The following are other examples that show the sensitivity of photostimulated $S_{RN}1$ reactions to the nature of the solvent and counterion. The reaction between 2-chloro-2-nitropropane and ethyl sodioacetylacetate in DMF yields ethyl 2-isopropylideneacetylacetate, but no reaction takes place with Li^+ in THF; potassium diethyl phosphite and 2-(*p*-tolylsulfonyl)-2-nitropropane in THF yield diethyl 2-nitroisopropylphosphate,[12] but no reaction occurs with Li^+ in THF; potassium diethyl thiophosphite reacts with 2-(*p*-tolylsulfonyl)-2-nitropropane in Me_2SO to give diethyl 2-nitroisopropylthiophosphonate, but with Li^+ in THF, the starting sulfone is recovered.

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(12) Russell, G. A.; Hershberger, J. *J. Chem. Soc., Chem. Commun.* **1980**, 216.

(13) Postdoctoral Fellow of the Consejo Superior de Investigaciones Cientificas de Espana, 1979–81.

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Substitution Reactions of Vinylmercurials by a Free-Radical Chain Mechanism[1]

Sir:

We have found that 1-alkenylmercury halides readily undergo photostimulated free-radical chain substitution reactions 1–3 (X = Cl, Br, OAc). In all cases the reactions are completely inhibited

$$\mathrm{RCH{=}CHHgX + R'Y{-}YR' \xrightarrow{h\nu} RCH{=}CHYR' + XHgYR'} \qquad (1)$$

$$\mathrm{Y = S,\ R' = alkyl\ or\ aryl;}$$
$$\mathrm{Y = Se,\ Te,\ R' = phenyl}$$

$$\mathrm{RCH{=}CHHgX + Z{-}Q \xrightarrow{h\nu} RCH{=}CHZ + XHgQ} \qquad (2)$$

$$\mathrm{Z = PhSO_2,\ Q = Cl;\ Z = Me_2CH,\ Q = I}$$

$$\mathrm{RCH{=}CHHgX + A^- \xrightarrow{h\nu} RCH{=}CHA + Hg^0 + X^-} \qquad (3)$$

$$\mathrm{A^- = (RO)_2PO^-,\ PhP(OBu)O^-,\ AlkSO_2^-,^2\ ArSO_2^-,^2\ AlkS^-,\ ArS^-}$$

by 5–10 mol % of di-*tert*-butyl nitroxide or galvinoxyl and fail to proceed significantly in the dark.

Reactions 1 and 2 or 3 with $A^- = RS^-$ clearly proceed by a free-radical addition–elimination mechanism (Scheme I).

In reaction 2 a vinyl radical intermediate is clearly excluded by the complete absence of the vinyl choride when the reactant is $PhSO_2Cl$ and only traces of the vinyl iodide when the reactant is Me_2CHI. A vinyl radical would attack these substrates to give halogen atom transfer. Furthermore, reactions 1, 2, or 3 with $A^- = RSO_2^-$ or RS^- fail to occur with phenyl- or benzylmercurials. This excludes reaction 1 occurring by the S_H2 attack of a carbon-centered radical on R′YYR′ or reaction 3 occurring by the $S_{RN}1$ mechanism.[2] Moreover, reaction 1 with Y = S will occur in PhH in the presence of 1 equiv of 2,6-di-*tert*-butylphenol to yield the vinyl sulfide in nearly quantitative yield with but a slight rate retardation.

In reaction 3 with $A^- = PhS^-$ the reaction is inhibited by an excess of the mercaptide ion.[3] However, the reaction is not inhibited by the presence of the free mercaptan, and the vinyl sulfide is still formed in nearly quantitative yield (the reaction is most conveniently performed by sunlamp irradiation of the alkenylmercury chloride and mercaptan in PhH in the presence of excess $NaHCO_3$). Again, a vinyl radical intermediate is excluded since this would have reacted with the mercaptan to form the olefin by hydrogen transfer. In reaction 3 with $A^- = R'S^-$, ligand exchange occurs readily to form the 1-alkenylmercury mercaptide (RCH=CHHgSR′), which can be isolated from solutions containing a trace of di-*tert*-butyl nitroxide. The pure mercaptide when irradiated in a variety of solvents (PhH, Et_2O, Me_2SO) decomposes cleanly according to reaction 4; again the

$$\mathrm{RCH{=}CHHgSR' \xrightarrow{h\nu} RCH{=}CHSR' + Hg^0} \qquad (4)$$

mercaptide ion inhibits the reaction while the free mercaptan has no effect on the rate or product. The decomposition of RCH=CHHgSR′ follows Scheme I, probably with the stepwise expulsion of Hg^0 from the intermediate β-mercurio radical.[3,4]

Table I gives some typical yields observed in these reactions. The processes are not completely stereoselective, which is consistent with Scheme I. With R = *tert*-butyl only the *E* products have been observed ($E/Z > 20{:}1$), but with smaller substituents (R = Ph, *n*-Pr) mixtures of the *E* and *Z* isomers are formed (Table I).

In an analogous series of reactions divinylmercurials undergo a photostimulated reaction with aryl disulfides (but not with primary alkyl disulfides) to form the vinyl sulfides (reaction 5).[5]

$$\mathrm{[(Ph)_2C{=}CH]_2Hg + PhSSPh \xrightarrow[PhH]{h\nu,\ 3\ h} \underset{99\%}{2(Ph)_2C{=}CHSPh} + Hg^0} \qquad (5)$$

At 0 °C in PhH–hexane solution the bis(vinyl)mecurial does not undergo significant electrophilic cleavage by PhSH, a dark reaction which occurs readily in Me_2SO or PhH at 25 °C. At 0 °C in PhH–hexane the presence of PhSH had no effect on the rate of reaction 5 and the vinyl sulfide was formed in quantitative yield. The reaction is, however, strongly inhibited by 5 mol % of galvinoxyl. We thus conclude that reaction 5 also does not involve intermediate vinyl radicals and chain propagation occurs by Scheme I followed by reactions 6 and 4. The failure of alkyl

$$\mathrm{(Ph)_2C{=}CHHg\ (from\ Scheme\ I) + PhSSPh \rightarrow (Ph)_2C{=}CHgSPh + PhS\cdot} \qquad (6)$$

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(1) Electron Transfer Reactions. 24. This work was supported by Grant CHE-7823866 from the National Science Foundation.

(2) Hershberger, J.; Russell, G. A. *Synthesis* 1980, 475.

(3) The inhibition by the thiolate anion may involve the trapping of the chain-carrying species HgSR (Scheme I). Trapping of RS· seems to be eliminated by the observation that PhS^- is not an inhibitor in reaction 5 where the intermediate Hg species can react rapidly with PhSSPh.

(4) The mercury substituent probably stabilizes the intermediate β-mercurio radical, leading to regioselectivity in the first step of Scheme I. It has been reported that a mercury substituent greatly activates β-hydrogen atoms toward attack by the trichloromethyl radical [Kochi, J. K.; Nugent, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 5406], although no dramatic activation has been noted in hydrogen abstraction by the less selective and less electrophilic phenyl radical in attack upon diethylmercury [unpublished results with J. D. Hunt].

(5) A number of thermal substitution reactions of $(CH_2{=}CH)_2Hg$ have been reported [Foster, D. J.; Tobler, E. *J. Am. Chem. Soc.* **1961**, *83*, 851; *J. Org. Chem.* **1962**, *27*, 834; U.S. Patents 3 087 952, April 30, 1963; Feb 15, 1966; 3 090 814, May 21, 1963; 3 153 074, Dec 23, 1963. Tobler, E.; Foster, D. J. *Z. Naturforsch.* **1962**, *176*, 135, 136] which follow the stoichiometry

$$\mathrm{(CH_2{=}CH)_2Hg + HX \xrightarrow{\Delta} CH_2{=}CH_2 + CH_2{=}CHX + Hg^0}$$

where X = SR, $SC({=}O)CH_3$, OPh, O_2CR, O_2SPhMe-*p*. This work has been extended to include $X^- = (EtO)_2P({=}O)O^-$, $MeP({=}O)(OR)O^-$, $(RO)_2P({=}S)S^-$ [Gololobov, Y. G.; Domitrieva, T. F.; Suborovskii, L. Z. *Probl. Organ. Sintoza, Akad. Nauk, SSSR, Otd. Obshsh. Tekhn. Khim* **1965**, 314; *Chem. Abstr.* **1966**, *64*, 6683h] and at 180 °C in the presence of hydroquinone, $C_nF_{2n+1}CO_2^-$ and $(CF_3)_2C{=}NO^-$ [Sterlin, R. N.; Euplov, B. N.; Knunyantz, I. L. *Zh. Vses. Khim. Obshchest.* **1967**, *12*, 591; *Chem. Abstr.* **1968**, *68*, 49706c]. It appears likely that some of these processes *may* proceed by a free-radical decomposition of the intermediate $CH_2{=}CHHgX$ formed by electrophilic cleavage of divinylmercury. In the present work $CH_2{=}CHHgCl$ failed to give a photostimulated substitution reaction with anions such as $(EtO)_2PO^-$ or RSO_2^-, but led instead to polymeric products. Foster and Tobler also report the thermal decompositions of $CH_2{=}CHHgSPh$, $CH_2{=}CHHgO_2CR$, $R'CH{=}CR'HgO_2CR$, and $CH_2{=}CHHgSCN$ to $CH_2{=}CHSPH$, $CH_2{=}CHOC({=}O)CH_3$, $CH_2{=}CHOC({=}O)Ph$, $R'CH{=}CR'O_2CCH_3$, $CH_2{=}CHSCN$, and $CH_2{=}CHNCS$ at 100–200 °C. At 35 °C, (*E*)-$Me_3CCH{=}CHHgOAc$ does not undergo decomposition to yield the vinyl acetate even with prolonged irradiation at 350 nm.

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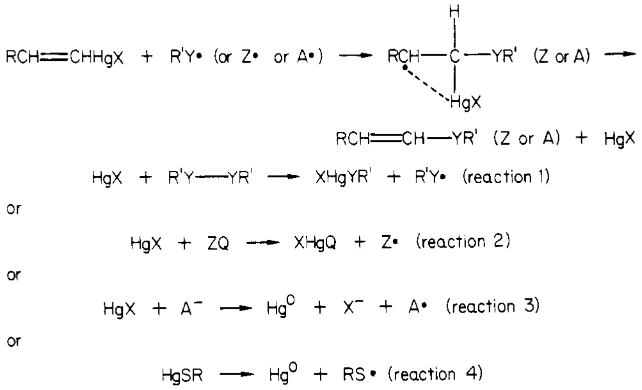
Table I. Photostimulated Reactions of Vinylmercurials

vinylmercurial	reactant	conditions[a]	products	% yield[b]
(E)-$\mathrm{Me_3CCH=CHHgCl}$	n-BuSSBu-n	PhH, 17 h	(E)-$\mathrm{Me_3CCH=CHSBu}$-n	100
(E)-$\mathrm{Me_3CCH=CHHgCl}$	PhSSPh	PhH, 6 h	(E)-$\mathrm{Me_3CCH=CHSPh}$	100
(E)-$\mathrm{Me_3CCH=CHHgCl}$	PhSeSePh	PhH, 2 h	(E)-$\mathrm{Me_3CCH=CHSePh}$	95
(E)-$\mathrm{Me_3CCH=CHHgCl}$	PhTeTePh	PhH, 18 h	(E)-$\mathrm{Me_3CCH=CHTePh}$	89
(E)-$\mathrm{Me_3CCH=CHHgCl}$	$\mathrm{PhSO_2Cl}$	PhH, 4 h[c]	(E)-$\mathrm{Me_3CCH=CHSO_2Ph}$	84
(E)-$\mathrm{Me_3CCH=CHHgCl}$	$\mathrm{(EtO)_2POK}$	$\mathrm{Me_2SO}$, 29 h	(E)-$\mathrm{Me_3CCH=CHP(O)(OEt)_2}$	76
(E)-$\mathrm{Me_3CCH=CHHgCl}$	PhP(OBu)OK	$\mathrm{Me_2SO}$, 3.5 h	(E)-$\mathrm{Me_3CCH=CHP(O)(OBu)Ph}$	84
(E)-$\mathrm{Me_3CCH=CHHgCl}$	p-$\mathrm{MePhSO_2Na}$	t-$\mathrm{BuOH/H_2O}$, 31 h	(E)-$\mathrm{Me_3CCH=CHSO_2PhMe}$-$p$	81[d]
(E)-$\mathrm{Me_3CCH=CHHgCl}$	n-$\mathrm{PrSO_2Na}$	$\mathrm{Me_2SO}/t$-$\mathrm{BuOH/H_2O}$, 30 h	(E)-$\mathrm{Me_3CCH=CHSO_2Pr}$-$n$	75[d]
(E)-$\mathrm{Me_3CCH=CHHgCl}$	PhSH	PhH, $\mathrm{NaHCO_3}$, 17 h	(E)-$\mathrm{Me_3CCH=CHSPh}$	99
(E)-$\mathrm{Me_3CCH=CHHgCl}$	t-BuSH	PhH, $\mathrm{NaHCO_3}$, 15 h	(E)-$\mathrm{Me_3CCH=CHSCMe_3}$	100
(E)-$\mathrm{Me_3CCH=CHHgCl}$	$\mathrm{PhCH_2SH}$	PhH, $\mathrm{NaHCO_3}$, 5 h	(E)-$\mathrm{Me_3CCH=CHSCH_2Ph}$	64
(Z)-$\mathrm{HOCH_2C(Cl)=CHHgCl}$	PhSH	PhH, $\mathrm{NaHCO_3}$, 5.25 h	$\mathrm{HOCH_2C(Cl)=CHSPh}$	61
$\mathrm{CH_2=CHHgCl}$	PhSH	PhH, $\mathrm{NaHCO_3}$, 3 h	$\mathrm{CH_2=CHSPh}$	100
(E)-EtC(OAc)=C(Et)HgCl	PhSH	PhH, $\mathrm{NaHCO_3}$, 11 h	EtC(OAc)=C(Et)SPh	92
(E)-$\mathrm{Me_3CCH=CHHgOAc}$	PhSH	PhH, 17 h	(E)-$\mathrm{Me_3CCH=CHSPh}$	100
(E)-$\mathrm{Me_3CCH=CHHgOAc}$	$\mathrm{PhCH_2SH}$	PhH, 18 h	(E)-$\mathrm{Me_3CCH=CHSCH_2Ph}$	97
$\mathrm{(Ph)_2CH=CHHgBr}$	MeSSMe	PhH, 8 h	$\mathrm{(Ph)_2CH=CHSMe}$	100
$\mathrm{(Ph)_2CH=CHHgBr}$	p-$\mathrm{MePhSO_2Na}$	DMSO, 40 h	$\mathrm{(Ph)_2CH=CHSO_2PhMe}$-$p$	61
$\mathrm{(Ph)_2CH=CHHgBr}$	$\mathrm{Me_2CHI}$	PhH, 2 h[c]	$\mathrm{(Ph)_2CH=CHCH(Me)_2}$	50
(E)-$\mathrm{Me_3CCH=CHHgSPh}$		PhH, 3 h	(E)-$\mathrm{Me_3CCH=CHSPh}$	99
(E)-$\mathrm{Me_3CCH=CHHgSBu}$-n		PhH, 6 h	(E)-$\mathrm{Me_3CCH=CHSBu}$-n	100
$\mathrm{(Ph)_2C=CHHgSPh}$		PhH, 15 h	$\mathrm{(Ph)_2C=CHSPh}$	100
$\mathrm{(Ph)_2C=C(CH_3)HgSPh}$		PhH, 6 h	$\mathrm{(Ph)_2C=C(CH_3)SPh}$	100
(E)-PhCH=CHHgSPh		PhH, 6 h	PhCH=CHSPh, $E{:}Z = 10{:}1$	100
(E)-n-PrCH=CHHgSPh		PhH, 4 h	n-PrCH=CHSPh, $E{:}Z = 1.2{:}1$	100
(E)-n-PrCH=CHHgCl	$\mathrm{(EtO)_2POK}$	$\mathrm{Me_2SO}$, 11 h	n-$\mathrm{PrCH=CHP(=O)(OEt)_2}$, $E{:}Z = 10{:}1$	56
(E)-n-PrCH=CHHgCl	p-$\mathrm{MePhSO_2Na}$	$\mathrm{Me_2SO}/t$-$\mathrm{BuOH/H_2O}$, 22 h	n-$\mathrm{PrCH=CHSO_2PhMe}$-p, $E{:}Z = 6{:}1$	71[d]
(E)-PhCH=CHHgCl	p-$\mathrm{MePhSO_2Na}$	$\mathrm{Me_2SO}/t$-BuOH, 19 h	(E)-$\mathrm{PhCH=CHSO_2PhMe}$-p, $E{:}Z > 20{:}1$	81[d]
(E)-PhCH=CHHgCl	n-BuSH	PhH, $\mathrm{NaHCO_3}$, 3 h	(E)-PhCH=CHSBu-n	100
(E)-PhCH=CHHgCl	PhSeSePh	PhH, 2h	(E)-PhCH=CHSePh	90
$\mathrm{CH_2=CHHgCl}$	PhSeSePh	PhH, 2h	$\mathrm{CH_2=CHSePh}$	91
$\mathrm{CH_2=CHSn(Bu}$-$n)_3$	PhSSPh	PhH, 4h	$\mathrm{CH_2=CHSPh}$	~100

[a] Reactants were irradiated with a 275-W sunlamp approximately 6 in. from the Pyrex reaction flask. The sunlamp maintained a temperature of approximately 35–45 °C. The mercurials (3 mmol) in 10–50 mL of solvent were reacted with a stoichiometric amount of the disulfide or $\mathrm{PhSO_2Cl}$, a 10–20% excess of the anions or free thiols, and a 10-fold excess of $\mathrm{Me_2CHI}$. The exclusion of molecular oxygen is essential. [b] Appropriate ^{1}H NMR, IR, and high-resolution mass spectra were obtained for all products. Satisfactory elemental analyses were obtained for all new compounds except for $\mathrm{Me_3CCH=CHTePh}$ (oxidatively reactive), $\mathrm{HOCH_2C(Cl)=CHSPh}$ (unstable), and n-$\mathrm{PrCH=CHP(O)(OEt)_2}$, for which an NMR yield is reported. The only previously reported 1-alkenylmercury mercaptide is $\mathrm{CH_2=CHHgSR}$.[5] [c] Irradiated in Pyrex in a RPR-100 Rayonet reactor at 350 nm. [d] Previously reported in ref 2.

Scheme I



disulfides to participate in reaction 5, although they react readily in reaction 1, may indicate that in the presence of the alkyl disulfide the vinylmercury intermediate ($\mathrm{(Ph)_2C{=}CHHg}$) at least partially decomposes to yield vinyl radicals which do not lead to chain propagation, possibly because of abstraction of the α-hydrogen atoms of the disulfide.

The reaction scheme attributes a surprisingly high reactivity to the species HgX which may be much more reactive than $\mathrm{Hg_2Cl_2}$ (as, for example, $\mathrm{R_3Sn}$ and $\mathrm{R_3SnSnR_3}$). Thus, in DMF $\mathrm{Hg_2Cl_2}$ is disproportionated to $\mathrm{Hg^0}$ and $\mathrm{HgCl_2}$ but not otherwise reduced by anions such as $\mathrm{PhSO_2^-}$. Furthermore, $\mathrm{Hg_2Cl_2}$ undergoes no reaction with $\mathrm{PhSO_2Cl}$ in PhH (heterogeneous).

Preliminary results indicate that reactions 1–3 or 5 may occur with other 1-alkenylmetals. Thus, we have found that a photostimulated free-radical chain reaction occurs between $(n\text{-Bu})_3\mathrm{SnCH{=}CH_2}$ and PhSSPh to afford $\mathrm{CH_2{=}CHSPh}$ in essentially a quantitative yield.

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Reduction of $\mathrm{CO_2}$ to CO by Transition-Metal Dianions[1]

Sir:

We wish to report an unusual $\mathrm{CO_2}$ reduction using electron transfer from transition-metal dianions, in which the oxygen sink is an alkali metal carbonate (eq 1). Since alkali metals provide the ultimate reducing power in the preparations of the transition-metal dianions and the carbon monoxide formed can be photochemically released from the product carbonyl complexes, the overall reaction can be summarized as in eq 2.

$$\mathrm{M_2[M'(CO)_n] + 2CO_2 \rightarrow M_2CO_3 + [M'(CO)_{n+1}]} \qquad (1)$$

$$n = 5,\ \mathrm{M = Na\ or\ Li,\ M' = W}$$

$$n = 4,\ \mathrm{M = Na,\ M' = Ru\ or\ Fe}$$

$$\mathrm{2M + 2CO_2 \rightarrow M_2CO_3 + CO} \qquad (2)$$

Treatment of a solution of $\mathrm{Li_2[W(CO)_5]}$ in tetrahydrofuran (thf)[2] with gaseous $\mathrm{CO_2}$ at −78 °C resulted in immediate bleaching

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(1) This paper is dedicated to the memory of Professor R. B. Woodward.