Reaction of 1-Alkenyl and 1-Alkynyl Derivatives of Tin and Mercury with Hetero-Centered Radicals

Glen A. Russell,* Preecha Ngoviwatchai, Hasan Tashtoush,[1] and James Hershberger

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received February 9, 1987

1-Alkenyl and 1-alkynyl derivatives of tin and mercury react with hetero-centered radicals such as RS•, PhSe•, $PhSO_2$•, or $(EtO)_2P(O)$• to undergo substitution of the metal atom in a free radical chain reaction involving addition-elimination. The hetero-centered radical can be formed in a chain propagation reaction by the attack of ClHg• or Bu_3Sn• upon reagents such as RSSR, $PhSeSO_2Ph$, PhSeSePh, or $PhSO_2Cl$ or mercurials such as $Hg(SPh)_2$, $Hg(SePh)_2$, $Hg(O_2SPh)_2$, or $Hg[(O)P(OEt)_2]_2$. In relative reactivity studies toward PhS•, vinylmercury chlorides are somewhat more reactive than the analogous tri-*n*-butylstannanes. Tri-*n*-butyl(phenylethynyl)stannane is 300 times less reactive than its β-styrenyl analogue. Toward PhS•, CH_2=$CHCH_2SnBu_3$ is 3 times as reactive as CH_2=$CHSnBu_3$ but only $^1/_{16}$ as reactive as (*E*)-PhCH=$CHSnBu_3$. An explanation is advanced for the observations that PhSeSePh participates in a free radical chain substitution reaction with allylstannanes or 1-alkenylmercury chlorides but not with 1-alkenylstannanes although PhSSPh or $(PhSe)_2Hg$ react readily with 1-alkenylmercurials or -stannanes.

We have previously reported the free radical chain reaction of the reagents Q-Y (Q-Y = RS-SR, $PhSO_2$-Cl, PhSe-SO_2Ar) with a variety of (2-substituted-1-alkenyl)-mercury derivatives (Scheme I, MX_n = HgX).[2] The addition-elimination sequence of Scheme I requires a regioselective addition of Q• to the alkene, a process which may be facilitated with hetero-centered radicals which can add reversibly to a carbon-carbon double bond. Thus, when applied to CH_2=$CHSnBu_3$, the substitution process of reaction 1 occurred cleanly with Q• = PhS•, $PhCH_2S$•, or $PhSO_2$• (Table I) although the addition of PhS• to the vinyl group is expected to occur preferentially at the terminal position. (Indeed, the free radical addition of *p*-MeC_6H_4SH to CH_2=$CHSnPh_3$ forms mainly *p*-$MeC_6H_4SCH_2CH_2SnPh_3$.[3]) (*E*)- and (*Z*)-MeO_2CCH=$CHSnBu_3$ gave the same ratio of (*E*)- and (*Z*)-MeO_2CCH=CHSPh or (*E*)- and (*Z*)-MeO_2CCH=$CHSO_2Ph$ under the conditions of Table I although at short reaction periods some evidence of stereospecificity was observed with PhSSPh.[4]

Scheme I

$$Q^{\bullet} + RCH{=}CHMX_n \rightarrow R\dot{C}H{-}CH(Q)MX_n$$

$$R\dot{C}H{-}CH(Q)MX_n \rightarrow RCH{=}CHQ + MX_n^{\bullet}$$

$$MX_n^{\bullet} + Y{-}Q \rightarrow YMX_n + Q^{\bullet}$$

$$RCH{=}CHMX_n + Y{-}Q \rightarrow RCH{=}CHQ + YMX_n \quad (1)$$

Reaction of (*E*)-PhCH=$CHSnBu_3$ with *N*-bromosuccinimide occurred rapidly in the dark or with UV irradiation to give the vinyl bromide by an electrophilic substitution reaction. Similarly, *N*-(phenylthio)phthalimide formed the phenyl vinyl sulfide. No reaction under the conditions of Table I was observed for *N*-chlorosuccinimide, $(PhO)_2PCl$, Ph_2PCl, or $(EtO)_2P(O)Cl$. Thermolysis of *t*-BuOOC(O)Ph in the presence of PhCH=$CHSnBu_3$ produced acetone as the major product, and PhCH=$CHSnBu_3$ was recovered.

Table II summarizes the reactions of Q-Y reagents with 1-alkenylmercurials. The most noticeable differences between the mercury compounds and the tin analogues is that substitution occurs in the mercury but not the tin series with PhSeSePh although both systems react with PhSSPh or $PhSeSO_2Ph$. With (*E*)- or (*Z*)-ClCH=CHHgCl the initial reaction product (ClCH=CHSPh) reacted further with PhS• to form (*E*)- and (*Z*)-PhSCH=CHSPh.

Reaction of (*E*)-*t*-BuCH=CHHgCl with MeCOSSCOMe gave only a 5% yield of the substitution product (14 h, sunlamp in PhH) while (1-(cyclohexylmethyl)ethenyl)-mercury bromide and MeSSMe gave ill-defined products after 67 h of sunlamp irradiation in PhH. Reaction of (*E*)-*t*-BuCH=CHHgCl with NBS in the dark or with UV irradiation gave a complex mixture of products. PhSeCl reacted in the dark (CH_2Cl_2) to form the phenyl vinyl selenide while no reaction was observed with UV irradiation for $(EtO)_2P(O)Cl$, PhCOCl, $Me_2C(NO_2)Br$, or 2,4-$(O_2N)_2C_6H_3SCl$. With PhHgCl no significant reaction was observed with any of the Q-Y reagents of Table II.

Substitution in vinylmercury halides can occur by easily oxidized anions such as PhS^-, $PhSO_2^-$, or $(EtO)_2PO^-$ (Q^- in Scheme II).[2,5] Alternately, vinyltin or -mercury reagents can react with the reagents Q_2Hg or QHgCl by the chain sequence of Scheme III.[6] The use of the reagents Q_2Hg or QHgCl avoids the problems of symmetrization which can occur in the reactions of vinylmercurials with anions in the dark.

Scheme II

$$Q^{\bullet} + RCH{=}CHHgCl \rightarrow R\dot{C}H{-}CH(Q)HgCl$$

$$R\dot{C}H{-}CH(Q)HgCl \rightarrow RCH{=}CHQ + HgCl$$

$$HgCl + Q^- \rightarrow Hg^0 + Cl^- + Q^{\bullet}$$

Scheme III

$$Q^{\bullet} + RCH{=}CHMX_n \rightarrow R\dot{C}H{-}CH(Q)MX_n$$

$$R\dot{C}H{-}CH(Q)MX_n \rightarrow RCH{=}CHQ + {}^{\bullet}MX_n$$

$${}^{\bullet}MX_n + Q_2Hg \rightarrow QMX_n + QHg^{\bullet}$$

$$QHg^{\bullet} \rightarrow Q^{\bullet} + Hg^0$$

Table III summarizes the observed substitutions utilizing the mercurials with Q = PhS, PhSe, $PhSO_2$, or $(EtO)_2PO$. In general, a slightly higher reactivity was displayed with

(1) Supported by a scholarship from Yarmouk University, Irbid, Jordan, 1980-1983.

(2) Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.

(3) Taylor, R. D.; Wardell, J. L. *J. Organomet. Chem.* **1974**, *77*, 311. See also: Voronkov, M. G.; Rakhlin, V. I.; Mirgkov, R. G. *Proc. Adad. Sci. USSR* **1973**, *209*, 261. Voronkov, M. G.; Mirgkov, R. G.; Rakhlin, V. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1978**, 1454.

(4) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1985**, *26*, 4975.

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

(6) Russell, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.* **1984**, *106*, 4622.

0276-7333/87/2306-1414$01.50/0

Table I. Reaction of Q–Y Reagents with $(R^1)(R^2)C{=}CHSnBu_3$

R^1	R^2	Q–Y (equiv)	conditns[a]	% $(R^1)(R^2)C{=}CHQ$[b]
H	H	PhS–SPh (1.2)	*hν*, 4 h	91 (I)
H	H	PhS–SPh (1.2)	AIBN (0.1 equiv), 80 °C, 4 h	82 (I)
H	H	PhS–SPh (1.2)	dark, 50 °C, 4 h	0 (GC)
H	H	PhS–SPh (1.2)	*hν*, $(t\text{-Bu})_2NO^\bullet$ (0.15 equiv), 2 h	0 (GC)
CH_3	CH_3	PhS–SPh (1.2)	*hν*, 2 h	97 (NMR), 74 (I)
CH_3	CH_3	PhS–SPh (1.2)	AIBN (0.1 equiv), 80 °C, 2 h	97 (NMR)
CH_3	CH_3	PhS–SPh (1.2)	*hν*, $(t\text{-Bu})_2NO^\bullet$ (0.05 equiv), 1 h	0 (NMR)
CH_3	CH_3	PhS–SPh (1.2)	dark, 80 °C, 2 h	0 (NMR)
(*E*)-Ph	H	PhS–SPh (1.2)	*hν*, 4 h	86 (I)
Ph	Ph	PhS–SPh (1.2)	*hν*, 2 h	93 (NMR)
H	H	$PhCH_2S$–SCH_2Ph (1.2)	*hν*, 2 h	82 (I)
CH_3	CH_3	$PhCH_2S$–SCH_2Ph (1.2)	*hν*, 2 h	84 (NMR)
(*E*)-Ph	H	$PhCH_2S$–SCH_2Ph (1.2)	*hν*, 10 h	85 (I)
H	H	$PhSO_2$–Cl (1.2)	*hν*, 6 h	89 (I)
CH_3	CH_3	$PhSO_2$–Cl (1.2)	*hν*, 4 h	90 (NMR)
(*E*)-Ph	H	$PhSO_2$–Cl (1.2)	*hν*, 4 h	88 (I); ((*E*)/(*Z*) > 50)
(*E*)-Ph	H	Cl_3CSO_2–Cl (1.5)	*hν*, 24 h	48 (GC)[c]
Ph	Ph	$PhSO_2$–Cl (1.2)	*hν*, 4 h	76 (NMR)
(*E*)-Ph	H	$PhSe$–$SO_2C_6H_4CH_3$-*p* (1.2)	*hν*, 6 h	84 (I); ((*E*)/(*Z*) > 50)
H	H	PhSe–SePh (1.2)	*hν*, 24 h	0 (GC)
CH_3	CH_3	PhSe–SePh (1.2)	*hν*, 4 h	0 (NMR)
(*E*)-Ph	H	PhSe–SePh (1.2)	*hν*, 24 h	0 (GC)
(*E*)-MeO_2C	H	PhS–SPh (1.6)	UV, 8 h	79 (NMR); (*E*)/(*Z*) = 3.8 (GC)
(*Z*)-MeO_2C	H	PhS–SPh (1.6)	UV, 8 h	91 (NMR); (*E*)/(*Z*) = 3.7 (GC)
(*E*)-MeO_2C	H	$PhSO_2$–Cl (1.6)	UV, 10 h	68 (NMR); (*E*)/(*Z*) > 50 (GC)
(*E*)-MeO_2C	H	$PhSO_2$–Cl (1.6)	UV, 10 h	76 (NMR); (*E*)/(*Z*) > 50 (GC)

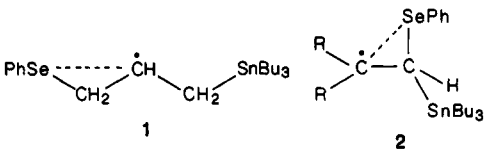
[a] Reactants (~0.1 M 1-alkenylstannane) were irradiated in PhH by a 275-W sunlamp ca. 15 cm from a Pyrex reaction vessel (*hν*) or in a 350-nm Rayonet Photoreactor (UV). The irradiation maintained a temperature of 35–40 °C. [b] Abbreviations: I, isolated yield; GC, yield by GLC using a calibrated standard; NMR, yield by ^1H NMR using an internal standard. [c] (*E*)-PhCH=$CHCCl_3$.

Table II. Reactions of Q–Y Reagents with $(R^1)(R^2)C{=}CHHgCl$

R^1	R^2	Q–Y (equiv)	conditns[a]	% $(R^1)(R^2)C{=}CHQ$ (*E*/*Z*)[b]
H	H	PhSe–SePh (1)	*hν*, 2 h	91
(*E*)-*t*-Bu	H	*n*-BuS–SBu-*n* (1)	*hν*, 17 h	100 (>50)
(*E*)-*t*-Bu	H	PhS–SPh (1)	*hν*, 6 h	100 (>50)
(*E*)-*t*-Bu	H	PhSe–SePh (1)	*hν*, 2 h	95 (>50)
(*E*)-*t*-Bu	H	PhTe–TePh (1)	*hν*, 18 h	89 (>50)
(*E*)-*t*-Bu	H	$PhSO_2$–Cl (1)	*hν*, 3 h	99 (>50)
(*E*)-*t*-Bu	H	*p*-MeC_6H_4-SO_2–Cl	*hν*, 25 h	75 (>50)
(*E*)-*t*-Bu	H	$MeSO_2$–Cl	*hν*, 22 h	32 (>50)
(*E*)-Ph	H	PhSe–SePh (1)	*hν*, 2 h	90 (>50)
Ph	Ph	MeS–SMe (1)	*hν*, 2 h	100
Ph	Ph	*i*-PrS–SPr-*i* (10)	*hν*, 24 h	98
(*E*)-Cl	H	PhS–SPh (2)	*hν*, Me_2SO, 0.5 h	14 (3.4); R^1 = PhS, 56 (0.9)
(*E*)-Cl	H	PhS–SPh (0.5)	UV, Me_2SO, 6 h	20 (2.5); R^1 = PhS, 40 (0.6)
(*E*)-Cl	H	PhS–SPh (1.2)	UV, Me_2SO, 6 h	R^1 = PhS, 81 (0.7)
(*Z*)-Cl[c]	H	PhS–SPh (0.5)	UV, Me_2SO, 6 h	16 (0.9); R^1 = PhS, 32 (0.7)
(*Z*)-Cl[c]	H	PhS–SPh (1.2)	UV, Me_2SO, 6 h	R^1 = PhS, 81 (0.8)

[a] See footnote *a*, Table I. $Ph_2C{=}CHHgBr$ was used for experiments with $R^1 = R^2$ = Ph. [b] Yields by ^1H NMR or GLC; (*E*)/(*Z*) ratios by GLC. [c] The starting material had a (*Z*)/(*E*) ratio of 3.0.

MX_n = HgCl than Bu_3Sn. Surprisingly, $(PhSe)_2Hg$ reacted cleanly with $Ph_2C{=}CHSnBu_3$ or $CH_2{=}CHSnBu_3$. The failure of PhSeSePh to lead to a free radical chain substitution reaction with vinylstannanes cannot be connected with the failure of $Bu_3Sn^\bullet$ to regenerate $PhSe^\bullet$ upon reaction with PhSeSePh. Thus, $Bu_3Sn^\bullet$ readily attacks $PhSeSO_2C_6H_4CH_3$-*p* to generate *p*-$CH_3C_6H_4SO_2^\bullet$ which leads to substitution in $PhCH{=}CHSnBu_3$. Furthermore, toward the 5-hexenyl radical, PhSeSePh is >100 times as reactive as PhSSPh,[7] and it would be expected that toward $Bu_3Sn^\bullet$, PhSeSePh would be more reactive than PhSSPh. Finally, with $CH_2{=}CHCH_2SnBu_3$ a free radical chain substitution is observed with either PhSSPh or PhSeSePh involving attack of $Bu_3Sn^\bullet$ upon the diaryl dichalcogenide.[8] What then can be the explanation for the absence of a reaction between PhSeSePh and vinylstannanes such as $CH_2{=}CHSnBu_3$, $Me_2C{=}CHSnBu_3$, or (*E*)-PhCH=$CHSnBu_3$? A possible explanation is that the high reactivity of PhSeSePh toward carbon radicals actually sabotages the chain reaction of Scheme I. If $MX_n^\bullet$ (i.e., $Bu_3Sn^\bullet$) is not eliminated immediately in Scheme I, then the intermediate adduct radical $RCHCH(SePh)SnBu_3$ might react with PhSeSePh to form $RCH(SePh)CH(SePh)SnBu_3$ which could eliminate PhSeSePh and regenerate the substrate $RCH{=}CHSnBu_3$. With the less reactive PhSSPh or $(PhSe)_2Hg$, the intermediate adduct radical can undergo the β-elimination of $Bu_3Sn^\bullet$, and the substitution reaction occurs with an appreciable kinetic chain length. Allylic substitution with PhSeSePh may occur because the β-elimination of $Bu_3Sn^\bullet$ is faster for **1** than for **2**, perhaps for conformational reasons. With



1-alkenylmercurials the β-elimination of $ClHg^\bullet$ is fast, and the substitution process according to Scheme I or III occurs with PhSSPh, PhSeSePh, $(PhS)_2Hg$, or $(PhSe)_2Hg$.

The acetylenic mercurial $[(PhC{\equiv}C)_2Hg]$ and stannane $(PhC{\equiv}CSnBu_3)$ gave rise to substitution products via a photostimulated free radical chain reaction with PhSSPh, $(PhS)_2Hg$, or $(EtO)_2P(O)HgCl$ (Table IV).[9,10] In the case of PhSSPh or $(PhS)_2Hg$, the initially formed $PhC{\equiv}CSPh$

(7) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.
(8) Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037.
(9) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1986**, *30*, 3479.
(10) $(PhCH{=}CH)_2Hg$ also reacts with excess PhSSPh to form 2 equiv of PhCH=CHSPh.[2]

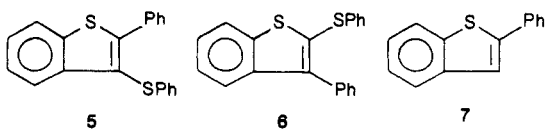
Table III. Reaction of $(R^1)(R^2)C{=}CHMX_n$ with Mercurials (HgQ_2 or QHgCl)

R^1	R^2	MX_n	mercurial (equiv)	conditns[a]	% $(R^1)(R^2)$-C=CHQ (*E*/*Z*)
Ph	Ph	HgBr	$Hg(SPh)_2$ (1)	UV, 20 h	100
(*E*)-Ph	H	HgCl	$Hg(SPh)_2$ (1)	UV, 20 h	97 (>50)
(*E*)-*t*-Bu	H	HgBr	$Hg(SPh)_2$ (1)	UV, 20 h	91 (>50)
Me	Me	HgBr	$Hg(SPh)_2$ (1)	UV, 20 h	39
H	H	HgCl	$Hg(SPh)_2$ (1)	UV, 20 h	46
Ph	Ph	$SnBu_3$	$Hg(SPh)_2$ (1)	UV, 20 h	66
Me	Me	$SnBu_3$	$Hg(SPh)_2$ (1)	UV, 20 h	56
H	H	$SnBu_3$	$Hg(SPh)_2$ (1)	UV, 20 h	45
Ph	Ph	HgBr	$Hg(SePh)_2$ (1)	UV, 20 h	80
(*E*)-*t*-Bu	H	HgBr	$Hg(SePh)_2$ (1)	UV, 20 h	35 (>50)
Me	Me	HgBr	$Hg(SePh)_2$ (1)	UV, 20 h	38
H	H	HgCl	$Hg(SePh)_2$ (1)	UV, 20 h	39
Ph	Ph	$SnBu_3$	$Hg(SePh)_2$ (1)	UV, 20 h	92
H	H	$SnBu_3$	$Hg(SePh)_2$ (1)	UV, 20 h	64
Ph	Ph	HgBr	$Hg(SO_2Ph)_2$ (5)	UV, 12 h	100
(*E*)-Ph	H	HgCl	$Hg(SO_2Ph)_2$ (5)	UV, 12 h	74 (>50)
(*E*)-*t*-Bu	H	HgBr	$Hg(SO_2Ph)_2$ (5)	UV, 12 h	42 (>50)
Me	Me	HgBr	$Hg(SO_2Ph)_2$ (5)	UV, 12 h	38
H	H	HgCl	$Hg(SO_2Ph)_2$ (5)	UV, 12 h	43
Ph	Ph	$SnBu_3$	$Hg(SO_2Ph)_2$ (5)	SL, 4 h	63
Me	Me	$SnBu_3$	$Hg(SO_2Ph)_2$ (5)	SL, 4 h	38
H	H	$SnBu_3$	$Hg(SO_2Ph)_2$ (5)	SL, 4 h	trace
Ph	Ph	HgBr	$[(EtO)_2P(O)]_2Hg$	UV, 24 h	86
(*E*)-Ph	H	HgCl	$[(EtO)_2P(O)]_2Hg$	UV, 8 h	68 (>10)
(*E*)-*t*-Bu	H	HgBr	$[(EtO)_2P(O)]_2Hg$	UV, 15 h	86 (>50)
Me	Me	HgBr	$[(EtO)_2P(O)]_2Hg$	UV, 15 h	trace
Ph	Ph	$SnBu_3$	$[(EtO)_2P(O)]_2Hg$	UV, 20 h	14[c]
Ph	Ph	HgBr	$(EtO)_2P(O)HgCl$	UV, 2 h	59
Ph	Ph	HgBr	$(EtO)_2P(O)HgCl$	$(t\text{-Bu})_2NO^\bullet$ (0.13 equiv), UV, 2 h	0
Ph	Ph	HgBr	$(EtO)_2P(O)HgCl$	UV, 4 h	85
Ph	Ph	HgBr	$(EtO)_2P(O)HgCl$	UV, 12 h	85
(*E*)-Ph	H	HgCl	$(EtO)_2P(O)HgCl$	UV, 4 h	57 (>50)
(*E*)-*t*-Bu	H	HgBr	$(EtO)_2P(O)HgCl$	UV, 24 h	67 (>50)
Me	Me	MgBr	$(EtO)_2P(O)HgCl$	UV, 24 h	31
H	H	HgCl	$(EtO)_2P(O)HgCl$	UV, 24 h	trace
Ph	Ph	$SnBu_3$	$(EtO)_2P(O)HgCl$	UV, 24 h	65
Me	Me	$SnBu_3$	$(EtO)_2P(O)HgCl$	UV, 24 h	36

[a] $R^1R^2C{=}CHMX_n$ (0.1 mmol) and the mercurial in 10 mL of nitrogen-purged Me_2SO were irradiated in a Pyrex tube. Abbreviations: UV, 350-nm Rayonet photoreactor; SL, 275-W sunlamp ca. 20 cm from reaction vessel. [b] Yields were determined by ^1H NMR; (*E*)/(*Z*) ratios were determined by GLC. [c] $Ph_2C{=}CHSnBu_3$ was recovered in 72% yield.

underwent further photostimulated reactions leading to **3–7**. A reasonable yield of PhC≡CSPh was observed only when a large excess of acetylenic reagent was employed.

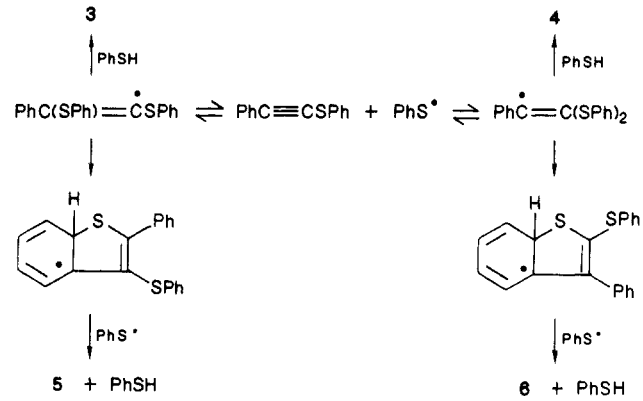
PhC(SPh)=CHSPh (*E*)- and (*Z*)-**3** PhCH=C(SPh)$_2$ **4**

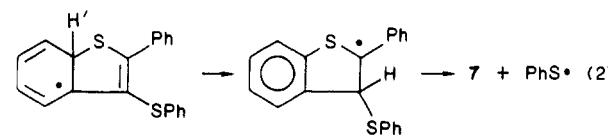


5 **6** **7**

The formation of **5** and **6** are readily explained by the nonregioselective addition of PhS• to PhC≡CSPh followed by cyclization and loss of H• to another PhS• (Scheme IV). The thiophenol from the aromatization reaction can serve as the hydrogen atom donor for the formation of **3** and **4**. The formation of **7** seems to require a hydrogen atom migration followed by loss of PhS• (reaction 2). Products

Scheme IV





3 and **4** were significant in the reactions involving PhC≡CSnBu$_3$ but not $(PhC{\equiv}C)_2Hg$, presumably because the mercurial was more effective in scavenging PhSH.

The relative reactivities of the 1-alkenyl- and 1-alkynylmercurials and 1-alkenyl- and 1-alkynylstannanes were measured by the competitive reaction of a 10-fold excess of 1:1 molar mixture of two unsaturated compounds with either $(PhS)_2Hg$ or PhSSPh (Table V). With $(PhS)_2Hg$ the compounds $Ph_2C{=}CHI$ and PhC≡CI could be used in the competitions by virtue of reactions 3 and 4 wherein I• attacks $(PhS)_2Hg$ to regenerate PhS•.

$$Ph_2C{=}CHI + (PhS)_2Hg \rightarrow Ph_2C{=}CHSPh + PhSHgI \quad (3)$$

$$PhC{\equiv}CI + (PhS)_2Hg \rightarrow PhC{\equiv}CSPh + PhSHgI \quad (4)$$

The reactions of PhS• with alkenes and alkynes are undoubtedly complicated by reversal of the PhS• addition step, and the reactivity is probably a function of k_a, k_{-a}, and k_e (reaction 5). The reactivity of a given substrate

$$PhS^\bullet + \pi\text{-}MX_n \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} PhS\text{-}\dot{\pi}\text{-}MX_n \xrightarrow{k_e} PhS\text{-}\pi + {}^\bullet MX_n \quad (5)$$

would be $k_ak_e/(k_{-a} + k_e)$, but if $k_e \gg k_{-a}$, the reactivity is a measure of k_a alone. The results summarized in Table V are internally consistent, suggesting that this indeed may be the case. Under the conditions used for the competitive reactions, the formation of **3–7** was not significant and the reactivity of PhC≡CSnBu$_3$ is based on the yield of PhC≡CSPh observed.

The results summarized in Table V indicate that PhCH=CHSnBu$_3$ is 300 times more reactive than PhC≡

Table IV. Reaction of $(PhC{\equiv}C)_2Hg$ and PhC≡CSnBu$_3$ with Mercurials

substrate	mercurial (equiv)	conditns[a]	products (equiv)[b]
$(PhC{\equiv}C)_2Hg$	$(EtO)_2P(O)HgCl$ (5)	Me_2SO, 24 h	$PhC{\equiv}CP(O)(OEt)_2$ (1.2)
$(PhC{\equiv}C)_2Hg$	$(PhS)_2Hg$ (0.2)	Me_2SO, 24 h	PhC≡CSPh (0.09); **5** and **6** (0.05); **7** (0.004)
$(PhC{\equiv}C)_2Hg$	PhSSPh (0.2)	Me_2SO, 24 h	PhC≡CSPh (0.05); **5** and **6** (0.05); **7** (0.016)
PhC≡CSnBu$_3$	$(PhS)_2Hg$ (0.2)	Me_2SO/PhH, 24 h	PhC≡CSPh (0.07); **3–6** (0.026)
PhC≡CSnBu$_3$	PhSSPh (0.2)	PhH, 12 h	PhC≡CSPh (0.12); **3–6** (0.016)

[a] 0.1 mmol of the substrate was irradiated in 10 mL of solvent in a 350-nm Rayonet Photoreactor. [b] Yields by GLC.

Table V. Relative Reactivities of 1-Alkenyl and 1-Alkynyl Derivatives toward PhS•[a]

reagent A	reagent B	Q–Y	k_A/k_B[b]
CH_2=$CHSnBu_3$	Ph_2C=CHI	$(PhS)_2Hg$	0.05
CH_2=$CHCH_2SnBu_3$	Ph_2C=CHI	$(PhS)_2Hg$	0.13
Me_2C=$CHSnBu_3$	Ph_2C=CHI	$(PhS)_2Hg$	0.60
Me_2C=$CHSnBu_3$	CH_2=$CHSnBu_3$	PhSSPh	11
CH_2=$CHSnBu_3$	PhC≡$CSnBu_3$	$(PhS)_2Hg$	6.0
PhC≡$CSnBu_3$	Ph_2C=CHI	$(PhS)_2Hg$	<0.01
(*E*)-PhCH=$CHSnBu_3$	Ph_2C=CHI	$(PhS)_2Hg$	2.4
(*E*)-PhCH=CHHgCl	Ph_2C=CHI	$(PhS)_2Hg$	5.2
(*E*)-PhCH=CHHgCl	Me_2C=$CHSnBu_3$	PhSSPh	7.0
PhC≡CI	Ph_2C=CHI	$(PhS)_2Hg$	0.23
Ph_2C=$CHSnBu_3$	PhC≡CI	$(PhS)_2Hg$	23
Ph_2C=$CHSnBu_3$	Me_2C=$CHSnBu_3$	PhSSPh	10
Ph_2C=CHHgCl	PhC≡CI	$(PhS)_2Hg$	30

[a] 0.1 mmol of the mercurial or PhSSPh was irradiated in a 350-nm Rayonet photoreactor in 10 mL of Me_2SO or PhH in the presence of 2 mmol of a 1:1 mixture of reagents A and B. [b] Based on the yields of sulfides measured by GLC.

$CSnBu_3$, that Ph_2C=$CHMX_n$ is about twice as reactive as PhCH=$CHMX_n$ (MX_n = Bu_3Sn or HgCl), and that β-styrenylmercurials are only slightly more reactive than the corresponding β-styrenylstannanes. The reactivity series observed is PhC≡$CSnBu_3$ (0.16) < CH_2=$CHSnBu_3$ (1.0) < CH_2=$CHCH_2SnBu_3$ (3.0) < Me_2C=$CHSnBu_3$ (12) < (*E*)-PhCH=$CHSnBu_3$ (50) < Ph_2C=$CHSnBu_3$ ≈ (*E*)-PhCH=CHHgCl (100) < Ph_2C=CHHgCl (140).[11] Included in the series is CH_2=$CHCH_2SnBu_3$ which reacts with PhSSPh[8] or $(PhS)_2Hg$ to form CH_2=$CHCH_2SPh$ by an S_H2' process.

Toward c-C_6H_{11}•, PhC≡$CSnBu_3$ is 0.3 as reactive as PhCH=$CHSnBu_3$ while $(PhC{\equiv}C)_2Hg$ is 0.13 as reactive as PhCH=CHHgCl.[9] The much greater selectivity observed with PhS• is in line with the lower reactivity of PhS• in relation to c-C_6H_{11}•. The difference in reactivity of alkynyl and alkenyl derivatives observed with both PhS• and c-C_6H_{11}• may be connected with the fact that neighboring group stabilization might be expected for PhĊH–$C(MX_n)$– but not for PhC=$\dot{C}(MX_n)$–.

By use of the reagents $(PhS)_2Hg$, $(PhSO_2)Hg$, or $[(EtO)_2P(O)]_2Hg$, it is possible to achieve free radical chain substitution in the compounds $(R^1)(R^2)C$=CHQ, PhC≡CQ, and CH_2=$CHCH_2Q$ where Q = halogen, $PhSO_2$, or PhS. The reactions proceed in a manner similar to Scheme I in which the eliminated radical Q• attacks the mercurial to displace PhS•, $PhSO_2$•, or $(EtO)_2PO$•.

Other vinylmetals besides the mercury and tin derivatives will participate in Scheme I. Thus, we have observed high yields of CH_2=CHSPh in the photostimulated reaction of PhSSPh with $(CH_2$=$CH)_4Pb$ (3 equiv of $PhSCH{=}CH_2$ in 12 h; no reaction was observed in the dark). Addition of $HZr(Cp)_2Cl$ to PhC≡CH in PhH followed by irradiation in the presence of PhSSPh produced a 35% yield of PhCH=CHSPh (based on the $HZr(Cp)_2Cl$ employed). No reaction was observed upon irradiation of CH_2=$CHSiMe_3$ or *t*-BuCH=$CHB(c\text{-}C_6H_{11})_2$ in the presence of PhSSPh.

Experimental Section

Tin Reagents. 1-Alkenylstannanes were prepared by the Grignard route in THF as reported for CH_2=$CHSnBu_3$[12] and (*E*)-PhCH=$CHSnBu_3$.[13] (2-Methyl-1-propenyl)tributylstannane: bp 84–85 °C at 0.07 torr; ^{1}H NMR ($CDCl_3$) δ 5.35 (br s, 1), 2.0–0.65 (m, 33). (2,2-Diphenylethenyl)tributylstannane, bp 162–164 °C at 0.35 torr, was purified by chromatography on silica gel with hexane eluent to give material having the following: ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 10), 6.65 (s, 1), 1.55–0.50 (m, 27). Methyl (*E*)-β-(tributylstannyl)acrylate, prepared by a literature procedure:[14] ^{1}H NMR ($CDCl_3$) δ 7.72 (d, 1, *J* = 19.5 Hz), 6.22 (d, 1, *J* = 19.5 Hz), 3.70 (s, 3), 1.8–0.7 (m, 27). Methyl (*Z*)-β-(tributylstannyl)acrylate:[14] bp 120–125 °C (1.5 torr); ^{1}H NMR ($CDCl_3$) δ 7.18 (d, 1, *J* = 13 Hz), 6.70 (d, 1, *J* = 13 Hz), 3.78 (s, 3), 1.8–0.6 (m, 27). (Phenylethynyl)tributylstannane[15] was prepared from PhC≡CLi and Bu_3SnCl and purified by chromatography on silica gel using hexane–ethyl acetate (90:10) as the eluent.

1-Alkenylmercury Halides. Vinylmercury choride was purchased from Organomet, Inc. ((*E*)-3,3-Dimethyl-1-butenyl)mercury chloride,[16] ((*E*)-2-phenyl-1-ethenyl)mercury chloride,[16] and (2,2-diphenylethenyl)mercury chloride,[17] mp 141–142 °C, and bromide,[17] mp 156–157 °C, were prepared according to the literature procedures. ((*E*)-β-Chlorovinyl)mercury chloride was prepared from C_2H_2, $HgCl_2$, and concentrated hydrochloric acid:[18] mp 115–123 °C; ^{1}H NMR ($CDCl_3$) δ 6.22 (s). Attempts to reproduce the literature procedure for ((*Z*)-β-chlorovinyl)mercury chloride led to a 3:1 mixture of *Z* and *E* isomers as analyzed by ^{1}H NMR. (*Z*)-isomer: ^{1}H NMR ($CDCl_3$) δ 6.98 (d, 1, *J* = 7.2 Hz), 6.22 (d, 1, *J* = 7.2 Hz).

Bis Mercurials. Bis(phenylethynyl)mercury, mp 122.5–123.0 °C, was synthesized by a literature procedure.[19] Attempts to prepare PhC≡CHgCl were unsucessful because of the facile symmetrization reaction. Also prepared by the literature procedures were mercuric phenylmercaptide,[20] mp 149–150 °C, mercuric phenylselenide,[21] mp 148.5–149.0 °C, mercuric benzenesulfinate,[22] mp 130 °C dec; bis(diethoxyphosphinyl)mercury,[23] mp 57–58 °C, and (diethoxyphosphinyl)mercury chloride, [23] mp 103–104 °C.

1-Alkenyl Sulfides. The following alkenyl sulfides were either prepared by literature procedures or isolated from reactions of the alkenylmercurials or -stannanes. Phenyl vinyl sulfide:[24] bp 35–37 °C at 0.5 torr; ^{1}H NMR ($CDCl_3$) δ 7.35–7.10 (m, 5), 6.44 (dd, 1, *J* = 16.5, 9 Hz), 5.33 (d, 1, *J* = 9 Hz), 5.24 (d, 1, *J* = 16.5 Hz). Benzyl vinyl sulfide: ^{1}H NMR ($CDCl_3$) δ 7.38–7.10 (m, 5), 6.4 (dd, 1, *J* = 16.9 Hz), 5.35 (d, 1, *J* = 9 Hz), 5.20 (d, 1, *J* = 16 Hz), 3.92 (s, 2); GCMS, *m/e* (relative intensity) 152 (1.2), 150 (M^+, 27), 91 (100). 2-Methyl-1-propenyl phenyl sulfide:[25] bp 40–53 °C at 0.007 torr; ^{1}H NMR ($CDCl_3$) δ 7.29–7.09 (m, 5), 5.91 (s, 1), 1.93 (s, 3), 1.87 (s, 3); GCMS, *m/e* (relative intensity) 166 (5), 164 (M^+, 100), 149 (31), 55 (46). Benzyl 2-methyl-1-propenyl sulfide:[25] ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5), 5.56 (s, 1), 3.73 (s, 2), 1.67 (s, 6); GCMS, *m/e* (relative intensity) 180 (1), 178 (M^+, 23), 91 (100), 65 (22). Phenyl (*E*)-2-phenyl-1-ethenyl sulfide:[26] bp 142–145 °C at 0.6 torr; ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, 10), 6.83 (d, 1, *J* = 15 Hz), 6.68 (d, 1, *J* = 15 Hz); GCMS, *m/e* (relative intensity) 214 (4.4), 212 (M^+, 93), 121 (69), 77 (100). Benzyl (*E*)-2-phenyl-1-ethenyl sulfide:[27] mp 65–67 °C; ^{1}H NMR ($CDCl_3$) δ

(11) The total reactivity of CH_2=$CHSnBu_3$ toward PhS• may be considerably higher than the measured reactivity toward α-attack since β-attack would be reversible (PhS• + CH_2=$CHSnBu_3$ ⇌ $PhSCH_2\dot{C}HSnBu_3$). Reaction of PhS• or PhSe• with CH_2=CHHgCl may also involve reversible β-addition or perhaps the formation of an unstable $PhSeCH_2CH(SePh)HgCl$ intermediate which decompose to CH_2=CHHgCl and PhSeSePh.

(12) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515.

(13) Seyferth, D.; Vaughan, L.; Susuki, R. *J. Organomet. Chem.* **1964**, *1*, 437.

(14) Seitz, D. E.; Lee, S. H. *Tetrahedron Lett.* **1981**, *22*, 4909.

(15) Centinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202.

(16) Larock, R. C.; Brown, H. C. *J. Organomet. Chem.* **1972**, *36*, 1.

(17) Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *J. Organomet. Chem.* **1978**, *162*, 271.

(18) Makarova, L. G.; Nesmeyanov, A. N. *Methods of Elemento Organic Chemistry*; North Holland Publishing Co.: Amsterdam, 1967; Vol. 4.

(19) Johnson, J. R.; McEwen, W. L. *J. Am. Chem. Soc.* **1926**, *48*, 469.

(20) Canty, A. J.; Kishimoto, R. *Inorg. Chim. Acta* **1977**, *24*, 109.

(21) Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99.

(22) Deacon, G. B. *Aust. J. Chem.* **1967**, *20*, 1367.

(23) Venezby, D. L.; Fox, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 1664.

(24) von Braun, J.; Kirschbaum, G. *Chem. Ber.* **1920**, *53*, 1399.

(25) Aida, T.; Harpp, D.; Chan, T. H. *Tetrahedron Lett.* **1980**, *21*, 3247.

(26) Smith, L. I.; Davis, H. R. *J. Org. Chem.* **1950**, *15*, 824.

7.5–7.1 (m, 10), 6.58 (d, 1, J = 15 Hz), 6.42 (d, 1, J = 15 Hz), 4.05 (s, 2); GCMS, m/e (relative intensity) 228 (0.4), 226 (M^+, 9), 91 (100). Methyl 2,2-diphenylethenyl sulfide:[28] mp 72–73 °C; ^{1}H NMR ($CDCl_3$) δ 7.72–7.33 (m, 10), 6.53 (s, 1), 2.33 (s, 3). Isopropyl 2,2-diphenyletheneyl sulfide: ^{1}H NMR ($CDCl_3$) 7.28 (s, 5), 7.18 (s, 5), 6.63 (s, 1), 3.16 (hept, 1, J = 7 Hz), 1.33 (d, 6, J = 7 Hz); MS calcd for $C_{17}H_{18}S$ 254.11293, found 254.11309. Phenyl 2,2-diphenylethenyl sulfide:[29] ^{1}H NMR ($CDCl_3$) δ 7.50–7.15 (m, 15), 6.88 (s, 1). (*E*)-3,3-Dimethyl-1-butenyl phenyl sulfide:[30] ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5), 6.02 (s, 2), 1.08 (s, 9). Butyl (*E*)-3,3-dimethyl-1-butenyl sulfide:[31] ^{1}H NMR ($CDCl_3$) δ 5.84 (d, 1, J = 15.5 Hz), 5.63 (d, 1, J = 15.5 Hz), 2.64 (t, 2, J = 6.5 Hz), 1.75–0.7 (m, 7), 1.02 (s, 9); MS calcd for $C_{10}H_{20}S$ 172.12858, found 172.12790. Methyl (*E*)-β-(phenylthio)acrylate:[32] ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 1, J = 15.6 Hz), 7.35 (m, 5), 5.68 (d, 1, J = 15.6 Hz), 3.67 (s, 3); GCMS, m/e (relative intensity) 196 (1), 194 (M^+, 48), 163 (46), 135 (100), 109 (77). Methyl (*Z*)-β-(phenylthio)acrylate: ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, 6), 5.9 (d, 1, J = 10 Hz), 3.7 (s, 3); GCMS, m/e (relative intensity) 196 (0.6), 194 (M^+, 77), 163 (53), 135 (100), 109 (56). (*E*)-β-Chlorovinyl phenyl sulfide:[33] bp 118 °C at 15 torr; ^{1}H NMR ($CDCl_3$) δ 7.32 (s, 5), 6.61 (d, 1, J = 13 Hz), 6.23 (d, 1, J = 13 Hz); ^{13}C NMR ($CDCl_3$) δ 133.9, 129.4, 129.1, 127.1, 125.5, 120.1; GCMS, m/e (relative intensity) 172 (26), 170 (M^+, 71), 130 (100), 91 (59). (*Z*)-β-Chlorovinyl phenyl sulfide: GCMS, m/e (relative intensity) 172 (26), 170 (M^+, 74), 135 (100), 91 (61). (*Z*)-1,2-Bis(phenylthio)ethene:[34] mp 30 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–7.0 (m, 10), 6.5 (s, 2); GCMS, m/e (relative intensity) 246 (8), 244 (M^+, 82), 135 (100), 134 (75), 91 (69). (*E*)-1,2-Bis-(phenylthio)ethene:[34] GCMS, m/e (relative intensity) 246 (10), 244 (M^+, 95), 135 (100), 134 (77), 91 (61).

Alkenyl Selenides. The following selenides were isolated from the reactions of Tables II and III. Phenyl vinyl selenide:[35] ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 5), 6.81 (dd, 1, J = 17, 8 Hz), 5.71 (d, 1, J = 8 Hz), 5.46 (d, 1, J = 17 Hz); MS calcd for C_8H_8Se 183.9791, found 183.9783; GCMS, m/e (relative intensity) 184 (M^+, 98), 183 (79), 182 (56), 181 (53), 180 (35), 104 (90), 103 (56), 91 (40), 78 (100). 2-Methyl-1-propenyl phenyl selenide:[35] ^{1}H NMR 7.5–7.1 (m, 5), 6.12 (s, 1), 1.9 (s, 3), 1.85 (s, 3); GCMS, m/e (relative intensity) 212 (M^+, 48), 210 (24), 132 (29), 131 (79), 117 (50), 116 (33), 115 (27), 105 (28), 91 (89), 78 (66), 77 (62), 55 (87), 53 (100). 3,3-Dimethyl-1-butenyl phenyl selenide:[36] ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 5), 6.37 (d, 1, J = 15 Hz), 6.18 (d, 1, J = 15 Hz), 1.05 (s, 9); MS calcd for $C_{12}H_{16}Se$ 240.0417, found 240.0409; GCMS, m/e (relative intensity) 240 (M^+, 22), 145 (27), 83 (100). Phenyl (*E*)-2-phenyl-1-ethenyl selenide:[36] ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 10), 7.13 (d, 1, J = 17 Hz), 6.75 (d, 1, J = 17 Hz); MS calcd for $C_{14}H_{12}Se$ 260.0104, found 260.0097; GCMS, m/e (relative intensity) 260 (M^+, 46), 258 (24), 180 (71), 179 (70), 178 (39), 169 (26), 165 (26), 103 (30), 102 (37), 78 (30), 77 (100). Phenyl (*Z*)-2-phenyl-1-ethenyl selenide: GCMS, m/e (relative intensity) 260 (M^+, 39), 258 (19), 180 (63), 179 (62), 178 (33), 169 (23), 165 (23), 103 (29), 102 (34), 78 (35), 77 (100). Phenyl 2,2-diphenylethenyl selenide: ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, 15), 7.1 (s, 1); GCMS, m/e (relative intensity) 336 (M^+, 47), 256 (22), 255 (25), 179 (34), 178 (100).

Alkenyl Sulfones. The following sulfones were prepared (Tables I, III). Phenyl vinyl sulfone:[37] mp 67–68 °C; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5), 6.7 (dd, 1, J = 16, 9 Hz), 6.47 (d, 1, J = 9 Hz), 6.05 (d, 1, J = 16 Hz); GCMS, m/e (relative intensity) 170 (0.7), 168 (M^+, 15), 125 (91), 77 (100). 2-Methyl-1-propenyl phenyl sulfone: mp 47.5–48.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.89–7.80 (m, 2), 7.59–7.44 (m, 3), 6.19 (s, 1), 2.15 (s, 2), 1.89 (s, 3); MS calcd for $C_{10}H_{12}O_2S$ 196.05581, found 196.05617. Methyl 3,3-dimethyl-1-butenyl sulfone: ^{1}H NMR ($CDCl_3$) δ 6.94 (d, 1, J = 15.5 Hz), 6.29 (d, 1, J = 15.5 Hz), 2.94 (s, 3), 1.12 (s, 9). 3,3-Dimethyl-1-butenyl phenyl sulfone: ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5), 6.87 (d, 1, J = 16 Hz), 6.11 (d, 1, J = 16 Hz), 1.09 (s, 9); MS calcd for $C_{12}H_{16}O_2S$ 224.08711, found: 224.08722. 3,3-Dimethyl-1-butenyl *p*-tolyl sulfone: bp 105 °C at 0.15 torr; ^{1}H NMR ($CDCl_3$) δ 7.80–7.20 (m, 4), 6.88 (d, 1, J = 15 Hz), 6.16 (d, 1, J = 15 Hz), 2.42 (s, 3), 1.09 (s, 9); MS calcd for $C_{13}H_{18}O_2S$ 238.10276, found 238.10282. Phenyl (*E*)-2-phenyl-1-ethenyl sulfone:[38] mp 73–74 °C; ^{1}H NMR δ 7.75 (d, 1, J = 16 Hz), 7.7–7.2 (m, 10), 6.9 (d, 1, J = 16 Hz); GCMS, m/e (relative intensity) 246 (0.5), 244 (M^+, 10), 102 (89), 91 (100), 77 (94). (*E*)-2-Phenyl-1-ethenyl *p*-tolyl sulfone:[39] ^{1}H NMR ($CDCl_3$) δ 7.8–7.2 (m, 9), 7.63 (d, 1, J = 15 Hz), 6.82 (d, 1, J = 15 Hz), 2.39 (s, 3); MS calcd for $C_{15}H_{14}O_2S$ 258.07145; found 258.07139; GCMS, m/e (relative intensity) 260 (0.8), 258 (M^+, 16), 139 (71), 102 (45), 91 (100), 77 (68). Phenyl 2,2-diphenylethenyl sulfone: mp 101.5–103.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m, 15), 6.97 (s, 1); MS calcd for $C_{21}H_{18}O_2S$ 334.10275, found 334.10407. Methyl (*E*)-β-(phenylsulfonyl)acrylate:[40] ^{1}H NMR ($CDCl_3$) δ 8.2–7.8 (m, 2), 7.8–7.3 (m, 3), 7.4 (d, 1, J = 16.2 Hz), 6.8 (d, 2, J = 16.2 Hz), 3.8 (s, 3); GCMS, m/e (relative intensity) 226 (M^+, 1.3), 125 (100), 77 (77), 51 (88).

1-Alkenylphosphonates. The following phosphonates were prepared (Table III). Diethyl ((*E*)-3,3-dimethyl-1-butenyl)-phosphonate: ^{1}H NMR ($CDCl_3$) δ 6.78 (dd, 1, J_H = 17.5, J_P = 23 Hz), 5.43 (dd, 1, J_H = 17.5, J_P = 20 Hz), 4.08 (m, 4), 1.32 (t, 6, J_H = 7 Hz), 1.05 (s, 9); MS calcd for $C_{10}H_{21}O_3P$ 220.12284, found 220.12290; GCMS, m/e (relative intensity) 220 (M^+, 8), 149 (29), 138 (32), 111 (49), 83 (100). Diethyl ((*E*)-2-phenyl-1-ethenyl)-phosphonate:[41] ^{1}H NMR ($CDCl_3$) δ 7.90–7.15 (m, 6), 6.6–5.7 (m, 1), 4.1 (m, 4), 1.34 (t, 6, J = 7 Hz); GCMS, m/e (relative intensity) 240 (M^+, 12), 131 (100). Diethyl (2-methyl-1-propenyl)-phosphonate: GCMS, m/e (relative intensity) 192 (M^+, 12), 136 (92), 121 (35), 83 (100). Diethyl (2,2-diphenylethenyl)phosphonate: ^{1}H NMR ($CDCl_3$) δ 7.50–7.15 (m, 10), 6.15 (d, 1, J_P = 16.8 Hz), 3.85 (m, 4), 1.10 (t, 6, J_H = 7 Hz); GCMS, m/e (relative intensity) 316 (M^+, 5), 207 (40), 180 (36), 178 (100).

Other Alkenyl and Alkynyl Derivatives. (*E*)-3,3-Dimethyl-1-butenyl phenyl telluride (Table I): ^{1}H NMR ($CDCl_3$) δ 7.7–7.1 (m, 5), 6.66 (d, 1, J = 16 Hz), 6.40 (d, 1, J = 16 Hz), 1.04 (s, 9); MS calcd for $C_{12}H_{16}Te$ 288.02990, found 288.02845. Reaction of (*E*)-PhCH=CHSnBu$_3$ with Cl_3CSO_2Cl (Table I) formed 3,3,3-trichloro-1-phenyl-1-propene: bp 86–90 °C at 0.7 torr; ^{1}H NMR ($CDCl_3$) δ 7.65–7.20 (m, 5), 6.0 (q, J_{AB} = 12 Hz, ν_{AB} = 0.59 ppm); MS calcd for $C_9H_7Cl_3$ 219.96151, found 219.96168; GCMS, m/e (relative intensity) 222 (0.2), 220 (M^+, 0.2), 189 (3), 187 (20), 185 (32), 151 (31), 149 (100). Photolysis of (*E*)-PhCH=CHSnBu$_3$ in CCl_4 for 38 h at 350 nm gave the same product in 62% yield with a *E*/*Z* ratio of 20:1. Reaction at 80 °C for 24 h in the presence of 5 mol % azobis(isobutyronitrile) gave the same product in 53% yield. Reaction of 1.5 equiv of $BrCCl_3$ with (*E*)-PhCH=CHSnBu$_3$ in PhH at 35 °C with 350-nm irradiation formed PhCH=CHCCl$_3$ in 55% yield. A comparable yield was obtained with 10 mol % azobis(isobutyronitrile) at 80 °C for 16 h.

Phenyl phenylethynyl sulfide (Table IV), bp 127 °C at 0.6 torr, was synthesized according to a literature procedure.[42] Diethyl (phenylethynyl)phosphonate (Table IV): ^{1}H NMR ($CDCl_3$) δ 7.7–7.1 (m, 5), 4.2 (m, 4), 1.4 (t, 6); GCMS, m/e (relative intensity) 238 (M^+, 11), 210 (16), 195 (15), 165 (21), 128 (29), 102 (100).

Photochemical Reaction of (PhC≡C)$_2$Hg and PhC≡CSnBu$_3$ with (PhS)$_2$Hg and PhSSPh. In addition to PhC≡CSPh, capillary column GC and GCMS indicated the formation of 2-phenylbenzo[*b*]thiophene (**7**), three isomers of $C_{20}H_{16}S_2$ (assigned as (*E*)- and (*Z*)-**3** and as **4**), and two isomers of $C_{20}H_{14}S_2$ (assigned as **5** and **6**). Photolysis of PhC≡CSPh with Hg(SPh)$_2$ (24 h, Me$_2$SO, 350 nm) yielded the same products, and only minor amounts of **3**–**7** were formed in the photolysis of PhC≡CSPh alone. 2-Phenylbenzo[*b*]thiophene (**7**) was isolated by preparative

(27) Pasto, D. J.; Snyder, S. *J. Org. Chem.* **1966**, *31*, 2777.
(28) Wittig, G.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 1373.
(29) Gröbel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867.
(30) Hartmann, J.; Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261.
(31) Gracheva, E. P.; Laba, V. I.; Kul'bovskaya, N. K.; Shostakovskii, M. F. *Zh. Obshch. Khim.* **1963**, *33*, 2493.
(32) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.
(33) Montanari, F. *Gazzetta* **1956**, 86.
(34) Truce, W. E.; McManime, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 5745.
(35) Okamoto, Y.; Homsany, R.; Yano, T. *Tetrahedron Lett.* **1972**, 2529.
(36) Raucher, S.; Hansen, M. R.; Cotter, M. A. *J. Org. Chem.* **1978**, *43*, 4885.
(37) McDowell, S. T.; Stirling, C. J. N. *J. Chem. Soc. B* **1967**, 348.
(38) Truce, W. E.; Badiger, V. V. *J. Org. Chem.* **1964**, *26*, 3277.
(39) Kohler, E. P.; Potter, H. *J. Am. Chem. Soc.* **1935**, *57*, 1316.
(40) Berdnikov, E. A.; Mukhitova, F. K.; Tantasheva, F. R.; Katane, E. G. *J. Org. Chem. USSR* **1977**, *13*, 1302.
(41) Tavs, P.; Weitkamp, H. *Tetrahedron* **1970**, *26*, 5529.
(42) Truce, W. E.; Hill, H. E.; Boudakian, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 2760.

GC or by silica gel chromatography with hexane eluent as a pure substance, mp 168–169 °C (lit.[43] 171–173 °C), but the two isomers $C_{20}H_{14}S_2$ could not be separated. The mixture had the following: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.00 (m); a GCMS consistent with those of **5** and **6**; MS (mixture) calcd for $C_{20}H_{14}S_2$ 318.053 699, found 318.053 55; GCMS, *m/e* (relative intensity) 320 (11), 318 (M^+, 100), 285 (20), 284 (25), 241 (36), 240 (67), 208 (29), 165 (25); IR (neat) 3043 (s), 1593 (w), 1576 (s), 1470 (s), 1448 (s), 1433 (s), 1422 (s), 1075 (m), 1063 (m), 1015 (s), 740 (s), 680 (s) cm^{-1}.

Irradiation of PhC≡CSPh with PhSH at 350 nm for 25 h yielded a mixture of **3** (*E* and *Z* isomers) and **4**. 2,2-Bis(phenylthio)-1-phenylethene (**4**)[44] was isolated by silica gel chromatography with hexane eluent: ^{1}H NMR ($CDCl_3$) δ 7.61 (m), 7.4–7.1 (m), 6.89 (s); GCMS (relative intensity) 322 (5), 320 (M^+, 45), 211 (97), 209 (40), 179 (23), 178 (100); IR (neat) 3062 (w), 1582 (m), 1479 (s), 1440 (s), 1025 (m), 738 (s), 688 (s) cm^{-1}. 1,2-Bis(phenylthio)phenylethene[45] (mixture of *E* and *Z* isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.10 (m); GCMS, *m/e* (relative intensity) 322 (5), 320 (M^+, 45), 211 (96), 210 (40), 179 (23), 178 (100); IR (neat) 3067 (m), 1587 (s), 1545 (m), 1485 (s), 1445 (s), 1030 (m), 740 (s), 680 (s). Compounds **3** and **4** were not significant products in the reaction of $(PhC{\equiv}C)_2Hg$ with $(PhS)_2Hg$ or PhSSPh. Compound **7** had the same retention time as $PhC{\equiv}CSnBu_3$ (7% OV-3, $^1/_8$ in. × 10 ft) and was not analyzed as a reaction product with $PhC{\equiv}CSnBu_3$ as the substrate.

Acknowledgment. This work was supported by Grants CHE-8415450 from the National Science Foundation and 14784-AC4 from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. (*Z*)-**3**, 41424-40-2; (*E*)-**3**, 41424-41-3; **4**, 35550-81-3; **5**, 108344-94-1; **6**, 77128-61-1; **7**, 1207-95-0; CH_2=CHSPh, 1822-73-7; $(CH_3)_2C$=CHSPh, 13640-71-6; (*E*)-PhCH=CHSPh, 7214-53-1; Ph_2C=CHSPh, 13112-46-4; CH_2=$CHSCH_2Ph$, 1822-76-0; $(CH_3)_2C$=$CHSCH_2Ph$, 63196-87-2; (*E*)-PhCH=$CHSCH_2Ph$, 13294-33-2; CH_2=$CHSO_2Ph$, 5535-48-8; $(CH_3)_2C$=$CHSO_2Ph$, 54897-35-7; (*E*)-PhCH=$CHSO_2Ph$, 16212-06-9; (*Z*)-PhCH=$CHSO_2Ph$, 32291-77-3; (*E*)-PhCH=$CHSO_2CCl_3$, 108344-83-8; Ph_2C=$CHSO_2Ph$, 26189-62-8; (*E*)-PhCH=CHSePh, 60466-40-2; (*Z*)-PhCH=CHSePh, 60466-30-0; (*E*)-MeO_2CCH=CHSPh, 49833-37-6; (*Z*)-MeO_2CCH=CHSPh, 49833-38-7; (*E*)-MeO_2CCH=$CHSO_2Ph$, 1865-13-0; (*Z*)-MeO_2CCH=$CHSO_2Ph$, 91077-67-7; CH_2=CHSePh, 35167-28-3; (*E*)-*t*-BuCH=CHSBu-*n*, 70127-58-1; (*Z*)-*t*-BuCH=CHSBu-*n*, 64228-42-8; (*E*)-*t*-BuCH=CHSPh, 53847-74-8; (*Z*)-*t*-BuCH=CHSPh, 58431-67-7; (*E*)-*t*-BuCH=CHSePh, 63831-89-0; (*Z*)-*t*-BuCH=CHSePh, 108344-84-9; (*E*)-*t*-BuCH=CHTePh, 75924-68-4; (*Z*)-*t*-BuCH=CHTePh, 108344-85-0; (*E*)-*t*-BuCH=$CHSO_2Ph$, 68969-27-7; (*Z*)-*t*-BuCH=$CHSO_2Ph$, 108344-86-1; (*E*)-*t*-BuCH=$CHSO_2C_6H_4$-*p*-Me, 74829-77-9; (*Z*)-*t*-BuCH=$CHSO_2C_6H_4$-*p*-Me, 108344-87-2; (*E*)-*t*-BuCH=$CHSO_2Me$, 108344-88-3; (*Z*)-*t*-BuCH=$CHSO_2Me$, 108344-89-4; Ph_2C=CHSMe, 15096-10-3; Ph_2C=CHSPr-*i*, 108344-90-7; (*E*)-ClCH=CHSPh, 26620-11-1; (*Z*)-ClCH=CHSPh, 60785-27-5; (*Z*)-PhCH=CHSPh, 7214-56-4; Ph_2C=CHSePh, 108365-51-1; $(CH_3)_2C$=CHSePh, 77461-45-1; Ph_2C=CHP(O)$(OEt)_2$, 78462-91-6; (*E*)-PhCH=CHP(O)$(OEt)_2$, 20408-33-7; (*Z*)-PhCH=CNP(O)$(OEt)_2$, 25362-01-0; (*E*)-*t*-BuCH=CHP(O)$(OEt)_2$, 75924-69-5; (*Z*)-*t*-BuCH=CHP(O)$(OEt)_2$, 108344-91-8; $(CH_3)_2C$=CHP(O)$(OEt)_2$, 58142-40-8; $PhC{\equiv}CP(O)(OEt)_2$, 3450-67-7; $PhC{\equiv}CSPh$, 35460-31-2; CH_2=$CHSnBu_3$, 7486-35-3; $(CH_3)_2C$=$CHSnBu_3$, 66680-86-2; (*E*)-PhCH=$CHSnBu_3$, 66680-88-4; Ph_2C=$CHSnBu_3$, 91083-76-0; (*E*)-MeO_2CCH=$CHSnBu_3$, 82101-74-4; (*Z*)-MeO_2CCH=$CHSnBu_3$, 82101-75-5; CH_2=CHHgCl, 762-55-0; (*E*)-*t*-BuCH=CHHgCl, 36525-02-7; (*E*)-PhCh=CHHgCl, 36525-03-8; Ph_2C=CHHgCl, 24522-19-8; (*E*)-ClCH=CHHgCl, 1190-78-9; (*Z*)-ClCH=CHHgCl, 2350-34-7; Ph_2C=CHHgBr, 67341-86-0; (*E*)-*t*-BuCH=CHHgBr, 108344-92-9; $(CH_3)_2C$=CHHgBr, 23010-28-8; Cl_3CSO_2-Cl, 2547-61-7; PhSe-$SO_2C_6H_4CH_3$-*p*, 68819-94-3; $Hg(SePh)_2$, 21514-25-0; $Hg(SO_2H)_2$, 15220-40-3; $[(EtO)_2P(O)]_2Hg$, 29105-14-4; $(EtO)_2P(O)HgCl$, 29120-01-2; Ph_2C=CHI, 19997-66-1; $PhC{\equiv}CI$, 932-88-7; (*Z*)-PhCH=$CHSO_2CCl_3$, 108344-93-0; (*E*)-PhSCH=CHSPh, 18893-63-5; (*Z*)-PhSCH=CHSPh, 18893-62-4; PhS—SPh, 882-33-7; $PhCH_2S$—SCH_2Ph, 150-60-7; $PhSO_2$—Cl, 98-09-9; PhSe—SePh, 1666-13-3; *n*-BuS—SBu-*n*, 629-45-8; PhTe—TePh, 32294-60-3; *p*-$MeC_6H_4SO_2$—Cl, 98-59-9; $MeSO_2$—Cl, 124-63-0; MeS—SMe, 624-92-0; *i*-PrS—SPr-*i*, 4253-89-8; $Hg(SPh)_2$, 21514-24-9; $(PhC{\equiv}C)_2Hg$, 6077-10-7; $PhC{\equiv}CSnBu_3$, 3757-88-8.

(43) Chow, A. W.; Hall, N. M.; Hoover, J. R. E.; Dolan, M. M.; Ferlauto, R. J. *J. Med. Chem.* **1966**, *9*, 551.
(44) Murahashi, S.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. Veenstra, G. E.; Zwanenberg, B. *Tetrahedron* **1978**, *34*, 1585.
(45) Oki, M.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 687.

^{125}Te NMR and Mössbauer Spectroscopy of Tellurium–Phosphine Complexes and the Tellurocyanates

C. H. W. Jones* and R. D. Sharma

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received December 23, 1986

The nature of the bonding to tellurium in the phosphine complexes R_3PTe and $(R_2P)_2Te$ and in the tellurocyanates $TeCN^-$, ArTeCN, $ArCH_2TeCN$, and $ArTe(X)CN^-$ (X = Cl, Br, I) has been studied by ^{125}Te solution NMR spectroscopy at ambient temperature and by ^{125}Te Mössbauer spectroscopy at 4.2 K. No evidence was found for multiple bonding to tellurium in either solution or the solid state. The phosphine complexes R_3PTe give ^{125}Te NMR shifts of −837 to −495 ppm (Me_2Te) and ^{125}Te quadrupole splittings of 10–12 mm s^{-1}. The $TeCN^-$ ion has a ^{125}Te NMR shift of −509 to −569 ppm dependent on solvent and counterion, ArTeCN and $ArCH_2TeCN$ shifts of +570–580 ppm, and the halide derivatives $ArCH_2Te(X)CN^-$ shifts of −586 to −604 ppm. The ^{125}Te Mössbauer quadrupole splitting of $TeCN^-$ is 12 mm s^{-1}, of ArTeCN and $ArCH_2TeCN$ is 13.7–14.1 mm s^{-1}, of $ArCH_2Te(X)CN$, X = Cl, is 14.5 mm s^{-1}, of $ArCH_2Te(X)CN$, X = Br, is 13.8 mm s^{-1}, and of $ArCH_2Te(X)CN$, X = I, is 14.0 mm s^{-1}.

Introduction

The application of ^{125}Te NMR and Mössbauer spectroscopy in the study of organotellurium compounds has attracted considerable attention in recent years. However, relatively little work has been reported on tellurium–phosphine complexes or on the tellurocyanates. Du Mont and Kroth[1] have reported ^{125}Te NMR data for $(t\text{-Bu})_3PTe$, $(n\text{-Bu})_3PTe$, and $Te[P(t\text{-Bu})_2)_2$, while the tellurocyanates have not been studied to date.

(1) du Mont, W.-W.; Kroth, H.-J. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *368*, 332.

0276-7333/87/2306-1419$01.50/0