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

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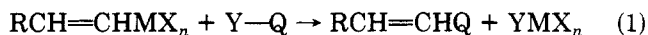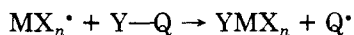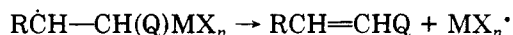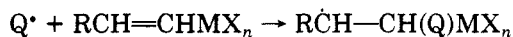
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1-Alkenyl and 1-alkynyl derivatives of tin and mercury react with hetero-centered radicals such as RS•, PhSe•, PhSO$_2$•, or (EtO)$_2$P(O)• to undergo substitution of the metal atom in a free radical chain reaction involving addition–elimination. The hetero-centered radical can be formed in a chain propagation reaction by the attack of ClHg• or Bu$_3$Sn• upon reagents such as RSSR, PhSeSO$_2$Ph, PhSeSePh, or PhSO$_2$Cl or mercurials such as Hg(SPh)$_2$, Hg(SePh)$_2$, Hg(O$_2$SPh)$_2$, 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$_2$SnBu$_3$ 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)$_2$Hg 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$_2$Ar) 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$_2$S•, 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$_6$H$_4$SH to CH$_2$=CHSnPh$_3$ forms mainly *p*-MeC$_6$H$_4$SCH$_2$CH$_2$SnPh$_3$.[3]) (*E*)- and (*Z*)-MeO$_2$CCH=CHSnBu$_3$ gave the same ratio of (*E*)- and (*Z*)-MeO$_2$CCH=CHSPh or (*E*)- and (*Z*)-MeO$_2$CCH=CHSO$_2$Ph under the conditions of Table I although at short reaction periods some evidence of stereospecificity was observed with PhSSPh.[4]

Scheme I

$$Q• + RCH=CHMX_n \rightarrow R\dot{C}H—CH(Q)MX_n$$

$$R\dot{C}H—CH(Q)MX_n \rightarrow RCH=CHQ + MX_n•$$

$$MX_n• + Y—Q \rightarrow YMX_n + Q•$$

$$RCH=CHMX_n + Y—Q \rightarrow RCH=CHQ + YMX_n \quad (1)$$

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)$_2$PCl, Ph$_2$PCl, or (EtO)$_2$P(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.
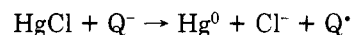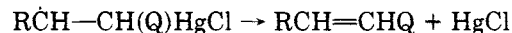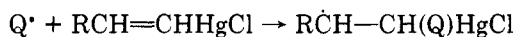
Table II summarizes the reactions of Q–Y reagents with 1-alkenylmercurials. The most noticeable differences be-

tween 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$_2$Ph. 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$_2$Cl$_2$) to form the phenyl vinyl selenide while no reaction was observed with UV irradiation for (EtO)$_2$P(O)Cl, PhCOCl, Me$_2$C(NO$_2$)Br, or 2,4-(O$_2$N)$_2$C$_6$H$_3$SCl. 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)$_2$PO⁻ (Q⁻ in Scheme II).[2,5] Alternately, vinyltin or -mercury reagents can react with the reagents Q$_2$Hg or QHgCl by the chain sequence of Scheme III.[6] The use of the reagents Q$_2$Hg or QHgCl avoids the problems of symmetrization which can occur in the reactions of vinylmercurials with anions in the dark.

Scheme II

$$Q• + RCH=CHHgCl \rightarrow R\dot{C}H—CH(Q)HgCl$$

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

$$HgCl + Q⁻ \rightarrow Hg^0 + Cl⁻ + Q•$$

Scheme III

$$Q• + RCH=CHMX_n \rightarrow R\dot{C}H—CH(Q)MX_n$$

$$R\dot{C}H—CH(Q)MX_n \rightarrow RCH=CHQ + •MX_n$$

$$•MX_n + Q_2Hg \rightarrow QMX_n + QHg•$$

$$QHg• \rightarrow Q• + Hg^0$$
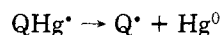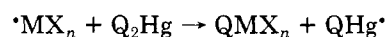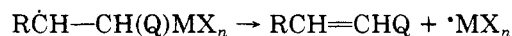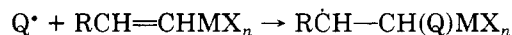
Table III summarizes the observed substitutions utilizing the mercurials with Q = PhS, PhSe, PhSO$_2$, or (EtO)$_2$PO. In general, a slightly higher reactivity was displayed with

(1) Supported by a scholarship from Yarmouk University, Irbid, Jordan, 1980–1983.
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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)	$h\nu$, 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)	$h\nu$, $(t$-Bu)$_2$NO$^\bullet$ (0.15 equiv), 2 h	0 (GC)
CH$_3$	CH$_3$	PhS–SPh (1.2)	$h\nu$, 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)	$h\nu$, $(t$-Bu)$_2$NO$^\bullet$ (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)	$h\nu$, 4 h	86 (I)
Ph	Ph	PhS–SPh (1.2)	$h\nu$, 2 h	93 (NMR)
H	H	PhCH$_2$S–SCH$_2$Ph (1.2)	$h\nu$, 2 h	82 (I)
CH$_3$	CH$_3$	PhCH$_2$S–SCH$_2$Ph (1.2)	$h\nu$, 2 h	84 (NMR)
(E)-Ph	H	PhCH$_2$S–SCH$_2$Ph (1.2)	$h\nu$, 10 h	85 (I)
H	H	PhSO$_2$–Cl (1.2)	$h\nu$, 6 h	89 (I)
CH$_3$	CH$_3$	PhSO$_2$–Cl (1.2)	$h\nu$, 4 h	90 (NMR)
(E)-Ph	H	PhSO$_2$–Cl (1.2)	$h\nu$, 4 h	88 (I); $((E)/(Z) > 50)$
(E)-Ph	H	Cl$_3$CSO$_2$–Cl (1.5)	$h\nu$, 24 h	48 (GC)^c
Ph	Ph	PhSO$_2$–Cl (1.2)	$h\nu$, 4 h	76 (NMR)
(E)-Ph	H	PhSe–SO$_2$C$_6$H$_4$CH$_3$-p (1.2)	$h\nu$, 6 h	84 (I); $((E)/(Z) > 50)$
H	H	PhSe–SePh (1.2)	$h\nu$, 24 h	0 (GC)
CH$_3$	CH$_3$	PhSe–SePh (1.2)	$h\nu$, 4 h	0 (NMR)
(E)-Ph	H	PhSe–SePh (1.2)	$h\nu$, 24 h	0 (GC)
(E)-MeO$_2$C	H	PhS–SPh (1.6)	UV, 8 h	79 (NMR); $(E)/(Z)$ = 3.8 (GC)
(Z)-MeO$_2$C	H	PhS–SPh (1.6)	UV, 8 h	91 (NMR); $(E)/(Z)$ = 3.7 (GC)
(E)-MeO$_2$C	H	PhSO$_2$–Cl (1.6)	UV, 10 h	68 (NMR); $(E)/(Z) > 50$ (GC)
(E)-MeO$_2$C	H	PhSO$_2$–Cl (1.6)	UV, 10 h	76 (NMR); $(E)/(Z) > 50$ (GC)

^{a} Reactants ($\sim$0.1 M 1-alkenylstannane) were irradiated in PhH by a 275-W sunlamp ca. 15 cm from a Pyrex reaction vessel ($h\nu$) or in a 350-nm Rayonet Photoreactor (UV). The irradiation maintained a temperature of 35–40 °C. ^{b} Abbreviations: I, isolated yield; GC, yield by GLC using a calibrated standard; NMR, yield by ^{1}H NMR using an internal standard. ^{c} (E)-PhCH=CHCCl$_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)	$h\nu$, 2 h	91
(E)-t-Bu	H	n-BuS–SBu-n (1)	$h\nu$, 17 h	100 (>50)
(E)-t-Bu	H	PhS–SPh (1)	$h\nu$, 6 h	100 (>50)
(E)-t-Bu	H	PhSe–SePh (1)	$h\nu$, 2 h	95 (>50)
(E)-t-Bu	H	PhTe–TePh (1)	$h\nu$, 18 h	89 (>50)
(E)-t-Bu	H	PhSO$_2$–Cl (1)	$h\nu$, 3 h	99 (>50)
(E)-t-Bu	H	p-MeC$_6$H$_4$-SO$_2$-Cl	$h\nu$, 25 h	75 (>50)
(E)-t-Bu	H	MeSO$_2$–Cl	$h\nu$, 22 h	32 (>50)
(E)-Ph	H	PhSe–SePh (1)	$h\nu$, 2 h	90 (>50)
Ph	Ph	MeS–SMe (1)	$h\nu$, 2 h	100
Ph	Ph	i-PrS–SPr-i (10)	$h\nu$, 24 h	98
(E)-Cl	H	PhS–SPh (2)	$h\nu$, Me$_2$SO, 0.5 h	14 (3.4); R^1 = PhS, 56 (0.9)
(E)-Cl	H	PhS–SPh (0.5)	UV, Me$_2$SO, 6 h	20 (2.5); R^1 = PhS, 40 (0.6)
(E)-Cl	H	PhS–SPh (1.2)	UV, Me$_2$SO, 6 h	R^1 = PhS, 81 (0.7)
(Z)-Cl^c	H	PhS–SPh (0.5)	UV, Me$_2$SO, 6 h	16 (0.9); R^1 = PhS, 32 (0.7)
(Z)-Cl^c	H	PhS–SPh (1.2)	UV, Me$_2$SO, 6 h	R^1 = PhS, 81 (0.8)

^{a} See footnote a, Table I. Ph$_2$C=CHHgBr was used for experiments with R^1 = R^2 = Ph. ^{b} Yields by ^{1}H 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$_3$Sn. Surprisingly, (PhSe)$_2$Hg reacted cleanly with Ph$_2$C=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$_3$Sn$^\bullet$ to regenerate PhSe$^\bullet$ upon reaction with PhSeSePh. Thus, Bu$_3$Sn$^\bullet$ readily attacks PhSeSO$_2$C$_6$H$_4$CH$_3$-p to generate p-CH$_3$C$_6$H$_4$SO$_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$_3$Sn$^\bullet$, PhSeSePh would be more reactive than PhSSPh. Finally, with CH$_2$=CHCH$_2$SnBu$_3$ a free radical chain substitution is observed with either PhSSPh or PhSeSePh involving attack of Bu$_3$Sn$^\bullet$ 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$_2$C=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$_3$Sn$^\bullet$) 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)$_2$Hg, the intermediate adduct radical can undergo the β-elimination of Bu$_3$Sn$^\bullet$, and the substitution reaction occurs with an appreciable kinetic chain length. Allylic substitution with PhSeSePh may occur because the β-elimination of Bu$_3$Sn$^\bullet$ is faster for 1 than for 2, perhaps for conformational reasons. With
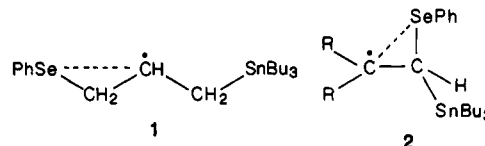
1-alkenylmercurials the β-elimination of ClHg$^\bullet$ is fast, and the substitution process according to Scheme I or III occurs with PhSSPh, PhSeSePh, (PhS)$_2$Hg, or (PhSe)$_2$Hg.

The acetylenic mercurial [(PhC≡C)$_2$Hg] and stannane (PhC≡CSnBu$_3$) gave rise to substitution products via a photostimulated free radical chain reaction with PhSSPh, (PhS)$_2$Hg, or (EtO)$_2$P(O)HgCl (Table IV).[9,10] In the case of PhSSPh or (PhS)$_2$Hg, the initially formed PhC≡CSPh

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(10) (PhCH=CH)$_2$Hg 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$_2$Ph)$_2$ (5)	UV, 12 h	100
(E)-Ph	H	HgCl	Hg(SO$_2$Ph)$_2$ (5)	UV, 12 h	74 (>50)
(E)-t-Bu	H	HgBr	Hg(SO$_2$Ph)$_2$ (5)	UV, 12 h	42 (>50)
Me	Me	HgBr	Hg(SO$_2$Ph)$_2$ (5)	UV, 12 h	38
H	H	HgCl	Hg(SO$_2$Ph)$_2$ (5)	UV, 12 h	43
Ph	Ph	SnBu$_3$	Hg(SO$_2$Ph)$_2$ (5)	SL, 4 h	63
Me	Me	SnBu$_3$	Hg(SO$_2$Ph)$_2$ (5)	SL, 4 h	38
H	H	SnBu$_3$	Hg(SO$_2$Ph)$_2$ (5)	SL, 4 h	trace
Ph	Ph	HgBr	[(EtO)$_2$P(O)]$_2$Hg	UV, 24 h	86
(E)-Ph	H	HgCl	[(EtO)$_2$P(O)]$_2$Hg	UV, 8 h	68 (>10)
(E)-t-Bu	H	HgBr	[(EtO)$_2$P(O)]$_2$Hg	UV, 15 h	86 (>50)
Me	Me	HgBr	[(EtO)$_2$P(O)]$_2$Hg	UV, 15 h	trace
Ph	Ph	SnBu$_3$	[(EtO)$_2$P(O)]$_2$Hg	UV, 20 h	14[c]
Ph	Ph	HgBr	(EtO)$_2$P(O)HgCl	UV, 2 h	59
Ph	Ph	HgBr	(EtO)$_2$P(O)HgCl	(t-Bu)$_2$NO• (0.13 equiv), UV, 2 h	0
Ph	Ph	HgBr	(EtO)$_2$P(O)HgCl	UV, 4 h	85
Ph	Ph	HgBr	(EtO)$_2$P(O)HgCl	UV, 12 h	85
(E)-Ph	H	HgCl	(EtO)$_2$P(O)HgCl	UV, 4 h	57 (>50)
(E)-t-Bu	H	HgBr	(EtO)$_2$P(O)HgCl	UV, 24 h	67 (>50)
Me	Me	MgBr	(EtO)$_2$P(O)HgCl	UV, 24 h	31
H	H	HgCl	(EtO)$_2$P(O)HgCl	UV, 24 h	trace
Ph	Ph	SnBu$_3$	(EtO)$_2$P(O)HgCl	UV, 24 h	65
Me	Me	SnBu$_3$	(EtO)$_2$P(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$_2$SO 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 ^{1}H NMR; $(E)/(Z)$ ratios were determined by GLC. [c] Ph$_2$C=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   PhCH=C(SPh)$_2$

(E)- and (Z)- 3   4

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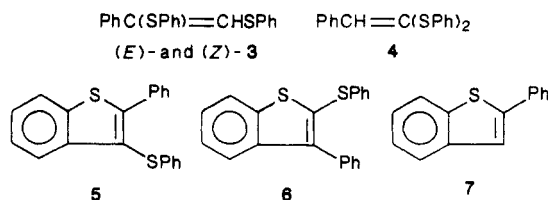
The formation of 5 and 6 are readily explained by the nonregioselective addition of PhS• to PhC≡CSPh followed
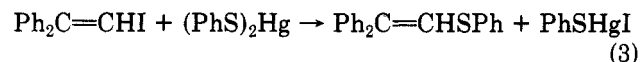
Scheme IV
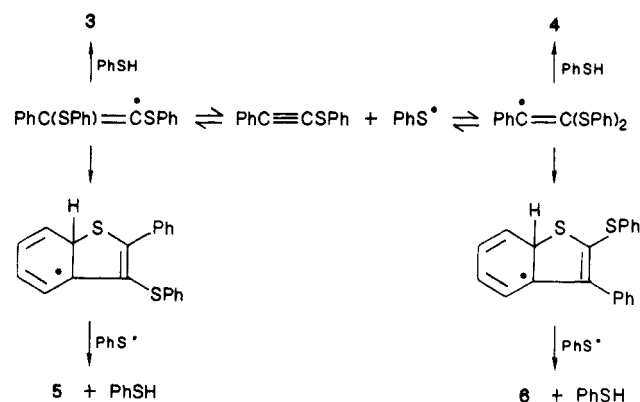
by cyclization and loss of H• to another PhS• (Scheme IV). The thiophenol from the aromatization reaction can serve as the hydrogen atom donor for the formation of 3 and 4. The formation of 7 seems to require a hydrogen atom migration followed by loss of PhS• (reaction 2). Products
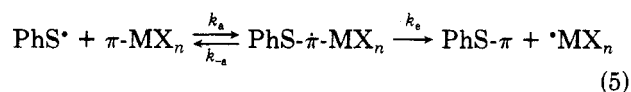

$$\text{(structures)} \longrightarrow \text{7} + \text{PhS• (2)}$$
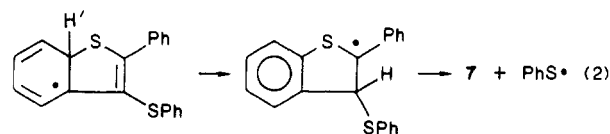
3 and 4 were significant in the reactions involving PhC≡CSnBu$_3$ but not (PhC≡C)$_2$Hg, presumably because the mercurial was more effective in scavenging PhSH.

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)$_2$Hg or PhSSPh (Table V). With (PhS)$_2$Hg the compounds Ph$_2$C=CHI and PhC≡CI could be used in the competitions by virtue of reactions 3 and 4 wherein I• attacks (PhS)$_2$Hg to regenerate PhS•.

$$\text{Ph}_2\text{C=CHI} + (\text{PhS})_2\text{Hg} \rightarrow \text{Ph}_2\text{C=CHSPh} + \text{PhSHgI} \tag{3}$$

$$\text{PhC≡CI} + (\text{PhS})_2\text{Hg} \rightarrow \text{PhC≡CSPh} + \text{PhSHgI} \tag{4}$$

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

$$\text{PhS•} + \pi\text{-MX}_n \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{PhS-}\dot{\pi}\text{-MX}_n \overset{k_e}{\longrightarrow} \text{PhS-}\pi + \text{•MX}_n \tag{5}$$

would be $k_a k_e/(k_{-a} + k_e)$, 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≡C)$_2$Hg and PhC≡CSnBu$_3$ with Mercurials

substrate	mercurial (equiv)	conditns[a]	products (equiv)[b]
(PhC≡C)$_2$Hg	(EtO)$_2$P(O)HgCl (5)	Me$_2$SO, 24 h	PhC≡CP(O)(OEt)$_2$ (1.2)
(PhC≡C)$_2$Hg	(PhS)$_2$Hg (0.2)	Me$_2$SO, 24 h	PhC≡CSPh (0.09); 5 and 6 (0.05); 7 (0.004)
(PhC≡C)$_2$Hg	PhSSPh (0.2)	Me$_2$SO, 24 h	PhC≡CSPh (0.05); 5 and 6 (0.05); 7 (0.016)
PhC≡CSnBu$_3$	(PhS)$_2$Hg (0.2)	Me$_2$SO/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$_2$C=CHI	(PhS)$_2$Hg	0.05
CH_2=CHCH$_2$SnBu$_3$	Ph$_2$C=CHI	(PhS)$_2$Hg	0.13
Me$_2$C=CHSnBu$_3$	Ph$_2$C=CHI	(PhS)$_2$Hg	0.60
Me$_2$C=CHSnBu$_3$	CH_2=CHSnBu$_3$	PhSSPh	11
CH_2=CHSnBu$_3$	PhC≡CSnBu$_3$	(PhS)$_2$Hg	6.0
PhC≡CSnBu$_3$	Ph$_2$C=CHI	(PhS)$_2$Hg	<0.01
(E)-PhCH=CHSnBu$_3$	Ph$_2$C=CHI	(PhS)$_2$Hg	2.4
(E)-PhCH=CHHgCl	Ph$_2$C=CHI	(PhS)$_2$Hg	5.2
(E)-PhCH=CHHgCl	Me$_2$C=CHSnBu$_3$	PhSSPh	7.0
PhC≡CI	Ph$_2$C=CHI	(PhS)$_2$Hg	0.23
Ph$_2$C=CHSnBu$_3$	PhC≡CI	(PhS)$_2$Hg	23
Ph$_2$C=CHSnBu$_3$	Me$_2$C=CHSnBu$_3$	PhSSPh	10
Ph$_2$C=CHHgCl	PhC≡CI	(PhS)$_2$Hg	30

[a] 0.1 mmol of the mercurial or PhSSPh was irradiated in a 350-nm Rayonet photoreactor in 10 mL of Me$_2$SO 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$_2$C=CHMX$_n$ is about twice as reactive as PhCH=CHMX$_n$ (MX$_n$ = Bu$_3$Sn 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$_2$SnBu$_3$ (3.0) < Me$_2$C=CHSnBu$_3$ (12) < (E)-PhCH=CHSnBu$_3$ (50) < Ph$_2$C=CHSnBu$_3$ ≈ (E)-PhCH=CHHgCl (100) < Ph$_2$C=CHHgCl (140).[11] Included in the series is CH_2=CHCH$_2$SnBu$_3$ which reacts with PhSSPh[8] or (PhS)$_2$Hg to form CH_2=CHCH$_2$SPh by an S$_H$2′ process.

Toward c-C$_6$H$_{11}$·, PhC≡CSnBu$_3$ is 0.3 as reactive as PhCH=CHSnBu$_3$ while (PhC≡C)$_2$Hg 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$_6$H$_{11}$·. The difference in reactivity of alkynyl and alkenyl derivatives observed with both PhS· and c-C$_6$H$_{11}$· may be connected with the fact that neighboring group stabilization might be expected for PhCH–C(MX$_n$)– but not for PhC=C(MX$_n$)–.

By use of the reagents (PhS)$_2$Hg, (PhSO$_2$)Hg, or [(EtO)$_2$P(O)]$_2$Hg, it is possible to achieve free radical chain substitution in the compounds (R^1)(R^2)C=CHQ, PhC≡CQ, and CH_2=CHCH$_2$Q 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)$_2$PO·.

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)$_4$Pb (3 equiv of PhSCH=CH$_2$ in 12 h; no reaction was observed in the dark). Addition of HZr(Cp)$_2$Cl 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)$_2$Cl employed). No reaction was observed upon irradiation of CH_2=CHSiMe$_3$ or t-BuCH=CHB(c-C$_6$H$_{11}$)$_2$ 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$_3$SnCl 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$_2$H$_2$, 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 unsuccessful 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

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(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$_2$CHSnBu$_3$). Reaction of PhS· or PhSe· with CH_2=CHHgCl may also involve reversible β-addition or perhaps the formation of an unstable PhSeCH$_2$CH(SePh)HgCl intermediate which decompose to CH_2=CHHgCl and PhSeSePh.

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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-diphenylethenyl 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 $C_{17}H_{18}S$ 254.112 93, found 254.113 09. 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 $C_{10}H_{20}S$ 172.128 58, found 172.127 90. 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 $C_{10}H_{12}O_2S$ 196.055 81, found 196.056 17. Methyl 3,3-di-

methyl-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 $C_{12}H_{16}O_2S$ 224.087 11, found: 224.087 22. 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 $C_{13}H_{18}O_2S$ 238.102 76, found 238.102 82. 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 $C_{15}H_{14}O_2S$ 258.071 45; found 258.071 39; 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 $C_{21}H_{18}O_2S$ 334.102 75, found 334.104 07. 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 $C_{10}H_{21}O_3P$ 220.122 84, found 220.122 90; 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 $C_{12}H_{16}Te$ 288.029 90, found 288.028 45. Reaction of (E)-PhCH=CHSnBu₃ 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, $\nu_{AB} = 0.59$ ppm); MS calcd for $C_9H_7Cl_3$ 219.961 51, found 219.961 68; 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=CHSnBu₃ 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=CHSnBu₃ in PhH at 35 °C with 350-nm irradiation formed PhCH=CHCCl₃ 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)₂Hg and PhC≡CSnBu₃ with (PhS)₂Hg 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, Me₂SO, 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

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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≡C)$_2$Hg with (PhS)$_2$Hg or PhSSPh. Compound 7 had the same retention time as PhC≡CSnBu$_3$ (7% OV-3, $^1/_8$ in. × 10 ft) and was not analyzed as a reaction product with PhC≡CSnBu$_3$ as the substrate.

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$_3$)$_2$C=CHSPh, 13640-71-6; (*E*)-PhCH=CHSPh, 7214-53-1; Ph$_2$C=CHSPh, 13112-46-4; CH$_2$=CHSCH$_2$Ph, 1822-76-0; (CH$_3$)$_2$C=CHSCH$_2$Ph, 63196-87-2; (*E*)-PhCH=CHSCH$_2$Ph, 13294-33-2; CH$_2$=CHSO$_2$Ph, 5535-48-8; (CH$_3$)$_2$C=CHSO$_2$Ph, 54897-35-7; (*E*)-PhCH=CHSO$_2$Ph, 16212-06-9; (*Z*)-PhCH=CHSO$_2$Ph, 32291-77-3; (*E*)-PhCH=CHSO$_2$CCl$_3$, 108344-83-8; Ph$_2$C=CHSO$_2$Ph, 26189-62-8; (*E*)-PhCH=CHSePh, 60466-40-2; (*Z*)-PhCH=CHSePh, 60466-30-0; (*E*)-MeO$_2$CCH=CHSPh, 49833-37-6; (*Z*)-MeO$_2$CCH=CHSPh, 49833-38-7; (*E*)-MeO$_2$CCH=CHSO$_2$Ph, 1865-13-0; (*Z*)-MeO$_2$CCH=CHSO$_2$Ph, 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$_2$Ph, 68969-27-7; (*Z*)-*t*-BuCH=CHSO$_2$Ph, 108344-86-1; (*E*)-*t*-BuCH=CHSO$_2$C$_6$H$_4$-*p*-Me, 74829-77-9; (*Z*)-*t*-BuCH=CHSO$_2$C$_6$H$_4$-*p*-Me, 108344-87-2; (*E*)-*t*-BuCH=CHSO$_2$Me, 108344-88-3; (*Z*)-*t*-BuCH=CHSO$_2$Me, 108344-89-4; Ph$_2$C=CHSMe, 15096-10-3; Ph$_2$C=CHSPr-*i*, 108344-90-7; (*E*)-ClCH=CHSPh, 26620-11-1; (*Z*)-ClCH=CHSPh, 60785-27-5; (*Z*)-PhCH=CHSePh, 7214-56-4; Ph$_2$C=CHSePh, 108365-51-1; (CH$_3$)$_2$C=CHSePh, 77461-45-1; Ph$_2$C=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$_3$)$_2$C=CHP(O)(OEt)$_2$, 58142-40-8; PhC≡CP(O)(OEt)$_2$, 3450-67-7; PhC≡CSPh, 35460-31-2; CH$_2$=CHSnBu$_3$, 7486-35-3; (CH$_3$)$_2$C=CHSnBu$_3$, 66680-86-2; (*E*)-PhCH=CHSnBu$_3$, 66680-88-4; Ph$_2$C=CHSnBu$_3$, 91083-76-0; (*E*)-MeO$_2$CCH=CHSnBu$_3$, 82101-74-4; (*Z*)-MeO$_2$CCH=CHSnBu$_3$, 82101-75-5; CH$_2$=CH-HgCl, 762-55-0; (*E*)-*t*-BuCH=CHHgCl, 36525-02-7; (*E*)-PhCh=CHHgCl, 36525-03-8; Ph$_2$C=CHHgCl, 24522-19-8; (*E*)-ClCH=CHHgCl, 1190-78-9; (*Z*)-ClCH=CHHgCl, 2350-34-7; Ph$_2$C=CHHgBr, 67341-86-0; (*E*)-*t*-BuCH=CHHgBr, 108344-92-9; (CH$_3$)$_2$C=CHHgBr, 23010-28-8; Cl$_3$CSO$_2$-Cl, 2547-61-7; PhSe-SO$_2$C$_6$H$_4$CH$_3$-*p*, 68819-94-3; Hg(SePh)$_2$, 21514-25-0; Hg(SO$_2$H)$_2$, 15220-40-3; [(EtO)$_2$P(O)]$_2$Hg, 29105-14-4; (EtO)$_2$P(O)HgCl, 29120-01-2; Ph$_2$C=CHI, 19997-66-1; PhC≡CI, 932-88-7; (*Z*)-PhCH=CHSO$_2$CCl$_3$, 108344-93-0; (*E*)-PhSCH=CHSPh, 18893-63-5; (*Z*)-PhSCH=CHSPh, 18893-62-4; PhS-SPh, 882-33-7; PhCH$_2$S-SCH$_2$Ph, 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$_6$H$_4$SO$_2$-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≡C)$_2$Hg, 6077-10-7; PhC≡CSnBu$_3$, 3757-88-8.

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

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The nature of the bonding to tellurium in the phosphine complexes R$_3$PTe and (R$_2$P)$_2$Te and in the tellurocyanates TeCN$^-$, ArTeCN, ArCH$_2$TeCN, 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$_3$PTe give [125]Te NMR shifts of −837 to −495 ppm (Me$_2$Te) 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$_2$TeCN shifts of +570–580 ppm, and the halide derivatives ArCH$_2$Te(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$_2$TeCN is 13.7–14.1 mm s^{-1}, of ArCH$_2$Te(X)CN, X = Cl, is 14.5 mm s^{-1}, of ArCH$_2$Te(X)CN, X = Br, is 13.8 mm s^{-1}, and of ArCH$_2$Te(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*-Bu)$_3$PTe, (*n*-Bu)$_3$PTe, and Te[P(*t*-Bu)$_2$]$_2$, while the tellurocyanates have not been studied to date.

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