NOTES

1,2,3,4-Tetrahydro-2-methoxynaphthalene

By Harry A. Arbit

The hydrogenation of 2-methoxynaphthalene to "*ac*-tetrahydro-β-naphthyl methyl ether" over Raney nickel in 71 to 73% has been described by Adkins and co-workers.[1] However, no physical properties of this compound other than a boiling point of 115-118° at 10 mm. pressure are given and no reason is presented for the statement that hydrogenation had taken place in the oxygenated ring.

We have carried out the hydrogenation[2] of 2-methoxynaphthalene as described by Musser and Adkins.[1] The product (58% yield) was a water-white liquid with a sweet odor, b. p. 113-115° (9 mm.), n^{25}_{D} 1.5293. In order to obtain clear evidence that the methoxyl group was on the reduced rather than on the aromatic ring, the following experiment was carried out. Two grams of the liquid was refluxed for ten minutes with 10 ml. of hydriodic acid (sp. gr. 1.7). Methyl iodide was evolved and the product obtained (b. p. 120° (10 mm.), n^{25}_{D} 1.5635) was insoluble in 10% sodium hydroxide and gave a positive qualitative test for iodine after sodium fusion. It was therefore 1,2,3,4-tetrahydro-2-iodonaphthalene, formed by action of the hydriodic acid on the secondary alcohol, *ac*-tetrahydro-β-naphthol, after demethylation of the original compound. This same iodide was obtained when a known sample of *ac*-tetrahydro-β-naphthol[3,4] was similarly treated with hydriodic acid.

The compound formed by the hydrogenation of 2-methoxynaphthalene is thus shown to be 1,2,3,4-tetrahydro-2-methoxynaphthalene. The latter has been obtained by v. Braun and Weissbach[5] by the hydrogenation of 3,4-dihydro-2-methoxynaphthalene. These authors give the boiling point of the compound as 123-124° (16 mm.), and mention its pleasant odor.

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[1] Van Duzee and Adkins, This Journal, **57**, 147 (1935); Musser and Adkins, *ibid.*, **60**, 664 (1938).

[2] The hydrogenation was carried out by Mr. W. M. Selby.

[3] Bamberger, *Ber.*, **23**, 197 (1890).

[4] Brochet and Cornubert, *Bull. soc. chim.*, [4] **31**, 1280 (1922).

[5] v. Braun and Weissbach, *Ber.*, **63**, 3052 (1930).

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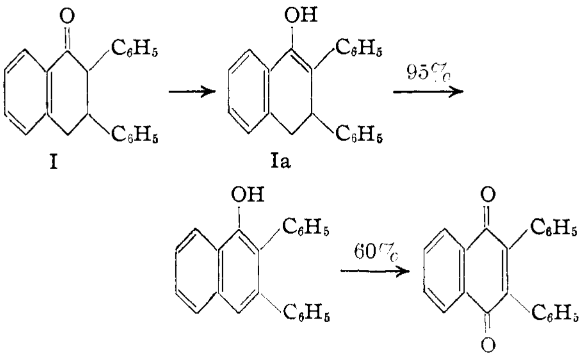
A Simple Route to 2,3-Diphenyl-1,4-naphthoquinone

By Felix Bergmann and Jacob Szmuszkovic

Crawford and Nelson[1] recently described an improved method for the conversion of 2,3-diphenyl-1-keto-1,2,3,4-tetrahydronaphthalene (I) into 2,3-diphenyl-1,4-naphthoquinone (III) in an over-all yield of 30%, using a four-step process. During our studies on polyphenylnaphthalenes[2] we observed that the ketone I shows a pronounced tendency to enolize to Ia. It seemed, therefore, possible that its direct dehydrogenation would lead to 2,3-diphenyl-1-naphthol (II). This is indeed the case. Heating of I with one equivalent of sulfur at 250-300° gives a nearly quantitative yield of the naphthol (II), which can be oxidized to the quinone (III) in about 60% yield.

Direct dehydrogenation of cyclic ketones to phenols has first been described by Darzens and Lévy.[3] The method was applied in a number of cases, using either sulfur or selenium,[4] but the yields are usually low. It is thus apparent that the enhanced enolizability of our ketone (I) has a favorable effect on the dehydrogenation to the corresponding naphthol (II), and one may presume that in every case the process consists essentially in the aromatization of an intermediate dihydronaphthalene derivative (such as Ia).



In this connection, it is of interest that catalytic dehydrogenation of cyclic ketones by means of palladium has been reported to give satisfactory yields (60-75%) of the corresponding phenols, especially if carried out in a solvent by prolonged heating.[5]

Experimental

2,3-Diphenyl-1-naphthol (II).—2,3-Diphenyl-1-keto-1,2,3,4-tetrahydronaphthalene (4.5 g.) and sulfur (530 mg.) were heated in a Pyrex tube. Reaction started at 250°, and this temperature was maintained for ten minutes and then raised slowly to 300° during thirty minutes. The black mass was distilled in a tube at 175-240° (0.6 mm.). The brown oil so obtained solidifies immediately; upon trituration with acetic acid, the substances showed a m. p. of 123-124°; yield, 4.3 g. The substance crystallized from acetic acid or petroleum ether (130°) in colorless plates, of m. p. 127-128°.[6]

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.1; H, 5.4. Found: C, 88.9; H, 5.4.

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[1] Crawford and Nelson, This Journal, **68**, 134 (1946).

[2] F. Bergmann, Schapiro and Eschinazi, *ibid.*, **64**, 559 (1942).

[3] Darzens and Lévy, *Compt. rend.*, **194**, 181 (1932).

[4] (a) Cook and Hewett, *J. Chem. Soc.*, 403 (1933); (b) Fieser, Hershberg and Newman, This Journal, **57**, 1509 (1935); (c) Peak and Robinson, *J. Chem. Soc.*, 759 (1936); (d) Ruzicka, *Helv. Chim. Acta*, **19**, 419 (1936).

[5] (a) Mosettig and Duvall, This Journal, **59**, 367 (1937); (b) Wilds and Shunk, *ibid.*, **65**, 469 (1943); Cook and Schoental, *J. Chem. Soc.*, 288 (1945).

[6] Weiss and Sonnenschein, *Ber.*, **58**, 1043 (1925), report a m. p. of 128-131°.

The picrate crystallized from ethanol in orange-red, flat rods of m. p. 127–128°.

Anal. Calcd. for $C_{28}H_{19}O_8N_3$: C, 64.0; H, 3.6. Found: C, 64.4; H, 3.9.

2,3-Diphenyl-1,4-naphthoquinone (III).—The naphthol II (2 g.) was dissolved in acetic acid (50 cc.) and, after addition of potassium dichromate (2 g.) in acetic acid (30 cc.), heated to boiling for two minutes. Upon pouring onto ice, a yellow precipitate (1.7 g.) was obtained. It crystallized from ethanol in yellow prisms of m. p. 135–136°. An additional recrystallization from acetic acid raised the m. p. to 140–141°, as reported in the literature.[6] The yield of pure product was 1.2 g. (60%).

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.1; H, 4.5. Found: C, 85.2; H, 4.7.

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The Resistance to Hydrogenation of β-Stenols in Ethyl Acetate with Adams Platinum Oxide Catalyst

BY SEYMOUR BERNSTEIN AND LOUIS DORFMAN

It is known that dehydroergostenol on hydrogenation with either platinum oxide in glacial acetic acid[1] or with palladium in ethyl acetate[2] affords α-ergostenol and not δ-ergostenol since the unhydrogenated double bond migrates to the α-position. It was therefore surprising to find that dehydroergostenol was not hydrogenated with platinum oxide catalyst in ethyl acetate and the starting material was recovered unchanged. Likewise β-ergostenol could not be hydrogenated under these conditions.

This hitherto unsuspected fact that β-stenols are resistant to hydrogenation with platinum oxide in ethyl acetate should prove useful in future synthetic and structural work in the steroid field, *e. g.*, in the cardiac aglucons.

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[1] Morrison and Simpson, *J. Chem. Soc.*, 1710 (1932).

[2] Windaus and Lüttringhaus, *Ann.*, **481**, 119 (1930).

[3] Original manuscript received September 19, 1945.

Some Substituted Acetophenones[1]

BY E. CAMPAIGNE AND WM. BRADLEY REID, JR.

Ortho- and *meta*-methyl- and *ortho-* and *meta*-phenylacetophenones, required in another investigation, were prepared from acetic anhydride by the low temperature Grignard procedure of Newman and Booth.[2] The required Grignard reagent and yield of the corresponding methyl ketones were as follows: *o*-tolylmagnesium bromide, 48.2%; *m*-tolylmagnesium bromide, 46.4%; *o*-xenylmagnesium iodide, 61.8%; *m*-xenylmagnesium iodide, 26.8%.

The biphenyl compounds, being new, were characterized by means of their crystalline semicarbazones and 2,4-dinitrophenylhydrazones.

Experimental

***o*-Phenylacetophenone.**—2-Iodobiphenyl was produced in 82.7% yield by the toluene extraction of a mixture obtained by treating a diazotized solution of 2-aminobiphenyl (Monsanto Chemical Company) with excess potassium iodide solution. The 2-iodobiphenyl was converted to the Grignard reagent and treated with acetic anhydride, yielding *o*-phenylacetophenone as a yellow oil, b. p. 104–105° at 1 mm. This oil yielded a semicarbazone in white plates, melting at 197°.

Anal.[3] Calcd. for $C_{15}H_{15}N_3O$: N, 16.59. Found: N, 16.67.

A 2,4-dinitrophenylhydrazone was also prepared, and obtained in light orange plates, melting at 169–170°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: N, 14.88. Found: N, 14.83.

3-Iodobiphenyl.—Using the method of Elks, Haworth and Hey,[4] *m*-nitroaniline was converted to 3-nitrobiphenyl in 43% yield. This nitro-compound, which melted at 59–61°, was reduced to the amine by hydrogenation over Adams platinum oxide catalyst in portions in 98.5% yield. The 3-aminobiphenyl, after distillation at 177–178° at 18 mm. pressure, solidified to a white solid melting at 31–31.5°. A solution of 53 g. (0.314 mole) of 3-aminobiphenyl in 500 ml. of 1.3 *M* sulfuric acid was diazotized with a solution of 22.5 g. (0.326 mole) of sodium nitrite in 50 ml. of water. The solid yellow diazo salt that formed was stirred vigorously in 500 ml. of toluene while a solution of 100.5 g. (0.628 mole) of potassium iodide in 250 ml. of water was added over a period of thirty minutes. The temperature of the reaction was maintained at +5° during the addition. The resulting red complex slowly decomposed at room temperature, and the black toluene layer that separated after several hours was dried and distilled at reduced pressure. The fraction which boiled at 145–155° at less than 1 mm. was redistilled at this pressure, and 3-iodobiphenyl was collected as a yellow oil, boiling at 149–152°. The yield was 42 g. or 48% of theoretical.

Anal. Calcd. for $C_{12}H_9I$: I, 45.42. Found: I, 45.69.

***m*-Phenylacetophenone.**—The Grignard reagent was prepared from 3-iodobiphenyl and converted to *m*-phenylacetophenone by treatment with acetic anhydride. The ketone was obtained as a light yellow oil boiling at 148–151° at less than 1 mm. pressure. It readily formed a semicarbazone which was obtained as white plates, melting at 222–223°.

Anal. Calcd. for $C_{15}H_{15}N_3O$: N, 16.59. Found: N, 16.47.

The 2,4-dinitrophenylhydrazone was also obtained as orange needles, m. p. 191–192°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: N, 14.88. Found: N, 14.68.

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[1] Abstracted from a part of the thesis submitted by Wm. Bradley Reid, Jr., to the faculty of the Graduate School in partial fulfillment of the requirements for the Degree, Doctor of Philosophy, in the Department of Chemistry, Indiana University.

[2] Newman and Booth, THIS JOURNAL, **67**, 154 (1945).

[3] All analyses are by Mrs. W. B. Reid, Jr., of this Laboratory.

[4] Elks, Haworth and Hey, *J. Chem. Soc.*, 1285 (1940).

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A Simple Purification Procedure for DDT[1]

BY KATHRYN H. COOK AND WALTER A. COOK

A survey of the literature on the new insecticide popularly known as DDT, discloses the fact

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[1] Presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, April 11, 1946.