Allylic and Propargylic Substitution Reactions Involving Radicals Generated from Alkylmercury Halides[1]

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Abstract: Addition of alkyl radicals to allyl or propargyl derivatives forms adduct radicals which can undergo β-elimination with substituents such as halogen, PhS, $PhSO_2$, Bu_3Sn, or HgCl to form the alkyl-substituted propene or allene and an eliminated radical which regenerates the alkyl radical by displacement from an alkylmercurial. With β-oxy substituents, such as O_2CR, $OP(O)(OEt)_2$, O_3SAr, OPh, $OSiMe_3$, or OH, the adduct radicals can displace the alkyl radical from the alkylmercurial to yield β-substituted alkylmercurials which spontaneously, or in the presence of nucleophiles, undergo an elimination reaction to yield the alkene or allene. Relative reactivities toward *tert*-butyl radical attack, such as k(allyl chloride)/k(propargyl chloride) ≅ 10, have been determined. A similar relative reactivity is observed in reaction with $(t\text{-Bu})_2CuLi$ implicating attack by free *tert*-butyl radicals. With allyl or propargyl iodide, radical attack leads to iodine atom abstraction. Reaction of propargyl iodide with *t*-BuHgCl/*hν*, $(t\text{-Bu})_2CuLi$, or $(t\text{-Bu})_3ZnLi$ leads to a mixture of hydrocarbons in which *tert*-butylallene is present in only trace amounts. Benzene is an important reaction product which seems to be formed via the cyclodimerization of two "propargyl" (C_3H_3•) radicals.

Hetero or carbon-centered electrophilic radicals readily displace secondary or tertiary alkyl radicals from alkylmercurials.[2,3] Chain reactions with allylic or propargylic systems can thus ensue, by the mechanism of Scheme I, a process of the general type previously recognized in the reactions of allyl[4-8] or propargyl[9,10] stannanes with alkyl halides, sulfides, or selenides, for the reaction of allylic sulfides with a mixture of hexabutyldistannane[11] or tributylstannane[12] and an alkyl halide or selenide, or for the reactions of allyl or propadienyl derivatives of Co, Rh, and Ir with polyhalomethanes.[13,14]

Scheme I

$$R^\bullet + CH_2{=}CHCH_2A \rightarrow RCH_2\dot{C}HCH_2A \quad (1)$$

$$RCH_2\dot{C}HCH_2A \rightarrow RCH_2CH{=}CH_2 + A^\bullet \quad (2)$$

$$A^\bullet + RHgCl \rightarrow AHgCl + R^\bullet \quad (3)$$

Similar S_H2' reactions are known for the attack of stannyl radicals upon allylic or propargylic sulfides[15] or sulfones.[16] Allylic sulfides similarly undergo S_H2' displacement reactions with phenyl[17a] or *tert*-alkyl[17b] radicals. Allylic substitutions are also observed for the reactions of phenyl radicals with allylic halides[17a] and an early report by Kharasch and Sage recognized allylic displacement of Br• as a side reaction in the addition of $BrCCl_3$ to allyl bromide.[18]

In the present report, we investigate the substituents A = halogen, PhS, $PhSO_2$, Bu_3Sn, HgCl, RCO_2, $ArSO_3$, $(EtO)_2P(O)O$, PhO, Me_3SiO, HO, and CN in the allylic system in photostimulated reactions with alkylmercury halides and the reactions of allylic halides with mercury(II) salts (HgY_2) where Y• = PhS•, $PhSO_2$•, or $(EtO)_2P(O)$• can take the place of R• in reaction 1 of Scheme I.[19] The reactions of *t*-BuHgCl with a variety of propargyl derivatives are also reported.

Results and Discussion

Reactions Proceeding by the S_H2' Process. Table I summarizes the yields of allylic or propadienylic products formed from allylic or propargylic halides, sulfides, sulfones, stannanes, and mercurials. The reactions of alkylmercury chloride with allyl or propargyl chloride in Me_2SO do not occur in the dark, and the photostimulated processes can be inhibited by the presence of 10 mol % $(t\text{-Bu})_2NO$•. From the inhibition period measured for allyl chloride (0.1 M) and *t*-BuHgCl (0.3 M) in Me_2SO at 40–45 °C, an initial kinetic chain length[3] of 50–70 was calculated. In a direct competition of allyl and propargyl chlorides for *t*-Bu•, it was found that the allylic system was about 10 times as reactive as the propargyl system. This reactivity difference is reflected in the yields of $t\text{-BuCH}_2\text{CH}{=}\text{CH}_2$ and $t\text{-BuCH}{=}\text{C}{=}\text{CH}_2$ reported in Table I. Because of the lower reactivity in the addition of an alkyl radical, the propargyl system is particularly vulnerable to reaction 4, which diverts the radical and terminates the chain sequence

$$HC{\equiv}CCH_2X + R^\bullet \rightarrow HC{\equiv}CCH_2^\bullet + RX \quad (4)$$

of Scheme I. Thus, under comparable conditions, the yields of substitution product decrease from the allyl to the propargyl system and as X is changed from Cl to Br to I. Alkylation at the allylic or propargylic carbon also increases the importance of reaction 4, and the substitution product was not observed for $CH_2{=}CHC(Me)_2Cl$ or HC≡CCH(Me)Cl. With $HC{\equiv}CCH(CH_3)$-OTs, where halogen atom transfer was not a problem, a 38% yield of $t\text{-BuCH}{=}\text{C}{=}\text{CHCH}_3$ was observed in 7 h with 5 equiv of *t*-BuHgCl. In a similar fashion, $CH_2{=}CHCMe_2SPh$ formed $t\text{-BuCH}_2\text{CH}{=}\text{CMe}_2$ (45%) and the isomerization product $PhSCH_2CH{=}CMe_2$ (22%).

The rates and yields of the reactions of allyl or propargyl chloride with *t*-BuHgCl in Me_2SO were increased by the presence of NaI. This reflects an increased rate of photoinitiation in the presence of I^-.[20] The rate of radical production by thermolysis

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Table I. Reaction of Allyl and Propargyl Derivatives with Alkylmercury Chlorides at 35–45 °C in Me_2SO

substrate (mmol)	mercurial (equiv)	conditions[a]	% product[b]
CH_2=$CHCH_2Cl$ (0.1)	*t*-BuHgCl (5)	4.5 h	92 (NMR)
CH_2=$CHCH_2Cl$ (0.1)	*t*-BuHgCl (5)	5 equiv NaI, 3 h	100 (NMR)
CH_2=$C(CH_3)CH_2Cl$ (0.1)	*t*-BuHgCl (5)	2 h	63 (NMR)
CH_2=CH_2CH_2Br (0.1)	*t*-BuHgCl (5)	2 h	94 (NMR)
CH_2=$CHCH_2Br$ (0.1)	*c*-$C_6H_{11}HgCl$ (1)	24 h	40 (GC)
CH_2=$CHCH_2I$ (0.1	*t*-BuHgCl (5)	2 h	65 (GC)
CH_2=$CHCH_2I$ (0.1)	*c*-$C_6H_{11}HgCl$ (2)	24 h	49 (GC)
CH_2=$CHCH_2SPh$ (0.1)	*t*-BuHgCl (5)	4 h	63 (GC)
CH_2=$CHCH_2SPh$ (0.1)	*t*-BuHgCl (5)	10 equiv NaI, 4 h	76 (GC)
CH_2=$CHCH_2SPh$ (0.5)	*c*-$C_6H_{11}HgCl$ (5)	24 h	57 (GC)
CH_2=$CHCMe_2SPh$ (0.1)	*t*-BuHgCl (5)	24 h	45 (NMR)[c,d]
CH_2=$CHCH_2SO_2Ph$ (0.1)	*t*-BuHgCl (5)	4 h	88 (GC)
CH_2=$CHCH_2SO_2Ph$ (0.1)	*c*-$C_6H_{11}HgCl$ (2)	24 h	42 (GC)
CH_2=$CHCMe_2SO_2Ph$ (0.1)	*t*-BuHgCl (5)	1.5 h	<10 (NMR)[c,e]
CH_2=$CHCH(CH_2Ph)SO_2Ph$ (0.1)	*t*-BuHgCl (5)	10 h	49 (NMR)[f]
CH_2=$CHCH(CH_2Ph)SO_2Ph$ (5)	*c*-$C_6H_{11}HgCl$ (25)	PhH/Me_2SO, 60 h	25 (GC)[g]
CH_2=$CHCH_2HgCl$ (0.1)	*t*-BuHgCl (5)	4 h	65 (GC)
CH_2=$CHCH_2SnBu_3$ (0.1)	*t*-BuHgCl (5)	Me_2SO (50)–PhH (50), 4 h	57 (GC)
CH_2=$CHCH_2SnBu_3$ (0.5)	*c*-$C_6H_{11}HgCl$ (5)	Me_2SO (50)–PhH (50), 23 h	12 (GC)
CH_2=$CHCH_2SnBu_3$ (0.1)	*t*-BuHgCl	10 equiv NaI, 1 h	73 (GC)
CH_2=$CHCH_2SnPh_3$ (0.1)	*t*-BuHgCl (5)	C_6D_6, 6 h	65 (NMR)
CH_2=$CHCH_2SnPh_3$ (0.1)	*t*-BuHgCl (5)	C_6D_6 (33)–Me_2SO-d_6 (67) 10 equiv NaI, 1.5 h	84 (NMR)
HC≡CCH_2Cl (0.1)	*t*-BuHgCl (5)	7 h	20 (NMR)
HC≡CCH_2Cl (0.1)	*t*-BuHgCl (5)	5 equiv NaI, 7 h	64 (NMR)
HC≡CCH_2Cl (0.1)	*t*-BuHgI (5)	7 h	39 (NMR)
HC≡CCH_2Cl (0.1)	*t*-BuHgI (5)	5 equiv NaI, 6 h	73 (NMR)
HC≡$CCH(CH_3)Cl$ (0.1)	*t*-BuHgCl (5)	7 h	0[h]
HC≡CCH_2Br (0.1)	*t*-BuHgCl (5)	7 h	6 (NMR)
HC≡CCH_2Br (0.1)	*t*-BuHgCl (5)	5 equiv NaI, 7 h	14 (NMR)
HC≡CCH_2Br (0.1)	*t*-BuHgI (5)	7 h	7 (NMR)
HC≡CCH_2Br (0.1)	*t*-BuHgI (5)	5 equiv NaI, 4 h	0 (NMR)
HC≡CCH_2SPh (0.1)	*t*-BuHgCl (5)	25 h	<10 (NMR)
HC≡CCH_2SPh (0.1)	*t*-BuHgCl (5)	5 equiv NaI, 7 h	26 (NMR)
HC≡CCH_2SO_2Ph (0.1)	*t*-BuHgCl (5)	23 h	<10 (NMR)

[a] Substrate (0.1 M) and mercurial in nitrogen-purged Me_2SO or Me_2SO-d_6 were irradiated with a 275-W sunlamp ca. 20 cm from the reaction flask. [b] Yields of RCH_2CH=CH_2 or RCH=C=CH_2 by GLC or ^1H NMR (in Me_2SO-d_6). [c] *t*-$BuCH_2CH$=CMe_2. [d] 22% $PhSCH_2CH$=CMe_2. [e] 86% $PhSO_2CH_2CH$=CMe_2. [f] *t*-$BuCH_2CH$=$CHCH_2Ph$ (*E*/*Z* = 5.2), 23% $PhSO_2CH_2CH$=$CHCH_2Ph$ (*E*/*Z* = 5.6). [g] *c*-$C_6H_{11}CH_2CH$=$CHCH_2Ph$, 70% $PhSO_2CH_2CH$=$CHCH_2Ph$. [h] 27% recovery of HC≡$CCH(CH_3)Cl$; in the presence of 5 equiv NaI, the substitution product was not observed and 62% HC≡$CCH(CH_3)Cl$ was recovered.

or 350-nm photolysis of *t*-BuHgI is considerably greater than that of *t*-BuHgCl, and the rate is further increased by the presence of excess I^-, possibly from the formation of the ate complex (*t*-$BuHgI_2^-$)[20] or even the labile (*t*-Bu)$_2$Hg. Electron transfer between the eliminated Cl$^\bullet$ and I^- may also lead to a more efficient chain reaction. However, iodide ion also increased the yield in the substitution reactions of CH_2=$CHCH_2SnBu_3$ and CH_2=$CHCH_2SnPh_3$, where electron transfer beteen the stannyl radical and I^- would not occur (the stannanes yielded $R_3SnCl(I)$ and Hg^0 as the reaction products).

The possibility of sulfoxonium salt formation from the allylic and propargylic halides in Me_2SO was investigated by ^1H NMR in Me_2SO-d_6. Propargyl iodide failed to form a salt at an appreciable rate and *t*-BuCH=C=CH_2 was not observed upon photolysis in the presence of *t*-BuHgCl, presumably because of the dominance of reaction 4. Allyl iodide slowly formed a single sulfoxonium salt [CH_2=$CHCH_2(SMe_2O)^+$][21] in a process which was greatly accelerated in the dark by the presence of *t*-BuHgCl. It was observed that the photostimulated formation of *t*-$BuCH_2CH$=CH_2 was not actually observed until the iodide had been completely converted to the sulfoxonium iodide (about 45 min for 0.1 M CH_2=$CHCH_2I$, 0.5 M *t*-BuHgCl in Me_2SO-d_6 at 25 °C). The substitution reaction of allyl iodide thus involves the addition of *t*-Bu$^\bullet$ to the sulfoxonium salt to yield *t*-$BuCH_2\dot{C}HCH_2(SMe_2O)^+$. It seems unlikely that the species $Me_2SO^{\bullet+}$ would be eliminated and instead the process of Scheme II is presumed to occur (A′ = SMe_2O^+), where A′HgCl = $Me_2SO\cdots{}^+HgCl$. The elimination reaction in this case must occur rapidly since there was no evidence from ^1H NMR for an intermediate organomercurial. Reaction 6 does not occur readily for a simple alkyl radical although it is a recognized process for an alkyl radical substituted with an electron withdrawing group (e.g., $RCH_2\dot{C}H$(EWG) with EWG = SO_2Ph, P(O)$(OEt)_2$, *p*-$NO_2C_6H_4$).[3] Apparently this polar effect extends to 2-substituted alkyl radicals such as *t*-$BuCH_2\dot{C}HCH_2(SMe_2O)^+$.

Scheme II

$$R^\bullet + CH_2{=}CHCH_2A' \rightarrow RCH_2\dot{C}HCH_2A' \quad (5)$$

$$RCH_2\dot{C}HCH_2A' + RHgX \rightarrow RCH_2CH(HgCl)CH_2A' + R^\bullet \quad (6)$$

$$RCH_2CH(HgCl)CH_2A' \rightarrow RCH_2CH{=}CH_2 + A'HgCl \quad (7)$$

Allyl cyanide reacted upon irradiation with 5 equiv of *t*-BuHgCl in the presence of 10 equiv of NaI in Me_2SO to yield the stable adduct expected from Reaction 6 (*t*-$BuCH_2CH(HgX)CH_2CN$) in 31% yield in 3 h. No elimination to form the alkene was observed in this case, and the adduct could be reduced by $NaBH_4$ to *t*-$BuCH_2CH_2CH_2CN$.

Substitution Reactions Involving Intermediate Organomercurials. Table II summarizes substitution yields for allyl and propargyl systems which are presumed to proceed via Scheme II and to involve the intermediates **1** or **2**. It is recognized that oxygen-

t-$BuCH_2CH(HgCl)CH_2A'$ (**1**) *t*-BuCH=$C(HgCl)CH_2A'$ (**2**)

centered radicals are not readily eliminated in reaction 2, and it seems unlikely that these substitutions could occur via Scheme I. In fact, with the substituents A′ = OAc, OH, OPh, or $OSiMe_3$, intermediate **1** can be detected by ^1H NMR while **2** as a mixture of *E* and *Z* isomers was detected with A′ = OAc or OBz. Reduction of the acetates with $NaBH_4$ yielded the expected *t*-$BuCH_2CH_2CH_2OAc$ and *t*-$BuCH$=$CHCH_2OAc$ (*E* and *Z* iso-

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Table II. Reaction of Oxy-Substituted $CH_2{=}CHCH_2A'$ (A) and $HC{\equiv}CCH_2A'$ (P) with *t*-BuHgCl[a]

system	A'[b]	equiv *t*-BuHgCl	equiv NaI	time, h	product[c]
A	OSO_2Ph	5	0	4	*t*-$BuCH_2CH{=}CH_2$, 73%
A	OSO_2Ph	5	10	1	*t*-$BuCH_2CH{=}CH_2$, 87%
A	$S(CD_3)_2O^+$[e]	2	0	7	*t*-$BuCH_2CH{=}CH_2$, 67%
P	OTs	5	0	7	*t*-$BuCH{=}C{=}CH_2$, 70%
P	OTs	5	5	7	*t*-$BuCH{=}C{=}CH_2$, 36%
P	OTs	5[d]	5	4	*t*-$BuCH{=}C{=}CH_2$, 5%
A	$OP(O)(OEt)_2$	5	0	2	*t*-$BuCH_2CH{=}CH_2$, 50%
P	$OP(O)(OEt)_2$	5	5	7	*t*-$BuCH{=}C{=}CH_2$, 56%
A	OH	5	0	2	**1** (A' = OH), 30%; *t*-$BuCH_2CH{=}CH_2$, 12%
A	OH	5	0	17	*t*-$BuCH_2CH{=}CH_2$, 40%
A	OAc	5	0	2	**1** (A' = OAc), 74%[f]
A	OAc	5[d]	0	1	**1** (A' = OAc), 13%; *t*-$BuCH_2CH{=}CH_2$, 20%
A	OAc	5	10	1	*t*-$BuCH_2CH{=}CH_2$, 64%
P	OAc	5	0	7	**2** (A' = OAc), E/Z = 2), 62%
P	O_2CPh	5	0	48	**2** (A' = O_2CPh), 95%
P	O_2CPh	5	5	7	*t*-$BuCH{=}C{=}CH_2$, 25%
A	OPh	5	0	4	**1** (A' = OPh), 25%; *t*-$BuCH_2CH{=}CH_2$, 20%
A	OPh	5	0	11	**1** (A' = OPh), 2%; *t*-$BuCH_2CH{=}CH_2$, 53%
A	OPh	5	10	1	*t*-$BuCH_2CH{=}CH_2$, 63%
A	$OSiMe_3$	5	0	4	**1** (A' = $OSiMe_3$), ~30%; *t*-$BuCH_2CH{=}CH_2$, 40%[g]
A	$OSiMe_3$	5	0	11	*t*-$BuCH_2CH{=}CH_2$, 69%
A	$OSiMe_3$	5	10	2	*t*-$BuCH_2CH{=}CH_2$, 60%

[a] Substrate (0.1 M) in Me_2SO-d_6 at 35–45 °C with photolysis by a 275-W sunlamp ca. 20 cm from the reaction vessel. [b] OTs = *p*-toluenesulfonate. [c] ^1H NMR yields relative to an internal standard. [d] *t*-BuHgI. [e] Prepared from 0.5 M $CH_2{=}CHCH_2I$ and 1 M *t*-BuHgCl in 1.5 h in a dark reaction in Me_2SO-d_6. [f] Converted to 53% yield of *t*-$BuCH_2CH{=}CH_2$ in 2 h at 45 °C in the dark or in 5 min by NaI or NaCN. [g] Increased to 70% after 12 h in the dark at 25 °C.

Table III. Relative Reactivities toward *tert*-Butyl Radical at 35–40 °C in Me_2SO-d_6

substrate A (0.5 M)	substrate B (0.5 M)	conditions[a]	k_a/k_b[b]	rel react. of A
$CH_2{=}CHCH_2SnPh_3$	$Ph_2C{=}CHI$	PhH, 1 h	11.6	2.9
$CH_2{=}CHCH_2Br$	$Ph_2C{=}CHI$	4 h	8.8	2.2
$CH_2{=}CHCH_2S(CD_3)_2O^+$[c]	$Ph_2C{=}CHI$	2 h	8.0	2.0
$CH_2{=}CHCH_2S(CD_3)_2O^+$[d]	$Ph_2C{=}CHI$	1 h	7.8	2.0
$CH_2{=}CHCH_2Cl$	$Ph_2C{=}CHI$	2 h	4.0	1.0
$CH_2{=}C(CH_3)CH_2Cl$	$Ph_2C{=}CHI$	4 h	3.8	0.80–0.95
$CH_2{=}C(CH_3)CH_2Cl$	$CH_2{=}CHCH_2Cl$	5 h	0.8	
$CH_2{=}CHCH_2HgCl$	$Ph_2C{=}CHI$	9 h	2.9	0.73
$CH_2{=}CHCH_2SO_2Ph$	$Ph_2C{=}CHI$	4 h	2.9	0.73
$CH_2{=}CHCH_2SPh$	$Ph_2C{=}CHI$	4 h	1.8	0.45
$HC{\equiv}CCH_2Cl$	$Ph_2C{=}CHI$	10 h	0.2	0.05–0.10
$HC{\equiv}CCH_2Cl$	$CH_2{=}CHCH_2Cl$	6 h	0.10	
$HC{\equiv}CCH_2OTs$	$CH_2{=}CHCH_2Cl$	5 h	0.28	0.28

[a] Substrates and 0.1 M *t*-BuHgCl in Me_2SO-d_6 with photolysis by a 275-W sunlamp ca. 20 cm from the reaction vessel. [b] By ^1H NMR of *tert*-butyl singlets. [c] From allyl tosylate in Me_2SO-d_6 for 24 h at 25 °C. [d] From 0.5 M allyl iodide and 0.5 M *t*-BuHgCl after 2 h in the dark. *tert*-Butyl-substitution products formed in 7% yield in the photostimulated reaction.

mers). Intermediate **1** (A' = OAc) was formed from allyl acetate in 74% yield during a 2-h period of photolysis (Table II), but in the presence of excess I^-, **1** was not detected and a 64% yield of *t*-$BuCH_2CH{=}CH_2$ was formed. The intermediate **1** from allyl acetate was converted to *t*-$BuCH_2CH{=}CH_2$ slowly in the dark at 45 °C and rapidly upon treatment with I^- or CN^- in Me_2SO. Apparently, the elimination of the elements HgCl and OAc can occur by an E2-type reaction initiated by the attack of a nucleophile upon the mercury atom. In a similar fashion, ^1H NMR evidence was also obtained for intermediate **1** with A' = OPh, $OSiMe_3$, or OH only in the absence of added iodide ion.

Propargyl tosylate reacted with *t*-BuHgCl upon photolysis in Me_2SO solution to form *t*-$BuCH{=}C{=}CH_2$. Intermediate **2** could not be detected, and in a ^1H NMR experiment in Me_2SO-d_6, the initial rate of formation of the allene was equal to the rate of disappearance of propargyl tosylate. Apparently, intermediate **2** with A' = OTs undergoes a very rapid elimination reaction. The substitution reaction was inhibited by $(t\text{-}Bu)_2NO^\bullet$, and from the initial rate of formation of the allene and the inhibition period, an initial kinetic chain length of >300 was calculated (0.1 M $HC{\equiv}CCH_2OTs$, 0.5 M *t*-BuHgCl). Iodide ion inhibited the reaction (Table II) apparently by forming the propargyl iodide which could enter into the chain-terminating halogen atom transfer reaction (reaction 4). Propargyl tosylate in Me_2SO is slowly converted into the sulfoxonium salt, which gave a poor yield of the allene when photolyzed with *t*-BuHgCl. On the other hand, allyl benzenesulfonate underwent the photostimulation reaction in the presence or absence of iodide ion. The sulfoxonium salt was formed more readily than in the propargyl system and could be detected by ^1H NMR during the substitution reaction. When the sulfoxonium salt was preformed by reacting allyl benzenesulfonate with Me_2SO in the presence of 5 equiv of *t*-BuHgCl in the dark for 6 h, photolysis gave a good yield (64%) of *t*-$BuCH_2CH{=}CH_2$. The allyl and propargyl diethyl phosphates also gave clean substitution reactions upon photolysis with *t*-BuHgCl in Me_2SO, and the iodide retardation observed with propargyl tosylate was not found for the phosphate.

Reactions of Allyl Derivatives with Mercury(II) Salts. Mercury(II) salts (HgY_2) are attacked by halogen atoms to yield $Y^\bullet$ = $PhSO_2^\bullet$, $PhS^\bullet$, $(EtO)_2PO^\bullet$, and $RCO_2^\bullet$ (reaction 8).[19] Equation

$$X^\bullet + HgY_2 \rightarrow XHgY + Y^\bullet \quad (8)$$

$$CH_2{=}CHCH_2X + HgY_2 \xrightarrow[24\ h]{h\nu} YCH_2CH{=}CH_2 + XHgY \quad (9)$$

X = I, Y = PhS; 75%
X = I, Y = $PhSO_2$; 51%
X = Br, Y = $(EtO)_2PO$; 22%

Table IV. Relative Reactivity in *tert*-Butylation Reactions

conditions	relative reactivity[a]		
	$HC{\equiv}CCH_2Cl$ (P)	$CH_2{=}CHCH_2Cl$ (A)	$CH_2{=}C(CH_3)CH_2Cl$ (MA)
t-BuHgCl/Me_2SO-d_6/*hν*/35 °C	0.096 ± 0.007	1.00	0.84 ± 0.02
t-BuHgCl/Et_2O/*hν*/35 °C	0.09	1.00	0.84
$(t\text{-Bu})_2CuLi/Et_2O$/−78 °C	0.097 ± 0.005[b]	1.00	0.64 ± 0.04
$(t\text{-Bu})_2Cu(CN)Li_2/Et_2O$/−78 °C	1.2–1.7	1.00	0.53 ± 0.10
$(t\text{-Bu})_2Cu(CN)Li_2/Et_2O$/0 °C	1.2–1.3	1.00	0.79 ± 0.04
$(t\text{-Bu})_3ZnLi/TMEDA/Et_2O$/0 °C	5.0–7.6	1.00	0.69 ± 0.01
$t\text{-BuCuPBu}_3/Et_2O$/0, −30, −78 °C	1.8–1.9	1.00	
$(t\text{-Bu})_2Cu(SMe_2)Li/Et_2O$/0, −78 °C	1.0	1.00	

[a] SD are given where 5 or more experiments were performed. [b] 0.086 ± 0.005 for $(t\text{-Bu})_2CuLi$ prepared at −78 °C and reacted at 0 °C.

9 summarizes allylic substitution yields observed from photolysis in Me_2SO at 40–45 °C of a 1:1 mixture of the allylic halide and the mercury salt. The yield of $(EtO)_2P(O)CH_2CH{=}CH_2$ was quite low from the allyl iodide and only 22% from allyl bromide. Perhaps the radical $(EtO)_2PO^{\bullet} \leftrightarrow (EtO)_2P^{+}{-}O^{-}$ can abstract the halogen atom in reaction 4. Vinyl and acetylenic substitution reactions of PhCH=CHI and PhC≡CI with $[(EtO)_2P(O)]_2Hg$ occur readily and in good yield by elimination of I• from the intermediate adduct radicals $PhCHCH(I)[P(O)(OEt)_2]$ and $PhC{=}C(I)[P(O)(OEt)_2]$.[19] Here halogen atom abstraction is not a competing process, and reaction 8 with X = I and Y = $(EtO)_2P(O)$ occurs readily.

Relative Reactivities of Allyl and Propargyl Derivatives toward *tert*-Butyl Radical. Competitive reactions between two substrates which individually react with *t*-BuHgCl by a chain process yield relative reactivity data concerning the product-determining steps. With long kinetic chain processes, product formation in the photoinitiation or the termination steps can be ignored and product formation will be determined by the irreversible addition of *t*-Bu• to the competing substrates. Table III summarizes data obtained using a 5-fold excess of each of two competing substrates in Me_2SO at 35–40 °C under conditions where kinetic chain lengths for the individual substrates have been measured by the nitroxide-inhibition technique under typical reactive conditions as 50–70 for allyl chloride, >300 for propargyl tosylate, and 100 for $Ph_2C{=}CHI$ (all measurements with a 2–5-fold excess of *t*-BuHgCl; longer kinetic chain lengths are probable when the radicaphile is used in excess).

Allyl chloride was 10 times as reactive as propargyl chloride and 3.6 times more reactive than propargyl tosylate in a direct competition experiment. The kinetic chain length of the reaction of propargyl chloride with *t*-BuHgCl has not been measured but is presumably about 0.1 that of allyl chloride since both reactions involve the same chain-carrying chlorine atoms and *t*-butyl radicals. The relative reactivities of propargyl and allyl chlorides were not affected by the presence of iodide ion, which is apparently not involved in the step (radical addition) that determines which product will be formed. In the presence of NaI, slow, thermally initiated free-radical reactions occurred which also gave a relative reactivity of allyl chloride to propargyl chloride of ~10.

The reactivities of the allyl derivatives seems to be at least partially controlled by the inductive effect of the substituents with the reactivity increasing from $CH_2{=}CHCH_2SPh$ to $CH_2{=}CHCH_2SO_2Ph$ to $CH_2{=}CHCH_2[S(CD_3)_2O^{+}]$ and from $CH_2{=}C(CH_3)CH_2Cl$ to $CH_2{=}CHCH_2Cl$ to $CH_2{=}CHCH_2Br$. However, the effect of a substituent in the allylic position is fairly small. The reactivities in the series PhC≡CA toward *c*-C_6H_{11}• (to yield $PhC{=}C(A)C_6H_{11}$) seems to be much better correlated with the polar nature of A with relative reactivity decreasing with a decrease in electronegativity of the substituent for the series SO_2Ph > I > SPh > $SnBu_3$, $HgC{\equiv}CPh$.[22,23] Presumably, bridging between the radical center and the substituent in $t\text{-BuC(A)}{=}CPh$ is not a factor in stabilizing the intermediate vinyl radical. In the allylic system, the high reactivity of $CH_2{=}CHCH_2SnPh_3$ suggests stabilization of the adduct radical ($t\text{-BuCH}_2\dot{C}HCH_2SnPh_3$) by either bridging or hyperconjugation involving the carbon–tin bond.[24]

Table IV examines the relative reactivities of $HC{\equiv}CCH_2Cl$ (P), $CH_2{=}CHCH_2Cl$ (A), and $CH_2{=}C(CH_3)CH_2Cl$ (MA) toward a variety of *tert*-butylating reagents. The experiments involved the competition of 1 equiv of A and 1 equiv of P or MA with 0.1–0.2 equiv of the organometallic reagent, and the relative reactivities are based on the yields of $t\text{-BuCH}_2CH{=}CH_2$ and $t\text{-BuCH}{=}C{=}CH_2$ or $t\text{-BuCH}_2C(CH_3){=}CH_2$ measured by GLC or ^1H NMR (in Me_2SO-d_6).

The relative reactivities observed with *t*-BuHgCl under fluorescent irradiation were not affected by the presence of I^{-} in Me_2SO or by a change in solvent from Me_2SO to Et_2O. At 35 °C, the relative reactivities toward *t*-Bu• generated from *t*-BuHgCl were P:A:MA = 0.096 ± 007:1.00:0.84 ± 0.02 while with $(t\text{-Bu})_2CuLi$ in Et_2O at −78 °C relative reactivities were 0.097 ± 0.005:1.00:0.64 ± 0.04. With $(t\text{-Bu})_2Cu(CN)Li_2$, the relative reactivity of A and MA decreased from 1.00:0.79 ± 0.04 at 0 °C to 1.00:0.48 ± 0.02 at −78 °C while with $(t\text{-Bu})_3ZnLi$/TMEDA at 0 °C a relative reactivity of 1.00:0.69 ± 0.01 was observed.

For the competition between allyl and methallyl chlorides, the data can be interpreted as indicating *t*-Bu• attack for all the reagents with an energy of activation favoring attack upon allyl chloride. However, the possibility exists that the relative reactivities measured for this pair of substrates is insensitive to the nature (radical, anionic) of the *tert*-butylating species. On the other hand, competitive reactions of these reagents with propargyl and allyl chlorides gave different relative reactivities. The relative reactivities observed with $(t\text{-Bu})_2CuLi$ of P:A = 0.097 ± 0.005 at −78 °C and 0.086 ± 0.005 at 0 °C are consistent with *t*-Bu• attack. (With *t*-BuLi a low yield of alkylation product was observed in which $t\text{-BuCH}_2CH{=}CH_2$ greatly predominated.) However, with $(t\text{-Bu})_2Cu(CN)Li_2$ at 0 or −78 °C, propargyl chloride was 1.3–1.7 as reactive as allyl chloride while with $(t\text{-Bu})_3ZnLi$ the propargyl derivative was more than 5 times as reactive. Furthermore, with $(t\text{-Bu})_2Cu(CN)Li_2$ and $(t\text{-Bu})_3ZnLi$, the reproducibility was poor in contrast to $(t\text{-Bu})_2CuLi$. This perhaps reflects competing reactions. However, it seems certain that $(t\text{-Bu})_3ZnLi$ and $(t\text{-Bu})_2Cu(CN)Li_2$ must be able to react with propargyl and possibly allyl chloride by a mechanism that does not involve *t*-Bu• attack at the carbon–carbon multiple bond. With the less stable $(t\text{-Bu})_2CuLi$, a radical process, e.g., Scheme III, seems to dominate for both the allyl and propargyl substrate.

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(24) In a previous publication[25] we have reported that toward *c*-C_6H_{11}•, $CH_2{=}CHCH_2SnBu_3$ is much less reactive than $Ph_2C{=}CHI$. In view of the results of Table III, where $CH_2{=}CHCH_2SnPh_3$ is 12 times as reactive as $Ph_2C{=}CHI$, the previous result requires verification. The allylstannanes may also undergo an electrophilic reaction with RHgCl to form $RHgCH_2CH{=}CH_2$, which is the precursor to $RCH_2CH{=}CH_2$ in a photostimulated reaction analogous to the decomposition of $PhCH{=}CHHgR$ to $PhCH{=}CHR$.[25] Further experiments in Me_2SO-d_6 have demonstrated the rapid formation of $CH_2{=}CHCH_2HgCl$ (isolation, ^1H NMR line broadening/coalescence of methylene groups) in dark reactions of $CH_2{=}CHCH_2SnR_3$ (R = Me, Bu, Ph) with *t*-BuHgCl. Similar processes may be involved in PhH solution with the apparent relative reactivity a function of R and of the experimental technique. The allylstannane/RHgCl system is obviously complicated and not suitable for relative reactivity studies. Probably $CH_2{=}CHCH_2SnR_3$ (R = Bu, Ph) has a low reactivity relative to $Ph_2C{=}CHI$ toward either c-C_6H_{11}• or *t*-Bu•.

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Scheme III

$$t\text{-Bu}^{\bullet} + CH_2{=}CHCH_2Cl \rightarrow t\text{-BuCH}_2\dot{C}HCH_2Cl$$

$$t\text{-BuCH}_2\dot{C}HCH_2Cl \rightarrow t\text{-BuCH}_2CH{=}CH_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + (t\text{-Bu})_2CuLi \rightarrow LiCl + (t\text{-Bu})_2Cu^{\bullet}$$

$$(t\text{-Bu})_2Cu^{\bullet} \rightarrow t\text{-Bu}^{\bullet} + t\text{-BuCu}$$

Reactions of Propargyl Iodide. The results with *t*-BuHgCl/*hν* demonstrated that *t*-Bu$^{\bullet}$ attack upon HC≡CCH$_2$I gives only traces of *t*-BuCH=C=CH$_2$, presumably because of reaction 4 leading to HC≡CCH$_2^{\bullet}$ ↔ $^{\bullet}$CH=C=CH$_2$. We, therefore, examined the reactions of several *tert*-butylating agents with propargyl iodide. Reaction in Et$_2$O with (*t*-Bu)$_2$CuLi (at −78 or 0 °C) gave a mixture of C$_6$H$_6$ hydrocarbons as well as *t*-BuI, *t*-BuCH$_2$C≡CH, and Me$_3$CCMe$_3$. However, only traces of *t*-BuCH=C=CH$_2$ were found. A 72% yield of *t*-BuI was found in the reaction of equal molar quantities of (*t*-Bu)$_3$ZnLi and HC≡CCH$_2$I at 0 °C and again only a trace of the allene could be detected. With (*t*-Bu)$_2$Cu(CN)Li$_2$ at 0 °C a good yield of *t*-BuCH=C=CH$_2$ was observed, but at −78 °C only a trace of the allene was observed and the product distribution resembled the reaction product from (*t*-Bu)$_2$CuLi.

The major C$_6$H$_6$ hydrocarbon formed was benzene. Smaller amounts of bipropargyl were found and a minor C$_6$H$_6$ isomer was detected by GCMS, but the retention time was too close to that of *t*-BuCH$_2$C≡CH to allow GCIR identification. We find the formation of benzene to be surprising since the reaction of propargyl bromide with Mg in THF is reported to give a mixture of bipropargyl, biallenyl, and propargylallene[26] or in Et$_2$O in the presence of CuCl to yield biallenyl and propargylallene exclusively.[27] We confirm the absence of benzene in the latter reaction although in our hands small amounts of bipropargyl were also formed. The C$_6$H$_6$ hydrocarbons formed in this way were distilled and photolyzed in Et$_2$O in the presence of *t*-BuHgCl. Although the concentrations of the hydrocarbons decreased and their relative concentrations changed considerably, there was no benzene formed. Reaction of *t*-BuHgCl/*hν* or (*t*-Bu)$_2$CuLi with bipropargyl in Et$_2$O also failed to yield detectable amounts of benzene.

Photolysis of HC≡CCH$_2$I in Et$_2$O formed bipropargyl and a dimeric compound C$_6$H$_6$I$_2$ but no benzene was detected. Apparently in this case the bipropargyl is formed by attack of HC≡CCH$_2^{\bullet}$ upon the propargyl iodide. Photolysis of *t*-BuHgCl in the presence of HC≡CCH$_2$I in Et$_2$O produced bipropargyl, benzene, and the dimeric diiodide although bipropargyl was now the major hydrocarbon. With 10 equiv of HC≡CCH$_2$I, the ratio of bipropargyl to benzene was 7:1, but with 0.5 equiv of HC≡CCH$_2$I the ratio decreased to 3:1. Photolysis of propargyl iodide and azobisisobutyronitrile in a 5:1 mol ratio also formed bipropargyl and benzene in a 7:1 ratio and the dimeric diiodide was again detected.

At present we see no other way to explain the formation of benzene in the reactions of HC≡CCH$_2$I except by the coupling of two C$_3$H$_3$ radicals. One possible pathway is a cyclodimerization leading to a cyclohexadiene-1,4-diyl which rearranges to benzene. Pyrolysis of dipropargyl oxalate at 600–660 °C yields benzene as the predominant product,[28] but bipropargyl is known to form benzene and fulvene at 380 °C[29] although at lower temperatures only 3,4-dimethylenecyclobutene is produced.[30]

The results obtained with propargyl iodide may not be pertinent to the mechanism of the reaction of propargyl chloride with cuprate reagents. It is known that the stereospecific reactions of optically active alkyl chlorides with alkyl cuprates often leads to racemization with the corresponding alkyl iodides[31] and that cuprate reactions involving 5-hexenyl radical cyclization are more apt to occur with the hexenyl iodide than with the chloride.[32] Thus, perhaps electron transfer between HC≡CCH$_2$I and the ate complexes leads to the formation of *t*-Bu$^{\bullet}$ and the ensuing *t*-BuI, Me$_3$CCMe$_3$, *t*-BuCH$_2$C≡CH, and C$_6$H$_6$ hydrocarbons.

It seems certain from the relative reactivity and product data that the reaction of (*t*-Bu)$_2$Cu(CN)Li$_2$ with either HC≡CCH$_2$Cl or HC≡CCH$_2$I at 0 °C can proceed by a process not involving the intermediacy of *t*-Bu$^{\bullet}$. The results with (*t*-Bu)$_2$Cu(CN)Li$_2$ illustrate a rather dramatic effect of temperature upon mechanism in that at 0 °C the reaction with HC≡CCH$_2$I yields *t*-BuCH=C=CH$_2$ by a process not involving *t*-Bu$^{\bullet}$, but at −78 °C the radical-coupling process dominates and more *t*-BuCH$_2$C≡CH than *t*-BuCH=C=CH$_2$ is observed.

Experimental Section

Analytical gas chromatography was performed on a varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. ^{1}H NMR spectra were recorded on a 300-MHz Nicolet NT300 spectrometer with tetramethylsilane as the internal standard. GCMS were recorded on a Finnegan 4000 spectrometer and GCIR with an IBM IR-98 FT spectrometer. 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. Me$_2$SO-d_6 and C$_6$D$_6$ were purchased from Cambridge Isotope Laboratories and dried over 4A molecular sieves. Allyl iodide, bromide, chloride, acetate, and cyanide, 3-chloro-2-methylpropene, allyloxytrimethylsilane, and propargyl chloride and bromide were purchased from Aldrich Chemical Co. Allyl alcohol was obtained from J. T. Baker Chemical Co. and 1,5-hexadiyne was from Alfa Products. Organomercurials were synthesized by the standard Grignard procedure.[25] Allyl phenyl sulfide,[33] allyl phenyl sulfone,[34] α,α-dimethylallyl phenyl sulfide,[35] allyl phenyl ether,[36] allyltributylstannane,[25] allyl benzenesulfonate,[37,38] allyl tosylate,[37] propargyl iodide,[39] 3-chloro-1-butyne,[40] propargyl tosylate (bp 117 °C, 0.1 torr),[37,41] propargyl phenyl sulfide,[41] propargyl phenyl sulfone (mp 92–93 °C),[41] propargyl acetate,[42] propargyl benzoate,[43] 2,2-diphenylethenyl iodide (mp 40–40.5 °C),[44] mercuric phenylmercaptide (mp 149–150 °C),[45] mercuric benzenesulfinate (mp 130 °C dec)[46] and bis(diethoxyphosphinyl)mercury (mp 57–58 °C)[47] were synthesized by the literature procedure. The following compounds were also prepared according to the literature procedure. α-Benzylallyl phenyl sulfone,[48] mp 83–84.5 °C: ^{1}H NMR (CDCl$_3$) δ 7.93–7.85 (m, 2 H), 7.68–7.60 (m, 1 H), 7.58–7.50 (m, 2 H), 7.30–7.05 (m, 5 H), 5.65 (td, J = 10.0, 17.1 Hz, 1 H), 5.14 (d, J = 10.0 Hz, 1 H), 4.78 (d, J = 17.1 Hz, 1 H), 3.74 (ddd, J = 3.0, 10.0, 11.3 Hz, 1 H), 3.55 (dd, J = 3.0, 13.6 Hz, 1 H), 2.90 (dd, J = 11.3, 13.6 Hz, 1 H). Allyltriphenylstannane,[49] mp 70.5–71.5 °C (recrystallized from hexane): ^{1}H NMR (CDCl$_3$) δ 7.65–7.46 (m, 6 H), 7.45–7.24 (m, 9 H), 6.20–5.98 (m, 1 H), 4.97 (d, J = 16.7 Hz, 1 H), 4.79 (d, J = 10.3 Hz, 1 H), 2.45 (d, J = 8.4 Hz, 2 H). Diethyl allyl phosphate,[50] bp 45–46

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Table V. ^{1}H NMR of Photoaddition Products in Me_2SO-d_6

A′	δ CH_3	δ H_B	δ H_C	J, Hz BC	J, Hz AB	J, Hz AC
	$(CH_3)_3CCH_2CH_A(HgCl)CH_BH_CA'$					
OAc	0.96	4.38	4.26	11.0	5.5	8.8
OH	0.95	3.69	3.59	10.6	6.3	7.3
OPh	0.97	4.31	4.23	9.8	5.9	7.8
$OSiMe_3$	0.91	3.69	3.59	10.8	6.3	7.8
CN	0.94	3.06	2.83	17.1	6.0	8.8
	$(CH_3)_3CCH_B=C(HgCl)C(H_C)_2A'$					
OAc (Z)	1.14	6.71	4.84	2.1		
OAc (E)	1.14	6.26	4.64	1.2		
OBz (Z)	1.14	6.76	5.11	2.1		
OBz (E)	1.14	6.37	4.93	1.2		

°C at 0.04 Torr: ^{1}H NMR ($CDCl_3$) δ 6.19–6.03 (m, 1 H), 5.53 (dd, J = 1.2, 17.1 Hz, 1 H), 5.40 (dd, J = 1.2, 10.2 Hz, 1 H), 4.73–4.64 (m, 2 H), 4.34–4.20 (m, 4 H), 1.49 (dt, J = 0.6, 7.0 Hz, 6 H). Diethyl propargyl phosphate,[50] bp 66–68 °C at 0.2 Torr: ^{1}H NMR ($CDCl_3$) δ 4.66 (dd, J = 2.4, 9.9 Hz, 2 H), 4.15 (pentet, J = 7.2 Hz, 4 H), 2.57 (t, J = 2.4 Hz, 1 H), 1.35 (t, J = 7.2 Hz, 6 H); GCMS m/z (relative intensity) 192 (M^+, 0.1), 136 (100), 119 (14), 99 (22), 81 (21), 57 (15), 55 (17). α,α-Dimethylallyl phenyl sulfone, mp 47–48 °C, was obtained from the oxidation of α,α-dimethylallyl phenyl sulfide[35] with 30% hydrogen peroxide in acetic acid (50%)–acetic anhydride (50%): ^{1}H NMR ($CDCl_3$) δ 7.87–7.78 (d, J = 7.5 Hz, 2 H), 7.67–7.59 (t, J = 7.5 Hz, 1 H), 7.56–7.47 (d, J = 7.5 Hz, 2 H), 6.03 (dd, J = 10.7, 17.3 Hz, 1 H), 5.27 (d, J = 10.7 Hz, 1 H), 5.08 (d, J = 17.3 Hz, 1 H), 1.45 (s, 6 H).

General Procedure for Photostimulated Reactions of Allyl and Propargyl Derivatives with Organomercurials (Tables I and II). The substrate (0.1 M) and the coreactant (see Table I for equivalents) were dissolved in a deoxygenated solvent under a nitrogen atmosphere in a Pyrex flask equipped with a rubber septum. The mixture was irradiated with a 275-W sunlamp ca. 20 cm from the reaction flask for the period of time indicated in the table. After irradiation, a known amount of the internal standard biphenyl was dissolved in the reaction mixture. The mixture was then poured into a saturated aqueous sodium chloride solution and extracted with diethyl ether. The ether extract was washed twice with 20% aqueous sodium thiosulfate solution to remove any organomercury halide, dried over anhydrous sodium sulfate, and carefully concentrated under vacuum. The mixture was then analyzed by GC and GCMS.

Reactions of allyl and propargyl derivatives with *tert*-butylmercury chloride were conveniently performed in an NMR tube and monitored by ^{1}H NMR. Thus, 0.1 mmol of the substrate and the coreactant (see Table I for equivalents) were dissolved in 1 mL of Me_2SO-d_6 in an NMR tube closed with a cap and sealed with parafilm. The ^{1}H NMR spectrum of the mixture was recorded before irradiation and the Me_2SO multiplet at 2.50 ppm used as the internal standard. The mixture was photolyzed by a 275-W sunlamp and the progress of the reaction was monitored periodically by ^{1}H NMR. The yield of the product was obtained from the integration of the appropriate peaks in the reaction product. The following products were obtained from the reactions outlined in Table I. 4,4-Dimethyl-1-pentene: ^{1}H NMR ($CDCl_3$) δ 6.0–5.8 (m, 1 H), 5.1–4.9 (m, 2 H), 1.92 (d, J = 7.5 Hz, 2 H), 0.88 (s, 9 H); ^{1}H NMR (Me_2SO-d_6) δ 5.88–5.73 (m, 1 H), 5.05–4.93 (m, 2 H), 1.91 (d, J = 7.5 Hz, 2 H), 0.86 (s, 9 H); GCMS m/z (relative intensity) 98 (M^+, 1.7), 83 (12), 57 (100), 55 (30), 41 (48), 39 (15). 2,5,5-Trimethyl-2-hexene: GCMS m/z (relative intensity) 126 (M^+, 14), 111 (9), 70 (54), 69 (25), 57 (100), 55 (20), 41 (59), 39 (14). 3-Methyl-2-butenyl phenyl sulfide:[35] ^{1}H NMR ($CDCl_3$) δ 7.40–7.15 (m, 5 H), 5.30 (t, J = 7.8 Hz, 1 H), 3.53 (d, J = 7.8 Hz, 2 H), 1.71 (s, 3 H), 1.58 (s, 3 H). 3-Methyl-2-butenyl phenyl sulfone[51] and 4-phenyl-2-butenyl phenyl sulfone[51] were identified by comparison of their spectra with those of the authentic compounds. (4-Phenyl-2-butenyl)cyclohexane was isolated by preparative GC as a mixture of the E and Z isomers: ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 5 H), 5.65–5.30 (m, 2 H), 3.5–3.2 (m, 2 H), 2.2–0.5 (m, 13 H); GCMS m/z (relative intensity) (E isomer) 214 (M^+, 23), 118 (46), 117 (36), 104 (82), 91 (51), 83 (48), 55 (100); (Z isomer) 214 (M^+, 16), 118 (39), 117 (30), 104 (80), 91 (45), 83 (45), 55 (100).

Reactions of allyloxy derivatives with *t*-BuHgCl (Table II) were performed in an NMR tube and monitored by ^{1}H NMR. The reactions gave adduct organomercurials, t-Bu$CH_2CH(HgCl)CH_2A'$, which were observed by their ^{1}H NMR spectra. Table V summarizes partial ^{1}H NMR spectra of these intermediate organomercurials. All the adduct organomercurials showed a singlet for the *tert*-butyl group at δ 0.91–0.97 and doublets of doublets (δ 2.83–4.38) for each diastereotopic allylic proton. Yields of the intermediates were obtained from the integration of the singlet and the doublets of doublets in comparison to that of Me_2SO, the internal standard. The decomposition of the mercurials to give 4,4-dimethyl-1-pentene under photolysis or in the dark was also followed by ^{1}H NMR. Reactions of allyloxy derivatives with *t*-BuHgCl in the presence of sodium iodide were also monitored by ^{1}H NMR. No intermediate was observed and only the alkene was formed.

Photoreactions of propargyl acetate and benzoate with *t*-BuHgCl in Me_2SO-d_6 also gave adduct organomercury compounds which could be observed by ^{1}H NMR (Table V). These intermediates also eliminated the mercury halide and the substituent to form *tert*-butylallene: ^{1}H NMR (Me_2SO-d_6) δ 5.18 (t, J = 6.6 Hz, 1 H), 4.79 (d, J = 6.6 Hz, 2 H), 1.01 (s, 9 H).

General Procedure for Photostimulated Reactions of Allyl Derivatives with *tert*-Butylmercury Chloride Followed by Sodium Borohydride Reduction. Allyl acetate (1 mmol) and *t*-BuHgCl (5 mmol) were dissolved in 10 mL of Me_2SO in a Pyrex flask equipped with a rubber septum. After deoxygenated by a stream of nitrogen gas for 10 min, the mixture was photolyzed for 2 h at 350 nm in a Rayonet photoreactor. The mixture was then added to an excess of sodium borohydride and 1 mL of water and stirred for 15 min. The mixture was decanted from the mercury bead, poured into water, and extracted with diethyl ether. The ether extract was washed twice with water, dried over Na_2SO_4 and concentrated under vacuum. The mixture was analyzed by GC, which indicated only one product. The product was identified by GCMS to be 4,4-dimethylpentyl acetate and was obtained in 20% yield: GCMS m/z (relative intensity) 159 (MH^+, 0.4), 83 (72), 61 (63), 57 (100), 55 (67), 43 (87), 42 (32), 41 (51).

Reaction of allyl phenyl ether with *t*-BuHgCl (4 h in Rayonet photoreactor) followed by sodium borohydride reduction gave [(4,4-dimethylpentyl)oxy]benzene in 11% yield: GCMS m/z (relative intensity) 192 (M^+, 16), 94 (100), 83 (47), 77 (13), 57 (80), 55 (34), 43 (36), 41 (42).

Reaction of allyl cyanide (0.1 M) and *t*-BuHgCl (0.5 M) in the presence of sodium iodide (1 M) with photolysis by a 275-W sunlamp for 4 h followed by sodium borohydride reduction gave a low yield (~10%) of 5,5-dimethylhexanenitrile. The product had GCMS m/z (relative intensity) 126 (MH^+, 0.3), 110 (34), 69 (40), 57 (100). Reduction of t-BuCH=C(HgCl)CH_2OAc (mixture of E and Z isomers) yielded 4,4-dimethyl-2-pentenyl acetate which had a GCMS m/z (relative intensity) 156 (M^+, 20), 141 (20), 114 (5), 96 (25), 81 (40), 70 (15), 57 (20), 55 (20), 43 (100). Treatment of t-BuCH=C(HgCl)CH_2O_2CPh (mixture of E and Z isomers) with $NaBH_4$ yielded the E and Z isomers of 4,4-dimethyl-2-pentenyl benzoate whose E or Z isomers had a similar GCMS: m/z (relative intensity) 218 (M^+, 2), 162 (5), 105 (100), 96 (10), 77 (25), 55 (20).

Formation and Reaction of Allyl and Propargyl Sulfoxonium Salts with *tert*-Butylmercury Chloride Monitored by ^{1}H NMR. Allyl benzenesulfonate (0.1 mmol) was dissolved in 1 mL of Me_2SO-d_6 in an NMR tube at 25 °C. The mixture was monitored periodically by ^{1}H NMR, which showed a downfield shift upon the formation of the sulfoxonium salt. The transformation was complete in about 6 h. ^{1}H NMR spectra of allyl benzenesulfonate and the allyl sulfoxonium salt in Me_2SO-d_6 are given in Table VI. Irradiation of a mixture of 0.1 mmol allyl benzenesulfonate and 0.5 mmol of *t*-BuHgCl in Me_2SO-d_6 (1 mL) with a 275-W sunlamp resulted in the formation of the allyl sulfoxonium salt which reacted with the mercurial to give 4,4-dimethyl-1-pentene in 73% yield (Table II). In the presence of 1 mmol of sodium iodide under the same conditions, the reaction was complete in 1 h to give an excellent yield (87%) of the alkene. In this case, no evidence of allylsulfoxonium salt was observed in the ^{1}H NMR. In another experiment, the allyl sulfoxonium salt was performed before irradiation from a mixture of allyl benzenesulfonate (0.1 mmol) and *t*-BuHgCl (0.5 mmol) in Me_2SO-d_6 (1 mL) for 6 h in the dark at 25 °C. Photolysis of this mixture with a 275-W sunlamp for 3 h gave 64% of the alkene.

A mixture of allyl iodide (0.5 mmol) in Me_2SO-d_6 (1 mL) in an NMR tube was monitored by ^{1}H NMR for a period of 40 min at 25 °C and no allyl sulfoxonium salt was observed. *tert*-Butylmercury chloride (1 mmol) was then added to this mixture, and ^{1}H NMR showed a rapid formation of the allyl sulfoxonium salt. The formation of the sulfoxonium salt was complete in 1.5 h at 25 °C (see Table VI for ^{1}H NMR). Irradiation of this mixture with a 275-W sunlamp for 7 h gave the alkene in 67% yield.

Reaction of propargyl tosylate and *t*-BuHgCl with photolysis by a 275-W sunlamp for 7 h gave only *t*-butylallene (70% yield), and no evidence for the propargyl sulfoxonium salt was observed. A quantitative yield of the propargyl sulfoxonium salt (see Table VI for ^{1}H NMR) was formed from propargyl tosylate (0.1 mmol) in Me_2SO-d_6 (1 mL) in the

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Table VI. ^{1}H NMR of Allyl and Propargyl Derivatives and Their Sulfoxonium Salts in Me_2SO-d_6[a]

A	CH_2=$CHCH_2A$, δ	CH_2=$CHCH_2$ $[S(CH_3)_2O^+]A^-$, δ
I	6.18–5.95 (m, 1 H), 5.28 (md, J = 16.7 Hz, 1 H), 4.95 (md, J = 9.8 Hz, 1 H), 3.98 (d, J = 7.6 Hz, 2 H)	6.01–5.85 (m, 1 H), 5.37 (md, J = 16.9 Hz, 1 H), 5.20 (md, J = 10.0 Hz, 1 H), 4.18 (d, J = 6.6 Hz, 2 H)
$PhSO_3$	7.98–7.96 (m, 2 H), 7.86–7.79 (m, 1 H), 7.76–7.63 (m, 2 H), 5.90–5.74 (m, 1 H), 5.33 (md, J = 17.4 Hz, 1 H), 5.24 (md, J = 10.5 Hz, 1 H), 4.59 (dd, J = 1.2, 5.7 Hz, 2 H)	7.65–7.60 (m, 2 H), 7.40–7.24 (m, 3 H), 6.10–5.90 (m, 1 H), 5.50 (md, J = 17.1 Hz, 1 H), 5.43 (md, J = 10.2 Hz, 1 H), 4.78 (d, J = 6.0 Hz, 2 H)
p-$MeC_6H_4SO_3$	7.79 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.1 Hz, 2 H), 5.89–5.70 (m, 1 H), 5.32 (d, J = 17.1 Hz, 1 H), 5.23 (d, J = 10.4 Hz, 1 H), 4.56 (d, J = 5.7 Hz, 2 H), 2.41 (s, 3 H)	7.51 (d, J = 6.1 Hz, 2 H), 7.47 (d, J = 6.1 Hz, 2 H), 6.08–5.90 (m, 1 H), 5.49 (d, J = 17.2 Hz, 1 H), 5.41 (d, J = 10.4 Hz, 1 H), 4.79 (d, J = 6.1 Hz, 2 H), 2.23 (s, 3 H)
A	HC≡CCH_2A (δ)	HC≡CCH_2 $[S(CD_3)_2O^+]A^-$ (δ)
p-$MeC_6H_4SO_3$	7.81 (d, J = 8.1 Hz, 2 H), 7.49 (d, J = 8.1 Hz, 2 H), 4.82 (d, J = 2.4 Hz, 2 H), 3.66 (t, J = 2.4 Hz, 1 H), 2.40 (s, 3 H)	7.55 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 5.03 (d, J = 2.4 Hz, 2 H), 4.09 (t, J = 2.4 Hz, 1 H), 2.28 (s, 3 H)

[a] Substrate = 0.1 M.

dark at 35–45 °C after 48 h. Photolysis of this preformed sulfoxonium salt in the presence of t-BuHgCl (0.5 mmol) by a sunlamp under our standard conditions gave the allene in only about 30% yield in 7 h.

General Procedure for the Reaction of Allyl Iodide with HgY_2. Allyl iodide (0.1 mmol) and the mercurial (0.1 mmol) were dissolved in 10 mL of nitrogen purged Me_2SO in a Pyrex tube equipped with a rubber septum. The mixture was irradiated for 24 h with a 275-W sunlamp ca. 20 cm from the vessel. After irradiation, the mixture was poured into water and extracted with benzene. The benzene extracted was washed twice with water, dried, and concentrated under vacuum. The concentrated mixture was then treated with hexane, and the precipitate of mercury was removed by filtering through a plug of cotton in a pipet. The mixture was concentrated again under vacuum and analyzed by GC, GCMS, and ^{1}H NMR. Diethyl allylphosphonate had a ^{1}H NMR which agreed with the literature;[51] GCMS m/z (relative intensity) 178 (M^+, 13), 151 (16), 134 (20), 109 (100), 97 (24), 96 (14), 91 (33), 81 (70), 65 (17), 41 (56), 39 (24).

General Procedure for the Determination of Relative Reactivities toward *tert*-Butyl Radical (Tables III and IV). Substrates A and B (0.5 mmol of each) and t-BuHgCl (0.1 mmol) were dissolved in 1 mL of Me_2SO-d_6 in an NMR tube equipped with a plastic cap and sealed with parafilm. The ^{1}H NMR spectrum of the mixture was recorded with Me_2SO as the internal standard. The mixture was irradiated with a 275-W sunlamp ca. 20 cm from the tube for the period of time as indicated in Table III. The ^{1}H NMR spectrum was recorded again after the photolysis. The ratio of the two substitution products was obtained from the integration of the ^{1}H NMR signals of the *tert*-butyl groups in the two products. Yields of each product were also obtained from comparison with the internal standard. The relative reactivities of Table IV were determined by ^{1}H NMR and by GC in Me_2SO-d_6 and by GC in Et_2O. The products were checked by GCMS to be sure that interference from t-$BuCH_2C$≡CH was not a problem.

General Procedures for the Reaction of *tert*-Butylcopper Reagents. $(t\text{-Bu})_2CuLi$ was prepared by the reaction of 2 equiv of t-BuLi with purified CuI[52] in Et_2O at −78 °C for 30 min. t-$BuCu(PBu_3)$[53] was prepared by the reaction of 1 equiv of t-BuLi with CuI in the presence of 2–3 equiv of Bu_3P while $(t\text{-Bu})_2Cu(Me_2S)Li$ was prepared by the reaction of t-BuLi with $CuI{\cdot}SMe_2$.[54] $(t\text{-Bu})_2Cu(CN)Li_2$ was prepared according to the procedure of Lipshutz,[55] and $(t\text{-Bu})_3ZnLi$ with prepared from $ZnCl_2$ and 3 equiv of t-BuLi at 0 °C in the presence of 1 equiv of tetramethylethylenediamine.[56] Reaction mixtures were prepared at the specified temperature by addition of a solution of the allyl and propargyl chloride to the organocopper reagent. Workup involved the addition of 1 mL of saturated aqueous NH_4Cl at 0 °C with stirring for 10 min. The mixture was then added to ice–water. The ether extract was washed twice with cold water, dried over Na_2SO_4 and analyzed by GLC with an internal standard or by ^{1}H NMR in Me_2SO-d_6.

Reactions of Propargyl Iodide with *tert*-Butylating Agents. The propargyl iodide was prepared by the reaction of NaI with propargyl bromide at 0 °C in acetone for 5 h. The reaction product was diluted with ether, washed with cold water, dried over Na_2SO_4, and distilled at room temperature at 15 Torr to give a product that by ^{1}H NMR contained 95% propargyl iodide and 5% of allenyl iodide. The propargyl iodide in $CDCl_3$ had ^{1}H NMR δ 3.65 (d, J = 2.7 Hz, 2 H), 2.42 (t, J = 2.7 Hz, 1 H).

The cuprate complexes were prepared by adding 2 equiv of t-butyllithium in pentane to 1 mmol of CuI or CuCN in 9 mL of ether at −78 °C. After stirring of the mixture for 30 min at −78 °C, 1 mmol of propargyl iodide was added dropwise over a period of 1 min and the resulting solution was stirred at −78 or 0 °C for 30 min. After hydrolysis the ether solution was analyzed by GC, GCMS, and GCIR. Blank experiments showed the complete absence of benzene in the final extract. The zincate complex was prepared from $ZnCl_2$·TMEDA with 3 equiv of t-BuLi which were mixed and stirred at 0 °C for 1 h before the addition of 1 equiv of propargyl iodide.

Benzene was identified by the GC retention time, GCMS, and by the GCIR, which matched the reported values.[57] 4,4-Dimethyl-1-pentyne: GCMS m/z (relative intensity) 81 (61), 79 (12), 57 (100), 53 (11), 41 (55), 39 (21), 29 (39); GCIR (relative intensity) 3329 (44), 2966 (100), 2122 (12), 1481 (20), 1373 (24), 1238 (28), 732 (10) cm^{-1}. 1,5-Hexadiyne: GCMS m/z (relative intensity) 78 (67), 77 (87), 76 (18), 74 (13), 63 (8), 52 (68), 51 (46), 39 (100), 38 (24); GCIR (relative intensity) 3336 (100), 3325 (99), 2939 (22), 2133 (7), 1439 (10), 1338 (7), 1261 (42), 1072 (3), 937 (6), 825 (3) cm^{-1}. The IR spectrum matched that reported previously.[58] 4,4-Dimethyl-1,2-pentadiene: GCMS m/z (relative intensity) 96 (25), 81 (72), 79 (30), 57 (100), 53 (32), 41 (85), 39 (52), 29 (53), 27 (34). The unidentified C_6H_6 hydrocarbon whose GC retention time was close to that of 4,4-dimethyl-1-pentyne: GCMS m/z (relative intensity) 78 (100), 77 (45), 76 (10), 74 (9), 63 (8), 56 (12), 52 (71), 51 (45), 50 (40), 42 (14), 41 (13), 39 (45), 38 (13).

Photolysis experiments utilized a 275-W GE fluorescent sunlamp and deoxygenated Pyrex reaction tubes.

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