fitted with stirrer, 2-liter dropping funnel and vent to the atmosphere. Ethanol (30 cc.) was added to 1200 ml. of anhydrous ammonia in the separatory funnel and 11.5 g. (0.50 mole) of sodium added in small pieces while the contents of the separatory funnel were stirred mechanically. The resulting sodium ethoxide suspension was added over a period of 10 minutes to the mixture in the main reaction flask. Both the sodium ethoxide suspension and the reaction mixture were stirred during the addition. The ammonia was then evaporated using an aspirator and a bath of running cold tap water. The residual salts were taken up in water, filtered to clarify, cooled with crushed ice and carefully acidified with sulfuric acid whereupon 43.6 g. (82%) of crude product, m.p. 143–149°, separated. Recrystallization from 140 cc. of 60% aqueous ethanol gave 24.5 g. (46%) of β-bromo-*cis*-cinnamic acid, m.p. 159–160°.

Acknowledgment.—We wish to thank Research Corporation for a grant in support of this work.

Summary

Dehydrobromination of α,β-dibromohydrocinnamic acid with two equivalents of sodium ethoxide or sodium hydroxide in liquid ammonia formed β-bromo-*cis*-cinnamic acid rather than the mixture of α-bromocinnamic acids which result from the use of aqueous or alcoholic alkalies. Excess of these alkaline reagents produced phenylpropiolic acid.

The reaction with an excess of sodamide or sodium acetylides formed cinnamic acid. The sodamide reaction apparently involved dehydrobromination to a mixture of α- and β-bromocinnamic acids followed by reductive cleavage of the remaining bromine.

PORTLAND 3, OREGON RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rearrangement and Reduction of Hindered 2-Hydroxy-3-alkyl-1,4-naphthoquinones

BY LOUIS F. FIESER AND ALFRED R. BADER[1]

When a solution of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone[2] (I) in 5% aqueous alkali is heated on the steam-bath with exclusion of air, the initially deep red solution becomes pure yellow in about 27 hours and acidification then precipitates a yellow, non-quinonoid isomer of I for which the structure of 2-cyclohexylindenone-3-carboxylic acid (III) has been tentatively suggested.[3] Further investigation has substantiated this assignment of structure. The yellow isomer has the ultraviolet absorption characteristics expected for III, it forms ester, amide and semicarbazone derivatives, and it is reduced by zinc dust and either acetic acid or alkali to a colorless dihydride of properties consistent with the indanone formula IX. Thus IX has an ultraviolet absorption spectrum similar to that of acetophenone and is reducible by the Clemmensen method to 2-cyclohexylindane-3-carboxylic acid. The indenone III also reacts with excess diazomethane to give a pyrazoline ester of the probable structure X.

Dr. Martin G. Ettlinger of this Laboratory observed in 1947 that 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone (Ia) is rapidly converted by alkali into a similar yellow non-quinone and that a colorless intermediate is formed at about the same rate when the rearrangement is conducted in a buffer of *p*H 9.2. We isolated these products and found the properties in accordance with the indenone structure IIIa for the yellow compound and the 3-hydroxyindanone-3-carboxylic acid structure II for the intermediate. Colorless II, of acetophenone-like spectrum, is converted rapidly by alkali into IIIa. Cooke and Somers[4] have reported the independent isolation of the *t*-butyl compound IIIa and the isolation and synthesis of the corresponding isopropyl derivative[5]; these authors comment on the analogy, considered also by Dr. Ettlinger, to the rearrangement of dunnione to allodunnione.[6]

According to our observations isomerization of 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone by 5% alkali at 90° is complete in 1 hour. 2-Hydroxy-3-cyclohexyl-1,4-naphthoquinone is isomerized by 5% alkali in some 27 to 30 hours, and a trace of the indanone IX was isolated from the reaction mixture. When the rearrangement was conducted in 2% alkali, no by-product was observed and pure III was isolated in 88% yield. When the compound I was heated in a buffer at *p*H 9.2, the sole product was the indenone III (91% yield). In this instance the hydroxyindanonecarboxylic acid is probably the initial product but undergoes dehydration at a rate exceeding the rate of formation. Whereas the dehydration is base catalyzed, the rate of rearrangement is independent of the concentration of hydroxide ion, provided this is sufficient to maintain the quinone largely in the form of the anion.

The mechanism suggested in the formulation is that the hydroxyquinone anion present in the red solution affords a hydrate that undergoes aldol cleavage and recondensation to II; the reaction can be regarded alternately as a benzilic acid rearrangement of the trione anion. The mechanism evidently is the same as that of the alkaline cleavage of 2- and 3-hydroxy-1,4-phenanthrenequinone observed by one of us.[7] In the case of the 2-hydroxy-3-alkyl-1,4-naphthoquinones, a possible explanation of the fact that a bulky alkyl group favors rearrangement is that hindrance in the planar anion is relieved by formation of the nonplanar hydrate.

The intermediates in the Hooker oxidation[8] of 2-hydroxy-3-alkyl-1,4-naphthoquinones, obtained in high yield by the action of alkaline hydrogen peroxide, have been shown to be 2,3-dihydroxy-2-alkylindanone-3-carboxylic acids,[9] but

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[1] Abbott Laboratories Fellow, 1948–1950.

[2] Fieser, THIS JOURNAL, **70**, 3165 (1948).

[3] Fieser, *ibid.*, **70**, 3237 (1948).

[4] Cooke and Somers, *Nature*, **165**, 314 (1950).

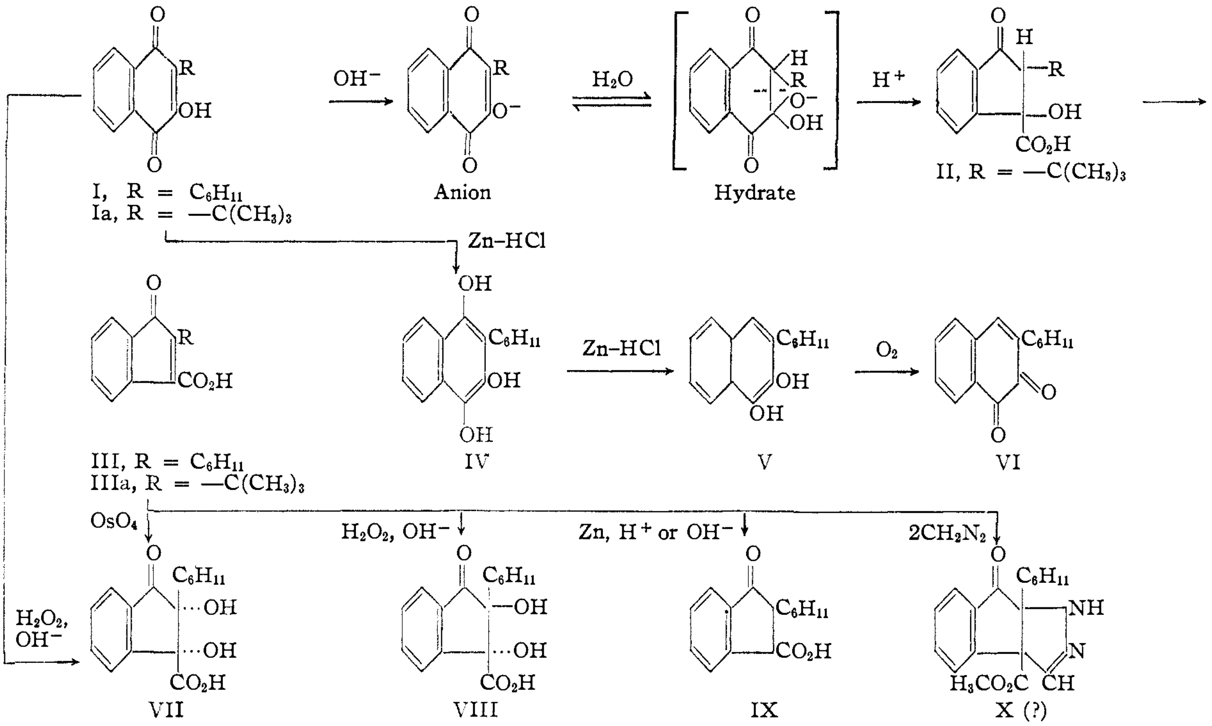
[5] See also Cooke, *ibid.*, **162**, 178 (1948); Shchukina, Kondrat'eva and Shemyakin, *J. Gen. Chem.*, **18**, 2121 (1948).

[6] Price and Robinson, *J. Chem. Soc.*, 1522 (1939).

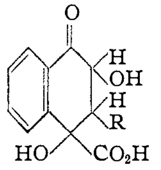
[7] Fieser, THIS JOURNAL, **51**, 940, 1896 (1929).

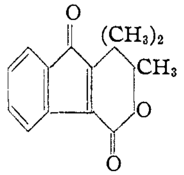
[8] Hooker, *ibid.*, **58**, 1164, 1174, 1179 1(936).

[9] Fieser and Fieser, *ibid.*, **70**, 3215 (1948).



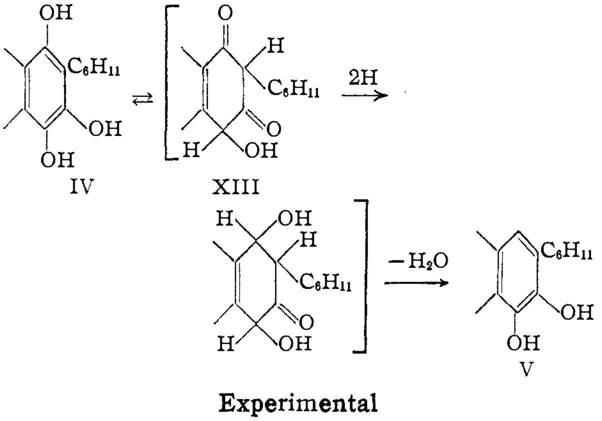
the configuration has not been established. We converted 2-cyclohexylindenone-3-carboxylic acid (III) with osmium tetroxide into the *cis*-diol VII (formulation of one of the two enantiomers) and with alkaline peroxide into the *trans*-diol VIII, and found the former diol (VII) to be identical with the previously described[9] Hooker intermediate. On titration with periodic acid, both the *cis*- and the *trans*-diol consumed two moles of reagent rapidly and a third mole more slowly; this behavior confirms the structures assigned and definitely excludes an open-chain formulation or the possible, if improbable, alternate cyclic formulation XI.


XI


XII

Allodunnione[6] corresponds to the 2-alkylindenone-3-carboxylic acids both in mode of formation and in ultraviolet absorption spectrum,[10] and hence the original formulation XII of Price and Robinson is substantiated. Our oxidation of III with alkaline hydrogen peroxide to the *trans*-diol VII was conducted by the procedure by which Price and Robinson converted allodunnione into a substance which they regarded as a lactone acid, $C_{12}H_{12}O_4$. The acid was not shown to be lactonic and the present results cast doubt on the formulation advanced.

A novel reaction was discovered as the result of an attempted Clemmensen reduction of a sample of III later found to have been contaminated with the starting hydroxyalkylnaphthoquinone (I). Clemmensen reduction of pure I, followed by air oxidation, was found to afford 3-cyclohexyl-1,2-naphthoquinone (VI), characterized by its bright orange-red color, by formation of a phenazine derivative, and by reconversion to I by Thiele reaction, hydrolysis and oxidation. 3-Isopropyl-, 3-phenyl- and 3-*p*-bromophenyl-1,2-naphthoquinone were obtained similarly from the 2-hydroxyl-3-alkyl- or aryl-1,4-naphthoquinones, but the reaction failed in the case of 2-hydroxy-1,4-naphthoquinone, its 3-methyl, 3-isoamyl and 3-triphenylmethyl derivatives, as well as with 2-cyclohexyl-1,4-naphthoquinone. In the case of I, the reaction proceeded equally well when applied to the hydroquinone, IV. Since the 2-hydroxyl group seems essential and since reduction was observed only with bulky 3-substituents, it seems possible that the reaction involves the 1,3-diketone XIII, whose formation is favored by hindrance between the 2-substituent in IV and the coplanar hydroxyl groups at C_1 and C_3.



Experimental

2-Cyclohexylindenone-3-carboxylic Acid (III).—In a repetition of the previous experiment,[3] 1 g. of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone[2] (I) was heated with 100

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(10) Cooke and Macbeth and Winzor, *J. Chem. Soc.*, 878 (1939).

cc. of 5% sodium hydroxide on the steam-bath in the absence of air for 30 hours (pure yellow solution). The cooled solution was extracted with ether to remove the blue pigment, acidified and the yellow product crystallized from acetic acid to give 0.6 g. of III, m.p. 168–169°. Fractionation of the mother liquor afforded 35 mg. of fine white needles of 2-cyclohexylindanone-3-carboxylic acid (IX, below), m.p. and mixed m.p. 149°.

When 2% alkali was used for the isomerization, the reaction took longer but the yield of III was improved and no blue pigment was produced. Thus 8.6 g. of I was heated with 1 l. of 2% sodium hydroxide solution under nitrogen until dissolved and the flask was stoppered and heated at 90° for 48 hours. Acidification of the cooled yellow solution precipitated 8.6 g. of crude product, m.p. 162–165°, and crystallization from ligroin (60–90°)–acetone (10:1) gave 7.6 g. (88%) of yellow needles of III, m.p. 169–170°, and a second crop of 0.6 g., m.p. 167–169°.

Isomerization at about *p*H 9.2, conducted as above with 10 g. of I, 100 cc. of 1 *N* NaOH, and 2 l. of 0.2 *M* disodium hydrogen phosphate appeared complete in two weeks and the yield of once-crystallized product, m.p. 169–170°, was 9.1 g. (91%).

The following constants were found for pure 2-cyclohexylindenone-3-carboxylic acid (m.p. 171–172°): $\lambda_{\max}^{C_2H_5OH}$ 245, 329 mμ (log ε 4.45, 3.15); $\lambda_{\max}^{Chf}$ 5.81, 5.88 μ. The maxima given for allodunnione are $\lambda_{\max}^{C_2H_5OH}$ 244, 334 mμ (log ε 4.49, 3.34).[10]

The ethyl ester (Fischer method) crystallized from ethanol in yellow needles, m.p. 69°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.91; H, 7.09.

The amide, prepared through the acid chloride (oxalyl chloride) and crystallized from aqueous ethanol, formed yellow needles, m.p. 178° (yield 86%).

Anal. Calcd. for $C_{16}H_{17}O_2N$: N, 5.49. Found: N, 5.73.

The semicarbazone was crystallized from ethanol, m.p. 246° dec.

Anal. Calcd. for $C_{17}H_{19}O_3N_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.24; H, 6.51; N, 13.45.

A pyrazolo derivative, of probable structure X, was obtained from III in dry ether with excess diazomethane. One crystallization from ligroin gave white plates, m.p. 111° (72% yield). Recrystallized material melted at 112°.

Anal. Calcd. for $C_{18}H_{20}O_3N_2$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.39, 69.34; H, 6.52, 6.48; N, 9.26.

2-Cyclohexylindanone-3-carboxylic Acid (IX).—To an ice-cold solution of 2 g. of 2-cyclohexylindenone-3-carboxylic acid (III) in 50 cc. of 10% sodium hydroxide 5 g. of zinc dust was added in small portions. The yellow color was discharged almost at once and the solution was then treated with 50 g. of ice and 30 cc. of acetic acid and extracted with ether. Evaporation of the solvent left a white residue and one crystallization from aqueous ethanol gave 1.92 g. (96%) of fine white needles, m.p. 149°; $\lambda_{\max}^{C_2H_5OH}$ 246, 292 mμ (log ε 4.06, 3.30).[11]

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.56; H, 7.25.

An identical product was obtained by warming 1 g. of III in 50 cc. of acetic acid with 3 g. of zinc dust for a few minutes until the solution was colorless. Dilution of the filtered solution gave a white solid that on crystallization afforded 0.8 g. of IX, m.p. 148–149°.

The methyl ester (diazomethane) formed fibrous needles from methanol, m.p. 88°.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.03; H, 7.45.

2-Cyclohexylindane-3-carboxylic Acid.—Clemmensen reduction of 1 g. of IX, with added toluene and acetic acid, afforded, after two crystallizations from aqueous alcohol, 0.84 g. (89%) of stout, colorless needles, m.p. 115°.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.37.

The methyl ester (diazomethane) formed white needles, m.p. 60°, from ether.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.59. Found: C, 79.23; H, 8.72.

***cis*-2,3-Dihydroxy-2-cyclohexylindanone-3-carboxylic Acid** (VII).—A solution of 0.95 g. of III and 1 g. of osmium tetroxide in 20 cc. of dry ether began to deposit a dark solid after standing for a few hours at room temperature. After 3 days the ether was removed in vacuum and a solution of the solid in 30 cc. of ethanol was refluxed with 5 g. of sodium sulfite in 25 cc. of water for 90 minutes. The filtered solution was acidified with hydrochloric acid, evaporated in vacuum to a small volume and extracted with ether. Evaporation of the ether left a colorless oil; this was dissolved in 1 l. of benzene and the solvent was largely distilled to effect dehydration. After extensive dilution with ligroin and cooling and scratching an amorphous solid was obtained, m.p. 180–183° (0.8 g.). Two recrystallizations from ethyl acetate–ligroin raised the m.p. to 190–191°; the sample did not depress the m.p. of the Hooker intermediate[9] and the infrared and ultraviolet spectra were identical.

The methyl and ethyl esters, prepared with use of the appropriate diazoalkane,[12] melted at 160° and at 96–100°, respectively, and were identical in melting point and infrared spectra with samples prepared from the Hooker intermediate.

Anal. Calcd. for $C_{17}H_{20}O_5$ and $C_{18}H_{22}O_5$ (respectively): C, 67.09, 67.91; H, 6.62, 6.97. Found: C, 67.35, 67.81; H.6.81, 7.03.

The *cis*-diol consumed two moles of periodic acid in aqueous solution at room temperature in about 2 hours and a third mole after a further 10 hours.

***trans*-2,3-Dihydroxy-2-cyclohexylindanone-3-carboxylic acid** (VIII).—A solution of 1 g. of III in 8 cc. of 10% sodium hydroxide and 50 cc. of water was heated on the steam-bath and treated in the course of 15 minutes with 5 cc. of 3% hydrogen peroxide. The resulting yellowish solution was cooled, acidified and extracted with ether to give a light yellow oil that on crystallization from 50% aqueous acetone gave 0.48 g. (43%) of shiny white platelets, m.p. 219–220°. The diol crystallized slowly and was accompanied by a few fine yellow needles of starting material that could be separated mechanically. Processing of the mother liquor afforded 30 mg. of phthalic acid. Recrystallized from ligroin-acetone, the diol melted at 223°; $\lambda_{\max}^{C_2H_5OH}$ 243.5, 287 mμ (log ε 4.12, 3.18); behavior toward periodic acid like that of the *cis*-diol.

Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.29, 66.19; H, 5.93, 6.34.

The methyl ester (diazomethane) formed stout needles, m.p. 157–158°, from methanol.

Anal. Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.11; H, 6.71.

2-*t*-Butyl-3-hydroxyindanone-3-carboxylic Acid (II).—A red solution of 150 mg. of 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone[13] (m.p. 92–93°) in 7.5 cc. of 0.1 *N* NaOH and 75 cc. of 0.01 *M* disodium hydrogen phosphate was heated on the steam-bath for 90 minutes, when it had become colorless. The solution was cooled in ice, acidified with 12 cc. of 1:1 hydrochloric acid, filtered and extracted with ether until a drop of the aqueous solution no longer turned yellow when heated with alkali. Evaporation and processing with benzene and then ligroin afforded 110 mg. (68%) of needles, m.p. 135–136°, and recrystallization from ligroin–ethyl acetate gave colorless needles, m.p. 137–138°; $\lambda_{\max}^{C_2H_5OH}$ 242.5, 288 mμ (log ε 4.08, 3.24).[11]

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.87, 67.87; H, 6.73, 6.32.

2-*t*-Butylindenone-3-carboxylic Acid (IIIa).—A solution of 50 mg. of 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone in 10 cc. of 5% sodium hydroxide was heated on the steam-bath for 1 hour, when the color had changed from red to pure yellow. Acidification precipitated 48 mg. of bright yellow solid, m.p. 158–160°, which on crystallization from ligroin gave 40 mg. of fine yellow needles, m.p. 166°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.14. Found: C, 73.39; 73.20; H, 6.20, 6.05.

An identical product was obtained quantitatively by heating the colorless hydrate II in 5% sodium hydroxide for 1 hour at 90°.

2-Isopropylindenone-3-carboxylic acid[4] resulted from isomerization of 2-hydroxy-3-isopropyl-1,4-naphthoquin-

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[11] Compare acetophenone. Ley and Winchen, *Ber.*, **67**, 501 (1934)

[12] McKay, THIS JOURNAL, **70**, 1974 (1948).

[13] Fieser, Leffler and co-workers, *ibid.*, **70**, 3175 (1948).

one[14] with alkali. On crystallization from ligroin–acetone, the substance formed yellow needles, m.p. 145–146°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.20; H, 5.60. Found: C, 72.03; H, 5.63.

Methyl 2,3-*cis*-Diacetoxy-2-β-isopentenyl-3-carboxylate.—This diacetate methyl ester of the ketol derived from lapachol[9] was obtained consistently by the following procedure. A solution of 1 g. of the anhydrous ketol (m.p. 157°) in 4 cc. of pyridine and 1 cc. of acetic anhydride was let stand at 25° for 4 days, diluted with water, acidified with hydrochloric acid and extracted with ether. The washed and dried solution was treated with excess diazomethane and evaporated to a small volume, when the product crystallized in stout needles; m.p. 136–137°, yield 0.9 g. Recrystallization from aqueous methanol raised the m.p. to 139°.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 63.88; H, 5.90.

3-Cyclohexyl-1,2-naphthoquinone (VI).—A mixture of 1 g. of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone, 3 g. of amalgamated zinc, 2 cc. of water, 1 cc. of acetic acid, 4 cc. of 36% hydrochloric acid and 3 cc. of toluene was refluxed for 24 hours, cooled and extracted with ether. Ten extractions with 10% carbonate solution (red extract) removed a total of 0.32 g. of starting material (m.p. 130–132°) and turned the initially colorless ethereal solution yellow (the naphthohydroquinone is not converted into the hydroxynaphthoquinone under these conditions). Evaporation of the dried ethereal solution and trituration with ligroin to effect separation from a red tar afforded shiny, micaceous orange-red leaflets, m.p. 159–160°; yield 0.31 g. (49%, allowing for recovery of starting material). Recrystallization from ethanol raised the m.p. to 161°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.12; H, 6.75.

In another experiment an ethereal solution of 2-hydroxy-3-cyclohexyl-1,4-naphthohydroquinone was added dropwise through an air condenser to a refluxing mixture of the reducing components and after the ether had been evaporated the mixture was refluxed for 36 hours and then processed as before. The yields of starting material and product were the same as in the experiment with the quinone cited.

The phenazine derivative, prepared by condensation of the *o*-quinone with *o*-phenylenediamine in acetic acid, formed fibrous yellow needles from ethanol, m.p. 189°.

Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.70; H, 6.40; N, 9.01.

Reductive acetylation gave **1,2-diacetoxy-3-cyclohexylnaphthalene,** which formed shiny white plates from ethanol, m.p. 180°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.68; H, 6.82.

Conversion to 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone was effected by the Thiele reaction without isolation of intermediates. An ice-cold suspension of 100 mg. of 3-cyclohexyl-1,2-naphthoquinone in 2 cc. of acetic anhydride was treated with 0.3 cc. of 96% sulfuric acid and eventually warmed to 60°. The resulting nearly colorless solution was cooled, treated with ice-water and the flocculent white precipitate of the hydroquinone triacetate was collected, washed well and dissolved in 6 cc. of ethanol and 6 cc. of 10% sodium hydroxide. The solution rapidly turned cherry red and acidification precipitated 75 mg. of yellow solid, m.p. 125–128°. One crystallization from ethanol raised the m.p. to 133–134° and identity with hydroxycyclohexylnaphthoquinone was established by mixed m.p. and infrared comparisons.

3-Isopropyl-1,2-naphthoquinone, obtained by Clemmensen reduction of 2-hydroxy-3-isopropyl-1,4-naphthoquinone[14] formed red plates from ethanol, m.p. 118°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.82; H, 5.89.

The phenazine formed needles from ethanol, m.p. 150°.

Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.87; H, 6.00; N, 10.36.

3-Phenyl-1,2-naphthoquinone, obtained similarly, crystallized from ethanol in red plates, m.p. 156°.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.16; H, 4.39.

The phenazine derivative melted at 205°.

Anal. Calcd. for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.15. Found: C, 86.13; H, 4.65; N, 9.24.

The required **2-hydroxy-3-phenyl-1,4-naphthoquinone,**[15] m.p. 143–144°, was obtained in 92% yield by the procedure described for preparation of the corresponding 3-cyclohexyl derivative[2] through **2-bromo-3-phenyl-1,4-naphthoquinone,** m.p. 84°, that resulted in 72% yield by bromination of 2-phenyl-1,4-naphthoquinone in acetic acid–sodium acetate.

Anal. Calcd. for $C_{16}H_9O_2Br$: C, 61.36; H, 2.90. Found: C, 61.53; H, 2.86.

3-*p*-Bromophenyl-1,2-naphthoquinone, obtained from the hydroxy-*p*-quinone,[16] melted at 203°.

Anal. Calcd. for $C_{16}H_9O_2Br$: C, 61.36; H, 2.90. Found: C, 61.26; H, 2.83.

The phenazine melted at 224°.

Anal. Calcd. for $C_{22}H_{13}N_2Br$: C, 68.58; H, 3.40; N, 7.27. Found: C, 68.45; H, 3.61; N, 7.41.

Attempts to produce 1,2-naphthoquinones by Clemmensen reduction were negative in the case of 2-hydroxy-1,4-naphthoquinone, phthiocol, hydrolapachol, 2-hydroxy-3-triphenylmethyl-1,4-naphthoquinone and 2-cyclohexyl-1,4-naphthoquinone.

Summary

Rearrangement of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone and of the 3-*t*-butyl derivative by alkali affords 2-alkylindenone-3-carboxylic acids in nearly quantitative yield; in the second instance an intermediate hydroxy acid can be isolated.

Hydroxylation of the cyclohexylindenonecarboxylic acid with osmium tetroxide afforded a *cis*-diol identical with the Hooker oxidation intermediate of Fieser and Fieser.

Clemmensen reduction of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone affords 3-cyclohexyl-1,2-naphthohydroquinone in 49% yield. This novel reduction was found applicable to the corresponding isopropyl, phenyl and *p*-bromophenyl derivatives, but not to the methyl, isoamyl or triphenylmethyl derivatives or to 2-hydroxy- or 2-cyclohexyl-1,4-naphthoquinone.

CAMBRIDGE 38, MASSACHUSETTS
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[14] Fieser, Hartwell and Seligman, THIS JOURNAL, **58**, 1223 (1936).

[15] Volhard, *Ann.*, **296**, 14 (1897).

[16] Fieser, Leffler and co-workers, THIS JOURNAL, **70**, 3203 (1948).