

791. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part III.¹ The Cleavage of Monosubstituted Dibenzyl Ethers by Grignard Reagents in the Presence of Cobaltous Chloride.*

By R. L. HUANG and (MISS) SING SOW SI-HOE.

Dibenzyl ether is considered to be cleaved by Grignard reagents in the presence of cobaltous chloride *via* the radical $\cdot\text{CHPh}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, which gives benzyl alcohol and toluene. Cleavage of a substituted dibenzyl ether would proceed *via* the radical $\text{R}\cdot\text{C}_6\text{H}_4\cdot\dot{\text{C}}\text{H}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ (I) provided R has more stabilising action than hydrogen on the intermediate benzyl radical. The direction of cleavage therefore enables such stabilising effects of R and H to be compared. All the six ethers studied (R = *p*-Ph, *p*-Cl, *p*-OMe, *p*-Me, *p*-Bu^t, and *m*-Me) were cleaved *via* the radical (as I) to give substituted benzyl alcohols $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ and toluene, indicating that all these substituents are relatively more stabilising than hydrogen.

A RECENT study² of the cleavage of substituted diphenyl ethers by Grignard reagents in the presence of anhydrous cobaltous chloride permitted a comparison of the relative stabilities of aryloxy-radicals. We now report the cleavage by the same method of six monosubstituted dibenzyl ethers, and propose a mechanism on the basis of which the direction of cleavage in each case indicates the relative stabilising influence of the phenyl and the substituted phenyl groups on free alkyl radicals.

This method of cleavage, first reported by Kharasch and Huang,³ affects a variety of ethers including benzyl aryl, allyl phenyl, diphenyl, and dibenzyl ethers. No mechanism was proposed for any of these cleavages, although free alkyl radicals and/or free hydrogen atoms were suggested as possible agents. In the case of diphenyl ethers, Huang² postulated the reaction as proceeding *via* aryloxy-radicals, produced by the agency of atomic hydrogen: $\text{Ph}\cdot\text{O}\cdot\text{Ph} \xrightarrow{\text{H}\cdot} \text{Ph}\cdot\text{O}\cdot + \text{PhH}$. Conclusions regarding the stabilising effects of substituent groups on aryloxy-radicals, on the whole, confirmed and extended the theory put forth by Ingold⁴ in 1934. In the case of dibenzyl ethers the mechanism of cleavage is probably different: indeed, it would be surprising if these two structurally divergent types of ethers, which represent extremes in behaviour towards ionic reagents,⁵ should be cleaved by the same mechanism. A satisfactory mechanism should be able to explain (a) the reaction conditions, which call for a large excess of the Grignard reagent (5 mols.) and of the cobaltous chloride (2.5 mols.), and (b) the products, which in the case of dibenzyl ether are toluene and benzyl alcohol, obtained in good yields and free from

¹ Part II, Huang, *J.*, 1957, 1342.

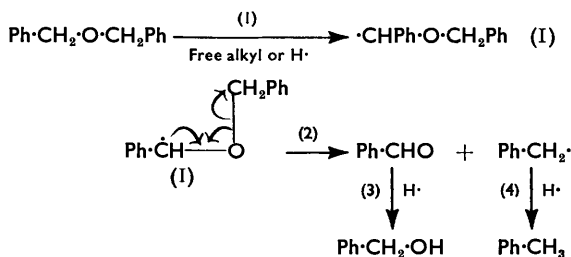
² Huang, *J.*, 1954, 3084; 3088.

³ Kharasch and Huang, *J. Org. Chem.*, 1952, **17**, 669.

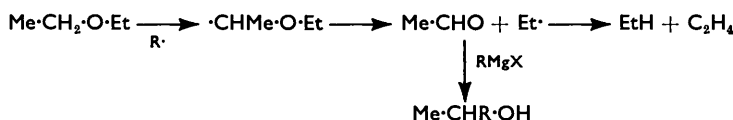
⁴ Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52.

⁵ See Burwell, *Chem. Rev.*, 1954, **54**, 615.

by-products. One such mechanism would be the following, involving the action of an excess of free alkyl radicals and hydrogen atoms:



Steps (1) and (2) are analogous to the processes postulated by Evans and his co-workers⁶ in a mechanism which satisfactorily explains the diverse products arising from the attack of free alkyl or aryl radicals, generated by the electrolysis of Grignard reagents, on aliphatic ethers, *e.g.*:



The abstraction of an active hydrogen (step 1) is a well-known specific reaction of free radicals, and occurs with a large variety of substances such as alkylbenzenes, ketones, and esters.⁷ Step (2), that of disproportionation, is again a common occurrence with free radicals and finds many analogies, such as the break-down of a free alkoxy-radical to a carbonyl compound and a free alkyl, *e.g.*, the *isopropoxy*-radical gives acetaldehyde and free methyl, and the *tert.*-butoxy-radical acetone and free methyl.⁸ The reductive nature of the Grignard reagent-cobaltous chloride system has been well demonstrated, and provides analogies for step (3) in the reduction of halogenobenzenes,⁹ and *isosafrole*.³ However, the possibility that benzyl alcohol was further reduced to toluene (giving two mols. of toluene per mol. of ether) was excluded by subjecting benzaldehyde itself to the cleavage conditions, and isolating a fair yield of benzyl alcohol, but no toluene. It might be presumed that the benzyl alcohol so produced was protected from further reduction by the formation of the magnesium complex ($\text{Ph}\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgX}$), thereby consuming yet another mol. of the Grignard reagent. Finally, the transient existence of the free benzyl radical finds strong support in the isolation, on cleavage of 4-methoxydibenzyl ether, of considerable amounts of 4:4'-dimethoxydibenzyl. The coupling of such radicals with atomic hydrogen (step 4) requires no comment.

The above mechanism is thus well substantiated by both analogy and experimental evidence,* which, nevertheless, do not exclude the alternative mechanism postulated for the cleavage of diphenyl ethers, involving direct reduction by hydrogen atoms. Evidence against the latter mechanism has, however, been found in the cleavage of a substituted ether, *viz.*, benzyl *p*-diphenylmethyl ether, as described below.

If the mechanism now proposed is operative, cleavage of a monosubstituted dibenzyl ether $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ would be expected to take one or both of two courses: (a) *via* the

* *Added, July 29th, 1957.*—Further evidence has recently been provided by the generation of the radical $\cdot\text{CHMe}\cdot\text{OEt}$ from diethyl ether by the Grignard reagent-cobaltous chloride mixture (Norman and Waters, *J.*, 1957, 950).

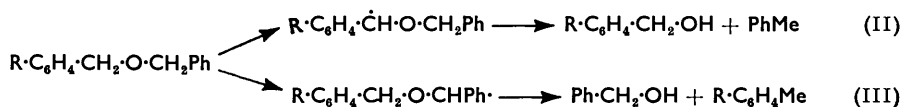
⁶ Evans and Braithwaite, *J. Amer. Chem. Soc.*, 1939, **61**, 898; Evans, Pearson, and Braithwaite, *ibid.*, 1941, **63**, 2574.

⁷ Cf., *e.g.*, Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401; Farmer and Moore, *J.*, 1951, **131**; Huang and Kum-Tatt, *J.*, 1954, 2570; 1955, 4229.

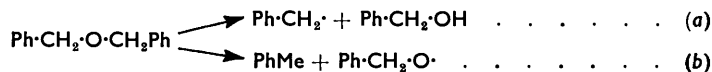
⁸ Rust, Seibold, and Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 338.

⁹ Kharasch, Sayles, and Fields, *ibid.*, 1944, **66**, 481.

intermediate radical (II) to give a substituted benzyl alcohol and toluene, and (b) *via* the radical (III) giving benzyl alcohol and a substituted toluene, as follows:



Since the course of the reaction should depend on the relative stability of the intermediate radical (steric factors being absent), the radical (II) would be the sole or major intermediate if it is more stable than (III), *i.e.*, if substituted phenyl has more stabilising effect than phenyl on the intermediate alkyl radical. Then R would appear in the benzyl alcohol produced. On the other hand, if hydrogen atoms effect cleavage in the same manner as in diphenyl ether, dibenzyl ether might be cleaved in one of the following ways:



Inasmuch as free benzyl is more resonance-stabilised than free benzyloxy, route (a) should be favoured. Cleavage of a monosubstituted dibenzyl ether should therefore proceed *via* the benzyl radical of greater stability, and if R has more stabilising effect on this radical than hydrogen, the substituent R would be found in the substituted toluene.

A decision between the two mechanisms can therefore be made by studying the cleavage of a monosubstituted ether the stabilising effect of whose substituent group R is already known. One such substituent is the *para*-phenyl group, whose stabilising influence on the benzyl radical has been expressed in terms of resonance¹⁰ and exemplified among other things in its effect on the triarylmethyl radicals.¹¹ Cleavage of benzyl *p*-diphenylmethyl ether gave a good yield of 4-phenylbenzyl alcohol.

A probable mechanism having been established, it was possible to extend the study to five other dibenzyl ethers bearing substituents whose stabilising influences on the benzyl radical are less well known. When both directions of cleavage were taken, quantitative isolation of all four possible cleavage products proved infeasible, especially as some toluene was invariably lost (presumably volatilised by the evolution³ of large volumes of gas during the cleavage). However, since cleavage in general is not complicated by side reactions, the isolation of any one product in a yield greater than 50% is sufficient indication of the main course of the reaction. Purification and attempts at quantitative isolation were accordingly directed at the more abundant of the constituents, although identification of the minor products was also undertaken. In most of the cases studied, cleavage was found to take one course predominantly.

The Grignard reagent of choice in previous studies² was *n*-butylmagnesium bromide, which gave small quantities of octane (b. p. 126°) which could not be separated by distillation from the toluene produced (Bryce-Smith¹² reports a similar inseparable mixture between octane and *isopropylbenzene*). *iso*Propylmagnesium bromide, found to be equally effective for the cleavage, was consequently employed throughout, the coupled product from this Grignard reagent, 2 : 3-dimethylbutane (b. p. 58°), being readily separated from toluene.

EXPERIMENTAL

Synthesis of Ethers.—The dibenzyl ethers (all new compounds) listed in Table I were prepared from the sodio-derivative of benzyl alcohol (except for 4-methoxybenzyl ether, for which anisyl alcohol was used), and the appropriate benzyl halide. A typical preparation follows: *p*-Chlorobenzyl chloride (Eastman, 60 g., 0.38 mole) in benzyl alcohol (20 g.) was added to

¹⁰ Pauling and Wheland, *J. Chem. Phys.*, 1933, **1**, 362.

¹¹ Müller, Müller-Rodloff, and Bunge, *Annalen*, 1935, **520**, 235; Marvel, Shackleton, Himel, and Whitson, *J. Amer. Chem. Soc.*, 1942, **64**, 1824.

¹² Bryce-Smith, *J.*, 1956, 1604.

a solution of sodium (12.2 g., 0.5 g.-atom) in benzyl alcohol (170 g., 1.5 moles) in about 15 min. with mixing. The mixture became warm and soon deposited sodium chloride. After 2 hours' heating at 120° the solid was filtered off, and the filtrate poured on ice and extracted with ether. After being dried (MgSO₄) the ether was distilled, and about two-thirds of the excess of benzyl alcohol was removed *in vacuo*. The residue was then distilled with a Vigreux column (benzyl alcohol co-distills with certain dibenzyl ethers, *e.g.*, dibenzyl ether and 4-methoxydibenzyl ether, if a Vigreux column is not used) to give 4-chlorodibenzyl ether, b. p. 114°/0.1 mm. (68 g.).

TABLE I. *Monosubstituted dibenzyl ethers*, R·C₆H₄·CH₂·O·CH₂Ph.

R	Ar·CH ₂ X	Yield (%)	B. p./mm.	n (temp.)	Found (%)			Formula	Required (%)		
					C	H	Cl		C	H	Cl
H ...	Ph·CH ₂ Cl	80	107—108°/0.3	1.5608 (23°)	—	—	—	—	—	—	—
<i>p</i> -Cl	<i>p</i> -Cl·C ₆ H ₄ ·CH ₂ Cl	78	114°/0.1	1.5698 (20°)	72.2	5.5	15.3	C ₁₄ H ₁₃ OCl	72.4	5.6	15.1
<i>p</i> -Me	<i>p</i> -Me·C ₆ H ₄ ·CH ₂ Br	73	110°/0.2	1.5558 (21°)	85.1	7.6	—	C ₁₅ H ₁₅ O	84.9	7.6	—
<i>m</i> -Me	<i>m</i> -Me·C ₆ H ₄ ·CH ₂ Br	70	104°/0.3	1.5560 (22°)	84.8	7.55	—	C ₁₅ H ₁₆ O	84.9	7.6	—
<i>p</i> -Bu ^t	<i>p</i> -Bu ^t ·C ₆ H ₄ ·CH ₂ Br	86	139—140°/0.2	1.5412 (23°)	85.3	8.7	—	C ₁₈ H ₂₂ O	85.1	8.7	—
<i>p</i> -Ph	<i>p</i> -C ₆ H ₅ ·C ₆ H ₄ ·CH ₂ Cl *	51	186—190°/0.2	1.6140 (23°)	87.7	6.7	—	C ₂₀ H ₁₈ O	87.6	6.6	—
<i>p</i> -OMe	Ph·CH ₂ Cl	59	146—147°/0.4	1.5625 (22°)	78.6	7.0	—	C ₁₅ H ₁₆ O ₂	78.9	7.1	—

* Prepared as described by von Braun (*Ber.*, 1933, **66**, 1471).

By this method, dibenzyl ether was obtained in 80% yield, having b. p. 107—108°/0.3 mm., n_D^{23} 1.5608. Dehydration of benzyl alcohol by Senderens's method¹³ gave a 60% yield of a product of b. p. 138—140°/5 mm., n_D^{20} 1.5640.

4-*tert*.-Butylbenzyl Bromide.¹⁴—Bromine (53 g.) was added during *ca.* 2 hr. to *p*-*tert*.-butyltoluene (50 g.) at 140—150° under nitrogen. The product was kept in a desiccator over potassium hydroxide for 48 hr., then distilled, giving *p*-*tert*.-butylbenzyl bromide, b. p. 80—84°/0.2 mm. (40 g.), n_D^{24} 1.5453.

Cleavage of Ethers.—*General procedure* (see Huang²). The ether (0.2 mole) was added to an approx. 1.5N-solution of isopropylmagnesium bromide (1 mole) in diethyl ether and vigorous stirring started. Anhydrous cobaltous chloride (0.5 mole) was then introduced in approx. 30 portions during 3 hr., the mixture being cooled with an ice-water bath to *ca.* 15—20°. In a few cases a sudden rise in temperature was noted after addition of about 0.2 mole of cobaltous chloride, causing gentle reflux of the solvent which subsided after 1 or 2 min. After addition was complete, stirring was continued for ½ hr. at *ca.* 28°, water (*ca.* 20 c.c.) being then cautiously added. Next day the mixture was poured on ice and dilute hydrochloric acid, and the product taken up in ether, washed with water, aqueous sodium hydrogen carbonate, and again with water, and dried (MgSO₄) and the solvent removed through a fractionating column. The products were then isolated by fractional distillation or recrystallisation, and identified by b. p. and refractive index or m. p., elemental analysis, and preparation of derivatives.

Benzyl p-Diphenylmethyl Ether.—This ether (8.3 g., 0.3 mole), treated as above, gave 4-phenylbenzyl alcohol, which crystallised from benzene-cyclohexane in plates, m. p. 91—95° (3.5 g., 0.019 mole), raised to m. p. 99—100° by further recrystallisations (Found: C, 84.5; H, 6.4; O, 8.9. C₁₃H₁₂O requires C, 84.75; H, 6.6; O, 8.7%). The α -naphthylurethane, needles from ligroin, melted at 126—127° (Found: C, 81.7; H, 5.3. C₂₄H₁₉O₂N requires C, 81.6; H, 5.4%). Some ether (1 g.) was recovered.

4-Methoxybenzyl Ether.—The cleavage products from this ether (45 g., 0.2 mole), fractionated through a 15-cm. Vigreux column, gave: (i) a forerun, b. p. 70—90° (bath)/100 mm. (0.6 g.); fractions (ii) b. p. 69—70°/100 mm. (7.6 g.); (iii) b. p. 40—42°/50 mm. (*ca.* 1—2 g.); (iv) b. p. 88—90°/50 mm. (4.1 g.); (v) b. p. 38°/0.9 mm. (*ca.* 1 g.); (vi) b. p. 59—60°/0.9 mm. (2.3 g.). The fractionating column was then replaced by a Claisen head, and distillation continued to

¹³ Senderens, *Compt. rend.*, 1928, **188**, 1073.

¹⁴ Shirley, "Preparation of Organic Intermediates," Wiley & Sons, 1951, p. 62; cf. Shoesmith and Mackie, *J.*, 1936, 300.

give (vii) material, b. p. 134—136°/0.9 mm., which partially crystallised (solid 3.1 g., liquid 1.3 g.), and (viii) a dark residue (13 g.).

The above fractions were then refractionated as follows. Fractions (i) and (ii) gave (a) a liquid, b. p. 54—62°/760 mm. (0.5 g.), probably mainly 2 : 3-dimethylbutane (lit., b. p. 58°), and (b) toluene, b. p. 109—111°/760 mm. (6.3 g.), n_D^{25} 1.4925 (toluene has b. p. 111°, n_D^{25} 1.4946) (2 : 4-dinitro-derivative, m. p. and mixed m. p. 69—70°). The residue from this distillation was combined with fractions (iii)—(v) and again fractionated, giving more toluene, b. p. 109—112°/760 mm. (1.0 g.), and a fraction, b. p. 175—176°/760 mm. (2.9 g.) n_D^{25} 1.5092. The last fraction on oxidation with alkaline potassium permanganate gave *p*-anisic acid, m. p. and mixed m. p. 183—185°, and was therefore *p*-methoxytoluene (lit.,¹⁵ b. p. 176°/760 mm.). Fraction (vi) together with the liquid from (vii) yielded more *p*-methoxytoluene (0.91 g.), n_D^{25} 1.5120, and benzyl alcohol, b. p. 46°/0.2 mm., 199°/755 mm. (1.3 g.), n_D^{25} 1.5431 (lit., b. p. 205°/760 mm., n_D^{20} 1.5400). The solid from fraction (vii) crystallised from 95% ethanol in needles, m. p. 126—127° (Found: C, 79.3; H, 7.4. Calc. for 4 : 4'-dimethoxydibenzyl, C₁₆H₁₈O₂: C, 79.3; H, 7.4%). On demethylation with hydrobromic acid in acetic acid it gave 4 : 4'-dihydroxydibenzyl, m. p. 200—201° (needles from benzene-cyclohexane). Richardson and Reid¹⁶ report m. p.s 125.7—127° and 198—199° respectively. Finally the residue (viii) (13 g.) was chromatographed on alumina, with benzene as eluant, to give more 4 : 4'-dimethoxydibenzyl m. p. 124—127° (2.0 g.), and unchanged ether (4.4 g.), b. p. 141—144°/0.3 mm. Hence high-boiling material unaccounted for totalled 6 g.

The main pure products isolated were: toluene (7.3 g., 0.081 mole), *p*-methoxytoluene (3.8 g., 0.031 mole), and 4 : 4'-dimethoxydibenzyl (5.0 g., 0.021 mole).

4-Chlorodibenzyl Ether.—The cleavage products (from 41 g., 0.17 mole, of the ether) on fractionation as described above yielded: (i) toluene (5.0 g., 0.054 mole); (ii) mixtures of *p*-chlorotoluene and benzyl alcohol; (iii) 4-chlorobenzyl alcohol, b. p. 62—74°/0.2 mm., needles (from benzene), m. p. 71—72° (11.1 g., 0.078 mole) (Mettler¹⁷ reports m. p. 73°) (Found: Cl, 24.3. Calc. for C₇H₇OCl: Cl 24.65%); (iv) unchanged ether (11.2 g.); and (v) a dark residue (4.1 g.). Chromatography of the residue gave negligible quantities of a solid, m. p. 180—195°, which could not be identified.

4-Methyldibenzyl Ether.—This ether (46.5 g., 0.21 mole) on cleavage gave: (i) toluene, b. p. 56—60°/100 mm., 109—111°/760 mm. (9.3 g., 0.10 mole), n_D^{25} 1.4925; (ii) mixtures of toluene and *p*-xylene, and of benzyl alcohol and 4-methylbenzyl alcohol; (iii) 4-methylbenzyl alcohol, m. p. 55—59° (18.9 g.), raised to 59—60° by recrystallisation from light petroleum (b. p. 60—80°) (lit., m. p. 60°) (Found: C, 78.6; H, 8.3. Calc. for C₈H₁₀O: C, 78.7; H, 8.2%) [3 : 5-dinitrobenzoate (from 95% ethanol), m. p. 117° (lit., 117—118°)]; and (iv) unchanged ether (1 g.).

3-Methyldibenzyl Ether.—The products from the cleavage of 3-methyldibenzyl ether (37.7 g., 0.17 mole) were fractionally distilled to give: (i) toluene (5.05 g. 0.055 mole); (ii) a mixture of toluene and *m*-xylene and possibly benzyl alcohol; (iii) 3-methylbenzyl alcohol, b. p. 69—70°/0.4 mm., 218—219°/759 mm. (13.8 g., 0.11 mole), n_D^{20} 1.5329 (Found: C, 78.1; H, 8.1%) (α -naphthylurethane, m. p. 117—118° after repeated recrystallisation from light petroleum) (lit.,¹⁵ b. p. 217°/760 mm.; m. p. 117°, respectively); (iv) unchanged ether (5.8 g.); and (v) an undistillable residue (1.1 g.).

4-tert.-Butyldibenzyl Ether.—The product from cleavage of this ether (30.3 g., 0.12 mole) on distillation gave only toluene (3.5 g., 0.038 mole) and 4-tert.-butylbenzyl alcohol, b. p. 87—88°/0.3 mm., 236—238°/761 mm. (14.8 g., 0.090 mole), n_D^{25} 1.5170 (Found: C, 80.7; H, 9.7. Calc. for C₁₁H₁₆O: C, 80.5; H, 9.75%) (α -naphthylurethane, m. p. 160°), there being practically no residue. Verley¹⁸ reports b. p. 140°/20 mm. and Wender *et al.*¹⁹ give m. p. 159—160°, respectively.

Reduction of Benzaldehyde.—Benzaldehyde (redistilled, 24 g., 0.23 mole) in ether (*ca.* 25 c.c.) was added in 10 portions during 2½ hr. to isopropylmagnesium bromide (0.46 mole) in diethyl ether (400 c.c.), each portion being immediately followed by cobaltous chloride (*ca.* 3 g. each time, total 0.23 mole). The product was worked up as usual and distilled, giving benzyl

¹⁵ Shriner and Fuson, "Identification of Organic Compounds," Wiley & Sons, 1948.

¹⁶ Richardson and Reid, *J. Amer. Chem. Soc.*, 1940, **62**, 413.

¹⁷ Mettler, *Ber.*, 1905, **38**, 1750.

¹⁸ Verley, *Bull. Soc. chim. France*, 1898, **19**, 68.

¹⁹ Wender, Greenfield, Metlin, and Orchin, *J. Amer. Chem. Soc.*, 1952, **74**, 4079.

alcohol, b. p. 56—58°/0.5 mm., 208°/760 mm. (9.5 g.) [α -naphthylurethane, m. p. 130—131° (lit.,¹⁵ m. p. 134°)].

DISCUSSION

The results of cleavage experiments are given in Table 2, the yields of products being calculated on the ethers actually cleaved. Except for 4-methoxydibenzyl ether, cleavage in every case gave a high yield of the substituted benzyl alcohol, with formation of little or no by-product or polymer. In the case of 4-methoxydibenzyl ether a 48% yield of toluene was obtained against 43% of *p*-methoxytoluene. Since loss of toluene was observed

TABLE 2. *Cleavage of dibenzyl ethers, R·C₆H₄·CH₂·O·CH₂Ph.*

R	Cleavage (%)	Products		R	Cleavage (%)	Products	
		R·C ₆ H ₄ ·CH ₂ ·OH (%)	PhMe (%)			R·C ₆ H ₄ ·CH ₂ ·OH (%)	PhMe (%)
H	100	73	55	<i>p</i> -Bu ^t ...	~100	75	32
<i>p</i> -Ph ...	88	71	—	<i>p</i> -Cl	73	61	39
<i>p</i> -Me ...	98	71	48	<i>p</i> -OMe *	87	—	48
<i>m</i> -Me ...	85	73	37				

* From this ether the products isolated were toluene (48%), *p*-methoxytoluene (18%), and 4 : 4'-dimethoxydibenzyl corresponding to a further yield (25%) of *p*-methoxytoluene (total 43%).

in every other case, it seems probable that the quantity of toluene formed was actually somewhat more than 48%, and so this ether was cleaved in the same direction as the other substituted ethers. Nevertheless, the directive effect of the *p*-methoxy-group appears to be the least decisive of all the substituents studied.

The conclusion is therefore reached that, of the substituents investigated, all influence the cleavage in the same manner, and hence it follows, if the above mechanism of cleavage be accepted, that all these substituents stabilise the benzyl radical with respect to hydrogen. It is noted that these are substituents capable of either (a) supplying electrons (alkyl groups) or (b) supplying and withdrawing electrons (Ph, Cl, OMe), operating by a purely inductive mechanism in some cases, and by a combination of inductive and mesomeric mechanisms in others. (A third type of substituents, that of a purely electron-withdrawing nature such as the nitro-group, cannot be studied by this method.²) In ionic reactions their diverse effects on the course and rate of reactions are well known, and this apparent lack of specificity when applied to homolytic reactions is reminiscent of the influence they exert on the benzene ring towards substitution by free radicals, recently investigated mainly by Hey and his co-workers.²⁰ In contrast to conclusions reached with regard to the aryloxy-radicals therefore, our findings so far concerning the benzyl radicals do not appear to corroborate Ingold's early theory.⁴ However, as further study is in progress, a fuller discussion is deferred.

The authors are much indebted to Professor C. K. Ingold, F.R.S., for a helpful discussion.

UNIVERSITY OF MALAYA, SINGAPORE.

[Received, May 6th, 1957.]

²⁰ Hey, Pengilly, and Williams, *J.*, 1956, 1463 (and earlier papers).