

none and the stable tautomer II can be converted into the same derivatives, but the acidic substance has not been reconverted into the quinone. Hydroxybenzalnaphthone (II) enters into various reactions involving a primary addition to the ends of the conjugated system. β -Naphthohydroquinone adds to give the condensation product I; an alcohol reacts to give a hydroquinone III, which is converted by air oxidation to the corresponding orthoquinone. The addition of acetic anhydride results in the formation of 1,2, α -tri-

acetoxy-4-benzyl-naphthalene, and the same product is obtained from 4-benzyl-1,2-naphthoquinone, evidently through tautomerism to II. It is suggested that a similar reaction is responsible for the abnormal acetylation of lapachol leading to the formation of a derivative of the substance characterized by Hooker as dehydro- α -lapachone (Paternò's "isolapachone").

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The Diphenylnaphthalenes¹

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There has been reported only one of the four possible diphenylnaphthalenes in which the phenyl groups are in the same ring. Franssen² reported the melting point of 1,4-diphenylnaphthalene as 308°, but it has since been shown by Weiss, Abeles and Knapp³ to melt at 135–137° and by Allen and Gilman⁴ to melt at 134–136°.

This paper reports the preparation of 1,2-, 1,3- and 2,3-diphenylnaphthalenes which were needed as reference compounds in connection with another problem. The series of reactions used in the preparation of these compounds is shown, followed by the descriptions of the procedures. The compounds whose melting points are indi-

cated in the equations are described for the first time.

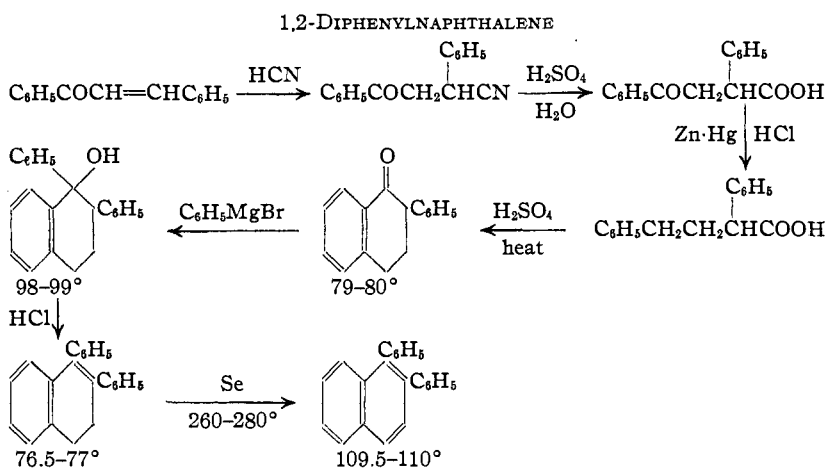
α -Phenyl- β -benzoylpropionitrile was made in 90% yields by the addition of hydrocyanic acid to benzalacetophenone.⁵

α -Phenyl- β -benzoylpropionic acid was prepared in 95% yields by the hydrolysis of the nitrile with sulfuric acid.⁶ Thirty to forty grams of the nitrile was hydrolyzed at one time.

α,γ -Diphenylbutyric acid was made by a Clemmensen reduction of the keto acid. Twenty grams of the keto acid was boiled for eighteen hours with 200 g. of amalgamated zinc and 260 cc. of concd. hydrochloric acid. The hydrochloric acid was added in several portions. Extraction of the cooled mixture with petroleum ether and evaporation of the solvent gave 14.5 g. (76%) of the saturated acid.

It melted at 75° as reported by Kohler and Kimball⁷ and not at 110° as reported by Ali, Desai, Hunter and Muhammad.⁸

1-Oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene was prepared by heating 10 g. of α,γ -diphenylbutyric acid with 42 cc. of concd. sulfuric acid and 14 cc. of glacial acetic acid on the steam-bath for one and one-half hours. The mixture was stirred mechanically. After cooling, the mixture was extracted with ether. The ether solution was then extracted with a solution of potassium hydroxide to remove unchanged acid. Evaporation of the ether solution gave



(1) Reported at the fall meeting of The American Chemical Society at Milwaukee, Wis., in September, 1938.

(2) Franssen, *Bull. soc. chim.*, **37**, 902 (1925).

(3) Weiss, Abeles and Knapp, *Monatsh.*, **61**, 162 (1932).

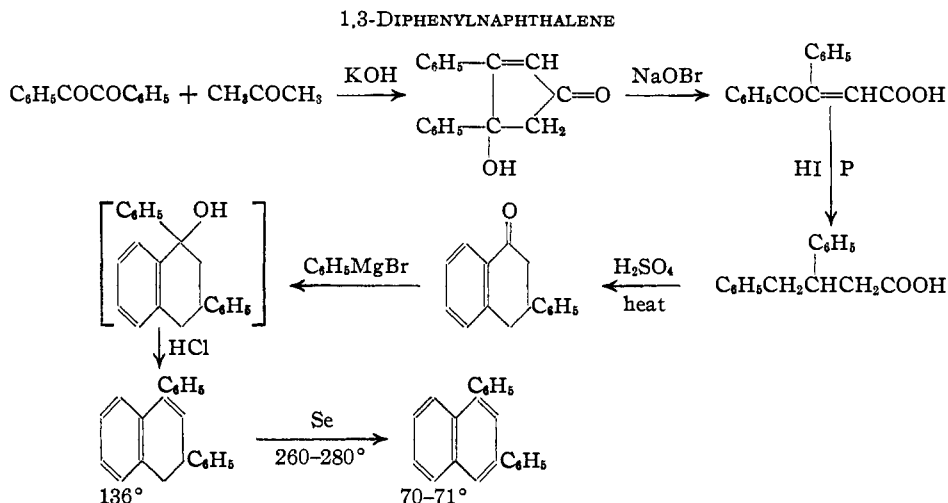
(4) Allen and Gilman, *THIS JOURNAL*, **58**, 937 (1936).

(5) *Org. Syntheses*, **10**, 80 (1930).

(6) Lapworth and Wechsler, *J. Chem. Soc.*, **97**, 42 (1910).

(7) Kohler and Kimball, *THIS JOURNAL*, **55**, 4637 (1933).

(8) Ali, Desai, Hunter and Muhammad, *J. Chem. Soc.*, 1016 (1937).



5.3 g. (57%) of 1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene. After two crystallizations from alcohol it separated in colorless leaflets melting at 79–80°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.45; H, 6.34. Found: C, 86.73; H, 6.49.

After this paper was submitted to the Journal, this compound was described by Newman [THIS JOURNAL, 60, 2949, (1938)] as melting at 76.2–77.0°.

1-Hydroxy-1,2-diphenyl-1,2,3,4-tetrahydronaphthalene was prepared by adding 0.03 mole of phenylmagnesium bromide to 2.2 g. (0.01 mole) of 1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene in ether. The ether boiled vigorously and the yellow-white precipitate first formed dissolved toward the end of the reaction. After a few minutes, the mixture was decomposed with dilute hydrochloric acid and extracted with ether. Evaporation of the solvent gave 1.6 g. (53%) of a white solid which melted at 98–99° after recrystallization from alcohol.

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}$: C, 87.96; H, 6.71. Found: C, 88.00; H, 6.84.

1,2-Diphenyl-3,4-dihydronaphthalene was obtained by heating the alcohol solution of the carbinol with a few drops of concd. hydrochloric acid. The hydrocarbon separated immediately from the alcohol, in which it was only slightly soluble, and was recrystallized from a mixture of alcohol and ethyl acetate. It separated in stout prisms melting at 76.5–77°.

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}$: C, 93.57; H, 6.42. Found: C, 93.49; H, 6.53.

1,2-Diphenyl-1,3,4-dihydronaphthalene was prepared by heating 1.2 g. of the dihydro compound with 1.5 g. of selenium for twenty-eight hours at 260–280°. After cooling, the hydrocarbon was dissolved in ether and filtered from selenium. Evaporation of the ether gave a white solid which is only slightly soluble in alcohol but very soluble in acetone, ethyl acetate and benzene. It was recrystallized from a mixture of alcohol and ethyl acetate from which it separated in clusters of needles melting at 109.5–110°.

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}$ (280.3): C, 94.25; H, 5.75. Found: C, 94.25; H, 5.90; mol. wt., 284.4.

Anhydroacetonebenzil was made in 78% yield according to the method of Japp and Lander.⁹

β -Benzoylcinnamic acid resulted in 44% yield by the oxidation of anhydroacetonebenzil.¹⁰

β,γ -Diphenylbutyric acid was obtained in 54% yield by reducing β -benzoylcinnamic acid with hydriodic acid and red phosphorus.¹¹

1-Oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene resulted when 10 g. of β,γ -diphenylbutyric acid was stirred and warmed on the steam-bath with 42 cc. of concd. sulfuric acid and 14 cc. of glacial acetic acid. The cooled mixture was poured into water and the organic material extracted with ether. Unchanged acid (about 0.1 g.) was extracted with potassium hydroxide. Evaporation of the ether solution gave 3.7 g. (40%) of the ketone melting at 65°.¹²

1,3-Diphenyl-3,4-dihydronaphthalene was prepared from 2.22 g. (0.01 mole) of 1-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene and 0.03 mole of phenylmagnesium bromide. The white precipitate first formed turned dark and partially dissolved in the excess of Grignard reagent. Ice and ammonium chloride were used to decompose the metallic compound and the solution was extracted with ether. The ether solution gave a white compound. Several solvents were tried for recrystallizing the carbinol, but were not satisfactory. When an alcohol solution of the carbinol was treated with a few drops of concd. hydrochloric acid there was an immediate precipitation of a white compound which was only slightly soluble in alcohol. Recrystallization from a mixture of alcohol and ethyl acetate gave a product melting at 136°. The yield was 2.3 g. (81%).

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}$: C, 93.57; H, 6.42. Found: C, 93.84; H, 6.57.

1,3-Diphenyl-1,2,3,4-tetrahydronaphthalene was prepared by dehydrogenating 1.4 g. of the dihydro compound by heating for twenty-four hours at 260° with 1.5 g. of selenium. The ether extract was filtered from unchanged selenium and allowed to evaporate. The resulting solid crystallized from

(9) Japp and Lander, *J. Chem. Soc.*, 71, 130 (1897).

(10) Japp and Lander, *ibid.*, 71, 132 (1897).

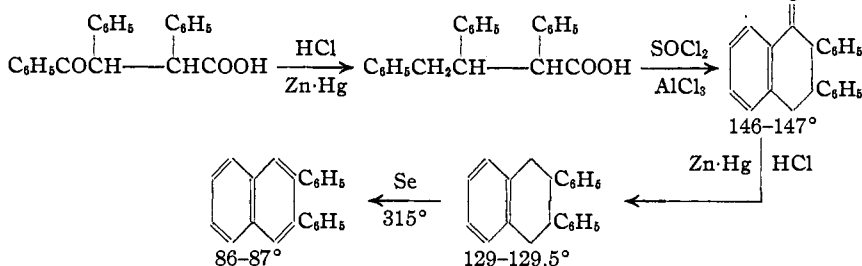
(11) Japp and Lander, *ibid.*, 71, 156 (1897).

(12) Spring, *ibid.*, 1334 (1934).

alcohol and ethyl acetate in colorless needles melting at 70–71°: yield, 0.9 g. (60%). It is only slightly soluble in alcohol but is quite soluble in acetone, ethyl acetate and benzene.

Anal. Calcd. for $C_{22}H_{18}$ (280.4): C, 94.25; H, 5.75. Found: C, 94.26; H, 5.86; mol. wt., 274.7.

2,3-DIPHENYLNAPHTHALENE



α,β -Diphenyl- β -benzoylpropionic acid was made as described previously¹³ and the lower melting racemic acid was used as it was formed in much larger quantities.

α,β,γ -Triphenylbutyric acid was prepared in 30% yields by a Clemmensen reduction of the keto acid melting at 201°. The cooled mixture was extracted with ether and the triphenylbutyric acid so obtained was recrystallized from 75% alcohol. It then melted at 153–154° and was apparently the same as the higher melting isomer obtained by de Schutzenbach.¹⁴ It was very soluble in alcohol, acetone, chloroform and ethyl acetate and insoluble in water.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.49; H, 6.43.

1-Oxo-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene was made by cyclizing α,β,γ -triphenylbutyric acid. Heating with concd. sulfuric acid and glacial acetic acid gave a very small yield (25%) of the cyclic ketone. A better yield (58%) was obtained by transforming 7.5 g. of α,β,γ -triphenylbutyric acid to the acid chloride by means of thionyl chloride. After removal of the excess thionyl chloride by suction, the acid chloride was dissolved in carbon disulfide and treated with 5 g. of anhydrous aluminum chloride. After the vigorous reaction had moderated, the mixture was heated on the steam-bath for ten minutes, cooled and decomposed with ice and concd. hydrochloric acid. The organic material was extracted with ether and the unchanged acid washed out with potassium hydroxide. The ether layer gave 3.7 g. (58%) of white solid which,

after recrystallization from ethyl acetate, melted at 146–147°. It dissolved easily in warm acetone or ethyl acetate, but only slightly in ether or alcohol.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.44; H, 6.22.

2,3-Diphenyl-1,2,3,4-tetrahydronaphthalene was prepared by a Clemmensen reduction of the ketone. One gram of the ketone was boiled for seven hours with 5 g. of amalgamated zinc, 10 cc. of alcohol, 10 cc. of concd. hydrochloric acid and 10 cc. of water. The cooled mixture was extracted with ether and the zinc washed with ethyl acetate. Evaporation of the ether gave a white solid (0.5 g., 50%) which crystallized

from alcohol and ethyl acetate in leaflets melting at 129–129.5°.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.75; H, 7.23.

2,3-Diphenylnaphthalene.—Dehydrogenation of the tetrahydro compound with sulfur at 265° gave very dark material from which there finally separated a white solid which contained sulfur. Attempts to dehydrogenate with selenium by heating for twenty-four hours at 260–280° gave only unchanged starting material. When the temperature was raised to 310–315° for twenty-four hours, most of the compound decomposed and a dark, tarry product resulted. Finally, a very small amount of crystalline material was obtained. It melted at 86–87° after several recrystallizations from alcohol and benzene. Although it was still colored slightly yellow, the analyses showed that it was 2,3-diphenylnaphthalene.

Anal. Calcd. for $C_{22}H_{18}$: C, 94.25; H, 5.75. Found: C, 94.29; H, 5.87.

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Summary

1,2-, 1,3- and 2,3-Diphenylnaphthalene and several intermediate compounds have been prepared.

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(13) Crawford, *THIS JOURNAL*, **60**, 3078 (1938).

(14) De Schutzenbach, *Ann. chim.*, **6**, 53 (1936).