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

The Reaction between 2-Methyl-1,4-naphthoquinone and Phenylmagnesium Bromide[1]

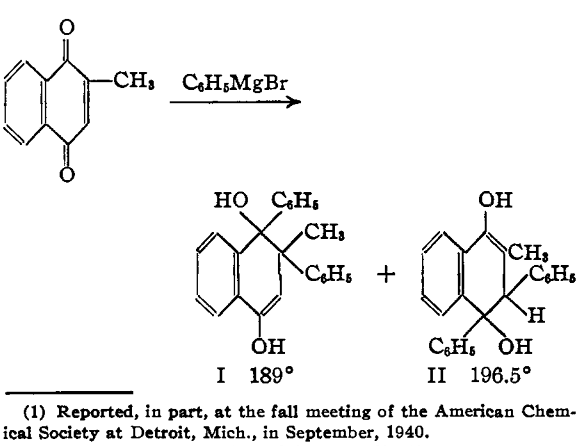
BY H. MARJORIE CRAWFORD

The reactions of phenylmagnesium bromide with 1,4-naphthoquinone[2,3] and with 2,3-dimethyl-1,4-naphthoquinone[4] have already been studied. This study of the reaction between phenylmagnesium bromide and 2-methyl-1,4-naphthoquinone was undertaken to complete the series, and to determine whether or not the resulting compounds would show Vitamin K activity.

Assays of three of these compounds (II, III and IV) by Dr. E. A. Doisy showed them to be inactive in a dosage of five milligrams, while 2-methyl-1,4-naphthoquinone has a potency of 2000 units per milligram.

The behavior of this quinone is more like that of the dimethyl compound, giving oils and several solid products, than like that of the unsubstituted naphthoquinone, which gave tars, colored amorphous products and only one crystalline compound. As in the case of the dimethyl quinone, the amount of crystalline material which could be isolated was small. It varied from 1 to 12% in different reactions and the total yield of solids from twenty reactions accounted for only 6% of the starting material. The main product was a thick, dark oil from which small amounts of solid continue to separate.

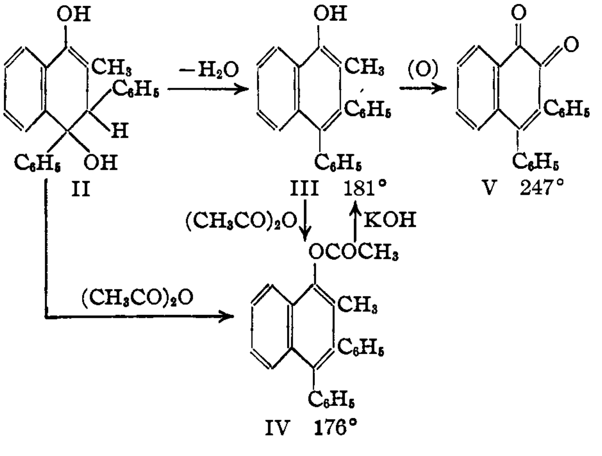
Two white, crystalline products, I and II, have been identified, both resulting from the 1,2- and 1,4-addition of two molecules of phenylmagnesium bromide to one molecule of the quinone.



I 189° II 196.5°

I was obtained in extremely small amounts after most of the II had separated. II was the main solid product in twenty of the twenty-one reactions carried out, regardless of the proportions of the reactants or of the method of carrying out the reaction. The oil from one run, which had given only a 2% yield of II, was acetylated and enough of the acetate IV was recovered to show that at least 27% of II had been formed even though only a small part of it could be separated from the oily mixture. In the one reaction in which II was not isolated, a few tenths of a gram of white solid VI, melting at 218–220°, was obtained. The analyses of this substance did not correspond to the theory for either a mono- or a di-addition product. I and II failed to give oximes, so have been written in the enol form. On oxidation, I gave *o*-benzoylbenzoic acid and acetophenone while II gave *o*-benzoylbenzoic acid, benzoic acid and a white compound VII, melting at 243–244°, for which no structure can be proposed at the present time.

II lost water readily and underwent the following series of reactions



IV was oxidized to *o*-benzoylbenzoic acid and a white compound VII. III was oxidized to *o*-benzoylbenzoic acid and V, which is already known.[3] The identity of this brilliant scarlet ortho quinone was established by the fact that it was also obtained by the oxidation of 1,2-diphenylnaphthalene and that it underwent reductive acetylation to give a diacetate. A mixed melting point of

---

[1] Reported, in part, at the fall meeting of the American Chemical Society at Detroit, Mich., in September, 1940.

[2] Franssen, *Bull. soc. chim.*, [4] **37**, 902 (1925).

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

[4] Crawford, *ibid.*, **57**, 2000 (1935); **61**, 3310 (1939).

this quinone with a sample kindly supplied by Dr. L. I. Smith showed no depression.

The reaction of 3-methyl-1,4-naphthoquinone with phenyllithium resulted in a clear, brown oil which has become rigid without the separation of any solid.

Experimental

All combustions were carried out using the semi-micro method of Lauer and Dobrovolny.[5]

Preparation of 2-Methyl-1,4-naphthoquinone.—The quinone was prepared in 29% yield according to the direction of Fieser.[6]

The Reaction between 2-Methyl-1,4-naphthoquinone and Phenylmagnesium Bromide.—As in other studies of this kind,[4,7] the reactions were carried out varying both the proportions of phenylmagnesium bromide to quinone and the method of addition to see whether these variations affected the nature and yield of the products. Phenylmagnesium bromide was made up in quantities of one mole or more, and aliquot parts were used for reactions with the quinone. One-tenth of a mole of quinone in 300 cc. of ether was added, with shaking, to 0.1, 0.2 and 0.3 mole of phenylmagnesium bromide, and 0.1, 0.2 and 0.3 mole of the Grignard reagent was added, with shaking, to 0.1 mole of the quinone in 300 cc. of ether. A vigorous reaction occurred in all cases, and a bright blue-green precipitate was formed. The precipitate dissolved in an excess of the Grignard reagent to give a brownish oily solid. In six reactions, the mixture was filtered after standing for twenty-four hours, and the solid and the ether solution worked up separately. The ether solutions were decomposed with ice and ammonium chloride, the ether layers dried and evaporated. The ether solutions were clear yellow and contained only the quinone and diphenyl. The solids were decomposed with ice and ammonium chloride and extracted with ether. A small amount of dilute sulfuric acid had to be added to bring about the separation of the layers. These ether solutions were then dried over anhydrous sodium sulfate, evaporated to about 75 cc. and allowed to stand. The solutions were dark brown to black. After several hours solid slowly separated, was filtered off, washed with diisopropyl ether and finally recrystallized from suitable solvents. The solids were compounds I and II. In later reactions, the whole reaction mixture was worked up without separating the ether and the solid magnesium compound. The yields of II varied from 0–12.2%, the average being 6%. The best results (5–12.2%) were obtained by adding one mole of quinone in 300 cc. of ether to 0.3 mole of phenylmagnesium bromide in ether. In one case, an oil, from which very little II could be isolated, was acetylated and gave the acetate IV in 25% yield.

In two cases an excess of acetyl chloride was added to the magnesium complex after it had stood for twenty-four hours. It reacted vigorously, and after standing for two hours longer these mixtures were worked up as described above. The acetate IV was obtained in 20% yields.

Phenyllithium was made from 0.3 mole of bromobenzene and 0.6 g. atom of lithium in 200 cc. of ether. Stirring and heating were continued for forty minutes, then 0.1 mole of 2-methyl-1,4-naphthoquinone in 400 cc. of ether was added. The green precipitate first formed dissolved at once. After the addition of water and dilute sulfuric acid, the dried ether solution was allowed to evaporate. It changed from a pale yellow solution to a thick red oil without the separation of any solid material after eight months.

2 - Methyl - 1,2 - diphenyl - 1,4 - dioxydihydronaphthalene, I, m. p. 189–190°.—This compound was obtained in very small amounts (2.5 g. from 360 g. of quinone). It is slightly more soluble than II, but can be separated from II only by a tedious process of growing the two kinds of crystals slowly and separating them by hand under a lens. I crystallizes in square, colorless, transparent plates. It is very soluble in acetone, fairly soluble in benzene, chloroform and ethyl acetate and slightly soluble in alcohol. The best solvent for recrystallization was a mixture of ethyl acetate and alcohol.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.24, 83.78; H, 6.21, 6.19.

An attempt to make the oxime by the method described by Smith and Hoehn[8] resulted in the recovery of the unchanged starting material.

Oxidation.—One gram of I was refluxed for four hours with 3 g. of potassium dichromate and 20 cc. of glacial acetic acid. The mixture was cooled, poured into water and most of the acid neutralized with sodium carbonate. The odor of acetophenone was very obvious. The organic material was extracted with ether and this ether solution extracted four times with 25 cc. of 10% sodium hydroxide. After working up in the usual way, the sodium hydroxide layer gave 0.2 g. of *o*-benzoylbenzoic acid which was identified by a mixed melting point with a known sample. The ether layer was dried, filtered and treated with 1 g. of semicarbazide hydrochloride, 1 g. of sodium acetate, 6 cc. of water and 10 cc. of alcohol. After this mixture was evaporated to a small volume and allowed to stand, it gave 0.25 g. of solid, m. p. 195–198°. A mixed melting point of this solid with a known sample of the semicarbazone of acetophenone showed no depression.

3 - Methyl - 1,2 - diphenyl - 1,4 - dioxydihydronaphthalene, II, m. p. 196.5–197°.—This compound was the chief solid product isolated from all twenty of the original reactions. It crystallized in stout prisms from a mixture of alcohol and ethyl acetate. It was very soluble in acetone, fairly soluble in benzene, chloroform and ethyl acetate and slightly soluble in alcohol.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.21, 83.87; H, 6.14, 6.22.

An attempt to make the oxime gave only unchanged starting material.

Dehydration.—Boiling with a trace of iodine in glacial acetic acid[4] and with concd. sulfuric acid in glacial acetic acid[8] resulted in incomplete dehydration and it was almost impossible to purify the resulting naphthol. Boiling with Lucas' reagent in benzene gave good yields of the naphthol III (details are given below).

Oxidation.—Two grams of II was boiled for five hours with 6 g. of potassium dichromate and 60 cc. of glacial

---

(5) Lauer and Dobrovolny, *Mikrochem.*, Pregl Festschr., 243 (1929).

(6) Fieser, THIS JOURNAL, 61, 3218 (1939).

(7) Smith and Crawford, *ibid.*, 50, 869 (1928).

acetic acid. The mixture was poured on ice, most of the acid neutralized with sodium carbonate and the organic material extracted with benzene. This benzene solution was then extracted four times with 25 cc. of 10% sodium hydroxide. The benzene solution gave 0.2 g. of a white solid VII which was identical with the solid from the oxidation of the acetate IV, and another white compound which is described with VII. The sodium hydroxide solution was acidified and steam distilled. The distillate gave a small amount of benzoic acid and the residue gave about 0.5 g. of *o*-benzoylbenzoic acid. The products were identified by mixed melting points with known samples.

Acetylation.—One gram of II was boiled for fifteen minutes with 7.5 cc. of acetic anhydride and two drops of concd. sulfuric acid, cooled and poured into water. After about fifteen minutes the tan solid was filtered off and dissolved in chloroform. This solution was dried over sodium sulfate, filtered and most of the solvent evaporated. Addition of alcohol to the chloroform solution caused the separation of the white acetate IV, in 89% yield.

2-Methyl-3,4-diphenyl-1-naphthol, III, m. p. 181–182°. —This compound could be formed either by the dehydration of II or by the alkaline hydrolysis of the acetate IV.

Seven-tenths of a gram of II was boiled for four hours in 25 cc. of benzene with 5 cc. of Lucas' reagent (zinc chloride–hydrochloric acid). The layers were separated, most of the benzene evaporated and the solution diluted with petroleum ether. The cream-colored solid (0.62 g., 94%) which separated melted at 180–181°. Recrystallization from benzene and petroleum ether gave a white compound melting at 181–182°.

One gram of the acetate IV was boiled for six hours with 40 cc. of alcohol, 1.5 g. of potassium hydroxide and 2 cc. of water. Dilution with water gave a voluminous creamy precipitate. It was filtered and recrystallized from diisopropyl ether and petroleum ether; yield, 0.7 g., 80%.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.18, 88.86; H, 6.19, 5.96.

The naphthol is very soluble in alcohol, diisopropyl ether, acetone and benzene, but is practically insoluble in petroleum ether. It is easily acetylated to the acetate IV by boiling for fifteen minutes with acetic anhydride and a drop of concd. sulfuric acid.

Oxidation.—Two grams of the naphthol was boiled for four hours with 6 g. of potassium dichromate, 4 cc. of water and 30 cc. of glacial acetic acid. On dilution with water a red solid separated. After neutralizing most of the acid with sodium carbonate, the mixture was extracted three times with ether and three times with benzene. The sodium hydroxide extract of this ether–benzene solution gave 0.2 g. of *o*-benzoylbenzoic acid and the ether–benzene solution gave 0.2 g. of the red ortho quinone V.

Acetate of 2-Methyl-3,4-diphenyl-1-naphthol, IV, m. p. 176–177°.—This compound could be formed by acetylating the di-addition product II, by acetylating the naphthol III, by acetylating the dark oils from the reaction of the quinone with phenylmagnesium bromide or by decomposing the magnesium complex from the original reaction with acetyl chloride.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.68, 84.77; H, 5.73, 5.75.

The acetate is only slightly soluble in alcohol and ethyl acetate but is quite soluble in chloroform. It crystallizes from alcohol and chloroform in small white cubes.

Oxidation.—Two grams of the acetate was boiled for five hours with 6 g. of potassium dichromate and 30 cc. of glacial acetic acid. The mixture was poured onto ice, most of the acid neutralized with sodium carbonate and the organic material extracted with ether and benzene. The sodium hydroxide extract of this ether–benzene layer gave 0.4 g. of *o*-benzoylbenzoic acid. The ether–benzene layer gave 0.2 g. of the white compound VII which was the same as one of the compounds obtained by the oxidation of II.

Alkaline hydrolysis of the acetate (described above) gave the naphthol III.

3,4-Diphenyl-1,2-naphthoquinone, V, m. p. 247–248°.—This compound was formed by the oxidation (described above) of the naphthol III. It was also formed by the oxidation of 0.3 g. of 1,2-diphenylnaphthalene[8] by boiling for two and one-half hours with 1 g. of potassium dichromate and 10 cc. of glacial acetic acid. The diluted solution was extracted with ether after neutralizing the acid with sodium carbonate. Evaporation of the ether gave a small amount of red solid. After recrystallization from alcohol and acetone it separated in glistening scarlet needles melting at 247–248°. A mixed melting point with the quinone from the oxidation of the naphthol was 247–248°, and a mixed melting point with a sample of the quinone kindly supplied by Dr. L. I. Smith[3] was 248–249°. This quinone is only slightly soluble in ether, alcohol and petroleum ether but is quite soluble in acetone. Reductive acetylation gave the diacetate described by Smith and Hoehn.[3]

White Compound, VI, m. p. 218–220°.—A gram of this compound was obtained in one of the twenty-one reactions carried out between phenylmagnesium bromide and 2-methyl-1,4-naphthoquinone.

Anal. Found: C, 79.27, 78.99; H, 5.25, 5.33.

White Compound, VII, m. p. 243–244°.—This compound was formed by the oxidation of both the di-addition product II and the acetate IV. It crystallized from alcohol and ethyl acetate in transparent rectangles. In the neutral oxidation product from II there was also a white substance, m. p. 215–217°, which formed branched crystals. It apparently was an isomer of the 243° compound since analyses of what later proved to be a mixture of the two gave the same results as the analyses of the pure 243° compound.

Anal. Found: (243° compound), C, 80.74, 80.13; H, 5.39, 5.32. Found: (mixture), C, 80.40, 80.71; H, 5.35, 5.51; mol. wt. of 243° (Rast), 280.

Summary

The reaction between 2-methyl-1,4-naphthoquinone and phenylmagnesium bromide has been studied.

Structures have been assigned to two new compounds resulting from the 1,2- and 1,4-addition of two molecules of phenylmagnesium bromide to one molecule of the quinone.

---

(8) Crawford, *This Journal*, **61**, 608 (1939).

Structures have been assigned to two new compounds resulting from a series of reactions, starting with one of the di-addition products.

The reaction of 2-methyl-1,4-naphthoquinone with phenyllithium gave no solid products.

The three products tested showed no Vitamin K activity.

POUGHKEEPSIE, N. Y. RECEIVED JANUARY 16, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectrum of 1,3-Cyclopentadiene*

BY LUCY W. PICKETT, ELEANOR PADDOCK AND ELINOR SACKTER

The absorption spectrum of 1,3-cyclopentadiene was measured as a part of an extensive spectroscopic study[1] of unsaturated hydrocarbons which has been in progress in this Laboratory for several years. This compound was of particular interest from two points of view: first, because measurements of the intense absorption band at 43,000 cm.$^{-1}$ could be made both of the vapor and of the solution in hexane under comparable conditions and thus afford a basis of study of the oscillator strength of this band and the effect of the solvent; and, second, because the far ultraviolet absorption beginning at 50,000 cm.$^{-1}$ consists of a group of sharply defined bands whose vibrational structure could be analyzed.

The absorption of cyclopentadiene and its dimer was measured by Stobbe and Dünnhaupt[2] between 23,000 and 27,000 cm.$^{-1}$ in the course of a study of the polymerization. A study of the spectrum at higher frequencies has been made by Scheibe and Grieneisen[3] and will be referred to later.

Experimental

Preparation of Cyclopentadiene.—The cyclopentadiene was prepared by repeatedly cracking and repolymerizing crude dicyclopentadiene using the method followed by Kistiakowsky and co-workers.[4] The technical dicyclopentadiene[5] was distilled once and then cracked by passing through a nitrogen filled 120-cm. column packed with glass beads and maintained at a temperature of 40–45°. The cyclopentadiene so obtained was purified by distillation in a long Crismer column and a product boiling between 39.4 and 40.2° was obtained. This was refluxed in air for ten hours on a steam-bath to form white crystals of the dimer which were then distilled twice at reduced pressure to purify them further. The pure dicyclopentadiene was cracked in a Fenske column in the absence of oxygen and the resulting cyclopentadiene, b. p. 40.2°, used immediately for the spectral measurements. A second series of measurements were made on material which had been subjected to further polymerization and cracking with agreeing results. Difficulty was experienced in determining the refractive index and density because of the polymerization of this compound when it is exposed to air. The lowest values recorded were $n^{20}{}_{D}$ 1.4437 and d^{20} 0.8073.

Measurement of Absorption.—The absorption spectrum from 32,000 to 46,000 cm.$^{-1}$ was photographed with a Hilger quartz prism spectrograph. Both the vapor and the solution were measured by the Henri method of comparisons using a copper–silver spark. The vapor was photographed in a 5-cm. quartz tube at measured pressures ranging from 0.01 to 80 mm. and its spectrum compared with that of the evacuated tube. The solutions in optically pure hexane were measured in matched Baly tubes. Photographs of both vapor and solution were taken using a hydrogen discharge tube as light source and ultraviolet sensitized plates in order to determine the positions of the narrow bands. The latter were measured both directly and from microphotometer records.

The vapor spectrum from 44,000 to 66,000 cm.$^{-1}$ was measured with a Hilger fluorite prism vacuum spectrograph using flowing vapor to minimize photodecomposition.[6] The spectra were recorded on Ilford Q plates and microphotometer records made.

Discussion of Results

The absorption curves of cyclopentadiene and dicyclopentadiene as measured with the quartz spectrograph are shown in Fig. 1, where the logarithm of the molecular extinction coefficient is plotted against the wave number. The curve of the cyclopentadiene vapor consists of an intense band with maximum about 43,000 cm.$^{-1}$ on which is superimposed a number of narrow bands while that of the solution of cyclopentadiene in optically pure hexane is of about the same intensity but is shifted toward the visible by about

---

* Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

[1] Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); **6**, 55 (1938).

[2] H. Stobbe and F. Dünnhaupt, *Ber.*, **52**, 1436 (1919); "I. C. T.," Vol. V, p. 363.

[3] Scheibe and Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

[4] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[5] Dicyclopentadiene was obtained from the Duisberg-Niederick Co. in Germany.

[6] For details of technique, see Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936).