Free Radical Reactions of 1,1-Diarylethylenes with t-Butylmercury Chloride

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The photostimulated reactions of Bu^tHgCl with 1,1-diarylethylenes yield different products for the aryl groups C_6H_5, p-$O_2NC_6H_4$, or p-$MeOC_6H_4$ reflecting the donor or acceptor properties of $Bu^tCB_2\dot{C}(Ar)_2$.

We have studied the products formed by trapping t-butyl radicals in the photostimulated reactions of diarylethylenes (**1a**—**c**) with Bu^tHgCl. Photolysis in Me_2SO of Bu^tHgCl and (**1a**) formed (**3a**)[1] and (**4a**)[2] in an approximately 1:1 ratio (Table 1). By g.c.–mass spectrometry a small amount of $(Bu^tCH_2CPh_2)_2$ was also detected. The rate of formation of (**3a**) and (**4a**) was not appreciably retarded by the presence of 10% of $Bu^t_2NO\cdot$. With (**1a**), the reaction follows a non-chain path, Scheme 1.† Under similar conditions, (**1b**) reacted to

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† Evidence for the reaction of monomeric HgCl with RHgCl to generate R· is provided by the free radical chain reaction of ArCH=CHHgCl with RHgCl to form ArCH=CHR + $HgCl_2$ + Hg^0.[3]

Table 1. Photostimulated reactions of Bu^tHgCl in Me_2SO at 35—40 °C.[a]

Equiv. of Bu^tHgCl	Reactant	Conditions[b]	Product (% Yield)[c]
3	**(1a)**	R, 90 h	**(3a)** (43); **(4a)** (35)
3	**(1a)**	R, 10 mol % DBNO, 90 h	**(3a)** (36); **(4a)** (29)
6	**(1a)**	S, 8 equiv. $MeC(CO_2Et)_2^-$, 12 h	**(5)** (68); **(3a)** (7); **(4a)** (0)
6	**(1a)**	S, 8 equiv. $MeC(CO_2Et)_2^-$, 10 mol % DBNO, 12 h	**(5)** (8); **(3a)** (3); **(4a)** (0)
3	**(1a)**	S, 8 equiv. $MeC(CO_2Et)_2^-$, 12 h	**(5)** (57); **(3a)** (16); **(4)** (0)[d]
6	**(1a)**	R, 8 equiv. $CH(CO_2Et)_2^-$, 12 h	**(3a)** (8); **(4a)** (12); **(5)** (4)
3	**(1b)**	R, 16 h	**(3b)** (<1); **(4b)** (84)
3	**(1b)**	R, 10 mol %, DBNO, 16 h	**(3b)** (<1); **(4b)** (19)
6	**(1b)**	R, 8 equiv. $MeC(CO_2Et)_2^-$, 16 h	**(3b)** (9); **(4b)** (69)
6	**(1b)**	R, 8 equiv. $CH(CO_2Et)_2^-$, 16 h	**(3b)** (2); **(4b)** (76)
3	**(1c)**	R, 30 h	**(3c)** (41); **(4c)** (<1)
3	**(1c)**	R, 10 mol % DBNO, 30 h	**(3c)** (16); **(4c)** (<1)
6	**(3a)**	S, 8 equiv. $MeC(CO_2Et)_2^-$, 12 h	**(5)** (7)
6	**(4a)**	S, 8 equiv. $MeC(CO_2Et)_2^-$, 12 h	No reaction
1	Ph_2CH^-	S, 2 h[e]	Bu^tCHPh_2 (36)
1	$(p\text{-}O_2NC_6N_4)_2CH^-$	S, 3 h	None detected
1	Ph_2P^-	S, 2 h	$Ph_2P(:O)Bu^t$ (38)
1	Ph_2P^-	S, 2 h[e]	Ph_2PBu^t (42)

[a] Reactions were performed in nitrogen-purged Me_2SO. Nucleophiles (N^-) were generated by the action of Bu^tOK on the conjugate acid. [b] R = Rayonet reactor with 350 nm irradiation; S = 275 W sunlamp *ca.* 15 cm from the reaction flask; DBNO = $Bu^t{}_2NO\cdot$. [c] Yields determined by ^1H n.m.r. and g.l.c. on a 1 mmol scale for reactions 0.1 M in the reactant. [d] A 35% yield of $MeC(CO_2Et)_2C(CO_2Et)_2Me$ was isolated. With 6 equiv. of Bu^tHgCl, only 2% of $MeC(CO_2Et)_2C(CO_2Et)_2Me$ was formed. [e] Hexamethylphosphoric triamide (HMPA) solvent.

$CH_2{=}CAr_2$	$Bu^tCH_2CAr_2$	$Bu^tCH_2CHAr_2$	$Bu^tCH{=}CAr_2$
(1)	**(2)**	**(3)**	**(4)**

a, Ar = C_6H_5; **b**, Ar = p-$MeOC_6H_4$; **c**, Ar = p-$O_2NC_6H_4$

$Bu^tCH_2CBu^tPh_2$
(5)

$$\begin{aligned}
&Bu^tHgCl \xrightarrow{h\nu} Bu^t\cdot + HgCl\\
&HgCl + Bu^tHgCl \rightarrow Bu^t\cdot + HgCl_2 + Hg^0\\
&Bu^t\cdot + (\mathbf{1a}) \rightarrow (\mathbf{2a})\cdot\\
&2(\mathbf{2a})\cdot \rightarrow (\mathbf{3a}) + (\mathbf{4a})
\end{aligned}$$

Scheme 1

$$\begin{aligned}
&Bu^t\cdot + (\mathbf{1b}) \rightarrow (\mathbf{2b})\cdot\\
&(\mathbf{2b})\cdot + Bu^tHgCl \rightarrow (\mathbf{2b})^+ + Bu^t\cdot + Hg^0 + Cl^-\\
&(\mathbf{2b})^+ \rightarrow (\mathbf{4b}) + H^+
\end{aligned}$$

Scheme 2

form nearly exclusively **(4b)**‡ (see Table 1). Now the rate of the reaction was drastically retarded by the presence of 10 mol % of $Bu^t{}_2NO\cdot$ and the chain process of Scheme 2 is suggested for the nucleophilic **(2b)**.

Reaction of Bu^tHgCl with **(1c)** leads to the formation of **(3c)**[1] as the major isolable product (Table 1). Apparently the electrophilic **(2c)**· reacts according to Scheme 3.

$$\begin{aligned}
&Bu^t\cdot + (\mathbf{1c}) \rightarrow (\mathbf{2c})\cdot\\
&(\mathbf{2c})\cdot + Bu^tHgCl \rightarrow (\mathbf{2c})^- + Bu^t\cdot + HgCl^+\\
&(\mathbf{2c})^- + H^+ \rightarrow (\mathbf{3c})
\end{aligned}$$

Scheme 3

$$\begin{aligned}
&Bu^t\cdot + (\mathbf{1a}) \rightarrow (\mathbf{2a})\cdot\\
&(\mathbf{2a})\cdot + MeC(CO_2Et)_2^- \rightleftharpoons (\mathbf{2a})^- + MeC(CO_2Et)_2\cdot\\
&(\mathbf{2a})^- + Bu^t\cdot \rightarrow (\mathbf{5})\cdot^-\\
&(\mathbf{5})\cdot^- + Bu^tHgCl \rightarrow (\mathbf{5}) + Bu^t\cdot + Hg^0 + Cl^-\\
&MeC(CO_2Et)_2\cdot + Bu^tHgCl \rightarrow MeC(CO_2Et)_2^- + Bu^t\cdot + HgCl^+
\end{aligned}$$

Scheme 4

The photostimulated reaction of **(1a)** with 6 equiv. of Bu^tHgCl in the presence of an excess (8 equiv.) of $MeC(CO_2Et)_2^-$ leads to the formation of $Bu^tCH_2CBu^tPh_2$ **(5)**[4] in good yield. This product is not observed in the absence of $MeC(CO_2Et)_2^-$ nor in the presence of the less easily oxidized $HC(CO_2Et)_2^-$. The formation of **(5)** occurs by a free radical chain process whose kinetic chain length is drastically retarded by the presence of $Bu^t{}_2NO\cdot$ (see Table 1). Under the reaction conditions, **(4a)** is not converted into **(5)** and the oxidative dimerization product $MeC(CO_2Et)_2C(CO_2Et)_2Me$[5] is not formed in significant yield when excess of Bu^tHgCl (6 equiv.) is employed. Di-t-butylation products analogous to **(5)** were not detected in similar reactions of **(1b)** and **(1c)**. The formation of **(5)** seems to be connected with the fact that Ph_2CR^- ions react with $Bu^t\cdot$ to form t-butylated products, whereas the less basic $(p\text{-}O_2NC_6H_4)_2CR^-$ is much less reactive[6] although Ph_2P^- reacts readily to form $Bu^tP(:O)Ph_2$

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‡ B.p. 220—224 °C (5 Torr); ^1H n.m.r. ($CDCl_3$) δ 0.92 (s, 9H), 3.76 (s, 3H), 3.83 (s, 3H), 5.82 (s, 1H), and 6.8—7.4 (m, 8H). All reaction products gave analytical data, including mass spectra, consistent with their structures.

in Me_2SO and Bu^tPPh_2 in HMPA (Table 1). The overall scheme suggested for the formation of (**5**) is shown in Scheme 4.

The results demonstrate that alkylmercurials can serve as electron acceptors[7] or donors towards free radicals which are either easily oxidized (nucleophilic) or easily reduced (electrophilic). The formally S_H2 process ($A\cdot + Bu^tHgCl \rightarrow AHgCl + Bu^t\cdot$) occurs readily only for electrophilic radicals,[8,9] *e.g.*, $MeC(CO_2Et)_2\cdot$, and may occur *via* electron transfer or at least by a transition state reflecting the electrophilic character of A.

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