Electron-Transfer Processes. 43. Attack of Alkyl Radicals upon 1-Alkenyl and 1-Alkynyl Derivatives of Tin and Mercury

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Alkyl radicals, obtained by reaction of $Bu_3Sn^\bullet$ or $ClHg^\bullet$ with alkylmercury halides, will undergo regioselective and in some cases stereospecific substitution by a free radical chain addition–elimination mechanism with 1-alkenylstannanes or -mercurials. The chain reaction is also observed for 1-alkynyl derivatives and in the photostimulated demercuration of mixed alkyl and 1-alkenyl- or 1-alkynylmercurials. Chain propagation with alkyl radical formation is also observed to occur in the reactions of β-eliminated $ClHg^\bullet$ with Grignard reagents in PhH–THF solution. In competitive reactions of $Bu_3Sn^\bullet$ or $ClHg^\bullet$ with pairs of alkylmercury chlorides, it is observed that a *tert*-butylmercurial is >1000 times more reactive than a *n*-butylmercurial, suggesting a concerted dissociate electron-transfer process not involving the intermediacy of $RHg^\bullet$ species.

We have previously reported free radical chain alkylation reactions involving alkylmercury halides and 2-substituted 1-alkenyl[1] and 1-alkynyl[2] derivatives of mercury and tin. The reactions involve the regioselective addition of an alkyl radical to the carbon bearing the mercury or tin substituent followed by β-elimination of $MX_n^\bullet$ ($^\bullet HgX$ or $Bu_3Sn^\bullet$) which reacts with RHgX to regenerate the alkyl radical (Scheme I).

Scheme I

MX_n = HgX or Bu_3Sn

$$R^\bullet + ZCH{=}CHMX_n \rightarrow Z\dot{C}HCH(R)MX_n \quad (1)$$

$$Z\dot{C}HCH(R)MX_n \rightarrow ZCH{=}CHR + MX_n^\bullet \quad (2)$$

$$XHg^\bullet + RHgX \rightarrow R^\bullet + HgX_2 + Hg^0 \quad (3)$$

$$Bu_3Sn^\bullet + RHgX \rightarrow R^\bullet + Bu_3SnX + Hg^0 \quad (4)$$

Tables I and II present a summary of yields and experimental observations that support the chain mechanism for alkenyl derivatives. With both 1-alkenylmercurials and -stannanes, a 2-substituent other than alkyl (e.g., Z = aryl, chlorine, carboalkoxy, benzenesulfonyl) is required for a high yield process. Apparently, if the addition of $R^\bullet$ is not highly directed to the 1-position, or if an allylic-type radical can be formed by hydrogen atom abstraction, the chain process of Scheme I is inhibited. Even with *t*-BuCH=C(H)HgCl, the substitution reaction occurred in only 10% yield with c-$C_6H_{11}HgCl$ although in this system substitution occurs readily in a chain fashion employing PhSSPh or PhS^- as a precursor to $PhS^\bullet$.[3] A low yield of the substitution product was observed with $CH_2{=}CHSnBu_3$ or $Me_2C{=}CHSnBu_3$ although again with $PhS^\bullet$ the substitution occurred cleanly.[3,4]

Further support for the radical chain nature of the substitution was obtained by measuring the initial kinetic chain length by the $(t\text{-Bu})_2NO^\bullet$ inhibition method. In the reaction of 0.1 M (*E*)-PhCH=CHSnBu$_3$ with 3 equiv of *t*-BuHgCl in Me_2SO-d_6, the formation of (*E*)-*t*-BuCH=CHPh could be conveniently followed by ^1H NMR using CH_2Cl_2 as an internal standard. Under standard conditions of irradiation by a 275-W fluorescent sunlamp at 35 °C, the initial rate of formation of the substitution product was 2.0×10^{-2} (mol/L)/min. In the presence of 0.0174 M $(t\text{-Bu})_2NO^\bullet$, the reaction was completely inhibited for 57 min after which it occurred at essentially the same rate as initially observed in the absence of the inhibitor. The rate of the photochemical radical formation from *t*-BuHgCl was 2.8×10^{-4} (mol/L)/min (~0.1%/min decomposition of *t*-BuHgCl), and if all radicals trapped by $(t\text{-Bu})_2NO^\bullet$ are effective in initiating the chain reaction, an initial kinetic chain length of 70 is indicated.[5] The kinetic chain length (kcl) was not reduced by the addition of 3 equiv of *n*-BuHgCl to the reaction. In a similar fashion, the initial kcl was found to be 56 for (*E*)-PhCH=C(H)HgCl reacting with *t*-BuHgCl in Me_2SO-d_6.

Tables I and II indicate that in general the yields and presumably the rates of the reactions increase from R = primary to secondary to tertiary alkyl. This may in part be due to the increased rate of photoinitiation from the *tert*-butylmercurial, but even with extended periods of irradiation, the yields were lower with primary alkylmercurials than for the secondary or tertiary alkyls. We thus examined the relative reactivities of pairs of alkylmercury chlorides toward the chain propagating $ClHg^\bullet$ and $Bu_3Sn^\bullet$. Since the substitutions involve an appreciable kinetic chain length, essentially every alkyl radical formed in reaction 3 or 4 must be trapped by the substrate to give the alkylation product. Under this condition, the relative yields of the two substitution products formed from a single substrate reacting with two alkylmercurials should be a fair measure of the relative reactivities of the alkylmercurials toward the attacking $^\bullet HgCl$ or $Bu_3Sn^\bullet$. Competitive reactions of 10 equiv each of 1:1 mixtures of *n*-BuHgCl/c-$C_6H_{11}HgCl$ and c-$C_6H_{11}HgCl$/*t*-BuHgCl with (*E*)-PhCH=C(H)HgCl or (*E*)-PhCH=CHSnBu$_3$ were performed and the substitution products analyzed by GLC. With PhCH=C(H)HgCl it was observed that *t*-BuHgCl was nearly 100 times more reactive than c-$C_6H_{11}HgCl$ which was in turn nearly 100 times more reactive than *n*-BuHgCl. The relative reactivity series for $^\bullet HgCl$ attack on RHgCl thus measured was *t*-Bu:c-C_6H_{11}:*n*-Bu = 1.0:0.011:0.0001 at 30–35 °C. Toward $Bu_3Sn^\bullet$ a similar series was observed, *t*-Bu:c-C_6H_{11}:*n*-Bu = 1.0:0.025:0.005.

We thus conclude that the rates of reactions 3 and 4 are controlled by the stabilities of the incipient alkyl radicals. Such an observation appears to exclude processes in which

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(4) The preferred addition of $PhS^\bullet$ to $CH_2{=}CHSnBu_3$ is at the β-position. The formation of the α-substitution product involves either the reversible addition of $PhS^\bullet$ or the rearrangement of $PhSCH_2\dot{C}HSnBu_3$ to $CH_2CH(SPh)SnBu_3$.
(5) If $(t\text{-Bu})_2NO^\bullet$ traps only *t*-Bu$^\bullet$, the occurrence of reaction 3 will assure that 2 mol of the nitroxide will be consumed for each mole of RHgCl which undergoes photolysis. The observed kinetic chain length should be independent of whether or not the nitroxide traps $^\bullet HgCl$.

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Table I. Reactions of 1-Alkenylmercury Halides with Organomercurials

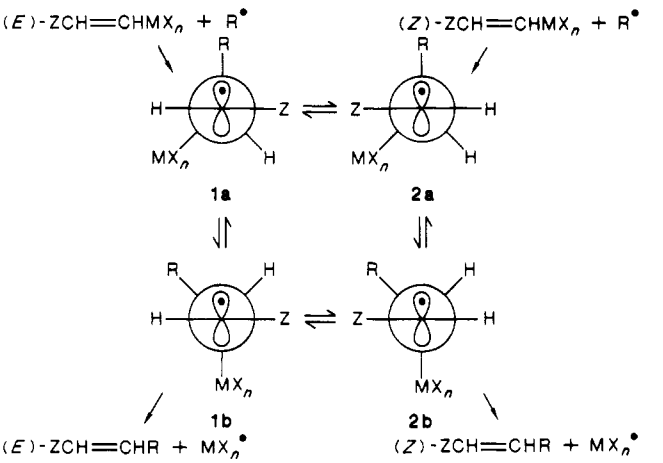
substrate	organomercurial (equiv)	conditions[a]	% yield (E/Z)[b]
(E)-PhCH=CHHgCl	*t*-BuHgCl (5)	Me_2SO, S, 4 h	97 (31.4)
(E)-PhCH=CHHgCl	*t*-BuHgCl (5)	Me_2SO, dark, 50 °C, 24 h	0
(E)-PhCH=CHHgCl	*t*-BuHgCl (3)	Me_2SO, *t*-Bu_2NO 10 mol %, S, 1 h	5
(E)-PhCH=CHHgCl	*t*-BuHgCl (3)	Me_2SO, S, 1 h	79
(E)-PhCH=CHHgCl	*t*-BuHgCl (1.2)	Me_2SO, S, 4 h	51
(E)-PhCH=CHHgCl	*t*-BuHgCl (1.2)	Me_2SO, NaI (1.2 equiv), S, 4 h	59
(E)-PhCH=CHHgCl	*t*-BuHgCl (1.2)	Me_2SO, NaI (2.4 equiv), S, 4 h	71
(E)-PhCH=CHHgCl	*t*-BuHgCl (5)	Me_2SO, NaI (10 equiv), dark, 25 °C, 24 h	23
(E)-PhCH=CHHgCl	c-C_6H_{11}HgCl (5)	Me_2SO, R, 12 h	78 (6.4)
(E)-PhCH=CHHgCl	*i*-PrHgCl (5)	Me_2SO, R, 12 h	83[c]
(E)-PhCH=CHHgCl	$PhCH_2HgCl$ (5)	Me_2SO, R, 12 h	31[c,d]
(E)-PhCH=CHHgCl	*t*-$BuCH_2HgCl$ (5)	Me_2SO, R, 12 h	23[c]
Ph_2C=CHHgBr	*t*-BuHgCl (5)	Me_2SO, R, 12 h	100
Ph_2C=CHHgBr	*i*-PrHgCl (5)	Me_2SO, R, 12 h	96
Ph_2C=CHHgBr	c-C_6H_{11}HgCl (5)	Me_2SO, R, 12 h	97
Ph_2C=CHHgCl	(E)-2-MeO-c-$C_6H_{10}HgO_2CCF_3$ (5)	MeOH, R, 24 h	69
Ph_2C=CHHgCl	$PhCH(OMe)CH_2HgO_2CCF_3$ (5)	MeOH/Me_2SO, R, 24 h	69
Ph_2C=CHHgBr	$(PhCOCH_2)_2Hg$ (1)	Me_2SO, R, 12 h	21
Ph_2C=CHHgBr	$PhCH_2HgCl$ (5)	Me_2SO, R, 12 h	56[e]
Ph_2C=CHHgBr	*t*-$BuCH_2HgCl$ (5)	Me_2SO, R, 12 h	30
(E)-Me_3CCH=CHHgBr	c-C_6H_{11}HgCl (5)	Me_2SO, R, 12 h	10[c]
Me_2C=CHHgBr	c-C_6H_{11}HgCl (5)	Me_2SO, R, 12 h	<10
(E)-ClCH=CHHgCl	*t*-BuHgCl (1.2)	Me_2SO, R, 10 h	33 (5.6)
(Z)-ClCH=CHHgCl[f]	*t*-BuHgCl (1.2)	Me_2SO, R, 10 h	44 (2.7)
(E)-ClCH=CHHgCl	c-C_6H_{11}HgCl (1.2)	Me_2SO, R, 10 h	28 (4.3)
(Z)-ClCH=CHHgCl[f]	c-C_6H_{11}HgCl (1.2)	Me_2SO, R, 10 h	38 (0.7)

[a] The substrate (0.1 mmol) and the mercurial in 10 mL of a nitrogen-purged solvent were irradiated in a Pyrex tube; S = 275-W sunlamp ca. 20 cm from reaction vessel; R = 350-nm Rayonet photoreactor. [b] Yields were determined by ^1H NMR; E/Z ratios were determined by GLC. [c] Mixture of E and Z isomers. [d] Bibenzyl was formed in 70% yield (based upon $PhCH_2HgCl$). [e] Bibenzyl was formed in 60% yield (based upon $PhCH_2HgCl$). [f] Starting material had a Z/E ratio of 3.0.

the rate-determining step is the formation of $RHg^•$ (as a precursor to R•) since the structure of R should have little effect on the formation of $RHg^•$. In particular, it is difficult to understand why *t*-$BuHg^•$ would be formed more readily than *n*-$BuHg^•$.[6] It appears that reactions 3 and 4 must be processes in which R• is formed in the rate-determining step and are most likely concerted reactions. Reaction of $Bu_3Sn^•$ with RHgCl to form[9] Bu_3SnCl and $RHg^•$ seems to be excluded, and the reaction most likely involves dissociative electron transfer to form Bu_3Sn^+, R•, Hg^0, and Cl^-. The oxidation potential of $Bu_3Sn^•$ is not known, and electron transfer to RHgCl may require Coulombic stabilization by the interaction between Bu_3Sn^+ and Cl^-. Alternately, $Bu_3Sn^•$ may attack at the mercury atom to displace R• and form $Bu_3SnHgCl$ which subsequently eliminates Hg^0.

A photostimulated radical chain reaction of PhCH=CHSnBu_3 with alkyl halides to yield PhCH=CHR and Bu_3SnX occurred with RX = CCl_4, MeO_2CCH_2Br, and *n*-BuI and in poor yield with *i*-PrI.[1,10] With *t*-BuBr no reaction was observed upon UV photolysis at 30 °C although inefficient reactions have been reported with other secondary and tertiary halides at 86 °C with 32–48 mol % of azobis(isobutyronitrile).[10c] The corresponding 1-alkenylmercury chloride gave poor yields of the alkylation products contaminated with the 1-alkenyl halides upon UV photolysis with MeI or *i*-PrI in PhH at 35–40 °C.[11] For both (E)-PhCH=CHSnBu_3 and (E)-PhCH=C(H)HgCl, faster reactions and higher yields are observed by using RHgCl instead of the alkyl halides, particularly when R = a secondary or tertiary alkyl.

Scheme II



The photostimulated reactions of *t*-BuHgCl in Me_2SO were faster in the presence of added NaI (Table I), but the final yields of alkylation products were only slightly improved. The increased rate of reaction is probably connected with a more rapid initiation process for *t*-BuHgI, possibly involving electron transfer from I^- to the mercurial. In fact, with the *t*-BuHgCl/NaI system in Me_2SO, a free radical process, completely inhibited by 10 mol % of (*t*-Bu)$_2$NO•, was initiated in the dark at 30 °C.

Tables I and II demonstrate that the substitution process can occur in a stereospecific manner with retention

(6) The reduction of RHgX by alkaline $NaBH_4$ involves a radical chain process in which RHgH reacts by hydrogen atom transfer to form $RHg^•$. Reaction of an excess of a 1:1 mixture of *t*-BuHgCl and *n*-BuHgCl with $NaBH_4$ in the presence of CH_2=C(Cl)CN forms *t*-$BuCH_2CH(Cl)CN$ and *n*-$BuCH_2CH(Cl)CN$ in approximately a 1:1 ratio at high CH_2=C(Cl)CN concentration. The results demonstrate that there is little kinetic effect of the structure of R for competing reactions which directly from $RHg^•$.[7,8]

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Table II. Reactions of 1-Alkenylstannanes with RHgCl

substrate	mercurial	conditions[a]	% yield (E/Z)[b]
(E)-PhCH=CHSnBu$_3$	*i*-PrHgCl	PhH, S, 18 h	86 (11.5)
(E)-PhCH=CHSnBu$_3$	*i*-PrHgCl	PhH, AIBN 4 mol %, 80 °C, 16 h	73 (15.6)
(E)-PhCH=CHSnBu$_3$	*i*-PrHgCl	PhH, dark, 50 °C, 24 h	0
(E)-PhCH=CHSnBu$_3$	*i*-PrHgCl	PhH, S, *t*-Bu$_2$NO 10 mol %, 16 h	35 (10.1)
(E)-PhCH=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	Me$_2$SO, S, 16 h	88 (19.0)
(E)-PhCH=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	PhH, S, 18 h	77 (19.0)
(E)-PhCH=CHSnBu$_3$	*t*-BuHgCl	PhH, S, 14 h	83 (49.0)
(E)-PhCH=CHSnBu$_3$	Δ^5-C$_6$H$_{11}$HgCl	PhH, R, 32 h	55[c] (7.3)
(E)-PhCH=CHSnBu$_3$	*n*-BuHgCl	PhH, R, 40 h	46 (6.1)
(E)-PhCH=CHSnBu$_3$	Δ^3-C$_4$H$_7$HgCl	PhH, R, 36 h	45 (7.3)
(E)-PhCH=CHSnBu$_3$	c-C$_5$H$_9$CH$_2$HgCl	PhH, R, 48 h	52 (5.7)
(E)-PhCH=CHSnBu$_3$	PhCH$_2$HgCl	PhH, S, 15 h	18[d] (10.1)
Ph$_2$C=CHSnBu$_3$	*t*-BuCH$_2$HgCl	PhH, S, 72 h	10
Ph$_2$C=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	Me$_2$SO, R, 32 h	76
Ph$_2$C=CHSnBu$_3$	*i*-PrHgCl	PhH, R, 28 h	73
Ph$_2$C=CHSnBu$_3$	*t*-BuHgCl	PhH, R, 18 h	78
Me$_2$C=CHSnBu$_3$	c-C$_5$H$_9$CH$_2$HgCl	PhH, R, 96 h	0
Me$_2$C=CHSnBu$_3$	*t*-BuHgCl	PhH, S, 18 h	0
(E)-MeO$_2$CCH=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	PhH/Me$_2$SO, R, 5 h	66 (23.0)
(Z)-MeO$_2$CCH=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	PhH/Me$_2$SO, R, 5 h	70 (2.1)
(E)-MeO$_2$CCH=CHSnBu$_3$	*t*-BuHgCl	PhH, R, 5 h	36 (>50)
(Z)-MeO$_2$CCH=CHSnBu$_3$	*t*-BuHgCl	PhH, R, 5 h	49 (>50)
CH$_2$=CHSnBu$_3$	c-C$_5$H$_9$HgCl	PhH, R, 24 h	10
CH$_2$=CHSnBu$_3$	c-C$_6$H$_{11}$HgCl	Me$_2$SO, R, 24 h	8
CH$_2$=CHSnBu$_3$	*t*-BuHgCl	PhH/Me$_2$SO, S, 2 h	<10[e]
(E)-PhSO$_2$CH=CHSnBu$_3$	*t*-BuHgCl	Me$_2$SO, S, 3 h	100[f] (>50)

[a] The substrate (1 mmol) and the mercurial (1.2–1.6 mmol) in 10 mL of a nitrogen-purged solvent in a Pyrex tube were irradiated with a 275-W sunlamp (S) ca. 15–20 cm from the reaction vessel or in a 350-nm Rayonet photoreactor (R). [b] Yields were determined by ^{1}H NMR; E/Z ratios were determined by GLC. [c] Only cyclized products ((E)- and (Z)-PhCH=CHCH$_2$-c-C$_5$H$_9$) were observed. [d] Bibenzyl was formed as the main product. [e] Me$_3$CCH$_2$CH$_2$SnBu$_3$ (~80% yield) was obtained when the reaction mixture was worked up with NaBH$_4$. [f] The substrate (0.1 mmol) and *t*-BuHgCl (0.5 mmol) in nitrogen-purged Me$_2$SO-d_6 (1 mL) in an NMR tube were irradiated with a 275-W sunlamp ca. 20 cm from the tube. Yield was determined by ^{1}H NMR using CH$_2$Cl$_2$ as an internal standard.

Table III. Photostimulated Reactions of 1-Alkenyl- or Alkylmercurials with Other Alkyl or 1-Alkenyl Organometallics

reactants			
mercurial	organometallic (equiv)	conditions[a]	coupling product,[b] %
t-BuHgCl	PhCH=CHMgBr[c] (0.6)	THF, R, 24 h	47 (GC)
t-BuHgCl	PhCH=CHMgBr[c] (4)	THF, R, 24 h	30 (GC)
c-C$_6$H$_{11}$HgCl	PhCH=CHMgBr[c] (4)	PhH/THF, R, 24 h	25 (GC)
n-BuHgCl	PhCH=CHMgBr[c] (4)	PhH/THF, R, 24 h	16 (GC)
PhCH$_2$HgCl	PhCH=CHMgBr (4)	PhH/THF, R, 24 h	23[d] (GC)
PhCH=CHHgBu-*t*[c]		PhH, R, 24 h	73 (I)
PhCH=CHHgC$_6$H$_{11}$-c[c]		PhH, R, 24 h	60 (I)
PhCH=CHHgBu-*n*[c]		PhH, R, 24 h	12 (GLC)
PhCH=CHHgCH$_2$Ph[c]		PhH, R, 24 h	30[d] (NMR)
(E)-PhCH=CHHgCl	*t*-BuMgCl (2)	PhH/THF, R, 5 h	63 (GC); E/Z = >50
(E)-PhCH=CHHgCl	*t*-BuLi (1)	PhH, R, 24 h	67 (GC); E/Z = 18.2
t-BuHgCl	Ph$_2$C=CHMgBr	THF, R, 24 h	<5 (NMR)
c-C$_6$H$_{11}$HgCl	Ph$_2$C=CHMgBr	THF, R, 24 h	0
PhCH$_2$HgCl	Ph$_2$C=CHMgBr	THF, R, 24 h	0
Ph$_2$C=CHHgCl	*t*-BuMgCl (2)	PhH/THF, R, 5 h	38 (GC)
Ph$_2$C=CHHgBr	*i*-PrMgBr	PhH/THF, R, 24 h	35 (NMR)
Ph$_2$C=CHHgCl	*t*-BuLi (1)	PhH, R, 24 h	56 (GC)
(E)-PhCH=CHHgCl	(c-C$_6$H$_{11}$)$_3$B (5)	PhH, R, 2 h	22 (NMR)
Ph$_2$C=CHHgBr	(c-C$_6$H$_{11}$)$_3$B (5)	PhH, S, 1 h	42 (NMR)
Ph$_2$C=CHHgBr	*i*-Pr$_3$Al (5)	PhH, R, 24 h	33 (NMR)

[a] The mercurial (1 mmol) and the organometallic compound in 5–10 mL of a nitrogen-purged solvent in a Pyrex tube were irradiated in a 350-nm Rayonet photoreactor (R) or with a 275-W sunlamp (S) ca. 15–20 cm from the reaction vessel. [b] Yields were determined by GLC (GC) or ^{1}H NMR (NMR), or isolated (I). E/Z ratios were determined by GLC. [c] Mixture of E and Z isomers. Products also consisted of both isomers in which the E isomer is the major isomer.

of configuration, at least for the E and Z substrates ClCH=C(H)HgCl and MeO$_2$CCH=CHSnBu$_3$.[12] Substitution by the homolytic addition–elimination mechanism presumably involves the conformational process shown in Scheme II. With MX$_n$ = HgCl and Z = Cl, stereospecificity is observed in reactions with R = c-C$_6$H$_{11}$ or *t*-Bu although the degree of selectivity is higher for c-C$_6$H$_{11}$ than *t*-Bu. Elimination of $^{\bullet}$HgCl from **1** and **2** must compete with their interconversion. However, with MX$_n$ = Bu$_3$Sn and Z = MeO$_2$C, the reaction is stereospecific for R = c-C$_6$H$_{11}$ but not for R = *t*-Bu since both E and Z substrates produce mainly (E)-*t*-BuCH=CHCO$_2$Me.[13] Apparently, with R = *t*-Bu, Z = MeO$_2$C, and MX$_n$ = Bu$_3$Sn, the formation of conformation **2b** and the β-elimination of Bu$_3$Sn$^{\bullet}$ must be slow relative to the **2** to **1** interconversion. Elimination from both the **1a** and **2a** adduct radicals thus proceed via the low-energy conformation **1b** rather than

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(13) With I$^{\bullet}$ as the leaving group, the reaction of (E)- or (Z)-MeO$_2$CCH=CHI with *t*-BuHgCl is stereospecific.[12]

Table IV. Photostimulated Reactions of 2-Phenylethynyl Derivatives with RHgCl

substrate (mmol)	RHgCl (mmol)	conditions[a]	% PhC≡CP[b] (mmol)	% Hg[0][c]
$(PhC{\equiv}C)_2Hg$ (0.1)	*n*-BuHgCl (0.5)	Me_2SO, 24 h	9 (0.018)	
$(PhC{\equiv}C)_2Hg$ (0.1)	c-C_6H_{11}HgCl (0.5)	Me_2SO, 24 h	26 (0.052)	
$(PhC{\equiv}C)_2Hg$ (0.1)	*t*-BuHgCl (0.5)	Me_2SO, 24 h	34 (0.068)	
$(PhC{\equiv}C)_2Hg$ (0.1)	$(EtO)_2P(O)HgCl$ (0.5)	Me_2SO, 24 h	61 (0.122)	
$PhC{\equiv}CSnBu_3$ (1)	*n*-BuHgCl (5)	PhH, 24 h	13[d] (0.13)	
$PhC{\equiv}CSnBu_3$ (1)	c-C_6H_{11}HgCl (5)	PhH, 24 h	43[e] (0.43)	
$PhC{\equiv}CSnBu_3$ (1)	*t*-BuHgCl (5)	PhH, 24 h	61[d] (0.61)	
PhC≡CLi (1)	*n*-BuHgCl (1)	PhH, 24 h	<10	10
PhC≡CLi (1)	$PhCH_2HgCl$ (1)	PhH, 24 h	10[f]	20
PhC≡CLi (1)	c-C_6H_{11}HgCl (1)	PhH, 24 h	23	20
PhC≡CLi (1)	*t*-BuHgCl (1)	PhH, 24 h	55	58
PhC≡CHgBu-*t*		PhH, 24 h	56 (isolated)	72
PhC≡CHgBu-*t*		Me_2SO, 24 h	36[g] (isolated)	65

[a] The reactants in 10 mL of a nitrogen-purged solvent in a Pyrex tube were irradiated in a 350-nm Rayonet photoreactor. [b] Yields were determined by GLC. [c] Mercury metal was formed in all of the reactions. [d] Bu_3SnCl was formed in 70% yield. [e] Bu_3SnCl was formed in 80% yield. [f] Bibenzyl (0.4 mmol) was obtained. [g] $(PhC{\equiv}C)_2Hg$ (0.25 mmol) was isolated.

Table V. Relative Reactivities of 1-Alkenyl and 1-Alkynyl Derivatives toward c-C_6H_{11}•

reagent A	reagent B	conditions[a]	k_A/k_B[b]	rel react of reagent A
$CH_2{=}CHCH_2SnBu_3$	$Ph_2C{=}CHI$	PhH, 24 h	≪0.1	≪1
$CH_2{=}CHSnBu_3$	$Ph_2C{=}CHI$	PhH, 24 h	<0.1[c]	<1
$Me_2C{=}CHSnBu_3$	$Ph_2C{=}CHI$	PhH, 24 h	0.1	1
(*E*)-$PhCH{=}CHSnBu_3$	$Ph_2C{=}CHI$	PhH, 24 h	0.7	7
(*E*)-PhCH=CHI	$Ph_2C{=}CHI$	PhH, 24 h	0.7	7
(*E*)-PhCH=CHHgCl	$Ph_2C{=}CHI$	PhH/Me_2SO, 24 h	1.5	15
(*E*)-$PhSO_2CH{=}CHSnBu_3$	PhC≡CI	PhH, 6 h	0.7	28
$Ph_2C{=}CHSnBu_3$	PhC≡CI	PhH, 5 h	0.2	8
$Ph_2C{=}CHHgCl$	PhC≡CI	PhH, 6 h	0.5	20
$PhC{\equiv}CSnBu_3$	$Ph_2C{=}CHI$	PhH, 20 h	0.2	2
$(PhC{\equiv}C)_2Hg$	$Ph_2C{=}CHI$	Me_2SO, 24 h	0.2	2
PhC≡CI	$Ph_2C{=}CHI$	PhH, 6 h	4[d]	40
$Ph_2C{=}CHI$				10

[a] Cyclohexylmercury chloride (0.1 mmol), reagent A (1 mmol), and reagent B (1 mmol) in 10 mL of a nitrogen-purged solvent in a Pyrex tube were irradiated in a 350-nm Rayonet photoreactor. [b] Based on the yields of the substitution products determined by GLC. [c] The major product (~80%) in the reaction of $CH_2{=}CHSnBu_3$ was derived from β-attack of c-C_6H_{11}•. [d] PhC≡CI and $Ph_2C{=}CHI$ react with c-C_6H_{11}• to form *c*-$C_6H_{11}C{\equiv}CPh$ and c-$C_6H_{11}CH{=}CPh_2$ in high yield.[2]

conformation **2b** with the destabilizing gauche interactions of *t*-Bu, MeO_2C, and Bu_3Sn. It appears that •HgCl is more readily eliminated than Bu_3Sn•.

The photostimulated reactions of 1-alkenylmercury halides with RMgX, R_3B, R_3Al, and *t*-BuLi also yield the alkyl substitution product (Table III). The reaction may involve the formation of intermediate alkyl-1-alkenylmercurials that can decompose as indicated in Scheme III. An analogous reaction to Scheme III has been previously reported for the conversion of R′CH=C(H)HgSR into R′CH=CHSR where the β-eliminated •HgSR decomposes to RS• and Hg^0.[11]

Scheme III

$$R^{\bullet} + PhCH{=}C(H)HgR \rightarrow PhCH\text{-}C(H)(R)HgR \quad (5)$$

$$PhCH\text{-}C(H)(R)HgR \rightarrow PhCH{=}CHR + RHg^{\bullet} \quad (6)$$

$$RHg^{\bullet} \rightarrow R^{\bullet} + Hg^0 \quad (7)$$

Reaction of PhCH=CHMgBr with RHgCl formed the isolable PhCH=C(H)HgR with R = *t*-Bu, c-C_6H_{11}, $PhCH_2$, or *n*-Bu. On the other hand, reaction of PhCH=C(H)HgCl with RMgCl failed to yield the β-styrenylalkylmercurial. Photolysis of PhCH=C(H)HgR yielded PhCH=CHR and Hg^0 (Table III) while photolysis of a 1:1 mixture of *t*-BuHgCH=CHPh and *n*-BuHgCH=CHPh gave initially *t*-BuCH=CHPh and *n*-BuCH=CHPh in a 1.4:1 ratio. Here the relative reactivity is controlled by attack of the alkyl radical upon PhCH=C(H)HgR, and there is but a slight effect upon reactivity when R is changed from *n*-Bu to *t*-Bu. This result excludes the possibility that alkyl-1-alkenylmercurials are involved in the reactions of 1-alkenylmercury halides or 1-alkenylstannanes with alkylmercury halides since now competition reaction between *t*-BuHgCl and *n*-BuHgCl yields essentially only the *tert*-butylation products. The result also confirms the stepwise nature of the addition–elimination process of Scheme I.

Reaction of either PhCH=C(H)HgCl or $Ph_2C{=}C(H)$-HgCl with *t*-BuLi followed by photolysis yielded the alkylation products, presumably via the intermediacy of the alkyl-1-alkenyl mercurial. Photolysis of PhCH=C(H)HgCl or $Ph_2C{=}C(H)HgCl$ with *t*-BuMgCl yielded Hg^0 and the *tert*-butylated product under conditions where the alkylalkenylmercurials were not formed on the basis of isolation experiments. These reactions appear to follow Scheme I with RMgCl in place of RHgCl (i.e., •HgCl + *t*-BuMgCl → *t*-Bu• + Hg^0 + $MgCl_2$).

Arylmercurials and -stannanes could in principle participate in Schemes I and III. However, these reactions are inefficient, at least with the parent phenyl derivatives. Photolysis of PhHgCl or $PhSnBu_3$ with an excess of *t*-BuHgCl typically yielded 10–15% of *t*-BuPh under the conditions of Tables I and II.

The reactions of Schemes I and III have been extended to 2-phenylethynyl derivatives (Table IV). Again, the substitutions are chain reactions that can be photostimulated or inhibited by nitroxides and that do not proceed in the dark. Reaction of PhC≡CLi with *t*-BuHgCl gave the isolable *t*-BuHgC≡CPh which could be photolyzed to *t*-BuC≡CPh and Hg^0. The somewhat low yields of this product observed are due to the concurrent symmetrization reaction ($2PhC{\equiv}CHgR \rightarrow (PhC{\equiv}C)_2Hg + R_2Hg$).

Table V summarizes competitive reactions of 2-phenylethenyl and 2-phenylethynyl derivatives (relative

to $Ph_2C{=}CHI$ or $PhC{\equiv}CI$) with c-$C_6H_{11}{}^{\bullet}$ from c-$C_6H_{11}HgCl$. The alkenyl or alkynyl iodides react with $R^{\bullet}$ to yield the substitution products by the homolytic addition–elimination sequence of Scheme I with MX_n = I.

The ethenyl- and ethynylstannanes were much more reactive than $Bu_3SnCH_2CH{=}CH_2$. The ethenylmercury halides were observed to be about twice as reactive as the corresponding tributylstannanes, while for both the stannanes or mercurials, the reactivity of the ethenyl derivatives are a factor of 3–4 greater than for the ethynyl analogues ($PhC{\equiv}CSnBu_3$ (1.0), $PhCH{=}CHSnBu_3$ (3.5), $Ph_2C{=}CHSnBu_3$ (4)).

Tin and mercury substituents could perhaps stabilize the adduct radicals by a neighboring group bridging effect. One might expect this effect to be greater in $PhC\dot{H}{-}C(H)(R)MX_n$ than in $Ph\dot{C}H{=}C(R)MX_n$ from stereoelectronic considerations. The results give little support for stabilization by bridging at least in the transition state for the addition of $R^{\bullet}$ to alkenyl- and alkynylmetals. On the other hand, the substituents HgCl and Bu_3Sn seem to have a fairly large effect in controlling the regioselectivity of the addition of $R^{\bullet}$ to $ZCH{=}CHMX_n$ systems. Of course, with Z = Ph addition occurs to give the adduct radicals with benzylic stabilization. With Z = Cl and MX_n = HgCl or with Z = MeO_2C and MX_n = Bu_3Sn, the preferred point of addition is still at the carbon with the MX_n substituent. However, the yields of substitution products are not quantitative and some attack at the other carbon atom may also be occurring. With $PhSO_2CH{=}CHSnBu_3$, a quantitative yield of the substitution product is observed in which t-$Bu^{\bullet}$ has attacked the carbon with the Bu_3Sn substituent. Since $PhSO_2$ should not stabilize a radical center, it might be argued that the Bu_3Sn substituent is somehow stabilizing a radical center at the β-carbon atom. However, such stabilization should also occur for $RCH_2\dot{C}HCH_2SnBu_3$ formed in the attack of $R^{\bullet}$ upon allylstannane. The low reactivity of $CH_2{=}CHCH_2SnBu_3$ relative to $PhSO_2CH{=}CHSnBu_3$ toward t-$Bu^{\bullet}$ (Table V) suggests that the relative reactivity and regioselectivity in alkyl radical attack is controlled to a large extent by the electron-withdrawing ability of the substituents.

Experimental Section

1-Alkenylmercury Halides. 2,2-Dimethylethenylmercury bromide was prepared from 2,2-dimethylethenylmagnesium bromide and mercuric bromide (1:1) in THF: ^{1}H NMR ($CDCl_3$) δ 5.55 (br s, 1), 1.95 (s, 3), 1.90 (s, 3). The preparation of the other 1-alkenylmercury halides employed in this study has been described previously.[3]

Alkylmercury Chlorides. The following general procedure was found convenient for the synthesis of several alkylmercury halides. To a Grignard reagent in THF was slowly added 1 equiv of mercuric chloride dissolved in THF. The reaction mixture was warmed to reflux for 1 h, cooled to room temperature, and poured into cold 2% aqueous acetic acid containing several equivalents of sodium chloride. The solid product was collected and dried. Inorganic salts were removed by dissolving the product in chloroform, filtering, and concentrating the solution under vacuum. Generally, a pure substance resulted. If desirable, the product was recrystallized from ethanol. Thus prepared were n-butylmercury chloride, mp 127.5 °C, isopropylmercury chloride, mp 94.5–95.5 °C,[15] cyclohexylmercury chloride, mp 163–164 °C,[16] cyclopentylmercury chloride, mp 53–54 °C,[16] and 5-hexenylmercury chloride, mp 100.5–101.5 °C.[16] $tert$-Butylmercury chloride, mp 110–113 °C,[17] was also synthesized by the Grignard route, but the reaction was carried out at 0–5 °C. After being stirred overnight in an ice bath, the mixture was poured into cold 2% aqueous acetic acid. The product was extracted with chloroform, washed with water, and dried over anhydrous sodium sulfate. A white solid was obtained after the removal of the solvent. The product was recrystallized from chloroform (10%)–hexane (90%) to give a white crystalline product in more than 50% yield. Literature procedures were employed for the preparations of benzylmercury chloride, mp 104 °C,[18] 3-butenylmercury chloride, mp 130 °C dec,[19] (diethoxyphosphinyl)-mercury chloride, mp 103–104 °C,[20] and bis(2-oxo-2-phenylethyl)mercury, mp 171–172.5 °C.[21]

Diorganomercurials. $tert$-Butyl(2-phenylethenyl)mercury was prepared from the Grignard reagent and $tert$-butylmercury chloride. To a solution of $tert$-butylmercury chloride (5 mmol) in 20 mL of THF cooled in an ice bath was added dropwise (from a syringe) the Grignard reagent in THF (~1 M) under a nitrogen atmosphere. The dark color of the Grignard reagent disappeared almost immediately, and the addition was continued until the dark color of the Grignard reagent remained for a few minutes (about 10 mL of the Grignard solution was added). The mixture was stirred in the ice bath for about 15 min and then poured into 2% aqueous acetic acid. The product was extracted with ether, washed twice with water, and dried over anhydrous sodium sulfate. The oily product after the removal of the solvent was purified by silica gel chromatography using ether (10%)–hexane (90%) as the eluent. The pale yellow oil (89% yield) was a mixture of E and Z isomers in a 4:1 ratio. The ^{1}H NMR($CDCl_3$) of the mixture had doublets at δ 7.07 (J = 19.5 Hz) and 6.68 (J = 19.5 Hz) for the E isomer and doublets at δ 7.94 (J = 12.9 Hz) and 6.57 (J = 12.9 Hz) for the Z isomer. The same procedure was also employed for the synthesis of the following mercurials that were obtained as pale yellow liquids. Cyclohexyl(2-phenylethenyl)mercury was obtained as a mixture of E and Z isomers (4:1) in 62% yield after silica gel chromatography using hexane as the eluent. The ^{1}H NMR ($CDCl_3$) of the mixture had doublets at δ 7.14 (J = 19.5 Hz) and 6.71 (J = 19.5 Hz) for the E isomer and doublets at δ 8.04 (J = 12.9 Hz) and 6.61 (J = 12.9 Hz) for the Z isomer. n-Butyl(2-phenylethenyl)mercury was obtained as 4:1 mixture of E and Z isomers in 72% yield after silica gel chromatography. The ^{1}H NMR ($CDCl_3$) of the mixture showed doublets at δ 7.13 (J = 19.5 Hz) and 6.73 (J = 19.5 Hz) for the E isomer and doublets at δ 8.06 (J = 12.9 Hz) and 6.60 (J = 12.9 Hz) for the Z isomer. Benzyl(2-phenylethenyl)mercury was obtained as a 4:1 mixture of E and Z isomers in 76% isolated yield. The ^{1}H NMR ($CDCl_3$) of the mixture had a resolved doublet at δ 6.61 (J = 19.2 Hz) for the E isomer and doublets at δ 7.85 (J = 12.6 Hz) and 6.46 (J = 12.6 Hz) for the Z isomer. $tert$-Butyl(phenylethynyl)mercury was synthesized as follows. To a well-stirred solution of phenylacetylene (5 mmol) in THF (10 mL) under a nitrogen atmosphere in a round-bottomed flask cooled in an ice bath was added dropwise a solution of n-butyllithium (5 mmol) in hexane. The mixture was stirred for a few minutes and then allowed to warm to room temperature for 5 min. The mixture was recooled in an ice bath, and $tert$-butylmercury chloride was added while the mixture was back-flushed with nitrogen. After the addition, the mixture was stirred at room temperature for 15 min, poured into water, and extracted with ether. The ether extract was washed twice with water and dried over anhydrous sodium sulfate. Ether was removed under vacuum to give a pale yellow oil which consisted of mainly the mercurial and a small amount of phenylacetylene. Attempts to purify the product by silica gel chromatography resulted in the decomposition of the mercurial to give a black precipitate of mercury. The mercurial had a ^{1}H NMR ($CDCl_3$) of δ 7.55–7.40 (m, 2), 7.35–7.25 (m, 3), and 1.38 (s, 9).

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Organostannanes. Allyltributylstannane was synthesized by the Grignard route as follows. To a solution of allylmagnesium chloride (0.25 mol) in 200 mL of THF was added tributyltin chloride (0.03 mol), and the mixture was refluxed for 2 h. The mixture was stirred at room temperature overnight and then decomposed by saturated aqueous ammonium chloride solution. The mixture was filtered, and the organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated. Distillation gave 6.5 g (65%) of a clear liquid product: bp 106 °C (0.1 Torr); ^{1}H NMR ($CDCl_3$) δ 6.05–5.83 (m, 1), 4.85–4.55 (m, 2), 1.77 (d, J = 8.4 Hz, 2), 1.6–1.2 (m, 18), 0.89 (t, J = 7.2 Hz, 9); IR (neat) 3080, 2920, 2880, 2840, 2820, 1605, 1445, 1400, 1355, 1170, 1050, 1000, 855 cm^{-1}. ((*E*)-2-(Phenylsulfonyl)ethenyl)tributylstannane was prepared by the literature procedure:[22] ^{1}H NMR ($CDCl_3$) δ 7.92–7.82 (m, 2), 7.73 (d, J = 18.3 Hz, 1), 7.65–7.45 (m, 3), 6.65 (d, J = 18.3 Hz, 1), 1.8–0.7 (m, 27). The preparation of all other organostannanes employed in this study has been described previously.[3]

Other Subtrates. Triisopropylaluminum was prepared by the same method reported for the synthesis of triisopentylaluminum.[23] Isopropylmagnesium bromide (0.3 mol) in 100 mL of diethyl ether was added dropwise to well-stirred and refluxing toluene and the ether allowed to distill. The suspension was cooled to room temperature, and anhydrous aluminum chloride (0.05 mol) was added slowly with stirring while the suspension was back-flushed with nitrogen. After the mixture was stirred at room temperature overnight, the precipitate was centrifuged. The product was isolated by vacuum distillation: bp 44–46 °C (2 torr); ^{1}H NMR ($CDCl_3$) δ 1.55–0.2 (m). The product was sensitive to moisture and was handled under a nitrogen atmosphere throughout the experiment. 2,2-Diphenylethenyl iodide, mp 40–40.5 °C,[24] phenylethynyl iodide, bp 74 °C (1.6 Torr),[25] and (*E*)-β-iodo-styrene[26] were synthesized by the literature procedures.

General Procedures for Photostimulated Reactions of 1-Alkenyl Derivatives. The substrates (see Table I–V) were dissolved in a nitrogen-purged solvent in a Pyrex tube equipped with rubber septum. The mixture was irradiated for a period of time in a 350-nm Rayonet photoreactor or with a 275-W sunlamp as indicated in the tables. The mixture was then poured into water, and the product was extracted with benzene or diethyl ether. The extract was washed twice with 10–20% aqueous sodium thiosulfate solution to remove the unreacted alkylmercury chloride, dried over anhydrous sodium sulfate, and concentrated under vacuum. The mixture was then analyzed by GLC and the E/Z ratio was obtained from the ratio of the peak areas. To determine the product yield, the solvent was completely removed from the product mixture under vacuum. A known amount of an internal standard, usually dibromomethane, was added to the crude product mixture dissolved in deuteriated chloroform. The yield was obtained from the intergration of the vinyl proton signal comparison with that of the internal standard.

Reaction Products. The following compounds were prepared (Tables I–IV). (*E*)-3,3-Dimethyl-1-phenyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.43–7.12 (m, 5), 6.31 (d, J = 16.2 Hz, 1), 6.24 (d, J = 16.2 Hz, 1), 1.11 (s, 9); GCMS, m/e (relative intensity) 160 (M$^+$, 38), 145 (100), 117 (36), 115 (22), 91 (50), 77 (21), 51 (21). (*Z*)-3,3-Dimethyl-1-phenyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.38–7.10 (m, 5), 6.40 (d, J = 12.6 Hz, 1), 5.59 (d, J = 12.6 Hz, 1), 0.97 (s, 9). ((*E*)-2-Phenylethenyl)cyclohexane: ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5), 6.33 (d, J = 15.9 Hz, 1), 6.16 (dd, J = 15.9, 6.9 Hz, 1), 2.20–2.05 (m, 1), 1.95–0.83 (m, 10); GCMS, m/e (relative intensity) 186 (M$^+$, 17), 104 (100), 91 (17). (*E*)-3-Methyl-1-phenyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.32–7.05 (m, 5), 6.32–6.20 (m, 2), 2.7–2.2 (m, 1), 1.05 (d, J = 7 Hz, 6); GCMS, m/e (relative intensity) 146 (M$^+$, 31), 131 (100), 91 (50). 1,3-Diphenylpropene: GCMS, m/e (relative intensity) 196 (M$^+$, 79), 115 (100), 91 (50). 4,4-Dimethyl-1-phenyl-1-pentene: GCMS, m/e (relative intensity) 174 (M$^+$, 10), 159 (3), 118 (31), 117 (35), 91 (12), 57 (100). 3,3-Dimethyl-1,1-diphenyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.5–6.9 (m, 10), 6.05 (s, 1), 0.98 (s, 9); GCMS, m/e (relative intensity) 236 (M$^+$, 62), 221 (100), 143 (72), 91 (37). 1,1-diphenyl-3-methyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.45–7.05 (m, 10), 5.9 (d, J = 9 Hz, 1), 2.8–2.1 (m, 1), 1.02 (d, J = 6.5 Hz, 6); GCMS, m/e (relative intensity) 222 (M$^+$, 50), 207 (92), 129 (100), 91 (44). (2,2-Diphenylethenyl)cyclohexane: ^{1}H NMR ($CDCl_3$) δ 7.45–6.90 (m, 10), 5.9 (d, J = 9 Hz, 1), 2.35–0.80 (m, 11); GCMS, m/e (relative intensity) 262 (M$^+$, 32), 180 (100), 91 (60). (2,2-Diphenylethenyl)-2-methoxycyclohexane: ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 5), 7.22 (s, 5), 5.98 (d, J = 9.5 Hz, 1), 3.52–2.8 (m, 4), 2.5–0.8 (m, 9); GCMS, m/e (relative intensity) 292 (M$^+$, 55), 260 (40), 217 (51), 205 (78), 112 (100), 91 (75). 4-Methoxy-1,1,4-triphenyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 7.5–6.9 (m, 15), 6.12 (t, J = 8 Hz, 1)8 4.18 (t, J = 6.5 Hz, 1), 3.2 (s, 3), 2.55 (m, 2); GCMS, m/e (relative intensity) 314 (M$^+$, 0.1), 121 (100), 91 (16), 77 (16). 4,4,1-Triphenyl-3-buten-1-one: ^{1}H NMR ($CDCl_3$) δ 8.2–6.9 (m, 15), 6.41 (t, J = 7 Hz, 1), 3.8 (d, J = 7 Hz, 2); GCMS, m/e (relative intensity) 298 (M$^+$, 2), 193 (25), 105 (100). 1,1,3-Triphenylpropene: GCMS, m/e (relative intensity) 270 (M$^+$, 19), 192 (100), 179 (49), 178 (49), 115 (65), 91 (71). 4,4-Dimethyl-1,1-diphenyl-1-pentene: GCMS, m/e (relative intensity) 250 (M$^+$, 10), 193 (89), 115 (100), 91 (40), 57 (56). ((*E*)-3,3-Dimethyl-1-butenyl)cyclohexane: GCMS, m/e (relative intensity) 166 (M$^+$, 12), 83 (39), 82 (100), 67 (47), 55 (70). (2-Methyl-1-propenyl)-cyclohexane: GCMS, m/e (relative intensity) 138 (M$^+$, 28), 123 (29), 95 (61), 81 (65), 67 (100), 55 (71). (*E*)-1-Chloro-3,3-dimethyl-1-butene: ^{1}H NMR ($CDCl_3$) δ 5.9 (s, 2), 1.05 (s, 9); GCMS, m/e (relative intensity) 118 (M$^+$, 10), 103 (44), 83 (100), 67 (52). ((*E*)-2-Chloroethenyl)cyclohexane: ^{1}H NMR ($CDCl_3$) δ 6.25–5.40 (m, 2), 2.7–0.5 (m, 11); IR (neat) 2920 (m), 2850 (s), 1620 (m), 1442 (s), 930 (s), 812 (s), 728 (s) cm^{-1}; GCMS, m/e (relative intensity) 144 (M$^+$, 15), 109 (26), 82 (64), 67 (100). ((*Z*)-2-Chloroethenyl)cyclohexane: ^{1}H NMR ($CDCl_3$) δ 6.01–5.42 (m, 2), 2.8–0.7 (m, 11); IR (neat) 2490 (s), 2870 (s), 1637 (m), 1458 (s), 1345 (m), 962 (m), 893 (m), 810 (w), 743 (s), 715 (s) cm^{-1}; GCMS, m/e (relative intensity) 144 (M$^+$, 15), 109 (31), 82 (74), 67 (100). 3-Cyclopentyl-1-propenylbenzene: ^{1}H NMR ($CDCl_3$) δ 7.55–7.2 (m, 5), 6.30–6.05 (m, 2), 2.25–1.10 (m, 11); GCMS, m/e (relative intensity) 186 (M$^+$, 14), 117 (98), 104 (100), 91 (25). 1-Phenyl-1-hexene: GCMS, m/e (relative intensity) 160 (M$^+$, 25), 117 (100), 104 (68). Methyl (*E*)-3-cyclohexylpropenoate: ^{1}H NMR ($CDCl_3$) δ 6.95 (dd, J_{trans} = 16.8 Hz, $J_{1,2}$ = 6 Hz, 1), 5.75 (dd, J_{trans} = 16.8 Hz, $J_{1,3}$ = 1.5 Hz, 1), 3.7 (s, 3), 2.9–0.8 (m, 11); GCMS, m/e (relative intensity) 168 (M$^+$, 31), 94 (45), 87 (82), 79 (61), 67 (99), 55 (100). Methyl (*Z*)-3-cyclohexylpropenoate: GCMS, m/e (relative intensity) 168 (M$^+$, 53), 94 (54), 87 (78), 79 (57), 67 (98), 55 (100). Methyl (*E*)-4,4-dimethyl-2-pentenoate: ^{1}H NMR ($CDCl_3$) δ 6.98 (d, J = 15.9 Hz, 1), 5.74 (d, J = 15.9 Hz, 1), 3.78 (s, 3), 1.08 (s, 9); GCMS, m/e (relative intensity) 142 (M$^+$, 20), 127 (55), 111 (41), 95 (56), 83 (100), 67 (56), 55 (67), 41 (71). (*E*)-3,3-Dimethyl-1-butenyl phenyl sulfone: ^{1}H NMR ($CDCl_3$) δ 7.92–7.90 (m, 2), 7.74–7.50 (m, 3), 6.99 (d, J = 15.6 Hz, 1), 6.21 (d, J = 15.6 Hz, 1), 1.09 (s, 9). 1-Phenyl-1-hexyne: ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 5), 2.65–0.6 (m, 9); GCMS, m/e (relative intensity) 158 (M$^+$, 41), 143 (58), 129 (69), 128 (47), 115 (100). (Phenylethynyl)-cyclohexane: ^{1}H NMR ($CDCl_3$) δ 7.70–7.05 (m, 5), 1.76–0.80 (m, 11); GCMS, m/e (relative intensity) 184 (M$^+$, 69), 156 (29), 155 (59), 142 (42), 141 (100), 130 (35), 129 (28), 128 (50), 115 (47), 102 (31). 3,3-Dimethyl-1-phenyl-1-butyne: ^{1}H NMR ($CDCl_3$) δ 7.40–7.33 (m, 2), 7.28–7.21 (m, 3), 1.31 (s, 9); GCMS, m/e (relative intensity) 158 (M$^+$, 38), 143 (100), 128 (42). Diethyl (phenylethynyl)phosphonate: ^{1}H NMR ($CDCl_3$) δ 7.7–7.1 (m, 5), 4.6–3.8 (m, 4), 1.4 (t, 6); GCMS, m/e (relative intensity) 238 (M$^+$, 11), 210 (16), 195 (15), 165 (21), 129 (24), 128 (29), 102 (100).

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Registry No. (*E*)-PhCH=CHHgCl, 36525-03-8; Ph_2C=CHHgBr, 67341-86-0; Ph_2C=CHHgCl, 24522-19-8; (*E*)-

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Synthesis of (Aminocarbene)chromium(0) Complexes by the Reaction of $Na_2Cr(CO)_5$ with Amides in the Presence of Trimethylsilyl Chloride

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Addition of trimethylsilyl chloride to a mixture of $Na_2Cr(CO)_5$ and a variety of tertiary amides produced (aminocarbene)pentacarbonylchromium(0) complexes in fair to excellent yield. The procedure developed is a rapid, convenient, one-pot process and permits the synthesis of carbene complexes not readily available by other synthetic routes. These carbene complexes have potential application in the synthesis of β-lactams and α-amino acids.

Introduction

Heteroatom-stabilized ("Fischer") chromium carbene complexes[1] are being extensively developed as reagents for use in organic synthesis.[2] Most extensively studied are the thermal reactions of methoxyaryl- and methoxyvinylcarbenes with alkynes to produce hydroquinone,[3] heteroaromatic,[4] or cyclic ketone[5] derivatives, while similar thermal reactions with amino arylcarbenes produce indenones or aminoindenes.[6] Thermal reactions of methoxycarbene complexes with isonitriles produces cyclic bis imines.[7] In contrast, photolytic reaction of methoxy[8] and aminocarbene[9] complexes with imines produce β-lactams and with nucleophiles produce α-amino acid derivatives.[10]

Methoxycarbene complexes are normally synthesized by the original Fischer procedure, involving the reaction of

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