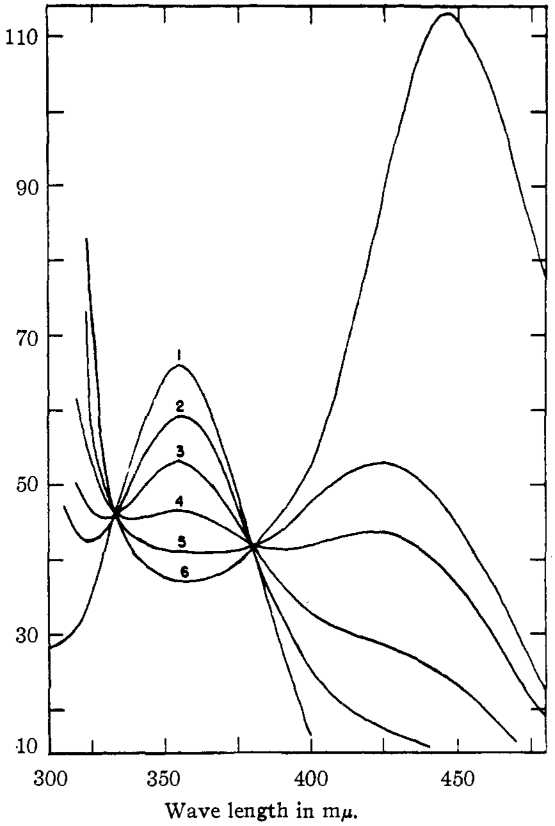

Fig. 1.—Spectrum of 3,3′,5,5′-tetranitro-4,4′-dihydroxydiphenyl (I) (approximately 2×10^{-4} *M* in I) in methanol of varying acidity: curve 1, 1.85×10^{-4} *M* and 1.85×10^{-3} *M* in hydrogen chloride; curve 2, in neutral methanol; curve 3, 3.9×10^{-5} *M;* curve 4, 7.8×10^{-5} *M;* curve 5, 1.04×10^{-4}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

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

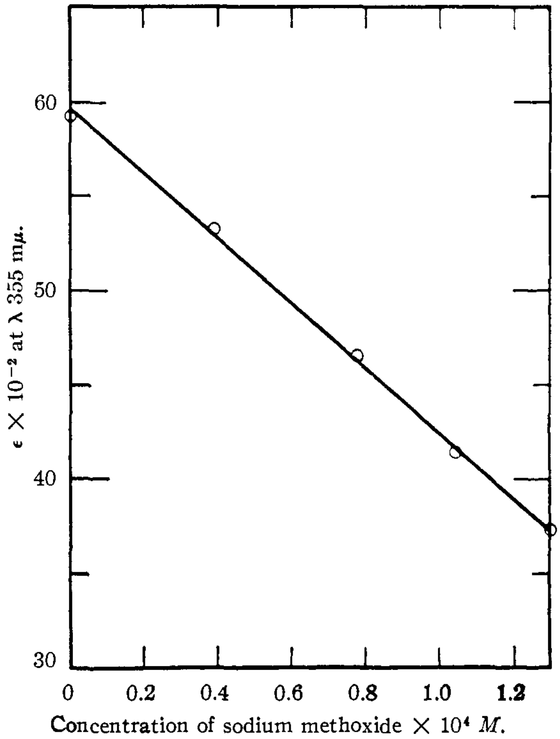

Fig. 2.—Linear dependence of the extinction coefficient of I at 355 mμ on the concentration of sodium methoxide in methanol.

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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RECEIVED JUNE 4, 1952

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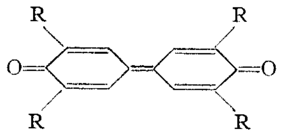
(1) Taken from the thesis presented for the Master of Science degree by W.J.D., March, 1952.

(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.



(R = H); II (R = CH$_3$); III (R = t-C$_4$H$_9$); IV (R = Cl)

I with a diene was that of Nara Boon-Long,[3] who reported the formation of ill-characterized and possibly polymeric products when a solution of I in benzene was heated with 2,3-dimethyl-1,3-butadiene in a sealed tube at 100° for 24 hours. The rather vigorous conditions and lack of control experiments prompted us to reinvestigate the reaction.

The first of our difficulties was encountered in the preparation of the parent compound, I. It had first been synthesized by Willstätter and Kalb[4] who oxidized an ether solution of 4,4′-diphenol by shaking with a suspension of lead dioxide at room temperature for 24 hours. Subsequent workers[3,5,6] also employed this procedure[7] but noted that the method was inconsistent, and did not always result in the desired product. In our hands, using commercially manufactured lead dioxide, the method was a complete failure. The state of subdivision or the recrystallization solvent for the 4,4′-diphenol, factors which were claimed to be of importance,[5] had little effect. It was found, however, that if the lead dioxide was freshly prepared from lead tetraacetate in a highly active form, according to the recent procedure of Kuhn and Hammer,[8] and the reaction time for the oxidation was decreased from 24 hours to about 30 minutes or less, a reasonable yield (55%) of the red crystalline modification of I was *consistently* obtained.

No exothermic reaction occurred between I and cyclopentadiene in alcohol, benzene, or chloroform solvents, nor could any well-defined adduct be obtained by refluxing. Blank experiments showed that I is readily polymerized by refluxing in the above solvents, but that II can be recovered quantitatively, even when cyclopentadiene is present.

The absorption spectra of I and of several substituted diphenoquinones were determined, and are summarized in Table I. Only the spectrum of I[5] and a portion of the spectrum of III[9] have been previously reported.

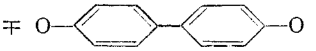
TABLE I

MAXIMA IN THE VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA OF SOME DIPHENOQUINONES

Compound	λ^c	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
I^a	395	62,600	261	2990	252	3130	...	...
II^a	414	67,600	...	...	...	...	...	...
III^a	420	70,800	269	4920	260	5480	251	4740
II^b	421	73,200	...	...	...	...	...	...
III^b	427	66,000	271	4240	262	4800	253	4320
IV^b	435	71,800	283	3470	273	4520	261	5390

^{a} In ethyl alcohol. ^{b} In chloroform. ^{c} All wave lengths are in mμ.

The principal maximum in the visible is probably due to contributions, in the first excited state, from resonance structures of the type



Substituents in the 3,3′,5,5′-positions apparently have only a slight effect on these principal contributing forms. The shift of 19 mμ (from 395 to 414 mμ) when a hydrogen atom is replaced by a methyl group may be interpreted in terms of hyperconjugation involving the methyl groups, and this shift is only slightly different (to 420 mμ) for the t-butyl group. Pianka, *et al.*,[10] have interpreted the similar bathochromic shift on going from the 2,4-dinitrophenylhydrazone of formaldehyde to those of acetaldehyde and higher aldehydes[11] in a similar manner, and point out the possible generality of bathochromic and hypsochromic shifts on alkyl substitution. The main feature of the spectra of the diphenoquinones, however, is their similarity, and the relative independence of the nature of the substituent.

Experimental

Diphenoquinone (I).—To 5 g. of 4,4′-dihydroxydiphenyl[12] dissolved in 720 ml. of ether there was added 25 g. of activated[8] lead dioxide. The mixture was shaken mechanically for about 30 minutes. After filtration, the lead dioxide residue containing I was extracted by refluxing for 15 minutes once with 1 l. and twice with 500 ml. of benzene. Cooling the combined extracts gave 1.69 g. of red crystalline I. Concentration of the mother liquors gave an additional 0.58 g. Additional product (0.40 g.) was precipitated from the mother liquors with ligroin, the gold crystalline modification of I being obtained. Recrystallization of the red crystals from benzene gave the gold form. The total yield was 2.67 g. (53.9%). The reaction time could be varied from 15 to 45 minutes without an appreciable effect on the yield.

Anal.[13] Calcd. for C$_{12}$H$_8$O$_2$: C, 78.25; H, 4.38. Found: red form, C, 78.55; H, 4.39; gold form, C, 78.42; H, 4.60.

Spectra.—Chloroform was purified by the method of Fieser,[14] and absolute alcohol was dried by distillation from calcium oxide. The spectra were determined with a Beckman model DU quartz spectrophotometer, using 1-cm. matched quartz cells. It should be noted that solutions of I in alcohol are unstable, and the spectrum must be determined rapidly. In chloroform I decomposes too rapidly for the determination of its spectrum. The same holds for alcoholic solutions of IV. Solutions of II and III in both solvents are stable.

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[3] N. Boon-Long, *J. Pharm. Assoc. Siam*, **1**, 5 (1948); *C. A.*, **43**, 5017 (1949).

[4] R. Willstätter and L. Kalb, *Ber.*, **38**, 1232 (1905).

[5] N. A. Valyashko and M. M. Shcherbak, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1597 (1938); *C. A.*, **33**, 4589 (1939).

[6] L. F. Fieser, THIS JOURNAL, **52**, 4915 (1930).

[7] After developing the successful procedure described below, we noted that L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 2nd Ed., 1941, p. 439, mentions the use of lead tetraacetate to oxidize diphenol to I. We could not find the details of this procedure in the literature, and after four unsuccessful attempts, gave this method up.

[8] R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950).

[9] H. Hart and F. A. Cassis, THIS JOURNAL, **73**, 3179 (1951).

[10] M. Pianka, H. C. Barany and C. G. Smith, *Nature*, **167**, 440 (1951).

[11] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 499 (1945).

[12] R. Hirsch, *Ber.*, **22**, 335 (1889).

[13] Clark Microanalytical Laboratories, Urbana, Illinois.

[14] L. F. Fieser, ref. 7, p. 365.

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Phenolphthalol

BY MAX H. HUBACHER

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By reduction of phenolphthalin (4′,4″-dihydroxytriphenylmethane-2-carboxylic acid) with sodium