reflux until the evolution of methyl mercaptan ceased. The picrate of the benzal hydrazone melted at 156–156.5° (dec.); orange, flat needles from 95% ethanol.

Anal. Calcd. for $C_{17}H_{19}N_7O_7$: C, 47.11; H, 4.42; N, 22.63. Found: C, 47.15; H, 4.69; N, 21.50.

Acknowledgment. We are indebted to Mr. E. M. Bens for many of the microanalyses.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Experiments with Quinone Imides. III. A Novel Synthesis of 1,4-Diphenylnaphthalene

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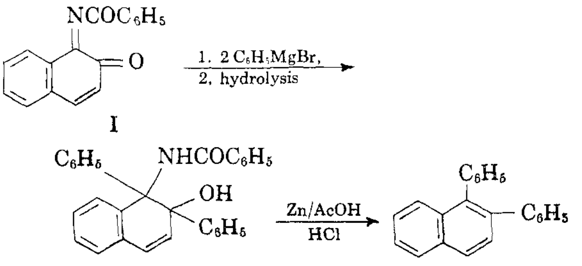
The action of phenylmagnesium bromide on 1,4-naphthoquinone dibenzimide, followed by the treatment of the hydrolyzed Grignard product with zinc dust and acetic and hydrochloric acids establishes a novel synthesis of 1,4-diphenylnaphthalene.

In Part II,[1] Mustafa and Kamel have shown that when 1,2-naphthoquinone-1-benzimide (I) is treated with an excess of phenylmagnesium bromide followed by hydrolysis, 1-benzamido-2-hydroxy-1,2-diphenyl-1,2-dihydronaphthalene (II) is obtained. Compound II, on treatment with zinc dust and acetic and hydrochloric acids gives 1,2-diphenylnaphthalene (III).

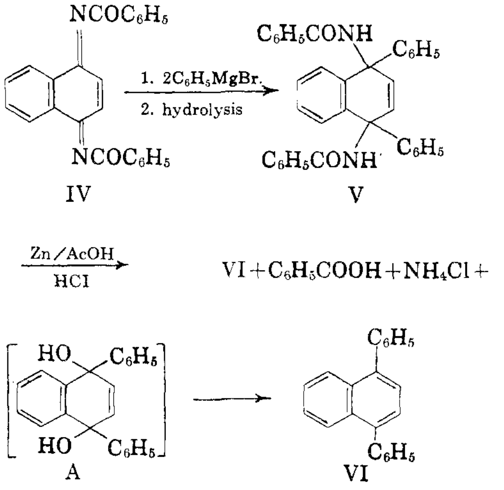


I

II III

We now have investigated the action of phenylmagnesium bromide on a *p*-quinone dibenzimide, namely 1,4-naphthoquinone dibenzimide (IV). Thus, when the pale yellow IV is treated with phenylmagnesium bromide, followed by hydrolysis, a colorless product believed to be 1,4-dibenzamido-1,4-diphenyl-1,4-dihydronaphthalene (V) is obtained.

Compound (V) gives correct analytical values: When its solution in glacial acetic acid is treated with a mixture of zinc dust and concentrated hydrochloric acid in the presence of a few drops of platinum chloride, it gives 1,4-diphenylnaphthalene (VI) in good yield, together with ammonium chloride and benzoic acid,[1] probably *via* the intermediate A. The ready transformation of the intermediate (A) to VI may be compared with the ready transformation of 9,10-dihydroxy-9-10-diphenyl-9,10-dihydroanthracene to 9,10-diphenylanthracene by the action of zinc dust and glacial acetic acid.[2]

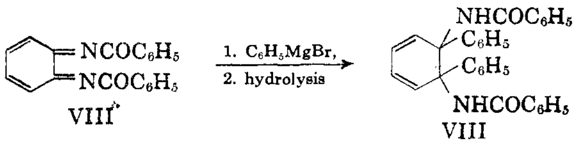


IV V

A VI

The action of phenylmagnesium bromide on IV, followed by the action of Zn/HCl/acetic acid, establishes a novel synthesis of 1,4-diphenylnaphthalene (VI). The new synthesis of VI may be considered as an extension of our previous finding for the synthesis of 1,2-diarynaphthalenes, *e.g.* II.

We also have investigated the action of phenylmagnesium bromide on *o*-quinone dibenzimides, *e.g.*, *o*-benzoquinone dibenzimide (VII). When VII is treated with phenylmagnesium bromide, followed by hydrolysis, a colorless compound, believed to have a structure like VIII and which is under further investigation, is obtained.



VIII VIII

On the other hand, when 4-methyl-*o*-benzoqui-

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[1] A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, 77, 5630 (1955).

[2] A. Haller and A. Guyot, *Compt. rend.*, 138, 1251 (1904).

none dibenzimide (IX) is treated with this reagent, only the diamide[3] (X) is obtained.

IX X

The quinone imides used in this investigation have been prepared after the procedure described by Adams and his co-workers. The dibenzimides (IV and IX) now have been prepared by the oxidation of their corresponding diamides with lead tetraacetate in chloroform[4] and in dry benzene,[5] respectively.

EXPERIMENTAL

Preparation of 1,4-naphthoquinone dibenzimide (IV). A suspension of 5.8 g. of 1,4-dibenzamidonaphthalene[6] and 7 g. of lead tetraacetate in 400 ml. of chloroform was refluxed with stirring for 1 hr. The orange suspension was then filtered hot and the lead salt precipitate washed with 50 ml. of chloroform. The filtrate and washings were concentrated in a vacuum to 15 ml. volume (water bath at 40–50°) and 170 ml. of petroleum ether (b.p. 60–80°) was added, whereby a yellow solid came down. This solid was filtered off and crystallized from ethyl acetate, m.p. 216–217°. Yield *ca.* 30%.

Anal. Calcd. for $C_{24}H_{16}N_2O_2$: C, 79.12; H, 4.39; N, 7.69. Found: C, 79.20; H, 4.23; N, 7.63.

IV is readily soluble in benzene, chloroform and ethyl acetate, but sparingly soluble in petroleum ether.

Preparation of 4-methyl-o-benzoquinone dibenzimide (IX). A suspension of 2.8 g. of 4-methyl-1,2-dibenzamidobenzene[7] and 3.7 g. of lead tetraacetate in 100 ml. of dry, thiophene-free benzene was heated under reflux for 10 hr. The reddish solution was filtered to remove the precipitated lead salt and reduced in volume to about 10 ml. Petroleum ether (b.p. 80–100°) was added and the solution was chilled in a Dry-Ice–methanol mixture. The red oil that formed by this treatment did not solidify after standing for 3 hr. The benzene-petroleum ether layer was decanted and left to evaporate slowly, whereby a yellow solid (*ca.* 0.3 g.) came down. This solid was crystallized from ethyl acetate, m.p. 191° and identified as IX.

Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.82; H, 4.87; N, 8.53. Found: C, 76.61; H, 4.55; N, 8.68.

When the red oil, obtained as above, was treated with ethyl acetate (10 ml.) a further crop of IX (0.2 g.) was obtained.

Action of phenylmagnesium bromide on 1,4-naphthoquinone dibenzimide. To a solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.5 g. of IV in 50 ml. of dry benzene. The ether was evaporated and the reaction mixture heated for 3 hr. on a steam bath. After the mixture had stood overnight at room temperature, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and extracted with ether. The ether-benzene mixture was washed twice with water (100 ml.), dried over sodium sulfate, filtered, and concentrated on a steam bath. The oil that remained was washed several times with light petroleum (*ca.* 40 ml.) until a viscous mass was obtained which was dissolved in alcohol (10 ml.). When to the alcoholic solution ether (*ca.* 30 ml.) was added and the mixture left to evaporate slowly, a colorless solid (*ca.* 0.7 g.) was formed. This material was filtered off and, after recrystallization from alcohol, gave V, m.p. 235° (clear melt).

Anal. Calcd. for $C_{36}H_{28}N_2O_2$: C, 83.07; H, 5.38; N, 5.38. Found: C, 82.82; H, 5.50; N, 5.12.

1,4-Dibenzamido-1,4-diphenyl-1,4-dihydronaphthalene (V) dissolves in alcohol, benzene, and glacial acetic acid, but sparingly in ether and light petroleum. It gives a brownish green color with concentrated sulfuric acid.

Action of phenylmagnesium bromide on o-benzoquinone dibenzimide (VII). A procedure identical to the above was used. On evaporation of the ether-benzene mixture, colorless crystals came down which, after recrystallization from a mixture of dioxane and light petroleum gave VIII, m.p. 248° (yellow-orange melt). Yield *ca.* 60%.

Anal. Calcd. for $C_{32}H_{26}N_2O_2$: C, 81.70; H, 5.53; N, 5.95. Found: C, 81.20; H, 5.28; N, 6.26.

VIII is soluble in glacial acetic acid and dioxane but sparingly soluble in petroleum ether. It gives no color with concentrated sulfuric acid.

Action of phenylmagnesium bromide on 4-methyl-o-benzoquinone dibenzimide (IX). When IX was treated with phenylmagnesium bromide in a manner identical to the above procedure, only the diamide X was obtained (m.p. and mixed m.p.[7]) in an almost quantitative yield.

Preparation of 1,4-Diphenylnaphthalene VI. To a mixture of 1 g. of V, 30 ml. of glacial acetic acid, 5 g. of zinc dust and 2 drops of (0.5%) solution of platinum chloride, was added 15 ml. of concentrated hydrochloric acid at intervals. The reaction mixture was heated on a sand bath for 15 hr. It was then cooled, decanted from the unreacted zinc and poured into 50 ml. of ice-cold water. Both the acidic mixture and the unreacted zinc dust were repeatedly extracted with ether. The combined ether extracts were washed with dilute aqueous sodium hydroxide solution (5%), then with water, and dried. The ether solution on evaporation gave colorless crystals which on repeated crystallization from alcohol gave a m.p. 136°, (undepressed when admixed with a sample of 1,4-diphenylnaphthalene prepared according to Dufraisse and Priou[8]). Yield 80%.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.29; H, 5.71. Found: C, 94.21; H, 5.65.

The alkaline solution was then acidified with hydrochloric acid and repeatedly extracted with ether; on evaporation of the ethereal solution, benzoic acid was identified (m.p. and mixed m.p.). Ammonium chloride was identified in the mother liquor.

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[3] Compare the ready reduction of quinone imides, *e.g.* 4-methyl-*o*-benzoquinone dibenzenesulfonimide, by Grignard reagent, A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, **75**, 2939 (1953).

[4] R. Adams and J. W. Way, *J. Am. Chem. Soc.*, **76**, 2763 (1954).

[5] R. Adams and J. L. Anderson, *J. Am. Chem. Soc.*, **72**, 5154 (1950).

[6] A. Wohl, *Ber.*, **36**, 4139 (1903).

[7] O. Hinsberg and L. v. Undranszky, *Ann.*, **254**, 252 (1889).

[8] C. Dufraisse and R. Priou, *Bull. soc. chim.* [5] **5**, 502 (1938).