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# Polyphenylnaphthalenes. I. 1,2-Diphenylnaphthalene

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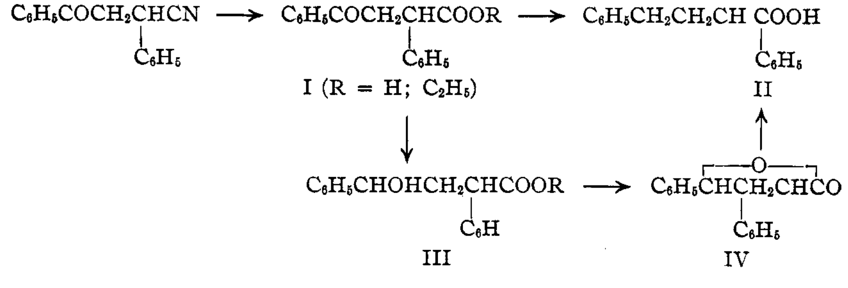
In the course of certain experiments in the polycyclic series, which will be described later on, we had to prepare a number of polyphenylnaphthalenes. The present paper deals with our experiences in the synthesis of 1,2-diphenylnaphthalene (VII).


$$C_6H_5COCH_2\underset{C_6H_5}{CH}CN \longrightarrow \underset{\text{I }(R = H;\ C_2H_5)}{C_6H_5COCH_2\underset{C_6H_5}{CH}COOR} \longrightarrow \underset{\text{II}}{C_6H_5CH_2CH_2\underset{C_6H_5}{CH}COOH}$$
$$\underset{\text{III}}{C_6H_5CHOHCH_2\underset{C_6H}{CH}COOR} \longrightarrow \underset{\text{IV}}{C_6H_5CHCH_2\underset{C_6H_5}{CH}CO}$$

This hydrocarbon has been prepared by Crawford[1] from 2-phenyl-α-tetralone (V) and phenyl magnesium bromide. The key substance in this synthesis was the α,γ-diphenylbutyric acid (II), which resulted from a Clemmensen reduction of α-phenyl-β-benzoylpropionic acid (I), in 76% yield. We met, however, with great difficulties in carrying out this reaction. Even with the modification of Martin,[2] the yield left very much to be desired. We have now found that II can be prepared in excellent yield, if the reduction process I → II is performed in two steps:

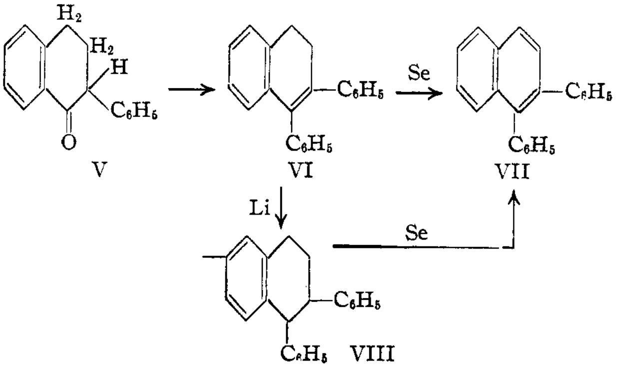
(a) α-Phenyl-β-benzoylpropionitrile is converted into the ethyl ester of I, according to Kohler.[3] The keto compound I ($R = C_2H_5$) is reduced to the γ-hydroxy ester III by means of aluminum isopropylate and III directly saponified to the lactone IV, m. p. 110°. In the saponification process, one obtains first a thick sirup, which still contains appreciable amounts of aluminum, apparently in complex binding. The complex is extremely stable, soluble in organic solvents like carbon tetrachloride, but cannot be distilled in a high vacuum, and can be decomposed only on treatment with concentrated sulfuric acid.

The same melting point as is reported above, 110°, was ascribed by Ali, *et al.*,[4] to the acid II, but apparently these workers had also the lactone IV in hand although they used the same reduction method as Crawford. This fact, therefore, can be considered as another illustration of the difficulties of Crawford's method.

(b) The lactone IV gives II in quantitative yield upon reduction with hydrogen iodide and red phosphorus.

Cyclization of II by the Friedel–Crafts reaction proved much superior to the method using sulfuric and acetic acid. We obtained a 90% yield of the tetralone V, in accordance with Newman,[5] in a high degree of purity.

By interaction of V with phenylmagnesium bromide, a non-crystallizable mixture resulted which gave the dihydronaphthalene derivative VI in about 55% yield calculated on the tetralone V. It melts at 94–95°, whereas Crawford reports 98–99° for the carbinol and 77° for VI. At present we are unable to explain this discrepancy. Addition of lithium to 1,2-diphenyl-3,4-dihydronaphthalene (VI) led to the liquid tetrahydronaphthalene derivative VIII.



VIII is more difficult to dehydrogenate to 1,2-diphenylnaphthalene (VII) than is VI, as indicated by duration and temperature of the reaction as well as yield and purity of dehydrogenated product. Therefore, it is improbable that in the reaction of VI with selenium disproportionation to VIII and VII occurs prior to the removal of the "excess" hydrogen.

## Experimental

**Ethyl α-Phenyl-β-benzoylpropionate** (I, $R = C_2H_5$).—

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[1] Crawford, THIS JOURNAL, **61**, 608 (1939).

[2] Martin, *ibid.*, **58**, 1438 (1936); see also Newman, footnote (5).

[3] Kohler, Peterson and Bickel, *ibid.*, **56**, 2000 (1934).

[4] Ali and co-workers, *J. Chem. Soc.*, 1013 (1937).

[5] Newman, THIS JOURNAL, **60**, 2947 (1938).

The crude α-phenyl-β-benzoylpropionitrile[6] was dissolved in boiling ethanol (5 parts), and treated with a stream of dry hydrogen chloride. After distilling off a maximal amount of alcohol, the residue was extracted with benzene, which left behind the dinitrile present in the crude product. The ester was then rectified, b. p. 200–205° (1 mm.). It formed a thick, yellow oil, which solidified in part on standing.

*Anal.* Calcd. for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4. Found: C, 76.2; H, 6.2.

**α,γ-Diphenyl-γ-butyrolactone** (IV).—The foregoing ester (235 g.) and aluminum isopropylate (125 g.) in isopropanol (500 cc.) were boiled for two hours. After distilling off the acetone formed and the solvent, solid sodium hydroxide (250 g.) and isopropanol (500 cc.) were added, and the mixture refluxed for two hours. After distilling off the solvent, the residue was converted into a thick paste by addition of 100 cc. of water. The paste was then poured slowly into concd. sulfuric acid while vigorously stirring, care having been taken to keep the temperature at 0°. The brown mass was then transferred into a flask connected with a reflux condenser and carbon tetrachloride (300 cc.) was added followed by small portions of water. The mixture became hot, and the boiling solvent immediately extracted the lactone formed from the water layer. After cooling, the two layers were separated. The residue of the carbon tetrachloride crystallized mostly on trituration with methanol. Sometimes, however, it was necessary to distil *in vacuo* before recrystallization; b. p. 195–198° (0.5 mm.); from isopropanol, long rods, m. p. 109–110°; yield, 95%. The lactone dissolved in boiling sodium hydroxide.

*Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.3; H, 5.9. Found: C, 80.2; H, 5.9.

If the alkaline solution of the above reduction product is acidified with dilute acid, the complex is not destroyed, but dissolves in large quantities of carbon tetrachloride. After removal of the solvent, a jelly remains, which crystallizes after treatment with ether, m. p. 190°. The material cannot be distilled.

**α,γ-Diphenylbutyric Acid** (II).—The alcohol-free lactone III (40 g.), hydriodic acid (125 cc., d. 1.7) and red phosphorus (17.5 g.) gave a vigorous reaction after short heating. When the spontaneous reaction subsided, boiling was continued for two hours. After that time, the phosphorus formed the upper layer, including all organic material. The lower layer was decanted, and the sirupy residue boiled with sodium hydroxide solution and filtered. The filtrate was acidified with dilute sulfuric acid and deposited a thick mass which solidified on standing overnight. The acid II was best purified by distillation, b. p. 190° (1 mm.), m. p. 75°; yield, 95%.

**2-Phenyl-1-keto-1,2,3,4-tetrahydronaphthalene** (V).—Cyclization of II with phosphorus pentoxide in boiling benzene failed. With a mixture of sulfuric and acetic acid, only a small amount of crystalline material was obtained. By the method of Newman[5] a 90% yield was obtained if the temperature was maintained at 0–20° throughout the Friedel–Crafts reaction (twenty hours). The crude reaction product was boiled with methanol, after which about a third of the tetralone crystallized out. The remaining oil was taken up in carbon tetrachloride and distilled; it then crystallized easily, m. p. 82°.

**1,2-Diphenyl-3,4-dihydronaphthalene** (VI).—The carbinol which resulted from V after interaction with phenylmagnesium bromide was not crystallizable and was therefore directly dehydrated with potassium bisulfate at 160°. The product was distilled, b. p. 210–215° (0.5 mm.), and recrystallized from methanol; plates, m. p. 94–95°; 11 g. of V yielded 8 g. of VI (57%).

*Anal.* Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.4; H, 6.3.

Dehydrogenation of VI with an equal weight of selenium at 280–290° for fifteen hours gave directly the crystalline 1,2-diphenylnaphthalene (VII) in 80% yield, m. p. 114° (ethanol). The picrate crystallized from ethanol in reddish needles, m. p. 148°.

*Anal.* Calcd. for $C_{28}H_{19}O_7N_3$: N, 8.2. Found: N, 7.9.

**1,2-Diphenyl-1,2,3,4-tetrahydronaphthalene** (VIII).—The dihydronaphthalene VI (4 g.) was shaken with lithium (0.5 g.) in ethereal solution for forty-eight hours. The reddish solution, after decolorization with methanol, gave an oil, b. p. 183–184° (1.5 mm.), in quantitative yield (VIII).

*Anal.* Calcd. for $C_{22}H_{20}$: C, 93.0; H, 7.0. Found: C, 92.5; H, 7.4.

VIII could be dehydrogenated with selenium only at 320°. From the reaction mixture ether extracted a thick oil, which could not be induced to crystallize and, therefore, was converted into the picrate of VII, m. p. 147–148°. Decomposition of the picrate with concd. ammonia gave the pure hydrocarbon VII in crystalline form.

## Summary

α,γ-Diphenylbutyric acid, the starting material for 1,2-diphenylnaphthalene, is prepared from α-phenyl-β-benzoylpropionic acid by a two-step reduction process, *via* the lactone of the corresponding γ-hydroxy acid.

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(6) Organic Syntheses, **X**, 80 (1930).