[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

2,3-Diphenyl-1,4-naphthoquinone[1]

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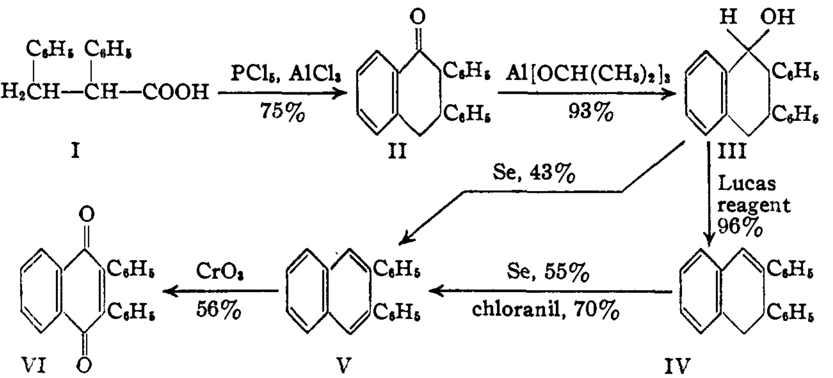
Two methods of preparing 2,3-diphenyl-1,4-naphthoquinone have been described[3,4] but all of our efforts to repeat these preparations have been unsuccessful. It seemed probable that the oxidation of the corresponding hydrocarbon would lead to the formation of the quinone. 2,3-Diphenylnaphthalene had been prepared previously,[5] but the yields were so poor that another route was sought.

The successful synthesis was as follows



Investigation of α,β,γ-triphenylbutyric acid[6] showed that cyclization of any of the three forms of the acid resulted in the formation of 2,3-diphenyltetralone-1 (II). Since the 157° acid was the most stable of the three, it was used in the preparation of the tetralone. The yields of tetralone were much better when phosphorus pentachloride was used (75%) than when thionyl chloride was used (46%) in the preparation of the acid chloride for the Friedel–Crafts reaction. Reduction of the tetralone to the corresponding secondary alcohol (III) was carried out according to the method of Lund[7] and gave average yields of 93%. The dehydration of the alcohol (III) to the hydrocarbon (IV), accomplished by refluxing a benzene solution with Lucas reagent, gave average yields of 96%. The dehydrogenation of IV to 2,3-diphenylnaphthalene was brought about either by heating the hydrocarbon with selenium (yield 50%) or by refluxing it in xylene with chloranil[8] (yield 70%).

The yield of 2,3-diphenylnaphthalene from the tetralone by this method (62%) was much better than that obtained by a Clemmensen reduction followed by selenium dehydrogenation[5] (9%).

Dehydration and dehydrogenation could be carried out in one step by heating the alcohol (III) with selenium. The yield in this case was 43% as compared to 53% when the steps were carried out consecutively.

Oxidation of the aromatic hydrocarbon (V) by chromium trioxide gave a 56% yield of 2,3-diphenyl-1,4-naphthoquinone (VI).

Experimental

Preparation of α,β,γ-Triphenylbutyric Acid (I).—This acid was prepared by the vigorous hydrolysis of both of the corresponding nitriles, using the procedure described as "Method 2" in an earlier publication.[6]

Preparation of 2,3-Diphenyltetralone-1 (II).—This compound was obtained in 75% yields by a modification of the method described by Newman.[9] α,β,γ-Triphenylbutyric acid (158.2 g., 0.5 mole) and phosphorus pentachloride (109.2 g., 0.5 mole) were dissolved in 300 ml. of benzene and refluxed for three hours. After removing part of the benzene on the steam-bath at atmospheric pressure, the phosphorus oxychloride and the rest of the benzene were removed under reduced pressure. The acid chloride was transferred to a three-necked flask carrying a condenser and a stirrer. After adding 400 ml. of thiophene-free benzene, the mixture was cooled in an ice-bath, the stirrer started, and anhydrous aluminum chloride (73.4 g., 0.55 mole) added over a period of thirty minutes. A chartreuse precipitate separated after about three-fourths of the aluminum chloride had been added. The mixture was allowed to stand overnight at room temperature, then poured onto ice and hydrochloric acid. The layers were separated and the water layer extracted once with benzene. The combined benzene layers were washed three times with 100 ml. of 10% sodium hydroxide to remove hydrochloric acid and traces of the unchanged starting material. After about half of the benzene was removed by distillation, cooling of the residue caused the separation of 84 g. of pure tetralone which, after washing with 95% ethyl alcohol, melted at 146–147°. A second crop (40 g.) was obtained later and was recrystallized from 95% ethyl alcohol. The total yield was 124 g., 83%. Refluxing for one hour instead of standing overnight reduced the yield to about 70%. When thionyl chloride was used instead of phosphorus pentachloride the yield was only 50%.

Preparation of 1-Hydroxy-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene (III).—This compound, which had not been reported before, was obtained by a modification of the method used by Lund[7] for preparing similar compounds. The solution of aluminum isopropylate in isopropyl alcohol was not used for three months and solid crystallized on the walls of the flask. This solid was re-

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[3] Weiss and Bloch, *Monatsh.*, **63**, 39 (1933); Weiss and Sonnenschein, *Ber.*, **58**, 1043 (1925).

[4] Kvalnes, THIS JOURNAL, **56**, 2478 (1934).

[5] Crawford, *ibid.*, **61**, 608 (1939).

[6] Crawford, Davidson and Plunkett, *ibid.*, **66**, 2010 (1944).

[7] Lund, *Ber.*, **70**, 1520 (1937).

[8] Arnold, Collins and Zenk, THIS JOURNAL, **62**, 983 (1940).

[9] Newman, *ibid.*, **62**, 870 (1940).

moved, weighed quickly and used in the reduction of the tetralone. 2,3-Diphenyltetralone-1 (59.6 g., 0.2 mole), aluminum isopropylate (40.8 g., 0.2 mole) and isopropyl alcohol (500 ml.) were placed in a 1000-ml. flask fitted with a Widmer column. This mixture was heated very gently until 20 drops of the distillate gave no precipitate with 5 ml. of the test solution (1 g. of 2,4-dinitrophenylhydrazine in 1000 ml. of 2 *N* hydrochloric acid). This required about thirteen hours, and during this time 190 ml. of distillate was collected. The alcohol was removed on the steam-bath under diminished pressure and the solid residue was treated with 800 ml. of water and 12 ml. of concentrated sulfuric acid. After standing for one-half hour the solid was filtered off, washed with water and crystallized from a mixture of ethyl alcohol and ethyl acetate. The average yield was 93% of the theoretical. 1-Hydroxy-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene is a white solid which melts at 139.5–140.5°. It is very soluble in acetone, ethyl acetate and benzene, somewhat soluble in ethyl alcohol and only slightly soluble in petroleum ether.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.85, 87.64; H, 6.99, 6.98.

Preparation of 2,3-Diphenyl-3,4-dihydronaphthalene (IV).—Various methods of dehydrating the alcohol III were tried and the following procedure gave the best results. 1-Hydroxy-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene (60 g., 0.2 mole) was refluxed on the steam-bath for two hours with 200 ml. of Lucas reagent[10] and 400 ml. of benzene. After cooling, the layers were separated and the benzene layer washed with water, sodium bicarbonate solution and finally with water. About 300 ml. of the benzene was distilled off and 150 ml. of 95% ethyl alcohol was added to the residue. The hydrocarbon (45.5 g.) precipitated at once. Later crops yielded an additional 9.3 g. The total yield was 54.8 g., 96%. After one recrystallization from benzene and alcohol it melted at 119.5–120.5°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.52, 93.34; H, 6.61, 6.75.

Preparation of 2,3-Diphenylnaphthalene (V).—An earlier preparation of this hydrocarbon from 2,3-diphenyl-1,2,3,4-tetrahydronaphthalene[5] by dehydrogenation with selenium resulted in extremely small yields of a yellow solid melting 86–87°. The yield was much better (55%) when 2 g. of IV was heated with 2.5 g. of selenium for twenty-seven hours at 260–280°. The cold mixture was treated with ether, filtered from selenium and the solvent evaporated. The hydrocarbon was crystallized from 95% ethyl alcohol using Norite to remove colored materials. The resulting crystals were long, flexible, pure white, needles which melted at 92–93°. The best solvent for recrystallization is ethyl alcohol, for it is extremely soluble in ethyl acetate and in benzene.

The dehydrogenation could also be accomplished by the method described by Arnold.[8] The yields were higher (70%) and the material was much more easily purified. 2,3-Diphenyl-3,4-dihydronaphthalene (28.2 g., 0.1 mole) and chloranil (36.9 g., 0.15 mole) were refluxed for seven hours in 150 ml. of xylene. After standing overnight, the solution was diluted with an equal volume of petroleum ether, cooled, and a large amount of tan solid filtered off. The solution was extracted several times with 4% potassium hydroxide solution to remove the small amount of tetrachlorohydroquinone still in solution. After removing most of the petroleum ether and xylene under reduced pressure on the steam-bath, addition of more petroleum ether caused the separation of solid which was recrystallized from 95% ethyl alcohol. This gave 2.7 g. of recovered starting material and 5.7 g. of 2,3-diphenylnaphthalene. The tan solid filtered from the original reaction mixture and that recovered from the potassium hydroxide solution by acidifying with hydrochloric acid weighed considerably more than the calculated amount of the hydroquinone. This solid was treated with 150 ml. of ethyl acetate (in which the hydrocarbon was known to be very soluble) and about half of it dissolved. About 75 ml. of benzene was added to the filtered solution and the hydroquinone was extracted with potassium hydroxide solution. The ethyl acetate–benzene solution was evaporated to a small volume and diluted with 100 ml. of 95% ethyl alcohol. Cooling this solution gave an additional 13.0 g. of 2,3-diphenylnaphthalene. The total yield was 18.7 g., 70%.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.23, 94.41; H, 6.03, 6.07.

Preparation of 2,3-Diphenyl-1,4-naphthoquinone (VI).—Oxidation of the hydrocarbon V to the quinone was carried out in the usual manner. 2,3-Diphenylnaphthalene (4.2 g., 0.015 mole) was suspended in 60 ml. of glacial acetic acid and the oxidizing mixture, 7.5 g. of chromium trioxide in 6 ml. of water and 6 ml. of glacial acetic acid, was added slowly from a dropping funnel. The mixture gradually warmed up and was kept below 60° by external cooling. After all of the chromium trioxide had been added and the temperature began to drop, the mixture was heated on the steam-bath for one hour, cooled and poured into 200 ml. of ice and water. Recrystallization of the resulting yellow solid from methyl alcohol gave 2.3 g., 50%, of bright yellow needles melting 138–139°. In previous preparations this quinone was described as melting at 136–139°,[3] 140–142°[8] and 135–136°.[4]

Summary

An improved method of making 2,3-diphenylnaphthalene from 2,3-diphenyltetralone-1 is described, the yield having been increased from about 5 to 62%.

Two new compounds, 1-hydroxy-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene and 2,3-diphenyl-3,4-dihydronaphthalene, are described.

2,3-Diphenyl-1,4-naphthoquinone is prepared in a new way—the oxidation of the corresponding aromatic hydrocarbon.

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(10) Lucas, THIS JOURNAL, 52, 803 (1930).