

1148. *Polar Influences in Radical Reactions. Part II.*¹ *The Abstraction of Benzylic Hydrogen Atoms from Substituted Dibenzyl Ethers by Atomic Bromine.*

By R. L. HUANG, H. H. LEE, and M. S. MALHOTRA.

In a Hammett study of the abstraction of benzylic α -hydrogen atoms at 80°, by atomic bromine generated from (a) *N*-bromosuccinimide and (b) molecular bromine, from five monosubstituted dibenzyl ethers, no polar effect has been detected.

In Part I¹ the abstraction of benzylic α -hydrogen atoms from substituted dibenzyl ethers by the *t*-butoxy- and benzoyloxy-radicals was shown to follow the Hammett relationship, giving a ρ -value of -0.5 at 110° for the former radical and -0.6 at 80° for the latter. We now report a similar study of the same system towards abstraction by atomic bromine generated from (a) *N*-bromosuccinimide and (b) molecular bromine under illumination.

It has been established² that in homolytic bromination by *N*-bromosuccinimide the hydrogen-abstracting species is atomic bromine (Goldfinger's mechanism)³ rather than the succinimidyl radical. However, in the bromination of substituted toluenes, the ρ -value in the Hammett plot for *N*-bromosuccinimide was found by Kooyman *et al.*,⁴ to differ from that for molecular bromine. This discrepancy has been ascribed to occurrence in the latter system of the reversible reaction $\text{HBr} + \text{R}\cdot \rightarrow \text{RH} + \text{Br}\cdot$ ($\text{R}\cdot$ = substituted benzyl radical), and can be minimised or eliminated by either removal of hydrogen bromide or, better, by increasing the concentration of bromine, as has been done by Pearson and Martin^{2c} who have recently obtained almost identical ρ -values (-1.46 and -1.36 , respectively, at 80°) for the two systems. In this work we have also made use of this latter method: effective removal of hydrogen bromide, *e.g.*, by sweeping out with an inert gas, would in any case be difficult owing to co-ordination of the bromide with the ether.

The reaction of dibenzyl ether (5-fold excess) with *N*-bromosuccinimide in carbon tetrachloride at 80° gave quantitative yields of benzaldehyde, isolated as the 2,4-dinitrophenylhydrazone, and benzyl bromide estimated by the titrimetric method of Patchornik and Rogozinski⁵ and identified through the methyl 9-fluorenyl-9-carboxylate. The

¹ Part I, R. L. Huang, H. H. Lee, and S. H. Ong, *J.*, 1962, 3336.

² (a) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, 1963, **85**, 3129; (b) G. A. Russell and K. M. Desmond, *ibid.*, p. 3139; (c) R. E. Pearson and J. C. Martin, *ibid.*, p. 3142.

³ J. Adam, P. Goldfinger, and P. A. Gosselain, *Bull. Soc. chim. belges*, 1956, **65**, 523; F. L. J. Sixma and R. H. Riem, *Proc. k. Ned. Akad. Wetenschap.*, 1958, **61**, B, 183; B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 1961, 80.

⁴ E. C. Kooyman, R. van Helden, and A. F. Bickel, *Proc. k. Ned. Akad. Wetenschap.*, 1953, **56**, B, 75; G. A. Russell, *J. Org. Chem.*, 1958, **23**, 1407.

⁵ A. Patchornik and S. E. Rogozinski, *Analyt. Chem.*, 1959, **31**, 985.

Reaction of monosubstituted dibenzyl ethers $R\text{-C}_6\text{H}_4\text{-CH}_2\text{-O-CH}_2\text{-Ph}$ with atomic bromine at 80° .

Ether		N-Bromo-succinimide (mmole)	Ratio $R\text{-C}_6\text{H}_4\text{-CHO:PhCHO}^*$ (Total % yield of aldehydes)		
R	(mmole)		1	2	Mean
H	107	21.0	1.00 (99.5)	—	1.00 (100)
	104	17.1	1.00 (100)	—	
<i>p</i> -Cl	101	20.0	0.93 (95)	0.89 (94)	0.92 (95)
	97	20.2	0.93 (95)	—	
<i>p</i> -Bu ^t	72	17.8	1.13 (84)	—	1.13 (87)
	100	20.6	1.14 (89)	1.11 (88)	
<i>p</i> -OMe	103	21.1	1.22 (95)	1.25 (96)	1.23 (94.5)
	108	19.4	1.23 (93)	1.24 (94)	
<i>m</i> -Cl	96	20.8	0.94 (91)	0.92 (90)	0.93 (90.5)
<i>p</i> -NO ₂	49	9.5	0.68 (65)	0.72 (67)	0.70 (66)
		Bromine (mmole)			
H	101	33.2	1.00 (99)	1.00 (100)	1.00 (99.5)
<i>p</i> -OMe	93	27.6	1.11 (80)	1.10 (80)	1.10 (79)
	88	22.7	1.11 (78)	1.08 (77)	
<i>m</i> -Cl	95	28.7	0.99 (85)	0.99 (85)	0.99 (85)
<i>p</i> -Cl	103	26.8	1.00 (96)	1.00 (95)	1.00 (95.5)
<i>p</i> -Bu ^t	54	17.3	1.11 (87)	1.14 (86)	1.125 (86.5)

* Isolated and estimated as the 2,4-dinitrophenylhydrazones.

σ or σ^+ constants of R gives straight lines, the slopes of both of which are negligible (σ -correlation¹¹: $\rho = -0.19$, $r = 0.942$, $s = 0.021$; σ^+ -correlation: $\rho = -0.12$, $r = 0.947$, $s = 0.020$). Data from bromination with molecular bromine give a less satisfactory correlation, the straight lines so obtained having also practically zero slopes (σ -correlation: $\rho = -0.09$, $r = 0.88$, $s = 0.015$; σ^+ -correlation: $\rho = -0.05$, $r = 0.81$, $s = 0.018$). These results are indicative of the virtual absence of polar effects. The similarity in reaction pattern of the two sets of experiments, incidentally, supports the Goldfinger mechanism. Fuller discussion is deferred.

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. Infrared spectra were determined in carbon tetrachloride solution with a Hilger H800 spectrophotometer and ultraviolet spectra in chloroform solution with a Hilger Uvispek instrument. Microanalyses were carried out by Mrs. H. K. Tong of Singapore.

"Petroleum" refers to a fraction of b. p. $40-60^\circ$, and "alumina" to neutral aluminium oxide (M.F.C.), activity 2-3, as supplied by Hopkin and Williams. *N*-Bromosuccinimide was purified according to the method of Dauben and McCoy,¹² and shown by iodometric titration to be at least 99% pure. Dibenzyl and substituted dibenzyl ethers were all distilled immediately before use, and were spectroscopically pure (infrared). Kieselguhr and bentonite (B.D.H.) were sieved (72 mesh) and dried at 150° for 2 days.

Preparation of Dibenzyl Ethers.—Substituted dibenzyl ethers (except the *p*-nitro-derivative) were prepared by reaction of the appropriate benzyl halide with sodium benzyloxy in benzyl alcohol as described elsewhere.¹³

p-Nitrodibenzyl Ether.—A solution of sodium (3.9 g., 0.17 mole) in benzyl alcohol (60 g.) was added with stirring over a period of 0.5 hr. to an ice-cold solution of *p*-nitrobenzyl bromide (30 g.) in benzyl alcohol (50 g.). After stirring for 27 hr. at room temperature (28°) the mixture was poured on to ice and the product extracted with diethyl ether, and then concentrated. The crude ether, dissolved in petroleum-benzene (1:1; 20 ml.), was adsorbed on alumina (50 g.) and eluted with the same solvent. Fractionation through a 6 in. Vigreux column under nitrogen then gave

¹¹ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

¹² H. J. Dauben, jun., and L. L. McCoy, *J. Amer. Chem. Soc.*, 1959, **81**, 4863.

¹³ R. L. Huang and S. S. Si-Hoe, *J.*, 1957, 3988.

p-nitrodibenzyl ether (20 g., 60%), b. p. 150—152°/0.15 mm., $n_D^{22.5}$ 1.5836 (Found: C, 69.2; H, 5.4; N, 6.2. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.8%), ν_{\max} . 1610, 1525, 1345, 1095, 842, and 693 cm^{-1} .

Analyses of Mixtures of Aldehyde 2,4-Dinitrophenylhydrazones.—Five mixtures of pairs of aldehyde 2,4-dinitrophenylhydrazones (from benzaldehyde, *p*-*t*-butyl-, *p*-methoxy-, and *p*-chloro-benzaldehyde) were made up, chromatographed,¹⁴ and the separated hydrazones determined (a) gravimetrically and (b) by ultraviolet spectroscopy. The absorbent used was bentonite-kieselguhr (4:1 by weight) and the eluant chloroform, followed by chloroform containing methanol (up to 5%). The results showed that for the gravimetric method, 0.5—1.0 g. samples were necessary, the recovery of the hydrazones being 100—105%. For the spectroscopic method, much smaller samples of ca. 0.05 g. sufficed, recovery being 97—100%. In view of its greater accuracy and convenience, this latter method was adopted.

The absorption maxima (λ_{\max} , in $m\mu$) and the molar extinction coefficients ($\epsilon \times 10^{-4}$) of the various aldehyde 2,4-dinitrophenylhydrazones (purified as suggested by Johnson¹⁵) are given below, followed by the literature^{15,16} values, where available, in parentheses: benzaldehyde, 378, 2.96 (378, 3.03; 377, 3.02); *p*-chloro, 378, 3.15 (377, 3.16; 375, 3.30); *m*-chloro, 375, 3.08; *p*-Bu^t, 385, 3.13; *p*-methoxy, 392, 3.06 (387, 3.05; 390, 3.09); *p*-nitro, 383, 3.60 (381, 3.69).

Reaction of Dibenzyl Ether with N-Bromosuccinimide.—(a) A mixture of *N*-bromosuccinimide (3.73 g., 21.0 mmoles), and dibenzyl ether (21.1 g., 107 mmoles), diluted to 100 ml. with carbon tetrachloride, was heated at 80° ± 1° (oil-bath) under nitrogen, illuminated with a 150-watt incandescent bulb, under reflux, and with efficient stirring. Reaction started in ca. 10 min. After 2 hr., the mixture was cooled and two 10 ml. aliquots were pipetted (a piece of cotton wool was placed at the tip of the pipette to prevent succinimide from being sucked up) and treated separately as follows.

(i) Alcohol method. 2,4-Dinitrophenylhydrazine (1.0 g.) and ethanol (10 ml.) were added to the aliquot, followed by concentrated hydrochloric acid (3 drops). The mixture was refluxed for 2 hr., cooled, and the 2,4-dinitrophenylhydrazone collected by filtration (0.80 g.).

(ii) Aqueous method. The aliquot was added to a saturated solution of 2,4-dinitrophenylhydrazine in 2*N*-hydrochloric acid (400 ml., containing 4 mg. reagent per ml.) and the mixture was shaken for 2 hr. Carbon tetrachloride was removed under reduced pressure and the 2,4-dinitrophenylhydrazone (0.61 g.) filtered, washed with 2*N*-hydrochloric acid, water, and cold ethanol (5 ml.).

The crude hydrazones obtained as in (i) and (ii) above were separately chromatographed, to remove unchanged reagent. Estimation by spectroscopy indicated yields of 2.09 and 2.08 mmoles (99.5 and 99.0%), respectively, calculated on the bromo-imide used. (Preliminary experiments with benzaldehyde showed that the presence of dibenzyl ether and carbon tetrachloride did not affect the yields of the hydrazone, when prepared by the above method.)

The remainder of the reaction mixture was filtered, concentrated under nitrogen and fractionally distilled to give (i) a liquid, b. p. 40—108°/0.3 mm. (2.9 g.), (ii) unreacted dibenzyl ether, b. p. 106—108°/0.3 mm. (6 g.), and (iii) a residue (1 g.). A portion (0.92 g.) of fraction (i) was added to a solution of methyl fluorene-9-carboxylate (1.1 g.) and sodium (0.23 g.) in dry methanol (10 ml.) as described by Bavin.¹⁷ A white solid (0.45 g., 36%) was obtained, m. p. 105—106° (from ethanol), undepressed by admixture with an authentic sample of methyl 9-benzylfluorene-9-carboxylate (Found: C, 84.2; H, 5.9. Calc. for $C_{22}H_{28}O_2$; C, 84.1; H, 5.7%). Bavin¹⁷ reported m. p. 74—75° for methyl 9-benzylfluorene-9-carboxylate. Saponification of the above derivative with sodium hydroxide yielded 9-benzylfluorene-9-carboxylic acid, m. p. 201—203° (lit.,¹⁷ 201—202°). Trituration of the residue (iii) with petroleum gave *N*-(α -benzyloxybenzyl)succinimide (0.05 g., 1.0%), m. p. 104—106° (from ethanol) (Found: C, 72.7; H, 5.65, N, 5.05. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.7%), ν_{\max} . 3035, 2860, 1725, 1495, 1453, 1362, 1269, 1107, 1095, 1070, 1027, 1027, 720, and 693 cm^{-1} . The infrared spectrum of the mother liquor showed the presence of only dibenzyl ether and no detectable amount of *N*-(α -benzyloxybenzyl)succinimide.

(b) In another experiment under similar conditions dibenzyl ether (20.5 g., 104 mmoles) and *N*-bromosuccinimide (3.05 g., 17.1 mmoles) gave benzaldehyde in yields of 99% and 100% (estimated as described above) and *N*-(α -benzyloxybenzyl)succinimide in 2% yield. The mixture

¹⁴ J. A. Elvidge and M. Whalley, *Chem. and Ind.*, 1955, 589.

¹⁵ G. D. Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 2720.

¹⁶ L. A. Jones and C. K. Hancock, *J. Org. Chem.*, 1960, **25**, 226.

¹⁷ P. M. G. Bavin, *Analyt. Chem.*, 1960, **32**, 554.

was also analysed for benzyl bromide by the method of Patchornik and Rogozinski,⁵ described below (preliminary experiments with authentic specimens of benzyl bromide having shown that the presence of benzaldehyde, dibenzyl ether, and carbon tetrachloride does not interfere with the determination). An aliquot (10 ml.) of the reaction mixture was titrated with a 0.1N-solution from sodium in methanol to the blue end-point of Thymol Blue (0.2% in dioxan). This gives an indication of acidic components present. Freshly distilled aniline (*ca.* 20 ml.) was then added, the mixture refluxed for 5 min., cooled, and further titrated with sodium methoxide to the green-blue end-point of Thymol Blue. The milliequivalent of sodium methoxide used in the second titration gave the milliequivalent of benzyl bromide present. Aliquots of 10, 10, and 20 ml., thus analysed, showed the presence of 1.71, 1.70, and 3.39 mmoles of benzyl bromide, corresponding to yields of 100%, 99%, and 99%, respectively. Acidic components (HBr) present amounted to 2.0%, 2.1%, and 2.0%, respectively.

Reaction of Substituted Dibenzyl Ethers with N-Bromosuccinimide.—This was carried out exactly as with dibenzyl ether. Aliquots (10 ml.) of the reaction mixture were withdrawn and treated with 2,4-dinitrophenylhydrazine by the two methods described earlier, and the mixture of hydrazones so obtained chromatographed and analysed by ultraviolet spectroscopy. Of the two methods employed in the preparation of the hydrazones, the alcohol method gave the more consistent results. The aqueous method sometimes gave slightly lower values, probably owing to incomplete formation of the hydrazones.

Reaction of Dibenzyl Ether with Molecular Bromine.—A solution (100 ml.) of dibenzyl ether (20.0 g., 101 mmoles) in carbon tetrachloride was placed in a three-neck flask fitted with a reflux condenser, a mechanical stirrer, and a nitrogen inlet tube leading almost to the bottom of the flask. The flask was then heated in a thermostatted oil-bath ($80 \pm 1^\circ$) and a rapid stream of nitrogen was bubbled through the solution. Bromine (5.3 g., 33.2 mmoles) was added during 2–3 min. to the stirred solution under illumination with a 150-watt incandescent bulb. After 2 hr., aliquots (10 ml.) were withdrawn and analysed for benzaldehyde and for benzyl bromide as described above.

Reactions of Substituted Dibenzyl Ethers with Molecular Bromine.—These were carried out as for dibenzyl ether.