Tetrahedron Letters,Vol.27,No.30,pp 3479-3482,1986 0040-4039/86 \$3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

FREE RADICAL SUBSTITUTION REACTIONS OF PHENYLACETYLENE DERIVATIVES BY AN ADDITION-ELIMINATION MECHANISM[1]

GLEN A. RUSSELL* and PREECHA NGOVIWATCHAI

Department of Chemistry
Iowa State University
Ames, Iowa 50011

Summary: Phenylacetylenes ($PhC{\equiv}CQ$ with Q = $PhSO_2$, I, SPh, Bu_3Sn $PhC{\equiv}CHg$) undergo free radical chain substitution reactions with RHgCl, R_2Hg, $(EtO)_2P(O)HgCl$, $(PhS)_2Hg$ or $(PhSO_2)_2Hg$. The relative reactivities of $PhC{\equiv}CQ$ towards $\underline{c}\text{-}C_6H_{11}\cdot$ are Q = $PhSO_2$ (65) > I (19) > Bu_3Sn (1.0).

Several recent reports of free radical reactions of $PhC{\equiv}CSO_2Ph$ have appeared.[2,3] These complement an earlier report by Nozaki et al. that $PhC{\equiv}CSO_2Me$ or $PhC{\equiv}CSOMe$ react with alkylboranes by a radical process to form $PhC{\equiv}CR$.[4] We have demonstrated that a variety of substituted alkenes including PhCH=CHQ and $Ph_2C{=}CHQ$ with Q = HgCl, Bu_3Sn, SO_2Ph, SOPh, I or SPh react with alkylmercury halides by a free radical chain process to form PhCH=CHR or $Ph_2C{=}CHR$.[5,6] It appears that the mechanism suggested for these vinyl systems (Scheme 1) is also applicable to acetylenic systems.[7]

Scheme 1

$$PhCH{=}CHQ + R\cdot \longrightarrow Ph\dot{C}HCH(R)(Q) \qquad (1)$$

$$Ph\dot{C}HCH(R)(Q) \longrightarrow PhCH{=}CHR + Q\cdot \qquad (2)$$

$$Q\cdot + RHgCl \longrightarrow QHgCl + R\cdot \qquad (3)$$

$$Bu_3Sn\cdot + RHgCl \longrightarrow Bu_3SnCl + Hg^\circ + R\cdot \qquad (3a)$$

$$HgCl\cdot + RHgCl \longrightarrow HgCl_2 + Hg^\circ + R\cdot \qquad (3b)$$

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 $PhCH{=}CHSO_2Ph$, PhCH=CHHgCl or $PhCH{=}CHSnBu_3$ with excesses of 1:1 mixtures of two alkylmercury chlorides, the relative reactivities of the alkylmercury chlorides as determined from product ratios are *t*-Bu > *c*-C_6H_{11} > *n*-Bu (for Q = HgCl, *t*-Bu:*c*-C_6H_{11}:*n*-Bu = 1.0:0.011:0.0001; for Q = Bu_3Sn, *t*-Bu:*c*-C_6H_{11}:*n*-Bu = 1.0:0.025:0.002).

Table 1 presents the results of the photostimulated reactions of a variety of mercurials with PhC≡C-Q (Reaction 4) where Q = $PhSO_2$, I, SPh, PhC≡CHg or Bu_3Sn. As in the case of

$$\mathrm{RHgCl + PhC{\equiv}C\text{-}Q \xrightarrow{350nm} PhC{\equiv}CR + QHgCl\ or\ QCl + Hg^{\circ}} \qquad (4)$$

PhCH=CHQ or Ph_2C=CHQ,[5] we find that the yields in general follow the order R = *t*-Bu > 2°-alkyl > 1°-alkyl. In addition to alkylmercury halides, the substitution reaction (Q = I) also occurs with $(EtO)_2P(O)HgCl$ (Table 1), $(PhS)_2Hg$, $(PhSO_2)_2Hg$ or $(Me_3C)_2Hg$. Use of $(Me_2CHCO_2)_2Hg$ to supply R• in Scheme 1 by a Hunsdiecker-type process has been unsuccessful with PhC≡CI although a good yield of Ph_2C=$CHCHMe_2$ is obtained from Ph_2C=CHI.

The relative reactivities of PhC≡C-Q, PhCH=CHQ and Ph_2C=CHQ towards *c*-C_6H_{11}• were determined by competitive reactions of *c*-$C_6H_{11}HgCl$ with an excess of mixtures of two substrates. The results of Table 2 indicate a surprisingly high reactivity for the substrates with Q = $PhSO_2$, particularly in the PhC≡CSO_2Ph system. Since there is no evidence that the addition of R• 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*-C_6H_{11}•. For PhC≡CQ the relative reactivities towards *c*-C_6H_{11}• increase from Q = Bu_3Sn to I to $PhSO_2$. Competitive reactions with a deficiency of $Hg(SPh)_2$ are admittedly complicated by the reversibility of the addition of PhS•. However, again a reactivity order of PhC≡CSO_2Ph (1.0) > PhC≡CI (0.2) > PhC≡$CSnBu_3$ (<0.01) is observed. Since the same reactivity order is found with both the nucleophilic *c*-C_6H_{11}• and the electrophilic PhS•, the relative reactivities apparently reflect the intrinsic reactivities of the alkynes.

The measured reactivities of Ph_2CH=CHQ towards PhS• (relative to PhC≡CSO_2Ph = 1.0) are Q = $PhSO_2$ (0.3) < I (0.8) < Bu_3Sn (4.5) < HgCl (6). The high reactivity of PhC≡CSO_2Ph relative to Ph_2C=$CHSO_2Ph$ (or PhCH=$CHSO_2Ph$) and the low reactivity of PhC≡$CSnBu_3$ relative to Ph_2C=$CHSNBu_3$ (or PhCH=$CHSnBu_3$) observed with both *c*-C_6H_{11}• and PhS• is puzzling. Perhaps the groups Q = Bu_3Sn or HgX can stabilize the transition states leading to Ph$\dot{C}$H-CH(R)Q, but not to Ph$\dot{C}$=C(R)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 $PhC{\equiv}C$-Q to Yield $PhC{\equiv}CR$

Q	R (equiv of RHgCl)	Conditions[a]	% Yield of $PhC{\equiv}CR$[b]
I	*t*-Bu (1.5)	Me_2SO, dark, 7 h	0
I	*t*-Bu (1.5)	Me_2SO, SL, 7 h	100
I	*t*-Bu (1.2)	Me_2SO, SL, 45 min	25
I	*t*-Bu (1.2)	Me_2SO, SL, 45 min, 10 mol % ($(t\text{-Bu})_2NO\cdot$)	<5
I	*c*-C_6H_{11} (1.5)	Me_2SO, SL, 7 h	93
I	*n*-Bu (1.5)	Me_2SO, SL, 7 h	48
I	$(EtO)_2PO$ (1.1)	Me_2SO, UV, 24 h	32
$PhSO_2$	*i*-Pr (5)	PhH, UV, 24 h	44
$PhSO_2$	*c*-C_6H_{11} (5)	PhH, UV, 24 h	67
$PhSO_2$	*t*-Bu (5)	PhH, UV, 24 h	55
$PhSO_2$	$(EtO)_2PO$ (5)	PhH, UV, 24 h	30
PhS	*i*-Pr (5)	PhH, UV, 24 h	37
PhS	*i*-Pr (5)	Me_2SO, UV 24 h	25
PhS	*i*-Pr (0.2)	Me_2SO, UV 24 h	42
PhS	*c*-C_6H_{11} (0.2)	Me_2SO, UV, 24 h	46
PhS	*t*-Bu (0.2)	Me_2SO, UV, 24 h	44
$PhC{\equiv}CHg$	*n*-Bu (5)	Me_2SO, UV, 24 h	9[c]
$PhC{\equiv}CHg$	*c*-C_6H_{11} (5)	Me_2SO, UV, 24 h	26[c]
$PhC{\equiv}CHg$	*t*-Bu (5)	Me_2SO, UV, 24 h	34[c]
$PhC{\equiv}CHg$	$(EtO)_2PO$ (5)	Me_2SO, UV, 24 h	61[c]
Bu_3Sn	*n*-Bu (5)	PhH, UV, 30 h	13
Bu_3Sn	*c*-C_6H_{11} (5)	PhH, UV, 30 h	43
Bu_3Sn	*t*-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 $PhC{\equiv}CR$/mol of $(PhC{\equiv}C)_2Hg$.

Table 2. Relative Reactivities towards c-C_6H_{11}•[a]

Q	PhC≡CQ	(E)-PhCH=CHQ	Ph_2C=CHQ
$PhSO_2$	$\underline{13}$	$\underline{3.3}$	6.4
I	$\underline{3.8}$	$\underline{0.7}$	1.0
n-Bu_3Sn	$\underline{0.2}$	$\underline{0.7}$	0.8
PhC≡CHg	$\underline{0.2}$[b]		
ClHg		$\underline{1.5}$	1.9

[a] At 35-40 °C in Me_2SO or PhH for Q = n-Bu_3Sn by a competitive reaction photostimulated by 350 nm irradiation in a Rayonet Reactor. Underlined reactivities were determined in direct competition with Ph_2C=CHI. Typical procedures involved 0.1 mmol of $C_6H_{11}HgCl$ and 2.0 mmoles of a 1:1 mixture of two substrates in 10 mL of Me_2SO 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_H2' 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)