HgCl$ with $(RO)_3P$ in Me_2SO.

The photostimulated reaction to form ketophosphonate **4** was always accompanied by a side reaction producing diketone **2** (Table 2) indicating a reaction of short kinetic chain length. Photolysis of $PhCOCH_2HgCl$ in Me_2SO formed **2** in 78% yield in the absence of $(RO)_3P$. Under standard conditions in Me_2SO-d_6, the formation of **2** was monitored by ^1H NMR. With $[PhCOCH_2HgCl]_o$=0.1M, the initial rate of formation of **2** was 2.7×10^{-5} M/s. In the presence of 0.02M $(t\text{-Bu})_2NO\cdot$, the appearence of **2** was delayed by 12 min giving a rate of formation of $PhCOCH_2\cdot$ of 6×10^{-5} M/s. (This calculation is based on the assumption that $(t\text{-Bu})_2NO\cdot$ traps only $PhCOCH_2\cdot$. Photolysis of $PhCOCH_2HgCl$ also produces $\cdot HgCl$, which may react with a second molecule of $PhCOCH_2HgCl$ to form $PhCOCH_2\cdot$, $HgCl_2$, and Hg^o).[15] The formation of diketone **2** is obviously not a chain process and very nearly one molecule of **2** is formed for every two radicals trapped by $(t\text{-Bu})_2NO\cdot$.

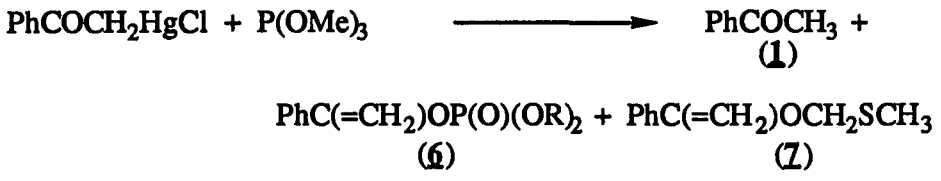
With $(PhCOCH_2)_2Hg$ similar experiments demonstrated that 0.9 mol of the mercurial was photochemically decomposed (in the absence of nitroxide) for every two radical trapped by the nitroxide.

Ionic Reactions of $PhCOCH_2HgCl$

$PhCOCH_2HgCl$ is stable in Me_2SO at room temperature and even at 80 °C in the dark. However it reacted slowly with $(MeO)_3P$ in Me_2SO to form the enol phosphate **6** and enol ether derivative of dimethyl sulfide **7**. The mercury was mainly reduced to the Hg^o state while significant amounts of acetophenone and trimethyl phosphate (**3**) were

also formed, none of the diketone **2** was detected (Table 3). The enol phosphate **6** was also formed in PhH or DMF in the dark or when refluxed at 80 °C in room light.

Table 3. Reaction of $PhCOCH_2HgCl$ with $P(OMe)_3$ in various aprotic solvents[a]



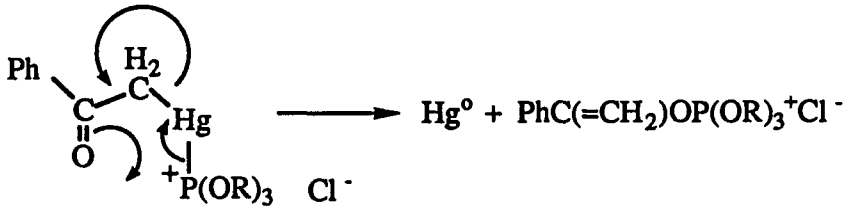
Solvent	Conditions	Time (h)	% Yield[b]		
			(1)	(6)	(7)
Me_2SO	dark, r.t.	48	53	13	25
PhH	dark, r.t.	48	40	56	0
DMF	dark, r.t.	24	82	14	0
PhH	room light 80 °C	2	13	68	0
DMF	room light 80 °C	2	40	45	0

[a]Reaction of 0.5 mmol $PhCOCH_2HgCl$ with 2.5 mmol $P(OMe)_3$ in 5 mL solvent.

[b]GC yield with biphenyl as internal standard.

[c]Test tube wrapped in aluminum foil.

The enol phosphate **6**, which is a Perkow-type product is probably not formed by nucleophilic attack at the carbonyl group because of the unfavorable polarity in $PhCOCH_2^{\delta-}\cdots HgCl^{\delta+}$. Instead we postulate nucleophilic attack of $(RO)_3P$ at mercury followed by electrophilic attack at the carbonyl oxygen with the electron flow as described in **8** of reaction 10.

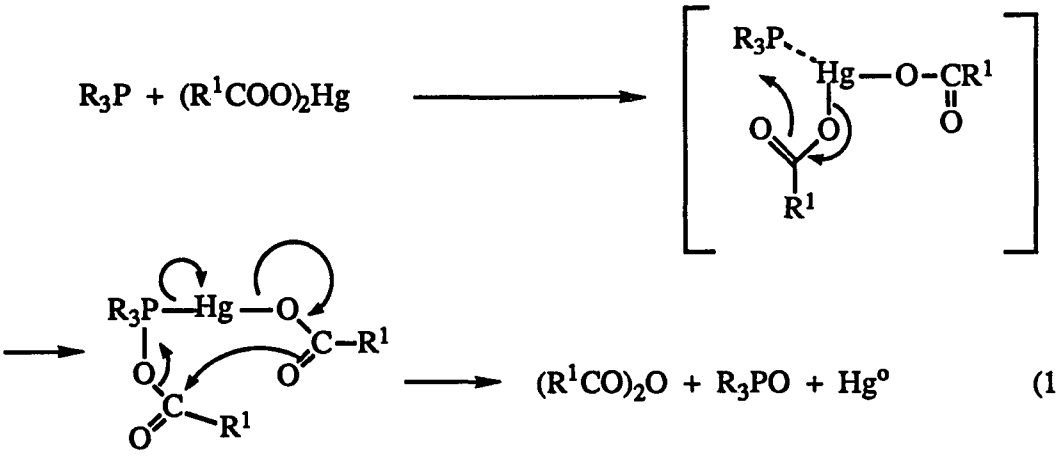


(10)

This is supported by observation by Mukaiyama[16] that a variety of mercury(II) salts of carboxylic acid give the corresponding carboxylic anhydrides, metallic mercury and trialkyl phosphates in good yields on reaction with trialkyl phosphites. He proposed that the coordination of phosphorus(III) compound to a mercury salt leads to an intermediate, which in turn, decomposes into an acid anhydride along with metallic mercury and a pentavalent phosphorus compound as shown in reaction 11.

Product **7** is reminiscent of the Pummerer reaction observed for sulfoxides.[17] However sulfoxonium salts such as $PhCOCH_2OSMe_2^+X^-$ are known to undergo elimination to PhCOCHO rather than react via the Pummerer route.[18] $PhCOCH_2HgCl$ in Me_2SO at 80 °C failed to form **7** in the absence of $(MeO)_3P$, While in the presence of $(EtO)_3P$ at 25 °C in Me_2SO, **6**(R=Et) but not **7** was formed. Furthermore, **7** was not formed when other proton acceptors such as Et_3N were substituted for $(MeO)_3P$.

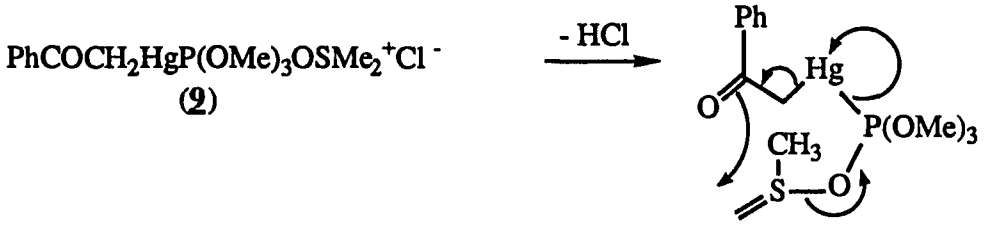
Compound **7** is also formed in the rearrangement of $PhCOCH_2S^+Me_2$ described by Ratts and Yao[19] in a process thought to proceed via $PhCOCH_2S(CH_3)=CH_2$. This



$$\longrightarrow (R^1CO)_2O + R_3PO + Hg^o \qquad (11)$$

suggests that in the presence of $(MeO)_3P$, perhaps Me_2SO is deoxygenated to Me_2S which reacts to form 7. However reaction of Me_2S with $PhCOCH_2HgCl$ and $(MeO)_3P$ in DMF also did not form 7, although enol phosphate 6 was formed. Finally $PhCOCH_2HgCl$ in Me_2SO-d_6 formed $PhC(=CH_2)OCD_2SCD_3$ devoid of non-deuterated species under conditions where the recovered Me_2S had not undergone appreciable deuterium exchange.

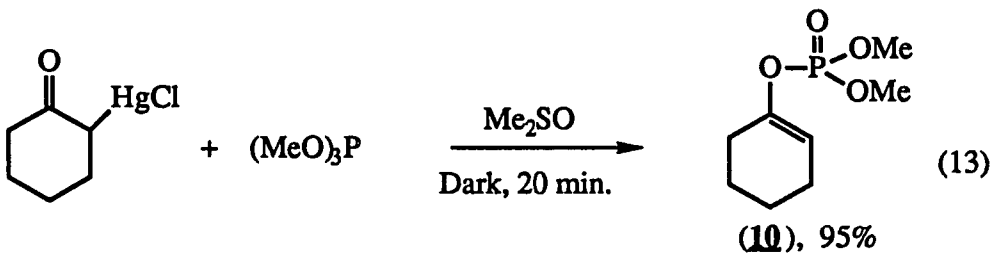
The formation of 7 from $PhCOCH_2HgCl$ and $(MeO)_3P$ in Me_2SO solution can be rationalized by the formation of a sulfoxonium intermediate 9 from a complex between $(MeO)_3P$ and the mercurial (reaction 12).



$$\longrightarrow (7) + Hg^o + (MeO)_3PO \qquad (12)$$

Indeed the dark reaction yielding a mixture of **6** and **7** was accompanied by the formation of phosphate **3**. Acetophenone was also observed, but it is difficult to determine its source since acetophenone was formed in the aqueous thiosulfate workup employed to remove any unreacted mercurial before GC analysis or product isolation. However the proton lost in coverting **9** to sulfur ylide presumably leads to the formation of some acetophenone by electrophilic attack upon $PhCOCH_2HgCl$.

Surprisingly reaction of (2-oxocyclohexyl)mercury chloride with $(MeO)_3P$ in Me_2SO in dark formed in 20 min. almost exclusively the enol phosphate **10** in 95% yield (reaction 13).



(13)

(**10**), 95%

Probably in this case the geometry of the complexed phosphite puts the phosphorus atom in close proximity of carbonyl oxygen and thus allows facile electrophilic attack of the carbonyl oxygen on the phosphorus atom.

Reactions in methanol

Reaction of $PhCOCH_2HgCl$ with 5 equivalents of $(RO)_3P$ in the dark or upon irradiation at 25 °C in MeOH, gave phosphonate **5** as the major product (24 h reaction period) accompanied by phosphate **3** and Hg^0 (Table 4). In MeOH with $(EtO)_3P$ (entry 3 of Table 4) **5** was detected indicating that the mercurial had catalyzed a rapid alkoxy

Table 4. Reactions of $PhCOCH_2HgCl$ with $(RO)_3P$ in methanol[a]

$$PhCOCH_2HgCl + (RO)_3P \xrightarrow{MeOH} \underset{(1)}{PhCOCH_3} + \underset{(5)}{PhC(OMe)(Me)P(O)(OMe)_2}$$

Mercurial	R	Conditions (h)	% Yield[b]	
			(1)	(5)
$PhCOCH_2HgCl$	Me	dark[c] (48)	18	42
$PhCOCH_2HgCl$	Me	hν[d] (8)	55	42
$PhCOCH_2HgCl$	Et	dark[c] (24)	46	33
$(PhCOCH_2)_2Hg$	Me	dark[c] (1)	96	0

[a]Reaction of 0.5 mmol mercurial with 2.5 mmol $(RO)_3P$ in 5 mL methanol.

[b]GC yield with biphenyl as internal standard.

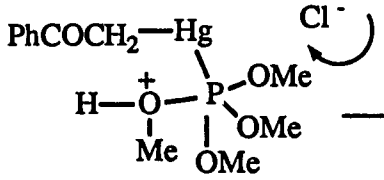
[c]Test tube wrapped in aluminum foil and kept at room temperature.

[d]Photolysis in a 350-nm Rayonet photoreactor at around 40 °C.

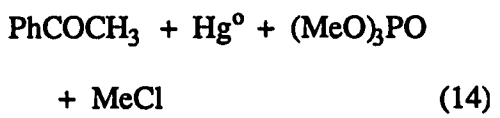
exchange in the trialkyl phosphite.

Reaction of $(PhCOCH_2)_2Hg$ in presence of $(MeO)_3P$ (entry 4 of Table 4) rapidly (5 min.) formed $PhCOCH_3$. Acetophenone also accompanied **5** in the reaction of $PhCOCH_2HgCl$, but only traces of ketal $PhC(OCH_3)_2CH_3$ were detected after 24 h. Acetophenone did not react with $(MeO)_3P$ in methanol but in presence of acids $HgCl_2$ or *p*- toluenesulfonic acid initially (5 min.) formed $PhC(OCH_3)_2CH_3$, but with time **5** was formed. With 10% PTSA after 24 h **5** was the only product and was formed in essentially quantitative yield.

These results suggest that the methanolysis of (benzoylmethyl)mercurials is strongly catalyzed by trialkyl phosphites in an overall process giving oxidation [$(RO)_3PO$] and reduction (Hg^o) products in the case of $PhCOCH_2HgCl$. One possible mechanism involves association of MeOH with the complex $PhCOCH_2HgP(OR)_3^+Cl^-$. This explains the rapid alkoxy exchange noted. The intermediate **11** could lead to acetophenone (reaction 14), which could react by Lewis acid [Hg(II)] catalysis to form $PhC(OCH_3)_2CH_3$, which is slowly but irreversibly converted to **5**.



11



(14)

Only traces of enol phosphate **6** were detected in the reactions of $PhCOCH_2HgCl/MeOH/(MeO)_3P$ or $PhCOCH_3/MeOH/(MeO)_3P/PTSA$. Methanolysis of $PhC(Me)(OSO_2Me)P(O)(OEt)_2$ in the presence of 2,6-lutidine is reported to form $PhC(Me)(OMe)P(O)(OEt)_2$ and **6** in a 5 : 1 ratio,[20] but in the absence of base **6** might be methanolyzed to acetophenone and $(MeO)_3PO$.

Reaction of $PhCOCH_2HgCl$ with $(RO)_2PO^-$

An excess of $(RO)_2PO^-$ converts $PhCOCH_2HgCl$ to $PhCOCH_3$ by nucleophilic attack at the mercury atom. Since products such as $PhC(=CH_2)OP(O)(OR)_2$, $PhC(=CH_2)OCH_2SCH_3$ and even $PhCOCH_2P(O)(OR)_2$ could be formulated as arising from further thermal or photochemical reactions of $PhCOCH_2HgP(O)(OR)_2$ (possibly formed from the decomposition of $PhCOCH_2HgP(OR)_3^+Cl^-$, we examined the products of

a stoichiometric reaction of $PhCOCH_2HgCl$ and $(MeO)_2PO^-$. However this reaction failed to produce the products observed upon reaction with $(MeO)_3P$. The reaction yielded after workup only acetophenone or upon photolysis only a mixture of acetophenone and diketone **2**. It does not appear that $PhCOCH_2HgP(O)(OMe)_2$ plays any significant role in the reactions involving $(MeO)_3P$.

CONCLUSION

The reaction of electrophilic benzoylmethyl radicals generated by photolysis of the corresponding mercurial with trialkyl phosphites in aprotic solvents represents a good method of producing β-keto phophonates free from enol phosphates. These reactions proceed by a S_{RN} type process which involves electron transfer from the intermediate phosphoranyl radical to the mercurial. The ability of the phosphites to form complexes with mercurials leads to a variety of ionic processes in protic solvents or in reactions carried out in the dark.

EXPERIMENTAL SECTION

General Considerations

Analytical gas chromatography (GC) was performed on a varian 3700 gas chromatograph packed with chromosorb W (80-100 mesh) coated with 7% OV-3. It was equipped with a Hewlett-Packard 3390A integrator. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained with a Nicolet NT 300 spectrometer. Chemical shifts are reported in ppm from internal standard TMS or from $CDCl_3$ (^{13}C NMR). Mass spectra were obtained in the GC mode with a Finnigan 4000 spectrometer with INCOS data system and in the high resolution mode with a Kratos MS-50 spectrometer. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated by column chromatography using 40-100 mesh silica-gel (J. T. Baker and Co.). Analytical thin layer chromatography was performed on glass silica gel plates (Aldrich Chemical Co.) with UV detection. GC yields were determined by using an internal standard (biphenyl) and were corrected with predetermined response factors.

Solvents and Reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (Me_2SO) was distilled from CaH_2 and stored over 4A° molecular sieves under nitrogen atmosphere. DMF was distilled from CaH_2. Benzene was distilled from sodium and methanol from

$Mg(OCH_3)_2$. Chemical reagents in high purity grades were purchased mainly from Aldrich and were used without further purification.

(Benzoylmethyl)mercury chloride ($PhCOCH_2HgCl$) was prepared from acetophenone in three steps.[21a] Acetophenone was first converted to its enol silyl ether using chlorotrimethylsilane and triethylamine in DMF. Then it was converted to the bis-mercurial $(PhCOCH_2)_2Hg$ by reacting it with HgO in presence of catalytic $Hg(OAc)_2$ in ethanol. Finally it was disproportionated with addition of stoichiometric amount of $HgCl_2$ to give after recrystallization from CH_2Cl_2-hexane pure $PhCOCH_2HgCl$ as white crystals: mp 144-145 °C (lit.[21b] mp 145-146 °C); ^1H NMR (Me_2SO-d_6) δ 3.10(s, 2H with ^{199}Hg satellites, J=330 Hz), 7.47(t, J=7.5 Hz, 2H), 7.57(t, J=7.5 Hz, 1H), 8.02(d, J=7.2 Hz, 2H). (2-oxocyclohexyl)mercury chloride: mp 134-135 °C (lit.[23] mp 134-135 °C) was prepared from cyclohexanone by the same procedure.[21a,22]

Procedures and Compounds

General procedure for photostimulated and dark reactions of RHgX

Photostimulated reactions were carried out in solvents deoxygenated by nitrogen bubbling in pyrex test tubes equipped with rubber septa. Photolysis was carried out in a 350-nm Rayonet photoreactor at around 40 °C. Dark reactions were performed in flasks wrapped in Aluminum foil.

Isolation procedures

The reaction mixture was diluted with 50 mL CH_2Cl_2, a known amount of the GC internal standard (biphenyl) was added and the resulting mixture was extracted three times

with 15% aqueous $Na_2S_2O_3$ followed by water. The CH_2Cl_2 solution was then dried over Na_2SO_4 and analyzed by GC or the solvent was removed and the products were isolated by column chromatography.

1,4-Diphenyl-1,4-butanedione (2)[24]

Photolysis of a solution of 0.5 mmol $PhCOCH_2HgCl$ in 5 mL Me_2SO in Rayonet for 8 h at around 40 °C gave 78% **2** after silica gel chromatography using hexane (80%)-ethylacetate (20%), as yellowish white crystals: mp 144-145 °C; ^1H NMR ($CDCl_3$) δ 3.46(s, 4H), 7.47(t, J=7.2 Hz, 4H), 7.57(t, J=7.2 Hz, 2H), 8.04(d, J=7.2 Hz, 4H); GCMS m/z(relative intensity) 238(M^+, 12), 133(10), 105(100), 77(38).

Dimethyl (benzoylmethyl)phosphonate (4)[25]

Pure $PhCOCH_2P(O)(OMe)_2$ was obtained as oily liquid by column chromatography using hexane (40%)-ethyl acetate (60%); ^1H NMR ($CDCl_3$) δ 3.65(d, $^2J_{P,H}$ =22.5 Hz, 2H), 3.78(d, $^3J_{P,H}$=11.4 Hz, 6H), 7.48(t, J=7.5 Hz, 2H), 7.60(t, J=7.2 Hz, 1H), 8.00(d, J=7.8 Hz, 2H); GCMS m/z(relative intensity) 228(M^+, 15), 200(2), 151(10), 105(100), 91(8), 77(33).

Dimethyl 1-phenylethenyl phosphate (6)[26]

It was obtained as an oily liquid by column chromatography using hexane (75%)-ethyl acetate (25%); ^1H NMR ($CDCl_3$) δ 3.86(d, $^3J_{P,H}$=11.1 Hz, 6H), 5.23(t, J=3H, 1H), 5.32(t, J=3H, 1H), 7.32-7.42(m, 3H), 7.56-7.64(m, 2H). The ^1H NMR compared favorably with that in the literature.[26]

Diethyl (benzoylmethyl)phosphonate[25]

It was identified using GCMS only. GCMS m/z(relative intensity) 256(M^+, 5), 211(3), 146(13), 120(17), 105(100), 77(28).

Dimethyl 1-cyclohexenyl phosphate (**10**)[27]

It was obtained as oily liquid; ^{1}H NMR ($CDCl_3$) δ 1.40-1.55(m, 2H), 1.60-1.70(m, 2H), 1.95-2.05(m, 2H), 2.07-2.20(m, 2H), 3.73(d, $^3J_{P,H}$=11.1 Hz, 6H), 5.37-5.45(m, 1H); GCMS m/z(relative intensity) 206(M^+,13), 127(100), 109(15), 97(12), 79(39).

[1-[(methylthio)methoxylethenyl]benzene (**7**)[19]

It was obtained as a liquid by column chromatography using hexane (96%)-ethyl acetate (4%); ^{1}H NMR ($CDCl_3$) δ 2.27(s, 2H), 4.29(d, J=3 Hz, 1H), 4.81(d, J=3 Hz, 1H), 5.02(s, 2H), 7.26-7.38(m, 3H), 7.60-7.68(m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.30, 135.98, 128.51, 128.06, 125.34, 84.90, 71.86, 15.01; HRMS m/z calcd for $C_{10}H_{12}OS$: 180.0609. Found: 180.0617. The ^{1}H NMR compared favorably with that in the literature.[19]

Dimethyl 1-methoxy-1-phenylethyl phosphate (**5**)[20]

Pure **5** was isolated by column chromatography using hexane (50%)-ethyl acetate (50%) as eluant; ^{1}H NMR ($CDCl_3$) δ 1.87(d, $^3J_{P,H}$=15.9 Hz, 3H), 3.22(s, 3H), 3.63(d, $^3J_{P,H}$=10.5 Hz, 3H), 3.68(d, $^3J_{P,H}$=10.2 Hz, 3H), 7.32(t, J=6.9 Hz, 1H), 7.39(t, J=7.2 Hz, 2H), 7.52(d, J=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.60, 128.07, 127.82, 127.62, 79.19(d, $J_{P,C}$=168 Hz), 53.85(d, $J_{P,C}$=6.5 Hz), 50.19(d, $J_{P,C}$=12.6 Hz), 18.73; HRMS m/z calcd for $C_{11}H_{17}O_4P$: 244.0865. Found: 244.0867.

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PART II. REACTION OF (BENZOYLMETHYL)MERCURIALS WITH *N*-METHYLPYRROLE AND ENAMINES

Reaction of (Benzoylmethyl)mercurials with *N*-methylpyrrole and enamines

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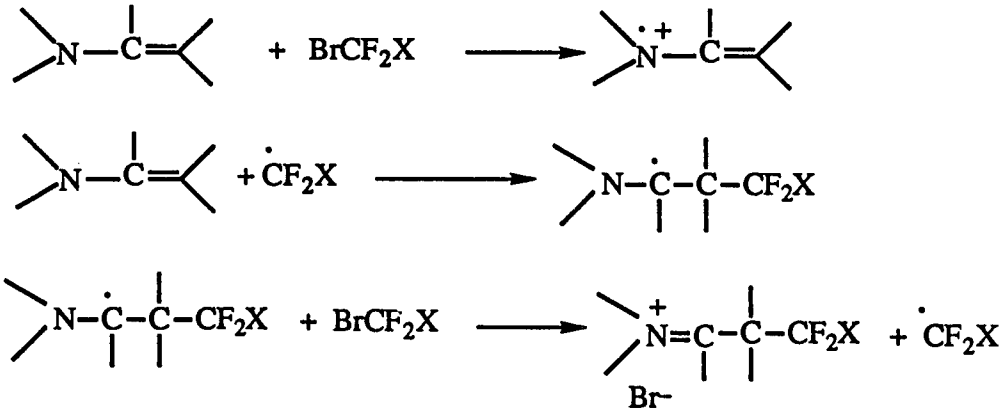
INTRODUCTION

tert-Butylmercury halides undergo a free radical chain reaction with pyridines or pyridinium salts[1] where the *t*-Bu· radical is trapped by PyH^+ or Py.....Hg(R)-X. With $PhCOCH_2HgCl$ these reactions are inefficient or do not occur at all. This is so because the *t*-Bu· radical is a nucleophilic radical, and reacts efficiently with electron poor pyridine complexes. Since $PhCOCH_2$· radical is an electrophilic radical, it shows a dramatically different reactivity as compared to the nucleophilic *t*-Bu· radical. Therefore it was expected to react more efficiently with the electron rich heterocycle such as pyrrole.

Enamines are a class of electron rich alkenes and as expected fail to undergo free radical substitution reactions with *t*-BuHgCl/hv. Electrophilic radicals, on the other hand, react with enamines due to favorable polar effect. For example, fluorinated alkyl radicals add to enamines to form adduct radicals capable of undergoing electron transfer to a variety of fluorohalocarbons (Scheme I).[2,3]

Scheme I

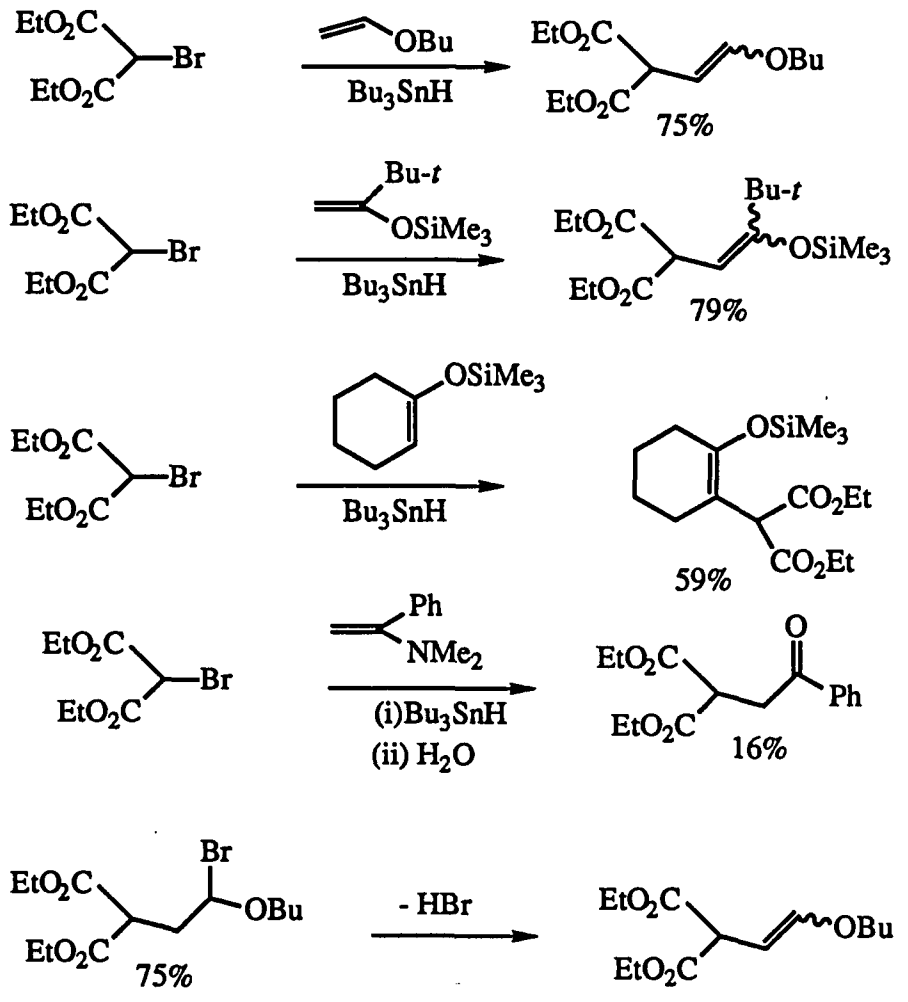


The electrophilic $(EtO_2C)_2CH$· is also reported to react with 5 to 10 fold excess of enamines and enol ethers to give substitution products (Scheme II).[4] The reaction

proceeds via an intermediate bromide which loses a molecule of HBr to give the substitution products.

Kinetic experiments with substituted styrenes showed that the malonyl radical reacts 23 times as readily with the electron rich enamine $CH_2=C(NMe_2)Ph$ as with the electron-poor unsaturated ester $CH_2=C(CO_2Et)Ph$.[4]

Scheme II

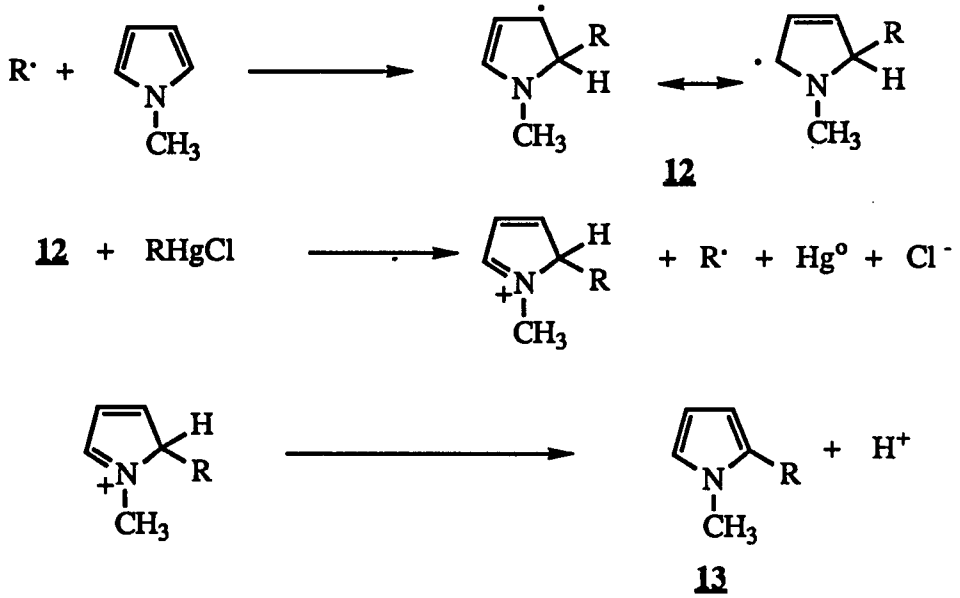


RESULTS AND DISCUSSION

Reactions with *N*-methylpyrrole

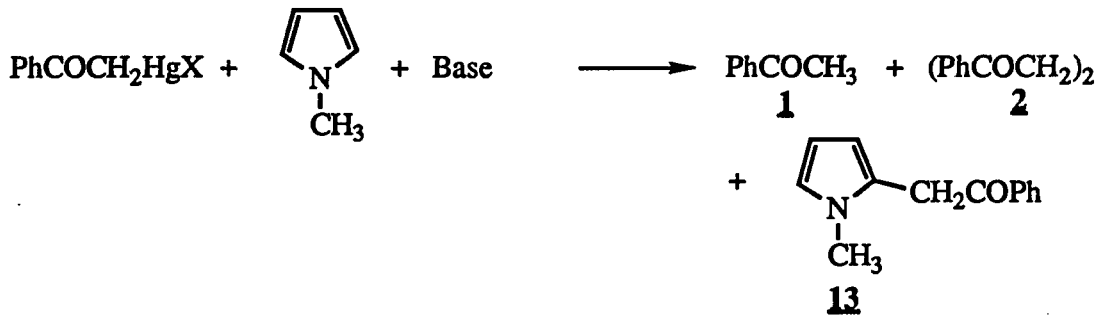
The photostimulated reaction of $PhCOCH_2HgCl$ with *N*-methylpyrrole gave regiospecifically the 2-substituted pyrrole derivative (Table 1). The possible mechanism is shown in Scheme III.

Scheme III



The $PhCOCH_2$· radical adds to the electron rich pyrrole nucleus to form an easily oxidizable adduct radical **12**. An electron is transferrred from **12** to $PhCOCH_2HgCl$ to form the iminium salt and another $PhCOCH_2$· radical which continues the chain. The

Table 1. Photostimulated reactions of $PhCOCH_2HgX$ with *N*-methylpyrrole[a]



X	Solvent	Base (equiv.)	% Yield[b]		
			1	**2**	**13**
Cl[c]	Me_2SO	-	43	7	9
Cl	Me_2SO	-	42	7	20
Cl	MeOH	-	41	1	14
Cl	PhH/Me_2SO(9/1)	-	19	29	7
Cl	Me_2SO	Li_2CO_3(5)	15	10	18
Cl	Me_2SO[d]	Li_2CO_3(5)	4	17	26
$PhCOCH_2$	Me_2SO	-	7[e]	46[e]	2[e]

[a]Reaction of 0.5 mmol of $PhCOCH_2HgCl$ with *N*-methylpyrrole (2.0 mmol) in 5 mL solvent at around 40 °C in a 350-nm Rayonet photoreactor for 4 h.

[b]GC yield with biphenyl as internal standard

[c]Reaction performed with 1:1 ratio of mercurial and *N*-methylpyrrole.

[d]20 mL solvent used.

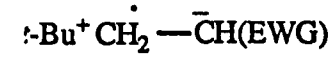
[e]Yield based on two equivalents of benzoylmethyl radicals from each equivalent of $(PhCOCH_2)_2Hg$.

iminium salt loses a proton to regain aromaticity and gives the substitution product.

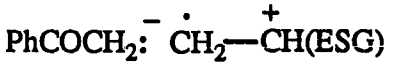
The results show that the yield of **13** is rather low and considerable amount of acetophenone and 1,4-diphenyl-1,4-butanedione (**2**) is formed. It was thought that the proton lost by the iminium ion (Scheme III) is probably responsible for the loss of some mercurial via an electrophilic attack[5] of the proton on $PhCOCH_2HgCl$ to form $PhCOCH_3$. The reaction was therefore performed in the presence of a base Li_2CO_3 to trap the proton. The base did reduce the amount of $PhCOCH_3$ but did not improve the yield of **13**. The reaction performed with reduced concentration of reactants in presence of Li_2CO_3, improved the yield slightly (entry 6, Table 1) and reduced the amount of acetophenone.

Reactions with Enamines

Enamines fail to undergo free radical substitution reactions with *t*-BuHgCl/hv but react readily with $PhCOCH_2HgCl$ upon irradiation. The low reactivity of electron rich systems such as enamines is apparently connected with the electron donating properties of *t*-Bu· radical where facile addition to electron poor alkenes occurs because of a polar contribution to the transition state described by **14** (EWG = electron-withdrawing group). Conversely addition of $PhCOCH_2$· to electron rich systems such as enamines should occur because of a stabilization from structure **15** (ESG = electron-supplying group).



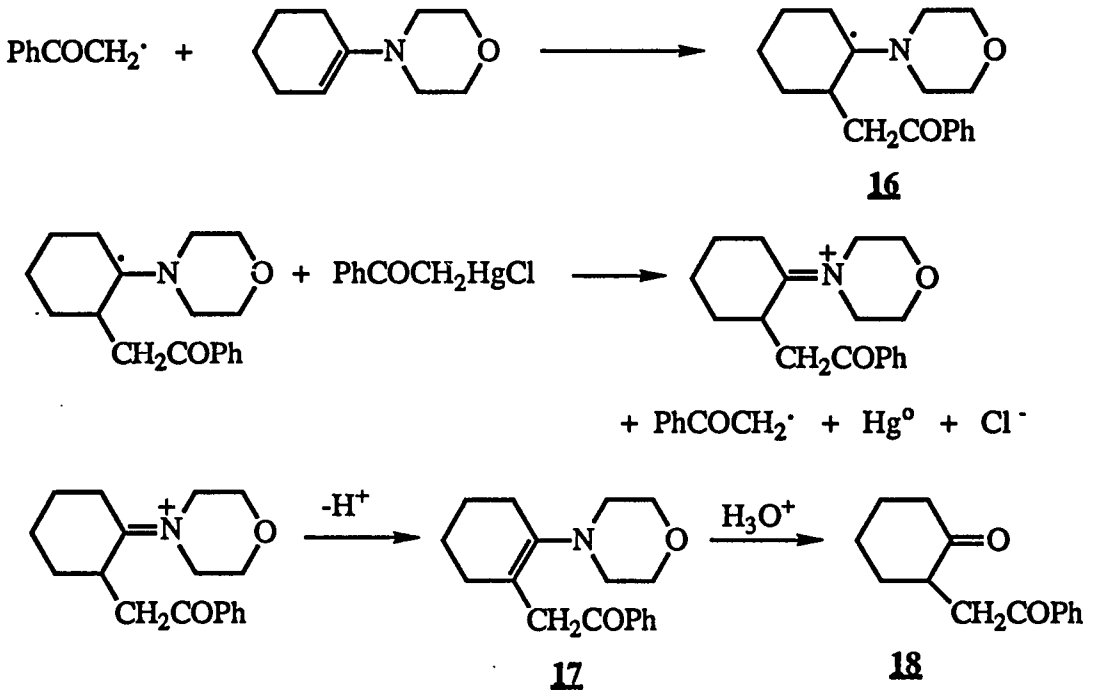
14



15

The photostimulated reactions of (benzoylmethyl)mercurials with *N*-morpholino-1-cyclohexene gave upon aqueous acid workup a 1,4-dicarbonyl compound **18** in good yield. When the reaction was analyzed by GCMS prior to aqueous acid treatment, it showed the presence of a substituted enamine **17**. Thus the possible mechanism for the formation of **18** in this reaction can be outlined as shown in Scheme IV.

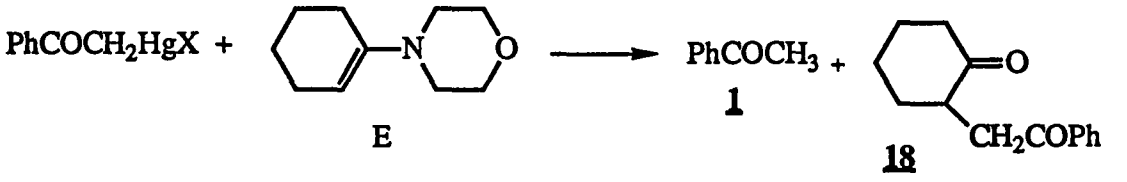
Scheme IV



Radicals of type **12** and **16** (which are intermediate adduct radicals in the reactions with pyrroles and enamines respectively) are known to have unusually low oxidation potentials with $E_{1/2}^{ox}$ in the range of -1V(SCE).[6] The irreversible half-wave reduction potentials of alkylmercury halides are typically more positive than -0.6V.[7] There is thus a

considerable driving force for **12** or **16** to undergo electron transfer to $PhCOCH_2HgCl$. The reactions of (benzoylmethyl)mercurials with *N*-morpholino-1-cyclohexene are summarized in Table 2.

Table 2. Photostimulated reactions of (benzoylmethyl)mercurials with *N*-morpholino-1-cyclohexene (E)



X	Equiv. of E	Base (equiv.)	Solvent	% Yield[b]	
				1	**18**[c]
Cl	1.0	-	Me_2SO	33	60
Cl	1.2	-	PhH/Me_2SO(9/1)	35	51
Cl	10.0	-	Me_2SO	38	59
Cl	1.2	Dabco (1.2)	Me_2SO	38	37
Cl	1.2	Li_2CO_3 (5)	Me_2SO	27	41
$PhCOCH_2$	2.0	-	Me_2SO	6[d]	10[d]

[a]Reaction of 0.5 mmol of $PhCOCH_2HgX$ with *N*-morpholino-1-cyclohexene in 5.0 mL solvent in a 350-nm Rayonet photoreactor at about 40 °C for 4 h.

[b]GC yield with biphenyl as internal standard.

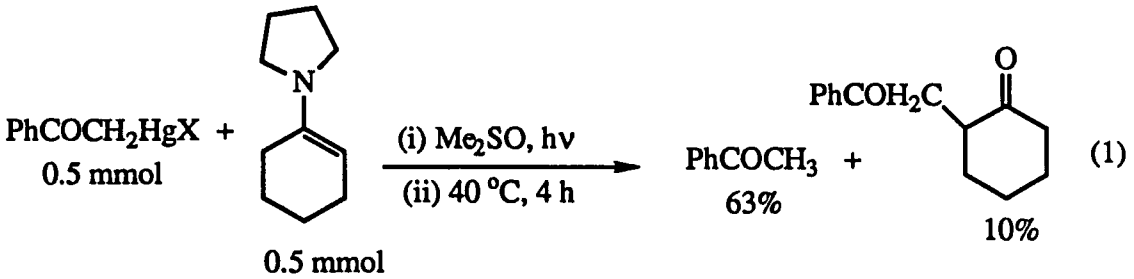
[c]After hydrolysis with 1M HCl.

[d]Yield based on two equivalents of benzoylmethyl radicals from each equivalent of $(PhCOCH_2)_2Hg$.

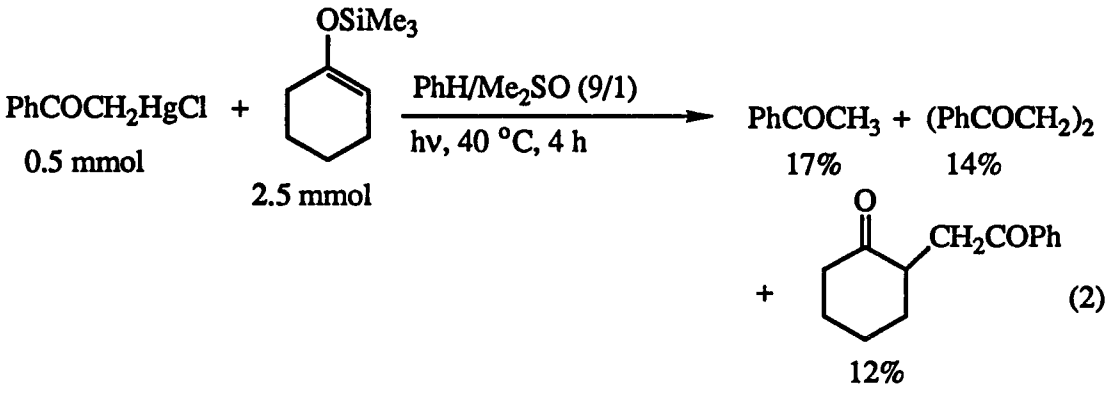
The reactions were fast and elemental mercury started separating from the reaction mixture immediately after the irradiation was started. These reactions were run only for 4 h since all the starting mercurial disappeared in less than 4 h as evidenced by ^1H NMR monitoring of the reaction mixture.

The yield of **18** was good even with a stoichiometric amount of enamine. Use of excess enamine did not improve the yield. The reactions were quite clean and acetophenone and **18** were the only products containing the $PhCOCH_2$ group that were observed. Diketone **2** was not observed indicating that the reaction probably took place via an efficient radical chain process. Use of bases such as Li_2CO_3 or Dabco to trap the proton lost from the cation (Scheme IV) in fact led to decreased yield of **18**. Me_2SO was again found to be the best solvent for this reaction. The bis-mercurial, $(PhCOCH_2)_2Hg$ gave very low yields of **18** suggesting that the electron transfer from adduct radical to the mercurial is probably not as efficient as in the case of $PhCOCH_2HgCl$.

The pyrrolidine enamine, *N*-pyrrolidino-1-cyclohexene however gave only 10% yield of **18** and 63% yield of acetophenone under similar conditions (reaction 1). The reaction also produced a number of other products in small amounts. The large amount of acetophenone obtained may be due to the S_N2 attack of this much more nucleophilic enamine[8] on the $PhCOCH_2HgCl$. This ionic reaction thus supercedes the slower radical reaction and acetophenone was the major product.



The trimethylsilyl enol ether of cyclohexanone also reacted with $PhCOCH_2HgCl$ upon photolysis to form the diketone **18** directly upon aqueous thiosulfate workup. However the yield was much lower (12%) than in the case of *N*-morpholino-1-cyclohexene (reaction 2).



(2)

CONCLUSION

Photostimulated reaction of (benzoylmethyl)mercurials with electron-rich *N*-methylpyrrole and enamines give benzoylmethyl substituted products via a S_{RN} type process. The reaction proceeds via easily oxidizable adduct radicals which transfer an electron to the mercurial to continue the chain. The reaction with *N*-methylpyrrole demonstrates an aromatic substitution by an electrophilic radical via an S_{RN} type process. The reaction with enamines provides a good method of producing 1,4-dicarbonyl compounds in good yield after hydrolysis of the substitution product.

EXPERIMENTAL SECTION

General Considerations

Analytical gas chromatography, ^{1}H and ^{13}C NMR spectroscopy, GCMS, high resolution mass spectroscopy were performed as discussed in Part I. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated by either flash column chromatography or preparative TLC technique as described in Part I. GC yields were determined using an internal standard (biphenyl) and were corrected with predetermined response factors.

Solvents and Reagents

Methanol was dried by distillation from $Mg(OMe)_2$, benzene was dried by distillation fron CaH_2. Dimethyl sulfoxide was dried as described in Part I. Reagents were purchased mainly from Aldrich and were used without further purification in most cases. *N*-methylpyrrole was distilled from CaH_2 prior to use. (Benzoylmethyl)mercury chloride and bis(benzoylmethyl)mercury were prepared as described in Part I.

Procedures and Compounds

N-Methyl-2-(benzoylmethyl)pyrrole (13)

A mixture of 0.50 mmol of $PhCOCH_2HgCl$ and 2.0 mmol *N*-methylpyrrole with or without a base in 5.0 mL deoxygenated Me_2SO was irradiated with stirring in a 350-nm

Rayonet photoreactor for 4 hours. The reaction mixture was then diluted with 50 mL CH_2Cl_2, a known amount of internal standard (biphenyl) added and was extracted three times with 15% $Na_2S_2O_3$ followed by water. The solvent was removed and a pure sample of **13** was obtained by column chromatography with hexane (90%)-ethyl acetate (10%) as eluent; ^1H NMR ($CDCl_3$) δ 3.55(s, 3H), 4.26(s, 2H), 6.05-5.95(m, 1H), 6.08(t, *J*=3 Hz, 1H), 6.61(t, *J*=2.4 Hz, 1H), 7.46(t, *J*=7.5 Hz, 2H), 7.57(t, *J*=7.5 Hz, 1H), 8.02(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.35, 136.21, 133.22, 128.58, 128.48, 125.27, 122.53, 108.90, 107.03, 37.07, 34.07; HRMS m/z Calcd for $C_{13}H_{13}NO$: 199.0997. Found: 199.0990.

Reaction of $PhCOCH_2HgCl$ with *N*-morpholino-1-cyclohexene to form 2-(benzoylmethyl)cyclohexanone (**18**)[9]

Photolysis (350-nm) of 0.50 mmol of $PhCOCH_2HgCl$ and 0.50 mmol of the enamine with or without the base with stirring for 4 hours in 5.0 mL deoxygenated Me_2SO produced after aqueous $Na_2S_2O_3$ workup (as described in Part I) a CH_2Cl_2 solution whose GCMS was consistent with the substitution of $PhCOCH_2$ for the vinyl hydrogen atom (compound **17**); GCMS m/z(relative intensity) 285(M^+, 8), 200(3), 180(100), 165(31), 105(12), 77(14). Hydrolysis of the extract with 20 mL of 1M HCl for 5 minutes yielded **18** and acetophenone (Table 2). Compound **18** was isolated by column chromatography using hexane (95%)-ethylacetate (5%): mp 42-44 °C; ^1H NMR ($CDCl_3$) δ 1.45(dq, *J*=3.9, 12.6 Hz, 1H), 1.58-1.95(m, 3H), 2.00-2.27(m, 2H), 2.45(q, *J*=4.5 Hz, 2H), 2.69(dd, *J*=5.7, 17.7 Hz, 1H), 3.18(sextet, *J*=6.3 Hz, 1H), 3.61(dd, *J*=6.6, 17.7 Hz, 1H), 7.46(t, *J*=7.5 Hz, 2H), 7.56(t, *J*=7.5 Hz, 1H), 7.99(d, *J*=7.2 Hz, 2H). The same ^1H NMR was observed for the diketone synthesized from the enamine and phenacyl bromide by ionic reaction. GCMS m/z(relative intensity) 216(M^+, 12), 159(3), 120(43), 105(100), 97(17), 77(42).

Reaction of $PhCOCH_2HgCl$ with *N*-pyrrolidino-1-cyclohexene

Photolysis (350-nm) of a mixture of 0.50 mmol $PhCOCH_2HgCl$ and 0.50 mmol *N*-pyrrolidino-1-cyclohexene in 5.0 mL deoxygenated Me_2SO for 4 hours gave after aqueous $Na_2S_2O_3$ workup and hydrolysis with 1M HCl a 10% yield of **18** and 63% yield of acetophenone.

Reaction of $PhCOCH_2HgCl$ with the trimethylsilyl enol ether of cyclohexanone

Photolysis (350-nm) of 0.50 mmol of $PhCOCH_2HgCl$ in the presence of 2.5 mmol of the enol ether for 4 hours in 5.0 mL deoxygenated PhH (90%)-Me_2SO (10%) gave after workup 12% **18**, 13% $PhCOCH_2CH_2COPh$ (**2**) and 14% acetophenone.

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PART III. REACTION OF (BENZOYLMETHYL)MERCURIALS WITH ALKENES: FORMATION OF α-TETRALONES

Reaction of (Benzoylmethyl)mercurials with alkenes: Formation of α-tetralones

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INTRODUCTION

Tetralines are a useful class of compounds, particularly for the synthesis of some pharmaceutically important drugs.[1] Much attention has been focussed on tetraline synthesis via free radical cyclizations.[2,3,4]

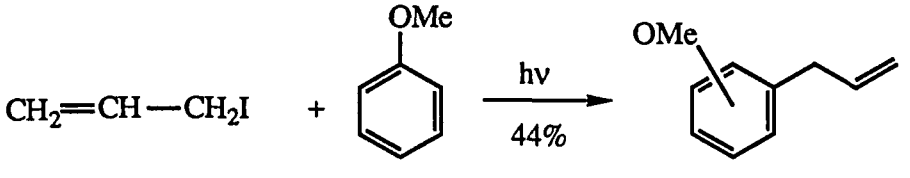
Aromatic substitution by radicals was first proposed by Hey and Waters[5] from their study of decomposition of diazonium salts in a variety of aromatic solvents. Since then arylation via homolytic aromatic substitution reactions has been developed because of its considerable synthetic utility.[6] Homolytic alkylation of aromatic compounds has been studied in much less detail than arylation.

Benzene behaves like an electron-rich alkene and therefore there is a weak interaction between the relatively high energy SOMO of nucleophilic alkyl radicals and the LUMO and HOMO of the benzene and its derivatives. For example Minisci[7] estimated the rate constants for attack upon benzene and anisole by butyl radicals to be 3.8×10^2 and 1.3×10^3 $Lmol^{-1}s^{-1}$ respectively at 79 °C in CH_3CN. The H-atom abstraction rates from C-H bonds of the alkyl groups by primary alkyl radicals are of the same order of magnitude as the addition to the benzene ring.[8] These rates are also only slightly slower than the addition to alkylated alkenes[9] and are hardly fast enough for synthetic applications involving a chain reaction (for chain reactions to occur the propogation steps require rate constants greater than 10^2 $Lmol^{-1}s^{-1}$).[10]

The nature of the attacking radical has a profound effect on the relative rates of addition to benzenes and H-atom abstraction from side chains. From the study of reactions of a series of radicals with toluene, Pryor[11] found that polar character of the radicals determines its addition/abstraction ratio. He obtained the following trend for the rate

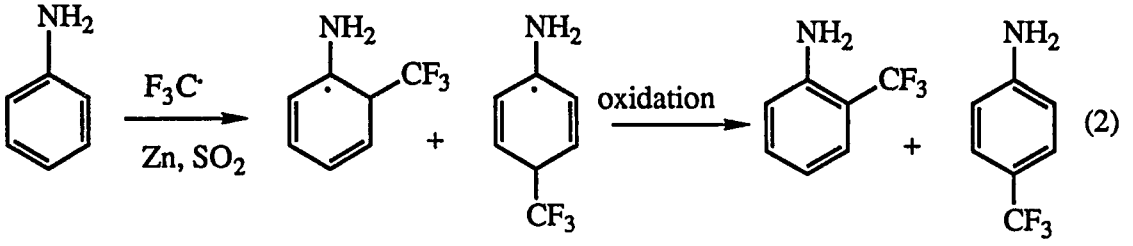
constant ratio $k_{add}/k_{abstraction}$ *p*-NO_2Ph· > *p*-BrPh· > CH_3·≅ Ph·≅H· > *i*-Pr· > *t*-Bu· indicating that radicals increasingly favor attack on benzene rings relative to attack on benzylic hydrogens [or CCl_4] as the radicals become increasingly electrophilic, with the *t*-Bu· radical completely failing to add to the aromatic ring of toluene. Aromatic homolytic substitution by nucleophilic alkyl radicals however takes place readily if the aromatic compounds are substituted by electron-withdrawing groups or if electron poor heterocyclic salts are used.

Intermolecular homolytic aromatic substitution by alkyl radicals has found little synthetic applicability because of lower addition rates and positional selectivities. For example allyl radicals give mixture of ortho, meta and para isomers with anisole (reaction 1)[12], while trifluoromethyl radicals give a mixture of ortho and para substitution products with aniline (reaction 2).[13]



(1)

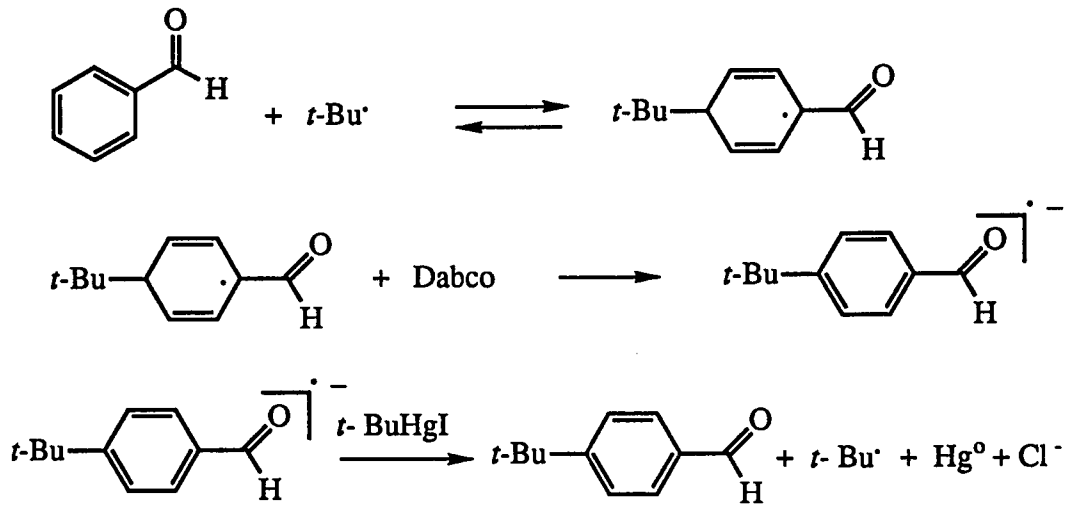
o : *m* : *p* = 48 : 16 : 46



(2)

The photostimulated reaction of *t*-BuHgl (6 equiv.) with benzaldehyde (1 equiv.) in presence of base Dabco (4 equiv.) however, gave exclusively *para*-alkylation product in 60% yield.[14] In this case the addition of *t*-Bu· radicals may be reversible and steric effect

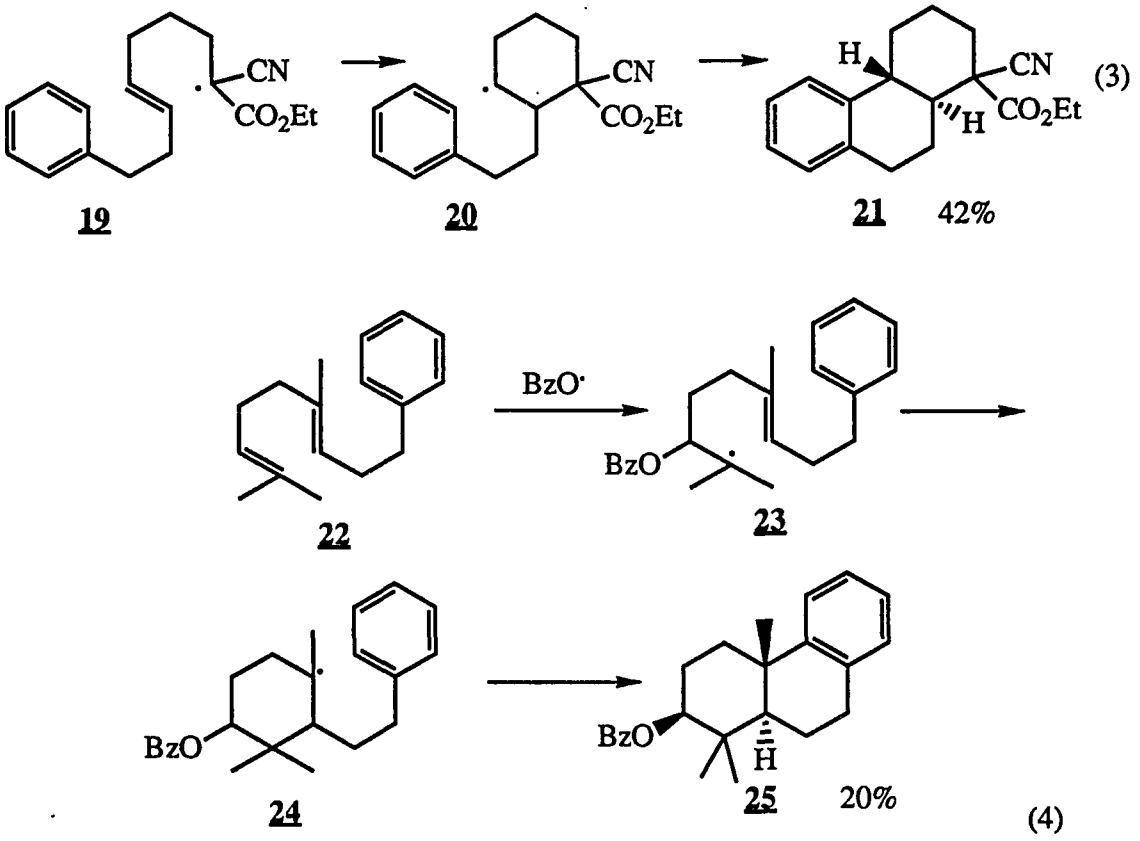
Scheme I



favors the para position.

This reaction apparently proceeds via a chain mechanism, which involves removal of a proton (Scheme I) from the adduct radical to form radical anion which transfers an electron to *t*-BuHgI to form the product and regenerate another *t*-Bu· radical to continue the chain.

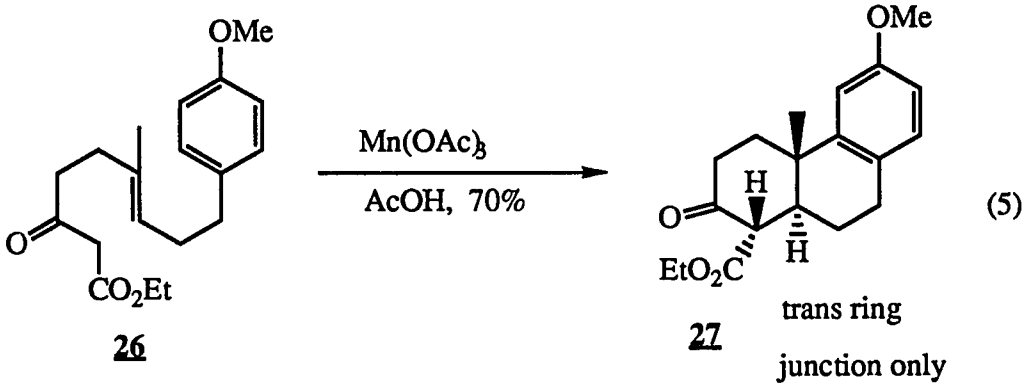
Radical cyclizations involving an intramolecular attack of a radical on the aromatic ring have sometimes been used in the synthesis of natural products. Julia[15] has described polycyclizations in which aromatic ring is attacked in the last step. For example radical **19** generated from the corresponding cyanoester by benzoyl peroxide in cyclohexane at 80 °C gave the cyclized trans product **21** (42% yield) in addition to the monocyclization product (reaction 3). Compound **22** when treated with benzoyl peroxide in refluxing benzene gave the trans compound **25** in 20% yield (reaction 4).



Snider[16] used the radical polycyclization strategy in the synthesis of (-)-podocarpic acid. Treatment of compound **26** with 2 equivalents of $Mn(OAc)_3$ in acetic acid gave compound **27**, which is a late intermediate in (-)-podocarpic acid synthesis, in 70% yield. Only a trans ring junction product was observed (reaction 5). It is not clear whether the intermediate cyclohexadienyl radical is oxidized by second equivalent of $Mn(OAc)_3$ to a cation which loses a proton to regenerate the aromatic ring or that the radical is oxidized to cation earlier in the cyclization sequence.

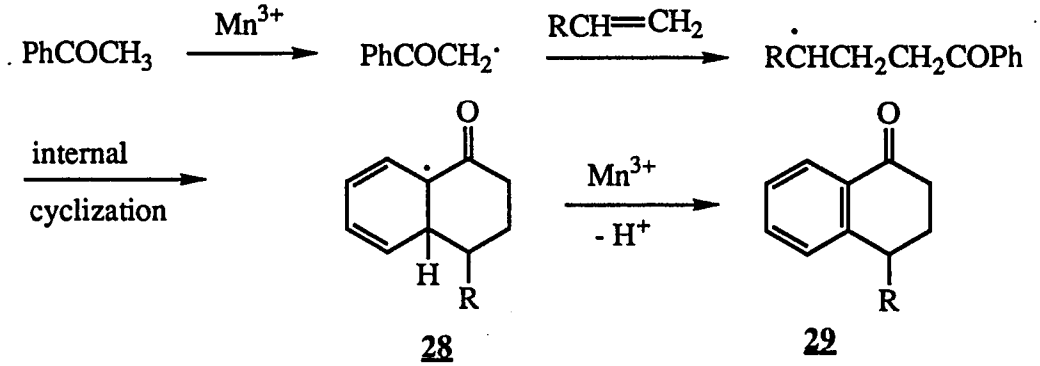
Synthesis of α-tetralones have been achieved by using intramolecular homolytic aromatic substitution reactions. Heiba[2] reported that reactions of olefins with ketones such as acetophenone in presence of manganic acetate gives α-tetralone **29** as the major product

in 50% yield based on Mn^{3+}. He explained the formation of **29** by mechanism shown in Scheme II.



26 **27** (5)

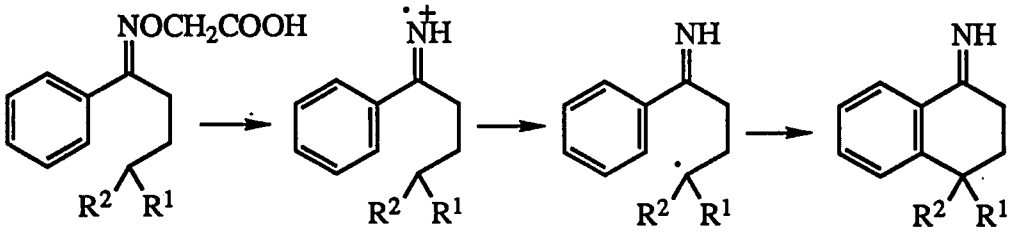
Scheme II



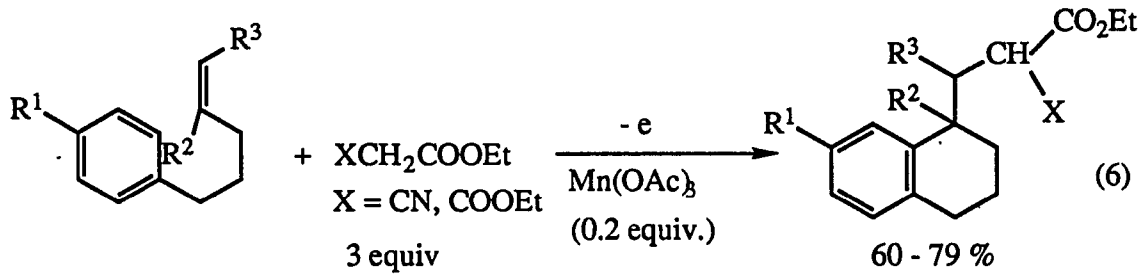
28 **29**

Oxidation of phenylalkylideneamino-oxyacetic acids with persulfate produced α-tetralones.[3] In this case the protonated iminyl radicals formed initially (Scheme III) abstract a γ-hydrogen from the alkyl chain and the resulting carbon radicals then cyclize on aryl ring.

Scheme III



Recently Mn^{3+}-mediated coupling/cyclization of 5-arylpent-1-enes with active methylene compounds to form tetralins by electrooxidation has been reported (reaction 6).[4]

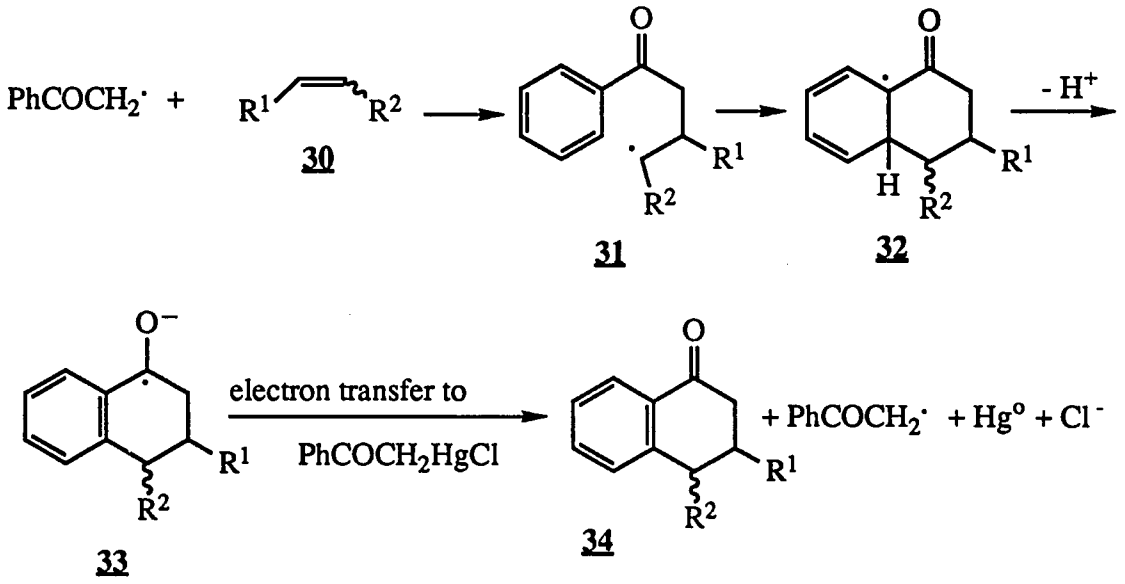


(6)

RESULTS AND DISCUSSION

Heiba[2] proposed in his synthesis of α-tetralones **29** that the reaction proceeds via an intermediate cyclohexadienyl radical **28**, which is oxidized by Mn^{3+}, followed by loss of proton to give **29**. It was thought that if the benzoylmethyl radical ($PhCOCH_2\cdot$) formed by the photolysis of either $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ would add to an alkene **30**, then the cyclization of benzoylpropyl radical **31** would produce the same cyclohexadienyl radical **32**. Radical **32** is expected to have a strong driving force to lose a proton and form an aromatic ketyl **33** which could induce a chain reaction since, **33** could serve as a powerful reducing agent for the (benzoylmethyl)mercurial to generate another $PhCOCH_2\cdot$ radical (Scheme IV).

Scheme IV



The rate of attack of the electrophilic $PhCOCH_2\cdot$ radical on the alkene was expected to be in the range of 10^6 $Lmol^{-1}s^{-1}$ (rate of addition of dicyanomethyl radical to 2-methyl-1-pentene is 1.6×10^6 $Lmol^{-1}s^{-1}$).[17] The adduct radical **31**, a nucleophilc radical could either cyclize to form the cyclohexadienyl radical **32** or abstract hydrogen atoms to form saturated product $PhCOCH_2CH(R^1)CH_2R^2$ (**35**). The rate of cyclization of radical **31** has been calculated[2] to be about 3×10^5 s^{-1}. This comparatively high rate of cyclization is probably due to stabilization of the cyclohexadienyl radical intermediate **32** by the carbonyl group.

Two methods were used to produce the $PhCOCH_2\cdot$ radical for this reaction. One method was photolysis of either $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$, which forms $PhCOCH_2\cdot$ radicals by homolysis of the carbon-mercury bond.

The second method was somewhat similar to the method developed by Minisci[18] which uses silver(I) and persulfate to generate alkyl radicals from the corresponding carboxylic acids (Scheme V).

Scheme V

$$S_2O_8^{2-} + Ag^+ \longrightarrow SO_4^{\cdot -} + SO_4^{2-} + Ag^{2+}$$

$$SO_4^{\cdot -} + Ag^+ \longrightarrow SO_4^{2-} + Ag^{2+}$$

$$RCOOH + Ag^{2+} \longrightarrow RCO_2^{\cdot} + H^+ + Ag^+$$

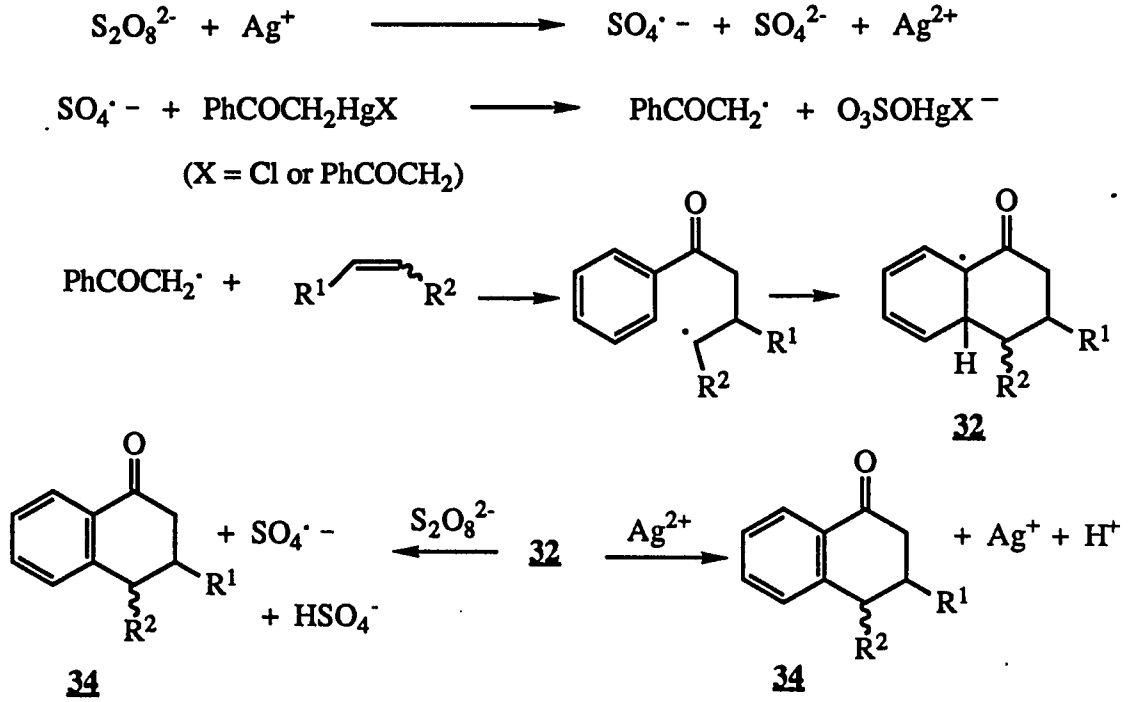
$$RCO_2^{\cdot} \longrightarrow R^{\cdot} + CO_2$$

In this second method the mercurial $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ was mixed with silver(I) and persulfate and was allowed to react with the alkenes in the dark or

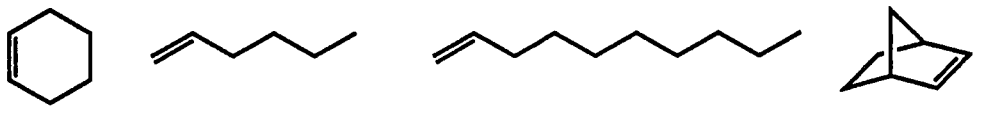
in room light. The following sequence of events was expected to produce the α-tetralone via $PhCOCH_2$· radical in this reaction mixture (Scheme VI).

It was expected that SO_4·⁻ would attack the mercurial to produce a $PhCOCH_2$· radical, which would produce the cyclohexadienyl radical **32** as described before (Scheme IV). This intermediate **32** could now probably be oxidized by either Ag^{2+} or by electron transfer to the $S_2O_8^{2-}$ present in the reaction mixture. Loss of proton was then expected to produce the α-tetralone **34**. In the present study $AgNO_3$ was used as the Ag^+ source and $K_2S_2O_8$ was used as the source of $S_2O_8^{2-}$ ion.

Scheme VI



Four different alkenes were studied using the two methods described above. Cyclohexene (36), which is a 1,2-disubstituted alkene, represents a somewhat sterically hindered alkene. 1-Hexene (37) and 1-decene (38), represent unhindered terminal alkenes, while norbornene (39), which is a bicyclic alkene, represents an alkene which has a reactive double bond due to the strain induced by the bicyclic structure.



36 37 38 39

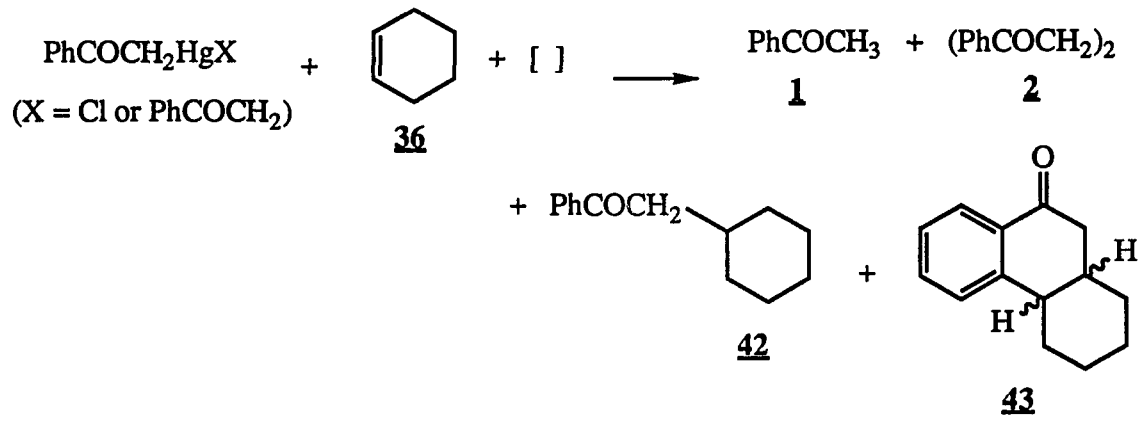
All the reactions of $PhCOCH_2HgCl$ and $(PhCOCH_2)_2Hg$ under photolytic conditions were run for eight hours to ensure complete homolysis of all the starting mercurials even in cases where it is a non-chain reaction. (Unimolecular homolytic decomposition of both these mercurials was complete in the absence of any other substrate in less than five hours under these reaction conditions.)

The reactions of $PhCOCH_2HgX$ (X = Cl or $PhCOCH_2$) with cyclohexene under various reaction conditions are summarized in Table 1. The results show that the yield of α-tetralone 43 is poor and a large amount of uncyclized product 42 always accompanies the α-tetralone.

The major factor responsible for the poor yield of 43 could be the abstraction of allylic H-atoms of cyclohexene by the $PhCOCH_2\cdot$ (due to slow rate addition of $PhCOCH_2\cdot$ to cyclohexene) and by the intermediate adduct radical formed by the attack of $PhCOCH_2\cdot$ on cyclohexene.

The cyclized product 43 is obtained as an inseparable mixture of two ring junction isomers in the ratio of approximately 6:1. The ^1H NMR of this mixture was too complex

Table 1. Reaction of $PhCOCH_2HgX$ with cyclohexene under various conditions[a]



Molar equivalents	Base	Solvent	% yield[b]			
$PhCOCH_2HgX$: **36** : $AgNO_3$: $K_2S_2O_8$	(equiv.)		**1**	**2**	**42**	**43**[c]
1(X = Cl) : 5 : 0 : 0	-	Me_2SO	45	tr	7	14
1(X = Cl) : 5 : 0 : 0	-	PhH	47	tr	13	11
1(X = Cl) : 5 : 0 : 0	-	PhH/Me_2SO (9/1)	26	14	3	5
1(X = Cl) : 5 : 0 : 0	$NaHCO_3$ (5)	Me_2SO	28	0	19	21
1(X = Cl) : 5 : 1 : 2	-	Me_2SO[d]	30	tr	15	22
1(X= CH_2COPh) : 10 : 1 : 2	-	Me_2SO[e]	38[f]	4[f]	13[f]	12[f]

[a]Reaction of 0.25 mmol $PhCOCH_2HgCl$ in 2.5 mL solvent in 350-nm Rayonet photoreactor at around 40 °C for 8 h.

[b]GC yield using biphenyl as internal standard.

[c]Mixture of cis and trans ring junction products in approximately 1 : 6 ratio respectively.

Table 1. (Continued)

[d]Reaction mixture stirred in dark for 60 h.

[e]Reaction mixture stirred in room light for 48 h.

[f]Yields based on two equivalents of $PhCOCH_2\cdot$ radicals from each equivalent of $(PhCOCH_2)_2Hg$.

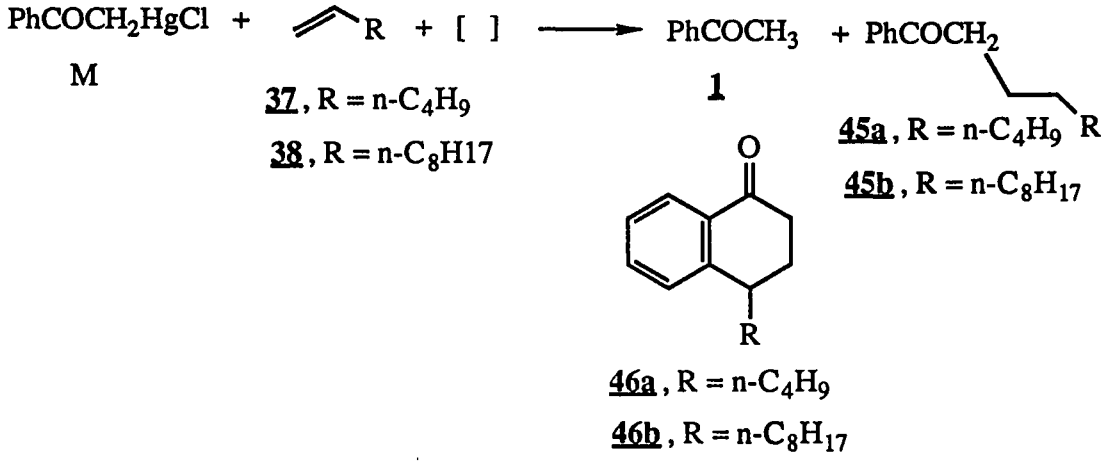
to assign the ring junction stereochemistry to these isomers. Cyclizations of this type reported so far[15,16] have resulted in trans ring junction product as the major or exclusive product. Therefore the major isomer was assumed to be the one having trans ring junction.

The reactions with sterically unhindered alkenes such as 1-hexene (**37**) and 1-decene (**38**) are summarized in Table 2. The reactions with norbornene (**39**) are summarized in Table 3.

The reaction of (benzoylmethyl)mercurials with terminal alkenes such as 1-hexene and 1-decene (Table 2) gave much better yield of α-tetralone derivatives (**46a,b**) than in the case of cyclohexene (Table 1). The amount of uncyclized products **45a,b** in these reactions was relatively low as compared to that in case of cyclohexene which is probably due to either faster rate of cyclization of the intermediate benzoylpropyl radical **31** (R^1=H, R^2=Bu or octyl) or a relatively slower rate of H-abstraction by **31** due to smaller number of allylic hydrogens in the alkene. The amount of 1,4-diphenyl-1,4-butanedione (**2**) obtained (due to radical-radical coupling of two $PhCOCH_2\cdot$ radicals) was in the range of 2-3% in case of $PhCOCH_2HgCl$ and about 4-5% in case of $(PhCOCH_2)_2Hg$ indicating a faster rate of attack on the terminal double bond than in case of 1,2-disubstituted alkene cyclohexene.

It is known that (benzoylmethyl)mercurials undergo electrophilic attack by H^+ readily to give $PhCOCH_3$.[19] It was therefore thought that perhaps the proton lost by **32**

Table 2. Reaction of $PhCOCH_2HgCl$ (M) with 1-alkenes under various conditions[a]



Molar equivalents	Base	Solvent	Product (% yield[c])		
M : 37 or 38 : A[b] : P[b]	(equiv.)		1	45a or b	46a or b
1 : 37 (5) : 0 : 0	-	Me_2SO	27	45a(5)	46a(43)
1[d] : 37 (5) : 0 : 0	-	Me_2SO	19[e]	45a(3)[e]	46a(29)[e]
1 : 37 (5) : 0 : 0	-	CH_3CN	22	45a(5)	46a(19)
1 : 37 (5) : 0 : 0	Dabco(1)	Me_2SO	28	45a(7)	46a(14)
1 : 37 (5) : 0 : 0	DTBP[b](1)	PhH/Me_2SO (9/1)	14	45a(7)	46a(30)
1 : 37 (5) : 0 : 0	Li_2CO_3(5)	Me_2SO	11	45a(12)	46a(32)
1 : 37 (5) : 1 : 1	-	Me_2SO[f]	29	45a(4)	46a(47)
1 : 37 (5) : 1 : 2	-	Me_2SO[g]	10	45a(6)	46a(49)
1 : 37 (5) : 1 : 1	Li_2CO_3(5)	Me_2SO[f]	49	45a(0)	46a(14)
1 : 38 (5) : 0 : 0	-	CH_3CN	14	45b(22)	46b(24)

Table 2. (continued)

1 : **38** (5) : 0 : 0	-	PhH/Me_2SO (9/1)	34	**45b**(17)	**46b**(44)
1 : **38** (5) : 1 : 2	-	Me_2SO[g]	11	**45b**(3)	**46b**(51)

[a]Reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL solvent in 350-nm Rayonet photoreactor at about 40 °C for 8 h.

[b]A = $AgNO_3$, P = $K_2S_2O_8$, DTBP = 2,6-Di-*tert*-butylpyridine.

[c]GC yield with biphenyl as internal standard.

[d]Reaction using 0.25 mmol of $(PhCOCH_2)_2Hg$ as the source of $PhCOCH_2\cdot$ radicals.

[e]Yields based on 2 equivalents of $PhCOCH_2\cdot$ radicals from one equivalent of $(PhCOCH_2)_2Hg$.

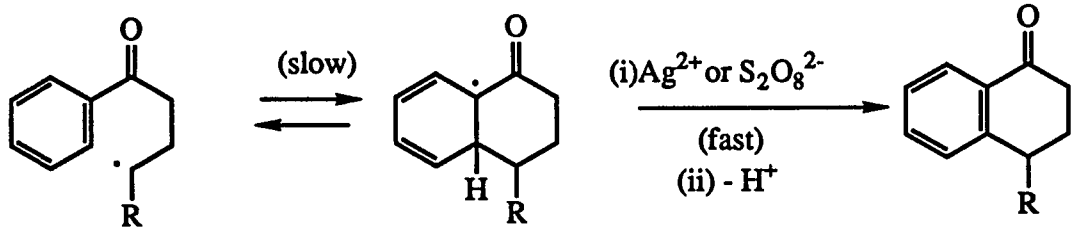
[f]Reaction mixture stirred in dark for 60 h.

[g]Reaction mixture stirred in room light for 48 h.

(Scheme IV) causes some loss of $PhCOCH_2HgX$ (X = Cl or $PhCOCH_2$) by formation of $PhCOCH_3$. The reaction was therefore studied in presence of some bases such as Dabco, 2,6,-di-*tert*-butylpyridine (DTBP) and Li_2CO_3. All these bases failed to increase the yield of α-tetralone derivatives **46a,b**. In fact Dabco reduced the yield of **46a,b** considerably.

The reactions performed using $Ag^+/S_2O_8^{2-}$ system gave moderately good yields. Use of Li_2CO_3 in this system to neutralize the proton lost in the conversion of **32** (R^1=H, R^2=n-C_4H_9) to **46a** actually led to a considerable decrease in the yield of **46a**. The comparatively smaller amount of uncyclized product obtained in this system probably suggests that the cyclization step is reversible and in this case the cyclohexadienyl radical is rapidly oxidized either by Ag^{2+} or $S_2O_8^{2-}$ before it can revert to open chain form (Scheme VII).

Scheme VII



R = n-C_4H_9 or n-C_8H_{17}

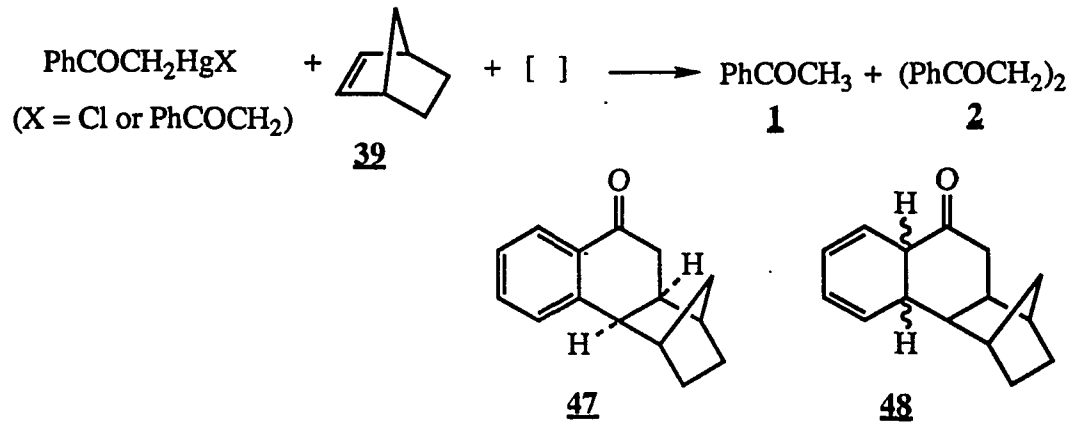
Reactions of $PhCOCH_2HgX$ (X = Cl or CH_2COPh) with norbornene (**39**) (Table 3) gave somewhat different results. Along with the α-tetralone **47**, product **48** was obtained, which was a dihydro derivative of **47**.

In these reactions the amount of uncyclized saturated product **49** was observed in very small amounts (3-4%). In all cases only one isomer of **47** was obtained making this reaction completely stereoselective. Addition of a radical to the double bond of norbornene is known to favor an exo attack. For example photoaddition of PhSH to norbornene gives cis-exo product (reaction 7).[20]

(7)

The attack of $PhCOCH_2\cdot$ is therefore from the exo side to generate the adduct radical **50**. The rate of inversion of configuration of the 2-norbornyl radical is estimated[21] to be greater than 10^5 s^{-1} at 25 °C making it a faster process than cyclization. The adduct radical will cyclize via the exo face to give the isomer **47** stereoselectively.

Table 3. Reaction of $PhCOCH_2HgCl$ and $(PhCOCH_2)_2Hg$ with norbornene[a]



Molar equivalents	Base	Solvent	% Yield[b]			
$PhCOCH_2HgX$: 39	(equiv.)		1	2	47	48
1 (X=Cl) : 5	-	Me_2SO	12	tr	32	13
1 (X=Cl) : 5	-	PhH/Me_2SO (9/1)	4	3	43	6
1 (X=Cl) : 5	-	CH_3CN	7	3	43	9
1 (X=Cl) : 5	Dabco(1)	Me_2SO	39	0	20	0
1 (X=Cl) : 5	DTBP[c](1)	Me_2SO	3	0	5	0
1 (X=Cl) : 5	DTBP[c](1)	PhH/Me_2SO (9/1)	0	0	55	tr
1 (X=Cl) : 5	Li_2CO_3(5)	Me_2SO	0	0	28	0
1 (X=Cl) : 5	-	Me_2SO[d]	33	0	11	0
1 (X=CH_2COPh):5	-	Me_2SO	49[e]	2[e]	13[e]	tr
1 (X=CH_2COPh):5	-	PhH/Me_2SO (9/1)	13[e]	4[e]	29[e]	6[e]
1 (X=CH_2COPh):5	-	Me_2SO[d]	53[e]	tr	11[e]	tr

[a]Reaction of 0.25 mmol $PhCOCH_2HgX$ in 2.5 mL solvent in a 350-nm Rayonet photoreactor for 8 h.

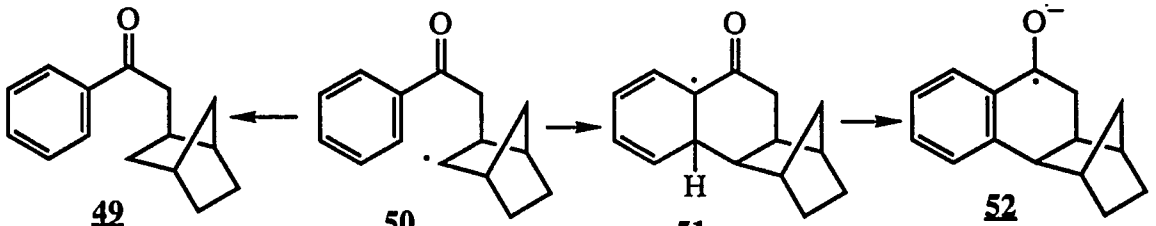
Table 3. (Continued)

[b]GC yield with biphenyl as internal standard.

[c]DTBP = 2,6-Di-*tert*-butylpyridine.

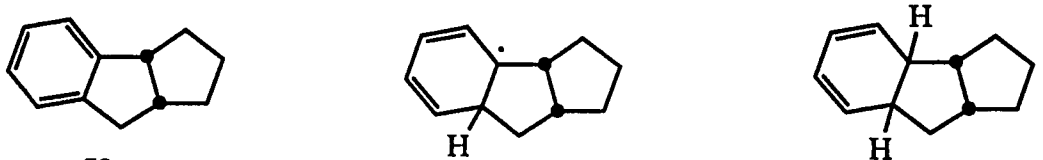
[d]Reaction mixture stirred in presence of 1 equiv. $AgNO_3$ and 2 equiv. $K_2S_2O_8$ in room light for 48 h.

[e]Yield based on two equivalents of $PhCOCH_2\cdot$ radicals from each equivalent of $(PhCOCH_2)_2Hg$.



49 50 51 52

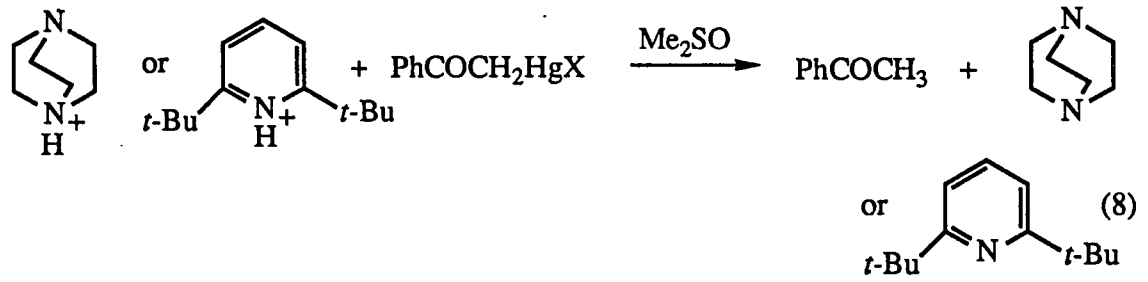
The dihydro compound **48** was obtained in variable amounts in different solvents in the absence of a base. It was thought that the intermediate cyclohexadienyl radical **51** has a lower tendency to lose a proton to form the ketyl, allowing some of these radicals to undergo disproportionation to form **48**. A similar dihydro compound has been proposed in the formation of, among other products, **53** (20% yield) during the reduction of cis-2-phenylcyclopentylmethyl bromide with 5 mole % Bu_3SnH or Et_3SiH.[22]



53 54 55

In this reaction it was believed that reaction of intermediate cyclohexadienyl radical **54** with stannane gives the dihydro derivative **55** which is oxidized during workup to give **53**.

In an effort to reduce or completely eliminate the dihydro derivative, the reaction was studied using various bases. These bases were expected to help pull out the proton from **51** facilitating the formation of ketyl **52** and thus eliminate the dihydro derivative **48**. The reactions in presence of bases such as Dabco, 2,6-di-*tert*-butylpyridine did completely eliminate the dihydro product **48**, but when Me_2SO was the solvent yield of **47** was considerably lower in case of base Dabco and 2,6-di-*tert*-butylpyridine. This is probably due to the fact that protonated forms of Dabco and 2,6-di-*tert*-butylpyridinium ions are still much too acidic in Me_2SO so that electrophilic attack of H^+ on $PhCOCH_2HgX$ (X = Cl or CH_2COPh) still takes place (reaction 8).



However when the reaction was carried out in PhH/Me_2SO (9/1) solvent combination, 2,6-di-*tert*-butylpyridine gave good yield of cyclized product **47** and no acetophenone was formed. Thus probably the acidity of the protonated pyridine base is much lower in this solvent system and reaction 8 does not take place. Dabco however did not give good yield in this solvent system probably due to its nucleophilic character (unlike the nonnucleophilic 2,6-di-*tert*-butylpyridine).

The organomercurials **56** were synthesized in hopes that cyclization of the adduct radicals **57** would occur by halogen atom eliminition to form **47** (Scheme VIII). The adduct radical **57** was expected to undergo intramolecular ipso attack on the aromatic ring to produce the cyclohexadienyl radical **58** which would then eliminate the halogen atom to give **47**. A competing intramolecular attack of **57** on the unsubstituted position of the aromatic ring to give **59** via the corresponding aromatic ketyl was also possible (Table 4).

Scheme VIII

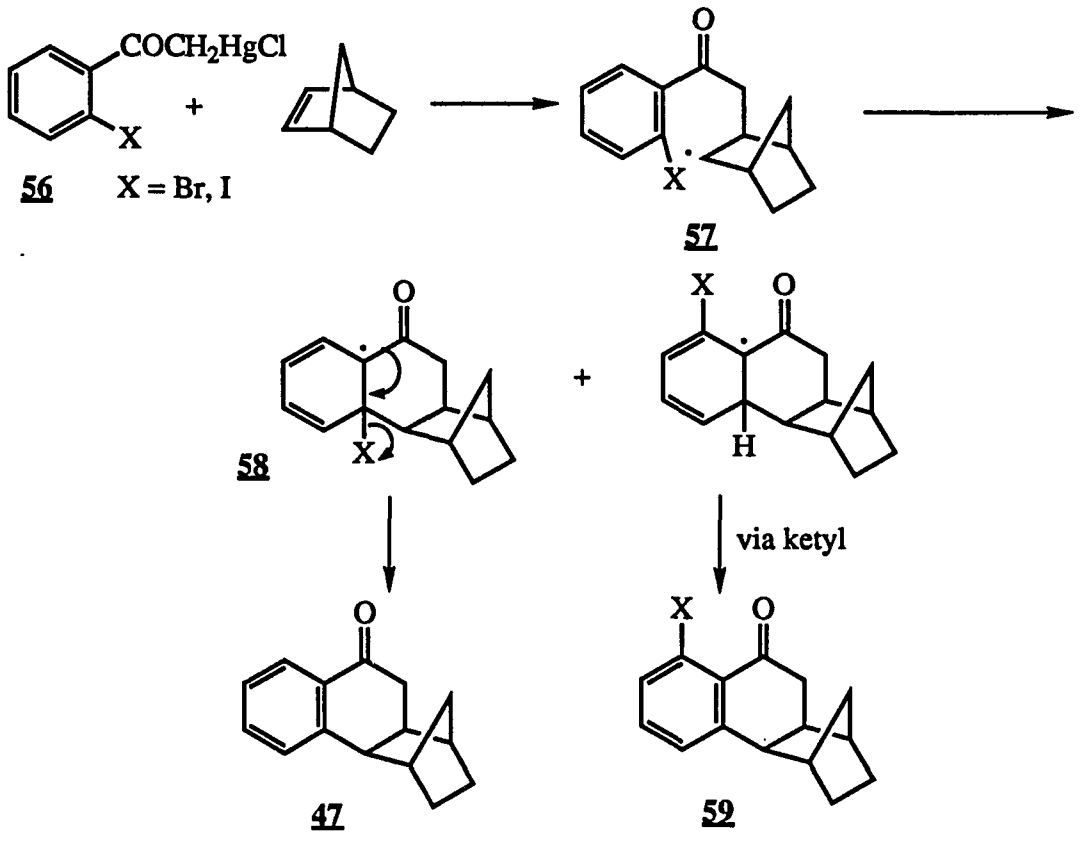
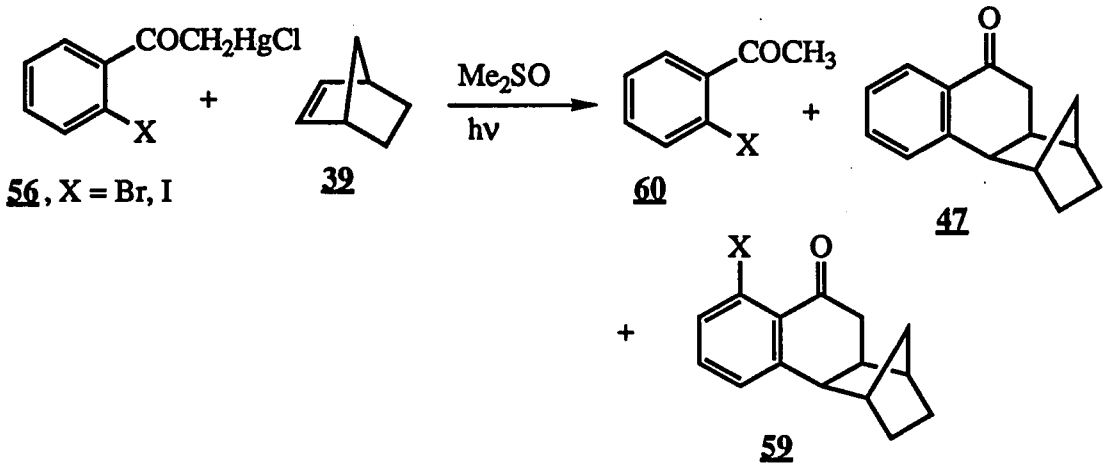


Table 4. Photostimulated reaction of (*o*-halobenzoylmethyl)mercury chlorides with norbornene[a]



56 (mmol)	39 (mmol)	% Yield[b]		
		60	47	59
0.25 (X=Br)	1.25	25 (X=Br)	8	28 (X=Br)
0.25 (X=I)	1.25	22 (X=I)	15	8[c] (X=I)

[a]Photostimulated reaction in 2.5 mL Me_2SO for 16 h.

[b]GC yield with biphenyl as internal standard

[c]Yield decreased with continued photolysis.

Ipso attack is known to occur when polar effects can intervene and stabilize the transition state of the addition.[23] Nucleophilic radicals easily add to the ipso positions of aromatic compounds containing electron withdrawing substituents. The relative rate of halogen displacements by nucleophilic cyclohexyl radicals has been found to be

F>I>Br>Cl by competitive elimination of halogen atoms by reaction of nucleophilic cyclohexyl radicals on aryldihalides.[24]

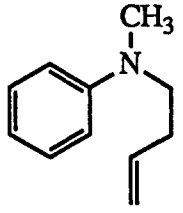
It can be seen from results in Table 4 that, although the process involving cyclization by elimination of halogen atom was demonstrated, the yield of the cyclized products and regioselectivity for the cyclization step were poor.

Reaction of (Benzoylmethyl)mercury chloride with Aromatic Alkenes: Competitive Cyclization Studies

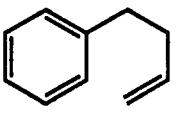
The attack of benzoylmethyl radical ($PhCOCH_2\cdot$) on an alkene to give ultimately a product arising from attack of the adduct radical on the aromatic ring, provided a unique opportunity to study the competitive cyclization of the adduct radical **61** when aromatic alkenes are used (Scheme IX).

The amounts of the two cyclization products formed were expected to reflect the relative cyclization rates with the two different aromatic rings.

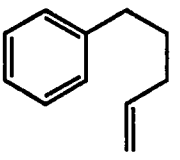
The reaction of $PhCOCH_2HgCl$ was studied in Me_2SO with the five different aromatic alkenes **64**-**68** shown below. In most cases a base such as Li_2CO_3 or Dabco was used since the reactions are generally cleaner than in the cases where base is not employed.



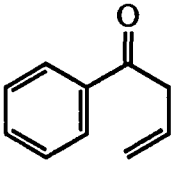
64



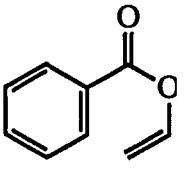
65



66



67



68

Scheme IX

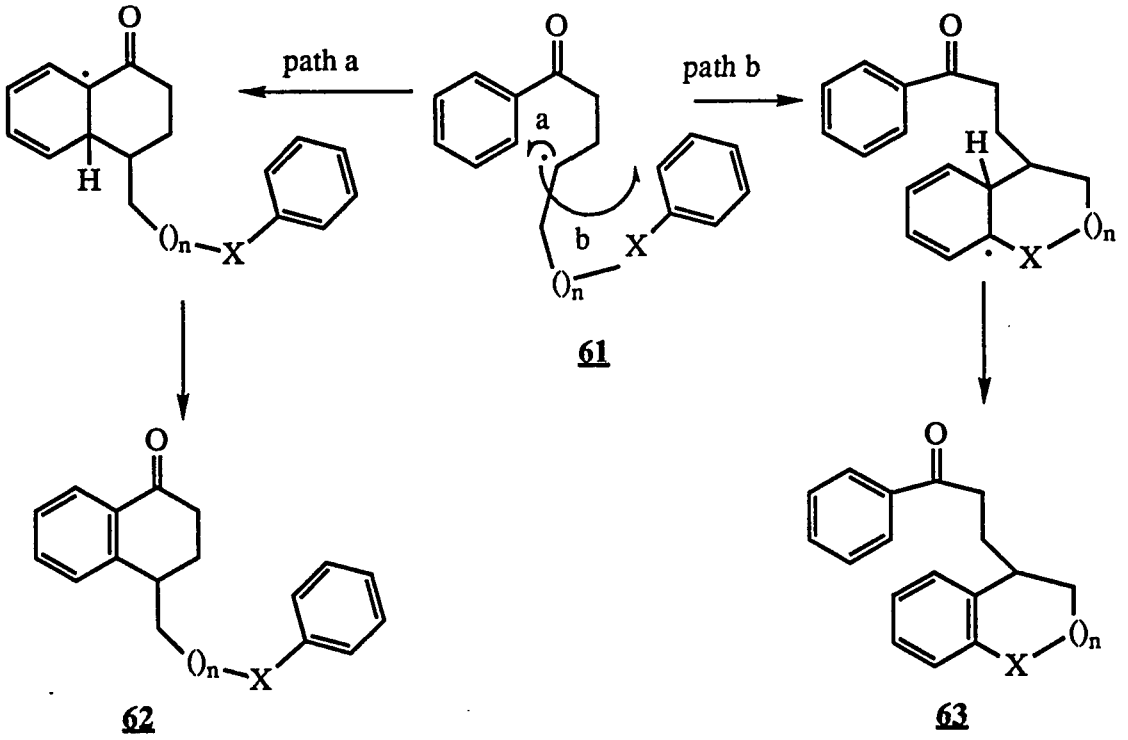
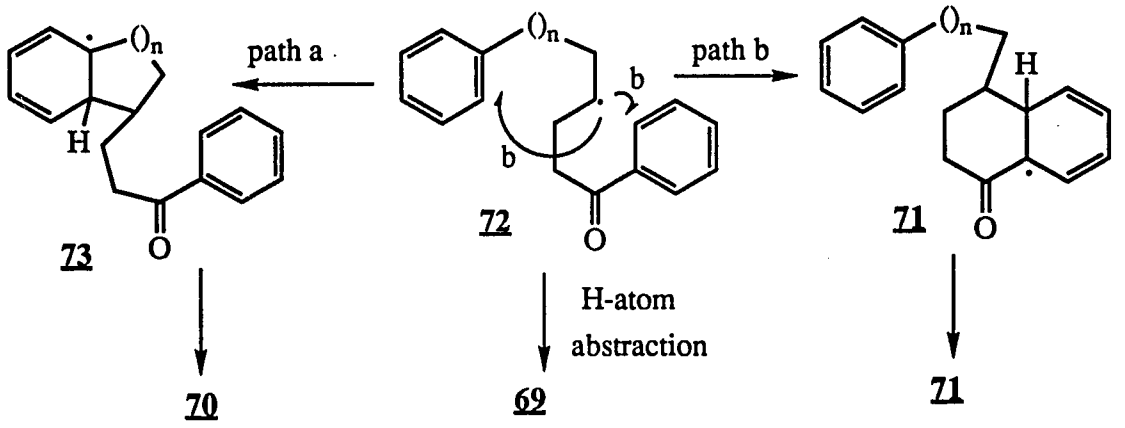


Table 5 shows the reactions of $PhCOCH_2HgCl$ with **65** and **66** in presence of a base.

In case of alkene **65** the adduct radical **72** (n = 1) can either cyclize with the aromatic ring of the alkene to form a five membered ring (path a, Scheme X) or with the aromatic ring of the benzoyl group to form a six-membered ring (path b). The absence of product **70** (n = 1) shows that path b is favored by a very large margin. The higher rate of cyclization of adduct radical **72** (n = 1) with the more electron deficient aromatic ring of the benzoyl group and the facile pathway for the formation of stable product **71** (n = 1) via the ketyl makes path b much more favorable than path a.

Scheme X

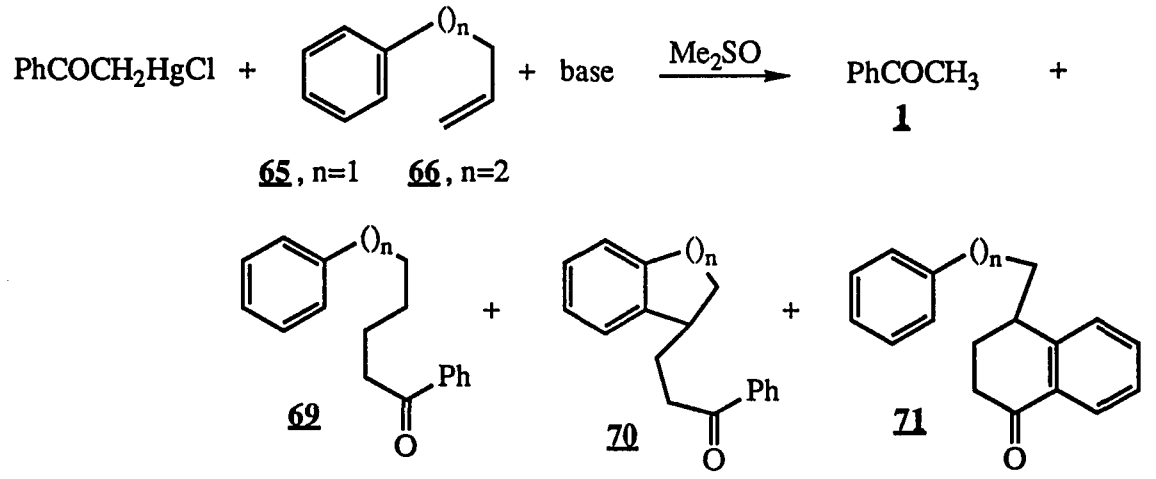


In the case of alkene 66, the adduct radical 72 (n = 2) can either cyclize with the aromatic ring of the alkene (path a, Scheme X) or the aromatic ring of the benzoyl group (path b) to form six membered rings. The formation of both products 70 (n = 2) and 71 (n = 2).suggest that the cyclization rates are of the same order of magnitude in both cases. The larger proportion of 71 (n = 2) is consistent with the expected higher rate of cyclization with the more electron deficient aromatic ring. Radical 73 (n = 2) is converted to the stable product 70 (n = 2) probably via a H-atom abstraction by $PhCOCH_2\cdot$ radical from 73 (n = 2).

Reaction of $PhCOCH_2HgCl$ with 67 presented an interesting case where the adduct radical 74 could cyclize to form either a 5-memebered ring (path a, Scheme XI) or a 6-membered ring (path b) by cyclizing with equally electron deficient aromatic rings, thus providing a direct measure of the 5 vs 6 ring size forming tendencies via radical cyclization with aromatic ring in this system.

The observation of only 77 in this reaction (Table 6) suggests that five membered ring formation is strongly disfavored as compared to six-membered ring formation.[2] When

Table 5. Photostimulated reactions of $PhCOCH_2HgCl$ with 4-phenyl-1-butene (**65**) and 5-phenyl-1-pentene (**66**) in presence of base[a]



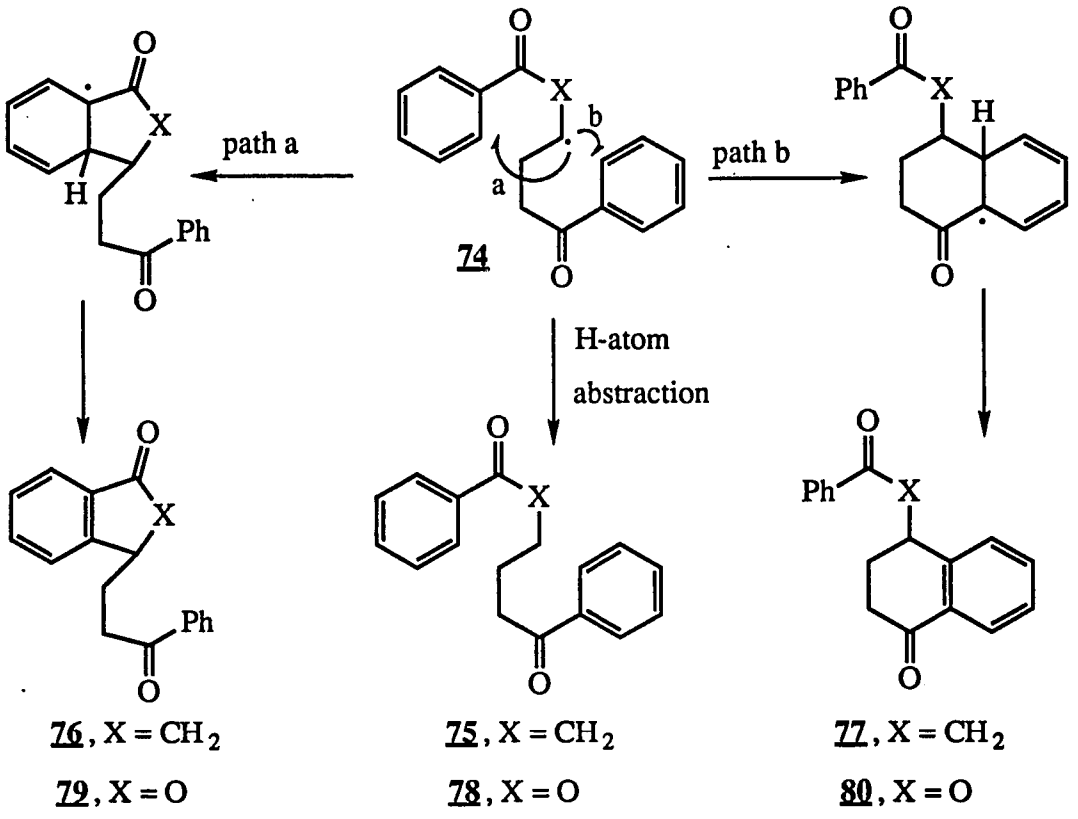
Alkene (mmol)	Base (mmol)	% Yield[b]			
		1	**69**	**70**	**71**
65 (1.25)	Li_2CO_3 (1.25)	5	14(n=1)	0(n=1)	30(n=1)
65 (1.25)	Dabco (0.50)	28	1 (n=1)	0 (n=1)	32(n=1)
66 (1.25)	Li_2CO_3 (1.25)	10	10(n=2)	9(n=2)	16(n=2)
66 (1.25)	Dabco (0.25)	33	1(n=2)	5(n=2)	18(n=2)

[a]Reaction of 0.25 mmol $PhCOCH_2HgCl$ in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at around 40 °C for 8 h.

[b]GC yield with biphenyl as internal standard.

the reaction was performed in presence of bases such as Li_2CO_3 and Dabco, the allylic ketone **67** isomerized completely to the conjugated α,β-unsaturated ketone and failed to give any addition products.

Scheme XI



A similar reluctance to form the 5-membered ring was found in case of reaction of $PhCOCH_2HgCl$ with the benzoate **68**.

The results with aniline derivative **64** were somewhat surprising. In this case the adduct radical **81** can cyclize with either an electron rich aromatic ring of the aniline derivative (path a, Scheme XII) or the electron deficient aromatic ring of the benzoyl group (path b). Considering the nucleophilic nature of the adduct radical **81**, it was expected that path b would be preferred to give predominantly **85**.

Table 6. Photostimulated reaction of $PhCOCH_2HgCl$ with allyl phenyl ketone (67), vinyl benzoate (68) and *N*-methyl-*N*-butenyl aniline (64) in Me_2SO[a]

$$PhCOCH_2HgCl + \text{alkene} \xrightarrow[h\nu]{Me_2SO} [\ ]$$

Alkene (mmol)	Base (mmol)	% Yield[b] of 1	products (% yield[b])		
67 (1.25)	-	30	75 (11)	76 (0)	77 (16)
68 (1.25)[c]	-	13	78 (1)	79 (0)	80 (13)
64 (1.25)	Li_2CO_3(1.25)	17	86 (3)	84 (27)	85 (10)
64 (1.25)	Dabco(0.50)	52	86 (2)	84 (11)	85 (7)

[a]Reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at around 40 °C for 8 h.

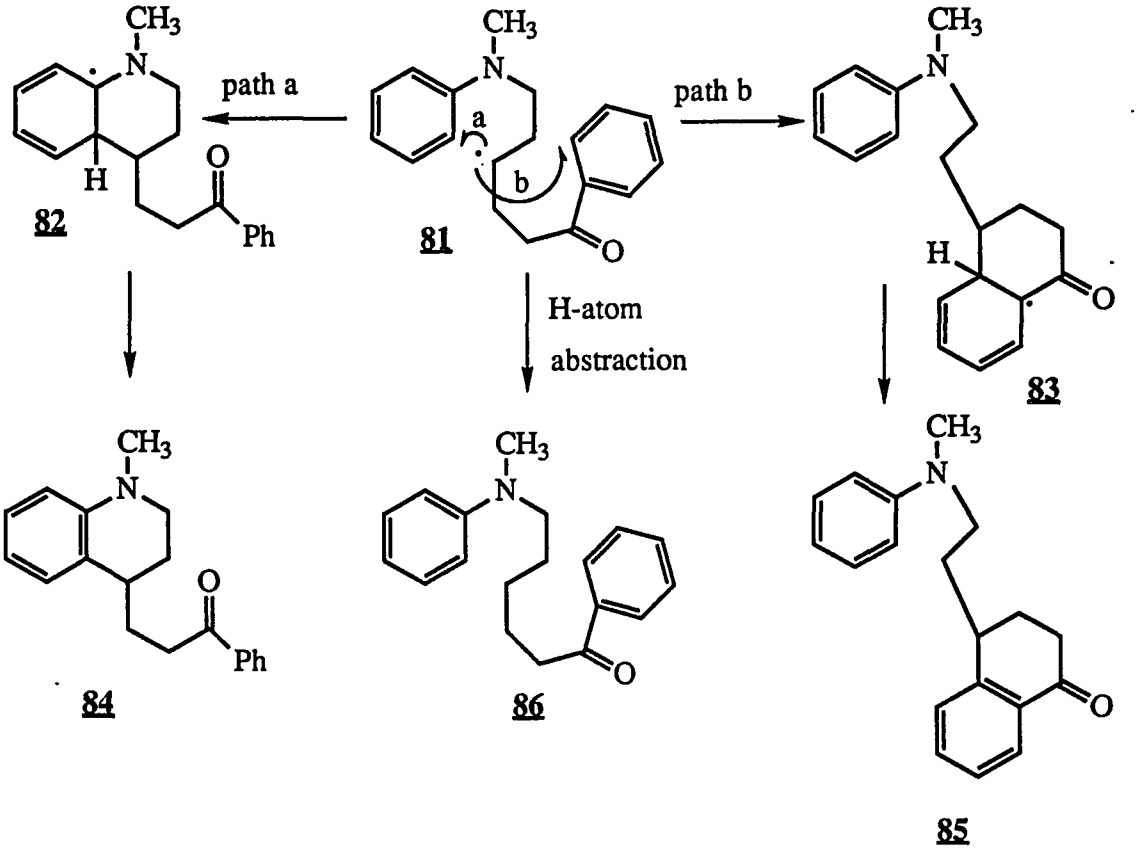
[b]GC yield with biphenyl as internal standard.

[c]Reaction carried out in 5 mL Me_2SO.

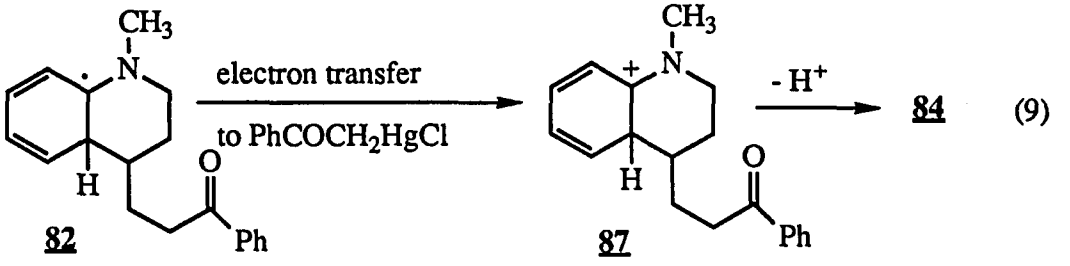
The intermediate cyclohexadienyl radicals 82 and 83 can be expected to follow different mechanisms to reach the final products. Radical 83 was expected to follow the usual course of losing a proton to form the ketyl and then electron transfer to $PhCOCH_2HgCl$ to give 85 as described earlier. On the other hand 82 was expected to first transfer an electron to $PhCOCH_2HgCl$ to form a cation 87 (stabilized by adjacent nitrogen) and then lose a proton to form 84 (reaction 9).

The reaction however gave 84 as the major product. This suggests that probably these cyclizations are reversible and in case of 82, the electron is transferred more rapidly than the reversal of the cyclization. The loss of a proton from 83 is probably much slower and therefore allows much more time for the radical 83 to equilibriate with the uncyclized

Scheme XII

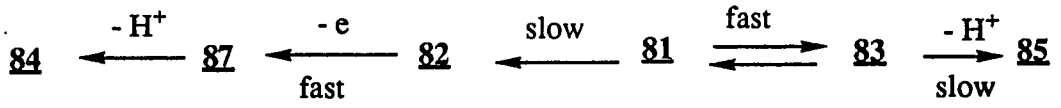


form (Scheme XIII). Another possible reason for the predominance of **84** may be that the stabilization of the radical center by adjacent nitrogen atom outweighs the electronically unfavorable cyclization of the nucleophilic radical with an electron rich aromatic ring.



(9)

Scheme XIII



Summarizing the results of the reactions of $PhCOCH_2HgCl$ with various aromatic alkenes it can be said that (1) In aromatic homolytic substitution six membered ring formation is favored over five membered ring. (2) Cyclization onto the aromatic ring of aniline is favored over the aromatic ring of the benzoyl group.

CONCLUSION

Reactions of benzoylmethyl radicals with simple alkenes represents a simple route to α-tetralone derivatives via cyclization of the adduct radicals with the aromatic ring. These reactions do not appear to be chain reactions and the intermediate cyclohexadienyl radicals do not seem to lose proton readily to form aromatic ketyls. Competitive cyclization studies with aromatic alkenes show a preference for a six-membered ring formation over five and provide some evidence for the reversibility of these cyclizations. Cyclization of the adduct radicals on the electron-rich aromatic ring of aniline was favored over electron deficient ring of the benzoyl group probably due to the ease of oxidation of the resulting α-amino radical or the stability accorded to the radical by the α-amino group.

EXPERIMENTAL SECTION

General Considerations

Analytical gas chromatography, ^{1}H and ^{13}C NMR spectroscopy, GCMS, high resolution mass spectroscopy and IR were performed as discussed in Part I. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated by either flash column chromatography on silica gel (kiesel gel, 230-400 mesh ASTM, purchased from EM reagents Co.) or by preparative TLC (silica gel) technique. GC yields were determined using an internal standard (biphenyl) and were corrected with predetermined response factors.

Solvents and Reagents

Acetonitrile and benzene were dried by distillation fron CaH_2. Dimethyl sulfoxide was dried as described in Part I. Reagents were purchased mainly form Aldrich and were used without further purification in most cases.

Procedures and Compounds

Preparation of starting materials

(Benzoylmethyl)mercury chloride and bis-(benzoylmethyl)mercury were prepared as described in Part I. (*o*-Bromobenzoylmethyl)mercury chloride was prepared from *o*-

bromoacetophenone by the same method[25]: mp 122-126 °C; ^{1}H NMR (Me_2SO-d_6) δ 3.01(s, 2H with ^{199}Hg satellites, *J*=330 Hz), 7.34(dt, *J*=1.5, 7.5 Hz, 1H), 7.43(dt, *J*=1.2, 7.5 Hz, 1H), 7.55-7.66(m, 2H). (*o*-Iodobenzoylmethyl)mercury chloride was also prepared by the same method[25] from *o*-iodoacetophenone: mp 99-100 °C (CH_2Cl_2-hexane); ^{1}H NMR (Me_2SO-d_6) δ 2.99(s, 2H with ^{199}Hg satellites, *J*=330 Hz), 7.15(t, *J*=7.5 Hz, 1H), 7.44(t, *J*=7.5 Hz, 1H), 7.58(d, *J*=7.5 Hz, 1H), 7.86(d, *J*=7.5 Hz, 1H). *N*-but-3-enyl-*N*-methylaminobenzene (64) was prepared by literature method;[26] ^{1}H NMR ($CDCl_3$) δ 2.27-2.36(m, 2H), 2.93(s, 3H), 3.38(br t, *J*=7.5 Hz, 2H), 5.00-5.14(m, 2H), 5.74-5.90(m, 1H), 6.65-6.72(m, 3H), 7.19-7.26(m, 2H). 4-Phenyl-1-butene (65) was prepared according to literature method;[27] ^{1}H NMR ($CDCl_3$) δ 2.37(br q, *J*=7.5 Hz, 2H), 2.70(t, *J*=7.5 Hz, 2H), 4.94-5.08(m, 2H), 5.78-5.93(m, 1H), 7.12-7.32(m, 5H). 5-Phenyl-1-pentene (66) was prepared from $C_6H_5CH_2CH_2MgBr$ and allyl bromide;[28] ^{1}H NMR ($CDCl_3$) δ 1.71(apparent pentet, *J*=7.5 Hz, 2H), 2.08(q, *J*=7.2 Hz, 2H), 2.61(t, *J*=7.8 Hz, 2H), 4.93-5.06(m, 2H), 5.75-5.90(m, 1H), 7.11-7.30(m, 5H). Allyl phenyl ketone (67) was prepared in 95% purity from allyl iodide and benzoyl chloride via allylmercury iodide;[29] ^{1}H NMR ($CDCl_3$) δ 3.76(td, *J*=1.5, 7.2 Hz, 2H), 5.17-5.26(m, 2H), 6.01-6.16(m, 1H), 7.46(t, *J*=7.2 Hz, 2H), 7.56(t, *J*=7.2 Hz, 1H), 7.96(d, *J*=7.2 Hz, 2H). Vinyl benzoate (68) was prepared from benzoic acid and vinyl acetate by a mercury catalysed transesterification reaction;[30] ^{1}H NMR ($CDCl_3$) δ 4.69(dd, *J*=1.5, 6.0 Hz, 1H), 5.06(dd, *J*=1.5, 13.8 Hz, 1H), 7.41-7.62(m, 4H), 8.10(d, *J*=7.2 Hz, 2H).

General procedure for the photostimulated reaction of (benzoylmethyl)mercurials with alkenes

The mercurial and the other solid reactants were placed in a dry pyrex test tube along with a magnetic stir bar and the solvent was added by a syringe through a rubber

septum fitted to the test tube. The mixture was deoxygenated by bubbling dry nitrogen through it for about 20 minutes and then previously deoxygenated alkene was added via a syringe through the septum. The mixture was then irradiated with stirring in a 350-nm Rayonet photoreactor maintained at about 40 °C for 8 hours.

General procedure for the reaction of (benzoylmethyl)mercurials with alkenes in presence of $AgNO_3$ and $K_2S_2O_8$

The mercurial and a magnetic stir bar were placed in a dry pyrex test tube fitted with a rubber septum and Me_2SO was added via a syringe through the septum. The solution was then deoxygenated by bubbling dry nitrogen for about 20 minutes and then $AgNO_3$ and $K_2S_2O_8$ were added quickly by opening the septum for a short time. After 5 minutes of further nitrogen bubbling, deoxygenated alkene was added via syringe and the reaction mixture was stirred in room light or dark (test tube wrapped in aluminum foil).

Isolation procedure

The reaction mixture was diluted with 50 mL CH_2Cl_2 in a separatory funnel, a known amount of internal standard (biphenyl) added and was extracted three times with 15% $Na_2S_2O_3$ solution followed by water. The CH_2Cl_2 layer was then dried over Na_2SO_4 and analyzed by GC or the solvent was removed and the products were isolated by column chromatography or preparative TLC. In most cases a mixture of solvents hexane : ethyl acetate in 98 : 2 ratio was used as eluant in flash column chromatography.

(Benzoylmethyl)cyclohexane (42)[31]

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.95-1.08(m, 2H), 1.12-1.33(m, 2H), 1.60-1.79(m, 4H), 1.90-2.05(m, 1H), 2.82(d, J=6.6 Hz, 2H), 7.45(t,

J=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.95(d, *J*=7.2 Hz, 2H); GCMS m/z(relative intensity) 202(M^+, 8), 120(100), 105(66), 77(41).

10-Phenanthrenone-4b,5,6,7,8,8a-hexahydro (trans-**43**) (major isomer)

This compound was isolated in about 83% purity as a part of an inseparable mixture containing the minor isomer (cis ring junction product); The ^1H NMR ($CDCl_3$) was very complex: δ 1.43-2.00(m, 8H), 2.31-2.72(m, 2H), 2.81-2.99(m, 2H), 7.29(t, *J*=7.2 Hz, 2H), 7.49(t, *J*=7.2 Hz, 1H), 8.02(d, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.06, 148.58, 133.62, 131.49, 128.35, 127.01, 126.39, 40.48, 39.76, 33.66, 30.03, 29.95, 25.22, 20.79; GCMS m/z(relative intensity) 200(M^+, 83), 185(8), 158(100), 144(26), 131(33), 115(42), 105(12), 77(18); HRMS m/z Calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1202.

(cis-**43**) (minor isomer)

This compound was identified by GCMS only; GCMS m/z(relative intensity) 200(M^+,100), 185(44), 158(81), 131(59), 115(45), 105(39), 91(20), 77(29).

1-Phenyl-1-octanone (**45a**)[32]

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.88(t, *J*=7.2 Hz, 3H), 1.10-1.50(m, 10H), 1.65-1.80(m, 2H), 2.96(t, *J*=7.2 Hz, 2H), 7.46(t, *J*=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.96(d, *J*=7.5 Hz, 2H); GCMS m/z(relative intensity) 204(M^+,6), 133(8), 120(81), 105(100), 77(50).

4-Butyl-1-tetralone (46a)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.92(t, *J*=6.9 Hz, 3H), 1.30-1.50(br s, 4H), 1.64-1.75(m, 2H), 1.99-2.13(m, 1H), 2.17-2.32(m, 1H), 2.51-2.63(m, 1H), 2.70-2.85(m, 1H), 2.86-2.97(m, 1H), 7.25-7.33(m, 2H), 7.48(t, *J*=7.2 Hz, 1H), 8.02(d, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.33, 148.53, 133.27, 131.79, 128.19, 127.22, 126.45, 37.94, 34.84, 34.34, 29.79, 26.63, 22.75, 14.01; GCMS m/z(relative intensity) 202(M^+, 29), 160(8), 145(100), 131(13), 117(36), 91(13), 77(7); HRMS m/z Calcd for $C_{14}H_{18}O$: 202.1358. Found: 202.1360.

1-Phenyl-1-dodecanone (45b)[33]

This compound was isolated as a solid: mp 41-42 °C; ^{1}H NMR ($CDCl_3$) δ 0.88(t, *J*=6.6 Hz, 3H), 1.18-1.42(br s, 16H), 1.67-1.79(m, 2H), 2.96(t, *J*=7.2 Hz, 2H), 7.45(t, *J*=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.96(d, *J*=7.2 Hz, 2H); GCMS m/z(relative intensity) 260(M^+, 6), 133(10), 120(100), 105(68), 77(27).

4-Octyl-1-tetralone (46b)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.88(t, *J*=6.9 Hz, 3H), 1.15-1.55(m, 12H), 1.63-1.73(m, 2H), 2.01-2.11(m, 1H), 2.17-2.31(m, 1H), 2.57(td, *J*=5.1, 18.0 Hz, 1H), 2.77(ddd, *J*=5.1, 11.7, 18 Hz, 1H), 2.87-2.96(m, 1H), 7.27-2.33(m, 1H), 7.48(t, *J*=7.5 Hz, 1H), 8.02(d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.39, 148.60, 133.30, 131.84, 128.22, 127.26, 126.48, 37.99, 34.88, 34.68, 31.87, 29.72, 29.54, 29.29, 27.64, 26.65, 22.66, 14.08; GCMS m/z(relative intensity) 258(M^+, 22), 216(4), 187(4), 159(5), 145(100), 131(11), 117(28), 105(17), 77(11).

2,3,4,4a,10,10a-Hexahydro-(1α,4α,4aα,10aα)-1H-1,4-methanophenanthren-9-one (47)

It was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.01(d, *J*=10.8 Hz, 1H), 1.26(d, *J*=10.8 Hz, 1H), 1.34-1.44(m, 1H), 1.48-1.74(m, 3H), 2.10(br s, 1H), 2.24(br s, 1H), 2.30-2.40(m, 1H), 2.50(dd, *J*=4.2, 15.6 Hz, 1H), 2.72(dd, *J*=9.0, 15.6 Hz, 1H), 3.05(d, *J*=8.4 Hz, 1H), 7.26(t, *J*=7.5 Hz, 1H), 7.32(d, *J*=7.5 Hz, 1H), 7.50(dt, *J*=1.5, 7.5 Hz, 1H), 7.78(dd, *J*=1.2, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.97, 145.43, 133.75, 133.27, 129.12, 125.79, 125.06, 46.89, 45.58, 44.79, 42.04, 39.44, 32.60, 30.00, 29.50; GCMS m/z(relative intensity) 212(M^+, 35), 170(8), 158(5), 145(92), 144(100), 128(14), 115(44), 77(8); HRMS m/z Calcd for $C_{15}H_{16}O$: 212.1201. Found: 212.1205.

Dihydro derivative of 47 (48)

This compound was identified by GCMS only; GCMS m/z(relative intensity) 214(M^+, 26), 213(26), 170(4), 145(11), 120(26), 105(100), 91(19), 77(27).

o-Bromo derivative of 47 (59, X = Br)

This compound was identified by GCMS only; GCMS m/z(relative intensity) 292(M^+, 36), 290(M^+, 37), 225(60), 224(88), 223(73), 222(78), 143(26), 128(21), 115(100).

o-iodo derivative of 47 (59, X = I)

This compound was identified by GCMS only; GCMS m/z(relative intensity) 338(M^+, 100), 271(67), 270(96), 144(20), 128(19), 127(7), 115(73).

1,6-Diphenyl-1-hexanone (69, n=1)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.35-1.49(m, 2H), 1.59-1.83(m, 4H), 2.62(t, *J*=7.5 Hz, 2H), 2.95(t, *J*=7.5 Hz, 2H), 7.12-7.21(m, 3H), 7.26(t, *J*=7.2 Hz, 2H), 7.44(t, *J*=7.5 Hz, 2H), 7.54(t, *J*=7.2 Hz, 1H), 7.94(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 200.30, 142.52, 137.02, 132.84, 128.51, 128.34, 128.22, 127.99, 125.60, 38.50, 35.78, 31.33, 28.99, 24.16; GCMS m/z(relative intensity) 252(M^+, 4), 234(5), 130(58), 120(84), 105(100), 91(38), 77(61).

4-(2-Phenylethyl)-1-tetralone (71, n = 1)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 2.00-2.09(m, 2H), 2.15(qd, *J*=5.1, 13.5 Hz, 1H), 2.31(tdd, *J*=4.5, 11.7, 13.8 Hz, 1H), 2.62(td, *J*=5.1, 18.5 Hz, 1H), 2.68-2.88(m, 3H), 2.95-3.03(m, 1H), 7.18-7.36(m, 7H), 7.50(t, *J*=7.5 Hz,1H), 8.05(d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.07, 147.92, 141.59, 133.36, 131.87, 128.42, 128.22, 128.16, 127.35, 126.66, 125.95, 37.49, 36.27, 34.81, 33.72, 26.60; GCMS m/z(relative intensity) 250(M^+, 28), 206(2), 159(100), 145(37), 131(25), 117(40), 115(39), 105(81), 92(90), 91(72), 77(30); HRMS m/z Calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1361.

1,7-Diphenyl-1-heptanone (69, n = 2)

This compound was identified by GCMS only due to separation problems; GCMS m/z(relative intensity) 266(M^+, 3), 248(3), 157(3), 144(35), 133(25), 120(93), 105(100), 91(46), 77(66).

1-(3-Oxo-3-phenylpropyl)tetralin (70, n = 2)

This compound was identified by GCMS only due to separation problems; GCMS m/z(relative intensity) 264(M^+, 2), 246(2), 144(100), 129(29), 120(11), 105(21), 91(25), 77(34).

4-(3-Phenylpropyl)-1-tetralone (71, n = 2)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.65-1.83(m, 4H), 2.05(qd, *J*=5.1, 13.5 Hz, 1H), 2.24(tdd, *J*=4.5, 11.7, 13.2 Hz, 1H), 2.56(td, *J*=5.1, 18 Hz, 1H), 2.62-2.80(m, 3H), 2.91-2.97(m, 1H), 7.15-7.33(m, 7H), 7.47(t, *J*=7.5 Hz, 1H), 8.01(d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.26, 148.18, 142.01, 133.36, 131.84, 128.52, 128.32, 128.21, 127.32, 126.60, 125.83, 37.89, 35.92, 34.84, 34.15, 29.44, 26.69; GCMS m/z(relative intensity) 264(M^+, 36), 173(9), 159(21), 145(73), 129(20), 117(53), 91(100), 77(21); HRMS m/z Calcd for $C_{19}H_{20}O$: 264.1514. Found: 264.1511.

1,6-Diphenyl-1,6-hexanedione (75)[34]

This compound was isolated as a solid: mp 104-105 °C (lit.[34] mp 106 °C); ^{1}H NMR ($CDCl_3$) δ 1.79-1.88(m, 4H), 3.05(br s, 4H), 7.46(t, *J*=7.5 Hz, 4H), 7.56(t, *J*=7.2 Hz, 2H), 7.96(d, *J*=7.8 Hz, 4H); GCMS m/z(relative intensity) 266(M^+, 0.2), 238(1), 146(33), 120(26), 105(100), 77(55).

4-(2-Oxo-2-phenylethyl)-1-tetralone (77)

This compound was isolated as a solid: mp 71-73 °C; ^{1}H NMR ($CDCl_3$) δ 2.05-2.17(m, 1H), 2.34(tdd, *J*=4.8, 10.8, 13.8 Hz, 1H), 2.65(td, *J*=5.4, 18.0 Hz, 1H), 2.79(ddd, *J*=5.1, 10.8, 17.7 Hz, 1H), 3.38(d, *J*=7.2 Hz, 2H), 3.83(apparent pentet, *J*=6.0 Hz, 1H),

7.29-7.37(m, 2H), 7.44-7.52(m, 3H), 7.59(t, *J*=7.5 Hz, 1H), 7.97(d, *J*=7.5 Hz, 2H), 8.06(d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.16, 197.77, 136.78, 133.79, 133.40, 132.11, 128.74, 128.06, 127.93, 127.49, 127.14, 127.03, 43.42, 35.34, 33.69, 27.53; GCMS m/z(relative intensity) 264(M^+, 3), 159(31), 144(91), 120(27), 105(100), 77(74); HRMS m/z Calcd for $C_{18}H_{16}O_2$: 264.1150. Found: 264.1147.

4-(Benzoyloxy)-1-tetralone (80)

This compound was isolated as a solid: mp 95-96 °C; ^{1}H NMR ($CDCl_3$) δ 2.30-2.60(m, 2H), 2.75(ddd, *J*=4.8, 7.2, 17.4 Hz, 1H), 3.02(ddd, *J*=5.1, 9.0, 17.4 Hz, 1H), 6.39(dd, *J*=3.6, 6.0 Hz, 1H), 7.40-7.61(m, 6H), 8.05(d, *J*=7.8 Hz, 2H), 8.09(d, *J*=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 196.73, 165.84, 140.73, 133.96, 133.26, 131.97, 129.80, 129.67, 129.02, 128.42, 128.30, 127.21, 69.60, 34.59, 28.66; GCMS m/z(relative intensity) 266(M^+, 3), 161(3), 144(49), 115(25), 105(100), 77(33); HRMS m/z Calcd for $C_{17}H_{14}O_3$: 266.0943. Found: 266.0942.

N-Methyl-4-(3-oxo-3-phenylpropyl)-1,2,3,4-tetrahydroquinoline (84)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.80-1.92(m, 1H), 1.93-2.17(m, 3H), 2.78-2.92(m, 1H), 2.89(s, 3H), 3.o3(dd, *J*=6.6,4.2 Hz, 1H), 3.06(dd, *J*=6.6,4.2 Hz, 1H), 3.17(td, *J*=4.8, 11.7 Hz, 1H), 3.33(dt, *J*=4.2, 10.5 Hz, 1H), 6.61(t, *J*=7.2 Hz, 2H), 7.01(br d, *J*=7.2 Hz, 1H), 7.09(t, *J*=7.5 Hz, 1H), 7.44(t, *J*=7.2 Hz, 2H), 7.54(t, *J*=7.5 Hz, 1H), 7.93(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.17, 145.86, 136.91, 132.86, 128.49, 127.94, 127.29, 125.52, 115.74, 110.75, 47.41, 38.79, 35.92, 35.69, 30.12, 26.74 (one aromatic carbon is missing probably due to a fortuitous overlap); GCMS m/z(relative intensity) 279(M^+, 27), 207(1), 159(100), 146(36), 144(43),

130(19), 118(5), 105(8), 77(17); HRMS m/z Calcd for $C_{19}H_{21}NO$: 279.1623. Found 279.1618.

4-[2-(*N*-Methyl-*N*-phenyl)aminoethyl]-1-tetralone (85)

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.91-2.01(m, 2H), 2.03-2.18(m, 1H), 2.25-2.38(m, 1H), 2.52(td, *J*=5.1, 18.0 Hz, 1H), 2.76(dd, *J*=5.1, 11.7 Hz, 1H), 2.93(s, 3H), 2.95-3.06(m, 1H), 3.35-3.56(m, 2H), 6.65-6.73(m, 3H), 7.18-7.27(m, 3H), 7.32(t, *J*=7.5 Hz, 1H), 7.49(t, *J*=7.5 Hz, 1H), 8.13(d, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.88, 149.03, 147.53, 133.49, 131.83, 129.21, 128.05, 127.47, 126.83, 116.48, 112.41, 50.90, 38.31, 36.08, 34.88, 30.96, 26.93; GCMS m/z(relative intensity) 279(M^+, 19), 144(1), 120(100), 107(11), 77(8); HRMS m/z Calcd for C19H21NO: 279.1623. Found: 279.1620.

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PART IV. REACTION OF CARBONYL SUBSTITUTED RADICALS WITH ALKENES IN PRESENCE OF DISULFIDES

Reaction of carbonyl substituted radicals with alkenes in presence of disulfides

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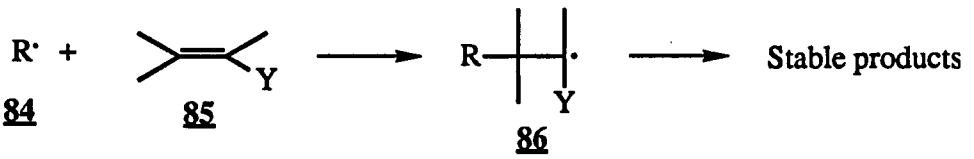
INTRODUCTION

The most important methodology for the synthesis of aliphatic C-C bond via radical reactions is the addition of alkyl radicals **84** to alkenes **85**. This reaction leads to adduct radicals **86** that must be converted to non-radical products before it can be consumed by undesired radical-radical reactions, radical solvent reactions or polymerization (Scheme I).

Scheme I



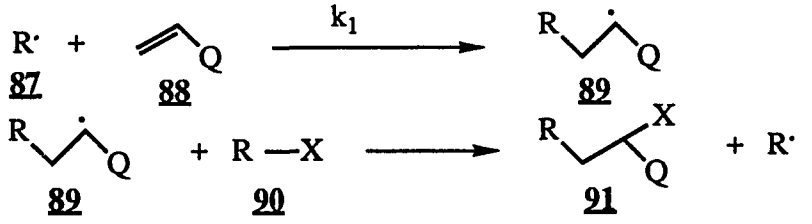
84 **85** **86**

Many such reactions (mostly chain reactions) have been developed in which the adduct radicals are trapped by a trapping reagent to convert it to a stable product. In general for the successful use of radical chains two conditions must be satisfied. (1) The selectivities of the radicals involved in the chain have to differ from each other. (2) The reaction between radicals and non-radicals must be faster than radical combination reactions. One type of chain reaction is shown in Scheme II.

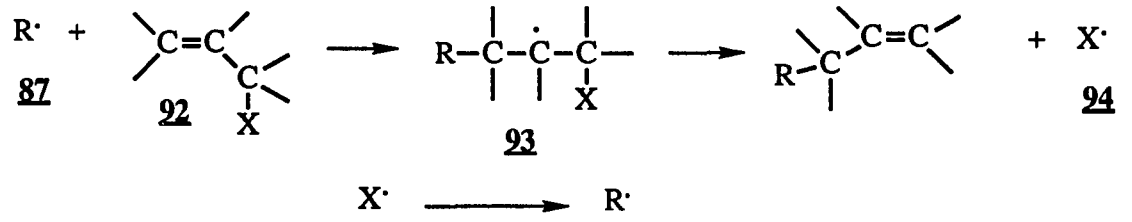
For this type of the chain reaction to succeed, the radical **87** must react faster with the alkene **88** than with the solvent and the adduct radical **89** must react faster with the radical precursor **90** than with the alkene **88**, because otherwise polymerization results.

Scheme III shows another kind of chain reaction in which the alkyl radical **87** reacts with a suitably substituted alkene **92** and the adduct radical **93** is converted to product by homolytic bond cleavage to release a new radical **94**.

Scheme II



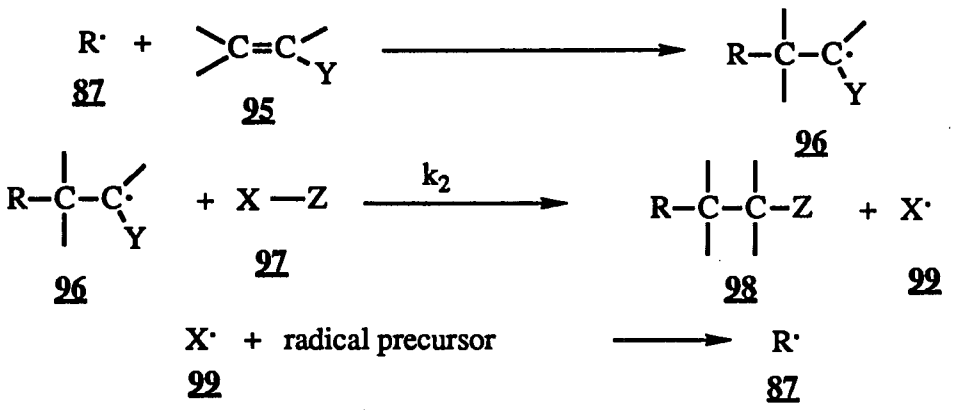
Scheme III



For the success of this chain reaction the newly formed radical **94** must react with the radical precursor to give back the starting radical R·. This condition severely limits the application of radical traps in synthesis.

Some chain reactions make use of a radical trap of the type shown in Scheme IV.In this sytem radicals **87**, **96**, and **99** are simultaneously present during the formation of product **98**. Alkyl radical **87** must attack alkene **95** to form adduct radical **96**. Radical **96** must react with trapping agent **97** to yield product **98** and radical **99**, which must react with the radical precursor to give back the starting radical **87**. This type of a chain will be synthetically useful only if these reactions are faster than all other possible reactions of radicals **87**, **96**, and **99**. Therefore, the radicals in the chain must meet certain selectivity and reactivity prerequisites and thus for a successful design of a radical chain reaction the

Scheme IV



selectivity of various radicals and the magnitude of the various rate constants should be known.

Some typical examples of various types of radical reactions which make use of a trapping agent are discussed below.

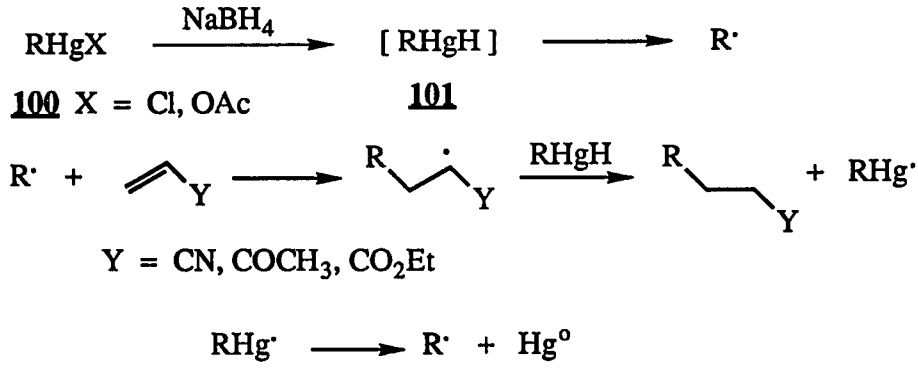
Reaction of Nucleophilic Alkyl Radicals with Electron-poor Alkenes

Trapping with hydrogen donors

Reduction of alkylmercury salts **100** with a hydrogen donor such as $NaBH_4$ or Bu_3SnH leads to alkylmercury hydrides **101** which undergo spontaneous decomposition to form alkyl radicals and start the chain (Scheme V).

High yields of C-C bond formation occur with very reactive alkenes like acrylonitrile, vinyl ketones, acrylates, fumaronitrile or maleic anhydride.[1,2] Lower yields are obtained with styrene, vinylidene chloride and crotonic esters because these alkenes are too unreactive[3] to compete with the reduction of the alkyl radical by mercury hydrides

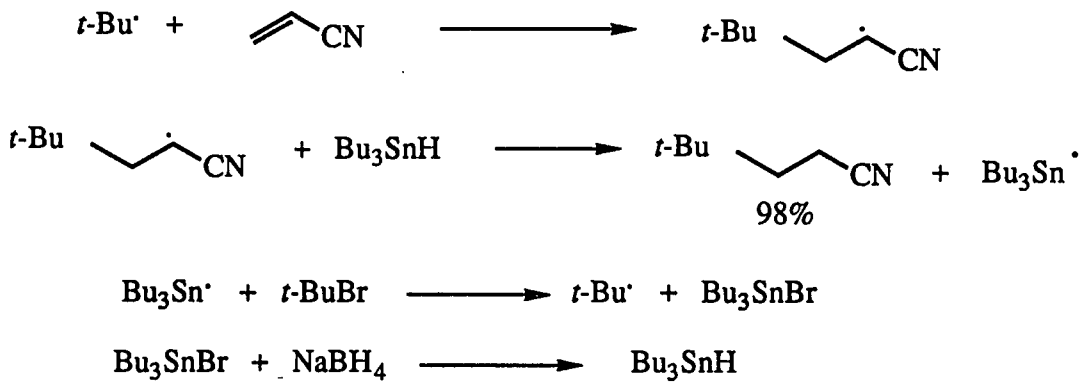
Scheme V



which trap alkyl radicals with rate coefficients of at least 10^7 $Lmol^{-1}s^{-1}$ at room temperature.[4]

Reaction of primary, secondary and tertiary bromides and iodides with electron-poor alkenes can be carried out successfully either photolytically at room temperature or thermally with radical initiators. Generally a catalytic amount of tin hydride with excess of $NaBH_4$ is used (Scheme VI).[5]

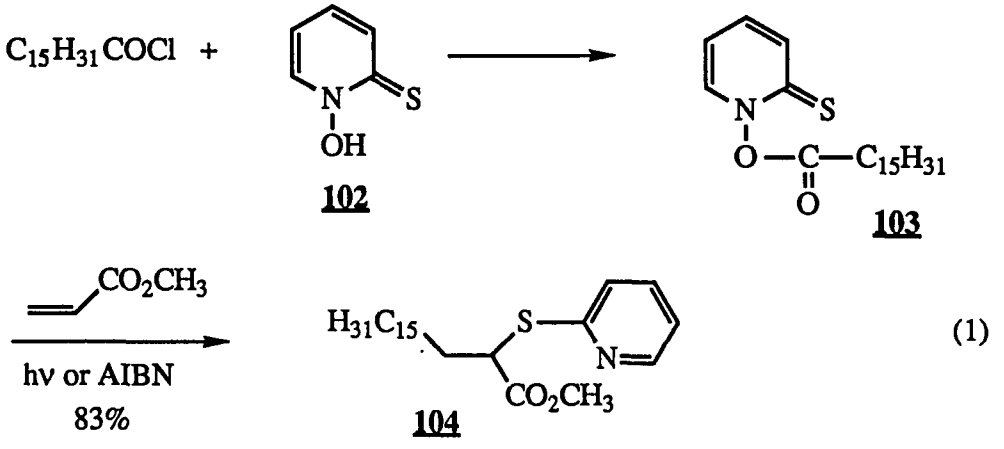
Scheme VI



Some disadvantages of using Bu_3SnH to mediate radical chain reactions are (1) Competing reduction of starting radicals when the rate of addition or cyclization is slow, (2) Difficulty in establishing different lifetimes for intermediate radicals due to similarities in rates for the reaction of many radicals with tin hydride and (3) Net reduction always results by H-atom transfer to the final radical which is particularly troublesome if functionality is required in the product for subsequent synthetic transformations.

Trapping with thio donors

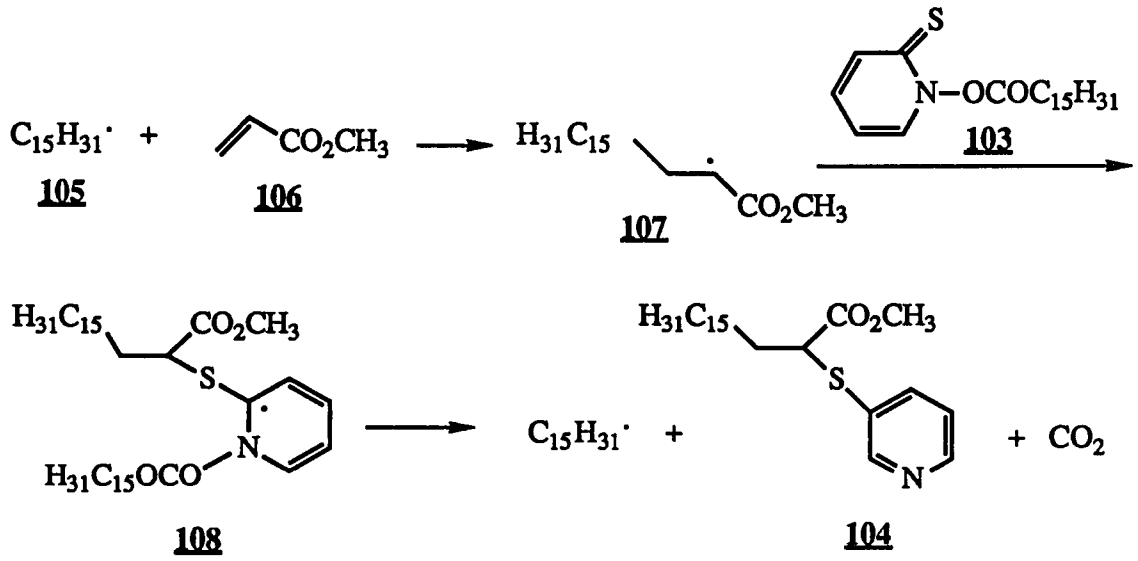
A very useful method in which radicals are trapped by a thiocarbonyl group has been developed by Barton.[6] Acid chloride is converted with N-hydroxypiperdine-2-thione **102** to mixed anhydride **103**, which is the radical precursor. Addition of electron-poor alkenes under either photolytical or thermal conditions leads to product **104** in which a C-C and C-S bonds have been formed (reaction 1).



(1)

In this reaction radical **105** is generated (Scheme VII) and attacks alkene **106** to give adduct radical **107** that is trapped by the thio-compound **103**. Two successive β-bond cleavage in **108** yield product **104** and the starting radical **105**.[7]

Scheme VII



This chain reaction can be successfully used with a variety of different carboxylic acids as long as electron-poor alkenes are used[6] which restricts its use since only nucleophilic radicals react well with electron-poor alkenes.

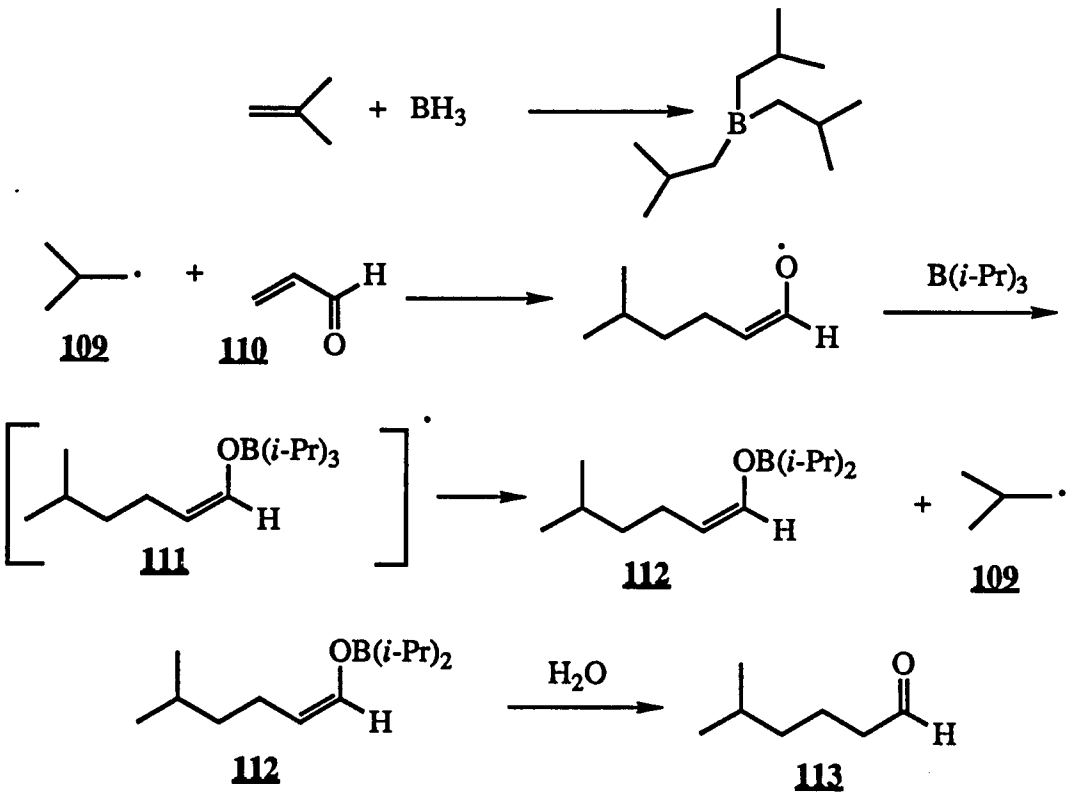
Trapping with borane donors

Brown[8] has shown that trialkylboranes are suitable precursors for alkyl radicals in C-C bond forming chain reactions with α,β-unsaturated ketones and aldehydes (reaction 2). The trialkyl boranes are generated by *in situ* hydroboration of alkenes.

Adduct radical is generated by the addition of radical **109** to alkene **110**. It is then trapped by the trialkylborane to give in a synchronous displacement or via intermediate **111**, the starting radical **109** and **112** which is hydrolysed to give product **113** (Scheme VIII).

This method is limited to use of α,β-unsaturated aldehydes, ketones and epoxides as alkenes[8] since with ester and nitrile groups, the intermediate adduct radical cannot be trapped fast enough by the trialkylborane and polymerization occurs.

Scheme VIII



Trapping by electron transfer reactions

During the past several years, Russell[9] has developed a series of free radical alkylations in which RHgX or R_2Hg partcipates in the propogation step of a chain process that does not usually involve RHg as an intermediate other than in the initiation step. Electron transfer from a donor radical to an alkylmercury halide generates the alkyl radical. Chain reaction can be achieved if a donor radical (D·) can be formed by further reactions of an alkyl radical which is itself not a strong donor or acceptor species (Scheme IX).[10]

Scheme IX

$$t\text{-Bu}^{\cdot} + CH_2{=}C(p\text{-}MeOC_6H_4)_2 \longrightarrow t\text{-}BuCH_2{-}\dot{C}(p\text{-}MeOC_6H_4)_2$$

$$t\text{-}BuCH_2{-}\dot{C}(p\text{-}MeOC_6H_4)_2 + t\text{-BuHgCl} \xrightarrow{(D^{\cdot})} t\text{-Bu}^{\cdot}$$

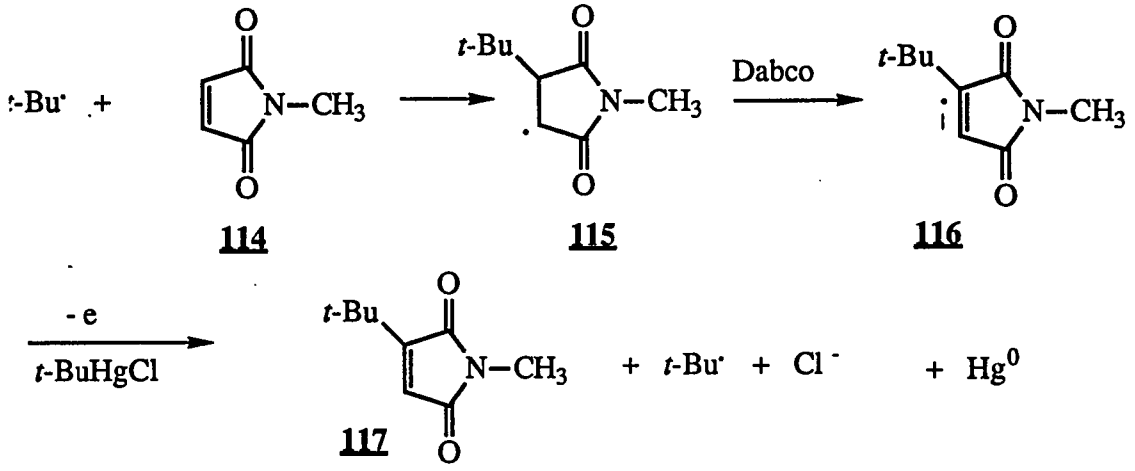
$$+ \quad t\text{-}BuCH_2{-}\overset{+}{C}(p\text{-}MeOC_6H_4)_2 + Hg^{\circ} + Cl^{-}$$

$$t\text{-}BuCH_2{-}\overset{+}{C}(p\text{-}MeOC_6H_4)_2 \xrightarrow{-H^{+}} t\text{-}BuCH{=}C(p\text{-}MeOC_6H_4)_2$$

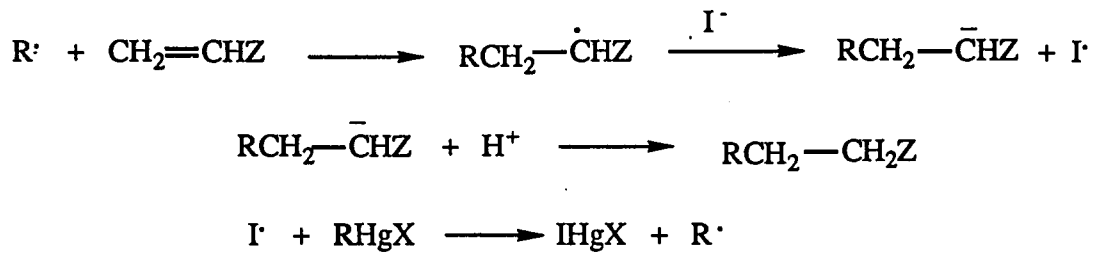
The enolyl radical **115** formed by the addition of an alkyl radical to a 1,4-enedione **114** is not a donor radical but in the presence of a base such as Dabco it is deprotonated to form a radical anion **116** which acts as a electron donor to the starting alkylmercurial[11] and thus continues the chain and gives an oxidative substitution product **117** (Scheme X).

In presence of iodide ion the intermediate adduct radical formed by attack of an alkyl radical on electron-poor alkene, is reduced to an anion by electron transfer from the iodide ion, giving a reductive alkylation product (Scheme XI).[11]

Scheme X



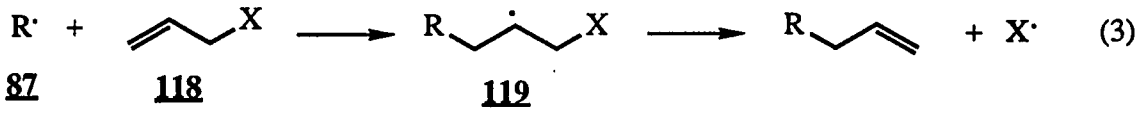
Scheme XI



The chain is continued by displacement of an alkyl radical from the starting organomercurial by iodine atom.

Fragmentation

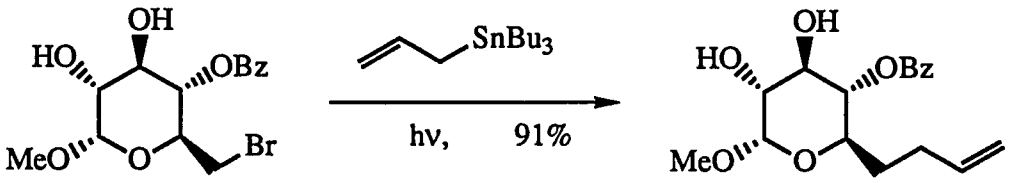
After construction of the C-C bond by radical addition to alkenes **118**, the adduct radical **119** can be transformed into non-radical products by splitting off a radical, for example in a β-bond cleavage (reaction 3).



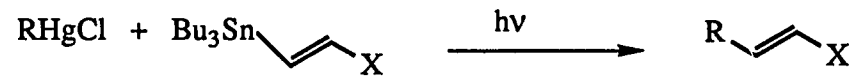
87 **118** **119** (3)

If the fragmentation is fast enough then radicals **87** and **119** need not be of different polarity, that is, even electron-rich alkenes can be used for C-C bond forming reactions with nucleophilic radicals.

Allylstannanes[12] (reaction 4), vinylstannanes[13,14] (reaction 5) have been used to take advantage of the β-bond cleavage of the tin radical.



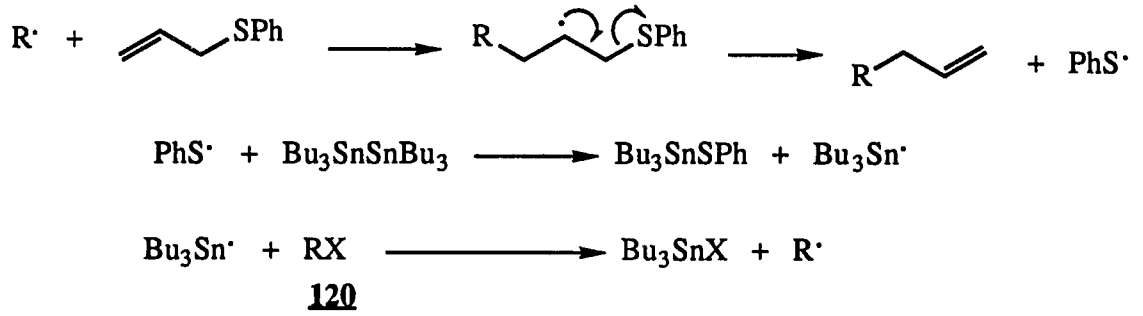
(4)



(5)

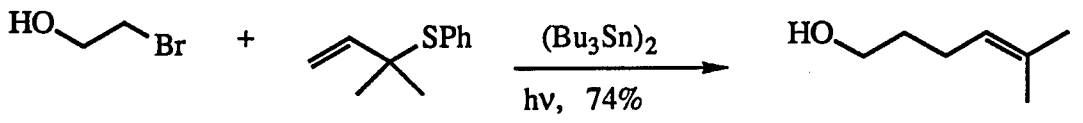
Keck[15] has shown how phenylthio radical carries the chain reaction by trapping it with hexabutylditin. The tributytin radical thus formed reacts with alkyl halide **120** and generates the starting alkyl radical (Scheme XII).

Scheme XII



120

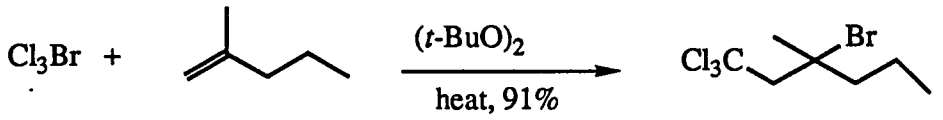
For example



Reaction of Electrophilic Alkyl Radicals with Electron-rich Alkenes

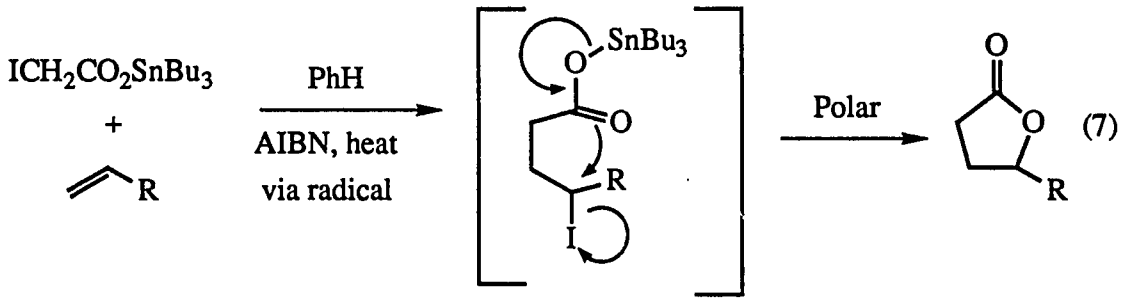
Trapping by atom transfer

The atom transfer addition of a C-X bond (where X is a univalent atom) across a double bond is a fundamental reaction of organic free radicals (reaction 6), the scope and underlying principles of which were pioneered by Kharasch.[16]



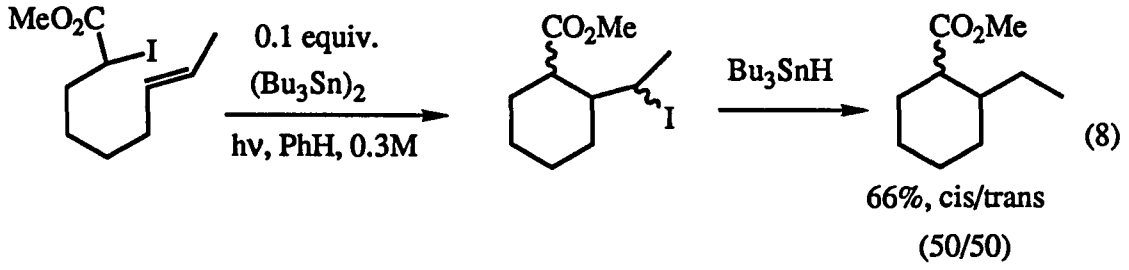
(6)

In 1984 Kraus[17] reported a convenient new synthesis of lactones from alkenes (reaction 7) which was ultimately shown[18] to proceed via an intermediate formed by an iodine atom transfer.



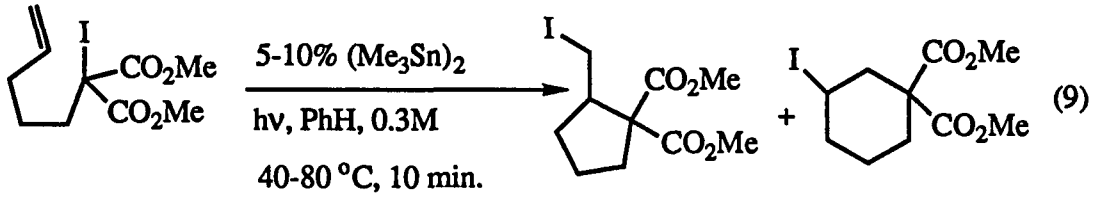
(7)

Taking the above example as a starting point Curran[19,20] has developed a number of atom transfer cyclization reactions (reactions 8 and 9) of α-iodo esters, ketones and malonates. This strategy has also been used successfully for macrocyclization.[21]



(8)

66%, cis/trans (50/50)



(9)

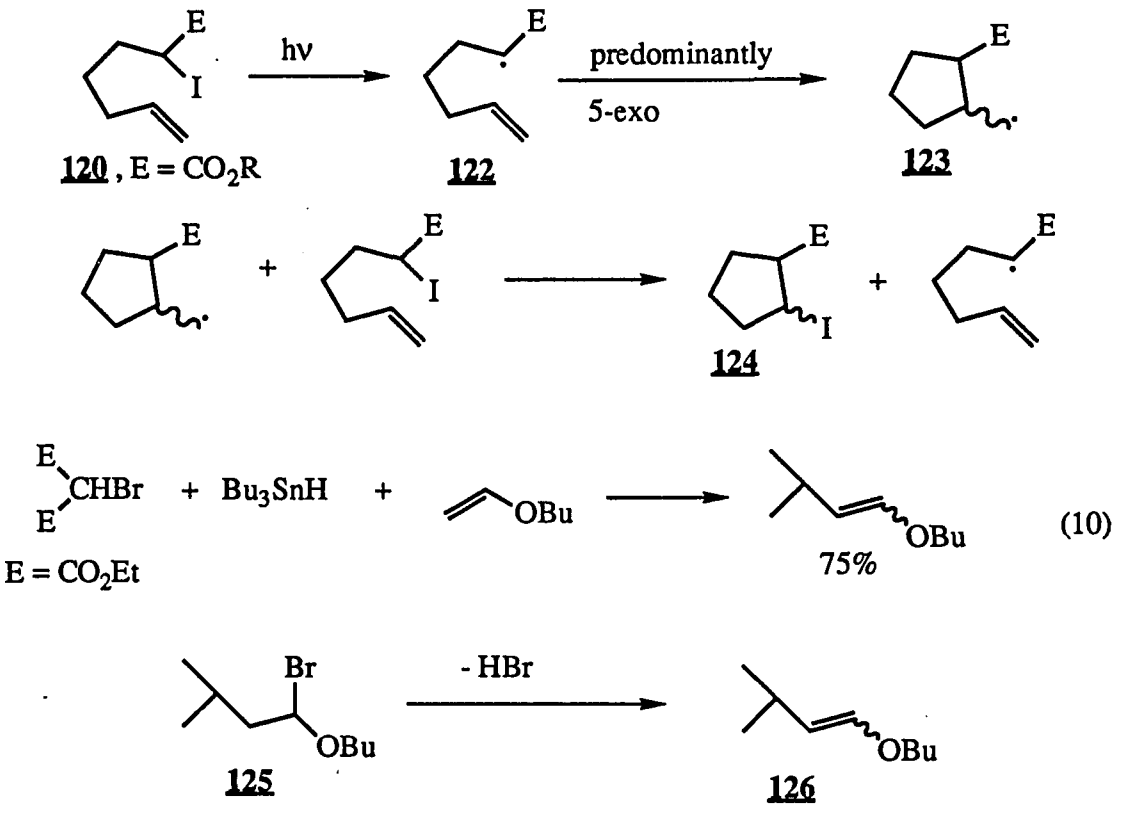
86% (90/10)

The mechanism is shown in Scheme XIII. Initiation takes place by photolytic cleavage of carbon-iodine bond of **121** to give a stabilized radical **122** which cyclizes predominantly in a 5-exo mode to give cis/trans mixture of radical **123**. This radical abstracts iodine atom from **121** in a rapid exothermic step with a rate of around[19] 10^7 to 10^9 $Lmol^{-1}s^{-1}$ to give the product **124** and starting radical **122**.

Giese[22] has also made use of an atom transfer method to add malonyl radical intermolecularly to electron-rich alkenes to give substitution products (reaction 10).

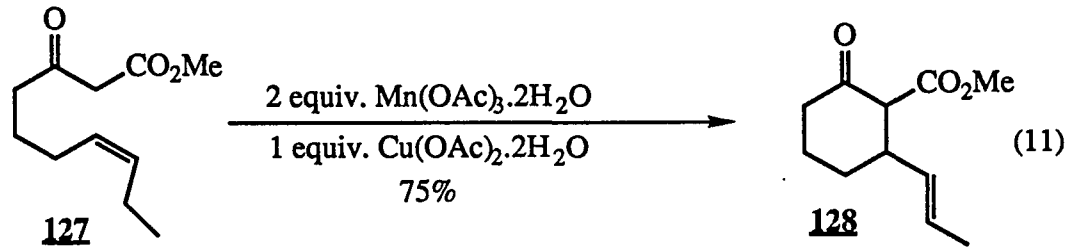
In this case the atom transfer addition yields the bromide **125** as an intermediate which loses a molecule of HBr to give the product **126**.

Scheme XIII



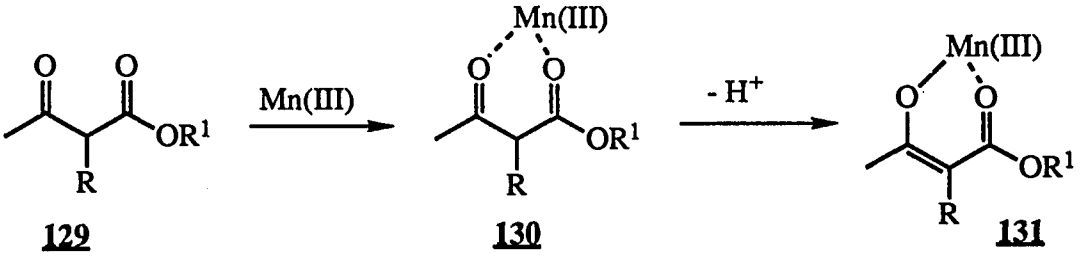
Trapping by oxidation of the adduct radicals

Manganese(III) oxidation of malonates, acetoacetates and related functional groups has emerged as a powerful method for the formation of lactones,[23] alkenes and alkyl chlorides.[24] Snider has used a variety of 1,3-dicarbonyl compounds such as β-keto esters in Mn(III)-based oxidative free radical cyclization reactions. For example the β-keto ester **127** gives a 75% yield of the cyclized product **128** in presence of 2 equivalents of $Mn(OAC)_3.2H_2O$ and 1 equivalent of $Cu(OAC)_2.H_2O$[25] (reaction 11).

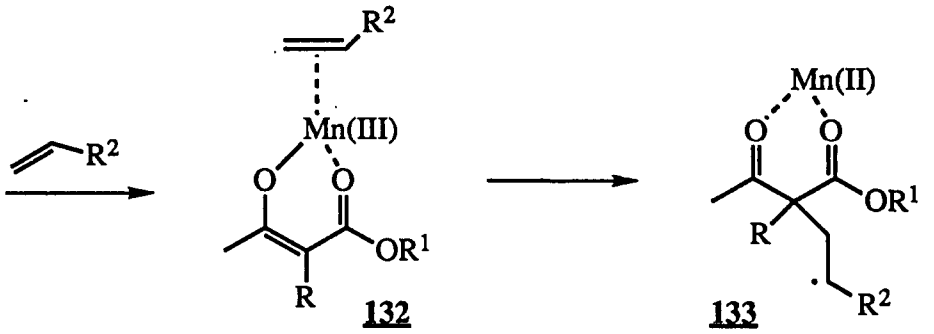


127 128 (11)

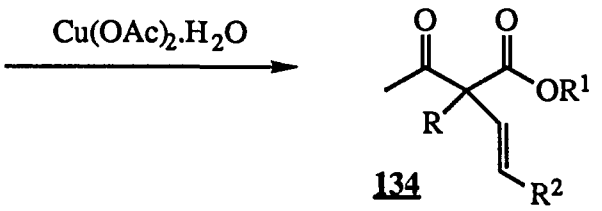
Scheme XIV



129 130 131



132 133

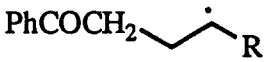


134

The mechanism (Scheme XIV)[25] involves first the formation of complex **131** from the β-keto ester which in the presence of alkene forms the complex **132**. The rate determining step for the overall reaction is the oxidation of this Mn(III)-**129**-alkene complex to give the addition product **133**. This secondary radical is not oxidized by Mn(III) but is rapidly oxidized by $Cu(OAC)_2.H_2O$ to give the product **134** via β-hydride elimination, without the intermediacy of a cation.

RESULTS AND DISCUSSION

The addition of benzoylmethyl radical, generated by photolysis of (benzoylmethyl)mercury chloride, to an electron-rich alkene forms the adduct radical **135** which if not trapped by any trapping agent, gives a mixture of products resulting from cyclization with the aromatic ring, abstraction of a hydrogen atom, telomers etc. as discussed in Part III. It was thought that trapping of this adduct radical with a suitable trapping agent would give a good yield of the addition product.

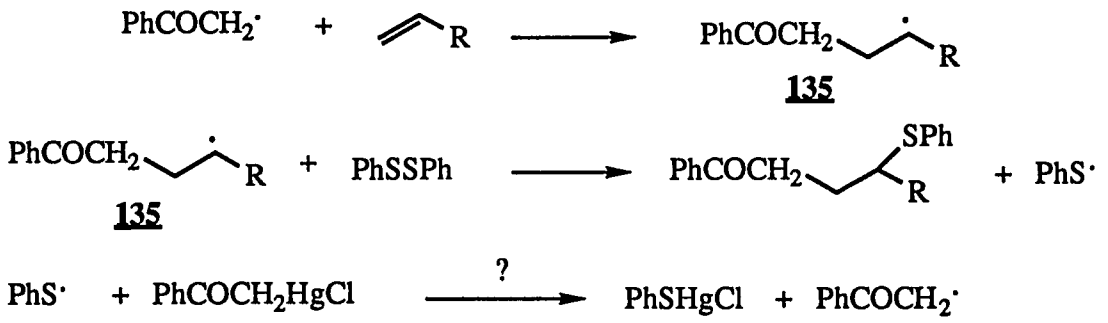


135

A suitable trapping agent for this reaction should react with the nucleophilic adduct radical **135** much faster than with the electrophilic $PhCOCH_2\cdot$ radical. It is known that chain transfer constant for a polystyryl radical (nucleophilic radical) is 1470 while that for the polymethylmethacrylate radical (electrophilic radical) is 85 with diphenyl disulphide at 60 °C.[26] This suggested that the nucleophilic radical **135** would probably react with diphenyl disulphide faster than the electrophilic benzoylmethyl radical. It is also known that PhS· radical rapidly displaces an alkyl radical from RHgCl[27] (reaction 12) which raises the possibility of a chain reaction. Thus the expected sequence of reactions is shown in Scheme XV.

$$PhS^{\cdot} + RHgCl \longrightarrow PhSHgCl + R^{\cdot} \qquad (12)$$

Scheme XV



To test the feasibility of this scheme some initial studies were performed with cyclohexene. These results are shown in Table 1.

The initial studies showed that the adduct radical could be trapped with PhSSPh giving good yields of the addition products. These results also gave some valuable information about some important aspects of this reaction. These are discussed below.

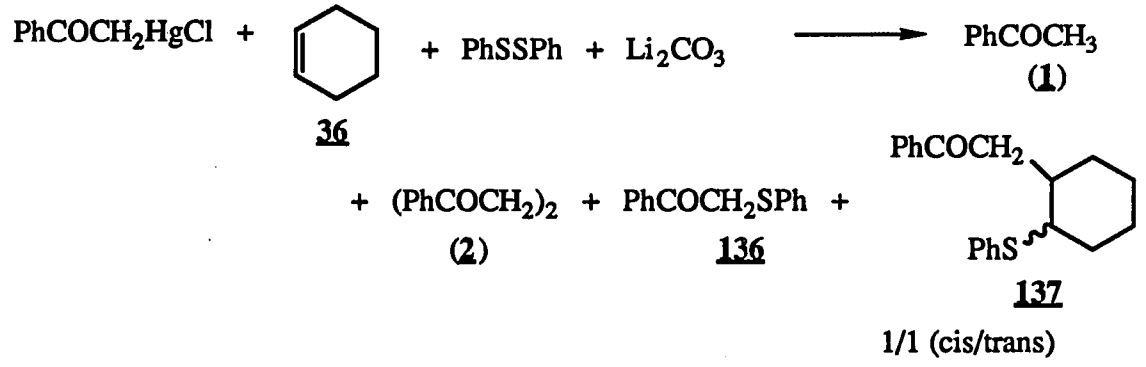
Selectivity of the Radicals Involved

Scheme XV shown earlier requires that there are three different radicals present in the reaction mixture at any time. These are $PhCOCH_2\cdot$, $PhS\cdot$ and the adduct radical **135**.

For the reaction to succeed the electrophilic $PhCOCH_2\cdot$ radical should react faster with the alkene than with PhSSPh. Thus the relative reactivity of $PhCOCH_2\cdot$ towards various alkenes as compared to that with PhSSPh is an important factor in this reaction.

Taking cyclohexene as the standard alkene, a series of experiments were performed taking varying ratios of cyclohexene and PhSSPh during the photolysis of $PhCOCH_2HgCl$ to determine the relative reactivity of $PhCOCH_2\cdot$ radicals with them

Table 1. Photostimulated reaction of $PhCOCH_2HgCl$ with cyclohexene in presence of diphenyl disulfide[a]



Molar equivalents $PhCOCH_2HgCl$:36: $PhSSPh$:Li_2CO_3	Reaction conditions	% Yield[b] 1	2	136	137
1 : 5 : 1 : 0	dark[c], 24 h	95[d]	0	0	0
1 : 5 : 1 : 0	hν, 6 h	53	44	tr	27
1 : 5 : 1 : 2	hν, 6 h	34	3	2	46
1 : 5 : 2 : 2	hν, 6 h	25	3	4	63
1 : 5 : 2 : 2	hν, 6 h[e]	34	tr	3	43

[a]Reaction of 0.5 mmol of $PhCOCH_2HgCl$ in 5 mL Me_2SO in a 350-nm Rayonet photoreactor at about 40 °C.

[b]GC yield with biphenyl as internal standard.

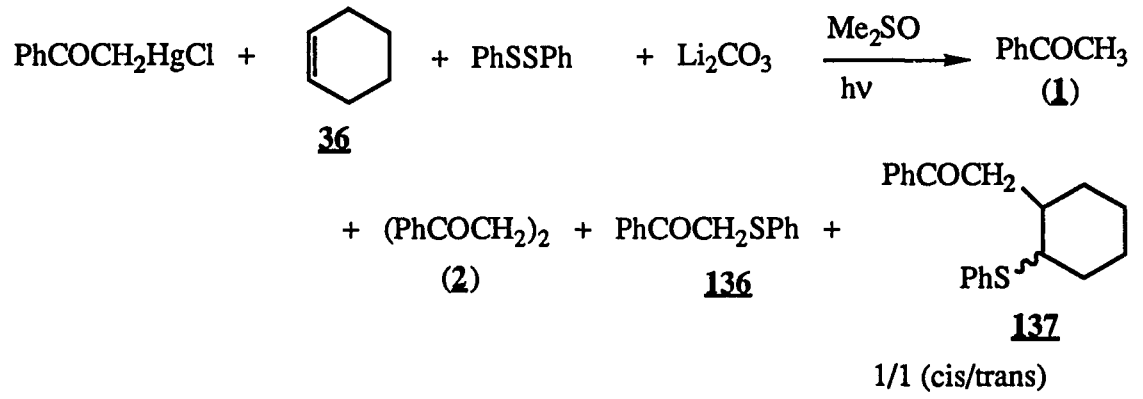
[c]Test tube covered with aluminum foil.

[d]Resulting from aqueous thiosulfate workup of unreacted $PhCOCH_2HgCl$.

[e]Reaction performed in DMF.

(Table 2). Since the yield of the product **137** was much higher in the presence of Li_2CO_3, these reactions were carried out using two equivalents of Li_2CO_3.

Table 2. Determination of the relative reactivity of $PhCOCH_2\cdot$ radicals toward cyclohexene and PhSSPh[a]



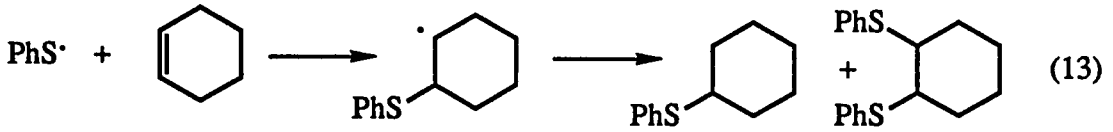
Molar equivalents	% Yield[b]				Relative reactivity[c]
$PhCOCH_2HgCl$:**36**:PhSSPh:Li_2CO_3	**1**	**2**	**136**	**137**	
1 : 5 : 1 : 2	34	3	2	46	4.6
1 : 5 : 5 : 2	18	9	11	43	3.9
1 : 5 : 10 : 2	11	16	15	30	4.0
1 : 5 : 20 : 2	tr	27	17	17	4.0

[a]Photostimulated reaction of 0.5 mmol $PhCOCH_2HgCl$ in a 350-nm Rayonet photoreactor in 5.0 mL Me_2SO for 6 h.

[b]GC yield with biphenyl as internal standard.

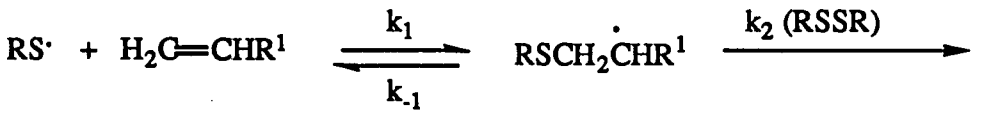
[c]Calculated as (%yield of **137**/%yield of **136**) x ($[PhSSPh]_o/[\mathbf{36}]_o$)

Thus $PhCOCH_2\cdot$ radical shows considerably greater selectivity towards cyclohexene than towards PhSSPh. The degree of substitution at the double bond of the olefin plays an important part in determining rate of addition of the radical to it.[28] Therefore it can be expected that $PhCOCH_2\cdot$ radical will show an even greater selectivity for a terminal alkene such as 1-hexene. For example methyl radical adds about 6.5 times more readily to 1-butene than to cis-2-butene at 65 °C.[29] Thus by using a suitable ratio of alkene to PhSSPh the loss of $PhCOCH_2\cdot$ in forming $PhCOCH_2SPh$ can almost be eliminated. The products resulting from the addition of PhS· radical to the alkene (reaction 13) were never observed in these reactions.



(13)

It is well known that addition of thiyl radical to olefins is reversible and has been shown to cause rapid cis/trans isomerization (reaction 14) of 2-butene.[30]



$$RSCH_2CH(SR)R^1 \quad + \quad RS\cdot \qquad (14)$$

In the above reaction 15, $k_{-1}/k_2(RSSR)$ has been determined to be relatively large.[31] Addition of PhS· to olefins is more readily reversible than the corresponding reactions involving alkylthiyl radicals like *t*-BuS· Thermochemistry accounts for the difference since bonds formed between'S' and 'C' are about 10 kcal/mole weaker for PhS·

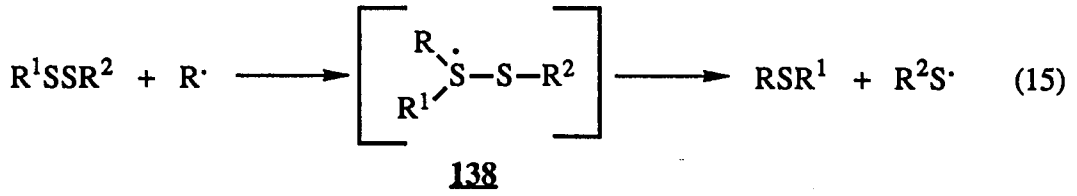
than for *t*-BuS·.[32] The rate constant for the addition of *p*-ClC_6H_5S· radical to cyclohexene has been determined to be 3.3 x 10^3 $Lmol^{-1}s^{-1}$ while the reverse rate has been estimated[33] to be 10^{-5}-10^{-8} s^{-1}. The observed results are consistent with the ready reversibility of PhS· attack on cyclohexene.

The most notable feature of this reaction is the almost complete absence of any products resulting from the cyclization with the benzene ring of the starting mercurial or H-atom abstraction by the adduct radical, which are observed in the absence of diphenyl disulphide. The obvious conclusion from this observation is that the rate at which adduct radical **135** reacts with diphenyl disulphide is much greater than the rate of cyclization with the aromatic ring as well as the rate of H-atom abstraction.

Adduct radical **135** is a nucleophilic radical formed from an exothermic addition of a resonance stabilized radical to an alkene. The rate constant for the homolytic bimolecular displacements of disulfides are known to be of the order of 10^6 $Lmol^{-1}s^{-1}$.[34] Thus the rate of this cyclohexyl radical is expected to be similar.

The high reactivity of disulfides toward alkyl radicals is probably due to the ease with which an intermediate sulfuranyl radical having nine electrons around sulfur can be formed.[35] Such sulfuranyl radicals are well documented.[36]

Sulfuranyl radicals **138** are intermediates in a variety of addition elimination reactions of sulfides, disulfides, sulfoxylates as well as in the reduction of triorgano and heteroorgano sulfonium salts (reaction 15).[37]



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The product obtained with cyclohexene was approximately a 50 : 50 mixture of cis and trans isomers. Thus the reaction takes place with no stereoselectivity. The mass balance obtained in this reaction for the $PhCOCH_2\cdot$ radical was always greater than 90% which suggests that telomerization of the adduct radicals does not take place and almost all the adduct radicals are efficently trapped by the disulfide.

The initial studies were successful enough to encourage us to explore the scope of the reaction with various kinds of electron-rich alkenes.

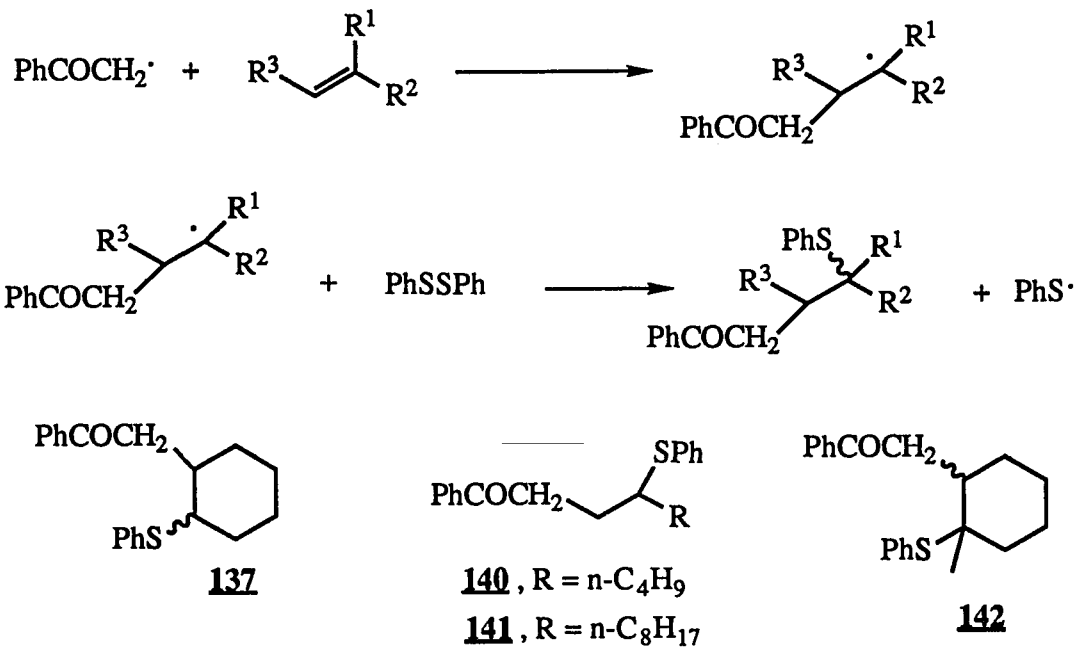
Higher yields of the addition products were obtained when Li_2CO_3 was used in the reaction. The role of Li_2CO_3 is not immediately obvious. The experiments performed to explore its role will be discussed later in this chapter. Since it gave higher yields, almost all the reactions hereafter were carried out with Li_2CO_3 as one of the components of the reaction mixture.

It was also found out that the optimum ratio of the mercurial to disulfide and Li_2CO_3 was 1 : 2 : 5. Therefore most of the reactions were carried out with this proportion of these reactants. Dimethyl sulfoxide was found to be the best solvent for this reaction.

Reaction with Simple Alkenes

Reaction with cyclohexene had already showed that the reaction works well with simple alkenes. The general scheme is shown in Scheme XVI. The reaction was performed with four simple alkenes viz. cyclohexene (**36**), 1-hexene (**37**), 1-decene (**38**) and 1-methyl-1-cyclohexene (**139**). The expected products were **137**, **140**, **141**, and **142** respectively. These reactions are summarized in Table 3.

Scheme XVI



These results show that terminal alkenes, which are relatively unhindered as compared to cyclohexene, give a much higher yield of the addition products. Even with only 1.2 equivalents of the alkenes the yields are quite good demonstrating the efficient trapping of the adduct radicals by PhSSPh.

In case of 1-methyl-1-cyclohexene, which is more sterically hindered than cyclohexene, the yield of the product obtained is much lower. There are two factors responsible for this lower yield. The first factor is, since the approach of $PhCOCH_2$· radical to the double bond is more difficult, the rate of addition to the double bond will be slowed down[28] and the rates of other processes such as hydrogen atom abstractions, radical-radical combinations and rearrangement of the radical will compete with the rate of addition. The second factor is the addition of the $PhCOCH_2$· radical to 1-methyl-1-

Table 3. Photostimulated reaction of $PhCOCH_2HgCl$ (M) with simple alkenes in presence of PhSSPh (D) and Li_2CO_3 (L)[a]

$$\underset{M}{PhCOCH_2HgCl} + \text{alkene} + \underset{D}{PhSSPh} + \underset{L}{Li_2CO_3} \longrightarrow \underset{\underline{1}}{PhCOCH_3} + \underset{\underline{136}}{PhCOCH_2SPh} + \underset{\underline{2}}{(PhCOCH_2)_2} + \text{addition product}$$

Molar equivalents	Alkene (equiv.)	% Yield[b]			Addition product
M : D : L		1	2	136	(% yield)
1 : 2 : 5	36 (5)	27	3	2	137 (63)[c]
1 : 2 : 5	139 (5)	11	5	tr	142 (37)[c]
1 : 2 : 5	37 (1.2)	tr	0	0	140 (67)
1 : 2 : 5	37 (5)	tr	0	0	140 (80)
1 : 2 : 5	38 (1.2)	4	tr	0	141 (68)
1 : 2 : 5	38 (5)	tr	tr	0	141 (62)

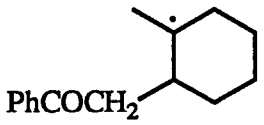
[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL Me_2SO for 6 h in a 350-nm Rayonet photoreactor at about 40 °C.

[b]GC yield with biphenyl as internal standard.

[c]Inseparable mixture of two diastereomers.

cyclohexene generates regioselectively the adduct radical **143** which is a tertiary radical and is more stable than a secondary radical generated in the case of cyclohexene. The attack of this tertiary radical on PhSSPh would be less exothermic and hence the rate will be slower than that of the secondary radical, again leading to more byproducts.

When styrene was used as the alkene only traces of addition products were



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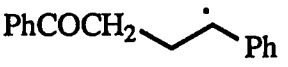
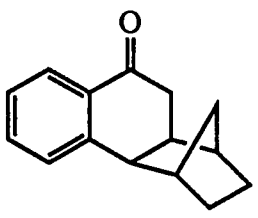


144

obtained, the major product being acetophenone. It is likely that the adduct radical **144** being a stabilized benzylic radical prefers to react with another styrene molecule to produce telomers rather than attack the disulfide. The absolute rate constants for the attack of polystyryl radical and methyl radical on CH_3SSCH_3 differ by almost four orders of magnitude.[38]

Reaction with norbornene gave under usual conditions 19% of cyclized product **47** and only traces of products **145**.

This suggests that the adduct radical **146** either is not easily accessible for the disulphide to trap bacause of the steric hindrance or that rate of cyclization with the benzene ring is much greater than the rate of reaction with disulfide. It is likely that the rate of cyclization could be greater in this case since the methano bridge of the norbornene moiety could provide enough steric hindrance for rotation around carbon-carbon bond, holding the radical center in close proximity of the benzene ring. Increasing the number of equivalents of PhSSPh to 5 did somewhat increase the yield of **145** but still **47** was the major product.



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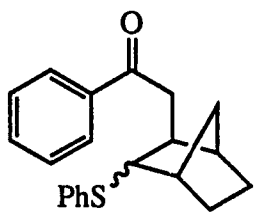

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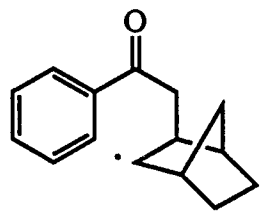
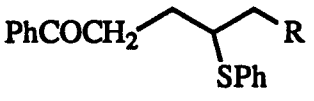


146

The reaction was then performed with four allylic alkenes viz. allyl alcohol (147), allyl acetate (148), allyloxytrimethylsilane (149) and allyltrimethylsilane (150). The expected products are shown below (151-154).



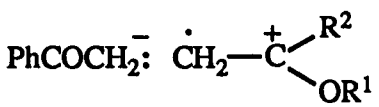
151, R = OH 152, R = OAc

153, R = $OSiMe_3$, 154, R = $SiMe_3$

The reaction with allylic alcohol or its derivatives (Table 4) was not as good as with simple terminal alkenes. However the reaction with allyltrimethylsilane gave very good yield of the addition product. In all these reactions the amounts of $PhCOCH_2CH_2COPh$ (2) and $PhCOCH_2SPh$ (136) were nil to traces. The poor mass balance in case of allylic alcohol and its derivatives probably suggests some degree of telomer formation in these cases.

Reaction with Enol Ethers

The electrophilic benzoylmethyl radical was expected to react faster with more electron-rich alkenes[39] such as enol ethers because of stabilization from structure 155.



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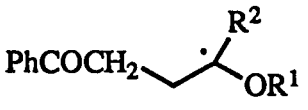
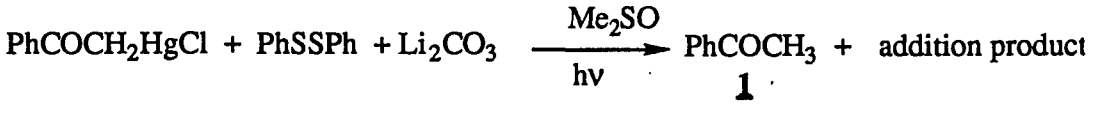


156

Addition of $PhCOCH_2\cdot$ to enol ether would form an adduct radical 156 which is stabilized by the adjacent alkoxy group by about 5-10 kcal/mole.[40] Trapping of this radical by diphenyl disulfide would produce the O,S-acetal or ketal 157 which could be hydrolysed to the corresponding aldehyde or ketone 158.

Table 4. Photostimulated reaction of $PhCOCH_2HgCl$ with allylic alkenes in presence of PhSSPh and Li_2CO_3[a]

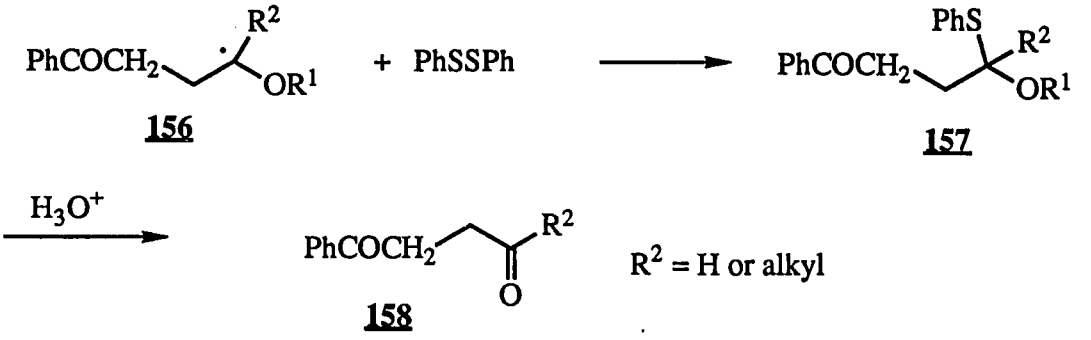


Alkene (mmol)	% Yield[b] of **1**	Addition product (% yield)[b]
147 (1.25)	13	**151** (26)
148 (1.25)	7	**152** (34)
149 (1.25)	7	**153** (38)[c]
150 (1.25)	0	**154** (84)

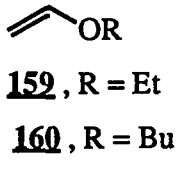
[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ in presence of 0.50 mmol PhSSPh and 1.25 mmol Li_2CO_3 in 2.5 mL Me_2SO at about 40 °C in a 350-nm Rayonet photoreactor for 6 h.

[b]GC yield with biphenyl as internal standard.

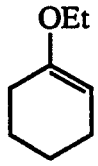
[c]Hydrolysed to alcohol during column chromatography.



The reaction was studied (Table 5) with a variety of enol ethers (**159**-**164**) such as simple alkyl vinyl ethers, cyclic enol ethers, enol silyl ethers etc.



159, R = Et
160, R = Bu
161, R = Ph



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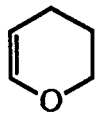

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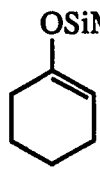
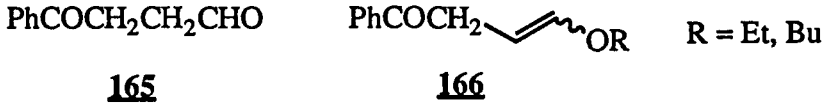


164

In case of the reactions with terminal alkyl vinyl ethers such as ethyl vinyl ether and butyl vinyl ether, the usual aqueous thiosulfate workup of the reaction mixture gave a mixture of O,S-acetal **157** (R^1=Et, Bu, R^2=H) and aldehyde **165**. The O,S-acetal decomposed under GC conditions giving PhSH and the substituted vinyl ether **166**.



$PhCOCH_2CH_2CHO$ (**165**) $PhCOCH_2$–OR (**166**) R = Et, Bu

Therefore the reaction mixture was hydrolysed by 2M aqueous HCl to convert the O,S-acetal **157** to the aldehyde **165** to get the yield of the reaction.

Reaction with phenyl vinyl ether gave the corresponding mixed O,S-acetal $PhCOCH_2CH_2CH(SPh)OPh$ (**167**) which did not hydrolyse to the aldehyde during workup, however it eliminated PhSH under GC conditions. In these reactions only traces of acetophenone, $PhCOCH_2SPh$ and $PhCOCH_2CH_2COPh$ were obtained indicating that the addition of $PhCOCH_2\cdot$ radical to these vinyl ethers was indeed faster and processes such as H-atom abstraction, radical-radical combination and attack of $PhCOCH_2\cdot$ on PhSSPh could not effectively compete with the addition to the double bond. The

Table 5. Photostimulated reaction of $PhCOCH_2HgCl$ (M) with enol ethers in presence of PhSSPh (D) and Li_2CO_3 (L)[a]

$$\underset{M}{PhCOCH_2HgCl} + \text{enol ether} + \underset{D}{PhSSPh} + \underset{L}{Li_2CO_3} \longrightarrow PhCOCH_3 + \text{addition product}$$

1

Molar equivalents M : D : L	Enol ether (equiv.)	% Yield[b] of **1**	Addition product (% yield[b])
1 : 2 : 5	**159** (5)	tr	**165** (55)[c]
1 : 2 : 5	**160** (5)	tr	**165** (56)[c]
1 : 2 : 2	**161** (5)	tr	**167** (37)[d]
1 : 2 : 5	**162** (5)	18	**18** (58)
1 : 2 : 5	**163** (5)	7	**168a** (43)[d]
1 : 2[e] : 5	**163** (5)	16	**168b** (43)
1 : 2 : 2	**164** (1.2)	27	**18** (40)
1 : 2 : 2	**164** (5)	40	**18** (51)

[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL Me_2SO in 350-nm Rayonet photoreactor for 6 h.

[b]GC yield with biphenyl as internal standard.

[c]After H_3O^+ hydrolysis.

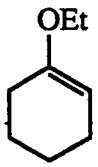
[d]Eliminated PhSH under GC conditions, yield calculated from the corresponding PhSH eliminated product.

[e]Dibutyl disulfide was used as the disulfide.

somewhat poor mass balance obtained indicates some loss of $PhCOCH_2$· radicals in telomerization reactions.

In case of reaction with ethyl cyclohexenyl ether **162** the diketone **18** was obtained directly upon workup. The somewhat larger proportion of acetophenone obtained in this reaction (18%) is probably due to 4 allylic hydrogens per enol ether available for H-atom abstraction.

An interesting reaction was observed in case of cyclic vinyl ether dihydropyran **163**. The products obtained in this case **168a,b** were a single isomer. Product **168a** eliminated PhSH under GC conditions while **168b** was stable and did not decompose probably due to lesser stability of BuS^- as compared to that of PhS^-.



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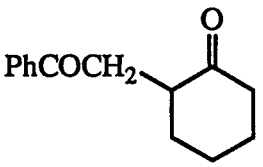

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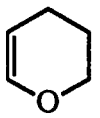
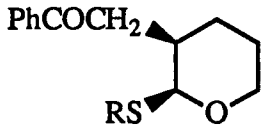


163

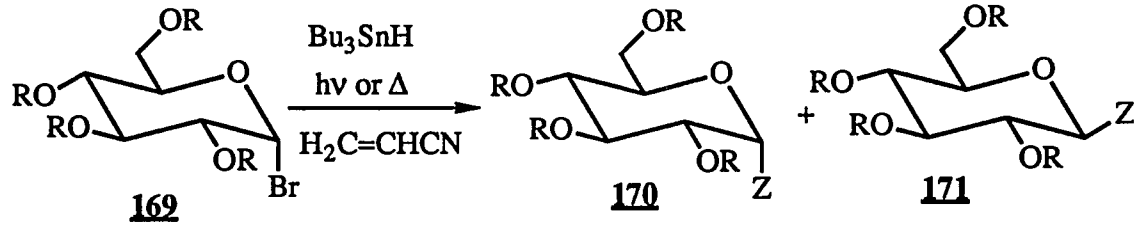


168a , R = Ph

168b , R = Bu

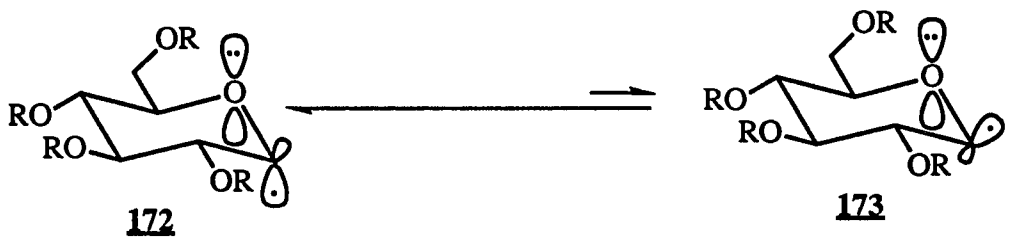
The ^1H NMR spectrum of **168a,b** showed that the SR group and the CH_2COPh to be in an axial-equatorial (cis-substitution) position. The equatorial-axial coupling of the corresponding protons being equal to 4.2 Hz, characteristic of such a coupling on a tetrahydropyran ring.[41]

Giese[42] has earlier demonstrated that reaction of tetraacetylglucosyl bromide **169** with Bu_3SnH in presence of acrylonitrile affords the C-C coupling product **170** with axial arrangement of the substituuents on C-1. The high stereoselectivity of the reaction decreased from over 50 (**170** : **171** = >98 : <2) to 3.5 (**170** : **171** = 78 : 22) when R was changed from Ac to Me (reaction 16).



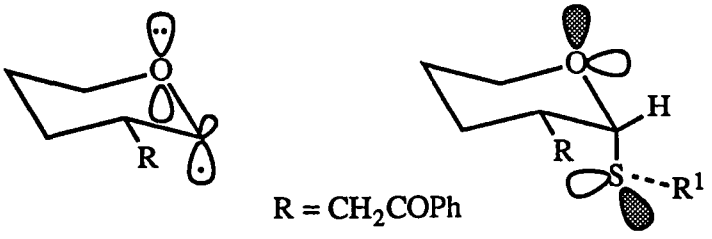
$Z = CH_2CH_2CN$ (16)

He ascribed this stereoselectivity to the interaction of intermediate σ radical **172** with non-bonding electron pair on the ring oxygen atom making it more stable and more nucleophilic than the σ-radical **173**.



In the present reaction it is likely that the adduct radical adopts a conformation **174** in which the bulky CH_2COPh group is equatorial and the radical is axial due to the interaction with non-bonding electron pair on the ring oxygen atom. Thus the product **168a,b** is an α-anomer existing almost completely in a conformation **175** with the SR group in an axial position and the CH_2COPh group in an equatorial position, because of the presence of anomeric effect in this conformation.

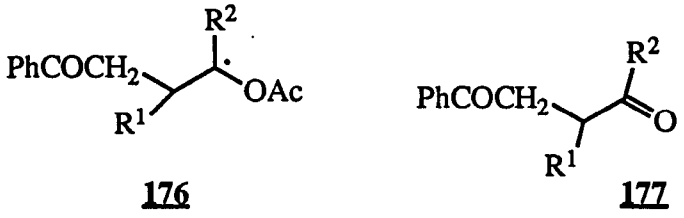
Reaction with the enol silyl ether of cyclohexanone **164** gave directly the diketone **18**, although most likely an unstable O,S-ketal is an intermediate. Again the high proportion of acetophenone may be due to the presence of four allylic hydrogens in **164**.



174 **175** (R^1 = Ph, Bu)

Reaction with Enol Acetates

Reaction of $PhCOCH_2HgCl$ with enol acetates was again expected to produce 1,4-dicarbonyl compounds **177** via trapping of the adduct radicals **176** by PhSSPh and subsequent hydrolysis.



176 **177**

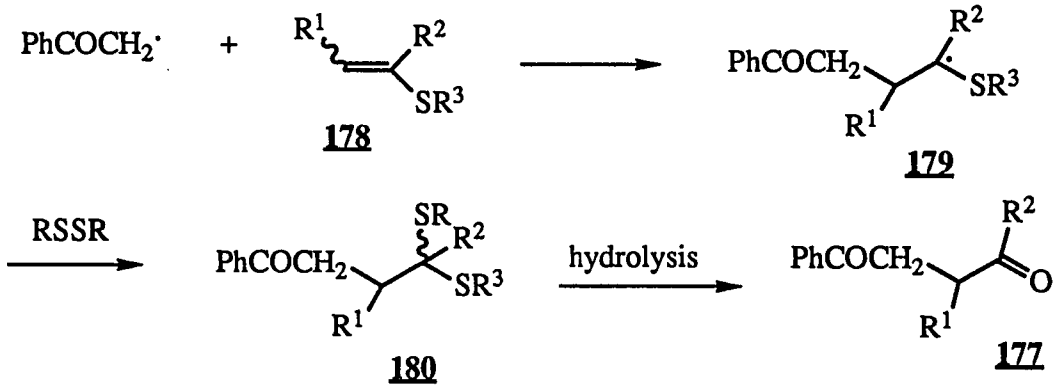
However the reaction of $PhCOCH_2HgCl$ with vinyl acetate and isopropenyl acetate in the presence of PhSSPh and Li_2CO_3 under the usual conditions gave only traces of the 1,4-dicarbonyl products **177** (R^1 = H, R^2 = H,Me) and the major product was acetophenone. It is likely that the adduct radicals **176** preferentially attack the monomers (enol acetates) rather than the diphenyl disulfide and telomerization results. Mayo and Walling[43] have deduced from copolymerization reactivity ratios that the effect of a substituent X of the alkene CH_2=CHX generally increased the reactivity of monomers towards attacking radicals in the following order -C_6H_5 > -$OCOCH_3$ > -OR. Thus the

combined effect of stabilization of the radical center by the adjacent oxygen and increased rate of attack of the adduct radicals on the monomers makes the trapping by PhSSPh a much slower and hence an inefficient process.

Reaction with Vinyl Sulfides

The reaction of $PhCOCH_2HgCl$ with vinyl sulfides **178** in the presence of RSSR and Li_2CO_3 was expected to generate adduct α-thiyl radicals **179** (Scheme XVII) regioselectively due to polar and steric effects which when trapped with disulfides would give the thioacetals **180**. These could then be hydrolysed to the corresponding ketones **177** to generate 1,4-dicarbonyl compounds.

Scheme XVII

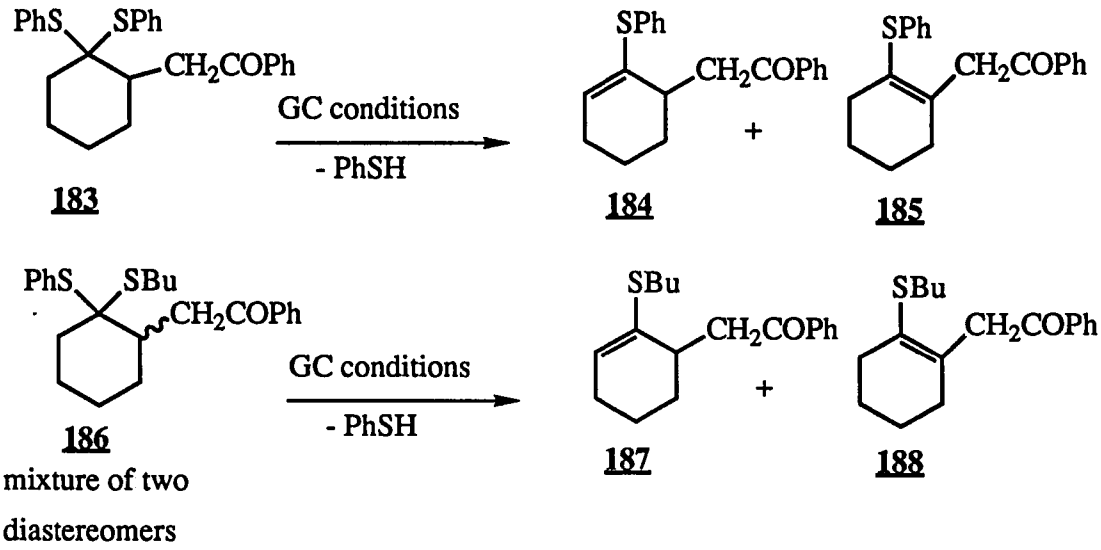


When the reaction was performed with phenyl vinyl sulfide only traces of the expected thioacetal $PhCOCH_2CH_2CH(SPh)SPh$ were obtained along with a poor mass balance of the reactants. Probably the unhindered vinyl sulfides undergo telomerization in

these reactions. It is known[44] that thioethers of the type $RSCH=CH_2$ where R = alkyl, aryl are polymerized much faster than corresponding alkyl vinyl ether at 60 °C with AIBN as initiator.

When the reactions were performed with more sterically hindered alkyl and aryl 1-cyclohexenyl thioethers a variety of addition products were obtained as shown in Table 6.

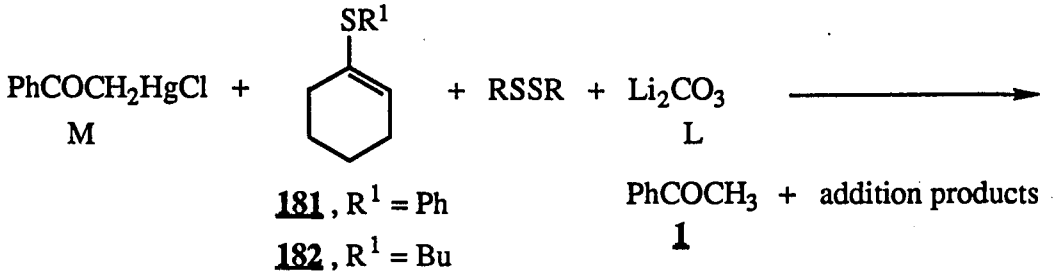
The thioacetals **183** and **186** decomposed under GC conditions eliminating PhSH to give two isomeric unsaturated sulfides which were identified by their mass spectra.



The selective expulsion of PhSH from the thioacetal is consistent with the fact that bonds formed between S and C are about 10 kcal/mole weaker for PhS than for RS (R = alkyl).[32]

The thioacetals were isolated using column chromatography and the yields determined. The saturated and unsaturated sulfides **137** and **184** did not separate on GC and also could not be separated by chromatography, even using preparative TLC.

Table 6. Photostimulated reaction of $PhCOCH_2HgCl$ (M) with vinyl sulfides in presence of disulfides and Li_2CO_3 (L)[a]



Molar equivalents M : **181** or **182** : RSSR : L	% Yield[b] of **1**	Addition products (% yield[b])
1 : **181** (5) : 2 (R=Ph) : 5	20	**183** (30)[c], **184** (3)[d], **137** (4)[e]
1 : **181** (5) : 2 (R=Bu) : 5	9	**184** (23)[d], **137** (26)[e]
1 : **182** (5) : 2 (R=Ph) : 5	7	**186** (51)[c]
1 : **182** (5) : 2 (R=Bu) : 5	5	**187** (23), **191** (34)[e]
1 : **181** (5) : 0 : 0	57	**184** (7)[d], **137** (10)[e]
1 : **182** (5) : 0 : 0	38	**187** (15), **191** (22)[e]

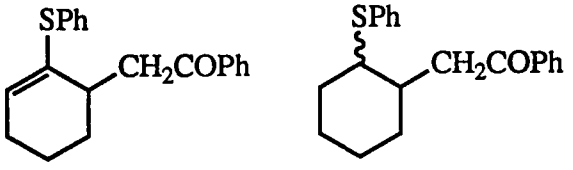
[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL Me_2SO in 350-nm Rayonet photoreactor for 6 h.

[b]GC yield with biphenyl as internal standard.

[c]isolated yield.

[d]Yield of diketone **18** after hydrolysis with $HgCl_2$ in 3 : 1 CH_3CN : H_2O.

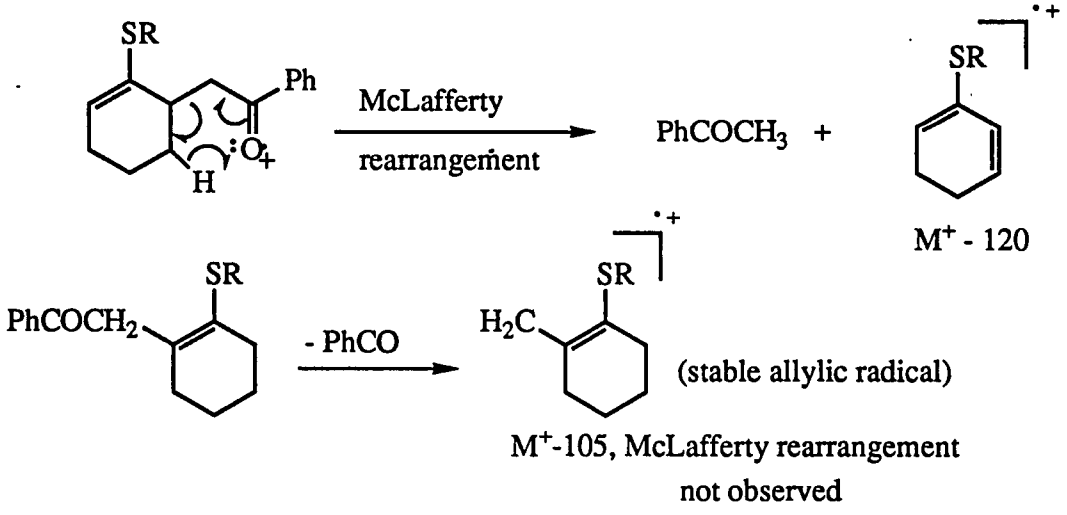
[e]Mixture of two diastereomers.



184 **137**

Therefore after removal of the thioacetal the mixture of these two products was subjected to hydrolysis using two equivalents of $HgCl_2$ in 3 : 1 CH_3CN : H_2O system[45] to convert the vinyl sulfide to the corresponding diketone **18** and then subjected to GC for the determination of the yield.

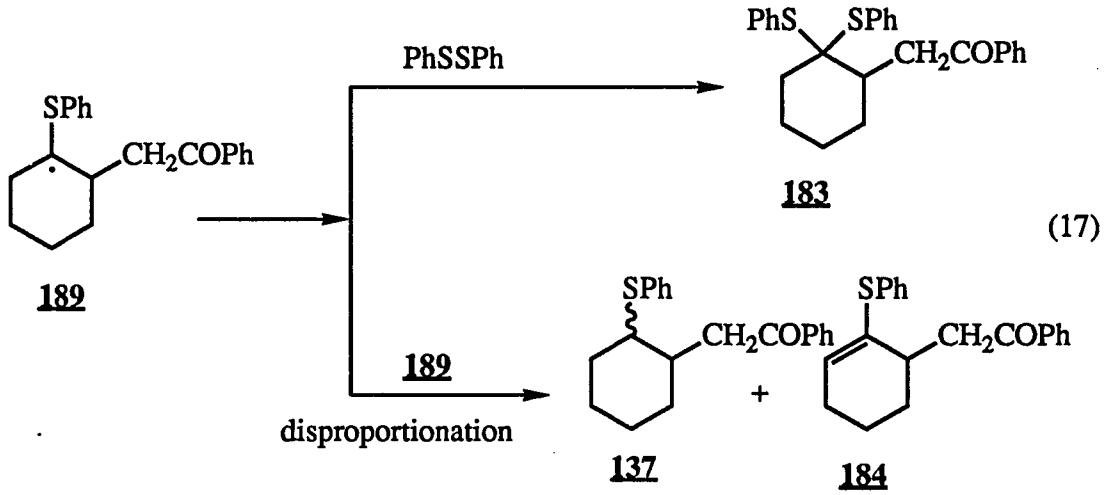
The assignment of the position of the double bond was based on the following expected fragmentation of two isomers.



The addition of $PhCOCH_2$· radical to phenyl 1-cyclohexenyl sulfide generates an adduct radical **189** which is stabilized by adjacent sulfur and by delocalization onto the aromatic ring through the sulfur atom. This increased stability makes it react slower with

the PhSSPh converting only some of the radicals **189** to thioacetal **183**, the remaining radicals undergoing disproportion[27] (reaction 17).

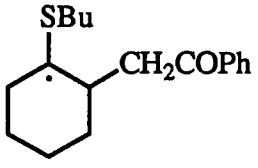
During disproportionation the sterically hindered tertiary radical **189** abstracts a H-atom from the less sterically hindered carbon adjacent to the radical center producing only isomer **184**.



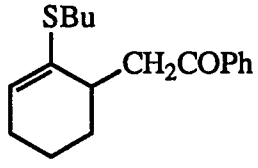
When the disulfide is BuSSBu, which has a much higher dissociation energy than PhSSPh,[46] the adduct radical attack on the disulfide is probably much less exothermic and hence all of it disproportionates giving saturated and unsaturated sulfides **137** and **184** respectively.

The less stabilized adduct radical **190** in case of butyl 1-cyclohexenyl sulfide (due to the absence of aromatic ring for delocalization of the radical) attacks the diphenyl disulfide efficiently to give only the thioacetal **186** as a mixture of two diastereomers. However its attack on BuSSBu is much slower than the disproportionation reaction and with BuSSBu the saturated and unsaturated sulfides **191** and **187** are formed.

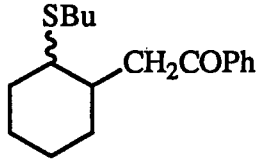
The presence of same products in the reaction mixture when the reactions were carried out in presence of BuSSBu (entries 2,4 of Table 6) and when they were performed in the absence of any disulfide (entries 5,6 of Table 6) confirms the disproportionation pathway for the origin of these products.



190



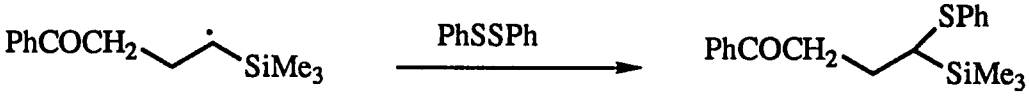
187



191

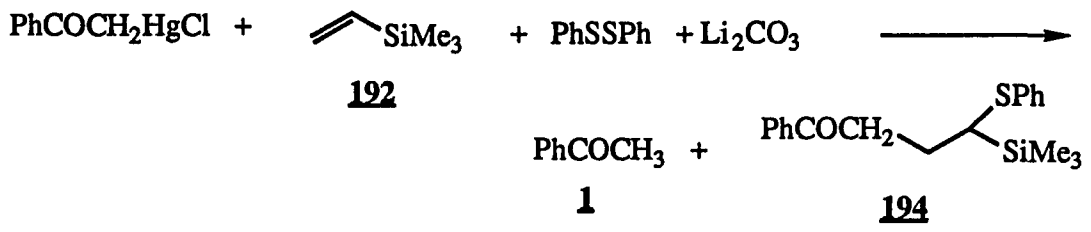
Reaction with Vinyltrimethylsilane

The reaction of $PhCOCH_2HgCl$ with vinyltrimethylsilane in presence of diphenyl disulfide and Li_2CO_3 gave very good yields of the addition product (Table 7). The rate of attack of intermediate adduct radical **193** (stabilized by about 2.6 kcal/mole[47] by the adjacent silyl group) on PhSSPh is fast enough to give sulfide product **194** without any evidence of disproportionation products.



193 **194**

Table 7. Photostimulated reaction of $PhCOCH_2HgCl$ with vinyltrimethylsilane in presence of PhSSPh and Li_2CO_3[a]



Molar equivalents	% Yield[b]	
$PhCOCH_2HgCl$: 192 : PhSSPh : Li_2CO_3	1	194
1 : 1.2 : 2 : 5	2	66
1 : 5 : 2 : 5	0	90

[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor for 6 h.

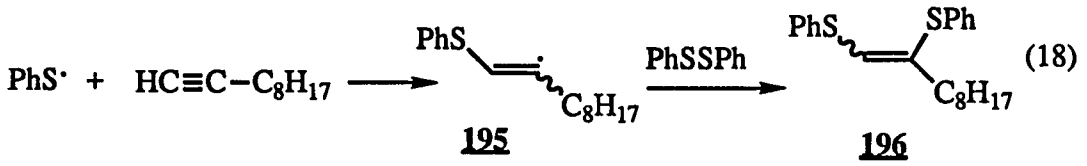
[b]GC yield with biphenyl as internal standard.

Reaction with Other Electron-Rich Unsaturated Compounds

The reaction of $PhCOCH_2HgCl$ under standard conditions was tried with a few other unsaturated compounds such as *N*-morpholino-1-cyclohexene, *N*-methyl pyrrole, dichloroethylene and 1-decyne. These substrates however gave very low yields of the expected products with a large number of byproducts.

The LUMO of alkynes lie higher than in alkenes.[48] Thus the interaction of the SOMO of the free radical and the frontier orbitals of the π-system is smaller for alkynes than for alkenes. Hence both nucleophilic and electrophilic radicals react slower with alkynes than with alkenes.

The main products obtained in low yields in the reaction with 1-decyne were found by mass spectroscopy to be a mixture of cis and trans **196**. This is probably due to the fact that addition of PhS· to alkynes is not as readily reversible as it is with alkenes[49] and the intermediate vinyl radical **195** is trapped by the disulfide before the reversible elimination occurs (reaction 18).

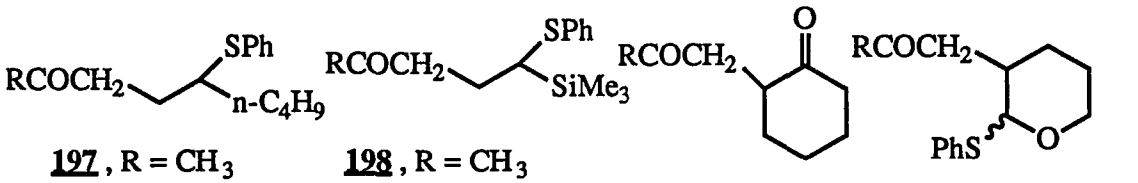


195 **196** (18)

Reaction of CH_3COCH_2HgCl and $OHCCH_2HgCl$ with Alkenes in Presence of PhSSPh and Li_2CO_3

To determine the generality of this reaction some studies were carried out using two other carbonyl substituted radicals CH_3COCH_2· and $OHCCH_2$· with various alkenes. The acetylmethyl radical has almost the same resonance stabilization as the benzoylmethyl radical since the C-H BDE of CH_3COCH_2-H and $PhCOCH_2$-H are 92 and 93 kcal/mole respectively[50]. In case of the ·CH2CHO radical the BDE was expected to be almost the same but the possibility of abstraction of the aldehydic hydrogen atom[51] was anticipated to be a possible problem.

The reactions were performed with the same alkenes as in the case of $PhCOCH_2HgCl$ under similar conditions. The expected products in this case were **197-204** shown below. Table 8 and Table 9 show the results of the reactions of CH_3COCH_2HgCl and $OHCCH_2HgCl$ with various alkenes under standard conditions respectively.



197, R = CH_3 **198**, R = CH_3 **199**, R = CH_3 **200**, R = CH_3

201, R = H **202**, R = H **203**, R = H **204**, R = H

Table 8. Photostimulated reaction of CH_3COCH_2HgCl with various alkenes in presence of PhSSPh and Li_2CO_3[a]

CH_3COCH_2HgCl + alkene + PhSSPh + Li_2CO_3 ⟶ addition product

Molar equivalents CH_3COCH_2HgCl : PhSSPh : Li_2CO_3	Alkene (equiv.)	Addition product (% Yield[b])
1 : 2 : 5	**37** (5)	**197** (92)
1 : 2 : 5	**192** (5)	**198** (90)
1 : 2 : 5	**162** (5)	**199** (35)
1 : 2 : 5	**164** (5)	**199** (40)
1 : 2 : 5	**163** (5)	**200** (32) (cis/trans=6/1)

[a]Photostimulated reaction of 0.25 mmol CH_3COCH_2HgCl in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at about 40 °C for 6 h.

[b]GC yield with biphenyl as internal standard.

Table 9. Photostimulated reaction of $OHCCH_2HgCl$ with various alkenes in presence of PhSSPh and Li_2CO_3[a]

$$OHCCH_2HgCl + \text{alkene} + PhSSPh + Li_2CO_3 \longrightarrow \text{addition product}$$

Molar equivalents $OHCCH_2HgCl$: PhSSPh : Li_2CO3	Alkene (equiv.)	Addition product (% yield[b])
1 : 2 : 5	**37** (5)	**201** (90)
1 : 2 : 5	**192** (5)	**202** (86)
1 : 2 : 5	**163** (5)	**203** (37)
1 : 2 : 5	**163** (5)	**204** (42) (cis/trans=5.5/1)

[a]Photostimulated reaction of 0.25 mmol of $OHCCH_2HgCl$ in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at about 40 °Cfor 6 h.

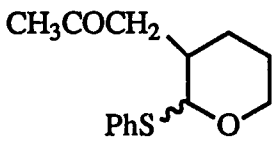
[b]GC yield with biphenyl as internal standard.

It can be seen from Table 8 and Table 9 that similar results are obtained with $CH_3COCH_2\cdot$ and $OHCCH_2\cdot$ radicals with various alkenes. The reaction with 1-hexene is in fact superior with these radicals than in the case of the $PhCOCH_2\cdot$ radical.

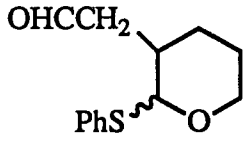
The success of the reaction of $OHCCH_2\cdot$ radicals especially with simple alkenes and the vinyl silane suggest that side reactions such as abstraction of the aldehydic H-atom etc. are minimal. Thus this is a very useful method to extend the carbon chain by a CH_2CHO group.

One major difference between the reaction of $PhCOCH_2HgCl$ and that of CH_3COCH_2HgCl and $OHCCH_2HgCl$ with dihydropyran is that the reactions in the latter case are not completely stereoselective unlike in the former case. Reaction of

CH_3COCH_2HgCl with dihydropyran (entry 5 of Table 8) gives a 6 : 1 (cis : trans) ratio of the product **200** while in case of $OHCCH_2HgCl$ the ratio is 5.5 : 1 (cis : trans) **204**.



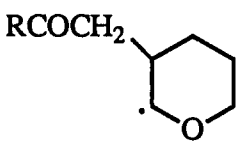
200



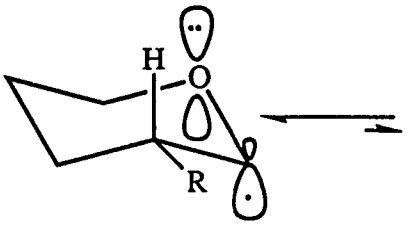
204

The trans isomers were found to exist in a conformation in which the two substituents were in diequatorial position. This was inferred from the characteristic coupling constant of the two axial protons of 7.2 Hz in these type of systems.[41]

In this case the adduct radical **205** which has a smaller substituent on the tetrahydropyran ring (i.e. CH_3COCH_2 or $OHCCH_2$) than in the case of radical **174** which has a $PhCOCH_2$ group, the conformational bias for keeping the substituent equatorial is less dominant. Thus the radical **205** exists as a mixture of two conformations **205a** and **205b** in which the σ-radical is axial to maximize the interaction with the non-bonding electron pair on ring oxygen and the substituent is in an equatorial and axial positions.

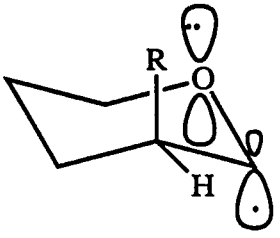


205 , R = Me, H



205a

R = Me, H



205b

The ratio of cis/trans product obtained, which is around 6 : 1 indicates that the conformation **205a** is favored over **205b** by a ratio of about 6 : 1. Similar loss of

stereoselectivity was observed by Giese[42] in the reaction of glycosyl radicals with alkenes when the ring substituents were changed from the larger acetoxy groups to smaller methoxy groups.

Another difference is that products **200** and **204** did not decompose under GC conditions unlike in case of **168a**. This may be bacause of the higher molecular weight of the product **168a** or another possibility is the anchimeric assistance by phenyl or the enolic oxygen of $PhCOCH_2$ group given to the departure of the SPh moiety in case of **168a**. The absence of the phenyl group and the lesser chance of enolization of the carbonyl (due to not being able to conjugate with the phenyl group) probably precludes any anchimeric assistance to the SPh moiety in case of **200** and **204**.

Kinetic Chain Length

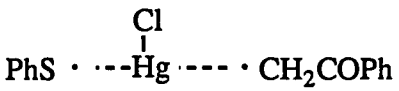
In general, in order to apply reactions between radicals and non-radicals for synthesis, chain reactions have to be built up. The good yields obtained in the foregoing reactions raised the question of whether it is a chain reaction. As discussed earlier one of the requirements of a chain reaction, i.e., that the selectivities of the radicals involved in the chain have to differ from each other, seems to be satisfied by the present system. Thus the important question was to determine the efficiency which the PhS· radical regenerates another $PhCOCH_2$· radical from starting mercurial viz. $PhCOCH_2HgCl$.

The displacement of an alkyl group by attack of a thiyl radical on an organometallic compounds such as organoboranes, organostibines, organobismuth compounds are well documented.[32,52] Russell has shown that alkylmercurials undergo substitution reaction with disubstituted dichalcogenides like RSSR, ArSSAr etc. by radical chain mechanism in which the chalcogenide-centered radical attacks RHgCl to form a

primary, secondary or tertiary alkyl radical[27]. Reaction of 0.25 M *t*-BuHgCl with 0.05 M PhSSPh formed *t*-BuSPh with an initial kinetic chain length of 400.[27]

The reaction of accepter radicals such as PhS· with RHgX can be pictured as a concerted reaction in which the stability of the incipient alkyl radical contributes to the stability of the transition state leading to its formation.[53]

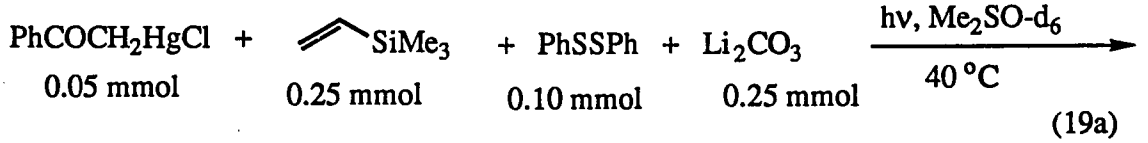
In the present reaction such a transition state could be shown by **206**, whose stability will depend on the stability of the incipient $PhCOCH_2$· radical. Since $PhCOCH_2$· radical is not as stable as *t*-Bu· radical the process is expected to be less efficient than that in the case of *t*-Bu· radical.



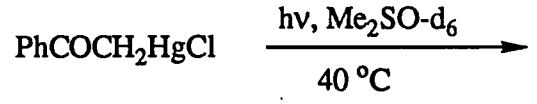
206

The usual method of using 10 mole % di-*tert*-butylnitroxide (DTBN) as an inhibitor to calculate the kinetic chain length could not be used here because of the possibility of the PhS· radicals formed by cleavage of PhSSPh during photolysis, reacting with the nitroxide radicals and thus giving anamolously short chain lengths. The kinetic chain length was therefore calculated using other methods as discussed below.

The rate of disappearance of $PhCOCH_2HgCl$ in the present reaction would be expected to be faster than that in the unimolecular decomposition in the absence of any other reactants, if the reaction is really a chain reaction. Thus the rate of disappearance of $PhCOCH_2HgCl$ with time was monitored by ^1H NMR in the following two reactions (reactions 19a and 19b) performed in NMR tubes.



(19a)



(19b)

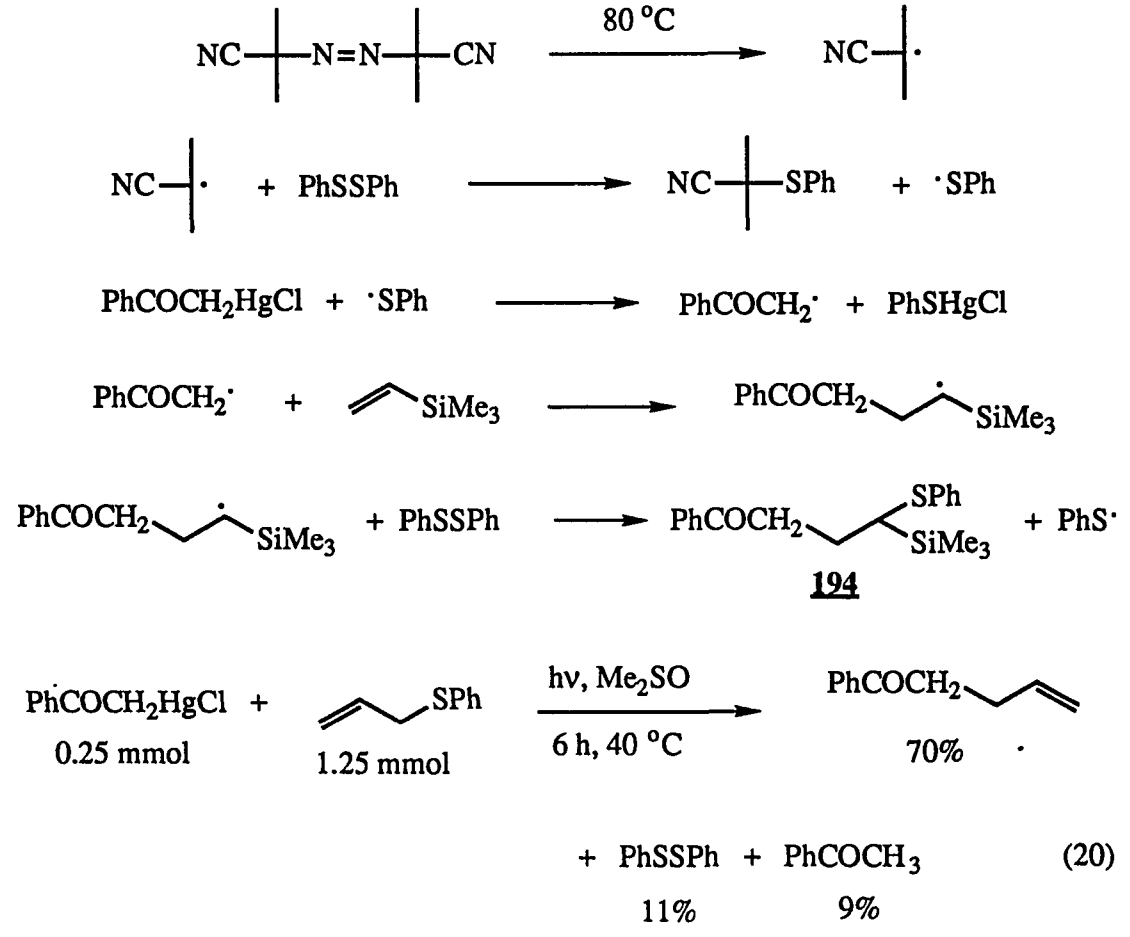
No noticable accelaration of the rate of disapperance of $PhCOCH_2HgCl$ in reaction 19a was observed indicating that PhS· radicals are not able to attack $PhCOCH_2HgCl$ to generate $PhCOCH_2$· radical.

Another experiment was carried in which a mixture of 1 equivalent of $PhCOCH_2HgCl$ with 5 equivalent of vinyltrimethyl silane in presence of 2 equivalent of PhSSPh, 5 equivalents of Li_2CO_3 and 0.1 equivalent AIBN was heated at 80 °C until all the AIBN had decomposed, as observed by ^1H NMR. If the reaction was a chain reaction, the expected sequence of reactions are shown in Scheme XVIII. It is known[54] that PhSSPh by itself does not undergo homolysis at 80 °C and it was found experimentally that $PhCOCH_2HgCl$ is stable to 80 °C in Me_2SO by itself.

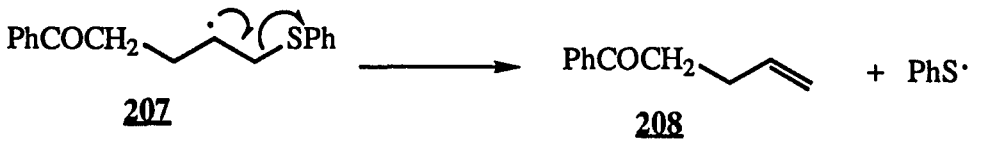
It was found that even after all the AIBN had decomposed none of the product **194** had formed and the $PhCOCH_2HgCl$ was mainly unaffected. This observation also supports the conclusion drawn earlier that the observed process is not a chain reaction.

An indirect method was also used, which again confirmed the conclusion that a chain reaction is not involved. In this method the kinetic chain length of the reaction between $PhCOCH_2HgCl$ with phenyl allyl sulfide was calculated by the usual DTBN inhibition method. The reaction of $PhCOCH_2HgCl$ with phenyl allyl sulfide gives a good yield (reaction 20) of allylated acetophenone derivative via an addition elimination sequence.

Scheme XVIII

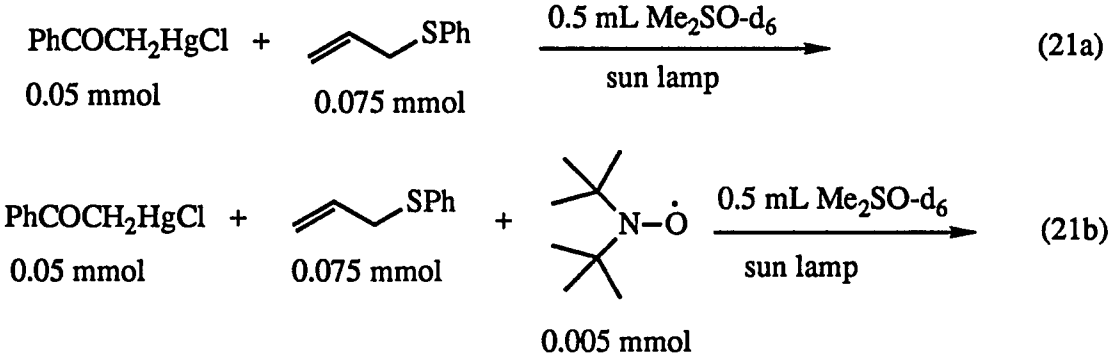


The above reaction would be a chain reaction if the PhS· eliminated by the adduct radical **207** attacked the $PhCOCH_2HgCl$ to generate another $PhCOCH_2$· radical, although the formation of PhSSPh indicates a facile termination process.



Thus a kinetic chain length greater than 1 for this reaction would indicate that the PhS· radicals are able to generate $PhCOCH_2$· by attack on $PhCOCH_2HgCl$ with olefins in presence of PhSSPh and Li_2CO_3.

The following two reactions 21a and 21b were followed by ^1H NMR to calculate the kinetic chain length of the reaction between $PhCOCH_2HgCl$ with phenyl allyl sulfide in Me_2SO-d_6.



Both the reactions 21a and 21b were performed under identical conditions and the rate of formation of product **208** with time was monitored (by monitoring the allylic CH_2 group of **208**) by ^1H NMR.

The initial rate of formation of product **208** in reaction 21a was found to be 6.4 x 10^{-4} $Lmol^{-1}min^{-1}$ while the inhibition time for reaction 21b was found to be 20 minutes. The initial concentration of di-*tert*-butylnitroxide (DTBN) in reaction 21b was 0.0125 $molL^{-1}$. The kinetic chain length (K.C.L.) was calculated as shown.

Thus it was confirmed that PhS· radicals are not able to attack $PhCOCH_2HgCl$ to generate $PhCOCH_2$· radical making the reaction of $PhCOCH_2HgCl$ with alkenes in presence of PhSSPh and Li_2CO_3 a non-chain reaction.

$$\text{K.C.L.} = \frac{\text{initial rate of formation of 208 in reaction 21a}}{\dfrac{\text{initial concentration of DTBN}}{\text{inhibition time in reaction 21b}}}$$

$$= \frac{6.4 \times 10^{-4}\ \text{molL}^{-1}\text{s}^{-1}}{\dfrac{0.0125\ \text{molL}^{-1}}{20\ \text{min}}}$$

$$= 1.02$$

The two most likely reasons for the inability of PhS· to displace $PhCOCH_2$· from $PhCOCH_2HgCl$ are (1) The considerably lower stability of the incipient $PhCOCH_2$· radical (BDE of $PhCOCH_2$-H = 93 kcal/mole) as compared to that of PhS· radical (BDE of PhS-H = 82 kcal/mole) and (2) The unfavourable polarity of $PhCOCH_2^{\delta-}$ $Hg^{\delta+}Cl$ making the attack of the electrophilic PhS· radical on the electron deficient Hg atom a less attractive process.

The good yields obtained in the present reaction inspite of it being a non-chain reaction, can thus be attributed to a high selectivity of the various radicals involved in the reaction sequence and the reversible adition of PhS· radicals to olefins.

The Role of Li_2CO_3

The reactions of $RCOCH_2HgCl$ (R = Ph, Me, H) with alkenes in presence of PhSSPh gave good yields of the phenylthio trapped addition products only when a base such as Li_2CO_3 was used. Table 10 clearly shows the importance of a carbonate base for the success of these reactions.

Table 10 shows that only carbonate bases like Li_2CO_3 and Na_2CO_3 give good yields, Li_2CO_3 being slightly better than Na_2CO_3. Reactions without the presence of a carbonate base or using bases such as 2,6-di-*tert*-butylpyridine (DTBP) or Dabco, give a higher proportion of acetophenone at the expense of the expected product.

The (benzoylmethyl)mercurials undergo electrophilic attack by H^+ quite readily to form acetophenone.[55] For example mixing one equivalent of proton donors such as HCl, ammonium salts or PhSH with $PhCOCH_2HgCl$ in Me_2SO, instantaneously converts it to $PhCOCH_3$ quantitatively.

Thus it was thought that Li_2CO_3 probably prevents buildup of acidic byproducts which otherwise would destroy some of the $PhCOCH_2HgCl$. The possible acidic byproducts could be either HCl or PhSH or both.

One possibility was that ionic reaction between the reactants at the reaction temperature produces an acidic byproduct causing conversion of some of the $PhCOCH_2HgCl$ to $PhCOCH_3$ in the absence of a base. To check this possibility the reaction of one equivalent $PhCOCH_2HgCl$ with two equivalent PhSSPh and five equivalents of cyclohexene in dark at around 40 °C in Me_2SO-d_6 was followed by ^1H NMR to find the rate of production of $PhCOCH_3$. The rate was found to be too slow to account for the large amount of $PhCOCH_3$ formed under standard conditions in the absence of a base. Thus it was evident that the acidic byproduct was formed via a radical reaction under photolytic reaction conditions.

Walling proposed in his review,[56] that the reaction in equation 22 would have negligible activation energy when polar and steric factors are favorable and when the resulting $R^{1\cdot}$ radicals are somewhat stabilized by resonance. This was later confirmed by Cohen and Wang.[57]

Table 10. Effect of various bases on the photostimulated reaction of $PhCOCH_2HgCl$ with alkenes in presence of PhSSPh in Me_2SO

$$PhCOCH_2HgCl + \text{alkene} + PhSSPh + [\ ] \xrightarrow{Me_2SO} PhCOCH_3 + \text{addition product}$$

1

Alkene (mmol)	Base (mmol)	% Yield[b] of **1**	Addition product (% yield[b])
36 (1.25)	-	53	**163** (27)[c]
36 (1.25)	Li_2CO_3 (1.25)	27	**137** (63)[c]
163 (1.25)	-	78	**168a** (4)
163 (1.25)	DTBP[d] (0.50)	70	**168a** (3)
163 (1.25)	Na_2CO_3 (1.25)	7	**168a** (33)
163 (1.25)	Li_2CO_3 (1.25)	7	**168a** (43)
37 (1.25)	-	36	**140** (47)
37 (1.25)	Na_2CO_3 (1.25)	tr	**140** (72)
37 (1.25)	Dabco (0.50)	76	**140** (7)
37 (1.25)	Li_2CO_3 (1.25)	tr	**140** (80)

[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$ and 0.50 mmol of PhSSPh in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at about 40 °C for 6 h.

[b]GC yield with biphenyl as internal standard.

[c]Mixture of two diastereomers.

[d]DTBP means 2,6-Di-*tert*-butylpyridine.

$$RS\cdot + R^1H \longrightarrow RSH + R^{1}\cdot \qquad (22)$$

It was likely that in the present reaction the PhS· radical produced from PhSSPh under photolysis abstracted hydrogen atoms from the alkenes to form PhSH. To confirm this a mixture of two equivalents of PhSSPh and five equivalents of cyclohexene in Me_2SO-d_6 was photolysed under standard conditions for six hours. At this point ^1H NMR showed a peak at 5.35 ppm belived to be of the thiol proton. When one equivalent of $PhCOCH_2HgCl$ was added to this reaction mixture and shaken for one minute, the ^1H NMR showed that almost all the $PhCOCH_2HgCl$ was converted to $PhCOCH_3$ and the peak at 5.35 ppm had disappeared. Thus it appears that substantial amounts of PhSH are formed under the standard reaction conditions via the H-atom abstractions by PhS· radicals, most likely from the allylic position of the alkenes.

As mentioned earlier PhSH instantaneously converts $PhCOCH_2HgCl$ to $PhCOCH_3$. However when 0.5 equivalents of PhSH in Me_2SO-d_6 is shaken with 10 equivalents of Li_2CO_3 intermittently for 10 minutes and then one equivalent of $PhCOCH_2HgCl$ added, ^1H NMR showed that no $PhCOCH_3$ had formed indicating that Li_2CO_3 does neutralize PhSH which otherwise would have caused the conversion of $PhCOCH_2HgCl$ to $PhCOCH_3$. However a peak was observed at 2.75 ppm which indicated that the PhSLi formed had caused symmetrization of some of $PhCOCH_2HgCl$ to the bis-mercurial $(PhCOCH_2)_2Hg$. Organomercurials are known to undergo symmetrization in presence of nucleophiles.

Surprisingly the reaction of $PhCOCH_2HgCl$ with 1-hexene in presence of PhSSPh and PhSLi (reaction 23) under standard conditions gave only $PhCOCH_3$.

$$\underset{0.25\ \text{mmol}}{PhCOCH_2HgCl} + \underset{1.25\ \text{mmol}}{C_4H_9} + \underset{0.50\ \text{mmol}}{PhSSPh} + \underset{0.25\ \text{mmol}}{PhSLi} \xrightarrow[6\ \text{h, 40 °C}]{h\nu,\ Me_2SO} \underset{57\%}{PhCOCH_3\ \text{only}} \quad (23)$$

^{1}H NMR of a mixture of one equivalent of PhSLi and one equivalent of $PhCOCH_2HgCl$ in Me_2SO-d_6 showed that some of the $PhCOCH_2HgCl$ had undergone symmetrization to form $(PhCOCH_2)_2Hg$. When this mixture was photolysed for two hours the reaction mixture became dark red-brown and ^{1}H NMR showed formation of $PhCOCH_3$ but no $(PhCOCH_2)_2$ was seen (reaction 24).

$$\underset{1\ \text{equiv.}}{PhSLi} + \underset{1\ \text{equiv.}}{PhCOCH_2HgCl} \xrightarrow[2\ \text{h, 40 °C}]{h\nu,\ Me_2SO\text{-}d_6} PhCOCH_3\ \text{but no}\ (PhCOCH_2)_2 \quad (24)$$

On the other hand, when first one equivalent of $HgCl_2$ was added to one equivalent of $PhCOCH_2HgCl$ in Me_2SO-d_6 and then one equivalent of PhSLi was added, the ^{1}H NMR showed that the bis-mercurial, $(PhCOCH_2)_2Hg$, had not formed. When this mixture was photolysed for two hours, the reaction mixture did not become red-brown and ^{1}H NMR showed the formation of $(PhCOCH_2)_2$ and the absence of $PhCOCH_3$ (reaction 25).

$$PhSLi + HgCl_2 \xrightarrow[Me_2SO\text{-}d_6]{\text{shake 1 min.}} \xrightarrow[PhCOCH_2HgCl]{\text{add 1 equiv.}} \xrightarrow[40\ °C]{h\nu,\ 2\ h} (PhCOCH_2)_2\ \text{but no}\ PhCOCH_3 \quad (25)$$

These observations suggested that when PhSLi is mixed with $PhCOCH_2HgCl$, some of the PhSLi symmetrizes the $PhCOCH_2HgCl$ to form $(PhCOCH_2)_2Hg$ but some PhSLi remains as such. When this mixture is photolyzed (reaction 24) the $PhCOCH_2\cdot$ radical formed either from $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ is immediately reduced by the PhS^- anion to form $PhS\cdot$ and $PhCOCH_2^-$ (reaction 26) and this enolate anion gives the characteristic red-brown color to the reaction mixture.

$$PhS^- + PhCOCH_2\cdot \longrightarrow PhS\cdot + PhCOCH_2^- \qquad (26)$$

However when PhSLi is first mixed with an equivalent amount of $HgCl_2$ it instantaneously reacts to form PhSHgCl and therefore when $PhCOCH_2HgCl$ is added afterwards it remains unsymmetrized due to absence of PhS^- in the reaction mixture. When this reaction mixture is photolyzed (reaction 25) the $PhCOCH_2\cdot$ radicals formed are not reduced due again to the absence of PhS^- anion in the reaction mixture and $(PhCOCH_2)_2$ is formed by radical-radical coupling.

In the reaction mixture under standard conditions, it is unlikely that $HgCl_2$ is present to react with PhSLi as described above. The most likely species that could be present is PhSHgCl formed by the attack of $\cdot HgCl$ (formed by photolytic cleavage of $PhCOCH_2HgCl$) on PhSSPh (reaction 27).

$$\cdot HgCl + PhSSPh \longrightarrow PhSHgCl + PhS\cdot \qquad (27)$$

Indeed when one equivalent of Hg_2Cl_2 was photolyzed in presence of PhSSPh (one equivalent) (reaction 28) it formed $(PhS)_2Hg$ and only 37% of the PhSSPh was

recovered, indicating that either the ·HgCl (formed by photolytic clevage of Hg-Hg bond in Hg_2Cl_2) attacked the PhSSPh or the PhS· radical attacked the Hg-Hg bond in a S_H2 fashion or both.

$$\underset{\text{1 equiv.}}{\text{Cl-Hg-Hg-Cl}} + \underset{\text{1 equiv.}}{\text{PhSSPh}} \xrightarrow[\text{4 h, 40 °C}]{Me_2SO\text{-}d_6,\ h\nu} (PhS)_2Hg + \underset{\text{0.37 equiv. unreacted}}{\text{PhSSPh}} \qquad (28)$$

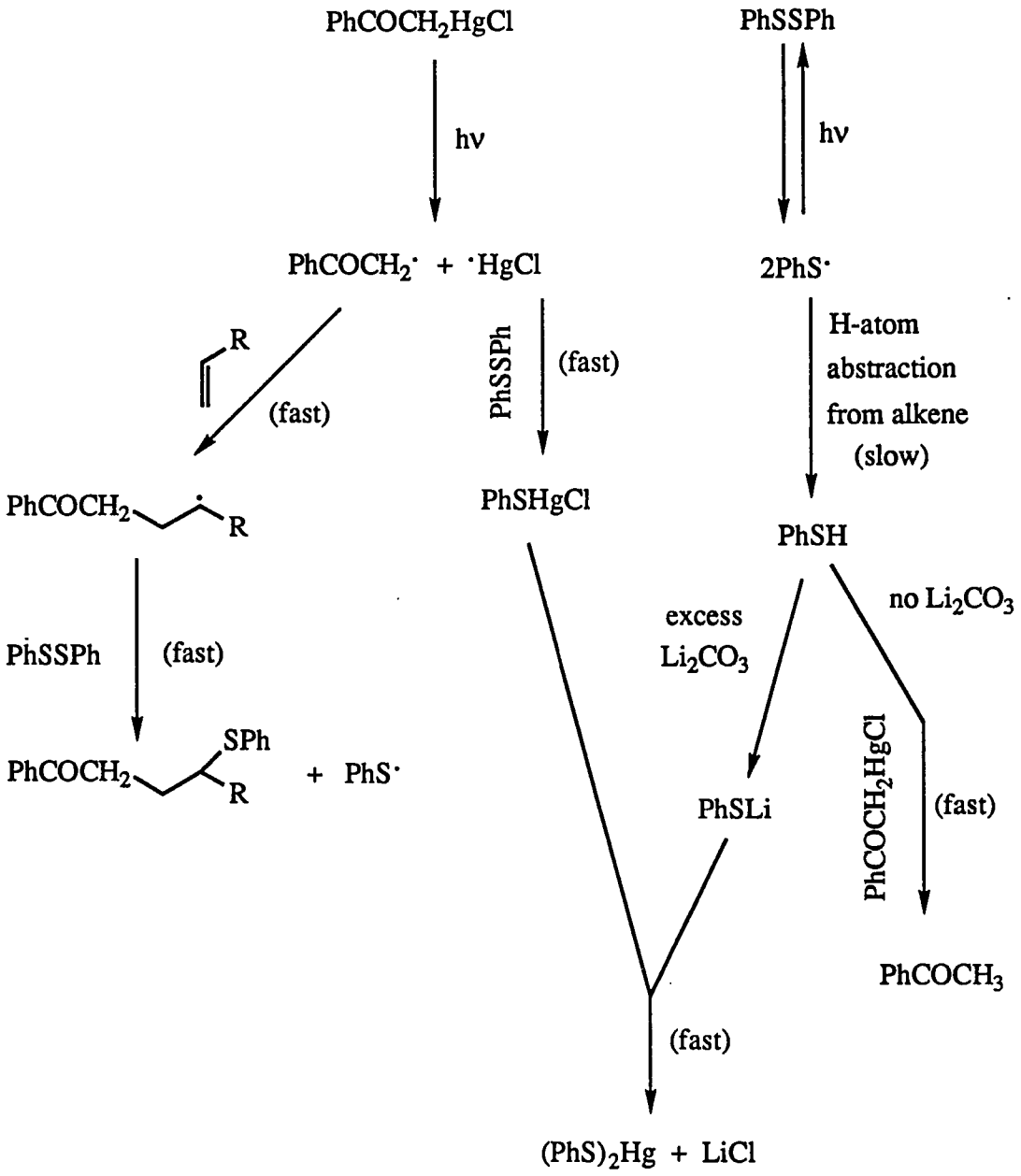
Formation of $(PhS)_2Hg$ as the reaction product in reaction 28 is not surprising since it is known that PhSHgCl is in equilibrium with $(PhS)_2Hg$ in solution (reaction 29)[58] and most probably the aqeous $Na_2S_2O_3$ workup pushes the equilibrium of equation 29 completely to the right by removing the $HgCl_2$ on the right hand side.

$$2PhSHgCl \rightleftharpoons (PhS)_2Hg + HgCl_2 \qquad (29)$$

This observation lent support to the assumption that PhSHgCl is the species present in the reaction mixture under standard reaction conditions. The question now was whether PhSLi can react with PhSHgCl to form $(PhS)_2Hg$ and thereby be removed from the reaction mixture. It is known[59] that one equivalent of $HgCl_2$ reacts with two equivalents PhSH in ethanol to form $(PhS)_2Hg$ in 98% yield demonstrating the readiness with which the first formed PhSHgCl reacts with another molecule of PhSH even in the absence of a base.

On the basis of these observations, the role of Li_2CO_3 in improving the yield of the reaction can now be summarized as shown below (Scheme XIX).

Scheme XIX


PhCOCH2HgCl
hν
PhCOCH2· + ·HgCl
R
(fast)
PhCOCH2
R
PhSSPh
(fast)
PhCOCH2
SPh
R
+ PhS·
PhSSPh
(fast)
PhSHgCl
PhSSPh
hν
2PhS·
H-atom
abstraction
from alkene
(slow)
PhSH
excess
Li2CO3
no Li2CO3
PhSLi
PhCOCH2HgCl
(fast)
PhCOCH3
(fast)
(PhS)2Hg + LiCl

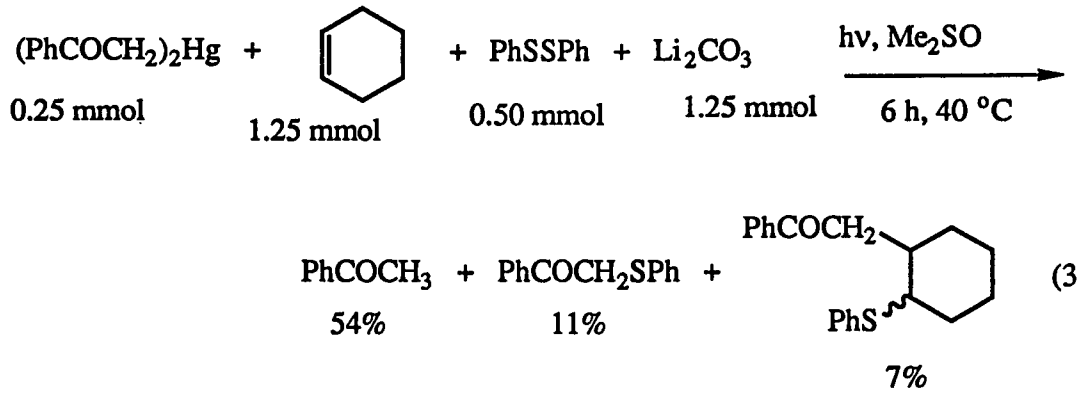
Scheme XIX shows that photolysis of the reaction mixture under standard conditions produces radicals $PhCOCH_2\cdot$, $\cdot HgCl$, and $PhS\cdot$ from the reactants, out of which $\cdot HgCl$ and $PhCOCH_2\cdot$ are rapidly consumed to form PhSHgCl and the adduct radical from the olefin respectively. The $PhS\cdot$ radicals slowly abstract H-atom from the alkene to form PhSH which is immediately neutralized by the comparatively large excess of Li_2CO_3 present to form PhSLi. The thiolate anion is immediately removed from the reaction mixture (before it can reduce $PhCOCH_2\cdot$) by reaction with the PhSHgCl (to form $(PhS)_2Hg$), which by then is present in large excess due to the rapid reaction of $\cdot HgCl$ with PhSSPh.

This elucidation of the role of Li_2CO_3 explained other observations which had earlier been intriguing. The reaction between $PhCOCH_2HgCl$, PhSSPh and 1-hexene in presence of PhSLi instead of Li_2CO_3 as mentioned earlier (reaction 23) gave only $PhCOCH_3$ due to the fact that at all times during that reaction there was an excess of PhSLi over PhSHgCl so that only reduction of $PhCOCH_2\cdot$ radicals to $PhCOCH_2^-$ took place.

The poor yields of the products obtained when $(PhCOCH_2)_2Hg$ is used as source of $PhCOCH_2\cdot$ radicals for reaction with alkenes such as cyclohexene (reaction 30) under standard conditions can also be understood readily.

In this case PhSLi formed reduces the $PhCOCH_2\cdot$ radicals by electron transfer due to the absence of PhSHgCl to consume the PhS^-. The $PhCOCH_2SPh$ observed is probably formed by attack of the acetophenone enolate ion on PhSSPh.

Na_2CO_3 is slightly less efficient than Li_2CO_3 probably bacause of its lower solubility in Me_2SO due to a more ionic character of the bonds as compared to those in Li_2CO_3.



Other bases such as Dabco and *t*-BuOK are too nucleophilic (unlike the non-nucleophilic CO_3^{2-}) and result in lower yield of the addition products to olefins, possibly due to the nucleophilic displacement of $PhCOCH_2^-$ from $PhCOCH_2HgCl$.

Effect of Other Trapping Agents

The success of the reaction in presence of PhSSPh as an adduct radical trap provided impetus to study the effect of other trapping agents. In almost all the reactions with these trapping agents the same ratio of $PhCOCH_2HgCl$, alkene, trapping agent and Li_2CO_3 was used viz. 1 : 5 : 2 : 5 respectively since it worked best with PhSSPh as radical trap.

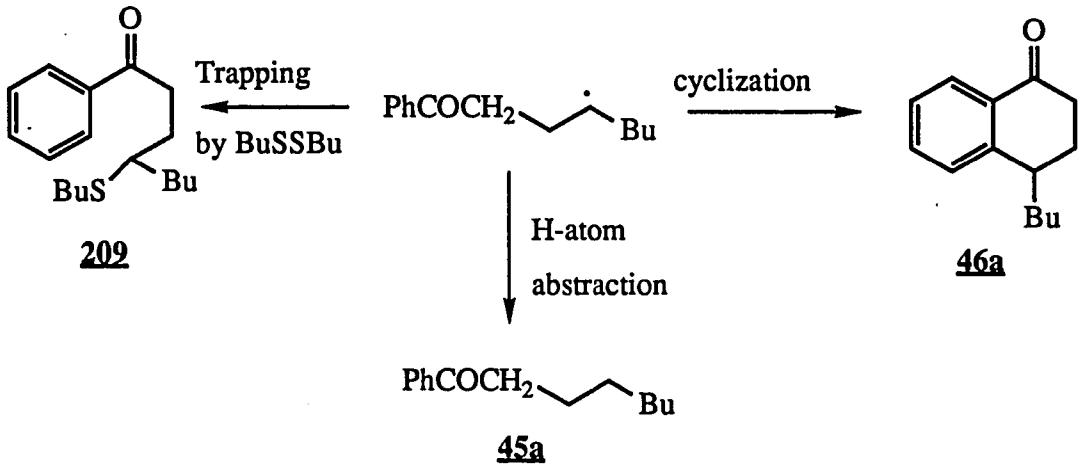
Other disulfides

Two other disulfides were tried apart from the PhSSPh discussed earlier, viz. dibutyldisulfide and di-*tert*-butyldisulfide. These two alkyl disulfides have considerably larger BDEs as compared to that of PhSSPh. For example, whereas PhSSPh has a BDE of about 23 kcal/mole, the alkyl disufide EtSSEt has a BDE of about 67 kcal/mole[46]. It was

therefore expected that the attack of the adduct radical on these two disulfides would be much slower than that in the case PhSSPh. In addition in the case of di-*tert*-butyldisulfide, a steric factor may further slow down this attack. These reactions are shown in Table 11.

The results in Table 11 show that BuSSBu does not trap the adduct radicals as efficiently as PhSSPh. This allows some of the adduct radicals to cyclize with the aromatic ring as discussed in Part III. This indicates that the S_H2 attack on BuSSBu by adduct radicals and cyclization with the aromatic ring occur at comparable rates, especially in the case of 1-hexene (Scheme XX).

Scheme XX



The enol ethers also behave similarly in case dibutyl disulfide but give much lower yields of the 1,4-dicarbonyl products.

In case of di-*tert*-butyl disulfide no product resulting from disulfide trapping of the adduct radical was obtained; probably the steric hindrance of *t*-butyl group completely prevents the bimolecular displacements at the sulfur atom. This is in agreement with the

Table 11. Photostimulated reaction of $PhCOCH_2HgCl$ with alkenes in presence of dibutyl disulfide and Li_2CO_3[a]

$$PhCOCH_2HgCl + alkene + BuSSBu + Li_2CO_3 \longrightarrow products$$

Alkene (mmol)	% Yield[b] of **1**	Addition products (% yield[b])
36 (1.25)	30	**191** (34)[c], **42** (11), **43** (5)[c]
37 (1.25)	tr	**209** (22), **45a** (9), **46a** (31)
159 (1.25)	tr	**165** (21)[d]
162 (1.25)	14	**18** (20)

[a]Photostimulated reaction of 0.25 mmol of $PhCOCH_2HgCl$, 0.50 mmol of BuSSBu and 1.25 mmol of Li_2CO_3 in 2.5 mL Me_2SO in a 350-nm Rayonet photoreactor at about 40 °C for 6 h.

[b]GC yield with biphenyl as internal standard

[c]Mixture of two diastereomers.

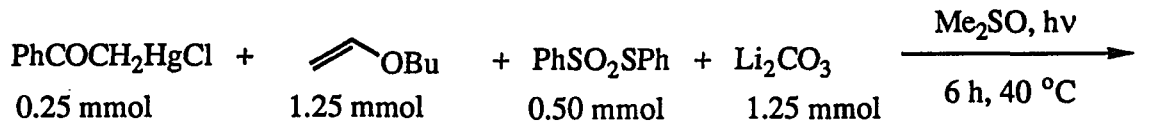
[d]After hydrolysis with H_3O^+.

observation[60] that Phenyl radicals attack dimethyl disulfide 112 times faster than di-*tert*-butyl disulfide.

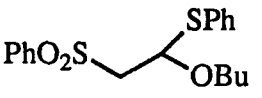
$PhSO_2SPh$ as a trapping agent

In this case it was expected that the adduct radical would attack $PhSO_2SPh$ to eliminate $PhSO_2\cdot$ radical which being less stable than PhS· radical[61] might regenerate another $PhCOCH_2\cdot$ radical from $PhCOCH_2HgCl$ and produce a chain reaction. Alkyl radicals formed by photolysis of RHgCl are known to enter into chain reaction with $PhSO_2Cl$ forming R-Cl, involving attack of $PhSO_2\cdot$ on RHgCl to form R· radicals.[27]

The reaction of $PhCOCH_2HgCl$ with butyl vinyl ether in presence of $PhSO_2SPh$ and Li_2CO_3 produced a product (**210**) resulting from the attack of $PhSO_2\cdot$ radical on the vinyl ether and trapping of the adduct radical by $PhSO_2SPh$ (reaction 31).



0.25 mmol 1.25 mmol 0.50 mmol 1.25 mmol



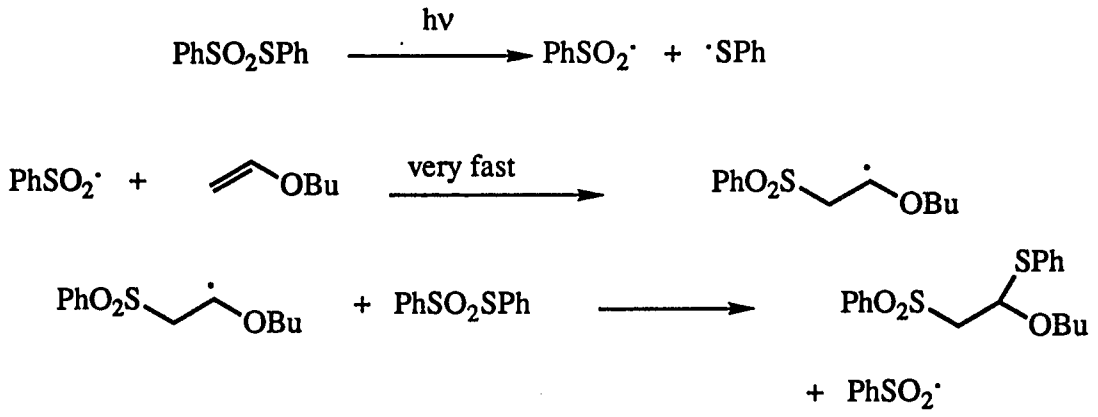
(31)

210, 40% based on $PhSO_2SPh$

The reaction was independent of the presence of $PhCOCH_2HgCl$ in the reaction mixture as demonstrated by the fact that the reaction of 1 equivalent of $PhSO_2SPh$ with 1.2 equivalent of butyl vinyl ether gave the same product **210** in 43% yield.

The rate of addition of $PhSO_2\cdot$ radical to alkenes is probably much faster than the addition of $PhCOCH_2\cdot$. For example the rate of addition of $CH_3SO_2\cdot$ radicals to 1-alkenes has been estimated[62] to have a rate constant of 1×10^9 $Lmol^{-1}s^{-1}$ in CH_3CN at 0 °C which is nearly one-tenth of the diffusion-limited rate. The rate of addition of $PhCOCH_2\cdot$ to alkenes, on the other hand is expected to be only about the order of 10^6 $Lmol^{-1}s^{-1}$. This addition of $PhSO_2SPh$ across alkenes probably takes place by a chain reaction (Scheme XXI).

Scheme XXI


hν
PhSO2SPh
PhSO2· + ·SPh
PhSO2· +
OBu
very fast
PhO2S
OBu
PhO2S
OBu
+ PhSO2SPh
SPh
PhO2S
OBu
+ PhSO2·

CONCLUSION

The photostimulated reaction of carbonyl substituted radicals $RCOCH_2\cdot$ (R = Ph, CH_3, H) with electron-rich alkenes in presence of alkyl or aryl disulfides and a base such as Li_2CO_3 represents a new method of carbon-carbon bond formation in high yields. In these reactions the adduct radicals resulting from the attack of the electrophilic $RCOCH_2\cdot$ radical on the alkenes are efficiently trapped by the disulfide to give γ-alkyl or arylthio carbonyl compounds. The presence of alkyl or arylthio group in the product provides an opportunity for further transformation of the products. The photostimulated reactions of $OHCCH_2HgCl$ with electron-rich alkenes in the presence of disulfides and Li_2CO_3 provides an efficient and useful method of extending the carbon chain by a CH_2CHO group. When enol ethers or vinyl sulfides are used as alkenes, 1,4-dicarbonyl compounds can be obtained on hydrolysis of the reaction products. These reactions proceed by a non-chain process and its success can be attributed to the high selectivity of the various radicals involved and the reversible addition of the phenylthio radicals to the alkenes.

EXPERIMENTAL SECTION

General Considerations

Analytical gas chromatography, ^{1}H and ^{13}C NMR spectroscopy, GCMS, high resolution mass spectroscopy and IR were performed as discussed in Part I. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis were performed by Galbraith laboratories Inc., Knoxville, TN 37921.

Most products were isolated by either flash column chromatography or preparative TLC technique as described in Part III. GC yields were determined using an internal standard (biphenyl) and were corrected with predetermined response factors.

Solvents and Reagents

Solvents were purchased and dried as mentioned in Part I. Reagents were purchased mainly from Aldrich and were used without further purification in most cases.

Procedures and Compounds

Preparation of starting materials

(Benzoylmethyl)mercury chloride and bis-(benzoylmethyl)mercury was prepared as described in Part I. (Acetylmethyl)mercury chloride was prepared by the reaction of isopropenylacetate and mercuric acetate followed by treatment with KCl[63]: mp 103-4 ^{o}C

(lit.[63] mp 103-104 °C); ^{1}H NMR (Me_2SO-d_6) δ 2.06(s, 3H), 2.56(s, 2H with ^{199}Hg satellites, *J*=324 Hz). $OHCCH_2HgCl$ was prepared by reaction of vinyl acetate and mercuric acetate followed by treatment with KCl[63]: mp 129-30 °C(dec.) (lit.[63] mp 129-30 °C (dec.)); ^{1}H NMR (Me_2SO-d_6) δ 2.61(d, *J*=5.1 Hz with ^{199}Hg satellites (d, *J*=5.1 Hz), *J*=325 Hz), 9.32(t, *J*=5.1 Hz, 1H). 1-[(Trimethylsilyl)oxy]cyclohexene was prepared from cyclohexanone;[64] ^{1}H NMR ($CDCl_3$) δ 0.17(s, 9H), 1.47-1.54(m, 2H), 1.61-1.70(m, 2H), 1.94-2.04(m, 4H), 4.33-4.68(m, 1H). Phenyl vinyl ether was prepared by a two step process from ethylene dibromide and phenol;[65] ^{1}H NMR ($CDCl_3$) δ 4.41(d, *J*=6.0 Hz, 1H), 4.75(d, *J*=13.8 Hz, 1H), 6.63(dd, *J*=6.6, 13.8, 1H), 6.99(d, *J*=7.8 Hz, 2H), 7.06(t, *J*=7.5 Hz, 1H), 7.30(t, *J*=7.8 Hz, 2H). 1-(Ethoxy)cyclohexene was prepared from cyclohexanone using triethylformate with catalytic amount of *p* -toluenesulfonic acid;[66] ^{1}H NMR ($CDCl_3$) δ 1.28(t, *J*=7.2 Hz, 3H), 1.47-1.57(m, 2H), 1.61-1.70(m, 2H), 2.00-2.08(m, 4H), 3.68(q, *J*=7.2 Hz, 2H), 4.59(t, *J*=3.0 Hz, 1H). 1-(Butylthio)cyclohexene was prepared from cyclohexanone and BuSH in presence of catalytic amount of *p* -toluenesulfonic acid by dehydration using Dean-stark apparatus;[67] ^{1}H NMR ($CDCl_3$) δ 0.92(t, *J*=7.2 Hz, 3H), 1.41(apparent sextet, *J*=7.5 Hz, 2H), 1.52-1.73(m, 2H), 2.06-2.15(m, 2H), 2.65(t, *J*=7.5 Hz, 2H), 5.61(br s, 1H). 1-(Phenylthio)cyclohexene was prepared from cyclohexanone and thiophenol by dehydration with P_2O_5;[67] ^{1}H NMR ($CDCl_3$) δ 1.57-1.69(m, 4H), 2.12-2.15(br s, 4H), , 6.06(br s, 1H), 7.17-7.32(m, 5H). Phenyl allyl sulfide was prepared from PhSH and allyl bromide with sodium ethoxide in ethanol;[68] ^{1}H NMR ($CDCl_3$) δ 3.54(d, *J*=6.9 Hz, 2H), 5.06(d, *J*=10.2 Hz, 1H), 5.13(d, *J*=17.1 Hz, 1H), 5.80-5.94(m, 1H), 7.17(t, *J*=7.2 Hz, 1H), 7.26(t, *J*=7.5 Hz, 2H), 7.33(d, *J*=7.5 Hz, 2H). $PhSO_2SPh$ was prepared by oxidation of diphenyldisulfide with 30% H_2O_2 in acetic acid.[69]

General procedure for the photostimulated reaction of $RCOCH_2HgCl$ (R = Ph, CH_3, H) with alkenes in presence of disulfides and Li_2CO_3

The mercurial, disulfide and Li_2CO_3 were placed in a dry pyrex test tube and Me_2SO was added by syringe through a rubber septum. The mixture was deoxygenated by bubbling dry nitrogen through it for about 20 minutes. After addition of previously deoxygenated alkene via a syringe through the septum, the reaction mixture was then irradiated with stirring in a 350-nm Rayonet photoreactor maintained at about 40 °C for 6 hours.

Isolation procedure

The reaction mixture was diluted with 50 mL CH_2Cl_2, a known amount of internal standard (biphenyl) was added and the resulting mixture was washed three times with 15% aqueous $Na_2S_2O_3$, followed by water. The CH_2Cl_2 layer was then dried over Na_2SO_4 and analyzed by GC or the solvent was removed and the products were isolated by column chromatography or preparative TLC. In most cases a mixture of solvents hexane and ethyl acetate in 98 : 2 ratio was used as eluant for flash column chromatography unless otherwise mentioned.

α-(Phenylthio)acetophenone (136)[70]

This compound was isolated as a solid: mp 53-54 °C; ^1H NMR ($CDCl_3$) δ 4.15(s, 2H), 7.20-7.70(m, 5H), 7.80-8.10(m, 5H); GCMS m/z(relative intensity) 230(M^+, 37), 123(9), 105(100), 91(5), 77(58). The ^1H NMR was identical to that given in the literature.[70]

1-(Benzoylmethyl)-2-(phenylthio)cyclohexane (137)

This compound was isolated as a mixture of inseparable cis and trans isomers in approximately 1 : 1 ratio; ^{1}H NMR ($CDCl_3$) (mixture of two isomers) δ 1.05-1.31(m, 2H), 1.34-1.38(m, 6H), 1.62-1.98(m, 7H), 2.05-2.20(m, 2H), 2.50-2.63(m, 1H), 2.74-2.99(m,3H), 3.36(dd, *J*=6.3, 17.1 Hz, 1H), 3.64(br s, 1H), 3.80(dd, *J*=3.0, 16.0 Hz, 1H), 7.04-7.58(m, 16H), 7.89(d, *J*=7.2 Hz, 2H), 7.96(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) (mixture of two isomers) δ 199.75, 199.63, 137.24, 136.08, 134.82, 132.81, 132.30, 131.22, 128.80, 128.48, 128.40, 128.10, 128.00, 126.86, 126.33, 52.80, 51.74, 43.95, 41.78, 38.91, 36.74, 34.63, 33.18, 31.29, 28.70, 26.58, 25.39, 24.71, 21.97; GCMS m/z(relative intensity) 310(M^+, 3), 201(1.5), 190(68), 105(100), 77(45); HRMS m/z Calcd for $C_{20}H_{22}OS$: 310.1391. Found: 310.1390; Anal. Calcd for $C_{20}H_{22}OS$: C, 77.37, H, 7.14, S, 10.33. Found: C, 77.65, H, 7.27, S, 10.19.

1-(Benzoylmethyl)-2-methyl-2-(phenylthio)cyclohexane (142)

Compound **142** was isolated as an inseparable mixture of two diastereomers in approximately 2 : 1 ratio. The ^{1}H NMR ($CDCl_3$) was very complicated. Some of the peaks of the major isomer that could be discerned were δ 3.87(dd, *J*=1.8, 16.8 Hz, 1H), 2.81(dd, *J*=10.8, 16.8 Hz) while those of the minor isomer were δ 3.37(dd, *J*=3.0, 17.1 Hz, 1H) and 3.03(dd, *J*=9.0, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) was also very complicated but the carbonyl carbon peaks for major isomer at δ 199.94 and that for the minor isomer at δ 199.85 could be distinguished; GCMS m/z(relative intensity) (minor isomer) 324(M^+, 1), 215(45), 105(100), 95(19), 77(20); HRMS m/z Calcd for $C_{21}H_{24}OS$: 324.1548. Found: 324.1542.

1-Phenyl-4-(phenylthio)-1-octanone (140)

This compound was isolated as a viscous liquid; ^{1}H NMR ($CDCl_3$) δ 0.89(t, *J*=7.2 Hz, 3H), 1.31(sextet, *J*=7.2 Hz, 2H), 1.41-1.69(m, 4H), 1.82-1.97(m, 1H), 2.07-2.21(m, 1H), 3.10-3.31(m, 3H), 7.19(t, *J*=7.2 Hz, 1H), 7.26(t, *J*=7.2 Hz, 2H), 7.38(d, *J*=7.2 Hz, 2H), 7.44(t, *J*=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.93(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199,88, 136.89, 135.14, 132.97, 131.90, 128.84, 128.53, 128.02, 126.72, 48.83, 35.69, 34.76, 29.13, 28.78, 22.58, 14.14; GCMS m/z(relative intensity) 312(M^+, 8), 203(24), 192(18), 150(61), 105(100), 77(41); HRMS m/z Calcd for $C_{20}H_{24}OS$: 312.1548. Found: 312.1544; Anal. Calcd for $C_{20}H_{24}OS$: C, 76.87, H, 7.74, S, 10.26. Found: C, 76.06, H, 7.89, S, 9.97.

1-Phenyl-4-(phenylthio)-1-dodecanone (141)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.88(t, *J*=6.6 Hz, 3H), 1.26(br s, 10H), 1.44-1.56(m, 2H), 1.57-1.68(m, 2H), 1.82-1.98(m, 1H), 2.08-2.22(m, 1H), 3.10-3.30(m, 3H), 7.19(t, *J*=7.2 Hz, 1H), 7.26(t, *J*=7.2 Hz, 2H), 7.39(d, *J*=7.2 Hz, 2H), 7.44(t, *J*=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.94(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.81, 136.86, 135.14, 132.93, 131.87, 128.81, 128.49, 127.99, 126.68, 48.82, 35.66, 35.03, 31.85, 29.47, 29.25, 28.76, 26.92, 22.65, 14.12; GCMS m/z(relative intensity) 368(M^+, 6), 281(5), 259(29), 248(11), 207(22), 150(55), 138(25), 105(100), 77(30); HRMS m/z Calcd for $C_{24}H_{32}OS$: 368.2174. Found: 368.2170.

5-Hydroxy-1-phenyl-4-(phenylthio)-1-pentanone (151)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.90-2.04(m, 1H), 2.17(dp, *J*=4.8, 7.2Hz, 1H), 2.46(br s, 1H), 3.16-3.37(m, 3H), 3.56-3.69(m, 2H), 7.20-

7.32(m, 3H), 7.39-7.49(m, 4H), 7.56(t, J=7.2 Hz, 1H), 7.96(d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHZ) δ 199.66, 136.66, 133.16, 132.62, 129.06, 128.90, 128.58, 128.03, 127.50, 63.97, 51.76, 35.50, 25.15; HRMS m/z Calcd for $C_{17}H_{18}OS$: 286.1027. Found: 286.1022.

5-Acetyloxy-1-phenyl-4-(phenylthio)-1-pentanone (152)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.78-1.95(m, 1H), 2.01(s, 3H), 2.21-2.35(m, 1H), 3.17-3.48(m, 3H), 4.11(dd, J=7.8, 11.1 Hz, 1H), 4.28(dd, J=5.4, 11.1 Hz, 1H), 7.20-7.32(m, 3H), 7.40-7.50(m, 4H), 7.57(t, J=7.2 Hz, 1H), 7.97(d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.17, 170.76, 136.70, 133.56, 133.11, 132.18, 129.03, 128.57, 127.96, 127.36, 66.61, 46.86, 35.55, 25.64, 20.78; HRMS m/z Calcd for $C_{19}H_{20}O_3$: 328.1133. Found: 328.1130.

1-Phenyl-4-(phenylthio)-5-(trimethylsilyloxy)-1-pentanone (153)

This compound hydrolyzed to the alcohol **151** during column chromatography. It was therefore identified by GCMS only; GCMS m/z(relative intensity) 358(M^+, 0.2), 343(1), 268(11), 249(2), 233(5), 159(100), 145(19), 129(30), 105(51), 77(24), 73(48).

1-Phenyl-4-(phenylthio)-5-(trimethylsilyl)-1-pentanone (154)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.05(s, 9H), 0.94(dd, J=8.4, 15.0 Hz, 1H), 1.04(dd, J=6.6, 15.0 Hz, 1H), 1.80-1.94(m, 1H), 2.03-2.16(m, 1H), 3.06(ddd, J=5.4, 9.0, 17.1 Hz, 1H), 3.25(ddd, J=6.3, 9.0, 17.1 Hz, 1H), 3.37-3.47(m, 1H), 7.15(t, J=7.2 Hz, 1H), 7.22(t, J=7.2 Hz, 2H), 7.33(d, J=7.2 Hz, 2H), 7.39(t, J=7.2 Hz, 2H), 7.50(t, J=7.2 Hz, 1H), 7.88(d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.81,

136.89, 135.41, 132.91, 131.73, 128.84, 128.49, 128.00, 126.69, 45.46, 35.23, 31.17, 23.57, -0.69; GCMS m/z(relative intensity) 342(M+, 0.5), 327(0.2), 233(40), 167(4), 105(6), 77(8), 73(100).

General procedure for the hydrolysis of O,S-acetals to aldehydes

The reaction mixture was diluted with CH_2Cl_2 and washed with 15% $Na_2S_2O_3$ solution as described before. It was then washed three times with 2M HCl and once with water and the products isolated as described before.

1-Phenyl-1,4-butanedione (165)[71]

This compound was isolated using 95 : 5 mixture of hexane and ethyl acetate as eluant; ^{1}H NMR ($CDCl_3$) δ 2.93(t, *J*=6.3 Hz, 2H), 3.33(t, *J*=6.3 Hz, 2H), 7.47(t, *J*=7.2 Hz, 2H), 7.58(t, *J*=7.2 Hz, 1H), 7.99(d, *J*=7.2 Hz, 2H), 9,90(s, 1H); GCMS m/z(relative intensity) 162(M^+, 0), 134(38), 120(20), 105(100), 77(66); CI(NH_3)=163(MH^+). The 1H NMR compared favorably with that in the literature.[71]

1-Phenyl-4-(phenylthio)-4-phenoxy-1-butanone (167)

This compound was isolated as a solid: mp 69-71 °C; ^{1}H NMR ($CDCl_3$) δ 2.38(q, *J*=6.9 Hz, 1H), 2.39(q, *J*=6.9 Hz, 1H), 3.23(t, *J*=6.9 Hz, 1H), 3.24(t, *J*=6.9 Hz, 1H), 5.61(t, *J*=6.6 Hz, 1H), 6.95-7.03(m, 3H), 7.22-7.31(m, 5H), 7.39-7.47(m, 4H), 7.54(t, *J*=7.2 Hz, 1H), 7.93(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.00, 156.62, 136.68, 134.39, 133.09, 131.26, 129.41, 128.79, 128.54, 128.13, 127.94, 121.99, 116.89, 84.59, 34.69, 30.22; GCMS: This compound decomposed under GC conditions

eliminating PhSH; Solid probe CI(NH_3) m/z(relative intensity) 366(M^++NH_4, 15), 255(M^+-OPh, 100), 239(M^+-SPh, 12); FTIR ($CDCl_3$) 1684 (s).

cis-3-(Benzoylmethyl)-2-(phenylthio)tetrahydropyran (168a)

This compound was isolated as a solid: mp 87-88 °C; ^1H NMR ($CDCl_3$) δ 1.50-1.90(m, 4H), 2.79-2.91(m, 1H), 2.98(dd, *J*=7.2, 17.4 Hz, 1H), 3.25(dd, *J*=6.0, 17.4 Hz, 1H), 3.65-3.75(m, 1H), 4.26(td, *J*=2.7, 11.4 Hz, 1H), 5.58(d, *J*=4.2 Hz, 1H), 7.15-7.28(m, 3H), 7.39-7.50(m, 4H), 7.56(t, *J*=7.2 Hz, 1H), 7.98(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.29, 131.13, 128.80, 128.55, 128.02, 126.69, 90.30, 60.95, 41.81, 36.89, 26.18, 25.36; GCMS: This compound decomposed under GC conditions eliminating PhSH; Solid probe CI(NH_3) m/z(relative intensity) 330(M^++NH_4, 18), 313(MH^+, 14), 203(M^+-SPh, 100); Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.03, H, 6.45, S, 10.26. Found: C, 72.91, H, 6.44, S, 10.06.

cis-3-(Benzoylmethyl)-2-(butylthio)tetrahydropyran (168b)

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.86(t, *J*=7.2 Hz, 3H), 1.34(sextet, *J*=7.2 Hz, 2H), 1.47-1.71(m, 6H), 2.45-2.61(m, 2H), 2.70-2.80(m, 1H), 2.85(dd, *J*=7.2, 17.1 Hz, 1H), 3.14(dd, *J*=6.3, 17.1 Hz, 1H), 3.55-3.63(m, 1H), 4.12(dt, *J*=2.7, 11.1 Hz, 1H), 5.24(d, *J*=3.9 Hz, 1H), 7.44(t, *J*=7.2 Hz, 2H), 7.55(t, *J*=7.2 Hz, 1H), 7.96(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.59, 137.12, 132.98, 128.59, 127.93, 86.54, 60.56, 41.52, 36.29, 31.92, 30.14, 26.30, 25.01, 22.00, 13.62; GCMS m/z(relative intensity) 292(M^+, 0), 203(M^+-SBu, 83), 185(5), 172(13), 161(4), 105(100), 77(24); HRMS m/z Calcd for $C_{17}H_{24}O_2S$: 292.1497. Found: 292.1497.

General procedure for the hydrolysis of thioacetals and vinyl sulfides[45]

The reaction mixture was diluted with CH_2Cl_2, internal standard (biphenyl) added and washed with 15% aqueous $Na_2S_2O_3$ as described before. The CH_2Cl_2 layer was then separated, the solvent was removed and 0.5 mmol $HgCl_2$ (135.75 mg) along with 25 mL 3 : 1 CH_3CN : H_2O mixture was added to the residue. This was then refluxed on an oil bath for 6 hours. After cooling, 50 mL CH_2Cl_2 was added and it was washed three times with 15% $Na_2S_2O_3$ and then once with water and dried over Na_2SO_4. The solvent was then removed and the residue was analyzed by GC.

1-(Benzoylmethyl)-2,2-bis(phenylthio)cyclohexane (183)

This compound was isolated as an oil; ^1H NMR ($CDCl_3$) δ 1.00-2.00(m, 8H), 2,63(dd, *J*=8.7, 15.3 Hz, 1H), 3.17(dd, *J*=10.5, 17.7 Hz, 1H), 4.20(d, *J*=17.7 Hz, 1H), 7.20-7.45(m, 8H), 7.50(t, *J*=7.2 Hz, 2H), 7.59(t, *J*=7.2 Hz, 1H), 7.81(d, *J*=7.8 Hz, 2H), 8.08(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.33, 137.60, 137.51, 137.28, 133.00, 131.30, 129.95, 129.21, 129.10, 128.80, 128.60, 128.54, 128.12, 70.75, 41.38, 40.84, 36.08, 29.10, 25.40, 22.65; GCMS: This compound decomposed under GC conditions eliminating PhSH; Anal. Calcd for $C_{26}H_{26}OS_2$: C, 74.41, H, 6.49, S, 15.29. Found: C, 74.15, H, 6.50, S, 16.45.

3-(Benzoylmethyl)-2-(phenylthio)cyclohexene (184)

This compound was identified by GCMS only because of separation problems; GCMS m/z(relative intensity) 308(M^+, 6), 199(18), 188(100), 155(9), 105(35), 77(33). It was hydrolysed to diketone **18** by the method described before to calculate the yield.

1-(Benzoylmethyl)-2-(butylthio)-2-(phenylthio)cyclohexane (186)

This compound was isolated as an inseparable mixture of two diastereomers in approximate ratio of 5 : 1; ^{1}H NMR ($CDCl_3$) (only peaks for the major isomer are given below) δ 0.98(t, *J*=7.2 Hz, 3H), 1.35-1.85(m, 11H), 2.05(br d, *J*=14.4 Hz, 1H), 2.53-2.69(m, 2H), 2.79(dd, *J*=6.6, 8.1 Hz, 1H), 2.82(dd, *J*=6.9, 7.8 HZ, 1H), 3.06(dd, *J*=7.2, 17.4 Hz, 1H), 4.03(dd, *J*=1.8, 17.4 Hz, 1H), 7.28-7.60(m, 8H), 8.05(d, *J*=7.2 Hz, 2H); GCMS: This compound decomposed under GC conditions eliminating PhSH. However CI(NH_3) gave following peaks m/z(relative intensity) 416(M^+ + NH4, 1), 309(M^+ - SBu, 24), 289(M^+ - SPh, 100).

3-(Benzoylmethyl)-2-(butylthio)cyclohexene (187)

This compound was identified by GCMS only because of separation problems; GCMS m/z(relative intensity) 288(M^+, 6), 199(4), 168(86), 112(100), 105(48), 91(7), 77(47).

1-(Benzoylmethyl)-2-(butylthio)cyclohexane (191)

This compound was identified by GCMS only; GCMS (major isomer) m/z(relative intensity) 290(M^+, 2), 201(1), 170(100), 114(38), 105(65), 77(30).

1-Phenyl-4-(phenylthio)-4-(trimethylsilyl)-1-butanone (194)

This compound was isolated as an off-white solid: mp 60-61 °C; ^{1}H NMR ($CDCl_3$) δ 0.18(s, 9H), 1.85-2.01(m, 1H), 2.22-2.36(m, 1H), 2.63(dd, *J*=4.2, 9.0 Hz, 1H), 3.07(ddd, *J*=5.4, 9.0, 17.1 Hz, 1H), 3.20(ddd, *J*=6.3, 9.0, 17.1 Hz, 1H), 7.08(t, *J*=7.2 Hz, 1H), 7.19(t, *J*=7.2 Hz, 2H), 7.31-7.42(m, 4H), 7.51(t, *J*=7.2 Hz, 1H), 7.80(d, *J*=7.2 Hz,

2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.05, 138.13, 136.77, 132.83, 129.43, 128.81, 128.42, 127.92, 125.82, 37.04, 34.17, 26.27, -2.30; GCMS m/z(relative intensity) 328(M^+, 1), 313(4), 219(55), 208(13), 203(17), 105(20), 77(16), 73(100); HRMS m/z Calcd for $C_{19}H_{24}OSSi$: 328.1317. Found: 328.1321; Anal. Calcd for $C_{19}H_{24}OSSi$: C, 69.46, H, 7.36, S, 9.76, Si, 8.55. Found: C, 69.55, H, 7.27, S, 8.23, Si, 8.32.

5-Phenylthio-2-nonanone (197)

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.88(t, *J*=7.2 Hz, 3H), 1.29(sextet, *J*=7.2 Hz, 2H), 1.38-1.62(m, 4H), 1.78-1.83(m, 1H), 1.87-2.03(m, 1H), 2.10(s, 3H), 2.61-2.71(m, 2H), 3.02-3.20(m, 1H), 7.21(t, *J*=7.2 Hz, 1H), 7.27(t, *J*=7.2 Hz, 2H), 7.36(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 208.37, 135.11, 131.88, 128.81, 126.72, 48.55, 40.57, 34.62, 30.00, 29.02, 28.18, 22.52, 13.98; GCMS m/z(relative intensity) 250(M^+, 7), 192(4), 150(17), 141(23), 123(19), 110(24), 97(3), 83(17), 43(100); HRMS m/z Calcd for $C_{15}H_{22}OS$: 250.1391. Found: 250.1386; Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95, H, 8.86, S, 12.81. Found: C, 71.90, H, 8.35, S, 13.21.

5-(Phenylthio)-5-(trimethylsilyl)-2-pentanone (198)

This compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.15(s, 9H), 1.64-1.81(m, 1H), 1.95(s, 3H), 2.04-2.15(m, 1H), 2.46-2.60(m, 2H), 2.62-2.75(m, 1H), 7.15(t, *J*=7.2 Hz, 1H), 7.25(t, *J*=7.5 Hz, 2H), 7.33(d, *J*=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 208.62, 138.18, 129.32, 128.82, 125.82, 41.67, 33.66, 29.86, 25.50, -2.38; GCMS m/z(relative intensity) 266(M^+, 2), 167(3), 151(5), 141(13), 137(11), 136(100), 115(19), 73(49); HRMS m/z Calcd for $C_{14}H_{22}OSSi$: 266.1161. Found: 266.1158.

2-(Acetylmethyl)cyclohexanone (199)[72]

This compound was isolated as a liquid using hexane : ethyl acetate (95 : 5) as eluant; ^{1}H NMR ($CDCl_3$) δ 1.18-1.44(m, 1H), 1.53-1.92(m, 3H), 2.01-2.18(m, 3H), 2.20(s, 3H), 2.29-2.43(m, 2H), 2.89-3.03(m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.40, 207.26, 46.39, 43.14, 41.80, 33.94, 30.43, 27.83, 25.24; GCMS m/z(relative intensity) 154(M^+, 17), 139(2), 121(3), 111(23), 97(33), 83(12), 55(40), 43(100); HRMS m/z Calcd for $C_9H_{14}O_2$: 154 0994. Found: 154.0998.

3-(Acetylmethyl)-2-(phenylthio)tetrahydropyran (cis-200)(major isomer)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.40-1.56(m, 1H), 1.57-1.83(m, 3H), 2.15(s, 3H), 2.45(dd, *J*=6.0, 16.8 Hz, 1H), 2.57-2.76(m, 2H), 3.63-3.72(m, 1H), 4.21(dt, *J*=3.0, 11.4 Hz, 1H), 5.49(d, *J*=3.9 Hz, 1H), 7.20(t, *J*=7.2 Hz, 1H), 7.27(t, *J*=7.2 Hz, 2H), 7.44(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.83, 135.11, 131.04, 128.84, 126.70, 89.84, 60.76, 46.80, 36.42, 30.63, 25.98, 25.30; GCMS m/z(relative intensity) 250(M^+, 0.5), 141(82), 123(16), 111(16), 99(12), 81(24), 43(100); HRMS m/z Calcd for $C_{14}H_{18}O_2S$: 250.1028. Found: 250. 1026.

3-(Acetylmethyl)-2-(phenylthio)tetrahydropyran (trans-200)(minor isomer)

This compound could be obtained only in 70% purity (contaminated with the major isomer); ^{1}H NMR ($CDCl_3$) δ 1.30-1.50(m, 1H), 1.56-1.73(m, 3H), 2.14(s, 3H), 2.30-2.38(m, 1H), 2.44(dd, *J*=7.5, 16.8 Hz, 1H), 2.95(dd, *J*=4.2, 16.8 Hz, 1H), 3.50-3.60(m, 1H), 4.12-4.21(m, 1H), 4.84(d, *J*=6.6 Hz, 1H), 7.19-7.31(m, 3H), 7.47(d, *J*=7.2 Hz, 2H); GCMS m/z(relative intensity) 250(M^+, 0), 141(67), 123(13), 111(14), 99(11), 81(20), 55(9), 43(100).

4-(Phenylthio)octanal (201)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.89(t, *J*=7.2 Hz, 3H), 1.30(sextet, *J*=7.2 Hz, 2H), 1.38-1.65(m, 4H), 1.71-1.86(m, 1H), 1.90-2.04(m, 1H), 2.67(t, *J*=7.2 Hz, 2H), 3.09(apparent pentet, *J*=6.6 Hz, 1H), 7.22(t, *J*=6.9 Hz, 1H), 7.28(t, *J*=7.2 Hz, 2H), 7.37(d, *J*=7.5 Hz, 2H), 9.75(s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.78, 134.79, 132.05, 128.90, 128.86, 48.57, 41.04, 34.42, 29.03, 26.59, 22.52, 13.98; GCMS m/z(relative intensity) 236(M^+, 11), 192(3), 179(3), 150(9), 127(20), 110(100), 109(61), 67(34); HRMS m/z Calcd for $C_{14}H_{20}OS$: 236.1235. Found: 236.1236; Anal. Calcd for $C_{14}H_{20}OS$: C, 71.13, H, 8.53, S, 13.57. Found: C, 71.16, H, 8.74, S, 13.68.

4-(Phenylthio)-4-(trimethylsilyl)butanal (202)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.15(s, 9H), 1.75-1.88(m, 1H), 2.06-2.20(m, 1H), 2.53(dd, *J*=4.2, 8.4 Hz, 1H), 2.55-2.73(m, 2H), 7.16(t, *J*=7.2 Hz, 1H), 7.26(t, *J*=7.2 Hz, 2H), 7.32(d, *J*=7.2 Hz, 2H), 9.66(s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.12, 137.63, 129.45, 128.87, 126.01, 42.39, 33.76, 23.93, -2.35; HRMS m/z Calcd for $C_{13}H_{20}OSSi$: 252.1004. Found: 252.1003.

2-(Formylmethyl)cyclohexanone (203)[73]

This compound was isolated using hexane : ethylacetate (95 : 5) as eluant; ^{1}H NMR ($CDCl_3$) δ 1.43(dq, *J*=3.6, 12.6 Hz, 1H), 1.59-1.83(m, 2H), 1.84-1.96(m, 1H), 2.00-2.50(m, 5H), 2.90-3.03(m, 2H), 9,81(s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 210.69, 200.68, 45.43, 43.58, 41.71, 33.99, 27.70, 25.20. HRMS m/z Calcd for $C_8H_{12}O_2$: 140.0837. Found: 140.0837.

3-(Formylmethyl)-2-(phenylthio)tetrahydropyran (cis-204)(major isomer)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.44-1.84(m, 4H), 2.44-2.56(m, 1H), 2.62-2.79(m, 2H), 3.64-3.74(m, 1H), 4.23(dt, *J*=3.0, 11.4 Hz, 1H), 5.47(d, *J*=3.9 Hz, 1H), 7.21(t, *J*=6.9 Hz, 1H), 7.28(t, *J*=6.9 Hz, 2H), 7.43(d, *J*=7.2 Hz, 2H), 9.77(s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.87, 131.13, 129.01, 128.82, 126.97, 89.39, 65.45, 46.75, 35.37, 27.76, 23.66; GCMS m/z(relative intensity) 236(M^+, 0.3), 127(100), 109(24), 97(11), 81(45); HRMS m/z Calcd for $C_{13}H_{16}O_2S$: 236.0871. Found: 236.0873.

3-(Formylmethyl)-2-(phenylthio)tetrahydropyran (trans-204)(minor isomer)

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.36-1.48(m, 1H), 1.62-1.72(m, 2H), 2.02-2.11(m, 1H), 2.30-2.42(m, 1H), 2.48(ddd, *J*=1.8, 7.2, 17.1, 1H), 2.93(ddd, *J*=1.2, 5.1, 17.1 Hz, 1H), 3.49-3.59(m, 1H), 4.12-4.22(m, 1H), 4.81(d, *J*=7.2 Hz, 1H), 7.23-7.34(m, 3H), 7.48(d, *J*=7.2 Hz, 2H), 9.75(s, 1H); GCMS m/z(relative intensity) 236(M^+, 0.3), 127(100), 109(26), 97(17), 81(47).

1-Phenyl-pent-4-ene-1-one (208)[74]

This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 2.43-2.48(m, 2H), 3.02-3.07(m, 2H), 5.00-5.08(m, 2H), 5.82-6.00(m, 2H), 7.40-7.60(m, 3H), 7.90-8.20(br d, *J*=7.2 Hz, 2H); GCMS m/z(relative intensity) 160(M^+, 2), 115(1), 105(100), 77(46).

Attempted determination of the initial kinetic chain length using AIBN

Nitrogen-purged Me_2SO-d_6 (0.4 mL) was added to a mixture of $PhCOCH_2HgCl$ (0.04 mmol), PhSSPh (0.08 mmol), Li_2CO_3 (0.20 mmol) and AIBN (0.004 mmol) in a

NMR tube. Previously deoxygenated vinyltrimethylsilane (0.20 mmol) was then added to this mixture and the NMR tube was capped with a rubber septum. After ^1H NMR spectrum of initial solution (after centrifuging it) was obtained, the reaction mixture was heated at 80 °C in an oil bath with intermittent shaking, in room light. The decomposition of AIBN was monitored at different periods of time by ^1H NMR integration of its protons by comparison with the integration of the residual non-deuterated Me_2SO protons. The expected addition product **194** did not form under these conditions leading to the failure of this experiment.

Determination of the initial kinetic chain length of the reaction between $PhCOCH_2HgCl$ and phenyl allyl sulfide

Nitrogen-purged Me_2SO-d_6 (1.0 mL) was added to $PhCOCH_2HgCl$ (0.10 mmol) and to this resulting solution nitrogen-purged phenyl allyl sulfide (0.15 mmol) was added. This solution was then divided into two NMR tubes (0.5 mL in each tube) equipped with rubber septa. Di-*tert*-butyl nitroxide (DTBN) (0.005 mmol) was added to one of these tubes. After ^1H NMR spectra of the initial solutions were obtained, these reaction mixtures were irradiated with a 275W GE sunlamp ca. 30 cm from the reaction tubes. The progress of the reaction was monitored at different periods of time by ^1H NMR integration of the allylic protons of the product **208** (multiplet at 2.33-2.40 ppm), taking the integration of the protons of the residual non-deuterated Me_2SO as reference.

1-Phenyl-4-(butylthio)-1-octanone (**209**)

This compound was identified by GCMS only; GCMS m/z(relative intensity) 292(M^+, 7), 235(2), 203(3), 172(15), 159(8), 145(4), 130(35), 115(100), 105(63).

1-Butoxy-2-(phenylsulfonyl)-1-(phenylthio)ethane (**210**)

This compound was isolated as an oil; ^{1}H NMR ($CDCl_3$) δ 0.85(t, *J*=7.2 Hz, 3H), 1.20(apparent sextet, *J*=7.2 Hz, 2H), 1.27-1.39(m, 2H), 3.30(td, *J*=6.3, 9.0 Hz, 1H), 3.88(td, *J*=6.9, 9.0 Hz, 1H), 5.11(dd, *J*=5.4, 6.9 Hz, 1H), 7.25-7.33(m, 3H), 7.35-7.41(m, 2H), 7.51(t, *J*=7.5 Hz, 2H), 7.62(t, *J*=7.5 Hz, 1H), 7.82(d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.12, 134.46, 133.43, 130.45, 129.03, 128.92, 128.54, 127.92, 82.09, 68.88, 62.22, 30.91, 19.15, 13.84.

Spectral data for **2** is given in Part I, for **18** is given in Part II while for **42**, **43**, **45a**, **46a** is given in Part III.

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GENERAL SUMMARY

Photostimulated reactions of the (benzoylmethyl)mercurials with electron-rich substrates such as trialkyl phosphites, *N*-methylpyrrole and enamines demonstrate that S_{RN} process can be observed with neutral substrates if electrophilic radicals are used. In these reactions an easily oxidizable adduct radical is formed which transfers an electron to the mercurial to continue the chain process. Photostimulated reaction of phosphites in aprotic solvents give β-keto phosphonates by an Arbuzov type process, while with *N*-methylpyrrole substitution at 2-position of the aromatic nucleus is observed. Good yields of 1,4-dicarbonyl compounds are observed from enamines by hydrolysis of the reaction product. Moderate yields of the α-tetralone derivatives are obtained via an intramolecular homolytic aromatic substitution in case of reaction of benzoylmethyl radicals with simple alkenes most likely via a non-chain process. When aromatic alkenes are used products resulting from cyclization to form six-membered ring are formed in preference to those containing a five membered ring. Reaction of $RCOCH_2HgCl$ (R = Ph, CH_3, H) with electron rich alkenes in presence of RSSR (R = alkyl or aryl) and Li_2CO_3 provides an efficient method of carbon-carbon bond formation in high yields. The presence of SR group in the product provides an opportunity for further transformation of the products (unlike in case of tin hydride mediated reactions). Reactions with enol ethers and vinyl sulfides give 1,4-dicarbonyl compounds after hydrolysis of the reaction products. These results also show that organomercurials are a convenient source of electrophilic radicals and sometimes permit transformations which otherwise are difficult to carry out with other radical sources.

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