

Hydroformylation of 1-Hexene in Place of 1-Iodohexane (eq 5). A mixture of 1-hexene (9.4 mmol), $\text{PtCl}_2(\text{PPh}_3)_2$ (0.50 mmol), K_2CO_3 (6.0 mmol), and dioxane (15 mL) was placed in a 100-mL stainless steel autoclave. The reactor was pressured with carbon monoxide (50 kg cm^{-2}) and molecular hydrogen (50 kg cm^{-2}) and stirred at 120 °C for 9 h. No carbonylated products were detected by GLC and IR measurements.

Carbonylation of 1-Bromohexane in the Presence of Potassium Iodide. A mixture of 1,4-dioxane (7.6 mL), methanol (30 mmol), 1-bromohexane (5.0 mmol), K_2CO_3 (3.0 mmol), $\text{PtCl}_2(\text{PPh}_3)_2$ (0.25 mmol), and potassium iodide (5.5 mmol) was placed in a 50-mL stainless steel autoclave (Yuasa Giken; SUS 304) equipped with a glass liner and a magnetic stirring bar. The reactor was pressured with carbon monoxide to 70 kg cm^{-2} and stirred at 120 °C for 9 h.

(E)- and (Z)-methyl 4-heptenoate: colorless oil; bp 86–88 °C (37 mmHg); IR (neat) 1742 cm^{-1} (C=O); ^1H NMR (300 MHz) (CDCl_3) δ 0.96 (t, 3 H, CH_3 , $J = 7.5$ Hz), 2.06 (quintet, 2 H, CH_2CH_3 , $J = 7.5$ Hz), 2.35 (m, 2 H, $-\text{CH}_2-$), 2.36 (m, 2 H, $-\text{CH}_2-$), 3.67 (s, 3 H, OCH_3), 5.25–5.55 (m, 2 H, $-\text{CH}=\text{CH}-$); ^{13}C NMR (25.05 MHz) (CDCl_3) δ 14.27 (q, CH_3), 20.49 (t, $\text{CH}_2\text{CH}_3(\text{Z})$), 22.72 (t, $\text{CH}_2\text{CH}=\text{Z}$), 25.54 (t, $\text{CH}_2\text{CH}_3(\text{E})$), 27.89 (t, $\text{CH}_2\text{CH}=\text{E}$), 34.23 (t, CH_2COOMe), 51.48 (q, OCH_3), 126.70 (d, $-\text{CH}=\text{CH}-$), 133.16 (d, $-\text{CH}=\text{CH}-$), 173.61 (s, C=O). Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: C, 67.57; H, 9.92; O, 22.50. Found: C, 67.39; H, 10.07; O, 22.25.

Methyl 2-nonynoate: IR (neat) 1721 cm^{-1} (C=O); ^1H NMR (90 MHz) (CDCl_3) δ 0.89 (t, 3 H, CH_3), 1.02–1.73 (m, 8 H, $-\text{CH}_2-$), 2.34 (t, 2 H, $-\text{CH}_2\text{C}\equiv\text{C}$), 3.76 (s, 3 H, OCH_3); ^{13}C NMR (25.05 MHz) (CDCl_3) δ 14.03 (q, CH_3), 18.67 (t, $-\text{CH}_2-$), 22.54 (t, $-\text{CH}_2-$), 27.59 (t, $-\text{CH}_2-$), 28.59 (t, $-\text{CH}_2-$), 31.29 (t, $-\text{CH}_2-$), 52.43 (q, OCH_3), 72.98 (s, $\text{C}\equiv\text{CCO}$), 89.77 (s, $-\text{C}\equiv\text{CCO}-$), 154.17 (s, C=O).

Isopropyl 2-nonynoate: ^{13}C NMR (25.05 MHz) (CDCl_3) δ 13.97 (q, CH_3), 18.67 (t, $-\text{CH}_2-$), 21.66 (q, $\text{CH}(\text{CH}_3)_2$), 22.49 (t, $-\text{CH}_2-$), 27.59 (t, $-\text{CH}_2-$), 28.53 (t, $-\text{CH}_2-$), 31.23 (t, $-\text{CH}_2-$), 69.45 (d, $-\text{CO}_2\text{CH}$), 73.56 (s, $\text{C}\equiv\text{CCO}$), 88.83 (s, $\text{C}\equiv\text{CCO}$), 153.35 (s, C=O).

7,9-Hexadecadiyne: colorless oil; bp 130 °C (0.08 mmHg); ^1H NMR (100 MHz) (CDCl_3) δ 0.89 (t, 6 H, 2 CH_3), 1.01–1.52 (m, 16 H, $-\text{CH}_2-$), 2.24 (t, 4 H, 2 $-\text{CH}_2\text{C}\equiv\text{C}$); ^{13}C NMR (25.05 MHz) (CDCl_3) δ 14.03 (q, CH_3), 19.25 (t, $-\text{CH}_2-$), 22.56 (t, $-\text{CH}_2-$), 28.41 (t, $-\text{CH}_2-$), 28.56 (t, $-\text{CH}_2-$), 31.33 (t, $-\text{CH}_2-$), 65.35 (s, $-\text{C}\equiv\text{CC}\equiv\text{C}-$), 77.48 (s, $-\text{C}\equiv\text{CC}\equiv\text{C}-$); MS, m/z 218.

Methyl 3-phenyl-2-propynoate: colorless oil; bp 130 °C (3 mmHg); IR (neat) 1717 cm^{-1} (C=O); ^{13}C NMR (25.05 MHz) (CDCl_3) δ 52.72 (q, OCH_3), 80.37 (s, $\text{PhC}\equiv\text{C}$), 86.42 (s, $\text{C}\equiv\text{CCO}_2-$), 119.53 (s, phenyl 1), 128.52 (d, phenyl 2,6), 130.63 (d, phenyl 4), 132.92 (d, phenyl 3,5), 154.40 (s, C=O). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_2$: C, 75.0; H, 5.0; O, 20.0. Found: C, 74.47; H, 5.22; O, 20.11.

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Registry No. $\text{PtCl}_2(\text{PPh}_3)_2$, 10199-34-5; $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$, 15377-00-1; $\text{Pt}(\text{PPh}_3)_4$, 14221-02-4; $\text{PtCl}_2(\text{AsPh}_3)_2$, 16242-55-0; $\text{PtCl}_2(\text{PCy}_3)_2$, 60158-99-8; $\text{Pd}(\text{PPh}_3)_4$, 14221-01-3; $\text{PdCl}_2(\text{PPh}_3)_2$, 13965-03-2; $\text{PtCl}_2(\text{PhCN})_2$, 14873-63-3; $\text{C}_{10}\text{H}_{21}\text{I}$, 2050-77-3; $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{I}$, 17376-04-4; cyclo- $\text{C}_6\text{H}_{11}\text{I}$, 626-62-0; $\text{C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{I}$, 557-36-8; (E)- $\text{C}_2\text{H}_5\text{CH}=\text{CHC}_2\text{H}_5\text{I}$, 119245-02-2; (Z)- $\text{C}_2\text{H}_5\text{CH}=\text{CHC}_2\text{H}_5\text{I}$, 21676-03-9; $\text{C}_6\text{H}_5\text{I}$, 591-50-4; $\text{C}_6\text{H}_{13}\text{I}$, 638-45-9; $\text{C}_{10}\text{H}_{21}\text{CO}_2\text{Me}$, 1731-86-8; $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CO}_2\text{Me}$, 103-25-3; cyclo- $\text{C}_6\text{H}_{11}\text{CO}_2\text{Me}$, 4630-82-4; $\text{C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{CO}_2\text{Me}$, 2177-86-8; (E)- $\text{C}_2\text{H}_5\text{CH}=\text{CHC}_2\text{H}_4\text{CO}_2\text{Me}$, 54004-29-4; (Z)- $\text{C}_2\text{H}_5\text{CH}=\text{CHC}_2\text{H}_4\text{CO}_2\text{Me}$, 39924-30-6; $\text{C}_6\text{H}_5\text{CO}_2\text{Me}$, 93-58-3; $\text{C}_6\text{H}_{13}\text{CO}_2\text{Me}$, 1119-06-8; $\text{C}_6\text{H}_{13}\text{CO}_2\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$, 119245-03-3; $\text{C}_6\text{H}_{13}\text{CHO}$, 111-71-7; $\text{C}_6\text{H}_{21}\text{CHO}$, 112-44-7; $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CHO}$, 104-53-0; cyclo- $\text{C}_6\text{H}_{11}\text{CHO}$, 2043-61-0; $\text{C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{CHO}$, 7786-29-0; $\text{C}_6\text{H}_{13}\text{C}\equiv\text{Cl}$, 81438-46-2; $\text{IC}\equiv\text{CC}_6\text{H}_5$, 932-88-7; 1-hexene, 592-41-6; 1-bromohexane, 111-25-1; methyl 2-nonynoate, 111-80-8; isopropyl 2-nonynoate, 119245-04-4; 7,9-hexadecadiyne, 18277-20-8; methyl 3-phenyl-2-propynoate, 4891-38-7; methyl heptanoate, 106-73-0; (E)-1-iodo-1-octene, 42599-17-7; (Z)-1-iodo-1-octene, 52356-93-1; (E)-methyl nonenoate, 14952-06-8; (Z)-methyl nonenoate, 68872-72-0.

Substitution Reactions in the β -Styryl and Phenylethynyl Systems¹

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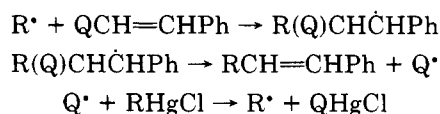
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Substitution for Q in the systems $\text{PhCH}=\text{CHQ}$, $\text{Ph}_2\text{C}=\text{CHQ}$, and $\text{PhC}\equiv\text{CQ}$ can occur by a free-radical chain mechanism where the attacking radical is alkyl ($\text{Q} = \text{HgX}$, Bu_3Sn , PhSO_2 , PhSO , PhS , Cl , Br , I) or $(\text{EtO})_2\text{PO}^\bullet$ ($\text{Q} = \text{HgX}$, Bu_3Sn , I). The Q^\bullet radicals formed by β -elimination can generate $t\text{-Bu}^\bullet$ or $(\text{EtO})_2\text{PO}^\bullet$ by reaction with $t\text{-BuHgCl}$, $\text{Hg}[\text{P}(\text{O})(\text{OEt})_2]_2$, $\text{ClHg}[\text{P}(\text{O})(\text{OEt})_2]$ or by electron transfer between HgCl and $(\text{EtO})_2\text{PO}^-$. With $\text{Q} = \text{PhS}$ or PhSO_2 , relative reactivity data indicates that the free radical addition-elimination sequence occurs for $t\text{-BuLi}$ at 0 or 45 °C and that this process may also be involved in reactions of $t\text{-BuMgCl}$ or *tert*-butyl cuprates with some of the substrates. Ionic reaction of $(\text{EtO})_2\text{PO}^-$ with the three substrates with $\text{Q} = \text{PhSO}_2$ or halogen are examined. With $\text{Q} = \text{PhSO}_2$, $\text{PhCH}[\text{P}(\text{O})(\text{OEt})_2]\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, $\text{Ph}_2\text{C}=\text{CHP}(\text{O})(\text{OEt})_2$, and $\text{PhC}\equiv\text{CP}(\text{O})(\text{OEt})_2$ are formed in good yield.

Substitution at an unsaturated carbon atom can occur by the addition-elimination of either nucleophiles or radicals. Alkyl substitution for a variety of electronegative or electropositive substituents in the β -styryl or phenylethynyl system occurs by the free-radical chain mechanism as shown in Scheme I in a photostimulated reaction with

Scheme I



alkylmercury halides.² In the present paper, we summarize the results of this homolytic process with $t\text{-BuHgCl}$ and examine the possibility of homolytic processes being involved in the reactions of other organometallic reactions and in the reactions involving $(\text{EtO})_2\text{PO}^-$ as a nucleophile, where the course of the reaction depends upon the structure of the substrate and the nature of the leaving group.

Summary of Reactions with *tert*-Butylmercury Chloride. For substitution by an alkyl radical, the leaving group Q in 1–3 can be HgX , Bu_3Sn , PhSO_2 , PhSO , PhS , Cl , Br , or I .²⁻⁷ The eliminated radical Q^\bullet will regenerate

(1) Electron Transfer Processes. 45. Work supported by the National Science Foundation (Grant CHE-8717871) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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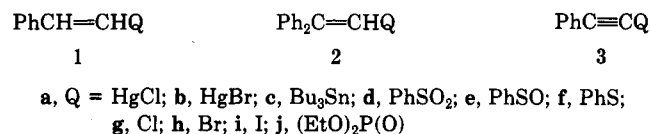
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Table I. Photostimulated Reaction of *t*-BuHgCl with 1-3 in Me₂SO at 35-40 °C

substrate	conditions (equiv <i>t</i> -BuHgCl, <i>hν</i> , time) ^a	% subst product (E/Z)	rel react. ^b	ref
(<i>E</i>)-1a	5, S, 4 h	97 (31)	[1.5]	6
2b	5, R, 12 h	100	[1.9]	6
(<i>E</i>)-1c	PhH, 1.2, S, 14 h	83 (49)	[0.7]	6
2c	PhH, 1.2, R, 18 h	78	[0.8]	6
3c	PhH, 5, R, 24 h	61	[0.2]	6
(<i>E</i>)-1d	5, S, 18 h	43 (>50) ^c	1.3	7
(<i>E</i>)-1d	5, 10 equiv of NaI, S, 24 h	73 (>50) ^d		
2d	2.5, R, 20 h	88	[6.5]	7
3d	5, R, 7 h	57	2.1	7
3d	5, 10 equiv of NaI, S, 24 h	85		
(<i>E</i>)-1e	5, R, 24 h	32 (21)		7
(<i>E</i>)-1f	5, R, 24 h	36 ^e	0.4	7
3f	0.2, S, 24 h	44	0.4	7
(<i>E</i>)-1g	5, S, 2 h, 5 of equiv NaI	53 (>50)	2.2	
(<i>E</i>)-1h	5, S, 2 h, 5 of equiv NaI	100 (>50)	3.5	
(<i>E</i>)-1i	5, S, 4 h	100 (25)	2.8	7
(<i>Z</i>)-1i	5, S, 6 h	90 (0.04)	1.8	7
2i	5, S, 12 h	86	1.0	7
3i	1.5, S, 7 h	100	[3.8]	7

^a[Substrate] = 0.01-0.1 M. R = Rayonet Photoreactor (350 nm); S = 275-W sunlamp ca. 20 cm from the reaction vessel. ^bTo form the substitution product, values in brackets are relative reactivities toward cyclohexyl radicals (ref 6). ^c16% of PhCH(Bu-*t*)CH₂SO₂Ph observed after NaBH₄ workup. ^d27% of PhCH(Bu-*t*)CH₂SO₂Ph formed. ^e12% of a mixture of PhCH(Bu-*t*)CH₂SPh and PhC(Bu-*t*)=CHSPh formed.

an alkyl radical by reaction with an alkylmercury halide, or in the case of Bu₃Sn[•], and less efficiently with [•]HgCl,⁸ by attack upon an alkyl halide. The formation of the alkyl



radical occurs most readily for the tertiary alkylmercurials and the yields decrease significantly between tertiary or secondary alkylmercurials and primary alkylmercury halides.^{6,9} Table I summarizes the observed yields and the competitive relative reactivities of 1-3 observed in photostimulated reactions with *t*-BuHgCl in Me₂SO at 35-40 °C.

The reactions with (*E*)- and (*Z*)-1-alkenyl iodides are stereospecific (retention)^{3,7} with the *E* isomer more reactive than *Z* isomer toward *t*-Bu[•].⁷ The reactions of 1-3 with *t*-Bu[•] were highly regioselective with preferential attack of *t*-Bu[•] at the carbon with the Q substituent. The only exceptions recognized are in attack of *t*-Bu[•] upon PhCH=CHSO₂Ph and PhCH=CHSPh where about 30% attack upon the phenyl-substituted carbon (α -position) is noted.⁷ The reactivities of the various derivatives of 1-3 show little effect of the nature of Q for attack at the β -carbon atom. In general, the halides and sulfones are more reactive than the corresponding stannane derivatives, which is consistent with a preferred attack of the nucleophilic (electron-donating) *t*-Bu[•] upon electron deficient

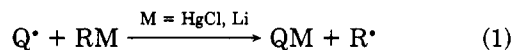
Table II. Relative Reactivities of PhCH=CHSPh (1f), PhC≡CSPH (3f), PhCH=CHSO₂Ph (1d), and PhC≡CSO₂Ph (3d) in Substitution Reactions

organometallic	conditions	<i>k</i> (rel), 1f:3f:1d:3d ^a	<i>k_α/k_β</i> for 1d ^b
<i>t</i> -BuHgCl	Me ₂ SO, 45 °C, <i>hν</i>	1.0:1.0:3.3:5.3	1:2.7
<i>t</i> -BuLi	THF, 45 °C	1.0:1.0:2.9:5.3	
<i>t</i> -BuLi	THF, 0 °C	1.0:1.3:3.4:6.8	1:2.8
<i>t</i> -BuMgCl	THF, 25 °C	1.0:0.7:2.2:9.2	1:3.7
<i>t</i> -BuLi	THF, -78 °C	1.0:0.7:2.9:5.0	1:3.2
(<i>t</i> -Bu) ₂ CuLi	THF, 0 °C	1.0:0.9:3.2:7.6	1:3.5
(<i>t</i> -Bu) ₂ CuLi	THF, -78 °C	1.0:0.8:1.8:3.7	1:1.3
(<i>t</i> -Bu) ₂ Cu(CN)Li ₂	THF, 0 °C		1:4
(<i>t</i> -Bu) ₂ Cu(PBu ₃)Li	THF, 0 °C		1:4

^aCompetition involved two substrates each 0.5 M reacting over a 2-4 period with the organometallic reagent at an initial concentration of 0.1 M. ^b α -Attack leads to PhCH(Bu-*t*)CH₂SO₂Ph; β -attack leads to PhCH=CHBu-*t*.

π -bonds. The phenylacetylene derivatives with Q = I or PhSO₂ are as reactive as the corresponding alkenes, but with Q = Bu₃Sn, 1 and 2 are more reactive than 3 by a factor of 4.

Reactions with Other *tert*-Butylating Agents. With the regioselectivity and kinetic selectivity defined for *t*-Bu[•] attack, we have examined the reactivity of other organometallic reagents in competitive reactions with the sulfides and sulfones, 1d,f and 3d,f. Table II summarizes competitive reactivity data observed in the reactions of an excess of a mixture of 1 and 3 with various *tert*-butylating agents while Table III summarizes the product yields observed in the reactions of an excess of the organometallic reagent with the various substrates. The data of Table II suggest that the reactions of *t*-BuLi (0 or 45 °C in THF) with these substrates occur in a free-radical fashion. The eliminated radical (Q[•] = PhSO₂[•], PhS[•]) apparently can attack lithium to regenerate *t*-Bu[•] as it does in the case of *t*-BuHgCl (reaction 1).^{10,11}



The reactions of *t*-BuLi and *t*-Bu₂CuLi gave similar selectivities at 0 or -78 °C, suggesting that in this case reaction of the cuprate may actually involve *t*-BuLi.¹² Alternately, (*t*-Bu)₂CuLi could react with Q[•] to form LiQ and (*t*-Bu)₂Cu, which would yield *t*-Bu[•] upon homolysis. With *t*-BuMgCl at 25 °C, 1d,f and 3f had relative reactivities consistent with radical attack, but the acetylenic sulfone had a greatly enhanced reactivity. The propensity of acetylenic sulfones to undergo substitution reactions with organolithium and magnesium reagents has been previously observed by Truce,¹³ and evidence for a mechanism involving electron transfer has been presented by Eisch.¹⁴ With *t*-BuLi or (*t*-Bu)₂CuLi at -78 °C, both the styryl and phenylethynyl sulfone showed an enhanced reactivity, presumably reflecting some process involving coordination of the alkylating agent. The cuprates (*t*-Bu)₂Cu(CN)Li₂ and (*t*-Bu)₂Cu(PBu₃)Li gave a regioselectivity with PhCH=CHSO₂Ph at 0 °C consistent with radical attack, but these cuprates reacted with PhC≡

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Table III. Reaction of Organometallic Reagents in THF with **1d,f** and **3d,f** (R = *t*-Bu)

substrate (mmol)	organometallic (mmol)	conditions ^a	products, %	
			substitution ^b	addition ^c
1d (0.5)	RLi (2.5)	0 °C, 2 h	71	25
1d (0.5)	RLi (2.5)	-78 °C, 2 h	97	3
1d (0.5)	R ₂ CuLi (2.5)	-78 °C, 2 h	93	7
1d (0.5)	RCu(I)Li (2.5)	-78 °C, 2 h	76	4
1d (0.5)	R ₂ Cu(CN)Li ₂ (2.5)	-78 °C, 2 h	0	0
1d (0.5)	R ₂ Cu(CN)Li ₂ (2.5)	0 °C, 2 h	46	12
1d (0.5)	R ₂ Cu(PBu ₃)Li (1.0)	0 °C, 2 h	48	12
1d (0.5)	R ₂ Cu(PBu ₃)Li (1.0)	-78 °C, 2 h	10	0
1d (0.5)	RMgCl (2.5)	25 °C, 4 h	22	6
3d (0.5)	RMgCl (2.5)	25 °C, 2.5 h	82	0
3d (0.5)	RLi (2.5)	0 °C, 2 h	93	2
3d (0.5)	RLi (2.5)	-78 °C, 2 h	73	2
3d (0.5)	R ₂ CuLi (2.5)	-78 °C, 2 h	93	7
3d (0.5)	RCu(I)Li (2.5)	0 °C, 2 h	0	95 ^d
3d (0.5)	RCu(I)Li (2.5)	-78 °C, 2 h	45	46 ^d
3d (0.5)	R ₂ Cu(CN)Li ₂ (2.5)	0 °C, 2 h	0	88 ^e
3d (0.5)	R ₂ Cu(CN)Li ₂ (2.5)	-78 °C, 2 h	0	81 ^e
3d (0.5)	R ₂ Cu(PBu ₃)Li (1.0)	0 °C, 2 h	21	69
3d (0.5)	R ₂ Cu(PBu ₃)Li (1.0)	-78 °C, 2 h	66	44
3d (0.5)	BuLi (2.5)	0 °C, 2 h	30	2
3d (0.5)	BuLi (2.5)	-78 to 25 °C, 2 h	98	0
3d (0.5)	Bu ₂ CuLi (2.5)	-78 °C, 2 h	88	12
1f (0.5)	RLi (2.5)	0 °C, 2 h	78	
1f (0.5)	RLi (2.5)	-78 °C, 2 h	96	
1f (0.5)	R ₂ CuLi (2.5)	-78 °C, 2 h	100	
3f (0.5)	RMgCl (2.5)	25 °C, 19 h	22	
3f (1.0)	RLi (5)	-78 °C, 2 h	84	
3f (1.0)	RuCu(I)Li (5)	-78 °C, 2 h	89	
3f (1.0)	R ₂ CuLi (5)	-78 °C, 2 h	86	
3f (1.0)	Bu ₂ CuLi (5)	-78 °C, 2.5 h	89	
1e (1.0)	RLi (5)	-78 °C, 2 h	30 ^f	
1e (1.0)	R ₂ CuLi (5)	-78 °C, 2 h	20 ^f	

^aIn 15 mL of THF. ^bSubstitution products are PhCH=CHBu-*t* or PhC≡CBu-*t*. ^cAddition products are PhCH(Bu-*t*)CH₂SO₂Ph or PhCH(Bu-*t*)=CHSO₂Ph. ^d*E* and *Z* isomers of PhC(Bu-*t*)=CHSO₂Ph. ^eOnly a single isomer of PhC(Bu-*t*)=CHSO₂Ph was observed by GLC. ^fSeveral unidentified products observed.

CSO₂Ph to give PhC(Bu-*t*)=CHSO₂Ph, the product expected from anionic but not radical attack. This mode of addition appears to be favored at higher temperatures for *t*-BuCu(I)Li and (*t*-Bu)₂Cu(PBu₃)Li (see Table III). Apparently, there are at least three distinct processes involved in the reaction of vinyl and acetylenic sulfides and sulfones with the organometallic reagents employed: (1) a process involving free *t*-Bu[•] characteristic of *t*-BuHgCl/*hν* and possibly *t*-BuLi and (*t*-Bu)₂CuLi, (2) a process resulting in enhanced reactivity of PhC≡CSO₂Ph in substitution reactions with *t*-BuMgCl, (3) a process involving addition in the anionic sense for PhC≡CSO₂Ph with (*t*-Bu)₂Cu(CN)Li₂, (*t*-Bu)₂Cu(PBu₃)Li, and *t*-BuCu(I)Li. The relative reactivities of PhCH=CHSPh and PhC≡CSPH in substitution reactions are essentially 1:1 with the reagents *t*-BuHgCl/*hν*/45 °C, *t*-BuLi (0 or -78 °C), (*t*-Bu)₂CuLi (0 or -78 °C) or *t*-BuMgCl (25 °C), suggesting that the substitution of *tert*-butyl for the PhS group occurs either by a common intermediate (i.e., *t*-Bu[•]) or that relative reactivity is independent of the nature of the attacking species. A similar conclusion is reached when the relative reactivities in substitution of PhCH=CHSO₂Ph and PhC≡CSO₂Ph are considered; with *t*-BuHgCl/*hν*, *t*-BuLi (0 or -78 °C) or (*t*-Bu)₂CuLi (0 or -78 °C), the acetylenic sulfone is about twice as reactive as the vinylic sulfone.

The regiochemistry observed in the reactions of *t*-BuLi or (*t*-Bu)₂CuLi with the sulfones is consistent with radical attack but by no means requires a homolytic substitution process as evidenced by the greatly increased reactivity in substitution of PhC≡CSO₂Ph but not PhCH=CHSO₂Ph toward *t*-BuMgCl. The large increase in β/α attack (i.e., substitution/addition) for PhCH=CHSO₂Ph and the increased reactivities of the sulfones relative to the sulfides

as the temperature is lowered is a bit surprising if only *t*-Bu[•] attack is involved since *E*_a for *t*-Bu[•] attack upon alkenes is only about 4 kcal/mol.¹⁵ However, preferential complexation of the organometallic reagents with either (or both) the PhS or PhSO₂ substituents could affect the reactivities of the substrates toward radical attack and lead to enhanced reactivities for the sulfones.

No direct evidence for radical involvement has been obtained for the reactions involving *t*-BuLi, *t*-BuMgCl, or (*t*-Bu)₂CuLi with the substrates of Table II. The reactions occur rapidly in the dark, and small amounts of free radical chain inhibitors (such as (*t*-Bu)₂NO[•]) have no appreciable effect on the yields. However, these observations are consistent with a radical process involving a rapid initiation step (i.e., a short kinetic chain length). Furthermore, it is difficult to find an inhibitor that is not destroyed by reaction with the organometallic reagent. If a free radical is involved, it may well be more important for *tert*-alkylating agents because of the increased stability of *tert*-alkyl radicals. However, *n*-BuLi or (*n*-Bu)₂CuLi also reacted with PhC≡CSPH or PhC≡CSO₂Ph to yield mainly the substitution products consistent with radical attack (*n*-BuLi with PhCH=CHSO₂Ph leads mainly to lithiation at the sulfone-substituted carbon atom¹⁴). The effects of stoichiometric amounts of radicaphiles (such as R₂PH, CH₂=CHCH₂I, Ph₂C=CH₂) are being investigated in these reactions. In general, they decrease the yields of the *tert*-butylation products from **1d,f** and **3d,f** but whether this results from competition for *t*-Bu[•] (as in the case of

(15) Fischer, H. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; NATO ASI Series C; D. Reidel: Dordrecht, 1986; Vol. 189, p 123.

Table IV. Formation of (*E*)-PhCH=CHP (1j) or Ph₂C=CHP (2j) in Photostimulated Reaction 2 (P = (EtO)₂P(O)) in Me₂SO at 35–40 °C

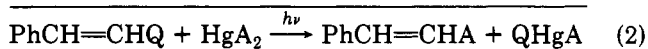
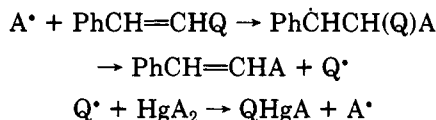
substrate ^a	% yield (reaction time, h) ^b	
	1 equiv of HgP ₂	3 equiv of ClHgP
(<i>E</i>)-1a	68 (3)	65 (8)
2b	86 (24)	85 (4)
2c	14 (20)	65 (24)
(<i>E</i>)-1d	0 (20)	1 (4)
2c	0 (20)	26 (24)
(<i>E</i>)-1f	0 (20)	0 (4)
2f	0 (20)	0 (24)
1h		3 (4)
2h	23 (24)	3 (4)
1i	85 (8)	88 (4)
2i	86 (24)	84 (12)

^aSubstrate (0.01 M) and mercurial in Me₂SO in a Pyrex tube was irradiated in a 350-nm Rayonet Photoreactor. ^b¹H NMR yield with an internal standard.

t-BuHgCl/*hν*) or for the organometallic reagent itself is difficult to ascertain.

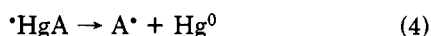
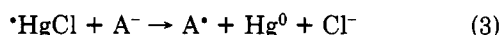
Nucleophilic Substitution Reactions Involving Free Radicals. Substitution of a heteroatom substituent for Q = I, HgCl, or Bu₃Sn in 1–3 can be achieved in a radical chain process by the use of Hg(II) salts such as HgA₂ with A = PhS, PhSe, PhSO₂, or (EtO)₂PO as shown in Scheme II.^{2–5} As demonstrated in Table IV, reaction

Scheme II



2 with Hg[P(O)(OEt)₂]₂ or ClHgP(O)(OEt)₂ works poorly or not at all with Q = Br, PhSO₂ or PhS for 1 and 2. Where reaction was not observed, or occurred poorly, the unreacted starting alkene could be recovered. Substitution for HgCl or Bu₃Sn in 1–3 by RS or PhSO₂ also occurs in a radical chain fashion with RSSR, PhSeSO₂Ph, or ClSO₂Ph by attack of the eliminated [•]HgCl or Bu₃Sn[•] upon the dichalcogenide or sulfonyl derivative.^{5,8}

Reactions of A[•] = PhS[•], PhSO₂[•], or (EtO)₂PO[•] with 1-alkenylmercurials also occurs in a free-radical chain fashion where the eliminated [•]HgCl or [•]HgA regenerates A[•] by reactions 3 and/or 4.^{8,15} Disproportionation of



RCH=CHHgX into (RCH=CH)₂Hg and HgX₂ is a serious problem in the presence of nucleophiles in Me₂SO, but with PhSO₂[•], the symmetrization of 1a or 2a could be minimized by use of a Me₂SO/*t*-BuOH/H₂O solvent.¹⁶

Photolysis of 1a with 1 equiv of (EtO)₂PO[•] = P[•] in Me₂SO formed the vinyl phosphonate (1j) and the symmetrized mercurial (Table V). The β-styryl phosphonate could also be formed cleanly in photostimulated reactions using an excess of (EtO)₂POH and KOH in Me₂SO or in a solvent system of Me₂SO (90%)–H₂O (10%). However, reaction of excess P[•] (5–10 equiv) with 1a in Me₂SO occurred in the dark to give significant amounts of PhCH=CH₂ and PhCH₂CH₂P. Apparently, nucleophilic attack of P[•] upon 1a and/or (PhCH=CH)₂Hg occurs at mercury to form PhCH=CH₂, which reacts slowly with P[•]

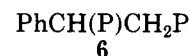
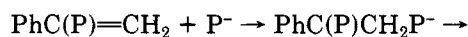
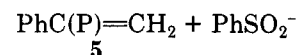
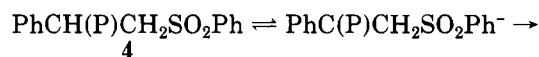
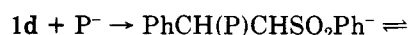
to form PhCH₂CH₂P (Table V). In Me₂SO (90%)–*t*-BuOH (10%) cleavage to PhCH=CH₂ occurred nearly quantitatively but now PhCH=CH₂ did not react with P[•] to form PhCH₂CH₂P. Reaction of 2a with 1–2 equiv of P[•] formed mainly Ph₂C=CH₂ and the symmetrized mercurial with only small amounts of 2j even upon photolysis.

Ionic Substitution Reactions with (EtO)₂PO[•]. With Q = PhSO₂, Br, or I, the substrates 1–3 react in an ionic fashion with P[•] in reactions that cannot be photostimulated or inhibited by (*t*-Bu)₃NO[•]. Substitution occurred cleanly for Ph₂C=CHSO₂Ph, Ph₂C=CHBr, or PhC≡CSO₂Ph (Table V). However, with PhC≡CBr or PhC≡CI, the major product was PhC≡CH in 70–80% yield, presumably from nucleophilic attack upon halogen to form PhC≡C[•]. This process may also be occurring for Ph₂C=CHI, which gave a much lower yield of Ph₂C=CHP (21%) than did Ph₂C=CHBr (70%) or Ph₂C=CHSO₂Ph (100%).

The rapid reaction of PhCH=CHSO₂Ph (1d) with excess P[•] gave an isolated yield of PhCH(P)CH₂P of 80%. The diphosphonate was also the major product when P[•] was not employed in excess. The β-styryl bromide (1h) reacted more slowly with P[•], but the diphosphonate was again formed in high yield. No reaction was observed between P[•] and PhCH=CHSPH and only a low yield of product was observed with PhCH=CHCl or PhCH=CHI. In these cases the unreacted substrate could be recovered even upon photolysis.

The presence of unionized (EtO)₂P(O)H had no effect upon the ionic reaction of PhCH=CHBr. However, with PhCH=CHSO₂Ph the presence of (EtO)₂P(O)H led to the formation of PhCH(P)CH₂SO₂Ph (4) in reaction times as short as 5 min at 25 °C (Table V). This observation suggested that the diphosphonate (6) was formed from 1d by the mechanism of Scheme III. Such a mechanism is

Scheme III [P = (EtO)₂P(O)]



also implicated by the observation that 6 is formed from 1d more rapidly than P[•] adds to the β-styryl phosphonate 1j. This scheme was verified by analysis for intermediates 4 and 5. Isolated 4 could be converted to 6 by reaction with P[•] or to 5 upon reaction with *t*-BuOK in Me₂SO (Table V). Reaction of 6 with EtO[•]/EtOH has been reported to rapidly form the EtO[•] adduct of 5,¹⁷ but strangely 6 with *t*-BuOK/Me₂SO in the absence of P[•] formed PhCOCH₂P, possibly from an α-elimination followed by oxygenation of the carbene by Me₂SO.^{18,19}

Reaction of PhCH=CHBr and Ph₂C=CHBr with P[•] apparently involves the addition of P[•] at the β-carbon followed by loss of Br[•]. Reaction of an equal molar mixture of PhCH=CHBr and PhCH=CHP with 2.5 equiv of P[•] at 50 °C for 5 h gave an 80% yield of 6, 20% of recovered PhCH=CHBr, and no unreacted PhCH=CHP. Thus, the reactivities toward P[•] are PhCH=CHSO₂Ph (α-attack) >

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(16) Hershberger, J.; Russell, G. A. *Synthesis* 1980, 475.

Table V. Reaction of $(\text{EtO})_2\text{PO}^-$ with 1-3 in Me_2SO

substrate (mol)	$(\text{EtO})_2\text{P}(\text{O})\text{H}$, mmol	KOCMe_3 , mmol	conditions ^a	product ^b
1a (0.5)	1.0	1.0	S, 19 h, 50 °C	1j (87%), $\text{PhCH}_2\text{CH}_2\text{P}$ (3%), $\text{PhCH}=\text{CH}_2$ (10%)
1a (0.5)	2.5	2.5	S, 21 h, 50 °C	1j (42%), $\text{PhCH}=\text{CH}_2$ (20%)
1a (0.5)	1.0	1.0	Me_2SO (90%)– H_2O (10%) S, 20 h, 50 °C	1j (70%), $\text{PhCH}_2\text{CH}_2\text{P}$ (13%), $\text{PhCH}=\text{CH}_2$ (8%)
1a (0.5)	1.0	1.0	(KOH) dark, 20 h, 50 °C	$(\text{PhCH}=\text{CH})_2\text{Hg}$, trace $\text{PhCH}=\text{CH}_2$
1a (0.5)	5.0	5.0	S, 19 h, 50 °C	$\text{PhCH}_2\text{CH}_2\text{P}$ (35%), $\text{PhCH}=\text{CH}_2$ (35%)
1a (0.5)	5.0	5.0	dark, 22 h, 50 °C	$\text{PhCH}_2\text{CH}_2\text{P}$ (29%), $\text{PhCH}=\text{CH}_2$ (37%)
1a (0.5)	2.5	2.5	Me_2SO (90%)– <i>t</i> -BuOH (10%), S, 21 h, 50 °C	$\text{PhCH}_2\text{CH}_2\text{P}$ (<10%), $\text{PhCH}=\text{CH}_2$ (68%)
1a (0.5)	2.5	2.5	Me_2SO (90%)– <i>t</i> -BuOH (10%), dark, 22 h 50 °C	$\text{PhCH}=\text{CH}_2$ (99%)
$\text{PhCH}=\text{CH}_2$ (1.0)	10.0	10.0	dark, 22 h, 50 °C	$\text{PhCH}_2\text{CH}_2\text{P}$ (68%), $\text{PhCH}=\text{CH}_2$ (21%)
$(\text{PhCH}=\text{CH})_2\text{Hg}$ (0.5)	5.0	5.0	dark, 22 h, 50 °C	$\text{PhCH}_2\text{CH}_2\text{P}$ (20%), $\text{PhCH}=\text{CH}_2$ (39%)
2a (0.5)	1.0	1.0	S, 22 h, 50 °C	2j (27%), $\text{Ph}_2\text{C}=\text{CH}_2$ (23%), $(\text{Ph}_2\text{C}=\text{CH})_2\text{Hg}$
2a (0.5)	1.5	0.5	S, 22 h, 50 °C	2j (10%), $\text{Ph}_2\text{C}=\text{CH}_2$ (58%), $(\text{Ph}_2\text{C}=\text{CH})_2\text{Hg}$
1d (0.5)	0.5		30 min, 25 °C	none
1d (0.5)	0.5	0.5	30 min, 25 °C	5 (0.02 mmol), 6 (0.24 mmol)
1d (3.0)	7.5	7.5	5 min, 25 °C	5 (5%), 6 (80%, I)
1d (5.0)	15.0	5.0	5 min, 25 °C	4 (95%; 80%, I)
1d (5.0)	15.0	5.0	10 min, 25 °C	4 (71%; 67%, I), 5 (16%), 6 (13%)
1d (0.5)	1.5	0.5	2 min, 25 °C	4 (77%), 5 (7%), 6 (14%)
1d (0.5)	1.5	0.5	4 h, 25 °C	4 (55%), 5 (16%), 6 (25%)
4 (1.0)	1.0	2.0	10 min, 25 °C	6 (53%, I)
4 (0.5)	0.5	1.0	5 min, 25 °C	5 (40%), 6 (53%)
4 (0.5)		0.6	5 min, 25 °C	4 (13%), 5 (87%)
4 (0.5)	0.5	0.5	5 min, 25 °C	4 (62%), 5 (13%), 6 (24%)
4 (0.5)	0.5	0.5	2 h, 25 °C	4 (50%), 5 (4%), 6 (41%)
6 (0.3)		0.4	30 min, 25 °C	PhCOCH_2P (78%)
1h (1.0)	5.0	5.0	S, 7 h, 50 °C	6 (100%)
1h (1.0)	5.0	5.0	dark, 4 h, 50 °C	6 (48%)
1h (1.0)	5.0	5.0	S, 4 h, 50 °C	6 (62%)
1h (1.0)	5.0	5.0	S, 4 h, 50 °C, 0.1 mmol $(t\text{-Bu})_2\text{NO}^*$	1j (1%), 6 (57%)
1h (1.0)	5.0	5.0	dark, 4 h, 50 °C, 0.1 mmol $(t\text{-Bu})_2\text{NO}^*$	1j (2%), 6 (39%)
1h (1.0)	2.5	1.5	S, 4 h, 50 °C	1j (2%), 6 (62%)
1i (1.0)	2.5	2.5	S, 6 h, 50 °C	1j (10%), 6 (20%)
1j (0.5)	1.0	1.0	4 h, 50 °C	1j (49%), 6 (51%)
1f (0.5)	2.5	2.5	S, 6 h, 50 °C	none
1g (0.5)	2.5	2.5	R, 2 h, 50 °C	6 (10%)
2d (0.5)	1.0	1.0	4 h, 25 °C	2j (100%)
2d (0.5)	1.5	0.5	4 h, 25 °C	2j (56%)
3d (0.5)	0.5	0.5	10 min, 25 °C	3j (78%)
3d (0.5)	0.5	0.5	10 min, 25 °C, 0.05 mmol $(t\text{-Bu})_2\text{NO}^*$	3j (61%)
3d (0.5)	1.0	0.5	10 min, 25 °C	3j (69%)
2h (0.5)	1.0	1.0	S, 7 h, 50 °C	2j (51%)
2h (0.5)	5.0	5.0	2 h, 50 °C	2j (51%)
2h (1.0)	5.0	5.0	2 h, 50 °C, 0.1 mmol $(t\text{-Bu})_2\text{NO}^*$	2j (48%)
3h (0.5)	1.0	1.0	S, 2 h, 50 °C	$\text{PhC}\equiv\text{CH}$ (80%)
2i (0.5)	1.0	1.0	S, 2 h, 50 °C	2j (21%)
3i (1.0)	1.5	1.5	S, 2 h, 50 °C	$\text{PhC}\equiv\text{CH}$ (70%)

^a[Substrate] = 0.1 M; S = 275-W sunlamp ca. 20 cm from reaction vessel; R = 350-nm Rayonet Photoreactor. ^bYields by GLC; I, isolated yield.

$\text{PhCH}=\text{CHP}$ (α -attack) > $\text{PhCH}=\text{CHBr}$ (β -attack). The formation of diphosponates is greatly retarded by an α -substituent in the β -styryl system, and no diphosponate was detected in the reactions of P^- with $\text{Ph}_2\text{C}=\text{CHBr}$, $\text{Ph}_2\text{C}=\text{CHSO}_2\text{Ph}$, or $\text{PhC}(\text{Me})=\text{CHBr}$. The latter system is reported to give a 16% yield of $\text{PhC}(\text{Me})=\text{CHP}$ upon reaction with $(\text{EtO})_2\text{PONa}$ in refluxing toluene while under similar conditions $\text{PhCH}=\text{CHBr}$ formed 6 in 12% yield.²⁰

Experimental Section

Analytical gas chromatography was performed on a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator using an internal standard. ¹H NMR spectra were recorded on a Nicolet NT 300 spectrometer with tetramethylsilane

as the internal standard. GCMS were recorded on a Finnegan 4000 spectrometer, and HRMS were measured by an AEI MS 902 spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

General Procedures for the Photostimulated Reactions of *t*-BuHgCl (Table I). The substrates were dissolved in nitrogen-purged Me_2SO in a Pyrex tube equipped with rubber septum. The mixture was irradiated for a period of time in a 350-nm Rayonet photoreactor or with a 275-W sunlamp as indicated in the table. The mixture was then poured into water, and the product was extracted with benzene or diethyl ether. The extract was washed twice with 10–20% aqueous sodium thiosulfate solution to remove the unreacted alkylmercury chloride, dried over anhydrous sodium sulfate, and concentrated under vacuum. The mixture was then analyzed by GLC, and the *E/Z* ratio was obtained from the ratio of the peak areas. To determine the product yield, the solvent was completely removed from the product mixture under vacuum. A known amount of an internal

(20) Arbuzov, B. A.; Lugovkin, B. D. *Zh. Obsch. Khim.* 1951, 21, 99.

standard, usually dibromomethane, was added to the crude product mixture dissolved in deuterated chloroform. The yield was obtained from the integration of the vinyl proton signal comparison with that of the internal standard.

The addition of an excess of NaI increased the yield and rate of the substitution reactions presumably from an increased rate of initiation and by the conversion of the eliminated Q^+ to I^+ by electron transfer.¹¹ The formation of R^+ from the reaction of I^+ with $RHgCl$ is known to occur efficiently.

(*E*)- β -Styrenyl bromide was prepared by treatment of the *cis*-*trans* mixture with NaOH in *i*-PrOH.²¹ The (*E*)- β -styrenyl chloride used was 90% *trans* and 10% *cis* by GLC analysis and was obtained by fractional distillation of commercial material from Frinton Laboratories. The 2,2-diphenylvinyl iodide used as a standard in competitive reactions was prepared by cleavage of 2,2-diphenylvinylmercury chloride by iodine.²² The other substrates and products have been previously described.^{6,7}

Competitive reactions with *t*-BuHgCl involved the photostimulated reaction of 10 equiv each of the substrate and $Ph_2C=CHI$ in deoxygenated Me_2SO . Iodide ion had no effect on the relative reactivities observed in the competitive substitution processes. After irradiation, the reaction mixtures were worked up as described previously and analyzed by GLC with appropriate calibration. The relative reactivities of **1d,f** and **3d,f** were determined in a similar fashion using mixtures of **1** and **3**.

3,3-Dimethyl-2-phenylbutyl Phenyl Sulfone. The sulfone was isolated from the photostimulated reaction of phenyl (*E*)-2-phenylethenyl sulfone, **1d** (3 mmol), and *t*-butylmercury chloride (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 milliliters 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,⁶ was eluted first (73% yield) followed by the sulfone. The addition product, 3,3-dimethyl-2-phenylbutyl phenyl sulfone, was obtained in 17% yield after recrystallization from hexane and had mp 131–132 °C: HRMS 302.13375 calcd for $C_{18}H_{26}O_2S$ 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).

3,3-Dimethyl-2-phenylbutyl Phenyl Sulfide and 3,3-Dimethyl-2-phenyl-1-butenyl Phenyl Sulfide. Reaction of **1f** with *t*-BuHgCl gave 36% of *t*-BuCH=CHPh and two minor products (workup with $NaBH_4$). 3,3-Dimethyl-2-phenylbutyl phenyl sulfide (9%) was identified from the ¹H NMR spectrum ($CDCl_3$) of the reaction mixture from three sets of doublets at δ 3.45 (1 H), 3.27 (1 H), 2.65 (benzylic, 1 H) and a *tert*-butyl singlet at δ 0.89 (9 H); GCMS *m/z* (relative intensity) 270 (M^+ , 12), 213 (29), 135 (100), 123 (20), 110 (53), 109 (17), 105 (31), 104 (23), 91 (51), 77 (15), 57 (44), 41 (32). 3,3-Dimethyl-2-phenyl-1-butenyl phenyl sulfide (3%) was assigned from the GCMS of *m/z* (relative intensity) 268 (M^+ , 78), 253 (100), 143 (29), 128 (51), 117 (23), 91 (33), 77 (23), 65 (22), 51 (21), 41 (68), 39 (38).

General Procedure for the Reactions with Organometallic Reagents (Tables II and III). Organocuprates were prepared by a 2-h reaction in 10 mL of THF under a nitrogen atmosphere. *t*-Bu₂CuLi was prepared from *t*-BuLi (2 equiv) and CuI (1 equiv) at –78 °C, *t*-BuCu(I)Li was prepared from equimolar amounts of *t*-BuLi and CuI at –78 °C, *t*-Bu₂Cu(CN)Li₂ was prepared from *t*-BuLi (2 equiv) and CuCN (1 equiv) at –30 °C, and *t*-Bu₂Cu(PBu₃)Li₂ was prepared from *t*-BuLi (2 equiv) and CuI·PBu₃ (1 equiv) at –78 °C.

To 10 mL of a THF solution of an organocopper reagent at the specified temperature was added 5 mL of a precooled THF solution of the substrate under a nitrogen atmosphere. After being stirred for a period of time, the mixture was poured into a sat-

urated 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 ¹H NMR.

For the reaction with *t*-BuLi, the substrate was 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. ¹H NMR and GCMS analyses of the reaction products have been reported in previous papers.^{6,7}

Competitive reactions involved the rapid addition of 10 equiv each of a mixture of **1** and **3** in THF at the desired reaction temperature to the preformed organometallic reagent. After a 2-h reaction period, the mixture was hydrolyzed, extracted, and analyzed by GLC.

3,3-Dimethyl-2-phenyl-1-butenyl Phenyl Sulfone. The sulfone was isolated from the reaction of **3d** with *t*-Bu₂Cu(CN)Li₂ at 0 °C as white crystals, mp 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, calcd for $C_{18}H_{26}O_2S$ 300.11841; ¹H NMR ($CDCl_3$) δ 7.50–6.73 (m, 10 H), 6.69 (s, 1 H), 1.07 (s, 9 H); ¹³C 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.

Reactions of Hg(II) Salts with **1 and **2** (Table IV).** Bis-(diethoxyphosphinyl)mercury, mp 57–58 °C, and (diethoxyphosphinyl)mercuric chloride, mp 103–104 °C, were synthesized according to a literature procedure.²³ The substrates were irradiated in Me_2SO or Me_2SO-d_6 under the conditions specified in Table IV. Only the *trans* substitution product was observed for **1** as judged by GLC. The yields of (*E*)-PhCH=CHP(O)(OEt)₂ and $Ph_2C=CHP(O)(OEt)_2$ were determined from the integrated ¹H NMR spectra either in Me_2SO-d_6 as the reaction solvent with an internal standard or after workup (hydrolysis, treatment with aqueous $Na_2S_2O_3$, extraction with Et_2O) in $CDCl_3$ with an internal standard. The properties of the diethyl 1-alkenyl phosphonates have been previously described.⁵

General Procedure for the Reaction of Diethyl Phosphite Ion with Phenyl (*E*)-2-Phenylethenyl Sulfone (Table V). Diethyl phosphite ion was generated in situ from diethyl phosphite and potassium *tert*-butoxide and was used immediately after preparation. The diethyl phosphite and potassium *tert*-butoxide (see Table V) were stirred at room temperature in a round-bottom flask equipped with a magnetic stirrer. After stirring for 5 min, the sulfone was added and stirring was continued for a period of time as indicated in Table V. In all cases, the mixture changed from colorless to yellow, and the reaction seemed to be complete almost immediately when the sulfone was added. The mixture was then poured into water and extracted with benzene or diethyl ether. The extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The mixture was then analyzed by GC, GCMS, and ¹H NMR.

1,2-Bis(diethylphosphono)-1-phenylethane (6).^{20,24} The diphosphonate was isolated as a yellow liquid whose ¹H NMR in CCl_4 agreed with the literature report:²⁴ GCMS *m/z* (relative intensity) 378 (M^+ , 9), 242 (15), 241 (100), 185 (37), 109 (19), 104 (23), 103 (12), 81 (17); ¹H NMR ($CDCl_3$) δ 7.45–7.20 (m, 5 H), 4.18–3.35 (m, 8 + 1 H), 2.55–2.40 (m, 2 H), 1.29 (t, *J* = 7.0 Hz, 3 H), 1.11 (t, *J* = 7.0 Hz, 3 H), 1.05 (t, *J* = 7.0 Hz, 3 H), 1.01 (t, *J* = 7.0 Hz, 3 H).

1-(Diethylphosphono)-2-(phenylsulfonyl)-1-phenylethane (4). Compound **4** was obtained from the reaction of the β -styryl sulfone and diethyl phosphite ion in the presence of diethyl phosphite (Table V). It was isolated by treating the reaction mixture (after the usual workup) with hexane. The product was filtered and recrystallized from 1:1 ethyl acetate/hexane to give white crystals, mp 82.5–84.0 °C: HRMS 382.0999, calcd for $C_{18}H_{26}O_5PS$ 382.0993; MS *m/z* (relative intensity) 383 (MH^+ , 0.4), 382 (M^+ , 0.3), 242 (22), 241 (100), 109 (29), 104 (46), 77 (27); ¹H

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NMR (CDCl₃) δ 7.57-7.51 (m, 2 H), 7.49-7.41 (m, 1 H), 7.33-7.25 (m, 2 H), 7.12 (s, 5 H), 4.15-3.50 (m, 7 H), 1.30 (t, *J* = 7.0 Hz, 3 H), 1.03 (t, *J* = 7.0 Hz, 3 H).

Diethyl (2-Phenylethyl)phosphonate.²⁵ PhCH₂CH₂P was prepared from the reaction of styrene and potassium diethyl phosphite. Styrene (1 mmol) was added to the solution of diethyl phosphite ion (10 mmol) generated by *t*-BuOK in Me₂SO (10 mL) under a nitrogen atmosphere. The mixture was stirred in the dark at 50 °C for 22 h, poured into water, and extracted with ether. The ether extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. GLC analysis of the mixture showed a 68% yield of the phosphonate and 21% of the unreacted styrene. The phosphonate, PhCH₂CH₂P, was also obtained from the reaction of (*E*)-(2-phenylethenyl)mercury chloride and potassium diethyl phosphite under photolysis or in the dark but in lower yield as shown in Table V. In a number of experiments where potassium *tert*-butoxide contaminated with potassium hydroxide was used to generate the diethyl phosphite ion, the photoreactions gave diethyl (*E*)-(2-phenylethenyl)phosphonate (1j) instead of the saturated product. PhCH₂CH₂P: GCMS *m/z* (relative intensity) 242 (M⁺, 37), 138 (100), 111 (96), 110 (29), 105 (28), 104 (65), 91 (19), 83 (27), 82 (53), 77 (24); ¹H NMR (CDCl₃) δ 7.33-7.24 (m, 2 H), 7.23-7.14 (m, 3 H), 4.15-4.00 (m, 4 H), 2.98-2.83 (m, 2 H), 2.15-1.93 (m, 2 H), 1.31 (t, *J* = 7.0 Hz, 6 H).

Diethyl (*E*)-(2-Phenylethynyl)phosphonate (1j).²⁶⁻²⁸ The β-styryl phosphonate was obtained from (*E*)-(2-phenylethenyl)mercury chloride and potassium diethyl phosphite generated from potassium hydroxide. The phosphite anion was generated by stirring diethyl phosphite (1.0 mmol) and potassium hydroxide (1.0 mmol) in Me₂SO (10 mL) in a Pyrex tube equipped with a rubber septum. After the mixture was stirred for 5 min, the mercurial (0.5 mmol) was added, and the mixture was deoxygenated for 5 min with a stream of nitrogen. The mixture was irradiated with a 275-W sunlamp placed ca. 20 cm from the reaction vessel. After the photolysis, the mixture was decanted from the shiny mercury bead formed during the reaction, poured into water, and extracted with ether. The ether extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The mixture consisted of the phosphonate in 70% yield, styrene in 8% yield, and PhCH(P)-CH₂P in 13% yield. The vinyl phosphonate had the following properties: GCMS *m/z* (relative intensity) 240 (M⁺, 12), 167 (13), 147 (17), 131 (100), 104 (20), 103 (12), 102 (15), 77 (17); ¹H NMR (CDCl₃) δ 7.60-7.44 (m, 2 + 1 H), 7.43-7.26 (m, 3 H), 6.26 (t, *J*

= 17.5 Hz, 1 H), 4.20-4.05 (m, 4 H), 1.35 (t, *J* = 7.0 Hz, 6 H).

Diethyl (1-Phenylethenyl)phosphonate (5).^{28,29} The α-styryl phosphonate was prepared from the reaction of 4 and potassium *tert*-butoxide. To the solution of 0.5 mmol of 4 in 10 mL of dry Me₂SO was added 0.6 mmol of *t*-BuOK. The resulting yellow mixture was stirred at room temperature for 5 min and then poured into water. The product was extracted with ether, washed with water, dried over anhydrous sodium sulfate, and concentrated. The mixture contained 87% of 5: GCMS *m/z* (relative intensity) 240 (M⁺, 45), 212 (41), 196 (21), 168 (20), 131 (38), 130 (70), 129 (37), 104 (59), 103 (100), 102 (22), 77 (50); ¹H NMR (CDCl₃) δ 7.60-7.05 (m, 5 H), 6.33 (dd, *J*_{HP(cis)} = 21.9 Hz, *J*_{HH} = 1.50 Hz, 1 H), 6.15 (dd, *J*_{HP(trans)} = 45.7 Hz, *J*_{HH} = 1.50 Hz, 1 H), 4.20-3.98 (m, 4 H), 1.28 (t, *J* = 7.0 Hz, 6 H).

Diethyl (2-Oxo-2-phenylethyl)phosphonate.³⁰ The keto phosphonate was obtained from 6 (0.3 mmol) and *t*-BuOK (0.4 mmol) in 5 mL of dry Me₂SO. The mixture was stirred at room temperature for 30 min and worked up by the usual procedure to give a mixture that contained the keto phosphonate in 78% yield and unreacted starting material. The keto phosphonate had the following properties: GCMS *m/z* (relative intensity) 256 (M⁺, 5), 146 (16), 120 (23), 105 (100), 77 (41); ¹H NMR (CDCl₃) δ 8.03-7.98 (m, 2 H), 7.60-7.40 (m, 3 H), 4.20-4.05 (m, 4 H), 3.62 (d, *J* = 22.6 Hz, 2 H), 1.27 (t, *J* = 7.0 Hz, 6 H).

Diethyl (2,2-Diphenylethenyl)phosphonate (2j). The reaction of Ph₂C=CHHgBr with [(EtO)₂P(O)]₂Hg to form 2j was reported previously.⁵

Diethyl (Phenylethynyl)phosphonate (3j). The reaction of (PhC≡C)₂Hg with [(EtO)₂P(O)]HgCl to form 3j was reported previously.⁵

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Registry No. (*E*)-1, Q = *t*-Bu, 3846-66-0; (*Z*)-1, Q = *t*-Bu, 3740-05-4; (*E*)-1a, 36525-03-8; (*E*)-1c, 66680-88-4; (*E*)-1d, 16212-06-9; (*E*)-1e, 40110-66-5; (*E*)-1f, 7214-53-1; (*E*)-1g, 4110-77-4; (*E*)-1h, 588-72-7; (*E*)-1i, 42599-24-6; (*Z*)-1i, 57918-63-5; (*E*)-1j, 20408-33-7; 1j dihydro derivative, 54553-21-8; 2, Q = *t*-Bu, 23586-64-3; 2a, 24522-19-8; 2b, 67341-86-0; 2c, 91083-76-0; 2d, 26189-62-8; 2h, 13249-58-6; 2i, 19997-66-1; 2j, 78462-91-6; 3, Q = *t*-Bu, 4250-82-2; 3c, 3757-88-8; 3d, 5324-64-1; 3f, 35460-31-2; 3i, 932-88-7; 3j, 3450-67-7; 4, 119337-14-3; 5, 25944-64-3; 6, 2519-12-2; PhCH(Bu-*t*)CH₂SO₂Ph, 113303-16-5; PhCH(Bu-*t*)CH₂SPh, 113303-14-3; PhC(Bu-*t*)=CHSPh, 113303-15-4; (*E*)-PhC(Bu-*t*)=CHSO₂Ph, 119337-13-2; (*Z*)-PhC(Bu-*t*)=CHSO₂Ph, 119337-15-4; PhCH=CH₂, 100-42-5; (PhCH=CH)₂Hg, 64984-50-5; Ph₂C=CH₂, 530-48-3; PhCOCH₂P(O)(OEt)₂, 3453-00-7.

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Photolysis of 2-Alkoxy-Δ³-1,3,4-oxadiazolines. A New Route to Diazoalkanes

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2-Alkoxy-2,5,5-trialkyl-Δ³-1,3,4-oxadiazolines (2), when photolyzed in solution with 300-nm light, afford the appropriate diazoalkane (3) and ester (4) in high yield. The diazoalkanes undergo intermolecular reaction, giving rise to azines (5), or they can be trapped in situ with 1,3-dipolarophiles to afford cycloadducts (7 or 11), which can in turn be photolyzed to the corresponding cyclopropenes (8) and cyclopropanes (12), respectively.

Diazo compounds are important reagents for organic synthesis.¹ Their major reactions include 1,3-dipolar cy-

cloadditions,² Wolff rearrangements,^{1,3} and carbene formation for cyclopropanations and single-bond insertions.^{1,3}