values of pK_a, obtained for each quinone in different buffers, was at most 0.06 and averaged 0.02 unit.

Summary

The acidities and visible spectra of certain 3-substituted 2-hydroxy-1,4-naphthoquinones were measured and correlated. Particular attention was given to the influence of groups separated from the chromophore by a saturated carbon atom.

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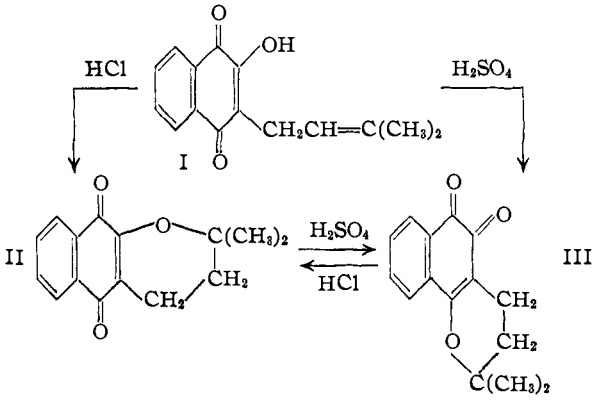
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Hydroxynaphthoquinones. II. Cyclization and the Basicity and Interconversion of *Ortho* and *Para* Quinones

BY MARTIN G. ETTLINGER[1]

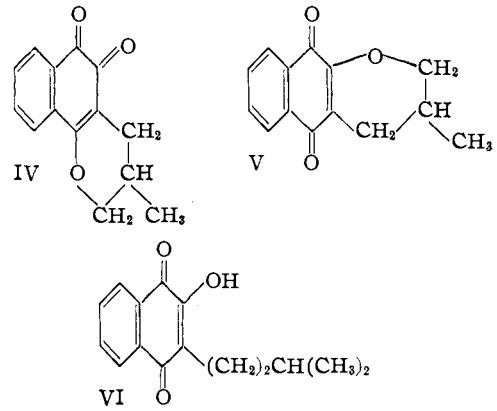
At the commencement of brilliant investigations of the natural pigment lapachol (I), Hooker discovered[2] that the course of reaction of lapachol and strong acids apparently depended on the specific acid employed. In concentrated hydrochloric acid lapachol was cyclized to the *para* quinone α-lapachone (II), but in concentrated sulfuric acid to the isomeric *ortho* quinone β-lapachone (III). Hooker also established a quantitative isomerization of α-



lapachone to β-lapachone in sulfuric acid and the reverse in hydrochloric acid, and hence a probable inversion of equilibrium. These observations, termed by Hooker "very remarkable," were confirmed after controversy,[3,4] and extended to the corresponding quinones derived from bromolapachol[5] and norlapachol[6] and to the isodunniones.[7] The lack of theoretical consideration of the problem[8] evoked the present paper.

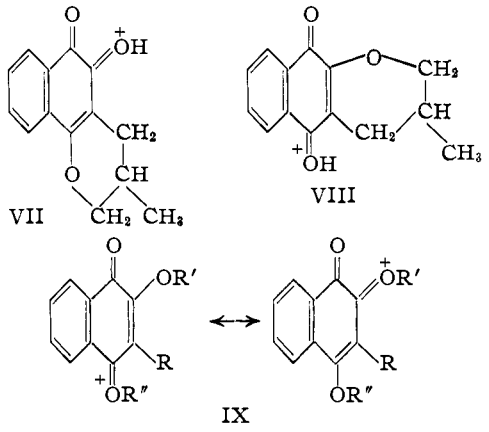
Largely from the work of Hammett[9] and collaborators, knowledge of solutions in sulfuric acid is now extensive. A useful acidity scale spanning all sulfuric acid–water mixtures has been devised and many oxygenated organic compounds proved to behave as simple neutral bases in these solvents. 2,5-Dihydroxybenzoquinone with pK_a −7.0[10] is nearly half ionized in 80% sulfuric acid, whereas anthraquinone (pK_a −8.15)[9] is over tenfold weaker. More strongly basic hydroxynaphthoquinone analogs are benzalacetophenone (pK_a −5.61)[9] and acetylacetone enol (pK_a −5.0).[11]

The ionization of hydroxynaphthoquinone ethers in sulfuric acid can be established spectroscopically. Since α-lapachone is unstable in concentrated sulfuric acid, the *ortho–para* isomeric pair of β-methyldihydropyranonaphthoquinones[12] (IV and V) was used. The absorption spectra of IV and V and hydrolapachol (VI)



appear in Fig. 1 for ethanol solutions, and in Fig. 2 for 95% sulfuric acid. Whereas in ethanol the *o*-quinone differs from the *p*-quinones in intensity of the 280 and 330 mμ bands and at long wave lengths,[13] the spectra in concentrated sulfuric acid, except for small differences in the inflection near 480 mμ which relatively deepen[14] the color of the *p*-isomers, are identical. The inference is that IV and V each add a proton in sulfuric acid to furnish, respectively, the ions VII and VIII, which, together with the cation (IX, R = $(CH_2)_2$-$CH(CH_3)_2$, R′ = R″ = H) of VI are examples

(1) Member of the Society of Fellows, Harvard University.
(2) Hooker, *J. Chem. Soc.*, **61**, 611 (1892).
(3) Monti, *Gass. chim. ital.*, **45**, II, 51 (1915).
(4) Hooker, THIS JOURNAL, **58**, 1190 (1936).
(5) Hooker, *J. Chem. Soc.*, **65**, 15 (1894).
(6) Hooker, THIS JOURNAL, **58**, 1168 (1936).
(7) Price and Robinson, *J. Chem. Soc.*, 1522 (1939); 1493 (1940).
(8) Fieser, *Record Chem. Progress*, **7**, 26 (1946).
(9) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapters II and IX.
(10) Schwarzenbach and Suter, *Helv. Chim. Acta*, **24**, 617 (1941).
(11) Schwarzenbach and Wittwer, *ibid.*, **30**, 659 (1947).
(12) Hooker and Steyermark, THIS JOURNAL, **58**, 1198 (1936).
(13) Cooke, Macbeth and Winzor, *J. Chem. Soc.*, 878 (1939).
(14) Fieser, THIS JOURNAL, **48**, 3201 (1926).



VII VIII IX

of the resonant ion IX. The chromophores of the cations of IV, V and VI are the same, and consequently the spectra are similar.

The ionization constants of three quinones in aqueous sulfuric acid were measured spectrophotometrically with the results: β-lapachone (III), pK_a −3.45; β-methyldihydropyrano - 1,2 - naphthoquinone (IV), −3.75; β-methyldihydropyrano-1,4-naphthoquinone (V), −6.65. β-Lapachone, which is half ionized in 52% sulfuric acid, is exceptionally basic for a non-nitrogenous substance and almost as strong as *p*-nitroazobenzene (pK_a −3.35)[9] or 2,4-dichloro-6-nitroaniline (pK_a −3.22),[9] whereas the *p*-quinone V is one eight hundredth as strong as its *o*-isomer IV. Since acid hydrolysis of an alkoxy quinone proceeds through a cation of type IX, the rapidity with which acid splits 4-methoxy-1,2-naphthoquinone compared to its *p*-isomer[15] accords with the smaller basicity of the latter. For calculation, the ratio of basicities of the lapachones may be taken the same as of IV and V, and α-lapachone (II) assigned pK_a −6.35.

The equilibrium between the lapachones in acid can now be elucidated. Qualitatively, the *p*-quinone is the more stable of the free quinones, and the *o*-quinone cation of the two cations, whence the greater basicity of the *o*-quinone follows. In concentrated sulfuric acid, which contains only 18 mole % of water and converts both isomers to their conjugate acids, the *o*-quinone predominates as the cation and is isolated in the metastable free condition on sudden dilution with water. In concentrated hydrochloric acid, which contains 77 mole % of water, equivalent to 62% sulfuric acid, the *o*-quinone ionizes largely but insufficiently to transform equilibrium from the side of the uncharged *p*-quinone. Furthermore, Hooker's experiments in hydrochloric acid were so performed that the less soluble α-lapachone precipitated as a solvate and the disappearance of β-lapachone thereby became more complete. In concentrated hydrobromic acid, containing 83 mole % of water, circumstances are similar. This interpretation was confirmed in the present work by experiments in aqueous sulfuric acid. Samples of lapachol or one of the lapachones were digested in acid of various concentrations, and the solutions quenched in water. The product obtained by recrystallization of the precipitate was α-lapachone from sulfuric acid of concentration 62% or less, β-lapachone from 75% or stronger acid, and a mixture of roughly equal parts of the isomers from 67% acid.

The lapachone isomerization formally resembles the enolization of acetylacetone in aqueous sulfuric acid, studied by Schwarzenbach and Witt-

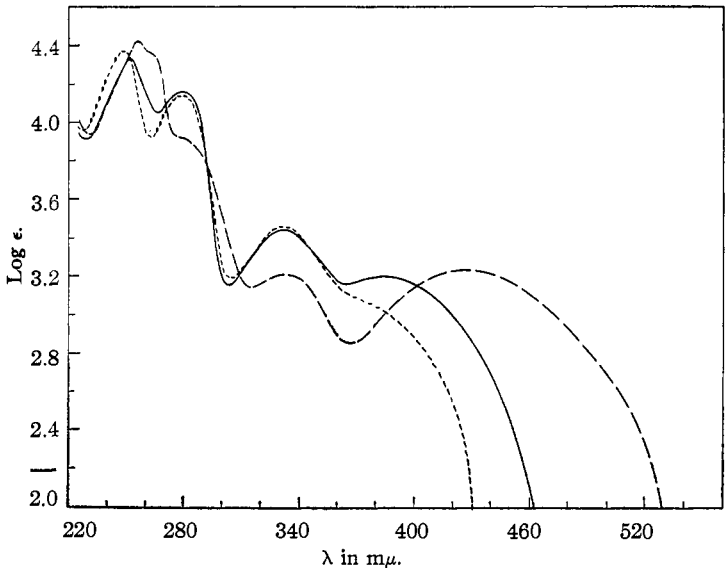


Fig. 1.—Absorption spectra in ethanol of hydrolapachol (VI), —; β-methyldihydropyrano-1,4-naphthoquinone (V), . . .; and β-methyldihydropyrano-1,2-naphthoquinone (IV), ---.

wer.[11] In their problem the equilibrium was mobile and measurable over the complete range of acid concentration, and from the results the ionization constants of enol and diketone were deduced. The basicities of the two forms differed only thirteen fold, corresponding to variation of the total enol–ketone ratio from 0.15 to 2.5. In the present investigation, the equilibrium varies more widely and is easily measurable in only a small region, but the independent determination of basicities enables calculation of the constants at extreme conditions. Let [α], [β], [Hα⁺] and [Hβ⁺] denote the concentrations of II, III and their respective cations, h_0 the Hammett function corresponding to oxonium ion concentration, and set

$$K_\alpha = \frac{h_0[\alpha]}{[H\alpha^+]} \cong 10^{6.35},\ K_\beta = \frac{h_0[\beta]}{[H\beta^+]} =$$

(15) Fieser, THIS JOURNAL, 48, 2922 (1926).

$$10^{3.45},\ K = \frac{[\alpha]}{[\beta]},\ K' = \frac{[H\alpha^+]}{[H\beta^+]} = KK_\beta/K_\alpha$$

As h_0 increases, $[\alpha]$ and $[\beta]$ decrease, $[H\alpha^+]$ and $[H\beta^+]$ increase, and the total α-β ratio

$$\frac{[\alpha] + [H\alpha^+]}{[\beta] + [H\beta^+]} = K\frac{1 + \frac{h_0}{K_\alpha}}{1 + \frac{h_0}{K_\beta}}$$

varies monotonically from K to K'. In the region $K_\beta \ll h_0 \ll K_\alpha$ of acid concentration, $[H\alpha^+] \ll [\alpha]$, $[\beta] \ll [H\beta^+]$, and $K = h_0[\alpha]/K_\beta[H\beta^+]$ can be determined from the total α-β ratio nearly independently of the uncertain value of K_α. Experimentally in 60–70% sulfuric acid at room temperature, $K \cong 25$, whence $K' \sim 0.03$. From the likelihood that the activity coefficients of the lapachones vary similarly, and analogous experience with acetylacetone,[11] K may be assumed roughly constant, within a factor of two, in all aqueous solvents.

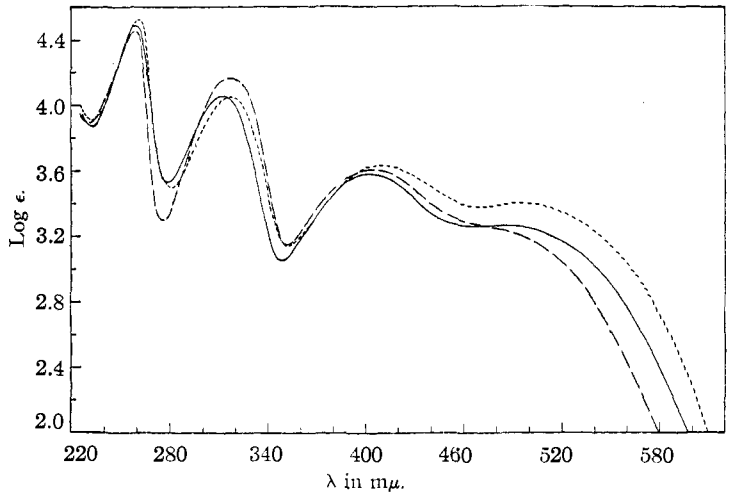
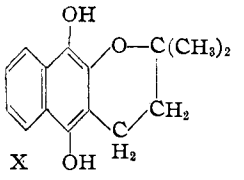
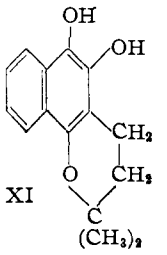


Fig. 2.—Absorption spectra in 95% sulfuric acid of hydrolapachol (VI), —; β-methyldihydropyrano-1,4-naphthoquinone (V), . . .; and β-methyldihydropyrano-1,2-naphthoquinone (IV), ---.

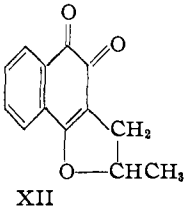
Equilibrium between the lapachones is less favorable to the *p*-quinone than in the tautomerism of 2-hydroxy-1,4-naphthoquinone, for which Fieser[16] plausibly derived a constant of 500 from oxidation–reduction potentials. The present data may be applied to the potentials[16] of the lapachones. Denote by K'' the equilibrium ratio of concentration of the hydroquinone X of II to XI of III. By extension of Fieser's calculation, $\log (K/K'') = (E_0^\beta - E_0^\alpha)/0.0296 = 0.099/0.0296 = 3.35$ in 50% ethanol at room temperature, $K/K'' = 2200$, $K'' \sim 0.01$. Even with allowance for uncertainties, the curious result is that the difference between the normal potentials of these isomer pairs is caused not only by greater stability of the *p*-quinone but at least equally by relative instability of the *p*-hydroquinone. Significantly, K' and K'', each of which measures the lability of linear compared to angular fusion of the three six-membered rings in otherwise roughly equivalent systems, are of similar magnitude.



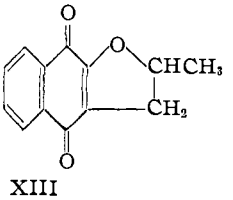


The potential of a naphthoquinone system is known to be influenced by the size of ring fused to it. Although β-methyldihydrofurano-1,2-naphthoquinone (XII) has practically the same potential as β-lapachone, the corresponding *p*-quinone XIII as well as phthiocol methyl ether are much higher in this respect than hydrolapachol or α-lapachone.[16,17] For the pair XIII and XII, accordingly, K/K'' is only 11. Since dihydrofurano-1,2-naphthoquinones are isomerized to *p*-quinones by dilute acid,[6,7,16] it is reasonable to conjecture that $K > 1$ in this series also, and consequently K'' is larger than for the lapachones, and nearer unity. An exact investigation by the present method would be interesting.

Certain unsaturated quinones display unusual properties as cations. Furano-1,4-naphthoquinones[18] (XIV) are slowly formed from their *o*-isomers in concentrated sulfuric acid, and by this change the color

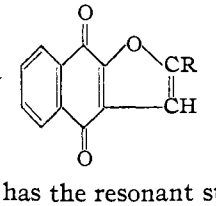


XII



XIII

of the solution lightens. Perhaps the cation of XIV differs from VIII or type IX in location



XIV

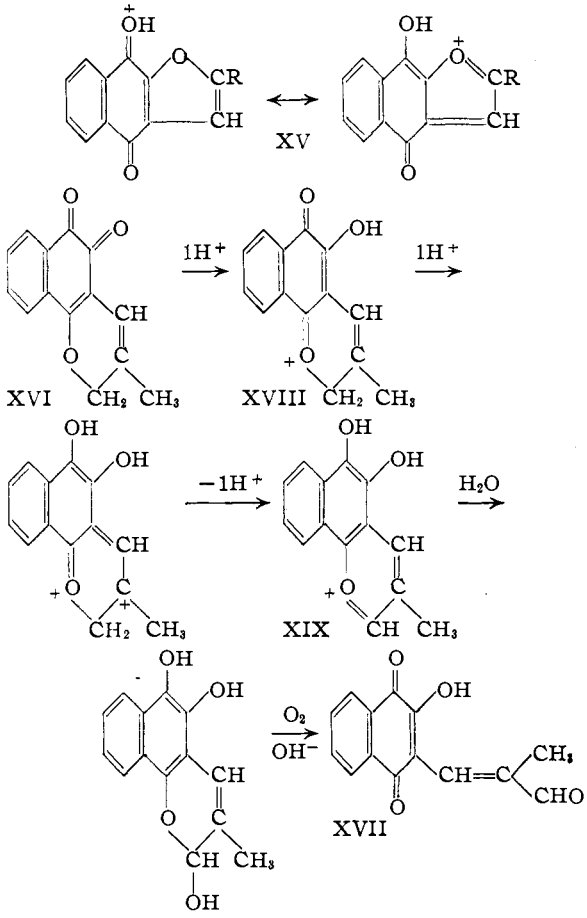
of the proton and has the resonant structure XV. A second anomaly is exhibited[19] by β-methylpy-

(16) Fieser, THIS JOURNAL, **50**, 439 (1928).

(17) Wallenfels and Moehle, *Ber.*, **76**, 924 (1943).

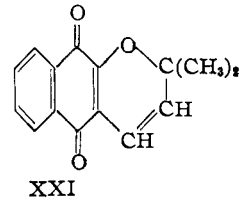
(18) Hooker and Steyermark, THIS JOURNAL, **58**, 1202 (1936).

(19) Hooker and Steyermark, *ibid.*, **58**, 1207 (1936).

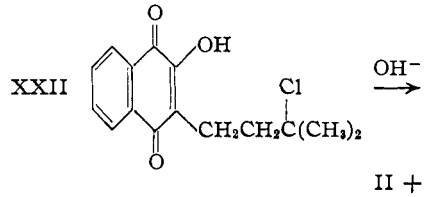


rano-1,2-naphthoquinone (XVI). If XVI is dissolved in concentrated sulfuric acid, it furnishes a blue solution, whence it may be reprecipitated by dilution with water, but if the solution is allowed to stand a few hours, the color changes to red, and the product formed on subsequent rapid dilution is the hydroquinone of XVII. Presumably the blue solution contains the simple cation XVIII, which is slowly converted to the red pyrylium salt XIX by a prototropic shift.

Rates of cyclization of 2-hydroxy-1,4-naphthoquinone derivatives, which are not included in the preceding discussion of equilibria, conform to rules that may be induced from Hooker's observations. Ring closure with acid of a compound hydroxylated in the side chain gives an *o*-quinone as first product. In weak acid, accordingly, the unstable ether is formed more rapidly than its *p*-quinone isomer. Examples are the cyclizations of hydroxyhydrolapachol[2] (XX) to β-lapachone (III), dihydroxyhydrolapachol[2] to hydroxy-β-lapachone, of norhydroxyhydrolapachol[6] and norhydrolomatiol,[12] the regeneration of dunnione[7] from alkaline solution, and the preparation[19] of XVI. If the side chain hydroxyl is allylic, however, both the reactions of ring closure and *o-p* isomerization are accelerated, with the result that the *p*-quinone ether may be the only product isolable. Examples are the cyclization of norlomatiol,[12] which simultaneously undergoes a *cis-trans* rearrangement, and the regeneration from alkaline solution of dehydro-α-lapachone[4] (XXI). The single instance wherein a *p*-quinone is unambiguously formed by initial ring closure

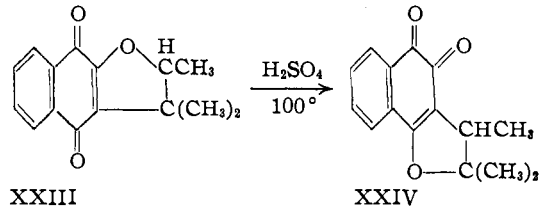


is the reaction of chlorohydrolapachol[2] (XXII) with alkali, which yields both lapachones. The partial transfer of reactivity from the 4- to the 2-



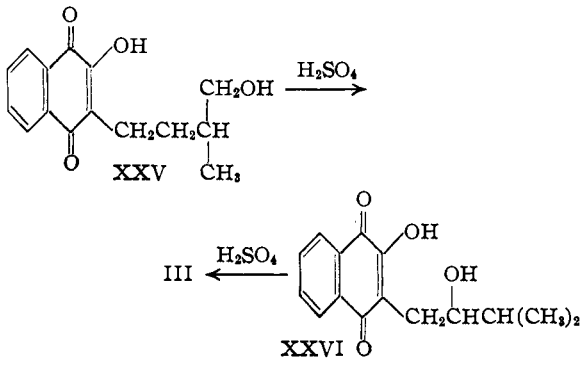
position in the anion accords with the electron attraction of the 1-carbonyl.

The condition for ready transformation of a cyclic 1,4-naphthoquinone ether to its *o*-quinone isomer in concentrated sulfuric acid is attachment of the ether oxygen to a tertiary carbon of the side chain. Whereas II, β,β-dimethyldihydrofurano-1,4-naphthoquinone[6] and α-isodunnione[7] are isomerized by cold sulfuric acid, V,[12] XIII,[14] α-dunnione[7] (XXIII) and apparently even β-methylpyrano-1,4-naphthoquinone[12] are not. It can be inferred that in the change from *para* to *ortho* quinone in sulfuric acid, the side chain separates from the 2-oxygen as a carbonium ion. The conversion[7] of α-dunnione (XXIII) to β-isodunnione (XXIV), whether by interchange



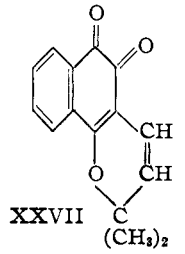
of methyl and hydrogen or migration of the quinone group, as well as the sulfuric acid cyclizations[20] of hydrolomatiol (XXV) and hydroisolo-

(20) Hooker, THIS JOURNAL, 58, 1181 (1936).



matiol (XXIV) to III with hydrogen shift, are typical carbonium ion rearrangements. Evidently the transformation of, for example, IV to V in hydrochloric acid proceeds by hydrolysis to norhydrolomatiol and ring closure, but the reverse reactions do not occur in concentrated sulfuric acid because of the dearth of water.

From the foregoing argument, it appears that dehydro-β-lapachone (XXVII), which Hooker



was unable to prepare, should be formed from XXI in concentrated sulfuric acid. However, the dilution of the acid necessary to isolation of XXVII tends to promote its rapid reconversion to XXI. Trials recorded at the end of the Experimental Part suggest that the obstacle can be overcome by suitable precautions and the elusive substance XXVII obtained.

Experimental

Absorption Spectra.—Determinations were made with Beckman Ultraviolet Spectrophotometers, Model DU, used by courtesy of Drs. J. J. Lingane and C. M. Williams. The solvents were absolute ethanol and du Pont C. P. reagent sulfuric acid. The positions and intensities of the maxima were: β-methyldihydropyrano-1,4-naphthoquinone (V); in ethanol 250 mμ (log ε 4.37), 281 (4.13), 333 (3.45), 375 (3.07) (inflection), in sulfuric acid 261 (4.52), 316 (4.05), 410 (3.63), 495 (3.40); hydrolapachol (VI), in ethanol containing 0.1% of acetic acid 252 (4.32), 282 (4.15), 332 (3.44), 387 (3.20), in sulfuric acid 260 (4.49), 312 (4.05), 402 (3.58), 485 (3.27); β-methyldihydropyrano-1,2-naphthoquinone (IV), in ethanol 256 (4.42), 280 (3.92) (inflection), 330 (3.20), 427 (3.24), in sulfuric acid 259 (4.45), 316 (4.16), 403 (3.61), 470 (3.27) (inflection).

Basicities.—A stock solution of a quinone at a concentration approximately 6 mg./100 cc. was prepared in 95.5% sulfuric acid for the *p*-quinone and 75% acid for the *o*-quinones. Known dilutions of the stock solution with water were made with cooling and their optical densities measured at 480 and 490 mμ for the *p*-quinone and 390 and 400 mμ for the *o*-quinones. From the optical densities, corrected for volume, the ratios *c* of ionized to un-ionized quinone were computed, with ionization taken to be complete in the stock solution and negligible in 62% acid for the *p*-quinone and 20–27% acid for the *o*-quinones. The acidity functions of the mixtures were interpolated from Hammett's table,[9] and the dissociation constants of the quinone cations calculated from the equation $pK_a = H_0 + \log c$. Results appear in Table I.

TABLE I

BASICITIES OF NAPHTHOQUINONES

H_2SO_4, %	H_0	*c* (average)	pK_a
β-Methyldihydropyrano-1,4-naphthoquinone (V)			
82	−8.8	3.5	−6.60
78.5	−7.15	0.87	−6.65
75	−6.6	0.33	−6.63
		Average	−6.65
β-Methyldihydropyrano-1,2-naphthoquinone (IV)			
60.5	−4.35	3.8	−3.77
55	−3.8	1.2	−3.72
50.7	−3.3	0.40	−3.70
		Average	−3.75
β-Lapachone (III)			
55	−3.8	2.02	−3.5
50.7	−3.3	0.82	−3.4
47	−2.9	0.37	−3.47
		Average	−3.45

Lapachone Equilibrium.—A mixture of 100 mg. of β-lapachone and 100 cc. of 38% hydrochloric acid was heated at 60–65° for three hours, the clear solution poured into 500 cc. of cold water and extracted with ether, and the ether washed with water, dried and evaporated. The orange–yellow residue, crystallized from 1 cc. of alcohol, afforded 70 mg. of crude, yellow α-lapachone, m. p. 115–119°.

A solution of 100 mg. of lapachol or a lapachone in 10 cc. of 96% sulfuric acid was diluted with a known quantity (4–15 cc.) of water, digested at 60–65° for one to two hours, quenched in 100 cc. of ice water, and the precipitate collected and crystallized from alcohol. Experimental results appear in Table II.

TABLE II

EQUILIBRIUM OF LAPACHONES

H_2SO_4, %	Product	Wt., mg.	M. p., °C.
79	β	61	157–159
75	β	41	156–160
67	Mixture[a]	67	100–130
62	α	41	119–120.5
58	α	67	119–122
53	α[b]	77	119–121

[a] Unrecrystallized. Spectrophotometric analysis at 460–470 mμ furnished a β-lapachone content of 51%; separation of a 50-mg. sample with alcoholic sodium bisulfite (Fieser, THIS JOURNAL, **70**, 3232 (1948)) yielded 21 mg. of crude α and 24 mg. of crude β-lapachone. [b] Crystallized directly from the reaction mixture.

To measure the lapachone equilibrium accurately at room temperature, a 50–100 mg. sample of β-lapachone or lapachol was digested for two hours at 60–65° in approximately 20 cc. of aqueous sulfuric acid and the solution allowed to stand for five days in a dark cupboard. Two 1-cc. aliquots were diluted to a convenient volume (25 or 50 cc.), one with acid of the same concentration, the other with 96% sulfuric acid, which converted α- to β-lapachone, and the optical densities at 470 mμ determined. The ratio *r* of the difference between the densities of the concentrated and dilute acids to the optical density of the dilute acid was 1.65 for 62% sulfuric acid (H_0 −4.55) and

0.42 for 66.6% acid (H_0 −5.1). Since in aqueous sulfuric acid the extinctions at 470 mμ of free and ionized *o*-quinone and ionized *p*-quinone are roughly the same, and that of uncharged *p*-quinone is 7.5% of the foregoing, the measured ratio

$$r = \frac{[\alpha](1 - 0.075)}{[H\beta^+]\left[1 + \frac{1}{K'} + (1 + 0.075\,K)\frac{[\beta]}{[H\beta^+]}\right]} \cong \frac{[\alpha]}{[H\beta^+]}\frac{0.925}{1.03 + 2.9\frac{h_0}{K_\beta}} \sim \frac{0.8[\alpha]}{[H\beta^+]}$$

in the original solution. Hence $K = h_0\,[\alpha]/K_\beta[H\beta^+] = 1.25\,(rh_0/K_\beta) = 26$ (62% acid) and 24 (66.6% acid).

Dehydrolapachone in Sulfuric Acid.—A solution of 15 mg. of dehydro-α-lapachone (XXI) in 1 cc. of concentrated sulfuric acid was allowed to stand for ten minutes, during which its initially green color changed to purple,[21] dropped into 80 cc. of ice-cold 5% sodium carbonate, and the purple suspension extracted immediately with 35 cc. of ether. The orange–red ether solution was washed with water, dried, and evaporated in vacuum. The residue, a purple solid, m. p. 102–107°, imparted an instantaneous purple color to sulfuric acid, dissolved in alcoholic sodium bisulfite to a yellow solution, and was converted by warm alcoholic hydrochloric acid to an orange substance, apparently dehydro-α-lapachone. These observations accord with the hypothesis that the purple substance is dehydro-β-lapachone (XXVII).

(21) Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

Summary

The interconversion of the lapachones in acid is explained from measurements of spectra and ionization in sulfuric acid. The discussion is extended to oxidation–reduction potentials and rates and mechanisms of hydroxyquinone cyclizations.

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Migration Aptitude as a Criterion of Ionic Mechanism in the Rearrangement of Mono-*p*-nitrotriphenylmethyl Hydroperoxide[1,2]

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Introduction.—The use of numerous acyl peroxides as initiators of polymerization is one of the most familiar pieces of evidence that these peroxides commonly undergo thermal decomposition by a mechanism involving free radicals. The same is true of hydrogen peroxide[3] and its monosubstitution products such as tetralin hydroperoxide.[4] It is now clear, however, that free radical mechanisms are not invariably operative in the decomposition of acyl peroxides and alkyl hydroperoxides. Decomposition of the peroxide of phenylacetic acid,[5] for example, is subject to general acid catalysis. *p*-Methoxy-*p'*-nitrobenzoyl peroxide[6] is capable of decomposition by either a free radical or a polar mechanism according to the conditions. 9-Decalyl hydroperoxide[7] yields a benzoate which decomposes only by way of a rearrangement favored by ionizing solvents. Other examples of duality of mechanism in the decomposition of peroxides have been given by Kharasch.[8] Criegee[7] and Leffler[9] have suggested that polar mechanisms for the rearrangement and decomposition of peroxidic substances are rather general and are particularly clearly indicated in such processes as the reaction of Caro's acid with ketones, the Dakin reaction, certain transformations of autoxidation products such as those of cyclohexene, and the rearrangement of primary into normal ozonides. A polar mechanism for the reaction of perbenzoic acid with ketones has been written by Friess.[10]

Migration Aptitudes as a Criterion of Mechanism.—The existing evidence for polar mechanisms in reactions of peroxides includes the different courses taken by polar and free radical decompositions,[6,7,8,9] susceptibility to general acid catalysis[5,6] and to ionizing media and reagents.[7,8] One of the general characteristics of polar rearrangements such as the Wagner–Meerwein and pinacol rearrangements is the order of migration aptitudes of the organic groups which migrate competitively during the rearrangement. Among aromatic groups the order of migration aptitudes in symmetrical pinacols is similar to the order of reactivity of the corresponding benzenes toward aromatic substitution.[11] This is a consequence of the fact that in both the Wagner–Meerwein rearrangement and aromatic substitution the transition state involves the attachment of an electrophilic reagent to the benzene ring before the old attachment (to carbon or hydrogen) is severed. One of the best criteria for a cationic mechanism in the rearrangement of a peroxide should be the observation that the relative migra-

(1) From a thesis presented by J. D. Cotman, Jr., for the degree of Doctor of Philosophy at Harvard University, 1949.

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