

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,<sup>12</sup> 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.

(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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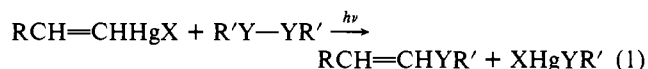
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### Substitution Reactions of Vinylmercurials by a Free-Radical Chain Mechanism<sup>1</sup>

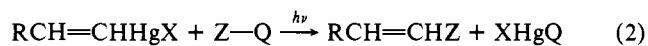
Sir:

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



$Y = S, R' = \text{alkyl or aryl};$

$Y = Se, Te, R' = \text{phenyl}$



$Z = PhSO_2, Q = Cl; Z = Me_2CH, Q = I$



$A^- =$

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

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 chloride 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  $S_H^2$  attack of a carbon-centered radical on  $R'YR'$  or reaction 3 occurring by the  $S_{RN}1$  mechanism.<sup>2</sup> 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.<sup>3</sup> However, the reaction is not

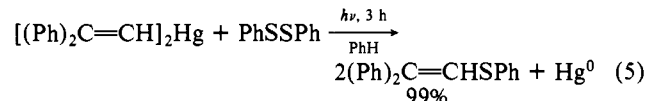
inhibited by the presence of the free mercaptan, and the vinyl sulfide is still formed in nearly quantitative yield (the reaction is most conveniently performed by sunlamp irradiation of the alkenylmercury chloride and mercaptan in PhH in the presence of excess  $NaHCO_3$ ). Again, a vinyl radical intermediate 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



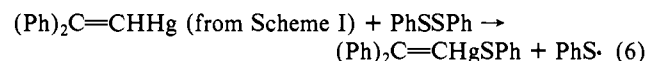
mercaptide ion inhibits the reaction while the free mercaptan has no effect on the rate or product. The decomposition of  $RCH=CHHgSR'$  follows Scheme I, probably with the stepwise expulsion of  $Hg^0$  from the intermediate  $\beta$ -mercurio radical.<sup>3,4</sup>

Table I gives some typical yields observed in these reactions. The processes are not completely stereoselective, which is consistent with Scheme I. With  $R = \textit{tert}$ -butyl only the *E* products have been observed ( $E/Z > 20:1$ ), but with smaller substituents ( $R = Ph, n\text{-Pr}$ ) 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).<sup>5</sup>

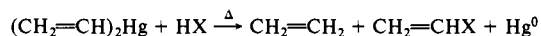


At 0 °C in PhH-hexane solution the bis(vinyl)mercurial does not undergo significant electrophilic cleavage by PhSH, a dark reaction which occurs readily in  $Me_2SO$  or PhH at 25 °C. At 0 °C in PhH-hexane the presence of PhSH had no effect on the rate of reaction 5 and the vinyl sulfide was formed in 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



(4) The mercury substituent probably stabilizes the intermediate  $\beta$ -mercurio radical, leading to regioselectivity in the first step of Scheme I. It has been reported that a mercury substituent greatly activates  $\beta$ -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 3087952, April 30, 1963; Feb 15, 1966; 3090814, May 21, 1963; 3153074, Dec 23, 1963. Tobler, E.; Foster, D. J. *Z. Naturforsch.* **1962**, *176*, 135, 136] which follow the stoichiometry



where  $X = SR, SC(=O)CH_3, OPh, O_2CR, O_2SPH\text{-}m\text{-}p$ . This work has been extended to include  $X^- = (EtO)_2P(=O)O^-, MeP(=O)(OR)O^-, (RO)_2P(=S)S^-$  [Golobobov, Y. G.; Domitrieva, T. F.; Suborovskii, L. Z. *Probl. Organ. Sintoz, 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  $CH_2=CHS-Ph, CH_2=CHOC(=O)CH_3, CH_2=CHOC(=O)Ph, R'CH=CR'O_2CCH_3, CH_2=CHSCN$ , 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.

(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.

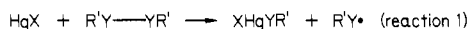
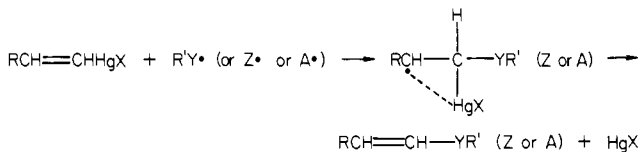
(3) The inhibition by the thiolate anion may involve the trapping of the chain-carrying species  $HgSR$  (Scheme I). Trapping of  $RS^-$  seems to be eliminated by the observation that  $PhS^-$  is not an inhibitor in reaction 5 where the intermediate  $Hg$  species can react rapidly with  $PhSSPh$ .

Table I. Photostimulated Reactions of Vinylmercurials

vinylmercurial	reactant	conditions <sup>a</sup>	products	% yield <sup>b</sup>
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	<i>n</i> -BuSSBu- <i>n</i>	PhH, 17 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSBu- <i>n</i>	100
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhSSPh	PhH, 6 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSPh	100
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhSeSePh	PhH, 2 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSePh	95
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhTeTePh	PhH, 18 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHTePh	89
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhSO <sub>2</sub> Cl	PhH, 4 h <sup>c</sup>	( <i>E</i> )-Me <sub>3</sub> CCH=CHSO <sub>2</sub> Ph	84
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	(EtO) <sub>2</sub> POK	Me <sub>2</sub> SO, 29 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHP(O)(OEt) <sub>2</sub>	76
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhP(OBu)OK	Me <sub>2</sub> SO, 3.5 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHP(O)(OBu)Ph	84 <sup>d</sup>
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	<i>p</i> -MePhSO <sub>2</sub> Na	<i>t</i> -BuOH/H <sub>2</sub> O, 31 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSO <sub>2</sub> PhMe- <i>p</i>	75 <sup>d</sup>
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	<i>n</i> -PrSO <sub>2</sub> Na	Me <sub>2</sub> SO/ <i>t</i> -BuOH/H <sub>2</sub> O, 30 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSO <sub>2</sub> Pr- <i>n</i>	81 <sup>d</sup>
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhSH	PhH, NaHCO <sub>3</sub> , 17 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSPh	99
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	<i>t</i> -BuSH	PhH, NaHCO <sub>3</sub> , 15 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSCMe <sub>3</sub>	100
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgCl	PhCH <sub>2</sub> SH	PhH, NaHCO <sub>3</sub> , 5 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSCH <sub>2</sub> Ph	64
( <i>Z</i> )-HOCH <sub>2</sub> C(Cl)=CHHgCl	PhSH	PhH, NaHCO <sub>3</sub> , 5.25 h	HOCH <sub>2</sub> C(Cl)=CHSPh	61
CH <sub>2</sub> =CHHgCl	PhSH	PhH, NaHCO <sub>3</sub> , 3 h	CH <sub>2</sub> =CHSPh	100
( <i>E</i> )-EtC(OAc)=C(Et)HgCl	PhSH	PhH, NaHCO <sub>3</sub> , 11 h	EtC(OAc)=C(Et)SPh	92
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgOAc	PhSH	PhH, 17 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSPh	100
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgOAc	PhCH <sub>2</sub> SH	PhH, 18 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSCH <sub>2</sub> Ph	97
(Ph) <sub>2</sub> CH=CHHgBr	MeSSMe	PhH, 8 h	(Ph) <sub>2</sub> CH=CHSMe	100
(Ph) <sub>2</sub> CH=CHHgBr	<i>p</i> -MePhSO <sub>2</sub> Na	DMSO, 40 h	(Ph) <sub>2</sub> CH=CHSO <sub>2</sub> PhMe- <i>p</i>	61
(Ph) <sub>2</sub> CH=CHHgBr	Me <sub>2</sub> CHI	PhH, 2 h <sup>c</sup>	(Ph) <sub>2</sub> CH=CHCH(Me) <sub>2</sub>	50
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgSPh	PhH, 3 h	PhH, 3 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSPh	99
( <i>E</i> )-Me <sub>3</sub> CCH=CHHgSBu- <i>n</i>	PhH, 6 h	PhH, 6 h	( <i>E</i> )-Me <sub>3</sub> CCH=CHSBu- <i>n</i>	100
(Ph) <sub>2</sub> C=CHHgSPh	PhH, 15 h	PhH, 15 h	(Ph) <sub>2</sub> C=CHSPh	100
(Ph) <sub>2</sub> C=C(CH <sub>3</sub> )HgSPh	PhH, 6 h	PhH, 6 h	(Ph) <sub>2</sub> C=C(CH <sub>3</sub> )SPh	100
( <i>E</i> )-PhCH=CHHgSPh	PhH, 6 h	PhH, 6 h	PhCH=CHSPh, <i>E</i> : <i>Z</i> = 10:1	100
( <i>E</i> )- <i>n</i> -PrCH=CHHgSPh	PhH, 4 h	PhH, 4 h	<i>n</i> -PrCH=CHSPh, <i>E</i> : <i>Z</i> = 1.2:1	100
( <i>E</i> )- <i>n</i> -PrCH=CHHgCl	(EtO) <sub>2</sub> POK	Me <sub>2</sub> SO, 11 h	<i>n</i> -PrCH=CHP(O)(OEt) <sub>2</sub> , <i>E</i> : <i>Z</i> = 10:1	56
( <i>E</i> )- <i>n</i> -PrCH=CHHgCl	<i>p</i> -MePhSO <sub>2</sub> Na	Me <sub>2</sub> SO/ <i>t</i> -BuOH/H <sub>2</sub> O, 22 h	<i>n</i> -PrCH=CHSO <sub>2</sub> PhMe- <i>p</i> , <i>E</i> : <i>Z</i> = 6:1	71 <sup>d</sup>
( <i>E</i> )-PhCH=CHHgCl	<i>p</i> -MePhSO <sub>2</sub> Na	Me <sub>2</sub> SO/ <i>t</i> -BuOH, 19 h	( <i>E</i> )-PhCH=CHSO <sub>2</sub> PhMe- <i>p</i> , <i>E</i> : <i>Z</i> > 20:1	81 <sup>d</sup>
( <i>E</i> )-PhCH=CHHgCl	<i>n</i> -BuSH	PhH, NaHCO <sub>3</sub> , 3 h	( <i>E</i> )-PhCH=CHSBu- <i>n</i>	100
( <i>E</i> )-PhCH=CHHgCl	PhSeSePh	PhH, 2h	( <i>E</i> )-PhCH=CHSePh	90
CH <sub>2</sub> =CHHgCl	PhSeSePh	PhH, 2h	CH <sub>2</sub> =CHSePh	91
CH <sub>2</sub> =CHSn(Bu- <i>n</i> ) <sub>3</sub>	PhSSPh	PhH, 4h	CH <sub>2</sub> =CHSPh	~100

<sup>a</sup> 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 PhSO<sub>2</sub>Cl, a 10–20% excess of the anions or free thiols, and a 10-fold excess of Me<sub>2</sub>CHI. The exclusion of molecular oxygen is essential. <sup>b</sup> Appropriate <sup>1</sup>H NMR, IR, and high-resolution mass spectra were obtained for all products. Satisfactory elemental analyses were obtained for all new compounds except for Me<sub>3</sub>CCH=CHTePh (oxidatively reactive), HOCH<sub>2</sub>C(Cl)=CHSPh (unstable), and *n*-PrCH=CHP(O)(OEt)<sub>2</sub>, for which an NMR yield is reported. The only previously reported 1-alkenylmercury mercaptide is CH<sub>2</sub>=CHHgSR.<sup>5</sup> <sup>c</sup> Irradiated in Pyrex in a RPR-100 Rayonet reactor at 350 nm. <sup>d</sup> Previously reported in ref 2.

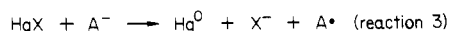
## Scheme I



or



or



or



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 ((Ph)<sub>2</sub>C=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 Hg<sub>2</sub>Cl<sub>2</sub> (as, for example, R<sub>3</sub>Sn and R<sub>3</sub>SnSnR<sub>3</sub>). Thus, in DMF Hg<sub>2</sub>Cl<sub>2</sub> is disproportionated to Hg<sup>0</sup> and HgCl<sub>2</sub> but not otherwise reduced by anions such as PhSO<sub>2</sub><sup>-</sup>. Furthermore, Hg<sub>2</sub>Cl<sub>2</sub> undergoes no reaction with PhSO<sub>2</sub>Cl 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*-

Bu)<sub>3</sub>SnCH=CH<sub>2</sub> and PhSSPh to afford CH<sub>2</sub>=CHSPh in essentially a quantitative yield.

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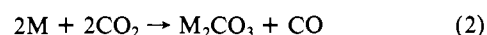
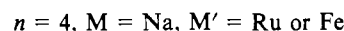
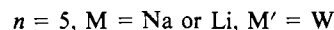
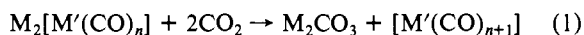
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Received July 25, 1980

Reduction of CO<sub>2</sub> to CO by Transition-Metal Dianions<sup>1</sup>

Sir:

We wish to report an unusual CO<sub>2</sub> 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.



Treatment of a solution of Li<sub>2</sub>[W(CO)<sub>5</sub>] in tetrahydrofuran (thf)<sup>2</sup> with gaseous CO<sub>2</sub> at –78 °C resulted in immediate bleaching

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