has given rise to a number of interesting lactones and dilactones of both the α- and the β-naphthoquinone series and reminiscent of some of the compounds of the lapachol and lomatiol group. These compounds have been investigated and the changes have been for the most part satisfactorily explained.

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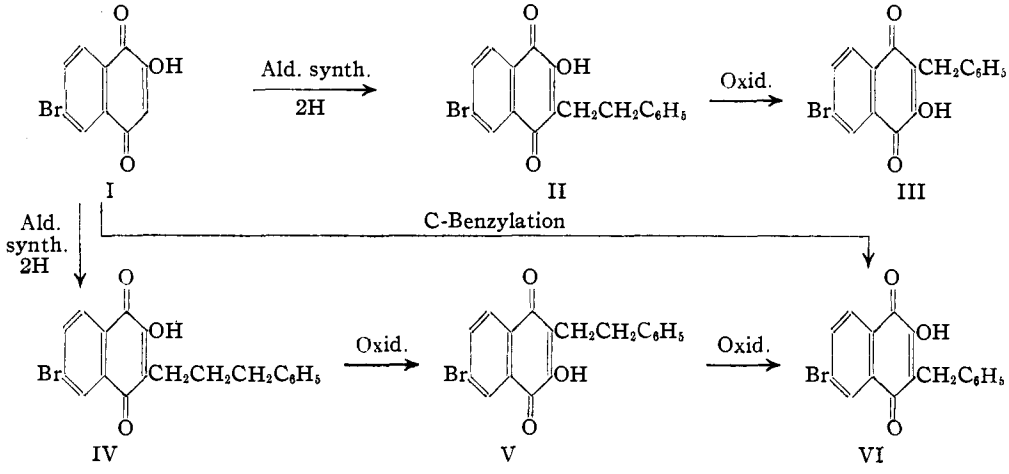
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Concerning the Mechanism of the Hooker Oxidation

BY L. F. FIESER, J. L. HARTWELL[1] AND A. M. SELIGMAN[1]

In the course of his investigations of the oxidation of alkyl and alkenyl derivatives of hydroxynaphthoquinone,[2] the late Dr. Samuel C. Hooker came to the conclusion that the essential step in the remarkable reaction discovered by him consists in the opening of the quinone ring and its subsequent closing in a different manner, and consequently that the alkyl and hydroxyl groups exchange places as a result of the oxidation. In understanding with Dr. Hooker, and as already mentioned in one of his papers,[2b] we undertook to provide a rigid test of this part of the mechanism by studying the oxidation of naphthoquinones marked with a distinguishing substituent in the aromatic ring.



2-Hydroxy-6-bromo-1,4-naphthoquinone,[3] I, served as a convenient starting material for the preparation of compounds of the type desired, and it was converted into the derivatives II and IV by condensation with the appropriate aldehydes and hydrogenation of the unsaturated side chain of the condensation products, following the general synthetic method of Hooker.[4] Submitted to the Hooker oxidation with alkaline permanganate, the hydrocinnamyl derivative IV yielded a lower homolog isomeric with the synthetic β-phenylethyl compound II but not identical with this substance. The oxidation product therefore has the alternate structure V and the hydroxyl and alkyl groups have assumed new positions with respect to the bromine atom, in accordance with the theory of Hooker. A second oxidation should result in a reversion to the original positions, with the hydroxyl and bromine located at 2 and 6, respectively. That the second oxidation product indeed has the structure VI was established by the independent synthesis of this compound from the silver salt of I by the method of Fieser.[5] According to the theory an isomer of this benzyl derivative should result from the oxidation of the synthetic β-phenylethyl compound II, and this prediction also was verified.

(1) The work on the bromonaphthoquinones and the experiments in the lapachol series were completed by J. L. Hartwell in 1933; the experiments with the alkylnaphthoquinones were carried out by A. M. Seligman in 1934.

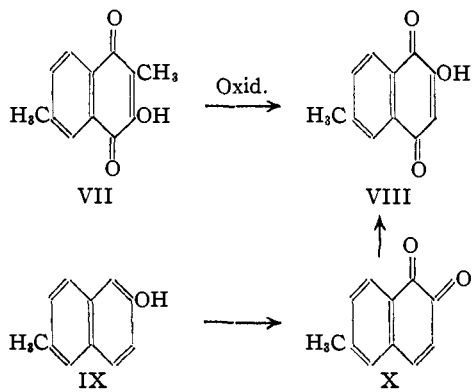
(2) Hooker, THIS JOURNAL, **58** (a) 1168; (b) 1174; Hooker and Steyermark, (c) 1179; (d) 1198 (1936).

(3) Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

(4) Hooker, THIS JOURNAL, **58**, 1163 (1936).

(5) Fieser, *ibid.*, **48**, 3201 (1926).

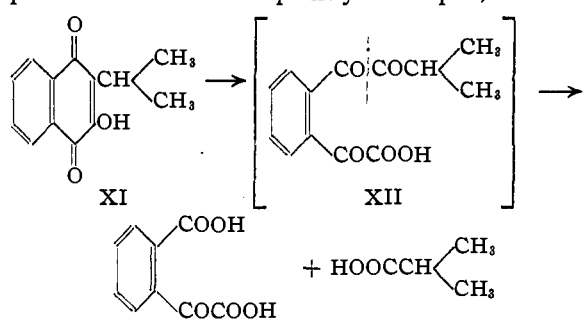
While these experiments adequately establish the point at issue it seemed desirable to include in the study a case in which the structure of the product of a single oxidation, rather than of two successive oxidations, could be proved by direct synthesis. 2,6-Dimethyl-3-hydroxy-1,4-naphthoquinone[6] (VII) was investigated for the purpose and when oxidized by the Hooker method it was found to give in good yield a hydroxynaphtho-



quinone having one less methyl group. That it is the methyl group of the quinone ring which has been eliminated is shown very clearly by the observation that the oxidation product easily yields an ether on reaction with methyl alcohol in the presence of a trace of mineral acid, whereas under similar conditions the starting material (VII) is unchanged.[6] As in other cases[7] a substituent in the hydroxyquinone ring effectively blocks the addition reaction. That the hydroxyl group assumes a new position with respect to the remaining methyl group as a result of the oxidation was established by the synthesis of a compound of the structure VIII from 6-methyl-2-naphthol,[8] IX, as indicated. The compound proved to be identical with the oxidation product from VII. Regarding the structure of the starting material IX, obtained from β-methylnaphthalene by sulfonation and fusion, it was found that the substance forms a characteristic 1,8-phthaloyl derivative which can be rearranged with concentrated sulfuric acid to a methylhydroxybenzanthraquinone, showing that the 7(β)-position of the methylnaphthol is unoccupied. This provides an independent proof in confirmation of other, less direct, evidence[8,9] that the substituents are located in the 2- and 6-positions as in formula IX.

(6) Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934).
(7) Fieser, *ibid.*, **48**, 2922 (1926).
(8) Dziewoński, Schoenówna and Waldmann, *Ber.*, **58** 1212 (1925).
(9) Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932).

It may be concluded from these results that the hydroxyl group and the modified alkyl substituent exchange places as a result of the oxidation, exactly as predicted on the theory that the quinone ring opens in the course of the reaction. In the hope of securing still more direct evidence on this point we undertook to investigate the oxidation of a compound of such a structure that the quinone ring, once opened, could not subsequently be reestablished. A compound suitable for the purpose was obtained by submitting hydrolapachol[4] to two successive oxidations with alkaline permanganate, 2-isopropyl-3-hydroxy-1,4-naphthoquinone (XI) being easily obtained in this way in good yield. When this was treated with alkaline permanganate in the regular manner oxidation proceeded to the colorless stage as usual, but no pink or red color subsequently developed, even on



long standing. According to the theory the oxidation should lead to the formation of the triketo acid XII which, lacking a methylene group in the proper position of the side chain, cannot undergo cyclization to a hydroxynaphthoquinone. On working up the acidified, colorless solution there was isolated in place of this substance phthalonic acid and isobutyric acid, which very probably arise from the oxidative cleavage of XII between the two adjacent carbonyl groups.

These observations lend considerable support to the view that the quinone ring opens in the first step of the Hooker oxidation, but our work casts no further light on the exact mechanism of the subsequent ring closure. There is perhaps a rough analogy in the conversion of 2-aceto-1-naphthylglyoxylic acid into 1,2-naphthindanedione,[10] but the reaction occurs in an acidic rather than an alkaline medium and the process definitely is one of oxidation, a point not yet clearly established in the case at hand.

In conclusion the senior author wishes to acknowledge his indebtedness to the late Dr. Hooker

(10) Fieser, THIS JOURNAL, **51**, 940 (1929).

both for the permission to collaborate on this problem and for the useful and inspiring advice of his esteemed friend.

Experimental Part

Condensation of Aldehydes with 2-Hydroxy-6-bromo-1,4-naphthoquinone, Hydrogenation

The starting material, previously mentioned only incidentally in the literature,[3] was prepared conveniently from 6-bromo-1,2-naphthoquinone[3,11] as follows. On reaction with acetic anhydride–sulfuric acid by the usual procedure[12] this gave **1,2,4-triacetoxy-6-bromonaphthalene** in 62% yield, the purified material forming colorless needles, m. p. 162°, from alcohol.

Anal. Calcd. for $C_{16}H_{13}O_6Br$: C, 50.4; H, 3.44. Found: C, 50.6; H, 3.69.

On adding 145 g. of the powdered triacetate to a cold solution of 160 g. of potassium hydroxide in 730 cc. of 95% alcohol the temperature soon rose nearly to the boiling point and the solid dissolved to give a solution which rapidly turned dark brown. Oxidation to the quinone was completed by bubbling in air for one-half hour, after which the potassium salt of the product soon separated completely as small red crystals. Washed with alcohol, then with ether, the material was obtained in a very pure condition and in quantitative yield. As the potassium salt is sparingly soluble in water it was merely suspended in hot water and treated with dilute acid. The hydroxyquinone was obtained as a lemon-yellow, crystalline precipitate. It formed beautiful yellow needles, m. p. 204–205°, from alcohol containing a trace of acetic acid.

2 - Hydroxy - 3 - β - phenylvinyl - 6 - bromo - 1,4 - naphthoquinone was prepared by Hooker's method[4] but using more solvent. A solution of 10 g. of the hydroxybromoquinone in 225 cc. of glacial acetic acid was treated at 93° with 30 cc. of previously warmed concentrated hydrochloric acid, followed immediately by 22 cc. of phenylacetaldehyde. After digestion at 80° for one hour a large crop of red, crystalline material had separated and this was collected while the solution was still hot, as on cooling a brown substance separated. The collected material, after being washed with acetic acid, was obtained in a good condition; yield 56%. Crystallized from benzene it formed glistening, deep red needles, m. p. 243–244°, violet solution in alkali.

Anal. Calcd. for $C_{18}H_{11}O_3Br$: C, 60.9; H, 3.12. Found: C, 60.8; H, 3.32.

Reductive acetylation with zinc dust, acetic anhydride, and sodium acetate gave the **hydroquinone triacetate** in 86% yield, the compound forming colorless needles, m. p. 197–198°, from benzene–absolute alcohol.

Anal. Calcd. for $C_{24}H_{19}O_6Br$: C, 59.6; H, 3.96. Found: C, 59.8; H, 4.12.

Hydrogenation of the hydroxyquinone proceeded smoothly in alcoholic solution using Adams catalyst, giving **2-hydroxy-3-β-phenylethyl-6-bromo-1,4-naphthoquinone (II)**, which crystallizes from alcohol containing a little acetic acid as flat, golden-yellow needles, m. p. 180–181°; red color in alkali.

Anal. Calcd. for $C_{18}H_{13}O_3Br$: C, 60.5; H, 3.67. Found: C, 60.3; H, 3.81.

The hydroquinone triacetate of II formed fine, colorless needles from alcohol–benzene, m. p. 188–189°.

Anal. Calcd. for $C_{24}H_{21}O_6Br$: C, 59.4; H, 4.36. Found: C, 59.3; H, 4.49.

2 - Hydroxy - 3 - γ - phenyl - α - propenyl - 6 - bromo - 1,4-naphthoquinone was prepared as above, using hydrocinnamaldehyde, but the product did not separate from the hot reaction mixture. On pouring this into water there was obtained a brown precipitate mixed with black tar. After decanting the aqueous liquor the material was warmed with two portions of alcohol, for although this extracted some of the product it effectively removed the tar and left a fairly clean, crystalline yellowish residue (40% yield). For further purification the product was dissolved in 2% alcoholic potassium hydroxide and the violet solution was filtered from some dark residue and acidified. The precipitated material then crystallized well from benzene–petroleum ether to which a small amount of acetic acid was added, finally forming bright orange needles, m. p. 177–178°.

Anal. Calcd. for $C_{19}H_{13}O_3Br$: C, 61.8; H, 3.55. Found: C, 61.8; H, 3.85.

The hydroquinone triacetate formed colorless needles, m. p. 170–171°, from alcohol, benzene, or glacial acetic acid.

Anal. Calcd. for $C_{25}H_{21}O_6Br$: C, 60.4; H, 4.26. Found: C, 60.4; H, 4.31.

This triacetate slowly absorbed hydrogen in the presence of Adams catalyst giving the corresponding saturated compound, **1,2,4-triacetoxy-3-hydrocinnamyl-6-bromonaphthalene,** which formed needles, m. p. 170–172° (depresses the m. p. of the starting material).

Anal. Calcd. for $C_{25}H_{23}O_6Br$: C, 60.1; H, 4.64. Found: C, 60.1; H, 4.80.

The saturated triacetate was dissolved in hot acetone and hydrolyzed with alcoholic alkali, the solution being exposed to the air until quite red, diluted, and acidified. The yellow precipitate of **2-hydroxy-3-hydrocinnamyl-6-bromo-1,4-naphthoquinone,** IV, (92% yield) crystallized from alcohol–benzene containing a trace of acetic acid as golden-yellow scales melting at 170–171°.

Anal. Calcd. for $C_{19}H_{15}O_3Br$: C, 61.5; H, 4.08. Found: C, 61.4; H, 4.35.

Benzylation of 2-Hydroxy-6-bromo-1,4-naphthoquinone

A suspension of 6.2 g. of the silver salt of the hydroxyquinone with 3 g. of benzyl bromide in 70 cc. of absolute ether was allowed to stand in a stoppered flask overnight, when the red salt had been replaced by silver bromide. Three products were obtained, namely, **4-benzyloxy-6-bromo-1,2-naphthoquinone** (a), **2-hydroxy-3-benzyl-6-bromo-1,4-naphthoquinone** (b), and **2-benzyloxy-6-bromo-1,4-naphthoquinone** (c), and they were separated in this order as follows. The ethereal solution was filtered and set aside, while the residue was extracted with 100 cc. of hot benzene. On cooling the benzene solution the *o*-quinone ether (a) separated in a nearly pure condition; yield 0.6 g. (10%); crystallized from benzene it formed orange-yellow needles, m. p. 227–228°. The benzene mother

(11) Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).
(12) Thiele and Winter, *Ann.*, **311**, 345 (1900).

liquor and the ethereal solution were combined and extracted with 2% alkali and the red alkaline solution on acidification gave 1.4 g. (24%) of the acidic isomer (b), which crystallized from absolute alcohol–benzene, with a trace of acetic acid, as golden-yellow plates, m. p. 192°. On drying and concentrating the benzene–ether mother liquor 0.6 g. (10%) of the *p*-quinone ether was obtained. It formed pale yellow needles from benzene, m. p. 201–202°.

Anal. Calcd. for $C_{17}H_{11}O_3Br$: C, 59.5; H, 3.23. Found: (a) C, 59.5; H, 3.59; (b) C, 59.5; H, 3.63; (c) C, 59.5; H, 3.49.

The structures of the non-acidic isomers (a) and (c) are inferred from the colors of the compounds, in analogy with known cases. It was noted that on the addition of a drop or two of sodium or potassium hydroxide to a solution of the *p*-quinone ether in acetone the solution became deep purplish-blue, the color changing after a few minutes to dull green with loss of strength. Both the alkali and the solvent acetone appear to be necessary for the production of the blue color, as other bases and other solvents were ineffective. The *o*-quinone ether gave only a faint pink coloration, and the test was negative with α-naphthoquinone and several of its simple derivatives. 2-Methoxy-1,4-naphthoquinone gave an exactly similar coloration.

Reductive acetylation of the acidic isomer gave **1,2,4-triacetoxy-3-benzyl-6-bromonaphthalene**; fine needles, m. p. 202–203°.

Anal. Calcd. for $C_{23}H_{19}O_6Br$: C, 58.6; H, 4.06. Found: C, 58.6; H, 4.29.

Oxidation of the Bromo Compounds

The Hydrocinnamyl Compound IV.—On account of the sparing solubility of the brominated quinones, the procedure was slightly modified as follows. A solution of 3 g. of IV in the required amount of hot benzene was stirred into 600 cc. of hot 1% sodium hydroxide solution and the red solution was cooled to 0° and treated with 189 cc. of 1% potassium permanganate solution, also at 0°. The color changes were as described by Hooker, the solution becoming practically colorless (spot test) and then reaching a maximum intensity of red in one to two hours. The yield of precipitated, nearly pure, material was 36%.[13] Crystallized from alcohol containing acetic acid the **3-hydroxy-2-β-phenylethyl-6-bromo-1,4-naphthoquinone** (V) formed golden-yellow needles, m. p. 173–175°. A mixture with the isomer II melted at 148–153°.

Anal. Calcd. for $C_{18}H_{13}O_3Br$: C, 60.5; H, 3.67. Found: C, 60.5; H, 3.93.

Further Oxidation of V.—From 0.9 g. of the above compound (V), oxidized in the same way, there was obtained in 54% yield a substance crystallizing as golden-yellow plates, m. p. 188–189°, and giving no depression with synthetic 2-hydroxy-3-benzyl-6-bromo-1,4-naphthoquinone, VI.

Oxidation of the Synthetic β-Phenylethyl Compound, II.—The oxidation product, obtained in 43% yield, crystallized from alcohol with a trace of acetic acid as golden-yellow needles, m. p. 158–159°. The melting point of the **3-hydroxy-2-benzyl-6-bromo-1,4-naphthoquinone** (III) was depressed about 10° by admixture with the isomeric 3-benzyl compound.

Anal. Calcd. for $C_{17}H_{11}O_3Br$: C, 59.5; H, 3.23. Found: C, 59.2; H, 3.43.

The **hydroquinone triacetate**, which formed colorless needles, m. p. 196–197°, also gave a depression with the isomeric 3-benzyl compound.

Anal. Calcd. for $C_{23}H_{19}O_6Br$: C, 58.6; H, 4.06. Found: C, 58.5; H, 4.34.

2-Isopropyl-3-hydroxy-1,4-naphthoquinone

Preparation.—Lapachol kindly supplied for the purpose by Dr. Hooker was converted into the hydro derivative[4] and this was oxidized[2a] to 2-isobutyl-3-hydroxy-1,4-naphthoquinone. The acetate of this substance formed pale yellow needles, m. p. 53.5–54° (Calcd.: C, 70.6; H, 5.93. Found: C, 70.6; H, 5.40). Oxidation of the hydroxy compound in 1% sodium hydroxide solution with 1% aqueous potassium permanganate gave **2-isopropyl-3-hydroxy-1,4-naphthoquinone** (XI) in 52% yield. The compound gave bright yellow needles, m. p. 92–93° from alcohol–acetic acid.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.60. Found: C, 72.4; H, 5.76.

Oxidation.—When a solution of 1 g. of the quinone in 1% alkali was treated with an aqueous solution of 1.08 g. of potassium permanganate according to Hooker's procedure the oxidation was somewhat slower than usual and the supernatant liquor became colorless only after about two hours. Air was bubbled through the solution for two hours, but no reddening occurred. After removing the manganese dioxide and acidifying the colorless solution a strong odor of isobutyric acid was noted and the substance was expelled by distilling the solution to a small volume, adding water and repeating the process. The acid distillate neutralized 42 cc. of 0.1038 *N* alkali, corresponding to a yield of 61% of isobutyric acid. In another experiment 5 g. of the starting material gave an acid distillate containing isobutyric acid equivalent to a 65% yield, on the basis of titration. The neutral solution of the salt on evaporation left a residue (1.25 g.) which was treated with hydrogen chloride in the presence of ether. After filtering, and removing the solvent, the free acid (0.91 g.) was refluxed with *p*-toluidine (3.2 g.), and after extracting the unused reagent with dilute hydrochloric acid the residue was dried and crystallized from ligroin. Colorless plates, m. p. 104–105°, were obtained and a mixed melting point with a known sample of the *p*-toluide of isobutyric acid, m. p. 106–106.5°, established the identity of the substance.

The residue from the steam distillation in the first experiment (1 g. of starting material) was made faintly alkaline and treated with 0.4 g. of phenylhydrazine hydrochloride and a few drops of acetic acid. After heating the mixture for four hours on the steam-bath and cooling, a pale yellow solid separated mixed with resinous matter. The yellow substance was extracted with soda solution, leaving the resin undissolved, and on acidifying the filtrate a pale yellow crystalline precipitate separated (0.25 g.). The substance melted at 215° with gas evolution and it was identified as 3-phenyl-4-phthalazone-1-carboxylic acid by a mixed melting point determination with a sample of the

(13) At the time of the experiment it was not recognized in Dr. Hooker's laboratory or in our own that the yield is generally improved by employing a higher concentration of alkali.

substance, m. p. 216–217°, dec., prepared from phthalonic acid and phenylhydrazine.[14]

Oxidation of 2,6-Dimethyl-3-hydroxy-1,4-naphthoquinone

Conversion to 2-Hydroxy-6-methyl-1,4-naphthoquinone.—In trial experiments it was found, in conformity with Hooker's observations,[2b] that the reaction proceeds best in a strongly alkaline medium, and the following method was adopted as the most satisfactory. A solution of 1.13 g. of the dimethylhydroxynaphthoquinone (VII) in 100 cc. of 6% sodium hydroxide was chilled in ice and treated all at once with a solution of 1.26 g. of potassium permanganate and 6 g. of sodium hydroxide in 126 cc. of water, also at 0°. After standing for two hours at room temperature, the manganese dioxide was removed and the filtered solution, which had become quite red, was acidified. Small yellow plates of the oxidation product separated in a good condition (0.78 g.) and a further amount (0.05 g.) was obtained by extracting the filtrate with ether; yield, 75%. The substance crystallized from benzene–ligroin as golden-yellow plates and from acetic acid as stout yellow needles; m. p. 199°, dec. It is sparingly soluble in water, moderately soluble in benzene, readily soluble in alcohol. The solutions in both alkali and sulfuric acid are red.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.19; H, 4.29. Found: C, 70.20; H, 4.30.

The methyl ether was obtained in good yield by refluxing for one and one-half hours a solution of 0.5 g. of the hydroxyquinone and 0.5 cc. of concentrated sulfuric acid in 25 cc. of methyl alcohol. The ether separated on cooling as fine, pale yellow needles, and after recrystallization it melted at 167–167.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.25; H, 4.99. Found: C, 71.31; H, 5.01.

The hydroquinone triacetate formed small, colorless needles from benzene–ligroin, m. p. 157–158°.

Anal. Calcd. for $C_{17}H_{16}O_6$: C, 64.53; H, 5.10. Found: C, 64.34; H, 5.04.

Synthetic Preparation of 2-Hydroxy-6-methyl-1,4-naphthoquinone.—β-Methylnaphthalene (100 g.) was sulfonated according to Dziewoński, Schoenówna and Waldmann[8] but the filtered solution of the reaction product in water (1 liter) was neutralized with concentrated alkali. The sodium salt which separated was obtained in a pure condition after one recrystallization; yield, 80%; *p*-toluidine salt, flat needles from dilute alcohol, m. p. 250–251°. For conversion to 6-methyl-2-naphthol[8] 140 g. of the sodium salt was fused with a melt from 460 g. of potassium hydroxide and 7 cc. of water and the crude, precipitated material was coagulated by boiling, dried, and vacuum distilled, giving 50 g. (55%) of slightly pink material melting at 123° and suitable for further use. The methylnaphthol was coupled with diazotized sulfanilic acid and the dye was reduced with hydrosulfite essentially as described for the case of β-naphthol,[15] with allowance for a lower solubility in the present series, the yield of very nearly colorless 1-amino-6-methyl-2-naphthol hydrochloride being 50%. The oxidation to 6-methyl-1,2-naphthoquinone presented some difficulties and ferric chloride gave only what appeared to be a dimolecular product. The following details can be supplemented to the brief statement in the literature.[8] A suspension of 7 g. of the amine hydrochloride in 200 cc. of water was neutralized with 14 g. of sodium acetate crystals, 10 cc. of concentrated sulfuric acid was added and the mixture was poured into 3 liters of water. After adding an additional 30 cc. of the acid the solution on filtration was water-clear, and it was stirred well and treated all at once with a cold solution of 7 g. of potassium dichromate and 30 cc. of concentrated sulfuric acid in 150 cc. of water. The quinone separated as orange micro-crystals, m. p. 126°, in 60% yield.

Potassium 6-Methyl-1,2-naphthoquinone-4-sulfonate.—Attempts to introduce an hydroxyl group by the Thiele reaction were unsuccessful; a colorless product, m. p. 156–158°, slowly separated from the mixture but it did not have the properties of a hydroquinone triacetate. The addition of bisulfite, on the other hand, proceeded normally. The quinone (3.5 g.) was added very slowly with stirring to a solution at 25° of 3.6 g. of sodium bisulfite in 40 cc. of water and after one-half hour the resulting solution was filtered, treated with 0.4 cc. of concentrated sulfuric acid, boiled, cooled to 25°, and treated with 2.4 g. of potassium dichromate and 1.8 cc. of concentrated sulfuric acid in 7 cc. of water, followed by 40 cc. of saturated potassium chloride solution, added in portions as crystallization of the quinone sulfonate proceeded. On dissolving the compound in water containing a trace of bromine at 60°, clarifying the solution and adding potassium chloride,[16] the quinone sulfonate separated as fine orange needles of a monohydrate; yield 50%.

Anal. Calcd. for $C_{11}H_7O_5SK \cdot H_2O$: S, 10.40. Found: S, 10.48.

2-Methoxy-6-methyl-1,4-naphthoquinone was obtained by mixing 0.8 g. of the above sulfonate with a solution of 0.5 cc. of concentrated sulfuric acid in 5 cc. of methyl alcohol at 0°, gradually warming the mixture on the steam-bath, adding 5 cc. more methyl alcohol, and refluxing until the salt had disappeared. On cooling the methoxy compound separated as very fine, pale yellow needles (70% yield). On recrystallization the substance melted at 167–167.5° and gave no depression when mixed with the ether of the quinone obtained above as an oxidation product. The hydroxy compound was obtained on hydrolysis of the synthetic ether and both this substance and its hydroquinone triacetate were compared with the above samples and the identity fully established.

1,8-Phthaloyl-6-methyl-2-naphthol (1-Hydroxy-5-methylpleiadenedione).—On condensing 6-methyl-2-naphthol (10 g.) with phthalic anhydride in the presence of aluminum chloride at 200° by the previously described procedure,[17] the reaction product was obtained in a pure condition after one crystallization from glacial acetic acid; yield, 14.7 g. (81%). It forms bright yellow needles, m. p. 194–194.5°.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 79.47; H, 4.44.

2'-Hydroxy-4-methyl-1,2-benzanthraquinone.—As with the parent compound,[18] the rearrangement proceeded

(14) Henriques, *Ber.*, **21**, 1610 (1888).

(15) Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

(16) See Martin's method for the parent compound, ref. 15.

(17) Fieser, THIS JOURNAL, **55**, 4977 (1933).

(18) Fieser and Fieser, *ibid.*, **55**, 3342 (1933).

poorly and much material was lost through sulfonation. Three grams of the pleiadenedione was quickly stirred into a solution of 160 cc. of concentrated sulfuric acid and 80 cc. of water preheated to 170°. The initially yellow-red solution soon turned brown and after three minutes it was poured into boiling water, and after boiling the mixture to coagulate the red precipitated material this was collected and washed; yield 0.9 g. The material was purified through the acetate which crystallizes from glacial acetic in cottony clusters of canary-yellow needles, m. p. 218–219°. This was hydrolyzed with alcoholic alkali giving, after dilution, an intensely blue solution of the sparingly soluble sodium salt from which the hydroxyquinone separated on acidification as a fiery red precipitate of hair-like micro-needles. From alcohol the substance crystallized as orange-red plates, m. p. 256–258°, dec. Treated with sodium hydrosulfite, the blue alkaline solution gives a transient red color and then an orange-yellow vat.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 78.84; H, 4.66. Acetate, calcd. for $C_{21}H_{14}O_4$: C, 76.34; H, 4.27. Found: C, 76.42; H, 4.39.

Summary

By using 2-alkyl-3-hydroxy-1,4-naphthoquinones having reference groups in the aromatic ring it has been possible to prove that the substituents in the 2- and 3-positions exchange places in the course of the Hooker oxidation in exactly the manner predicted by the discoverer of the reaction. Hooker's view that the quinone ring is opened in the first step of the process has been substantiated by the isolation of products evidently arising from the type of intermediate postulated.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 16, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. X. A Potentiometric Method for Determining ΔF for the Addition of Sodium to an Organic Compound[1]

BY H. E. BENT AND N. B. KEEVIL

Most compounds containing sodium are very stable. A reaction leading to the formation of a compound involving the pure metal goes so nearly to completion that it is not possible to obtain an equilibrium constant from the concentration of unreacting material. Such reactions can be studied, however, with the aid of mercury.[2] Sodium forms compounds with mercury which are so stable that it is possible to remove sodium from other compounds by shaking them with mercury or a dilute amalgam. By choosing an amalgam of the proper concentration an equilibrium can be established favorable for analysis and the computation of an equilibrium constant. At equilibrium the reaction may be considered as a distribution experiment, the sodium in the mercury being in equilibrium with the sodium in the solution of the compound being studied. Since the thermodynamic properties of amalgams have been rather thoroughly studied, it is possible to calculate the free energy change which would have accompanied the reaction if solid sodium had been used.

The method is capable of quite general application but has certain disadvantages. In the first place the range of concentration of sodium amalgams which are liquid at room temperature is small. The increase in temperature necessary to extend the range of concentration appreciably would be so great as to decompose many organic compounds. The consequence of this rather narrow range of liquid amalgam is that only compounds which have a correspondingly narrow range of stability can be studied by this method. A second difficulty was encountered when studying reactions characterized by a large activation energy. Sometimes many months were required for the establishment of substantially equilibrium concentrations. The potentiometric method to be described seems likely to be free from these objections.

Both difficulties are inherently absent in a potentiometric method since a reaction does not need to proceed to the equilibrium point. The potential is a measure of the distance the system is from equilibrium and hence one might expect to be able to study with the aid of liquid amalgams reactions which would require solid amalgams by the analytical method. Furthermore, a reaction which proceeds very slowly might be expected to supply sufficient energy for a delicate electrical measurement while requiring years for substantial completion. Preliminary calculations indicated this to be the case.

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(2) Bent, THIS JOURNAL, **52**, 1498 (1930).