light yellow crystals which melted at 94–95°. When mixed with III (m. p. 97–98°), the substance melted at 94–96°.

## Summary

1. Phenyldiphenylacetylacetylene III has been synthesized and its structure has been proved.

2. This ketone cannot be cyclized to the naphthol I, from which it follows that the ketone III is not an intermediate in the formation of the naphthol from diphenylketene and phenylacetylene.

MINNEAPOLIS, MINNESOTA

RECEIVED DECEMBER 13, 1940

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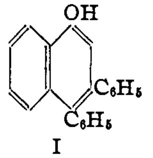
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

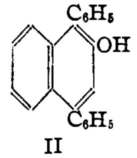
# The Reaction between Diphenylketene and Arylacetylenes. IV. Synthesis of 1,4-Diphenyl-β-naphthol[1]

BY LEE IRVIN SMITH AND HARVEY H. HOEHN[2]

In the first paper of this series[3] it was shown that diphenylketene and phenylacetylene reacted to form 3,4-diphenyl-α-naphthol, I. Before the structure of the reaction product was definitely known, however, an isomeric naphthol, 1,4-diphenyl-β-naphthol (II) had to be considered because it was possible to write a reaction between the ketene and the acetylene which led to the β (II) rather than to the α (I) naphthol.



I

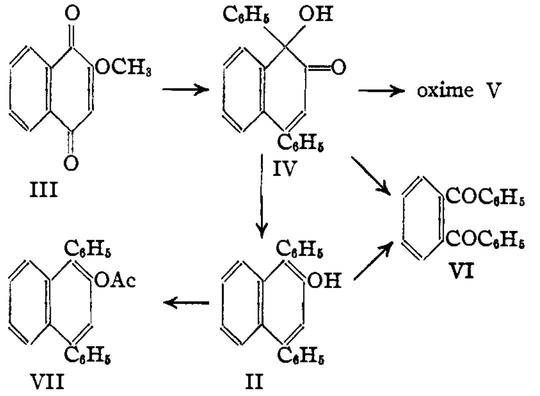


II

In order to reach a decision, 1,4-diphenyl-β-naphthol (II) was synthesized. This substance was not identical with the product of the reaction between diphenylketene and phenylacetylene, but because the synthesis of II presented some interesting features, a description of it is presented at this time.

The starting material was 2-methoxy-1,4-naphthoquinone (III). The methoxyquinone reacted with phenylmagnesium bromide to give a good yield of 1-hydroxy-2-keto-1,4-diphenyldihydronaphthalene (IV), which formed an oxime V and which, on oxidation, gave o-dibenzoylbenzene (VI).

This is an interesting reaction between a 1,4-quinone and a Grignard reagent, for the reagent adds largely 1,2 to both carbonyl groups. The simultaneous cleavage of the methoxyl group by the reagent is not surprising, since the methoxyl group of III is more like an ester group than an ether group. Thus III is converted into the hydroxyquinone by dilute alkali and, conversely, the hydroxyquinone can be converted into III by the action of methyl alcohol containing a little mineral acid.



Reduction of the ketol IV by zinc and acetic acid gave the naphthol II, which formed an acetate (VII) and which, on oxidation, gave o-dibenzoylbenzene (VI).

## Experimental Part[4]

2-Methoxy-1,4-naphthoquinone (III) (41 g.) was prepared from 1-amino-2-naphthol-4-sulfonic acid (87.5 g.) essentially as described by Fieser and Fieser.[5] The crude product was heated with dilute sodium hydroxide (2.5%, 375 cc.) until solution was complete (ten minutes). The deep red solution was filtered while hot, the cooled filtrate was acidified with dilute sulfuric acid and the precipitate (41 g.) was removed. The hydroxyquinone (35 g.) was dissolved in methanol (350 cc.), hydrochloric acid (25 cc.) was added and the mixture was refluxed for thirty minutes. 2-Methoxy-1,4-naphthoquinone (30 g.) was obtained from the cooled reaction mixture. It melted at 181–183°.

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[1] Paper III, THIS JOURNAL, 63, 1176 (1941).

[2] Abstracted from a thesis by Harvey H. Hoehn, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

[3] Smith and Hoehn, THIS JOURNAL, 61, 2619 (1939).

[4] Microanalyses by C. O. Guss.

[5] Fieser and Fieser, THIS JOURNAL, 57, 494 (1935).

**1-Hydroxy-2-keto-1,4-diphenyldihydronaphthalene (IV).**—The above methoxyquinone (30 g.) suspended in a mixture of ether (300 cc.) and benzene (100 cc.) was added slowly (one hour) and with vigorous stirring to a solution of phenylmagnesium bromide (prepared from bromobenzene (157 g.), magnesium (24 g.) and ether (600 cc.)). The mixture was refluxed and stirred for an additional ninety minutes and was then decomposed by pouring it into iced hydrochloric acid. The mixture was thoroughly extracted with ether and the ether was evaporated. The residue, a light red oil, was dissolved in acetic acid (100 cc.). The solution, when cooled, deposited a light yellow solid (20 g.), which after crystallization from acetic acid melted at 103°. This product consisted of a molecular compound of IV and acetic acid. After this substance was heated under reduced pressure in a drying pistol, it melted at 122°; the same substance, m. p. 122°, was obtained when the 103° compound was crystallized from petroleum ether–benzene.

*Anal.* Calcd. for $C_{33}H_{16}O_2$: C, 84.58; H, 5.17. Found: C, 84.67; H, 5.30.

**Oxime V.**—The ketol IV (600 mg.), hydroxylamine hydrochloride (1.5 g.), sodium hydroxide (3 cc., 20%), water (9 cc.) and ethanol (20 cc.) were mixed and refluxed for fifteen minutes. Most of the ethanol was removed by distillation and the residue, on cooling, deposited light yellow plates which melted at 193–194° with decomposition after crystallization from aqueous ethanol.

*Anal.* Calcd. for $C_{22}H_{17}O_2N$: C, 80.70; H, 5.24. Found: C, 79.62; H, 4.98.

**Oxidation of IV.**—The ketol IV (500 mg.) was refluxed for fifteen minutes with a solution of chromic acid (300 mg.) in acetic acid (10 cc.). The reaction mixture was diluted with water and extracted with ether. The ethereal solution was washed with water, then with potassium carbonate solution, and finally with water again. The ether was evaporated and the residue was taken up in a little ethanol. The cooled solution deposited *o*-dibenzoylbenzene (200 mg.) which melted at 145–146° alone or when mixed with an authentic specimen.[6]

**1,4-Diphenyl-β-naphthol (II).**—A solution of the ketol IV (3 g.) in acetic acid (30 cc.) was stirred and refluxed for six hours during which zinc dust (total 25 g.) was added in small portions from time to time. The reaction mixture was cooled and filtered and the filtrate was diluted with water. The white precipitate (2 g.) was removed and crystallized from dil. acetic acid. The white naphthol II melted at 117–118°. It gave a negative ferric chloride test, but a positive Folin test. It was soluble in Claisen alkali but precipitated when water was added to the solution.

*Anal.* Calcd. for $C_{22}H_{16}O$: C, 89.15; H, 5.45. Found: C, 88.95; H, 5.35.

**Acetate (VII).**—The naphthol (500 mg.) was acetylated by adding a drop of sulfuric acid to its solution in acetic acid (10 cc.) and heating to the boiling point. The mixture was poured into water and the product was removed, taken up in chloroform and decolorized with Norit. Most of the chloroform was replaced by ethanol. The cooled solution deposited white cubes (485 mg.) of the acetate, which melted at 157°.

*Anal.* Calcd. for $C_{24}H_{18}O_2$: C, 85.17; H, 5.37. Found: C, 85.39; H, 5.33.

**Oxidation of II.**—The naphthol II (500 mg.) was refluxed for one hour with a solution of chromic acid (680 mg.) in acetic acid (10 cc.). The reaction mixture, processed as described above for the oxidation of IV, yielded *o*-dibenzoylbenzene (100 mg.) which melted at 142–143° and did not depress the melting point of an authentic sample.

## Summary

1. A synthesis of 1,4-diphenyl-β-naphthol (II) from 2-methoxy-1,4-naphthoquinone (III) is described.

2. The addition of phenylmagnesium bromide to the methoxyquinone III is noteworthy in that the reaction consists chiefly of 1,2-addition of the reagent to both carbonyl groups of the quinone.

3. The product obtained when diphenylketene reacts with phenylacetylene is not 1,4-diphenyl-β-naphthol (II).

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RECEIVED DECEMBER 13, 1940

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(6) Prepared by Dr. H. M. Crawford.