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MOLECULAR REARRANGEMENTS—II

THE PYROLYSIS OF BENZYL-β-NAPHTHYL ETHER

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Abstract—When purified benzyl-β-naphthyl ether was heated at 260°, in absence of any promotor, the benzyl group migrated to the α-position of the naphthol nucleus. β-Naphthol, toluene, dibenzyl and 9-phenyl-1,2,7,8-dibenzoxanthene also were formed. When quinoline was used as a solvent, the normal rearrangement products were obtained together with 2- and 4-benzylquinolines and 1(2-quinolyl)2-naphthol and its isomeric 1(4-quinolyl)2-naphthol. When phenol and anisole were used as solvents, the rearrangement was accompanied with benzylation of the solvent.

It is concluded that the pyrolysis of benzyl-β-naphthyl ether depends on homolytic fission of the ether to benzyl and naphthyloxy radicals.

IT WAS reported by Behagel and Friensehner,[1] that benzyl-β-naphthyl ether gave 1-benzyl-2-naphthol and 10% β-naphthol, together with unidentified higher boiling materials, when it was heated at 240–250° for 48 hr. Benzyl-α-naphthyl ether and other aryl benzyl ethers also rearranged under similar conditions. However, the ether on heating in a sealed tube with 38% HCl, gave rearrangement products from which β-naphthol was identified as reported.[2] There are good reasons for believing that under the conditions used by Behagel, the change is proton catalysed by hydrogen chloride resulting from the hydrolysis of benzyl chloride in the crude ethers used. Indeed, benzyl chloride is persistently retained by benzyl ethers made from benzyl chloride and the phenols, and is removed only by repeated treatment with pyridine. Furthermore, the accelerating effect of zinc on the rearrangement,[3] can be interpreted as due to the formation of zinc chloride (which acts as a powerful promoter for that change) from the hydrochloric acid formed from the benzyl chloride present as impurity.

A more detailed study was made of the pyrolysis of benzyl-β-naphthyl ether, carefully freed from benzyl chloride. In contrast to Behagel's observations, the pyrolysis required prolonged heating at 260° and the products differed in many respects from those reported by Behagel. Thus, benzyl-β-naphthyl ether, changed on heating for some days at its boiling point under reflux or in sealed tubes at about 260°. 1-Benzyl-2-naphthol was formed together with β-naphthol, 9-phenyl-1,2,7,8-dibenzoxanthene, some water, toluene, dibenzyl, 2,2'-dinaphthol(2,2'-dihydroxy-1,1'dinaphthol) and higher boiling products not yet resolved.

The products of these thermal rearrangements differ markedly from those of the proton catalysed rearrangements, from which neither benzoxanthene, nor toluene or dibenzyl have been reported.[1,2]

The presence of toluene and dibenzyl in the product strongly suggests that the change depends on a free radical mechanism. In order to study this suggestion further, the thermal rearrangement in high boiling solvents was examined. In phenol, the

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normal products of the rearrangement were obtained together with 2- and 4-benzylphenol; in anisole, benzylation of the solvent occurred.

The thermal rearrangement of benzyl-β-naphthyl ether in quinoline gave the normal rearrangement products accompanied by 2- and 4-benzylquinolines together with 1-(2-quinolyl)2-naphthol and another isomer which was identified as 1-(4-quinolyl)2-naphthol. Other products were, 2,2′-biquinolyl, 2,2′-dinaphthol and β-dinaphthylene oxide, as summarized in Table (1).

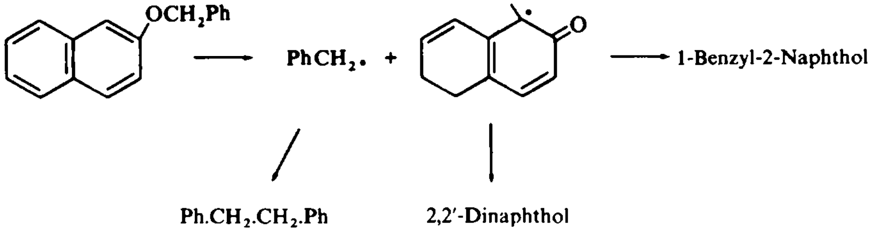
Table 1. Products of pyrolysis of β-benzylnaphthyl ether in different solvents

Exp. No.	1	2	3	4
Solvent used (g)	—	Phenol (7 g)	Anisole (11 g)	Quinoline[a] (40 g)
Temp./days	260/6	225/6	260/10	260/10
Ether used (g)	38	25	45	70
Ether recovered (g)	6	—	11·8	17·5
Water (g)	0·5	0·6	0·35	0·38
Toluene (g)	1·8	1	2·5	9·2
Dibenzyl (g)	0·3	0·2	0·5	0·33
2-Naphthol and Binaphthol (g)	5·6	5[c]	7·4	13·5
1-Benzyl-2-naphthol (g)	8	6	6·8	5
Dibenzoxanthene (g)	1·3	2·3	2·5	3
Benzyl isomers of solvent used (g)	—	3	2	6·8
Non-volatile residue[b] (g)	—	8	3·7	6·1[i]

[a] β-Dinaphthylene oxide (0·4 g), 2,2′-biquinolyl (6·5 g) and isomeric quinolyl naphthols (1·5 g) were separated; [b] Neutral and phenolic products, [i] together with amino products; [c] Binaphthol not isolated.

Substitution in quinoline by both benzyl and hydroxynaphthyl group in the same positions is consistent only with an initial dissociation of the ether into free radicals.

On this basis, it is possible to provide a satisfactory picture of the ether rearrangement and of the formation of all products, through its initial homolytic fission to benzyl and naphthyloxy free radicals. Their subsequent recombination give 1-benzyl-2-naphthol, while combination of, two benzyl radicals give dibenzyl, and two naphthyloxy radicals give 2,2′-dinaphthol, then β-dinaphthylene oxide.



Substitution by benzyl radical on solvent nuclei, phenol and anisole, gives the expected products separated as in Table 2.

In quinoline, the formation of 2,2′-biquinolyl, strongly suggests the formation of quinolyl free radical from quinoline by reaction with other free radicals in the reaction.

Combination of two of the quinolyl free radicals, gives 2,2′-biquinolyl, while with

TABLE 2. RATIO OF ISOMERIC BENZYL DERIVATIVES OF THE AROMATIC SOLVENTS

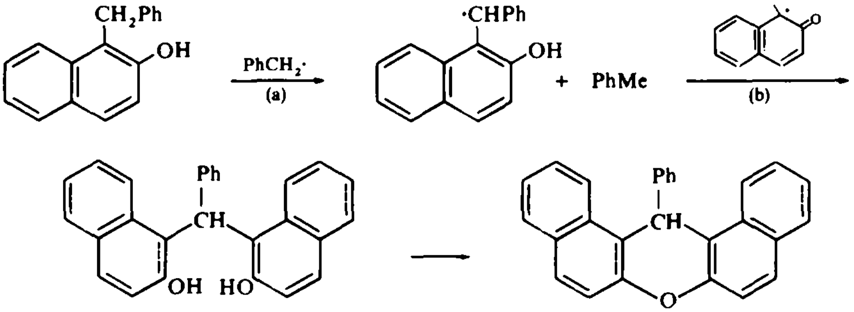
Isomeric products	Phenol	Anisole	Quinoline[a]
2-Benzyl-	66	30·4	40
4-Benzyl-	34	69·6	60

[a] Separated as their picrates

a benzyl radical, 2- and 4-benzylquinolines are formed: while naphthyloxy radicals give the different isomeric quinolyl-naphthols.

2-Benzyl-1-naphthol, was recovered unchanged, after heating alone in a sealed tube under the rearrangement conditions, thus excluding the possibility of its condensation to produce the dibenzoxanthene and toluene byproducts. Moreover, there is no evidence for the formation of benzyldehyde, as a byproduct, thus excluding the possibility of its condensation with β-naphthol separated to produce dibenzoxanthene.

The most satisfactory explanation for the formation of 9-phenyl-1,2,7,8-dibenzoxanthene which is a characteristic product, depends on the reaction of benzyl or β-naphthyloxy radicals with 2-benzyl-1-naphthol(a), followed by reaction with an oxynaphthylradical(b), according to the following scheme:



The attack of aryl radicals on the side chain of alkyl benzenes[4a], and the attack of benzyl radicals on the 9,10-positions of anthrathene[4b], are reported.

EXPERIMENTAL

Analysis. The lower boiling products of the rearrangement were analyzed by high-temperature gas chromatography, Model 1709, flame ionization attachment of F. and M. scientific corporation, Model 500, with copper columns, 6 ft × 4 mm. The column used was 20% SE30 on Chromosorb W(35–80 mesh) at 200° for the phenolic products and 215° for the neutral products. The IR spectroscopic analysis was carried out by Pye–Unicam IR spectrophotometer, Model SP200G.

Benzyl-β-naphthyl ether was prepared[5] from benzyl chloride, β-naphthol and anhyd K_2CO_3 in acetone It was freed from any traces of benzyl chloride by refluxing several times with pyridine. then extracting with ether. After neutralization with acid, washing, drying and evaporation, it was obtained from EtOH, m.p. 101–102°.

Pyrolysis of benzyl-β-napthyl ether. Benzyl-β-naphthyl ether (38 g), heated at 260° in a sealed tube for 6 days, became a thick red brown liquid with a greenish fluorescence. Toluene (1·8 g) and water (0·3 g) were removed by initial distillation.

The residue was diluted with ether and benzene, and extracted with aqueous methyl alcoholic potash (Claisen solution) to remove phenols (A). The neutral products (B) were distilled to give unchanged benzyl-β-naphthyl ether (6 g), m.p. and mixed m.p. 101°; 9-phenyl-1,2,7,8,-dibenzoxanthene, as yellow white crystals (1·3 g), from AcOH, m.p. and mixed m.p. 189°. From the fraction 180–200°/24 mm, dibenzyl (0·3 g), was isolated, m.p. and mixed m.p. 52° from aqueous EtOH (4,4′-dinitroderivative m.p. and mixed m.p. 180°). It was further identified by its IR spectra and its retention time in GLC.

The phenol (A), were resolved into β-naphthol (5 g), 1-benzyl-2-naphthol (8 g), m.p. and mixed m.p. 108–109°, benzoate, m.p. and mixed m.p. 96°, and 2.2′-dinaphthol (0·6 g), m.p. and mixed m.p. 212–213°, dibenzoate, white needles, m.p. and mixed m.p. 160°. Its IR spectrum was identical to that of a reference sample.

Thermal rearrangements in aromatic solvents

(a) *Phenol.* The ether (25 g) and phenol (7 g) were heated together in a sealed tube at 225° for 6 days. The contents of the tube changed to dark brown thick oil, and had a strong naphthol odour. Distillation of the product up to 200° removed toluene (1 g), $n_D^{17\cdot5}$. 1·4957 (2,4-dinitroderivative, m.p. and mixed m.p. 70–71° and water (0·6 g), $n_D^{27\cdot8}$: 1·3395.

The higher boiling material was separated into phenolic (A) and neutral products (B) by extraction with Claisen solution after dilution with ether and benzene.

From the phenolic products, phenol and β-naphthol (5g) were isolated together with 1-benzyl-2-naphthol, m.p. and mixed m.p. 108–109° (6 g).

From the liquid phenolic fractions (3 g), 2- and 4-benzylphenols were resolved by fractional crystallization from benzene–light petroleum (60–80), the 4-benzylphenol separated, m.p. and mixed m.p. 84°, benzoate, m.p. and mixed m.p. 87°. These were also confirmed by their IR spectra and by GLC analysis (25% of the phenolic fraction, with the ratio of 66% *ortho* isomer and 34% for the *p*-benzylphenol).

From the neutral fractions, b.p. 250–260°/13 mm, and b.p. 280°/13 mm, 9-phenyl-1,2,7,8-dibenzoxanthene was isolated, m.p. and mixed m.p. 189° (2·3 g).

In the liquid fractions, b.p. 180–200°/13 mm, and b.p. 210–230°/13 mm, by fractional crystallization from dilute EtOH, dibenzyl (0·2 g) was separated, m.p. and mixed m.p. 52°, (4,4′-dinitro derivative, m.p. and mixed m.p. 180°). It was further identified by its IR spectrum and its retention time in GLC analysis.

(b) *Anisole.* The ether (45 g) and anisole (11 g) heated together at about 260° for 10 days in a sealed tube. Distillation of the products up to 200° removed toluene (2·5 g), $n_D^{22\cdot5}$: 1·5010 (2,4-dinitro derivative, m.p. and mixed m.p. 72°), and water (0·35 g) $n_D^{22\cdot5}$: 1·3310, together with some anisole 6·2 g).

The higher boiling material was separated into phenolic (A) and neutral products (B).

From the phenolic products, β-naphthol (6·85 g) was isolated together with 1-benzyl-2-naphthol (6·8 g), m.p. and mixed m.p. 110°, benzoate, m.p. and mixed m.p. 97°. From the phenolic fraction, b.p. 195–230°/8 mm, 2,2′-dinaphthol (0·5 g) was isolated, m.p. and mixed m.p. 212–213°, dibenzoate, m.p. and mixed m.p. 160°.

From the neutral fraction, b.p. 180–200°/24 mm, dibenzyl (0·5 g) was isolated by fractional crystallization from dilute MeOH, m.p. and mixed m.p. with reference sample, 52°, (4,4′-dinitro derivative, m.p. and mixed m.p. 180°), the remaining oil (2 g) was identified by GLC analysis, as *o*-benzylanisole 30% and *p*-benzylanisole 68·8%, together with some dibenzyl up to 1·2%. They were further identified by comparison of their IR spectra with those of reference samples. Unchanged benzyl-β-naphthyl ether (11·8 g) was isolated from the fraction b.p. 120–140°/7 mm.

From the neutral fraction, b.p. 250–280°/10 mm, 9-phenyl-1,2,7,8-dibenzoxanthene (2·5 g) was isolated, m.p. and mixed m.p. 189°.

(c) *Quinoline.* The ether (70 g) and redistilled quinoline (40 g) were heated together in a sealed tube at about 260° for 10 days. Toluene (9·2 g) and water (0·38 g) were removed from the product by distilling up to 200°.

The higher boiling material was diluted with ether. The phenols and aminophenols (A) were extracted with Claisen solution. The neutral layer, after its separation from Claisen solution, was shaken with HCl to extract the amines (B), (47 g).

The remaining ether soln of neutral materials (C), (27 g) was distilled and the fraction b.p. 115–130°/15 mm, gave dibenzyl (0·33 g), m.p. and mixed m.p. 52° (4,4′-dinitro derivative m.p. and mixed m.p. 180°). It was further identified by its IR spectrum and its retention time in GLC analysis. Unchanged ether (17·5 g) was separated. 9-Phenyl-1,2,7,8-dibenzoxanthene (3g), m.p. and mixed m.p. 189°, was isolated from a fraction b.p. 200–225°/15 mm, together with β-dinaphthylene oxide (0·4 g) which was separated from the mother liquour, m.p. and mixed m.p. 154-156°. (Found: C, 89·0: H, 4·4: $C_{20}H_{10}O$ requires: C, 89·5: H, 4·5%).

The amines separated from the acid extract (B), were, quinoline (24 g) and a mixture of 2- and 4-benzylquinolines, b.p. 160–173°/15 mm, which were separated by fractional crystallization of thier picrates. 4-Benzylquinoline picrate (9 g) m.p. and mixed m.p. 178–179°, and 2-benzylquinoline picrate (6 g), m.p. and mixed m.p. 156°. From the fraction b.p. 220–240°/15 mm, 2,2'-biquinolyl was separated (6·5 g), m.p. and mixed m.p. 195°, picrate, m.p. and mixed m.p. 213–214°. Its IR spectrum was identical with that of reference sample.

The phenol and aminophenol extract (A) was concentrated to remove some of the MeOH and then acidified with HCl to liberate the phenols (D), (20 g), which were extracted with ether. The aqueous acid soln, which contained the hydrochloride of the aminophenols was neutralized to liberate the aminophenols (E), (3g), which were extracted with ether.

Fractional distillation of the phenols (D) liberated, β-naphthol (13 g) and 1-benzyl-2-naphthol (5 g) m.p. and mixed m.p. 110°, benzoate, m.p. and mixed m.p. 97°.

From a fraction, b·p. 235–240°/10 mm, 2,2'-dinaphthol (0·5 g) was isolated, m.p. and mixed m.p. 212-213°, dibenzoate, m.p. and mixed m.p. 160°. Its IR spectrum was the same as that of the reference sample.

The aminophenols (E) were triturated with light petroleum (60–80) to give one isomeric solid product, which was crystallized from benzene–light petroleum (60–80) giving colourless crystals (0·8 g), m.p. 280-281°, which were not changed by mixing with a sample of 1-(2-quinolyl)2-naphthol, and their IR spectra were the same. (Found: C, 84·6; H, 4·5; N, 4·9; $C_{19}H_{18}NO$ requires: C, 84·1; H, 4·8; N, 5·2%), picrate, m.p. and mixed m.p. 156–157°. The mother liquor, after evaporation yielded another isomeric quinolyl-2-naphthol which was recrystallized from light petroleum (40–60), (0·65 g), m.p. 28–29°. (Found: C, 84·4; H, 4·7; N, 5·0; $C_{19}H_{13}NO$ requires: C, 84·1; H, 4·8; N, 5·2%), picrate, m.p. 197–198° (dec), benzoate, m.p. 81–82°. The isomeric structure was identified as 1-(4-quinolyl)2-naphthol, since its IR spectrum has bands of free and associated OH, at 3490 cm^{-1} and 3410 cm^{-1}. Moreover, its UV absorption shows a hyperchromic effect[6], in comparison to that observed for the 2-quinolyl isomer, as shown in the table.

TABLE 3. U.V. ABSORPTION OF ISOMERIC QUINOLYL NAPHTHOLS*

Isomer	λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{max}
1-(2-quinolyl)2-naphthol	273	10650	340	8990
1-(4-quinolyl)2-napthol	237	8700	313	2600

* The UV spectra was measured in ethanol solution

(d) *Heating of authentic 1-benzyl-2-naphthol in a sealed tube.* Pure 1-benzyl-2-naphthol (6 g) was heated in a sealed tube at 260° for 6 days. Identification of the products, by GLC, IR spectra and mixed m.p., confirmed that the starting isomer was recovered unchanged.

Preparation of reference compounds

1-*Benzyl*-2-*naphthol*:[7] pale brown crystals from benzene–light petroleum (60–80), m.p. 110°. (Found: C, 87·4: H, 5·9; $C_{17}H_{14}O$ requires: C, 87·2: H, 6·0%), benzoate, m.p. 97°.

2-*Benzylanisole*:[8] white crystals from EtOH, m.p. 28°. (Found: C, 84·8; H, 7·3; $C_{14}H_{14}O$ requires: C, 84·8; H, 7·1%).

4-*Benzylanisole*:[9] pale yellow oil, b.p. 152–155°/7 mm, n_D^{20}: 1·5781' (Found: C, 84·9; H, 7·0: $C_{14}H_{14}O$ requires: C, 84·8; H, 7·1%).

4-*Benzylphenol*:[10] hairy needles from light petroleum (60-80), m.p. 84°, benzoate, m.p. 87°.

2-*Benzylquinoline*:[11] pale yellow oil, b.p. 235°/14 mm. (Found: C, 87·3; H, 6·1; N, 6·5; $C_{16}H_{13}N$ requires: C, 87·6: H, 6·0: N, 6·4%), picrate, m.p. 157°; methiodide, m.p. 219° (dec).

4-*Benzylquinoline*:[12] brownish crystals, b.p. 230°/14 mm, m.p. 52·5–53°. (Found: C, 87·5; H, 6·2; N, 6·3; $C_{16}H_{13}N$ requires: C, 87·6; H, 6·0; N, 6·4%), picrate, m.p. 178–179°.

2,2'-*Dinaphthol*: (2,2'-*dihydroxy*-1,1'-*binaphthyl*;[13] white crystals from toluene, m.p. 217–218. (Found: C, 83·6; H, 5·1; $C_{10}H_{14}O$ requires: C, 83·9; H, 4·9%), dibenzoate, m.p. 160°.

β-*Dinaphthylene oxide*:[14] white crystals from glacial AcOH, m.p. 156°. (Found: C, 89·0: H, 4·4: $C_{20}H_{12}O$ requires: C, 89·5: H, 4·5%).

9-*Phenyl*-1,2,7,8-*dibenzoxanthene*:[15] light rhombic crystals from AcOH, m.p. 189°. (Found: C, 90·6: H, 5·2: $C_{27}H_{18}O$ requires: C, 90·5: H, 5·0%).

2,2′-*Biquinolyl*:[16] white crystals from EtOH, m.p. 192°. (Found: C, 80·4: H, 5·9: N, 13·2: $C_{14}H_{12}N_2$ requires: C, 80·7: H, 5·8: N, 13·5%), picrate, m.p. 210°.

1-(2-*Quinolyl*)2-*naphthol* was prepared from *o*-aminobenzaldehyde (1 g), 10% EtONa (10 ml) and 1-acetyl-2-naphthol (1g) by heating in abs EtOH (30 ml). After keeping overnight at room temp, the quinolyl naphthol product was extracted with HCl aq and precipitated. After recrystallization from benzene–light petroleum (60–80) it was obtained as colourless crystals, m.p. 280°. (Found: C, 84·2: H, 4·6: N, 4·9: $C_{19}H_{13}NO$ requires: C, 84·1: H, 4·8: N, 5·2%), picrate, from EtOH, m.p. 157°.

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