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REACTIONS OF THE α-METHOXY- AND α,α-DIMETHOXYBENZYL RADICALS

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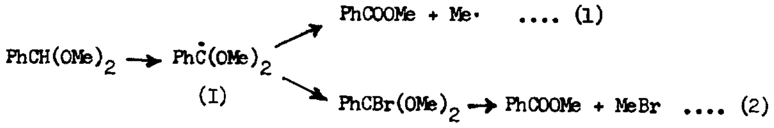
THE substituted benzyl radicals $Ph\dot{C}HOR$ and $Ph\dot{C}HNRR'$ (R, R' = Me, Ph, $PhCH_2$, etc.) have been prepared from benzyl ethers[1] and t-benzylamines,[2] respectively, by dehydrogenation with t-butoxy radicals, and shown to disproportionate provided the radical R· so produced is resonance-stabilised. The analogous dimethoxybenzyl radical (I) has now been prepared from the dimethyl acetal of benzaldehyde through hydrogen-abstraction by a variety of radicals namely, t-butoxy, trichloromethyl, or succinimidyl radicals. By itself (I) disproportionates (reaction 1) to methyl benzoate and free methyl, which then carries on the chain. When generated in the presence of N-bromosuccinimide or bromotrichloromethane, however, (I) readily abstracts a bromine atom from these substances to give an unstable bromo-compound which breaks down into methyl bromide and methyl benzoate (reaction 2), no chain characteristics being exhibited in this case.



$$PhCH(OMe)_2 \rightarrow \underset{(I)}{Ph\dot{C}(OMe)_2} \rightarrow PhCOOMe + Me\cdot \quad .... (1)$$

$$Ph\dot{C}(OMe)_2 \rightarrow PhCBr(OMe)_2 \rightarrow PhCOOMe + MeBr \quad .... (2)$$

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[1] Huang and Si-Hoe, Proc. Chem. Soc. 354 (1957); idem in "Vistas in Free-Radical Chemistry" ed. W. A. Waters, Pergamon Press, London (1959), p.242.

[2] Huang, J. Chem. Soc. 1816 (1959).

TABLE

	Reactants				Products			
Expt. No.	Starting Material (m.mole)	Radical Source (m.mole)	Reaction Time[a] hr.	Starting Material Recovered m.mole	PhCOOMe m.mole	PhCHO m.mole	MeBr	Other Products (m.moles)
1	$PhCH(OMe)_2$ (100)	$t-Bu_2O_2$ (10)	40	24.5	14.4			t-BuOH (5.0), MeCOMe (0.2), $t-Bu_2O_2$ (6.3)
2	" (30)	NBS[b] (15)	0.75	15.0	14.8	trace		
3	" (30)	$BrCCl_3$ (22.5)	45	19.2	8.4	2.0	(c)	$CHCl_3$, MeOH, $MeOCH_2OMe$
4	" (30)	" (20)	45	20.9	7.3	1.8	(d)	$CHCl_3$, MeOH, $MeOCH_2OMe$ (0.4)
5	$PhCH_2OMe$ (30)	" (20)	42	11.7		14.6	(d)	PhCOBr (1.4), $CHCl_3$
6	" (40)	" (30)	41	11.9		20.8	(c)	PhCOBr (trace), $CHCl_3$
7	(25)	NBS[b] (6)	0.5	18.2		4.4		

Foot-notes:

(a) The reactants were heated at 110° in Expt.1, in refluxing CCl_4 in Expts. 2 and 7 and in boiling CCl_4 under illumination by a 150 watt incandescent lamp in the other Expts.

(b) NBS = N-Bromosuccinimide

(c) Identified as methyl 9-methylfluorine-9-carboxylate and the acid (see Bavin, Analyt. Chem., 32, 554(1960)

(d) Isolation not attempted

It has also been found that the $\mathrm{Ph\dot{C}HOMe}$ radical, previously shown[1] to be a relatively stable entity which persists in solution until dimerisation, in contact with N-bromosuccinimide or bromotrichloromethane similarly combines with the bromine atom in these substances to form PhCHBr(OMe) which readily breaks down to benzaldehyde and methyl bromide.

Results from typical experiments are given in the Table. The products were analysed by infra-red spectropcopy and/or chemical identification.

These systems afford new avenues whereby the Hammett relationship in hydrogen-abstraction from aromatic side chains may be studied. Work in this direction is under way.