tungsten lamp for 10–30 min. Afterward, a measured amount of an appropriate internal standard was added, and the reaction mixtures were analyzed directly by GLC (triplicate determinations). Tables containing the experimental data used to construct the figures are available as supplementary material.

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Registry No. DMB, 79-29-8; C_6F_6, 392-56-3; $C_6H_5CF_3$, 98-08-8; C_6H_5CN, 100-47-0; $(C_6H_5)_2O$, 101-84-8; $(C_6H_5)_2CO$, 119-61-9; C_6H_5-C_6H_5, 92-52-4; $(CH_3)_4C$, 463-82-1.

Supplementary Material Available: Tables on the effect of neopentane and various arenes on the neopentane M/P ratios (6 pages). Ordering information is given on any current masthead page.

Reactions of Alkylmercurials with Heteroatom-Centered Acceptor Radicals[1]

Glen A. Russell,* Preecha Ngoviwatchai, Hasan I. Tashtoush,[2] Anna Pla-Dalmau, and Rajive K. Khanna

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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Abstract: The relative reactivities of alkylmercury halides toward PhS$^\bullet$, PhSe$^\bullet$, or I$^\bullet$ decrease drastically from R = *tert*-butyl to R = *sec*-alkyl to R = *n*-butyl, indicative that R$^\bullet$ is formed in the rate-determining step in the attack of these radicals upon RHgCl. The alkyl radicals thus formed will enter into chain reactions in which a heteroatom-centered radical (A$^\bullet$) is regenerated from substrates such as RS–SR, ArSe–SeAr, ArTe–TeAr, PhSe–SO_2Ar, Cl–SO_2Ph; ZCH=CHA (A = Cl, I, SPh, SO_2Ph); or PhC≡CHA (A = I, SPh, SO_2Ph). β-Styrenyl (PhCH=CHA, Ph_2C=CHA) and β-phenethynyl (PhC≡CA) systems with A = I, Br, SO_2Ph also enter into chain reactions with mercury(II) salts with the ligands PhS, PhSe, $PhSO_2$, or $(EtO)_2PO$. The relative reactivities of a series of reagents toward *t*-Bu$^\bullet$ and of PhCH=CHA, Ph_2C=CHA, and PhC≡CA toward *c*-$C_6H_{11}^\bullet$ are reported as well as the regioselectivity of *t*-Bu$^\bullet$ attack observed for 1,2-disubstituted ethylenes (ZCH=CHA) with Z and A from the group Ph, Cl, Br, I, SO_2Ph, SPh, Bu_3Sn. Reactions of (*E*)- and (*Z*)-PhCH=CHI or MeO_2CCH=CHI with *t*-Bu$^\bullet$ or *c*-$C_6H_{11}^\bullet$ occurred in a regioselective and stereospecific (retention) manner. Reactions of (*E*)- and (*Z*)-ClCH=CHCl occurred in a nonstereospecific manner in which the *E*/*Z* product ratio increased with the bulk of the attacking radical. A similar effect on the *E*/*Z* product ratios was observed for (*Z*)-MeO_2CCH=CHCl.

Alkylmercurials (RHgX, R_2Hg) are recognized to undergo attack at mercury by halogen atoms to form alkyl radicals.[3-5] Reactions of alkylmercurials with halogen molecules yield the alkyl halides by both homolytic attack at mercury and electrophilic attack at carbon although in many cases it is possible to select conditions which will favor either the ionic or homolytic process.[3] The reactions between alkylmercurials and vicinal dihalides (e.g., C_2Cl_6) leads to dehalogenation by a free-radical chain process involving halogen atom abstraction by R$^\bullet$ followed by a β-elimination of a halogen atom which regenerates R$^\bullet$ by attack upon the mercurial.[6,7]

The reactions of alkylmercurials with disubstituted dichalcogenides (RSSR, ArSSAr, ArSeSeAr, ArTeTeAr) have been known for some time as thermal processes,[8] but only recently has it been recognized that these substitutions occur by a radical chain mechanism in which the chalcogenide-centered radical attacks RHgCl to form a primary, secondary, or tertiary alkyl radical.[9] The free-radical chain reactions of halogens or dichalcogenides with alkylmercurials involve the attack of an electron-accepting radical (A$^\bullet$ = I$^\bullet$, Cl$^\bullet$, RS$^\bullet$, etc.) at the mercury atom (reaction 1). The chain reaction propagates by reaction of the alkyl radical

$$A^\bullet + RHgX(R_2Hg) \rightarrow AHgX(RHgA) + R^\bullet \quad (1)$$

$$R^\bullet + Y\text{-}A \rightarrow RY + A^\bullet \quad (2)$$

thus formed with the substrate Y–A (e.g., I–I, RS–SR). Other reagents which will react with alkyl radicals to furnish a heteroatom-centered acceptor radical which will participate in reaction 1 are benzenethiol and the arylsulfonyl halides, sulfides, and selenides. With the sulfonyl derivatives, Reaction 2 yields the arylsulfonyl radical ($ArSO_2^\bullet$) which serves as A$^\bullet$ in reaction 1. *N*-Bromosuccinimide and arylsulfenyl halides might be expected to react with RHgCl by a radical chain reaction. However, electrophilic substitution processes occur so readily for these materials that no evidence for a free-radical process was observed at 30 °C in PhH or CH_2Cl_2 solution.

Another route to acceptor radicals involves the addition–elimination sequence of reactions 3 and 4[10] and the analogous processes

$$ZCH{=}CHA + R^\bullet \rightarrow Z\dot{C}H\text{-}C(H)(R)A \quad (3)$$

$$Z\dot{C}H\text{-}C(H)(R)A \rightarrow ZCH{=}CHR + A^\bullet \quad (4)$$

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Table I. Poststimulated Reactions of Alkylmercurials with Y–A Reagents, RHgX(R) + YA → RY + AHgX (or A_2Hg)

mercurial and Y–A (equiv)	conditions[a]	% yield R–Y[b]
CH_2=$CHCH_2CH_2HgCl$ and PhS–SPh (1.2)	4; D, 50 °C, 6.5; 10% DBNO, 4 h; D, 10% AIBN, 80 °C, 10	92; 0; 0; 64 (I)
CH_2=$CHCH_2CH_2HgCl$ and Y–A (1.2), Y–A = PhSe–SePh; PhTe–TePh; PhSe–$SO_2C_6H_4Me$-*p*; *n*-BuS–SBu-*n*	5; 3; 4; 20	85; 92; 87; 60 (GC)
$CH_3(CH_2)_4CH_2HgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh; PhTe–TePh; PhSe–$SO_2C_6H_4Me$-*p*; Cl–SO_2Ph	3; 4; 4; 5; 48	79; 82; 83; 82; 46
$(CH_3)CCH_2HgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh; PhTe–TePh; PhSe–$SO_2C_6H_4Me$-*p*	12; 5; 6; 10	74; 86; 78; 75
$(CH_3)_2CHHgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh; PhTe–TePh	6; 6; 4	100; 100; 96
c-$C_6H_{11}HgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhTe–TePh	Me_2SO, 16	65 (I); 72 (I)
c-$C_5H_9CH_2HgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh	4	86, 73 (I); 84
7-norbornyl-HgBr and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh; PhTe–TePh; PhSe–$SO_2C_6H_4Me$-*p*	6; 4; 4; 10	43;[c] 53;[c] 45;[c] 48[c]
CH_2=$CH(CH_2)_3CH_2HgCl$ and Y–A (1.2), Y–A = PhS–SPh; PhSe–SePh; PhTe–TePh; PhSe–$SO_2C_6H_4Me$-*p*	3; 3; 3; 6	88 (GC);[d] 93 (GC);[d] 88 (GC);[d] 81 (GC)[d]
CH_2=$CH(CH_2)_3CH_2HgCl$ and PhSH (1.2)	5; D, 10% DBNO, 38	58 (GC);[d] 0 (GC)
RHgCl and PhSSPh (1.2), R = $CH_3(CH_2)_3CH_2$; $(CH_3)_2CHCH_2$; $(CH_3)_3C$	6; 6; 8	84 (GC); 86 (GC); 78 (GC)
$[CH_3(CH_2)_2CH_2]_2Hg$ and PhS–SPh (1.2; 1.2; 2.5; 2.5; 2.5)	2.5; 21; 2.5; 10% DBNO, 1.5; D, 45 °C, 4	50 (GC); 85 (GC); 100 (GC); 5 (GC); 0 (GC)
1,6-dihexanediylmercury and PhSSPh (2.0)	2.5	95
$[(CH_3)_2CH]_2Hg$ and PhS–SPh (1.2; 2.5)	12; 2	92 (GC); 95 (GC)
R_2Hg and PhSe–SePh (1.2), R = *n*-Bu; *i*-Bu; 5-hexenyl	2.5; 5; 4	92 (GC); 90 (GC); 95 (GC)[d]

[a] The mercurial (1–5 mmol) in 10 mL of deoxygenated C_6H_6 was irradiated by a 275-W sunlamp ca. 20 cm from a Pyrex reaction vessel at 35–40 °C; D = dark; DBNO = di-*tert*-butylnitroxide; AIBN = azobisisobutyronitrile. The numbers not followed by a percent (%) or temperature sign (°C) designate the number of hours. [b] Yield determined by ^1H NMR, isolation (I), or by GLC after aqueous $Na_2S_2O_3/CH_2Cl_2$ extraction (GC). [c] Coupling product (7,7'-binorbornyl) observed. [d] Mixture of 5-hexenyl and cyclopentylcarbinyl products whose ratio was dependent upon the structure and concentration of A–Y.[9]

involving PhC≡CA,[11] CH_2=$CHCH_2A$, or HC≡CCH_2A where A can be halogen or $ArSO_n$ (n = 0, 1, 2). In the substitution processes described by reactions 1, 3, and 4, it is possible to employ mercury(II) salts such as $(PhS)_2Hg$, $(PhSO_2)_2Hg$, $[(EtO)_2P(O)]_2Hg$, or $(RCO_2)_2Hg$ (with decarboxylation of $RCO_2^\bullet$ to $R^\bullet$) with 1-alkenyl or 1-alkynyl derivatives, particularly the iodides.[10-12] The iodine atom, or other acceptor radical formed in reaction 4, will continue the chain via ractions 5 and 6.

$$I^\bullet + HgL_2 \rightarrow IHgL + L^\bullet \quad (5)$$

$$L^\bullet + ZCH{=}CHI \rightarrow \rightarrow ZCH{=}CHL + I^\bullet \quad (6)$$

Reactions Involving Attack of R• upon Y–A. Table I presents a summary of yields observed in the reaction of RHgCl with a variety of Y–A reagents. Evidence for the chain sequence of reactions 1 and 2 includes the cyclization observed when R = 5-hexenyl, the photostimulation of the reactions at 35 °C, and the inhibition by 10 mol% $(t\text{-Bu})_2NO^\bullet$ of the photostimulated reaction.[9] With RHgCl the reactions do not occur in the dark at 35 °C although slow reactions can be observed at about 60 °C for *t*-BuHgCl. At this temperature the reactions are dramatically accelerated by 10 mol% of the free-radical initiation azobisisobutyronitrile (AIBN).

Yields and rates of the photostimulated reactions generally increase from R = primary to secondary to tertiary alkyl. This is in part due to the rate of chain initiation, but even at long irradiation periods, the yields with *t*-BuHgCl nearly always exceed the yields with *n*-BuHgCl. Further investigation led to the conclusion that in reaction 1 the reactivity of RHgX increases sharply from R = primary to secondary to tertiary alkyl. For example, under standard conditions with fluorescent sunlamp irradiation, the photodissociation of 0.25 M RHgCl in Me_2SO at 30 °C as measured by ^1H NMR was 1.38×10^{-6} mol/L-s (0.03%/min) for R = *t*-Bu and 9.13×10^{-8} mol/L-s (0.002%/min) for R = *n*-Bu.[13] With the same irradiation, reaction of 0.25 M *t*-BuHgCl with 0.05 M PhSSPh formed *t*-BuSPh with an initial rate of 5.42×10^{-4} mol/L-s leading to an initial kinetic chain length (kcl) of 400. In the presence of 0.25 M *n*-BuHgCl, the reaction still gave essentially all *t*-BuSPh with an initial rate of 5.92×10^{-4} mol/L-s (kcl 420). Further competitive experiments using GC analysis with a 5–10-fold excess of a mixture of two organomercurials showed that *t*-BuHgCl was much more reactive than *i*-PrHgCl which in turn was much more reactive than *n*-BuHgCl toward PhS•, PhSe•, or I• (Table II).[14] Reaction 1 is obviously controlled by the stability of the incipient alkyl radical. Reaction 1 must involve the formation of R• in the rate-determining step and is most likely a concerted one-step process. Exchange processes involving $^1R^\bullet + {}^2RHgX \rightleftharpoons {}^2R^\bullet + {}^1RHgX$ can be excluded because there is no effect of the concentration of the radical-trapping reagent (e.g., PhSSPh, PhSeSePh) upon the ratios of substitution products. With PhSeSePh, which is ~5000 times more reactive than PhSSPh toward alkyl radicals,[9] the exchange process can be excluded even if it occurs at an encounter-controlled rate. The reaction of acceptor radicals with RHgX is thus pictured as a concerted reaction in which the stability of the incipient alkyl radical contributes to the stability of the transition state leading to its formation.[15,16]

Table II. Relative Reactivities of Alkylmercury Halides toward Acceptor Radicals at 35–40 °C

attacking radical	radical precursor	solvent	rel reactivity: *t*-BuHgCl:*i*-PrHgCl:*n*-BuHgCl
PhS•	PhSSPh	Me_2SO	1.0:0.008:<0.003
PhSe•	PhSeSePh	PhH	1.0:<0.004
I•	(*E*)-PhCh=CHI or Ph_2C=CHI	Me_2SO	1.0:0.006:[a]<0.0001

[a] *c*-$C_6H_{11}HgCl$.

With 1 equiv of PhSSPh or PhSeSePh in PhH, $(n\text{-Bu})_2Hg$ reacts rapidly upon irradiation to give a mixture of *n*-BuYPh and *n*-BuHgYPh (Y = S, Se). Further irradiation decomposes *n*-BuHgYPh to form *n*-BuYPh and Hg°, possibly by a process involving a Hg(I) intermediate ($R^\bullet + RHgYPh \rightarrow RYPh + RHg^\bullet \rightarrow R^\bullet + Hg^\circ$). With excess PhYYPh, the first formed *n*-

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(12) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1985**, *26*, 4975.
(13) The disappearance of RHgCl upon photolysis involves $RHgCl \rightarrow R^\bullet + {}^\bullet HgCl$; ${}^\bullet HgCl + RHgCl \rightarrow R^\bullet + HgCl_2 + Hg^\circ$. Two molecules of RHgCl may disappear for each photodissociation step.
(14) The reactivity of R_2Hg toward $PhCO_2^\bullet$ or $n\text{-BuCO}_2^\bullet$ apparently follows the sequence R = *i*-Pr > *n*-Bu > Me based on the degree of decarboxylation observed.[6]
(15) Russell, G. A.; Jiang, W.; Hu, S. S.; Khanna, R. K. *J. Org. Chem.* **1986**, *51*, 5498.
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Table III. Photostimulated Reaction of $PhCH_2HgX$ with Diaryldichalcogenides[a]

X	coreactant (equiv)	time, h	% yield $PhCH_2YPh$	% yield $PhCH_2CH_2Ph$
$PhCH_2$		21[b,c]	0	86
PhS		6[b]	tr	85
PhSe[d]		5	22	65
PhSe[d]		3.5[b]	25	69
$PhCH_2$	PhSSPh (2.5)	6	8	75
$PhCH_2$	PhTeTePh (2.0)	1	100	0
$PhCH_2$	PhSeSePh (2.0)	5	78	10
$PhCH_2$	PhSeSePh (1.0)	6	42[e]	40[e]
$PhCH_2$	NBS (2.5)/CH_2Cl_2	6	84[f]	4
$PhCH_2$	NBS (2.5)/CH_2Cl_2	4[g]	46[f]	2
Cl	PhSSPh (1.2)	4[c]	15	66
Cl	PhSeSePh (1.2)	2[c]	72	7
Cl	PhTePh (1.2)	1[c]	80	0
Cl	$PhSeSO_2C_6H_4$-Me-*p* (1.2)	6[c]	68	5

[a] Typical procedures involved 1 mmol of the mercuiral in 10 mL of C_6H_6 irradiated at 40 °C with a 275-W sunlamp. Products were analyzed by ^1H NMR. [b] Irradiation at 350 nm in a Rayonet Photoreactor. [c] Reactions completely inhibited by 7–10 mol% $(t\text{-Bu})_2NO^\bullet$. [d] Me_2SO solvent. [e] $PhCH_2SePh$ and $PhCH_2CH_2Ph$ were formed in a 2:1 mol ratio. [f] $PhCH_2Br$. [g] In the presence of 20 mol% of $(t\text{-Bu})_2NO^\bullet$.

BuHgYPh reacts rapidly via reactions 1 and 2 to form *n*-BuYPh and $(PhY)_2Hg$. With 1,6-hexanediylmercury, 2 equiv of PhSSPh react in the expected fashion to form 1,6-bis(thiophenyl)hexane (reaction 7). With $PhS^\bullet$ or $PhSO_2^\bullet$ radicals, there is no indication

$$+ \ 2PhSSPh \xrightarrow[PhH]{h\nu} PhS(CH_2)_6SPh + (PhS)_2Hg \quad (7)$$

of β-hydrogen atom abstraction from *n*-butyl-, isobutyl-, or *tert*-butylmercurials although such a process has been reported for $CCl_3^\bullet$ attack at more elevated temperatures ($CCl_3^\bullet$ + $(i\text{-Bu})_2Hg \rightarrow HCCl_3 + Me_2C{=}CH_2 + i\text{-Bu}^\bullet + Hg^\circ$).[17]

Photostimulated reactions of benzylmercurials led to significant amounts of $PhCH_2CH_2Ph$ in the presence of PhSSPh (Table III), although by the use of the more reactive radical trap PhSeSePh (excess) or PhTeTePh, high yields of $PhCH_2SePh$ or $PhCH_2TePh$ were observed in chain reactions which could be inhibited by 10–15 mol% of $(t\text{-Bu})_2NO^\bullet$ for discrete periods of time. Under standard sunlamp irradiation, the formation of $PhCH_2CH_2Ph$ from 0.125 M $(PhCH_2)_2Hg$ in C_6D_6 was completely inhibited (as measured by ^1H NMR) by 15 mol% $(t\text{-Bu})_2NO^\bullet$ for 1 h. The rate of photodissociation ($(PhCH_2)_2Hg \rightarrow 2PhCH_2^\bullet + Hg^\circ$) was thus 3×10^{-6} mol/L-s (0.15%/min). In the presence of $CH_2{=}CPh_2$(60%)–C_6D_6(40%), the photodecomposition of $(PhCH_2)_2Hg$ from ^1H NMR was measured to be 0.05%/min. However, in the absence of a radical trap, the initial disappearance of $(PhCH_2)_2Hg$ (equal to the rate of appearance of $PhCH_2CH_2Ph$) was 1.5×10^{-5} mol/L-s (0.7%/min). The photostimulated decomposition of $(PhCH_2)_2Hg$ thus involves a short kcl. We believe this decomposition involves reactions 8 and 9. Similar reactions occur with $PhCH_2HgSPh$, $PhCH_2HgSePh$, and $PhCH_2HgTePh$ in which PhYHg decomposes to $PhY^\bullet$ and Hg°.[18]

$$PhCH_2^\bullet + PhCH_2HgCH_2Ph \rightarrow PhCH_2CH_2Ph + PhCH_2Hg^\bullet \quad (8)$$

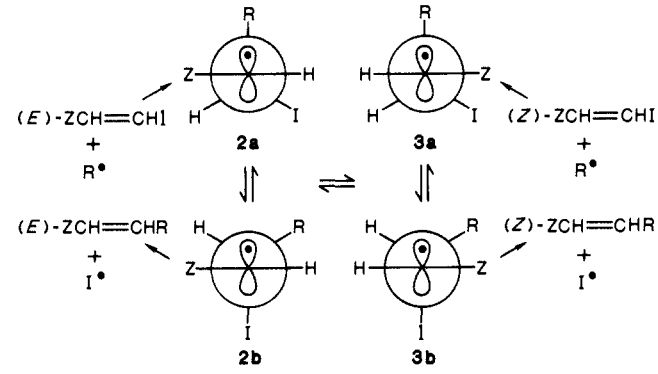
$$PhCH_2Hg^\bullet \rightarrow Hg^\circ + PhCH_2^\bullet \quad (9)$$

The photostimulated decomposition of $PhCH_2HgSePh$ leads mainly to $PhCH_2CH_2Ph$ in PhH (Table III). On the other hand, the reaction of $(PhCH_2)Hg$ or $PhCH_2HgSePh$ with excess PhSeSePh leads mainly to $PhCH_2SePh$. From the ratio of

(17) Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *97*, 5405, Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 327.

(18) The decomposition of $PhSHg^\bullet$ to $PhS^\bullet$ and Hg° has been previously described: Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.

Scheme I



$PhCH_2SePh$ and $PhCH_2CH_2Ph$ observed and with the assumption that the rate constant for attack of $PhCH_2^\bullet$ upon PhSeSePh is similar in value to 1.2×10^7 L/mol-s observed with 5-hexenyl radical,[9] it is concluded that *k* for reaction 8 must be $\sim 10^6$ L/mol-s; since *k* for attack of the 5-hexenyl radical upon PhSSPh is only 7.6×10^4, the formation of large amounts of $PhCH_2CH_2Ph$ in the photostimulated decomposition of $PhCH_2HgX$ (X = Cl, SPh, CH_2Ph) in the presence of PhSSPh is reasonable. The formation of $PhCH_2CH_2Ph$ could occur by the formation and decomposition of an intermediate such as $(PhCH_2)_2Hg(X)^\bullet$ with X = CH_2Ph, SPh, or SePh. We think this is unlkely because the photostimulated reaction of excess PhSeSePh with $(PhCH_2)_2Hg$ yielded mainly $PhCH_2SePh$, whereas the photostimulated decomposition of $PhCH_2HgSePh$ yielded mainly $PhCH_2CH_2Ph$. Obviously, both reactions cannot involve a common intermediate. We feel that if **1** is involved in the attack of $PhCH_2^\bullet$ upon $PhCH_2HgSePh$, it should also be formed in the attack of $PhSe^\bullet$ upon $(PhCH_2)Hg$. Attack of $PhCH_2^\bullet$ upon $PhCH_2HgSePh$ to

$$PhSe^\bullet + (PhCH_2)_2Hg \xrightarrow{?} \underset{\mathbf{1}}{(PhCH_2)_2\dot{H}gSePh} \xleftarrow{?} PhCH_2HgSePh + PhCH_2^\bullet$$

yield mainly $PhCH_2CH_2Ph$ thus appears to involve direct attack on the benzylic carbon atom in an S_H2 fashion, while attack of $PhSe^\bullet$ upon $PhCH_2HgSePh$ yields $PhCH_2^\bullet$ and $Hg(SePh)_2$ in a reaction whose rate increases with stability of the incipient alkyl radical.[19] The relative reactivities of *t*-BuHgCl > *i*-PrHgCl > *n*-BuHgCl toward $PhS^\bullet$, $PhSe^\bullet$, or $I^\bullet$ could be explained by the reversible formation of Hg(III) intermediates similar to **1** (e.g., $R\dot{H}g(Cl)(A)$ with A = PhS, PhSe, or I). However, it seems unreasonable that such intermediates would preferentially decompose to $A^\bullet$ and RHgCl in view of the more exergonic decomposition to $R^\bullet$ and AHgCl.

Reactions of Alkyl Radicals with 1-Alkenyl and 1-Alkynyl Substrates. Table IV summarizes yields for the reactions of RHgCl with substrates ZCH=CHA (Z = Ph, MeO_2C), $Ph_2C{=}CHA$, PhC≡CA, and 2-substituted benzothiazoles. Table V extends the substitution process to 1,2-disubstituted ethenes (ZCH=CHA) where both A and Z can in theory be displaced in reactions 3 and 4 to give heteroatom-centered acceptor radicals. The displaced groups in Tables IV and V included I, Br, Cl, PhS, PhSO, and $PhSO_2$. The reactions with primary secondary, or tertiary alkylmercury chlorides did not occur in the dark at 35 °C but could be photostimulated or initiated by AIBN. The reactions were inhibited by $(t\text{-Bu})_2NO^\bullet$, and cyclization was observed for R = 5-hexenyl. In general, the photostimulated reactions were faster and yields higher with R = *tert*-butyl than for *n*-butyl. The reactions were not observed with Z = H, Me,

(19) Reaction of $BrCCl_3$ with $(PhCH_2)Hg$ proceeds in a fast chain reaction in which $PhCH_2Br$ and $PhCH_2CCl_3$ are formed in a 1:1 ratio. Apparently, $CCl_3^\bullet$ can take the place of $PhCH_2^\bullet$ in this substitution process. Substitution by $CCl_3^\bullet$ or $p\text{-}MeC_6H_4SO_2^\bullet$ at the benzylic carbon atom in benzylcobaloxime has been suggested to occur by S_H2 attack at carbon: (a) Funabiki, T.; Gupta, B. D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1977**, 653. (b) Bougeard, P.; Gupta, B. D.; Johnson, M. D. *J. Organomet. Chem.* **1981**, 206, 211. (c) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343.

Table IV. Photostimulated Reactions of Alkylmercury Chlorides with 1-Alkenyl and 1-Alkynyl Derivatives

substrate (mmol) and RHgX (mmol)	conditions[a]	substitutn prod % yield; $(E/Z)^b$
(*E*)-PhCH=CHI (1) and RHgX (2), R = *n*-Bu, *i*-Pr, C-C_6H_{11}	48	22;[c] 70 (9); 84 (11.5)
(*E*)-PhCH=CHI (0.1) and *t*-BuHgCl (0.5)	S, 4	100 (25)
(*Z*)-PhCH=CHI (0.1) and *t*-BuHgCl (0.5)	S, 2; S, 6; S, 2, 1 mmol NaI; D, 2, 50 °C, 1 mmol NaI	48 (0.09), GC; 90 (0.04), GC; 75 (0.03), GC; 8 (0.04), GC
Ph_2C=CHI (0.1) and RHgX (0.5), R = *n*-Bu; *i*-Pr; *c*-C_6H_{11}; *t*-Bu	12	38, 89; 95; 86
Ph_2C=CHI (0.2) and $MeOC(R^1)HCH(R^2)HgO_2CCF_3$ (0.2), R^1, R^2 = $-(CH_2)_4-$; Ph, H	MeOH, 24	75; 63
R_2C=CHI (0.1) and *c*-$C_6H_{11}HgCl$ (0.2) R = H; Me	12	<5, (GC); <10 (GC)
2-iodobenzothiazole (0.5) and RHgCl (2.5), R = *n*-Bu; *i*-Pr; *c*-C_6H_{11}; *t*-Bu	42; 22; 18; 72	38; 55; 62; 10
(*E*)-MeO_2CCH=CHI (0.3) and RHgCl, R = *i*-Pr (0.5); *c*-C_6H_{11} (0.5); *t*-Bu (1.5)	PhH, S, 4; Ph/Me_2SO, 6; PhH, S, 6	36 (30); 34 (20); 43 (>50)
(*Z*)-MeO_2CCH=CHI (0.3) and RHgCl, R = *i*-Pr (0.5); *c*-C_6H_{11} (0.5); *t*-Bu (1.5)	PhH, 23; PhH/Me_2SO, 6; PhH, S, 6	45 (0.5); 45 (0.9); 41 (0.1)
(*Z*)-MeO_2CCH=CHCl (0.3) and RHgCl (0.5), R = *c*-C_6H_{11}; *t*-Bu	S, 24	34 (0.1); 49 (>50)
PhC≡CI (0.1) and RHgCl (0.15), R = *n*-Bu; *c*-C_6H_{11}; *t*-Bu	S, 7	48 (GC); 93 (GC); 100 (GC)
PhC≡CSPh (0.5) and RHgCl (0.1), R = *i*-Pr, *c*-C_6H_{11}, *t*-Bu	24	42 (GC); 46 (GC); 44 (GC)
PhC≡CSO_2Ph (0.1) and RHgCl (0.5), R = *i*-Pr, *c*-C_6H_{11}, *t*-Bu	24; 7; 7	44 (GC); 66 (GC); 57 (GC)
(*E*)-PhCH=CHSPh (1.0) and RHgCl (2.0), R = *i*-Pr, *c*-C_6H_{11}	40	32 (5.2); 43 (4.9)
(*E*)-PhCH=CHSPh (0.1) and *t*-BuHgCl (0.5)	24	36[d]
Ph_2C=CHSPh (0.1) and RHgCl (0.5), R = *i*-Pr; *c*-C_6H_{11}	96	55 (GC); 58 (GC)
(*E*)-PhCH=$CHSO_2Ph$ (1.0) and RHgCl (2.0), R = *i*-Pr; *c*-C_6H_{11}; *t*-Bu	24; 38; 48 h	68 (5.6); 74 (7.3); 43 (>50)[e]
(*E*)-PhCH=CHSOPh (0.1) and RHgCl (0.5), R = *i*-Pr; *t*-Bu	24	20 (19), GC; 32 (21), GC
Ph_2C=$CHSO_2Ph$ (0.1) and RHgCl (0.5), R = *i*-Pr; *c*-C_6H_{11}; *t*-Bu	20	87 (GC); 91 (GC); 88 (GC)
2-(phenylsulfonyl)benzothiazole (0.5) and RHgCl (2.5), R = *i*-Pr; *c*-C_6H_{11}; *t*-Bu	38; 38; 80	35; 38; 5

[a] The substrates in 5–10 mL of a nitrogen-purged MeSO in a Pyrex tube at 35–40 °C were irradiated in a 350-nm Rayonet photoreactor; S = irradiation with a 275-W sunlamp ca. 20 cm from the Pyrex reaction vessel; D = dark. The numbers which are not followed by mmol or a temperature sign (°C) designate the number of hours. [b] Yields were determined by ^1H NMR or GLC (GC); *E*/*Z* ratios were determined by GLC. [c] Mixture of *E* and *Z* isomers; *E*/*Z* ratio was not determined. [d] PhCH(*t*-Bu)CH_2SPh (9%) and Ph(*t*-Bu)C=CHSPh (3%) were obtained after workup with $NaBH_4$; 50% of PhCH=CHSPh was recovered. [e] Ph(*t*-Bu)$CHCH_2SO_2Ph$ (16%) was obtained upon workup with $NaBH_4$.

or *t*-Bu. Thus, photolysis of ICH=CHI or ICH=CHCl with an excess of *t*-BuHgCl formed *t*-BuCH=CHI and *t*-BuCH=CHCl, respectively, with only a trace of *t*-BuCH=CHBu-*t*.

Reactions of *t*-BuHgCl or *c*-$C_6H_{11}HgCl$ with (*E*)- and (*Z*)-MeO_2CCH=CHI and (*E*)- and (*Z*)-PhCH=CHI were stereospecific with retention of configuration. The interconversion of conformations **2** and **3** (Scheme I) must be slow relative to the elimination of I·. However, although (*Z*)-MeO_2CCH=CHCl reacted with *c*-$C_6H_{11}HgCl$ to produce mainly (*Z*)-MeO_2CCH=CHC_6H_{11}, reaction with *t*-BuHgCl yielded nearly exclusively the more stable *E* isomer. With Cl in place of I, the rate of the β-elimination reaction is slower, and, apparently with a bulky R, the **3** to **2** interconversion is fast enough that the elmination proceeds mainly from the more stable conformation **2b** when R = *t*-Bu but not for cyclohexyl. A similar effect has been observed with R = *t*-Bu and *c*-C_6H_{11} with Bu_3Sn as the leaving group.[11] With (*E*)- and (*Z*)-ClCH=CHCl stereospecificity was not observed with R = *n*-Bu, *c*-C_6H_{11}, or *t*-Bu. However, with ClCH=CHCl or (*Z*)-MeO_2CCH=CHCl, the *E*/*Z* product ratio increased with the bulk of the attacking radical with *E*/*Z* > 50 observed for R = *t*-Bu·.

The effect of added NaI on the reaction of PhCH=CHI with *t*-BuHgCl was investigated (Table IV). In the presence of NaI, a slow thermal substitution reaction was observed at 50 °C, presumably initiated by electron transfer from I^- to *t*-BuHgI or the thermal homolysis of *t*-BuHgI/*t*-$BuHgI_2^-$. Photolysis of *t*-BuHgCl/NaI mixtures led to a somewhat faster substitution than in the absence of I^- but with no appreciable effect on the stereospecificity observed for the reaction with (*Z*)-PhCH=CHI. Because of the stereospecificity observed in the photostimulated reactions of (*E*)- or (*Z*)-PhCH=CHI with RHgCl, it was possible to measure the relative reactivity of the *E* and *Z* isomers by a direct competition of a mixture of the isomers with 0.1 equiv of *t*-BuHgCl. The results of this experiment demonstrated that the *E* isomer is 1.75 times more reactive than the *Z* isomer toward attack by the *tert*-butyl radical in Me_2SO at 35–40 °C.

Completely regioselective attack of *t*-Bu· in reaction 3 with displacement of I· was observed for PhCH=CHI, Ph_2C=CHI, PhC≡CI, $PhSO_2CH$=CHI, MeO_2CCH=CHI, and ClCH=CHI. However, with PhCH=$CHSO_2Ph$ or PhCH=CHSPh, attack of *t*-Bu· occurred at both vinyl carbon atoms. Attack at the phenyl-substituted carbon led to PhCH(*t*-Bu)$\dot{C}HSO_2Ph$ and PhCH(*t*-Bu)$\dot{C}$HSPh. The α-sulfonyl-substituted radical reacted with *t*-BuHgCl as a carbon-centered acceptor radical to form PhCH(*t*-Bu)CH(HgCl)SO_2Ph which could be converted to RCH(*t*-Bu)CH_2SO_2Ph by reaction with alkaline $NaBH_4$ in workup.[15] The α-thiyl radical mainly disproportionated to form PhCH(*t*-Bu)C=CHSPh and PhCH(*t*-Bu)CH_2SPh in a chain-terminating reaction.

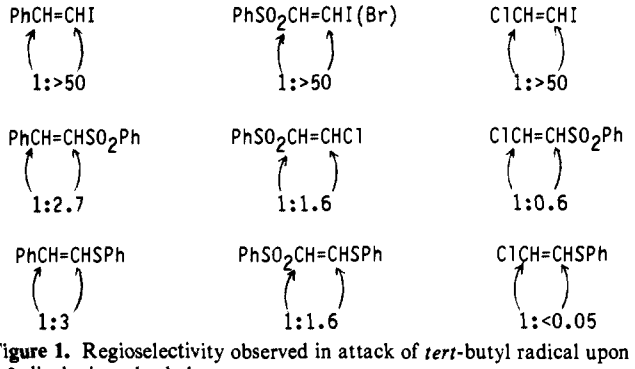


Figure 1. Regioselectivity observed in attack of *tert*-butyl radical upon 1,2-disubstituted ethylenes.

Figure 1 summarizes the regioselectivity toward *t*-Bu· attack based on the reaction products for a group of related 1,2-disubstituted ethenes. From the data summarized in Figure 1, the ability of a substituent (A) to direct attack of R· to the vinyl carbon atom to which the substituent is bound follows the general trend of I > Cl > $PhSO_2$ or PhS. This trend is observed in ZCH=CHA as Z is changed from Ph to $PhSO_2$ to Cl.[20] The observed selectivities probably result from a variety of factors including steric and polar effects as well as the ability of both Z and A to stabilize a radical center at the α-position by conjugation and at the β-position by hyperconjugation or possibly bridging. As shown in Figure 1, iodine or bromine have a very strong directing effect. One might expect that β-elimination of I· or Br· from the adduct radical would occur more readily than the

(20) Other substituents which are effective in inducing the attack of *t*-Bu· at the substituted carbon atom are Bu_3Sn and HgCl: Russell G. A.; Ngoviwatchai, P.; Tashtoush, H. *Organometallics* **1988**, *7*, 696.

Table V. Reaction of Alkylmercury Chlorides with 1,2-Disubstituted Ethylenes, ZCH=CHA + RHgCl $\xrightarrow{h\nu}$ RCH=CHA + ZCH=CHR

ZCH-CHA (mmol)	RHgX (equiv)	conditions[a]	% yield[b] RCH=CHA; (E/Z)	% yield[b] ZCH=CHR; (E/Z)
(Z)-ClCH=CHCl (2)	n-BuHgCl (1)	R, 21		41 (GC); (0.5)
(E)-ClCH=CHCl (2)	n-BuHgCl (1)	R, 20		59 (GC); (0.5)
(Z)-ClCH=CHCl (2)	c-C_6H_{11}HgCl (1)	R, 21		70 (GC); (0.8)
(E)-ClCH=CHCl (3)	c-C_6H_{11}HgCl (1)	R, 20		63 (GC); (0.7)
(Z)-ClCH=CHCl (2)	t-BuHgCl (1)	R, 21		63 (GC); (41.0)
(E)-ClCH=CHCl (3)	t-BuHgCl (1)	R, 20		75 (GC); (>50)
(E)-ICH=CHI (1)	n-BuHgCl (1)	S, 7		14 (GC); (3.8)
(E)-ICH=CHI (1)	c-C_6H_{11}HgCl (1)	S, 7		15 (GC); (8.4)
(E)-ICH=CHI (1)	t-BuHgCl (1)	S, 7		48 (GC); (>50)
(E)-ICH=CHI (1)	t-BuHgCl (5)	S, 7		86 (NMR); (>50)
(E)-ClCH=CHI (1)	n-BuHgCl (2.5)	S, 10	[c]	60 (GC); (1.7)
(E)-ClCH=CHI (1)	c-C_6H_{11}HgCl (1.5)	S, 10	[c]	63 (GC); (2.3)
(E)-ClCH=CHI (1)	t-BuHgCl (1.5)	S, 10	[c]	60 (GC); (>30)
(E)-ClCH=CHSPh (1)	n-BuHgCl (1)	R, 30	11 (GC); (2.8)[d,e]	[c]
(E)-ClCH=CHSPh (1)	c-C_6H_{11}HgCl (1)	R, 30	49 (GC); (2.6)[d,f]	8 (GC); (2.1)
(E)-ClCH=CHSPh (0.1)	t-BuHgCl (5)	S, 10	95 (NMR); (>50)[d,g]	<5
(E)-ClCH=CHSO$_2$Ph (1)	c-C_6H_{11}HgCl (1)	S, 11	5 (GC); (>50)	28 (GC); (1.4)[h]
(E)-ClCH=CHSO$_2$Ph (0.1)	t-BuHgCl (5)	S, 4	40 (NMR); (>50)[g]	60 (NMR); (<50)[g]
(E)-BrCH=CHSO$_2$Ph (0.1)	t-BuHgCl (5)	S, 1	92 (NMR); (>50)[g]	[c]
(Z)-BrCH=CHSO$_2$Ph (0.1)	t-BuHgCl (5)	S, 0.5	95 (NMR); (5.8)[g]	[c]
(E)-ICH=CHSO$_2$Ph (0.1)	c-C_6H_{11}HgCl (0.5)	S, 10	76 (GC); (40.5)	[c]
(E)-ICH=CHSO$_2$Ph (0.1)	t-BuHgCl (5)	S, 4	98 (NMR); (>50)[g]	[c]
(E)-PhSCH=CHSO$_2$Ph (0.1)	t-BuHgCl (5)	S, 28	34 (NMR)[g,i]	53 (NMR); (>50)[g,i]
(E)-Bu$_3$SnCH=CHSO$_2$Ph	t-BuHgCl (1)	S, 3	100 (NMR); (>50)[g]	

[a] Substrates in 10 mL of nitrogen-purged Me_2SO in a Pyrex tube were irradiated with a 275-W sunlamp (S) ca. 20 cm from the reaction vessel or in a 350-nm Rayonet photoreactor (R). The numbers in the column designate the number of hours. [b] Yields were determined by GLC (GC) or by ^1H NMR (NMR); stereochemistry was established by GLC. [c] Product not detected. [d] 1,2-Bis(phenylthio)ethylene was detected. [e] Starting material (71%) recovered. [f] Starting material (26%) recovered. [g] Reaction performed in an NMR tube by using 1 mL of Me_2SO-d_6. Yield determined by using CH_2Cl_2 as the internal standard. [h] Starting material (61%) recovered. [i] At 3 h of irradiation the ratio of t-BuCH=CHSO$_2$Ph:PhSCH=CHBu-t was 20%:21%.

Table VI. Estimated Relative Reactivities of PhCH=CHA toward Alkyl Radicals

A	prod. (with t-BuHgCl)	rel reactivity (toward c-C_6H_{11}•)	total reactivity[a]
I	PhCH=CHBu-t (100%)	1.00	1.00
SO_2Ph	PhCH=CHBu-t (43%)	4.70[b]	6.5
	PhCH(t-Bu)CH_2SO_2Ph (16%)	1.75[c]	
SPh	PhCH=CHBu-t (36%)	1.57[b]	2.1
	PhCH(t-Bu)CH_2SPh and PhC(t-Bu)=CHSPh (12%)	0.52[c]	

[a] Assuming t-Bu• and c-C_6H_{11}• have similar chemo and regioselectivities. [b] Observed. [c] Assuming t-Bu• and c-C_6H_{11}• have similar regioselectivities.

elimination of Cl•, $PhSO_2$•, or PhS•. This raises the possibility that the addition of t-Bu• may be reversible, but this seems unlikely. Another possibility is that vinylic homolytic substitutions can involve a concerted addition of t-Bu• with migration of A to the β-position or perhaps the concerted elimination of A, particularly with the iodo substituent. If such processes are involved for vinyl iodides such as PhCH=CHI, one would expect to see an increased reactivity relative to a substrate which reacted with a lower regioselectivity, e.g., PhCH=CHSO$_2$Ph or PhCH=CHSPh. Relative reactivities of various 1-alkenyl and 1-alkynyl derivatives toward c-C_6H_{11}• are given in the next section. Some pertinent data for PhCH=CHA with A = I, $PhSO_2$, PhS are collected in Table VI. As demonstrated in Table VI, both the sulfide and sulfone are actually more reactive than the iodide, and there is no correlation between chemo and regioselectivity. The high regioselectivity observed for 1-alkenyl iodides is not connected with an enhanced reactivity for alkyl radical attack. Giese has concluded[21] that the reactivities of electronegatively substituted alkenes toward alkyl radicals are controlled mainly by the electron-withdrawing ability of the substituent while regiochemistry is controlled by steric effects. The data of Figure 1 indicate that certainly other factors besides steric effect are important in determining the regiochemistry of radical attack on 1,2-disubstituted ethenes.

Relative Reactivities toward Alkyl Radicals of Precursors to Heteroatom-Centered Acceptor Radicals. The chain processes involving reactions 1 and 2 or 1, 3, and 4 proceed by reasonably long kinetic chains. This means that essentially every adduct radical, e.g., PhĊH–CH(R)A, gives rise to the substitution product and generates A• which continues the chain reaction. The products of competitive reactions should thus be a true measure of the reactivity of the substrates toward R•. The alkylmercury halides appear to be an excellent source of alkyl radicals for such relative reactivity studies. Table VII summarizes the relative reactivities observed in competition of a large excess of two substrates (more than 10 equiv each) for either t-BuHgCl or c-C_6H_{11}HgCl. Also included in Table VII are relative reactivities of 1-alkenyl and 1-alkynyl mercurials and stannanes which have been previously reported.[11] Toward the ZCH=CHA and PhCH=CHA substrates there is actually quite a small spread of relative reactivities in the substitution process of reactions 3 and 4 with all the substrates having a reactivity spread of no more than a factor of 60. Toward c-C_6H_{11}• the sulfones are more reactive than the iodides, sulfides, stannanes, or mercury chlorides for PhCH=CHA, Ph_2C=CHA, and PhC≡CA. For the vinyl systems (Ph_2C=CHA, PhCH=CHA), a reactivity order of A = $PhSO_2$ > PhS, HgCl > Bu_3Sn, I is observed. However, in the PhC≡CA series, the reactivity order is $PhSO_2$ (60) > I (19) > SPh (4) > $SnBu_3$ (1). For the phenylacetylenes, the reactivity toward c-C_6H_{11}• appears to follow the polar effect of the substituents with highest reactivity observed for attack of the electron-donating (nucleophilic) c-C_6H_{11}• upon the system with the most powerful electron-withdrawing group.[21] For the vinyl derivatives, steric and stereoelectronic considerations may be more important and a much compressed scale of reactivities (eightfold for Ph_2C=CHA, fivefold for PhCH=CHA) is observed. The low reactivitiy of the vinyl iodides is noteworthy and seems to exclude any bridging effect by iodine atoms in the transition state for the regioselective addition of c-C_6H_{11}• to the 1-iodoalkenes.

In S_H2 substitution reactions of Y–A reagents with t-Bu•, a 2000-fold range in reactivities was measured between the highly reactive $PhSO_2Cl$ and the unreactive t-BuSSBu-t. The reactivity

(21) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 771.

Table VII. Relative Reactivities toward Alkyl Radicals

substrate A (mmol)	substrate B (mmol)	conditions[a]	k_A/k_B[b]	rel react. of A[c]
	Toward Cyclohexyl Radical (Reactivity in Substitutions Only)			
PhSSPh (1)	Ph_2C=CHI (1)	PhH, R, 4 h	36	36
PhC≡CSO_2Ph (1)	Ph_2C=CHI (1)	PhH, R, 20 h	12.2	12
Ph_2C=$CHSO_2Ph$ (1)	PhC≡CI (1)	PhH, R, 6 h	1.7	6.5
Ph_2C=CHSPh (1)	PhC≡CI (1)	PhH, R, 6 h	1.1	4.2
PhC≡CI (1)	Ph_2C=CHI (1)	PhH, R, 6 h	3.8	3.8
(*E*)-PhCH=$CHSO_2Ph$ (1)	Ph_2C=CHI (1)	PhH, R, 24 h	3.3	3.3
(*E*)-$PhSO_2CH$=$CHSnBu_3$	PhC≡CI (1)	PhH, S, 6 h	0.7	2.7
Ph_2C=C(H)HgCl (1)	PhC≡CI (1)	PhH, R, 6 h	0.5	1.9
(*E*)-MeO_2CCH=CHI (1)	(*E*)-PhCH=CHI (1)	Me_2SO, S, 6 h	2.4	1.7
(*E*)-PhCH=C(H)HgCl (1)	Ph_2C=CHI (1)	PhH/Me_2SO, R, 24 h	1.5	1.5
(*E*)-PhCH=CHSPh (1)	Ph_2C=CHI (1)	PhH, R, 24 h	1.1	1.1
PhC≡CSPh (1)	Ph_2C=CHI (1)	PhH, R, 20 h	0.8	0.8
Ph_2C=$CHSnBu_3$ (1)	PhC≡CI (1)	PhH, R, 5 h	0.2	0.8
(*E*)-PhCH=CHI (1)	Ph_2C=CHI (1)	PhH, R, 24 h	0.7	0.7
(*E*)-PhCH=$CHSnBu_3$ (1)	Ph_2C=CHI (1)	PhH, R, 24 h	0.7	0.7
PhC≡$CSnBu_3$ (1)	Ph_2C=CHI (1)	PhH, R, 20 h	0.2	0.2
$(PhC≡C)_2Hg$ (1)	Ph_2C=CHI (1)	Me_2SO, R, 24 h	0.2	0.2
CH_2=$CHSnBu_3$ (1)	Ph_2C=CHI (1)	PhH, R, 24 h	<0.1	<0.1
CH_2=$CHCH_2SnBu_3$ (1)	Ph_2C=CHI (1)	PhH, R, 24 h	≪0.1	≪0.1
	Toward *tert*-Butyl Radical			
$PhSO_2Cl$ (0.5)	*n*-BuSSBu-*n* (3)	PhH, S, 30 min	134	107
PhSSPh (1)	Ph_2C=CHI (1)	PhH, S, 10 min	43	43
$PhCH_2Br$ (0.5)	*n*-BuSSBu-*n*	PhH, S, 50 min	18	14
CH_2=$CHP(O)(OEt)_2$ (0.5)[d]	PhSSPh (0.5)	Me_2SO, R, 21 h	0.25	11
CH_2=$CHP(O)(OEt)_2$ (0.5)[d]	Ph_2C=CHI (0.5)	Me_2SO, R, 21 h	8	8
CH_2=CPh_2 (0.5)[e]	*n*-BuSSBu-*n* (0.5)	Me_2SO, S, 16 h	4.2	3
MeSSMe (1)	Ph_2C=CHI (1)	Me_2SO, S, 30 min	3	3
n-BuSSBu-*n* (1)	Ph_2C=CHI (1)	Me_2SO, S, 30 min	0.8	0.8
$PhCH_2SCH_2Ph$ (1)	Ph_2C=CHI (1)	Me_2SO, S, 30 min	0.6	0.6
Me_2C=NO_2^-·K^+,18-*c*-6 (0.5)[f]	*n*-BuSSBu-*n* (0.5)	Me_2SO, S, 2 h	0.3	0.2
i-PrSSPr-*i* (10)	Ph_2C=CHI (1)	Me_2SO, S, 30 min	0.035	0.035
t-BuSSBu-*t* (21)	Ph_2C=CHI (0.5)	Me_2SO, S, 2 h	0.0045	0.0045

[a] The mercurial (0.1 mmol of c-$C_6H_{11}HgCl$ or *t*-BuHgCl) was reacted with an excess of two substitutes in 3–10 mL of deoxygenated solvent; (S), sunlamp irradiation (R), irradiation at 350 mm in a Rayonet photoreactor at 35–40 °C. [b] From the ratio of substitution or addition products which accounted for more than 80% of the RHgCl. With disulfides, values of k_A/k_B were calculated by extrapolating the rates of product formation to t = 0. [c] Reactivity of Ph_2C=CHI = 1.0. Toward *t*-Bu•, the absolute rate constant for addition to CH_2=$CHP(O)(OET)_2$ is 5.9×10^4 M^{-1} s^{-1} at 233 K: Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1981**, 161. [d] Product after $NaBH_4$ workup is *t*-$BuCH_2CH_2P(O)(OET)_2$. [e] Products are *t*-$BuCH_2CHPh_2$ and *t*-BuCH=CPh_2. [f] Product is *t*-$BuCMe_2NO_2$.

of the disulfides reflect steric effects (*t*-BuSSBu-*t* < *i*-PrSSPr-*i* < *n*-BuSSBu-*n* < MeSSMe) and stabilization of the thiyl radical formed (PhSSPh is 10 times as reactive as MeSSMe).

Reaction of 1-Alkenyl and 1-Alkynyl Iodides with Hg(II) Salts. Table VIII summarizes free radical chain photostimulated substitutions of alkenyl and alkynyl iodides with the highly covalent $Hg(SPh)_2$, $Hg(SO_2Ph)_2$, $Hg[P(O)(OEt)_2]_2$, $ClHg[P(O)(OEt)_2]$, and $Hg(O_2CR)_2$ salts. With $Hg(O_2CR)_2$ no more than one of the ligands of the mercury salt could be utilized in the substitution process. Additional evidence for the chain process of reactions 5 and 6 was provided by the observation that RCO_2• (R = Et, *i*-Pr, *t*-Bu), formed by the attack of I• upon $(RCO_2)_2Hg$, underwent decarboxylation to yield the alkylation product of reaction 10. Substitution reactions involving mercury(II) salts have also

$$PhCH{=}CHI + (RCO_2)_2 \xrightarrow{h\nu} PhCH{=}CHR + IHgO_2CR + CO_2 \quad (10)$$

been reported for 1-alkenyl stannanes and mercurials with $Hg(SPh)_2$, $Hg(SO_2Ph)_2$, and $Hg[P(O)(OEt)_2]_2$.[16] Bis(*N*-succinimidyl)mercury[22] or bis(*N*-phthalimidyl)mercury failed to react in these photostimulated processes.

Experimental Section

Analytical gas chromatography was performed on a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. ^1H NMR spectra were recorded on a 60 MHz Varian EM 360A or EM 360L or on a 300 MHz Nicolet NT 300 spectrometer and are reported in δ values with tetramethylsilane as the internal standard. GCMS were recorded on a Finnegan 4000 spectrometer. High resolution mass spectra were recorded on an AEI MS 902. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Materials. Dimethyl sulfoxide was distilled from calcium hydride; benzene and tetrahydrofuran were distilled from lithium aluminum hydride and stored over 4A molecular sieves under nitrogen. Diphenyl disulfide, diphenyl diselenide, dimethyl disulfide, dibenzyl disulfide, di-*n*-butyl disulfide, diisopropyl disulfide, di-*tert*-butyl disulfide, benzenesulfonyl chloride, azobisisobutyronitrile, (*E*)- and (*Z*)-1,2-dichloroethene, benzyl bromide, diethyl vinyl phosphonate, and 1,1-diphenylethylene were purchased from Aldrich Chemical Co. Benzenethiol was purchased from Eastman Organic Co. and *N*-bromosuccinimide from Fisher Scientific Co. Diphenyl ditelluride,[23] *Se*-phenyl *p*-tolylsulfonoselenoate,[24] (*E*)-β-iodostyrene,[25] (*Z*)-β-iodostyrene,[26] 2,2-diphenylethenyl iodide,[27] 1-iodocyclopentene,[28] 2-iodobenzothiazole,[29] 2-phenylsulfonylbenzothiazole,[30] methyl (*E*)-β-iodoacrylate,[31] methyl (*Z*)-β-iodoacrylate,[31] methyl (*Z*)-β-chloroacrylate,[32] phenylethynyl iodide,[33] phenyl (*E*)-2-phenylethenyl sulfide,[34] phenyl 2,2-diphenylethenyl sulfide,[18,35] phenyl phenylethynyl sulfide,[36] phenyl (*E*)-2-phenylethenyl sulfoxide,[37] phenyl (*E*)-2-phenyl-

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ethenyl sulfone,[38] phenyl 2,2-diphenylethenyl sulfone,[39] phenyl phenylethynyl sulfone,[36] (*E*)-1,2-diiodoethene,[40] (*E*)-2-chloroethenyl phenyl sulfide,[41] 1-phenylsulfonyl-2-(phenylthio)ethene,[42] ((*E*)-2-(phenylsulfonyl)ethenyl)tributylstanane,[43] 2,2-diphenylethenylmercury chloride,[27] ((*E*)-2-phenylethenyl)tributylstannane,[44] phenylethynyltributylstannane,[45] bis(phenylethynyl)mercury,[46] vinyltributyltin,[47] and allyltributyltin[48] were synthesized according to the literature procedures. (*E*)-2-Chloroethenyl phenyl sulfone, mp 46–47 °C, was prepared by the oxidation of (*E*)-2-chloroethenyl phenyl sulfide by H_2O_2 in 1:1 AcOH/Ac_2O: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.95–7.85 (m, 2 H), 7.72–7.52 (m, 3 H), 7.46 (d, J = 13.2 Hz, 1 H), 6.75 (d, J = 13.2 Hz, 1 H); GCMS *m/e* (rel intensity) 202 (M^+, 15), 125 (100), 77 (76), 51 (52). (*E*)-2-Bromoethenyl phenyl sulfone: mp 56–57 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.93–7.85 (m, 2 H), 7.73–7.50 (m, 3 H), 7.70 (d, J = 13.5 Hz, 1 H), 6.70 (d, J = 13.5 Hz, 1 H). (*Z*)-2-Bromoethenyl phenyl sulfone: mp 38–39 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 8.05–7.96 (m, 2 H), 7.72–7.50 (m, 3 H), 7.22 (d, J = 8.1 Hz, 1 H), 7.13 (d, J = 8.1 Hz, 1 H) were obtained from the oxidation of a mixture of (*E*)- and (*Z*)-2-bromoethenyl phenyl sulfide[49] by hydrogen peroxide in a 1:1 mixture of AcOH/Ac_2O followed by chromatography on silica gel. (*E*)-2-Iodoethenyl phenyl sulfone was prepared as follows. (*E*)-1,2-Diiodoethene (1.4 g, 5 mmol) and mercuric benzenesulfinate[50] (2.4 g, 5 mmol) were dissolved in Me_2SO (30 mL) in a Pyrex flask equipped with a rubber septum. After a nitrogen purge for 5 min, the mixture was irradiated for 16 h with a 275-W sunlamp ca. 15 cm from the flask. The reaction mixture was poured into water, and the product was extracted with benzene. The benzene extract was washed twice with 20% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. Benzene was removed under vacuum to give a gray precipitate which was chromatographed on silica gel by using a mixture of hexane and chloroform (50:50) as the eluent. The product was obtained as a white solid (1.1 g, 75% yield): 300 MHz ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 14.4 Hz, 1 H), 8.0–7.75 (m, 2 H), 7.75–7.53 (m, 3 H), 7.28 (d, J = 14.4 Hz, 1 H); GCMS *m/e* (rel intensity) 294 (M^+, 11), 125 (85), 77 (100). (*E*)-2-Methoxycyclohexylmercury trifluoroacetate and 2-methoxy-2-phenylethylmercury trifluoroacetate were prepared from a 1:1 mixture of the alkene (cyclohexene or styrene) and mercuric trifluoroacetate[51] in methanol and used without isolation. Mercuric dimethyl acetate, mp 102–105 °C, and mercuric propionate, mp 108–112 °C, were prepared from reaction of yellow mercuric oxide and the carboxylic acids. Mercuric oxide (0.1 mol) was slowly addedto 30 mL of the acid with stirring. After the evolution of heat, an additional 10 mL of the acid was added, and the mixture was heated on a steam bath until all of the mercuric oxide dissolved. The mixture was cooled in an ice bath, and the white crystalline product was filtered and dried under vacuum or recrystallized from chloroform. Benzylmercury thiophenoxide,[52] mp 83–83.5 °C, was prepared from benzylmercury chloride[53] (3.0 g, 9.2 mmol), potassium *tert*-butoxide (1.3 g, 11.6 mmol), and thiophenol (1.29 g, 11.7 mmol) in 30 mL of nitrogen-purged Me_2SO. After having been stirred for 5 min, the solution was poured into 250 mL of 10% aqueous potassium carbonate, and the product was extracted with benzene. The extract was washed with aqueous potassium carbonate, dried ($MgSO_4$), and concentrated under vacuum to afford 3.6 g of crude product. Recrystallization from ethanol–benzene yielded 3.1 g (84% yield) of the pure compound: ^{1}H NMR ($CDCl_3$) δ 7.45–7.0 (m, 10 H), 2.92 (s, 2 H). *n*-Butylmercury thiophenoxide, bp 135–138 °C (0.3 Torr), was prepared from *n*-butylmercury chloride[53] and potassium thiophenoxide in Me_2SO: ^{1}H NMR ($CDCl_3$) δ 7.55–7.05 (m, 5 H), 1.9–0.8 (m, 9 H); MS, 368.05104, calcd for $C_{10}H_{14}HgS$ 368.05225. Benzylmercury phenyl selenide was prepared in 83% yield from benzylmercury chloride and potassium phenyl selenide in Me_2SO. The pale yellow precipitate was recrystallized from methanol, mp 128–130 °C dec: ^{1}H NMR (Me_2SO-d_6) δ 7.8–7.1 (m, 10 H), 3.9 (s, 2 H). 1,6-Hexanediylmercury was prepared by the reaction of 1,6-dibromohexane with sodium amalgam[54] followed by several recrystallizations to remove traces of di-*n*-hexylmercury. *n*-Hexyl phenyl sulfide or *n*-hexyl bromide were not detected in the reactions of the recrystallized material with PhSSPh or $BrCCl_3$. All other mercurials were synthesized according to the literature procedure.[16,48,53]

General Procedure for Photostimulated Reactions of Mercurials with Diaryldichalcogenides and Other Y–A Reagents (Tables I and III). The mercurial and the coreactant were dissolved in 10 mL of a deoxygenated solvent under a nitrogen atmosphere in a Pyrex flask equipped with a magnetic stirring bar and a rubber septum. The stirred mixture was irradiated by either a 275-W sunlamp ca. 20 cm from the flask or in a 350-nm Rayonet photoreactor. After the completion of the reaction, the mixture was decanted from mercury metal or filtered from the precipitate of mercury salt. Benzene was removed under vacuum, and the residue was analyzed by ^{1}H NMR, GLC, and GCMS. When Me_2SO was used as the solvent, the reaction mixture was poured into water, and the product was extracted with benzene. The extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated. The residue was then analyzed by ^{1}H NMR, GLC, and GCMS. ^{1}H NMR spectra of 2,2-dimethyl-1-propyl phenyl sulfide,[55] isopropyl phenyl selenide,[56] *n*-butyl phenyl selenide,[56] benzyl phenyl selenide,[56] and isopropyl phenyl telluride[56] agreed with those reported in the literatures. The following data were obtained for other products reported in Tables I and III. 3-Butenyl phenyl sulfide:[52] ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 5.7–5.42 (m, 1 H), 5.15–4.8 (m, 2 H), 2.85–2.6 (m, 2 H), 2.15–2.13 (m, 2 H); GCMS *m/e* (rel intensity) 166 (1.7), 164 (M^+, 37), 123 (100), 110 (18). 1 Hexyl phenyl sulfide:[57] ^{1}H NMR (C_6D_6) δ 7.45–7.0 (m, 5 H), 2.71 (t, J = 6.5 Hz, 2 H), 1.7–0.8 (m, 11 H); GCMS *m/e* (rel intensity) 196 (7), 194 (M^+, 21), 123 (17), 110 (100). Isopropyl phenyl sulfide:[58] ^{1}H NMR (C_6D_6) δ 7.4–7.1 (m, 5 H), 3.02 (septet, J = 6 Hz, 1 H), 1.1 (d, J = 6.5 Hz, 6 H); GCMS *m/e* (rel intensity) 154 (2.3), 152 (M^+, 50) 110 (100). Cyclopentylmethyl phenyl sulfide: ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m, 5 H), 2.85 (d, J = 6.5 Hz, 2 H), 2.1–1.1 (m, 9 H); GCMS *m/e* (rel intensity) 194 (1), 192 (M^+, 22), 123 (12), 110 (100). Cyclohexyl phenyl sulfide: ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 3.2–2.7 (m, 1 H), 1.7–0.9 (m, 10 H); GCMS *m/e* (rel intensity) 194 (7), 192 (M^+, 20), 110 (100), 56 (66). 7-Norbornyl phenyl sulfide: GCMS *m/e* (rel intensity) 206 (3.7), 204 (M^+, 76), 110 (73), 95 (94), 67 (100). 5-Hexenyl phenyl sulfide: ^{1}H NMR ($CDCl_3$) δ 7.45–7.05 (m, 5 H), 5.95–5.4 (m, 1 H), 5.1–4.8 (m, 2 H), 2.9 (t, J = 6.5 Hz, 2 H), 1.9–0.9 (m, 6 H); GCMS *m/e* (rel intensity) 194 (1), 192 (M^+, 22), 123 (49), 110 (100). *n*-Butyl phenyl sulfide:[58] ^{1}H NMR ($CDCl_3$) δ 7.5–7.15 (m, 5 H), 3.01 (t, J = 6 Hz, 2 H), 1.8–0.7 (m, 7 H); GCMS *m/e* (rel intensity) 168 (1.8), 166 (M^+, 39), 123 (22), 110 (100). 2-Methyl-1-propyl phenyl sulfide:[59] ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 2.85 (d, J = 7 Hz, 2 H), 2.3–1.8 (m, 1 H), 1.15 (d, J = 7 Hz, 6 H); GCMS *m/e* (rel intensity) 168 (2.1), 166 (M^+, 47), 123 (46), 110 (100). Benzyl phenyl sulfide: ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m, 5 H), 4.1 (s, 2 H); GCMS *m/e* (rel intensity) 202 (0.6), 200 (M^+, 12), 91 (100). 3-Butenyl phenyl selenide: ^{1}H NMR (C_6D_6) δ 7.45–6.95 (m, 5 H), 5.9–5.3 (m, 1 H), 5.1–4.75 (m, 2 H), 2.8–2.4 (m, 2 H), 2.3–2.1 (m, 2 H), GCMS *m/e* (rel intensity) 212 (M^+, 17), 158 (21), 55 (100). 1-Hexyl phenyl selenide:[52] ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 5 H), 2.9 (t, J = 6.5 Hz, 2 H), 1.9–0.7 (m, 11 H); GCMS *m/e* (rel intensity) 242 (M^+, 21), 158 (100), 78 (65). 2,2-Dimethyl-1-propyl phenyl selenide: ^{1}H NMR (C_6D_6) δ 7.45–6.9 (m, 5 H), 2.75 (s, 2 H), 0.9 (s, 9 H); GCMS *m/e* (rel intensity) 228 (M^+, 15), 158 (35), 71 (100). Cyclopentylmethyl phenyl selenide:[60] ^{1}H NMR (C_6D_6) δ 7.4–6.85 (m, 5 H), 2.75 (d, J = 6.5 Hz, 2 H), 1.8–0.9 (m, 9 H); GCMS *m/e* (rel intensity) 240 (M^+, 6), 158 (31), 83 (38), 55 (100). Cyclohexyl phenyl selenide: ^{1}H NMR ($CDCl_3$) δ 7.65–7.1 (m, 5 H), 3.5–3.0 (m, 1), 2.2–0.9 (m, 10 H); GCMS *m/e* (rel intensity) 240 (M^+, 6), 158 (44), 83 (27), 55 (100). 5-Hexenyl phenyl selenide:[60] ^{1}H NMR ($CDCl_3$) δ 7.65–7.1 (m, 5 H), 5.8–5.2 (m, 1 H), 5.0–4.75 (m, 2 H), 2.65 (t, J = 7 Hz, 2 H), 2.0–1.2 (m, 6 H); GCMS *m/e* (rel intensity) 240 (M^+, 7), 158 (25), 83 (43), 55 (100). 7-Norbornyl phenyl selenide: GCMS *m/e* (rel intensity) 252 (M^+, 12), 158 (18), 95 (93), 67 (100).

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Table VIII. Photostimulated Reaction of Hg(II) Salts with 1-Alkenyl and 1-Alkynyl Derivatives

substrate (mmol) and mercurial (mmol)	conditions[a]	substitutn prod.[b] % yield; (*E*/*Z*)
(*E*)-PhCH=CHI (0.1) and HgL_2 (0.1), L = PhS; PhSe; $PhSO_2$; $(EtO)_2PO$	20; 20; 12; 8	97 (>50), GC; 34 (1.1); 88 (>50), GC; 78 (>50)
(*E*)-PhCH=$CHSO_2Ph$ (0.1) and HgL_2 (0.1), L = PhS; $(EtO)_2PO$	24; 20	50 (>50);[c] <5[d]
Ph_2C=CHI (0.1) and HgL_2 (0.1), L = PhS; PhSe; $PhSO_2$; $PhCOCH_2$; $(EtO)_2PO$	20; 20; 12; 13; 24	100, GC; 78; 93, GC; 64; 86
Ph_2C=$CHSO_2Ph$ (0.1) and HgL_2 (0.1), L = PhS; PhSe; $(EtO)_2PO$	24; 20; 20	100, GC; 12; <5[d]
PhC≡CA (1) and $Hg(SPh)_2$ (0.1), A = I; $PhSO_2$	4; 4	0.17 mmol, GC; 0.16 mmol, GC
PhC≡CA (0.1) and $(EtO)_2P(O)HgCl$ (5), A = I; $PhSO_2$	24; PhH, 24	32; 30, GC
Ph_2C=CHI (1) and $(RCO_2)_2Hg$ (1), R = Et, *t*-Bu	PhH, 24	58;[e] 28[e]
Ph_2C=CHI (2) and $(i\text{-}PrCO_2)_2Hg$ (1)	PhH, 21; PhH, 49	0.95 mmol;[e] 0.81 mmol[e]
Ph_2=CHI (0.2) and $(i\text{-}PrCO_2)_2Hg$ (0.4)	PhH, 24	0.16 mmol[e]

[a] Reactions performed in deoxygenated Me_2SO with 350-nm irradiation in a Rayonet photoreactor at 35–45 °C. The numbers designate the number of hours. [b] Yields determined by ^1H NMR or GLC (GC); *E*/*Z* ratios determined by GLC. [c] 42% of PhCH=$CHSO_2Ph$ recovered. [d] Not detected, substrate recovered. [e] The substitution product was Ph_2C=CHR, R = Et, *i*-Pr, *t*-Bu.

2-Methyl-1-propyl phenyl selenide: ^1H NMR ($CDCl_3$) δ 7.6–7.15 (m, 5 H), 2.92 (d, *J* = 6.5 Hz, 2 H), 2.1–1.7 (m, 1 H), 1.05 (d, *J* = 6.5 Hz, 6 H); GCMS *m*/*e* (rel intensity) 214 (M^+, 22), 158 (58), 78 (40), 57 (100). 3-Butenyl phenyl telluride: ^1H NMR (C_6D_6) δ 7.7–6.8 (m, 5 H), 5.8–5.1 (m, 1 H), 4.9–4.6 (m, 2 H), 3.0–2.7 (m, 2 H), 2.45–2.1 (m, 2 H); GCMS *m*/*e* (rel intensity) 260 (M^+, 15), 77 (43), 55 (100). 1-Hexyl phenyl telluride: ^1H NMR ($CDCl_3$) δ 7.75–7.1 (m, 5 H), 2.85 (t, *J* = 7 Hz, 2 H), 1.8–0.8 (m, 11 H); GCMS *m*/*e* (rel intensity) 290 (M^+, 6), 206 (13), 77 (100). 2,2-Dimethyl-1-propyl phenyl telluride: ^1H NMR (C_6D_6) δ 7.72–6.95 (m, 5 H), 3.0 (s, 2 H), 0.85 (s, 9 H); GCMS *m*/*e* (rel intensity) 276 (M^+, 3), 77 (51), 71 (100). 5-Hexenyl phenyl telluride: ^1H NMR (C_6D_6) δ 7.8–6.9 (m, 5 H), 6.0–5.3 (m, 1 H), 5.1–4.7 (m, 2 H), 2.82 (t, *J* = 6.5 Hz, 2 H), 2.1–0.9 (m, 6 H); GCMS *m*/*e* (rel intensity) 288 (M^+, 2), 83 (31), 77 (45), 55 (100). Cyclopentylmethyl phenyl telluride: GCMS *m*/*e* (rel intensity) 288 (M^+, 1), 83 (44), 77 (58), 55 (100). 7-Norbornyl phenyl telluride: GCMS *m*/*e* (rel intensity) 300 (M^+, 3), 95 (92), 77 (42), 67 (100). Benzyl phenyl telluride:[56] ^1H NMR (C_6D_6) δ 7.4–6.8 (m, 10 H), 3.95 (s, 2 H); GCMS *m*/*e* (rel intensity) 296 (M^+, 3), 91 (100).

General Procedure for the Competitive Reactions of Alkylmercury Halides with Acceptor Radical (Table II). The radicalphile (0.1 mmol) and two alkylmercury halides (1 mmol of each) were dissolved in 10 mL of nitrogen-purged Me_2SO in a Pyrex flask equipped with a rubber septum. The mixture was irradiated with a 275-W sunlamp ca. 20 cm from the flask until all of the radicalphile was consumed (max 8 h). The mixture was poured into water, and the product was extracted with benzene. The extract was washed twice with 10–20% aqueous sodium thiosulfate, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was then treated with hexane, and any precipitate of the remaining alkylmercury halides was filtered off. The concentration mixture was analyzed by GLC, and the relative reactivity was obtained from the ratio of the products.

General Procedure for the Reactions of Mercurials with 1-Alkenyl and 1-Alkynyl Derivatives (Tables IV and VIII) and 1,2-Disubstituted Ethylenes (Table V). The substrate and the mercurial were dissolved in 10 mL of a nitrogen-purged solvent in a Pyrex flask equipped with a rubber septum. The mixture was irradiated as described previously. After completion of the reaction, the reaction mixture was poured into water and extracted with benzene. The extract was washed twice with 10–20% aqueous sodium thiosulfate solution, dried (Na_2SO_4), and concentrated under vacuum. The residue was then analyzed by ^1H NMR and GLC.

In the cases where the reaction mixture was worked up with sodium borohydride, an excess amount of sodium borohydride was added, and the mixture was stirred in Me_2SO for 10–15 min. Benzene was then added, and the mixture was washed 3 times with water, dried (Na_2SO_4), concentrated, and analyzed.

For the reaction performed in an NMR tube, the substrate (0.1 mmol) and the mercurial (0.5 mmol) were dissolved in 1 mL of nitrogen-purged Me_2SO-d_6 in an NMR tube. Methylene chloride (0.1 mmol, the internal standard) was added from a microsyringe, and the tube was capped and sealed with parafilm. The mixture was irradiated with a sunlamp ca. 20 cm from the tube, and the reaction was monitored periodically by 300 MHz ^1H NMR until the reaction was completed. The yield of the product was obtained from the integration of the vinyl proton signal in comparison with that of the internal standard. Most of the reaction products have been reported previously.[16,48] The following data were obtained for previously unreported reaction products (Tables IV, V, and VIII). 2-*n*-Butylbenzothiazole: GCMS *m*/*e* (rel intensity) 193 (1.2), 191 (M^+, 26), 149 (100). 2-Isopropylbenzothiazole: ^1H NMR ($CDCl_3$) δ 7.95–7.7 (m, 2 H), 7.5–7.2 (m, 2 H), 3.1–2.7 (m, 1 H), 1.21 (d, *J* = 7 Hz, 6 H); GCMS *m*/*e* (rel intensity) 179 (1.5), 177 (M^+, 34), 162 (100). 2-Cyclohexylbenzothiazole: ^1H NMR ($CDCl_3$) δ 8.05–7.8 (m, 2 H), 7.55–7.2 (m, 2 H), 3.05–2.7 (m, 1 H), 2.2–1.4 (m, 10 H); GCMS *m*/*e* (rel intensity) 219 (0.5), 217 (M^+, 9), 162 (100), 149 (86). 3-Methyl-1-phenyl-1-butyne:[61] GCMS *m*/*e* (rel intensity) 144 (M^+, 43), 129 (100), 128 (63), 127 (24). 1-Chloro-1-hexene:[62] GCMS *m*/*e* (rel intensity) 120 (6), 118 (M^+, 20), 56 (100). (*E*)-(2-Chloroethenyl)-cyclohexane:[62] ^1H NMR ($CDCl_3$) δ 6.25–5.4 (m, 2 H), 2.7–0.5 (m, 11 H); IR (neat, NaCl plates, cm^{-1}) 2920 (s), 2850 (vs), 1620 (m), 1442 (s), 930 (s), 812 (s), 728 (s); GCMS *m*/*e* (rel intensity) 146 (5), 144 (M^+, 15), 109 (26), 82 (64), 67 (100). (*Z*)-(2-Chloroethenyl)cyclohexane: ^1H NMR ($CDCl_3$) δ 6.01–5.42 (m, 2 H), 2.8–0.7 (m, 11 H); IR (neat, NaCl plates, cm^{-1}) 2940 (vs), 2870 (s), 1637 (m), 1458 (s), 1345 (m), 962 (m), 893 (m), 810 (w), 743 (s), 715 (s); GCMS *m*/*e* (rel intensity) 146 (5), 144 (M^+, 15), 109 (31), 82 (74), 67 (100). (*E*)-1-Iodo-1-hexene:[63] GCMS *m*/*e* (rel intensity) 210 (M^+, 65), 167 (21), 154 (41), 83 (16), 55 (100). (*Z*)-1-Iodo-1-hexene: GCMS *m*/*e* (rel intensity) 210 (M^+, 77), 167 (18), 154 (48), 83 (35), 55 (100). (*E*)-(2-Iodoethenyl)cyclohexane: GCMS *m*/*e* (rel intensity) 236 (M^+, 21), 109 (45), 67 (100), 55 (28). (*Z*)-(2-Iodoethenyl)cyclohexane:[64] GCMS *m*/*e* (rel intensity) 236 (M^+, 34), 109 (48), 67 (100), 55 (28). (*E*)-3,3-Dimethyl-1-iodo-1-butene:[62] ^1H NMR ($CDCl_3$) δ 6.65 (d, *J* = 14.5 Hz, 1 H), 5.98 (d, *J* = 14.5 Hz, 1 H), 1.05 (s, 9 H); GCMS *m*/*e* (rel intensity) 210 (M^+, 18), 83 (72), 68 (53), 67 (41), 55 (100). (*E*)-2-Cyclohexylethenyl phenyl sulfide: GCMS *m*/*e* (rel intensity) 220 (5), 218 (M^+, 100), 109 (57), 67 (86). (*Z*)-2-Cyclohexylethenyl phenyl sulfide: GCMS *m*/*e* (rel intensity) 220 (5), 218 (M^+, 99), 109 (95), 67 (100). (*E*)-3,3-Dimethyl-1-butenyl phenyl sulfide: ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 6.05 (s, 2 H), 1.08 (s, 9 H); GCMS *m*/*e* (rel intensity) 194 (2), 192 (M^+, 46), 177 (92), 83 (100), 65 (62), 55 (82). (*E*)-2-Cyclohexylethenyl phenyl sulfone: GCMS *m*/*e* (rel intensity) 250 (M^+, 2), 109 (100), 67 (62). 1,1-Diphenyl-1-butene: ^1H NMR ($CDCl_3$) δ 7.3 (m, 10 H), 6.08 (t, 1 H), 2.12 (m, 2 H), 0.99 (t, 3 H).

General Procedure for the Determination of Relative Reactivities toward Alkyl Radicals (Table VII). Substrates A and B and the mercurial (0.1 mmol of cyclohexyl- or *tert*-butylmercury chloride) in a deoxygenated solvent in a Pyrex flask were irradiated with either a 275-W sunlamp ca. 20 cm from the flask or in a 350-nm Rayonet photoreactor. After irradiation, the mixture was worked up as described previously. The concentrated reaction mixture was analyzed by GLC, and the relative reactivities were obtained from the ratio of the product corrected by the initial mol ratio of the substrates.

Registry No. CH_2=$CHCH_2H_9Cl$, 14155-77-2; $CH_3(CH_2)_4CH_2HgCl$, 17774-09-3; $(CH_3)_3CCH_2HgCl$, 10284-47-6; $(CH_3)_2CHHgCl$, 30615-19-1; *c*-$C_6H_{11}HgCl$, 24371-94-6; *c*-$C_5H_9CH_2HgCl$, 33631-66-2; CH_2=$CH(CH_2)_3CH_2HgCl$, 63668-13-3; $CH_3(CH_2)_3CH_2HgCl$, 544-15-0; $(CH_3)_2CHCH_2HgCl$, 27151-74-2; $(CH_3)_3CHgCl$, 38442-51-2; [CH_2=$CH(CH_2)_2CH_2]_2Hg$, 53103-00-7; $(i\text{-}Pr)_2Hg$, 1071-39-2; *n*-BuHgCl, 543-63-5; $(n\text{-}Bu)_2Hg$, 629-35-6; PhSSPh, 882-33-7; PhSeSePh, 1666-13-3; PhTeTePh, 32294-60-3; $PhSeSO_2C_6H_4$-Me-*p*, 68819-94-3; *n*-BuS-SBu-*n*, 629-45-8; Cl-SO_2Ph, 98-09-9; PhSH, 108-98-5; CH_2=$CHCH_2CH_2SPh$, 4285-49-8; CH_2=$CHCH_2CH_2SePh$, 113303-06-3; CH_2=$CHCH_2CH_2TePh$, 113303-07-4; CH_2=$CHCH_2CH_2S$-*n*-Bu, 20218-02-4; $CH_3(CH_2)_4CH_2SPh$, 943-78-2; $CH_3(CH_2)_4CH_2SePh$, 63866-88-6; $CH_3(CH_2)_4CH_2TePh$, 85055-59-0; $CH_3(CH_2)_4CH_2Cl$, 544-10-5; $(CH_3)_3CCH_2SPh$, 7210-80-2; $(CH_3)_3CCH_2SePh$, 96503-15-0;

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$(CH_3)_3CCH_2TePh$, 113303-08-5; $(CH_3)_2CHSPh$, 3019-20-3; $(CH_3)_2CHSePh$, 22233-89-2; $(CH_3)_2CHTePh$, 32343-99-0; c-$C_6H_{11}SPh$, 7570-92-5; c-$C_6H_{11}TePh$, 56950-05-1; c-$C_5H_9CH_2SPh$, 100258-36-4; c-$C_5H_9CH_2SePh$, 78872-19-2; $CH_2{=}CH(CH_2)_3CH_2SPh$, 39984-84-4; $CH_2{=}CH(CH_2)_3CH_2SePh$, 78872-18-1; $CH_2{=}CH(CH_2)_3CH_2TePh$, 113303-11-0; $CH_2{=}CH(CH_2)_3CH_2SH$, 17651-39-7; $CH_3(CH_2)_3CH_2SPh$, 1129-70-0; $(CH_3)_2CHCH_2SPh$, 13307-61-4; $(CH_3)_3CSPh$, 3019-19-0; $PhS(CH_2)_6SPh$, 55129-89-0; n-BuSePh, 28622-61-9; $(i\text{-Bu})_2Hg$, 24470-76-6; $PhCH_2HgCHPh$, 780-24-5; $PhCH_2HgSPh$, 113303-12-1; $PhCH_2HgSePh$, 113303-13-2; $PhCH_2HgCl$, 2117-39-7; $PhCH_2SePh$, 18255-05-5; $PhCH_2SPh$, 831-91-4; $PhCH_2TePh$, 32344-00-6; $PhCH_2CH_2Ph$, 103-29-7; $PhCH_2Br$, 100-39-0; (E)-PhCH=CHI, 42599-24-6; (Z)-PhCH=CHI, 57918-63-5; $Ph_2C{=}CHI$, 19997-66-1; $H_2C{=}CHI$, 593-66-8; $Me_2C{=}CHI$, 20687-01-8; (E)-$MeO_2CCH{=}CHI$, 6213-88-3; (Z)-$MeO_2CCH{=}CHI$, 6214-23-9; (Z)-$MeO_2CCH{=}CHCl$, 3510-44-9; PhC≡CI, 932-88-7; PhC≡CSPh, 35460-31-2; $PhC{\equiv}CSO_2Ph$, 5324-64-1; (E)-PhCH=CHSPh, 7214-53-1; $Ph_2C{=}CHSPh$, 13112-46-4; (E)-$PhCH{=}CHSO_2Ph$, 16212-06-9; $Ph_2C{=}CHSO_2Ph$, 26189-62-8; $MeOC(CH_2)_4HCHHgO_2CCF_3$, 720-77-4; $MeOC(Ph)HCH_2HgO_2CCF_3$, 111823-11-1; (E)-PhCH=CH-n-Bu, 6111-82-6; (Z)-PhCH=CH-n-Bu, 15325-54-9; (E)-PhCH=CH-i-Pr, 15325-61-8; (Z)-PhCH=CH-i-Pr, 15325-56-1; (E)-PhCH=CH-c-C_6H_{11}, 18869-27-7; (Z)-PhCH=CH-c-C_6H_{11}, 40132-69-2; (E)-PhCH=CH-t-Bu, 3846-66-0; (Z)-PhCH=CH-t-Bu, 3740-05-4; $Ph_2C{=}CH\text{-}n\text{-}Bu$, 1530-19-4; $Ph_2C{=}CH\text{-}i\text{-}Pr$, 35467-39-1; $Ph_2C{=}CH\text{-}c\text{-}C_6H_{11}$, 91083-83-9; $Ph_2C{=}CH\text{-}t\text{-}Bu$, 23586-64-3; $MeOC(CH_2)_4HCHCH{=}CPh_2$, 111823-12-2; $MeOC(Ph)HCH_2CH{=}CPh_2$, 111823-13-3; $Me_2C{=}CH\text{-}c\text{-}C_6H_{11}$, 89656-98-4; ($E$)-$MeO_2CH{=}CH\text{-}i\text{-}Pr$, 20515-15-5; ($Z$)-$MeO_2CCH{=}CH\text{-}i\text{-}Pr$, 20515-16-6; ($E$)-$MeO_2CCH{=}CH\text{-}c\text{-}C_6H_{11}$, 26429-99-2; ($Z$)-$MeO_2CCH{=}CH\text{-}c\text{-}C_6H_{11}$, 26429-98-1; ($E$)-$MeO_2CCH{=}CH\text{-}t\text{-}Bu$, 20664-51-1; ($Z$)-$MeO_2CCH{=}CH\text{-}t\text{-}Bu$, 57539-96-5; PhC≡C-$n$-Bu, 1129-65-3; PhC≡C-$c$-$C_6H_{11}$, 33414-83-4; PhC≡C-$t$-Bu, 4250-82-2; PhC≡C-$i$-Pr, 1612-03-9; PhCH($t$-Bu)$CH_2SPh$, 113303-14-3; Ph($t$-Bu)C=CHSPh, 113303-15-4; Ph(t-Bu)$CHCH_2SO_2Ph$, 113303-16-5; (E)-PhCH=CHSOPh, 40110-66-5; (Z)-ClCH=CHCl, 156-59-2; (E)-ClCH=CHCl, 156-60-5; (E)-ICH=CHI, 590-27-2; $Ph_2C{=}CHSePh$, 108365-51-1; (E)-ClCH=CHI, 28540-81-0; (E)-ClCH=CHSPh, 26620-11-1; (E)-$ClCH{=}CHSO_2Ph$, 38238-75-4; (E)-$BrCH{=}CHSO_2Ph$, 20408-25-7; (Z)-$BrCH{=}CHSO_2Ph$, 52244-26-5; (E)-$ICH{=}CHSO_2Ph$, 58202-75-8; (E)-$PhSCH{=}CHSO_2Ph$, 37530-86-2; (E)-$Bu_3SnCH{=}CHSO_2Ph$, 88486-41-3; (E)-ClCH=CH-n-Bu, 50586-19-1; (Z)-ClCH=CH-n-Bu, 50586-18-0; (E)-ClCH=CH-c-C_6H_{11}, 67404-71-1; (Z)-ClCH=CH-c-C_6H_{11}, 67404-70-0; (E)-ClCH=CH-t-Bu, 18314-62-0; (Z)-ClCH=CH-t-Bu, 18314-61-9; (E)-ICH=CH-n-Bu, 16644-98-7; (Z)-ICH=CH-n-Bu, 16538-47-9; (E)-ICH=CH-c-C_6H_{11}, 42599-23-5; (Z)-ICH=CH-c-C_6H_{11}, 67404-69-7; (E)-ICH=CH-t-Bu, 61382-45-4; (Z)-ICH=CH-t-Bu, 64245-24-5; $PhS(CH_2)_2SPh$, 622-20-8; (E)-n-BuCH=CHSPh, 62839-73-0; (Z)-n-BuCH=CHSPh, 70197-34-1; (Z)-c-$C_6H_{11}CH{=}CHSPh$, 94633-43-9; (E)-c-$C_6H_{11}CH{=}CHSPh$, 94633-42-8; (Z)-t-BuCH=CHSPh, 58431-67-7; (E)-t-BuCH=CHSPh, 53847-74-8; (E)-c-$C_6H_{11}CH{=}CHSO_2Ph$, 112863-50-0; (Z)-c-$C_6H_{11}CH{=}CHSO_2Ph$, 113303-17-6; (E)-t-$BuCH{=}CHSO_2Ph$, 68969-27-7; (Z)-t-$BuCH{=}CHSO_2Ph$, 108344-86-1; $(PhS)_2Hg$, 21514-24-9; $(PhSe)_2Hg$, 21514-25-0; $(PhSO_2)_2Hg$, 26186-79-8; $[(EtO)_2PO]_2Hg$, 74475-14-2; $(PhCOCH_2)_2Hg$, 37160-45-5; $(EtCO_2)_2Hg$, 26719-04-0; $(t\text{-}BuCO_2)_2Hg$, 32276-77-0; $(i\text{-}PrCO_2)_2Hg$, 19348-33-5; (Z)-PhCH=CHSPh, 7214-56-4; (E)-PhCH=CHSePh, 60466-40-2; (Z)-PhCH=CHSePh, 60466-30-0; (Z)-$PhCH{=}CHSO_2Ph$, 32291-77-3; (E)-$PhCH{=}CHP(O)(OEt)_2$, 20408-33-7; (Z)-$PhCH{=}CHP(O)(OEt)_2$, 25362-01-0; $Ph_2C{=}CHCH_2COPh$, 57694-83-4; $Ph_2C{=}CHP(O)(OEt)_2$, 78462-91-6; PhC≡CP(O)$(OEt)_2$, 3450-67-7; $Ph_2C{=}CHEt$, 1726-14-3; $(EtO)_2POHgCl$, 29120-01-2; 7-norbornylmercury, 83020-42-2; 1,6-dihexanediylmercury, 6675-64-5; 7-norbornylphenyl sulfide, 94110-62-0; 7-norbornylphenyl selenide, 113303-09-6; 7-norbornylphenyl teluride, 113303-10-9; 7,7′-dinorbornyl, 1712-32-9; 2-iodobenzothiazole, 120-75-2; 2-phenylsulfonylbenzothiazole, 64345-00-2; 2-butylbenzothiazole, 54798-95-7; 2-isopropylbenzothiazole, 17626-86-7; 2-cyclohexylbenzothiazole, 40115-03-5; 2-*tert*-butylbenzothiazole, 17626-88-9.

Does Formal Intramolecular Transfer of an Acidic Deuterium to a Site of Halogen–Lithium Exchange Show That Lithium–Halogen Exchange Is Faster than Loss of the Acidic Deuterium? Evidence in Favor of an Alternative Mechanism

Peter Beak,* Timothy J. Musick, and Chin-wen Chen

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801.
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Abstract: Reactions in which there is formal intramolecular transfer of an acidic deuterium to a site of halogen–lithium exchange could be interpreted to show that initial halogen–lithium exchange occurs faster than loss of the acidic deuterium. However studies of the competition between halogen–metal–deuterium exchange and deuterium loss for *N*-deuterio-*N*-alkyl-*o*, -*m*-, and -*p*-halobenzimides are not consistent with that mechanism. We suggest an alternative in which initial loss of the acidic deuterium is followed by halogen–lithium exchange to give a dilithiated intermediate. Deuterium transfer to the site of halogen–lithium exchange then occurs by reaction of the dilithiated species intermolecularly with unreacted N-deuteriated amide. The halogen–lithium exchange is faster than complete mixing of the reactants and can occur either in an initially formed deprotonated complex or in a transient high local concentration of organolithium reagent. Evidence for both possibilities is provided. Two reactions from the literature in which halogen–lithium exchange appears to be faster than transfer of an acidic hydrogen have been reinvestigated and found to be interpretable in terms of similar sequences.

The relative rates of competitive reactions of organolithium compounds are important for the use and to the understanding of these reagents.[1] Particularly interesting are reactions of polyfunctional molecules in which a kinetically driven reaction takes precedence over a thermodynamically favored alternative.[2] Perhaps the most dramatic apparent examples of such reactions are those in which a highly acidic hydrogen appears not to react

(1) For a summary of pertinent literature and elegant uses of selective reactions of organolithium reagents in competitive situations, see: Cooke, M. P., Jr.; Widner, R. K. *J. Org. Chem.* **1987**, *52*, 1382. Parham, W. F.; Bradsher, C. K. *Acc. Chem. Res.* **1982**, *15*, 300 and references cited therein.

(2) A number of such reactions have been attributed to complex-induced proximity effects: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

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