Working up the filtrates and ether extract yielded 8.2 g. of crude ortho isomer melting at 52–87°.

Separation of Naphthols. Aqueous Process.—A mixture consisting of 2.6 g. (0.01 mole) each of 8-benzamido-1-naphthol and 5-benzamido-1-naphthol was dissolved in 10 cc. of water by addition of 4.2 cc. of 5 *N* sodium hydroxide. Addition of 1.7 g. (0.02 mole) of sodium bicarbonate precipitated the naphthols. Then 2.8 g. (0.015 mole) of triethylamine–SO_3 was added. After stirring for six hours at 30°, 10 cc. of 5 *N* sodium hydroxide was added and the triethylamine was extracted with ether. Acidification with 20% acetic acid precipitated 2.6 g. of product identified as being principally 5-benzamido-1-naphthol.

From the filtrate the sulfuric ester of 8-benzamido-1-naphthol was isolated in 81% yield.

Separation of Naphthols. Anhydrous Process.—A mixture consisting of 1.3 g. (0.005 mole) each of 5-benzamido-1-naphthol and 8-benzamido-1-naphthol was placed in 15 cc. of dry pyridine and 1 g. (0.005 mole) of triethylamine–SO_3 was added. The clear brown solution was allowed to stand for 24 hours at room temperature. Ten cc. of water and 5 cc. of 5 *N* sodium hydroxide were added and the organic bases were extracted with ether. The aqueous layer was neutralized with 80% acetic acid and the upper layer was decanted from the oil and clarified. A 50-cc. portion was taken from the total volume of 115 cc. and boiled with hydrochloric acid. The dried product resulting from this hydrolysis weighed 0.3 g. and melted at 233–242°. Thus, the principal product isolated is 5-benzamido-1-naphthol formed in about 53% yield.

Separation of Anilines.—A mixture consisting of 12.1 g. (0.1 mole) each of *o*-ethylaniline and *p*-ethylaniline was placed in 100 cc. of chloroform in a flask fitted with mechanical stirrer and 20.2 g. (0.11 mole) of triethylamine–SO_3 was added. While stirring, the temperature was allowed to rise gradually from 15 to 25° during a five-hour period. The white solid was filtered off at 7° and washed with hexane. It weighed 19.4 g., 64.2% yield, m.p. 101–103°. The identity of this material as the para isomer is shown by the fact that no depression in melting point occurs when it is mixed with an authentic sample of the para isomer. Furthermore, the ortho isomer yields an oil under these conditions.

Separation of Alcohols.—A mixture of 30 g. (0.5 mole) each of 2-propanol and 1-propanol was treated in 125 cc. of chloroform with 97 g. (0.525 mole) of triethylamine–SO_3. The clear solution was allowed to stand at room temperature for two and one-half days. The solvent was then evaporated under reduced pressure so that the liquid temperature did not exceed 40°. Addition of 200 cc. of hexane caused a layer separation and the lower layer weighing 177 g. was separated and cooled. Since crystallization could not be induced, a 3.5-g. (0.01 mole real) aliquot was added to 10 cc. of water containing 2.2 g. of benzylisothiouronium chloride. The vacuum-dried product obtained weighed 2.4 g., a 77.2% yield of the sulfuric ester of 1-propanol as the benzylisothiouronium salt; sintering point 113°, m.p. 115–116°.

Anal. Calcd. for $C_{11}H_{17}N_2O_4S_2$: C, 43.2; H, 5.6; S, 20.9. Found: C, 43.2; H, 5.8; S, 20.6.

***o*-Phenylphenol Sulfuric Ester.**—A 17-g. (0.1 mole) sample of *o*-phenylphenol was dissolved to a clear solution in 90 cc. of water by addition of 20 cc. of 5 *N* sodium hydroxide. Then 8.4 g. (0.1 mole) of sodium bicarbonate, 5.3 g. (0.05 mole) of sodium carbonate and 28 g. (0.15 mole) of triethylamine–SO_3 were added. The mixture was stirred for three hours at 45–50° to give a two-layer system. The cooled reaction mixture was extracted with ether. The two remaining lower layers were neutralized with dilute hydrochloric acid and again extracted with ether. The aqueous layer was salted to 15% concentration with potassium chloride at 50°, and the white solid was filtered off at 10° and washed with 15% potassium chloride–2% potassium hydroxide solution. The wet cake weighed 68.5 g. One-fourth of this was clarified from 75 cc. of water and resalted. The dry product weighed 7.6 g., an 83% yield based on the carbon content.

Anal. Calcd. for $C_{12}H_9KO_4S$: C, 51.4; H, 3.1; S, 11.0; C/S, 12.0. Found: C, 38.5; H, 2.93; S, 8.62; C/S, 11.9.

8-Benzamido-1-naphthol Sulfuric Ester.—A 2.6-g. portion (0.01 mole) of 8-benzamido-1-naphthol was treated with triethylamine–SO_3 in aqueous carbonate solution as described in the preparation of the ester of *p*-phenylphenol. The product weighed 4.3 g., a yield of 72%.

Under these same conditions 1-benzamido-5-naphthol was recovered unchanged.

Anal. Calcd. for $C_{17}H_{12}KO_5NS$: C, 53.4; H, 3.19; N, 3.68; S, 8.40; C/S, 17.0; N/S, 1.00. Found: C, 42.2; H, 3.34; N, 2.93; S, 6.57; C/S, 17.0; N/S, 1.03.

***p*-Ethylaniline Sulfamic Acid.**—Six grams (0.049 mole) of *p*-ethylaniline and 9.5 g. (5% excess) of triethylamine–SO_3 were dissolved in 50 cc. of chloroform. After warming at 60° for 15 minutes, the solution was cooled to 10° and the product was filtered off and washed with hexane. The crude dry product weighed 16.0 g. and melted at 75–80°. An 8.0-g. sample recrystallized from 50 cc. of chloroform gave 6.6 g. of white solid melting at 99–102°, an 89% yield as the triethylamine salt of *p*-ethylanilinesulfamic acid.

Anal. Calcd. for $C_{14}H_{26}N_2O_3S$: C, 55.6; H, 8.6; N, 9.28; S, 10.6. Found: C, 55.7; H, 8.48; N, 9.29; S, 10.8.

Under the same conditions, *o*-ethylaniline failed to yield a solid derivative.

2-Propanol Sulfuric Ester.—Six grams (0.1 mole) of 2-propanol was heated with 18.1 g. (0.1 mole) of triethylamine–SO_3 at a bath temperature of 125° for two hours. Since the viscous reaction mixture could not be crystallized, 4.5 g. (0.019 mole) of the mixture was dissolved in 20 cc. of water and the product was precipitated by addition of 4.0 g. (0.02 mole) of benzylisothiouronium chloride in 16 cc. of water. After recrystallization from water, 1.4 g. of dry product sintering at 141°, m.p. 142–144°, was obtained, a yield of 24%.

Anal. Calcd. for $C_{11}H_{17}N_2O_4S_2$: C, 43.2; H, 5.6; N, 9.2; S, 20.9. Found: C, 43.3; H, 5.0; N, 9.8; S, 20.7.

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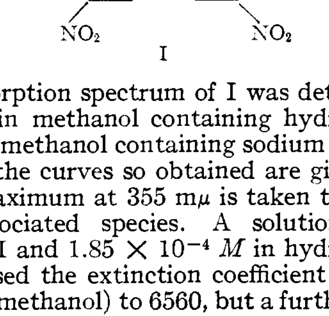
The Dissociation of 3,3',5,5'-Tetranitro-4,4'-dihydroxydiphenyl in Methanol[1]

BY HAROLD HART AND WILLIAM J. DETROIT

RECEIVED MAY 12, 1952

The effect of nitro groups ortho or para to the hydroxyl function of phenols on the acidity of the latter is well known. It was of interest to determine the acidity of a dihydric phenol in which two such arrangements were present in the same molecule, but isolated from each other. Accordingly, the dissociation constant of 3,3',5,5'-tetranitro-4,4'-dihydroxydiphenyl (I) was measured.



I

The absorption spectrum of I was determined in methanol, in methanol containing hydrogen chloride and in methanol containing sodium methoxide. Several of the curves so obtained are given in Fig. 1. The maximum at 355 mμ is taken to represent the undissociated species. A solution 1.87 × 10^{-4} *M* in I and 1.85 × 10^{-4} *M* in hydrogen chloride increased the extinction coefficient from 5920 (in neutral methanol) to 6560, but a further increase (tenfold) in the hydrogen chloride concentration had a negligible effect. Curve 1, therefore, represents I in the undissociated form. Addition of in-

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[1] Taken in part from the Master of Science thesis of W. J. D., March, 1952.

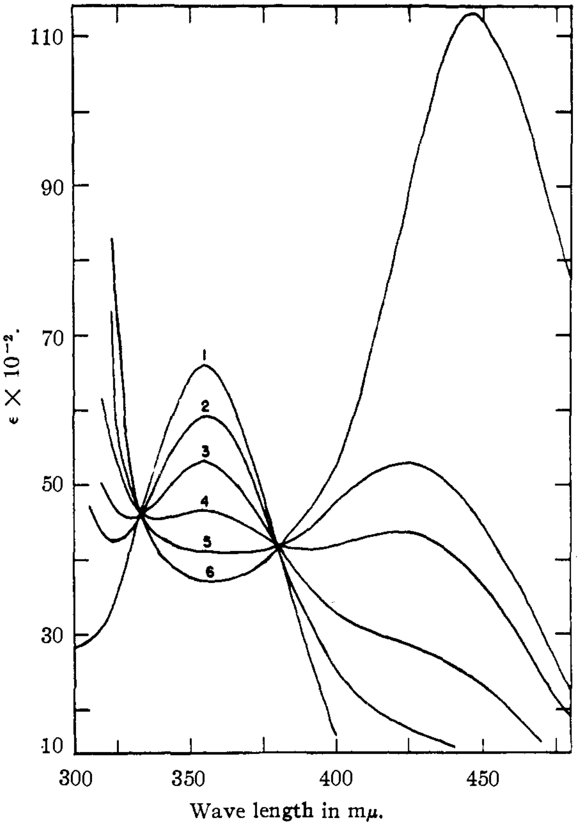

Fig. 1.—Spectrum of 3,3′,5,5′-tetranitro-4,4′-dihydroxydiphenyl (I) (approximately 2×10^{-4} M in I) in methanol of varying acidity: curve 1, 1.85×10^{-4} M and 1.85×10^{-3} M in hydrogen chloride; curve 2, in neutral methanol; curve 3, 3.9×10^{-5} M; curve 4, 7.8×10^{-5} M; curve 5, 1.04×10^{-4} M; and curve 6, 1.3×10^{-4} M in sodium methoxide.

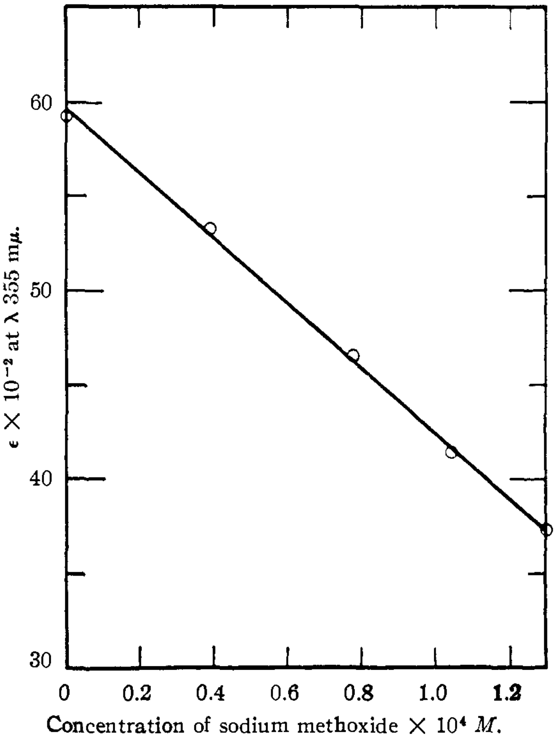

Fig. 2.—Linear dependence of the extinction coefficient of I at 355 mμ on the concentration of sodium methoxide in methanol.

creasing quantities of sodium methoxide decreased the extinction at 355 mμ linearly, as shown in Fig. 2. Curve 6, of Fig. 1, the last curve which continued to pass through the isobestic points, was taken to represent complete disappearance of the undissociated form of I. As methoxide concentration was increased, another maximum appeared, shifting gradually from 422 to 477 mμ and becoming more intense. This probably represents the monovalent anion. When further methoxide was added, the curve no longer passed through the isobestic points. This probably represents loss of the second proton and conversion to the divalent anion. This second dissociation, unfortunately, could not be measured spectrophotometrically, due to crystallization from the alcohol–sodium methoxide solution of red crystals, probably the sodium salt.

The first dissociation constant of I in methanol was evaluated from the spectra, using data at several different wave lengths between the isobestic points, in the usual manner. It was found to be $1.27 \pm 0.18 \times 10^{-6}$ (pK 4.90 ± 0.06, room temperature). The pK of 2,6-dinitrophenol[2] in water at 18° is 3.58. Schwarzenbach and Rudin[3] have shown that the measured acidity may decrease by as much as 2.5 pK units in going from water to 95% ethanol for *o*- and *p*-nitrophenol. The dissociation constant we have determined for I in methanol is, therefore, a reasonable one.

Experimental

Materials.—3,3′,5,5′-Tetranitro-4,4′-dihydroxydiphenyl was prepared from benzidine in 70% yield by the procedure of Borsche and Scholten.[4] Absolute methanol was the solvent for the spectra. When acidic or basic methanol solutions were required, anhydrous hydrogen chloride or sodium methylate, respectively, were dissolved in absolute methanol. The solutions were standardized in the usual manner.

Spectra.—A Beckman model DU spectrophotometer, with 1-cm. quartz cells, was used for determination of the spectra.

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[2] D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1366 (1939).

[3] G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939).

[4] W. Borsche and B. G. B. Scholten, *Ber.*, **50**, 508 (1917).

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Studies in the Diphenoquinone Series[1]

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The reaction of dienes proceeds well with *p*- and *o*-quinones, naphthoquinones, and other cyclenones.[2] Because of the nature of the products which might be obtained, we became interested in studying the possible reaction of diphenoquinone (I) and related compounds with dienes. The only previously reported attempt at the condensation of

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[1] Taken from the thesis presented for the Master of Science degree by W.J.D., March, 1952.

[2] L. W. Butz and A. W. Rytina, Chapter in R. Adams, "Organic Reactions," Volume 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 136.