

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

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The photostimulated reactions of Bu<sup>t</sup>HgCl with 1,1-diarylethylenes yield different products for the aryl groups C<sub>6</sub>H<sub>5</sub>, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, or *p*-MeOC<sub>6</sub>H<sub>4</sub> reflecting the donor or acceptor properties of Bu<sup>t</sup>CB<sub>2</sub>Ċ(Ar)<sub>2</sub>.

We have studied the products formed by trapping t-butyl radicals in the photostimulated reactions of diarylethylenes (**1a–c**) with Bu<sup>t</sup>HgCl. Photolysis in Me<sub>2</sub>SO of Bu<sup>t</sup>HgCl and (**1a**) formed (**3a**)<sup>1</sup> and (**4a**)<sup>2</sup> in an approximately 1:1 ratio (Table 1). By g.c.–mass spectrometry a small amount of (Bu<sup>t</sup>CH<sub>2</sub>CPh<sub>2</sub>)<sub>2</sub> was also detected. The rate of formation of (**3a**) and (**4a**) was not appreciably retarded by the presence of

10% of Bu<sup>t</sup><sub>2</sub>NO•. With (**1a**), the reaction follows a non-chain path, Scheme 1.† Under similar conditions, (**1b**) reacted to

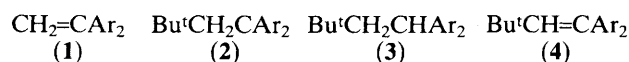
† Evidence for the reaction of monomeric HgCl with RHgCl to generate R• is provided by the free radical chain reaction of ArCH=CHHgCl with RHgCl to form ArCH=CHR + HgCl<sub>2</sub> + Hg<sup>0</sup>.<sup>3</sup>

**Table 1.** Photostimulated reactions of Bu<sup>t</sup>HgCl in Me<sub>2</sub>SO at 35–40 °C.<sup>a</sup>

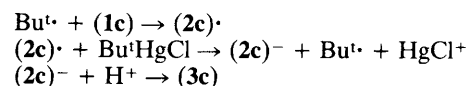
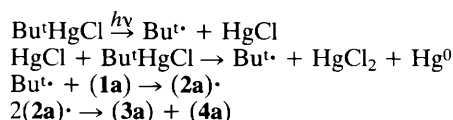
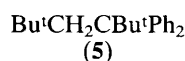
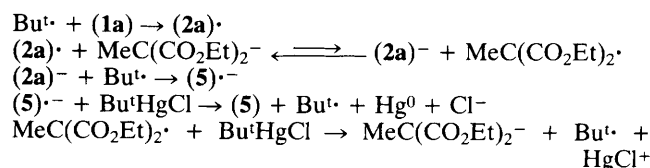
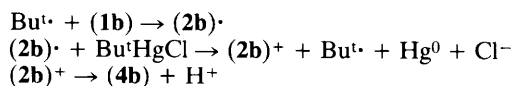
Equiv. of Bu <sup>t</sup> HgCl	Reactant	Conditions <sup>b</sup>	Product (% Yield) <sup>c</sup>
3	(1a)	R, 90 h	(3a) (43); (4a) (35)
3	(1a)	R, 10 mol % DBNO, 90 h	(3a) (36); (4a) (29)
6	(1a)	S, 8 equiv. MeC(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 12 h	(5) (68); (3a) (7); (4a) (0)
6	(1a)	S, 8 equiv. MeC(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 10 mol % DBNO, 12 h	(5) (8); (3a) (3); (4a) (0)
3	(1a)	S, 8 equiv. MeC(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 12 h	(5) (57); (3a) (16); (4) (0) <sup>d</sup>
6	(1a)	R, 8 equiv. CH(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 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 <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 16 h	(3b) (9); (4b) (69)
6	(1b)	R, 8 equiv. CH(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 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 <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 12 h	(5) (7)
6	(4a)	S, 8 equiv. MeC(CO <sub>2</sub> Et) <sub>2</sub> <sup>-</sup> , 12 h	No reaction
1	Ph <sub>2</sub> CH <sup>-</sup>	S, 2 h <sup>e</sup>	Bu <sup>t</sup> CHPh <sub>2</sub> (36)
1	( <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CH <sup>-</sup>	S, 3 h	None detected
1	Ph <sub>2</sub> P <sup>-</sup>	S, 2 h	Ph <sub>2</sub> P(:O)Bu <sup>t</sup> (38)
1	Ph <sub>2</sub> P <sup>-</sup>	S, 2 h <sup>e</sup>	Ph <sub>2</sub> PBu <sup>t</sup> (42)

<sup>a</sup> Reactions were performed in nitrogen-purged Me<sub>2</sub>SO. Nucleophiles (N<sup>-</sup>) were generated by the action of Bu<sup>t</sup>OK on the conjugate acid.

<sup>b</sup> R = Rayonet reactor with 350 nm irradiation; S = 275 W sunlamp ca. 15 cm from the reaction flask; DBNO = Bu<sup>t</sup><sub>2</sub>NO<sup>•</sup>. <sup>c</sup> Yields determined by <sup>1</sup>H n.m.r. and g.l.c. on a 1 mmol scale for reactions 0.1 M in the reactant. <sup>d</sup> A 35% yield of MeC(CO<sub>2</sub>Et)<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub>Me was isolated. With 6 equiv. of Bu<sup>t</sup>HgCl, only 2% of MeC(CO<sub>2</sub>Et)<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub>Me was formed. <sup>e</sup> Hexamethylphosphoric triamide (HMPA) solvent.



a, Ar = C<sub>6</sub>H<sub>5</sub>; b, Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>; c, Ar = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>

**Scheme 3****Scheme 1****Scheme 4****Scheme 2**

form nearly exclusively (4b)<sup>‡</sup> (see Table 1). Now the rate of the reaction was drastically retarded by the presence of 10 mol % of Bu<sup>t</sup><sub>2</sub>NO<sup>•</sup> and the chain process of Scheme 2 is suggested for the nucleophilic (2b).

Reaction of Bu<sup>t</sup>HgCl with (1c) leads to the formation of (3c)<sup>‡</sup> as the major isolable product (Table 1). Apparently the electrophilic (2c)<sup>•</sup> reacts according to Scheme 3.

<sup>‡</sup> B.p. 220–224 °C (5 Torr); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) 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.

The photostimulated reaction of (1a) with 6 equiv. of Bu<sup>t</sup>HgCl in the presence of an excess (8 equiv.) of MeC(CO<sub>2</sub>Et)<sub>2</sub><sup>-</sup> leads to the formation of Bu<sup>t</sup>CH<sub>2</sub>CBu<sup>t</sup>Ph<sub>2</sub> (5)<sup>4</sup> in good yield. This product is not observed in the absence of MeC(CO<sub>2</sub>Et)<sub>2</sub><sup>-</sup> nor in the presence of the less easily oxidized HC(CO<sub>2</sub>Et)<sub>2</sub><sup>-</sup>. The formation of (5) occurs by a free radical chain process whose kinetic chain length is drastically retarded by the presence of Bu<sup>t</sup><sub>2</sub>NO<sup>•</sup> (see Table 1). Under the reaction conditions, (4a) is not converted into (5) and the oxidative dimerization product MeC(CO<sub>2</sub>Et)<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub>Me<sup>5</sup> is not formed in significant yield when excess of Bu<sup>t</sup>HgCl (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<sub>2</sub>CR<sup>-</sup> ions react with Bu<sup>t</sup>• to form *t*-butylated products, whereas the less basic (*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CR<sup>-</sup> is much less reactive<sup>6</sup> although Ph<sub>2</sub>P<sup>-</sup> reacts readily to form Bu<sup>t</sup>P(:O)Ph<sub>2</sub>

in Me<sub>2</sub>SO and Bu<sup>t</sup>PPh<sub>2</sub> 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<sup>7</sup> or donors towards free radicals which are either easily oxidized (nucleophilic) or easily reduced (electrophilic). The formally S<sub>H</sub>2 process (A<sup>•</sup> + Bu<sup>t</sup>HgCl → AHgCl + Bu<sup>t•</sup>) occurs readily only for electrophilic radicals,<sup>8,9</sup> e.g., MeC(CO<sub>2</sub>Et)<sub>2</sub><sup>•</sup>, and may occur *via* electron transfer or at least by a transition state reflecting the electrophilic character of A.

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