Electron Transfer Processes. Part 47.* Reactions of Organometallic Reagents Involving Electron Transfer†

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Radical chain processes occur in conjugate addition reactions of 2-cycloalkenones with t-$BuHgI_2^-$, $(t\text{-Bu})_2CuLi$ or $(t\text{-Bu})_3ZnLi$ as judged by the relative reactivity of 2-cyclopentenone > 2-cyclohexenone and by the effect of $CH_2{=}CPh_2$ as a radical trap. On the other hand, $(n\text{-Bu})_2CuLi$ or $(t\text{-Bu})_2Cu(CN)Li_2$ react by a mechanism involving preferential attack upon 2-cyclohexenone. Vinyl substitution reactions of $PhCH{=}CHSO_nPh$ and $PhC{\equiv}CSO_nPh$, where $n = 0$ or 2, occur by a radical process with t-BuHgCl, t-BuLi or $(t\text{-Bu})_2CuLi$ as judged by chemo- and regio-selectivity. Radicals such as $PhSO_n^{\cdot}$ or enolyl radicals are postulated to undergo electron transfer reactions with t-$BuHgI_2^-$, $(t\text{-Bu})_2Cu^-$ or $(t\text{-Bu})_3Zn^-$, leading to the regeneration of *tert*-butyl radicals.

Organomercury halides have proved to be a convenient source of alkyl radicals for a number of free radical chain processes.[1,2] Reactions involving borohydride reduction to form RHgH spontaneously form free radials at room temperature.[1] In the absence of BH_4^-, chain reactions are conveniently initiated by fluorescent light, by ultrasound, or by oxidation–reduction such as $I^-/S_2O_8^{2-}$.[2] The latter system is known to produce $I^{\cdot}$ which readily displaces $R^{\cdot}$ from RHgX.

Alkylmercury halides are readily reduced ($E_{1/2} \sim -0.5$ v) by easily oxidized radicals or radical anions ($D^{\cdot}$) leading to the chain propagating reaction (1). Donor species

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

can be radical anions such as $RNO_2^{-\cdot}$, $RCH_2NO_2^{-\cdot}$, $RCH_2\dot{C}(O^-)Ph$ formed by the addition of $R^{\cdot} = t\text{-Bu}^{\cdot}$ to the appropriate anion.[3,4] Among the easily oxidized neutral radicals which participate in reaction (1) with R = t-Bu are $RCH_2\dot{C}(C_6H_4OMe\text{-}p)_2$ and the *ortho*- and *para*-alkylpyridinyl radicals.[5,6] With $R = PhCOCH_2$, the adduct radicals formed by the addition of $R^{\cdot}$ to trialkyl phosphites, enamines or *N*-methylpyrrole will participate in reaction (1). The adduct radical of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine with benzyl or primary alkyl radicals will also participate in reaction (1). [For the couple $R_2N\dot{C}</R_2\dot{N}{=}C<$ the value of E° is ca. -1 v].[7]

A second general chain propagating reaction of alkylmercurials is the formal S_H2 displacement of $R^{\cdot}$ by attack of an acceptor radical ($A^{\cdot}$) at the mercury atom, reaction (2).[8] This process occurs readily with electronegative hetero-

$$A^{\cdot} + RHgX \rightarrow R^{\cdot} + AHgX \qquad (2)$$

atom-centered species such as halogen atoms or chalcogenide-centered radicals. Such radicals can be formed in chain processes by S_H2 attack of $R^{\cdot}$ upon an appropriate group such as Y = H, halogen or chalcogenide atom in reaction (3),[8] or by the radical addition–elimination process of reaction (4).[9]

$$R^{\cdot} + Y\text{–}A \rightarrow RY + A^{\cdot} \qquad (3)$$

$$R^{\cdot} + PhCH{=}CHA \rightarrow\rightarrow PhCH{=}CHR + A^{\cdot} \qquad (4)$$

Among the carbon-centered radicals which participate in reaction (2) are vinyl radicals in general and electronegatively substituted alkyl radicals such as $RCH_2\dot{C}H(EWG)$ with EWG = $(EtO)_2P(O)$, $PhSO_2$ or $p\text{-}O_2NC_6H_4$.[10] However, enolyl-type radicals react rather inefficiently in reaction (2) with alkylmercury chlorides or carboxylates.[11]

Substrates which form an initial adduct radical with $R^{\cdot}$, but which otherwise fail to participate effectively in a free radical chain reaction with an alkylmercurial, can sometimes be coerced into reaction by additional chain propagating steps which involve either activation of the adduct radical or the alkylmercurial. An example of activation of an adduct radical is the loss of a proton to yield a conjugated radical anion, a species with a favorable potential to the ready transfer of an electron to RHgX in reaction (1).[12] Such a process has been documented in the photostim-

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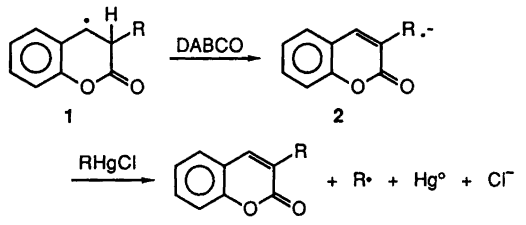


1 2

Scheme 1. R = alkyl.

ulated reaction of alkylmercury chlorides with coumarin where the initial adduct radical is benzylic and fails to react with RHgX via reaction (1) or (2). Extended photolysis produces a mixture of products resulting from intermolecular radical reactions of the adduct radical **1**. However, in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) the adduct radical yields the ketyl radical anion **2** ($E° \sim -1.6$ v) which can continue a chain reaction by electron transfer to RHgCl (Scheme 1). Similar reactions are observed for the benzylic radicals obtained by the addition of *t*-Bu$^{\cdot}$ to perinaphthenone or *N*-methyl-2-quinolinone.[12]

Activation of the organomercurial for reaction with acceptor radicals is observed when complexing ligands are added, particularly I^-, which can form ate complexes with the mercurial ($RHgI_2^-$).[11] This is particularly effective with enolyl-type radicals where apparently an ineffective S_H2 process [reaction (2)] is replaced by an efficient electron transfer process, reaction (5).

$$RCH_2\dot{C}HC(O)R^1 + RHgI_2^- \rightarrow RCH_2CH{=}C(O^-)R^1 + R^{\cdot} + HgI_2 \quad (5)$$

We have extended the concept that ate complexes may react by electron transfer with acceptor-type adduct radicals to reactions of *tert*-butyl cuprates and zincates in both conjugate addition and vinyl substitution processes.[11,13] For these processes, as well as nucleophilic substitution at a saturated carbon atom, there exists a series of mechanisms involving the classical two-electron processes (S_N2, Michael addition, nucleophilic addition/elimination) as one extreme and radical chain processes as the other extreme (Fig. 1).*

Radical chain mechanisms can be expected to predominate when the classical two-electron processes are inhibited by steric or electronic effects and when the intermediate radicals in the chain processes are stabilized but still reactive. The alkylmercury halides represent a class of compound where two-electron processes are rare because of the polarity of the carbon–mercury bond ($R^{\delta-}$–$HgX^{\delta+}$). This polarity effectively prevents S_N2 or E2 reactions but is not sufficient to allow carbanionic reactivity. Thus, alkylmercury halides undergo only the free radical chain alkylations for the three processes of Fig. 1. Furthermore, the rates and efficiencies of these processes, in general, increase with the stability of the incipient alkyl radical (*t*-Bu > *i*-Pr > *n*-Bu).[2]

*Whether processes such as the S_N2 and $S_N(ET)$ reactions occur in competition, or are merged, or if there is a gradual transition from one process to another is uncertain; Lund, T. and Lund, H. *Acta Chem. Scand. B 42* (1988) 269.

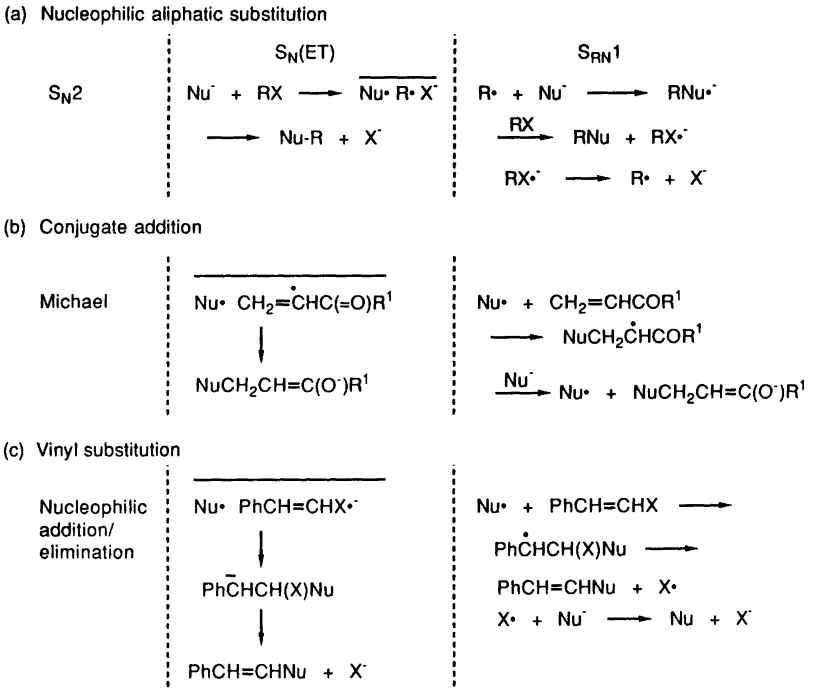


Fig. 1. The transition from two-electron processes to radical chain mechanisms.

Table 1. Photostimulated reactions of *tert*-butylmercury chloride.

Substrate	Product	% yield (equiv. *t*-BuHgCl; *hν*; time)[a]	
		t-BuHgCl[b]	*t*-BuHgCl/2 NaI[c]
CH_2=$CHSO_2Ph$	*t*-$BuCH_2CH_2SO_2Ph$	39 (1; R; 4 h)	85 (1; R; 4 h)[d]
CH_2=$CHP(O)(OEt)_2$	*t*-$BuCH_2CH_2P(O)(OEt)_2$	30 (1; S; 2 h)	86 (1; S; 2 h)[d]
CH_2=CHCOMe	*t*-$BuCH_2CH_2COMe$	7 (2; R; 10 h)	85 (2; R; 6 h)[d]
CH_2=$CHCO_2Et$	*t*-$BuCH_2CH_2CO_2R$	5 (2; R; 10 h)	80 (1; R; 6 h)[d,e]
5,6-Dihydro-2*H*-pyran-2-one	β-*tert*-Butylvalerolactone	Low	81 (2; R; 3 h)
Uracil	6-*tert*-Butyldihydrouracil	Low	62 (1.6; D; 15 h)[f]
2-Cyclohexenone	3-*tert*-Butylcyclohexanone	32 (2; R; 10 h)	85 (2; S; 2 h)
2-Cyclohexenone	3-Isopropylcyclohexanone	Low[g]	75 (2; S; 5 h)[g]
2-Cyclohexenone	3-Butylcyclohexanone	Low[h]	36 (2; S; 12 h)[h]
PhC≡CSO_2Ph	PhC≡CBu-*t*	49 (5; S; 17 h)	85 (5; S; 2 h)
(*E*)-PhCH=$CHSO_2Ph$	(*E*)-PhCH=CHBu-*t*	45 (5; S; 24 h)	73 (5; S; 24 h)
	PhCH(Bu-*t*)CH_2SO_2Ph	16 (5; S; 24 h)	27 (5; S; 24 h)
(*E*)-PhCOCH=CHCl	(*E*)-PhCOCH=CHBu-*t*	80 (5; S; 3 h)[j]	100 (5; S; 1 h)[j]

[a]Reaction mixtures containing the substrate (0.2–0.4 mmol) in 10 ml of deoxygenated Me_2SO were irradiated at 35–40 °C; 275 W sunlamp ca. 20 cm from the reaction vessel; R, Rayonet 350 nm photoreactor. [b]Work-up by $NaBH_4$ or H_3O^+. [c]Work-up with 1 % hydrochloric acid or $Na_2S_2O_3$. [d]Me_2SO (60 %)–MeOH (40 %). [e]*t*-$BuCH_2CH_2CO_2Me$, no telomer observed. [f]In the dark in the presence of 1 equiv. of $(NH_4)_2S_2O_8$. [g]^1H NMR yield in Me_2SO-d_6. [h]*i*-PrHgCl. [i]*n*-BuHgCl. [j](*E*)/(*Z*) = 70/30. A 100 % yield of (*E*)-PhCOCH=CHBu-*t* was also produced in 6 h in room light.

Results

Conjugate additions to α,β-unsaturated carbonyl compounds. Table 1 summarizes the effect of I^- in Me_2SO upon the photostimulated reaction of *t*-BuHgCl and a variety of α,β-unsaturated compounds. In the absence of I^- the reaction of ethyl acrylate leads mainly to the telomer *t*-$BuCH_2CH(CO_2Et)CH_2CH_2CO_2Et$ but in the presence of I^- the 1:1 addition product is formed in high yield. The combination RHgCl/2 I^- is much more effective than RHgCl alone in trapping the adduct radical *t*-$BuCH_2\dot{C}HCO_2Et$. This is interpreted in terms of a chain reaction involving reaction (5) instead of the inefficient S_H2 process of reaction (2). By ^{13}C NMR spectroscopy and the measurement of J (^{199}Hg–^{13}C) it is estimated that in Me_2SO at 25 °C that $[t\text{-}BuHgI_2^-]/[t\text{-}BuHgI][I^-] = 1\ M^{-1}$ whereas from ^1H NMR spectroscopy the complexation constant of *i*-PrHgI and I^- is ca. 9 M^{-1}.[11]

The addition products of Table 1 are formulated as arising from the chain process of Scheme 2 since no reaction occurs in the dark or in the presence of $(t\text{-}Bu)_2NO^{\cdot}$.

Competition of 2-cyclopentenone (C_5) and 2-cyclohexenone (C_6) for R$^{\cdot}$ in the RHgCl/NaI/Me_2SO system at 40 °C led to the reactivity ratio of $C_5/C_6 = 3.3$ for *t*-Bu; 2.9 for *i*-Pr$^{\cdot}$ and 2.3 for *n*-Bu$^{\cdot}$. On the other hand, towards $(n\text{-}Bu)_2CuLi$ at 0 °C or −78 °C, 2-cyclohexenone was five times as reactive as 2-cyclopentenone. From these results it appears that the C_5/C_6 reactivity ratio can be used as a mechanistic probe in conjugate addition reactions. Some pertinent results are summarized in Table 2. Both $(t\text{-}Bu)_2CuLi$ and $(t\text{-}Bu)_3ZnLi$/TMEDA gave a relative reactivity similar to that observed for *t*-Bu$^{\cdot}$ attack. On the other hand, $(t\text{-}Bu)_2Cu(Bu_3P)Li$ and $(t\text{-}Bu)_2Cu(CN)Li_2$ gave relative reactivities similar to that observed for $(n\text{-}Bu)_2CuLi$ and inconsistent with free radical attack. Extension to 2-cycloheptenone (C_7) was not particularly illuminating. Towards *t*-Bu$^{\cdot}$ at 40 °C in Me_2SO, the relative reactivity of C_6/C_7 was 2.5 but towards *n*-Bu$^{\cdot}$ only 1.1. In Et_2O at −78 °C $(t\text{-}Bu)_2CuLi$ or $(t\text{-}Bu)_2Cu(CN)Li_2$ gave a similar relative reactivity of 2.5±0.1 while $(n\text{-}Bu)_2CuLi$ and $(n\text{-}Bu)_2Cu(CN)Li_2$ gave reactivities of 1.2±0.1. All of the relative reactivities for the C_6/C_7 pair are consistent with radical attack. However, an alternative explanation is that the C_6/C_7 relative reactivity is not sensitive to the mechanism of the conjugate addition reaction. However, for the C_5/C_6 pair there seems to be a definite change in mechanism as reflected by a change in relative reactivity between $(t\text{-}Bu)_2CuLi$ or $(t\text{-}Bu)_3ZnLi$ and $(n\text{-}Bu)_2CuLi$ or $(t\text{-}Bu)_2Cu(CN)Li_2$ and this is attributed to a change from a radical to an ionic or cage mechanism.

The stereoselectivity of alkylation of 5-methyl-2-cyclohexenone [reaction (6)] was also consistent with this interpretation. The *cis*/*trans* product ratios for RHgCl/2 NaI/*hν* in Me_2SO at 40 °C were 45/55 for R = *t*-Bu, 26/74 for R = *i*-Pr and 19/81 for R = *n*-Bu. In Et_2O at −78 °C the *cis*/*trans* ratios observed for $(t\text{-}Bu)_2CiLi$ (41/59) and $(t\text{-}Bu)_3ZnLi$ (46/54) were similar to those observed for *t*-Bu$^{\cdot}$ attack. On the other hand, $(t\text{-}Bu)_2Cu(CN)Li_2$ gave *cis*/*trans* =

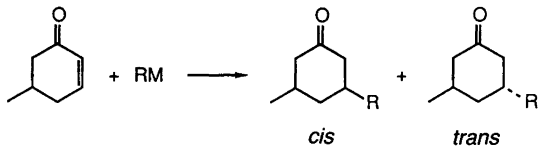
$$t\text{-}BuHgCl + 2\,I^- \rightleftarrows t\text{-}BuHgI_2^- \xrightarrow{h\nu} t\text{-}Bu^{\cdot} + {}^{\cdot}HgI + I^-$$

$$^{\cdot}HgI + t\text{-}BuHgI \rightarrow t\text{-}Bu^{\cdot} + HgI_2 + Hg^0$$

$$t\text{-}Bu^{\cdot} + CH_2{=}CH(EWG) \rightarrow t\text{-}BuCH_2\dot{C}H(EWG)$$

$$t\text{-}BuCH_2\dot{C}H(EWG) + t\text{-}BuHgI_2^- \rightarrow t\text{-}BuCH_2CH(EWG)^- + t\text{-}Bu^{\cdot} + HgI_2$$

Scheme 2.



(6)

9/91 and approximately the same value was observed for $(n\text{-Bu})_2$CuLi (−30 °C) and $(sec\text{-Bu})_2$CuLi (−78 °C).

Use of $CH_2{=}CPh_2$ as a radical trap provided further confirmation of a change in mechanism between $(t\text{-Bu})_2$CuLi and $(n\text{-Bu})_2$CuLi. With *t*-BuHgCl/Me_2SO/*hv*/40 °C the reaction with 2-cyclohexenone in the presence of a fivefold excess of $CH_2{=}CPh_2$ produced only 21 % 3-*tert*-butylcyclohexanone and a 38 % yield of a 1.2:1 mixture of *t*-BuCH=CPh_2 and *t*-$BuCH_2CHPh_2$, the disproportionation products of *t*-$BuCH_2\dot{C}Ph_2$.[5] With $(t\text{-Bu})_2$CuLi/Et_2O/−78 °C a 42 % yield of the alkylated cyclohexanone was observed and a 36 % yield of a 1.3:1 mixture of the disproportionation products. On the other hand, $CH_2{=}CPh_2$ had no effect on the alkylation with $(n\text{-Bu})_2$CuLi and even when 10 equiv. of $CH_2{=}CPh_2$ were employed, the yield of 3-butylcyclohexanone was 95 % at −30 or −78 °C. With $(t\text{-Bu})_2$Cu(CN)Li_2 at −78 °C or $(t\text{-Bu})_2$Cu(Bu_3P)Li at −30 °C the yield of 3-*tert*-butylcyclohexanone (83–85 %) was not diminished significantly and only traces of products derived from $CH_2{=}CPh_2$ were observed.

Our conclusion is that with $(t\text{-Bu})_2$CuLi or $(t\text{-Bu})_3$ZnLi in Et_2O, a free radical chain process is readily initiated and that alkylation by radical addition is the preferred course for the reaction with 2-cycloalkenones. With the more stable $(t\text{-Bu})_2$Cu(CN)Li_2 and $(t\text{-Bu})_2$Cu(Bu_3P)Li, or with $(n\text{-Bu})_2$CuLi, the radical process can be excluded. The radical reactions may involve electron transfer from the ate complexes to the adduct enolyl radical with generation of a thermally unstable $(t\text{-Bu})_2$Cu or $(t\text{-Bu})_3$Zn species which continues the chain reaction by decomposition to yield *t*-Bu· (Scheme 3).

Table 2. Relative reactivities of 2-cyclopentenone (C_5) and 2-cyclohexenone (C_6) with ate complexes in Et_2O.[a]

Reagent (°C)	Rel. react., C_5/C_6[b]	Product yield (%)
$(n\text{-Bu})_2$CuLi (−78)	0.18	78
$(n\text{-Bu})_2$CuLi (0)	0.20	62
$(n\text{-Bu})_3$ZnLi (−78)	0.45	88
$(t\text{-Bu})_2$CuLi (−78)	3.6	91
$(t\text{-Bu})_2$CuLi (−30)	4.2	79
$(t\text{-Bu})_3$ZnLi (−78)	3.5	62
$(t\text{-Bu})_2$Cu(CN)Li_2 (−78)	0.30	96
$(t\text{-Bu})_2$Cu(CN)Li_2 (−30)	0.14	79
$(t\text{-Bu})_2$Cu(Bu_3P)Li (−78)	0.27	85
$(t\text{-Bu})_2$Cu(Bu_3P)Li (−30)	0.18	92

[a]Reaction of 0.1 M C_5, 0.1 M C_6 and 0.01–0.02 M of the ate complex for 2–3 h. [b]Based on the ratio of 3-*tert*-butylcyclopentanone to 3-*tert*-butylcyclohexanone by GLC.

$$R\cdot + CH_2{=}CH(EWG) \rightarrow RCH_2\dot{C}H(EWG)$$
$$RCH_2\dot{C}H(EWG) + R_2CuLi \rightarrow RCH_2CH(EWG)^-Li^+ + R_2Cu$$
$$R_2Cu \rightarrow R\cdot + RCu$$

Scheme 3. R = *t*-Bu.

Scheme 3 with R = *n*-Bu would be much less likely to occur because of the greater thermal stability of $(n\text{-Bu})_2$CuLi and $(n\text{-Bu})_2$Cu.

Radical chain alkylations of enones are known to occur with a variety of trialkylboranes and trialkylalanes particularly with a trace of oxygen as the initiator.[14,15] Here the adduct enolyl radical displaces R· from R_3B or R_3Al by an S_H2 reaction analogous to reaction (2).

Vinyl substitution reactions of phenylethenyl and phenylethynyl sulfides and sulfones. The reaction of (*E*)-PhCH=$CHSO_2Ph$ with *t*-BuHgCl/*hv* with $NaBH_4$ work-up yields a 2.7:1 mixture of the α-addition [PhCH(*t*-Bu)CH_2SO_2Ph] and β-substitution [(*E*)-PhCH=CH-Bu-*t*)] products in a reaction which is facilitated by the presence of I^- (Table 1). However, I^- has no effect on the observed regioselectivity of *t*-Bu· attack. The reaction is formulated as involving the competing chain process of Scheme 4.

In the presence of I^- a more efficient chain process may occur because of electron transfer trom *t*-$BuHgI_2^-$ to $PhSO_2\cdot$ or PhCH(*t*-Bu)$\dot{C}HSO_2Ph$ although the increased yields (Table 1) may also be due to the increased rate of photoinitiation.[11] With PhC≡CSO_2Ph reaction with *t*-BuHgCl/*hv* leads to the substitution product PhC≡CBu-*t* with only traces of the addition product. Table 3 presents the ratio of substitution and addition products from PhCH=$CHSO_2Ph$ observed with other *tert*-butylating agents. The data suggest that radical attack is a possibility, at least at 0 °C, for all the reagents listed. With $(t\text{-Bu})_2$Cu(CN)Li_2 reaction was not observed at −78 °C but at 0 °C a reaction was observed with the regioselectivity expected for a radical process and not for carbanionic addition.

With (*E*)-PhCH=CHSPh, *t*-Bu· attack also occurred at the α and β carbon atoms while PhC≡CSPh yielded only the substitution product. Table 4 presents relative reactivity data for the competitive substitution reactions (β-attack) of (*E*)-PhCH=CHSPh (**3**), PhC≡CSPh (**4**) (*E*)-PhCH=$CHSO_2Ph$ (**5**) and PhC≡CSO_2Ph (**6**).

Anionic addition to an α,β-unsaturated sulfone would be expected to form the carbanion stabilized by the sulfone group. Such regioselectivity was not observed for any of the

$$R\cdot + PhCH{=}CHSO_2Ph \rightleftarrows \begin{cases} PhCHCH(SO_2Ph)R \\ PhCH(R)\dot{C}HSO_2Ph \end{cases}$$
$$PhCHCH(SO_2Ph)R \rightarrow PhCH{=}CHR + PhSO_2\cdot$$
$$PhCH(R)\dot{C}HSO_2Ph + RHgCl \rightarrow PhCH(R)CH(HgCl)SO_2Ph + R\cdot$$
$$PhSO_2\cdot + RHgCl \rightarrow PhSO_2HgCl + R\cdot$$

Scheme 4. R = *t*-Bu.

Table 3. Regioselectivity in the alkylation of (*E*)-PhCH=CHSO$_2$Ph.

Alkylating agent	k_α/k_β[a]
t-BuHgCl/Me$_2$SO/*hv*/40 °C	1/2.7
t-BuLi/THF/0 °C	1/2.8
t-BuMgCl/THF/25 °C	1/3.7
(*t*-Bu)$_2$CuLi/THF/0 °C	1/3.5
(*t*-Bu)$_2$Cu(CN)Li$_2$/THF/0 °C	1/4
(*t*-Bu)$_2$Cu(Bu$_3$P)Li/THF/0 °C	1/4
t-BuLi/THF/−78 °C	1/32
(*t*-Bu)$_2$CuLi/THF/−78 °C	1/13

[a]Based on the GLC ratio of PhCH(Bu-*t*)CH$_2$SO$_2$Ph (α-attack) and (*E*)-PhCH=CHBu-*t* (β-attack) formed.

reagents in Table 4 although with PhC≡CSO$_2$Ph, reaction with (*t*-Bu)$_2$Cu(CN)Li$_2$ or (*t*-Bu)$_2$Cu(Bu$_3$P)Li at 0 °C yielded PhC(*t*-Bu)=CHSO$_2$Ph in high yield.

The data of Table 4 is very suggestive of free radical attack when the organometallic reagent is *t*-BuLi. Elimination of PhS$^\cdot$ or PhSO$_2^\cdot$ from PhĊHCH(SO$_n$Ph)Bu-*t* or PhĊH=C(SO$_n$Ph)Bu-*t* is apparently followed by reaction (7) which can be considered to be either an electron trans-

$$PhSO_n^\cdot + t\text{-BuLi} \rightarrow PhSO_nLi + t\text{-Bu}^\cdot \quad (7)$$

fer or a lithium atom transfer process. Towards *t*-BuMgCl at 25 °C the relative reactivities of **3**:**4**:**5** are also consistent with radical attack but the high reactivity of **6** in exclusively β-substitution suggests another mode of reaction. It has been previously recognized that acetylenic sulfones undergo facile substitution reactions with a variety of organolithium or magnesium reagents including aromatic derivatives where the aryl radical would be an unlikely intermediate.[16,17]

With (*t*-Bu)$_2$CuLi at 0 °C the chemoselectivity is essentially the same as that observed with *t*-BuLi and the possibility exists that reaction proceeds via *t*-BuLi in equilibrium with (*t*-Bu)$_2$CuLi. [In reactions with 2-cycloalkenones *t*-BuLi fails to yield the conjugate addition products which are formed in high yields with (*t*-Bu)$_2$CuLi.] The increased reactivity of PhC≡CSO$_2$Ph and PhCH=CHSO$_2$Ph towards β-substitution with *t*-BuLi or (*t*-Bu)$_2$CuLi at −78 °C may reflect a non-radical process of the same type observed for PhC≡CSO$_2$Ph reacting with *t*-BuMgCl at 25 °C. It is presumed, but not proven, that the addition of *t*-Bu$^\cdot$ to **3**–**6** is an irreversible process. If the addition of *t*-Bu$^\cdot$ is reversible, complexation of the sulfone with Li$^+$ might lead to an increased rate of β-elimination of PhSO$_2$Li$^{\cdot+}$ resulting in the increased reactivity of the sulfones in the substitution reaction at −78 °C. However, at 0 °C the relative reactivities towards *t*-Bu$^\cdot$ from *t*-BuHgCl and towards the alkylating agent from *t*-BuLi are essentially the same. Furthermore, the relative reactivities of the two sulfones **5** and **6** in displacement of the sulfone group by *tert*-butyl are nearly constant ($k_6/k_5 \sim 2$) for the reagents of Table 4 with the notable exception of *t*-BuMgCl.

Table 4. Relative reactivities in β-substitution reactions for (*E*)-PhCH=CHSPh (**3**), PhC≡CSPh (**4**), (*E*)-PhCH=CHSO$_2$Ph (**5**) and PhC≡CSO$_2$Ph (**6**).[a]

Reagent	*k*(rel), **3**:**4**:**5**:**6**
t-BuHgCl/Me$_2$SO/*hv*/40 °C	1.0:1.0:3.3:5.3
t-BuLi/THF/40 °C	1.0:1.0:2.9:5.3
t-BuLi/THF/0 °C	1.0:1.3:3.4:6.8
t-BuLi/THF/−78 °C	1.0:0.7:29:50
(*t*-Bu)$_2$CuLi/THF/0 °C	1.0:0.9:3.2:7.6
(*t*-Bu)$_2$CuLi/THF/−78 °C	1.0:0.8:18:37
t-BuMgCl/THF/25 °C	1.0:0.7:2.2:92

[a]Based on the yields of (*E*)-PhCH=CHBu-*t* and PhC≡CBu-*t* by GLC observed from the reaction of two substrates each 0.5 M reacting over a period of 2–4 h with the organometallic reagent at an initial concentration of 0.1 M.

Combining the regioselectivity data of Table 3 and the chemoselectivity data of Table 4 leads to the conlcusion that the relative reactivities of PhCH=CHSPh (β-substitution), PhC≡CSPh (β-substitution) and PhCH=CHSO$_2$Ph (α-addition) are about equal for all the reagents of Table 4 and do not vary significantly with temperature. Since the reactions with *t*-BuHgCl are clearly free radical in nature, it seems probable that the other reactions also involve attack of *t*-Bu$^\cdot$.

It should be emphasized that tertiary alkyl organometallic reagents may well be unique in their propensity to undergo reactions involving the alkyl radical because the stability of the alkyl radical and the instability of the organometallic reagent increase the probability of the formation of the alkyl radical. Whether a given reagent participates in a radical chain process or in alkylation by some different process depends upon the rates of these competing processes. Radical processes are less likely to be observed when a feasible alternative ionic process is available. Thus, with 2-cycloalkenones the thermally stable (*t*-Bu)$_2$Cu(CN)Li$_2$ gave no evidence of reacting by a radical process at −78 °C although possibly the observed alkylation occurs by the electron-transfer cage mechanism of House.[18] On the other hand, PhCH=CHSO$_2$Ph which fails to react with (*t*-Bu)$_2$Cu(CN)Li$_2$ at −78 °C gave a regioselectivity at 0 °C which is quite consistent with *t*-Bu$^\cdot$ attack.

Experimental

General. ^{1}H and ^{13}C NMR spectra were obtained with a Nicolet NT300 spectrometer with tetramethylsilane as an internal standard. ^{31}P NMR spectra were obtained with a Bruker WM-300 spectrometer and reported in δ units 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 with a Kratos MS-50 spectrometer. Infrared spectra were obtained with a Beckman IR 4250 spectrometer. Neat spectra were recorded

between NaCl plates. Elemental analyses were performed by Galbraith Laboratories, Inc. All m.p.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 (Kieselgel 60, 230–400 mesh ASTM). Analytical gas chromatography was performed with a Varian 3700 chromatograph with a Hewlett Packard 3390A integrator employing naphthalene or biphenyl as the internal standard. Photostimulated reactions utilized a G.E. 275-W fluorescent sunlamp or a Rayonet Photoreactor (350 nm) and Pyrex reaction vessels. Both irradiation sources maintain the reaction mixtures at 35–40 °C.

Materials. Me_2SO was stirred over CaH_2 for 12 h at 80 °C, distilled and stored over 4 Å molecular sieves. THF was refluxed with $Ph_2C{=}O$/Na followed by distillation and storage over molecular sieves. Phenyl phenylethynyl sulfide[19] and sulfone[19] and phenyl (*E*)-phenylethenyl sulfide[20] and sulfone[20] were synthesized by literature procedures. The other substrates employed were purchased from Aldrich Chemical Company.

Alkylmercury halides were prepared according to literature procedures.[21] *tert*-Butylmercury chloride (m.p. 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 dark at 0 °C. Lithium dialkylcuprates were formed by the reaction of copper(I) salts with 2 equiv. of RLi in Et_2O or THF. Copper(I) iodide was flame-dried under a stream of nitrogen before the addition of the solvent. BuLi was allowed to react at −30 °C and *t*-BuLi or *sec*-BuLi at −78 °C. The reactions were vigorously stirred until the CuI had dissolved. $R_2Cu(CN)Li_2$ was similarly prepared at −30 °C from CuCN[22] and $R_2Cu(Bu_3P)Li$ from tetrakis{iodo[tributylphosphinecopper(I)]} at −78 °C.[23] Trialkylzincates were prepared from $ZnCl_2 \cdot$ TMEDA complex by reaction with BuLi at 0 °C or *t*-BuLi at −40 °C.[24]

General procedure for reactions of RHgCl with alkenyl substrates (Table 1). A tube containing RHgCl and the substrate in 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 solid $NaBH_4$ with a few drops of water added after 10 min. The product was hydrolyzed, separated from the mercury metal and extracted with Et_2O and concentrated to give the reaction product which was purified by flash column chromatography.

General procedure for the reactions of alkylmercury halides in presence of iodide salts. Sodium iodide was dissolved in 10 ml of Me_2SO under a nitrogen atmosphere. The alkylmercury halide was added followed by the α,β-unsaturated compound. The reaction mixture was irradiated with a 275 W sunlamp placed 15 cm from the reaction flask. Usually a dark brown solution resulted after 1 h of irradiation. For work-up, aqueous $Na_2S_2O_3$ (20 ml) was added and the mixture stirred for 10 min. The mixture was extracted with CH_2Cl_2, the extract dried over $MgSO_4$ and concentrated. Pure products were isolated by flash column chromatography. Reactions employing a mixture of NaI and $(NH_4)_2S_2O_8$ occurred in the dark and were conveniently followed by ^1H NMR spectroscopy in Me_2SO-d_6.

Diethyl 3,3-dimethylbutylphosphonate. The product had ^1H NMR ($CDCl_3$) δ 4.11 (q, *J* 4.2 Hz, 4 H), 1.72–1.70 (m, 4 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 33.430; MS *m/z* (relative intensity) Calc. for $C_{10}H_{22}O_3P$ (M^+-H): 221.13060; Found: 222 (0.2), 221.13036 (1.1), 207 (49), 166 (58), 165 (100), 151 (52), 138 (96), 111 (63), 57 (66); IR (neat) 2980, 2870, 1470, 1440, 1390, 1360, 1245, 1155, 1058, 960, 780 cm^{-1}. Anal. ($C_{10}H_{23}O_3P$) C, H, P.

3,3-Dimethylbutyl phenyl sulfone. The product had m.p. 52–53.5 °C (lit.[25] m.p. 59–60 °C); and the expected IR, NMR and GCMS; MS Calc. for $C_{12}H_{19}O_2S$ (M^++H): 227.1106; Found: 227.1104.

3-tert-Butylcyclopentanone. Material obtained by flash column chromatography with hexane (90 %)–ethyl acetate (10 %) elution had ^1H NMR ($CDCl_3$) δ 0.89 (s, 9 H), 1.85–2.05 (m, 3 H), 2.07–2.25 (m, 4 H); IR (neat) 1755, 1345 cm^{-1}; MS Calc. for $C_9H_{16}O$ (M^+): 140.24965. Found: *m/z* (relative intensity) 140.24694 (20), 125 (9), 97 (3), 84 (46), 83 (40), 69 (15), 57 (100).

3-tert-Butylcyclohexanone. The material had ^1H NMR ($CDCl_3$) δ 2.40–2.10 (m, 4 H), 1.82–1.31 (m, 5 H), 0.85 (s, 9 H); IR (neat) 1702, 1365 cm^{-1}; MS *m/z* (relative intensity) Calc. for $C_{10}H_{18}O$: 154.13577; Found: 154.13575 (32), 139 (8), 121 (6), 98 (85), 97 (30), 83 (30), 57 (100), 41 (61).

3-Isopropylcyclohexanone. The material had ^1H NMR ($CDCl_3$) δ 2.40–1.38 (m, 10 H), 0.84 (d, *J* 6.6 Hz, 6 H); IR (neat) 1742, 1465, 1455, 1405, 1155 cm^{-1}; MS *m/z* (relative intensity) Calc. for $C_9H_{16}O$: 140.12012; Found: 140.12001 (21), 125 (11), 110 (9), 98 (79), 83 (21), 69 (10), 42 (100).

3-Butylcyclohexanone and 3-butylcyclopentanone. These products had ^1H NMR, IR and GCMS properties identical with that of authentic samples.[26]

3-tert-Butylcycloheptanone. The product had ^1H NMR ($CDCl_3$) δ 2.51–1.80 (m, 11 H), 0.88 (s, 9 H); IR (neat) 1702, 1365 cm^{-1}; MS Calc. for $C_{11}H_{20}O$: 168.15142; Found: 168.15157.

γ-tert-*Butyl-δ-valerolactone.* The product had ^1H NMR ($CDCl_3$) δ 4.35–4.25 (m, 1 H), 4.18–4.08 (m, 1 H), 2.55–2.45 (m, 1 H), 2.25–2.10 (m, 1 H), 1.85–1.42 (m, 3 H),

0.80 (s, 9 H); IR (neat) 1745, 1600, 1530, 1350, 1200 cm^{-1}; MS *m/z* (relative intensity) Calc. for $C_8H_{13}O_2$ (M^+-CH_3): 141.09156; Found: 157 (M^++1.9), 141.09121 (8), 100 (100), 85 (4), 69 (21), 57 (76), 41 (56).

6-tert-Butyl-5,6-dihydrouracil. The product had ^1H NMR ($CDCl_3$) δ 8.07 [N(3)H, 1 H], 5.69 [N(1)H, 1 H], 3.35 (m, 1 H), 2.55 (m, 2 H), 0.98 (s, 9 H); MS *m/z* (relative intensity) Calc. for $C_8H_{14}N_2O_2$: 170.10553; Found: 170.10545 (3), 153 (6), 114 (100), 86 (22), 70 (25), 57 (50); MSCI (isobutane) 171 (M^++1).

3,3-Dimethyl-2-phenylbutyl phenyl sulfone. The sulfone was isolated from the photostimulated reaction of (*E*)-PhCH=CHSO$_2$Ph (3 mmol) and *t*-BuHgCl (15 mmol) in Me_2SO (30 ml). After photolysis with a 275 W sunlamp in a Pyrex tube under a nitrogen atmosphere for 65 h, the mixture was stirred for 10 min with an excess of sodium borohydride in the presence of a few millimeters of water. More water was added, and products were extracted with benzene. The benzene extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated. The two reaction products were isolated by column chromatography on silica gel using hexane–chloroform (60:40) as the eluent. The substitution product, 3,3-dimethyl-1-phenyl-1-butene,[27] was eluted first (73 % yield) followed by the sulfone. The addition product, 3,3-dimethyl-2-phenylbutyl phenyl sulfone, was obtained in 27 % yield after recrystallization from hexane and had m.p. 131–132 °C: HRMS 302.13375. Calc. for $C_{18}H_{22}O_2S$: 302.13406; GCMS *m/z* (relative intensity) 302 (M^+, 0.08), 104 (100), 77 (12), 57 (74); ^1H NMR ($CDCl_3$) δ 7.55–6.85 (m, 10 H), 3.67 (dd, *J* 10.5, 14.4 Hz, 1 H), 3.56 (dd, *J* 2.1, 14.4 Hz, 1 H), 2.97 (dd, *J* 2.1, 10.5 Hz, 1 H), 0.85 (s, 9 H).

Competitive alkylations of 2-cycloalkenones (Table 2). For alkylmercury chloride reactions, 1 mmol of NaI was flame-dried under a stream of N_2. Me_2SO (10 ml) was added by a hypodermic syringe through a rubber septum and the solution stirred until the NaI had dissolved. Solid alkylmercury chloride was added under nitrogen flushing and the two 2-cycloalkenones added by syringe. The reaction mixture was irradiated in a Rayonet photoreactor at ca. 40 °C. After work-up with 20 ml of aqueous $Na_2S_2O_3$ solution, the mixture was extracted with 2×10 ml of CH_2Cl_2 and the extract was dried over $MgSO_4$ and concentrated. The product ratio and yield were determined by GLC analysis corrected by independently determined response factors. All products were confirmed by GCMS.

Reaction with cuprate or zincate reagents involved the addition of a precooled solution of a mixture of the two ketones in Et_2O to the performed organometallic compounds. After reaction the mixture was poured into aqueous NH_4Cl, the pH adjusted to 8–9 by NH_4OH and the solution extracted with Et_2O three times. The ether extract was washed with brine, dried, concentrated and analyzed by GLC usually with biphenyl as an internal standard.

Alkylation of 5-methyl-2-cyclohexenone. The *trans*- and *cis*-3-alkyl-5-methylcyclohexenones isolated by flash column chromatography could be separated by capillary GLC but were more conveniently analyzed by ^1H NMR spectroscopy taking advantage of a smaller chemical shift and a larger coupling constant for the methyl group in the *trans*-isomer. 3-*tert*-Butyl-5-methylcyclohexenone gave a ^1H NMR spectrum of the *cis*-isomer ($CDCl_3$) of δ 0.899 (s, 9 H), 1.058 (d, 3 H, *J* 6.3 Hz), 1.40–2.60 (m, 8 H); *trans*-isomer δ 0.888 (s, 9 H), 0.964 (d, 3 H, *J* 7.5 Hz), 1.40–2.60 (m, 8 H). The mixture had IR (neat) 2965 (m), 2880 (s), 1715 (s), 1365 (s) cm^{-1}. HRMS (mixture) 168.15203. Calc. for $C_{11}H_{20}O$ (M^+): 168.15142. 3-Isopropyl-5-methylcyclohexanone gave a ^1H NMR spectrum of the *cis*-isomer ($CDCl_3$) δ 0.859 (d, 6 H, *J* 6.9 Hz), 0.997 (d, 3 H, *J* 6.3 Hz), 1.40–2.40 (m, 9 H); *trans*-isomer δ 0.859 (d, 6 H, *J* 6.9 Hz), 0.926 (d, 3 H, *J* 7.0 Hz), 140–2.40 (m, 9 H). HRMS (mixture) 154.13597. Calc. for $C_{10}H_{18}O$ (M^+): 154.13577. The 3-butyl-5-methylcyclohexanone isomers were confirmed by comparison of ^1H NMR and GCMS data with an authentic sample.[28] ^1H NMR of *cis*-isomer ($CDCl_3$) δ 0.851 (br t, 3 H), 1.004 (d, 3 H, *J* 4.8 Hz), 1.15–1.40 (m, 6 H), 1.70–2.39 (m, 8 H); *trans*-isomer, δ 0.851 (br t, 3 H), 0.959 (d, 3 H, *J* 6.9 Hz), 1.15–1.40 (m, 6 H), 1.70–2.39 (m, 8 H).

Regioselectivity for the tert-*butylation of (E)-PhCH=CHSO$_2$Ph (Table 3).* The reaction with *t*-BuHgCl was worked up with $NaBH_4$ or in the presence of I^- with aq. $Na_2S_2O_3$. Reaction with the other alkylating agents followed the procedure described below for competitive alkylations.

Chemoselectivity of alkylation of **3–6** *(Table 4).* Competitive reactions of alkenyl and alkynyl substrates were analyzed by GLC for PhC≡CBu-*t* and (*E*)-PhCH=CHBu-*t*. ^1H NMR and GCMS data for these products have been reported previously.[27]

To 10 ml of a THF solution of an organocopper reagent at the specified temperature were added 5 ml of a precooled THF solution of the substrate or mixture of substrates under a nitrogen atmosphere. After being stirred for a period of time, the mixture was poured into a satd. aqueous ammonium chloride solution and extracted with benzene. The benzene extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude product was analyzed by GC, GCMS, and ^1N NMR spectroscopy.

For the reaction with *t*-BuLi, the substrate or substrates were dissolved in 15 ml of dry THF under a nitrogen atmosphere in a round-bottom flask equipped with a rubber septum. The mixture was cooled to −78 or 0 °C, a precooled solution of *t*-BuLi at the same temperature was added via a syringe, and the mixture was stirred at the reaction temperature for a period of time. The reaction

with *t*-BuMgCl at 25 °C was carried out by a similar procedure. The reaction mixtures were worked up as mentioned above.

3,3-Dimethyl-2-phenyl-1-butenyl phenyl sulfone. The sulfone was isolated from the reaction of $PhC{\equiv}CSO_2Ph$ and $t\text{-}Bu_2Cu(CN)Li_2$ at 0 °C as white crystals, m.p. 102–102.5 °C (recrystallized from hexane): GCMS *m/z* (relative intensity) 300 (M^+, 5), 159 (53), 158 (14), 143 (13), 119 (21), 117 (20), 103 (27), 102 (38), 77 (23), 57 (100); HRMS 300.11892. Calc. for $C_{18}H_{20}O_2S$: 300.11841; ^1H NMR ($CDCl_3$) δ 7.50–6.73 (m, 10 H), 6.69 (s, 1 H), 1.07 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 141.85, 134.34, 132.49, 128.91, 128.76, 128.52, 128.40, 127.52, 127.43, 127.07, 38.20, 28.78.

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