# 647. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part VI.*[1] *The Cleavage of Substituted Dibenzyl Ethers by Grignard Reagents in the Presence of Cobaltous Chloride.*

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From the cleavage of nine mono- and seven di-substituted dibenzyl ethers by the cobalt-catalysed Grignard reaction, the following scales of stabilising influence on free benzyl radicals have been established: *m*- and *p*-Me and -Cl, *p*-Bu$^t$, -OMe, and -Ph > H; *p*-Bu$^t$ > *p*-Me $\sim$ *p*-Cl > *p*-OMe > H; *m*- and *p*-Me > *m*-Cl $\geqslant$ *p*-OMe > H; and *p*-Me > *p*-Ph > H. The results are explained in terms of radical-stabilisation by homomesomerism, in conjunction with polar effects, due to the substituents.

THE cleavage of dibenzyl ether by Grignard reagents in the presence of cobaltous chloride proceeds *via* the radical $\cdot CHPh\cdot O\cdot CH_2Ph$ which disproportionates to benzaldehyde and free benzyl, and these in turn are reduced, respectively, to benzyl alcohol and toluene.[2] By studying the direction of fission of monosubstituted dibenzyl ethers, it was possible to compare the relative stabilising influences of the substituents, with respect to hydrogen, on the intermediate benzyl radical. We now report (*a*) further work on the monosubstituted ethers, and (*b*) the cleavage of disubstituted ethers $R\cdot C_6H_4\cdot CH_2\cdot O\cdot CH_2\cdot C_6H_4R'$ in which comparison is made of the stabilising effects of R and R′.

The method of cleavage previously reported[2] (isopropylmagnesium bromide and cobaltous chloride) was used. For the monosubstituted ethers, the technique of isolating, in a 50% or higher yield, one of the benzyl alcohols to determine the main course of fission was adopted. For the disubstituted ethers, however, a more quantitative approach was attempted wherever possible, involving estimation of the molar ratio of the two benzyl alcohols formed, each of the minor products being identified, but not all quantitatively isolated. In most cases it was possible, from the alcohols produced, to account for 80—90% of the ether which reacted.

## EXPERIMENTAL

*Synthesis of Ethers*.—The ethers (all new compounds) were prepared as previously described, and are listed in Table 1.

TABLE 1. *Synthesis of dibenzyl ethers,* $R\cdot C_6H_4\cdot CH_2\cdot O\cdot CH_2\cdot C_6H_4R'$.

| | | | $X\cdot C_6H_4\cdot CH_2Hal$ | | Yield | | | Found (%) | | | Reqd. (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | R | R′ | X | Hal | (%) | B. p./mm. | $n_D$ (temp.) | C | H | Formula | C | H |
| 1 | H | *m*-Cl | *m*-Cl | Br | 73 | 112—116°/0·2 | 1·5694(22°) | | | $C_{14}H_{13}OCl$ [a] | | |
| 2 | H | *o*-Cl | *o*-Cl | Br | 67 | 130°/0·4 | 1·5682(23·5°) | 72·7 | 5·6 | $C_{14}H_{13}OCl$ | 72·4 | 5·6 |
| 3 | H | *o*-Me | *o*-Me | Br | 81 | 117°/0·2 | 1·5588(24°) | 84·4 | 7·7 | $C_{15}H_{16}O$ | 84·9 | 7·6 |
| 4 | *p*-Me | *p*-Cl | *p*-Me | Br | 85 | m. p. 63—64° | — | 72·5 | 6·2 | $C_{15}H_{15}OCl$ | 73·0 | 6·1 |
| 5 | *p*-Me | *m*-Cl | *m*-Cl | Br | 85 | 110—112°/0·1 | 1·5632(23°) | 73·3 | 6·3 | $C_{15}H_{15}OCl$ [b] | 73·0 | 6·1 |
| 6 | *p*-Me | *p*-Bu$^t$ | *p*-Bu$^t$ | Br | 81 | 124—128°/0·2 | 1·5383(25°) | 85·0 | 8·8 | $C_{19}H_{24}O$ | 85·1 | 9·0 |
| 7 | *p*-Me | *p*-Ph | *p*-Ph | Cl | 86 | m. p. 62—63° | | 87·6 | 7·1 | $C_{21}H_{20}O$ | 87·5 | 6·9 |
| 8 | *m*-Me | *m*-Cl | *m*-Cl | Br | 91 | 124—127°/0·1 | 1·5637(24°) | 73·0 | 6·1 | $C_{15}H_{15}OCl$ | 73·0 | 6·1 |
| 9 | *p*-Cl | *p*-OMe | *p*-Cl | Cl | 87 | 164—166°/0·3 | 1·5692(23°) | | | $C_{15}H_{15}O_2Cl$ [c] | | |
| 10 | *m*-Cl | *p*-OMe | *m*-Cl | Br | 85 | 164—168°/0·3 | 1·5693(22°) | | | $C_{15}H_{15}O_2Cl$ [d] | | |

[a] Found: Cl, 15·3. Reqd.: Cl, 15·3%. [b] Found: Cl, 14·0. Reqd.: Cl, 14·4%. [c] Found: Cl, 13·0. Reqd.: Cl, 13·5%. [d] Found: OMe, 12·3. Reqd.: OMe, 11·8%.

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[1] Part V, Huang and Williams, *J.*, 1958, 2637.
[2] Huang and Si-Hoe, *J.*, 1957, 3988.

3-*Chlorodibenzyl Ether*.—(*a*) [3] The cleavage products from this ether (21·2 g., 0·086 mole) were fractionally distilled to give (i) a liquid, b. p. 54—60°/760 mm. (2 g.), probably 2 : 3-dimethylbutane; (ii) toluene, b. p. 109—111°/760 mm. (2·8 g.), $n_D^{22\cdot5}$ 1·4908, oxidised by alkaline potassium permanganate to benzoic acid, m. p. and mixed m. p. 121°; (iii) benzyl alcohol, b. p. 64—66/0·5 mm. (2·0 g., 0·0185 mole), $n_D^{23\cdot5}$ 1·5378 [3 : 5-dinitrobenzoate, m. p. and mixed m. p. 112°] (lit., $n_D^{20}$ 1·5395, m. p. 112°); (iv) 3-chlorobenzyl alcohol, b. p. 84— 85°/0·5 mm. (6·35 g., 0·045 mole, 52% yield), $n_D^{24}$ 1·5513 (Found: Cl, 24·5. Calc. for $C_7H_7OCl$: Cl, 24·9%), [3,5-dinitrobenzoate, needles (from light petroleum), m. p. 97—98° (Found: O, 28·7. $C_{14}H_9O_6N_2Cl$ requires O, 28·6%)].

(*b*) The cleavage products from the ether (24·0 g., 0·10 mole) on distillation gave the following fractions: (i) Toluene, b. p. 109—110°/761 mm., $n_D^{21}$ 1·4942 (4·35 g., 0·047 mole). (ii) A mixture of benzyl and 3-chlorobenzyl alcohol, b. p. 58—66°/0·5 mm., $n_D^{21.5}$ 1·5362 (3·30 g.), the chlorine content of which (Found: Cl, 7·9%) indicated that it consisted of 0·021 mole of benzyl alcohol and 0·0074 mole of 3-chlorobenzyl alcohol. The phenylurethane prepared from the mixture had m. p. 77—78°, alone or mixed with that prepared from benzyl alcohol. (iii) A mixture (8·57 g.), b. p. 70—74°/0·5 mm., 233—234°/760 mm., $n_D^{21\cdot5}$ 1·5515 (Found: Cl, 23·0%), containing 0·0061 and 0·055 mole, respectively, of the same alcohols. It gave the phenylurethane of 3-chlorobenzyl alcohol, needles (from light petroleum), m. p. 92—93° (Found: N, 5·25. $C_{14}H_{12}O_2NCl$ requires N, 5·4%). (iv) A small residue (bath up to 140°/0·5 mm.). The products therefore consisted of toluene (0·047 mole), benzyl alcohol (0·027 mole), and 3-chlorobenzyl alcohol (0·063 mole, 63%).

2-*Chlorodibenzyl Ether*.[3]—The fission products from this ether (34 g., 0·15 mole) were fractionated to give (i) toluene (4·2 g., 0·046 mole), (ii) benzyl alcohol (2·3 g., 0·029 mole), (iii) 2-chlorobenzyl alcohol, b. p. 80°/0·5 mm. (8·2 g., 0·058 mole), needles (from benzene), m. p. 73—74° (Mettler [4] reports m. p. 72°), and (iv) a residue (1·3 g.).

2-*Methyldibenzyl Ether*.[3]—This ether (30 g., 0·14 mole) on cleavage gave (i) toluene (4·75 g., 0·052 mole), (ii) *o*-xylene, with some toluene, b. p. 143—144°/760 mm., $n_D^{25}$ 1·4985 (2·6 g., 0·025 mole), (iii) benzyl alcohol (3·5 g., 0·032 mole), (iv) 2-methylbenzyl alcohol, b. p. 62—65°/0·2 mm. (9·3 g., 0·076 mole, 54%), m. p. 34—35° (lit., m. p. 36°) (Found: C, 78·8; H, 8·1. Calc. for $C_8H_{10}O$: C, 78·7; H, 8·2%) [*p*-nitrobenzoate, m. p. 99—100° (lit., m. p. 100—101°)], and (v) a residue (0·5 g.).

4-*Chloro-4′-methyldibenzyl Ether*.—This (19·5 g., 0·080 mole) yielded the following products:—(i) A mixture of toluene and *p*-xylene, b. p. 64—74°/100 mm., 116—120°/760 mm. (1·4 g.), $n_D^{22\cdot5}$ 1·4920. A portion (0·5 g.) was oxidised with alkaline potassium permanganate and the mixture of products extracted with chloroform to give benzoic acid, m. p. and mixed m. p. 122° (0·34 g.), and with ether to give terephthalic acid, m. p. >300° (sublimes) (0·09 g.) (dimethyl ester, m. p. and mixed m. p. 141°). (ii) *p*-Xylene, b. p. 74—82°/100 mm., 135—136°/760 mm. (1·4 g., 0·013 mole), $n_D^{23}$ 1·4932 (2,3,5-trinitro-derivative, m. p. and mixed m. p. 139°) (lit., b. p. 137°/760 mm., $n_D^{21}$ 1·5004). (iii) 4-*Methylbenzyl alcohol*, b. p. 70—75°/0·3 mm. (1·63 g., 0·013 mole), m. p. and mixed m. p. 54—55° (from light petroleum) (lit.,[5] m. p. 57—58°). To ascertain the absence of benzyl alcohol the mother-liquors from the above recrystallisations were concentrated and the residue was treated with phenyl isocyanate, giving a crude urethane (1·55 g.), recrystallisation of which from ligroin gave two crops (1·3 g.) of the phenylurethane of 4-methylbenzyl alcohol, m. p. and mixed m. p. 74—76° (mixed m. p. with benzylphenylurethane, 55—58°). (iv) A mixture of 4-methyl- and 4-chloro-benzyl alcohol, b. p. 75—82°/0·3 mm. (3·97 g.), which was redistilled (see below). (v) 4-Chlorobenzyl alcohol, b. p. 84—86°/0·3 mm., needles (from cyclohexane), m. p. and mixed m. p. 71—72° (1·47 g., 0·010 mole). (vi) Unchanged ether (4·65 g.). The cyclohexane mother-liquor from fraction (v) was concentrated, combined with fraction (iv), and redistilled, giving (*a*) material, b. p. 68—70°/0·3 mm. (0·15 g.), probably mainly 4-methylbenzyl alcohol; (*b*) a mixture, b. p. 70—74°/0·3 mm. (2·2 g.) (Found: Cl, 8·6%) of 4-methyl- (1·44 g.), and 4-chloro-benzyl alcohol (0·76 g.); (*c*) a mixture, b. p. 78—82°/0·3 mm. (1·2 g.) (Found: Cl, 20·7%) of the same alcohols (0·20 and 0·99 g., respectively); and (*d*) a residue of 4-chlorobenzyl alcohol (*ca.* 0·45 g.). Thus the main products from the ether which reacted (14·8 g., 0·060 mole) were 4-methyl- (3·4 g., 0·028 mole) and 4-chlorobenzyl alcohol (3·7 g., 0·026 mole).

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[3] We thank Miss S. Si-Hoe for collaboration in this experiment.

[4] Mettler, *Ber.*, 1905, **38**, 1750.

[5] Mozingo and Folkers, *J. Amer. Chem. Soc.*, 1948, **70**, 230.

3-*Chloro-4′-methyldibenzyl Ether*.—This ether (25 g., 0·10 mole) gave products which were fractionated as follows: (i) Material, b. p. 40°/100 mm. (0·6 g.), mainly 2,3-dimethylbutane, b. p. 50—60°/760 mm., and traces of toluene, b. p. 110°/760 mm., $n_D^{23}$ 1·4905. (ii) A mixture of toluene and *p*-xylene, b. p. 80°/100 mm., 116—118°/761 mm. (1·5 g.), $n_D^{24}$ 1·4850, a portion (0·50 g.) of which on oxidation with alkaline potassium permanganate yielded benzoic acid (0·29 g.), and terephthalic acid (0·10 g.) (identified as the dimethyl ester). (iii) *p*-Xylene, b. p. 50—60°/30 mm. (1·5 g.), which was redistilled, (b. p. 130—136°/760 mm., $n_D^{26}$ 1·4918; 1·0 g.) (2,3,5-trinitro-derivative, m. p. and mixed m. p. 139°). (iv) Material, b. p. 72—76°/1 mm., 218°/760 mm., $n_D^{27}$ 1·5278 (1·69 g.), whose b. p. and chlorine content (Found: Cl, 2·2, 1·9%) indicated that it was a mixture of 4-chloro- (0·14 g.) and 4-methyl-benzyl alcohol (1·55 g.). It gave the phenylurethane of the latter alcohol (m. p. and mixed m. p. 79—80°). (v) A mixture, b. p. 76—80°/1 mm., m. p. 51—54° (3·08 g.) (Found: Cl, 3·4; 3·4%), of 4-chloro- (0·42 g.) and 4-methyl-benzyl alcohol (2·66 g.). It gave the phenylurethane of the latter alcohol. (vi) A mixture, b. p. 83—86°/1 mm., $n_D^{27}$ 1·5416 (3·44 g.) (Found: Cl, 13·9, 13·9%), of 3-chloro- (1·92 g.) and 4-methyl-benzyl alcohol (1·52 g.), a portion (0·52 g.) of which with alkaline potassium permanganate yielded *m*-chlorobenzoic acid, m. p. and mixed m. p. 157—158° (0·53 g.), and terephthalic acid (0·15 g.) identified as previously. The mixture gave a phenylurethane which after five recrystallisations from ligroin had m. p. 92—93°, alone or mixed with that prepared from 3-chlorobenzyl alcohol. (vii) Unchanged ether, b. p. 114—116°/0·1 mm. (7·84 g., 0·032 mole). The main products from the ether cleaved (0·070 mole) are thus *p*-xylene (1·5 g., 0·013 mole) and 4-methyl- (5·73 g., 0·047 mole) and 3-chloro-benzyl alcohol (2·50 g., 0·017 mole).

4-*Methyl-4′-t-butyldibenzyl Ether*.—This ether (30 g., 0·11 mole) gave the following fission products: (i) *p*-Xylene, b. p. 72—74/45 mm., 138—139°/760 mm., $n_D^{26·5}$ 1·4920 (6·25 g., 0·059 mole) (2,3,5-trinitro derivative, m. p. and mixed m. p. 139—140°; and oxidised to terephthalic acid). (ii) *p*-t-Butyltoluene, mixed with some *p*-xylene, b. p. 178°/760 mm., $n_D^{24·5}$ 1·4889 (1·55 g.), a portion (0·52 g.) of which gave *p*-t-butylbenzoic acid, m. p. and mixed m. p. 164° (0·29 g.), and terephthalic acid (0·12 g.). (iii) Material, b. p. 92—96°/1 mm., 248°/759 mm. (5·10 g.), $n_D^{27}$ 1·5145, consisting mainly of 4-t-butylbenzyl alcohol. A sample (0·55 g.) was oxidised to *p*-t-butylbenzoic (0·47 g.) and terephthalic acid (0·016 g.). (iv) 4-t-Butylbenzyl alcohol, b. p. 96—100°/1 mm., 254°/760 mm. (7·85 g., 0·048 mole), $n_D^{27}$ 1·5150, a portion (0·53 g.) of which afforded *p*-t-butylbenzoic acid (0·49 g.) only. The 3,5-dinitrobenzoate, needles (from ligroin), melted at 162° (Found: C, 60·4; H, 5·0. $C_{18}H_{18}O_6N_2$ requires C, 60·3; H, 5·0%). (v) Uncleaved ether (5·6 g., 0·021 mole). The main cleavage products were thus *p*-xylene (6·25 g., 0·059 mole) and 4-t-butylbenzyl alcohol (12·2 g., 0·074 mole).

3-*Chloro-3′-methyldibenzyl Ether*.—Fractionation of the cleavage products from this ether (25 g., 0·10 mole) gave the following: (i) *m*-Xylene mixed with some toluene, b. p. 124—130°/760 mm., $n_D^{25}$ 1·4920 (1·80 g.). A sample (0·50 g.) yielded benzoic (0·063 g.) and isophthalic acid (0·42 g.) (dimethyl ester, m. p. and mixed m. p. 64—65°). (ii) *m*-Xylene, b. p. 139—140°/760 mm., $n_D^{25}$ 1·4930 (1·20 g.) (2,4,6-trinitro-derivative, m. p. and mixed m. p. 182—183°). (iii) A mixture, b. p. 76—80°/1 mm., 215°/761 mm., $n_D^{23}$ 1·5339 (Found: Cl, 3·1; 3·3%), of 3-methyl- (2·53 g.) and 3-chloro-benzyl alcohol (0·37 g.), a portion of which (0·53 g.) gave isophthalic acid (0·53 g.), identified as previously. Another portion of the mixture, with 3,5-dinitrobenzoyl chloride at 100° (10 min.), yielded 3-*methylbenzyl* 3,5-*dinitrobenzoate*, needles (from ligroin), m. p. 108—109° (Found: N, 8·8. $C_{15}H_{12}O_6N_2$ requires N, 8·9%). (iv) A mixture, b. p. 80—83°/1 mm., 222°/761 mm., $n_D^{23}$ 1·5383 (Found: Cl, 7·8, 7·9%), of 3-chloro- (1·0 g.) and 3-methyl-benzyl alcohol (2·15 g.). Oxidation of this (0·61 g.) produced *m*-chlorobenzoic (0·16 g.), m. p. and mixed m. p. 157—158°, and isophthalic acid (0·58 g.), separated by extraction with benzene, in which only the former acid is soluble. (v) Material, b. p. 84—86°/1 mm., 237°/760 mm., $n_D^{23}$ 1·5447 (Found: Cl, 17·6, 17·7%), consisting of the same alcohols (1·80 and 0·72 g., respectively). Oxidation again gave a mixture of *m*-chlorobenzoic and isophthalic acid. Treatment with phenyl isocyanate and recrystallisation of the product gave the phenylurethane of 3-chlorobenzyl alcohol. (vi) Unchanged ether (6·13 g.). The chief products are thus 3-methyl- (5·40 g., 0·044 mole) and 3-chloro-benzyl alcohol (3·17 g., 0·022 mole).

4-*Chloro-4′-methoxydibenzyl Ether*.—Cleavage of this substance (30·0 g., 0·11 mole) gave the following: (i) Toluene (2·0 g.). (ii) *p*-Methoxytoluene, b. p. 62—66°/35 mm., 174—175°/760 mm., $n_D^{22·5}$ 1·5100 (5·68 g., 0·046 mole) (lit.,[6] b. p. 176°, $n_D^{20}$ 1·512), oxidised by alkaline

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[6] Huntress and Mulliken, " Identification of Pure Organic Compounds," 1946, Wiley and Sons, New York, p. 532.

potassium permanganate to *p*-anisic acid, m. p. and mixed m. p. 182—183°. (iii) 4-Chlorobenzyl alcohol, b. p. 92—97°/1 mm. (5·17 g., 0·036 mole), needles (from cyclohexane), m. p. 71—72°, undepressed by admixture with a sample prepared from 4-chlorobenzyl chloride by hydrolysis. (iv) Material, b. p. 160—164°/1 mm. (4·23 g.), which on addition of a few drops of ethanol deposited 4,4′-dimethoxybibenzyl (1·0 g., 0·004 mole), needles, m. p. 125—127° (Found: C, 79·5; H, 7·4. Calc. for $C_{16}H_{18}O_2$: C, 79·3; H, 7·4%). The supernatant liquid was mostly unchanged ether, b. p. 164°/1 mm., $n_D^{22}$ 1·5695 (3·23 g., 0·012 mole). (v) An undistillable residue (2·6 g.). The principal products were thus toluene (0·022 mole), *p*-methoxytoluene (0·046 mole), 4-chlorobenzyl alcohol (0·036 mole) and 4,4′-dimethoxybibenzyl (0·004 mole).

3-*Chloro-4′-methoxydibenzyl Ether*.—The following fission products were obtained (from 30 g., 0·11 mole, of the ether): (i) 2,3-Dimethylbutane (0·3 g.); (ii) toluene (1·35 g., 0·015 mole); (iii) material, b. p. 92—94°/40 mm. (4·48 g.), $n_D^{24}$ 1·5076 (further fractionated as described below), a sample of which (0·50 g.) gave *p*-anisic acid (0·47 g.); (iv) 3-chlorobenzyl alcohol, b. p. 76—78°/0·5 mm., 237°/763 mm. (1·43 g., 0·010 mole), $n_D^{24\cdot5}$ 1·5445 (phenylurethane, m. p. and mixed m. p. 92—93°); (v) uncleaved ether (12·4 g., 0·047 mole); and (vi) a dark residue (4·8 g.) (bath up to 220°). Fraction (iii) above was redistilled, giving (*a*) material, b. p. 172—174°/760 mm. (0·70 g.), whose chlorine content (Found: Cl, 1·80%) showed it to be mostly *p*-methoxytoluene (0·65 g.), and (*b*) *p*-methoxytoluene, b. p. 175—176°/760 mm., $n_D^{24}$ 1·5076 (3·7 g.) (lit., *m*-chlorotoluene, b. p. 162°; *p*-methoxytoluene, b. p. 175—176°). The main products isolated were thus *p*-methoxytoluene (0·036 mole) and 3-chlorobenzyl alcohol (0·010 mole). Ether cleaved was 0·067 mole.

4-*Methyl-4′-phenyldibenzyl Ether*.—The fission products from this ether (35 g., 0·12 mole) on distillation gave the following: (i) *p*-Xylene, b. p. 60°/75 mm. (2·3 g.), b. p. 138—140°/761 mm., $n_D^{23}$ 1·4921, identified as previously. (ii) A mixture, b. p. 62—67°/0·1 mm. (7·65 g.), of 4-methylbenzyl alcohol and 4-methylbiphenyl whose oxygen content (Found: O, 9·15; 9·14%) showed it to consist of 5·33 g. of the former and 2·32 g. of the latter. It gave with phenyl isocyanate the phenylurethane of 4-methylbenzyl alcohol, m. p. and mixed m. p. 79—80°, and, on oxidation, 0·62 g. gave terephthalic (0·70 g.), and *p*-phenylbenzoic acid, m. p. 225—227° (0·09 g.) (lit., m. p. 228°) (Found: C, 78·6; H, 5·2. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·05%). (iii) Material, b. p. 78—82°/0·1 mm. (5·8 g.) (Found: O, 1·89; 1·72%), consisting of 4-methylbenzyl alcohol (0·80 g.) and 4-methylbiphenyl (5·0 g.), a portion of which (0·61 g.) on oxidation yielded *p*-phenylbenzoic (0·48 g.) and terephthalic acid (0·23 g.). When recrystallised from methanol, the 4-methylbiphenyl had m. p. 48—48·5° (lit., m. p. 49—50°). (iv) 4-Phenylbenzyl alcohol, b. p. 120—126°/0·1 mm. (6·30 g.), which crystallised from benzene–cyclohexane in plates, m. p. and mixed m. p. 100—100·5° (α-naphthylurethane, m. p. and mixed m. p. 125—126°) (unchanged ether has b. p. ~178°/0·07 mm., m. p. 62—63°). (v). A residue (11·5 g.) which percolated in benzene–light petroleum (1 : 4) through alumina, giving unchanged ether, m. p. 62—63° (7·9 g.). The main cleavage products from the ether (27·1 g., 0·094 mole) were thus 4-methyl- (6·14 g., 0·050 mole) and 4-phenyl-benzyl alcohol (6·30 g., 0·034 mole).

## DISCUSSION

The cleavage mechanism proposed by Huang and Si-Hoe,[2] in which free alkyl radicals or hydrogen atoms are considered to be the reacting entities, has been confirmed by Norman and Waters,[7] who unambiguously demonstrated the existence of free radicals in the catalysed Grignard reaction and showed that such radicals dehydrogenated diethyl ether to the radical $CHMe{\cdot}EOt$. More recently, the radical $\cdot CHPh{\cdot}O{\cdot}CH_2Ph$ has been prepared from dibenzyl ether by the action of t-butoxy-radicals, and found to disproportionate to benzaldehyde and free benzyl.[8] If this mechanism is accepted, the fission of the dibenzyl ether $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_4R'$ to give a 50% or higher yield of the benzyl alcohol $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ or of the toluene $R'{\cdot}C_6H_4Me$ would indicate that scission proceeds *via* the radical $R{\cdot}C_6H_4{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2{\cdot}C_6H_4R'$, and, since reaction takes the course involving the more stable radical-intermediate (steric factors being absent), it follows

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[7] Norman and Waters, *J.*, 1957, 950.

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

that, in stabilising power on the intermediate benzyl radical, R is superior to R′, or *vice versa*.

Among the monosubstituted ethers (See Table 2, in which for completeness the results from Part III[2] have been included), 2-chlorodibenzyl ether gave inconclusive results, while the 2-methyl homologue was split in the same direction as the 4-isomer. Of greater significance is the finding that the 3-chloro-atom stabilises the benzyl radical more than hydrogen does. This leads to the conclusion that, except for the *ortho*-substituents in which steric effects might be of consequence, all the substituents studied, despite their divergent electronic effects, stabilise benzyl radicals with respect to hydrogen.

TABLE 2. *Cleavage of monosubstituted dibenzyl ethers,* $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph$.

| R | Cleavage (%) | Products | |
|---|---|---|---|
| | | $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ (%) | PhMe (%) |
| *o*-Me | 100 | 54 | 37 |
| *m*-Me | 85 | 73 | 37 |
| *p*-Me | 98 | 71 | 48 |
| *p*-Bu$^{t}$ | 100 | 75 | 32 |
| *p*-Ph | 88 | 71 | — |
| *o*-Cl | 83 | 46 | 37 |
| *m*-Cl | 100 | 52 | 35 |
| „ | 100 | 63 * | 47 |
| *p*-Cl | 73 | 61 | 39 |
| *p*-OMe | 87 | — | 48 |

* Estimated by chlorine analyses of alcohol fractions (as for disubstituted ethers). Benzyl alcohol formed = 27%.

TABLE 3. *Cleavage of disubstituted dibenzyl ethers* $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_4R'$.

| | R | R′ | Ether reacting (%) | Products | | Inference (*re* stabilising influence) |
|---|---|---|---|---|---|---|
| | | | | $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ (%) | $R'{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ (%) | |
| 1 | *p*-Me | *p*-Cl | 76 | 47 | 43 | *p*-Me $\sim$ *p*-Cl |
| 2 | *p*-Me | *m*-Cl | 69 | 68 | 25 | *p*-Me $>$ *m*-Cl |
| 3 | *p*-Me | *p*-Bu$^{t}$ | 80 | 1 | 79 | *p*-Bu$^{t}$ $>$ *p*-Me |
| 4 | *p*-Me | *p*-Ph | 78 | 54 | 36 | *p*-Me $>$ *p*-Ph |
| 5 | *m*-Me | *m*-Cl | 76 | 57 | 29 | *m*-Me $>$ *m*-Cl |
| 6 | *p*-Cl | *p*-OMe | 89 | 36 | Traces * | *p*-Cl $>$ *p*-OMe |
| 7 | *m*-Cl | *p*-OMe | 59 | 15 | Traces † | *m*-Cl $\geqslant$ *p*-OMe |

* *p*-Methoxytoluene isolated in 55% yield. † *p*-Methoxytoluene isolated in 50% yield.

The results for the disubstituted ethers (see Table 3) allow a comparison to be made among the substituents themselves. The following scales of relative stabilising capacities can be set up: *p*-Bu$^{t}$ $>$ *p*-Me $\sim$ *p*-Cl $>$ *p*-OMe $>$ H; *m*- and *p*-Me $>$ *m*-Cl $\geqslant$ *p*-OMe $>$ H; and *p*-Me $>$ *p*-Ph $>$ H. The high stabilising capacities of the alkyl groups are evident from all three scales, while the relation *m*-Cl $\geqslant$ *p*-OMe confirms the result from 3-chlorodibenzyl ether.

The uniformly greater stabilising influence, compared with hydrogen, of substituents of diverse electronic nature has been encountered in the substituted triphenylmethyls, which can be considered as substituted benzyl radicals, as measured by the degree of dissociation in solution of the corresponding hexa-arylethanes. This has been extensively investigated by Bowden and his co-workers[9] using the cryscopic technique, and by Marvel *et al.*,[10] who employ the magnetic susceptibility method. Unfortunately serious discrepancies exist

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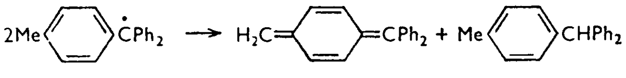
[9] (*a*) Bowden and Thomas, *J.*, 1940, 1242; Bowden and Clarke, *J.*, 1940, 883; (*b*) Bowden, *J.*, 1957, 4235; (*c*) Beynon and Bowden, *J.*, 1957, 4257; and other papers in the series.

[10] (*a*) Marvel, Riegel, and Mueller, *J. Amer. Chem. Soc.*, 1939, **61**, 2769; Marvel, Mueller, Himel, and Kaplan, *ibid.*, p. 2771; Marvel, Kaplan, and Himel, *ibid.*, 1941, **63**, 1892; (*b*) Marvel, Dietz, and Himel, *J. Org. Chem.*, 1942, **7**, 392; (*c*) Marvel, Whitson, and Johnston, *J. Amer. Chem. Soc.*, 1944, **66**, 415; (*d*) Marvel, Mueller, and Ginsberg, *ibid.*, 1939, **61**, 2008.

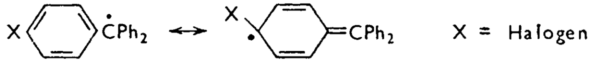
between results obtained by the two schools, although the validity of the magnetic method has recently been questioned.[9b,9c,11] Nevertheless, from both approaches the concordant conclusion emerges that, of the substituents studied, which included certain *m*- and *p*-alkyl, halogen, methoxy, and phenyl groups, all stabilise the resulting triphenylmethyl radical with respect to hydrogen.

Substituents whose effects could not satisfactorily be evaluated from dissociation of the hexa-arylethanes are the *p*-methyl group [9a,10a] and the *p*-halogen-atom.[9c,10b] With the former, the radical (I) is in part destroyed by intermolecular disproportionation:



(I)

while the latter is to some extent reduced by " molecular " silver, an effect attributed by Beynon and Bowden [9c] to the partially aliphatic character of the halogen atom due to participation by canonical structures such as (II). Side reactions of this nature (namely, intermolecular disproportionation or reduction [12] by the cobalt chloride–Grignard reagent) could occur with radicals derived from the dibenzyl ethers containing 4-methyl and 4-chloro-substituents, and would introduce moderate errors in the analysis of the cleavage products, especially where 4-chlorobenzyl alcohol is produced. However, that these side-reactions, if they took place, did so only to a small extent is evident from the following observations. (*a*) In the cleavage of 4-methyl- and 4-chloro-dibenzyl ether, good yields of the substituted benzyl alcohols were obtained. (*b*) With 3-chloro-4′-methyl- and 4-chloro-4′-methyl-dibenzyl ether, no less than 93 and 90%, respectively, of the ethers which reacted were accounted for as 4-methyl- and chloro-benzyl alcohol. (*c*) In the alcoholic fraction of the cleavage products of the last-named ether, a search for benzyl alcohol showed that none was present. It is concluded that the radicals formed from the dibenzyl ethers undergo intramolecular disproportionation into an aldehyde and a free benzyl radical relatively rapidly, before reduction by the Grignard reagent–cobaltous chloride mixture, or intermolecular disproportionation with a similar radical, can occur to any considerable extent. On the other hand, reduction of chlorine was quite appreciable in the 4-chlorobenzyl radicals, as shown, for instance, by the isolation of toluene from 4-chloro-4′-methyldibenzyl ether. This is not surprising considering the relatively long life of radicals of this type.



(II)

The greater stabilising capacity on benzyl radicals of all the substituents studied, compared with hydrogen, can be explained in terms of increased delocalisation of the unpaired electron by " homo-mesomerism " [13] due to the presence of the substituents. Thus, for the radicals obtained from 4-chloro-, 4-methoxy-, and 4-phenyl-dibenzyl ether, it would be expected that resonance hybrids such as (III), (IV), and (V), respectively, contribute to radical stability, while for the 4-methyl homologue, hyperconjugation would result in canonical structures such as (VI). For the 4-t-butyl group a hyperconjugative-like effect, analogous to that proposed by Brown *et al.*[14] in the solvolysis of αα-dimethylbenzyl chloride, could conceivably be invoked, resulting in resonance forms such as (VII) for the radical. However, the insufficiency of homo-mesomerism alone to account for

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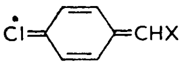
[11] Selwood and Dobres, *J. Amer. Chem. Soc.*, 1950, **72**, 3860.

[12] Cf. Huang, *J.*, 1954, 3084.

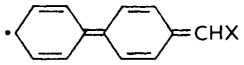
[13] See Remick, " Electronic Interpretations of Organic Chemistry," Chapman and Hall, London, 2nd edn., 1949, p. 62.

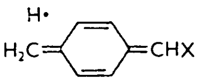
[14] Brown, Brady, Grayson, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

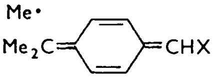
all the observed results is soon apparent. Thus the stabilising influence of the 3-methyl and the 3-chloro-substituent remains unexplained, while the contrasting electronic effects of such groups as 4-t-butyl and 3-chloro playing no part in determining radical-stability, seems difficult to understand. Moreover, the strikingly high stabilising power of the alkyl groups would have to be attributed entirely to hyperconjugation. This effect, if appreciable, is known to be small.

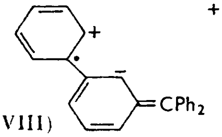

(III)

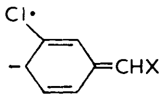

(IV)

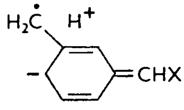

(V)


(VI)


(VII)


(VIII)


(IX)


(X)

X = O·CH$_2$Ph

It appears clear that, in conjunction with the homo-mesomeric mechanism, polar effects must also operate in some measure to control radical-stability. For the *m*-phenyl group in the substituted triphenylmethyls,[10d] it has been suggested [15] that stabilisation is due to participation of dipolar-radicals such as (VIII). This could be envisaged for the radicals derived from 3-chloro- and 3-methyl-dibenzyl ether, resulting in contributions from radical-ions such as (IX) and (X). Thus the effects of the 3-chloro and the 3-methyl group could be rationalised in terms of a homo-mesomeric process dependent on the operation of a polar (mesomeric) mechanism. However, to explain the results for the substituents examined it appears to us that a more general effect, operating jointly with those above, has to be postulated, involving electronic interaction of the substituents with the radical centre (the α-carbon), relayed through both the inductive and the mesomeric mechanism. By this effect it is envisaged that electronegative substituents, such as 3- and 4-chloro, tend to withdraw the unpaired electron into the ring, thereby imparting to the radical some of the character of the benzylic cation, whereas with electron-repelling groups, such as 3- or 4-methyl or 4-t-butyl, the reverse occurs, the radical in this case acquiring the attributes of the benzylic anion. The resulting polar nature of the radical would then be expected to be conducive to radical-stabilisation (*a*) externally, by solvation with the solvent, and (*b*) internally, if the not unreasonable assumption is made that these resonance-stabilised ions are relatively more stable than the radical. The assumption that the benzyl cation is more stabilised than the corresponding radical finds experimental evidence from the electron impact measurements by Halpern,[16] who concludes that allyl and cumyl cations possess resonance energies an order of magnitude higher than the respective radicals, and derives theoretical support from the calculation by Muller and Mulliken [17] on the allyl ion and radical. That the benzyl anion is also relatively more stable than the radical, however, requires substantiation.

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[15] Lichtin and Glazer, *ibid.*, 1951, **73**, 5537.
[16] Halpern, *J. Chem. Phys.*, 1952, **20**, 744.
[17] Muller and Mulliken, *J. Amer. Chem. Soc.*, 1958, **80**, 3489.