

260. *Molecular Rearrangements. Part V.* The Course of the Thermal Rearrangement of Benzyl Phenyl Ether.*

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Thermal rearrangement of benzyl phenyl ether in a suitable solvent results in the transfer of the benzyl group, in part, to the solvent. In α - or β -naphthol the normal products of the rearrangement are accompanied by benzyl-naphthols and 9-phenylbenzoxanthenes. In quinoline 2- and 4-benzyl-quinoline are obtained together with 2-*o*-hydroxyphenylquinoline and the normal products of rearrangement of the ether. In isoquinoline the ether similarly gives benzyl- and hydroxyphenyl-isoquinolines.

It is concluded that this rearrangement depends primarily on homolysis into benzyl and phenoxy-radicals. The nature of the fission is inferred from the fact that benzyl and hydroxyphenyl groups substitute quinoline in the same positions. Intervention of free benzyl radicals is deduced because benzyl 2,4,6-trimethylphenyl ether, when heated alone or in quinoline, gives dibenzyl as one of the products. Diphenylmethyl phenyl ether also decomposes on being heated, forming tetraphenylethane, phenol, and some diphenylmethane.

It has been established¹ that aryl benzyl ethers rearrange at $\sim 270^\circ$ with the migration of the benzyl group from the oxygen to give *ortho*- and *para*-substituted phenols. This change is distinguished from that induced by acids or Lewis acids in that toluene and 9-phenylxanthenes are always present in the products. The work described in this paper was planned to obtain more information about the thermal change.

Behagel and Friensehner² reported that benzyl phenyl ether, heated with β -naphthol, gave 1-benzyl-2-naphthol, among other products; methyl 1-naphthyl ether was similarly benzylated in the nucleus. For reasons indicated earlier¹ it was considered necessary to repeat these observations. It has now been confirmed that benzyl phenyl ether and β -naphthol at $\sim 260^\circ$ give 1-benzyl-2-naphthol as well as the normal products of rearrangement of the ether: a mixture 9-phenyl-7,8-benzo- and -1,2,7,8-dibenz-oxanthen and 9-phenylxanthen was also obtained, showing that the essential character of the thermal rearrangement had not been modified by the presence of a phenol. Using

* Part IV, *J.*, 1960, 520.

¹ Part III, Elkobaisi and Hickinbottom, *J.*, 1959, 1873.

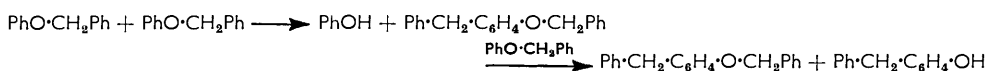
² Behagel and Friensehner, *Ber.*, 1934, **67**, 1368.

α -naphthol, instead of β -naphthol, led to 2- and 4-benzyl-1-naphthol, 9-phenyl-5,6-benzoxanthen, and the normal products of rearrangement.

Thermal rearrangement of benzyl phenyl ether in quinoline gives the normal products and substituted quinolines—2- and 4-benzylquinoline and 2-*o*-hydroxyphenylquinoline with a little 2-*p*-hydroxyphenylquinoline.

Similar substitution occurs when isoquinoline is the solvent. 1-Benzylisoquinoline is formed together with a hydroxyphenylisoquinoline which has not yet been definitively identified: its infrared spectrum provides evidence of bonding between the phenolic hydrogen and the nitrogen atom, so that it has an *o*-hydroxyphenyl group in the 1- or the 3-position. Attempts to synthesise compounds having these structures have not yet been successful.

From these observations it is a reasonable conclusion that the thermal rearrangement of benzyl phenyl ether is not an intramolecular change. The benzyl group must be considered to migrate by some other process. In general terms, two main routes are possible: (a) a bimolecular reaction with benzyl phenyl ether as a benzylating agent and represented by the scheme:



(b) fission of the bond between the benzyl and the phenoxy-group, followed by recombination of the benzyl group with the mesomeric oxyphenyl group.

Both schemes depend essentially on fission of the benzyl-oxygen bond. The nature of this rupture can be accurately and surely deduced from the substitution products formed in quinoline. Only two types of fission are possible, homolysis and heterolysis; for heterolysis, it is reasonable to assume that the benzyl and oxyphenyl groups would substitute quinoline at different positions in the nucleus since one of the groups must be electrophilic and the other nucleophilic. The fact that both the benzyl and oxyphenyl groups attack the same position is consistent only with the conclusion that both groups react as free radicals and that the fission is a homolysis.

It is possible to decide between a homolytic bimolecular reaction (a) and a thermal fission into free radicals (b) from the behaviour of benzyl 2,4,6-trimethylphenyl ether at 270°. Here the opportunity of the benzyl group to substitute the nucleus is restricted by the *ortho*- and *para*-substituents of the phenyl group. As a consequence, dibenzyl is formed—a result which can be satisfactorily explained only if the benzyl group has some existence in the reaction as a free radical.

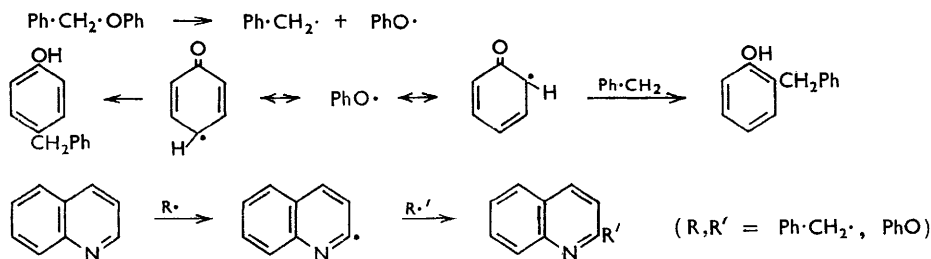
This conclusion has been tested by replacing the benzyl group in benzyl phenyl ether by diphenylmethyl which has relatively low reactivity and little or no capacity to substitute the aromatic nucleus. At its boiling point, diphenylmethyl phenyl ether decomposes to give 1,1,2,2-tetraphenylethane, phenol, and some diphenylmethane. This is conclusive evidence of pyrolysis into diphenylmethyl- and phenoxy-radicals.

The only valid evidence in favour of intermolecular benzylation (a) is Hart and Eleuterio's observation³ that the optical activity of the α -phenylethyl group is retained in the thermal rearrangement of phenyl α -phenylethyl ether. But migration of the α -phenylethyl group is accompanied by very extensive racemisation, so that it may be concluded that intermolecular phenylethylation can account for only a small fraction of the product. Hart and Eleuterio suggest that this retention of optical activity indicates an intramolecular migration, but until there is more detailed information on the optical activity of the *ortho*- and *para*-alkylated phenols from the rearrangement their conclusion should be accepted only with reserve.

On the basis of a preliminary fission of benzyl phenyl ether into benzyl and phenoxy-radicals by heat, the course of the rearrangement can be represented simply as shown in

³ Hart and Eleuterio, *J. Amer. Chem. Soc.*, 1954, **76**, 519.

the annexed scheme. This also explains the formation of benzylnaphthols in α - or β -

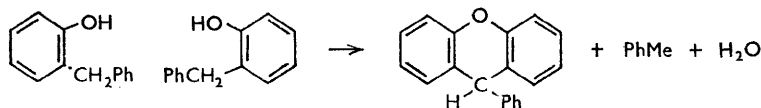


naphthol, and of 2-hydroxyphenylquinoline. In an elaboration of it we can suppose that the more reactive benzyl radicals interact with unchanged ether:



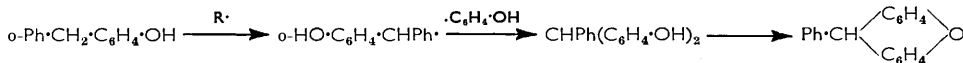
However, the thermal rearrangement is more complicated than these simple schemes suggest. Account must also be taken of the formation of toluene and of 9-phenylxanthen which are characteristic products, formed generally in much greater amounts than the benzyphenols.

Formation of xanthenes and xanthens when suitably substituted phenols are heated is well known and it seemed possible that 9-phenylxanthen could be formed by the interaction of two molecules of *o*-benzylphenol with the elimination of toluene and water:



However, heating *o*-benzylphenol in sealed tubes under conditions which cause thermal rearrangement yielded neither toluene nor 9-phenylxanthen. It was also possible that benzaldehyde, which is formed when benzyl phenyl ether is heated at its boiling point for some hours, might yield 9-phenylxanthen by reaction with phenol, for it is known that *para*-substituted phenols and benzaldehyde do so react in suitable solvents. But the amount of benzaldehyde formed as a result of several hours' heating does not account for the amount of 9-phenylxanthen formed, nor is there evidence that benzaldehyde is formed when benzyl phenyl ether is heated in sealed tubes. It is probable that the benzaldehyde is formed by aerial oxidation of the ether.

A more satisfactory explanation depends on reaction of benzyl or phenoxy-radicals with a benzyphenol (*a*) followed by reaction with an oxyphenyl radical (*b*).



There is already evidence that reaction of aryl radicals with alkylbenzenes involves attack on the side chain⁴ and that benzyl radicals attack the 9,10-positions of anthracene.⁵ Thus benzyl radicals may dehydrogenate the CH₂ group of benzyphenols, and in support is the observation that the yield of toluene increases with that of 9-aryl-xanthen. In the thermal rearrangement of benzyl 2,4,6-trimethylphenyl ether there is formed in addition to dibenzyl, mesitol, and toluene, a phenol which has been provisionally identified as 2,4-dimethyl-6-phenethylphenol mainly for the reason that it is not the product that would be expected from attack of the benzyl group on the only vacant position in the mesitol nucleus.

⁴ Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, **4**, 386; Cadogan, Gold, and Satchell, *J.*, 1955, 561; Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.

⁵ Norman and Waters, *J.*, 1957, 950; 1958, 167; Beckwith, Norman, and Waters, *J.*, 1957, 171.

Its precise identification has only minor bearing on the principal arguments developed in this paper, yet its formation gives point to the suggestion that the attack of benzyl radical is not confined to the aromatic nucleus.

EXPERIMENTAL

Thermal Rearrangement of Benzyl Phenyl Ether.—(a) *In α -naphthol.* Benzyl phenyl ether (40 g.) and α -naphthol (15 g.) were heated together in sealed tubes at 260° for 12 days. The contents of the tube were dark brown and had a strong phenolic odour. Distillation up to 200° gave water (1 g.), toluene (5.8 g.), and phenol (10.0 g.). The higher-boiling products were separated by treatment with methyl-alcoholic potassium hydroxide (Claisen's solution) into neutral and phenolic products. The former gave two main fractions: (a) b. p. 230—240°/14 mm. (3.5 g.), (b) b. p. 250—260°/14 mm. (8.0 g.). A dark tar remained (7.0 g.) from which nothing homogeneous was isolated. Fraction (a) solidified under ethanol, and crystallisation therefrom gave 9-phenylxanthen, m. p. and mixed m. p. 145°. Fraction (b) afforded 9-phenyl-5,6-benzoxanthen, prisms, m. p. 182°, by crystallisation from ethanol (Found: C, 89.0; H, 5.3. $C_{23}H_{16}O$ requires C, 89.5; H, 5.2%). Distillation of the phenolic material gave: (a) α -naphthol (7.5 g.); (b) *o*-benzylphenol (4.0 g.) (Found: C, 84.5; H, 6.6. Calc. for $C_{13}H_{10}O$: C, 84.75; H, 6.6%) from a fraction of b. p. 175—185°/13 mm. (phenylurethane, m. p. and mixed m. p. 117°); (c) *p*-benzylphenol (6.5 g.), b. p. 195—205°/13 mm., m. p. and mixed m. p. 84° (from light petroleum) (Found: C, 84.3; H, 6.6%) (benzoate, m. p. and mixed m. p. 87°); (d) a mixture (7.0 g.), b. p. 235—245°/13 mm., from which 2-benzyl-1-naphthol, m. p. and mixed m. p. 74°, was isolated by crystallisation from 3 : 17 acetic-formic acid (Found: C, 87.0; H, 6.0. Calc. for $C_{17}H_{14}O$: C, 87.1; H, 6.0%) [from the more soluble fractions of this crystallisation, 2,4-dibenzylphenyl α -naphthylurethane, m. p. and mixed m. p. 145°, was obtained; it was estimated from the infrared spectrum of the mixture that these two components were present in about equal amounts); (e) 4-benzyl-1-naphthol (0.8 g.), m. p. and mixed m. p. 126° (from benzene), from a fraction of b. p. 255—265°/13 mm. (Found: C, 86.8; H, 6.0. Calc. for $C_{17}H_{14}O$: C, 87.1; H, 6.0%) (benzoate, m. p. and mixed m. p. 103°).

For comparison, 2-benzyl-1-naphthol was prepared by reaction of benzyl chloride (48 g.) on a suspension of sodium 1-naphthyl oxide in toluene (from α -naphthol 42 g., and sodium hydride 8 g.); this (yield, 52 g.) had b. p. 233°/12 mm., m. p. 74° (Found: C, 86.9; H, 5.8%).

4-Benzyl-1-naphthol was prepared by reaction of benzyl alcohol (27 g.) and α -naphthol (30 g.) in light petroleum with aluminium chloride at 35—40°, the yield being 38 g., the b. p. 245—255°/12 mm., and the m. p. 126° (Found: C, 86.8; H, 6.1%).

(b) *In β -naphthol.* Benzyl phenyl ether (40 g.) and β -naphthol (15 g.) were heated together at 260° for 12 days in sealed tubes. The product was worked up as described for α -naphthol and the following were isolated: water (0.8 g.); toluene (5.4 g.); phenol (8.4 g.); β -naphthol (4.0 g.); *o*-benzylphenol (3.6 g.), b. p. 170—180°/12 mm. (Found: C, 84.5; H, 6.5. Calc. for $C_{13}H_{10}O$: C, 84.75; H, 6.6%) (phenylurethane, m. p. and mixed m. p. 117°); *p*-benzylphenol (5.5 g.), m. p. and mixed m. p. 84° (Found: C, 84.7; H, 6.6%) (benzoate, m. p. and mixed m. p. 87°); 1-benzyl-2-naphthol, b. p. 220—230°/12 mm. (1.6 g.), m. p. 112° [from light petroleum (b. p. 80—100°)] (Found: C, 87.0; H, 6.0%) (acetate, m. p. and mixed m. p. 65°; benzoate, m. p. and mixed m. p. 97°); a mixture, b. p. 230—240°/12 mm. (5.0 g.) of 1-benzyl-2-naphthol and 2,4-dibenzylphenol in about equal proportions (infrared estimation). From this mixture 1-benzyl- β -naphthol was isolated by crystallisation from light petroleum (b. p. 80—100°): from the more soluble fractions, 2,4-dibenzylphenol was isolated as α -naphthylurethane, m. p. and mixed m. p. 145°.

The neutral products were separated by distillation and crystallisation into the following: 9-phenylxanthen, m. p. and mixed m. p. 145°, from a fraction of b. p. 225—235°/12 mm. (5.5 g.); 9-phenyl-1,2,7,8-dibenzoxanthen (0.8 g.), m. p. and mixed m. p. 190° (Claisen⁶ gives m. p. 189—190°) (Found: C, 90.2; H, 5.0. Calc. for $C_{27}H_{18}O$: C, 90.5; H, 5.0%) (red colour with sulphuric acid); 9-phenyl-7,8-benzoxanthen (5.5 g.), m. p. 163—164° [from ethanol or light petroleum (b. p. 60—80°)] (Found: C, 89.0; H, 5.3. Calc. for $C_{23}H_{16}O$: C, 89.5; H, 5.2%) (yellow colour with sulphuric acid).

(c) *In quinoline.* Benzyl phenyl ether (70 g.) and redistilled quinoline (60 g.) were heated together at 270° for 14 days in sealed tubes. Distillation, first at atmospheric pressure and then

⁶ Claisen, *Annalen*, 1887, **237**, 266.

up to 140°/15 mm., removed toluene (16.6 g.), phenol (1.0 g.), unchanged quinoline (28 g.) and benzyl phenyl ether. The remaining semisolid mass was diluted with ether; the phenols and aminophenols (A) were extracted with Claisen's solution. The ether solution was then shaken several times with hydrochloric acid to remove the amines (B) and leave an ethereal solution of the neutral products (C).

The neutral products (C) consisted essentially of 9-phenylxanthen (10 g.), b. p. 230—240°, m. p. and mixed m. p. 145° (from ethanol) (Found: C, 88.4; H, 5.4. Calc. for C₁₈H₁₄O: C, 88.3; H, 5.4%) (correct infrared spectrum).

The Claisen extracts (A) were concentrated to remove alcohol, then acidified with hydrochloric acid to liberate the phenols (D). The aqueous acid solution, freed from phenols by ether-extraction, was neutralised with sodium carbonate to liberate the aminophenols (E) which were taken up into ether. Distillation of the phenols (D) gave *o*-benzylphenol, b. p. 180—190°/17 mm. (4.5 g.) (Found: C, 84.4; H, 6.5%) (phenylurethane, m. p. and mixed m. p. 117°), *p*-benzylphenol, b. p. 200—210°/17 mm., m. p. and mixed m. p. 84° (Found: C, 84.7; H, 6.4%) (benzoate, m. p. and mixed m. p. 87°), and 2,4-dibenzylphenol, b. p. 235—245°/17 mm. (0.8 g.) (1-naphthylurethane, m. p. and mixed m. p. 144°). The main constituent of fraction (E) was 2-*o*-hydroxyphenylquinoline (12 g.), yellow needles (from methanol), the mother-liquors from which gave 2-*p*-hydroxyphenylquinoline, m. p. 234—237°.

The amines (B), on distillation, gave fractions, (a) b. p. 220—230°/17 mm. (8 g.) and (b) b. p. 245—260°/17 mm. (12 g.), and a solid residue (6 g.). Fraction (a) was essentially a mixture of 2- and 4-benzylquinoline and was separated by crystallisation of the picrates from ethanol (4-benzylquinoline picrate separated first). Fraction (b) on trituration with ethanol and crystallisation from the same solvent gave 2,2'-biquinolyl, m. p. and mixed m. p. 195° (Found: C, 84.0; H, 4.6; N, 10.8. Calc. for C₁₈H₁₂N₂: C, 84.3; H, 4.7; N, 10.9%) (picrate, prisms, m. p. and mixed m. p. 213°) (Smirnoff ⁷ gives m. p. 196° and 210—215° respectively), the mother-liquors on evaporation giving an unidentified yellow compound, m. p. 142° (from ethanol).

2-Benzylquinoline, liberated from the pure picrate, boiled at 230°/14 mm. (Found: C, 87.0; H, 6.0; N, 6.5. Calc. for C₁₆H₁₃N: C, 87.6; H, 6.0; N, 6.4%) [*picrate*, m. p. 158—159° (Found: C, 58.9; H, 3.7; N, 12.75. C₁₆H₁₃N, C₆H₅O₇N₃ requires C, 58.9; H, 3.7; N, 12.5%); *methiodide*, yellow needles (from acetone), m. p. 218—219° (decomp.) (Found: C, 56.85; H, 4.8; N, 3.8; I, 35.1. C₁₇H₁₆NI requires C, 56.6; H, 4.5; N, 3.9; I, 35.0%)]. A specimen prepared from 1-methylquinolone as described by Decker and Pschorr ⁸ had the same appearance, the same infrared spectrum and the same crystallographic constants as the sample prepared from 2-benzylquinoline, and gave an undepressed mixed m. p.

4-Benzylquinoline had b. p. 230°/17 mm. (Found: C, 87.4; H, 5.9; N, 6.5. Calc. for C₁₆H₁₃N: C, 87.6; H, 6.0; N, 6.4%), and gave a picrate, platelets, m. p. 178—179° (Found: C, 59.1; H, 3.6; N, 12.5. Calc. for C₁₆H₁₃N, C₆H₅O₇N₃: C, 58.9; H, 3.7; N, 12.5%), and *methiodide*, orange prisms, m. p. 224—228° (decomp.) (Found: C, 56.4; H, 4.7; N, 4.0. C₁₇H₁₆NI requires C, 56.6; H, 4.5; N, 3.9%). Rabe and Pasterneck ⁹ describe 4-benzylquinoline, b. p. 222—223°/19 mm. (*picrate*, m. p. 178°).

2-*o*-Hydroxyphenylquinoline formed pale yellow needles (from methanol), m. p. 116° (lit.,¹⁰ 116°) (Found: C, 81.2; H, 4.6; N, 6.6. Calc. for C₁₅H₁₁ON: C, 81.4; H, 5.0; N, 6.3%) [*picrate*, needles, m. p. 185° (lit.,¹⁰ 184°) (Found: C, 56.0; H, 3.0; N, 12.2. Calc. for C₁₅H₁₁ON, C₆H₅O₇N₃: C, 56.0; H, 3.1; N, 12.4%); *hydrochloride*, light yellow needles from dilute hydrochloric acid (Found: C, 61.35; H, 5.4; N, 4.9. C₁₅H₁₁ON, HCl, 2H₂O requires C, 61.3; H, 5.5; N, 4.8%); *hydrobromide*, bronze-coloured needles from dilute hydrobromic acid (Found: C, 56.4; H, 4.3; N, 4.5; Br, 24.75. C₁₅H₁₁ON, HBr, H₂O requires C, 56.3; H, 4.4; N, 4.4; Br, 25.0%); *O*-benzoate, stout colourless crystals (from aqueous alcohol), m. p. 86—87° (Found: C, 81.3; H, 4.6; N, 4.4. C₂₂H₁₅O₂N requires C, 81.2; H, 4.6; N, 4.3%); *O*-benzoate *picrate*, prisms (from methanol), m. p. 167° (Found: C, 60.7; H, 3.6. C₂₂H₁₅O₂N, C₆H₅O₇N₃ requires C, 60.6; H, 3.3%); *O*-acetate, m. p. 78—79°, long white needles from light petroleum]. It was identical in m. p., mixed m. p., and infrared spectrum with a specimen prepared by Doebner's method.¹⁰

2-*p*-Hydroxyphenylquinoline formed thin flattened plates (from aqueous alcohol), m. p.

⁷ Smirnoff, *Helv. Chem. Acta*, 1921, **4**, 807.

⁸ Decker and Pschorr, *Ber.*, 1904, **37**, 3400.

⁹ Rabe and Pasterneck, *Ber.*, 1913, **46**, 1027.

¹⁰ Doebner, *Annalen*, 1888, **249**, 99.

236—237° not depressed on admixture with an authentic specimen¹¹ [hydrochloride (Found: C, 61.3; H, 5.0; Cl, 12.5. Calc. for C₁₅H₁₁ON.HCl: C, 61.2; H, 5.5; Cl, 12.1%); acetyl derivative, m. p. 123—124° (Found: C, 77.4; H, 4.7; N, 5.5. Calc. for C₁₇H₁₃O₂N: C, 77.5; H, 4.9; N, 5.4%); picrate needles (from acetone), m. p. 196—197° (Found: C, 55.9; H, 3.6; N, 11.7. C₁₇H₁₃O₂N.C₆H₃O₇N₃ requires C, 56.1; H, 3.3; N, 11.4%)].

(d) *In isoquinoline.* Benzyl phenyl ether (70 g.) and isoquinoline (60 g.) were heated together in sealed tubes at 270° for 15 days. The product was worked up as described for quinoline, giving toluene (12 g.), phenol (17 g.), isoquinoline, m. p. 25° (33 g.), benzyl phenyl ether, m. p. 39° (25 g.), *o*-benzylphenol (6 g.), *p*-benzylphenol (4.2 g.), 2,4-dibenzylphenol (2.0 g.), 1-benzylisoquinoline (15 g.), 1-*o*-hydroxyphenylisoquinoline (10.5 g.), and 9-phenylxanthen (7.5 g.).

1-Benzylisoquinoline, b. p. 212—215°/15 mm., m. p. 55.5—56° (Found: C, 87.9; H, 6.2; N, 6.4. Calc. for C₁₆H₁₃N: C, 87.6; H, 6.0; N, 6.4%), was characterised as its *picrate*, m. p. 182° (Found: C, 59.1; H, 3.7; N, 12.5. C₁₆H₁₃N.C₆H₃O₇N₃ requires C, 58.9; H, 3.6; N, 12.5%), and *methiodide*, yellow needles, m. p. 247—247.5° (Found: C, 56.0; H, 4.4; N, 3.9; I, 34.7. C₁₇H₁₆NI requires C, 56.5; H, 4.5; N, 3.9; I, 35.0%). It was identical (m. p. and infrared spectrum) with 1-benzylquinoline prepared by cyclisation of *N*- α -hydroxybenzylphenylacetamide.¹² The picrates and methiodides from both sources had the same m. p. and were not depressed on admixture.

1-*o*-Hydroxyphenylisoquinoline formed prisms, b. p. 240—250°/15 mm., m. p. 166° (Found: C, 81.8; H, 5.0; N, 6.2. C₁₅H₁₁ON requires C, 81.4; H, 5.0; N, 6.3%); soluble in dilute alkali. Its *picrate* crystallises from chloroform in light yellow crystals, m. p. 183° (Found: C, 56.0; H, 3.2; N, 11.9. C₁₅H₁₁ON.C₆H₃O₇N₃ requires C, 56.0; H, 3.1; N, 12.4%). Its phenylurethane has m. p. 173—174°.

Thermal Rearrangement of Benzyl 2,4,6-Trimethylphenyl Ether.—This ether, b. p. 180—182°/14 mm., n_D^{20} 1.5555, was prepared by refluxing a mixture of benzyl chloride, 2,4,6-trimethylphenol, and potassium carbonate in acetone for 35 hr. (Found: C, 84.9; H, 8.1. C₁₆H₁₈O requires C, 84.9; H, 8.0%).

(a) *Alone.* The phenol (38 g.) was heated in sealed tubes for 10 days at 280°. By distillation and treatment of each fraction with aqueous alkali the product was resolved into toluene (7.4 g.), mesitol (11.2 g.), m. p. and mixed m. p. 92°, dibenzyl (3.5 g.), m. p. and mixed m. p. 52° (decomp.), benzyl mesityl ether (2 g.), 2,4-dimethyl-6-phenethylphenol (7 g.), m. p. 87° (Found: C, 84.9; H, 8.1. C₁₆H₁₈O requires C, 84.9; H, 8.0%) (phenylurethane, m. p. 145.5°; *p*-nitrobenzoate, m. p. 142°), and tar (4 g.).

Dibenzyl was further identified by means of its infrared spectrum and dinitro-compound, m. p. and mixed m. p. 180°.

3-Benzyl-2,4,6-trimethylphenol was prepared by adding, in 1 hr., finely powdered aluminium chloride (17 g.) to mesitol (35 g.) and benzyl alcohol (25 g.) in light petroleum, with stirring at 35°. Next morning, acidification, and distillation of the phenols, gave mesitol (5 g.), 3-benzyl-2,4,6-trimethylphenol (23 g.), and 3,5-dibenzyl-2,4,6-trimethylphenol (10 g.). The monobenzyl product, b. p. 200—210°/15 mm., m. p. 59—59.5° (from light petroleum) (Found: C, 84.9; H, 8.0. C₁₆H₁₈O requires C, 84.9; H, 8.0%), gave a phenylurethane, m. p. 138—139°, and its infrared spectrum was distinct from that of 2,4-dimethyl-6-phenethylphenol with which it gave a depression of the m. p.

3,5-Dibenzyl-2,4,6-trimethylphenol, b. p. 290—295°/15 mm., m. p. 111° (from light petroleum) (Found: C, 87.2; H, 7.4. C₂₃H₂₄O requires C, 87.3; H, 7.6%) gave a phenylurethane, m. p. 129°.

The same two phenols were formed by reaction of benzyl chloride with mesitol in light petroleum in presence of aluminium chloride.

(b) *In quinoline.* Benzyl 2,4,6-trimethylphenyl ether (50 g.) and quinoline (20 g.) were heated together at 270° for 17 days in sealed tubes. The lower-boiling products were toluene (12 g.) and 2,4,6-trimethylphenol (13.5 g.). The higher-boiling material was freed from phenols by washing with Claisen's solution and then from amines by means of acid. The neutral product was essentially dibenzyl, m. p. and mixed m. p. 52° (3.0 g.). The amines were separated by distillation into quinoline (8 g.), 2,2'-biquinolyl, m. p. and mixed m. p. 195° (4.5 g.), and mixed benzylquinolines (7.8 g.) from which 2- and 4-benzylquinoline were isolated by fractional crystallisation of their picrates.

¹¹ Weidel, *Monatsh.*, 1887, **8**, 127.

¹² Pictet, *Ber.*, 1910, **43**, 2386.

Thermal Decomposition of Diphenylmethyl Phenyl Ether.—This ether was prepared by adding bromodiphenylmethane (25 g.) in ether (120 c.c.) to sodium phenoxide in an excess of phenol (from phenol, 120 g., and sodium, 5 g.). Reaction was completed on a steam-bath in $1\frac{1}{2}$ hr. After treatment with water, the ether extract was washed repeatedly with aqueous alkali, diluted with light petroleum, and extracted with Claisen's solution. Distillation gave the ether, b. p. $210^{\circ}/14$ mm., m. p. 54° (from light petroleum) (Found: C, 87.5; H, 6.1. Calc. for $C_{19}H_{16}O$: C, 87.7; H, 6.2%); Schorigin¹³ gives b. p. 233 — $243^{\circ}/23$ mm., m. p. 54° .

At its b. p. the ether decomposes and the temperature of the boiling liquid falls from 295° to 235° . After 3 hr. 30 g. of ether gave phenol (7 g.), unchanged ether (2.8 g.), 1,1,2,2-tetra-phenylethane (10.5 g.), and a dark residue.

Heating 20 g. of ether at 250° for 20 hr. gave phenol (3 g.), diphenylmethane (1.5 g.), tetra-phenylethane (13 g.), and a residue (2.5 g.).

1,1,2,2-Tetraphenylethane, m. p. and mixed m. p. 210° (Found: C, 93.3; H, 6.5. Calc. for $C_{26}H_{22}$: C, 93.4; H, 6.6%), was further identified by means of its infrared spectrum and by its tetranitro-compound, m. p. and mixed m. p. 143° . Diphenylmethane, m. p. and mixed m. p. 26° (tetranitro-compound, m. p. and mixed m. p. 172°), also had the correct infrared spectrum.

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¹³ Schorigin, *Ber.*, 1926, **59**, 2502.