Reductive Alkylation of Electronegatively-Substituted Alkenes by Alkylmercury Halides[1]

Glen A. Russell,* Bing Zhi Shi, Wan Jiang, Shuiesheng Hu, Byeong H. Kim, and Woonphil Baik

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received October 11, 1994[⊗]

Abstract: Photolysis of alkylmercury halides in the presence of electronegatively-substituted 1-alkenes yields adduct radicals [$RCH_2CH(EWG)^•$] that in some cases react with RHgX to form $RCH_2CH(HgX)(EWG)$, e.g., EWG = $(EtO)_2PO$ or $PhSO_2$. When the EWG is carbonyl or cyano, the resonance stabilized adduct radicals fail to react with the alkyl mercury halide. In these cases photolysis with RHgCl/KI in Me_2SO leads to the adduct mercurial via reaction of the adduct radicals with $RHgI_2^-$. The reactions of tertiary-enolyl adduct radicals are inefficient with RHgX/KI, and disproportionation of the adduct radicals is the major reaction pathway. For secondary- or tertiary-adduct radicals the reductive alkylation products are formed in excellent yield by reaction with RHgCl and silyl hydrides in Me_2SO solution in a process postulated to involve RHgH as an intermediate. The relative reactivities of a number of α,β-unsaturated systems toward *t*-Bu• have been measured by competitive techniques. The results demonstrate a high reactivity of *s-cis* enones relative to the *s-trans* conformers.

Introduction

Terminal alkenes with electronegative substituents are readily attacked by nucleophilic alkyl radicals, e.g., *t*-Bu•. Reactivity is controlled mainly by the SOMO−LUMO interactions as visualized in the polar transition state structure **1**. To convert the adduct radical (formed regioselectively via **1**) to the alkylation product in a chain reaction we have examined a

$$R^+\,[CH_2{=}CH{-}EWG]^{\bullet\,-}$$
1

number of routes starting from alkylmercury halides. In some cases [EWG = $PhSO_2$, $(EtO)_2P(O)$] the electron-accepting adduct radical will react with RHgX to continue a chain reaction, Scheme 1.[2] The addition product **2** can be converted to $RCH_2CH_2(EWG)$ by reduction with BH_4^- or by protonolysis.

Scheme 1

$$RHgX \xrightarrow{h\nu} R^• + HgX^• \xrightarrow{RHgX} R^• + HgX_2 + Hg^0 \quad (1)$$

$$R^• + CH_2{=}CH(EWG) \rightarrow RCH_2CH(EWG)^• \quad (2)$$

$$RCH_2CH(EWG)^• + RHgX \rightarrow \underset{\mathbf{2}}{RCH_2CH(HgX)(EWG)} + R^• \quad (3)$$

Electron-accepting heteroatom-centered radicals or •HgX are known to displace R• from RHgX in reactions whose rates increase dramatically from R = Bu to *i*-Pr to *t*-Bu or $PhCH_2$.[2,3] However, when EWG is cyano or carbonyl, reaction 3 with X = Cl or I is ineffective and cannot compete with the addition of the adduct radical to the substrate or disproportionation of the adduct radical. To overcome this reactivity problem we have developed iodide promoted reactions where the intermediate mercury species reacts readily with secondary α-cyano or α-keto radicals, reaction 4 (Z = alkyl, aryl, or NH_2).[4−7] However, reaction 4 occurs inefficiently with tertiary-enolyl

$$RCH_2CHCOZ^• \xrightarrow{RHgX/I^-} RCH_2CH(COZ)HgI \xrightarrow[\text{or } BH_4^-]{H^+} RCH_2CH_2COZ \quad (4)$$

radicals. In these cases conversion of the adduct radicals to the reductive alkylation product can be achieved by hydrogen atom transfer from Bu_3SnH or RHgH formed by the reaction of RHgCl with BH_4^- or Bu_3SnH.[8] Because of the high reactivity of Bu_3SnH or RHgH, a serious side reaction is the trapping of R• to form RH. We have developed an alternative route to RHgH from the reaction of silyl hydrides with RHgX in Me_2SO solution, reaction 5.[9] Because of the low steady

$$\equiv SiH + RHgX \underset{}{\overset{Me_2SO}{\rightleftharpoons}} \equiv SiX + RHgH \quad (5)$$

concentration of the RHgH formed in this manner, hydrogen atom transfer to R• is minimized, particularly when the alkene has a low reactivity toward R•. Use of the three different procedures (*t*-BuHgCl/*hν*; *t*-BuHgCl/KI/*hν*; *t*-BuHgCl/≡SiH) allows an extensive series of relative reactivities toward *t*-Bu• to be measured in Me_2SO by competitive techniques.

Results and Discussion

Photostimulated Reactions of RHgX. Extended photolysis of 2−4 equiv of RHgCl or RHgI with $CH_2{=}CHSO_2Ph$ or

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1995.

(1) Electron Transfer Processes. 57.

(2) Russell, G. A.; Jiang, W.; Hu, S. S.; Khanna, R. K. *J. Org. Chem.* **1986**, *51*, 5498.

(3) Russell, G. A. *Acc. Chem. Res.* **1989**, *22*, 1.

(4) Russell, G. A.; Hu, S.; Herron, S.; Baik, W.; Ngovwatchai, P.; Jiang, W.; Nebgen, M.; Wu, Y.-W. *J. Phys. Org. Chem.* **1988**, *1*, 299.

(5) Russell, G. A.; Yao, C.-F.; Rajaratnam, R.; Kim, B. H. *J. Am. Chem. Soc.* **1991**, *113*, 373.

(6) Russell, G. A.; Baik, W.; Ngovwatchai, P.; Kim, B. H. *Acta Chem. Scand.* **1990**, *44*, 170.

(7) (a) Russell, G. A.; Kim, B. H. *Tetrahedron Lett.* **1990**, *31*, 6273. (b) Russell, G. A.; Kim, B. H. *Synlett* **1990**, 87.

(8) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon: Oxford, 1986.

(9) Russell, G. A.; Shi, B. Z. *Synlett.* **1993**, 701.

0002-7863/95/1517-3952$09.00/0

Table 1. Photostimulated reactions of RHgCl with CH_2=CH(EWG)

EWG	R (equiv)	conditions[a]	products (%)[b] 4[c]	products (%)[b] $RCH_2CH(I)(EWG)$[d]
$(EtO)_2P(O)$	*t*-Bu (4)	PhH, 24 h	98, 88I	88, 72I
$(EtO)_2P(O)$	*t*-Bu (4)	Me_2SO, NaI (6 equiv), 20 min	75	
$(EtO)_2P(O)$	*t*-Bu (4)	Me_2SO, NaI (6 equiv), 24 h	**4a** (17%), **5**a (24%)[e]	
$(EtO)_2P(O)$	*t*-Bu (2)	Me_2SO (60%)-MeOH (40%), NaI (2 equiv), 3 h	98[f]	
$(EtO)_2P(O)$	*t*-Bu (1)	Me_2SO (60%)-MeOH (40%), Me_4NI (3 equiv), 2 h	**4a** (78%), **5a** (9%)[f]	
$(EtO)_2P(O)$	*t*-Bu (4)	CCl_4, 24 h	52I[g]	45I[g]
$(EtO)_2P(O)$	*i*-Pr (4)	PhH, 24 h	52, 44I	48, 40I
$(EtO)_2P(O)$	*c*-C_6H_{11} (4)	PhH (80%)-Me_2SO (20%), 24 h	65	41
$(EtO)_2P(O)$	Bu (5)	PhH (80%)-Me_2SO (20%), 24 h	32, 26I	
$PhSO_2$	*t*-Bu (2)	PhH, 3 h	*t*-$BuCH_2CH(SO_2Ph)HgCl$ (44%)[h]	
$PhSO_2$	*t*-Bu (3)	PhH, 24 h	96, 87I	81, 75I
$PhSO_2$	*t*-Bu (2)	Me_2SO (60%)-MeOH (40%), NaI (4 equiv), 5 h	95, 89I[f]	
$PhSO_2$	*i*-Pr (3)	PhH, 24 h	70, 62I	46, 38I
$PhSO_2$	*c*-C_6H_{11} (3)	PhH (80%)-Me_2SO (20%), 24 h	69	37
$PhSO_2$	Bu (5)	PhH (80%)-Me_2SO (20%), 24 h	60, 56I	
Ph_3Si	*t*-Bu (3)[i,j]	Me_2SO, 20 h	*t*-$BuCH_2CH(SiPh_3)HgI$ (58%)[h]	
Ph_3Si	*t*-Bu (3)[i]	Me_2SO (80%)-PhH (20%), 24 h	**4c** (90%); **5c** (8%)[c]	

[a] Photolysis at 350 nm in a Rayonet Photoreactor at 40–45 °C; 0.05–0.1 M substrate. [b] By GC with internal standard; I, isolated by column chromatography. [c] After reaction with $NaBH_4/H_2O$. [d] After reaction with I_2. [e] Workup with either $NaBH_4/H_2O$ or aqueous $Na_2S_2O_3$; ~30% of the dimer of **2a** was formed. [f] Workup with aqueous $Na_2S_2O_3$. [g] $CCl_3CH_2CH_2P(O)(OEt)_2$ and $CCl_3CH_2CH(I)P(O)(OEt)_2$. [h] Isolated after workup with H_2O. [i] 0.12 M. [j] *t*-BuHgI with fluorescent sunlamp irradiation for 20 h.

CH_2=$CHP(O)(OEt)_2$ in Me_2SO for 24 h with irradiation at 350 nm leads to an ~1:1 mixture of **4** and **5** from disproportionation of the adduct radical **3**, reaction 6, a major chain termination step of Scheme 1. The dimer of **3a** is also a significant product upon extended photolysis. However, **2** is apparently first formed via Scheme 1; the mercurials are photolabile in Me_2SO and

$$\underset{\mathbf{3}}{2RCH_2CH(Q)^\bullet} \rightarrow \underset{\mathbf{4}}{RCH_2CH_2(Q)} + \underset{\mathbf{5}}{RCH{=}CH(Q)} \quad (6)$$

a, Q = $(EtO)_2P(O)$
b, Q = $PhSO_2$
c, Q = Ph_3Si
d, Q = PhS

eventually form the disproportionation and dimerization products of **3**. In PhH or PhH (80%)–Me_2SO (20%) the adduct mercurials undergo little photodecomposition. The mercurials can now be detected by ^1H NMR in C_6D_6 or isolated upon aqueous workup. Treatment of the products formed in PhH with $NaBH_4$ leads to the formation of **4a** or **4b** with R = *t*-Bu in 96–98% yield, while treatment with I_2 forms *t*-$BuCH_2CH(I)SO_2Ph$ or *t*-$BuCH_2CH(I)P(O)(OEt)_2$ in high yield, Table 1. Under similar conditions with 3 equiv of RHgCl and $NaBH_4$ workup, CH_2=$CHSiPh_3$ forms **4c** in 85–90% yield with R = *t*-Bu or *i*-Pr but now 8–10% of **5c** is also formed ($[RHgCl]_0$ = 0.12 M, irradiation at 350 nm). At lower concentrations of $[RHgCl]_0$ reaction 3 is not as effective, and reaction 6 becomes more important. Thus, with 0.04 M $[t\text{-}BuHgCl]_o$, $NaBH_4$ workup gives **4c** (65%) and **5c** (31%). The mercurial *t*-$BuCH_2CH(SiPh_3)HgI$ can be isolated upon sunlamp photolysis with *t*-BuHgI in Me_2SO-d_6 for 20 h, and little decomposition of this mercurial is observed under these conditions. The isolated mercurial can be reduced by $NaBH_4$ to **4c** (58%) accompanied by only 3% of **5c**. Irrespective of solvent or workup procedure, CH_2=CHSPh gives a mixture of **4d** and **5d** with considerable amounts of $[t\text{-}BuCH_2CH(SPh)]_2$. In the case of **3d**, reaction 3 occurs slowly, if at all, and the products result mainly from bimolecular radical reactions. For reaction 3 to occur readily the adduct radical **3** must be easily reduced suggesting a transition state for reaction 3 with considerable ionic character, e.g., **6**.

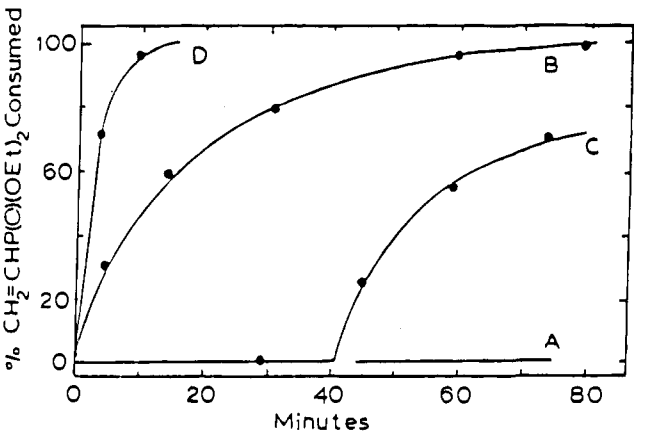


Figure 1. Reactions in Me_2SO of diethyl vinylphosphonate and *tert*-butylmercury chloride (initial concentrations 0.12 and 0.45 M, respectively); A, dark (25 °C); B, sunlamp irradiation, 35 °C; C, sunlamp irradiation in presence of 0.012 M di-*tert*-butyl nitroxide; initial kinetic chain length ~100; D, sunlamp irradiation with 6 equiv of NaI; initial kinetic chain length ~16 (from di-*tert*-butyl nitroxide inhibition). Product after workup with $NaBH_4$ was diethyl 3,3-dimethylbutylphosphonate.

$$RCH_2CH(EWG):^- HgCl^+ R^\bullet$$
6

Evidence for the chain reaction of Scheme 1 in the reactions of *t*-BuHgX with the vinylphosphonate is presented in Figure 1. The reactions with the vinylphosphonate or sulfone do not occur in the dark, while the photostimulated processes are inhibited by $(t\text{-}Bu)_2NO^\bullet$. From the inhibition period in Me_2SO-d_6 an initial kinetic chain length of ~100 is calculated for 0.1 M CH_2=$CHP(O)(OEt)_2$ in the presence of 4 equiv of *t*-BuHgCl at 35 °C. A similar initial kinetic chain length is observed in C_6D_6 and for CH_2=$CHSO_2Ph$ in Me_2SO or PhH. In the presence of 6 equiv of NaI the consumption of the phosphonate is faster (Figure 1), but the reaction occurs with a shorter kinetic chain length. Photolysis of *t*-BuHgCl/KI forms radicals rapidly, possibly via ate-complexes such as *t*-$BuHgI_2^-$ or from $(t\text{-}Bu)_2Hg$.[4] In many cases the iodide-promoted

reactions will occur in the dark from thermal initiation (with kinetic chain lengths >500) and more rapidly in the presence of $(NH_4)_2S_2O_8$.[10]

Some evidence in regard to the rate constant for reaction 3 can be presented. Telomers such as t-$BuCH_2CH[P(O)(OEt)_2]$-$CH_2CH_2P(O)(OEt)_2$ are not observed in reactions with 2 equiv of t-BuHgCl in PhH. Since k_p for vinyl phosphonate polymerization is 1.2×10^2 M^{-1} s^{-1}at 40 °C,[11] it follows that if k_3 is $<1 \times 10^3$ M^{-1} s^{-1}, ~5% of the telomer should be formed from a solution 0.1 M in CH_2=CHP(O)$(OEt)_2$. Photolysis of t-BuHgCl (0.2 M) with CH_2=CHP(O)$(OEt)_2$ (0.05 M) in 10 M CCl_4 forms $CCl_3CH_2CH[P(O)(OEt)_2]HgCl$ as evidenced by the conversion to $CCl_3CH_2CH_2P(O)(OEt)_2$ (52%) or CCl_3CH_2CH-(I)P(O)$(OEt)_2$ (48%) upon workup with $NaBH_4$ or I_2. The adduct $CCl_3CH_2CH(Cl)P(O)(OEt)_2$ is not detected (<5%) although with $BrCCl_3$ (2 M) in Me_2SO only the adduct CCl_3-$CH_2CH(Br)P(O)(OEt)_2$ is formed (reflecting the fact that $BrCCl_3$ is ~5000 more reactive than CCl_4 in halogen atom transfer reactions). From the chain transfer constant for the polymer radical of the vinylphosphonate with CCl_4, which has been measured as $>3k_p$ at 130 °C,[12] it follows that if k_3 for CCl_3-$CH_2CHP(O)(OEt)_2$• reacting with t-BuHgCl is $<1.5 \times 10^5$ M^{-1} s^{-1}, more than 5% of the CCl_4 adduct should have been formed while to form >90% of the adduct with 2 M $BrCCl_3$ limits k_3 to $<1.5 \times 10^6$ M^{-1} s^{-1}. Reaction 3 with t-BuHgCl and EWG = P(O)$(OEt)_2$ thus occurs with a rate constant of 10^5-10^6 M^{-1} s^{-1}.

With CH_2=CHCOCH$_3$, CH_2=CHCOPh, CH_2=CHCO$_2$Et or CH_2=CHCN only low yields of the reductive alkylation products are formed in PhH or Me_2SO upon photolysis with t-BuHgCl or t-BuHgI. For delocalized adduct enolyl radicals, reaction 3 cannot compete effectively with the addition of the adduct radical to the substrate or with radical−radical interactions such as reaction 6.

Reductive Alkylations with t-BuHgX/M^+I^-. Addition of iodide salts to t-BuHgCl in Me_2SO forms t-BuHgI and ate-complexes such as t-$BuHgI_2^-$.[4] Comproportionation to yield $(t\text{-Bu})_2Hg$ is also a possibility. The yields of the reductive alkylation products are often dramatically improved in the presence of I^- because of a faster initiation processes,[4] and a more rapid conversion of the adduct radical to the mercurial **2**. Thus, photolysis of t-BuHgCl (1 equiv) with CH_2=CHP(O)$(OEt)_2$ in Me_2SO (60%)−MeOH (40%) for 2 h with acidic workup forms **4a** (R = t-Bu) in 31% yield. Addition of I^- increases the yield of **4a** to 65% with 2 equiv of NaI and 78% with 3 equiv of Me_4NI. With 1 equiv of t-BuHgI and 2 equiv of NaI the yield of **4a** increases to 86%, while 2 equiv each of t-BuHgCl or t-BuHgI and NaI gives 98% of **4a** after 3 h. In a similar fashion, the yield of **4b** observed in Me_2SO upon photolysis of CH_2=CHSO$_2$Ph at 350 nm in Me_2SO with 1 equiv of t-BuHgCl for 4 h followed by acidic workup increases from 39 to 85% by the addition of 2 equiv of NaI while in Me_2SO (60%)−MeOH (40%) with 2 equiv each of t-BuHgCl or t-BuHgI and NaI the yield of **4b** is 95−98% upon acidic workup after 2−5 h of photolysis.

With α,β-unsaturated carbonyl compounds which form secondary-enolyl radicals the effect of added I^- is even more pronounced, Table 2. With added I^- there is no evidence for telomerization or disproportionation of the adduct radicals and high yields of the reductive alkylation products are observed in Me_2SO solution upon workup with H_2O or aqueous $Na_2S_2O_3$ (to remove unreacted mercurial). For unreactive substrates which add t-Bu• to form secondary-enolyl radicals, e.g., chalcone or uracil, 40−60% yields of the reductive alkylation products can be achieved in Me_2SO by reaction with a mixture of t-BuHgCl/NaI/$(NH_4)_2S_2O_8$ which generates a high flux of t-Bu• as evidenced by the strong CIDNP signals for Me_3CH and Me_2C=CH_2 observed in the absence of any t-Bu• traps.[10] α,β-Unsaturated carbonyls that form β-carbonyl-substituted radicals do not undergo reductive alkylation with t-BuHgCl/KI. Thus, coumarin (which forms mainly the benzylic adduct radical) gives a mixture of products resulting from bimolecular radical reactions.[13]

Table 2. Photostimulated Reactions of t-BuHgCl with α,β-unsaturated carbonyls in Me_2SO in the presence of iodide ion.[a]

	% yield (equiv t-BuHgCl, time)[c]	
tert-butylation product[b]	t-BuHgCl	t-BuHgCl + 2NaI
t-$BuCH_2CH_2CO_2Et$	5 (2, 10 h)[d]	80, 75I (2, 6 h)
t-$BuCH_2CH_2COCH_3$	7 (2, 10 h)	85, 81I (2, 6 h)
t-$BuCH_2CH_2COPh$	29 (4, 18 h)	57 (4, 18 h)
t-$BuCH_2CH_2CONH_2$		83 (1.2, 1 h)[e,f]
t-$BuCH_2CH_2CONHPh$	12 (6, 31 h)	92 (6, 22 h)
3-t-Bu-cyclopentanone		89, 72I (2, 4 h)
3-t-Bu-cyclohexanone	35 (2, 10 h)	85, 73I (2, 6 h)
3-t-Bu-cycloheptanone		69I (2, 5 h)
4-t-Bu-tetrahydra-2H-pyran-2-one		81I (2, 3 h)
6-t-Bu-5,6-dihydrouracil		61 (1.5, 10 h)[e,f]
t-BuCH(Ph)CH_2COPh	<10 (4, 22 H)	50 (8, 24 h)[f]
t-$BuCH(CO_2Et)CH_2CO_2Et$	37 (4, 20 h)	100 (4, 3 h)[g]
t-BuCH(COPh)CH_2COPh	10 (4, 24 h)	76 (4, 24 h)[h]
t-$BuCH(CO_2Et)CH_2COPh$	6 (4, 24 h)	63 (4, 24 h)[i,j]
3-t-Bu-1-Me-2,5-pyrrolidinedione		91 (4, 5 min)[k]
t-$BuCH_2CH(CO_2Et)_2$		90 (4, 4 h)l[l]

[a] Photolysis by a 275 W fluorescent sunlamp at 30−35 °C; workup with aqueous $Na_2S_2O_3$. [b] Substrates were CH_2=CHCO$_2$Et, CH_2=CH-COCH$_3$, CH_2=CHCOPh, CH_2=CHCONH$_2$, CH_2=CHCONHPh, 2-cycloalkenones, 5,6-dihydro-2H-pyran-2-one, uracil, chalcone, ethyl maleate or fumarate, PhCOCH=CHCOPh, PhCOCH=CHCO$_2$Et, N-methylmaleimide, and CH_2=C(CO$_2$Et)$_2$. [c] By GC or ^{1}H NMR with internal standards on a 0.2−0.4 mmol scale; I, isolated yields after column chromatography on a 1−5 mmol scale. [d] Major product was t-$BuCH_2$-CH(CO$_2$Et)CH$_2$CH$_2$CO$_2$Et. [e] ^{1}H NMR yield in Me_2SO-d_6 in a dark reaction at 25 °C. [f] 8 equiv of KI, 4 equiv $K_2S_2O_8$. [g] 4 equiv of KI. [h] 4 equiv each KI and $K_2S_2O_8$. [i] 4 equiv KI, 2 equiv $K_2S_2O_8$. [j] ~8% of PhCOCH(Bu-t)CH$_2$CO$_2$Et also formed. [k] 8 equiv KI. [l] 8 equiv of KI, 4 equiv of PTSA; product not detected in the absence of a proton donor.

The reactions of CH_2=CHCN or CH_2=CHCO$_2$Me with t-BuHgI/I^- are conveniently followed in Me_2SO-d_6 by ^{1}H NMR. Rapid reaction leading to **2** with Q = CO$_2$Me or CN are observed even in the presence of water or alcohol while in the presence of ND_4^+, **2** is initially formed and then protonalized to form the monodeuterated reductive alkylation product.[14] Since similar reactions are not observed with $(t\text{-Bu})_2Hg$ or $(t\text{-Bu})_2Hg$/I^-, the promotion by I^- must be connected with the formation of t-$BuHgI_2^-$ and its rapid reaction with the adduct radicals, reaction 7.[14] Electron transfer from the ate-complex to the adduct radical to form the carbanion is excluded with Q = CN or CO$_2$Me.

$$t\text{-}BuCH_2CH(Q)^\bullet + t\text{-}BuHgI_2^- \rightarrow t\text{-}BuCH_2CH(Q)HgI_2^- + t\text{-}Bu^\bullet \quad (7)$$

(10) Russell, G. A.; Guo, D.; Baik, W.; Herron, S. J. *Heterocycles* **1989**, *28*, 143.
(11) Levin, Y. A.; Breus, A. A.; Ivanov, B. E. *Dokl. Akad. Navk, SSSR* **1977**, *236*, 387.
(12) Raynal, S. *Phosphorus Sulfur* **1981**, *11*, 287.
(13) Russell, G. A.; Kim, B. H.; Kulkarni, S. V. *J. Org. Chem.* **1984**, *54*, 3768.
(14) The reactions of t-BuHgI/KI with CH_2=CHCN or CH_2=CHCO$_2$-Me in Me_2SO are quite fast and with 1.1 equiv of t-BuHgI/2−4 equiv of KI are complete in 5−30 min in the dark at room temperature. These reactions are free radical chain processes since 10 mol % of $(t\text{-Bu})_2NO$• completely inhibits them for 12−24 h; unpublished results with Mr. Ping Chen and Dr. Chaozhong Li.

Electron transfer from I^- or t-$BuHgI_2^-$ can be observed for more easily reduced adduct radicals. This is possibly the case for t-$BuCH_2C(CO_2Et)_2^{\bullet}$ where the iodide-promoted reaction leads to polymerization of $CH_2{=}C(CO_2Et)_2$ which can be completely suppressed by the presence of a proton donor, Table 2. Protonated Schiff bases are excellent traps for alkyl radicals and in the presence of I^- reductive alkylation occurs rapidly by the chain sequence of Scheme 2.[5] Similar reductive alkylations involving electron transfer from I^- or $RHgI_2^-$ occur in the reductive alkylations of certain pyridinium-type cations.[15]

Scheme 2

$$R^{\bullet} + PhCH{=}NHPh^+ \rightarrow PhCH(R)NHPh^{\bullet+}$$

$$PhCH(R)NHPh^{\bullet+} + RHgI_2^- \rightarrow PhCH(R)NHPh + R^{\bullet} + HgI_2$$

The RHgX/KI system is relatively ineffective for reductive alkylations involving tertiary-enolyl radicals. Thus photolysis of 4 equiv of t-BuHgCl with ethyl methacrylate in the presence of KI slowly forms a mixture of t-$BuCH_2CH(Me)CO_2Et$ and $(t\text{-}BuCH_2)_2CHCO_2Et$ in a ratio of ~1:1 with 4 equiv and ~4:1 with 8 equiv of KI in Me_2SO (Table 3). The di-*tert*-butylated product results from t-Bu$^{\bullet}$ addition to t-$BuCH(=CH_2)CO_2Et$ formed by the disproportionation of t-$BuCH_2C(CH_3)CO_2Et^{\bullet}$, Scheme 3.[16] In the presence of Me_3SiCl/D_2O, or with

Scheme 3

$$2t\text{-}BuCH_2CH(Me)CO_2Et^{\bullet} \rightarrow \underset{\mathbf{3e}}{}$$

$$t\text{-}BuCH_2CH(Me)CO_2Et + t\text{-}BuCH_2C(=CH_2)CO_2Et$$
$$\mathbf{4e} \qquad\qquad \mathbf{5e}$$

$$\mathbf{5e} + t\text{-}Bu^{\bullet} \rightarrow (t\text{-}BuCH_2)_2CCO_2Et^{\bullet} \rightarrow \rightarrow (t\text{-}BuCH_2)_2CHCO_2Et$$
$$\mathbf{7}$$

D_3O^+ workup, deuterium is not appreciably incorporated into the products.

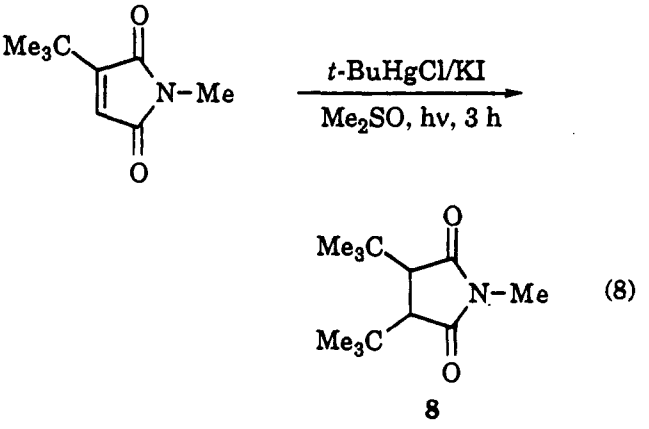
Reductive alkylation products are sometimes observed in the absence of reaction 7 or of electron transfer. Thus, reaction of *tert*-butyl-*N*-methylmaleimide with t-BuHgCl (4 equiv)/KI (8 equiv) forms 71% of the saturated di-*tert*-butylated derivative (**8**) as a 2.5:1 ratio of *cis* to *trans* isomers, reaction 8.[7] Compound **8** apparently results from hydrogen atom transfer from t-Bu$^{\bullet}$, t-BuHgX, $(t\text{-}Bu)_2Hg$ or t-$BuHgI_2^-$ to the adduct radical. Consistent with this conclusion, workup with D_2O incorporates no more than 10% of deuterium into **8**. Apparently this route to the reductive alkylation product becomes important only when other reactions of the adduct radical are blocked for steric reasons.

Reductive Alkylations by ≡SiH/RHgCl in Me_2SO. Table 3 illustrates the efficiency of Et_3SiH for promoting the reductive alkylation of ethyl methacrylate by t-BuHgCl in Me_2SO in the dark at room temperature. The reactions with added hydrides form Hg^0 in quantitative yield and can be easily monitored by the cloudiness of the solution when Hg^0 is being precipitated.

Table 3. *tert*-Butylation of Ethyl Methacrylate by t-BuHgX.[a]

X (equiv)	added reagent (equiv)	conditions (time)[b]	% yield[c] 4e	7
Cl (4)	KI (4)	Me_2SO, *hν* (12 h)	18	13
Cl (4)	KI (8)	Me_2SO, *hν* (12 h)	28	6
Cl (4)	KI (8)	Me_2SO/Et_3N,[d] *hν* (12 h)	35	12
I (4)		Me_2SO, *hν* (12 h)	10	10
I (4)	KI (8)	Me_2SO, *hν* (12 h)	22	16
I (2)	$NH_4^+HCO_2^-$ (2)	Me_2SO, *hν* (1 h)	22	1
I (2)	Bu_3SnH (2)	Me_2SO (10 min)	67	0
Cl (2)	$NaBH_4$ (2)/OH^-	CH_2Cl_2 (20 min)	60	0
Cl (2)	Et_3SiH (2)	Me_2SO, *hν* (11 h)	90	0
Cl (2)	Et_3SiH (2)	Me_2SO (11 h)	93	0
Cl (4)	$PhSiH_3$ (4)	Me_2SO (1 h)	54	0

[a] 0.05 M $CH_2{=}C(Me)CO_2Et$. [b] *hν*, irradiation by a 275 W fluorescent sunlamp which gave a reaction temperature of 35–40 °C. [c] By GC or ^1H NMR integration with $PhCH_3$ as an added internal standard. [d] 25 vol %.



(8)

8

The reaction apparently proceeds in a manner similar to the Giese procedure employing $RHgX/OH^-/BH_4^-$ in CH_2Cl_2.[8] An unstable RHgH is formed that readily generates R$^{\bullet}$ and also undergoes facile hydrogen atom transfer to R$^{\bullet}$ or to an adduct radical formed by the addition of R$^{\bullet}$ to an alkene. The concentration of RHgH will play an important role in determining whether R$^{\bullet}$ is trapped by RHgH (to form RH) or can add to some radicophile to form the adduct radical. Silyl hydrides apparently react slowly in Me_2SO with RHgX to yield a low steady state concentration of RHgH, reaction 5.[17] Silyl hydride promoted alkylations do not occur, or are much less effective, with Et_3SiH in solvents such as CH_2Cl_2, THF, PhH, or DMF. The reaction of ≡SiCl with Me_2SO to form ≡SiOSi≡ undoubtedly plays an important role in the formation of RHgH via reaction 5. The disappearance of Et_3SiH in reaction 5 can be followed by ^1H NMR in Me_2SO-d_6 in the absence of an alkene. This reaction is not affected by sunlamp irradiation or by the presence of $(t\text{-}Bu)_2NO^{\bullet}$. However, product formation in the alkylation of ethyl methacrylate by t-BuHgCl/Et_3SiH in the dark at 25 °C does show inhibition by $(t\text{-}Bu)_2NO^{\bullet}$ with an initial kinetic chain length of 8 (0.13 M ethyl methacrylate with 2 equiv each of t-BuHgCl and Et_3SiH). Thermal initiation via RHgH must be quite rapid which is also indicated by the lack of an appreciable effect of irradiation (Table 3). Further evidence for a free radical reaction is the observation that reaction of 5-hexenylmercury bromide with Et_3SiH and $CH_2{=}CHCO_2Et$ forms mainly ethyl 4-cyclopentylbutyrate (52%).

Faster formation of RHgH from RHgCl in Me_2SO is observed with $PhSiH_3$ in place of Et_3SiH or by the addition of KI which

(15) Russell, G. A.; Rajaratnam, R.; Wang, L.; Shi, B. Z.; Kim, B. H.; Yao, C. F. *J. Am. Chem. Soc.* **1993**, *115*, 10596.

(16) An 80% yield of **7** can be achieved in the reaction of $CH_2{=}CH(CH_2Cl)CO_2Et$ with t-BuHgCl/KI/*hν*. Here the intermediate adduct radical undergoes β-elimination of Cl$^{\bullet}$ to continue a chain reaction (Cl$^{\bullet}$ + t-BuHgX → ClHgX + t-Bu$^{\bullet}$).

(17) A similar reaction with Bu_3SnH occurs: Quirk, R. P. *J. Org. Chem.* **1972**, *37*, 3554.

forms the more reactive RHgI.[18] The use of $PhSiH_3$ can be advantageous because upon aqueous workup an insoluble resin is formed that is easily separated from the reductive alkylation product. With Et_3SiH workup leads to a mixture of Et_3SiOH and $Et_3SiOSiEt_3$ which are best separated from the alkylation product by chromatography.

Triethylsilane has such a low reactivity in hydrogen atom transfer reactions that its reaction with the adduct radical can be discounted.[8] However, with Bu_3SnH reductive alkylation can involve both hydrogen atom transfer from Bu_3SnH and RHgH.[19] Thus, Et_3SiH (4 equiv) was found to have no effect on the ~1:1 ratio of **4e** and **7** formed upon photolysis of 4 equiv of $(t\text{-Bu})_2Hg$ with ethyl methacrylate in Me_2SO. On the other hand, under the same conditions 4 equiv of $PhSiH_3$ had an effect on the ratio; **4e** and **7** were formed in a ratio of 9:1 suggesting that hydrogen atom transfer from $PhSiH_3$ occurred. However, **7** was always a detectable product from photolysis with $(t\text{-Bu})_2Hg$ in the presence of silyl hydrides whereas with *t*-BuHgX and Et_3SiH or $PhSiH_3$ there was no indication of any disproportionation of **3e** to yield eventually **7** (see Table 3).

Although the reactions promoted by $PhSiH_3$ are routinely faster (~1 vs ~12 h for completion), the yields of the reductive alkylation products are in general higher with Et_3SiH. For relatively unreactive radicophiles (e.g., $CH_2{=}C(Me)CO_2Et$ in Table 3), Et_3SiH gives a higher yield of the reductive alkylation product presumably because a lower steady state concentration of RHgH is maintained which favors trapping of R• by the alkene. However, with more reactive radicophiles, e.g., $CH_2{=}CHCOPh$ or $CH_2{=}C(Cl)CO_2Et$), the yields are about equivalent for reactions of *t*-BuHgCl promoted by Et_3SiH or $PhSiH_3$. With BuHgX the differences between $PhSiH_3$ and Et_3SiH are accentuated still further. Table 4 gives the yields of the reductive alkylation products observed with a number of electronegatively substituted 1-alkenes. Excellent yields of *tert*-butylation products are observed from alkenes that yield tertiary-enolyl adduct radicals such as dimethyl itaconate ($CH_2{=}C(CO_2Me)CH_2CO_2Me$) or citraconate ($MeO_2CC(Me){=}CHCO_2Me$), substrates which fail to form the reductive alkylation products with *t*-BuHgI/KI/*hv*.

Side Reactions in Reductive Alkylation with RHgX/≡SiH. 1,1-Disubstituted alkenes with substituents that can complex RHgX give rise to a side reaction involving the hydrogenation of the alkene, reaction 9. Electrophilic catalysis by Hg(II)

$$CH_2{=}C[N(CH_2CH_2)_2O]CO_2Et + {\equiv}SiH \xrightarrow[Me_2SO]{RHgCl} CH_3CH[N(CH_2CH_2)_2O]CO_2Et \quad (9)$$
9

species for silyl hydride reduction processes has been documented.[20] With ethyl α-morpholinoacrylate reduction to **9** also occurs with PhHgCl or $HgCl_2$ (Table 5). When reduction is a competing side reaction it is more important for BuHgCl or $PhSiH_3$ than for *t*-BuHgCl or Et_3SiH. The chain alkylation reaction generally occurs more slowly for BuHgCl than for *t*-BuHgCl. This allows an ionic hydrogenation reaction catalyzed by the mercurial to compete more effectively. Although $CH_2{=}C(CO_2Et)_2$ gave only the reduction product with *t*-BuHgCl/Et_3SiH or $PhSiH_3$, $CH_2{=}C(CO_2Bu\text{-}t)$ gave an excellent yield of $t\text{-BuCH}_2CH(CO_2Bu\text{-}t)_2$ with *t*-BuHgCl/$PhSiH_3$ (Table 4).[9]

(18) The half-life of 0.1 M Et_3SiH in the presence of 1 equiv of *t*-BuHgI in Me_2SO-d_6 is ~15 min (by ^1H NMR), while with *t*-BuHgCl the half-life is much longer, ~3 h.

(19) BH_4^- is quite unreactive towards alkyl radicals. Reductive alkylation by RHgCl/OH^-/$NaBH_4$ in CH_2Cl_2 must occur via RHgH: Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

(20) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

Table 4. Reactions of $CH_2{=}C(R^1)(R^2)$ with 4 equiv of RHgCl and Silyl Hydrides in Me_2SO To Form $RCH_2CH(R^1)(R^2)$[a]

R^1, R^2	R	≡SiH[b]	time (h)	yield, %[c]
H, CO_2Et	*t*-Bu	Et	12	84
H, CO_2Et	*t*-Bu	Ph	1	88
H, CO_2Et	*n*-Bu	Et	14	93
H, CO_2Et	*n*-Bu	Ph	14	12
Me, CO_2Et	*t*-Bu	Et	11	93
Me, CO_2Et	*t*-Bu	Ph	1	54
Me, CO_2Et	*n*-Bu	Et	20	74
Me, CO_2Et	*n*-Bu	Ph	2	10
CH_2CO_2Me, CO_2Me	*t*-Bu	Et	12	88
Ph, CO_2Et	*t*-Bu	Ph	8	78
Ph, CO_2Et	*n*-Bu	Et	12	41
Cl, CO_2Et	*t*-Bu	Ph	10	95
Cl, CO_2Et	*n*-Bu	Ph	7	93
PhS, CO_2Et	*t*-Bu	Et	17	57 (34)
CO_2Et, CO_2Et	*t*-Bu	Et	12	8 (34)
CO_2Et, CO_2Et	*t*-Bu	Ph	12	33 (57)
CO_2Et, CO_2Et	*n*-Bu	Et	12	– (60)
CO_2Et, CO_2Et	*n*-Bu	Ph	12	– (62)
$CO_2Bu\text{-}t$, $CO_2Bu\text{-}t$	*t*-Bu	Ph	8	80
$N(CH_2CH_2)_2O$, CO_2Et	*t*-Bu	Et	12	– (82)
$N(CH_2CH_2)_2O$, CO_2Et	*t*-Bu	Ph	1	– (87)
NEt_2, CO_2Et	*t*-Bu	Et	3	– (60)
$NHCOCH_3$, CO_2Me	*t*-Bu	Ph	2	55
H, CN	*t*-Bu	Et	12	90
H, CN	*t*-Bu	Ph	1	95
H, CN	*n*-Bu	Et	20	73
Me, CN	*t*-Bu	Et	22	86
Me, CN	*n*-Bu	Et	22	86
Cl, CN	*t*-Bu	Et	12	76
Cl, CN	*t*-Bu	Ph	1	85
Cl, CN	*n*-Bu	Ph	1	86
H, COPh	*t*-Bu	Ph	2	91
H, COPh	*n*-Bu	Et	3	90
Me, COPh	*t*-Bu	Et	12	54
Me, COPh	*t*-Bu	Ph	1	47
Me, COPh	*n*-Bu	Et	22	40
Ph, COPh	*t*-Bu	Et	12	64 (17)
Ph, COPh	*t*-Bu	Ph	1	62 (6)
Cl, COPh	*t*-Bu	Et	22	43
Cl, COPh	*t*-Bu	Ph	1	69
Cl, COPh	*n*-Bu	Ph	3	35 (41)
H, $COC_6H_4OMe\text{-}p$	*t*-Bu	Et	12	95
H, COMe	*t*-Bu	Et	5	69
H, $COCMe_3$	*t*-Bu	Et	8	78
Me, CHO	*t*-Bu	Et	1	30
H, $PO(OEt)_2$	*t*-Bu	Et	2	87
H, SPh	*t*-Bu	Et	24	52
H, SOPh	*t*-Bu	Et	12	60
H, SO_2Ph	*t*-Bu	Et	4	91
Cl, Cl	*t*-Bu	Et	12	75
H, $SiPh_3$	*t*-Bu	Et	9	74

[a] 0.025 M alkene under N_2. Reactions were terminated when the cloudiness from Hg^0 precipitation cleared. For BuHgCl/Et_3SiH reactions 4 equiv of KI were added to increase the reaction rate. [b] Et = Et_3SiH, Ph = $PhSiH_3$. [c] By GC and ^1H NMR with internal standards. Values in parentheses are the yields of the reduction products, $CH_3CH(R^1)(R^2)$.

Table 5. Silyl Hydride Reduction of Ethyl α-Morpholinoacrylate by ≡SiH and Hg(II) Compounds in Me_2SO[a]

mercurial	silane	time	% **9**[b]
t-BuHgCl	Et_3SiH	12 h	82
t-BuHgCl	$PhSiH_3$	35 min	87
PhHgCl	$PhSiH_3$	40 min	84
$HgCl_2$	Et_3SiH	1 h	27
$HgCl_2$	$PhSiH_3$	1 h	60

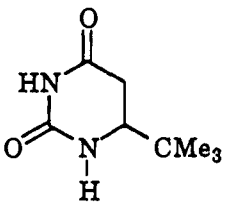
[a] Reaction of 0.025 M ethyl α-morpholinoacrylate with 4 equiv each of the mercurial and silane. [b] By GC and ^1H NMR.

Apparently complexation of Hg(II) by the di-*tert*-butyl ester is not as important and only the homolytic reductive alkylation is observed.

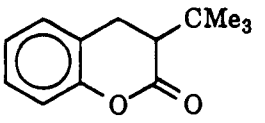
1,2-Disubstituted alkenes generally give low yields of reductive alkylation products in the *t*-BuHgCl/Et_3SiH system unless both substituents are electron withdrawing, e.g., maleates, fumarates, citraconates. Without two electron-withdrawing substituents the rate of radical trapping by the alkene is usually too low to compete effectively with hydrogen atom transfer from RHgH. For unreactive substrates where a secondary-enolyl adduct radical is formed, reaction in the *t*-BuHgCl/KI system is preferred for reductive alkylation. Thus, chalcone and uracil yield **10** and **11** with *t*-BuHgCl/KI/$K_2S_2O_8$ (Table 2) but with

t-BuCH(Ph)CH_2COPh

10



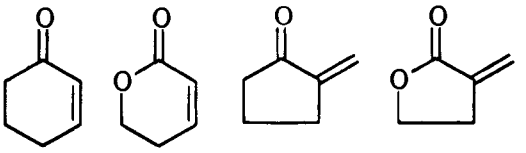
11



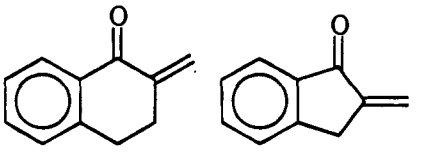
12

Et_3SiH/*t*-BuHgCl the reactions fail completely. 2-Cyclohexenone or 5,6-dihydro-2*H*-pyran-2-one give excellent yields of the alkylation products with *t*-BuHgCl/KI/hν (Table 2) but only low yields with *t*-BuHgCl/Et_3SiH (~30%). However, coumarin, which yields a variety of products from the benzylic adduct radical with *t*-BuHgCl/KI/*hv*,[13] does react with Et_3SiH/*t*-BuHgCl to form **12** in 55% yield accompanied by ~4% of the 4-*tert*-butyl isomer.

Reactivities of Alkenes towards *t*-Bu•. Competitive *tert*-butylation in Me_2SO of various pairs of alkenes including **13**–**18** are reported in Tables 6 and 7. The primary standards used were (E)-PhCH=CHI (which yields (*E*)-PhCH=$CHCMe_3$)[21,22] and CH_2=$CHCO_2Et$ and CH_2=$CHP(O)(OEt)_2$ (which yield the reductive alkylation products **4** with *t*-BuHgCl/KI/*hv* or *t*-BuHgCl/Et_3SiH). The absolute rate constant for *t*-Bu• additions to CH_2=$CHP(O)(OEt)_2$ has been measured at 233 K.[23] Using log $A = 7.5 \pm 0.5$ (a value observed for many 1-alkenes),[24] the rate constants for *t*-Bu• addition to (*E*)-PhCH=CHI and CH_2=$CHCO_2Et$ at 25 °C are estimated to be $1.6 \pm 1 \times 10^4$ and $1.3 \pm 0.8 \times 10^6$ L/mol-s, respectively based on the measured relative reactivities of CH_2=$CHCO_2Et$:CH_2=CHP(O)$(OEt)_2$:(*E*)-PhCH=CHI of 82:19:1.0. The absolute rate constants for *t*-Bu• addition to a variety of alkenes is isopropyl alcohol at 27 °C as measured by ESR techniques have been reported by Fischer.[24] There is fair agreement (within a factor of ~ 3) between these rate constants and those calculated in Me_2SO from Table 7. Thus, from Table 7, CH_2=CCl_2 adds *t*-Bu• with a rate constant of $2.6 \pm 1.6 \times 10^5$ L/mol-s, whereas Fischer reports $3.5 \pm 0.2 \times 10^5$. The reactivity of 4-vinylpyridine from Table 7 is $1.6 \pm 1 \times 10^5$, whereas Fischer reports $4.6 \pm 1 \times 10^5$. With acrylonitrile Table 7 yields $3.4 \pm 2.1 \times 10^6$, while Fischer reports $1 \pm 0.4 \times 10^6$ in isopropyl alcohol and $2.4 \pm 0.2 \times 10^6$ in isobutene. Solvent polarity may effect the rate constant for *t*-Bu• addition by solvation of resonance structure **1** in this early transition state reaction. Thus, in Me_2SO the relative reactivities of CH_2=$CHCO_2Et$:CH_2=CHCN:(*E*)-EtO_2CCH=$CHCO_2Et$ towards *t*-Bu• are 1:3:6, while Giese et. al.[25] report in CH_2Cl_2 a reactivity series of 1(CH_2=$CHCO_2$-Me):5:3. [Toward *c*-C_6H_{11}• in CH_2Cl_2 the reactivities are 1:3:5,[25] while towards polystyrenyl radical in mixed alkene solvents at 60 °C the relative reactivities are 1:2:3.[26]]



13 **14** **15** **16**



17 **18**

In Table 6 the reactivities of α-substituted vinyl ketones and esters are compared. The α-methyl substituted compounds are less reactive than the unsubstituted compounds as expected on the basis of **1**. Similarly, the α-chloro derivatives are much more reactive. With esters, α-substitution of phenyl for hydrogen results in a large increase in reactivity, presumably because of an increase in the stability of the benzylic adduct radical. However, for CH_2=C(R)COPh, the reactivity is considerably higher for R = H than for either R = Me or Ph. We believe this to be a result of changes in the preferred *s-cis* or *s-trans* geometries as the bulk of R is changed. It is known that CH_2=CHCOPh exists primarily in the *s-cis* conformation (84%), whereas the α-substituted derivatives prefer the *s-trans* conformations.[27] The reactivity towards *t*-Bu• also increases from CH_2=CHCOMe (react. 90; 29% *s-cis*[28]) to CH_2=CH-$COCMe_3$ (react. 190, 100% *s-cis*[28]). The α-methylene carbonyls **15**–**18** with *s-cis* geometries have much higher reactivities than CH_2=C(Me)COPh (reactivity 70) or CH_2=C(Me)CO_2Et (reactivity 50); reactivities of **15**–**18** = 180, 150, 370, 780, respectively. The high reactivities of *s-cis* carbonyl compounds relative to their *s-trans* analogues is presumably connected with a favorable SOMO–LUMO interaction (**1**) in the orthogonal approach of *t*-Bu• to the conjugated π-systems. The phenyl group of PhCOCH=CH_2 plays a small role in activating the enone group toward *t*-Bu• attack. Thus, for the *s-cis* enones, PhCOCH=CH_2 is ca. twice as reactive as *t*-BuCOCH=CH_2, while **18** is ca. five-times as reactive as **15**. Ketones and

Table 6. Relative reactivities towards *t*-Bu• [a]

R	CH_2=C(R)COPh	CH_2=C(R)CO_2Et
Me	70 ± 10	50 ± 10
H	470 ± 20	80 ± 10
MeCONH		115 ± 10
PhS		210 ± 10
Ph	175 ± 10	310 ± 10
Cl	700 ± 100	1300 ± 200

[a] Relative to (*E*)-PHCH=CHI.

(21) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1985**, *26*, 4975.
(22) Russell, G. A.; Ngoviwatchai, P. *J. Org. Chem.* **1989**, *54*, 1836.
(23) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. II* **1981**, 161.
(24) Fischer, H. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janovsek, Z., Merenyi, R., Eds.; Reidel: Dordrecht, 1988; p 123.
(25) Giese, B.; Kretzschmer, G.; Meixner, J. *Chem. Ber.* **1980**, *113*, 2787.
(26) Walling, C. *Free Radicals in Solution*, Wiley: New York, 1957; p 118.
(27) Gottlieb, H. in *The Chemistry of Enones*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989, Part 1; Chapter 5.
(28) Hayes, W. P.; Timmons, C. T. *Spectrochim. Acta* **1968**, *24A*, 323.

Table 7. Relative Reactivities of Alkenes in the Addition of *t*-Bu• in Me_2SO

A	B[a]	method[b]	rel react.[c]	react. of A[d]
PhCH=NPh	I	A	0.79	0.8
13	I	A	1.3	1.3
14	**13**	A	1.1	1.4
CH_2=CHSiPh$_3$	I	B	1.6	1.6
CH_2=CHSPh	I	B	4.0	4.0
PhCH=NHPh$^+$	I	A	4.0	4.0
PhCH=CHCOPh	I	A	5.8	5.8
CH_2=CHS(O)Ph	CH_2=CHSPh	B	2.75	11
CH_2=CHS(O)Ph	CH_2=CHSO$_2$Ph	B	0.080	8
4-CH_2=CHPy	I	A	9.8	10[e]
coumarin	I	B	14	14
CH_2=CCl$_2$	I	B	16	16
CH_2=CHP(O)(OEt)$_2$	I	B	19	19
EtO$_2$CC≡CH	EM	B	0.64	20
(*Z*)-EtO$_2$CCH=CHCO$_2$Et	EA	B	0.38	31
CH_2=C(Me)CO$_2$Et	I	B	60	60
CH_2=C(Me)CO$_2$Et	EA	B	0.685	55
CH_2=C(Me)CO$_2$Et	CH_2=C(Ph)CO$_2$Et	B	0.13	40
CH_2=C(Me)CN	I	B	59	59
CH_2=C(Me)CN	EA	B	0.63	52
CH_2=C(Me)COPh	I	B	73	73
CH_2=C(Me)COPh	MMA	B	1.2	70
EtO$_2$CC≡CCO$_2$Et	HC≡CCO$_2$Et	*f*	4.1	82
CH_2=CHCO$_2$Et	P	B	4.3	82
CH_2=CHCOMe	EA	B	1.1	90
CH_2=CHSO$_2$Ph	EA	B	1.1	90
CH_2=CHSO$_2$Ph	P	B	5.8	110
CH_2=CHSO$_2$Ph	MMA	B	1.6	93
CH_2=C(NHCOMe)CO$_2$Me	EA	B	1.3	110
CH_2=C(NHCOMe)CO$_2$Me	MMA	B	2.0	120
16	EA	B	1.8	150
CH_2=C(Ph)COPh	CH_2=CHCOPh	B	0.39	180
CH_2=C(Ph)COPh	CH_2=C(Me)COPh	B	2.7	170
15	**16**	B	1.2	180
CH_2=CHCOCMe$_3$	EA	B	2.45	190
CH_2=CHCOCMe$_3$	CH_2=CHCOMe	B	2.3	210
CH_2=C(SPh)CO$_2$Et	EA	B	2.5	205
CH_2=C(SPh)CO$_2$Et	MMA	B	3.6	210
CH_2=CHCN	EA	B	2.6	210
CH_2=CHCN	CH_2=C(Me)CN	B	3.9	230
CH_2=C(Ph)CO$_2$Et	EA	B	3.7	300
CH_2=C(Ph)CO2Et	CH_2=C(Ph)COPh	B	1.8	320
CH_2=C(Ph)CO$_2$Et	CH_2=C(NHCOCH$_3$)CO$_2$Me	B	2.8	320
17	CH_2=CHCOPh	B	0.81	380
17	**18**	B	0.45	360
CH_2=CHCONHPh	CH_2=CHCOPh	A	0.62	390
CH_2=CHCOC$_6$H$_4$OMe-*p*	CH_2=CHCOPh	B	0.64	400
CH_2=CHCOPh	EA	B	5.5	450
CH_2=CHCOPh	CH_2=C(Me)COPh	B	6.9	490
(*E*)-EtO$_2$CCH=CHCO$_2$Et	EA	B	5.6[g]	460
4-CH_2=CHPyH$^+$	I	A	>500[e]	>500
CH_2=C(Cl)COPh	CH_2=CHCOPh	B	1.7	710
18	AN	B	3.4	750
18	CH_2=CHCOPh	B	1.7	800
CH_2=C(Cl)CN	AN	B	4.7	1000
CH_2=C(Cl)CN	CH_2=C(Cl)CO$_2$Et	B	0.67	900
(*E*)-PhCOCH=CHCOPh	EA	B	12	1000
(*E*)-PhCOCH=CHCOPh	EF	B	2.15	1000
CH_2=C(Cl)CO$_2$Et	EA	B	18	1500
CH_2=C(Cl)CO$_2$Et	MMA	B	22	1300
CH_2=C(Cl)CO$_2$Et	CH_2=C(Ph)CO$_2$Et	B	3.3	1100
N-methylmaleimide	EF	B	6.0	2800
N-methylmaleimide	EF	A	5.1	2300
(*E*)-NCCH=CHCN	NMM	A	2.5	6400
CH_2=C(CO2Et)$_2$	EA	A[h]	~100	~8000

[a] I = (*E*)-PhCH=CHI, EA = CH_2=CHCO$_2$Et, MMA = CH_2=C(Me)CO$_2$Et; AN = CH_2=CHCN; EF = diethyl fumarate; EM = diethyl maleate; NMM = *N*-methylmaleimide. [b] Method A, *t*-BuHgCl/KI/hν at 35 °C; method B, *t*-BuHgCl/Et$_3$SiH at 25 °C. [c] As calculated from the observed alkylation products. [d] Relative to (*E*)-PhCH=CHI, $k_{add.}$ = 1.6 × 10^4 L/mol-s at 25 °C; experimental uncertainty is estimated to be ±15%. [e] In the absence of a proton donor the reactivity depends on the concentration of *t*-BuHgX (because of complexation) and of KI (reversible *t*-Bu• addition). A rel react. of 9.8 was observed for 0.025 M 4-vinylpyridine with 4 equiv each of *t*-BuHgI and KI. [f] Photolysis with *t*-BuHgCl to yield vinyl mercurials (ref 2) followed by $NaBH_4$ workup. [g] With Bu_3SnH, $PhSiH_3$, or $NaBH_4$ in Me_2SO. [h] In the presence of PTSA.

lactones, e.g., **13** and **14** or **15** and **16**, have nearly the same reactivity towards *t*-Bu• with the *s-cis exo*-methylene compounds **15** and **16** being ca. 100 times more reactive than compounds with internal 1,2-disubstituted double bonds such as **13** or **14**.

Experimental Section

^{1}H NMR spectra were obtained with a Nicolet NT300 spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded with JEOL FX-90Q and Nicolet NT300 spectrometers. ^{31}P NMR spectra were obtained with a Bruker WM-300 spectrometer and reported in δ relative to external 85% phosphoric acid. Mass spectra were obtained with a Finnigan 4000 (INCOS data system) in the GC mode and high resolution spectra obtained by a Kratos MS-50 spectrometer. Infrared spectra were obtained with a Beckman IR 4250, Digital FTS-7FT, or IBM IR-98FT spectrometers. Neat spectra were recorded between NaCl plates. Elemental analyses were performed by Galbraith Laboratories, Inc. All mp's were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Most products were isolated by flash column chromatography on silica gel (Kiesel gel 60, 230−400 mesh ASTM) usually with hexane (99%)−ethyl acetate (1%). Analytical gas chromatography was performed with a Varian 3700 chromatograph with a Hewlett Packard 3390A integrator employing toluene, naphthalene, or biphenyl as the internal standard. Photostimulated reactions utilized a Sylvania 275 W fluorescent sunlamp or a Rayonet Photoreactor (350 nm) and Pyrex reaction vessels. Both irradiation sources maintained the reaction mixtures at ca. 35−40 °C.

Solvents and Materials. Me_2SO was stirred over CaH_2 for 12 h at 80 °C, distilled, and stored over 4A molecular sieves. Benzene and THF were refluxed with $Ph_2C{=}O$/Na followed by distillation and storage over molecular sieves. Carbon tetrachloride was distilled from P_2O_5.

Alkylmercury halides were prepared according to literature procedures.[29] *tert*-Butylmercury chloride (mp 110−113 °C) was prepared in 50% yield after recrystallization from hexane (90%)−ethanol (10%) by reaction of *t*-BuMgCl with $HgCl_2$ in THF at 0 °C. The mercurial was stored in the absence of light at 0 °C. In CH_3CN the λ_{max} of 210 nm was not affected by 1−3 equiv of vinyl phosphonate. Di-*tert*-butylmercury, mp 52−55 °C, was prepared by a literature procedure.[30] *t*-BuHgI was prepared by reaction of *t*-BuHgCl (0.03 mol) with KI (0.06 mol) in 50 mL of Me_2SO.[31] After 2 h at 25 °C the solution was treated with 100 mL of water and extracted with Et_2O. After drying over $MgSO_4$ the solvent was evaporated to give white crystals which turned yellow when exposed to air [^{1}H NMR ($CDCl_3$) δ 1.54 (s, 9 H); ^{1}H NMR (Me_2SO-d_6) δ 1.43 (s, 9 H)]. The compound decomposes upon heating and does not give a well-defined mp.

The preparation of substrates that were not available from Aldrich Chemical Co. are summarized in the supplementary material.

General Procedure for Reactions of RHgCl with Alkenyl Substrates (Table 1). A Pyrex tube containing RHgX and the substrate in PhH or Me_2SO under a positive pressure of N_2 was irradiated at 35−40 °C. The reaction product was transferred to a flask and treated with either solid $NaBH_4$ or I_2. For the $NaBH_4$ reduction, a few drops of water were added after 10 min. The product was hydrolyzed, separated from mercury metal, extracted with Et_2O, concentrated, and isolated by flash column chromatography. The iodine cleavage was allowed to proceed for 4−8 h in PhH after which HgI_2 was removed by filtration. The filtrate was washed until colorless with 5% aqueous $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated to afford a reaction product which was purified by flash column chromatography. The crude or purified iodides were converted to alkenes by reaction with 3 equiv of diazabicycloundecane in PhH or neat at 80−90 °C. The product was dissolved in Et_2O and washed with 5% aqueous $Na_2S_2O_3$ and water, dried over $MgSO_4$, and after concentration purified by flash column chromatography.

Reaction Products from Diethyl Vinyl Phosphonate. Diethyl 3,3-Dimethylbutylphosphonate (4a, R = *t*-Bu). ^{1}H NMR ($CDCl_3$) δ 4.11 (p, J = 4.2 Hz, 4 H), 1.76−1.62 (m, 2 H), 1.53−1.39 (m, 2 H), 1.33 (t, 6 H), 0.90 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 61.4 (d, J_{COP} = 6.1 Hz), 35.8 (d, J_{CCP} = 6.1 Hz), 29.4 (d, J_{CCCP} = 6.1 Hz), 28.7, 21.2 (d, J_{CP} = 141.6 Hz), 16.4 (d, J_{CCOP} = 6.1 Hz); ^{31}P NMR (C_6D_6) δ 33.43; GC and HRMS *m/z* (%) calcd for $C_{10}H_{22}O_3P$ ($M^+ - H$) 221.1306; found 222 (0.2), 221.1304 (1.1), 207 (49), 166 (58), 165 (100), 151 (52), 138 (96), 111 (63), 57 (66); IR (neat) ν = 2980, 2870, 1470, 1440, 1390, 1360, 1245, 1155, 1058, 960, 780 cm^{-1}. Anal. Calcd for $C_{10}H_{23}O_3P$: C, 54.02; H, 10.46; P, 13.94. Found: C, 54.24; H, 10.06; P, 13.70.

Diethyl 1-Iodo-3,3-dimethylbutylphosphonate. ^{1}H NMR ($CDCl_3$) δ 4.17 (p, J = 7.1 Hz, 4 H), 2.41−1.93 (m, 3 H), 1.34 (t, 6 H), 0.93 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 63.5 (t, J_{COP} = 12.2 Hz), 36.6, 31.7 (d, J_{CCCP} = 12.2 Hz), 29.2, 16.25 (d, J_{CCOP} = 6.1 Hz), 8.64 (d, J_{CP} = 153.8 Hz); ^{31}P NMR (C_6D_6) δ 23.68; GC and HRMS *m/z* (%) calcd for $C_{10}H_{22}IO_3P$ 348.0351; found 349 (0.08), 348.0352 (0.85), 347 (0.02), 221 (24), 165 (83), 137 (18), 109 (45), 83 (87), 57 (100); IR (neat) ν = 2990−2880, 1475, 1445, 1395, 1370, 1255, 1160, 1060−1020, 970, 820−780, 750 cm^{-1}.

Diethyl 3,3-Dimethyl-1-butenylphosphonate (5a, R = *t*-Bu). The alkene was prepared in 90% yield from 0.1 g of *t*-$BuCH_2CH(I)P(O)(OEt)_2$ and 0.13 g of DBU at 90 °C for 4 h: ^{1}H NMR ($CDCl_3$) δ 6.80 (d of d, $J_{H,P}$ = 24 Hz, $J_{H,H}$ = 17.6 Hz, 1 H), 5.50 (d of d, $J_{H,P}$ = 20 Hz, $J_{H,H}$ = 17.6 Hz, 1 H), 4.32−3.80 (p, J = 7.5 Hz, 4 H), 1.30 (t, J = 7.5 Hz, 6 H), 1.07 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 162.7 (d, J_{CCP} = 3.67 Hz), 111.6 (d, J_{CP} = 188.0 Hz), 61.13 (d, J_{POC} = 4.89 Hz), 35.51 (d, J_{CCCP} = 4.89 Hz), 28.09, 15.98 (d, J_{POCC} = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 20.70; GC and HRMS *m/z* (%) calcd for $C_{10}H_{21}O_3P$ 220.1228, found 222 (0.8), 221 (7.4), 220.1226 (39), 204 (35), 163 (19), 149 (44), 138 (54), 111 (60), 110 (19), 83 (100). IR (neat) ν = 2575−2880, 1630, 1480, 1395, 1370, 1250, 1165, 1060, 1030, 970, 850, 820, 780 cm^{-1}.

Tetraethyl 2,2,7,7-Tetramethyloctane-4,5-diphosphonate. Photolysis for 24 h of *t*-BuHgCl and $CH_2{=}CHP(O)(OEt)_2$ in a 1:1 mole ratio in Me_2SO followed workup with aqueous $Na_2S_2O_3$ and CH_2Cl_2 extraction yielded *t*-$BuCH_2CH_2P(O)(OEt)_2$, *t*-$BuCH{=}CHP(O)(OEt)_2$, and *t*-$BuCH_2CH[P(O)(OEt)_2]CH[P(O)(OEt)_2]CH_2Bu$-*t* in a 1:1:1.5 ratio. The diphosphonate was formed as an ~1:1 mixture of diastereomers having GCMS *m/z* (%) = 427 ($M\text{-}CH_3^+$, 0.3), 385 (28), 305 (23), 222 ($M^+/2$, 91), 165 (8), 138 (5), 170 (10), 135 (9), 111 (20), 109 (35), 57 (100) and 427 ($M\text{-}CH_3^+$, 1), 385 (4), 305 (5), 221 ($M^+/2$, 75), 165 (51), 138 (4), 137 (8), 135 (6), 111 (16), 104 (30), 57 (100).

Diethyl 3,3,3-Trichloropropylphosphonate (4a, R = CCl_3). Reaction of *t*-BuHgCl (2 mmol) with $CH_2{=}CHP(O)(OEt)_2$ (0.5 mmol) in CCl_4 (10 mL) for 24 h in a Rayonet Photoreactor precipitated hexachloroethane [mp 189−193 °C; ^{13}C NMR ($CDCl_3$) δ 104.9]. Reduction with $NaBH_4$ followed by CH_2Cl_2 extraction yielded 62% of the crude phosphonate isolated in 52% yield by flash column chromatography: ^{1}H NMR ($CDCl_3$) δ 4.16 (p, J = 8.3 Hz, 4 H), 3.08−2.83 (m, 2 H), 2.41−2.01 (m, 2 H), 2.36 (t, J = 8.3 Hz, 5 H); ^{13}C NMR ($CDCl_3$) δ 99.00 (d, J_{PCCC} = 29.3 Hz), 61.92 (d, J_{POC} = 6.1 Hz), 48.40, 23.40 (d, J_{PC} = 142.8 Hz), 16.30 (d, J_{POCC} = 6.1 Hz); GC and HRMS *m/z* (%) calcd for $C_7H_{14}Cl_2O_3P$ (M^+ − Cl) 247.0059, found 287 (0.7), 285 (0.5), 282 (0.6), 257 (20), 255 (10), 249 (35), 247.0059 (50), 165 (61), 109 (100), 55 (87), IR (neat) ν = 2950−2930, 1430, 1390, 1255, 1220, 1160, 1050, 975, 950, 840, 790−770, 750 cm^{-1}.

Diethyl 3,3,3-Trichloro-1-iodopropylphosphonate. Iodine cleavage of the mercurial gave 60% of the crude phosphonate isolated in 40% yield by flash column chromatography: ^{1}H NMR ($CDCl_3$) δ 4.24 (p, J = 7.9 Hz, 4 H), 3.62−3.16 (m, 3 H), 1.40 (t, J = 7.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 97.13 (d, J_{PCCC} = 18.3 Hz), 63.68 (t, J_{POC} = 12.2 Hz), 56.80 (d, J_{POCC} = 6.1 Hz), 5.26 (d, J_{PC} = 155 Hz); ^{31}P NMR ($CDCl_3$) δ 20.96; GC and HRMS *m/z* (%) calcd for $C_7H_{13}Cl_3IO_3P$ 407.8713, found 411 (0.03), 410 (1.6), 407.8713 (1.5), 191 (31), 189 (46), 111 (20), 109 (100), 81 (69), 65 (46); IR (neat) ν = 2950−2920, 1440, 1420, 1390, 1260, 1190, 1160, 1050, 1020, 970, 840, 770, 720, 690 cm^{-1}.

Diethyl 3,3,3-Trichloro-1-propenylphosphonate (5a, R = CCl_3). Reaction of the iodide (0.08 g, 0.2 mmol) with DBU (0.09 g, 0.6 mmol) in 6 mL of PhH at 90 °C for 4 h yielded 68% of the phosphonate: ^{1}H

(29) Makarova, L. G.; Nesmeyanov, A. N. *The Organic Compounds of Mercury*; North-Holland Publishing Co.: Amsterdam, 1967; Vol. 4.
(30) Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 371.
(31) Seyferth, D.; Towe, R. H. *Inorg. Chem.* **1962**, *1*, 185.
(32) Bordwell, F. G.; Drucker, G. E.; McCollum, G. J. *J. Org. Chem.* **1982**, *47*, 2504.
(33) Hershberger, J.; Russell, G. A. *Synthesis* **1980**, 475.
(34) Manescalchi, F.; Orena, M.; Savoia, D. *Synthesis* **1979**, 445.
(35) Lewis, L. N.; Sy, K. G.; Bryant, G. L.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.
(36) Boustany, K. *J. Chem. Eng. Data* **1972**, *17*, 104.
(37) Hartmann, J.; Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261.

NMR ($CDCl_3$) δ 7.05 (d of d, $J_{P,H}$ = 19.6, $J_{H,H}$ = 15.5 Hz, 1 H), 6.31 (d of d, $J_{P,H}$ = 15.3 Hz, $J_{H,H}$ = 15.5 Hz), 4.16 (p, J = 8.97 Hz, 4 H), 1.35 (t, J = 8.97 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 149 (d, J_{CCP} = 10.19 Hz), 118.2 (d, J_{CP} = 186.2 Hz), 65.58, 62.44, 16.14; ^{31}P NMR ($CDCl_3$) δ 6.84; GC and HRMS m/z (%) calcd for $C_7H_{12}Cl_2O_3P$ (M^+ − Cl) 244.9901, found 282 (2.0), 280 (M^+, 2.5), 247 (39) 244.9904 (62), 219 (65), 217 (100), 211 (15), 209 (25), 191 (26), 189 (39), 183 (17), 181 (37), 153 (72), 109 (82); IR (neat) ν = 3250, 2990−2970, 1560, 1530, 1300, 1250, 1150, 1120, 1060, 980 cm^{-1}.

Diethyl 3-Methylbutylphosphonate (4a, R = *i*-Pr). Material isolated by flash column chromatography had ^1H NMR ($CDCl_3$) δ 4.33 (p, J = 7.5 Hz, 4 H), 1.90−1.38 (m, 5 H), 1.33 (t, J = 7.5 Hz, 6 H), 0.90 (d, 6 H); ^{13}C NMR ($CDCl_3$) δ 61.21 (d, J_{POC} = 6.11 Hz), 30.90 (d, J_{PCCC} = 4.88 Hz), 29.01, 23.51 (d, J_{PC} = 140.4 Hz), 21.80, 16.30 (d, J_{POCC} = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 33.39; GC and HRMS m/z (%) calcd for $C_9H_{20}O_3P$ (M^+ − H) 207.1150, found 209 (0.20), 208 (0.14), 207.1149 (1.7), 165 (69), 152 (100), 138 (58), 137 (49), 125 (82), 111 (59), 109 (38), 69 (41); IR (neat) ν = 2970, 1450, 1380, 1360, 1240, 1210, 1155, 1090, 1060, 1010, 960 cm^{-1}. Anal. Calcd for $C_9H_{21}O_3P$: C, 51.89; H, 10.19; P, 14.88. Found: C, 51.63; H, 10.06; P, 14.79.

Diethyl 1-Iodo-3-methylbutylphosphonate. ^1H NMR ($CDCl_3$) δ 4.21 (p, J = 7.13 Hz, 4 H), 2.24−1.58 (m, 4 H), 1.34 (t, J = 7.13 Hz, 6 H), 0.96 (d of d, 6 H); ^{13}C NMR ($CDCl_3$) δ 63.10 ((t, J_{POC} = 10.98 Hz), 41.09 (d, J_{PCCC} = 2.44 Hz), 27.71 (d, J_{PCC} = 12.2 Hz), 22.51, 16.14 (d, J_{PC} = 157.5 Hz), 16.03 (d, J_{POCC} = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 23.57; GC and HRMS m/z (%) calcd for $C_9H_{20}IO_3P$ 334.0194, found 335 (0.04), 334.0190 (0.4), 207 (40), 179 (9), 165 (12), 151 (65), 137 (9), 109 (36), 91 (23), 69 (100); IR (neat) ν = 2900−2880, 1470, 1390−1370, 1245, 1050, 1025, 970, 810, 730 cm^{-1}.

Diethyl 3-Methyl-2-butenylphosphonate (5a, R = *i*-Pr). Elimination of HI from the iodide by DBU at 90 °C formed the nonconjugated alkene in 52% yield: ^1H NMR ($CDCl_3$) δ 5.18 (m, 1 H), 4.15 (p, J = 7.8 Hz, 4 H), 2.48 (d of d, J_{HCP} = 22 Hz, $J_{H,H}$ = 8.4 Hz, 2 H), 1.75 (s, 3 H), 1.68 (s, 3 H), 1.31 (t, J = 7.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 136.1 (d, $J_{C,P}$ = 14.7 Hz), 112.25 (d, $J_{C,P}$ = 11.0 Hz), 61.11 (d, J_{POC} = 6.1 Hz), 25.95 (d, J_{PC} = 140.4 Hz), 25.05, 17.36; 15.87 (d, J_{POCC} = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 29.24; GC and HMRS m/z (%) calcd for $C_9H_{19}O_3P$ 206.1073, found 208 (0.4), 207 (4.7), 206.1075 (41), 150 (46), 138 (48), 111 (100), 97 (27), 83 (49), 82 (76), 81 (37), 69 (79), 68 (31); IR (neat) ν = 2990−2960, 1520, 1470, 1330, 1300, 1150−1120, 1050 cm^{-1}.

Diethyl 2-Cyclohexylethylphosphonate (4a, R = *c*-C_6H_{11}). ^1H NMR ($CDCl_3$) δ 4.30 (p, J = 7.15 Hz, 4 H), 2.20−1.32 (m, 15 H), 1.30 (t, J = 7.15 Hz, 6 H); GCMS: m/z (%) = 248 (M^+, 0.3), 247 (0.7), 166 (28), 165 (89), 152 (100), 138 (49).

Diethyl 2-Cyclohexyl-1-iodoethylphosphonate. ^1H NMR ($CDCl_3$) δ 4.18 (p, J = 5.05 Hz, 4 H), 2.28−1.61 (m, 3 H), 1.36 (t, J = 5.05 Hz, 6 H), 1.31−1.20 (m, 11 H); GCMS m/z (%) = 374 (M^+, 0.06), 247 (0.09), 165 (54), 138 (100), 125 (39), 109 (26), 55 (40).

Diethyl Hexylphosphonate (4a, R = Bu). ^1H NMR ($CDCl_3$) δ 4.11 (p, J = 7.0 Hz, 4 H), 2.41−1.25 (m, 10 H), 1.4 (t, J = 7.0 Hz, 6 H), 0.95 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 61.13 (d, J_{POC} = 5.86 Hz), 31.02, 30.37, 29.65, 25.39 (d, J_{CP} = 145 Hz), 18.08, 16.19 (d, J_{POCC} = 5.86 Hz), 13.72; ^{31}P NMR ($CDCl_3$) δ 33.19; GC and HRMS m/z (%) calcd for $C_{10}H_{22}O_3P$ (M^+ − H) 221.1307, found 222 (1.5), 221.1305 (5.1), 166 (29), 165 (100), 138 (27), 111 (16), 55 (29); IR (neat) ν = 2980, 2960−2920, 2880, 1450, 1380, 1245, 1160, 1030, 950 cm^{-1}. Anal. Calcd for $C_{10}H_{23}O_3P$: C, 54.02; H, 10.46; P, 13.94. Found: C, 54.06; H, 10.47; P, 13.92.

Reaction Products from Phenyl Vinyl Sulfone. 3,3-Dimethyl-1-(Phenylsulfonyl)butylmercury Chloride (2, R = *t*-Bu, EWG = $PhSO_2$). Photolysis at 350 nm of CH_2=$CHSO_2Ph$ (0.12 mmol) and *t*-BuHgCl (0.6 mmol) in C_6D_6 for 3 h completely consumed the CH_2=$CHSO_2Ph$ and 50% of the *t*-BuHgCl. Aqueous workup and CH_2Cl_2 extraction yielded 44% of the mercurial: ^1H NMR (C_6D_6) δ 7.93−7.87 (m, 2 H), 7.15−7.08 (m, 3 H), 3.65 (dd, J = 11.7, 1.8 Hz, 1 H), 2.20 (dd, J = 14.1, 11.7 Hz, 1 H), 1.67 (dd, J = 14.1, 1.8 Hz, 1 H), 0.69 (s, 9 H). The mercurial was unstable to GC conditions but could be reduced to *t*-$BuCH_2CH_2SO_2Ph$ by $NaBH_4$ in 80% yield.

3,3-Dimethylbutyl Phenyl Sulfone (4b, R = *t*-Bu). Isolated material with mp 52−53.5 °C (lit.[31] mp 59−60 °C) had the expected IR, NMR and GCMS; HRMS m/z calcd for $C_{12}H_{18}O_2S$ 226.1028, found 226.1031.

1-Iodo-3,3-dimethylbutyl Phenyl Sulfone. Isolated material had mp 98−100 °C; ^1H NMR ($CDCl_3$) δ 8.13−7.40 (m, 5 H), 4.84 (d of d, 1 H), 2.12 (q, 2 H), 0.90 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 134.7, 134.3, 130.1, 129.1, 46.80, 37.10, 31.31, 29.25; GC and HRMS m/z (%) calcd for $C_{12}H_{17}IO_2S$ 351.9995, found 354 (0.06), 353 (0.2), 351.9998 (1.3), 211 (16), 169 (10), 143 (14), 125 (13), 83 (15), 77 (14), 57 (100); IR (KBr pellet), ν = 3000−2900, 1590, 1480, 1455, 1400, 1350, 1330−1305, 1200, 1155, 1090, 780, 760, 735, 690 cm^{-1}.

3,3-Dimethyl-1-butenyl Phenyl Sulfone (5b, R = *t*-Bu). Elimination of HI by DBU in PhH gave 78% of the alkene whose NMR, GCMS and IR were consistent with lit. values:[32] HRMS m/z calcd for $C_{12}H_{16}O_2S$ 224.0871, found 224.0869.

3-Methylbutyl Phenyl Sulfone (4b, R = *i*-Pr). ^1H NMR ($CDCl_3$) δ 7.80−7.44 (m, 5 H), 3.06 (t, 2 H), 1.71−1.49 (m, 3 H), 0.87 (d, 6 H); ^{13}C NMR ($CDCl_3$) δ 138.95, 133.4, 129.0, 127.7, 54.38, 30.77, 26.91, 21.80; GC and HRMS m/z (%) calcd for $C_{11}H_{16}O_2S$, 212.0871, found 212.0870 (0.14), 143 (100), 78 (20), 77 (34), 70 (39), 55 (22), IR (neat) ν = 3070, 2980, 2890, 1590, 1470, 1450, 1370, 1320, 1280, 1150, 1090, 790, 690 cm^{-1}.

1-Iodo-3-methylbutyl Phenyl Sulfone. Isolated material had ^1H NMR ($CDCl_3$) δ 8.05−7.50 (m, 5 H), 4.90 (dd, 1 H), 1.98−1.70 (m, 3 H), 0.99 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 134.94, 134.25, 129.79, 129.00, 44.01, 41.16, 27.99, 22.93; GC and HRMS m/z (%) calcd for $C_{11}H_{15}IO_2S$ 337.9838, found 340 (0.2), 337.9836 (4.8), 211 (30), 197 (43), 143 (75), 125 (37), 77 (38), 69 (100); IR (neat) ν = 3080, 2980, 2940, 2880, 1580, 1470, 1450, 1390, 1370, 1310, 1150, 1080, 750, 710, 690 cm^{-1}.

3-Methyl-2-butenyl Phenyl Sulfone (5b, R = *i*-Pr). Elimination of DBU in refluxing PhH for 6 h gave in 92% of the nonconjugated alkene; ^1H NMR ($CDCl_3$) δ 7.95−7.48 (m, 5 H), 5.19 (t, 1 H), 3.79 (d, 2 H), 1.65 (s, 3 H), 1.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 133.4, 129.2, 128.9, 128.3, 127.9, 110.3, 56.12, 25.80, 17.66; GC and HRMS m/z (%) calcd for $C_{11}H_{14}O_2S$ 210.0715, found 212 (0.03), 211 (0.07), 210.0718 (0.6), 131 (1), 79 (2), 77 (8), 70 (8), 69 (100), 68 (4), 67 (5), 51 (7); IR (neat) ν = 3060, 2980, 2940, 2870, 1670, 1620, 1590, 1450, 1310, 1240, 1150, 1090, 770, 740, 690 cm^{-1}.

2-Cyclohexylethyl Phenyl Sulfonate (4b, R = *c*-C_6H_{11}). ^1H NMR ($CDCl_3$) δ 7.90−7.40 (m, 5 H), 3.05 (t, 2 H), 1.53−1.48 (m, 2 H), 1.26−1.19 (m, 11 H); GCMS m/z (%) = 254 (0.2), 253 (0.6), 252 (M^+, 0.7), 187 (17), 143 (100), 110 (87), 81 (49), 77 (40), 55 (97).

2-Cyclohexyl-1-iodoethyl Phenyl Sulfone. ^1H NMR ($CDCl_3$) δ 8.10−7.70 (m, 5 H), 4.85 (d of d, 1 H), 2.10−1.97 (m, 2 H), 1.36−1.19 (m, 11 H); GCMS m/z (%) = 380 (0.02), 379 (0.06), 378 (M^+, 0.7), 251 (13), 143 (36), 109 (100), 83 (33), 77 (26), 67 (34).

Hexyl Vinyl Sulfone (4b, R = Bu). IR, GCMS, and NMR were consistent with literature values:[33] HMRS calcd for $C_{12}H_{18}O_2S$ 226.1076, found 226.1022.

Reaction Products from Vinyl Triphenylsilane. 3,3-Dimethyl-1-(triphenylsilyl)butylmercury Chloride. Sunlamp photolysis of CH_2=$CHSiPh_3$ with 4 equiv of *t*-BuHgCl in Me_2SO for 24 h followed by aqueous $Na_2S_2O_3$ workup, and CH_2Cl_2 extraction gave 50% of the mercurial and 5% of *t*-$BuCH_2CH_2SiPh_3$. The mercurial had ^1H NMR ($CDCl_3$) δ 7.70−7.60 (m, 2 H), 7.50−7.30 (m, 3 H), 2.47 (dd, J = 12.6, 1.8 Hz, 1 H), 2.17 (dd, J = 15.0, 1.8 Hz, 1 H), 1.80 (dd, J = 15.0, 12.6 Hz, 1 H), 0.995 (s, 9 H).

(3,3-Dimethylbutyl)triphenylsilane (4c, R = *t*-Bu). ^1H NMR ($CDCl_3$) 7.53−7.48 (m, 6 H), 7.41−7.32 (m, 9 H), 1.34 (m, 4 H), 0.87 (s, 9 H); ^{13}C NMR 135.62, 135.53, 129.28, 127.78, 37.67, 31.36, 28.80, 7.49; GC and HRMS m/z (%) calcd for $C_{24}H_{28}Si$ 344.1960, found 344.1958 (0.2), 260 (22), 259 (100), 183 (12), 181 (39), 180 (14), 155 (13), 105 (38), 57 (8), 41 (9).

(*E*)-(3,3-Dimethyl-1-butenyl)triphenylsilane (5c, R = *t*-Bu). The compound was isolated as a solid, mp 84−86 °C with spectral data consistent with literature values.[34]

Reaction Products from Phenyl Vinyl Sulfide. Photolysis of *t*-BuHgCl or *t*-BuHgI with CH_2=$CHSPh$ gave low yields of *t*-$BuCH_2CH_2SPh$, *t*-$BuCH$=$CHSPh$, and *t*-$BuCH_2CH(SPh)CH(SPh)CH_2Bu$-*t* in the presence or absence of added iodide ion. Reaction with 4 equiv of

t-BuHgCl and 4 equiv of Et_3SiH for 24 h in Me_2SO gave 52% of *t*-$BuCH_2CH_2SPh$ and 5% of *t*-BuCH=CHSPh.

3,3-Dimethylpropyl Phenyl Sulfide (4d, R = *t*-Bu).[35] GCMS *m/z* (%) = 194 (M^+, 35), 137 (83), 123 (66), 110 (84), 109 (37), 85 (15), 84 (12), 77 (20), 69 (22), 65 (27), 57 (100).

(*E*)-3,3-Dimethyl-1-propenyl Phenyl Sulfide (5d, R = *t*-Bu).[36] GCMS *m/z* (%) = 192 (M^+, 53), 177 (94), 135 (28), 110 (17), 109 (20), 91 (19), 83 (100), 77 (20), 57 (12).

2,2,7,7-Tetramethyl-4,5-bis(phenylthio)octane. The dimer was formed as an ~1:1 mixture of two diastereomers; GCMS *m/z* (%) = 386 (M^+, 0.4), 277 (19), 193 (9), 137 (42), 111 (8), 110 (5), 109 (6), 69 (10), 57 (100) and 386 (M^+, 0.2), 277 (3), 193 (8), 137 (43), 111 (4), 110 (4), 109 (6), 69 (7), 57 (100).

General Procedure for the Reactions of Alkylmercury Halides in Presence of Iodide Salts. Sodium, potassium, or ammonium iodide was dissolved in 5−10 mL of deoxygenated Me_2SO in a Pyrex tube with a rubber septum under a positive nitrogen pressure. The alkylmercury halide was added followed by the α,β-unsaturated compound. The reaction mixture was irradiated with a 275 W sunlamp placed 15−25 cm from the reaction flask. Usually a dark brown solution resulted after 1 h of irradiation. For workup, 22 mL of aqueous $Na_2S_2O_3$ was added, and the mixture was stirred for 10 min. The mixture was extracted with CH_2Cl_2, and the extract was dried over $MgSO_4$ and concentrated. The reaction product was analyzed by GLC, and pure products were isolated by flash column chromatography. Yields were usually determined by ^1H NMR integration with toluene as an internal standard. Many of the reactions in the presence of I^- proceed in the dark at 25 °C by a thermally initiated free radical chain leading to the adduct organomercurial whose formation can be monitored by ^1H NMR in Me_2SO-d_6. In the presence of NH_4^+ the organomercurials are slowly cleaved to form the reductive alkylation product. The reactions are not appreciably affected by the presence of 10 mol % water.

General Procedure for the Alkylation of Alkenes by RHgX in the Presence of Silanes. The substrate (0.1 mmol) and alkylmercury halide were dissolved in 4 mL of deoxygenated Me_2SO under positive nitrogen pressure in a Pyrex tube equipped with a rubber septum. A silyl hydride (0.4 mmol) was added by syringe, and the reaction was stirred until the precipitation of metallic mercury ceased. The reaction mixture was added to 15 mL of saturated aqueous $Na_2S_2O_3$ and worked up in the standard manner.

Alkylation of Acrylate Esters. The properties of most of the alkylation products are given in the supplementary material. Photolysis of mixtures of *t*-BuHgCl or *t*-BuHgI and ethyl acrylate followed by $NaBH_4$ reduction produced *t*-$BuCH_2CH(CO_2Et)CH_2CH_2CO_2Et$: GCMS *m/z* (%) = 259 ($M^+$ + 1, 0.4), 243 (7), 214 (13), 213 (100), 202 (18), 201 (76), 197 (20), 185 (11), 169 (60), 158 (22), 157 (22), 156 (34), 155 (93), 151 (33), 139 (29), 129 (17), 128 (88), 127 (25), 115 (21), 102 (39), 101 (38), 99 (22), 97 (25), 95 (38), 88 (9), 83 (29), 81 (14), 73 (16), 69 (20), 67 (11), 57 (85). Also detected by GCMS were *t*-$BuCH_2CH(CO_2Et)CH_2CH(CO_2Et)$Bu-*t* and *t*-$BuCH_2CH(CO_2Et)CH_2$-$CH(CO_2Et)CH_2CH(CO_2Et)$Bu-*t*. On the other hand, photolysis or dark reactions of *t*-BuHgCl or *t*-BuHgI in the presence of KI gave excellent yields of *t*-$BuCH_2CH_2CO_2Et$ after hydrolytic workup. Photolysis of $(t\text{-Bu})_2Hg$ with CH_2=$CHCO_2Et$ in PhH also produced a variety of products including *t*-$BuCH_2CH_2CO_2Et$ (18%), *t*-$BuCH$=$CHCO_2Et$ (5%), *t*-$BuCH_2CH(CO_2Et)$Bu-*t* (5%), and two diastereomers of *t*-$BuCH_2$-$CH(CO_2Et)CH(CO_2Et)CH_2$Bu-*t* (7%).

Ethyl 2,4,4-Trimethylpentanoate (4e). The isolated material had ^1H NMR ($CDCl_3$) δ 4.11 (q, *J* = 7.2 Hz, 2 H), 2.48 (m, 1 H), 1.85 (dd, J = 14.1, 9.3 Hz, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.16 (dd, J = 14.1, 3.0 Hz, 1 H), 1.15 (d, *J* = 7.2 Hz, 3 H), 0.88 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 178.02, 60.19, 47.81, 36.32, 30.84, 29.45, 20.45, 14.19; HRMS *m/z* calcd for $C_{10}H_{20}O_2$ 172.1463, found 172.1462.

Ethyl 2-(2,2-Dimethylpropyl)-4,4-dimethylpentanoate (7). ^1H NMR ($CDCl_3$) 4.08 (q, *J* = 7.2 Hz, 2 H), 2.48 (m, 1 H), 1.73 (dd, *J* = 14.1, 9.3 Hz, 2 H), 1.255 (t, *J* = 7.2 Hz, 3 H), 1.23 (dd, *J* = 14.1, 6.0 Hz, 2 H), 0.89 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 178.5(s), 60.1(t), 49.3-(t), 38.4(d), 31.2(s), 29.5(q), 14.0(q); GCMS, *m/z* (%) = 229 (M + 1^+, 10), 213 (85), 157 (37), 142 (35), 129 (33), 102 (55), 83 (48), 57 (100).

Diethyl (2,2-Dimethylpropyl)malonate. ^1H NMR ($CDCl_3$) δ 4.16 (m, 4 H), 3.37 (t, *J* = 6.0 Hz, 1 H), 1.92 (d, *J* = 6.3 Hz, 2 H), 1.24 (t, *J* = 7.2 Hz, 6 H), 0.89 (s, 9 H); GCMS, *m/z* (%) = 231 (M + 1^+, 0.5), 215 (20), 185 (38), 175 (33), 141 (54), 128, 86, 101 (65), 73 (39), 57 (100).

Bis(1,1-dimethylethyl) (2,2-Dimethylpropyl)malonate. ^1H NMR ($CDCl_3$) δ 3.17 (t, *J* = 6.0 Hz, 1 H), 1.83 (d, *J* = 6.0 Hz, 2 H), 1.455 (s, 18 H), 0.90 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 169.6 (s), 81.14 (s), 50.83 (d), 41.67 (t), 30.41 (s), 29.25 (q), 27.89 (q); HRMS *m/z* calcd for $C_{12}H_{21}O_3$ (M^+ − $OCMe_3$) 213.1491, found, 213.1486.

Diethyl (1,2,2-Trimethylpropyl)maleate. Sunlamp photoysis of 0.05 M diethyl ethylidenemalonate with 4 equiv of *t*-BuHgCl and 8 equiv. of KI in Me_2SO for 19 h produced 50% of the reductive alkylation product whose yield was increased to 64% by the addition of 2 equiv of $K_2S_2O_8$: ^1H NMR ($CDCl_3$) δ 4.23−4.13 (m, 4 H), 3.51 (d, *J* = 5.4 Hz, 1 H), 2.24 (dq, J = 5.2, 7.2 Hz, 1 H), 1.30−1.23 (m, 6 H), 1.01 (d, *J* = 7.2 Hz, 3 H), 0.90 (s, 9 H); GC and HRMS *m/z* (%) calcd for $C_{12}H_{21}O_4$ (M − 15) 229.1434, found 245.1753 (M + 1^+, 9), 229.1439 (15), 199 (50), 142 (9), 115 (100); CIMS (NH_3) *m/z* = 245; FTIR (neat) ν = 2972, 1755, 1732 cm^{-1}.

Diethyl (2,2-Dimethyl-1-phenylpropyl)malonate. Sunlamp photolysis of 0.05 M diethyl benzalmalonate with 4 equiv each of *t*-BuHgI and KI for 19 h gave 70% of the alkylation product: ^1H NMR ($CDCl_3$) δ 7.26−7.12 (m, 5 H), 4.22 (m, 2 H), 3.98 (d, *J* = 11.1 Hz, 1 H), 3.71 (dq, *J* = 3.3, 6.9 Hz, 2 H), 1.30 (t, *J* = 6.9 Hz, 3 H), 0.88 (s, 9 H), 0.80 (t, *J* = 6.9 Hz, 3 H); GC and HRMS *m/z* (%) calcd for $C_{18}H_{26}O_4$ 306.1831, found 307 (0.1), 306.1830 (0.03), 291 (1), 250 (47), 176 (100); FTIR (neat) ν = 2974, 1759, 1732 cm^{-1}.

Reaction of Alkylmercury Halides with Other α,β-Unsaturated Compounds. Properties of the other reductive alkylation products listed in Tables 2, 4 and 6 are given in the supplementary material.

(a) Chalcone. Sunlamp photolysis of chalcone with *t*-BuHgCl (4 equiv), KI (4 equiv), and $K_2S_2O_8$ (2 equiv) for 24 h produced 60% of **10**. The regiochemistry of the addition was proven by deuteration in Me_2SO/*t*-BuOK/D_2O to give a dideuterio derivative and by reduction with LAH to give the alcohol in which the benzylic proton at δ 2.84 was coupled to two diastereotopic methylene protons with *J* = 11.7 and 3.0 Hz.

4,4-Dimethyl-1,3-diphenyl-1-pentanone (10). The compound was a solid: mp 112−113 °C; ^1H NMR ($CDCl_3$) δ 7.87−7.84 (m, 2 H), 7.54−7.38 (m, 3 H), 7.26−7.12 (m, 5 H), 3.51 (dd, *J* = 16.5, 9.9 Hz, 1 H), 3.33 (dd, *J* = 16.5, 3.9 Hz, 1 H), 3.26 (dd, *J* = 9.9, 3.9 Hz, 1 H), 0.94 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 199.4 (s), 142.3 (s), 137.3 (s), 132.7 (d), 129.3 (d), 128.4 (d), 127.8 (d), 127.5 (d), 126.0 (d), 51.0 (d), 39.7 (t), 33.8 (s), 28.0 (q); GC and HRMS *m/z* (%) calcd for $C_{19}H_{22}O$ 266.16 71, found 266.1667 (0.2), 209 (100), 105 (80), 91 (24), 72 (29), 57 (8). The dideuterated compound had aliphatic ^1H NMR signals at δ 3.23 (1 H), and 0.94 (9 H) while in the ^{13}C spectrum the peak at δ 39.7 was not detected. The dideuterated compound gave EIMS *m/z* (%) = 268 (M^+, 1), 253 (0.8), 212 (44), 105 (100); CIMS (isobutane) = 269 (M + 1^+, 100), 212 (15); CIMS (NH_3) = 305 (M + 35^+, 5), 268 (M + 18^+, 100), 269 (M + 1^+, 10).

(b) Coumarin. Photolysis of coumarin with *t*-BuHgCl in the presence of DABCO gave 90% of the oxidative alkylation product,[13] while reaction with *t*-BuHgCl/Et_3SiH formed mainly 3-*tert*-butyldihydrocoumarin.

3-(1,1-Dimethylethyl)coumarin. The compound had mp 82−83 °C; ^1H NMR ($CDCl_3$) δ 7.54 (s, 1 H), 7.50−7.35 (m, 2 H), 7.35−7.20 (m, 2 H), 1.40 (s, 9 H); GC and HMRS *m/z* (%) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0991 (45), 187 (100), 160 (85), 144 (11), 133 (17), 115 (31); FTIR ($CDCl_3$) ν = 2964, 1722, 1705 cm^{-1}.

3-(1,1-Dimethylethyl)dihydrocoumarin (12). The compound had mp 45−46 °C; ^1H NMR ($CDCl_3$) δ 7.27−6.96 (m, 4 H), 3.065 (dd, *J* = 16.2, 6.6 Hz, 1 H), 2.95 (dd, *J* = 16.2, 9.6 Hz, 1 H), 2.50 (dd, *J* = 9.6, 6.6 Hz, 1 H), 1.08 (s, 9 H); GC and HRMS *m/z* (%) calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1149 (6), 189 (77), 168 (39), 148 (60), 133 (100), 120 (26), 119 (15), 107 (92), 91 (29), 83 (18), 77 (15), 57 (42).

4-(1,1-Dimethylethyl)dihydrocoumarin. The compound was a solid: mp 43−45 °C; ^1H NMR ($CDCl_3$) δ 7.31−7.04 (m, 4 H), 3.05 (d, J = 15.9 Hz, 1 H), 2.75 (d, J = 7.5 Hz, 1 H), 2.68 (dd, *J* = 15.9, 7.5 Hz, 1 H), 0.95 (s, 9 H); GC and HMRS *m/z* (%) calcd for $C_{13}H_{16}O_2$

204.1150, found 204.1151 (11), 148 (100), 91 (20), 57 (85); FTIR ($CDCl_3$) ν = 2966, 2901, 1765 cm^{-1}.

(c) ***N*-Methylmaleimide.** The reductive and oxidative mono-*tert*-butylation products of *N*-methylmaleimide have been previously reported.[7b]

***trans*-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione (*trans*-8).** The compound was isolated as a solid, mp 128−131 °C. The structure was assigned on the basis of isomer stability: ^1H NMR ($CDCl_3$) δ 2.94 (s, 3 H), 2.37 (s, 2 H), 0.98 (s, 18 H); GC and HRMS *m/z* (%) calcd for $C_{13}H_{23}NO_2$ 225.1729, found 225.1730 (0.2), 210 (2), 169 (20), 113 (100), 57 (14); FTIR ($CDCl_3$) ν = 2963, 1692 cm^{-1}.

***cis*-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione (*cis*-8).** The compound was a solid, mp 74−87 °C; ^1H NMR ($CDCl_3$) δ 2.93 (s, 3 H), 2.80 (s, 2 H), 1.20 (s, 18 H); GC and HRMS *m/z* (%) calcd for $C_{13}H_{23}NO_2$ 225.1729; calcd for $C_{13}H_{20}NO_2$ (M-Me) 210.1494, found 225.1721 (0.1), 210.1491 (1), 169 (18), 113 (100), 57 (25); CIMS (NH_3) 226 ($M + 1^+$); FTIR ($CDCl_3$) ν = 2963, 1769, 1699 cm^{-1}.

(d) **Benzylideneanilines.** Dark reactions with *t*-BuHgI/KI were not observed while photolysis with 1 equiv each of *t*-BuHgI and KI produced ~50% of the reductive alkylation product in 12 h. Alkylation was not observed in the absence of KI. In the presence of 1 equiv of PTSA, *t*-BuHgI, and KI the reactions were much faster and produced the reductive alkylation products in ~100% yield. The reactions were complete in ~3 h with sunlamp photolysis and in ~24 h in the dark. Competition of (*E*)-PhCH=CHI with PhCH=NPh and with PhCH=NPh plus 6 equiv of PTSA with *t*-BuHgCl/KI indicated a relative reactivity of PhCH=NPh:(*E*)-PhCH=CHI:$PhCH{=}NHPh^+$ of 0.8:1.0:4.0.

***N*-(2,2-Dimethyl-1-phenylpropyl)aniline.** ^1H NMR ($CDCl_3$) δ 7.30−7.15 (m, 5 H), 7.01 (*t*, *J* = 7.8 Hz, 2 H), 6.57 (*t*, *J* = 7.2 Hz, 1 H), 6.48 (d, *J* = 7.8 Hz, 2 H), 4.25 (s, 1 H), 4.03 (2, 1 H), 1.00 (s, 9 H); GCMS and HRMS *m/z* (%) calcd for $C_{17}H_{21}N$ 239.1674, found 239.1678 (4), 182 (100), 104 (10), 77 (19), 57 (1).

4-[2′,2′-Dimethyl-1′-(phenylamino)propyl]benzonitrile. The compound had mp 159−160 °C; ^1H NMR ($CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.07−7.02 (m, 2 H), 6.62 (t, *J* = 7.2 Hz, 1 H), 6.43−6.40 (m, 2 H), 4.26 (br. d, *J* = 5.1 Hz, 1 H), 4.08 (d, *J* = 5.4 Hz, 1 H), 0.99 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 147.2 (s), 146.9 (s), 131.6 (d), 129.14 (d), 129.10 (d), 118.9 (s), 117.5 (d), 113.1 (d), 110.73 (s), 67.07 (d), 34.93 (s); GC and HRMS *m/z* (%) calcd for $C_{18}H_{20}N_2$ 264.1632, found 246.1627 (5), 207 (100), 105 (5), 77 (10). Anal. Calcd: C, 81.78; H, 7.62; N, 10.60. Found: C, 82.12; H, 7.79; N, 10.40.

General Procedure for Competitive *tert*-Butylations, Table 7. Reaction of a pair of alkenes of known concentrations with *t*-BuHgX was stopped short of completion so that less than 50% of any alkene had been consumed. After workup the yields of the *tert*-butylation products were determined by ^1H NMR using toluene as an internal standard. The relative reactivities were calculated by the integrated expression for two competing first order reactions assuming that the final alkene concentration was equal to the initial concentration minus the alkylation product formed.

Acknowledgment. We are grateful for financial support provided by the National Science Foundation (CHE-9220639).

Supplementary Material Available: Preparation of substrates and physical properties of *tert*-butylation products of Tables 2, 4, and 6 (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information.

JA9433277