648. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part VII.*[1] *The Cleavage of Monosubstituted Dibenzyl Ethers by Free t-Butoxy-radicals.*

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In the abstraction of α-hydrogens by t-butoxy-radicals from the ether $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph$ the substituents R = 4-Bu^t, 4-OMe, and 4-Cl facilitate the reaction, while 3-Cl has little effect. The results are explained in terms of the stabilising influence of R on the benzyl radical produced, in conjunction with a polar effect.

Evidence for hydrogen-abstraction from the ether by the benzyl radicals $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}$ is presented.

The cleavage of substituted dibenzyl ethers (I) by free alkyl radicals formed from Grignard reagents in the presence of cobaltous chloride has been studied in a comparison of the stabilising influences, relative to hydrogen, of the substituents R on free benzyl radicals.[1,2] The radical-intermediate (II) involved in the cleavage has since been shown in the case of dibenzyl ether to be generated also by free t-butoxy-radicals; its disproportionation products, benzaldehyde and free benzyl, being obtained, respectively, as the free aldehyde and substances derived from the radical.[3] Since aldehydes can readily be isolated, *e.g.*, *via* the bisulphite compounds, this reaction of t-butoxy-radicals provides a convenient method for studying the substituent effect on the cleavage of dibenzyl ethers. The fission by this method of five such ethers (I; R = 4-Me, -Bu^t, and -OMe, 3- and 4-Cl) is now reported.

$$(\mathrm{I})\quad \mathrm{R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph} \qquad\qquad \mathrm{R{\cdot}C_6H_4{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2Ph}\quad (\mathrm{II})$$

Whereas in the catalysed Grignard reaction the aldehyde and free benzyl formed are efficiently reduced to the corresponding benzyl alcohol and toluene, which being immune to further reaction are obtained in good yield, with t-butoxy-radicals these disproportionation products react further to give a variety of substances.[3] Inasmuch as a 50% or higher yield of the main product is essential for a decision of the main direction of cleavage, it is important to ascertain the optimum conditions. Experiments conducted with this in view are summarised in the Table.

Among the secondary products (see Table), the substituted benzoic acids probably result mainly from oxidation of the aldehydes, while 3- and 4-chlorobenzyl alcohol, isolated in traces, probably arose by hydrolysis (during exhaustive extraction with aqueous sodium hydrogen sulphite) of the corresponding benzyl benzoate, derived from the radical (III), itself formed from the aldehyde as follows:

$$\mathrm{Ar{\cdot}CHO} \xrightarrow{\mathrm{Bu^tO\cdot}} \mathrm{Ar{\cdot}\dot{C}{:}O} \xrightarrow{\mathrm{Ar{\cdot}CHO}} \mathrm{Ar{\cdot}CO{\cdot}O{\cdot}\dot{C}HAr}\ (\mathrm{III}) \xrightarrow{\text{Ether}} \mathrm{Ar{\cdot}CO{\cdot}O{\cdot}CH_2Ar}$$

$$\mathrm{Ar} = m\text{- and } p\text{-}\mathrm{Cl{\cdot}C_6H_4}\text{–}$$

The formation of the radical (III; Ar = Ph) from benzaldehyde and free t-butoxy-radicals is well known.[4] Of greater interest is the isolation, in yields of 12—24%, of the substituted toluene $R{\cdot}C_6H_4Me$ from most of the ethers. Formation of these toluenes probably occurs by hydrogen-abstraction by the free benzyl from the solvent ether, and strongly suggests

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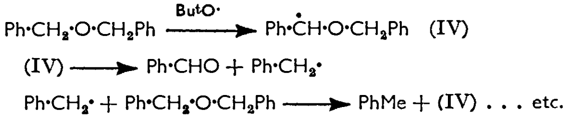
[1] Part VI, Huang and Singh, preceding paper.

[2] Huang and Si-Hoe, *J.*, 1957, 3988.

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

[4] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258.

that cleavage proceeds in part by a chain mechanism (though undoubtedly of a short chain-length) which for dibenzyl ether may be represented as follows:



$$Ph\cdot CH_2\cdot O\cdot CH_2Ph \xrightarrow{Bu^tO\cdot} Ph\cdot\dot{C}H\cdot O\cdot CH_2Ph \quad (IV)$$
$$(IV) \longrightarrow Ph\cdot CHO + Ph\cdot CH_2\cdot$$
$$Ph\cdot CH_2\cdot + Ph\cdot CH_2\cdot O\cdot CH_2Ph \longrightarrow PhMe + (IV)\ .\ .\ .\ etc.$$

Benzyl ethers thus appear to be susceptible to fission by radicals of a range of electronegativity, including substituted benzyl radicals, and free alkyl and alkyloxy-radicals.

Cleavage of monosubstituted dibenzyl ethers $R\cdot C_6H_4\cdot CH_2\cdot O\cdot CH_2Ph$ *by free t-butoxy-radicals.*

		Ether			Products					
	R	Quantity used (mmole)	Quantity reacted (mmole)	Peroxide (mmole) (ratio, ether : peroxide)	$R\cdot C_6H_4\cdot CHO$ bisulphite compound (mmole) (%)	$Ph\cdot CHO$ bisulphite compound (mmole) (%)	$R\cdot C_6H_4\cdot CO_2H$ (mmole)	$R\cdot C_6H_4\cdot Me$ (mmole) (%)	Polymer (g.)	Yield of $R\cdot C_6H_4\cdot CHO$ + $R\cdot C_6H_4\cdot CO_2H$ (%)
1	*p*-Me	95	53	48 (2 : 1)	14 (26)	7 (13)	0·2	—	6·3	26
2	*p*-Bu^t	160	110	78 (2 : 1)	31 (28)	4 (4)	0·7	14 (13) *	17·5	28
3	,,	79	36	20 (4 : 1)	16 (45)	2 (5)	0·6	6·3 (19)	3·8	47
4	,,	91	41	18 (5 : 1)	25 (61)	3 (8)	0·7	10 (24)	3·6	63
5	*p*-OMe	92	38	18 (5 : 1)	19 (50)	3 (8)	0·5	4·9 (13)	3·5	51
6	*m*-Cl	110	55	22 (5 : 1)	22 (40)	22 (40)	0·6	13 (24)	2·1 §	41
7	*p*-Cl	110	42	22 (5 : 1)	13 (31)	5 (12)	0·8	6·3 (15)	3·1	33
8	,,	130	71	65 (2 : 1)	29 (41)	13 (18)	1·4	—	6·8 ‡	42
9	,,	170	97	69 (2·5 : 1)	27 (28)	12 (12)	1·3	—	9·1 ‡ §	29
10	,,	170	35	86 (2 : 1) ¶	18 (51)	5 (14)	2·0	4·1 (12)	1·8 ¶	57

* Also isolated $[p\text{-}Bu^t\cdot C_6H_4\cdot CH_2]_2$ (3 mmoles). ‡ In open vessel under N_2. ¶ In open vessel at 110—115° for 38 hr., peroxide only partially decomposed. We thank Mr. Surinder Singh for collaboration in this experiment. § Traces of $R\cdot C_6H_4\cdot CH_2\cdot OH$ isolated.

EXPERIMENTAL

Cleavage Experiments.—A mixture of the ether and di-t-butyl peroxide was sealed under nitrogen in a glass tube, and heated at 110° for 96 hr. (experiments nos. 1—7). In some cases (nos. 8—10) the mixture was heated in an open flask under reflux, in an atmosphere of nitrogen. Optimum yields (nos. 4, 5, 6, and 10) were obtained by using a 5-fold excess of the ether, except for 4-chlorodibenzyl ether, for which a 2-fold excess for a shorter time (38 hr.) was preferable.

Analysis of Cleavage Products: *Typical Procedures.*—*4-t-Butyldibenzyl ether.* The reaction mixture from this ether (40·0 g., 160 mmoles) and t-butyl peroxide (11·4 g., 78 mmoles) was diluted with light petroleum (40 c.c.) and the homogeneous mixture was shaken with a saturated aqueous solution of sodium hydrogen sulphite (2 hr.). The bisulphite compounds (8·9 g.) were filtered off and washed with ether. The petroleum solution was further extracted with 10% aqueous sodium carbonate, dried ($MgSO_4$), concentrated, and distilled to give the following fractions: (i) *p*-t-Butyltoluene, b. p. 32—34°/0·5 mm., 191·5°/762 mm. (2·1 g.), n_D^{24} 1·4919 (lit.,[5] b. p. 192—193°/760 mm., n_D^{20} 1·4919) [dinitro-derivative, yellow plates (from ethanol), m. p. and mixed m. p. 96—97°, alone or mixed with an authentic sample]. (ii) Material, b. p. 144—158°/0·5 mm., n_D^{23} 1·5425 (12·5 g.) which deposited small quantities of *4,4'-di-t-butylbibenzyl* (0·61 g.) which crystallised from light petroleum in rhombic prisms, m. p. 150—151° (Found: C, 89·4; H, 10·2. $C_{22}H_{30}$ requires C, 89·8; H, 10·2%), the liquid being mostly unchanged ether (b. p. and *n*). (iii) A residue (17·8 g.), a portion (6·2 g.) of which was chromatographed in light petroleum on alumina, ten 30 c.c. fractions being collected. The first two of these gave traces (0·09 g.) of the above bibenzyl, and the later fractions intractable oils.

The sodium carbonate extract was washed with ether, and, after expulsion of dissolved ether by warming, was acidified with concentrated hydrochloric acid to give *p*-t-butylbenzoic acid, m. p. 159—163° (0·13 g.), raised to 163—164° by recrystallisation from light petroleum (Found: C, 74·4; H, 7·8. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%). Marvel *et al.*[6] report m. p. 164°.

The mixture of aldehyde bisulphite compounds obtained as above was treated with 2N-sulphuric acid under nitrogen, and the aldehydes were liberated taken up in ether, washed with water, dried, and concentrated to a mixture (4·0 g.). A portion of this gave the *p*-t-butylbenzaldehyde *p*-nitrophenylhydrazone, yellow leaflets (from ethanol), m. p. 215—216° (Baker *et al.*[7] report m. p. 214°). Another portion (1·0 g.) was shaken with saturated aqueous alkaline potassium permanganate (*ca.* 20 c.c.) for 10 min., then heated with shaking at 60° for 30 min., cooled, and acidified with dilute sulphuric acid. After clarification with aqueous sodium hydrogen sulphite, the products were extracted with much ether, washed with water once, dried, and concentrated to give a solid, m. p. 158—165° (0·7 g.), which was mostly *p*-t-butylbenzoic acid. Fractional sublimation (at 110°/0·2 mm.) removed traces of benzoic acid (0·05 g.; m. p. and mixed m. p.), the *p*-t-butylbenzoic acid being then obtained as needles (from petroleum), m. p. and mixed m. p. 164—165° (0·65 g.). From the molar ratio of butylbenzoic and benzoic acid obtained, it is thus estimated that the mixture of bisulphite compounds obtained above (8·9 g.) is composed of approx. 31 and 4 mmoles of the bisulphite compounds of the respective aldehydes.

4-Chlorodibenzyl ether. This ether (25 g., 110 mmoles) and the peroxide (3·2 g., 22 mmoles) gave, as above, a mixture of bisulphite compounds, *p*-chlorobenzoic acid, m. p. and mixed m. p. 239—242° (0·13 g.), and a neutral fraction which was distilled to give (i) *p*-chlorotoluene, b. p. 42—50°/0·5 mm., 162°/760 mm. (0·8 g.), n_D^{23} 1·5187 (lit., b. p. 162°/760 mm., n_D^{19} 1·5199), (ii) unchanged ether (11·0 g.), and (iii) a residue (7·45 g.). The residue, on chromatography and distillation, gave more unchanged ether (4·4 g.). (In one experiment, traces of 4-chlorobenzyl alcohol were isolated; m. p. and mixed m. p. 70—71°.) The bisulphite compounds were decomposed as before, and the aldehyde mixture distilled *in vacuo*, a small forerun and residue being rejected (<10%). A chlorine analysis of the main distillate (Found: Cl, 19·0, 19·0%) enabled the molar ratio of chlorobenzaldehyde and benzaldehyde to be computed (subject probably to a maximum error of *ca.* 5%). A sample of the aldehyde mixture gave *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 267—268° and an oxime, m. p. 109—110° (lit., m. p. 110°).

The cleavage products from 3-chlorodibenzyl ether were similarly worked up. The mixture of aldehydes from 4-methoxydibenzyl ether was estimated by methoxyl determinations.

DISCUSSION

If the course of cleavage is governed soley by the relative stability of the radical intermediate, the results obtained (Table, nos. 4, 5, 6, and 10) show that, in their ability to stabilise benzyl radicals, the substituents 4-Bu^t, 4-OMe, and 4-Cl are all greater than, and 3-Cl is of the same order as, hydrogen. Recently, however, evidence has accumulated which indicates that in reactions involving radicals of relatively high electronegativity polar factors can also play an effective directing part, as for example in the abstraction of hydrogen, by chlorine atoms and by free benzoyloxy-radicals, from substituted toluenes,[8] aliphatic acids,[9] and aromatic aldehydes.[10] These effects appear significant only with

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[5] Lacourt, *Bull. Soc. chim. belges*, 1929, **38**, 1.

[6] Marvel, Johnston, Meier, Mastin, Whitson, and Himel, *J. Amer. Chem. Soc.*, 1944, **66**, 914.

[7] Baker, Nathan, and Shoppee, *J.*, 1935, 1846.

[8] Helden and Kooyman, *Rec. Trav. chim.*, 1954, **73**, 269; Russell and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 4578; Russell, *ibid.*, 1956, **78**, 1047; Walling and Miller, *ibid.*, 1957, **79**, 4181.

[9] Price, *ibid.*, 1953, **75**, 3686.

[10] Walling and McElhill, *ibid.*, 1951, **73**, 2927.

highly electronegative radicals such as mentioned above (and presumably with electropositive ones also) but, as would be expected, not with relatively neutral radicals such as free alkyls,[9] or even trichloromethyl.[11] Since free t-butoxy is intermediate in electron-withdrawing character between the free alkyls and benzoyloxy, its reactions might similarly be influenced by polar effects. This has been found to be the case by Johnston and Williams,[12] who showed, contemporaneously with this work, that in the attack by this radical on substituted toluenes and cumenes the substituent assists or retards α-hydrogen-abstraction according to whether it is electron-repelling or -attracting. Such polar influence must to some extent operate also in the reaction with dibenzyl ethers. Thus the facilitating action of the 4-butyl and 4-methoxy-groups is attributed to two complementary effects: radical-stabilisation and electron-release. The 4-chloro-substituent represents a case of opposing influences: but, whereas in *p*-chlorotoluene the hindering polar factor seems overpowering (the rate of hydrogen-abstraction being 0·85 against 1 for toluene),[12] in the benzyl ether the reverse is the case, and this must be due to the presence of the electron-donating and resonance-stabilising benzyl ether grouping $-O{\cdot}CH_2Ph$. The same effect of this group has earlier been encountered by Russell [8] in the reaction of peroxy-radicals. The 3-chloro-atom is a similar combination of conflicting influences, and its indifferent directive capacity, compared with that of the 4-chloro-atom, can be explained in terms of a greater adverse polar effect coupled probably with decreased stabilisation. It is noteworthy that in the cleavage of 3-chlorodibenzyl ether by the cobalt chloride-catalysed Grignard reaction,[1] the radicals $3\text{-}Cl{\cdot}C_6H_4{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2Ph$ and $3\text{-}Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}\dot{C}HPh$ are formed in a molar ratio of 63 : 27, whereas with t-butyl peroxide this ratio becomes 41 : 40. In the former fission, relatively neutral alkyl radicals (or hydrogen atoms) react, and hence the stability factor predominates; in the latter, the unfavourable polar effect of the 3-chloro-substituent becomes significant, and the direction of cleavage is all but reversed. Again, with 4-chloro-4′-methoxydibenzyl ether, attacking alkyl radicals (from the catalysed Grignard reaction) rupture the ether largely via the radical-intermediate $4\text{-}Cl{\cdot}C_6H_4{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe\text{-}4$,[1] whereas free t-butoxy-radicals bring about fission equally in both directions, giving a mixture of *p*-chloro- and *p*-methoxybenzaldehyde in approximately the same molar proportions.[13] Here a favourable polar effect towards the electrophilic t-butoxy-radical is exerted by the 4-methoxy-group, probably augmented by the $-I$ effect of the 4-chlorine atom. It would be of interest to study cleavages by more strongly polar radicals, of both electropositive and electronegative character.

The authors thank Dr. W. A. Waters, F.R.S., for stimulating discussions.

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[*Received, February 6th*, 1959.]

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[11] Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163.
[12] Johnston and Williams, *Chem. and Ind.*, 1958, 328.
[13] Huang and Singh, unpublished result.