372. *Molecular Rearrangements. Part III.* The Thermal Rearrangement of Aryl Benzyl Ethers.*

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When purified benzyl phenyl ether is heated at about 250° for some days, it rearranges to give *o*- and *p*-benzylphenols and 2 : 4-dibenzylphenol, together with phenol, toluene, and 9-phenylxanthen.

o- and *p*-Tolyl, 2 : 4-dimethylphenyl, and 2 : 6-dimethylphenyl benzyl ethers similarly rearrange and also yield toluene and the corresponding xanthen.

The rearrangement is not proton-catalysed: it is essentially a migration of the benzyl group brought about by heating to a sufficiently high temperature.

Benzyl phenyl ether was reported by Powell and Adams [1] to change slowly on heating under reflux to toluene, phenol, and unidentified high-boiling material. Behagel and Freiensehner [2] found that by longer boiling some *p*-benzylphenol was formed as well as

* Part II, *J.*, 1958, 2982.

[1] Powell and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 656.
[2] Behagel and Freiensehner, *Ber.*, 1934, **67**, 1368.

phenol and some high-boiling products. The formation of benzylphenols occurred more readily if zinc were present. Other aryl benzyl ethers also rearrange under similar condition.

It appeared possible that these migrations are proton-catalysed as a result of hydrolysis of traces of benzyl chloride by moisture. If this were so, the action of zinc in accelerating the change can be explained simply and rationally in terms of known observation.[3] Support for this view is provided by the observation that benzyl chloride is often a persistent impurity in benzyl phenyl ether as ordinarily prepared.

A method of preparing benzyl phenyl ether very pure and free from traces of benzyl chloride has been developed. Using it we have established that it decomposes when heated at its boiling point: after about 20 hours toluene, phenol, and benzaldehyde are obtained in small yields together with some *p*-benzylphenol. More complete rearrangement is brought about by heating in sealed tubes for some days at 250°; *o*- and *p*-benzylphenols are formed together with phenol, toluene, 2 : 4-dibenzylphenol, and 9-phenylxanthen. The benzyl ethers of *o*- and *p*-cresol, of 2 : 4- and 2 : 6-dimethylphenol, and of *p*-chlorophenol similarly rearrange to form toluene, the phenol, and a substituted 9-phenylxanthen.

The production of toluene and 9-phenylxanthen distinguishes this rearrangement from that induced by proton catalysis or Lewis acids. There can be little doubt that this is a thermal isomerisation of the same type, although not necessarily the same mechanism as the Claisen rearrangement of allyl aryl ethers.

Experimental

Preparation of Aryl Benzyl Ethers.—All ethers were prepared by refluxing benzyl chloride with a slight excess (1·1 moles) of the appropriate phenol in acetone containing an excess of finely powdered potassium carbonate in suspension.

To ensure the absence of traces of benzyl chloride, the crude redistilled ether was heated under reflux with dry pyridine for some hours. The ether was recovered by dilution with water; the oil which separated was taken up in ether and freed from pyridine by repeated washing with dilute hydrochloric acid. After a final treatment with sodium hydroxide solution, the dried ethereal solution was distilled, and the whole process of purification repeated on the aryl benzyl ether until there was no detectable trace of chloride in the product.

Thermal Rearrangement of Aryl Benzyl Ethers.—Benzyl phenyl ether: (a) *Under reflux.* Benzyl phenyl ether (50 g., m. p. 42°) was boiled under reflux. The temperature of the boiling liquid fell from 270° to 250° during the first 3 hr. and remained thereat. The colour changed through pale yellow to dark brown as the heating continued. After 20 hours' heating the liquid was distilled, first at atmospheric pressure up to 200° and thereafter under reduced pressure. There were obtained (*a*) water (0·5 g.), (*b*) toluene [2·8 g. (2 : 4-dinitro-derivative, m. p. and mixed m. p. 72°)], (*c*) benzaldehyde [0·8 g. (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158°)], (*d*) phenol, m. p. 42° (5·5 g.), (*e*) benzyl phenyl ether, b. p. 130—150°/14 mm. (26·5 g.) (after crystallisation from alcohol this fraction melted at 42°), (*f*) *p*-benzylphenol (1·8 g.), m. p. 84° after crystallisation from alcohol, unchanged by admixture with an authentic sample. A tar (10 g.) remained which did not give recognisable components.

(b) *In sealed tubes.* Benzyl phenyl ether (70 g.) become thick and dark brown with a greenish fluorescence after it had been heated at 250° for 7 days in sealed tubes; it also had a pronounced phenolic odour.

The lower-boiling fractions (b. p. up to 200°) from the rearrangement product were separated into water (1·5 g.), toluene (10 g.), and phenol (2·6 g.). The higher-boiling material was separated into neutral (*A*) and phenolic (*B*) products by extraction with Claisen's solution [4] after dilution with ether and light petroleum.

From the neutral matter there was separated, by distillation, benzyl phenyl ether (10·2 g.) and a fraction of b. p. 220—240°/14 mm. (16·5 g.) which became semisolid on cooling. By trituration with alcohol and crystallisation from the same solvent the main constituent was

[3] (*a*) Von Alphen, *Rec. Trav. chim.*, 1927, **46**, 804; (*b*) Short, *J.*, 1928, 528; (*c*) Short and Stewart, *J.*, 1929, 558.

[4] Claisen, *Annalen*, 1925, **442**, 224, footnote.

obtained pure, m. p. 145° (Found: C, 87·9; H, 5·4. Calc. for $C_{19}H_{14}O$: C, 88·3; H, 5·4%). It dissolved in concentrated sulphuric acid with development of a yellow colour and it was identified as 9-phenylxanthen by comparison with an authentic specimen prepared from xanthone and phenylmagnesium bromide with subsequent reduction of the 9-phenylxanthhydrol by zinc and platinum chloride in aqueous acetic acid.[5]

The phenolic products of the rearrangement were separated by distillation into (*a*) phenol (1·1 g.), (*b*) crude *o*-benzylphenol, b. p. 170—180°/14 mm. (2·2 g.), (*c*) crude *p*-benzylphenol, b. p. 180—200°/14 mm. (5·0 g.), and (*d*) 2 : 4-dibenzylphenol, b. p. 260—270°/14 mm. (0·4 g.).

o-Benzylphenol was characterised by its phenylurethane, m. p. and mixed m. p. 117°; *p*-benzylphenol was obtained solid and after crystallisation had m. p. 84°, not depressed by admixture with an authentic specimen (Found: C, 87·6; H, 6·8. Calc. for $C_{13}H_{12}O$: C, 87·6; H, 6·6%); 2 : 4-dibenzylphenol after crystallisation had m. p. and mixed m. p. 48—49° (Found: 84·9; H, 6·6. Calc. for $C_{20}H_{18}O$: C, 84·8; H, 6·6%) (α-naphthylurethane, m. p. and mixed m. p. 114°).

Benzyl o-*tolyl ether.* This ether (b. p. 158°/14 mm.; Schorigin[6] gives b. p. 284° or 183°/24 mm.) does not rearrange readily on boiling under reflux. When it was heated in sealed tubes for 10 days at 250°, water (2·2 g.), toluene (18·5 g.), and *o*-cresol, m. p. 30° (31 g.), were obtained from 130 g. of ether.

The neutral components of the rearrangement product were unchanged ether (20 g.) and 4 : 5-*dimethyl*-9-*phenylxanthen* (20 g.), b. p. 240—260°/18 mm., m. p. 120° after crystallisation from alcohol (Found: C, 88·2; H, 6·4. $C_{21}H_{18}O$ requires C, 88·0; H, 6·3%).

The phenolic components were separated by careful fractionation into 2-benzyl-6-methylphenol, b. p. 137—140°/1 mm., m. p. and mixed m. p. 50·5° (Found: C, 84·7; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%) (4-bromo-derivative, m. p. and mixed m. p. 64°); 4-benzyl-2-methylphenol, b. p. 140—150°/0·8 mm., m. p. and mixed m. p. 49·5° (Found: C, 84·9; H, 7·0%) (benzoate, m. p. and mixed m. p. 55°), and an orange oil, b. p. 210°/0·8 mm. (Found: C, 87·3; H, 7·0. Calc. for $C_{21}H_{20}O$: C, 87·45; H, 7·0%). It is indifferent to bromine and is presumably 2 : 4-dibenzyl-6-methylphenol. The total weight of these phenols was 14·2 g. of which about 1/5 was the last and the remainder approximately equal weights of the benzyl-*o*-cresols.

For comparison 4-benzyl-2-methyl phenol[7] was prepared by adding aluminium chloride (65 g.) to *o*-cresol (100 g.) and benzyl alcohol (100 g.) in light petroleum (200 g.), the temperature being kept at 30—35°. Next morning evolution of hydrogen chloride had ceased; it was then decomposed and 4-benzyl-2-methylphenol isolated by distillation, b. p. 185°/13 mm., m. p. 49° (benzoate, m. p. 55°).

Preparation of 4 : 5-*Dimethyl*-9-*phenylxanthen.*—4 : 5-Dimethylxanthone, m. p. 170°, was prepared in relatively poor yield from 2-hydroxy-3-methylbenzoic acid by boiling it with acetic anhydride and then distilling.[8]

By reaction with phenylmagnesium bromide in ether, 4 : 5-dimethyl-9-phenylxanthhydrol was obtained, yellow prisms from light petroleum (b. p. 60—80°), m. p. 137°. It was reduced by zinc dust in acetic acid to which a few drops of platinic chloride had been added. There resulted 4 : 5-dimethyl-9-phenylxanthen (colourless needles from alcohol), m. p. 117—117·5°, not depressed by admixture with that isolated from the rearrangement product.

Thermal Rearrangement of Aryl Benzyl Ethers.—Benzyl p-*tolyl ether.* The purified ether (70 g., m. p. 40°; Claisen[9] gives m. p. 41°; Baw,[10] m. p. 40°), heated under reflux for 40 hr., gave water (0·6 g.), toluene (3·8 g.), *p*-cresol (11·5 g.), unchanged ether (25 g.), 2-benzyl-4-methylphenol (4·0 g.), 2 : 7-dimethyl-9-phenylxanthen (4·0 g.), and a tar (12 g.).

When the ether (90 g.) was heated in sealed tubes at 280° for 14 days, the following products were obtained: water (1·0 g.), toluene (16·6 g.), *p*-cresol (14 g.), 2-benzyl-4-methylphenol (10·5 g.), 2 : 7-dimethyl-9-phenylxanthen (23·5 g.), and a tar (10 g.).

2-Benzyl-4-methylphenol was identified by comparison with an authentic sample,[11] m. p. and mixed m. p. 36° (Found: C, 84·2; H, 7·1%), and by its phenylurethane, m. p. and mixed m. p. 146°.

[5] Ullman and Engi, *Ber.*, 1904, **37**, 2370.
[6] Schorigin, *Ber.*, 1925, **58**, 2032, footnote 14.
[7] Huston, *J. Amer. Chem. Soc.*, 1930, **52**, 4486.
[8] Schopff, *Ber.*, 1892, **25**, 3647.
[9] Claisen, *Annalen*, 1925, **442**, 242.
[10] Baw, *Quart. J. Indian Chem. Soc.*, 1926, **3**, 101.
[11] Elkobaisi and Hickinbottom, *J.*, 1958, 2431.

2 : 7-Dimethyl-9-phenylxanthen, m. p. 195° from alcohol (Found: C, 88·0; H, 6·5%), gives a yellow colour with concentrated sulphuric acid. It was identical with the product obtained by distilling 2 : 2′-dihydroxy-5 : 5′-dimethyltriphenylmethane.[12]

Benzyl 2 : 4-dimethylphenyl ether. This is a somewhat viscous faint yellow *liquid*, b. p. 180°/15 mm. (Found: C, 84·9; H, 7·5. $C_{15}H_{18}O$ requires C, 84·9; H, 7·6%). Heated in sealed tubes at 270° for 17 days, 70 g. of it gave water (1·3 g.), toluene (12·0 g.), 2 : 4-dimethylphenol (11·5 g.), 6-benzyl-2 : 4-dimethylphenol (18 g.), and 2 : 4 : 5 : 7-tetramethyl-9-phenylxanthen (12 g.).

6-Benzyl-2 : 4-dimethylphenol, m. p. 67° (Found: C, 84·6; H, 7·7. Calc. for $C_{15}H_{16}O$: C, 84·9; H, 7·6%) (phenylurethane, m. p. 138°), was identical (mixed m. p.) with a sample prepared in another way.[10]

2 : 4 : 5 : 7-*Tetramethyl-9-phenylxanthen*, colourless prisms, m. p. 108° (Found: C, 87·9; H, 7·1. $C_{23}H_{22}O$ requires C, 87·9; H, 7·1%), gives an orange-yellow colour with concentrated sulphuric acid.

Benzyl 2 : 6-dimethylphenyl ether.[13] This, b. p. 162°/14 mm. (Found: C, 84·8; H, 7·6%), was heated at 260° for 14 days. From 106 g. of ether there were obtained water (1·8 g.), toluene (21·4 g.), 2 : 6-dimethylphenol (20 g.), 4-benzyl-2 : 6-dimethylphenol (27 g.), and an unidentified product, b. p. 234—250°/14 mm. (18 g.).

4-Benzyl-2 : 6-dimethylphenol, b. p. 190—196°/14 mm., m. p. 66° (Found: C, 84·3; H, 7·8%) (phenylurethane, m. p. 153°), was identified by comparison with an authentic sample prepared by reaction of 2 : 6-dimethylphenol with benzyl alcohol and aluminium chloride in light petroleum at 30—35°. Two main products were isolated, 4-benzyl-2 : 6-dimethylphenol, b. p. 196°/14 mm., m. p. 66° not depressed by admixture with that isolated from the rearrangement (Found: C, 84·5; H, 7·7%), and its benzyl ether, m. p. 118°, needles from light petroleum.

Benzyl 4-chlorophenyl ether. By refluxing this ether (40 g.) for 12 hr. there were obtained water (0·3 g.), toluene (2·9 g.), *p*-chlorophenol (7·7 g.), 2-benzyl-4-chlorophenol (7·5 g.), and 2 : 7-dichloro-9-phenylxanthen (1·5 g.); a dense black tar (17 g.) remained.

The ether (60 g.), heated in sealed tubes for 9 days at 260°, gave toluene (2·1 g.), *p*-chlorophenol (14·1 g.), unchanged ether (0·7 g.), 2-benzyl-4-chlorophenol (12·6 g.), 2 : 7-dichloro-9-phenylxanthen (15·8 g.), and tar (15 g.).

2-Benzyl-4-chlorophenol, m. p. 53° (Found: C, 71·4; H, 4·95; Cl, 16·1. Calc. for $C_{13}H_{11}OCl$: C, 71·4; H, 5·0; Cl, 16·2%), is identical with that prepared in another way.

2 : 7-*Dichloro-9-phenylxanthen* had m. p. 195° (from acetic acid) (Found: C, 70·0; H, 3·4; Cl, 21·4. $C_{19}H_{12}OCl_2$ requires C, 69·7; H, 3·7; Cl, 21·7%).

Benzyl 4-chlorophenyl ether had b. p. 180—182°/mm., m. p. 71—72° (Baw [10] gives m. p. 71°) (Found: C, 71·2; H, 5·0; Cl, 16·6. Calc. for $C_{13}H_{11}OCl$: C, 71·4; H, 5·0; Cl, 16·2%).

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[12] Feuerstein and Lipp, *Ber.*, 1902, **35**, 3252.
[13] Curtin, *J. Amer. Chem. Soc.*, 1958, **80**, 1397.