Table III. Effect of Reaction Conditions on the Cocyclizations of 1a

$$\mathbf{1a} + (CH_3)_3SiC{\equiv}CSi(CH_3)_3 \xrightarrow{CpCo(L)_2,\ h\nu} \mathbf{2a} + \mathbf{3a} + \mathbf{4a}$$

L	$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, equiv	temp, °C	yield, %		
C_2H_4	solvent	134	37	0	58
CO	solvent	134	25	0	49
CO	15	110	10	0	17
C_2H_4	solvent	25	74	18	0
CO	solvent	25	51	13	0
CO	5	25	38	10	0
C_2H_4	5	0	40	13	0
C_2H_4	5	−78	35	0	0

confirmed by X-ray analysis.

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Supplementary Material Available: Mp, bp, spectral, and analytical data on 25 new compounds, general experimental procedures employing $CpCoL_2$ (L = CO or $CH_2{=}CH_2$), and optimized procedure for the preparation of **2a** and **3a** (12 pages). Ordering information is given on any current masthead page.

George S. Sheppard, K. Peter C. Vollhardt*

Department of Chemistry
University of California, Berkeley
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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Free Radical Reactions of Organomercury Halides with Alkenes and Alkynes[1]

Summary: Substituted acetylenes or electronegatively monosubstituted ethylenes react with *t*-BuHgCl in photostimulated free radical chain processes in PhH or Me_2SO to form $R^1C(t\text{-}Bu){=}C(HgCl)R^2$ (R^1, R^2 = H, Ph; H, COMe; EtO_2C, Ph; EtO_2C, EtO_2C) or $t\text{-}BuCH_2CH(HgCl)E$ (E = $(EtO)_2PO$, $PhSO_2$, $p\text{-}O_2NC_6H_4$, $SiPh_3$). Reduction by BH_4^- or cleavage by I_2 forms $R^1C(t\text{-}Bu){=}CHR^2$ and $t\text{-}BuCH_2CH_2E$ or $R^1C(t\text{-}Bu){=}C(I)R^2$ and $t\text{-}BuCH_2CH(I)E$.

Sir: We have previously reported the photostimulated free radical chain reaction of alylmercury halides with substituted alkenes[2] and alkynes[3] occurring by an addition–elimination mechanism with retention of configuration for Q = I or HgCl (eq 1).[4,5] Alkenes that are effective traps

$$RHgCl + R'CH{=}CHQ \xrightarrow[\substack{Q\,=\,Bu_3Sn,\ PhS,\\ PhSO_2,\ I,\ HgCl\\ R'\,=\,Ph,\ Cl,\ MeO_2C}]{h\nu} R'CH{=}CHR \qquad (1)$$

for alkyl radicals but that are not susceptible to such addition–elimination processes can also react cleanly with RHgCl by chain or nonchain processes. Chain reactions occur when the radical formed by addition of R$^\bullet$ to the alkene is either a good donor (D$^\bullet$) or acceptor (A$^\bullet$) (reactions 2 and 3).

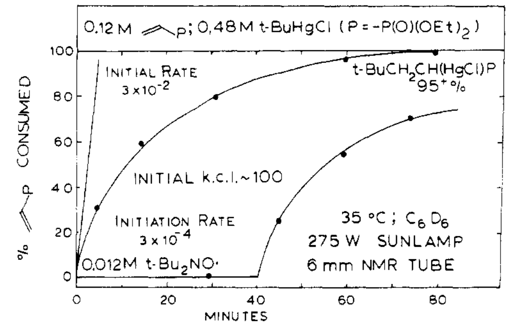

Figure 1. Measurement of initial kinetic chain length in PhH at 35–40 °C determined by ^1H NMR. In Me_2SO the rates are ~20% faster with the same inhibition period. Reactions in Me_2SO are considerably faster than in PhH at the latter stages of the reaction; the build-up of the terminating HgCl may be more important in PhH than in Me_2SO.

Table I. Reaction Products from $R^1C{\equiv}CR^2$[a]

R^1, R^2	kinetic chain length[b]	products (%)[c] *t*-BuC-$(R^1){=}$C-(R^2)H	 *t*-BuC-$(R^1){=}$C-(I)R^2
H, Ph	15 (Me_2SO); 10 (PhH)	63	41
H, COMe	25 (Me_2SO); 15 (PhH)	90[d]	85
EtO_2C, Ph		72	94
EtO_2C, CO_2Et		97	96

[a] Reaction of 3 equiv of *t*-BuHgCl for 1–2 h with 0.2–0.4 mmol of alkyne in 2.5 mL of Me_2SO or PhH with irradiation from a 275-W sunlamp at 35–40 °C. [b] $[PhC{\equiv}CH]_0$ = 0.166 M; $[MeC(O)C{\equiv}CH]_0$ = 0.137 M. [c] Mixtures of *E* and *Z* isomers.[9] [d] $t\text{-}BuCH{=}CHCH(OH)CH_3$ (70%), $t\text{-}BuCH{=}CHCOCH_3$ (20%).

$$RHgCl + D\cdot \rightarrow D^+ + R\cdot + Hg^0 + Cl^- \qquad (2)$$

$$RHgCl + A\cdot \rightarrow AHgCl + R\cdot \qquad (3)$$

Competition reactions of excesses of *t*-BuHgCl and *n*-BuHgCl with $Me_2C{=}NO_2^-$, $PhCH{=}CHSnBu_3$, PhSSPh, or $CH_2{=}CHP(O)(OEt)_2$ (VP) give a 3°/1° relative reactivity of >200, >200, >300, and >1000, respectively, where the chain-carrying radicals are either D$^\bullet$ ($RCMe_2NO_2^{\bullet-}$, $Bu_3Sn^\bullet$) or A$^\bullet$ ($PhS^\bullet$, $RCH_2\dot{C}HP(O)(OEt)_2$) and kinetic chain lengths measured by $(t\text{-}Bu)_2NO\cdot$ inhibition are 50, 40, 400, and 116, respectively. The high 3°/1° reactivity requires that reactions 2 and 3 are one-step processes.[6] *Such high 3°/1° reactivities appear to be characteristics of dissociative electron transfer processes*, or perhaps, in the case of reaction 3, of a process with extensive electron shift in the transition state.[7]

Photostimulated reactions of RHgCl with VP, $CH_2{=}CHSO_2Ph$, or $CH_2{=}CHC_6H_4NO_2\text{-}p$ in PhH or Me_2SO proceed by chain reactions in which the consumption of the alkene is drastically retarded by the presence of $(t\text{-}Bu)_2NO^\bullet$ (Figure 1). An initial kinetic chain length (kcl) of 95 (C_6D_6) and 116 ($Me_2SO\text{-}d_6$) is calculated for reaction 4 under the concentrations and conditions employed. In

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(1) Electron Transfer Processes. 41.

(2) Russell, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.* **1984**, *106*, 4622.

(3) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1986**, *27*, 3479.

(4) Russell, G. A. Ngoviwatchai, P. *Tetrahedron lett.* **1985**, *26*, 4975.

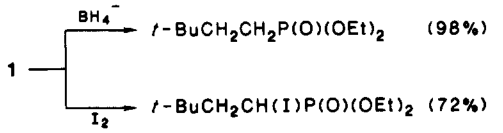
(5) Similar substitutions are observed for allyl iodides, sulfides, sulfones, or stannanes and for alkenyloxystannnes.

(6) The reaction of RHgCl with BH_4^- involves the intermediates RHgH, RHg·, R· (Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239). Relative reactivities of *t*-BuHgH and *n*-BuHgH toward the adduct radicals from reactive alkenes such as $CH_2{=}C(Cl)CN$ or $CH_2{=}CHCO_2Et$ are ~1:1.

(7) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

$$t\text{-BuHgCl (4 equiv)} + \text{VP} \xrightarrow{h\nu} \underset{\mathbf{1}}{t\text{-BuCH}_2\text{CH(HgCl)P(O)(OEt)}_2} \quad (4)$$

reaction 4, the intermediate t-BuCH$_2\dot{\text{C}}$HP(O)(OEt)$_2$ is an acceptor radical which readily enters into reaction 3 with t-BuHgCl with $k > 10^5$ M^{-1} s^{-1}.[8] The resulting **1** can be reduced by BH$_4^-$ or cleaved by I$_2$ in high overall yields



(based on starting alkene). For CH$_2$=CHSO$_2$Ph in Me$_2$SO, a kcl of 108 ([CH$_2$=CHSO$_2$Ph]$_0$ = 0.19 M) was measured at 35–40 °C, and yields of t-BuCH$_2$CH$_2$SO$_2$Ph and t-BuCH$_2$CH(I)SO$_2$Ph of 87% and 75% were obtained. In a similar fashion, CH$_2$=CHSiPh$_3$ yielded t-BuCH$_2$H$_2$SiPh$_3$ (68%) and i-PrCH$_2$CH$_2$SiPh$_3$ (85%) after BH$_4^-$ reduction (kcl = 14 at 0.12 M CH$_2$=CHSiPh$_3$ in Me$_2$SO).

Vinyl radicals also react as A$^\bullet$ in reaction 3. Thus, reaction 5 has been observed to occur by a chain process to

$$\text{R}^1\text{C}\equiv\text{CR}^2 + t\text{-BuHgCl} \xrightarrow{h\nu} \underset{\mathbf{2}}{t\text{-BuC(R}^1\text{)=C(HgCl)R}^2} \quad (5)$$

yield the vinylmercurial (**2**) which can be reduced by NaBH$_4$ or cleaved by I$_2$ (Table I) to form a mixture of the appropriate E and Z isomers.[9]

When addition of R$^\bullet$ to an alkene yields a donor radical, reaction 2 can occur. Thus, in Me$_2$SO, CH$_2$=C(C$_6$H$_4$OMe-p)$_2$ (0.04 M) reacts with t-BuHgCl (0.12 M) in a photostimulated process with an initial kcl of 18 to form t-BuCH=C(C$_6$H$_4$OMe)$_2$ (85%) with only traces of t-BuCH$_2$CH(C$_6$H$_4$OMe)$_2$.[10]

Reaction of alkenes with RHgCl and BH$_4^-$ leads to reaction 6,[11] provided the alkene can compete effectively with

$$\text{RHgCl} + \text{CH}_2\text{=CHE} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{NaBH}_4} \text{RCH}_2\text{CH}_2\text{E} + \text{Hg}^0 \quad (6)$$

RHgH in the trapping of R$^\bullet$.[6] Some relative reactivities of pertinent alkenes and alkynes in reaction 6 at 25 °C are CH$_2$=C(Cl)CN (52); CH$_2$=CHCN (3.8); CH$_2$=CHSO$_2$Ph (2.5); CH$_2$=CHCO$_2$Et (1.0); EtO$_2$CC≡CCO$_2$Et (0.9); VP (0.53);[12] CH$_2$=CPh$_2$ (0.21); HC≡CCO$_2$Et (0.19); CH$_2$=CHPh (0.15); CH$_2$=C(C$_6$H$_4$OMe-p)$_2$ (0.11);[13] CH$_2$=CCl$_2$ (0.06); CH$_2$=CHSPh (0.03); HC≡CPh (0.02); EtO$_2$CC≡CPh (0.014); CH$_2$=CHSOPh (0.005); CH$_2$=CHOEt, CH$_2$=CHSiMe$_3$, CH$_2$=CHSnBu$_3$, CH$_2$=CHCMe$_3$, CH$_2$=CHNH$_2$, norbornene (all <0.005). When applied to a reactive alkene such as VP, both reactions 6 and 4 (followed by BH$_4^-$) give high yields of RCH$_2$CH$_2$P(O)(OEt)$_2$. However, when applied to less reactive substrates such as PhC≡CH or norbornene, the Giese reaction gives low yield (8–10% for PhC≡CH, 0% for norbornene) because R$^\bullet$ is preferentially trapped by RHgH.[6] In such cases, the two-step process involving addition of RHgCl to the double or triple bond followed by NaBH$_4$ reduction is preferable.

Alkenes which lead to adduct radicals without strong polar character can yield products of nonchain reactions. Thus, CH$_2$=CPh$_2$ readily traps t-Bu$^\bullet$ from the photolysis of t-BuHgCl, but the resulting t-BuCH$_2\dot{\text{C}}$Ph$_2$ mainly disproportionate to form t-BuCH$_2$CHPh$_2$ and t-BuCH=CPh$_2$ (~1:1 ratio).[10] Here, trapping of t-BuCH$_2\dot{\text{C}}$Ph$_2$ by HgCl (from the photolysis of t-BuHgCl) would undoubtedly be reversible and not lead to a stable organometallic. On the other hand, excess norbornene (4 equiv in Me$_2$SO) forms an adduct radical with t-Bu$^\bullet$ which is cleanly trapped by HgCl to form a new organomercurial (isolated in 50% yield after 24 h irradiation) which can be reduced by NaBH$_4$ to *exo*-2-*tert*-butylnorbornane.[14] The rate of consumption of norbornene determined by ^{1}H NMR is equal to the rate of the photochemical dissociation of t-BuHgCl as measured by the "inhibition" period observed in the presence of (t-Bu)$_2$NO$^\bullet$.

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Glen A. Russell,* Wan Jiang
Shui Sheng Hu, Rajive K. Khanna
Department of Chemistry
Iowa State University
Ames, Iowa 50011

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[8] Based on k_p for polymerization of VP of 1 × 10^2 M^{-1} s^{-1} at 40 °C (Levin, Y. A.; Breus, A. A.; Ivanov, B. E. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 154); a 3-fold excess of t-BuHgCl eliminates products derived from attack of t-BuCH$_2\dot{\text{C}}$HP(O)(OEt)$_2$ upon VP. The chain transfer rate constant of VP radical with CCl$_4$ is >3 × 10^2 M^{-1} s^{-1} (Raynal, S. *Phosphorous Sulfur* **1981**, *11*, 287), but in competition with 10 M CCl$_4$, 0.1 M t-BuHgCl is also an effective trap for RCH$_2\dot{\text{C}}$HP(O)(OEt)$_2$. Reaction 4 in CCl$_4$ solution yields Cl$_3$CCH$_2$CH(HgCl)P(O)(OEt)$_2$ in 52% (based on the yield of Cl$_3$CCH$_2$CH$_2$P(O)(OEt)$_2$ after BH$_4^-$ reduction).

[9] For example, t-BuCH=CHPh (Table I) is formed with Z/E = 79/21, the stereoselectivity being controlled by attack of RHgH upon linear t-BuCH=$\dot{\text{C}}$Ph. Assignment is based upon the known decarboxylation (Cu$_2$O, quinoline) of t-BuC(CO$_2$H)=CHPh to predominantly (Z)-t-BuCH=CHPh (Buckles, R. E.; Wheeler, N. G. *Organic Synthesis*; Wiley: New York, 1983; Collect. Vol. 4, p 857). From the chemical shift of the vinyl H (δ 7.1 (83%), 6.55 (17%)), the major isomer of t-BuC(CO$_2$Et)=CHPh (Table I) can be assigned as E (i.e., t-Bu and H are trans). For t-BuC(CO$_2$Et)=CHCO$_2$Et, the chemical shifts of δ 5.81 (62%) and 6.18 (38%) allow the assignment of the Z isomer (t-Bu and H are cis) as the major product.

[10] Russell, G. A.; Khanna, R. K.; Guo, D. *J. Chem. Soc., Chem. Commun.* **1986**, 632.

[11] Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753; **1985**, *24*, 553. Giese, B.; Horlen, H. *Tetrahedron* **1985**, *41*, 4025. Giese, B.; Gröninger, K. *Tetrahedron Lett.* **1984**, *25*, 2473.

[12] Attack of t-Bu$^\bullet$ upon VP has a rate constant of 5.9 × 10^4 M^{-1} s^{-1} at 233 K: Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1981**, 161.

[13] Diarylmethyl radicals apparently react slowly with RHgH. Thus, in reaction 6, CH$_2$=C(C$_6$H$_4$OMe)$_2$ yields exclusively t-BuCH=C(C$_6$H$_4$OMe)$_2$ and CH$_2$=C(Ph)$_2$ yields either t-BuCH$_2$CHPh$_2$ or a mixture of t-BuCH$_2$CHPh$_2$ and t-BuCH=CPh$_2$ at low RHgH concentration.

[14] ^{1}H NMR evidence (300 MHz) favors the *exo*-2-*tert*-butyl-*exo*-3-(chloromercurio)norborane structure with H(3),H(4) δ 2.28–2.32; H(2) δ 1.64 (d), $J_{2,3}$ = 7.44 Hz; H(1) δ 2.52–2.54 (q); H(*exo*-t-Bu) δ 0.89.

Carboxylative Coupling of Propargylic Alcohols with Allyl Chloride

Summary: Palladium-mediated reaction of lithium 2-alkynyl carbonates with allyl chloride affords cyclic carbonates whose alkaline hydrolysis gives keto alcohols in good yields. The combination of the above procedure with the formation of lithium 2-alkynolates from lithioalkynes and carbonyl compounds provides novel use of lithioalkynes as acyl anion equivalents in the reaction of carbonyl compounds.

Sir: Insertion of carbon dioxide into oxiranes[1-7] or 2-

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[1] Matsuda, H.; Ninagawa, A.; Nomura, R.; Tsuchida, T. *Chem. Lett.* **1979**, 573.

[2] Matsuda, H.; Ninagawa, A.; Nomura, R. *Chem. Lett.* **1979**, 1261.

[3] Nomura, R.; Ninagawa, A.; Matsuda, H. *J. Org. Chem.* **1980**, *45*, 3735.