

LXXXI.—*The Rearrangement of Phenyl Benzyl Ethers.*

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THE rearrangement of phenyl benzyl ether has been observed by van Alphen (*Rec. trav. chim.*, 1927, **46**, 804) and by Short (J., 1928, 528). The former obtained a small quantity of 4-hydroxydiphenylmethane by heating phenyl benzyl ether to 160° with 40% of anhydrous zinc chloride. Short heated phenyl benzyl ether with the catalyst until a visible reaction set in (225° with zinc chloride * alone, 180° with zinc chloride and a current of hydrogen chloride) and isolated phenol and 2- and 4-hydroxydiphenylmethane. Van Alphen holds that the reaction is intramolecular, but in view of the experimental results set out below we consider that the reaction, like the rearrangement of alkylaniline hydrochlorides (Beckmann and Correns, *Ber.*, 1922, **55**, 852; compare, however, Derrick, *J. Amer. Chem. Soc.*, 1924, **46**, 166; Hickinbottom, J., 1927, 64) and of the diacylanilines (Chapman, J., 1925, **127**, 2818), is intermolecular.

(i) 2:4-Dibenzylphenol is one of the main products of the rearrangement of phenyl benzyl ether under all the conditions tried.

(ii) Phenyl benzyl ether is attacked by hydrogen chloride at 100° with the formation of benzyl chloride and phenol, which are known to react to form 2- and 4-hydroxydiphenylmethane. Table I shows the products obtained from 100 g. of phenyl benzyl ether.

The necessity for a catalyst and the absence of dibenzyl in the products show that the benzyl does not migrate as a free radical.

(iii) When the rearrangement of phenyl benzyl ether is carried out in presence of anisole (1 mol.), more than half the benzyl becomes attached to the anisole nucleus (B, Table II). Appropriation by the anisole is probably favoured by the smaller initial concentration of the phenol, and competition experiments (A, Table II) in which benzyl chloride was heated with equivalent quantities of phenol and anisole bear this out.

* It is well known that zinc chloride, if it is at all damp, may contain free hydrogen chloride.

TABLE I.

	A.	B.	C.
Temperature	160°	100°	100°
Catalyst	ZnCl ₂ (40 g.)	ZnCl ₂ (2 g.); HCl	HCl
Duration (hours)	1	3	3
Phenol	23·8	13·4	25·0
Benzyl chloride	—	—	9·0
2-Hydroxydiphenylmethane	9·0	—	7·6
4-Hydroxydiphenylmethane ...	19·4	28·4	12·6
2 : 4-Dibenzylphenol	40·4	15·0	12·6
Resinous material	27·4 *	36·6	33·2 *

* By difference.

TABLE II.

Products (g.) from 0·4 g.-mol. quantities.	A.	B.
	Condensation.	Rearrangement.
Hydroxydiphenylmethanes	17·0	14·0
2 : 4-Dibenzylphenol	6·6	12·6
4-Methoxydiphenylmethane	21·7	28·5
2 : 4-Dibenzylanisole	1·9	3·4
Partition of benzyl chloride, PhOMe/PhOH	1·07	1·35

Condensation of quinol monomethyl ether with benzyl chloride gives a homogeneous product in which the benzyl is doubtless directed ortho by the hydroxyl. This is another illustration of the fact first established by Wibaut (*Rec. trav. chim.*, 1915, **34**, 241) that the velocity of substitution induced by the simultaneous presence of two substituents in the benzene nucleus may be wholly different from that induced by the substituents separately.

The identification of 2- and 4-hydroxydiphenylmethane was confirmed in all cases by the preparation of their *benzyl* ethers, which we have synthesised. A very small capacity for crystallisation appears to be characteristic of the dibenzylphenols and their derivatives. 2 : 4- and 2 : 6-*Dibenzylphenol*, which are strongly cryptophenolic, were prepared from benzyl chloride and the sodium derivative of 4- and 2-hydroxydiphenylmethane, respectively, in dry toluene. Claisen has shown (*Annalen*, 1925, **442**, 238) that phenols are benzylated in the ortho-position by this method, and potash fusion of the isomeride believed to be 2 : 4-dibenzylphenol now gives a small yield of 4-hydroxyisophthalic acid, which helps to confirm this. 2 : 4-Dibenzylphenol was identified in all cases by the preparation of its α -*naphthylurethane*.

EXPERIMENTAL.

Phenyl benzyl ether was obtained in 73% yield by a modification of the method due to Gomberg and Buchler (*J. Amer. Chem. Soc.*, 1920, **42**, 2066). A solution of phenol (140 g.; 1·5 mols.) in 600 c.c. of aqueous sodium hydroxide (60 g.; 1·5 mols.) was boiled gently for 1 hour with benzyl chloride (126 g.; 1 mol.). Unchanged

phenol was removed from an ethereal solution of the product by extraction with alkali. The solvent was removed from the dried solution, and the residue yielded pure phenyl benzyl ether (m. p. 39°) on recrystallisation from 95% alcohol.

2-Hydroxydiphenylmethane and 2:6-Dibenzylphenol.—Sodium phenoxide (from 94 g. of phenol) was condensed with benzyl chloride (126 g.) in dry toluene as described by Claisen (*Annalen*, 1925, **442**, 238). Phenol and 2-hydroxydiphenylmethane (m. p. 21°) were extracted from the product by means of alkali. The residue from the toluene solution was repeatedly fractionated at 10 mm. and yielded two main fractions: (1) 150—153°, (2) 237.5—238°. The first fraction solidified completely and after recrystallisation from alcohol melted at 38—39° and did not depress the m. p. of phenyl benzyl ether. The production of this ether is probably due to the presence of phenol, produced in the reaction $2\text{PhONa} + 2\text{CH}_2\text{PhCl} = (\text{CH}_2\text{Ph})_2\text{C}_6\text{H}_3\cdot\text{OH} + \text{PhOH} + 2\text{NaCl}$, which, as a dissociating solvent, promotes the formation of *O*-alkyl derivatives from sodium phenoxides and alkyl halides (Claisen, *loc. cit.*; Busch, *Ber.*, 1927, **60**, 2244). Fraction (2) consisted of a light yellow, viscous oil which could not be induced to solidify. Analysis showed it to be a dibenzylphenol (Found: C, 87.4; H, 6.6. $\text{C}_{20}\text{H}_{18}\text{O}$ requires C, 87.6; H, 6.6%) and the orientation of the benzyl groups is indicated by the method of preparation and by comparison with the 2:4-isomeride. The *benzyl ether* of 2:6-dibenzylphenol was prepared by the interaction of the phenol (3.4 g.), sodium (0.3 g.), and benzyl chloride (1.5 g.) in solution in 95% alcohol (110 c.c.) at 100°. It crystallised from ligroin-methyl alcohol in colourless plates, m. p. 65° (Found: C, 88.9; H, 7.2. $\text{C}_{27}\text{H}_{24}\text{O}$ requires C, 89.0; H, 6.6%). The α -*naphthylurethane* of 2:6-dibenzylphenol was obtained by heating a mixture of α -naphthylcarbimide (1.3 g.) with the phenol (2.2 g.) almost to the b. p. for 3 minutes. The oily product was extracted with hot ligroin and filtered from the di- α -naphthylcarbamide. The product softened slightly at 161° and melted at 165—166° (Found: N, 3.3. $\text{C}_{31}\text{H}_{25}\text{O}_2\text{N}$ requires N, 3.2%).

4-Hydroxydiphenylmethane.—The method of van Alphen (*Rec. trav. chim.*, 1927, **46**, 803) was found to give poor yields and was therefore modified. Phenol (110 g.; 1.2 mols.) was condensed with benzyl chloride (126.5 g.; 1 mol.) in presence of anhydrous zinc chloride (2 g.) in the following manner. A mixture of the phenol, zinc chloride, and half the benzyl chloride was warmed gently until reaction set in, the remainder of the benzyl chloride was added in two portions at intervals of 1 hour, and the mixture was finally heated to 100° to complete the reaction. The product was dissolved in ether, washed with a small quantity of sodium

carbonate solution, dried, and fractionated at 10 mm. through a jacketed Vigreux column. The following fractions were separated : (1) 70—180° (75 g.), (2) 180—190° (70 g.), (3) 254—256° (31 g.). Fraction (1) consisted mainly of phenol. Fraction (2) contained 2- and 4-hydroxydiphenylmethane. A sharp separation of these two substances could not be effected by making use of the different solubilities of the barium salts (Friedr. Bayer Patentanmeldung 53443, 1923), but they were easily separated by taking advantage of the fact that the ortho-compound separates completely as a heavy oil as soon as a hot solution of the mixture in ligroin is cooled slightly. The pure para-compound (62 g., m. p. 84°) was deposited by the mother-liquor on cooling. Fraction (3) proved to be 2:4-dibenzylphenol and was identified by conversion into the α -naphthylurethane, m. p. 143—144° (see below).

2- and 4-Benzyloxydiphenylmethane.—These benzyl ethers were prepared by heating the phenol (8 g.), benzyl chloride (5.5 g.), and a solution of sodium ethoxide (from 1 g. of sodium) in 95% alcohol (300 c.c.) for 3 hours at 100°. The product was poured into water, extracted with ether, dried, and freed from the solvents.

2-Benzyloxydiphenylmethane may be recrystallised from warm methyl alcohol and melts at 38° (Found : C, 87.5; H, 6.7. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%). *4-Benzyloxydiphenylmethane* crystallises from ethyl alcohol in glistening needles, m. p. 49.5° (Found : C, 87.6; H, 6.6%). These ethers are not hydrolysed by concentrated boiling hydrochloric acid or sodium hydroxide, but boiling hydriodic acid causes fission of the molecule with production of benzyl iodide.

2:4-Dibenzylphenol.—A solution of 4-hydroxydiphenylmethane (46 g.; 1 mol.) in dry toluene (200 c.c.) was added to sodium wire (5.8 g.; 0.8 mol.) immersed in 400 c.c. of toluene. The mixture was cautiously warmed, and a solution of benzyl chloride (31.7 g.; 1 mol.) in toluene (100 c.c.) added during 1 hour. The mixture was then slowly heated to the b. p. and boiled gently for 5 hours. The product was washed with water and sodium hydroxide solution, dried over calcium chloride, and freed from toluene. The residue was fractionated at 10 mm. and gave a pale yellow oil (25 g.; yield, 36%), b. p. 252—254° (Found : C, 87.3; H, 6.7. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%). The position of the benzyl groups was determined by fusion with potash. Dibenzylphenol (6 g.), potassium hydroxide (120 g.), and water (24 g.) were heated to 220°, and lead dioxide (22 g.) introduced during an hour. The product was lixiviated with water, filtered from litharge and resin, acidified, and extracted with ether. The solvent was removed and the residue distilled in a current of steam. The distillate contained benzoic acid (1.7 g., m. p. 122°). The residue was boiled with water and

passed through a hot filter to remove resinous material. The cream-coloured solid deposited by the filtrate on cooling was recrystallised from boiling water; the acid obtained (0.05 g.) melted at 308—309° and gave an intense cherry-red coloration with aqueous ferric chloride. The melting point of 4-hydroxyisophthalic acid is 310° (Graebe and Krafft, *Ber.*, 1906, **39**, 798).

The benzyl ether, benzoate and diphenylurethane of 2:4-dibenzylphenol could not be induced to crystallise, but the α -naphthylurethane formed light yellow crystals (from ligroin), m. p. 143—144° (Found: N, 3.2. $C_{31}H_{25}O_2N$ requires N, 3.2%).

Identification of 4-Methoxydiphenylmethane.—This compound, which melts at 20—21° (Späth, *Monatsh.*, 1913, **34**, 2007), is liquid at atmospheric temperature and, since it was encountered during our experiments, we developed the following methods for its identification. (1) The methoxy-compound (5 g.) was demethylated in the usual way by heating for 1 hour with 58% hydriodic acid (12 g.). The resulting 4-hydroxydiphenylmethane melted at 84° after crystallisation from petroleum spirit. (2) Contrary to the statement of Rennie (*J.*, 1882, **41**, 37, 227), the oxidation of 4-methoxydiphenylmethane with alkaline permanganate yields benzoic acid, and not 4-methoxybenzophenone, as main product. Oxidation with sodium dichromate and sulphuric acid also proved unsatisfactory and, after numerous trials, the following method, which gives a 56% yield of the desired product, was ultimately evolved.

4-Methoxydiphenylmethane (3 g.), dissolved in acetic acid (35 c.c.), was oxidised with chromic anhydride (7.9 g.) in the apparatus described by one of us (*J.*, 1928, 2630). The product, isolated in the usual manner, was recrystallised from light petroleum and melted at 61—62°, which is the m. p. of 4-methoxybenzophenone recorded in the literature.

Rearrangement of Phenyl Benzyl Ether.—(A) Phenyl benzyl ether (70 g.) and zinc chloride (28 g.) were heated at 160° for 1 hour. The product was poured into water (200 c.c.), and extracted with ether, and the solution dried. After the solvent had been removed, the residue was distilled at 10 mm. and the following fractions were collected: (1) 73—78° (16 g.), (2) 160—180° (22 g.), (3) 240—260° (27 g.). Fraction (1), most of which distilled at 75°, consisted of phenol (benzoate, m. p. 68°). Extraction of fraction (2) with alkali removed 2- and 4-hydroxydiphenylmethane and left phenyl benzyl ether (3 g., m. p. 39°). The mixture of hydroxydiphenylmethanes contained 6 g. of the *o*-compound (benzyl ether, m. p. 38°) and 13 g. of the *p*-compound (m. p. 84°). Fraction (3) consisted of 2:4-dibenzylphenol (α -naphthylurethane, m. p. 143—144°).

(B) Phenyl benzyl ether (60 g.) was heated at 100° for 3 hours with anhydrous zinc chloride (2 g.), a slow stream of dry hydrogen chloride being passed through the liquid, which was stirred mechanically. A rapid current of steam was passed through the mixture for a few minutes and phenol (8 g.) was recovered from the distillate. The residue, when treated as described under (A), yielded 4-hydroxydiphenylmethane (17 g., m. p. 84°), 2 : 4-dibenzylphenol (9 g.), and resinous material (22 g.).

(C) Phenyl benzyl ether (40 g.) was heated at 100° for 3 hours, a slow stream of dry hydrogen chloride being passed through the liquid, which was stirred mechanically. The product was diluted with water, neutralised with sodium bicarbonate, and extracted with ether. The solution was dried, freed from the solvent, and distilled. The following fractions were collected : (1) 82—84°/15 mm. (13.5 g.), (2) 180—184°/10 mm. (8 g.), (3) 220—240°/2 mm. (5 g.). Fraction (1) yielded to sodium hydroxide 10 g. of phenol and the residue was identified as benzyl chloride by oxidation to benzoic acid (m. p. 122°). Solution of fraction (2) in light petroleum resolved it into 2-hydroxydiphenylmethane (3 g.; benzyl ether, m. p. 38°) and 4-hydroxydiphenylmethane (5 g.; m. p. 84°). Fraction (3) consisted of 2 : 4-dibenzylphenol (α -naphthylurethane, m. p. 143—144°).

Condensation of Anisole and Phenol with Benzyl Chloride.—Anisole (43.2 g.; 1 mol.), phenol (37.7 g.; 1 mol.), and anhydrous zinc chloride (1 g.) were heated to 100° and a slow stream of dry hydrogen chloride was passed through the vigorously agitated liquid. Benzyl chloride (50.6 g.; 1 mol.) was introduced in small portions during 20 minutes, and heating was continued for a total period of 3 hours. The product was diluted with ether and extracted with moderately concentrated sodium hydroxide solution, to which it yielded phenol and the two hydroxydiphenylmethanes. The ether retained anisole, 4-hydroxydiphenylmethane, dibenzylanisole, and the cryptophenolic 2 : 4-dibenzylphenol. Each of these mixtures was systematically fractionated under diminished pressure. In this way, phenol (25 g.), 2-hydroxydiphenylmethane (5 g.), and 4-hydroxydiphenylmethane (12 g.) were separated from the alkali-soluble portion : they were identified as described in the previous sections. The alkali-insoluble mixture could easily be resolved into anisole (27 g.), 4-methoxydiphenylmethane (21.7 g.; b. p. 172—174°/10 mm.; identified by oxidation to 4-methoxybenzophenone, m. p. 61—62°), and a mixture (8.5 g.; b. p. 240—260°/10 mm.) of 2 : 4-dibenzylphenol and 2 : 4-dibenzylanisole. It was found impracticable to separate this mixture into its constituents by fractionation. A portion of it was demethylated with 58% hydriodic

acid and the product gave an excellent yield of the α -naphthylurethane (m. p. 143—144°) of 2 : 4-dibenzylphenol. This indicated the constitution of the mixture, and a quantitative determination of the methoxy-content showed the presence of 23% of dibenzylanisole.

Rearrangement of Phenyl Benzyl Ether in Presence of Anisole.—Phenyl benzyl ether (73.6 g.; 1 mol.) and anisole (43.2 g.; 1 mol.) were heated to 100°, anhydrous zinc chloride (1 g.) was added, and a slow stream of dry hydrogen chloride passed through the liquid. At the end of 3 hours the product was worked up by the method already described. The alkali-soluble portion consisted of phenol (24 g.) and 4-hydroxydiphenylmethane (14 g., m. p. 84°). The alkali-insoluble products contained anisole (23 g.), 4-methoxydiphenylmethane (28.5 g.; identified by oxidation to 4-methoxybenzophenone, m. p. 61—62°), and a mixture (16 g., b. p. 240—255°/10 mm.) of 2 : 4-dibenzylanisole and 2 : 4-dibenzylphenol. The product obtained by demethylating a portion of this mixture gave a high yield of the α -naphthylurethane (m. p. 143—144°) of 2 : 4-dibenzylphenol. A methoxy-determination showed that the mixture in question contained 21% of dibenzylanisole.

Quinol Monomethyl Ether and Benzyl Chloride.—Quinol monomethyl ether, m. p. 56° (Robinson and Smith, J., 1926, 393) (8 g.), mixed with benzyl chloride (9 g.) and anhydrous zinc chloride (1 g.), was warmed until reaction set in and finally maintained at 100° for 0.5 hour. The product was taken up in ether and extracted with alkali. The alkali-soluble products were distilled and the following fractions collected : (1) 120—165°/10 mm. (3 g.), (2) 190—240°/10 mm. (6 g.). A small quantity of high-boiling yellow oil was not distilled. Fraction (1) solidified on cooling and consisted of unchanged quinol monomethyl ether. The majority of fraction (2) distilled at 200°/10 mm. and solidified on cooling. It was recrystallised from ligroin until a constant m. p., viz., 77°, was attained (Found: C, 78.6; H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.5%). As the relative directive power of the hydroxy-group is superior to that of the methoxy-group, this product must be *2-hydroxy-4-methoxydiphenylmethane*. This result agrees with the observation (Irvine and Smith, J., 1927, 74) that quinol monomethyl ether gives a homogeneous monobromination product.

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