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Iowa State University, 1987

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Photostimulated reactions of organomercurials with alkenes and alkynes

by

Wan Jiang

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1987

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INTRODUCTION

This thesis is divided into five parts. Part I considers the photostimulated reactions of alkylmercury halides with substituted alkenes. The reactions of alkylmercury chlorides with alkynes are presented in Part II. In Part III, the experimental determination of the initial kinetic chain lengths for these reactions is presented. Parts IV and V examine the reactions of alkylmercury chloride with dihaloalkenes and the reactions of dialkylmercurials with several alkenes.

I. PHOTOSTIMULATED REACTIONS OF ORGANOMERCURY HALIDES WITH ALKENES

A. Introduction

Organomercury chemistry has attracted more interest of chemists in recent years as the development of organometallic chemistry has increased explosively. Although some organomercury compounds are very toxic because of their low boiling points,[1] the majority of them are crystalline solids which have fairly high melting points[2] and are easy to handle in the laboratory. Since organomercurials, which are easily prepared,[3] have the remarkable potential to tolerate a variety of organic functional groups, they have been more and more broadly used in organic synthesis. Organomercury reagents have been found useful in many organic reactions, such as substitution reactions,[4,5] solvomercuration-demercuration reactions,[6,7] divalent carbon transfer reactions,[8,9] and esterification reactions.[10,11] They have even been employed in the synthesis of natural products.[12]

Although for a number of years, free radical chemistry has been dominated by the exploration of addition reactions, addition of free radicals derived from organomercurials to the carbon-carbon double bonds has not been well studied, especially, under the photostimulated conditions. Recently, Giese and his co-workers reported that electron-deficient olefins can be alkylated by free radicals which are generated from the reaction of organomercury halides with $NaBH_4$ or $NaBH(OCH_3)_3$ (Eq. 1).[13-17] In these reactions, organomercury

$$RHgX + CH_2{=}CR^1R^2 \xrightarrow[\text{or } NaBH(OMe)_3]{NaBH_4} RCH_2CHR^1R^2 + Hg° \qquad (1)$$

halides can be primary, secondary, tertiary alkyl and benzylic mercurials. Usually, 5-10 fold excess of the olefins are employed and methylene chloride is the most commonly used solvent in the reactions. The reaction proceeds via a free radical chain mechanism as shown in Scheme 1.[18] In the

<u>Scheme 1</u>

Initiation:

$$RHgX + NaBH_4 \xrightarrow{h\nu} RHgH + NaBH_3X$$

$$RHgH \longrightarrow R\cdot + H\cdot + Hg°$$

Chain:

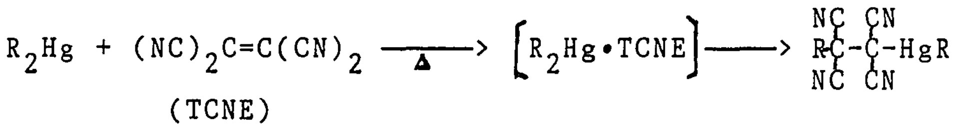
$$CH_2{=}CR^1R^2 + R\cdot \longrightarrow RCH_2\dot{C}R^1R^2$$

$$RCH_2\dot{C}R^1R^2 + RHgH \longrightarrow RCH_2CHR^1R^2 + RHg\cdot$$

$$RHg\cdot \longrightarrow R\cdot + Hg°$$

initiation step, the alkylmercury halide is reduced by $NaBH_4$ to produce the alkylmercury hydride, a reaction known for some time.[19,20] Alkylmercury hydrides are not stable and undergo decomposition to generate the alkyl radical (R•). In the absence of the alkenes, the alkyl radical reacts with RHgH to form RH and RHg• as proved by Russell and Guo.[21] In the presence of a reactive alkene, the alkyl radical adds to the alkene to generate an adduct radical, which reacts with RHgH to form the addition product and RHg• which decomposes readily to form another alkyl radical which continues the chain reaction. This reaction involves the polar effect in the addition of alkyl radicals to carbon-carbon double bonds. The reason for olefins being limited to electron-deficient ones has been discussed in a recent review.[22]

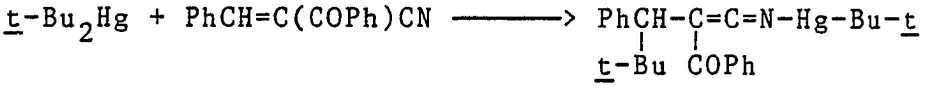
It was reported that thermal reaction of dialkylmercury and dibenzylmercurials with a highly electron-deficient olefin, tetracyanoethylene (TCNE) afforded the corresponding addition products (Eq. 2).[23-26] The reaction occurs after



$$R_2Hg + \underset{\text{(TCNE)}}{(NC)_2C{=}C(CN)_2} \xrightarrow[\Delta]{} \left[R_2Hg{\bullet}TCNE\right] \longrightarrow R\underset{NC}{\overset{NC}{C}}-\underset{CN}{\overset{CN}{C}}-HgR \qquad (2)$$

R = Et, i-Pr, n-Bu, $PhCH_2$, p-$CH_3C_6H_4CH_2$.

charge transfer in the alkylmercurial-TCNE complexes, [R_2Hg-TCNE].[24,27] Charge transfer bands have been observed in the absorption spectra of solution containing TCNE and dialkylmercurials by ultraviolet-visible spectrometry.[24] A solution of $(PhCH_2)_2Hg$ and TCNE in CH_2Cl_2 at 30 °C is initially dark blue, but turns red when the reaction is completed.[23] The 1:1 adducts have been characterized by their proton NMR spectra. Blaukat and Neumann[26] also reported that a 1,4-addition product was obtained from the thermal reaction of di-*tert*-butylmercury with a conjugated olefin PhCH=C(COPh)CN (Eq. 3).



$$\underline{t}\text{-}Bu_2Hg + PhCH{=}C(COPh)CN \longrightarrow Ph\underset{\underline{t}\text{-}Bu}{CH}\text{-}\underset{COPh}{C}{=}C{=}N\text{-}Hg\text{-}Bu\text{-}\underline{t} \qquad (3)$$

Photostimulation to generate radicals which can undergo a variety of reactions is a fairly well-known technique. But up to now only a few examples of the photostimulated addition of free radicals derived from organomercurials to alkenes have appeared in the literature. Russell and Hershberger have reported that 1-alkenylmercury halides can undergo photostimulated radical substitution reactions (Eq. 4).[28]

$$RCH{=}CHHgX + R'Y\text{-}YR' \xrightarrow{h\nu} RCH{=}CHY\text{-}R' + R'YHgX \qquad (4)$$

Recently, extensive work on this reaction has been reported (Eq. 5).[29,30] The reaction is believed to involve a radical

$$RR'C{=}CHZ + QHgX \xrightarrow{h\nu} RR'C{=}CHQ + ZHgX \qquad (5)$$

Z = *n*-Bu$_3$Sn, I, HgCl, SO$_2$Ph. X = Cl, SPh.

Q = cyclo-C$_6$H$_{11}$, *i*-Pr, *t*-Bu, SPh.

chain addition-elimination process as shown in Scheme 2. In

Scheme 2

Initiation:

$$QHgX \xrightarrow{h\nu} Q\cdot + \cdot HgX$$

Chain:

$$Q\cdot + RR'C{=}CHZ \xrightarrow{\text{add.}} \underset{\mathbf{1}}{RR'\dot{C}{-}CHQZ}$$

$$\mathbf{1} \xrightarrow{\text{elim.}} RR'C{=}CHQ + Z\cdot$$

$$Z\cdot + QHgX \longrightarrow Q\cdot + ZHgX$$

Or $\underline{n}\text{-}Bu_3Sn\cdot + QHgCl \longrightarrow \underline{n}\text{-}Bu_3SnCl + Q\cdot + Hg^\circ$

Or $\cdot HgCl + QHgCl \longrightarrow Q\cdot + HgCl_2 + Hg^\circ$

this reaction mechanism, the radical (Q·), which is generated by the reaction of radical Z· with QHgX, adds to the alkene to form a new adduct radical **1**. Since group Z in RR'C=CHZ is a good leaving group, radical 1 readily undergoes a beta-elimination to afford the substituted olefin. The eliminated radical Z• then reacts with QHgX to generate another radical Q• which continues the chain reaction. The addition and elimination reaction in the chain sequence can lead to the substitution with the retention of configuration of alkenes RR'C=CHZ.[31]

Thus, the photostimulated reaction of organomercurials with certain substituted alkenes can form the substitution products, but the photostimulated addition of alkylmercurials to alkenes has not been reported. The work represented in this thesis considers the photostimulated addition of organomercurials to carbon-carbon multiple bonds and, especially, the alkylation of alkenes with organomercury halides.

B. Results and Discussion

1. Photostimulated reactions of alkylmercury halides with diethyl vinylphosphonate(VP), phenyl vinyl sulfone(VS) followed by $NaBH_4$ reduction

Alkylmercury halides (RHgX) do not react with diethyl vinylphosphonate (VP) or phenyl vinyl sulfone (VS) at any appreciate rate in the absence of a free radical initiator. Thus, alkylmercury halide, such as t-BuHgCl, with VP or VS in either benzene or dimethyl sulfoxide (DMSO) did not react when kept in the dark at room temperature for 24 h. However, the reaction occurred when the pyrex reaction vessel was placed in a Rayonet Photoreactor (350 nm). When benzene was employed as the solvent, a gray precipitate appeared within 15-30 min of the initiation of irradiation. When dimethyl sulfoxide was used as the solvent, the mercury was observed at the bottom of the reaction vessel after irradiation for 30-45 min. After irradiation for 24 h (the kinetic study in Part III showed that the reactions were completed in 2 h), the reaction mixture was treated with $NaBH_4$ to give the corresponding diethyl alkylphosphonates, alkyl phenyl sulfones as shown in Eq. 6 and Table 1. The reaction apparently involves the formation of $RCH_2CH(HgX)Q$ as an intermediate which is reduced to RCH_2CH_2Q by reaction with $NaBH_4$. Thus in experiments in which after the irradiation, instead of treating with $NaBH_4$, the reaction mixture was washed with 5% $Na_2S_2O_3$ solution, only 10-20% yields of alkylated products were obtained and no starting materials were recovered. Aqueous sodium thiosulfate solution is often employed in the workup

$$CH_2{=}CHQ + RHgX \xrightarrow[2.\ NaBH_4]{1.\ h\nu} RCH_2CH_2Q \qquad (6)$$

$Q = P(O)(OEt)_2$, SO_2Ph.

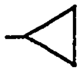
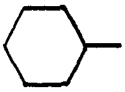
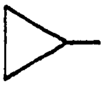
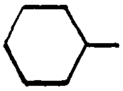
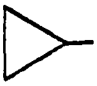
X = Cl, except when R = , X = Br.

Table 1. Photoreaction of alkylmercury halides with VP·, VS followed by reduction of $NaBH_4$

$$RHgCl + CH_2{=}CHQ \xrightarrow[\text{2. } NaBH_4]{\text{1. UV, 24 h}} RCH_2CH_2Q$$

R(equiv.)	Q	Concn. of $CH_2{=}CHQ$	Solvent	% Yield^a
t-Bu (4)	$P(O)(OEt)_2$	0.06 M	PhH	98 (88)
i-Pr (4)	$P(O)(OEt)_2$	0.05 M	PhH	52 (44)
n-Bu (5)	$P(O)(OEt)_2$	0.05 M	DMSO/PhH	32 (26)
 (4)	$P(O)(OEt)_2$	0.06 M	DMSO/PhH	65
 ^{b}(5)	$P(O)(OEt)_2$	0.07 M	DMSO	25
t-$BuCH_2$ (5)	$P(O)(OEt)_2$	0.07 M	DMSO	12
t-Bu (3)	SO_2Ph	0.08 M	PhH	96 (87)
i-Pr (3)	SO_2Ph	0.07 M	PhH	70 (62)
n-Bu (5)	SO_2Ph	0.05 M	DMSO/PhH	64 (56)
 (3)	SO_2Ph	0.06 M	DMSO/PhH	69

[a] GLC yields measured by adding internal standard, and isolated yields in parentheses.

[b] RHgX = HgBr.

procedure as a convenient method for removing organomercury compounds from organic medium by formation of water soluble mercury-thiosulfate complexes. Therefore, in the second step of the reaction, $NaBH_4$ reduces the $RCH_2CH(HgCl)Q$ and the excess alkylmercury halide. This reaction is a free radical chain reaction since the rate of the reaction is drastically retarded by the present of 10 mol% of di-*tert*-butylnitroxide. Examination of the UV-visible spectra of *t*-BuHgCl, VP and the mixture of *t*-BuHgCl and VP showed that there was no complex between the alkylmercury chloride and VP. Although this reaction leads to the same products as the Giese reaction (Eq.1 and Scheme 1), the reaction involves a different mechanism due to the absence of RHgH during the photostimulated free radical chain reaction (Scheme 3). Upon irradiation, an alkyl radical is generated from RHgX which adds to the double bond of CH_2=CHQ to generate radical **2**. Radical **2** then reacts with RHgCl to give a new mercury compound **3** and an alkyl radical which continues the chain reaction. Compound **3** is converted by $NaBH_4$ to the corresponding alkanes.[9] When two equivalent of *t*-BuHgCl was employed, 5-10% of the telomer (2:1) of radical **2** with VP was observed. In order to completely avoid the telomerization of the adduct radical **2** with diethyl vinylphosphonate, the excess alkylmercury halide must be employed in the reactions.

Scheme 3

Initiation:

$$\mathrm{RHgCl} \xrightarrow{h\nu} \mathrm{R\cdot} + \mathrm{\cdot HgCl}$$

Chain:

$$\mathrm{R\cdot} + \mathrm{CH_2{=}CHQ} \longrightarrow \underset{\mathbf{2}}{\mathrm{RCH_2\dot{C}HQ}}$$

$$\mathbf{2} + \mathrm{RHgCl} \longrightarrow \underset{\mathbf{3}}{\mathrm{RCH_2CH(HgCl)Q}} + \mathrm{R\cdot}$$

Reduction:

$$\mathbf{3} + \mathrm{NaBH_4} \longrightarrow \mathrm{RCH_2CH_2Q} + \mathrm{NaBH_3Cl} + \mathrm{Hg^\circ}$$

2. Photostimulated reactions of organomercury halides with VP, VS followed by reaction with iodine

It is known that halogens decompose diorganomercurials in a two step process (Eqs. 7,8).[32] The cleavage of organo-

$$\mathrm{R_2Hg} + \mathrm{X_2} \longrightarrow \mathrm{RHgX} + \mathrm{RX} \qquad (7)$$

$$\mathrm{RHgX} + \mathrm{X_2} \longrightarrow \mathrm{RX} + \mathrm{HgX_2} \qquad (8)$$

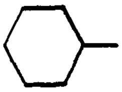
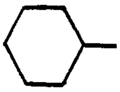
mercury compounds by halogens (such as I_2, Br_2 and Cl_2) may occur via a homolytic mechanism or heterolytic process depending on the experimental conditions such as solvent, reaction temperature and pressure or absence of free radical initiators or inhibitors.[33,34] In the proposed radical chain addition mechanism shown in Scheme 3, the formation of intermediate $\underset{\sim}{3}$ ($RCH_2CH(HgCl)Q$) is a key point in the mechanism. Thus, evidence to prove the existence of the organomercury halide $\underset{\sim}{3}$ is an important substantiation of the proposed chain mechanism. If the intermediate $\underset{\sim}{3}$ does form in the reaction, then by treating the reaction mixture with halogen, the corresponding halide should be obtained. Therefore, the following reactions were carried out (Eq. 9). As expected from

$$CH_2{=}CHQ + RHgCl \xrightarrow[2.\ I_2]{1.\ h\nu} RCH_2CH(I)Q + HgI_2 + HgICl \quad (9)$$

Scheme 3, substantial yields of the iodides were obtained (Table 2). All the reactions were carried out in benzene solution and an excess of iodine was employed in the cleavage reaction. The cleavage reaction was readily completed in a few hours in the presence or absence of light. The excess iodine can be easily removed by washing with aqueous sodium thiosulfate solution. The formation of $RCH_2CH(I)P(O)(OEt)_2$ is strong evidence for the formation of $RCH_2CH(HgCl)P(O)(OEt)_2$ as an intermediate. However, one might argue that $RCH_2CH(I)$-$P(O)(OEt)_2$ could be formed without the intermediary of RCH_2-$CH(HgCl)P(O)(OEt)_2$. As shown in Eq. 10, to exclude this possibility, a solution containing a 6.5 fold excess iodine in benzene was added dropwise to a stirred mixture of <u>t</u>-BuHgCl

Table 2. Photoreactions of alkylmercury chlorides with VP, VS followed by reaction with iodine

$$CH_2{=}CHQ \quad + \quad RHgCl \xrightarrow[2.\ I_2]{1.\ UV, 24\ h} RCH_2CH(I)Q$$

R (equiv.)	Q	Concn. of $CH_2{=}CHQ$	Solvent	Ratio of I_2/RHgCl	%Yield[a]
t-Bu (4)	$P(O)(OEt)_2$	0.06 *M*	PhH	1.5	88 (72)
i-Pr (4)	$P(O)(OEt)_2$	0.06 *M*	PhH	1.8	48 (40)
 (4)	$P(O)(OEt)_2$	0.07 *M*	PhH/DMSO (80%:20%)	1.5	41
t-Bu (3)	SO_2Ph	0.08 *M*	PhH	1.5	81 (75)
i-Pr (3)	SO_2Ph	0.10 *M*	PhH	1.8	46 (38)
 (3)	SO_2Ph	0.11 *M*	PhH/DMSO (80%:20%)	1.5	37

[a] GLC yields measured by adding internal standard; and isolated yields in parentheses.

and VP with irradiation from a 275 W sunlamp. As expected,

$$CH_2{=}CHP(O)(OEt)_2 + \underline{t}\text{-}BuHgCl + I_2 \xrightarrow[PhH]{h\nu} \underline{t}\text{-}BuI + HgICl$$

$$+ \underline{t}\text{-}BuCH_2CH(I)P(O)(OEt)_2 \qquad (10')$$

the tert-butyl radical reacted with iodine much faster than it added to olefin, and only 20% of the iodide, $\underline{t}$-$BuCH_2CH(I)$-$P(O)(OEt)_2$ was obtained. Moreover, when the reaction mixture containing 3 was treated with diphenyl disulfide (PhSSPh) or bromine (Br_2), the corresponding sulfide, $\underline{t}$-$BuCH_2CH(SPh)$-$P(O)(OEt)_2$, and bromide, $\underline{t}$-$BuCH_2CH(Br)P(O)(OEt)_2$, were observed in the yields of 8% and 48%, respectively.

3. Mechanism consideration

As mentioned previously, the alkylmercury halides did not react with $CH_2{=}CHP(O)(OEt)_2$ or $CH_2{=}CHSO_2Ph$ in the dark. Photostimulated reaction of RHgCl with VP or VS in DMSO or PhH proceeds by a radical chain reaction in which the consumption of alkenes is drastically retarded by the presence of 10 mol% of di-tert-butylnitroxide. An initial kinetic chain length of 95 (in C_6D_6) and 116 (in d_6-DMSO) is calculated for the reaction of $\underline{t}$-BuHgCl with $CH_2{=}CHP(O)(OEt)_2$; and the initial kinetic chain length of 103 (in d_6-DMSO) is calculated for the reaction of $\underline{t}$-BuHgCl with $CH_2{=}CHSO_2Ph$

(the kinetic study will be discussed in detail in Part III). Thus, the reaction proceeds via a free radical chain mechanism as in Scheme 4. Because of the electron-withdrawing

Scheme **4**

Initiation:

$$\mathrm{RHgCl} \xrightarrow{h\nu} \mathrm{R}\cdot + \cdot\mathrm{HgCl}$$

Chain:

$$\mathrm{R}\cdot + \mathrm{CH_2{=}CHQ} \xrightarrow{\text{1st}} \underset{\mathbf{2}}{\mathrm{RCH_2\dot{C}HQ}}$$

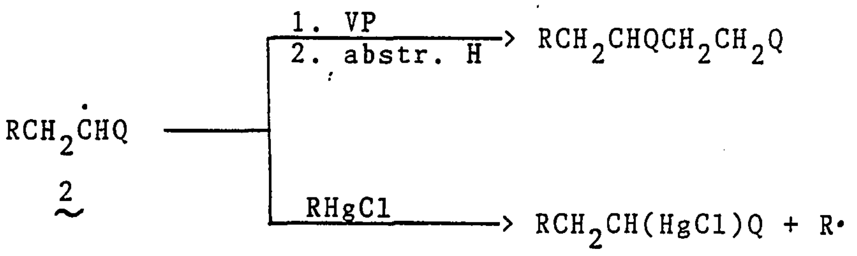
$$\mathbf{2} + \mathrm{RHgCl} \xrightarrow{\text{2nd}} \underset{\mathbf{3}}{\mathrm{RCH_2CH(HgCl)Q}} + \mathrm{R}\cdot$$

Substitution:

$$\begin{tikzcd} & \mathrm{RCH_2CH_2Q} \\ \mathbf{3} \arrow[ur, "\mathrm{NaBH_4}"] \arrow[dr, "\mathrm{I_2}"'] & \\ & \mathrm{RCH_2CH(I)Q} \end{tikzcd}$$

and carbanion-stabilizing nature of groups such as $(\mathrm{EtO})_2\mathrm{P(O)}$, $\mathrm{PhSO_2}$, the intermediate **2** is an electron-acceptor radical which easily undergoes the second step in the chain process with RHgCl to give **3** and an electron-donor alkyl radical. However, the telomer (2:1) of radical **2** with VP is observed when only two equivalents of _t_-BuHgCl was employed in the reaction. This indicated that the following competition occurred in the reaction when RHgCl was not employed in excess (Scheme 5). It has been found that when the ratio of

Scheme 5



RHgCl/VP = 4 and RHgCl/VS = 3, the telomerization of radical 2 with VP or VS can be completely avoided.

In reactions (Eqs. 6 and 9), products such as $CH_3CH(Q)R$ or $CH_2(I)CH(Q)R$ were not observed. This is due to the fact that the alkyl radical preferentially attacks the less substituted carbon atom of the olefins to form the more stable intermediate $RCH_2\dot{C}HQ$ and not the 1° radical, $\cdot CH_2CH(Q)R$.

The relative reactivity of RHgCl in this reaction has measured from the competition reactions (Eq. 11) and results are arranged in Table 3. These results showed that the

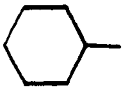
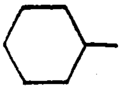
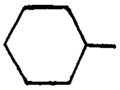
$$RHgCl + R'HgCl + CH_2{=}CHP \xrightarrow[2.\ NaBH_4]{1.\ h\nu} RCH_2CH_2P + R'CH_2CH_2P \quad (11)$$

$P = P(O)(OEt)_2$

Table 3. Competition reactions of alkylmercury chlorides with VP followed by reduction of $NaBH_4$

$$RHgCl + R'HgCl + CH_2{=}CHP \xrightarrow[2.\ NaBH_4]{1.\ UV^{a},21\ h} RCH_2CH_2P + R'CH_2CH_2P$$

$P = P(O)(OEt)_2$

R (Equiv.)	R' (Equiv.)	% Yield	
		RCH_2CH_2P	$R'CH_2CH_2P$
t-Bu (4)	n-Bu (4)	96	0
t-Bu (4)	i-Pr (4)	81	15
t-Bu (4)	 (4)	82	10
i-Pr (4)	n-Bu (4)	64	5
i-Pr (4)	 (4)	63	18
 (4)	n-Bu (4)	61	5

[a] All the reactions were carried out in DMSO with the initial concentration of $CH_2{=}CHP$ of 0.05 M.

relative reactivity of RHgCl towards radical **2** has the order of *t*-BuHgCl > *i*-PrHgCl ~ cyclo-C_6H_{11}HgCl >> *n*-BuHgCl. This is consistent with the expected stabilities of alkyl radicals and suggests that the reaction of radical **2** with RHgCl involves a one-step process with a transition state in which the incipient alkyl radical is nearly completely formed, i.e., a transition state with extensive breaking of R-Hg bond. The present work does not provide any data from which the reactivity of different alkyl radicals towards VP or VS can be measured. On the basis of polar effects, it is expected that towards an electron-deficient olefin like VP or VS, that the radical addition step involves a transition state in which a considerable electron shift has occurred (**5**).

$$R\cdot CH_2{=}CHQ \longleftrightarrow R^{+}CH_2\overset{\dot{-}}{=}CHQ$$

5

This suggests that the absolute rate constant for the addition of an alkyl radical R• to VP should decrease from R = *t*-Bu, to R = 2° alkyl and to R = 1° alkyl as the ionization potential of R• increases.[35] This sequence is consistent with the observed yields of $RCH_2CH_2P(O)(OEt)_2$ (Table 1) and $RCH_2CH(I)P(O)(OEt)_2$ (Table 2), and is also consistent with the values of absolute rate constant (K_{add}) of alkyl radical R• towards VP reported by Baban and Robert with ESR spectroscopy shown in Table 4.[36,37]

Table 4. ESR parameters for the adducts $RCH_2\dot{C}HP(O)(OEt)_2$ and rate constants for addition of R• to VP

$$R\cdot + CH_2{=}CHP(O)(OEt)_2 \xrightarrow{K_{add}} RCH_2\dot{C}HP(O)(OEt)_2$$

R•	Temp./°K	g-Factor	$K_{add}(mol^{-1}s^{-1})$
Me•	230	2.0025	1.7×10^2
Et•	225	2.0025	4.2×10^2
i-Pr•	243	2.0025	2.5×10^3
t-Bu•	239	2.0024	3.1×10^4

4. Photostimulated reaction of diethyl vinylphosphonate (VP) with tert-butylmercury chloride in CCl_4 solution

When the photostimulated reaction of VP with *t*-BuHgCl was carried out in CCl_4 solution, interestingly, the product obtained was not formed by addition of the *tert*-butyl radical to the VP, but was formed by the addition of the trichloromethyl radical to VP (Eq. 12). The reaction occurred readily

$$\underline{t}\text{-BuHgCl} + CH_2{=}CHP \xrightarrow[CCl_4]{1.\ h\nu\quad 24h} \begin{cases} \xrightarrow{2.\ NaBH_4} Cl_3CCH_2CH_2P\ (52\%) \\ \xrightarrow{2.\ I_2} Cl_3CCH_2CH(I)P\ (45\%) \end{cases} \qquad (12)$$

$P = P(O)(OEt)_2$; initial concentration of VP = 0.05 $\underline{M}$,
[$\underline{t}$-BuHgCl] = 0.2 $\underline{M}$, [CCl_4] = 10 $\underline{M}$.

and after irradiation for 5 min, a white precipitate appeared which was identified as hexachloroethane, Cl_3CCCl_3, from the melting point and ^{13}C NMR. The product diethyl 3,3,3-trichloropropylphosphonate ($Cl_3CCH_2CH_2P(O)(OEt)_2$) was isolated in 52% yield after $NaBH_4$ reduction and the corresponding iodide ($Cl_3CCH_2CH(I)P(O)(OEt)_2$) was obtained in 45% upon workup with iodine. The reaction of certain dialkylmercury with CCl_4 at higher temperature (100 °C) or in the presence of the free radical initiator di-$\underline{n}$-butyl peroxide, has been reported by Nugent and Kochi (Eq. 13).[38] In addition, it has

$$\underline{i}\text{-PrCH}_2HgCH_3 \xrightarrow[CCl_4]{100\ ^\circ C} CH_2{=}CMe_2 + CHCl_3 + CH_3Cl + Hg^\circ \qquad (13)$$

reported by Tashtoush[39] that when diisobutylmercury in CCl_4 was irradiated for 48 h in a Rayonet Photoreactor at 350 nm, the products isobutyl chloride, chloroform and 1,1,1,3-tetrachloro-3-methylbutane were formed in an approximately 1:1:1 ratio (Eq. 14). A radical chain mechanism in which the $\cdot CCl_3$

$$(\underline{i}\text{-}PrCH_2)_2Hg + CCl_4 \xrightarrow[48\ h]{UV} \underline{i}\text{-}PrCH_2Cl + Cl_3CCH_2C(Cl)Me_2 + CHCl_3 \tag{14}$$

adds to the mercury atom displacing an alkyl radical was discussed in his thesis.[39]

Since there was no reaction between VP and $\underline{t}$-BuHgCl in CCl_4 in the dark for 24 h and the photoaddition rate was significantly inhibited by the presence of 10 mol% of di-tert-butylnitroxide, the addition reaction apparently is a radical chain reaction as shown in Scheme 6. In this reaction, tert-butyl radical can either react with CCl_4 to give the tert-butyl chloride and a trichloromethyl radical or react with VP to give the adduct $\underline{t}\text{-}BuCH_2\dot{C}HP(O)(OEt)_2$. Due to the 200 fold excess of CCl_4 in the reaction, tert-butyl radical apparently only reacts with CCl_4 because the alkane ($\underline{t}\text{-}BuCH_2CH_2P(O)(OEt)_2$) was not observed as a reaction product. Thus, once the tert-butyl radical is generated, it reacts with CCl_4 to form a trichloromethyl radical which adds to VP to form radical **6**. Radical **6** then reacts with $\underline{t}$-BuHgCl to form **7** and regenerates the tert-butyl radical which continues the chain reaction. Similarly, as shown in Scheme 4, when **7**

Scheme 6

Initiation:

$$\underline{t}\text{-BuHgCl} \xrightarrow{h\nu} \underline{t}\text{-Bu}\cdot + \cdot\text{HgCl}$$

Chain:

$$\underline{t}\text{-Bu}\cdot + \text{CCl}_4 \xrightarrow{\text{1st.}} \underline{t}\text{-BuCl} + \text{Cl}_3\text{C}\cdot$$

$$\text{Cl}_3\text{C}\cdot + \text{CH}_2\text{=CHP} \xrightarrow{\text{2nd.}} \underset{\underset{\sim}{6}}{\text{Cl}_3\text{CCH}_2\dot{\text{C}}\text{HP}}$$

$$\underset{\sim}{6} + \underline{t}\text{-BuHgCl} \xrightarrow{\text{3rd.}} \underset{\underset{\sim}{7}}{\text{Cl}_3\text{CCH}_2\text{CH(HgCl)P}} + \underline{t}\text{-Bu}\cdot$$

Substitution:

$$\begin{tikzcd}
 & \text{Cl}_3\text{CCH}_2\text{CH}_2\text{P} \\
\underset{\sim}{7} \arrow[ur, "\text{NaBH}_4"] \arrow[dr, "\text{I}_2"'] & \\
 & \text{Cl}_3\text{CCH}_2\text{CH(I)P}
\end{tikzcd}$$

$\text{P} = \text{P(O)(OEt)}_2$

reacts with NaBH_4, the corresponding hydrogenated product is obtained; when $\underset{\sim}{7}$ reacts with iodine, the substituted iodide is isolated. Because of the nature of the electron-withdrawing group $(\text{EtO})_2\text{P(O)}$, radical $\underset{\sim}{6}$ is an electrophile which easily reacts with the nucleophilic $\underline{t}$-BuHgCl in the third step of the chain sequence of Scheme 6 to form $\underset{\sim}{7}$ and a <u>tert</u>-butyl radical.

The rate constant (k) for this step (Eq. 15) has been estimated by the following method. Based on the data reported by Raynal[40] the chain transfer rate constant (k_{CCl_4}) of VP radical with CCl_4 (Eq. 16) is 3 times the propagation rate

$$Cl_3CCH_2\dot{C}HP + t\text{-}BuHgCl \xrightarrow{k} Cl_3CCH_2CH(HgCl)P + t\text{-}Bu\cdot \quad (15)$$

$$Cl_3CCH_2\dot{C}HP + CCl_4 \xrightarrow{k_{CCl_4}} Cl_3CCH_2CH(Cl)P + Cl_3C\cdot \quad (16)$$

$P = P(O)(OEt)_2$

constant for the free radical polymerization of VP at 130 °C. The propagation rate constant of VP (attack of $\sim\!\sim CH_2$-$\dot{C}HP(O)(OEt)_2$ upon VP) is known from the literature to be $1 \times 10^2\ M^{-1}\ s^{-1}$ at 15-35 °C.[41] Thus leads to k_{CCl_4} of $> 3 \times 10^2\ M^{-1}\ s^{-1}$ at 40 °C. In competition with 10 M CCl_4, 0.2 M of t-BuHgCl is an effective trap for $Cl_3CCH_2\dot{C}HP(O)(OEt)_2$ with Reaction 12 in CCl_4 solution yielding $Cl_3CCH_2CH(HgCl)$-$P(O)(OEt)_2$ in 52% (based on the yield of $Cl_3CCH_2CH_2P(O)(OEt)_2$ after $NaBH_4$ reduction). Thus, on the basis of the assumption that 48% of $Cl_3CCH_2CH(Cl)P(O)(OEt)_2$ was also formed in the reaction (even though it was not observed), Eq. 17 would apply. At the end of the reaction ($t = \infty$), the concentration of t-BuHgCl had changed from 0.2 M to 0.15 M due to the initial ratio of t-BuHgCl/VP = 4 (VP is 100% consumed). Thus, the minimum value of the rate constant ($\underline{k}$) for the reaction of $Cl_3CCH_2\dot{C}HP(O)(OEt)_2$ with $\underline{t}$-BuHgCl is estimated from Eq.17 as $\underline{k} > 2 \times 10^4\ \underline{M}^{-1}\ s^{-1}$.[42] The value of $\underline{k}$ may actually be

$$\frac{52\%}{48\%} = \frac{\underline{k}[\underline{t}\text{-BuHgCl}]}{\underline{k}_{CCl_4}[CCl_4]} = \frac{\underline{k} \times 0.2\ \underline{M}^*}{> 3 \times 10^2 \times 10\ \underline{M}} \qquad (17)$$

$[^*\ 0.2\ \underline{M}\ (t = 0) \longrightarrow 0.15\ \underline{M}\ (t = \infty)]$

greater than $10^4\ \underline{M}^{-1}\ s^{-1}$. If a reasonable assumption is made that 5% of $Cl_3CCH_2CH(Cl)P(O)(OEt)_2$ would have been detected by GLC, the rate $\underline{k}[\underline{t}\text{-BuHgCl}]/\underline{k}_{CCl_4}[CCl_4]$ must be > 10 (52%/less than 5%), this leads to a minimum value of $\underline{k}$ of $> 2 \times 10^5\ \underline{M}^{-1}\ s^{-1}$. The reaction of $Cl_3CCH_2\dot{C}HP(O)(OEt)_2$ with $\underline{t}$-BuHgCl to yield $Cl_3CCH_2CH(HgCl)P(O)(OEt)_2$ occurs very rapidly in view of the steric effects which appear to be present.

Hexachloroethane was formed by the coupling of two trichloromethyl radicals in the termination step. The rapid combination of trichloromethyl radicals to form hexachloroethane may be one of the reasons why only 50% of the addition product was obtained in the reaction.

Because of the low solubility of phenyl vinyl sulfone in CCl_4 solution, the reaction of $\underline{t}$-BuHgCl with CH_2=$CHSO_2Ph$ in carbon tetrachloride gave the addition product $Cl_3CCH_2CH_2SO_2Ph$ in a low yield.

5. Formation of substituted alkenes by elimination of iodides with DBU

The reaction of halides with bases to eliminate hydrogen halide to form the corresponding olefins is a common and useful method in organic synthesis. Thus the iodides which were obtained from the photoaddition of alkylmercury chlorides to alkenes $CH_2{=}CHQ$ (Eq. 9), when treated with 1,8-diazabicyclo-[5,4,0]undec-7-ene (DBU)[43] at 80-90 °C for a few hours, yielded the corresponding alkenes (Eq. 18 and Table 5).

$$RCH_2CH(I)Q \xrightarrow[80\text{-}90\ ^\circ C]{DBU} RCH{=}CHQ \qquad (18)$$

Treatment of the iodides with R = i-Pr by DBU did not lead to the expected product i-PrCH=CHQ, but the isomer $Me_2C{=}CHCH_2Q$ was formed (see Table 5). This isomerization is known as a prototropic transformation which quite often occurs in a three-carbon system containing an activated unsaturated group.[44] Ionin and Petrov have studied the prototropic isomerization of several alkenylphosphonates with the catalyst sodium ethoxide (Eq. 19).[45] It was found that the isomer

$$RR'C{=}CHCH_2P(O)(OEt)_2 \rightleftarrows RR'CHCH{=}CHP(O)(OEt)_2 \qquad (19)$$

containing the structure $>C{=}CHCH_2P{=}O$ is more stable when $R' \neq H$. Thus, the iodide in Eq. 20 undergoes the elimination

Table 5. Elimination reactions of iodides with DBU[a]

$$RCH_2CH(I)Q + DBU \xrightarrow{80\text{-}90\ ^\circ C} RCH{=}CHQ$$

R	Q	Condition	Products[b]	% Yield[c]
t-Bu	$P(O)(OEt)_2$	4 h	*t*-$BuCH{=}CHP(O)(OEt)_2$	92 (88)
i-Pr	$P(O)(OEt)_2$	6 h	$Me_2C{=}CHCH_2P(O)(OEt)_2$	52 (43)
Cl_3C	$P(O)(OEt)_2$	PhH 4 h	$Cl_3CCH{=}CHP(O)(OEt)_2$	68 (54)
t-Bu	SO_2Ph	PhH 3 h	*t*-$BuCH{=}CHSO_2Ph$	78 (58)
i-Pr	SO_2Ph	PhH 6 h	$Me_2C{=}CHCH_2SO_2Ph$	92 (88)

[a] The iodide (1 mmol) was treated with 3 mmol of DBU either neat or in 5-8 mL of PhH.

[b] Only the (*E*)-isomers were detected by GLC; the stereoselectivity must be > 95%.

[c] GLC yields measured by adding internal standard; isolated yields in parentheses.

of HI with DBU to give alkene **8**, which is then isomerized by the excess base into the more stable alkene **9**.

$$Me_2CHCH_2CH(I)Q \xrightarrow{DBU} \underset{\mathbf{8}}{Me_2CHCH{=}CHQ} \rightleftarrows \underset{\mathbf{9}}{Me_2C{=}CHCH_2Q} \qquad (20)$$

The conversion in Eq. 21 from starting olefins $CH_2=CHQ$ via photoaddition with RHgCl, followed by substitution with

$$CH_2=CHQ + RHgCl \xrightarrow[3.DBU]{1.h\nu,\ 2.I_2} RCH=CHQ \qquad (21)$$

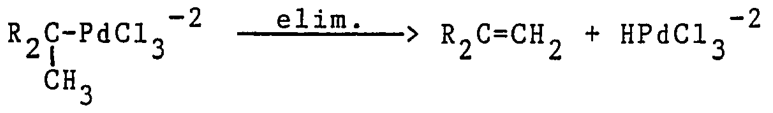
$Q = P(O)(OEt)_2, SO_2Ph.$

$R = \underline{t}\text{-Bu}, \underline{i}\text{-Pr}, \text{cyclo-}C_6H_{11}, \underline{n}\text{-Bu}, Cl_3C.$

iodine, and then elimination to give product RCH=CHQ may be useful in organic synthesis. The Heck reaction involves an addition reaction in which certain organomercurials react with alkenes to produce the substituted olefins in the presence of palladium chloride plus lithium chloride (Eq.22).[46]

$$R'HgX + CH_2=CHR \xrightarrow{Li_2PdCl_4} R'CH=CHR \qquad (22)$$

However, organomercurials (R'HgX) bearing beta-hydrogen cannot be used in this reaction because of the fact that the intermediate ($R'PdCl_3^{-2}$) readily undergoes beta-hydrogen elimination as shown in Eq. 23.[47] The conversion in Eq. 21



$$R_2\underset{CH_3}{C}\text{-}PdCl_3^{-2} \xrightarrow{elim.} R_2C=CH_2 + HPdCl_3^{-2} \qquad (23)$$

is not restricted by the presence of beta-hydrogen atoms. Thus reactions of $CH_2=CHQ$ with $\underline{t}$-BuHgCl (bearing 9 beta-hydrogen atoms) and with $\underline{i}$-PrHgCl (bearing 6 beta-hydrogen atoms) lead to the substituted alkenes t-BuCH=CHQ and $Me_2C=CHCH_2Q$ in good yields (Table 2 and 5).

6. Photostimulated reactions of alkylmercury chlorides with triphenylvinylsilane

Photostimulated reactions of alkylmercury chlorides with triphenylvinylsilane were also carried out (Eq. 24 and Table 6). This reaction is a little different than the previously

$$RHgCl + CH_2{=}CHSiPh_3 \xrightarrow[2.\ NaBH_4]{1.\ h\nu} RCH_2CH_2SiPh_3 \qquad (24)$$

discussed reactions. As shown in Table 6, a small amount of the corresponding olefin ($RCH{=}CHSiPh_3$) was also formed in the reaction. The results reported in Table 7 indicate that the solvent appears to have an effect on the reaction yields and that the workup procedure with $NaBH_4$ is not necessary. The same yields of $RCH_2CH_2SiPh_3$ and $RCH{=}CHSiPh_3$ were obtained when parallel reactions were worked-up with $NaBH_4$ or by treatment with aqueous $Na_2S_2O_3$ (see Table 7, entries 1,2 and 4,5). The different yields obtained in benzene and the mixed solvent of PhH/DMSO could be interpreted by the different solubility of olefin $CH_2{=}CHSiPh_3$ because t-BuHgCl is known to easily dissolve in both solvents. About 50% of the starting material was recovered in PhH solution perhaps because of the low solubility of $CH_2{=}CHSiPh_3$ in benzene.

Table 6. Photoreactions of $CH_2{=}CHSiPh_3$ with RHgCl followed by $NaBH_4$ reduction

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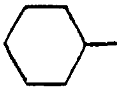
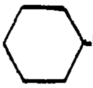
$$CH_2{=}CHSiPh_3 + RHgCl \xrightarrow[2.\ NaBH_4]{1.\ UV,\ 24\ h} RCH_2CH_2SiPh_3$$

R (Equiv.)	Concn. of $CH_2{=}CHSiPh_3$	Solvent	% Yield
t-Bu (3)	0.04 M	DMSO/PhH (80%:20%)	90[a]
i-Pr (5)	0.02 M	DMSO/PhH (80%:20%)	85[b]
 (5)	0.02 M	DMSO	60[c]
n-Bu (5)	0.02 M	DMSO/PhH (83%:17%)	30[d]

[a] 8% of t-BuCH=CHSiPh$_3$ was obtained.

[b] 10% of i-PrCH=CHSiPh$_3$ was obtained.

[c] 5% of  CH=CHSiPh$_3$ was observed.

[d] 17% of n-BuCH=CHSiPh$_3$ was obtained.

Tabele 7. Photoreactions of *t*-BuHgCl with $CH_2{=}CHSiPh_3$[a]

$$\underline{t}\text{-BuHgCl} + CH_2{=}CHSiPh_3 \xrightarrow[\text{2. workup}]{\text{1. UV}} \underline{t}\text{-BuCH}_2CH_2SiPh_3 + \underline{t}\text{-BuCH}{=}CHSiPh_3$$

No.	Solvent	UV(h)	workup with	% Yield		
				t-$BuCH_2CH_2SiPh_3$	*t*-$BuCH{=}CHSiPh_3$	$CH_2{=}CHSiPh_3$
1	DMSO/PhH (80%:20%)	24 h	$NaBH_4$	60	31	
2	DMSO/PhH (80%:20%)	24 h	$Na_2S_2O_3$	58	30	
3	DMSO/PhH (20%:80%)	24 h	$NaBH_4$	65	31	
4	PhH[b]	36 h	$NaBH_4$	26	10	44
5	PhH[b]	36 h	$Na_2S_2O_3$	24	5	51

[a] Reaction of 0.1 mmol of $CH_2{=}CHSiPh_3$ with 0.3 mmol of *t*-BuHgCl in 8 mL of solvent.

[b] $CH_2{=}CHSiPh_3$ did not completely dissolve in PhH.

The fact that the different workup procedure led to the same yields of products indicates that this reaction did not undergo the same mechanism as Scheme 4. Because there was no reaction between RHgCl and $CH_2{=}CHSiPh_3$ in the dark at room temperature for 3 days, the addition must occur by a free radical generated from photolysis of RHgCl. In order to ascertain if $RCH_2CH(HgCl)SiPh_3$ was formed in the reaction, the photolysis product was cleaved with molecular iodine (Eq. 25).

$$\underline{t}\text{-BuHgCl} + CH_2{=}CHSiPh_3 \xrightarrow[2.\ I_2]{1.UV,\ PhH} \underset{(28\%)}{\underline{t}\text{-BuCH}_2CH(I)SiPh_3}$$

$$+ \underset{(42\%)}{\underline{t}\text{-BuCH}_2CH_2SiPh_3} + \underset{(17\%)}{\underline{t}\text{-BuCH=CHSiPh}_3} + \underset{(12\%)}{CH_2{=}CHSiPh_3} \qquad (25)$$

The result showed that 12% of unreacted olefin was left, perhaps because of the low solubility of $CH_2{=}CHSiPh_3$ in PhH. Only 28% of the expected iodide was obtained, and the substituted alkane and alkene were observed in 42% and 17%, respectively. These results may be rationalized by the proposed reaction process presented in Scheme 7. Upon irradiation, the alkyl radical generated from RHgCl adds to the double bond of $CH_2{=}CHSiPh_3$, probably because of the absence of a strong electron-withdrawing group. Thus, radical **10** undergoes three competition reactions to lead to three different products. Besides the expectant reaction with RHgCl to form **11** and a

Scheme 7

Initiation:

$$RHgCl \xrightarrow{h\nu} R\cdot + \cdot HgCl$$

Addition:

$$R\cdot + CH_2{=}CHSiPh_3 \longrightarrow \underset{10}{RCH_2\dot{C}HSiPh_3}$$

Competition:

$$\underset{10}{RCH_2\dot{C}HSiPh_3} \xrightarrow{1.RHgCl} \underset{11}{RCH_2CH(HgCl)SiPh_3} + R\cdot$$

$$\underset{10}{RCH_2\dot{C}HSiPh_3} \xrightarrow{2.elim.[H\cdot]} \underset{12}{RCH{=}CHSiPh_3}$$

$$\underset{10}{RCH_2\dot{C}HSiPh_3} \xrightarrow{3.abstr.H\cdot} \underset{13}{RCH_2CH_2SiPh_3}$$

radical (R·) in a chain sequence; radical 10 can eliminate a hydrogen from the beta-carbon to give the addition-elimination product 12. Radical 10 also can abstract a hydrogen from the reaction medium, the reactant, or the reaction intermediate to give saturated product 13. In addition, compound 11 may undergo self-decomposition to lead to product 12 by elimination or to product 13 by hydrogen abstraction. The product 13 always appeared as the major product of reaction indicating that hydrogen abstraction by radical 10 was almost 2 times faster than the hydrogen elimination from radical 10. If the radical 10 underwent a termination reaction by disproportionation, product 12 and 13 should be formed in a 1:1 ratio (Eq. 26). The excess of product 13 particularly at high

$$2\ \underset{\sim}{10} \longrightarrow \underset{\underset{\sim}{12}}{RCH{=}CHSiPh_3} + \underset{\underset{\sim}{13}}{RCH_2CH_2SiPh_3} \qquad (26)$$

[t-BuHgCl] (compare Tables 6 and 7), suggests that perhaps 13 can be formed in part by Reaction 27. Reaction of ·HgCl with RHgCl (Eq. 28) could continue a chain reaction.

$$\underset{\sim}{10} + \textit{t}\text{-BuHgCl} \longrightarrow \underset{\sim}{13} + Me_2C{=}CH_2 + \cdot HgCl \qquad (27)$$

$$RHgCl + \cdot HgCl \longrightarrow R\cdot + HgCl_2 + Hg^\circ \qquad (28)$$

Although this reaction did not give exclusively the alkylated product, it did give much higher yields of product 13 than the Giese method.[22] Results of a Giese-type reaction of triphenylvinylsilane with tert-butylmercury chloride are summarized in Table 8.

Table 8. Reactions[a] of t-BuHgCl with $CH_2=CHSiPh_3$ and $NaBH_4$

$$t\text{-BuHgCl} + CH_2=CHSiPh_3 + NaBH_4 \longrightarrow t\text{-BuCH}_2CH_2SiPh_3$$

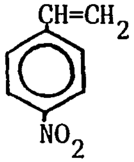
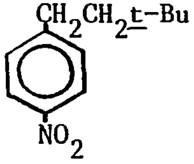
No.	Solvent	Reaction time(min)	% Yield	
			t-$BuCH_2CH_2SiPh_3$	$CH_2=CHSiPh_3$
1	DMSO	15	0	98
2	DMSO/PhH (33%:67%)	30	0	97
3	PhH	60	4.3	95
4	CH_2Cl_2	90	4.5	94

[a] Reaction of 0.1 mmol of $CH_2=CHSiPh_3$ with 0.3 mmol of t-BuHgCl in 8 mL of solvent by adding 0.4 mmol of $NaBH_4$.

7. Photoreactions of t-BuHgCl with other alkenes

Photostimulated reactions of tert-butylmercury chloride with several other alkenes followed by reduction with $NaBH_4$ were also examined. The results are summarized in Table 9. The poor yields were observed in these reactions except for the reaction with p-nitrostyrene which formed 1-(p-nitrophenyl)-3,3-dimethylbutane in 62% yield. The reasons for the low yields observed with the other substituted alkenes of Table 9

Table 9. Photoreaction of t-BuHgCl with olefins followed by $NaBH_4$ reduction

No.	Olefins	t-BuHgCl (equiv.)	Conditions	Products	% Yield
1.		5	DMSO,UV,24h		62
2.	$CH_2=C(Cl)CN$	5	PhH,UV,20h	t-$BuCH_2CH(Cl)CN$	26[a]
3.	$CH_2=CHSPh$	5	PhH,UV,20h	t-$BuCH_2CH_2SPh$	26[b]
				t-BuCH=CHSPh	30
4.	$CH_2=CHCOCH_3$	0.5	PhH,UV,22h	t-$BuCH_2CH_2COCH_3$	33[c]
5.	$CH_2=CHCOPh$	5	DMSO,UV,24h	t-$BuCH_2CH_2COPh$	10[d]

---

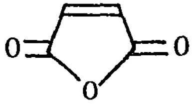
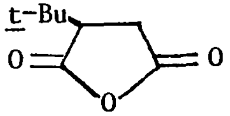
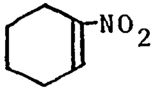
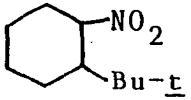
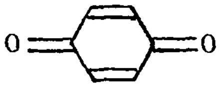
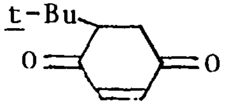
[a] 2% of (t-$BuCH_2C(Cl)CN)_2$ was formed.

[b] 41% of t-$BuCH_2CH(SPh)CH(SPh)CH_2Bu$-t was formed.

[c] 2% of t-$BuCH_2CH_2CH(OH)CH_3$ was observed.

[d] 50% of $CH_2=CHCOPh$ was recovered.

Table 9. (Continued)

No.	Olefins	t-BuHgCl (equiv.)	Conditions	Products	% Yield
6.	$CH_2{=}CPh_2$	2	PhH,UV,20h	$t\text{-BuCH}_2\text{CHPh}_2$	12
				$t\text{-BuCH}{=}\text{CPh}_2$	15
7.		3	PhH,UV,24h		16[e]
8.	$CH_2{=}C(CO_2Me)CH_2CO_2Me$	5	PhH,UV,20h	$t\text{-BuCH}_2\text{CH--CO}_2\text{Me}$ $\text{CH}_2\text{CO}_2\text{Me}$	10
9.		1	PhH,UV,20h		10
10.		3	PhH,UV,20h		8

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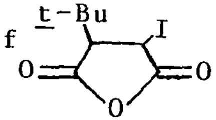
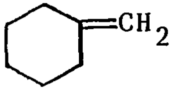
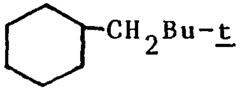
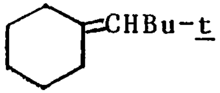
[e] 14% of  was obtained by workup with iodine.

Table 9. (Continued)

No.	Olefins	*t*-BuHgCl (equiv.)	Conditions	Products	% Yield
11	CH$_2$=CHCO$_2$Et	4	PhH,UV,20h	*t*-BuCH$_2$CH$_2$CO$_2$Et	8[e]
12		3	PhH,UV,18h		10
					10
13	CH$_2$=CHSOPh	5	PhH,UV,20h	*t*-BuCH$_2$CH$_2$SOPh	5
14	MeO$_2$CCH=CHCO$_2$Me	5	PhH,UV,24h	MeO$_2$CCH(*t*-Bu)CH$_2$CO$_2$Me	31[f]
15	PhCH=CHCO$_2$Et	5	PhH,UV,24h	PhCH$_2$CH(*t*-Bu)CO$_2$Et	7[g]
16	PhO$_2$CCH=CHNO$_2$	3	PhH,UV,12h	PhO$_2$CCH(*t*-Bu)CH$_2$NO$_2$	0

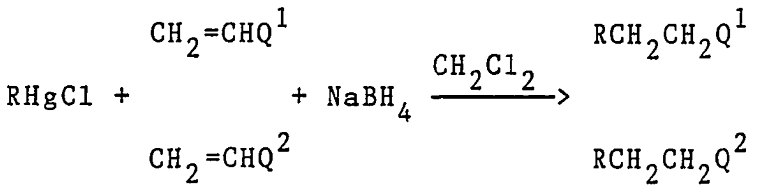
[e] 5% of *t*-BuCH$_2$CH(I)CO$_2$Et was obtained by workup with iodine.

[f] 21% of a telomer was obtained.

[g] 22% of a telomer was observed.

can only be surmised. In the formation of the 1:1 adduct with *t*-BuHgCl via a free radical chain process, the two propagation steps are (a) the addition of *tert*-butyl radical to the alkene and (b) the reaction of the adduct radical with *t*-BuHgCl to generate the *tert*-butyl radical. If either step fails, the telomerization process is doomed.

The reactivity of alkenes towards alkyl radicals has been measured by competitive reactions by Giese[15,22] and others[42] (Eq. 29). Some pertinent results are summarized in

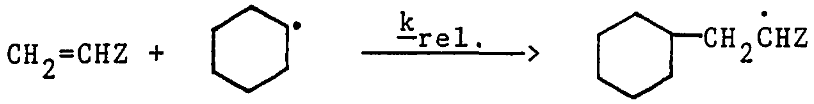


$$\text{RHgCl} + \begin{array}{c} \text{CH}_2\text{=CHQ}^1 \\ \\ \text{CH}_2\text{=CHQ}^2 \end{array} + \text{NaBH}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} \begin{array}{c} \text{RCH}_2\text{CH}_2\text{Q}^1 \\ \\ \text{RCH}_2\text{CH}_2\text{Q}^2 \end{array} + \text{Hg}° \qquad (29)$$

Tables 10 and 11. The reactivity of the olefinic substrate may be an important factor with some of the substrates in Table 9, particularly the 1,2-disubstituted compounds (entries 14-16 of Table 9) and possibly phenyl vinyl sulfoxide. However, substrates as unreactive as a vinylstannane are fairly efficient in trapping a *tert*-butyl radical when there is no other reaction channel available (see Section 6 of Part I,A).

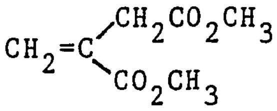
The major problem with a chain reaction involving the substrates in Table 9 appears to be the reaction between the adduct radical ($t\text{-BuCH}_2\dot{\text{C}}\text{HQ}$) and *t*-BuHgCl to regenerate a

Table 10. Relative reactivities of substituted alkenes towards cyclohexyl radical[22]



No.	Z	$k_{rel.}$
1	CHO	34
2	CN	24
3	$COCH_3$	13
4	CO_2CH_3	6.7
5	$CONH_2$	1.1
6	Ph	= 1.0
7	Cl	0.12
8	$OCOCH_3$	0.016
9	H	0.015
10	n-Bu	0.004

Table 11. Relative reactivities of substituted alkenes towards alkyl radicals

Alkenes	Radicals	
	Cyclohexyl[a]	*tert*-Butyl[b]
$CH_2=C(Cl)CN$	31	52
$CH_2=C(Cl)CO_2CH_3$	12	
$CH_2=CHCN$	3.6	3.8
$CH_2=CHSO_2Ph$		2.5
 $CH_2=C(CH_2CO_2CH_3)CO_2CH_3$	1.4	
$CH_2=CHCO_2Et$	= 1.0	= 1.0
$CH_2=CHP(O)(OEt)_2$		0.53
$CH_2=CPh_2$	0.51	0.21
$CH_2=CHPh$	0.15	0.15
$CH_2=C(C_6H_4OCH_3\text{-}\underline{p})_2$		0.11
$CH_2=CCl_2$		0.06
$CH_2=CHSPh$		0.03
$CH_2=CHSOPh$		0.005

[a] Reference [22].

[b] Reference [42].

Table 11. (Continued)

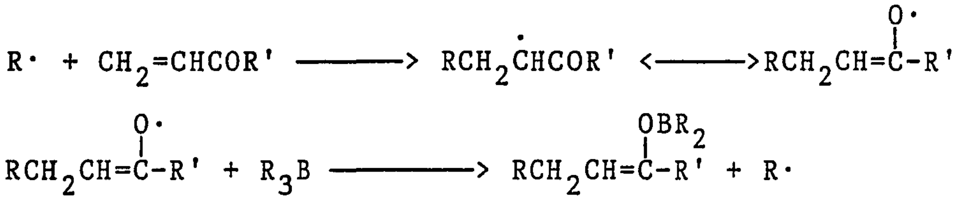
Alkenes	Radicals	
	Cyclohexyl[a]	*tert*-Butyl[b]
CH_2=CHOEt		< 0.005
CH_2=CHSiMe_3		< 0.005
CH_2=CHSnBu_3		< 0.005
CH_2=CHCMe_3		< 0.005
CH_2=CHNH_2		< 0.005

tert-butyl radical. This is clearly the case with CH_2=CHSPh, CH_2=CPh_2 and methylenecyclohexane where *t*-BuCH=CHQ and *t*-Bu-CH_2CH_2Q are formed in a 1:1 ratio from the disproportionation of *t*-Bu$CH_2\dot{C}$HQ. Apparently, only adduct radicals with a Q substituent that can stablize the anion (*t*-Bu$CH_2\ddot{C}HQ^-$) react readily with *t*-BuHgCl to regenerate *t*-Bu· (e.g. Q = PhSO_2, $(EtO)_2$P(O), *p*-$NO_2C_6H_4$). In the case of CH_2=C(Cl)CN, the adduct radical may be too sterically hinder to react with *t*-BuHgCl even though a strong polar effect should occur.

The failure of α, β -unsaturated ketones, esters or anhydrides (entries 4, 5, 7, 8, 10, 11, 14 and 15 in Table 9) is noteworthy. Compounds like ethyl acrylate is quite reactive towards the tert-butyl radical (see Table 11) and these substrates gave good yields of $\underline{t}\text{-BuCH}_2\text{CH}_2\text{Q}$ in the Giese reaction. The failure of the telomerization reaction with t-BuHgCl must be connected with the failure of the adduct radical ($\underline{t}\text{-BuCH}_2\dot{\text{C}}\text{HCOR}$, $\underline{t}\text{-BuCH}_2\dot{\text{C}}\text{HCO}_2\text{Et}$) to react with t-BuHgCl. No real explanation can be advanced for this effect at this time. Perhaps it is connected with the fact that the electron spin is delocalized into the carbonyl group and that oxygen-centered radical appears to have low reactivity in homolytic displacement on mercury. We must conclude that the reactivity of $\underline{t}\text{-BuCH}_2\dot{\text{C}}\text{HQ}$ towards t-BuHgCl depends on more than just steric effects and the ability of Q to stabilize a negative charge.

α, β-Unsaturated esters and ketones do participate in a free radical chain reaction with trialkylboranes.[48,49] Here, coordination of the R_3B with the carbonyl group may be important. Ignoring this coordination, the reaction mechanism of Scheme 8 can be written. Thus, alkylboranes participate in a free radical telomerization reaction with α, β-unsaturated ketones and esters whereas alkylmercury halides are ineffective. It could appear that the major difference between

Scheme 8



$$R\cdot + CH_2{=}CHCOR' \longrightarrow RCH_2\dot{C}HCOR' \longleftrightarrow RCH_2CH{=}\overset{O\cdot}{\overset{|}{C}}{-}R'$$

$$RCH_2CH{=}\overset{O\cdot}{\overset{|}{C}}{-}R' + R_3B \longrightarrow RCH_2CH{=}\overset{OBR_2}{\overset{|}{C}}{-}R' + R\cdot$$

mercury and boron is the strength of the bonds being formed to the oxy-substituent; in any event, apparently, an alkoxyl-type radical readily attacks the boron atom of an alkylborane, but has little reactivity towards the mercury atom of an alkylmercury chloride. Trialkylboranes are easily autoxidized by a chain reaction involving peroxy and alkoxy radicals which displace R· from R_3B. Dialkylmercurials are much more resistent to reaction with molecular oxygen even though the carbon-mercury bond is relatively weak.

8. Photostimulated reactions of tert-butylmercury thiophenoxide with diethyl vinylphosphonate(VP)

The photostimulated reaction of tert-butylmercury thiophenoxide (t-BuHgSPh) with VP was performed (Eq. 30) and the results are given in Table 12. Three products were obtained from the reaction. The major product in a mixture (about 40%) of t-$BuCH_2CH_2P(O)(OEt)_2$ and t-$BuCH{=}CHP(O)(OEt)_2$, possibly

Table 12. Photoreactions of *t*-BuHgSPh with VP[a]

$$t\text{-BuHgSPh} + \underset{(VP)}{CH_2{=}CHP} \xrightarrow[2.\ Na_2S_2O_3]{1.\ h\nu} \underset{\mathbf{14}}{t\text{-BuCH}_2\text{CH(SPh)P}}$$

$$+ \underset{\mathbf{15}}{t\text{-BuCH}_2\text{CH}_2\text{P}} + \underset{\mathbf{16}}{t\text{-BuCH{=}CHP}}$$

$P = P(O)(OEt)_2$

No.	Ratio of *t*-BuHgSPh/VP	Conditions	% Yield	
			14	**15** + **16**
1	2	PhH,UV,24h	19	41
2	5	PhH,UV,24h	17	29
3	3	PhH,UV,24h	12	38
4	3	PhH,UV,6.5h	12	37
5	3	PhH,UV,30h	9	49

[a] Reaction of 0.2 mmol of VP with excess *t*-BuHgSPh in 4 mL of benzene.

formed by the disproportionation of *t*-$BuCH_2\dot{C}HP(O)(OEt)_2$. In addition, about 17% of *t*-$BuCH_2CH(SPh)P(O)(OEt)_2$ was obtained and 50-70% of mercury metal was formed after irradiation even when the reactions were carried out in PhH solution.

$$CH_2{=}CHP + \underline{t}\text{-BuHgSPh} \xrightarrow[2.\ Na_2S_2O_3]{1.\ h\nu} \underset{\mathbf{14}}{\underline{t}\text{-BuCH}_2CH(SPh)P}$$

$$P = P(O)(OEt)_2 \qquad + \underset{\mathbf{15}}{\underline{t}\text{-BuCH}_2CH_2P} + \underset{\mathbf{16}}{\underline{t}\text{-BuCH{=}CHP}} + Hg^\circ \qquad (30)$$

The reaction of VP with *t*-BuHgCl (Table 1) leads to one product in an excellent yield. The only difference between these two reactions is the mercurial employed. The results indicate that *t*-BuHgSPh is either much less reactive than *tert*-butylmercury chloride towards $\underline{t}\text{-BuCH}_2\dot{C}HP(O)(OEt)_2$ (**17**) or *t*-BuHgSPh reacts in a different manner than *t*-BuHgCl. One possibility is that *t*-BuHgSPh is much more prone to undergo a beta-hydrogen abstraction (Eq. 30). If Reaction 31 occurs in

$$\underset{\mathbf{17}}{\underline{t}\text{-BuCH}_2\dot{C}HP} + \underline{t}\text{-BuHgSPh} \longrightarrow \underline{t}\text{-BuCH}_2CH_2P + Me_2C{=}CH_2 + Hg^\circ + PhS\cdot \qquad (31)$$

a concerted manner there is a considerable thermochemical driving force because of the stability of PhS· formed. Reaction of PhS· with **17** would explain the formation of product **14**. Alternately, **17** might react with *t*-BuHgSPh to form **14** directly or to form $\underline{t}\text{-BuCH}_2CH(HgSPh)P(O)(OEt)_2$ which might decompose thermally or photochemically to **14** and Hg°. Some insight further into the reaction mechanism might have been obtained if the ratio of 15/16 had been measured.

9. Photoreactions of diethyl phosphonyl mercurials with alkenes

The Giese reaction (Scheme 1) is limited to electron-deficient olefins and to alkylmercurials capable of forming donor radicals, the reaction of such donor radicals with electron-deficient olefins has been interpreted by the frontier orbital method, in terms of the interaction between the SOMO of the free radical and the LUMO and HOMO of the alkenes (Fig. 1).[22,50]

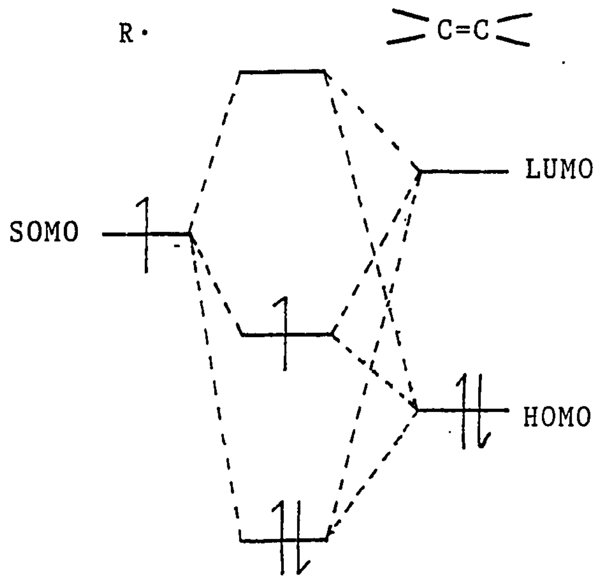


Figure 1. Interaction between the SOMO of a free radical and the HOMO and LUMO of an alkene

The polar effect in free radical addition to double bonds is often explained by structures such as 18 and 19 (D = donor, A = acceptor). Such structure represents SOMO-LUMO (18) and

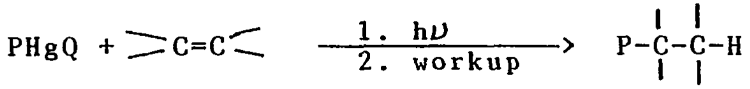
$$D^{+}\ \dot{C}H_2\text{-}\ddot{C}HA^{-} \qquad\qquad A\bar{:}\ \dot{C}H_2\text{-}\overset{+}{C}HD$$

18 19

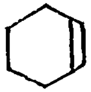
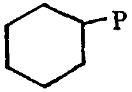
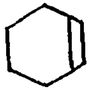
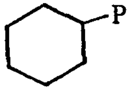
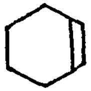
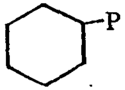
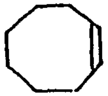
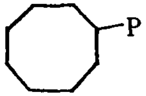
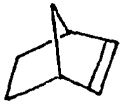
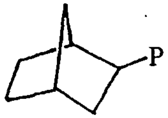
SOMO-HOMO (19) interaction and should be most important when the substituents in the radical and alkene cause the SOMO-LUMO or SOMO-HOMO energy gaps to be small. Diethylphosphonyl mercurials ($(EtO)_2P(O)HgX$, $[(EtO)_2P(O)]_2Hg$, etc.) are known to generate the $(EtO)_2\dot{P}(O)$ radical[31] which is an electron-deficient radical. Thus, photoreactions of $(EtO)_2P(O)HgQ$ with some electron-rich olefins were carried out and the results are given in Table 13. The yields of telomers formed were modest and it is not obvious that chain reactions are involved in view of the long irradiation periods employed. In addition, the photolysis of $(EtO)_2P(O)HgCl$ with $(\underline{p}\text{-}NO_2C_6H_4)_2C{=}CH_2$ and $(\underline{p}\text{-}MeOC_6H_4)_2C{=}CH_2$ led to none of the expecting products, the olefins being recovered in nearly 100%.

The results listed in Table 13 apparently show that although an electron-deficient radical like diethyl phosphonyl radical can add to the electron-rich olefins, the adduct radicals $(EtO)_2P(O)\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot$ formed by addition do not react readily

Table 13. Photoreactions of PHgQ with alkenes (P = $P(O)(OEt)_2$)



$$PHgQ + {>}C{=}C{<} \xrightarrow[\text{2. workup}]{\text{1. } h\nu} P{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H$$

Q (equiv.)	Olefins	Conditions	Workup with	Products	% Yield
Cl (1)		PhH UV 24h	$NaBH_4$		48
CF_3CO_2 (1)		DMSO UV 24h	$NaBH_4$		40
P (1)		DMSO UV 12h	$Na_2S_2O_3$		10
CF_3CO_2 (1)	t-BuCH=CH_2	DMSO UV 24h	$NaBH_4$	t-BuCH_2CH_2P	38
Cl (1.5)		DMSO UV 24h	$NaBH_4$		42
Cl (1)		DMSO UV 24h	$NaBH_4$		7[a]

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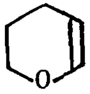
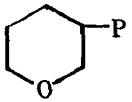
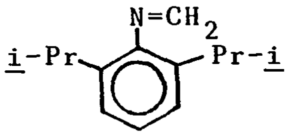
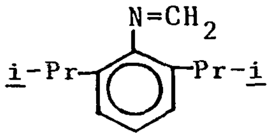
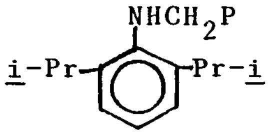
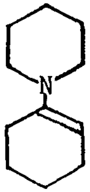
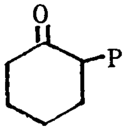
[a] 3% of the dimer,  , was formed.

Table 13. (Continued)

Q (equiv.)	Olefins	Conditions	Workup with	Products	% Yield
Cl (2.5)	$(MeO)_2C=CH_2$	PhH UV 24h	$NaBH_4$	$(MeO)_2CHCH_2P$	20[b]
Cl (5)		DMSO UV 22h	$NaBH_4$		10[b]
P (2)		DMSO SL 24h	$Na_2S_2O_3$		35[c]
Cl (5)		DMSO UV 3 days	$Na_2S_2O_3$		65
Cl (5)		DMSO UV 3 days	0.1M HCl		15

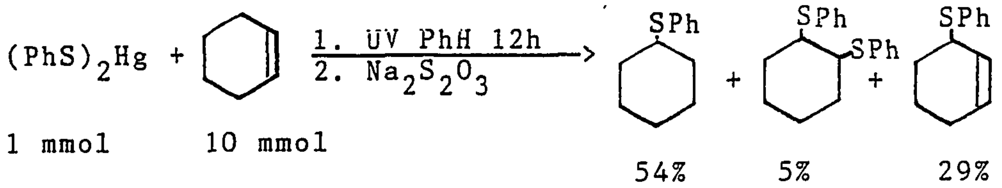
[b] Polymers were also formed.

[c] 50% of olefin was recovered.

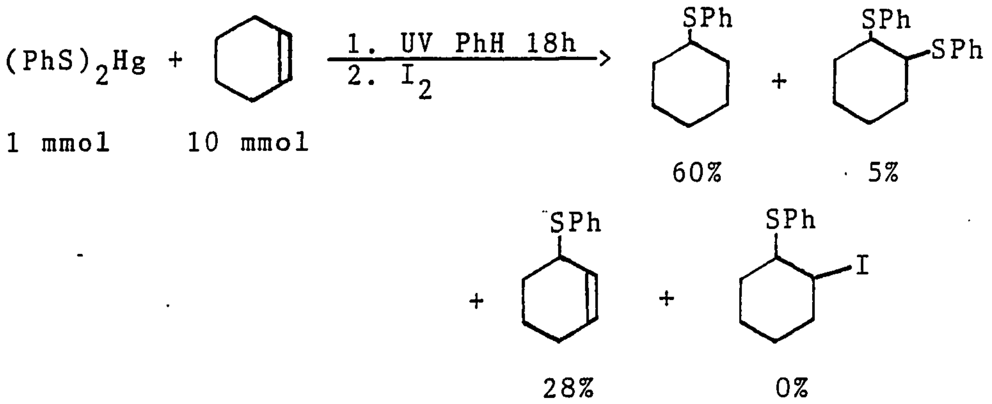
with diethyl phosphonyl mercurials.

10. Reactions of bis(thiophenyl)mercury with cyclohexene

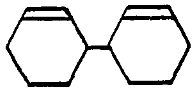
The reaction of bis(thiophenyl)mercury with cyclohexene was also carried out (Eqs. 31 and 32). Three major products



(31)



(32)

plus the dimer () were obtained in the reaction. Cleavage of the reaction product with molecular iodine did not produce a detectable amount of phenyl 2-iodocyclohexyl sulfide and it thus appears that a simple addition of PhS-HgSPh to the cyclohexene bond to form a new mercurial did not occur. It appears that PhS· from the photolysis of $(PhS)_2Hg$ adds to the double bond of cyclohexene or abstracts the allylic hydrogen atom forming thiophenol. Radical attacks upon $(PhS)_2Hg$ to form 3-cyclohexenyl phenyl sulfide, PhS·, and Hg° may have occurred. Alternately, the 3-cyclohexenyl phenyl sulfide could be formed by the attack of the allylic radical upon PhSSPh or by coupling of radical PhS· with the allylic radical.

C. Conclusion

Alkylmercury chlorides (RHgCl, R = t-Bu, i-Pr, cyclo-C_6H_{11}, n-Bu) react with alkenes (CH_2=CHQ; Q = $P(O)(OEt)_2$, SO_2Ph) under the influence of ultraviolet light irradiation followed by $NaBH_4$ reduction to afford respectively diethyl alkylphosphonates and alkyl phenyl sulfones in good yields. The reactions proceed via a free radical chain mechanism involving alkyl radicals, evidence to support this mechanism includes the facts that the reactions fail to proceed in the dark but can be readily initiated by photoirradiation. The rate of addition of alkyl radical to alkenes is drastically retarded by the presence of 10 mol% of di-tert-butylnitroxide. Furthermore, the UV-visible spectra showed that there was no complexion between alkylmercury chloride and VP. The intermediate $RCH_2CH(HgCl)Q$ involved in free radical chain sequence has been quantitatively trapped by formation of the corresponding iodide $RCH_2CH(I)Q$ with workup by reaction of iodine, and the possibility of the iodides formed without the intermediacy of $RCH_2CH(HgCl)Q$ has been excluded. The relative reactivity of RHgCl in this addition reaction has been measured as the order of _t_-BuHgCl > _i_-PrHgCl ~ cyclo-$C_6H_{11}HgCl$ >> _n_-BuHgCl, which is consistent with the results measured by ESR spectroscopy.[36,37]

The interesting product $Cl_3CCH_2CH_2P(O)(OEt)_2$ was isolated from the reaction of _t_-BuHgCl with VP in CCl_4 solution followed by $NaBH_4$ reduction. Mechanistically, the reaction has been shown by a free radical chain process involving trichloromethyl radical which generated from the reaction of _t_-Bu· with CCl_4. The reaction did not proceed in the dark, but occurred smoothly under photostimulation, and the reaction is completely inhibited by the presence of 10 mol% of di-_tert_-butylnitroxide. In addition, the iodide Cl_3CCH_2-$CH(I)P(O)(OEt)_2$ was also isolated from the reaction by workup with iodine, proving the existence of intermediate compound $Cl_3CCH_2CH(HgCl)P(O)(OEt)_2$. The iodides $RCH_2CH(I)Q$ (R = _t_-Bu, _i_-Pr, Cl_3C) can easily eliminate HI with DBU to accomplish the conversion from olefins CH_2=CHQ into substituted olefins RCH=CHQ in good yields. The described reaction of RHgCl with CH_2=CHQ synthetically provides a convenient method for preparation of alkylphosphonates, alkyl phenyl sulfones and the corresponding substituted olefins.

Alkylmercury chlorides have been found to react with olefin CH_2=$CHSiPh_3$ somewhat differently from the reaction with CH_2=CHQ. This reaction is a free radical reaction due to fail to occur in the dark, but two products were obtained from the reaction and only 28% of iodide t-$BuCH_2CH(I)SiPh_3$ was obtained by workup with iodine.

The reaction of t-BuHgCl with other alkenes were also examined. The incongruitive results show that the reactivity of the adduct radical towards t-BuHgCl in these reactions depends on more than just steric effects and the ability of substituents to stablize a radical intermediate.

The electron-deficient radical $(EtO)_2(O)P\cdot$ derived from $(EtO)_2(O)PHgQ$ (Q = Cl, F_3CCOO, $P(O)(OEt)_2$) photochemically adds to the electron-rich olefins. However, the reaction did not lead to the good yields because the adduct radicals do not react readily with diethyl phosphonyl mercurials.

D. Experimental

1. Instrumentation and techniques

Proton NMR spectra were recorded by Varian EM 360A, EM-360L and Nicolet NT300 spectrometers. Carbon NMR spectra were recorded by JOEL FX-90Q and Nicolet NT300 spectrometers. Phosphorus NMR spectra were recorded by a Bruker WM-300 spectrometer and are reported in ppm (δ) related to 85%

H_3PO_4. Analytic gas chromatography (GLC) was performed with a Varian 3700 gas chromatography equipped with a Hewlett-Packard 3390A integrator. G.C. mass spectra (GCMS) were recorded by a Finnegan 4000 with an INCOS data system. High resolution mass spectra (MS) were recorded with a Kratos MS-50 spectrometer. Infrared spectra (IR) were recorded by a Beckman IR 4250 spectrophotometer, and elemental analyses were measured by Galbraith Laboratories, Inc. All the melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated by flash column chromatography on silica gel (Kiesel gel 60, 230-400 mesh ASTM, purchased from EM Reagents Co.) with eluents of ether or mixed solvents. GLC yields were determined by using an internal standard of naphthalene or biphenyl.

2. Solvents and reagents

Solvents were purchased from Fisher or Baker. Dimethyl sulfoxide (DMSO) was stirred with calcium hydride at 80 °C overnight, then distilled and stored over 4A Molecular Sieves. Benzene and tetrahydrofuran (THF) were refluxed with sodium metal by using benzophenone as an indicator to form sodium benzophenone ketyl (deep blue). After a few hours, the solvent was distilled and stored over 4A Molecular Sieves.

Carbon tetrachloride was distilled from phosphorus pentoxide (P_2O_5), and other solvents were used without purification.

Chemical reagents including most of the olefins were purchased from Aldrich Chem. Co. and were used without further purification in most cases since analysis of the olefins purchased by GLC indicated a high degree of purity. Some olefins were prepared by literature procedures. Thus prepared were methylenecyclohexane (Lit.[51] bp 94-96 °C), N-methylene-2,6-diisopropylaniline (Lit.[52] bp 58-60 °C/0.15 mmHg), phenyl vinyl ketone (Lit.[53] bp 58-59 °C/2 mmHg) and *p*-nitrostyrene[54] (the method employed was a variation of that reported by Wittig and Schoellkopf[51]). All of the olefins prepared had physical constants which agreed with the literature values.

3. Preparation of organomercurials

Most of the alkylmercury halides were prepared by the literature procedures.[3] Usually, they were prepared by the reaction of the corresponding Grignard reagents with mercury salts in 1:1 ratio in THF or ether. Thus prepared were *n*-butylmercury chloride (Lit.[55] mp 127 °C), neopentylmercury chloride (Lit.[56] mp 117-118 °C), isopropylmercury chloride (Lit.[57] mp 94.5-95.5 °C), cyclohexylmercury chloride (Lit.[58] mp 163-164 °C), and *tert*-butylmercury chloride (mp 110-113 °C, Lit.[59] mp 123 °C). The preparation of _t_-BuHgCl by refluxing the mixture in THF, as described in the literature, afforded a low yield (20-30%) of the product because of the instability of _t_-BuHgCl. However, the yield is improved to over 50% by performing the reaction at low temperature. Thus, a solution containing mercury chloride ($HgCl_2$ 0.2 mole, dried at 80 °C) in dry THF was stirred in an ice bath under nitrogen while a solution of 0.2 mole of _tert_-butylmagnesium chloride prepared from _tert_-butyl chloride and Mg in THF was added dropwise. After addition, the mixture was then stirred overnight at room temperature. At 0 °C, ether (75 mL) and water (75 mL) were then slowly added to the mixture. After stirring for 10 min, the mixture was separated and the aqueous layer was extracted by ether (2 x 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The white precipitate was recrystallized from hexane-ethanol (90%:10%). Unlike other alkylmercury chlorides, _tert_-butylmercury chloride slowly decomposes to give mercury metal at room temperature. Therefore, it was wrapped with aluminum foil and kept in a closed container in a refrigerator.

Bis(diethylphosphonyl)mercury (Lit.[60] mp 56.8-58 °C), diethyl phosphonylmercury chloride (Lit.[60] mp 103-104 °C), diethyl phosphonylmercury trifluoroacetate (Lit.[61] mp 119-122 °C) and _tert_-butylmercury thiophenoxide (Lit.[62] mp 66-

68 °C) were synthesized by the methods described in the literature. All the mercurials employed had melting points in agreement with the literature values.

4. General procedure for photoreactions of RHgCl with CH_2=CHQ followed by $NaBH_4$ reduction

To an oven-dried pyrex tube was added RHgCl, CH_2=CHQ and solvent (PhH or DMSO). The tube was irradiated in a Rayonet Photoreactor at 40 °C. After irradiation, the mixture was transferred to a flask and solid $NaBH_4$ was added. After stirring for 10 min, a few drops of water was added to precipitate the mercury metal, and then more water (8-10 mL) was added. The mixture was separated, and the aqueous layer was extracted with ether (2 x 5 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated to afford a liquid or a solid which was analyzed by GLC and GCMS. The pure reaction products were isolated by flash column chromatography and characterized by ^1H NMR, ^{13}C NMR, MS and IR. The following reactions in Section 5 to 12 were carried out using this procedure.

5. Photoreaction of t-BuHgCl with VP followed by $NaBH_4$ reduction

A pyrex tube containing *t*-BuHgCl (0.2 g, 0.72 mmol), VP (0.03 g, 0.18 mmol) and PhH (3 mL) was irradiated for 24 h. After irradiation, $NaBH_4$ (0.04 g, 0.86 mmol) was added and the mixture was worked up as described in Section 4. After removing the solvent, a colorless liquid containing diethyl 3,3-dimethylbutylphosphonate in 98% yield was isolated by flash column chromatography with ether as the eluent.

^1H NMR ($CDCl_3$) δ 4.11 (p, 4H, *J* = 7.2 Hz), 1.72-1.70 (m, 4H), 1.33 (t, 6H), 0.90 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 61.37 (d, J_{COP} = 6.1 Hz), 35.80 (d, J_{CCP} = 6.1 Hz), 29. 37 (d, J_{CCCP} = 6.1 Hz), 28.68, 21.20 (d, J_{CP} = 141.6 Hz), 16.41 (d, J_{CCOP} = 6.1 Hz).

GCMS, *m*/*e* (relative intensity) 222 (0.2, M^+), 221 (1.1), 207 (49), 166 (58), 165 (100), 151 (52), 138 (96), 111 (63), 57 (66).

M.S. Calculated for $C_{10}H_{22}O_3P$ (M^+-H): 221.13060. Found: 221.13036. Error: -1.0 ppm.

IR (neat, NaCl plate, cm^{-1}) 2980, 2870, 1470, 1440, 1390, 1360, 1245, 1155, 1058, 960, 780.

^{31}P NMR (C_6D_6) δ33.4299.

Elemental analysis, calculated for $C_{10}H_{23}O_3P$: C, 54.02; H, 10.46; P, 13.94. Found: C, 54.24; H, 10.06; P, 13.70.

6. Photoreaction of i-PrHgCl with VP followed by $NaBH_4$ reduction

To a pyrex tube was added *i*-PrHgCl (0.28 g, 0.96 mmol), diethyl vinylphosphonate (0.04 g, 0.24 mmol) and benzene (5 mL). The tube was sealed with a rubber septum and irradiated for 24 h. After irradiation, $NaBH_4$ (0.07 g, 1.44 mmol) was added to the mixture, and the mixture was worked up according to the general procedure. After removing the solvent, a liquid remained from which 52% of diethyl 3-methylbutylphosphonate was isolated by flash column chromatography with the eluent of CH_3CO_2Et-Et_2O (40%:60%).

^1H NMR ($CDCl_3$) δ 4.33 (p, 4H, *J* = 7.5 Hz), 1.90-1.38 (m, 5H), 1.33 (t, 6H), 0.90 (d, 6H).

^{13}C NMR ($CDCl_3$) δ 61.21 (d, J_{POC} = 6.11 Hz), 30.90 (d, J_{PCCC} = 4.88 Hz), 29.01, 23.51 (d, J_{PC} = 140.38 Hz), 21.80, 16.30 (d, J_{POCC} = 6.11 Hz).

GCMS, *m*/*e* (relative intensity) 209 (0.2), 208 (0.14, M^+), 207 (1.7), 165 (69), 152 (100), 138 (58), 137 (49), 125 (82), 111 (59), 109 (38), 69 (41).

M.S. Calculated for $C_9H_{20}O_3P$ (M^+-H): 207.1150. Found: 207.1149. Error: -0.5 ppm.

IR (neat, NaCl plate, cm^{-1}) 2970, 1450, 1380, 1360, 1240, 1210, 1155, 1090, 1060, 1010, 960.

^{31}P NMR ($CDCl_3$) δ 33.3863.

Elemental analysis, calculated for $C_9H_{21}O_3P$: C, 51.89; H, 10.19; P, 14.88. Found: C, 51.63; H, 10.06; P, 14.79.

7. Photoreaction of cyclohexylmercury chloride with VP followed by $NaBH_4$ reduction

A dry pyrex tube containing cyclohexylmercury chloride (0.38 g, 1.2 mmol), diethyl vinylphosphonate (0.05 g, 0.3 mmol), DMSO (3 mL) and PhH (2 mL) was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor for 24 h. After reduction with $NaBH_4$ (0.07 g, 1.4 mmol), the mixture was worked up according to the general procedure to give a liquid containing a 65% yield of diethyl 2-cyclohexylethylphosphonate.

^1H NMR ($CDCl_3$) δ 4.30 (p, 4H, *J* = 7.15 Hz), 2.2-1.32 (m, 15H), 1.30 (t, 6H).

GCMS, *m/e* (relative intensity) 248 (0.26, M^+), 247 (0.7), 166 (28), 165 (89), 152 (100), 138 (49).

8. Photoreaction of n-BuHgCl with VP followed by $NaBH_4$ reduction

A dry pyrex tube containing *n*-BuHgCl (1.1 g, 3.73 mmol), diethyl vinylphosphonate (0.12 g, 0.75 mmol), DMSO (10 mL) and PhH (5 mL) was sealed with a rubber septum and irradiated for 24 h. After reduction with $NaBH_4$ (0.17 g, 4.5 mmol), the mixture was worked up by the general procedure. The product, diethyl n-hexylphosphonate was isolated by flash column chromatography with the eluent of CH_3COOEt and ether (40%:60%).

^1H NMR ($CDCl_3$) δ 4.11 (p, 4H, J = 7.0 Hz), 2.41-1.25 (m, 10H), 1.4 (t, 6H), 0.95 (t, 3H).

^{13}C NMR ($CDCl_3$) δ 61.13 (d, J_{COP} = 5.86 Hz), 31.02, 30.37, 29.65, 25.39 (d, J_{CP} = 145.11 Hz), 18.08, 16.19 (d, J_{POCC} = 5.86 Hz), 13.72.

GCMS, m/e (relative intensity) 222 (21,52, M^+), 221 (5.1), 2.8 (35), 166 (29), 165 (100), 138 (27), 111 (16) 55 (29).

M.S. Calculated for $C_{10}H_{22}O_3P$ (M^+-H): 221.1307. Found: 221.1305. Error: -0.9 ppm.

IR (neat, NaCl plate, cm^{-1}) 2980, 2960-2920, 2880, 1450, 1380, 1245, 1160, 1030, 950.

^{31}P NMR ($CDCl_3$) δ 33.1933.

Elemental analysis, calculated for $C_{10}H_{23}O_3P$: C, 54.02; H, 10.46; P. 13.94. Found: C, 54.06; H, 10.47; P, 13.92.

9. Photoreaction of t-BuHgCl with VS followed by $NaBH_4$ reduction

A pyrex tube containing tert-butylmercury chloride (1.0 g, 3.40 mmol), phenyl vinyl sulfone (0.19 g, 1.13 mmol) and benzene (14 mL) was irradiated in a Rayonet Photoreactor for 24 h. After irradiation, $NaBH_4$ (0.13 g, 3.40 mmol) was added and the mixture was worked up by the general procedure. After removing the solvent with a rotary evaporator, the yellow solid was identified as 3,3-dimethylbutyl phenyl sulfone in 96% yield and was purified by flash column chromatography with the eluent of CH_3COOEt and ether (10%:90%). The melting point is 52-53.5 °C (Lit.[63] mp 59-60 °C).

^1H NMR ($CDCl_3$) δ 7.93-7.50 (m, 5H), 3.08-3.04 (p, 2H), 1.63-1.57 (p, 2H), 0.87 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 138.98, 133.46, 129.07, 127.78, 52.68, 35.46, 29.77, 28.68.

GCMS, *m/e* (relative intensity) 228 (0.03), 227 (0.33), 226 (0.84, M^+), 169 (11), 143 (40), 142 (12), 77 (20), 69 (19), 57 (100).

M.S. Calculated for $C_{12}H_{19}O_2S$ (M^++H): 227.1106. Found: 227.1104. Error: -0.9 ppm.

IR (melt, NaCl plate, cm^{-1}) 3080, 2980, 2880, 1590, 1480, 1450, 1400, 1370, 1320, 1250, 1150, 1090, 1080, 805, 750.

10. Photoreaction of i-PrHgCl with VS followed by $NaBH_4$ reduction

A dry pyrex tube containing *i*-PrHgCl (0.6 g, 2.1 mmol), phenyl vinyl sulfone (o.12 g, 0.70 mmol) and PhH (10 mL) was irradiated for 24 h in a Rayonet Photoreactor. After the mixture reacted with $NaBH_4$ (0.12 g, 2.50 mmol), it was worked up by the general procedure. A pure product, 3-methylbutyl phenyl sulfone was isolated in 62% yield by flash column chromatography with the eluent of CH_3COOEt and ether (10%:90%).

^1H NMR ($CDCl_3$) δ7.80-7.44 (m, 5H), 3.06 (t, 2H), 1.71-1.49 (m, 3H), 0.87 (d, 6H).

^{13}C NMR ($CDCl_3$) δ138.95, 133. 38, 129.00, 127.69, 127.69, 54.38, 30.77, 26.91, 21.80.

GCMS, m/e (relative intensity) 212 (0.14, M^+), 143 (100), 78 (20), 77 (34), 70 (39), 55 (22).

M.S. Calculated for $C_{11}H_{16}O_2S$: 221.08711. Found: 212.08701. Error: -0.5 ppm.

IR (neat, NaCl plate, cm^{-1}) 3070, 2980, 2890, 1590, 1470, 1450, 1370, 1320, 1280, 1150, 1090, 790, 740, 690.

11. Photoreaction of cyclohexylmercury chloride with VS followed by $NaBH_4$ reduction

To a dry pyrex tube was added cyclohexylmercury chloride (0.57 g, 1.8 mmol), phenyl vinyl sulfone (0.1 g, 0.6 mmol), DMSO (6 mL) and PhH (4 mL). The tube was equipped with a rubber septum and was irradiated for 24 h in a Rayonet Photoreactor. After reduction with $NaBH_4$ (0.08 g, 1.8 mmol), the mixture was worked up by the general procedure. After removing the solvent under the reduced pressure, a yellow adhensive liquid was left which contained a 65% yield of 2-cyclohexylethyl phenyl sulfone.

^1H NMR ($CDCl_3$) δ 7.9-7.4 (m, 5H), 3.05 (t, 2H), 1.53-1.48 (m, 2H), 1.26-1.19 (m, 11H).

GCMS, *m/e* (relative intensity) 254 (0.15), 253 (0.61), 252 (0.74, M^+), 187 (17), 143 (100), 110 (87), 81 (49), 77 (40), 55 (97).

12. Photoreaction of n-BuHgCl with VS followed by $NaBH_4$ reduction

A dry pyrex tube containing *n*-butylmercury chloride (1.7 g, 6 mmol), phenyl vinyl sulfone (0.2 g, 1.2 mmol), DMSO (15 mL) and PhH (7 mL) was irradiated for 24 h in a Rayonet Photoreactor. After reaction with $NaBH_4$ (0.29 g, 6 mmol), the mixture was worked up by the general procedure. The thick liquid obtained by evaporating the solvent was identified as *n*-hexyl phenyl sulfone which was isolated in pure form by flash column chromatography with the eluent of CH_3COOEt and ether (20%:80%).

^1H NMR ($CDCl_3$) δ 7.99-7.30 (m, 5H), 3.23-3.72 (m, 2H), 1.87-0.85 (m, 11H). Lit.[64] ^1H NMR δ 7.5-8.2 (m, 5H), 3.0-3.3 (m, 2H), 1.1-2.1 (m, 8H), 0.85 (t, 3H).

^{13}C NMR ($CDCl_3$) δ 138.17, 133.75, 129.19, 127.95, 56.29, 35.42, 31.12, 27.90, 22.60, 19.88.

GCMS, m/e (relative intensity) 228 (0.07), 226 (1.05, M^+), 161 (9), 143 (100), 142 (20), 133 (13), 91 (24), 85 (18), 78 (34), 77 (49).

M.S. Calculated for $C_{12}H_{18}O_2S$: 226.1076. Found: 226.1022. Error: -2.31 ppm.

IR (melt, NaCl plate, cm^{-1}) 3050, 2970, 2940, 2880, 1450, 1410, 1300, 1150, 1090, 1030, 1000, 750, 690.

13. UV-visible absorption spectra of t-BuHgCl and VP

The UV-visible spectra were recorded with a Perkin-Elmer 320 Spectrometer in HPLC-grade CH_3CN. A solution of *tert*-butylmercury chloride had a λ_{max} of 210 nm, while a solution of diethyl vinylphosphonate had no absorption from 500 nm to 185 nm. The mixture of *t*-BuHgCl/VP (1:1 or 1:3) had λ_{max} of 210 nm. Thus, there was no indication of any association between *t*-BuHgCl and VP.

14. General procedure for photoreaction of RHgCl with CH_2=CHQ followed by iodine cleavage

To an oven-dried pyrex tube was added the alkylmercury chloride, olefin (CH_2=CHQ, Q = $P(O)(OEt)_2$, SO_2Ph) and PhH. The tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation, the mixture was transferred to a flask with a magnetic stirring bar, iodine was added, and the cleavage reaction was completed in a few hours. Then, benzene (8-10 mL) was added and the mercury iodide (HgI_2) was filtered. The red-purple filtrate was washed until colorless with 5% $Na_2S_2O_3$ solution, dried over $MgSO_4$ and concentrated to afford a liquid or solid which was identified by ^{1}H NMR and GCMS, and isolated by the column chromatography. The following reactions in Section 15 to 20 were carried out and worked up according to this procedure.

15. Photoreaction of t-BuHgCl with diethyl vinylphosphonate followed by iodine cleavage

A dry pyrex tube containing *tert*-butylmercury chloride (0.4 g, 1.44 mmol), VP (0.06 g, 0.36 mmol) and benzene (6 mL) was irradiated for 24 h in a Rayonet Photoreactor. After reaction with iodine (0.5 g, 2.1 mmol) for 4 h, the reaction mixture was worked up according to the general procedure (in Section 14). A yellow liquid contained diethyl 3,3-dimethyl-1-iodobutylphosphonate was isolated in 72% yield by flash column chromatography with ether as the eluent.

^{1}H NMR ($CDCl_3$) δ4.17 (p, 4H, $\underline{J}$ = 7.1 Hz), 2.41-1.93 (m, 3H), 1.34 (t, 6H), 0.93 (s, 9H).

^{13}C NMR ($CDCl_3$) δ63.46 (t, $\underline{J}_{COP}$ = 12.2 Hz), 36.61, 31.66 (d, $\underline{J}_{CCCP}$ = 12.2 Hz), 29.17, 16.25 (d, $\underline{J}_{CCOP}$ = 6.1 Hz), 8.64 (d, $\underline{J}_{CP}$ = 153.8 Hz).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 349 (0.08), 348 (0.85, M^+), 347 (0.02), 221 (24), 165 (83), 137 (18), 109 (45), 83 (87), 57 (100), 55 (35).

M.S. Calculated for $C_{10}H_{22}IO_3P$: 348.03514. Found: 348.03520. Error: +0.2 ppm.

IR (neat, NaCl plate, cm^{-1}) 2990-2880, 1475, 1445, 1395, 1370, 1255, 1160, 1060-1020, 970, 820-780, 750.

^{31}P NMR (C_6D_6) δ23.6825.

16. Photoreaction of i-PrHgCl with VP followed by iodine cleavage

A dry pyrex tube containing isopropylmercury chloride (0.7 g, 2.4 mmol), diethyl vinylphosphonate (0.10 g, 0.6 mmol) and benzene (10 mL) was irradiated for 24 h in a Rayonet

Photoreactor. After reaction with iodine (1.1 g, 4.3 mmol), the mixture was worked up by the general procedure. A yellow liquid containing diethyl 3-methyl-1-iodobutylphosphonate in 48% yield was isolated by flash column chromatography using CH_3COOEt and ether (10%:90%) as the eluent.

^1H NMR ($CDCl_3$) δ 4.21 (p, 4H, *J* = 7.13 Hz), 2.24-1.58 (m, 4H), 1.34 (t, 6H), 0.96 (d,d, 6H).

^{13}C NMR ($CDCl_3$) δ 63.10 (t, J_{POC} = 10.98 Hz), 41.09 (d, J_{PCCC} = 2.44 Hz), 27.71 (d, J_{PCC} = 12.2 Hz), 22.51, 16.03 (d, J_{POCC} = 6.1 Hz), 16.14 (d, J_{PC} = 157.47 Hz).

GCMS, *m/e* (relative intensity) 335 (0.04), 334 (0.39, M^+), 207 (40), 179 (9), 165 (12), 151 (65), 137 (9), 109 (36), 91 (23), 69 (100).

M.S. Calculated for $C_9H_{20}IO_3P$: 334.0194. Found: 334.0190. Error: -1.2 ppm.

IR (neat, NaCl plate, cm^{-1}) 2900-2880, 1470, 1390-1370, 1245, 1050, 1025, 970, 810, 730.

^{31}P NMR ($CDCl_3$) δ 23.5650.

17. Photoreaction of cyclohexylmercury chloride with VP followed by iodine cleavage

A dry pyrex tube containing cyclohexylmercury chloride (0.75 g, 2.4 mmol), diethyl vinylphosphonate (1.0 g, 0.6 mmol), DMSO (2 mL) and PhH (6 mL) was irradiated for 24 h. After reaction with iodine (0.9 g, 3.6 mmol) for 5 h, the mixture was worked up according to the general procedure. The resulting adhensive liquid was identified as diethyl 2-cyclohexyl-1-iodoethylphosphonate in 41% yield.

^{1}H NMR ($CDCl_3$) δ 4.18 (p, 4H, *J* = 5.05 Hz), 2.28-1.61 (m, 3H), 1.36 (t, 6H), 1.31-1.20 (m, 11H).

GCMS, *m/e* (relative intensity) 374 (0.06, M^+), 247 (0.09), 165 (54), 138 (100), 125 (39), 109 (26), 55 (40).

18. Photoreaction of t-BuHgCl with VS followed by iodine cleavage

A pyrex tube containing *tert*-butylmercury chloride (1.1 g, 3.6 mmol), phenyl vinyl sulfone (VS) (0.2 g, 1.2 mmol) and benzene (15 mL) was irradiated for 24 h in a Rayonet Photoreactor. After reaction with iodine (1.4 g, 5.4 mmol) for 4 h, the mixture was worked up by the general procedure. After removing the solvent, a yellow solid was obtained which was dried under vacuum line and identified as 3,3-dimethyl-1-iodobutyl phenyl sulfone in 75% yield, mp 98-100 °C.

^{1}H NMR ($CDCl_3$) δ 8.13-7.40 (m, 5H), 4.84 (d,d, 1H), 2.12 (q, 2H), 0.90 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 134.67, 134.30, 130.05, 129.09, 46.80, 37.10, 31.31, 29.25.

GCMS, m/e (relative intensity) 354 (0.06), 353 (0.16), 352 (1.25, M^+), 211 (16), 169 (10), 143 (14), 125 (13), 83 (15), 77 (14), 57 (100).

M.S. Calculated for $C_{12}H_{17}IO_2S$: 351.9995. Found: 351.9998. Error: +0.8 ppm.

IR (KBr pellet, cm^{-1}) 3000-2900, 1590, 1480, 1455, 1400, 1350, 1330-1305, 1200, 1155, 1090, 780, 760, 735, 690.

19. Photoreaction of i-PrHgCl with VS followed by iodine cleavage

A dry pyrex tube containing isopropylmercury chloride (1.0 g, 3.6 mmol), phenyl vinyl sulfone (0.2 g, 1.2 mmol) and benzene (12mL) was irradiated for 24 h in a Rayonet Photoreactor at 350 nm. After reaction with iodine (1.6 g, 6.5 mmol) for 6 h, the mixture was worked up by the general procedure. After removing the solvent, an adhensive solid was left which was identified as 3-methyl-1-iodobutyl phenyl sulfone in 46% yield.

^1H NMR ($CDCl_3$) δ8.05-7.50 (m, 5H), 4.90(d,d, 1H), 1.98-1.70 (m, 3H), 0.99 (d, 6H).

^{13}C NMR ($CDCl_3$) δ134.94, 134.25, 129.79, 129.00, 44.01, 41.16, 27.99, 22.93.

GCMS, m/e (relative intensity) 340 (0.22), 339 (0.76), 338

(4.78, M^+), 211 (30), 197 (43), 143 (75), 125 (37), 77 (38), 69 (100), 51 (23).

M.S. Calculated for $C_{11}H_{15}IO_2S$: 337.98376. Found: 337.98356. Error: -0.6 ppm.

IR (melt, NaCl plate, cm^{-1}) 3080, 2980, 2940, 2880, 1580, 1470, 1450, 1390, 1370, 1310, 1150, 1080, 750, 710, 690.

20. Photoreaction of cyclohexylmercury chloride with VS followed by iodine cleavage

A dry pyrex tube containing cyclohexylmercury chloride (1.1 g, 3.3 mmol), phenyl vinyl sulfone (0.18 g, 1.1 mmol), DMSO (2 mL) and PhH (8 mL) was equipped with a rubber septum and was irradiated for 24 h in a Rayonet Photoreactor at 350 nm. After reaction with iodine (1.2 g, 5 mmol) for 6 h, the mixture was worked up according to the general procedure. By evaporating the solvent, an adhensive liquid was left which was identified as 2-cyclohexyl-1-iodoethyl phenyl sulfone in 37% yield.

^1H NMR ($CDCl_3$) δ 8.10-7.70 (m, 5H), 4.85 (d,d, 1H), 2.1-1.97 (m, 2H), 1.36-1.19 (m, 11H).

GCMS, m/e (relative intensity) 380 (0.02), 379 (0.06), 378 (0.67; M^+), 251 (13), 143 (36), 109 (100), 83 (33), 77 (26), 67 (34).

21. Dark reaction between t-BuHgCl with VP followed by iodine cleavage

tert-Butylmercury chloride (0.2 g, 0.72 mmol) and VP (0.03 g, 0.18 mmol) were dissolved in 3 mL of benzene and the reaction flask was wrapped with aluminum foil to exclude light. After stirring the reaction mixture at room temperature for 24 h, iodine (0.25 g, 1.1 mmol) was added. The red precipitate of HgI_2 was filtered, the red-purple filtrate was washed until colorless with 5% $Na_2S_2O_3$ solution, and dried over $MgSO_4$. After the solvent was removed under reduced pressure, GLC analysis of the crude isolate revealed unchanged starting material, diethyl vinylphosphonate, in 98% recovery.

22. Effect of di-tert-butylnitroxide on the reaction of t-BuHgCl with VP followed by iodine cleavage

tert-Butylmercury chloride (0.4 g, 1.4 mmol), VP (0.06 g, 0.36 mmol) and di-*tert*-butylnitroxide (5.7 mg, 0.04 mmol) were dissolved in 6 mL benzene. The pyrex tube was sealed with a rubber septum and irradiated in a Rayonet Photoreactor. After irradiation for 6 h, the solution was transferred into a flask with a magnetic stirring bar, iodine (0.5 g, 2.2 mmol) was added and the solution stirred for 4 h. Benzene (10 mL) was added, the precipitate (HgI_2) was filtered and the mixture was washed with 5% $Na_2S_2O_3$ solution, dried over $MgSO_4$

and concentrated. GLC analysis showed that the crude liquid contained mainly unreacted diethyl vinylphosphonate in over 90% recovery.

23. Photoreaction of t-BuHgCl with VP in CCl_4 solution followed by $NaBH_4$ reduction

tert-Butylmercury chloride (0.59 g, 2.0 mmol) and VP (0.08 g, 0.5 mmol) were dissolved in CCl_4 (10 mL). The pyrex tube was equipped with a rubber septum and was irradiated for 24 h in a Rayonet Photoreactor. After irradiation for 5 min, a white precipitate appeared. After 24 h irradiation, the white precipitate was filtered and was identified as hexachloroethane, mp 189-193 °C (Lit.[65] 190-195 °C) and ^{13}C NMR ($CDCl_3$) δ104.90 (Lit.[66] δ105.30). $NaBH_4$ (0.12 g, 2.4 mmol) was added to the filtrate. After stirring for 15 min, a few drops of water was added to precipitate the mercury metal. Then, more water (8 mL) was added. The CCl_4 layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The CCl_4 and CH_2Cl_2 solution were combined, dried over $MgSO_4$ and concentrated to afford a yellow oil which was identified as diethyl 3,3,3-trichloropropylphosphonate in 62% yield. The pure product was isolated in 52% yield by flash column chromatography using hexane and ether (15%:85%) as the eluent.

^{1}H NMR ($CDCl_3$) δ 4.16 (p, 4H, *J* = 8.3 Hz), 3.08-2.83 (m, 2H), 2.41-2.01 (m, 2H), 2.36 (t, 6H).

^{13}C NMR ($CDCl_3$) δ 99.00 (d, J_{PCCC} = 29.3 Hz), 61.92 (d, J_{POC} = 6.1 Hz), 48.40, 23.40 (d, J_{PC} = 142.80 Hz), 16.30 (d, J_{POCC} = 6.1 Hz).

GCMS, *m/e* (relative intensity) 287 (0.07), 285 (0.51), 282 (0.6, M^+), 257 (10), 255 (10), 249 (35), 247 (50), 165 (61), 109 (100), 55 (87).

M.S. Calculated for $C_7H_{14}Cl_2O_3P$ (M^+-Cl): 247.00577. Found: 247.00589. Error: +0.5 ppm.

IR (neat, NaCl plate, cm^{-1}) 2950-2930, 1430, 1390, 1255, 1220, 1160, 1050, 1025, 975, 950, 840, 790-770, 750.

^{31}P NMR ($CDCl_3$) δ 28.6289.

Elemental analysis, calculated for $C_7H_{14}Cl_3O_3P$: C, 29.79; H, 5.01; Cl, 37.21; P, 10.98. Found: C, 29.90; H, 4.91; Cl, 37.54; P, 10.61.

24. Photoreaction of t-BuHgCl with VP in CCl_4 solution followed by iodine cleavage

tert-Butylmercury chloride (0.59 g, 2.0 mmol) and VP (0.08 g, 0.5 mmol) were dissolved in CCl_4 solution (10 mL). The mixture was irradiated for 24 h in a Rayonet Photoreactor.

After the white precipitate of C_2Cl_6 was filtered, the CCl_4 was removed from the filtrate with a rotatory evaporator. Benzene (10 mL) was added, the mixture reacted with iodine (0.6 g, 2.4 mmol) for 6 h, HgI_2 removed by filtration. The red-purple solution was washed until colorless with 5% $Na_2S_2O_3$ solution, dried over $MgSO_4$ and concentrated to afford a yellow oil which contained diethyl 3,3,3-trichloro-1-iodopropylphosphonate in 60% yield. The pure product was isolated in 40% yield by flash column chromatography with the eluent of hexane and ether (40%:60%).

^1H NMR ($CDCl_3$) δ 4.24 (p, 4H, $\underline{J}$ = 7.9 Hz), 3.62-3.16 (m, 3H), 1.40 (t, 6H).

^{13}C NMR ($CDCl_3$) δ 97.13 (d, $\underline{J}_{PCCC}$ = 18.31 Hz), 63.68 (t, $\underline{J}_{POC}$ = 12.2 Hz), 56.80, 15.98 (d, $\underline{J}_{POCC}$ = 6.1 Hz), 5.26 (d, $\underline{J}_{PC}$ = 154.9 Hz).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 411 (0.03), 410 (1.57), 408 (1.47, M^+), 191 (31), 189 (46), 111 (20), 109 (100), 81 (69), 65 (46).

M.S. Calculated for $C_7H_{13}Cl_3IO_3P$: 407.87127. Found: 407.87133. Error: +0.1 ppm.

IR (neat, NaCl plate, cm^{-1}) 2950-2920, 1440, 1420, 1390, 1260, 1190, 1160, 1050, 1020, 970, 840, 770, 720, 690.

^{31}P NMR ($CDCl_3$) δ 20.9607.

25. General procedure for elimination of iodides with DBU

To a round-bottom flask fitted with a magnetic stirring bar and a refluxing condenser was added the iodide, RCH_2-CH(I)Q, (or a crude iodide mixture from the previous reaction), DBU (DBU:iodide = 3:1) with or without PhH as a solvent. Under nitrogen, the mixture was heated in an oil bath at 80-90 °C. After the reaction, the mixture was cooled, ether (15-20 mL) was added and the mixture was stirred for 10 min, washed 2 times with 5% $Na_2S_2O_3$ and 3 times with water, and dried over $MgSO_4$. After removing the solvent, the crude liquid was analyzed by GLC, and then isolated by flash column chromatography. The following reactions in Section 26 to 30 were carried out according to this general procedure.

26. Elimination reaction of $t\text{-}BuCH_2CH(I)P(O)(OEt)_2$ with DBU

The mixture of $\underline{t}\text{-}BuCH_2CH(I)P(O)(OEt)_2$ (0.1 g, 0.29 mmol) and DBU (0.13 g, 0.87 mmol) was heated at 85-90 °C in an oil bath. After reaction for 4 h, the mixture was worked up by the general procedure. The ether was removed and GLC analysis of the crude residue revealed the product, diethyl 3,3-dimethyl-1-butenylphosphonate in 92% yield. The pure product was obtained by flash column chromatography with the eluent of CH_3COOEt and ether (30%:70%) in 88% yield.

^{1}H NMR ($CDCl_3$) δ 6.80 (d,d, 1H, $\underline{J}_{H-P}$ = 24 Hz, $\underline{J}_{H-H}$ = 17.6 Hz), 5.50 (d,d, 1H, $\underline{J}_{H-P}$ = 20 Hz, $\underline{J}_{H-H}$ = 17.6 Hz), 4.32-3.80 (p, 4H, $\underline{J}$ = 7.5 Hz), 1.30 (t, 6H), 1.07 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 162.74 (d, $\underline{J}_{C=C-P}$ = 3.67 Hz), 111.62 (d, $\underline{J}_{C-P}$ = 187.99 Hz), 61.13 (d, $\underline{J}_{POC}$ = 4.89 Hz), 35.51 (d, $\underline{J}_{CCCP}$ = 4.89 Hz), 28.09, 15.98 (d, $\underline{J}_{POCC}$ = 6.1 Hz).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 222 (0.81), 221 (7.4), 220 (38.9, M^+), 205 (35), 163 (19), 149 (44), 138 (54), 111 (60), 110 (19), 83 (100).

M.S. Calculated for $C_{10}H_{21}O_3P$: 220.1228. Found: 220.1226. Error: -0.9 ppm.

IR (neat, NaCl plate, cm^{-1}) 2975-2880, 1630, 1480, 1395, 1370, 1250, 1165, 1060, 1030, 970, 850, 820, 780.

^{31}P NMR ($CDCl_3$) δ 20.6969.

27. <u>Elimination reaction of i-PrCH$_2$CH(I)P(O)(OEt)$_2$ with DBU</u>

The mixture of $\underline{i}$-PrCH$_2$CH(I)P(O)(OEt)$_2$ (0.08 g, 0.2 mmol) and DBU (0.09 g, 0.6 mmol) was heated at 82-90 °C in an oil bath. After reaction for 6 h, the mixture was worked up as the general procedure described in Section 25. After the ether was removed under reduced pressure, GLC analysis of the crude residue revealed the product, diethyl 3-methylbuten-2-ylphosphonate, in 52% yield. The pure product was separated in 43% yield by flash column chromatography with the eluent of CH_3COOEt and ether (30%:70%).

^1H NMR ($CDCl_3$) δ 5.18 (m, 1H), 4.15 (p, 4H, $\underline{J}$ = 7.8 Hz), 2.48 (d,d, 2H, $\underline{J}_{HCP}$ = 22 Hz, $\underline{J}_{H-H}$ = 8.4 Hz), 1.75 (s, 3H), 1.68 (s, 3H), 1.31 (t, 6H).

^{13}C NMR ($CDCl_3$) δ 136.06 (d, $\underline{J}$ = 14.65 Hz), 112.25 (d, $\underline{J}$ = 10.98 Hz), 61.11 (d, $\underline{J}_{POC}$ = 6.1 Hz), 25.95 (d, $\underline{J}_{P-C}$ = 140.38 Hz), 25.05, 17.36, 15.87 (d, $\underline{J}_{POCC}$ = 6.1 Hz).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 208 (0.4), 207 (4.7), 206 (40.6, M^+), 150 (46), 138 (48), 111 (100), 97 (27), 83 (49), 82 (76), 81 (37), 69 (79), 68 (31).

M.S. Calculated for $C_9H_{19}O_3P$: 206.10727. Found: 206.10750. Error: -1.4 ppm.

IR (neat, NaCl plate, cm^{-1}) 2990-2960, 1520, 1470, 1330, 1300, 1150-1120, 1050-1000.

^{31}P NMR ($CDCl_3$) δ 29.2423.

28. Elimination reaction of $Cl_3CCH_2CH(I)P(O)(OEt)_2$ with DBU

The mixture of $Cl_3CCH_2CH(I)P(O)(OEt)_2$ (0.08 g, 0.2 mmol), DBU (0.09 g, 0.6 mmol) and benzene (6 mL) was heated at 84-89 °C in an oil bath. After refluxing for 4 h, the mixture was worked up by the general procedure. After the solvent was removed under reduced pressure, GLC analysis of concentrated liquid revealed the product, diethyl 3,3,3-trichloropropen-1-ylphosphonate in 68% yield. The pure product was isolated by flash column chromatography with the eluent of CH_3COOEt and ether (10%:90%).

^1H NMR ($CDCl_3$) δ 7.05 (d,d, 1H, J_{P-H} = 19.6 Hz, J_{H-H} = 15.5 Hz), 6.31 (d,d, 1H, J_{PCH} = 15.3 Hz, J_{H-H} = 14.5 Hz), 4.16 (p, 4H, J = 8.97 Hz), 1.35 (t, 6H).

^{13}C NMR ($CDCl_3$) δ 148.89 (d, $J_{C=C-P}$ = 10.19 Hz), 118.24 (d, J_{C-P} = 186.20 Hz), 65.58, 62.44, 16.14.

GCMS, *m/e* (relative intensity) 282(1.96), 280 (2.52, M^+), 247 (39), 245 (62), 219 (65), 217 (100), 211 (15), 209 (25), 191 (26), 189 (39), 183 (17), 181 (37), 153 (72), 109 (82).

M.S. Calculated for $C_7H_{12}Cl_2O_3P$ (M^+-Cl): 244.99012. Found: 244.99037. Error: +1.0 ppm.

IR (neat, NaCl plate, cm^{-1}) 3250, 2990-2970, 1560, 1530, 1300, 1250, 1150, 1120, 1060, 980.

^{31}P NMR ($CDCl_3$) δ 6.8423.

29. Elimination reaction of t-$BuCH_2CH(I)SO_2Ph$ with DBU

The mixture of *t*-$BuCH_2CH(I)SO_2Ph$ (0.1 g, 0.28 mmol), DBU (0.13 g, 0.84 mmol) and PhH (8 mL) was refluxed at 86-90 °C in an oil bath. After reaction for 3 h, the mixture was worked up by the general procedure. After the solvent was removed under reduced pressure, GLC analysis of the adhensive liquid revealed the product to be 3,3-dimethylbuten-1-yl phenyl sulfone in 78% yield. The pure product was isolated by flash column chromatography with ether as the eluent.

^{1}H NMR ($CDCl_3$) δ7.95-7.49 (m, 5H), 6.99 (d, 1H, *J* = 15.24 Hz), 6.21 (d, 1H, *J* = 15.62 Hz), 1.15 (s, 9H). This is consistent with the literature values,[67] δ 7.4-7.9 (m, 5H), 6.87 (d, 1H, *J* = 16 Hz), 6.11 (d, 1H, *J* = 16 Hz), 1.09 (s, 9H).

^{13}C NMR ($CDCl_3$) δ156.38, 133.13, 129.18, 127.94, 127.44, 126.50, 34.10, 28.33.

GCMS, *m/e* (relative intensity) 225 (0.02), 224 (0.10, M^+), 125 (12), 97 (3), 84 (6), 83 (100), 82 (6), 77 (14), 67 (17), 55 (42).

M.S. Calculated for $C_{12}H_{16}O_2S$: 224.0871. Found: 224.0869. Error: -0.89 ppm.

IR (melt, NaCl plate, cm^{-1}) 3060, 2975, 2890, 2320, 1648, 1450, 1370, 1300, 1145, 1090, 978, 840, 750, 720, 690.

30. Elimination reaction of i-PrCH$_2$CH(I)SO$_2$Ph with DBU

The mixture of *i*-PrCH$_2$CH(I)SO$_2$Ph (0.3 g, 0.89 mmol), DBU (0.4 g, 2.7 mmol) and PhH (6 mL) was refluxed at an oil bath of 86-90 °C. After reaction for 6 h, the mixture was worked up by the general procedure. After the solvent was removed under reduced pressure, GLC analysis of the concentrated liquid revealed the product to be 3-methylbuten-2-yl phenyl sulfone in 92% yield. The pure product was isolated by flash column chromatography with the eluent of CH_3COOEt and ether (5%:95%).

^1H NMR ($CDCl_3$) δ7.95-7.48 (m, 5H), 5.19 (t, 1H), 3.79 (d, 2H), 1.65 (s, 3H), 1.28 (s, 3H).

^{13}C NMR ($CDCl_3$) δ133.42, 129.16, 128.87, 128.34, 127.90, 110.34, 56.12, 25.80, 17.66.

GCMS, m/e (relative intensity) 212 (0.03), 211 (0.07), 210 (0.56, M^+), 131 (1), 78 (2), 77 (8), 70 (8), 69 (100), 68 (4), 67 (5), 51 (7).

M.S. Calculated for $C_{11}H_{14}O_2S$: 210.0715. Found: 210.0718. Error: +1.4 ppm.

IR (neat, NaCl plate, cm^{-1}) 3060, 2980, 2940, 2870, 1670, 1620, 1590, 1450, 1310, 1240, 1150, 1090, 770, 740, 690.

31. General procedure for the photoreaction of alkylmercury chlorides with CH_2=$CHSiPh_3$ followed by $NaBH_4$ reduction

To a dry pyrex tube was added alkylmercury chloride (RHgCl, R = t-Bu, i-Pr, cyclo-C_6H_{11}, n-Bu), triphenylvinylsilane and the solvent (DMSO and PhH). The tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation for 24 h, the mixture was transferred into a flask, $NaBH_4$ ($RHgCl:NaBH_4$ = 1:1.2) was added, the mixture stirred for 10-15 min. A few drops of water was added to precipitate the mercury metal and then more water (8-10 mL) was added. The mixture was separated and the aqueous layer was extracted with ether (3 x 5 mL). The organic layers were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure and the concentrated liquid was analyzed by GLC and ^1H NMR.

32. Photoreaction of t-BuHgCl with $CH_2=CHSiPh_3$ followed by $NaBH_4$ reduction

Triphenylvinylsilane (0.03 g, 0.1 mmol) and *tert*-butylmercury chloride (0.09 g, 0.3 mmol) were dissolved in the mixed solvent (8 mL, DMSO and PhH, see Table 7), the mixture was irradiated in a Rayonet Photoreactor at 350 nm for 24-36 h. After reaction with $NaBH_4$ (0.02 g, 0.32 mmol), the mixture was worked up by the general procedure described in Section 31. After the solvent was removed under reduced pressure, GLC and GCMS analysis of the concentrated liquid revealed two products, 3,3-dimethylbutyltriphenylsilane and 3, 3-dimethyl-buten-1-yltriphenylsilane.

GCMS for *t*-$BuCH_2CH_2SiPh_3$, *m/e* (relative intensity) 346 (0.1), 345 (0.3), 344 (1, M^+), 266 (3), 260 (30), 259 (100), 155 (3), 105 (5), 77 (0.3), 57 (1).

GCMS for *t*-BuCH=CHSiPh$_3$, *m/e* (relative intensity) 343 (8), 342 (29, M^+), 286 (26), 285 (100), 259 (76), 207 (85), 183 (73), 181 (79), 105 (55), 77 (4), 57 (7), 53 (14).

33. Photoreaction of t-BuHgCl with CH$_2$=CHSiPh$_3$ followed by workup with Na$_2$S$_2$O$_3$ solution

Similar to the above procedure, a tube containing *tert*-butylmercury chloride (0.09 g, 0.3 mmol), triphenylvinylsilane (0.03 g, 0.1 mmol) and the solvent (8 mL, DMSO and PhH) was irradiated in a Rayonet Photoreactor for 24-36 h. The mixture was then transferred to a separatory funnel, ether (10 mL) was added. The mixture was washed 3 times with 5% $Na_2S_2O_3$ solution, dried with $MgSO_4$, and concentrated to afford a liquid which contained *t*-BuCH$_2$CH$_2$SiPh$_3$ and *t*-BuCH=CHSiPh$_3$.

34. Photoreaction of t-BuHgCl with CH$_2$=CHSiPh$_3$ followed by iodine cleavage

A pyrex tube containing *t*-BuHgCl (0.09 g, 0.3 mmol), triphenylvinylsilane (0.03 g, 0.1 mmol) and PhH (8 mL) was irradiated in a Rayonet Photoreactor for 24 h. The reaction mixture was transferred to a flask with a magnetic stirring bar, iodine (0.1 g, 0.45 mmol) was added and after stirring overnight, benzene (10 mL) was added. The mixture was washed 3 times with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure, leaving a liquid product which was analyzed by GLC to contain $\underline{t}$-$BuCH_2CH(I)$-$SiPh_3$ (28%), $\underline{t}$-$BuCH_2CH_2SiPh_3$ (42%) and $\underline{t}$-$BuCH{=}CHSiPh_3$ (17%). GCMS for $\underline{t}$-$BuCH_2CH(I)SiPh_3$, $\underline{m}/\underline{e}$ (relative intensity) 470 (5, M^+), 399 (50), 343 (8), 309 (12), 258 (36), 259 (100), 181 (28), 105 (18), 57 (11).

35. General procedure for the reaction of $CH_2{=}CHSiPh_3$, t-BuHgCl and $NaBH_4$

The reactions were carried out according to the general procedure reported by Giese and Meister.[68] $NaBH_4$ (0.02 g, 0.4 mmol) was added into a stirred mixture of $\underline{t}$-BuHgCl (0.09 g, 0.3 mmol), triphenylvinylsilane (0.03 g, 0.1 mmol) and the solvent (see Table 8). After the reaction, a few drops of water was added to precipitate the mercury metal, then more water (8-10 mL) was added, the mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 8 mL). The organic layers were combined and dried with $MgSO_4$. After the solvent was removed, the concentrated liquid was analyzed by

GLC.

36. General procedure for the photoreactions of t-BuHgCl with alkenes (see Table 9) followed by $NaBH_4$ reduction

A pyrex tube contained *t*-BuHgCl, alkene and the solvent (PhH or DMSO) was irradiated at 350 nm. After irradiation, the mixture was transferred to a flask and $NaBH_4$ (*t*-BuHgCl: $NaBH_4$ = 1:1.2) was added. After the mixture was stirred for 10-15 min, a few drops of water was added, then more water (8-10 mL) was added and the aqueous layer was separated and extracted with ether (2 x 8 mL). The organic layers were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure and the concentrated liquid was analyzed by GLC, GCMS and ^1H NMR.

37. General procedure for photoreaction of t-BuHgSPh with diethyl vinylphosphonate

tert-Butylmercury chloride (0.4-1.0 mmol as in Table 12) and VP (0.03 g, 0.2 mmol) dissolved in benzene (4 mL). The mixture was irradiated in a Rayonet Photoreactor at 350 nm for 6.5-30 h, PhH (10 mL) was added, the mixture was washed 3 times with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. The solvent was evaporated under a rotatory evaporator and the concentrated liquid was analyzed.

GCMS for *t*-BuCH$_2$CH(SPh)P(O)(OEt)$_2$, *m/e* (relative intensity) 330 (8, M$^+$), 221 (2), 193 (7), 137 (36), 65 (14), 57 (100).

38. General procedure for photoreaction of (EtO)$_2$P(O)HgQ with alkenes (see Table 13)

To a pyrex tube was added (EtO)$_2$P(O)HgQ (Q = Cl, CF$_3$CO$_2$, P(O)(OEt)$_2$), alkene and the solvent (PhH or DMSO). The tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation, the mixture was transferred into a flask and NaBH$_4$ ((EtO)$_2$P(O)HgQ: NaBH$_4$ = 1:1.5) was added. After stirring for 10-15 min, a few drops of water was added to precipitate the mercury metal, then more water (10 mL) was added, the mixture was separated and aqueous layer was extracted with ether (2 x 8 mL). The organic layers were combined and dried over MgSO$_4$. The solvent was removed under reduced pressure and the concentrated liquid was analyzed.

39. Photoreaction of (EtO)$_2$P(O)HgCl with cyclohexene followed by NaBH$_4$ reduction

A pyrex tube containing (EtO)$_2$P(O)HgCl (0.08 g, 0.2 mmol) and cyclohexene (0.02 g, 0.2 mmol) and PhH (4 mL) was irradiated in a Rayonet Photoreactor for 24 h. The mixture was then transferred into a flask with a magnetic stirring bar. After reaction with $NaBH_4$ (15 mg, 0.3 mmol), a few drops of water was added and then more water (8 mL) was added. The layers were separated and the aqueous layer was extracted with ether (2 x 10 mL). The organic layers were combined, dried with $MgSO_4$. The solvent was removed under the reduced pressure to yield a liquid containing diethyl cyclohexylphosphonate in 48% yield.

^{1}H NMR ($CDCl_3$) δ 4.29 (p, 4H), 2.11-1.19 (m, 11H), 1.28 (t, 6H).

GCMS, m/e (relative intensity) 221 (1), 220 (10, M^+), 139 (40), 138 (100), 111 (85), 83 (67), 82 (57), 81 (56).

40. Photoreaction of bis(thiophenyl)mercury with cyclohexene

A tube containing bis(thiophenyl)mercury (0.1 g, 0.2 mmol), cyclohexene (0.2 g, 2.0 mmol) and PhH (2 mL) was irradiated for 12 h in a Rayonet Photoreactor at 350 nm. After irradiation, benzene (10 mL) was added, the mixture was then washed 3 times with 5% $Na_2S_2O_3$ and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the concentrated liquid contained cyclohexyl phenyl sulfide in 54% yield, 3-(phenylthio)cyclohexene in 29% and 1,2-di(phenylthio)cyclohexene in 29% and 1,2-di(phenylthio)cyclohexane in 5% yield.

GCMS of cyclohexyl phenyl sulfide, *m*/*e* (relative intensity) 194 (2), 193 (4), 192 (28, M^+), 111 (11), 110 (100), 83 (14), 65 (12), 55 (64).

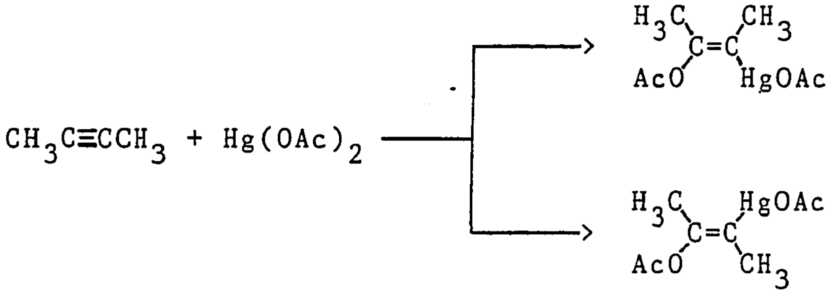
GCMS of 3-(phenylthio)cyclohexene, *m*/*e* (relative intensity) 192 (3), 190 (16, M^+), 110 (20), 81 (100), 80 (78), 79 (40), 65 (17).

GCMS of 1,2-di(phenylthio)cyclohexane, *m*/*e* (relative intensity) 302 (4), 301 (8), 300 (45, M^+), 219 (14), 218 (100), 185 (15), 184 (18), 55 (17).

II. PHOTOSTIMULATED REACTIONS OF ORGANOMERCURY HALIDES WITH ALKYNES

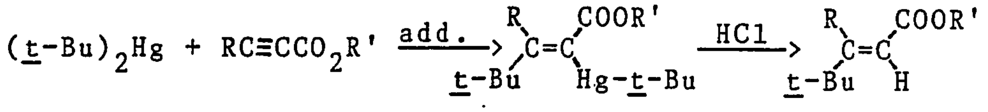
A. Introduction

Formation of the carbon-carbon double bond is one of the most important synthetic steps in the construction of organic molecules. In the last few years, it has been increasingly achieved by the addition of organomercurials to alkynes, which leads to organomercury compounds useful in this synthetic process.[69] It is known that mercury (II) acetate readily reacts with alkynes in acetic acid to give beta-(acetoxyl)-vinylmercurials.[70] As shown in Eq. 33, the reaction of $Hg(OAc)_2$ with 2-butyne leads to either the trans or the cis addition product depending upon the reaction conditions.[71]



(33)

Di-tert-butylmercury has been found to add to some electron poor triple bonds, forming the adduct containing the t-BuHg- group which can be protodemercurated to give the corresponding olefins as shown in Eq. 34.[26,72] These reac-



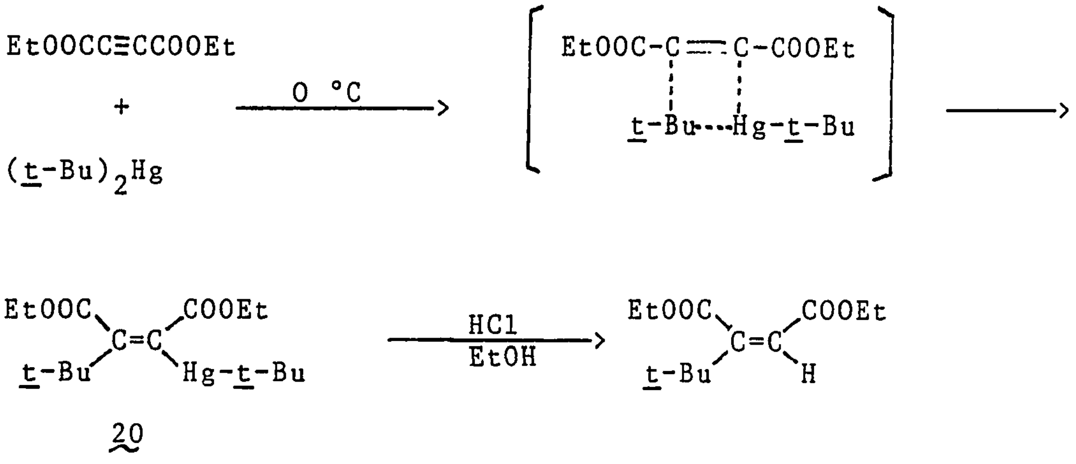
(34)

R = H, COOEt.

R' = Me, Et.

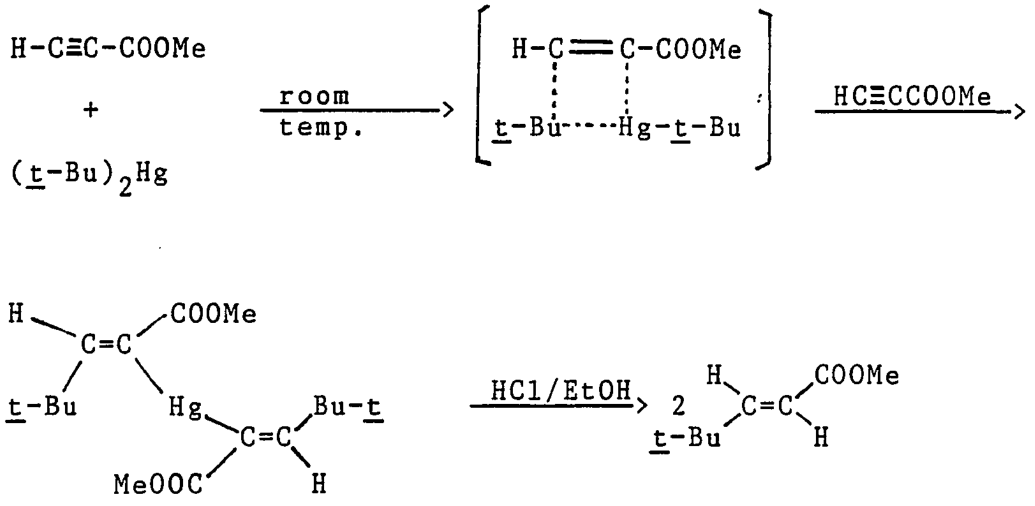
tions were carried out at room temperature or at 0 °C because of the high reactivity of di-tert-butylmercury. At 0 °C, the reaction was presumed to occur via a concerted process to lead to the cis-addition product exclusively as shown in Scheme 9 although there was no direct evidence presented for

Scheme 9



the formation of the 1:1 adduct 20 which contains the t-BuHg group. However, when the ratio of alkyne/($(t\text{-Bu})_2$Hg = 2 was employed, the reaction at room temperature leads to 21 in which two cis additions have occurred as shown in Scheme 10.

Scheme 10



21

Blaukat and Neumann claimed that the vinylic proton signals of 21 were observed in the ^{1}H NMR spectra.[26]

Recently, Giese and Lachhein have reported that alkyl radicals generated from the reaction of alkylmercury chlorides with sodium borohydride add to some alkynes to form the substituted olefins in the yields of 8-54% (Eq. 35 and Table 14).

$$\mathrm{RHgCl} + \mathrm{X\text{-}C{\equiv}C\text{-}Y} + \mathrm{NaBH_4} \xrightarrow[\mathrm{CH_2Cl_2}]{} \underset{(\underline{E} + \underline{Z})}{\mathrm{RXC{=}CHY}} \qquad (35)$$

Table 14. Reactions of alkyl radicals with alkynes at 293°K[73]

R	X	Y	syn.:anti. addition	% Yield
c-C_6H_{11}	H	Ph	30:70	8
t-Bu	H	Ph	7:93	10
n-C_6H_{13}	H	CO_2Me	69:31	10
c-C_6H_{11}	H	CO_2Me	56:44	35
t-Bu	H	CO_2Me	28:72	41
c-C_6H_{11}	CO_2Me	CO_2Me	64:36	21
t-Bu	CO_2Me	CO_2Me	42:58	54

Similar to the reaction with alkenes (Eq. 1), this reaction apparently occurs by a free radical mechanism as shown in Scheme 11. Alkyl radicals add to the alkyne to form vinylic radical **22** which react with RHgH via a syn-addition or anti-addition to lead to the (*Z*) and (*E*) olefins, and an alkyl radical which continues the chain reaction. In contrast to the reaction with alkenes, the reaction with alkynes leads to the addition products in low yields because alkynes are less reactive than alkenes towards free radicals. The reason for

Scheme 11

Initiation:

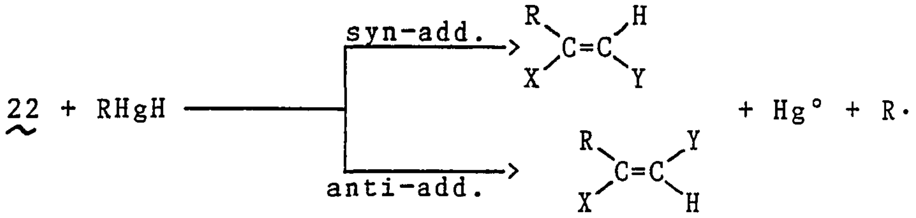
$$RHgCl + NaBH_4 \longrightarrow RHgH + NaBH_3Cl$$

$$RHgH \longrightarrow R\cdot + Hg^\circ + H\cdot$$

Chain:

$$R\cdot + X\text{-}C\equiv C\text{-}Y \longrightarrow R(X)C=\dot{C}\text{-}Y$$

22



the lower rate of addition of alkyl radicals to alkynes than to alkenes has been accounted for by the fact that the LUMO of an alkyne is energetically higher than the LUMO of an alkene.[74]

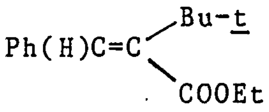
Although an alkyl radical generated from the reaction of organomercury halides with $NaBH_4$ can add to some alkynes to form the corresponding olefins in a low yield, up to now, the photostimulated reaction of organomercury halides with alkyne has not been reported. The work presented in this part considers the photochemical behavior of alkylmercury chlorides towards alkynes.

B. Results and Discussion

1. Photostimulated reaction of tert-butylmercury chloride with ethyl phenylpropiolate followed by $NaBH_4$ reduction

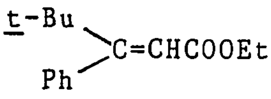
Ethyl phenylpropiolate was found to undergo a photostimulated reaction with t-BuHgCl which after reduction with $NaBH_4$ yielded the cis and trans adducts in 94%. Thus, when a mixture of ethyl phenylpropiolate and tert-butylmercury chloride in a solution of DMSO/PhH (50%:50%) was irradiated in a Rayonet Photoreactor at 350 nm for 20 h, a reaction took place as evidenced by the formation of a gray precipitate about 40 min after the irradiation was initiated. The reaction mixture was reacted with $NaBH_4$, and worked up by the addition of water followed by extraction of the aqueous layer with ether. The combined organic layers were dried over $MgSO_4$. After removing the solvent, a yellow oil remained which was identified by GLC and GCMS as the products of cis and trans adduct olefins containing the tert-butyl group.

However, it is not quite clear from the ^1H NMR spectrum that the product obtained from the reaction is olefin 23 or olefin 24. To determine the structure of this product, the



$\mathrm{Ph(H)C{=}C(Bu\text{-}t)(COOEt)}$

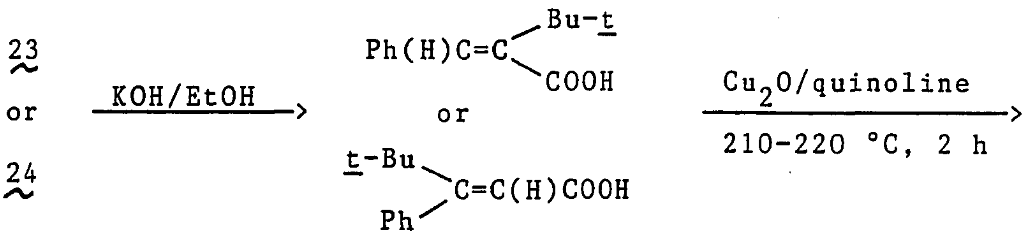
23

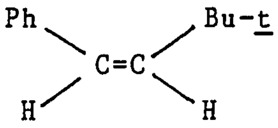


$\mathrm{(t\text{-}Bu)(Ph)C{=}CHCOOEt}$

24

reaction product was hydrolyzed with KOH/EtOH to give the carboxylic acid which was then decarboxylated with Cu_2O and quinoline. This decarboxylation process is known to lead predominately to cis-1,2-disubstituted alkenes (Eq. 36).[75]



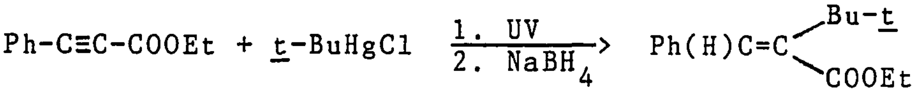


^{1}H NMR for vinylic hydrogen:

6.40 (d, 1H, *J* = 12 Hz) (36)

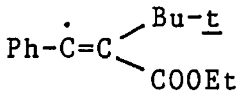
5.65 (d, 1H, *J* = 12 Hz)

Analysis of the product from Reaction 36 proved that the olefin obtained from the reaction of ethyl phenylpropiolate with *t*-BuHgCl is olefin 23, ethyl α-*tert*-butyl cinnamate as shown in Eq. 37.

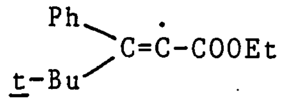


$$\text{Ph-C}\equiv\text{C-COOEt} + \underline{t}\text{-BuHgCl} \xrightarrow[\text{2. NaBH}_4]{\text{1. UV}} \text{Ph(H)C=C}\begin{matrix}\text{Bu-}\underline{t}\\ \text{COOEt}\end{matrix} \quad (37)$$

This reaction apparently involves the formation of an intermediate (Ph(HgCl)C=C(*t*-Bu)COOEt) which is reduced to Ph(H)C=C(*t*-Bu)COOEt by reaction with $NaBH_4$. Therefore, in an experiment in which after the irradiation, the reaction mixture was washed with 5% $Na_2S_2O_3$ solution instead of reacting with $NaBH_4$, less than 5% of the adduct olefin was detected and starting alkyne was not observed at all. Treatment of the reaction product with aqueous $Na_2S_2O_3$ solution presumably solublizes the vinylmercurial in water which is the initial reaction product. The fact that olefin 23 is formed in Reaction 37 indicates that the tert-butyl radical preferentially adds α to the ester group to form vinylic radical 25. The vinylic radical 26 involving the addition of the tert-butyl



25

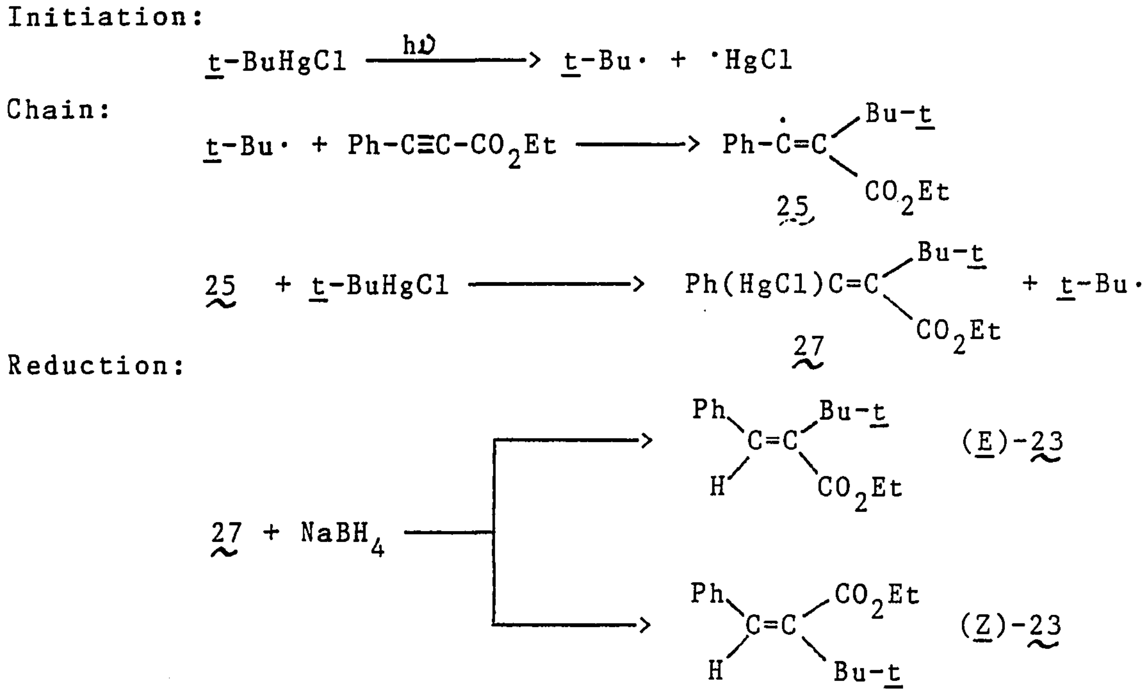


26

radical to the other end of the alkyne does not form. This can best be explained by the stability of the vinylic radical 25 over vinylic radical 26 because in 25 the electron can be delocalized by the π system of the phenyl ring.

This reaction is believed to occur by a radical chain process because the reaction fails to occur in the dark at room temperature for 3 days and the rate of photostimulated reaction is significantly inhibited by the presence of 10 mol% of di-tert-butylnitroxide. Thus, this reaction is proposed to occur in a process as shown in Scheme 12.

Scheme 12



The olefin 23 as a mixture of (E) and (Z) isomers, has been isolated in 72% yield by column chromatography, and the ratio of cis/trans isomer has been determined by high resolution ^1H NMR spectral analysis as Z/E = 13/87.

2. Photostimulated reaction of t-BuHgCl with alkynes followed by NaBH$_4$ reduction

Photostimulated reaction of *tert*-butylmercury chloride with some alkynes has been carried out. The reaction was occurred readily either in a Rayonet Photoreactor at 350 nm or under a 275 W sunlamp. After the irradiation, the reaction mixture was treated with $NaBH_4$, followed by hydrolysis with water. The adduct olefins (in Eq. 38) were isolated and identified as shown in Table 15. The reaction of _t_-BuHgCl

$$t\text{-BuHgCl} + \text{Q-C}\equiv\text{C-Y} \xrightarrow[\text{2. NaBH}_4]{\text{1. h}\nu} \text{QHC=C(}t\text{-Bu)Y} \qquad (38)$$

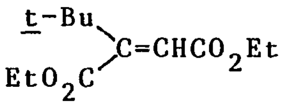
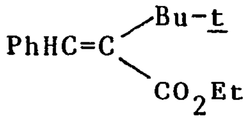
with 3-butyn-2-one only formed 20% of _t_-$BuCH=CHCOCH_3$ because 70% of this product was further reduced into _t_-BuCH=CHCH(OH)-CH_3 by the sodium borohydride.

The cis-olefin was obtained predominantly from the reaction of _tert_-butylmercury chloride with phenylacetylene as demonstrated by the ^1H NMR spectrum and a GLC retention time matching that of an authentic sample obtained from Reaction 36.[75]

Similar to the previous Reaction 37, these reactions did not occur in the dark and the addition reaction was drastically inhibited by the presence of 10 mol% of di-_tert_-butylnitroxide. When the reaction mixture was worked up with 5% $Na_2S_2O_3$ solution after the irradiation, none of the starting alkynes (except for unreacted PhC≡CPh) was detected, and only

Table 15. Photostimulated reaction of t-BuHgCl with alkynes followed by $NaBH_4$ reduction[a]

$$Q\text{-}C\equiv C\text{-}Y \ + \ \textit{t}\text{-BuHgCl} \xrightarrow[2.\ NaBH_4]{1.\ h\nu} QCH{=}C(\textit{t}\text{-Bu})Y$$

Q	Y	Ratio of RHgCl/$QC\equiv CY$	Conditions	Products	E/Z	% Yield[b]
CO_2Et	CO_2Et	3.5	DMSO SL 6h	 $(\textit{t}\text{-Bu})(EtO_2C)C{=}CHCO_2Et$	38/62[c]	97 (86)
Ph	CO_2Et	4	DMSO/PhH (50%:50%) UV 20h	 $PhHC{=}C(Bu\text{-}\textit{t})(CO_2Et)$	87/13[c]	94 (72)
CO_2Et	H	4	DMSO/PhH (50%:50%) SL 20h	$\textit{t}\text{-}BuCH{=}CHCO_2Et$		64

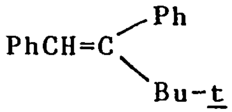
---

[a] The initial concentration of alkynes was 0.04 M to 0.1 M; a ratio of t-BuHgCl/$NaBH_4$ = 1.0/1.2 was employed.

[b] (E) and (Z) mixture yields. The GLC yields measured by adding internal standard; isolated yields in parentheses.

[c] The ^1H NMR "assigned" E/Z ratios.

Table 15. (Continued)

Q	Y	Ratio of RHgCl/QC≡CY	Conditions	Products	E/Z	% Yield[b]
$COCH_3$	H	0.33	DMSO/PhH (50%:50%) SL 20h	<u>t</u>-BuCH=CHCOCH_3		20[d]
Ph	H	5	DMSO UV 20h	PhCH=CHCMe_3	13/87[e]	71 (60)
Ph	Ph	5	DMSO/PhH (50%:50%) SL 20h			19

[d] 70% of <u>t</u>-BuCH=CHCH(OH)CH_3 was obtained.

[e] Determined by the GLC retention time matching with that of an authentic sample.[75]

[f] 60% of PhC≡CPh was recovered.

very small amount of the olefin was observed. Thus, these reactions apparently are free radical chain reactions occurring by the same mechanism presented in Scheme 12.

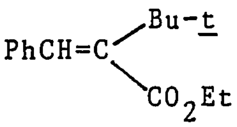
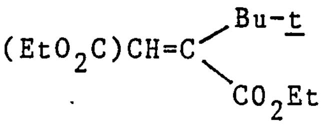
As previous mentioned, Giese and Lachhein reported that an alkyl radical generated by the reaction of alkylmercury chlorides with $NaBH_4$ adds to some alkynes to form cis and trans olefins (Eq. 35 and Table 14). In order to compare these two methods, the reactions of *t*-BuHgCl with three alkynes were carried out with Giese method, the reaction results are arranged in Table 16. Comparing the results in Tables 14, 15 and 16, a conclusion can be made that the photostimulated reaction of *t*-BuHgCl with alkynes provides adduct olefins in much higher yields than the Giese method.

3. Photostimulated reaction of t-BuHgCl with alkynes followed by iodine cleavage

The reaction mechanism for the photostimulated reaction of *tert*-butylmercury chloride with alkynes has been proposed in Scheme 12. It is known that alkylmercury halides can be converted into alkyl halides by reaction with halogen.[32] In order to prove the existence of the intermediate , Ph(HgCl)C=C(*t*-Bu)CO_2Et or Q(HgCl)C=C(*t*-Bu)Y, in this reaction, the cleavage reaction by iodine was carried out (Eq. 39). As expected, the corresponding iodides were obtained, the results

Table 16. Reactions of *t*-BuHgCl with alkynes and NaBH$_4$[a]

$$\mathrm{Q{-}C{\equiv}C{-}Y} + t\text{-}\mathrm{BuHgCl} + \mathrm{NaBH_4} \xrightarrow[\text{1 h}]{\mathrm{CH_2Cl_2}} \mathrm{QCH{=}C(}t\text{-}\mathrm{Bu)Y}$$

Q	Y	Initial concn. of Q-C≡C-Y	Products (*E* + *Z*)	% Yield
Ph	CO_2Et	0.05 *M*	 $\mathrm{PhCH{=}C}\begin{matrix}\diagup \mathrm{Bu\text{-}}t\\ \diagdown \mathrm{CO_2Et}\end{matrix}$	21[b]
Ph	H	0.04 *M*	PhCH=CH(*t*-Bu)	7[c]
CO_2Et	CO_2Et	0.04 *M*	 $\mathrm{(EtO_2C)CH{=}C}\begin{matrix}\diagup \mathrm{Bu\text{-}}t\\ \diagdown \mathrm{CO_2Et}\end{matrix}$	32[d]

[a] Ratio of alkyne/*t*-BuHgCl/NaBH$_4$ = 1:4:4.5.

[b] 65% Of Ph-C≡C-CO$_2$Et was recovered.

[c] 70% of Ph-C≡C-H was recovered.

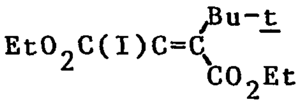
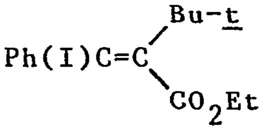
[d] 50% of EtO$_2$C-C≡C-CO$_2$Et was recovered.

being given in Table 17. The high yields of iodides obtained in this reaction provided good evidence to support the

$$\mathrm{Q{-}C{\equiv}C{-}Y} + t\text{-}\mathrm{BuHgCl} \xrightarrow[\text{2. } \mathrm{I_2}]{\text{1. } h\nu} \mathrm{Q(I)C{=}C(}t\text{-}\mathrm{Bu)Y} \qquad (39)$$

Table 17. Photostimulated reactions of *t*-BuHgCl with alkynes followed by iodine reduction[a]

$$\mathrm{Q\text{-}C{\equiv}C\text{-}Y} + t\text{-}\mathrm{BuHgCl} \xrightarrow[2.\ \mathrm{I_2}]{1.\mathrm{UV\ 20h\ PhH}} \mathrm{Q(I)C{=}C(}t\text{-}\mathrm{Bu)Y}$$

Q	Y	Ratio of RHgCl/QC≡CY	Initial concn. of Q-C≡C-Y	Products	Z/E[b]	% Yield[c]
CO_2Et	CO_2Et	5	0.05 *M*	 $\mathrm{EtO_2C(I)C{=}C(Bu\text{-}}t\mathrm{)(CO_2Et)}$		98 (77)
Ph	CO_2Et	5	0.05 *M*	 $\mathrm{Ph(I)C{=}C(Bu\text{-}}t\mathrm{)(CO_2Et)}$		94 (86)
$COCH_3$	H	0.33	0.30 *M*	$t\text{-}\mathrm{BuCH{=}C(I)COCH_3}$	71/29	(76)
Ph	H	5	0.06 *M*	$t\text{-}\mathrm{BuCH{=}C(I)Ph}$	63/37	41 (37)[d]

[a] The ratio of *t*-BuHgCl/I_2 = 1.0/1.2 was employed.

[b] The ^{1}H NMR "assigned" Z/E ratios.

[c] (*E*) and (*Z*) mixture yields. GLC yields measured by adding internal standards; isolated yields in parentheses.

[d] 7% of PhCH=CH(*t*-Bu) was obtained.

intermediacy of Q(HgCl)C=C(_t_-Bu)Y.

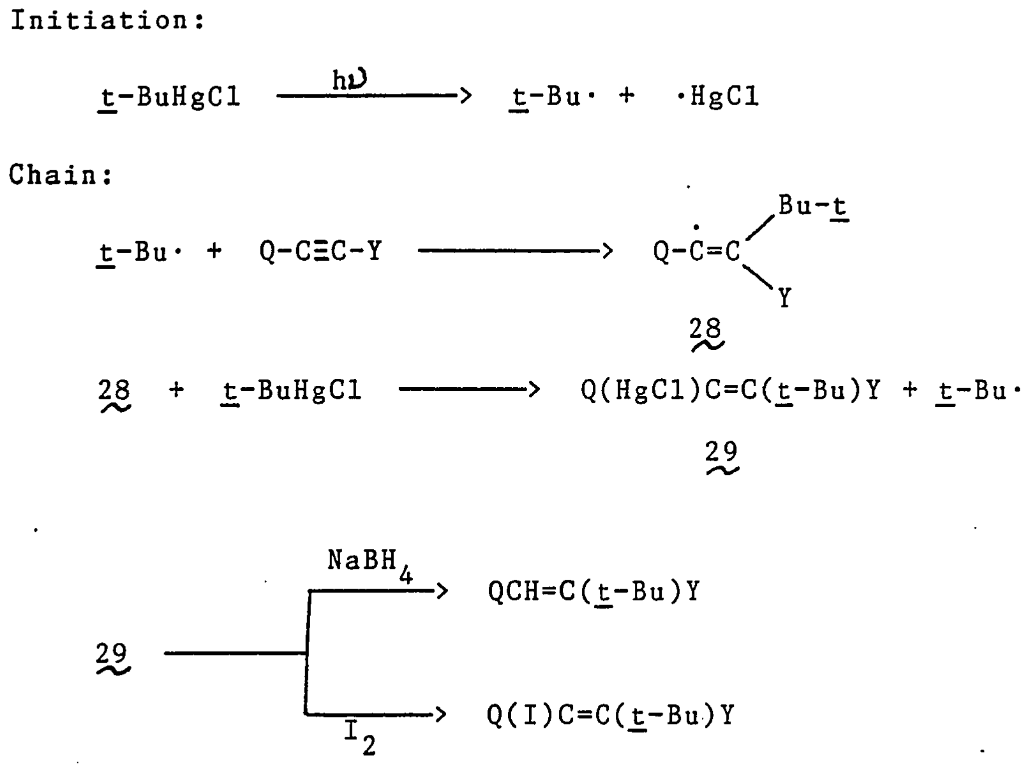
4. Mechanism consideration

It was found that _tert_-butylmercury chloride did not react with any of the alkynes employed in the absence of a radical initiator. Thus, there was no reaction of alkynes with _t_-BuHgCl in the dark, even upon stirring at room temperature for 3 days. In addition, the presence of 10 mol% of di-_tert_-butylnitroxide significantly retarded the rate of the addition of _t_-BuHgCl to the alkynes. Therefore, these reactions are free radical chain reaction precesses leading to **29** as presented in Scheme 13. Upon irradiation, a _tert_-butyl radical formed from _t_-BuHgCl which adds to the triple bond of Q-C≡C-Y to form a vinylic radical **28**. Radical **28** then reacts with _tert_-butylmercury chloride to form **29** and another _tert_-butyl radical which continues the chain reaction. **29** reacts readily with $NaBH_4$ or I_2 to give the proto and iodo demercurated products.

C. Conclusion

tert-Butylmercury chloride has found to photochemically react with alkynes (Q-C≡C-Y, Q = Ph, CO_2Et, $COCH_3$; Y = H, Ph, CO_2Et) to form the (_E_) and (_Z_) adduct olefins in high yields. The structure of the product from the reaction of ethyl phenyl-

Scheme 13



propiolate with *t*-BuHgCl indicated that the adduct radical 25 (Ph$\dot{\mathrm{C}}$=C(*t*-Bu)CO$_2$Et) is more stable than radical 26 (EtO$_2$C$\dot{\mathrm{C}}$=C(*t*-Bu)Ph) even though the carboethoxy group is an electron-withdrawing group. This is because in radical 25 the electron can be well delocalized by the π system of the phenyl ring. Because these reactions fail to occur in the dark and the addition reaction was significantly retarded by the presence of 10 mol% of di-*tert*-butylnitroxide, these reactions apparently proceed by a free radical chain process as presented in Scheme 13. The adduct (Q(HgCl)C=C(*t*-Bu)Y) in the reaction has been converted in a high yields to Q(I)C=C(Y)Bu-*t* by the cleavage reaction with elemental iodine. Compared to the results obtained with Gises method, the photostimulated reaction of *t*-BuHgCl with these alkynes followed by $NaBH_4$ reduction, lead to the corresponding olefins in a much higher yield.

D. Experimental

1. General consideration

All the instrumentation and techniques employed in the experiments have already been described in Part I, D. *tert*-Butylmercury chloride was prepared in over 50% yield with the modified method described before. All of the alkynes employed were commercially available from Aldrich Chem. Co. and were used without further purification.

2. General procedure for photoreactions of t-BuHgCl with alkynes followed by $NaBH_4$ reduction

To an oven-dried pyrex tube was added *tert*-butylmercury chloride, alkyne and solvent (PhH and DMSO). The tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation, the reaction mixture was transferred to a flask with a magnetic stirring bar and solid $NaBH_4$ was added. After reacting with the $NaBH_4$ for 10-15 min, a few drops of water was added to coagulate the mercury. After 5 min, more water (10-15 mL) was added and the aqueous layer was separated, extracted with ether (2 x 10 mL). The organic layers were combined and dried over $MgSO_4$. Upon removing the solvent, the concentrated liquid was analyzed by GLC and GCMS. The pure products were isolated by flash column chromatography. The following reactions, Sections 3 and 6 to 10, were carried out according to this procedure.

3. Photoreaction of t-BuHgCl with ethyl phenylpropiolate followed by $NaBH_4$ reduction

A dry pyrex tube containing ethyl phenylpropiolate (0.08 g, 0.45 mmol), *tert*-butylmercury chloride (0.5 g, 1.8 mmol) and the solvent of DMSO (6 mL) and PhH (6 mL) was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor for 20 h. After reaction with $NaBH_4$ (0.1 g, 2.2 mmol), the mixture was worked up according to the general procedure described in Section 2. After evaporation of solvent, a liquid remained which was analyzed to contain the (*E*) and (*Z*) isomers of ethyl α-*tert*-butylcinnamate in 94% yield. The mixture of (*E*) and (*Z*) isomers was isolated in 72% yield by flash column chromatography with the eluent of hexane and ether (40%:60%). The ratio of (E) and (Z) isomers as 87/13 was determined by the ^{1}H NMR of the vinylic protons: δ 7.11 (s, 0.87H) as (E) isomer and δ 6.55 (s, 0.13H) as (Z) isomer. According to the literature data, (E)-PhH$_a$C=CH$_b$COOEt has H$_a$ = δ 7.70, H$_b$ = 6.44.[76] For $H_3CCH{=}C(CH_3)CO_2CH_3$, resonance for the vinylic proton occurs at δ 6.73 for the (E)-isomer and at δ 5.98 for the (Z)-isomer.[77]

^{1}H NMR of (E) and (Z) mixture ($CDCl_3$) δ 7.35-7.18 (m, 5H), 7.11 (s, 0.87H), 6.55 (s, 0.13H), 4.25 (q, 2H), 1.39 (t, 3H), 1.12 (s, 9H).

^{13}C NMR ($CDCl_3$, mixture of (E) and (Z) isomers) δ 170.85, 145.04, 137.95, 133.58, 128.13, 127.78, 126.90, 60.54, 35.49, 30.88, 14.30.

GCMS, m/e (relative intensity) 233 (3), 232 (18, M^+), 217 (28), 187 (27), 171 (26), 159 (100), 145 (22), 143 (58), 129 (33), 117 (98), 91 (36), 57 (29).

M.S. Calculated for $C_{15}H_{20}O_2$: 232.14633. Found: 232.14638. Error: +0.2 ppm.

IR (neat, NaCl plate, cm^{-1}) 2960, 2900, 2860, 1730, 1580, 1470, 1360, 1240, 1220, 1190, 1050, 1020, 780, 730, 690.

4. Hydrolysis of ethyl α-tert-butylcinnamate

The mixture of ethyl α-*tert*-butylcinnamate (0.12 mmol) and KOH (70 mg)/EtOH (8 mL) was heated to reflux for 3 h in an oil bath at 100 °C. Then about one-thirds of EtOH was removed by use of a rotatory evaporator, and 10 mL of water was added, the mixture was neutralized with hexane (3 x 8 mL). The organic layers were combined, washed with water and dried over $MgSO_4$. After removing the solvent, a yellow solid remained was identified as the isomers, -*tert*-butylcinnamic acids, PhCH=C(*t*-Bu)COOH.

^{1}H NMR ($CDCl_3$) 11.68 (s, 1H), 7.46 (s, 0.90H), 7.38-7.15 (m, 5H), 1.19 (s, 9H).

5. Decarboxylation of α-tert-butylcinnamic acids

The reaction was carried out similar to the procedure described in the literature.[75] To a flask equipped with a thermometer and a refluxing condenser was added α-*tert*-butylcinnamic acid (0.1 mmol) prepared in the previous section, Cu_2O (0.02 g) and quinoline (1.0 mmol). Under nitrogen, the mixture was heated at 210-220 °C by a heating mantle for 2 h. After the reaction, the mixture was allowed to cool to room temperature and about 50 mL of 10% HCl solution was added to dissolve the excess quinoline. The brown solution was extracted with ether (3 x 20 mL), the organic layers were combined and filtered. The filtrate was washed 3 times with 10% K_2CO_3 solution, then washed with water and dried over $MgSO_4$. After removing the solvent, a liquid remained was identified as (Z)-1-tert-butyl-2-phenylethene.

^1H NMR ($CDCl_3$) δ 7.40-7.06 (m, 5H), 6.40 (d, 1H, J = 12 Hz), 5.65 (d, 1H, J = 12 Hz), 1.01 (s, 9H).

In GLC, the product showed only one peak with the retention time of 5.15 min (column: OV-3, 7%, $\frac{1}{8}$" x 6'. Program: 100 °C, initial time 05 min, 10 °C/min, 310 °C).

6. Photoreaction of t-BuHgCl with diethyl acetylenedicarboxylate followed by sodium borohydride reduction

A pyrex tube containing tert-butylmercury chloride (0.24 g, 0.8 mmol), diethyl acetylenedicarboxylate (0.04 g, 0.23 mmol) and DMSO (6 mL) was irradiated under a 275 W sunlamp for 6 h. After reaction with $NaBH_4$ (0.05 g, 0.96 mmol), the mixture was worked up according to the general procedure in Section 2. By evaporating the solvent, the concentrated liquid was dried under vaccum for 2 h and was characterized as (E)- and (Z)-$EtO_2CCH{=}C(t\text{-}Bu)CO_2Et$ in 86% yield (further purification was not needed).

The ratio of (E) and (Z) isomers as 38/62 was determined from the ^1H NMR of the vinylic protons: δ 6.18 (s, 0.38H) as (E) isomer and δ5.81 (s, 0.62H) as (Z) isomer. According to the literature data for $EtO_2CCH=CHCO_2Et$, the vinylic protons resonate at δ6.89 in the (E)-isomer and at δ6.23 in the (Z)-isomer.[78]

^1H NMR ($CDCl_3$) δ6.18 (s, 0.38H), 5.81 (s, 0.62H), 4.10-4.30 (q, 4H), 1.32-1.30 (t, 6H), 1.18 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 168.56, 165.24, 122.97, 116.21, 61.00, 60.81, 35.64, 28.94, 14.18.

GCMS, *m/e* (relative intensity) 230 (0.01), 228 (0.02, M^+), 183 (26), 155 (100), 127 (64), 111 (28), 109 (64), 81 (44), 67 (22), 59 (22), 41 (49).

IR (neat, NaCl plate, cm^{-1}) 2970, 2910, 2870, 1730, 1640, 1370, 1340, 1019, 1250, 1170, 1050, 1030.

7. Photoreaction of t-BuHgCl with phenylacetylene followed by $NaBH_4$ reduction

To a pyrex tube was added *t*-BuHgCl (0.44 g, 1.5 mmol), phenylacetylene (0.03 g, 0.3 mmol) and DMSO (6 mL). The tube was sealed with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm for 20 h. After reaction with $NaBH_4$ (0.09 g, 1.8 mmol), the mixture was worked up by the general procedure. By removing the solvent, the concentrated liquid was analyzed as the product, 1-*tert*-butyl-2-phenylethylene, in 71% yield. The product (over 90% (Z)-isomer) was isolated in 60% yield by flash column chromatography with ether as the eluent.

The ratio of (*E*) and (*Z*) isomers of 13/87 was determined by GLC. The isomer with the retention time of 5.25 min was assigned to the (*Z*)-isomer because the retention time matched that of the authentic sample in Section 5. Another peak with the retention time of 7.43 min was assigned to the (*E*)-isomer. In GCMS, both peaks showed the parent ion of *m*/*e* = 160.

^{1}H NMR of isolated product ($CDCl_3$) δ 7.42-7.09 (m, 5H), 6.40 (d, 1H, *J* = 12 Hz), 5.65 (d, 1H, *J* = 12 Hz), 1.02 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 142.72, 131.61, 129.01, 128.55, 127.60, 126.25, 40.98, 31.28.

GCMS, *m*/*e* (relative intensity) 161 (5), 160 (42, M^+), 145 (100), 130 (19), 128 (15), 117 (38), 115 (16), 91 (46).

8. Photoreaction of t-BuHgCl with 3-butyn-2-one followed by $NaBH_4$ reduction

A pyrex tube containing *t*-BuHgCl (0.1 g, 0.3 mmol), 3-butyn-2-one (69 mg, 1.0 mmol) and the solvent of DMSO (2 mL) and PhH (2 mL) was irradiated under a 275 W sunlamp for 20 h. After reaction with $NaBH_4$ (0.02 g, 0.36 mmol), the mixture was worked up according to the general procedure. After the solvent was removed, GLC analysis of the concentrated liquid revealed two products, *t*-BuCH=CHCOCH$_3$ in 20% yield and *t*-Bu-

$-CH=CHCH(OH)CH_3$ in 70% yield.

GCMS of *t*-$BuCH=CHCOCH_3$, *m*/*e* (relative intensity) 127 (0.3), 126 (3, M^+), 111 (63), 83 (30), 67 (12), 55 (55), 43 (100).

GCMS of *t*-$BuCH=CHCH(OH)CH_3$, *m*/*e* (relative intensity) 128 (0.04, M^+), 95 (15), 85 (11), 83 (10), 72 (20), 71 (34), 70 (12), 69 (16), 67 (11), 59 (26), 55 (29), 43 (100), 41 (33).

9. Photoreaction of t-BuHgCl with ethyl propiolate followed $NaBH_4$ reduction

To a pyrex tube was added *t*-BuHgCl (0.24 g, 0.8 mmol), ethyl propiolate (20 mg, 0.2 mmol) and the solvent of DMSO (1.5 mL) and PhH (1.5 mL). The tube was equipped with a rubber septum and was irradiated under a 275 W sunlamp for 20 h. After reaction with $NaBH_4$ (0.05 g, 0.96 mmol), the mixture was worked up according to the general procedure. After removing the solvent, GLC analysis of the remained liquid revealed two isomers of *t*-$BuCH=CHCO_2Et$ in 62% yield.

GCMS of one isomer (*E* or *Z*), *m*/*e* (relative intensity) 157 (1), 156 (10, M^+), 141 (38), 113 (52), 111 (66), 95 (45), 83 (100), 67 (37), 55 (60), 43 (41).

GCMS of another isomer (*E* or *Z*), *m*/*e* (relative intensity) 157 (2), 156 (17, M^+), 141 (42), 113 (39), 111 (66), 95 (35), 83 (100), 69 (22), 67 (36), 55 (55).

10. Photoreaction of t-BuHgCl with diphenylacatylene followed by $NaBH_4$ reduction

A pyrex tube containing *t*-BuHgCl (0.15 g, 0.5 mmol), diphenylacetylene (0.02 g, 0.1 mmol) and the solvent of DMSO (1.5 mL) and PhH (1.5 mL) was irradiated under a 275 W sunlamp for 20 h. After reaction with $NaBH_4$, the mixture was worked up by the general procedure. After removing the solvent, GLC analysis of the concentrated liquid revealed the expecting products (*E* and *Z*), Ph(*t*-Bu)C=CHPh, in 20% yield and the starting alkyne, PhC≡CPh, in over 60% recovered. GCMS of one isomer, *m/e* (relative intensity) 237 (4), 236 (21, M^+), 221 (26), 179 (17), 178 (26), 143 (89), 128 (26), 105 (32), 91 (100), 77 (17).

11. General procedure for photoreaction of t-BuHgCl with alkynes followed by iodine cleavage

To a dry pyrex tube was added *t*-BuHgCl, alkyne and PhH. The tube was sealed with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation, the reaction mixture was transferred to a flask with a magnetic stirring bar, iodine was added and the cleavage reaction was completed in a few hours. Then, PhH (10 mL) was added and the mercury iodide (HgI_2) was filtered. The red-purple filtrate was washed until colorless with 5% $Na_2S_2O_3$, dried over

$MgSO_4$ and concentrated to afford an adhensive liquid or an oil which was analyzed by ^1H NMR, GLC and GCMS, and the pure product was isolated. The reactions in Sections 12 to 15 were carried out and worked up according to this procedure.

12. Photoreaction of t-BuHgCl with diethyl acetylenedicarboxylate followed by iodine cleavage

A pyrex tube containing t-BuHgCl (0.43 g, 1.45 mmol), diethyl acetylenedicarboxylate (0.05 g, 0.29 mmol) and PhH (6 mL) was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor for 20 h. After reaction with I_2 (0.4 g, 1.74 mmol), the reaction mixture was worked up by the general procedure described in Section 11. After removing the solvent, GLC analysis of the adhensive liquid revealed the products to be the (E) and (Z) isomers of $EtO_2C(t\text{-}Bu)C=C(I)CO_2Et$ in 98% yield. The concentrated liquid was dissolved in hexane (5 mL) and filtered. After removing the hexane, the liquid remaining was dissolved in hexane (5 mL) and filtered again. By evaporating the solvent and drying under vacuum for 2-3 h, the mixture of (E) and (Z) isomers was isolated in 77% yield (further purification was not necessary).

GCMS of one isomer (E or Z), m/e (relative intensity) 355 (3), 354 (7, M^+), 281 (76), 253 (68), 126 (55), 125 (30), 87

(100), 81 (30), 59 (43), 57 (67), 53 (34), 43 (40), 41 (68).
GCMS of another isomer (E or Z), m/e (relative intensity) 354 (1, M^+), 281 (73), 253 (47), 227 (5), 154 (36), 153 (37), 126 (64), 125 (54), 87 (48), 57 (78), 43 (61), 41 (100).

^1H NMR ($CDCl_3$) δ4.43-4.01 (m, 4H), 1.40-1.28 (m, 6H), 1.23 (s, 9H).

^{13}C NMR ($CDCl_3$) δ167.98, 166.85, 153.21, 81.97, 62.18, 61.43, 38.95, 29.44, 14.01, 13.60.

M.S. Calculated for $C_{12}H_{19}O_4I$: 354.03281. Found: 354.03303. Error: +0.6 ppm.

IR (melt, NaCl plate, cm^{-1}) 2980, 2920, 2880, 1740-1720, 1620, 1470, 1390, 1370, 1270-1200, 1100, 1070, 1020, 920, 860.

13. Photoreaction of t-BuHgCl with ethyl phenylpropiolate followed by iodine cleavage

To a pyrex tube was added t-BuHgCl (0.66 g, 2.25 mmol), ethyl phenylpropiolate (0.08 g, 0.45 mmol) and PhH (8 mL). The tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor for 20 h. After reaction with iodine (0.69 g, 2.7 mmol), the mixture was worked up by the general procedure. The solvent was removed under reduced pressure, a yellow oil was analyzed as the products, (E) and (Z)-Ph(I)C=C(t-Bu)CO_2Et, in 94% yield. The purification was carried out by dissolving the oil in hexane (5 mL) followed

by filtration, then repeating this procedure once more. By removing the hexane and drying under vacuum for 2-3 h, the mixture of (E) and (Z) isomers was isolated in 86% yield.
GCMS of one isomer (E or Z), m/e (relative intensity) 358 (7, M^+), 231 (10), 185 (51), 157 (61), 147 (51), 142 (31), 129 (94), 102 (47), 77 (29), 57 (100), 43 (53).
GCMS of another isomer (E or Z), m/e (relative intensity) 358 (0.2, M^+), 231 (89), 175 (69), 147 (96), 129 (43), 128 (33), 115 (16), 77 (18), 57 (100).
^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5H), 4.35 (q, 2H), 1.43 (t, 3H), 0.95 (s, 9H).
^{13}C NMR ($CDCl_3$) δ 169.60, 152.11, 144.82, 128.04, 127.52, 114.78, 95.79, 61.32, 38.63, 31.08, 14.18.
M.S. Calculated for $C_{15}H_{19}O_2I$: 358.04307. Found: 358.04354. Error: +1.3 ppm.
IR (melt, NaCl plate, cm^{-1}) 2970, 2920, 2900, 1730, 1620, 1590, 1470, 1440, 1360, 1250, 1230, 1210, 1050, 1025, 840, 780, 760, 690.

14. Photoreaction of t-BuHgCl with 3-butyn-2-one followed by iodine cleavage

To a dry pyrex tube was added t-BuHgCl (0.1 g, 0.3 mmol), 3-butyn-3-one (69 mg, 1.0 mmol) and PhH (3 mL). The tube was sealed with a rubber septum and was irradiated in a Rayonet

Photoreactor at 350 nm for 20 h. After reaction with iodine (0.1 g, 0.36 mmol), the mixture was worked up according to the general procedure. By removing the solvent and drying under vacuum for 2 h, a yellow liquid was identified as the mixture of (E) and (Z) isomers of t-BuCH=C(I)$COCH_3$ isolated in 76% yield without further purification.

The ratio of (E) and (Z) isomers as 29/71 was determined by the ^1H NMR. In ^1H NMR, the vinylic proton at δ 7.36 (s, 0.71H) was assigned to the (Z)-isomer and the proton at δ 6.14 to the (E)-isomer according to the literature data for the compound of $CH_3CH=C(CH_3)CO_2CH_3$.[77]

^1H NMR ($CDCl_3$) δ 7.36 (s, 0.71H), 6.14 (s, 0.29H), 2.52 (s, 3H), 1.28 (s, 2.70H), 1.09 (s, 6.30H).

^{13}C NMR ($CDCl_3$) δ 206.57, 128.37, 93.24, 38.45, 29.21, 29.85.

GCMS, m/e (relative intensity) 253 (0.4), 252 (6, M^+), 237 (6), 125 (27), 110 (27), 67 (17), 43 (100).

15. Photoreaction of t-BuHgCl with phenylacetylene followed by iodine cleavage

A pyrex tube containing t-BuHgCl (0.44 g, 1.5 mmol), phenylacetylene (0.03 g, 0.3 mmol) and PhH (5 mL) was irradiated in a Rayonet Photoreactor for 20 h. After reaction with iodine (0.46 g, 1.8 mmol), the mixture was worked up by the general procedure. After removing the solvent, GLC analysis of the concentrated liquid revealed the isomers of Ph(I)C=CH(t-Bu) in 41% yield. The purification was carried out by dissolving the concentrated liquid in hexane (5 mL) followed by filtration. After removing the solvent under the reduced pressure, the mixture of (E) and (Z) isomers was obtained in 37% yield.

The ratio of (E) and (Z) isomers as 37/63 was determined by the ^1H NMR. The vinylic proton at δ6.40 (s, 0.63H) was assigned as the (Z) isomer and at δ6.20 (s, 0.37H) as (E) isomer according to the data for the authentic sample reported in Section 5.

^1H NMR ($CDCl_3$) δ 7.11-7.30 (m, 5H), 6.40 (s, 0.63H), 6.20 (s, 0.37H), 1.30 (s, 9H).

GCMS, m/e (relative intensity) 286 (0.3, M^+), 159 (74), 129 (19), 117 (43), 105 (5), 102 (13), 57 (100).

16. Dark reaction between t-BuHgCl with ethyl phenylpropiolate followed by iodine cleavage

Ethyl phenylpropiolate (0.08 g, 0.45 mmol) and t-BuHgCl (0.66 g, 2.25 mmol) were dissolved in 8 mL of benzene and the reaction flask was wrapped with aluminum foil to exclude the light. After stirring the reaction mixture at room temperature for 3 days, iodine (0.69 g, 2.7 mmol) was added. The mixture was stirred overnight and PhH (10 mL) was added. The red precipitate of HgI_2 was filtered, the red-purple filtrate was washed until colorless with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. After the solvent was evaporated, GLC analysis of the crude isolate revealed unchanged starting material, ethyl phenylpropiolate, in 97% recovery.

17. Effect of di-tert-butylnitroxide on the reaction of t-BuHgCl with ethyl phenylpropiolate followed by iodine cleavage

Ethyl phenylpropiolate (0.04 g, 0.23 mmol), *t*-BuHgCl (0.33 g, 1.13 mmol) and di-*tert*-butylnitroxide (0.3 mg, 0.02 mmol) were dissolved in the solvent of DMSO (2 mL) and PhH (2 mL). The pyrex tube was equipped with a rubber septum and was irradiated in a Rayonet Photoreactor at 350 nm. After irradiation for 6 h, the mixture was transferred into a flask with a magnetic stirring bar, iodine (0.35 g, 1.4 mmol) was added and the solution stirred overnight. PhH (6 mL) was added, the precipitate (HgI_2) was filtered and the mixture was first washed with 6 mL of water, then washed with 5% $Na_2S_2O_3$ solution, dried over $MgSO_4$ and concentrated. GLC analysis showed that the concentrated liquid contained mainly unreacted ethyl phenylpropiolate in 93% recovery.

18. Photoreaction of t-BuHgCl with ethyl phenylpropiolate followed by workup with 5% $Na_2S_2O_3$ solution

To a dry pyrex tube was added ethyl phenylpropiolate (0.04 g, 0.23 mmol), t-BuHgCl (0.25 g, 0.9 mmol) and PhH (6 mL). The tube was irradiated under a 275 W sunlamp for 24 h. The mixture was transferred to a separatory funnel, PhH (10 mL) was added. The mixture was washed with 5% $Na_2S_2O_3$ for 3 times, dried over $MgSO_4$ and concentrated. GLC analysis of the residue revealed the product in only 4% yield and none of the starting alkyne was detected.

19. General procedure for reaction of t-BuHgCl, alkynes and $NaBH_4$ (see Table 16)

The reactions were carried out according to the general procedure reported by Giese and his co-workers.[68,73] $NaBH_4$ was added into a stirred mixture of t-BuHgCl, alkyne and CH_2Cl_2 (alkyne/t-BuHgCl/$NaBH_4$ = 1/4/4.5). After reaction for 15-20 min, a few drops of water was added to coagulate the mercury metal, then more water (8-10 mL) was added and the mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined and dried with $MgSO_4$. After removing the solvent, the liquid remained was analyzed by GLC.

III. KINETIC CHAIN LENGTHS AND REACTION KINETICS

A. Introduction

Kinetic chain length is the average number of monomer (or reactant) molecules consumed for every radical which initiates a chain reaction.[79] Therefore, the magnitude of the kinetic chain length measured for a reaction can be a criterion to determine whether the reaction is a chain reaction. The reactions of alkylmercury halides with olefins, $CH_2=CHQ$ ($Q = (EtO)_2P(O)$, SO_2Ph) and the reactions of tert-butylmercury chloride with alkynes, $Q-C\equiv C-Y$ (Q = H, Ph, COOEt; Y = COOEt, $COCH_3$, Ph) have been shown to be radical processes (Parts I and II). These reactions are believed to involve a free radical chain mechanism since the reactions fail to occur in the dark and the reactions are significantly retarded by the presence of 10 mol% of di-tert-butylnitroxide. However, the kinetic chain length of these reactions is not known. In order to provide evidence to support the chain process of these reactions, it was necessary to measure the kinetic chain length for these reactions.

The work in this part presents the results on the determination of the kinetic chain lengths for some of these reactions and studies the kinetics of the reaction between the tert-butylmercury chloride and diethyl vinylphosphonate.

B. Results and Discussion

1. Determination of kinetic chain length of the reaction between diethyl vinylphosphonate and t-BuHgCl

For the radical addition reactions, the kinetic chain length at any time can be expressed as shown in Eq. 40. The

$$\text{Kinetic Chain Length} = \frac{\text{Rate of Reaction}}{\text{Rate of Initiation}} \qquad (40)$$

kinetic chain length varies over the course of a reaction and depends upon the concentration of reagents as well as the rate of initiation. Experimentally, it is possible to measure the initial kinetic chain length at the beginning of a reaction if the initial reaction rate and the rate of the free radical initiation reaction are known. As the reactant is consumed and the rate of the reaction approaches zero, the kinetic chain length will also approach zero.

The rate of initiation can be measured from the inhibition period observed with a known amount of an inhibitor which traps free radicals with a known stoichiometry. The initial rate of the reaction can be measured experimentally by following either the consumption of the substrate or the formation of the product. The progress of the reaction of *t*-BuHgCl with diethyl vinylphosphonate is conveniently monitored by the ^{1}H

NMR.

Thus, diethyl vinylphosphonate (0.12 M) and t-BuHgCl (0.48 M) in nitrogen-purged deuterated DMSO were placed in a 5 mm NMR tube. The solution was irradiated with a 275 W sunlamp at 30-35 °C and was checked at different periods of time by the ^{1}H NMR. The consumption of the substrate, CH_2=C-HP(O)(OEt)$_2$, was determined by the integration of decrease of the signal of three vinylic protons comparing with the unchanged signal of four protons $(-OCH_2-)_2$ of the group of $-P(O)(OCH_2CH_3)_2$ as the internal reference. The reaction in the presence of 10 mol% of di-tert-butylnitroxide (DTBN) was carried out in the same condition. Table 18 listed the results from both reactions and the plot of the consumption of the olefin (VP) vs. time is shown in Figure 2.

The initial rate of the reaction is obtained from the slope of the curve at the beginning of the reaction drawn by using a tangent meter as shown in Figure 2 and calculated as 3.4×10^{-2} M/min. The rate of initiation with the inhibitor (DTBN) presented is obtained from the concentration of DTBN divided by the time needed to consume all of the DTBN which can be determined from the Figure 2. The calculation, of course, assumes that DTBN captures the initiating radical in a 1:1 stoichiometry. From Figure 2 it is calculated that:

Table 18. Reaction of VP with t-BuHgCl in $DMSO\text{-}d_6$[a]

$$\underset{\text{(VP)}}{\text{CH}_2\text{=CHP(O)(OEt)}_2} + \underline{\text{t}}\text{-BuHgCl} \xrightarrow[\text{DMSO-d}_6]{h\nu^{b}} \underline{\text{t}}\text{-BuCH}_2\text{CH(HgCl)P(O)(OEt)}_2$$

Time	% Consumption of VP[c]	
(min)	without DTBN	with DTBN
5	15.7	0
15	50.8	0
30	85.1	0
40	95.0	9.4
45	99.1	35.1
55		67.6

[a] Reactions of VP (0.12 M) and t-BuHgCl (0.48 M) without and with DTBN (0.012 M) were carried out in 0.5 mL $DMSO\text{-}d_6$.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

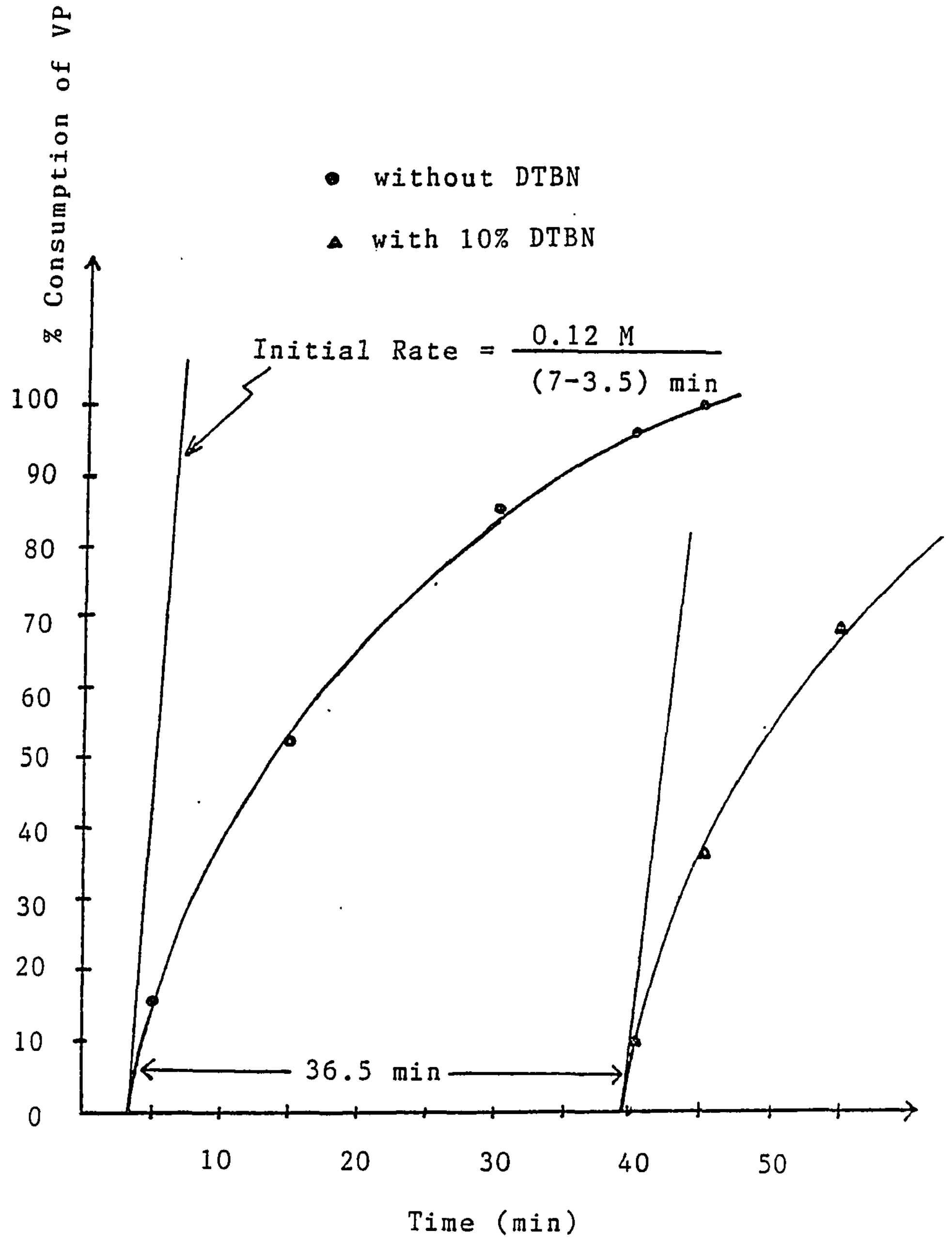


Figure 2. Consumption of VP vs. time for the reaction of diethyl vinylphosphonate and tert-butylmercury chloride

Initial Rate = 0.12 $\underline{M}$ / (7-3.5) min

Rate of Initiation = 0.012 $\underline{M}$ / 36.5 min

$$\text{Initial Kinetic Chain Length} = \frac{0.12\ \underline{M}/3.5\ \text{min}}{0.012\ \underline{M}/36.5\ \text{min}} = 105$$

Thus, with a kinetic chain length of 105, reaction of VP with t-BuHgCl is definitely a chain process. However, the measured kinetic chain length is based on the assumption that DTBN is consumed only by tert-butyl radical but not by the monomeric ·HgCl. In fact, the DTBN could trap both tert-butyl radical and ·HgCl, and if ·HgCl cannot initiate the chain, the initial kinetic chain length would be 105 x 2. Actually, Reaction 41 may occur, namely, ·HgCl may initiate the chain

$$\underline{t}\text{-BuHgCl} + \cdot\text{HgCl} \longrightarrow \underline{t}\text{-Bu}\cdot + \text{Hg}^\circ + \text{HgCl}_2 \qquad (41)$$

by forming tert-butyl radical. If Reaction 41 occurs, trapping or lack of trapping of the ·HgCl by DTBN will have no effect on the calculation of the kinetic chain length.

Similarly, the initial kinetic chain length of this reaction in deuterated benzene (C_6D_6) was also measured (Table 19 and Figure 3). From Figure 3 it is calculated that:

Table 19. Reaction of VP with *t*-BuHgCl in C_6D_6[a]

$$\underset{\text{(VP)}}{CH_2{=}CHP(O)(OEt)_2} + \textit{t}\text{-}BuHgCl \xrightarrow[C_6D_6]{h\nu^{b}} \textit{t}\text{-}BuCH_2CH(HgCl)P(O)(OEt)_2$$

Time (min)	% Consumption of VP[c]	
	without DTBN	with DTBN
5	31.7	0
15	59.7	0
30	62.5	0
40	90.1	9.2
45		24.2
60	95.7	51.5
75		70.7
90	99.5	76.0
123		99.8

[a] Reactions of VP (0.12 *M*) and *t*-BuHgCl (0.48 *M*) without and with DTBN (0.012 *M*) were carried out in 0.5 mL C_6D_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

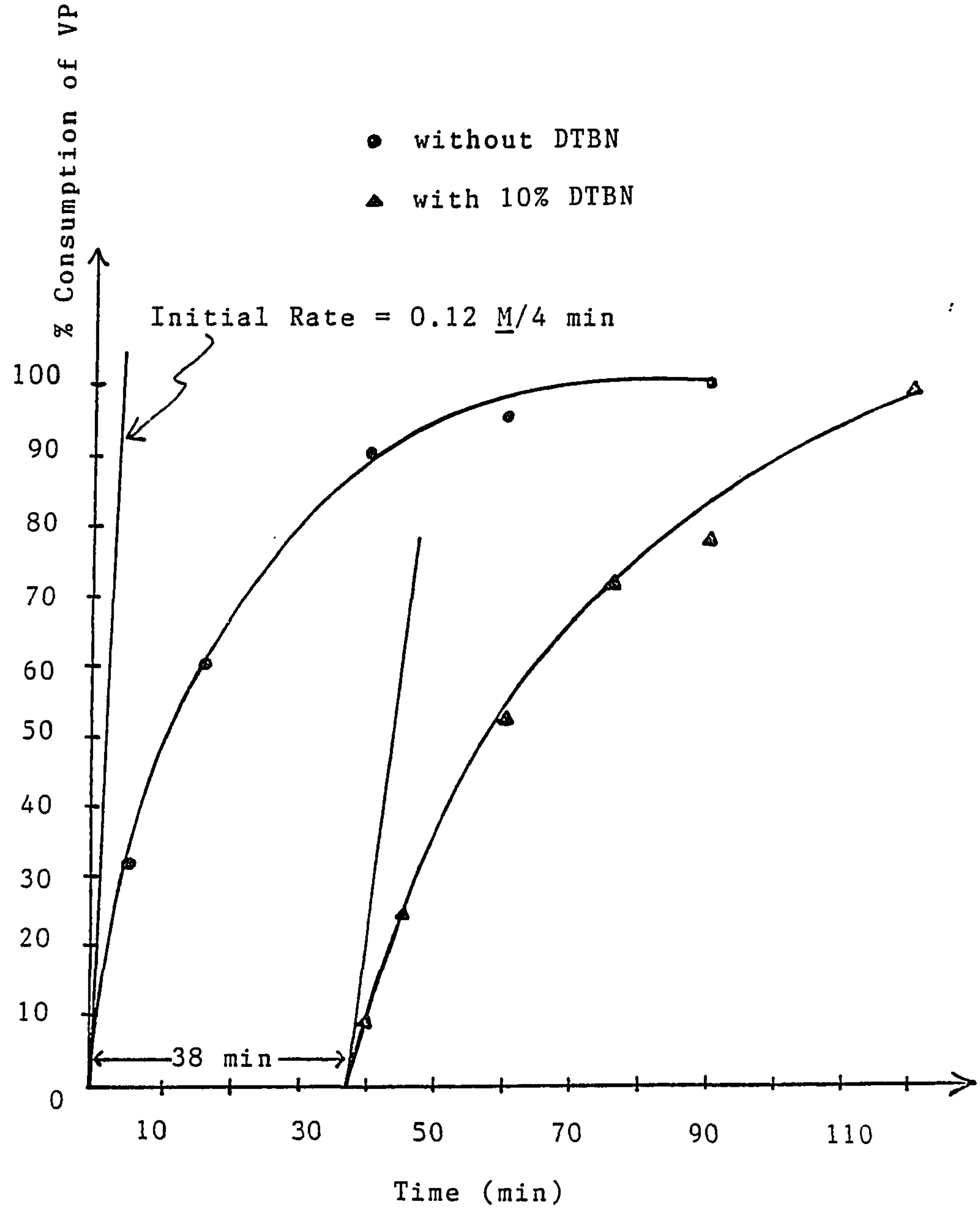


Figure 3. Consumption of VP vs. time for the reaction of diethyl vinylphosphonate and tert-butylmercury chloride in C_6D_6

Initial Rate = 0.12 M / 4 min

Rate of Initiation = 0.012 M / 38 min

$$\text{Initial Kinetic Chain Length} = \frac{0.12\ \underline{M}\ /\ 4\ \text{min}}{0.012\ \underline{M}\ /\ 38\ \text{min}} = 95$$

This reaction with an initial kinetic chain length of 95 in C_6D_6 and an initial kinetic chain length of 105 in DMSO-d_6 is doubtlessly a chain reaction. It is quite clear from the data in Tables 18 and 19 that the substrate, diethyl vinylphosphonate (VP), was completely consumed in 2 h in this photostimulated process. Thus, this reaction need not be irradiated under UV for 24 h (see Section 1 of Part I). A white precipitate was always observed when the reaction was carried out in benzene solution, while mercury metal was observed when DMSO was employed as the solvent. One explanation is that the mercuric chloride ($HgCl_2$) formed in Reaction 41 does not dissolve in PhH and is observed as a white precipitate. In DMSO, the $HgCl_2$ is soluble and is reduced to mercury metal under irradiation. Although in C_6D_6 the ·HgCl from the photoinitiation step may dimerize and precipitate as Hg_2Cl_2 while in DMSO Reaction 41 occurs to yield mercury metal (Hg°).

2. Determination of kinetic chain length of the reaction between phenyl vinyl sulfone and t-BuHgCl

The experimental procedure employed to determine the kinetic chain length of the reaction of phenyl vinyl sulfone (VS) and *tert*-butylmercury chloride is similar to that employed in the previous section. Thus, the VS (0.119 *M*) and *t*-BuHgCl (0.47 *M*) in nitrogen-purged deuterated DMSO in a 5 mm NMR tube were irradiated with a 275 W sunlamp at 30-35 °C. The reaction was monitored periodically by the ^1H NMR. The consumption of the substrate, $CH_2=CHSO_2Ph$ (VS), was obtained by the integration of the decreased signal of three vinylic protons comparing with that of the unchanged signal of five protons of the phenyl group as the reaction progressed. The reaction results without and with 10 mol% of DTBN are given in Table 20. Figure 4 shows the plot of the consumption of olefin (VS) vs. time. From Figure 4 it is calculated that:

Initial Rate = 0.119 *M* / (12-9) min

Rate of Initiation = 0.0119 *M* / 31 min

$$\text{Initial Kinetic Chain Length} = \frac{0.119\ \underline{M}/3\ \text{min}}{0.0119\ \underline{M}/31\ \text{min}} = 103$$

Table 20. Reaction of VS with t-BuHgCl in DMSO-d_6[a]

$$\underset{\text{(VS)}}{CH_2{=}CHSO_2Ph} + \text{t-BuHgCl} \xrightarrow[\text{DMSO-}d_6]{h\nu^{b}} \text{t-BuCH}_2\text{CH(HgCl)P(O)(OEt)}_2$$

Time (min)	% Consumption of VS[c]	
	without DTBN	with DTBN
5	0	0
10	17	0
15	57	0
30	98	0
40		2
55		26
70		77

[a] Reactions of VS (0.119 M) and t-BuHgCl (0.47 M) without and with DTBN (0.0119 M) were carried out in 0.5 mL DMSO-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

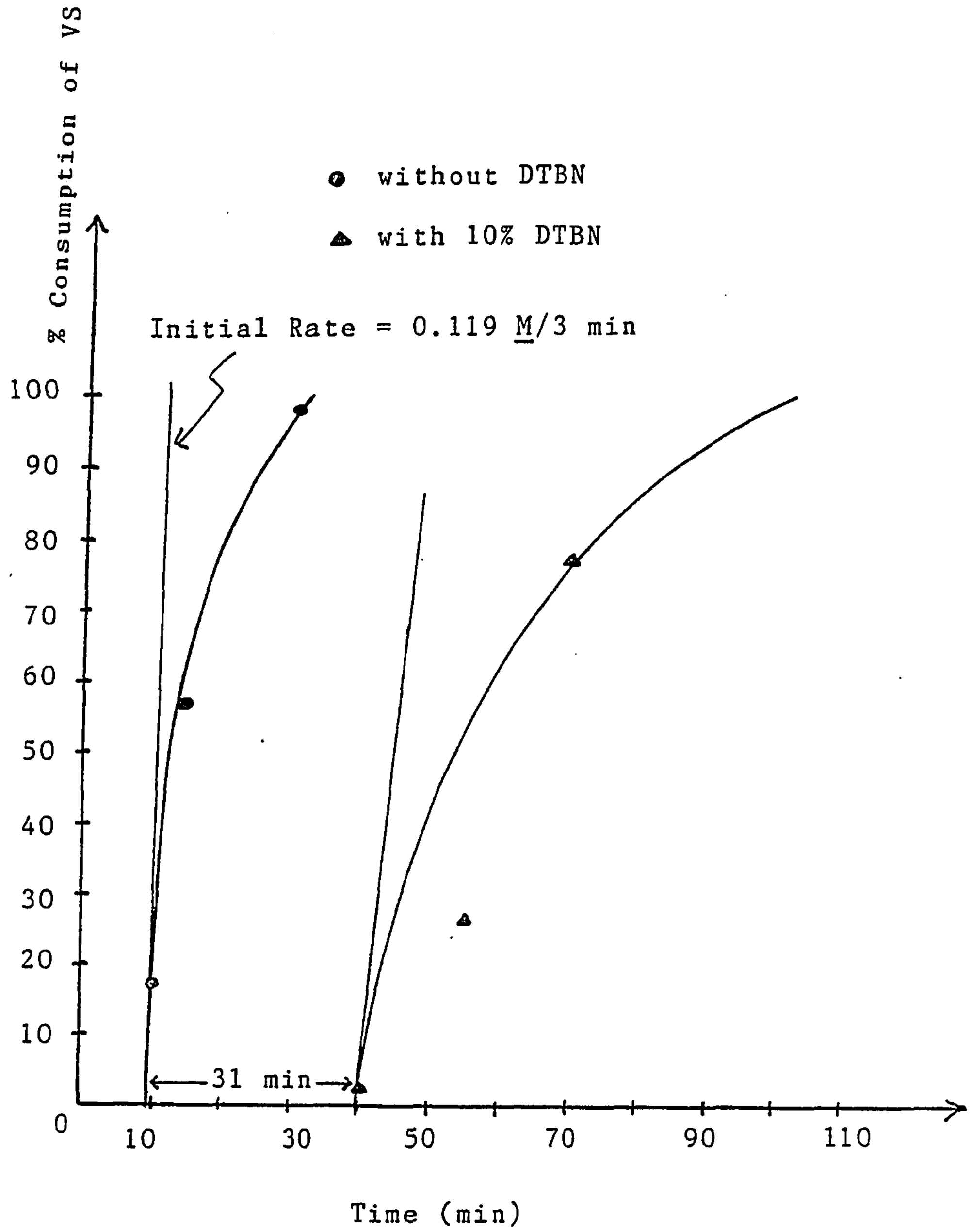


Figure 4. Consumption of VS vs. time for the reaction of phenyl vinyl sulfone and tert-butylmercury chloride in DMSO-d_6

The reaction of phenyl vinyl sulfone with t-BuHgCl with an initial kinetic chain length of 103 is a free radical chain reaction. If both tert-butyl radical and ·HgCl are trapped by the di-tert-butylnitroxide (DTBN), the actual kinetic chain length would be 103 x 2 provided ·HgCl is effective in initiating the chain. This reaction had an appreciable induction period even with a nitrogen-purged solvent. This may be caused by the solvent, DMSO, containing some inhibitors.

3. Determination of kinetic chain length of the reaction between phenylacetylene and t-BuHgCl

The kinetic chain length of the reaction of phenylacetylene and t-BuHgCl in both DMSO-d_6 and C_6D_6 has been determined. Thus, phenylacetylene (0.14 M) and t-BuHgCl (0.42 M) in nitrogen-purged deuterated DMSO in a 5 mm NMR tube were irradiated with a 275 W sunlamp at 30-35 °C. The progress of the reaction was monitored by the ^{1}H NMR at different periods of time. The consumption of the substrate, Ph-C≡C-H, was obtained by the integration of the signal of the acetylenic proton comparing with the unchanged signal of five protons of phenyl group as the internal reference. Since the signal of the acetylenic proton was not easy to monitor when the ratio of t-BuHgCl / Ph-C≡C-H = 5 was employed, both reactions in

DMSO-d_6 and C_6D_6 were carried out with the ratio of t-BuHgCl /Ph-C≡C-H = 3. The results are given in Tables 21 and 22. Similar to Sections 1 and 2, by plotting the consumption of phenylacetylene vs. time, the initial kinetic chain length of the reaction has calculated. Thus, for the reaction carried out in DMSO-d_6, the kinetic chain length of 15 was obtained. In DMSO-d_6 solvent, plotting the data of Table 21 yielded:

Initial Rate = 0.14 M / (16.5-3.5) min

Rate of Initiation = 0.014 M / (23.5-3.5) min

$$\text{Initial Kinetic Chain Length} = \frac{0.14\ \underline{M}/13\ \text{min}}{0.014\ \underline{M}/20\ \text{min}} = 15$$

The initial kinetic chain length of 14 was calculated when the reaction was carried out in C_6D_6. In deuterated benzene solvent, plotting of the data of Table 22 yielded:

Initial Rate = 0.14 M / (13.5-0.5) min

Rate of Initiation = 0.014 M / (18.5-0.5) min

$$\text{Initial Kinetic Chain Length} = \frac{0.14\ \underline{M}/13\ \text{min}}{0.014\ \underline{M}/18\ \text{min}} = 14$$

If in the reaction, both tert-butyl radical and monomer ·HgCl are trapped by the DTBN, the measured initial kinetic chain

Table 21. Reaction of $\mathrm{Ph{-}C{\equiv}C{-}H}$ with $\underline{t}$-BuHgCl in DMSO-d_6[a]

$$\mathrm{Ph{-}C{\equiv}C{-}H} \;+\; \underline{t}\text{-}\mathrm{BuHgCl} \xrightarrow[\mathrm{DMSO{-}d_6}]{h\nu^{b}} \mathrm{Ph(HgCl)C{=}CH(}\underline{t}\text{-}\mathrm{Bu)}$$

Time (min)	% Consumption of $\mathrm{PhC{\equiv}CH}$[c]	
	without DTBN	with DTBN
5	9	0
20	50	0
25	61	12
40	88	38
55	92	81

[a] Reactions of $\mathrm{Ph{-}C{\equiv}C{-}H}$ (0.14 $\underline{M}$) and $\underline{t}$-BuHgCl (0.42 $\underline{M}$) without and with DTBN (0.014 $\underline{M}$) were carried out in 0.5 mL DMSO-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^{1}H NMR.

Table 22. Reaction of $Ph\text{-}C{\equiv}C\text{-}H$ with *t*-BuHgCl in C_6D_6[a]

$$Ph\text{-}C{\equiv}C\text{-}H \quad + \quad \underline{t}\text{-}BuHgCl \xrightarrow[C_6D_6]{h\nu^{b}} Ph(HgCl)C{=}CH(\underline{t}\text{-}Bu)$$

Time (min)	% Consumption of $PhC{\equiv}CH$[c] without DTBN	 with DTBN
5	17	0
10	29	0
20	49	3
40	78	26
55		54

[a] Reactions of $Ph\text{-}C{\equiv}C\text{-}H$ (0.14 *M*) and *t*-BuHgCl (0.42 *M*) without and with DTBN (0.014 *M*) were carried out in 0.5 mL C_6D_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

length for the reaction would be 15 x 2 in DMSO-d_6 and 14 x 2 in C_6D_6.

4. Determination of kinetic chain length of the reaction between butyn-3-one and t-BuHgCl

Determination of the initial kinetic chain length for reaction of butyn-3-one and *t*-BuHgCl in DMSO-d_6 and C_6D_6 has been carried out. The reaction was periodically monitored by the ^1H NMR. The consumption of the alkyne, $H-C\equiv C-COCH_3$, was obtained from the integration of the decreased signal of the acetylenic proton comparing with the unchanged signal of the three protons of the methyl group as the internal reference. Thus, butyn-3-one (0.17 *M*) and *t*-BuHgCl (0.51 *M*) without and with 9 mol% of DTBN in a 5 mm NMR tube were irradiated with a 275 W sunlamp at 30-35 °C. The results for the reaction in DMSO-d_6 and in C_6D_6 are given in Tables 23 and 24.

By plotting the consumption of alkyne vs. time from the data in Table 23, the initial kinetic chain length for the reaction in DMSO-d_6 was calculated as 32:

Initial Rate = 0.17 *M* / (13-4) min

Rate of Initiation = 0.015 *M* / (29-4) min

$$\text{Initial Kinetic Chain Length} = \frac{0.17\ \underline{M}/9\ \text{min}}{0.015\ \underline{M}/25\ \text{min}} = 32$$

Table 23. Reaction of butyn-3-one and *t*-BuHgCl in DMSO-d_6[a]

$$H\text{-}C\equiv C\text{-}COCH_3 + \underline{t}\text{-}BuHgCl \xrightarrow[DMSO\text{-}d_6]{h\nu^{b}} \underline{t}\text{-}BuCH{=}C(HgCl)COCH_3$$

Time (min)	% Consumption of $HC\equiv CCOCH_3$[c]	
	without DTBN	with DTBN
5	10	0
10	36	0
20	83	0
25	98	0
30		7
40		45
55		87

[a] Reactions of $H\text{-}C\equiv C\text{-}COCH_3$ (0.17 M) and *t*-BuHgCl (0.51 M) without and with DTBN (0.015 M) were carried out in 0.5 mL DMSO-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

Table 24. Reaction of butyn-3-one and t-BuHgCl in C_6D_6[a]

$$\text{H-C}\equiv\text{C-COCH}_3 + \underline{\text{t}}\text{-BuHgCl} \xrightarrow[C_6D_6]{h\nu\ ^{b}} \underline{\text{t}}\text{-BuCH=C(HgCl)COCH}_3$$

Time (min)	% Consumption of $HC\equiv CCOCH_3$[c]	
	without DTBN	with DTBN
5	12	0
10	31	0
20	38	0
25	67	6
40	98	40
55		69

[a] Reactions of $H\text{-}C\equiv C\text{-}COMe$ (0.17 M) and t-BuHgCl (0.51 M) without and with DTBN (0.015 M) were carried out in 0.5 mL C_6D_6.

[b] The mixture in a 5 mm NMR tube was irradiated at 30-35 °C with a 275 W sunlamp ca. 20 cm. from the tube.

[c] Determined by the ^1H NMR.

The initial kinetic chain length for the reaction in C_6D_6 was calculated as 26:

Initial Rate = 0.17 M / (12-3) min

Rate of Initiation = 0.015 M / (23.5-3) min

$$\text{Initial Kinetic Chain Length} = \frac{0.17\ \underline{M}/9\ \text{min}}{0.015\ \underline{M}/20.5\ \text{min}} = 26$$

In these reactions, if tert-butyl radical and monomeric ·HgCl can both be trapped by the DTBN, the measured kinetic chain length would be 32 x 2 in DMSO-d_6 and 26 x 2 in C_6D_6, provided ·HgCl is effective in initiating the chain reaction.

5. Solvent effect consideration

The initial kinetic chain length measured for the reactions carried out in benzene and DMSO indicate that the reaction in DMSO are somewhat faster and have longer kinetic chain length than that in benzene. Even though the reactions in DMSO-d_6 have a longer induction period before the reaction started, due to the existence of some inhibitors, the reactions were completed in a short time. This probably can be interpreted by the different chemical behavior of the monomeric ·HgCl in the DMSO and PhH, the ·HgCl is presumably formed in the photoinitiation process.

In the solvent of DMSO, monomeric ·HgCl may be effective in initiating the chain reaction and thus increases the reaction rate as shown in Scheme 14. Therefore, when DMSO was employed as the solvent, a certain amount of mercury metal (about 20% mercury) was always observed from the reactions.

Scheme 14 (in DMSO solvent):

$$\underline{t}\text{-BuHgCl} \xrightarrow{h\nu} \underline{t}\text{-Bu}\cdot + \cdot\text{HgCl}$$

$$\cdot\text{HgCl} + \underline{t}\text{-BuHgCl} \longrightarrow \underline{t}\text{-Bu}\cdot + \text{HgCl}_2 + \text{Hg}^\circ$$

However, when the reactions are carried out in the PhH solution, perhaps monomeric ·HgCl can build up and acts as a chain terminator as shown in Eq. 42 and 43. Thus, the kinetic chain lengths may decrease more rapidly with the present reaction in benzene than in DMSO because of the build-up of monomeric ·HgCl.

$$\underline{t}\text{-BuCH}_2\dot{\text{C}}\text{HQ} + \cdot\text{HgCl} \longrightarrow \underline{t}\text{-BuCH}_2\text{CH(HgCl)Q} \qquad (42)$$

$Q = P(O)(OEt)_2, SO_2Ph.$

$$\text{Q(}\underline{t}\text{-Bu)C=}\dot{\text{C}}\text{-Y} + \cdot\text{HgCl} \longrightarrow \text{Q(}\underline{t}\text{-Bu)C=C(HgCl)Y} \qquad (43)$$

Q = H, Ph, COOEt. Y = COOEt, $COCH_3$, Ph.

6. Kinetic study on reaction of t-BuHgCl with diethyl vinylphosphonate

For the photostimulated reaction of diethyl vinylphosphonate and t-BuHgCl, it is known from the previous results that: (1) this reaction is a free radical chain reaction with an initial kinetic chain length of 105 (in DMSO-d_6) and 95 (in C_6D_6); (2) the initial reaction product is t-$BuCH_2$-$CH(HgCl)P(O)(OEt)_2$. Reaction kinetics consulates the rate of a chemical reaction with all factors which influence it and provides an explanation of the rate in terms of the reaction mechanism. Therefore, determining the kinetic equation of this reaction from the experimental data will definitely provide a strong evidence for the reaction mechanism in terms of the reaction rate. Thus, the reaction kinetics of this reaction was studied by carrying out several reactions with the different concentration on CH_2=$CHP(O)(OEt)_2$ (VP) and with the different ratios between VP and t-BuHgCl. These reactions were carried out in NMR tubes with nitrogen-purged DMSO-d_6 as the solvent. The progress of the reaction was periodically monitored by the ^1H NMR. The consumption of the substrate, VP, was determined by the integration of the decreased signal of three vinylic protons comparing with the internal reference of the unchanged signal of four protons of the two methylene groups of $-P(O)(OCH_2CH_3)_2$. To minimize the experimental error, two reactions were performed at the same time with one of the two reactions in a set serving as a reference reaction. Similar to Section 1, by plotting the consumption of the substrate VP vs. time, the initial rate of the reaction was calculated from the slope of the curve. The results are given in Table 25. The reference reactions in the four reaction sets (1a, 2a, 3a and 4a in Table 25) demonstrate good agreement and provide evidence that the rate of the photoinitiation (Ri) was constant. The results indicate that the rate of the reaction is independent of the concentration of VP because the initial rate of the reactions do not significantly change when the concentration of VP changed from 0.06 <u>M</u> to 0.12 <u>M</u> with [<u>t</u>-BuHgCl] = 0.48 <u>M</u> (Experiments 1b and 2b). However, the initial rate of the reaction is dependent upon the concentration of the <u>t</u>-BuHgCl (see Sets 1 and 3 in Table 25). Thus, Equation 45 holds at least initially for Reaction 44.

$$\underset{\text{(VP)}}{CH_2{=}CHP(O)(OEt)_2} + \underline{t}\text{-}BuHgCl \xrightarrow{h\nu} \underline{t}\text{-}BuCH_2CH(HgCl)P(O)(OEt)_2 \quad (44)$$

$$-\frac{d[VP]}{dt} = k\,[\underline{t}\text{-}BuHgCl]^n[VP]^0 \quad (45)$$

Table 25. Kinetic studies on the reaction of VP and t-BuHgCl[a]

Set No.	No.	[VP] (M)	[t-BuHgCl] (M)	Ratio of t-BuHgCl/VP	Initial Rate (Ri) 10^{-2} (M/min)
1	1a[b]	0.06	0.24	4	0.50
	1b	0.06	0.48	8	1.09
2	2a[b]	0.06	0.24	4	0.57
	2b	0.12	0.48	4	1.26
3	3a[b]	0.06	0.24	4	0.48
	3b	0.06	0.31	5	0.66
4	4a[b]	0.06	0.24	4	0.55
	4b	0.13	0.63	4.8	1.73
5	5b	0.24	0.96	4	2.40

[a] Reactions were carried out in the 5 mm NMR tubes with 0.5 mL of nitrogen-purged DMSO-d_6 and were irradiated with a 275 W sunlamp.

[b] Reference reaction.

According to the general method of determining the reaction order (n),[80] Equation 45 can be written in the form of Equation 46 (Ri = -d[VP] / dt). Thus, the reaction order (n),

$$\text{Log Ri} = n \text{ Log } [\underline{t}\text{-BuHgCl}] + \text{Log } k \tag{46}$$

the slope of this equation can be obtained from the plot of Log Ri vs. Log [t-BuHgCl]. Based on the data given in Table 26, the plot of logarithm of initial rate (Ri) vs. the logarithm of concentration of t-BuHgCl is given in Figure 5. From Figure 5, the slope was calculated as 1.10. Thus, Equation 47 appears to represent the initial rate of the consumption of VP. Therefore, the photostimulated reaction of VP and *tert*-butylmercury chloride is a first-order reaction.

$$-\frac{d[\text{VP}]}{dt} = k[\underline{t}\text{-BuHgCl}]^1 \tag{47}$$

According to the kinetic study and based on the mechanism previously proposed in Scheme 4, a reaction process in terms of the reaction rate for this reaction is shown in Scheme 15.

Table 26. Logarithm Ri and logarithm of concentration of *t*-BuHgCl

No.[a]	[VP] (*M*)	[*t*-BuHgCl] (*M*)	Log[*t*-BuHgCl]	Ri x 10^{-2} (*M*/min)	Log Ri
1 (5b)	0.24	0.96	-0.018	2.40	-1.620
2 (4b)	0.13	0.63	-0.200	1.73	-1.762
3 (1b)	0.06	0.48	-0.319	1.09	-1.963
4 (3b)	0.06	0.31	-0.510	0.67	-2.176
5 (2a)	0.06	0.24	-0.620	0.57	-2.244

[a] The numbers in parentheses come from Table 25.

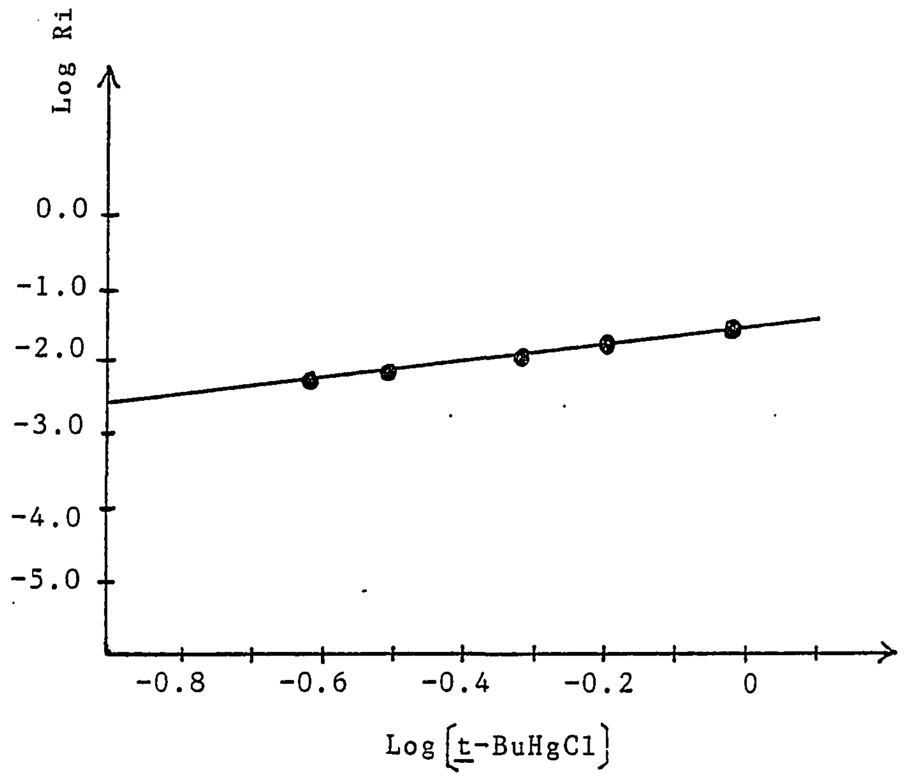


Figure 5. Plot of logarithm of Initial Rate(Ri) vs. logarithm of concentration of _t_-BuHgCl

Scheme 15

$$\mathrm{RHgCl} \xrightarrow[k_i]{h\nu} \mathrm{R\cdot + \cdot HgCl}$$

$$\mathrm{R\cdot} + \underset{(\mathrm{VP})}{\mathrm{CH_2{=}CHP}} \xrightarrow{\text{fast}} \underset{\mathbf{30}}{\mathrm{RCH_2\dot{C}HP}}$$

$$\mathbf{30} + \mathrm{RHgCl} \xrightarrow{k_2} \underset{\mathbf{31}}{\mathrm{RCH_2CH(HgCl)P}} + \mathrm{R\cdot}$$

$$\mathbf{30} + \mathrm{CH_2{=}CHP} \xrightarrow[\text{when RHgCl/VP = 4}]{k_2' = 0} \mathrm{RCH_2CHPCH_2\dot{C}HP}$$

$$\mathbf{30} + \mathrm{RHgCl} \xrightarrow[k_t]{} \text{non-radical products}$$

e.g. $\mathrm{RCH_2CH_2P}$

$\mathrm{Me_2C{=}CH_2}$

$\mathrm{\cdot HgCl}$

$$\xrightarrow[\text{very slow}]{\mathrm{RHgCl}} \mathrm{Hg^\circ + HgCl_2 + R\cdot}$$

$\mathrm{P = P(O)(OEt)_2}$.

R = *t*-Bu, *i*-Pr, *c*-$\mathrm{C_6H_{11}}$, *n*-Bu.

From Scheme 15, it follows that under the steady state condition (*i.e.* Ri = Rt) that:

$$\mathrm{Ri} = k_i[\mathrm{RHgCl}]$$

$$\mathrm{Rt} = k_t[\mathbf{30}][\mathrm{RHgCl}]$$

$$[\underset{\sim}{30}] = \underline{k}_i \ / \ \underline{k}_t$$

$$- \frac{d[VP]}{dt} = \underline{k}_2[\underset{\sim}{30}][RHgCl]$$

$$\text{Thus:} \quad - \frac{d[VP]}{dt} = \frac{\underline{k}_i \ \underline{k}_2}{\underline{k}_t} [RHgCl] \qquad (48)$$

Therefore, the kinetic equation for this reaction, at $t \cong 0$ is given in Eq. 48. According to the kinetic analysis *t*-BuHgCl is involved in the photoinitiation, in the slow propagation reaction, and in the termination step at least when $t \cong 0$.

C. Conclusion

The initial kinetic chain lengths of the reactions of diethyl vinylphosphonate with *t*-BuHgCl in DMSO-d_6 and in C_6D_6 were determined. The measured initial kinetic chain lengths are 105 (or 105 x 2) and 95 (or 95 x 2), respectively. The initial kinetic chain length of 103 was measured from the reaction of phenyl vinyl sulfone with *t*-BuHgCl in DMSO-d_6. These results indicate that these reactions are definitely radical chain processes and nearly all of the addition product must be formed in the propagation step.

The initial kinetic chain lengths of the reactions of phenylacetylene and butyn-3-one with *t*-BuHgCl in the solvents

DMSO-d_6 and C_6D_6 were determined. With the ratio of t-BuHgCl /alkyne = 3, the measured kinetic chain lengths for the reaction of phenylacetylene and t-BuHgCl are 15 (or 15 x 2) in DMSO-d_6 and 14 (or 14 x 2) in C_6D_6, and for the reaction of butyn-3-one with t-BuHgCl are 32 (or 32 x 2) in DMSO-d_6 and 26 (or 23 x 2) in C_6D_6. These results indicate that these reactions are free radical chain reactions. Apparently, the reactions go to completion faster in DMSO than in PhH since the reactions in DMSO have longer initial kinetic chain lengths than in PhH. Compared with the reactions of alkenes, the reactions of alkynes with t-BuHgCl occur with shorter kinetic chains.

From the kinetic studies, the reaction of t-BuHgCl with VP is found as the first-order reaction in which the reaction rate only depends on the concentration of the t-BuHgCl and is independent of the concentration of VP. Scheme 15 suggests a reaction mechanism which is consistent with the observed reaction kinetics, at least at the beginning of the reaction.

D. Experimental

1. General consideration

All the experiments were carried out in standard NMR (5 mm, 7") tubes and the reactions were periodically monitored by ^1H NMR at 300 MHz (Nicolet). The DMSO-d_6 and C_6D_6

were purchased from Aldrich Chem. Co. and were degassed with nitrogen for 10-15 min before use.

2. Determination of initial kinetic chain lengths in the reaction of VP with t-BuHgCl

t-BuHgCl (0.24 mmol) and VP (0.06 mmol) were dissolved in 0.5 mL of nitrogen-purged DMSO-d_6 or C_6D_6 in a NMR tube equipped with a rubber septum and sealed with a piece of parafilm. After a ^1H NMR spectrum was obtained, the tube was irradiated at 30-35 °C with a 275 W sunlamp placed about 20 cm. from the tube. The progress of the reaction was monitored by the ^1H NMR and the consumption of the substrate VP was obtained by the integration of the decreased signal of three vinylic protons comparing with the internal reference. The consumptions of the olefin (VP) at different periods of time are given in Table 18 for DMSO-d_6 and in Table 19 for C_6D_6. The reactions of VP with t-BuHgCl in the presence of 10 mol% of DTBN were carried out under the same conditions. Thus, VP (0.06 mmol), t-BuHgCl (0.24 mmol) and DTBN (0.006 mmol) were dissolved in 0.5 mL of nitrogen-purged DMSO-d_6 or C_6D_6 in a NMR tube. After a ^1H NMR spectrum was obtained, the mixture was irradiated with a sunlamp under exactly the same condition described above. The progress of the reaction was followed by ^1H NMR and the consumptions of the olefin VP obtained at different periods of time are given in Tables 18 (in DMSO-d_6) and 19 (in C_6D_6).

3. Determination of initial kinetic chain length in the reaction of phenyl vinyl sulfone with t-BuHgCl

Phenyl vinyl sulfone (0.094 mmol) and t-BuHgCl (0.37 mmol) were dissolved in 0.5 mL of DMSO-d_6 in a NMR tube equipped with a rubber septum and sealed with a piece of parafilm. After a ^1H NMR spectrum was obtained, the mixture was irradiated at 30-35 °C with a 275 W sunlamp placed about 20 cm. from the tube. The reaction was monitored by the ^1H NMR and the consumption of the olefin (VS) was obtained by the integration of the decreased signal of three vinylic protons comparing with that of the internal reference (phenyl group in VS). The results are given in Table 20. The reaction of VS with t-BuHgCl in the presence of 10 mol% of DTBN (0.009 mmol) was also carried out under exactly the same condition. The results are given in Table 20.

4. Determination of initial kinetic chain length in the reaction of phenylacetylene with t-BuHgCl

Phenylacetylene (0.068 mmol) and t-BuHgCl (0.20 mmol) were dissolved in 0.5 mL of DMSO-d_6 or C_6D_6 in a NMR tube. The tube was equipped with a septum and sealed with a piece of parafilm, after a ^{1}H NMR was obtained, the mixture was irradiated at 30-35 °C with a 275 W sunlamp. The progress of the reaction was monitored by the ^{1}H NMR. The consumption of the phenylacetylene was determined by the integration of the acetylenic proton comparing with the internal standard (phenyl group in PhC≡CH). The results are given in Table 21 (in DMSO-d_6) and Table 22 (in C_6D_6). The reactions of PhC≡CH and t-BuHgCl in the presence of 10 mol% of DTBN (0.0068 mmol) in both solvents were carried out under the same condition and the results are given in Tables 21 and 22.

5. Determination of initial kinetic chain length in the reaction of butyn-3-one with t-BuHgCl

Butyn-3-one (0.1 mmol) and t-BuHgCl (0.3 mmol) were dissolved in 0.6 mL of DMSO-d_6 or C_6D_6 in a NMR tube which was equipped with a septum and sealed with a piece of parafilm. After a ^{1}H NMR spectrum was obtained, the mixture was irradiated with a 275 W sunlamp placed about 20 cm. from the tube. The reaction was monitored periodically by the ^{1}H NMR. The consumption of butyn-3-one was determined by the integration of the acetylenic proton comparing with the internal standard (methyl group in $HC\equiv CCOCH_3$). The results are given in Table 23 and in Table 24. The reactions of $HC\equiv CCOCH_3$ with t-BuHgCl in the presence of 9 mol% of DTBN (0.009 mmol) in both solvents were carried out under the same condition. The results are listed in Tables 23 and 24.

6. General procedure for the determination of initial rate of the reaction between VP and t-BuHgCl (in Table 25)

t-BuHgCl and VP were dissolved in 0.5 mL of DMSO-d_6 in a NMR tube. The tube was equipped with a septum and sealed with a piece of parafilm. After the ^1H NMR spectrum was obtained, the mixture was irradiated at 30-35 °C with a 275 W sunlamp placed about 20 cm. from the tube. The progress of the reaction was monitored by the ^1H NMR at different periods of time. The consumption of the VP was determined by the integration of the three vinylic protons comparing with that of the internal standard (four protons of $-P(O)(OCH_2CH_3)_2$). To minimize the experimental error, two reactions in each set were carried out at the same time. One of the two reactions in each set was the reference reaction in which VP (0.03 mmol) and *t*-BuHgCl (0.12 mmol) were dissolved in 0.5 mL of DMSO-d_6. The reactions from Section 7 to 11 were carried out according to this general procedure.

7. Determination of initial rate of the reaction of VP and t-BuHgCl with [VP] = 0.06 M and the ratio of RHgCl/VP = 8

(Reaction set 1 in Table 25)

t-BuHgCl (0.24 mmol) and VP (0.03 mmol) were dissolved in 0.5 mL of DMSO-d_6 in a NMR tube. This mixture (Reaction 1b) and the reference reaction (1a) were irradiated with a 275 W sunlamp. The consumption of the VP was monitored by the ^1H NMR and the results are given in Table 27.

Table 27. The reaction of VP with t-BuHgCl (Reaction set 1)

Time (min)	% Consumption of VP	
	Reaction 1b	Reaction 1a(ref.)
5	35	16
10	67	41
15	98	59
20		78
25		98

8. Determination of initial rate of the reaction of VP and t-BuHgCl with [VP] = 0.12 M and the ratio of RHgCl/VP = 4 (Reaction set 2 in Table 25)

t-BuHgCl (0.24 mmol) and VP (0.06 mmol) were dissolved in 0.5 mL of DMSO-d_6. This mixture (Reaction 2b) and the reference reaction (2a) were irradiated with a 275 W sunlamp after a ^1H NMR spectra were obtained. Table 28 shows the results of the consumption of VP at the different periods of time.

Table 28. The reaction of VP with *t*-BuHgCl (Reaction set 2)

Time (min)	% Consumption of VP Reaction 2b	 Reaction 2a(ref.)
5	23	11
10	61	47
15	78	68
20	96	89
25		99

9. Determination of initial rate of the reaction of VP and t-BuHgCl with [VP] = 0.06 M and the ratio of RHgCl/VP = 5 (Reaction set 3 in Table 25)

t-BuHgCl (0.15 mmol) and VP (0.03 mmol) were dissolved in 0.5 mL of DMSO-d_6 in a NMR tube (Reaction 3b). After the ^1H NMR spectra were obtained for both reactions (Reactions 3a and 3b), the two tubes were irradiated with a 275 W sunlamp. The consumption of the VP monitored by the ^1H NMR is given in Table 29.

10. Determination of initial rate of the reaction of VP and t-BuHgCl with [VP] = 0.13 M and the ratio of RHgCl/VP=4.8 (Reaction set 4 in Table 25)

t-BuHgCl (0.312 mmol) and VP (0.065 mmol) were dissolved

Table 29. The reaction of VP with t-BuHgCl (Reaction set 3)

Time (min)	% Consumption of VP	
	Reaction 3b	Reaction 3a(ref.)
5	18	16
10	35	30
15	46	49
20	61	60

in 0.5 mL of DMSO-d_6 in a NMR tube (Reaction 4b). After the ^{1}H NMR spectra were obtained, both reaction tubes (4a and 4b) were irradiated with a 275 W sunlamp. Table 30 showed the results of the consumption of the VP at the different periods of time.

Table 30. The reaction of VP with t-BuHgCl (Reaction set 4)

Time (min)	% Consumption of VP	
	Reaction 4b	Reaction 4a(ref.)
5	26	14
10	59	40
15	76	55
20	96	74

11. Determination of initial rate of the reaction of VP and t-BuHgCl with [VP] = 0.24 M and the ratio of RHgCl/VP=4 (Reaction 5b in Table 25)

t-BuHgCl (0.48 mmol) and VP (0.12 mmol) were dissolved in 0.5 mL of DMSO-d_6 in a NMR tube. After a ^{1}H NMR spectrum was obtained, the mixture was irradiated with a 275 W sunlamp placed about 20 cm. from the tube. The consumption of the VP was periodically monitored by the ^{1}H NMR and the results are listed in Table 31.

Table 31. The reaction of VP with *t*-BuHgCl (Reaction 5b)

Time(min)	% Consumption of VP
5	17
10	32
15	46
20	59

IV. PHOTOSTIMULATED REACTIONS OF ORGANOMERCURIALS WITH DIHALOALKENES

A. Introduction

Alkenyl chlorides of the type of ClCH=CHX where X = alkyl are not reactive towards alkyl radicals due to the nucleophilic character of alkyl radicals. However, with X equal to an electron-withdrawing group such as CO_2R, the alkenes ($ClCH=CHCO_2R$) can react with alkyl radicals to give the substituted olefin $R'CH=CHCO_2R$.[81] Recently, Russell and Ngoviwatchai reported that (E)- and (Z)-1,2-dichloroethene react with alkylmercury chlorides to give the substitution products in 41-75% yields (Eq. 49).[30] The reactions only led to the mono-

$$ClCH=CHCl + RHgCl \xrightarrow[DMSO]{h\nu} RCH=CHCl \qquad (49)$$

R = t-Bu, c-C_6H_{11}.

substituted products even when an excess amount of RHgCl was employed. Mercuric phenylmercaptide was also found to photochemically react with (E)- and (Z)-dichloroethene to give 84% yield of (E)- and (Z)-1,2-bis(phenylthio)ethene and a 14% yield of β-chlorovinyl phenyl sulfide with a ratio of ClCH=CHCl/PhSHg-

$$ClCH=CHCl + (PhS)_2Hg \xrightarrow[DMSO]{UV} PhSCH=CHSPh + PhSCH=CHCl \qquad (50)$$

SPh = 5; when the ratio was equal to 1, only a 43% yield of 1,2-bis(phenylthio)-ethene was obtained.[30] The reactions apparently involve a radical addition and elimination process as shown in Scheme 16.[81] The formation of 1,2-bis(phenylthio)-ethene from this reaction is consistent with the chlorine being a stronger electron-withdrawing group than sulfur which makes 1,2-dichloroethene less reactive than beta-chlorovinyl phenyl sulfide towards benzenethiyl radical.

Scheme 16

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

$$\text{Cl}\cdot + (\text{PhS})_2\text{Hg} \longrightarrow \text{PhS}\cdot + \text{PhSHgCl}$$

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

(E)-1,2-Dichloroethene was also found to react with thiols to give the substitution product and other products (Eq. 51).[82] However, when benzenethiol was employed, the di-substituted product was not formed in Reaction 52. These

$$\text{RSH} + \text{ClCH=CHCl} \xrightarrow{h\nu} \text{RSCH}_2\text{CHCl}_2 + \text{RSSR} + \text{RSCH=CHCl}(\underline{E} + \underline{Z})$$
$$+ \text{RSCH=CHSR}(\underline{E} + \underline{Z}) \qquad (51)$$

$R = \underline{n}\text{-Bu}, \underline{n}\text{-C}_6\text{H}_{13}.$

$$\text{PhSH} + \text{ClCH=CHCl} \xrightarrow{h\nu} \text{PhSCH}_2\text{CHCl}_2 + \text{PhSSPh} + \underset{(\underline{E} + \underline{Z})}{\text{PhSCH=CHCl}} \qquad (52)$$

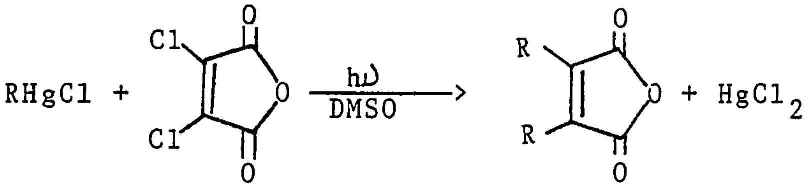
reactions were complicated because of the addition of the thiol with α,β-chlorotropic rearrangement.

Though some work has been reported for the photostimulated reaction of 1,2-dichloroethene with organomercurials, the reactions of dichloromaleic anhydride and 1,2-dibromoethene with organomercurials have not been studied. The work in this part considers these reactions.

B. Results and Discussion

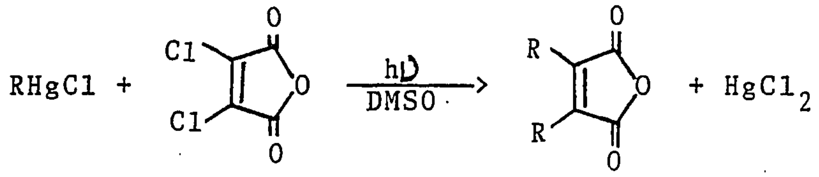
1. Photostimulated reaction of alkylmercury chlorides with dichloromaleic anhydride in DMSO

Alkylmercury chlorides and dichloromaleic anhydride dissolved in DMSO were irradiated at 30-35 °C with a 275 W sunlamp. After irradiation for 60 min, a white precipitate was observed which was identified as mercuric chloride ($HgCl_2$). After the reaction, the mixture was worked up by extracting with hexane and washing with 5% $Na_2S_2O_3$ solution. The product remaining after evaporation of the solvent was identified as the 1,2-disubstituted maleic anhydride (Eq. 53 and Table 32). These reactions are free radical reactions because the



(53)

Table 32. Reactions of alkylmercury chlorides with dichloromaleic anhydride



R	Ratio of RHgCl/anhydride	Condition[a]	% Product[b]
t-Bu	5	SL 24h	25
t-Bu	5	SL 8h	27 (24)
t-Bu	5	Dark 24h	0[c]
c-C_6H_{11}	5	SL 24h	21
c-C_6H_{11}	5	Dark 24h	0[c]

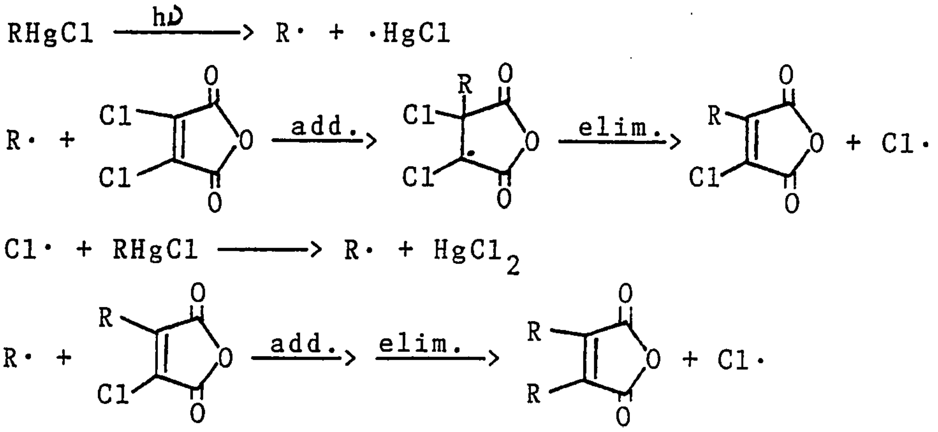
[a] The reactions were carried out with the initial concentration of dichloromaleic anhydride as 0.04 M.

[b] GLC yields and isolated yield in parentheses.

[c] Over 95% of dichloromaleic anhydride was recovered.

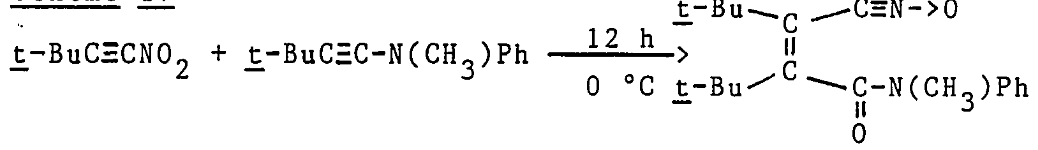
reactions fail to occur in the dark for 24 h and the reaction of dichloromaleic anhydride with *t*-BuHgCl was inhibited by the presence of 10 mol% of DTBN. The mechanism for the reactions is proposed in Scheme 16.

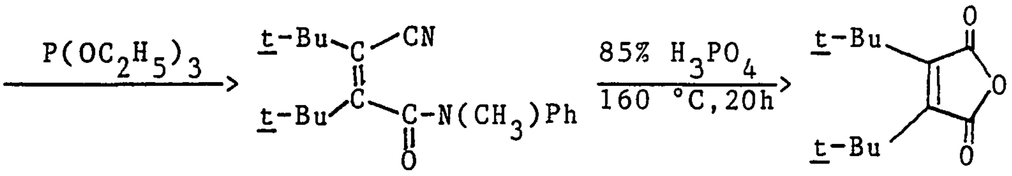
Scheme 16



The two free radical addition and elimination steps lead to the disubstituted maleic anhydrides, which are remarkable compounds because of the adjacent *tert*-butyl or cyclohexyl groups. It is worthy to mention that the synthesis of the dicyclohexylmaleic anhydride has not been reported in the literature and up to now only one method has been reported for the preparation of di-*tert*-butylmaleic anhydride which involved three reaction steps with the ratio of reactants, *t*-BuC≡C-N(CH_3)Ph/*t*-BuC≡CNO_2 = 4 as shown in Scheme 17.[83]

Scheme 17

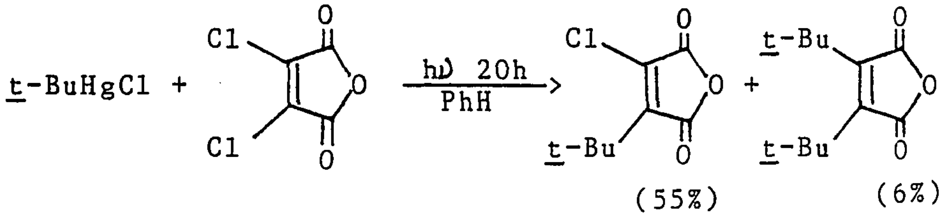




In comparison with the literature method, the formation of di-*tert*-butylmaleic anhydride from the reaction of maleic anhydride with *t*-BuHgCl definitely has the advantages of simplicity and convenient short reaction time. Thus, this method will be useful in organic synthesis if the yield can be improved.

2. Photostimulated reaction of *t*-BuHgCl with dichloromaleic anhydride in benzene

When benzene was employed as the solvent, the reaction of dichloromaleic anhydride with *t*-BuHgCl led to the monosubstituted product predominantly and only a small amount of the disubstituted maleic anhydride (Eq. 54). A white precipitate ($HgCl_2$) was observed when the reaction was irradiated with a 275 W sunlamp for 30 min. After irradiation for 20 h, the reaction tube contained a slurry of the white precipitate.



(54)

The reaction was worked up by filtering and the filtrate was washed with 5% $Na_2S_2O_3$ solution. The synthesis of chloro-*tert*-butylmaleic anhydride has not been reported in the literature. Thus, Reaction 54 provides a convenient synthesis since chloro-*tert*-butylmaleic anhydride has been isolated in 52% yield.

The results from Reaction 54 indicate that: (1) di-*tert*-butylmaleic anhydride, the only product obtained from Reaction 53, must be the secondary addition and elimination product from the chloro-*tert*-butylmaleic anhydride which is consistent with the proposed mechanism in Scheme 16. (2) When the PhH was employed as the solvent, the further reaction of *t*-BuHgCl with chloro-*tert*-butylmaleic anhydride was somehow blocked. The reason why the monosubstituted olefin is the major product in the reaction with PhH as the solvent is not clear. One possible reason is that the large amount of the white precipitate ($HgCl_2$) formed in the reaction which does not dissolve in PhH reflects the light and prevents the 2nd step of the photostimulated reaction from occurring. The high yield of the monosubstituted product, chloro-*tert*-butylmaleic anhydride, obtained from Reaction 54 indicates that the yield of the disubstituted product, di-*tert*-butylmaleic anhydride, actually should be higher than 27%. However, the reaction with the solvents of PhH/DMSO (80%:20%) only gave the disubstituted olefin in 18% yield and the monosubstituted product in 12% yield.

In addition, the reaction of maleic anhydride with t-BuHgCl followed by $NaBH_4$ reduction gave only a 16% yield of the monoaddition product (see entry 7 of Table 9). This indicates that dichloromaleic anhydride is much more reactive than maleic anhydride towards a nucleophilic radical because of the effect of the chlorine being a strong electron-withdrawing group.

3. Photostimulated reaction of alkylmercury chlorides with 1,2-dibromoethene

The photostimulated reactions of (E)-1,2-dibromoethene with t-BuHgCl and with cyclohexylmercury chloride have been carried out. The reactions occurred smoothly under the irradiation of a 275 W sunlamp and led to (E) and (Z)-1-bromo-2-tert-butylethene in 63% yield, and (E) and (Z)-1-bromo-2-cyclohexylethene in 45% yield, respectively, with the ratio of RHgCl / BrCH=CHBr = 1. These reactions only afforded

$$\text{RHgCl} + \text{BrCH=CHBr} \xrightarrow[\text{DMSO}]{h\nu} \text{RCH=CHBr } (\underline{E} + \underline{Z}) \qquad (55)$$

$$\text{R} = \underline{c}\text{-}C_6H_{11} \quad 45\%$$

$$\underline{t}\text{-Bu} \quad 63\%$$

monosubstituted product because the product RCH=CHBr is less reactive than the reactant BrCH=CHBr towards a nucleophilic radical. This is consistent with the reaction results of ClCH=CHCl with _t_-BuHgCl.[30]

C. Conclusion

The photostimulated reactions of dichloromaleic anhydride with alkylmercury chlorides in DMSO led to di-_tert_-butylmaleic anhydride in 27% yield and dicyclohexylmaleic anhydride in 21% yield. The reaction is a free radical reaction occurring via two addition-elimination steps to give the disubstituted product. However, when the reaction was carried out in PhH, the monosubstituted product, chloro-_tert_-butylmaleic anhydride was obtained in 55% yield. In addition, (_E_)-1,2-dibromoethene was found to react photochemically with alkylmercury chloride to lead to the (_E_) and (_Z_) monosubstituted products in good yields.

D. Experimental

1. Photostimulated reaction of t-BuHgCl with dichloromaleic anhydride in DMSO

To a pyrex tube was added dichloromaleic anhydride (0.1 g, 0.6 mmol), _t_-BuHgCl (0.84 g, 2.9 mmol) and DMSO (9 mL). The tube was irradiated with a 275 W sunlamp for 8 h. After irradiation, the mixture was transferred to a separatory funnel and was extracted with ether (2 x 6 mL). Water (10 mL) was added and the mixture of DMSO-water was extracted with hexane (3 x 10 mL). The organic layers were combined and washed with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. After the solvent was evaporated, the white solid which remained was dried under vacuum for 4 h and was identified as di-_tert_-butylmaleic anhydride in 24% yield with mp 80-81 °C (Lit.[83] 88.5-89.5 °C).

^{1}H NMR ($CDCl_3$) δ 1.55 (s).

^{13}C NMR ($CDCl_3$) δ 164.86, 150.53, 34.73, 31.56.

GCMS, _m/e_ (relative intensity) 210 (6.2, M^+), 112 (100), 81 (43), 57 (96), 41 (77).

M.S. Calculated for $C_{12}H_{18}O_3$: 210.12560. Found: 210.12569. Error: +0.6 ppm.

2. Photostimulated reaction of cyclohexylmercury chloride with dichloromaleic anhydride

Dichloromaleic anhydride (0.02 g, 0.11 mmol) and cyclohexylmercury chloride (0.18 g, 0.56 mmol) were dissolved in DMSO (3 mL). The mixture was irradiated with a 275 W sunlamp for 24 h and was transferred into a separatory funnel. Water (8 mL) was added, the mixture was extracted with hexane (3 x 10 mL). The hexane solution was then washed with 5% $Na_2S_2O_3$

solution and dried with $MgSO_4$. After the solvent was removed under a rotary evaporator, GLC analysis of the yellow oil revealed that product, di-cyclohexylmaleic anhydride in 45% yield.

^1H NMR ($CDCl_3$) δ 1.63-1.46 (m).

GCMS, m/e (relative intensity) 262 (24, M^+), 107 (26), 91 (58), 79 (58), 67 (61), 55 (60), 41 (100).

3. Photostimulated reaction of t-BuHgCl with dichloromaleic anhydride in benzene

To a pyrex tube was added dichloromaleic anhydride (0.1 g, 0.6 mmol), t-BuHgCl (0.84 g, 2.9 mmol) and PhH (8 mL). The tube was irradiated with a 275 W sunlamp for 20 h and the white precipitate ($HgCl_2$) was suction filtered and hexane (15 mL) was added to the filtrate. The filtrate was washed with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. After the solvent was evaporated, a residue of yellow adhensive oil and white crystals was identified as the mixture of chloro-tert-butylmaleic anhydride in 55% yield and di-tert-butylmaleic anhydride in 6% yield. The pure chloro-tert-butylmaleic anhydride was obtained in 52% yield by dissolving the mixture in ether (5 mL), followed by cooling in an ice bath to remove the white solid of di-tert-butylmaleic anhydride which has a low solubility in ether.

^{1}H NMR ($CDCl_3$) δ 1.54 (s).

^{13}C NMR ($CDCl_3$) δ 162.92, 161.89, 157.30, 148.52, 34.93, 28.51.

GCMS, m/e (relative intensity) 188 (0.1, M^+), 129 (63), 81 (100), 65 (58), 57 (13), 41 (47).

M.S. Calculated for $C_8H_9O_3Cl$: 188.02403. Found: 188.02392. Error: -0.6 ppm.

4. Photostimulated reaction of t-BuHgCl with 1,2-dibromoethene

A pyrex tube containing (E)-1,2-dibromoethene (0.05 g, 0.26 mmol), t-BuHgCl (0.08 g, 0.26 mmol) and DMSO (2 mL) was irradiated with a 275 W sunlamp for 24 h. The reaction mixture was transferred to a separatory funnel and water (5-8 mL) was added. The mixture was extracted with ether (3 x 8 mL). The ether layer was washed with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. After the solvent was evaporated, GLC analysis of the remained liquid revealed the products as (E) and (Z)-1-bromo-2-tert-butylethene in 63% yield.

GCMS of one isomer (E or Z), m/e (relative intensity) 162 (8, M^+), 147 (24), 83 (100), 67 (86), 55 (96).

GCMS of another isomer (Z or E), m/e (relative intensity) 162 (2, M^+), 83 (100), 55 (97), 41 (90).

5. Photostimulated reaction of cyclohexylmercury chloride with 1,2-dibromoethene

Cyclohexylmercury chloride (0.04 g, 0.13 mmol) and (*E*)-1,2-dibromoethene (0.025 g, 0.13 mmol) were dissolved in DMSO (2 mL). The mixture was irradiated with a 275 W sunlamp for 24 h. Then, water (8 mL) was added, the mixture was extracted with ether (3 x 8 mL). The ether layer was washed with 5% $Na_2S_2O_3$ solution and dried over $MgSO_4$. After evaporating the solvent, the remained liquid was identified as the mixture of (*E*) and (*Z*)-1-bromo-2-cyclohexylethene in 45% yield.

GCMS of one isomer (*E* or *Z*), *m*/*e* (relative intensity) 188 (1, M^+), 109 (53), 82 (13), 67 (100).

GCMS of another isomer (*Z* or *E*), *m*/*e* (relative intensity) 188 (1, M^+), 109 (56), 82 (13), 67 (100).

V. PHOTOSTIMULATED REACTIONS OF DIALKYLMERCURIALS WITH ALKENES AND ALKYNES

A. Introduction

Dialkylmercurials (R_2Hg, R = Et, i-Pr, n-Bu, $PhCH_2$ and p-$CH_3C_6H_4CH_2$) have been found to thermally react with tetracyanoethylene (TCNE) to lead to the 1:1 addition products (see Part I, A).[23-26] Blaukat and Neumann[26,27] reported that at room temperature or at 0 °C, di-tert-butylmercury can add to some electron-deficient alkynes to form adducts containing the t-BuHg- group which were protodemercurated with HCl/EtOH to give the corresponding olefins (see Part II, A).

The work presented in this part concerns the photochemical behavior of dialkylmercurials (R_2Hg, R = t-Bu, i-Pr) towards several alkenes and a few alkynes.

B. Results and Discussion

1. Photostimulated reactions of dialkylmercurials with 2-chloroacrylonitrile

The reactions of dialkylmercurials with 2-chloroacrylonitrile were carried out under the irradiation of a 275 W sunlamp. The reactions occurred readily by forming mercury metal and some gray precipitate after irradiation for 10-30 min and gave two products which were identified as the alkylmercury chloride and the coupled olefin as shown in Eq. 56. The

$$R_2Hg + CH_2{=}C(Cl)CN \xrightarrow{h\nu} RCH_2(NC)C{=}C(CN)CH_2R + RHgCl \quad (56)$$

$$R = \underline{t}\text{-Bu, } 27\%$$

$$\underline{i}\text{-Pr, } 17\%$$

coupled olefin with R = t-Bu was isolated by column chromatography and the structure assigned on the basis of the high resolution mass spectrum and the NMR spectra. The (E) and (Z)-coupled olefins with one isomer predominating in over 70% were obtained from the reaction of $\underline{t}$-Bu_2Hg with $CH_2{=}C(Cl)CN$. A mixture of (E) and (Z)-coupled olefins was also obtained from the reaction of $\underline{i}$-Pr_2Hg with $CH_2{=}C(Cl)CN$. The alkylmercury chlorides obtained in the reactions were identified by the melting points and the ^1H NMR spectra.

It is known that dialkylmercurials can be cleaved by vicinal dihalides. Thus, the pair of diastereomeric 2,3-dibromobutanes reacted with di-n-propylmercury at 80 °C to give (E) and (Z)-2-butenes (Eq. 57).[84]

$$CH_3CHBrCHBrCH_3 + \underline{n}\text{-}Pr_2Hg \xrightarrow[2h]{80\ ^\circ C} CH_3CH{=}CHCH_3 + \underline{n}\text{-}PrHgBr$$

$$+ \underline{n}\text{-}PrBr \quad (57)$$

To test this reaction, the reactions of di-i-propylmercury with ethyl 2,3-dichloropropiolate and 1,2-dibromo-1-phenylethane were carried out. The solid products obtained from the reactions were separated and identified as *i*-PrHgCl and *i*-PrHgBr, respectively. Therefore, a reaction mechanism

$$CH_2ClCHClCO_2Et + \underline{i}\text{-}Pr_2Hg \xrightarrow[PhH]{h\nu} \underline{i}\text{-}PrHgCl + CH_2{=}CHCO_2Et \tag{58}$$

$$PhCHBrCH_2Br + \underline{i}\text{-}Pr_2Hg \xrightarrow[PhH]{h\nu} \underline{i}\text{-}PrHgBr + CH_2{=}CHPh \tag{59}$$

is proposed for the reaction of dialkylmercurials with 2-chloroacrylonitrile as shown in Scheme 18. An alkyl radical

<u>Scheme 18</u>

$$RHgR \xrightarrow{h\nu} R\cdot + \cdot HgR$$

$$\cdot HgR \longrightarrow R\cdot + Hg^\circ$$

$$R\cdot + CH_2{=}C(Cl)CN \longrightarrow \underset{\mathbf{32}}{RCH_2\dot{C}(Cl)CN}$$

$$2\ \mathbf{32} \longrightarrow \underset{\mathbf{33}}{RCH_2C(CN)ClC(CN)ClCH_2R}$$

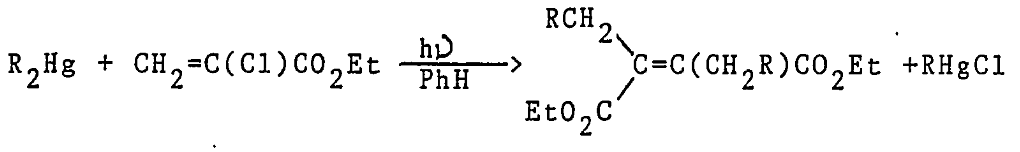
$$\mathbf{33} + RHgR \longrightarrow \underset{\mathbf{34}}{RCH_2(NC)C{=}C(CN)CH_2R} + RHgCl + RCl$$

generated from dialkylmercurial adds to the less substituted side of 2-chloroacrylonitrile to form **32**. The coupling of the two of the radical **32** leads to **33** which reacts further with

R_2Hg to give the olefin **34**, alkylmercury chloride and alkyl chloride. The alkylchloride was not observed by GLC analysis of the reaction mixtures after work-up possibly because of its low boiling point.

2. Photostimulated reactions of dialkylmercurials with ethyl 2-chloroacrylate

The reactions of dialkylmercurials with ethyl 2-chloroacrylate were carried out under similar condition to the reactions of dialkylmercurials with 2-chloroacrylonitrile. As expected, the reactions led to the coupled olefins and the corresponding alkylmercury chlorides (Eq. 60). The reaction



$$R_2Hg + CH_2{=}C(Cl)CO_2Et \xrightarrow[PhH]{h\nu} \begin{matrix} RCH_2 \\ EtO_2C \end{matrix}\!\!>\!C{=}C(CH_2R)CO_2Et + RHgCl \quad (60)$$

R = *t*-Bu, 14%
i-Pr, 9%

is believed to occur by the same pathway as proposed in Scheme 18. The low yields of the coupled olefins probably are due to the inefficiency of the coupling reaction of the radical intermediate ($RCH_2\dot{C}(Cl)CO_2Et$), because of the steric hindrance of the carboethoxy group.

The reactions of dialkylmercurials with 1,1-dichloroethene led to complicated results. Besides the formation of the alkylmercury chloride, only a trace amount of the coupled olefin, $RCH_2(Cl)C=C(Cl)CH_2R$, was observed in the reaction and four other unidentified products in major amounts were formed in the reaction.

3. Photostimulated reactions of dialkylmercurials with diethyl vinylphosphonate (VP)

The photostimulated reactions of dialkylmercurials with VP gave the corresponding addition products as shown in Eq. 61 and Table 33. As to the products obtained from the reaction of t-Bu_2Hg with VP, there was not much difference between this reaction and the reaction of t-BuHgCl with VP (see Table 1) except the 20% of t-$BuCH_2CH_2P$ was formed when the reaction was worked up by iodine cleavage. Furthermore, t-$BuCH_2CH_2P$ was formed in good yield in the absence of $NaBH_4$ reduction. The reaction of i-Pr_2Hg with VP was different from the reaction of i-PrHgCl with VP. This reaction not only led to the addition product, but also led to another product i-$PrCH_2CH$(i-Pr)P. Thus, these reactions may undergo

$$R_2Hg + CH_2{=}CHP \xrightarrow{h\nu} RCH_2CH_2P + RCH_2CH(R)P \qquad (61)$$

$P = P(O)(OEt)_2$.

Table 33. Reactions of dialkylmercurials with VP

R	Ratio of R_2Hg/VP	Concn. of [VP] (*M*)	Condition	Work-up with	Products[a]	% Yield
t-Bu	3	0.06	UV 18h	$Na_2S_2O_3$	*t*-BuCH$_2$CH$_2$P	55
t-Bu	3	0.05	UV 18h	I_2^b	*t*-BuCH$_2$CH$_2$P	21
					t-BuCH$_2$CH(I)P	35
i-Pr	2	0.06	SL 17h	$Na_2S_2O_3$	*i*-PrCH$_2$CH$_2$P	42
					i-PrCH$_2$CH(*i*-Pr)P	7[c]
i-Pr	2	0.06	SL 3h	$Na_2S_2O_3$	*i*-PrCH$_2$CH$_2$P	28
					i-PrCH$_2$CH(*i*-Pr)P	7[d]
i-Pr	2	0.06	SL 3h (with 10 mol% of DTBN)	$Na_2S_2O_3$	*i*-PrCH$_2$CH$_2$P	3

[a] P = P(O)(OEt)$_2$.

[b] Ratio of I_2 / R_2Hg = 2.5 was employed.

[c] 5% of *i*-PrCH$_2$CH(HgPr-*i*)P was formed.

[d] 3% of *i*-PrCH$_2$CH(HgPr-*i*)P was observed.

the reaction process as shown in Scheme 19. The reaction is

Scheme 19

$$R_2Hg \xrightarrow{h\nu} R\cdot + \cdot HgR$$

$$\cdot HgR \longrightarrow R\cdot + Hg^\circ$$

$$R\cdot + CH_2{=}CHP \longrightarrow RCH_2\dot{C}HP$$

$$RCH_2\dot{C}HP + R_2Hg \longrightarrow \underset{\mathbf{35}}{RCH_2CH(HgR)P} + R\cdot$$

$$\mathbf{35} \longrightarrow RCH_2CH_2P + Hg^\circ + \text{alkene}$$

$$\mathbf{35} \longrightarrow RCH_2CH(R)P + Hg^\circ$$

$$\mathbf{35} \xrightarrow{I_2} RCH_2CH(I)P + RI + HgI_2$$

$P = P(O)(OEt)_2$. alkene = $Me_2C{=}CH_2$, $CH_3CH{=}CH_2$.

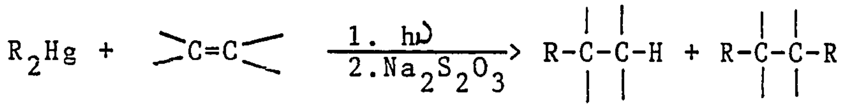
a free radical chain process since the reaction was inhibited by the presence of 10 mol% of DTBN. Unlike the intermediate ($RCH_2CH(HgCl)P$) in the reactions of RHgCl with VP, the intermediate **35** formed in these reactions is not stable and undergoes decomposition to give the products of RCH_2CH_2P and RCH_2-$CH(R)P$ before the reaction is worked up. Thus, when the reaction of _t_-Bu_2Hg with VP was worked up with iodine, only 35% of intermediate **35** was converted to the iodide (based on starting VP) and about 20% of **35** had decomposed to give _t_-$BuCH_2CH_2P$. The product _t_-$BuCH_2CH$(_t_-Bu)P was not observed in the reaction probably due to the strong tendency for the formation of the olefin, $Me_2C=CH_2$, from the dehydrogenation of the *tert*-butyl radical. Another process which may be occurring in these reactions is hydrogen atom transfer from R_2Hg to the adduct radical, $RCH_2\dot{C}HP$ (Eq. 62). There was no

$$RCH_2\dot{C}HP + R_2Hg \longrightarrow RCH_2CH_2P + \text{alkene} + RHg\cdot \qquad (62)$$

evidence for such a hydrogen atom transfer in the reaction of RHgCl with VP discussed in Part I.

4. Photostimulated reactions of dialkylmercurials with other alkenes

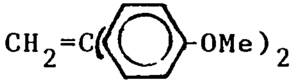
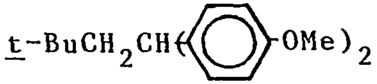
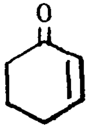
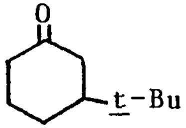
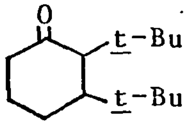
Dialkylmercurials were reacted with some other alkenes either in a Rayonet Photoreactor at 350 nm or with the irradiation of a 275 W sunlamp. Work-up with $Na_2S_2O_3$ solution gave the corresponding addition products (Eq. 63). The reaction results are given in Table 34. Similar to the previous



$$R_2Hg + {>}C{=}C{<} \xrightarrow[2.\,Na_2S_2O_3]{1.\ h\nu} R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R \qquad (63)$$

reactions in Section 3, the reactions of R_2Hg with alkenes led to more than one addition product. Besides the product $R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$, another product $R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R$ was also formed particularly in the reactions of *i*-Pr_2Hg with alkenes.

Table 34. Reactions of dialkylmercurials with alkenes

R(equiv.)	Alkenes	Concn. of [Alkene]	Condition	Products	% Yield
t-Bu (1)	$CH_2=CHCO_2Et$	0.18 M	PhH UV 8h	t-$BuCH_2CH_2CO_2Et$	18[a]
				t-$BuCH_2CH($t-$Bu)CO_2Et$	5
t-Bu (2)	$CH_2=CHSPh$	0.12 M	PhH UV 18h	t-$BuCH_2CH_2SPh$	17[b]
				t-$BuCH=CHSPh$	15
t-Bu (3)		0.01 M	PhH/hexane (50%:50%) SL 8.5h		90
t-Bu (3)		0.05 M	PhH SL 6h		35[c]
					6

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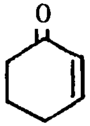
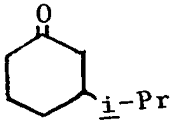
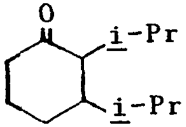
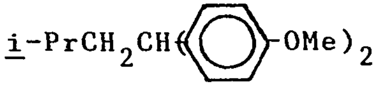
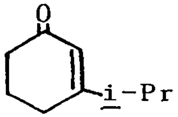
[a] 7% of t-$BuCH_2CH(CO_2Et)CH_2CH_2CO_2Et$ was formed.

[b] 25% of t-$BuCH_2CH(SPh)CH(SPh)CH_2Bu$-t was formed.

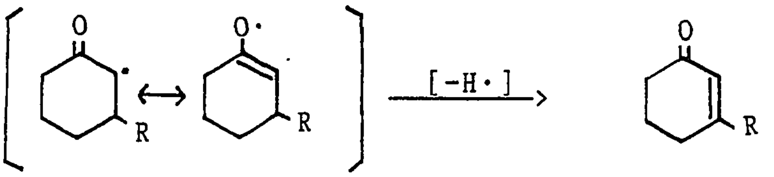
[c] 26% of  was formed.

Table 34. (Continued)

R(equiv.)	Alkenes	Concn. of [Alkene]	Condition	Products	% Yield
i-Pr (2)		0.07 *M*	DMSO/PhH (66%:34%) SL 17h	 	31[d] 9
i-Pr (2)	$CH_2=CHSiPh_3$	0.035 *M*	DMSO/PhH (50%:50%) SL 24h	*i*-Pr$CH_2CH_2SiPh_3$ *i*-Pr$CH=CHSiPh_3$ *i*-PrCH_2CH(*i*-Pr)$SiPh_3$	40 18 10
i-Pr (2)		0.06 *M*	DMSO/PhH (50%:50%) SL 18h		44
i-Pr (2)	$CH_2=CPh_2$	0.08 *M*	DMSO/PhH (50%:50%) SL 20h	*i*-PrCH_2CHPh_2 *i*-Pr$CH=CPh_2$ *i*-PrCH_2C(*i*-Pr)Ph_2	30 18 12

[d] 15% of  was formed.

Only one product was obtained in a good yield from the reaction of R_2Hg with 1,1-di-(p-anisyl)ethylene indicating that the radical intermediate, $RCH_2\dot{C}(C_6H_4\text{-OMe-}p)_2$, with the large steric hindrance from the two substituted phenyl groups, completely avoided the coupling reaction with the alkyl radical. The reactions of R_2Hg with 2-cyclohexen-1-one gave two addition products and one substituted olefin which was formed by the dehydrogenation of the intermediate 36.

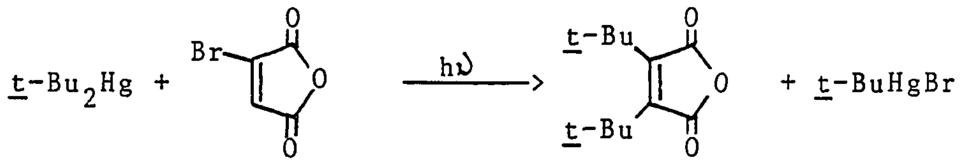


36

(64)

5. Photostimulated reaction of di-tert-butylmercury with bromomaleic anhydride

A mixture of t-Bu_2Hg and bromomaleic anhydride in the solvent of PhH/DMSO (66%:34%) was irradiated with a 275 W sunlamp for 12 h to give a 38% yield of di-tert-butylmaleic anhydride and tert-butylmercury bromide (Eq.65). The reaction

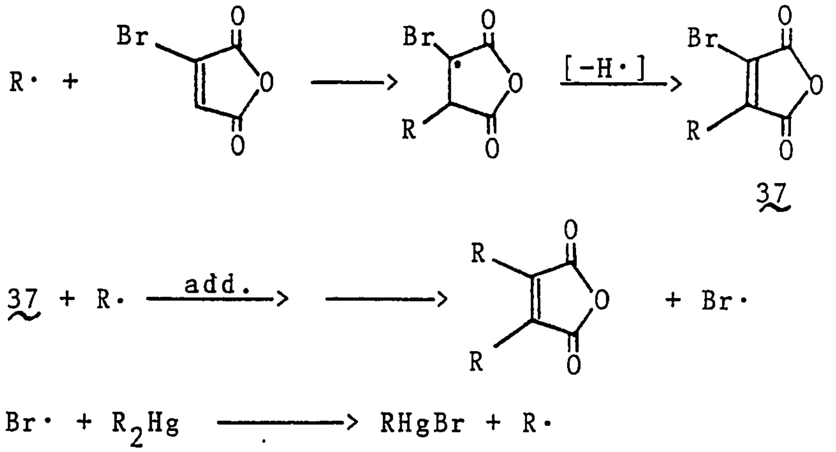


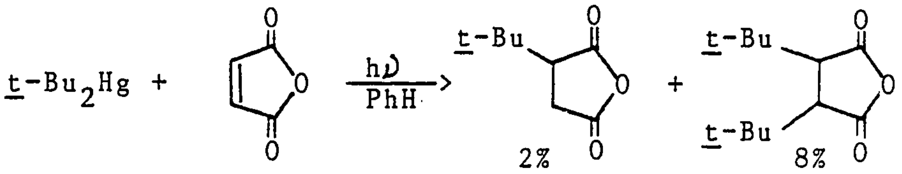
(65)

occurred smoothly and even when irradiated for only 2 h, about

8% of the disubstituted maleic anhydride was observed. The mechanism for this reaction is not clear. The reaction might undergo the process shown in Scheme 20, which is similar to the mechanism proposed for the reaction of t-BuHgCl with dichloromaleic anhydride (in Scheme 16). However, t-Bu_2Hg when reacted with maleic anhydride led to only a trace amount of the addition product and 8% of monoaddition product. This result indicates that the substituent bromine on the maleic anhydride made bromomaleic anhydride more reactive than maleic anhydride towards the nucleophilic tert-butyl radical. Furthermore, the formation of the disubstituted product cannot

Scheme 20

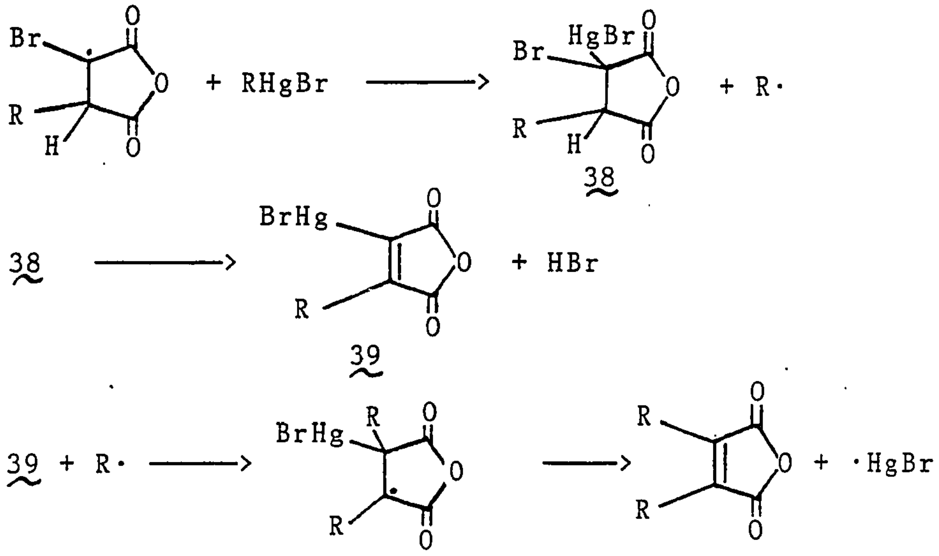




(66)

be occurring via the intermediacy of the tert-butylmaleic anhydride. The formation of the disubstituted maleic anhydride as the only product from the reaction of R_2Hg with halomaleic anhydride may be connected with the formation of the alkylmercury halide (compare Reactions 65 and 66). One possible pathway is shown in Scheme 21.

Scheme 21

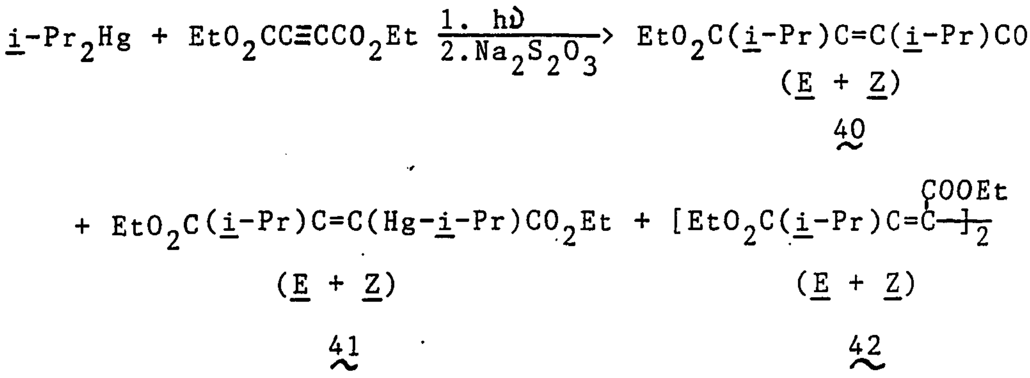


$$HBr + R_2Hg \longrightarrow RHgBr + RH$$

$$\cdot HgBr + R_2Hg \longrightarrow RHgBr + Hg^\circ + R\cdot$$

6. Photostimulated reactions of dialkylmercurials with alkynes

Di-isopropylmercurial reacted with diethyl dicarboxylacetylene to lead to three products (Eq. 67). To examine the



$$\underline{i}\text{-}Pr_2Hg + EtO_2CC{\equiv}CCO_2Et \xrightarrow[2.\,Na_2S_2O_3]{1.\ h\nu} \underset{\underset{\mathbf{40}}{(\underline{E} + \underline{Z})}}{EtO_2C(\underline{i}\text{-}Pr)C{=}C(\underline{i}\text{-}Pr)CO_2Et}$$

$$+ \underset{\underset{\mathbf{41}}{(\underline{E} + \underline{Z})}}{EtO_2C(\underline{i}\text{-}Pr)C{=}C(Hg\text{-}\underline{i}\text{-}Pr)CO_2Et} + \underset{\underset{\mathbf{42}}{(\underline{E} + \underline{Z})}}{[EtO_2C(\underline{i}\text{-}Pr)C{=}\overset{COOEt}{\overset{|}{C}}\text{-}]_2} \quad (67)$$

reaction process, several reactions under the different conditions were carried out and the results are arranged in Table 35. The reaction failed to occur in the dark and was significantly retarded by the presence of 10 mol% of DTBN. This indicates that the reaction is a free radical chain process. Based on the results listed in Table 35, the reaction is believed to undergo the reaction process shown in Scheme 22.

Scheme 22 (R = $\underline{i}$-Pr, E = CO_2Et)

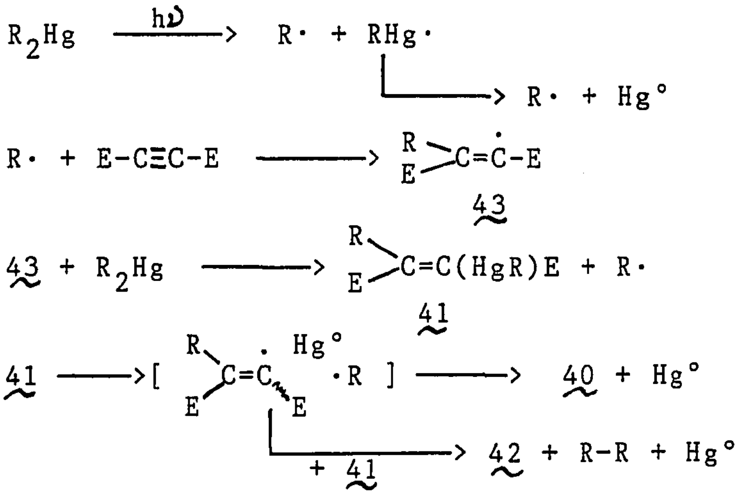


Table 35. Reactions of *i*-Pr_2Hg with $EtO_2CC\equiv CCO_2Et$[a]

$$\textit{i}\text{-Pr}_2\text{Hg} + \text{EtO}_2\text{CC}\equiv\text{CCO}_2\text{Et} \xrightarrow[2.\,\text{Na}_2\text{S}_2\text{O}_3]{1.\ h\nu} \mathbf{40} + \mathbf{41} + \mathbf{42}$$

No.	Reaction condition	% Yield (*E* + *Z*)[b]		
		40	**41**	**42**
1	SL 2h	11	70	3
2	SL 7h	15	68	12
3	SL 18h	41	35	19
4	SL 24h	50	11	26
5	SL 60h	59	4	32
6	SL 7h (with 10 mol% DTBN)	0	7	0
7	Dark 12h	0	6	0
8	Heat at 100-110 °C for 24h	17	20	10

[a] All the reactions carried out with the initial concentration of alkyne as 0.11 *M* in the solvent of DMSO/PhH (1:1).

[b] GLC relative yields based on the peak areas only.

In Scheme 22, an alkyl radical adds to the alkyne to form the vinylic radical **43** which reacts with R_2Hg to give 1:1 addition product **41**, which is consistent with the literature results.[26] With irradiation, **41** undergoes decomposition to give the products **40** (possibly via a radical cage process). Thus, as the irradiation time increased, the amount of **41** decreased and the yields of **40** and **42** increased (see entries 2 and 4 in Table 35).

However, the reactions of di-*tert*-butylmercurial with phenylethynyl phenyl sulfone and 2,2-diphenylethenyl phenyl sulfone gave the substituted products (Eqs. 68 and 69). These

$$\underline{t}\text{-}Bu_2Hg + PhC{\equiv}CSO_2Ph \xrightarrow[2\ h]{UV} PhC{\equiv}C\text{-}\underline{t}\text{-}Bu \quad (84\%) \qquad (68)$$

$$\underline{t}\text{-}Bu_2Hg + Ph_2C{=}CHSO_2Ph \xrightarrow[2\ h]{UV} Ph_2C{=}CH\text{-}\underline{t}\text{-}Bu \quad (88\%) \qquad (69)$$

reactions undergo an addition-elimination process due to the existence of the good leaving group of SO_2Ph.[30,31]

C. Conclusion

Dialkylmercurials have been found to react with 2-chloroacrylonitrile and ethyl 2-chloroacrylate to give the coupled olefins, $RCH_2(Q)C{=}C(Q)CH_2R$ (R = *t*-Bu, *i*-Pr; Q = CN, CO_2Et), and the alkylmercury chloride. The reaction undergoes a process involved a coupling reaction of the radical intermediate

32, $RCH_2\dot{C}(Cl)Q$.[26] Di-*tert*-butylmaleic anhydride was obtained in 38% yield from the reaction of *t*-Bu_2Hg with bromomaleic anhydride while a trace amount of the diaddition product was obtained from the reaction of *t*-Bu_2Hg with maleic anhydride. 3-*tert*-Butylcyclohexanone, 1,1'-di(*p*-anisyl)-3,3-dimethylbutane and several addition products were obtained from the reaction of dialkylmercurial with other alkenes. The reactions undergo a radical process which is somewhat different from the reactions of RHgCl with the same olefins as shown in Scheme 19. Di-isopropylmercury reacted with alkyne, $EtO_2CC{\equiv}CCO_2Et$, to give three addition products. The reaction is a free radical chain process involving the formation of the 1:1 adduct **41**.

D. Experimental

1. General consideration

Di-*tert*-butylmercury was synthesized from the reaction of $HgCl_2$ with an excess *t*-BuMgCl according to the literature procedure (mp 52-55 °C, Lit.[85] 58-60 °C). Due to its instability, it must be stored in a freezer. Di-isopropylmercury, a colorless liquid with bp 49 °C/5 mmHg, was prepared in 64% yield by the method reported by Cowan and Mosher.[86] Ethyl 2-chloroacrylate was prepared according to the procedure described in the literature (bp 42-45 °C/17 mmHg, Lit.[87] 51-53 °C/18 mmHg). Bromomaleic anhydride and other olefins were purchased from Aldrich Chem. Co. and used without further purification. Except the isolated yields, all the yields were determined by GLC without the correction factors.

2. Reaction of t-Bu_2Hg with 2-chloroacrylonitrile

To a pyrex tube containing t-Bu_2Hg (0.28 g, 0.88 mmol), PhH (2 mL) and hexane (3 mL) was added 2-chloroacrylonitrile (0.04 g, 0.44 mmol). The tube was irradiated with a 275 W sunlamp for 5 h. After the reaction, the mercury metal was separated and hexane (10 mL) was added to the yellow solution. The solution was washed once with 0.1 M HCl (8 mL), twice with water and dried over $MgSO_4$. After evaporating the solvent, the residue was identified as a mixture of t-BuHgCl and the olefin coupling product. The t-BuHgCl (mp 120-124 °C, ^1H NMR ($CDCl_3$) δ 1.45) was removed from the mixture by crystallization with hexane (3 x 5 mL). The coupled olefins, (E) and (Z)-4,5-dicyano-2,2,7,7-tetramethyl-4-octene, were isolated in 20% yield by flash column chromatography with the eluent of ether.

^1H NMR ($CDCl_3$) δ 2.55-2.51 (s, 4H), 1.10-1.06 (s, 18H).

^{13}C NMR ($CDCl_3$) δ 129.19, 128.33, 117.17, 113.17, 47.73, 34.01, 29.57.

GCMS, m/e (relative intensity) 218 (0.12, M^+), 147 (4), 105 (3), 58 (5), 57 (100).

M.S. Calculated for $C_{14}H_{22}N_2$: 218.17830. Found: 218.17778. Error: +2.4 ppm.

3. Reaction of i-Pr_2Hg with 2-chloroacrylonitrile

A pyrex tube containing *i*-Pr_2Hg (0.13 g, 0.46 mmol), 2-chloroacrylonitrile (0.04 g, 0.46 mmol), hexane (1 mL) and PhH (2 mL) was irradiated with a 275 W sunlamp for 22 h. After the reaction, mercury metal was separated and hexane (10 mL) was added to the yellow solution. The solution was washed once with 0.1 *M* HCl, twice with 5% $Na_2S_2O_3$ solution and dried with $MgSO_4$. After evaporating the solvent, a white precipitate (*i*-PrHgCl) and a yellow residue remained. *i*-PrHgCl (mp 92-93 °C, ^1H NMR ($CDCl_3$) δ 2.65 (h, 1H), 1.54 (d, 6H), ^{13}C NMR ($CDCl_3$) δ 23.86, 43.04) was removed by the crystallization with hexane (3 x 6 mL). The yellow residue was identified as (*E*) and (*Z*)-4,5-dicyano-2,7-dimethyl-4-octene in 17% yield.

GCMS, *m/e* (relative intensity) 190 (3, M^+), 148 (27), 133 (68), 105 (74), 103 (11), 43 (100), 41 (50).

4. Reaction of t-Bu_2Hg with ethyl 2-chloroacrylate

The mixture of *t*-Bu_2Hg (0.2 g, 0.99 mmol), CH_2=C(Cl)CO_2Et (0.05 g, 0.33 mmol) and PhH (4 mL) was irradiated with a 275

W sunlamp for 5 h. The mercury and gray precipitate were separated and hexane (8 mL) was added to the solution. The solution was washed with 5% $Na_2S_2O_3$ solution (3 x 20 mL) and dried over $MgSO_4$. t-BuHgCl (mp 116-119 °C) was separated from the residue by crystallization from pentane (3 x 6 mL). The residue was identified as the mixture of (E) and (Z)-diethyl 1,2-dineopentyl-ethenyldicarboxylate in 14% yield.

^1H NMR ($CDCl_3$) δ 4.37-4.11 (q, 4H), 2.28-2.25 (s, 4H), 1.31-1.25 (t, 6H), 1.10 (s, 18H).

^{13}C NMR ($CDCl_3$) δ 168.36, 167.97, 128.76, 127.58, 65.55, 47.80, 31.80, 30.69, 15.20.

GCMS, m/e (relative intensity) 312 (0.7, M^+), 192 (35), 137 (17), 135 (56), 57 (100).

5. Reaction of i-Pr_2Hg with ethyl 2-chloroacrylate

A pyrex tube containing i-Pr_2Hg (0.14 g, 0.5 mmol), $CH_2=C(Cl)CO_2Et$ (0.04 g, 0.25 mmol) and PhH (2.5 mL) was irradiated with sunlamp for 17 h. The mercury metal was separated and ether (10 mL) was added to the yellow solution. The solution was washed twice with 5% $Na_2S_2O_3$ solution and dried with $MgSO_4$. After evaporating the solvent, i-PrHgCl and a yellow residue remained. i-PrHgCl was removed from the mixture by the crystallization from pentane (3 x 6 mL) and the yellow liquid was identified as the mixture of (E) and (Z)-

diethyl 1,2-diisobutyl-ethenyldicarboxylate in 10% yield. GCMS, *m/e* (relative intensity) 284 (2, M^+), 273 (25), 178 (59), 177 (24), 137 (29), 135 (100), 107 (36), 95 (21).

6. Reaction of t-Bu_2Hg with ethyl acrylate

A pyrex tube containing *t*-Bu_2Hg (0.2 g, 0.7 mmol), ethyl acrylate (0.07 g, 0.7 mmol) and PhH (4 mL) was irradiated in a Rayonet Photoreactor for 8 h. Then ether (15 mL) was added and the solution was washed with 5% $Na_2S_2O_3$ (3 x 18 mL) and dried over $MgSO_4$. After evaporating the solvent, the concentrated liquid was analyzed as ethyl 4,4-dimethylpentanonate in 18% yield, ethyl 4,4-dimethyl-2-*tert*-butylpentanonate in 5% and diethyl 2-neopentylpentane-1,5-dionate in 7% yield. GCMS of ethyl 4,4-dimethylpentanonate, *m/e* (relative intensity) 158 (0.06, M^+), 113 (28), 97 (42), 69 (56), 57 (100). GCMS of *t*-$BuCH_2CH$(*t*-Bu)CO_2Et, *m/e* (relative intensity) 214 (3, M^+), 155 (51), 128 (69), 57 (100), 55 (64).
GCMS of *t*-$BuCH_2CH(CO_2Et)CH_2CH_2CO_2Et$, *m/e* (relative intensity) 258 (1, M^+), 158 (29), 157 (53), 101 (100), 57 (71).

7. Reaction of t-Bu_2Hg with 1,1-di(p-anisyl)ethylene

1,1-Di(*p*-anisyl)ethylene (0.01 g, 0.04 mmol) and *t*-Bu_2Hg (0.04 g, 0.12 mmol) were dissolved in PhH (1.5 mL) and hexane (1.5 mL). The mixture was irradiated with a sunlamp for 8.5

h. The mercury metal was separated and hexane (10 mL) was added. The solution was washed with 5% $Na_2S_2O_3$ (3 x 15 mL) and dried over $MgSO_4$. After evaporating the solvent, GLC analysis of the remained liquid revealed 90% yield of addition product 1,1-di(p-anisyl)-3,3-dimethylbutane.

GCMS, m/e (relative intensity) 298 (4, M^+), 296 (3), 228 (17), 227 (100), 135 (25), 57 (4).

8. Reaction of t-BuHgBu-t with 2-cyclohexen-1-one

A pyrex tube containing t-Bu_2Hg (0.6 g, 1.8 mmol), 2-cyclohexen-1-one (0.06 g, 0.6 mmol) and PhH (3 mL) was irradiated with a 275 W sunlamp for 6 h. The mercury metal was separated and the solvent was evaporated under a rotatory evaporator. The yellow-orange oil which remained was analyzed as a mixture of 3-tert-butylcyclohexanone in 35% yield, 3-tert-butyl-2-cyclohexen-1-one in 26% and 2,3-di-tert-butylcyclohexanone in 6% yields.

GCMS of 3-tert-butylcyclohexanone, m/e (relative intensity) 154 (15, M^+), 98 (78), 83 (26), 57 (100).

GCMS of 3-tert-butyl-2-cyclohexen-1-one, m/e (relative intensity) 152 (62, M^+), 137 (71), 109 (57), 95 (78), 81 (55), 44 (91), 41 (100).

GCMS of 2,3-di-tert-butylcyclohexanone, m/e (relative intensity) 210 (0.2, M^+), 97 (100), 57 (11), 41 (12).

9. General procedure for the reactions of i-PrHgPr-i with alkenes

A pyrex tube containing *i*-Pr_2Hg, alkene and solvent (PhH and DMSO) was irradiated with a 275 W sunlamp. After irradiation, mercury metal was separated and the liquid was transferred to a separatory funnel. Water (5 mL) was added and the mixture was extracted with PhH (6 mL) and with ether (2 x 8 mL). The organic layers were combined and washed with 5% $Na_2S_2O_3$ (3 x 8 mL) and dried with $MgSO_4$. After evaporating the solvent, the concentrated liquid was analyzed by GLC and GCMS.

10. Reaction of i-Pr_2Hg with 2-cyclohexen-1-one

To a pyrex tube was added *i*-Pr_2Hg (0.12 g, 0.42 mmol), 2-cyclohexen-1-one (0.02 g, 0.21 mmol), DMSO (2 mL) and PhH (1 mL). The tube was irradiated with a sunlamp for 17 h and the mixture was worked up according to the general procedure. After removing the solvents, the residue was identified as 3-*i*-propylcyclohexanone in 31% yield, 3-*i*-propyl-2-cyclohexen-1-one in 15% and 2,3-di-*i*-propylcyclohexanone in 9% yields.
GCMS of 3-*i*-propylcyclohexanone, *m*/*e* (relative intensity) 140 (17, M^+), 97 (100), 82 (21), 69 (56), 55 (78).
GCMS of 3-*i*-propyl-2-cyclohexen-1-one, *m*/*e* (relative intensity) 138 (35, M^+), 110 (80), 95 (100), 67 (74).

GCMS of 2,3-di-*i*-propylcyclohexanone, *m*/*e* (relative intensity) 182 (2, M^+), 139 (11), 97 (100), 55 (12).

11. Reaction of i-Pr_2Hg with triphenylvinylsilane

The mixture of *i*-Pr_2Hg (40 mg, 0.14 mmol), CH_2=$CHSiPh_3$ (20 mg, 0.07 mmol), DMSO (1 mL) and PhH (1 mL) was irradiated under a sunlamp for 24 h. The mixture was then worked up by the general procedure. After evaporating the solvents, GLC analysis of the residue revealed 40% yield of (3-methylbutyl) triphenylsilane, 18% yield of (3-methyl-1-butenyl)triphenylsilane and 10% yield of (2,6-dimethyl-3-hexyl)triphenylsilane.

GCMS of *i*-$PrCH_2CH_2SiPh_3$, *m*/*e* (relative intensity) 330 (0.01, M^+), 259 (100), 252 (21), 181 (29), 105 (34).

GCMS of *i*-PrCH=$CHSiPh_3$, *m*/*e* (relative intensity) 328 (8, M^+), 285 (31), 183 (100), 181 (55), 105 (75).

GCMS of *i*-$PrCH_2CH$(*i*-Pr)$SiPh_3$, *m*/*e* (relative intensity) 372 (5, M^+), 294 (78), 259 (100), 181 (50), 105 (40).

12. Reaction of i-Pr_2Hg with 1,1-di(p-anisyl)ethylene

To a pyrex tube was added *i*-Pr_2Hg (0.07 g, 0.24 mmol), 1,1-di(*p*-anisyl)ethylene (30 mg, 0.12 mmol) and the solvents of DMSO (1 mL) and PhH (1 mL). The mixture was irradiated with a sunlamp for 18 h and was worked up according to the general procedure. After evaporating the solvent, the addition product, 1,1-di(*p*-anisyl)-3-methylbutane, was identified in 44% yield by GLC.

GCMS, *m/e* (relative intensity) 284 (8, M^+), 228 (16), 227 (100), 153 (4), 114 (14).

13. Reaction of t-Bu_2Hg with bromomaleic anhydride

To a pyrex tube containing bromomaleic anhydride (0.04 g, 0.22 mmol), PhH (2.5 mL) and DMSO (0.5 mL) was added *t*-Bu_2Hg (0.17 g, 0.55 mmol). The reaction tube was irradiated under a sunlamp for 12 h. The mercury metal was separated and the water (6 mL) was added to the mixture. The mixture was separated and aqueous layer was extracted with hexane (2 x 8 mL). The organic layers were combined and dried with $MgSO_4$. After the solvent was removed, the residue was identified as di-*tert*-butylmaleic anhydride by GLC. The retention time was the same as that of the previously isolated sample (Part IV).

14. General procedure for the reaction of i-PrHgPr-i with diethyl dicarboxylacetylene (Table 35)

Di-isopropylmercury (0.06 g, 0.22 mmol), diethyl dicarboxylacetylene (0.02 g, 0.11 mmol), DMSO (1 mL) and PhH (1 mL) were placed in a pyrex tube. The tube was irradiated with a sunlamp (275 W). After irradiation, mercury metal was separated and water (3 mL) was added to the mixture, and the solution was extracted with ether (3 x 10 mL). The organic layers were combined, washed with a 5% $Na_2S_2O_3$ solution (2 x 15 mL) and dried over $MgSO_4$. After the solvent was evaporated, the products, (*E*) and (*Z*)-diethyl 1,2-diisopropylethenyl-1,2-dicarboxylate (**40**), (*E*) and (*Z*)-1,2-dicarboethoxyl-3-methyl-1-butenyl-(isopropyl)mercury (**41**) and tetraethyl-1,4-diisopropyl-1,2,3,4-butadienetetracarboxylate (**42**) were identified by GLC and GCMS.

GCMS of **40**, *m*/*e* (relative intensity) 256 (2, M^+), 211 (43), 210 (49), 183 (100), 109 (59), 87 (51), 59 (34).

GCMS of **41**, *m*/*e* (relative intensity) 458 (0.2, M^+), 213 (30), 169 (71), 141 (100), 139 (67), 113 (96), 112 (93), 67 (74).

GCMS of **42**, *m*/*e* (relative intensity) 426 (0.04, M^+), 213 (32), 169 (66), 141 (100), 113 (90), 112 (82), 67 (67).

15. Thermal reaction of i-PrHgPr-i with diethyl dicarboxylacetylene

To a flask equipped with a reflux condenser and a magnetic stirring bar was added *i*-Pr_2Hg (0.06 g, 0.22 mmol), $EtO_2CC{\equiv}CCO_2Et$ (0.02 g, 0.11 mmol), DMSO (1 mL) and PhH (1 mL). Under nitrogen, the mixture was stirred and heated by an oil bath at 100-110 °C for 24 h. After the reaction, a little mercury metal was formed. The reaction mixture was worked up according to the general procedure in Section 14. After the solvent was removed, the residue was identified as product 40 in 17% yield, product 41 in 20% yield and product 42 in 10% yield.

16. Reaction of t-Bu_2Hg with $PhC{\equiv}CSO_2Ph$

A pyrex tube containing *t*-Bu_2Hg (0.2 g, 0.6 mmol), $PhC{\equiv}C$-SO_2Ph (0.07 g, 0.3 mmol) and PhH (4 mL) was irradiated in a Rayonet Photoreactor for 2 h. The mercury metal (0.08 g in 67% yield) was separated and PhH (8 mL) was added to the solution. The solution was washed with 5% $Na_2S_2O_3$ (3 x 10 mL) and dried over $MgSO_4$. After evaporating the PhH, the yellow oil remaining was identified as 1-phenyl-3,3-dimethyl-1-butyne in 84% yield which matched the retention time of an authentic sample in GLC.

GCMS, *m*/*e* (relative intensity) 158 (38, M^+), 143 (100), 128 (52), 115 (15), 77 (13).

17. Reaction of t-Bu_2Hg with $Ph_2C{=}CHSO_2Ph$

Di-*tert*-butylmercury (0.2 g, 0.6 mmol) and $Ph_2C{=}CHSO_2Ph$ (0.09 g, 0.3 mmol) were dissolved in PhH (6 mL). The mixture was irradiated in a Rayonet Photoreactor at 350 nm for 2 h. After the reaction, mercury metal (0.14 g in 98% yield) was separated and PhH (8 mL) was added to the solution, which was then washed with a 5% $Na_2S_2O_3$ solution (3 x 15 mL) and dried with $MgSO_4$. After evaporating the solvent, the concentrated liquid was analyzed as 1,1-diphenyl-3,3-dimethyl-1-butene in 88% yield which matched the retention time of an authentic sample in GLC.

GCMS, m/e (relative intensity) 236 (42, $M^{+\cdot}$), 221 (75), 180 (35), 143 (100), 105 (56), 91 (79).

SUMMARY

The photostimulated reactions of alkylmercury chloride (RHgCl) with several alkenes have been studied. The reaction occurs by a free radical chain process which forms RCH_2--CH(HgCl)Q. Evidence for this initial product includes the fact that the hydroalkylation products (RCH_2CH_2Q) were formed when the reactions were worked up with $NaBH_4$ and the iodides ($RCH_2CH(I)Q$) were isolated in high yields when the reactions were worked up by reaction with iodine. The relative reactivity of RHgCl in the addition reactions has been found to follow the order t-BuHgCl > i-PrHgCl ~ c-C_6H_{11}HgCl >> n-BuHgCl.

The reactions of t-BuHgCl with alkynes gave the corresponding alkylated alkenes in excellent yields upon workup with $NaBH_4$ reduction. The intermediate R(X)C=C(HgCl)Y which is formed in a free radical chain sequence has been trapped by I_2 as R(X)C=C(I)Y in a quantitative yield.

The initial kinetic chain lengths have been measured for the reactions of t-BuHgCl with alkenes and alkynes by ^1H NMR. The results indicate that these reactions are definitely free radical chain processes. The kinetic study found that the photostimulated reaction of RHgCl with diethyl vinylphosphonate is a first-order reaction in which the reaction rate

only depends on the concentration of RHgCl.

Alkylmercury chlorides photochemically reacted with some haloalkenes to give the alkylated coupled olefins and alkylmercury halides. The photochemical behavior of dialkylmercurials towards several alkenes has been examined and the formation of the 1:1 adduct and its decomposition products from the reaction of diisopropylmercury with diethyl dicarboxylacetylene is reported.

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