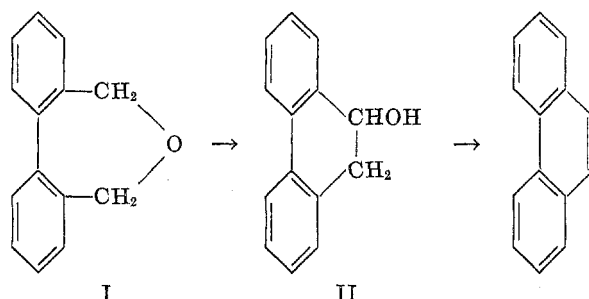


REARRANGEMENT OF DIPHENAN TO 9,10-DIHYDRO-9-PHENANTHROL BY POTASSIUM AMIDE AND DEHYDRATION TO PHENANTHRENE. RESULTS WITH 1,8-NAPHTHALAN, PHTHALAN, AND 2,5-DIHYDROFURAN¹

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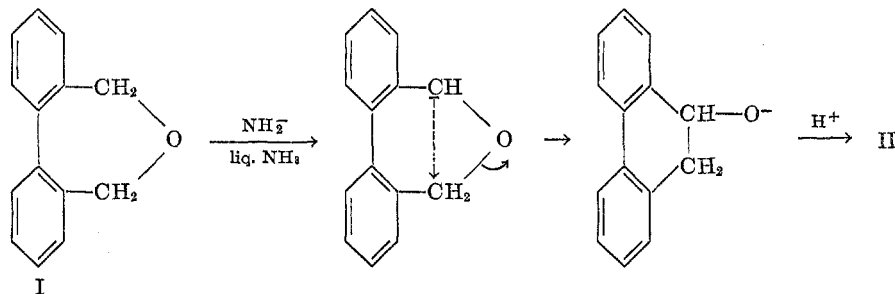
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Wittig and coworkers (1) recently effected the rearrangement of diphenan (I) with phenyllithium during one week to form 9,10-dihydro-9-phenanthrol (II) which was dehydrated by sulfuric acid in acetic acid to give phenanthrene. This type of rearrangement had previously been realized with dibenzyl ether and certain other straight chain ethers (2).



In the present investigation this novel route to phenanthrene was effected employing potassium amide in liquid ammonia for the rearrangement, and acetyl chloride for the dehydration. The potassium amide method, which was developed in this laboratory for the rearrangements of dibenzyl ether and certain other straight chain ethers (3), is convenient and rapid, producing a 90% yield of carbinol (II) from diphenan (I) within one hour. This rearrangement was also effected with sodium amide in liquid ammonia, but the pure carbinol was not isolated.

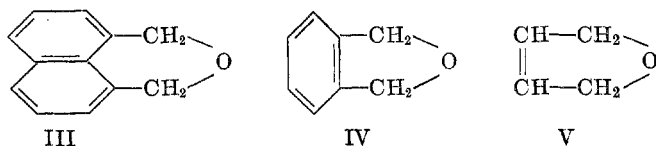
The mechanism for the rearrangement of diphenan involves presumably an internal displacement (S_N1) within an intermediate carbanion (Stevens type of 1,2-shift) (3).

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This conversion of the seven-membered ring ether carbanion to the six-membered ring carbinol anion evidently takes place more readily than that of the carbanion of dibenzyl ether to the anion of benzyl phenyl carbinol (3). Thus, the rearrangement of diphenan (I) by potassium amide in liquid ammonia was essentially complete within one hour, whereas that of dibenzyl ether with this reagent appeared to require more than three hours (3). Moreover, the maximum yield was better (90%) with the cyclic ether than that (51–61%) with dibenzyl ether which underwent partly a β -elimination to form benzaldehyde and toluene (3). The latter type of reaction was not observed with diphenan.

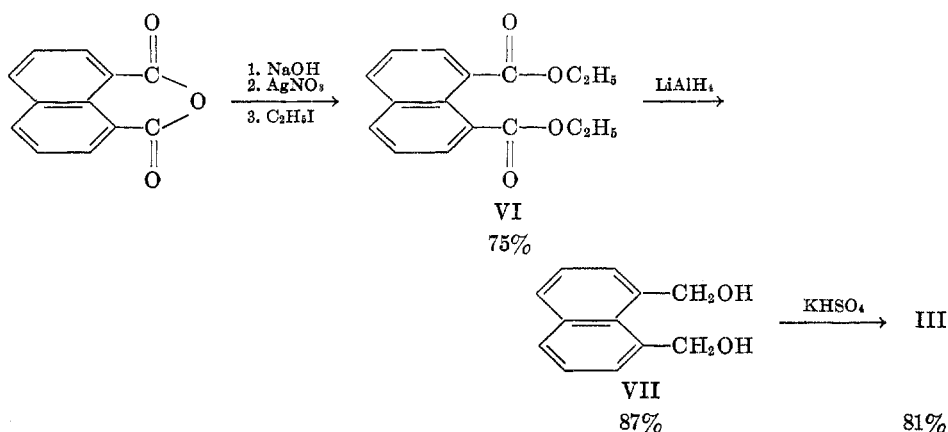
In connection with the present work it was found that, like potassium amide (3), sodium amide in liquid ammonia during three or more hours effects the rearrangement of dibenzyl ether to form benzyl phenyl carbinol (55%) along with some benzaldehyde (9.5%) and toluene (7%). When the reaction was stopped after $1\frac{1}{2}$ hours the yield of the carbinol was only 32%, and 36% of the dibenzyl ether was recovered. However, in contrast to potassium amide which produced the best yield (61%) in refluxing ether, sodium amide in this medium was found unsatisfactory.

In contrast to the seven-membered ring diphenan (I), 1,8-naphthalan (III), phthalan (IV), and 2,5-dihydrofuran (V), which have six- or five-membered rings, failed to yield rearranged carbinols with potassium amide in liquid ammonia or in higher-boiling solvents. Naphthalan was largely recovered after treatment in liquid ammonia, and only gum was obtained after 20 hours of refluxing in tetrahydrofuran. Phthalan was largely recovered (partly as its peroxide) after treatment in liquid ammonia or in refluxing di-*n*-butyl ether (18 hours). Dihydrofuran gave polymeric material on treatment in either liquid ammonia or refluxing pentane (20 hours). The former conditions gave partly a liquid polymer which, on distillation at 150–250°, decomposed evolving ammonia.

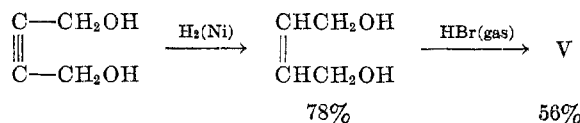


The syntheses of diphenan (I), naphthalan (III), and phthalan (IV) were effected by cyclization of the appropriate glycols, which were prepared by the reduction of the corresponding carboxylic acid or ester with lithium aluminum hydride. For example, naphthalan (III) was synthesized in good over-all yield by the cyclization of 1,8-naphthalyl alcohol (VII) obtained by the reduction of diethyl 1,8-naphthalate, which in turn was prepared from 1,8-naphthalic anhydride. Both naphthalan and the intermediate glycol appear not to have been isolated previously.

In the synthesis of phthalan (IV), contact with air should be avoided since this cyclic ether is quite susceptible to oxidation to its peroxide, although complete conversion to this product on exposure to air was realized only after several weeks. Incidentally the melting point of the peroxide obtained by us was somewhat higher than that reported recently for this product (4).



The synthesis of dihydrofuran (V) was effected by the cyclization of 2-butene-1,4-diol, which was prepared by the catalytic hydrogenation of 2-butyne-1,4-diol. The cyclization of the glycol has previously been reported by Valette (5) in connection with the preparation of 1,4-dibromo-2-butene in which ether (V) was obtained as a by-product in only 32% yield.



EXPERIMENTAL

Diphenan (I). Diphenic acid (6) (78.5 g., 0.324 mole), was introduced into a refluxing solution of 16.5 g. (0.434 mole) of lithium aluminum hydride in 1500 ml. of ether over a four-day period (Soxhlet extractor) according to the general method of Nystrom and Brown (7) for compounds difficultly soluble in ether. After decomposing the excess hydride by the cautious addition of water, the mixture was poured onto ice and excess alkali, and the ether distilled. The residue was heated briefly at the boiling point (to dissolve acidic material), cooled, and the solid glycol was separated. After recrystallization from benzene there was obtained 56.0 g. (80%) of *o,o'*-bis(hydroxymethyl)biphenyl, m.p. 110.5–111.5°.

Anal. Calc'd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59.

Found: C, 78.62; H, 6.47.

Wittig (1) prepared this product, m.p. 111–112°, by the reduction of the ether-soluble dimethyl ester.

An intimate mixture of 37.6 g. of *o,o'*-bis(hydroxymethyl)biphenyl and 108 g. of freshly fused potassium bisulfate was heated gradually with occasional shaking to 160° over a 40-minute period. On cooling, the melt was dissolved in 500 ml. of water and 200 ml. of benzene. The benzene solution was separated and passed through a short column of alumina to remove colored impurities. The solvent was removed and the solid residue was recrystallized from 70–90° ligroin to give 30.8 g. (89%) of diphenan, m.p. 71.5–72° [reported m.p. 72.5–73° (1)].

Anal. Calc'd for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.17.

Found: C, 85.39; H, 6.20.

Rearrangement of diphenan (I) to *9,10-dihydro-9-phenanthrol* (II). A solution of 19.6 g. (0.1 mole) of diphenan in 75 ml. of ether was added during 5 minutes to a stirred suspension of 0.2 mole of potassium amide (8) in 250 ml. of liquid ammonia. After one hour, the mix-

ture was neutralized with an excess of solid ammonium chloride, and the ammonia was allowed to evaporate. The mixture was dissolved in ether and water, and after drying over Drierite, the slightly colored ether solution (250 ml.) was passed through a short column of alumina. The first 25 ml. of the filtrate was evaporated to give 0.05 g. of phenanthrene, m.p. and mixture m.p. 99–100°. The remainder of the filtrate, together with ether washings, was evaporated to give 18.1 g. (92%) of cream-colored 9,10-dihydro-9-phenanthrol, melting at 82–90°, and at 105–105.5° [reported m.p. 105–105.5° (1)] after recrystallization from ether.

Phenanthrene. The crude 9,10-dihydro-9-phenanthrol (2 g.) was refluxed for one hour in 25 ml. of acetyl chloride. The solution was poured onto ice, and after hydrolysis of the acetyl chloride, the solid was separated and recrystallized from ethanol to give 1.55 g. (85%) of phenanthrene, m.p. 99.5–100°.

1,8-Naphthalyl alcohol. Naphthalic anhydride, m.p. 274–276°, was obtained by recrystallizing Eastman Practical material first from methyl benzoate, and then from acetic acid using Norit.

To a solution of 8.94 g. (0.045 mole) of 1,8-naphthalic anhydride in one liter of water containing 3.72 g. (0.090 mole) of sodium hydroxide, was added a solution of 15.35 g. (0.090 mole) of silver nitrate in 75 ml. of water. After filtering and drying overnight at 60–70° the silver salt was heated with 35 ml. of ethyl iodide in a pressure bottle at 100° for 13 hours. After cooling, the mixture was shaken with ether and filtered. The ether solution was shaken with aqueous sodium thiosulfate, dried, and the solvent removed. The residual oil was triturated with a small quantity of ligroin, giving 9.3 g. (75%) of crude crystalline diethyl 1,8-naphthalate. Larger scale runs employing variations of this procedure gave lower yields.

A solution of 24.2 g. of the crude diethyl 1,8-naphthalate in 150 ml. of ether was added to a stirred solution of 4.2 g. of lithium aluminum hydride in 700 ml. of ether, and the resulting mixture was refluxed for six hours. After destroying the excess hydride with water, the mixture was poured onto ice and hydrochloric acid. The ether layer containing suspended solid was concentrated to 200 ml., and filtered to give 14.6 g. (87%) of white, crystalline 1,8-naphthalyl alcohol, m.p. 154–154.5° after recrystallization from ethanol.

Anal. Calc'd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43.

Found: C, 76.70; H, 6.45.

Naphthalan. An intimate mixture of 14.6 g. of naphthalyl alcohol and 27.7 g. of freshly fused potassium bisulfate was heated at 120° for ten minutes and then steam-distilled. The distillate was filtered to give 10.7 g. (81%) of white, crystalline naphthalan, melting at 83.0–83.5° after recrystallization from 70–90° ligroin.

Anal. Calc'd for $C_{12}H_{10}O$: C, 84.68; H, 5.92.

Found: C, 84.30; H, 5.81.

The *picrate*, after recrystallization from ethanol, melted at 177.5–178°, [reported m.p. 173.5–175° (9)].

Anal. Calc'd for $C_{13}H_{13}N_3O_5$: N, 10.52. Found: N, 10.56.

Phthalan. Phthalyl alcohol, 103 g., prepared by the reduction of diethyl phthalate with lithium aluminum hydride, was dissolved in 150 ml. of Dowtherm at 125°, and a solution of 1 g. of *p*-toluenesulfonic acid in 15 ml. of hot Dowtherm was added. A rapid stream of air was pulled through the solution while its temperature was raised to 250°. The vapors of phthalan, Dowtherm, and water carried from the reaction mixture were condensed in an ice-cooled trap. When the distillation had ceased, the trap contents were shaken with ether, and the water was separated. The ether solution was dried and the solvent removed. The residue was distilled in an atmosphere of nitrogen through a 25-cm. column packed with glass helices to give 50.8 g. (57%) of phthalan boiling at 85° at 20 mm. [reported b.p. 106° at 36 mm. (4)]. The analytical sample was sealed rapidly under an atmosphere of nitrogen to prevent air oxidation.

Anal. Calc'd for C_8H_8O : C, 79.96; H, 6.71.

Found: C, 79.30; H, 6.60.

Samples of phthalan were allowed to stand in air in an open container. Within three to

four weeks the original liquid was converted completely to a solid. After two recrystallizations from commercial absolute alcohol, the product melted at 151–152° and analyzed for phthalan peroxide [m.p. 137.5–139.5° has been reported (4)].

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 71.10; H, 5.22.

Found: C, 71.48; H, 5.16.

2-Butene-1,4-diol. A 35% aqueous solution of 2-butyne-1,4-diol² (500 g.) was heated under a vacuum to the maximum temperature of 50° until water no longer distilled. The dark brown solid was recrystallized from 500 ml. of ether with a Soxhlet extractor. The ether was evaporated and, on trituration with an equal volume of ligroin, the residual oil gave 170 g. of pale yellow crystals, m.p. 55–56°. A solution of 144.5 g. of the purified 2-butyne-1,4-diol in 1500 ml. of commercial absolute alcohol containing 30 ml. of Raney nickel was stirred vigorously while hydrogen at slightly more than atmospheric pressure was admitted to the reaction flask. When 94% of the theoretical hydrogen had been taken up, the mixture was filtered and the ethanol was removed under reduced pressure. The residue was distilled to give 115.2 g. (78%) of 2-butene-1,4-diol, b.p. 118–120° at 4.5 mm. [reported b.p. 132° at 16 mm. (5)].

2,5-Dihydrofuran. A rapid stream of dry hydrogen bromide was passed through 128.7 g. of 2-butene-1,4-diol contained in a flask fitted with a 15-cm. Vigreux column and immersed in a bath maintained at 140–150°. The distillate containing the 2,5-dihydrofuran was collected until the sharp odor of 1,4-dibromo-2-butene was detected. The distillate was dried over two portions of solid potassium hydroxide and distilled, giving 57.4 g. (56%) of 2,5-dihydrofuran, b.p. 66–67°. After refluxing over sodium wire the product boiled at 66.5–67°, n_D^{25} 1.4289–1.4294 [reported, b.p. 67°; n_D^{18} 1.428 (5)]. A sample treated with 2,4-dinitrobenzenesulfonyl chloride according to the method of Kharasch and Buess (10), gave an adduct which melted at 160–161° after recrystallization from acetic acid.

Anal. Calc'd for $C_{10}H_8ClN_2O_5S$: C, 39.41; H, 2.98; Cl, 11.64.

Found: C, 39.41; H, 2.85; Cl, 11.41.

SUMMARY

1. Diphenan was rearranged by potassium amide in liquid ammonia to form 9,10-dihydro-9-phenanthrol which was dehydrated to give phenanthrene.
2. Unsuccessful attempts were made to effect the analogous rearrangement with 1,8-naphthalan, phthalan, and 2,5-dihydrofuran.
3. Dibenzyl ether was rearranged to form benzyl phenyl carbinol in satisfactory yield by sodium amide in liquid ammonia but not in refluxing ether.
4. New or improved methods of synthesis were developed for the cyclic ethers studied.

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² We are indebted to the General Aniline and Film Company for a generous sample of this material.