

FREE RADICAL SUBSTITUTION REACTIONS OF
 PHENYLACETYLENE DERIVATIVES BY AN ADDITION-ELIMINATION MECHANISM¹

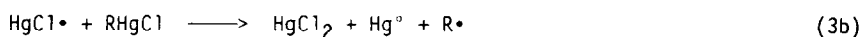
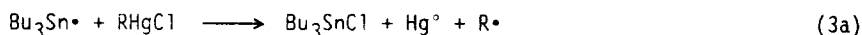
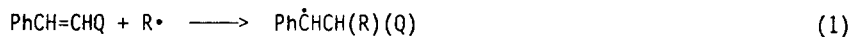
GLEN A. RUSSELL* and PREECHA NGOVIWATCHAI

Department of Chemistry
 Iowa State University
 Ames, Iowa 50011

Summary: Phenylacetylenes ($\text{PhC}\equiv\text{CQ}$ with $\text{Q} = \text{PhSO}_2, \text{I}, \text{SPh}, \text{Bu}_3\text{Sn PhC}\equiv\text{CHg}$) undergo free radical chain substitution reactions with $\text{RHgCl}, \text{R}_2\text{Hg}, (\text{EtO})_2\text{P}(\text{O})\text{HgCl}, (\text{PhS})_2\text{Hg}$ or $(\text{PhSO}_2)_2\text{Hg}$. The relative reactivities of $\text{PhC}\equiv\text{CQ}$ towards $\underline{\text{C}}\text{-C}_6\text{H}_{11}\cdot$ are $\text{Q} = \text{PhSO}_2 (65) > \text{I} (19) > \text{Bu}_3\text{Sn} (1.0)$.

Several recent reports of free radical reactions of $\text{PhC}\equiv\text{CSO}_2\text{Ph}$ have appeared.^{2,3} These complement an earlier report by Nozaki et al. that $\text{PhC}\equiv\text{CSO}_2\text{Me}$ or $\text{PhC}\equiv\text{CSOMe}$ react with alkylboranes by a radical process to form $\text{PhC}\equiv\text{CR}$.⁴ We have demonstrated that a variety of substituted alkenes including $\text{PhCH}=\text{CHQ}$ and $\text{Ph}_2\text{C}=\text{CHQ}$ with $\text{Q} = \text{HgCl}, \text{Bu}_3\text{Sn}, \text{SO}_2\text{Ph}, \text{SOPh}, \text{I}$ or SPh react with alkylmercury halides by a free radical chain process to form $\text{PhCH}=\text{CHR}$ or $\text{Ph}_2\text{C}=\text{CHR}$.^{5,6} It appears that the mechanism suggested for these vinyl systems (Scheme 1) is also applicable to acetylenic systems.⁷

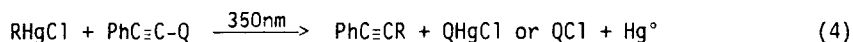
Scheme 1



In specific cases the combination of Reactions 1 and 2 can lead to stereospecific substitution with retention of configuration.⁶ Evidence for Reactions 3-3b occurring in a concerted one-step process is furnished by the observations that in the reactions of $\text{PhCH}=\text{CHSO}_2\text{Ph}, \text{PhCH}=\text{CHHgCl}$ or $\text{PhCH}=\text{CHSnBu}_3$ with excesses of 1:1 mixtures of two alkylmercury chlorides, the relative reactivities of the alkylmercury chlorides as determined from product

ratios are $t\text{-Bu} > c\text{-C}_6\text{H}_{11} > n\text{-Bu}$ (for $Q = \text{HgCl}$, $t\text{-Bu}:c\text{-C}_6\text{H}_{11}:n\text{-Bu} = 1.0:0.011:0.0001$; for $Q = \text{Bu}_3\text{Sn}$, $t\text{-Bu}:c\text{-C}_6\text{H}_{11}:n\text{-Bu} = 1.0:0.025:0.002$).

Table 1 presents the results of the photostimulated reactions of a variety of mercurials with $\text{PhC}\equiv\text{C}-\text{Q}$ (Reaction 4) where $Q = \text{PhSO}_2$, I, SPh, $\text{PhC}\equiv\text{CHg}$ or Bu_3Sn . As in the case of



$\text{PhCH}=\text{CHQ}$ or $\text{Ph}_2\text{C}=\text{CHQ}$,⁵ we find that the yields in general follow the order $R = t\text{-Bu} > 2^\circ\text{-alkyl} > 1^\circ\text{-alkyl}$. In addition to alkylmercury halides, the substitution reaction ($Q = \text{I}$) also occurs with $(\text{EtO})_2\text{P}(\text{O})\text{HgCl}$ (Table 1), $(\text{PhS})_2\text{Hg}$, $(\text{PhSO}_2)_2\text{Hg}$ or $(\text{Me}_3\text{C})_2\text{Hg}$. Use of $(\text{Me}_2\text{CHCO}_2)_2\text{Hg}$ to supply R^\bullet in Scheme 1 by a Hunsdiecker-type process has been unsuccessful with $\text{PhC}\equiv\text{CI}$ although a good yield of $\text{Ph}_2\text{C}=\text{CHCHMe}_2$ is obtained from $\text{Ph}_2\text{C}=\text{CHI}$.

The relative reactivities of $\text{PhC}\equiv\text{C}-\text{Q}$, $\text{PhCH}=\text{CHQ}$ and $\text{Ph}_2\text{C}=\text{CHQ}$ towards $c\text{-C}_6\text{H}_{11}^\bullet$ were determined by competitive reactions of $c\text{-C}_6\text{H}_{11}\text{HgCl}$ with an excess of mixtures of two substrates. The results of Table 2 indicate a surprisingly high reactivity for the substrates with $Q = \text{PhSO}_2$, particularly in the $\text{PhC}\equiv\text{CSO}_2\text{Ph}$ system. Since there is no evidence that the addition of R^\bullet to vinyl or acetylenic substrates is reversible, the data of Table 2 are believed to present the true reactivities of these substrates towards the addition of $c\text{-C}_6\text{H}_{11}^\bullet$. For $\text{PhC}\equiv\text{CQ}$ the relative reactivities towards $c\text{-C}_6\text{H}_{11}^\bullet$ increase from $Q = \text{Bu}_3\text{Sn}$ to I to PhSO_2 . Competitive reactions with a deficiency of $\text{Hg}(\text{SPh})_2$ are admittedly complicated by the reversibility of the addition of PhS^\bullet . However, again a reactivity order of $\text{PhC}\equiv\text{CSO}_2\text{Ph}$ (1.0) $>$ $\text{PhC}\equiv\text{CI}$ (0.2) $>$ $\text{PhC}\equiv\text{CSnBu}_3$ (<0.01) is observed. Since the same reactivity order is found with both the nucleophilic $c\text{-C}_6\text{H}_{11}^\bullet$ and the electrophilic PhS^\bullet , the relative reactivities apparently reflect the intrinsic reactivities of the alkynes.

The measured reactivities of $\text{Ph}_2\text{CH}=\text{CHQ}$ towards PhS^\bullet (relative to $\text{PhC}\equiv\text{CSO}_2\text{Ph} = 1.0$) are $Q = \text{PhSO}_2$ (0.3) $<$ I (0.8) $<$ Bu_3Sn (4.5) $<$ HgCl (6). The high reactivity of $\text{PhC}\equiv\text{CSO}_2\text{Ph}$ relative to $\text{Ph}_2\text{C}=\text{CHSO}_2\text{Ph}$ (or $\text{PhCH}=\text{CHSO}_2\text{Ph}$) and the low reactivity of $\text{PhC}\equiv\text{CSnBu}_3$ relative to $\text{Ph}_2\text{C}=\text{CHSnBu}_3$ (or $\text{PhCH}=\text{CHSnBu}_3$) observed with both $c\text{-C}_6\text{H}_{11}^\bullet$ and PhS^\bullet is puzzling. Perhaps the groups $Q = \text{Bu}_3\text{Sn}$ or HgX can stabilize the transition states leading to $\text{Ph}\dot{\text{C}}\text{H}-\text{CH}(\text{R})\text{Q}$, but not to $\text{Ph}\dot{\text{C}}=\text{C}(\text{R})\text{Q}$, by hyperconjugation or bridging, particularly when the attacking radical is electrophilic in nature.

The results indicate that the preferred group for free radical substitution by an addition-elimination mechanism depends on the nature of the center being attacked (sp or sp^2) and on the nature of the attacking radical with PhSO_2 being the preferred group in alkynes but often Bu_3Sn or HgCl in the alkenes. However, when stereospecificity is desired, the iodo substituent seems to be the preferred leaving group.⁶

Table 1. Photostimulated Reaction of RHgCl with $\text{PhC}\equiv\text{C-Q}$ to Yield $\text{PhC}\equiv\text{CR}$

Q	R (equiv of RHgCl)	Conditions ^a	% Yield of $\text{PhC}\equiv\text{CR}$ ^b
I	<i>t</i> -Bu (1.5)	Me_2SO , dark, 7 h	0
I	<i>t</i> -Bu (1.5)	Me_2SO , SL, 7 h	100
I	<i>t</i> -Bu (1.2)	Me_2SO , SL, 45 min	25
I	<i>t</i> -Bu (1.2)	Me_2SO , SL, 45 min, 10 mol % (<i>t</i> -Bu) ₂ NO ⁺	<5
I	<i>c</i> -C ₆ H ₁₁ (1.5)	Me_2SO , SL, 7 h	93
I	<i>n</i> -Bu (1.5)	Me_2SO , SL, 7 h	48
I	(EtO) ₂ PO (1.1)	Me_2SO , UV, 24 h	32
PhSO ₂	<i>i</i> -Pr (5)	PhH, UV, 24 h	44
PhSO ₂	<i>c</i> -C ₆ H ₁₁ (5)	PhH, UV, 24 h	67
PhSO ₂	<i>t</i> -Bu (5)	PhH, UV, 24 h	55
PhSO ₂	(EtO) ₂ PO (5)	PhH, UV, 24 h	30
PhS	<i>i</i> -Pr (5)	PhH, UV, 24 h	37
PhS	<i>i</i> -Pr (5)	Me_2SO , UV 24 h	25
PhS	<i>i</i> -Pr (0.2)	Me_2SO , UV 24 h	42
PhS	<i>c</i> -C ₆ H ₁₁ (0.2)	Me_2SO , UV, 24 h	46
PhS	<i>t</i> -Bu (0.2)	Me_2SO , UV, 24 h	44
PhC≡CHg	<i>n</i> -Bu (5)	Me_2SO , UV, 24 h	9 ^c
PhC≡CHg	<i>c</i> -C ₆ H ₁₁ (5)	Me_2SO , UV, 24 h	26 ^c
PhC≡CHg	<i>t</i> -Bu (5)	Me_2SO , UV, 24 h	34 ^c
PhC≡CHg	(EtO) ₂ PO (5)	Me_2SO , UV, 24 h	61 ^c
Bu ₃ Sn	<i>n</i> -Bu (5)	PhH, UV, 30 h	13
Bu ₃ Sn	<i>c</i> -C ₆ H ₁₁ (5)	PhH, UV, 30 h	43
Bu ₃ Sn	<i>t</i> -Bu (5)	PhH, UV, 30 h	61

^a Reactions performed on a 0.1 mmol scale in 5 mL of solvent at 35-40 °C with irradiation from a 275 W sunlamp (SL) or at 350 nm in a Rayonet Reactor (UV). ^b Yield determined by GLPC. ^c Based on a stoichiometry of 2 mol of $\text{PhC}\equiv\text{CR}$ /mol of $(\text{PhC}\equiv\text{C})_2\text{Hg}$.

Table 2. Relative Reactivities towards $\underline{C}-C_6H_{11} \cdot^a$

Q	PhC \equiv CQ	(E)-PhCH=CHQ	Ph ₂ C=CHQ
PhSO ₂	<u>13</u>	<u>3.3</u>	6.4
I	<u>3.8</u>	<u>0.7</u>	1.0
<i>n</i> -Bu ₃ Sn	<u>0.2</u>	<u>0.7</u>	0.8
PhC \equiv CHg	<u>0.2^b</u>		
ClHg		<u>1.5</u>	1.9

^a At 35-40 °C in Me₂SO or PhH for Q = *n*-Bu₃Sn by a competitive reaction photostimulated by 350 nm irradiation in a Rayonet Reactor. Underlined reactivities were determined in direct competition with Ph₂C=CHI. Typical procedures involved 0.1 mmol of C₆H₁₁HgCl and 2.0 mmoles of a 1:1 mixture of two substrates in 10 mL of Me₂SO or PhH. ^b Molar reactivity of (PhC \equiv C)₂Hg.

References:

- (1) Electron Transfer Processes. 41. This work was supported by grant CHE-841540 from the National Science Foundation.
- (2) De Lucchi, O.; Licini, G.; Pasquato, L.; Senta, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1597.
- (3) Eisch, J. J.; Behrooz, M.; Galle, J. E. *Tetrahedron Lett.* **1984**, 25, 4851.
- (4) Miyamoto, N.; Fukuoka, D.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1974**, 47, 503.
- (5) Russell, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.* **1984**, 106, 4622.
- (6) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1985**, 26, 4975; see also Saihi, M. L.; Pereyre, M. *Bull. Chem. Soc. Fr.* **1977**, 1251; Baldwin, J. E.; Kelly, D. R.; Ziegler, C. B. *J. Chem. Soc., Chem. Commun.* **1984**, 133.
- (7) Substitution by addition-elimination in a variety of allylic, propargylic, allenic and alkenyloxy systems is also well recognized. For some recent examples of S_N2' reactions see: Ueno, Y.; Chino, K.; Okawara, M. *Tetrahedron Lett.* **1982**, 23, 2575; Baldwin, J. E.; Adlington, R. M.; Basak, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1284; Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, 50, 1037; Keck, G. E.; Byers, J. H. *J. Org. Chem.* **1985**, 50, 5442.

(Received in USA 11 February 1986)