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Free Radical Chain Reactions Involving Alkyl- and Alkenylmercurials

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Alkylmercurials are readily available organometallic reagents possessing moderate reactivity in electrophilic substitution and low reactivity in nucleophilic attack at carbon.[1] Pyrolysis of organomercurials has been utilized as a method to generate alkyl radicals useful in homolytic aromatic substitution processes[2] and in defining a set of σ-constants for substituent stabilization of benzylic radicals.[3] One of the most widely studied chain reactions of an organomercurial has been the alkaline $NaBH_4$ reduction of alkylmercury halides or carboxylates to yield the alkane[4] or products derived from alkyl radical attack upon a suitable coreactant.[5] Both the pyrolysis of R_2Hg and the alkaline $NaBH_4$ reduction of RHgCl are reactions that involve unstable mercury(I) intermediates.

During the past several years, we have developed a series of free radical reactions in which RHgX or R_2Hg participates in the propagation step of a chain process that does not usually involve $RHg^\bullet$ as an intermediate other than in the initiation step.[6-26] One group of these reactions involves the homolytic displacement of an alkyl radical from a mercury atom by an electron-accepting carbon- or heteroatom-centered radical. This type of homolytic displacement is not unexpected since it has been recognized for some time in the cleavage of R_2Hg or RHgX by molecular halogens.[27] Competing electrophilic substitution by halogen can occur, but it has been possible to define conditions where either the free radical or ionic substitution will predominate.[28] Another group of reactions involves electron transfer to RHgX from an electron-donating free radical or radical ion and leads directly to the alkyl radical, mercury metal, and X^-.[6] The unusual reactivity of carbon–mercury bonds toward both electron-accepting and electron-donating paramagnetic species is the focus

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Formation of Alkyl Radicals from Alkylmercurials

Alkylmercury(I) species have only transitory existence because of their facile fragmentation to alkyl radicals and mercury metal.[29] Alkylmercury(II) compounds also generate alkyl radicals upon thermolysis or photolysis. It appears that the rate of spontaneous (thermal) formation of radicals from *tert*-butylmercurials decreases from the unisolable t-BuHgH to $(t\text{-Bu})_2$Hg to t-BuHgX (X = Cl, Br, I, OAc). Formation of $t\text{-Bu}^\bullet$ can be measured by spin trapping with N-t-butylphenylnitrone.[30] In Me_2SO at 100 °C this technique leads to $d[t\text{-Bu}^\bullet]/dt = k[t\text{-BuHgX}]$, where k increases from 1.4×10^{-6} with X = Cl to 1.4×10^{-5} for X = I and 4.4×10^{-3} s^{-1} with X = t-Bu.[26] The secondary alkyl- and primary alkylmercury derivatives are, of course, considerably more stable in thermal or photochemical radical-forming processes. With irradiation from a 275-W fluorescent sunlamp through Pyrex, typical decomposition rates for 0.1 M t-BuHgCl of a few percent per hour are observed as measured by the consumption of the radical trap $(t\text{-Bu})_2NO^\bullet$.

Alkylmercury hydrides, formed by the reaction of RHgX with alkaline $NaBH_4$, react with alkyl radicals by hydrogen atom transfer to form $RHg^\bullet$.[12] A free radical chain process leads to the formation of the alkane (RH) or, in the presence of an olefinic radical trap, to the reduced addition product (Scheme I).[31] For such processes involving $RHg^\bullet$, the structure of the alkyl group has little effect on the reactivity of its precursor; competitive reactions involving *tert*-butyl- and n-butylmercury chlorides with $NaBH_4$ lead to approximately equal amounts of *tert*-butylation and n-butylation products, particularly when a reactive radicaphile (e.g., $CH_2{=}C(Cl)CN$) is present to trap $R^\bullet$.[19]

Scheme I

$$RHg^\bullet \rightarrow R^\bullet + Hg^0$$

$$R^\bullet + CH_2{=}CHCO_2Et \rightarrow RCH_2\dot{C}HCO_2Et(R'^\bullet)$$

$$R^\bullet\ (R'^\bullet) + RHgH \rightarrow RH\ (R'H) + RHg^\bullet$$

Dialkylmercurials react cleanly with heteroatom-centered acceptor radicals such as $RS^\bullet$, $PhSe^\bullet$, $PhTe^\bullet$, $RSO_2^\bullet$, or halogen atoms to form the Hg(II) salt and $R^\bullet$ (Scheme IIa).[10] With carbon-centered radicals (e.g., $CCl_3^\bullet$), hydrogen atom abstraction and β-elimination of $RHg^\bullet$ becomes an important process, and a chain reaction leading to alkene and Hg^0 has been reported (Scheme IIb).[32]

Scheme II

$$\text{(a)}\ RS^\bullet + (i\text{-Bu})_2Hg \rightarrow i\text{-BuHgSR} + i\text{-Bu}^\bullet$$

$$i\text{-Bu}^\bullet + RSSR \rightarrow i\text{-BuSR} + RS^\bullet$$

$$RS^\bullet + i\text{-BuHgSR} \rightarrow (RS)_2Hg + i\text{-Bu}^\bullet$$

$$\text{(b)}\ CCl_3^\bullet + (i\text{-Bu})_2Hg \rightarrow HCCl_3 + Me_2C{=}CH_2 + i\text{-BuHg}^\bullet$$

$$i\text{-BuHg}^\bullet \rightarrow i\text{-Bu}^\bullet + Hg^0$$

$$i\text{-Bu}^\bullet + CCl_4 \rightarrow i\text{-BuCl} + CCl_3^\bullet$$

Table I
Relative Reactivities of Alkylmercury Chlorides toward Free Radicals at 35–40 °C

radical[a]	solvent	t-BuHgCl: i-PrHgCl: n-BuHgCl
$RCMe_2NO_2^{\bullet-}$	Me_2SO	1.0[b]:0.07:<0.005
$Bu_3Sn^\bullet$	PhH	1.0:0.025[c]:0.005
$ClHg^\bullet$	PhH	1.0:0.011[c]:0.0001
$PhS^\bullet$	Me_2SO	1.0:0.08:<0.003
$PhSe^\bullet$	PhH	1.0:–:<0.004
$RCH_2\dot{C}HP(O)(OEt)_2$	Me_2SO	1.0:–:<0.003
$I^\bullet$	Me_2SO	1.0:0.006[c]:<0.0001

[a] Radical precursors were $Me_2C{=}NO_2^-$, (E)-PhCH=CHSnBu$_3$, (E)-PhCH=C(H)HgCl, PhSSPh, PhSeSePh, $CH_2{=}CHP(O)(OEt)_2$, and (E)-PhCH=CHI or $Ph_2C{=}CHI$. [b] $PhCH_2HgCl$ is 4.7 times as reactive. [c] c-$C_6H_{11}^\bullet$.

Monoalkylmercurials (RHgX) also react readily with acceptor radicals ($A^\bullet$). For example, $SO_4^{\bullet-}$, generated by reaction of $S_2O_8^{2-}$ with I^- or Ag^+, readily displaces $R^\bullet$; in Me_2SO at 25 °C strong CIDNP multiplet signals (A/E) for RH, R(–H) and R–R can be observed from the diffusive encounter of primary, secondary, or tertiary alkyl radicals. Alkylmercury salts will also undergo electron transfer with easily oxidized donor radicals ($D^\bullet$) or radical anions ($D^{\bullet-}$). Competing elimination reactions are seldom observed. Thus, reactions 1 and 2 can serve as propagation steps in a number of

$$RHgX + D^\bullet\ (D^{\bullet-}) \rightarrow R^\bullet + Hg^0 + X^- + D^+\ (D) \qquad (1)$$

$$RHgX + A^\bullet \rightarrow R^\bullet + AHgX \qquad (2)$$

chain reactions. In a similar fashion, monomeric HgCl formed in a β-elimination process will regenerate $R^\bullet$ (reaction 3).[11] This process contributes to the efficiency

$$RHgX + HgX \rightarrow R^\bullet + HgX_2 + Hg^0 \qquad (3)$$

$$^\bullet HgX + Y\text{–}A \rightarrow A^\bullet + YHgX \qquad (4)$$

of RHgX in thermal or photochemical initiation reactions. Monomeric $^\bullet$HgX also reacts in a radical manner with reagents Y–A (reaction 4) such as the dichalcogenides or sulfonyl halides, sulfides, and selenides to generate a heteroatom-centered radical ($A^\bullet$), which serves as the acceptor radical in reaction 2.[10]

In direct-competition experiments with an excess of a mixture of two alkylmercury chlorides, it is observed that in reactions 1–3 the stability of the incipient $R^\bullet$ has a large effect upon the rate of its production, with $k_{t\text{-Bu}}/k_{n\text{-Bu}}$ as great as 10^3).[19] We conclude that reactions 1–3 are processes in which the radical is formed in the rate-determining step; the reactions are probably concerted and quite certainly do not involve $RHg^\bullet$ intermediates. Table I lists relative reactivity data observed when excesses of mixtures of two alkylmercury chlorides are attacked by acceptor or donor radicals in free radical chain processes.

Reactions 1–3 occur to yield substituted alkyl radicals, e.g., $PhCOCH_2^\bullet$ or 2-methoxycyclohexyl radical. However, the reactions are very inefficient or do not occur at all when $R^\bullet = CF_3^\bullet$, 1-alkenyl, 1-alkynyl, or aryl, presumably because of the stability of the radical that would be formed. Heteroatom-centered acceptor radicals such as $PhS^\bullet$, $PhSO_2^\bullet$, $(EtO)_2PO^\bullet$, and $RCO_2^\bullet$

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Table II
Substitutions Occurring by a Homolytic Addition–Elimination Chain Process

reactants (equiv)	conditions[a]	product	% yield, (*E*/*Z*)	ref
(*E*)-PhCH=C(H)HgCl and RHgCl (5), R = *t*-$BuCH_2$; c-C_6C_{11}; *t*-Bu	Me_2SO, R, 12 h; 12 h; 4 h	PhCH=CHR	23; 78 (6); 97 (31)	11
Ph_2C=C(H)HgBr and *i*-PrMgI (2); *t*-BuMgCl (2); (c-$C_6H_{11})_3B$ (5)	PhH, R, 12 h; R, 5 h; S, 1 h	Ph_2C=CHR	35; 38; 42	24
PhCH=C(H)HgR, R = *n*-Bu; c-C_6H_{11}; *t*-Bu	PhH, R, 24 h	PhCH=CHR	12; 60; 73	24
(*E*)-*t*-BuCH=C(H)HgSR, R = Ph; *n*-Bu	PhH, S (PhH, S, 3 h; 12 h) 3 h; 12 h	*t*-BuCH=CHSR	100 (>50); 100 (>50)	8
(*E*)-*t*-BuCH=C(H)HgCl and PhYYPh, Y = S; Se; Te	PhH, S, 6 h; 2 h; 18 h	*t*-BuCH=CHYPh	100 (>50); 95 (>50); 89 (>50)	8
(*E*)-*t*-BuCH=C(H)HgCl and $PhSO_2Cl$ (1); $(PhSO_2)_2Hg$ (5); $PhSO_2Na$ (1.2)	Me_2SO, S, 3 h; 12 h; *t*-BuOH/H_2O, S, 30 h	*t*-BuCH=$CHSO_2Ph$	99 (>50); 42 (>50); 81 (>50)	10
(*E*)-*t*-BuCH=C(H)HgCl and A^- (1.2), A = $(EtO)_2POK$; PhP(OBu)OK; *n*-$PrSO_2Na$	Me_2SO, S, 29 h; 3.5 h; *t*-BuOH/H_2O, S, 30 h	*t*-BuCH=CHA	76; 84; 75	8
CH_2=C(H)HgCl and A_2Hg, A = PhS (1); PhSe (1); $PhSO_2$ (5)	Me_2SO, R, 20 h; 20 h; 12 h	CH_2=CHA	76; 39; 43	21
(*E*)-PhCH=$CHSnBu_3$ and RHgCl (1.2), R = *n*-Bu; *i*-Pr; *t*-Bu	PhH, R, 40 h; S, 18 h; S, 14 h	PhCH=CHR	46 (6); 86 (12); 83 (49)	11
(*E*)-PhCH=CHI and RHgCl, R = *n*-Bu (2); *i*-Pr (2); *t*-Bu (5)	Me_2SO, R, 48 h; 48 h; 1 h	PhCH=CHR	22; 70 (9); 100 (25)	11
(*Z*)-PhCH=CHI and *t*-BuHgCl (5)	Me_2SO, S, 6 h	PhCH=CHBu-*t*	90 (0.04)	25
(*E*)-PhCH=C(H)Q, Q = PhS; PhSO; $PhSO_2$ and *t*-BuHgCl (5; 5; 2)	Me_2SO, R, 24 h	PhCH=CHBu-*t*	36; 32 (21); 43 (81)	11
Ph_2C=C(H)Q, Q = Bu_3Sn; HgBr; $PhSO_2$ and *t*-BuHgCl (2; 5; 5)	PhH, R, 18 h; Me_2SO, R, 12 h; 12 h	Ph_2C=CHBu-*t*	78; 100; 88	11
Ph_2C=C(H)Q, Q = HgBr; I; SPh and *i*-PrHgCl (5)	Me_2SO, R, 12 h; 8 h; 96 h	Ph_2C=CHPr-*i*	96; 89; 55	11
Ph_2C=C(H)I and A_2Hg (1), A = PhS; $PhSO_2$; $(EtO)_2PO$	Me_2SO, R, 12 h	Ph_2C=CHA	100; 93; 86	11
Ph_2C=C(H)I and $(RCO_2)_2Hg$, R = Et (1); *i*-Pr (2); *t*-Bu (1)	Me_2SO, R, 24 h	Ph_2C=CHR	48; 39; 28	16
PhC≡CX, X = Bu_3Sn; SO_2Ph; SPh and *t*-BuHgCl (5; 5; 0.2)	Me_2SO, R, 24 h	PhC≡CBu-*t*	61; 57; 44	18
PhC≡CI and RHgCl (1.5), R = *n*-Bu; *c*-C_6H_{11}; *t*-Bu	Me_2SO, S, 7 h	PhC≡CR	48; 93; 100	18
CH_2=$CHCH_2X$, X = Bu_3Sn; Br; SO_2Ph and *t*-BuHgCl (5)	PhH, S, 4 h; Me_2SO, S, 2 h; 4 h	*t*-$BuCH_2CH$=CH_2	55; 91; 85	26
HC≡CCH_2Cl and *t*-BuHgCl (5), NaI (5)	Me_2SO, S, 7 h	*t*-BuCH=C=CH_2	71	26

[a] R = 350-nm Rayonet photoreactor; S = 275-W sunlamp ca. 20 cm from Pyrex reaction vessel.

(which decarboxylates to $R^\bullet + CO_2$) are also readily formed in reaction 2 or 3 by radical attack upon the appropriate Hg(II) salt.[11]

Substitution Processes Occurring by a Homolytic Addition–Elimination Mechanism

1-Alkenyl- and 1-alkynylmercurials open up a radical reaction channel in which substitution can occur by an addition–elimination process (Scheme III).[8,11] Monomeric HgCl thus formed regenerates an alkyl radical by reaction with RHgCl (reaction 3) or by the analogous reaction with RMgCl.[24] Heteroatom-centered radicals, which can take the place of $R^\bullet$ in Scheme III, can be formed by reaction with Y–A reagents (reaction 4),[8] with HgA_2 (reaction 5),[11] or in certain cases by electron

$$HgCl + HgA_2 \rightarrow A^\bullet + AHgCl + Hg^0 \quad (5)$$

$$HgCl + A^- \rightarrow A^\bullet + Hg^0 + Cl^- \quad (6)$$

transfer with $A^- = RSO_2^-$, $(EtO)_2PO^-$, $RP(OR')O^-$, or RS^- (reaction 6).[8] Examples of photostimulated radical chain substitution reactions of vinylmercurials are given in Scheme IV and in Table II.

Scheme III

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

$$Ph\dot{C}H{-}CH(R)HgCl \rightarrow PhCH{=}CHR + HgCl$$

The radical addition–elimination sequence occurs with a variety of leaving groups in addition to Hg(I) species. Thus, reaction 7a occurs by a radical chain process where the leaving group Q can be not only HgCl but also Bu_3Sn, PhS, $PhSO_2$, and halogen.[11] Mercury(II) salts participate in the free radical exchange of one group for another (reaction 7b). Whether exchange

$$PhCH{=}CHQ + RHgCl \xrightarrow{h\nu} PhCH{=}CHR + QHgX \text{ (or } QX + Hg^0) \quad (7a)$$

$$PhCH{=}CHQ + A_2Hg \xrightarrow{h\nu} PhCH{=}CHA + QHgA \quad (7b)$$

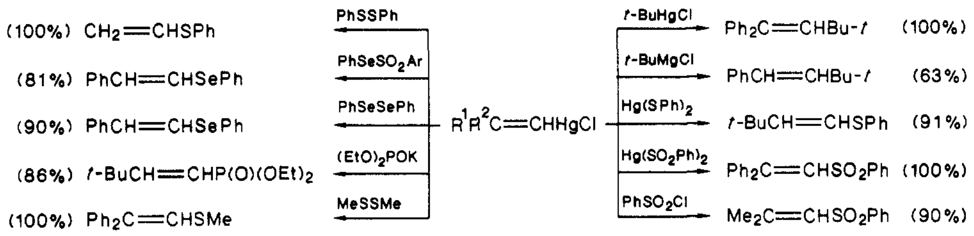
occurs readily depends upon the leaving-group abilities of $Q^\bullet$ and $A^\bullet$. Thus, in the β-styrenyl system, $(EtO)_2PO^\bullet$ displaces $I^\bullet$, $Bu_3Sn^\bullet$, or $XHg^\bullet$ readily but $Br^\bullet$, $PhS^\bullet$, or $PhSO_2^\bullet$ ineffectively or not at all.

With PhSSPh reaction 8 is observed with $R^1 = R^2 = H$ not only for Q = HgCl but also for Bu_3Sn, R_3Rb, or $Zr(Cp)_2Cl$.[21] When the attacking radical is $PhS^\bullet$ or

$$(R^1)(R^2)C{=}CHQ + PhSSPh \xrightarrow{h\nu} (R^1)(R^2)C{=}CHSPh + QSPh \quad (8)$$

$PhSO_2^\bullet$, reversal of the addition step is possible, and in reaction 8 only products from α-addition are observed even though the preferred site of radical attack is at the β-carbon atom. Thus, reaction of $CH_2{=}CHSnPh_3$ with p-MeC_6H_4SH proceeds in a chain fashion to yield mainly p-$MeC_6H_4SCH_2CH_2SnPh_3$ as expected for preferred terminal attack followed by a facile hydrogen atom transfer.[33] However, in reaction with the less reactive PhSSPh or $(PhS)_2Hg$, only the products from α-substitution ($CH_2{=}CHSPh$) are observed for $CH_2{=}CHSnBu_3$.[21]

Scheme IV

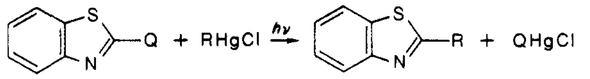


1-Alkenyl- or 1-alkynylmercurials such as PhCH=C(H)HgSR, PhCH=C(H)HgR, or PhC≡CHgR undergo a radical chain decomposition involving the addition–elimination sequence followed by decomposition of the eliminated Hg(I) species to form $\mathrm{Hg^0}$ and PhS• and PhS• (reaction 9).[8] The photostimulated decomposi-

$$\mathrm{PhCH{=}C(H)HgR} \xrightarrow[\substack{\mathrm{R\ =\ alkyl}\\ \mathrm{or\ thiyl}}]{h\nu} \mathrm{PhCH{=}CHR} + \mathrm{Hg^0} \quad (9)$$

tion of a 1:1 mixture of *t*-BuHgCH=CHPh and *n*-BuHgCH=CHPh initially forms *t*-BuCH=CHPh and *n*-BuCH=CHPh in an approximately equal ratio ($k_{n\text{-Bu}}/k_{t\text{-Bu}} = 0.7$) since there is little effect of the structure of R on the reactivity of PhCH=C(H)HgR toward alkyl radicals.[24]

Homolytic aromatic substitution by an addition–elimination mechanism occurs less efficiently than alkenyl substitutions. However, with activated aromatic systems, such as 2-benzothiazole derivatives, a chain reaction with RHgCl has been observed (reaction 10, Q = I, $\mathrm{PhSO_2}$).[11]



(10)

Substitution by alkyl radical attack in allylic, propargylic, and allenic systems by the $\mathrm{S_H2'}$ addition–elimination mechanism (reaction 11) is well-known for substrates with Q = $\mathrm{Bu_3Sn}$,[34] PhS,[35] or cobaloximes.[36]

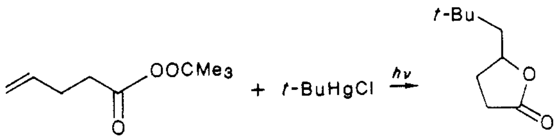
$$\mathrm{R^\bullet + CH_2{=}CHCH_2Q \rightarrow RCH_2\dot{C}HCH_2Q \rightarrow RCH_2CH{=}CH_2 + Q^\bullet} \quad (11)$$

With alkylmercurials as the radical precursor, such substitutions also occur readily in a chain fashion with halogen as the leaving groups (e.g., reacton 12). With

$$\mathrm{CH_2{=}CHCH_2Q} + t\text{-}\mathrm{BuHgX} \xrightarrow[\mathrm{Q\ =\ Cl,\ Br,\ I}]{h\nu,\ \mathrm{Me_2SO}} t\text{-}\mathrm{BuCH_2CH{=}CH_2 + QHgX} \quad (12)$$

poor leaving groups that are also electron withdrawing, e.g., Q = $\mathrm{O_2CR}$, CN, OTos, or $\mathrm{OP(O)(OEt)_2}$, the intermediate radicals ($\mathrm{RCH_2\dot{C}HCH_2Q}$, $\mathrm{RCH{=}\dot{C}CH_2Q}$) react with RHgX as an acceptor species to form $\mathrm{RCH_2CH(HgX)CH_2Q}$ or $\mathrm{RCH{=}CH(HgX)CH_2Q}$. When Q is the tosyl or diethyl phosphate group, these intermediates readily undergo elimination to form the allyl or allenyl products, particularly in the presence of iodide ions.

Addition–elimination in 3-butenyl and 5-hexenyl systems can lead to cyclized products containing 3- and 5-membered rings.[37] One example of such a process involving an alkylmercurial as the alkylating agent is given in reaction 13, a process previously described for solvent-derived radicals.[38]



(13)

Table II presents some representative examples of homolytic substitutions involving mercury reagents that proceed by the addition–elimination mechanism. In those substitutions where reactions 1–3 are involved, the processes are usually more efficient with R = *t*-Bu than for *i*-Pr or *n*-Bu. As demonstrated in Table II, homolytic substitution in 1-alkenyl derivatives can occur in a stereospecific manner with retention of configuration.[16] The degree of stereospecificity depends uon the nature of the leaving group, the size of the attacking radical, and presumably the lifetime of the intermediate radical undergoing β-elimination. Thus, c-$\mathrm{C_6H_{11}}^\bullet$ gives retention of configuration with (*E*)- or (*Z*)-$\mathrm{MeO_2CCH{=}CHSnBu_3}$, $\mathrm{MeO_2CCH{=}CHI}$, PhCH=CHI, or $\mathrm{MeO_2CCH{=}CHCl}$, but *t*-Bu• reacts in a stereospecific manner only with the iodides. Apparently, in the β-elimination of Scheme III, I• is a better leaving group than $\mathrm{Bu_3Sn^\bullet}$ or Cl•. With Q = $\mathrm{Bu_3Sn}$ or Cl and R = *t*-Bu in Scheme V, the β-elimination is apparently slow enough and the concentration of the high-energy conformation **1** so low, that both *E* and *Z* substrates react via the low-energy conformation **2** leading to the *E* product. With a smaller R group and Q = $\mathrm{Bu_3Sn}$ or Cl or with Q = I and R = *t*-Bu, elimination from conformation **1** occurs more rapidly than the interconversion of **1** to **2**. Stereospecificity is also observed in the reactions of *t*-BuHgCl with (*E*)- or (*Z*)-ClCH=CHHgCl.

Substitution Processes Involving $\mathrm{S_H2}$ Reactions of Alkyl Radicals

The addition–elimination sequence of Scheme III is but one example of a process in which an alkyl radical is recycled to yield a species capable of participating in reactions 1 and 2. Scheme VI presents another general chain sequence involving the formation of donor or acceptor radicals. An example of this process has already been given in Scheme IIa. Atom-transfer reactions of R• followed by reaction 2 can be involved in the homolytic cleavage of alkylmercury bonds by the halogens or HBr. Other Y–Q reagents that have been observed to participate in Scheme VI are $\mathrm{HSnR_3}$,[39,40]

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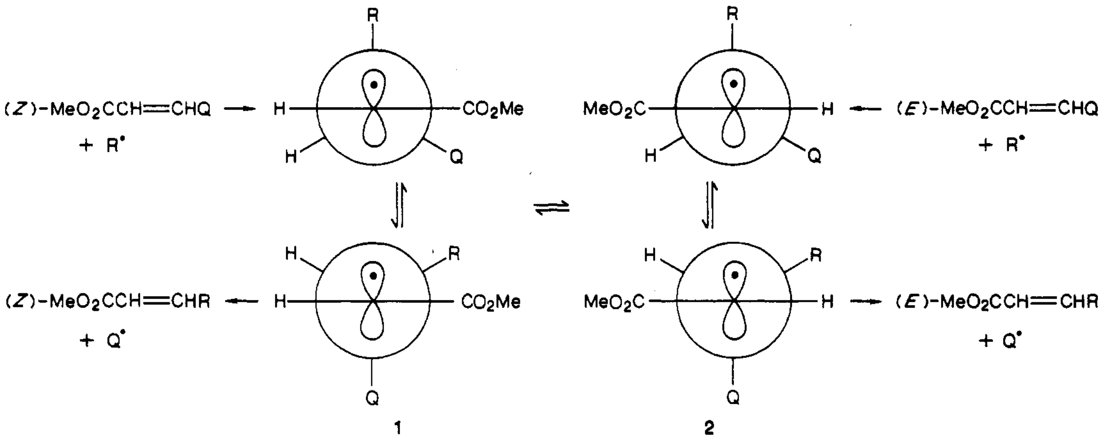
Scheme V



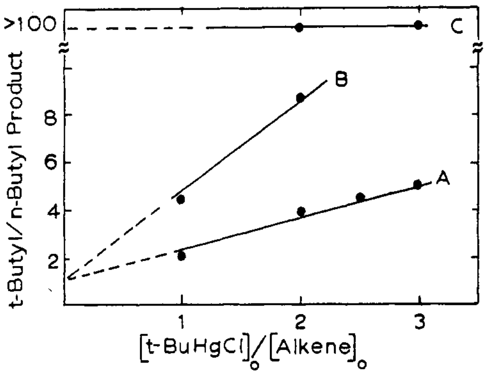


Figure 1. Reaction of 1:1 mixture of *t*-BuHgCl and *n*-BuHgCl with substituted alkenes (initially 0.10 M) in the presence of an excess of $NaBH_4$ or Bu_3SnH at 25 °C: (A) $CH_2{=}C(Cl)CN$ and $NaBH_4$ in CH_2Cl_2; (B) $CH_2{=}CHCO_2Et$ and $NaBH_4$ in CH_2Cl_2; (C) $CH_3{=}C(Cl)CN$ and Bu_3SnH in PhH.

N-benzyl-1,4-dihydronicotinamide,[41] HSPh, RSSR, PhSeSePh, PhTeTePh, $ClSO_2Ar$, and $PhSeSO_2Ar$.[10]

Scheme VI

$$R^\bullet + Y\text{-}Q \xrightarrow[Q\,=\,D\text{ or }A]{} RY + Q^\bullet$$

$$D^\bullet + RHgX \rightarrow R^\bullet + Hg^0 + X^- + D^+$$

$$A^\bullet + RHgX \rightarrow R^\bullet + AHgX$$

The reaction of RHgCl with Bu_3SnH has been formulated to involve RHgH as an intermediate[39] or to involve halogen atom abstraction by $Bu_3Sn^\bullet$.[40] As shown in Table I, the reactivity of RHgCl toward $Bu_3Sn^\bullet$ increases with the stability of the incipient $R^\bullet$, an observation that we believe excludes $RHg^\bullet$ as an intermediate. When applied in the Giese reaction with $CH_2{=}C(Cl)CN$ as the substrate (reaction 14, Figure 1)

$$RHgCl + CH_2{=}C(Cl)CN + MH \rightarrow RCH_2CH(Cl)CN + Hg^0 + MCl \quad (14)$$

and with an excess of a 1:1 mixture of *t*-BuHgCl and *n*-BuHgCl, the use of Bu_3SnH in PhH or alkaline $NaBH_4$ in CH_2Cl_2 gives dramatically different results.[42] With $NaBH_4$ essentially a 1:1 mixture of *t*-$BuCH_2CH(Cl)CN$ and *n*-$BuCH_2CH(Cl)CN$ is formed, particularly at high concentrations of $CH_2{=}C(Cl)CN$. With Bu_3SnH the initial reaction products are more than 100:1 in favor of the *tert*-butylated product. The borohydride reaction involves the intermediates RHgH and $RHg^\bullet$, which appear to be excluded at least in the initial reaction sequence involving Bu_3SnH.

The reaction of an alkyl radical with BH_4^- could in principle form RH and the donor species $BH_3^{\bullet-}$. However, BH_4^- is unreactive toward alkyl radical attack. When (5-hexenyl)mercury chloride is reduced by alkaline $NaBH_4$, the cyclized (methylcyclopentane) and uncyclized (1-hexene) products are formed. With excess BH_4^- the uncyclized/cyclized ratio is a linear function of the concentration of RHgCl (presumably rapidly converted to RHgH) employed. However, excess BH_4^- itself has no effect on the amount of cyclization, indicating a low reactivity of BH_4^- with the 5-hexenyl radical.[12] Reactions of $RHgX/BH_4^-$ thus involves Hg(I) intermediates formed by radical attack upon RHgH. On the other hand, the $RHgX/Bu_3SnH$ system involves mainly a chain process in which $R^\bullet$ is displaced by the attack of $Bu_3Sn^\bullet$ at mercury.

Formation of Donor and Acceptor Radicals by Addition of R• to Unsaturated Systems

Unsaturated systems with polar substituents yield carbon-centered adduct radicals that react as donors or acceptors in reactions 1 and 2. Reactions of 1,1-diarylethylenes with *t*-BuHgCl are illustrative.[17] With $CH_2{=}CPh_2$, photolysis of *t*-BuHgCl yields *t*-$BuCH_2CPh_2^\bullet$, which does not attack *t*-BuHgCl at 40 °C. The radicals disproportionate to yield *t*-$BuCH_2CHPh_2$ and *t*-$BuCH{=}CPh_2$ in a 1:1 ratio by a nonchain process. With $CH_2{=}C(C_6H_4OMe\text{-}p)_2$ the resulting adduct radical is a donor species that undergoes electron transfer with *t*-BuHgCl, thereby establishing a chain process. Loss of a proton from the dianisylcarbinyl cation gives the substitution product, *t*-$BuCH{=}C(C_6H_4OMe\text{-}p)_2$, in good yield. 1,1-Bis(*p*-nitrophenyl)ethylene also reacts with *t*-BuHgCl by a chain process, but now the product after protonation is *t*-$BuCH_2CH(C_6H_4NO_2\text{-}p)_2$. The intermediate bis(*p*-nitrophenyl)carbinyl radical is an acceptor species that reacts with *t*-BuHgCl to form the anion (whether *t*-$BuCH_2CH(HgCl)(C_6H_4NO_2\text{-}p)_2$ is an intermediate is unknown; with powerful electron acceptors reaction 2 may proceed directly to $A^- + HgX^+ + R^\bullet$).

With the unsaturated radicaphile is an anion, the resulting adduct is a radical anion (reaction 15), which

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Table III
Reaction of *t*-BuHgCl with $CH_2{=}CH(EWG)$ To Give *t*-$BuCH_2CH_2(EWG)$

	% yield (equiv of *t*-BuHgCl; *hν*; time)[a]	
substrates (mmol)	*t*-BuHgCl/Me_2SO[b]	*t*-BuHgCl/2NaI/Me_2SO[c]
$CH_2{=}CHSO_2Ph$ (0.2)	39 (1; R; 4 h)	85 (1; R; 4 h)
$CH_2{=}CHSO_2Ph$ (0.2)	87 (4; S; 24 h)	95 (2; R; 24 h)
$CH_2{=}CHP(O)(OEt)_2$ (0.4)	30 (1; S; 2 h)	86 (1; S; 2 h)
$CH_2{=}CHCO_2Et$ (0.4)	5 (2; R; 10 h)[d]	80 (1; R; 6 h)[e]
$CH_2{=}CHCOCH_3$ (0.4)	6.2 (2; R; 10 h)	85 (2; R; 6 h)
2-cyclohexen-1-one (0.4)	35 (2; R; 10 h)	85 (2; R; 6 h)
2,3-dichloromaleic anhydride[f]	27 (5; S; 8 h)	98 (3; S; 5 h)
$HC{\equiv}CCH_2Cl$ (0.1)[g]	20 (5; S; 7 h)	71 (5; S; 5 h)
$PhCOCH{=}CHCl$ (0.2)[h]	<10 (5; S; 12 h)	100 (5; S; 1 h)
$PhC{\equiv}CSO_2Ph$[i]	49 (5; S; 17 h)	85 (5; S; 2 h)

[a] Substrate in 1–10 mL of deoxygenated solvent at 35–45 °C; S, 275-W sunlamp ca. 20 cm from Pyrex reaction vessel; R, Rayonet photoreactor (350 nm). [b] Workup by $NaBH_4$ or H_3O^+. [c] Workup with 1% hydrochloric acid or aqueous $Na_2S_2O_3$. [d] Major product is *t*-$BuCH_2CH(CO_2Et)CH_2CH_2CO_2Et$. [e] Me_2SO (60%)–MeOH (40%); product was *t*-$BuCH_2CH_2CO_2Me$, and no higher telomers were observed. [f] Product was 2,3-di-*tert*-butylmaleic anhydride. [g] Product is *t*-$BuCH{=}C{=}CH_2$. [h] Product is $PhCOCH{=}CHBu$-*t*. [i] Product is *t*-$BuC{\equiv}CPh$.

readily transfers an electron to RHgX to regenerate $R^\bullet$ (reaction 16).[6] Alkylmercurials have a low reactivity

$$R^\bullet + Nu^- \rightarrow RNu^{\bullet-} \qquad (15)$$

$$RNu^{\bullet-} + RHgX \rightarrow RNu + R^\bullet + Hg^0 + X^- \qquad (16)$$

in S_N2 substitution at carbon because of the unfavorable polarity of the carbon–mercury bond. However, by initiating a chain reaction involving reactions 1, 15, and 16, nucleophiles that readily trap $R^\bullet$ can be induced to react cleanly. With R = *t*-$Bu^\bullet$ such reactions have been observed for NO_2^-, N_3^-, $(R^1)(R^2)C{=}NO_2^-$, $(R^1)(R^2)C{=}C(O^-)Ph$, phthalimide$^-$, $Ph_2C{=}C{=}N^-$, Ph_3C^-, Ph_2CH^-, Ph_2P^-, and fluorenyl$^-$.[13,14,20,22] Ambident anions such as $Ph_2C{=}C{=}N^-$ or Ph_3C^- yield mixtures of alkylation products from C- and N-alkylation or from *α*- and *p*-alkylation, respectively.

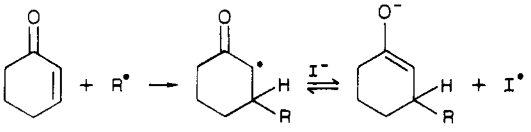
Loss of a proton makes an adduct radical a better donor. Thus, attack of $R^\bullet$ upon pyridinium ion followed by loss of a proton, or attack upon pyridine followed by protic tautomerization, forms the easily oxidized ortho- or para-substituted pyridinyl radical that transfers an electron to RHgX in reaction 1 to yield the substituted pyridinium ion.[15] This process occurs readily upon photolysis of a variety of solvomercuration products of alkenes in pyridine solution, particularly for the mercury trifluoroacetates. Addition of alkyl radicals to tetramethyl-*p*-phenylenediamine forms an adduct radical that is again easily oxidized to the immonium ion by RHgX.[15]

Carbon-centered acceptor radicals are formed by the attack of $R^\bullet$ upon olefins with electron-withdrawing groups (EWG).[19] In photostimulated reactions of $CH_2{=}CH(EWG)$ with RHgX, reaction 17 involving the formation of $RCH_2CH(HgX)(EWG)$ via reaction 2 is observed with EWG = $(EtO)_2PO$, $PhSO_2$, *p*-$NO_2C_6H_4$, COR, and CO_2R (Table III). When the intermediate

$$RHgX + CH_2{=}CH(EWG) \xrightarrow{h\nu} RCH_2CH(HgX)(EWG) \qquad (17)$$

adduct radical possesses enolate stabilization, reaction 2 occurs inefficiently with *t*-BuHgCl. Now, the use of *t*-BuHgX + NaI in Me_2SO greatly increases the rate and yield of the reaction (Table III). *tert*-Butylmercury iodide may be more reactive than the chloride in reaction 2, but the iodide ion may be more intimately involved in the reaction, for example, by electron transfer to the adduct radical (Scheme VII).

Scheme VII



$$I^\bullet + RHgX \longrightarrow R^\bullet + IHgX$$

The increased reactivity of the iodide system toward the adduct radical is not only evident in the yields and rates of the reactions but also in the reaction products. Thus, with the polymerizable alkene $CH_2{=}CHP(O)(OEt)_2$, the 1:1 adduct free of higher telomers can be obtained exclusively only with a 4-fold excess of *t*-BuHgCl.[19] However, in the presence of 2 equiv of NaI in Me_2SO, a good yield of the 1:1 adduct (*t*-$BuCH_2CH_2P(O)(OEt)_2$) is obtained after hydrolytic workup with 1.2 equiv of *t*-BuHgCl. Similarly, photolysis of excess *t*-BuHgCl in Me_2SO in the presence of $CH_2{=}CHCO_2Et$ yields ~5% of the 1:1 adduct and 95% of higher telomers. However, with 1.2 equiv of *t*-BuHgCl in the presence of 2.4 equiv of NaI in Me_2SO–MeOH, the 1:1 adduct is obtained in high yield without the formation of higher telomers.

The reducing agent in the $RHgI/I^-$ system may well be the ate complex, $RHgI_2^-$, rather than I^- itself. Electron transfer to an enolyl-type radical from the ate complex would form the enolate anion, HgI_2, and regenerate the $R^\bullet$ radical. The ate complex, *i*-$PrHgI_2^-$ seems to be definitely involved in the reaction of *i*-$PrHgI/I^-$ with $BrCCl_3$, a process that occurs with kinetic chain lengths in the order of 10^4 (Scheme VIII).[26]

Scheme VIII

$$i\text{-}PrHgI + I^- \underset{}{\overset{k_e\,=\,9\ M}{\rightleftharpoons}} i\text{-}PrHgI_2^-$$

$$i\text{-}Pr^\bullet + BrCCl_3 \rightarrow i\text{-}PrBr + CCl_3^\bullet$$

$$CCl_3^\bullet + i\text{-}PrHgI_2^- \rightarrow CCl_3^- + i\text{-}Pr^\bullet + HgI_2$$

$$CCl_3^- + NH_4^+ \rightarrow HCCl_3 + NH_3$$

Vinyl radicals function as acceptor radicals in reaction 2 with or without an EWG (reaction 18).[19] Reaction

$$t\text{-}BuHgCl + HC{\equiv}CY \xrightarrow{h\nu} t\text{-}BuCH{=}C(HgCl)Y \qquad (18)$$

of vinyl radicals with *t*-BuHgCl occurs readily when the vinyl radical is conjugated with carbonyl substituents, and reaction 18 occurs in a chain manner with Y = Ph, PhS, $PhSO_2$, MeO_2C, and MeCO.

Competitive chain reactions can occur with 1,2-disubstituted alkenes when the EWG is capable of undergoing *β*-elimination. Thus, addition of *t*-$Bu^\bullet$ to (*E*)-$PhCH{=}CHSO_2Ph$ forms adduct radicals **3** and **4**

$Ph\dot{C}H{-}CH(R)SO_2Ph$
3

$PhCH(R){-}\dot{C}HSO_2Ph$
4

in a ratio of 2.7:1. Radical **3** undergoes *β*-elimination of $PhSO_2$ to form (*E*)-$PhCH{=}CHBu$-*t* (overall reaction 7a) while **4** is an acceptor radical that displaces *t*-$Bu^\bullet$ from *t*-BuHgCl (overall reaction 17).

Table IV
Kinetic Chain Lengths (kcl) in Photostimulated Reaction of *t*-BuHgCl at 35–40 °C in Me_2SO[a]

substrate (equiv)	product	init kcl
PhSSPh (0.2)	*t*-BuSPh	400[b]
$Me_2C{=}NO_2^-$ (1)	*t*-$BuCMe_2NO_2$	50[c]
$CH_2{=}CHP(O)(OEt)_2$ (0.25)	*t*-$BuCH_2C(H)(HgCl)P(O)(OEt)_2$	105 (95)[d]
$CH_2{=}CHSO_2Ph$ (0.4)	*t*-$BuCH_2CH(HgCl)SO_2Ph$	103
$HC{\equiv}CCOCH_3$ (0.3)	*t*-$BuCH{=}C(HgCl)COCH_3$	32 (26)[d]
$HC{\equiv}CPh$ (0.3)	*t*-$BuCH{=}C(HgCl)Ph$	15 (14)[d]
$Ph_2C{=}CHI$ (0.3)	*t*-$BuCH{=}CPh_2$	100
(*E*)-$PhCH{=}CHSnBu_3$ (0.3)	(*E*)-*t*-BuCH=CHPh	71
(*E*)-PhCH=CHHgCl (0.3)	(*E*)-*t*-BuCH=CHPh	56
$CH_2{=}C(C_6H_4OMe\text{-}p)_2$ (0.3)	*t*-$BuCH{=}C(C_6H_4OMe\text{-}p)_2$	18

[a] $[t\text{-BuHgCl}]_0$ = 0.5 M; irradiation by a 275-W fluorescent sunlamp in 6-mm NMR tubes. Irradiation conditions were only approximately the same for different substrates. [b] 420 in the presence of 1 equiv of *n*-BuHgCl. [c] In the presence of 18-crown-6; longer kinetic chain lengths were observed in its absence. [d] PhH solvent.

The products of addition of RHgX to an alkene ($RCH_2CH(HgX)(EWG)$) or alkyne ($RCH{=}C(HgX)Y$) can be converted by reaction with BH_4^- to $RCH_2CH_2(EWG)$ or RCH=CHY or with I_2 to $RCH_2CH(I)(EWG)$ or RCH=C(I)Y. The saturated adducts with electron-withdrawing groups are also susceptible to hydrolytic electrophilic cleavage to form $RCH_2CH_2(EWG)$. This product can be formed in one step in reaction 14 but only if the alkene or alkyne has a high reactivity towards $R^\bullet$. Otherwise, the alkyl radical is trapped by the intermediate RHgH or MH to form RH, and the alkene or alkyne fails to participate significantly in the chain reaction of Scheme I.[19]

Kinetic Chain Lengths and Relative Reactivities

Free radical chain reactions of alkylmercurials with mixtures of substrates is a convenient technique for measuring their relative reactivities (e.g., R′CH=CHQ, $CH_2{=}CHCH_2Q$, Y–Q, $CH_2{=}CH(EWG)$) toward an alkyl radical. This technique has been applied to electronegatively substituted alkenes using $NaBH_4$ in reaction 14[43,44] and to a variety of unsaturated anions in reaction 15.[13,14,20] The technique requires that the relative yields of the substitution or addition products are a measure of the ratio k_A/k_B in Scheme IX. If the chain reactions have a significant kinetic chain length (kcl) with both reactant A and reactant B, the values of k'_A and k'_B in Scheme IX do not influence the ratio of the products P_A and P_B formed in a competition because a significant kcl requires that essentially all adduct radicals ($RA^\bullet$, $RB^\bullet$) will react to continue the chain. Under such conditions, $k_A/k_B = [P_A][B]/[P_B][A]$ or if the ratio of [A]/[B] changes during the reaction, $k_A/k_B = \log\{(1 - [P_A])/[A]_0\}/\log\{(1 - [PB])/[B]_0\}$.

Scheme IX

$$R^\bullet + A \xrightarrow{k_A} RA^\bullet \xrightarrow[RHgX]{k'_A} P_A + R^\bullet$$

$$R^\bullet + B \xrightarrow[k_B]{} RB^\bullet \xrightarrow[RHgX]{k'_B} P_B + R^\bullet$$

The initial kcl's of the photochemical reactions of alkylmercurials are conveniently measured by the nitroxide inhibition method using ^1H NMR to follow the course of the reaction (Figure 2).[19] If $(t\text{-Bu})_2NO^\bullet$ traps the radicals that would have otherwise initiated a chain reaction, the initial kcl can be obtained from the initial reaction rate divided by the rate of chain initiation, provided the rate of initiation is maintained at a constant value, for example, in a photostimulated process. The kcl is a function of the rate of initiation, and as the reaction proceeds, the kcl decreases as the reactants are consumed. Table IV gives the measured values of the initial kcl observed in some photostimulated reactions of *t*-BuHgCl. The reactions are of moderate kcl but are suitable for relative reactivity studies at least under the initial reaction conditions.

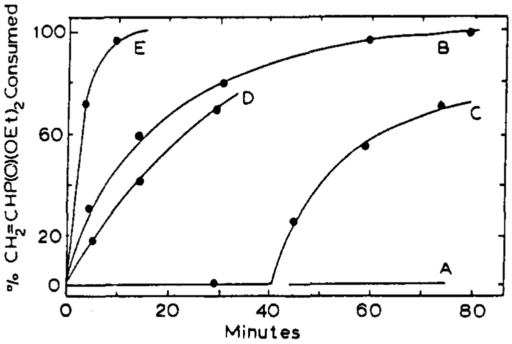


Figure 2. Reaction of 0.12 M $CH_2{=}CHP(O)(OEt)_2$ with 4 equiv of *t*-BuHgCl in Me_2SO at 25 °C (dark) or 40 °C ($h\nu$): (A) dark; (B) sunlamp irradiation; (C) sunlamp irradiation, 0.012 M $(t\text{-Bu})_2NO^\bullet$, initial kcl ~ 100; (D) dark, 6 equiv of NaI; initial kcl ~ 500; (E) sunlamp irradiation, 6 equiv of NaI. Product after $NaBH_4$ workup was *t*-$BuCH_2CH_2P(O)(OEt)_2$.

Alkylmercurials react with a variety of substrates by reactions that are clearly radical in nature and that do not occur in the dark in the absence of an initiation reaction. The reactions of *t*-BuHgX thus define the chemo-, regio-, and stereospecificity of *t*-Bu• addition or substitution. The resulting reactivity data can be used as a diagnostic test for free radical intervention in the reactions of other *tert*-butylating agents. For example, the reaction of *t*-Bu• with (*E*)- or (*Z*)-PhCH=CHI gives substitution with 96 ± 1% retention of configuration, a stereospecificity quantitatively different from that observed for substitution with *t*-BuMgCl.[23] On the other hand, (*E*)-$PhCH{=}CHSO_2Ph$ reacts with *t*-BuHgCl by competing chain reactions to yield (*E*)-PhCH=CHBu-*t* (73%) and PhCH(Bu-*t*)CH(HgCl)SO_2Ph (27%), a regiochemistry essentially the same as observed for reactions with *t*-BuLi or *t*-BuMgCl.[23,26] The relative reactivities for substitution of PhS or $PhSO_2$ via reaction 7a for the series $PhC{\equiv}CSPh$, $PhC{\equiv}CSO_2Ph$, and $PhCH{=}CHSO_2Ph$ observed for *t*-Bu• at 40 °C in Me_2SO are 0.3:1.6:1.0, while with *t*-BuLi at 0 °C in THF the reactivity series is

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Table V
Relative Reactivities toward *tert*-Butyl Radical at 35–40 °C

substrate	final product	rel react
$CH_2{=}C(Cl)CN$	t-BuCH$_2$CH(Cl)CN^a	160
PhSO$_2$Cl	t-BuCl	11
$CH_2{=}CHSO_2Ph$	t-BuCH$_2$CH(HgCl)SO$_2$Ph	7.4
PhSSPh	t-BuSPh	4.3
$CH_2{=}CHCO_2Et$	t-BuCH$_2$CH(HgCl)CO$_2$Et	3.0
$CH_2{=}CHP(O)(OEt)_2$	t-BuCH$_2$CH(HgCl)P(O)(OEt)$_2$	1.0^b
$HC{\equiv}CCO_2Et$	t-BuCH=C(HgCl)CO$_2$Et	0.6
$CH_2{=}CPh_2$	t-BuCH$_2$CHPh$_2$ + t-BuCH=CPh$_2$	0.4
MeSSMe	t-BuSMe	0.3
$CH_2{=}CHSOPh$	t-BuCH$_2$CH(HgCl)SOPh	0.2
$CH_2{=}CHSPh$	t-BuCH$_2$CH$_2$SPh^a	0.1
$Ph_2C{=}CHI$	t-BuCH=CPh$_2$	0.1
(E)-PhCH=CHI	(E)-t-BuCH=CHPh	0.28
(Z)-PhCH=CHI	(Z)-t-BuCH=CHPh	0.18
(E)-PhCH=CHBr	(E)-t-BuCH=CHPh	0.35
(E)-PhCH=CHCl	(E)-t-BuCH=CHPh	0.22
(Z)-PhCH=CHCl	(E)-t-BuCH=CHPh	0.03
$PhC{\equiv}CH$	t-BuCH=C(HgCl)Ph	0.04
$Me_2C{=}NO_2Li$	t-BuCMe$_2$NO$_2$	0.02
i-PrSSPr-i	t-BuSPr-i	4×10^{-3}
t-BuSSBu-t	(t-Bu)$_2$S	5×10^{-4}

^{a} Observed with NaBH$_4$/CH$_2$Cl$_2$. ^{b} Data of ref 45 with E_a = 4 kcal/mol yields 4.8×10^5 M^{-1} s^{-1} for the rate of attack of t-Bu$^\bullet$ at 35 °C.

0.3:1.8:1.0.[26] Evidence for t-Bu$^\bullet$ attack is also provided in a comparison of the reactivity of 2-cyclopentenone and 2-cyclohexanone with t-BuHgI/I$^-$ ($h\nu$/40 °C, Me$_2$SO), (t-Bu)$_2$CuLi (−30 °C, Et$_2$O), and (t-Bu)$_3$ZnLi/TMEDA (0 °C, Et$_2$O). The C$_5$/C$_6$ relative reactivities are 3.8 for t-Bu$^\bullet$, 4.2 for (t-Bu)$_2$CuLi, and 3.9 for (t-Bu)$_3$ZnLi.[26] Reaction with n-Bu$^\bullet$ gives C$_5$/C$_6$ = 2.4 but now the n-butylcuprate or -zincate reacts preferentially with 2-cyclohexenone (C$_5$/C$_6$ ~ 0.2) by a mechanism obviously not involving attack by the butyl radical. Table V lists some additional relative reactivities toward t-Bu$^\bullet$ from which the absolute rate constants can be calculated from the known rate constant for addition of t-Bu$^\bullet$ to CH$_2$=CHP(O)(OEt)$_2$.[45] Relative reactivities and regioselectivities of attack of c-C$_6$H$_{11}$$^\bullet$ and PhS$^\bullet$ upon 1,2-disubstituted alkenes or alkynes are reported elsewhere.[24,25]

Conclusions

Alkylmercurials are excellent sources of alkyl radicals that can be utilized in a variety of alkylation reactions proceeding by a chain process. *tert*-Butylmercury halides are more reactive than primary alkylmercurials in many of these processes not only in chain initiation but also in the chain propagation reactions 1–3 with a variety of donor or acceptor radicals formed by addition, addition–elimination, or S$_H$2 reactions of the *tert*-butyl radical.

It is a pleasure to acknowledge the contributions, many of which are unpublished, of my collaborators, J. Hershberger, H. Tashtoush, P. Ngoviwatchi, W. Jiang, S. Hu, R. K. Khanna, S. Herron, D. Guo, Y.-W. Wu, and A. Pla Dalmau. Financial support has been provided by the National Science Foundation and the Petroleum Research Fund.

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Probing Ring Conformations with EPR Spectroscopy[1]

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The conformational options open to alicyclic molecules have far-reaching chemical consequences. NMR spectroscopy has proved to be an extremely valuable tool for studying ring conformations. The equatorial preferences of substituents and, particularly, the dynamic stereochemistry of cyclohexanes and of medium-ring compounds have been investigated in this way.[3-5] The analogous technique of EPR spectroscopy has been used to study the conformations of some persistent radicals such as mono- and bicyclic semidiones[6] and nitroxides.[7] This technique has also been used to study ring inversions for a few transient cyclic radicals such as cyclohexyl and other radicals in which the unpaired electron is localized on one or more ring carbon atoms.[8-13] Unfortunately, such radicals contain the planar radical center in the ring, which drastically alters the ring's conformation in comparison with that of the

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