

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

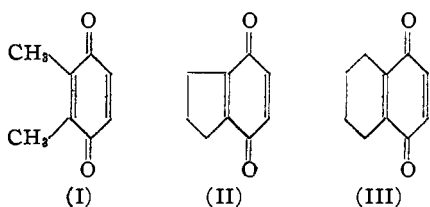
The Mills-Nixon Effect. II

BY RICHARD T. ARNOLD AND HAROLD E. ZAUGG

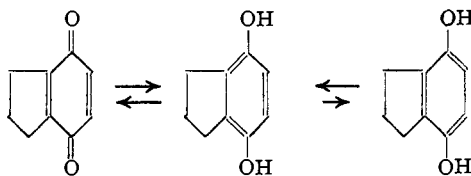
In an earlier study dealing with the acidity of nitroxyls, nitrohydrindenols, and nitrotetraols it was indicated that the Mills-Nixon effect was probably small or non-existent.¹

This study however was complicated by the presence of external hydrogen bonding found in all *o*-nitrophenols, which reduced the sensitivity of this method as a tool for locating stabilized double bonds.

In the present attack on this problem, the oxidation-reduction potentials of *o*-xyloquinone (I), 4,7-hydrindenequinone (II), and 1,2,3,4-tetrahydronaphthoquinone-5,8 (III) have been measured both potentiometrically and polarographically.



Any geometric strain in the hydrindenequinone caused by the presence of the double bond in the five membered ring (*i. e.*, a positive Mills-Nixon effect) can be partly relieved by reduction to the benzenoid nucleus accompanied by partial stabilization.



This being the case, hydrindenequinone would be expected to have a higher oxidation potential than either (I) or (III). Actually the quinones (I) and (III) have oxidation-reduction potentials which are nearly the same, while that of hydrindenequinone is greater than these by roughly fifty millivolts as shown in Table I.

The agreement obtained by these two methods is quite satisfactory. It should be pointed out that the introduction of the two methyl groups in passing from *p*-benzoquinone to *o*-xyloquinone results in a decrease in the E_0 value of 123 millivolts, which obviously is more than twice the

(1) Arnold and Evans, *THIS JOURNAL*, **62**, 556 (1940).

TABLE I

Name	E_0 (potentiometric)	E_0 (polarographic) ²
<i>o</i> -Xyloquinone (I)	0.588	0.589
4,7-Hydrindenequinone (II)	.641	.638
1,2,3,4-Tetrahydronaphthoquinone (III)	.585	.585
<i>p</i> -Benzoquinone	.711 ³	

effect (53 millivolts) attributed by us to a Mills-Nixon type of stabilization.

The insignificant difference found between the values for compounds (I) and (III) seems to indicate the lack of any Mills-Nixon effect in the tetralin nucleus.

Methods used for the synthesis of 4,7-hydrindenequinone and reactions leading to a proof of structure are shown (next page).

Experimental

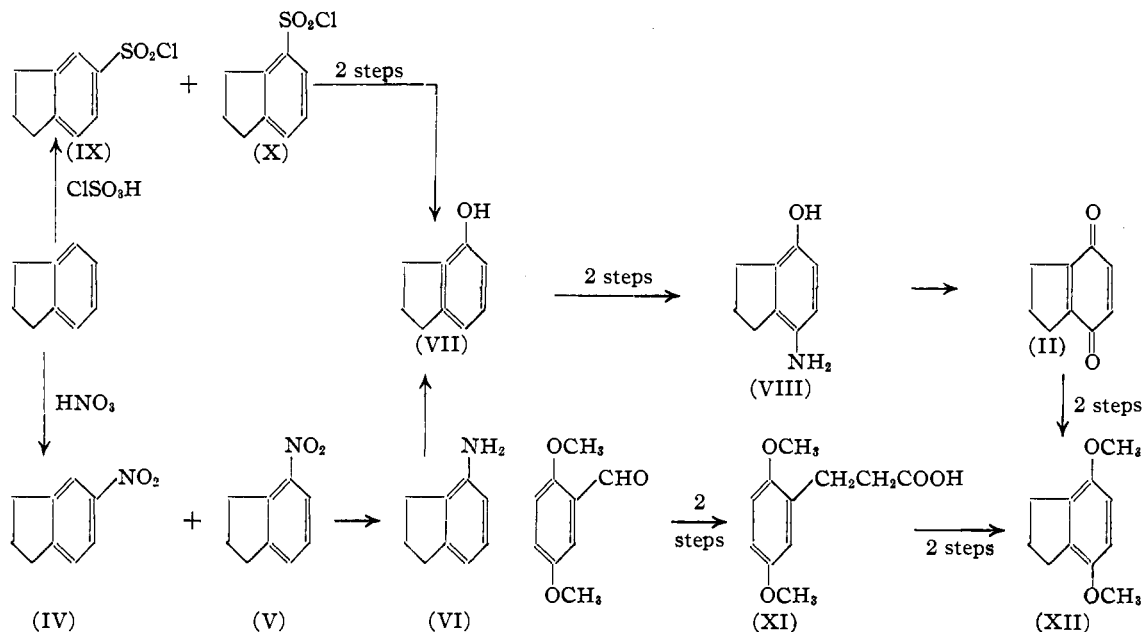
1,2,3,4-Tetrahydronaphthoquinone-5,8.—A completely modified procedure similar to that of Jacobson and Turnbull⁴ was used in the preparation of this quinone.

A cold suspension of diazonium salt, prepared from 31.5 g. of sulfanilic acid, was poured with stirring into a cooled solution of 20.4 g. of 1,2,3,4-tetrahydronaphthol-5 in 150 cc. of water containing 22.5 g. of sodium hydroxide. The resulting azo solution was allowed to stand overnight. It was then cooled to 5° and 65 g. of sodium hydrosulfite was added in one portion with stirring. The mixture was allowed to warm to room temperature and stirring was continued for several hours. The yellow aminophenol that was finally precipitated was filtered by suction and immediately dissolved by warming in 350 cc. water containing 25 cc. of concd. sulfuric acid. The resulting deep red solution of the amine salt was clarified by charcoal and then oxidized by dropwise addition of it to a suspension of 80 g. of manganese dioxide in 300 cc. of water containing 9 cc. of concd. sulfuric acid, through which steam (at 55° (95 mm.)) was being passed. The aqueous distillate was extracted with ether until colorless. The extract was dried and distilled under reduced pressure. The quinone, left as the residue, was obtained in a 60% over-all yield from the phenol. Recrystallization from petroleum ether (b. p. 30–60°) gave golden-yellow needles of m. p. 55–56°.

1,2,3,4-Tetrahydronaphthohydroquinone-5,8 was obtained by reduction of an ether solution of the quinone with aqueous sodium hydrosulfite. Evaporation of the ether solution and recrystallization from ether and petroleum ether gave the pure hydroquinone, m. p. 178–179°.

(2) The authors are indebted to Mr. Leo J. Spillane for the values obtained by the polarograph.

(3) Value reported by Conant and Fieser, *THIS JOURNAL*, **45**, 2208 (1923).(4) Jacobson and Turnbull, *Ber.*, **31**, 898 (1898).



o-Xyloquinone (I).—A cold suspension of diazonium salt from 21.0 g. of sulfanilic acid was added to a solution containing 11.2 g. of 2,3-dimethylphenol, 60 cc. of water, and 15.0 g. of sodium hydroxide. After standing overnight at ice-bath temperature, 44.0 g. of sodium hydrosulfite was added in one portion with good stirring, and the solution was allowed to warm to room temperature. After several hours the precipitated aminophenol was filtered and immediately dissolved in a warm solution of 12 cc. of concd. sulfuric acid in 200 cc. of water. This solution was added dropwise into a vacuum steam distillation apparatus containing 60 g. of manganese dioxide, 200 cc. of water, and 6 cc. of concd. sulfuric acid. The steam distillation was continued (at 55° (95 mm.)) until 600 cc. of distillate was collected. Ether extraction followed by evaporation of the ether at diminished pressure gave yellow prisms of the quinone; weight, 7.7 g. (62% from the dimethylphenol); m. p. $56.5\text{--}57.5^\circ$.⁵

o-Xylohydroquinone was prepared from the quinone by reduction with zinc and acetic acid according to the method of Emerson and Smith⁶; colorless prisms from acetone, m. p. $223\text{--}224^\circ$ (with slight decomposition).

4-Nitrohydrindene (V).—From 210 g. of a mixture of 4- and 5-nitrohydrindenes prepared according to Lindner,⁶ there was obtained, after sixteen fractionations through a six-inch (16-cm.) helix-packed column followed by fractional crystallization after each distillation, 44.0 g. of pure (V) and 72.0 g. of pure (IV).

4-Aminohydrindene (VI).—Reduction of 37.2 g. of (V) dissolved in 50 cc. of ethanol over Raney nickel at 150° and under a pressure of 800–1300 pounds of hydrogen, gave 28.5 g. (94%) of pure (VI). This procedure was reported by Erich Goth⁷ but no yield was given.

4-Hydroxy- and 4-Iodohydrindene.—Twenty-eight and one-half grams of 4-aminohydrindene (VI) dissolved in a

warm solution of 19.3 cc. of concd. sulfuric acid in 400 cc. of water was cooled and diazotized with 16 g. of sodium nitrite in 60 cc. of water. A slight excess of nitrous acid was decomposed with urea. To this solution at 5° was added 39.1 g. of potassium iodide in 50 cc. of water. After standing overnight in an ice-bath, the solution was warmed until the evolution of nitrogen had ceased, and then was steam distilled. Ether extraction followed by fractionation gave 14.1 g. of a yellow oil, b. p. $97\text{--}99^\circ$ (6 mm.). Extraction with alkali gave 6.9 g. of 4-hydroxyhydrindene (VII), m. p. $49\text{--}50^\circ$.^{6,7} The alkali insoluble 4-iodohydrindene (5.6 g.) could not be obtained pure, but at 275° in the presence of sodium hydroxide (3.0 g. in 20 cc. of water) and a few copper turnings it yielded 1.13 g. of pure (VII).

Chlorosulfonation of Hydrindene.—To 500 g. of chlorosulfonic acid (Eastman Kodak Co. Practical) cooled to -10° was added dropwise, with vigorous stirring, 118 g. (1 mole) of hydrindene (b. p. $174\text{--}176^\circ$). The temperature was maintained at -10° by efficient dry-ice cooling and the addition of the hydrindene required two and one-quarter hours. After the addition was complete, the mixture was stirred for another fifteen minutes and then poured carefully with stirring into a two-liter beaker half filled with ice. Carbon tetrachloride (250 cc.) was added to the mixture in a separatory funnel and the organic layer drawn off. The aqueous layer was extracted with 300 cc. more carbon tetrachloride, and the combined extracts were then washed with dilute sodium carbonate solution until the wash liquid remained basic to litmus. (The reaction mixture must be freed from all unchanged sulfonic acid since the presence of this material catalyzes the decomposition of the sulfonyl chlorides during the distillation.) After one washing with 300 cc. of water, the carbon tetrachloride was taken off under reduced pressure and the residue distilled. There was obtained 164 g. (76%) of yellow oil, b. p. $161\text{--}171^\circ$ (9–10 mm.) consisting of a mixture of the sulfonyl chlorides (IX) and (X).

(5) Emerson and Smith, *THIS JOURNAL*, **62**, 141 (1940).

(6) Lindner, Schmitt and Zaunbauer, *Monatsh.*, **72**, 216 (1939).

(7) Erich Goth, *Ber.*, **61**, 1459 (1928).

Separation of the Isomeric Hydrindenesulfonyl Chlorides.—The liquid chlorosulfonylation product was fractionated seven times through a six-inch, helix-packed column. The boiling point of hydrindene-4-sulfonyl chloride (X) is about 140–141° (4 mm.), and of hydrindene-5-sulfonyl chloride (IX), about 148–149° (4 mm.). Compound (X) solidified in large flat plates and melted, after several crystallizations from low-boiling petroleum ether, at 53–53.5°.

Anal. Calcd. for $C_9H_9O_2SCl$: C, 49.88; H, 4.18. Found: C, 49.68; H, 4.01.

A small quantity of (X) was heated with concd. ammonium hydroxide on the steam-bath. On cooling and recrystallization of the resulting solid from dilute ethanol, hydrindene-4-sulfonamide was obtained in thin white needles of m. p. 118–119°.

Anal. Calcd. for $C_9H_{11}O_2SN$: C, 54.81; H, 5.62. Found: C, 54.79; H, 5.74.

The hydrindene-5-sulfonyl chloride (IX) also solidified in large rhombic prisms. One recrystallization from low-boiling petroleum ether gave a product melting at 46–47°. The sulfonamide prepared from (IX) and recrystallized once from dilute ethanol gave shiny white platelets of m. p. 135–136°.

Spilker⁸ reported melting points of 45° for hydrindene-5-sulfonyl chloride (IX) and 135.5–136° for the corresponding sulfonamide. These values have been checked as shown above. However, he did not isolate any hydrindene-4-sulfonyl chloride (X) but reported a melting point for the 4-sulfonamide at 91–92°. Approximately equal quantities of the 5-sulfonamide (m. p. 135–136°) and 4-sulfonamide (m. p. 118–119°) were mixed and the melting point was found to be very sharp (for a mixed melting point) at 90–93°. This seems to indicate that Spilker's 91–92° compound was actually a eutectic mixture of the two isomeric sulfonamides. This evidence is further substantiated by the fact that potassium hydroxide fusion of what Spilker thought was pure sodium hydrindene-4-sulfonate gave a phenolic non-crystallizable oil.⁹ As shown in a later procedure, potassium hydroxide fusion of the sodium salt of the sulfonic acid obtained by the hydrolysis of (X) gives solid 4-hydroxyhydrindene (VII).

Sodium Hydrindene-4-sulfonate.—Hydrindene-4-sulfonyl chloride (X) (15.3 g.) was refluxed with 250 cc. of water for two hours during which the mixture became homogeneous. The volume of liquid was then decreased to 100 cc. by distillation and 8.4 g. of sodium bicarbonate was added carefully in portions, followed by 13 g. of sodium chloride, which was dissolved by heating. On cooling, the sodium hydrindene-4-sulfonate crystallized in small shiny white leaflets; weight of dry product, 13.0 g. or 81%.

4-Hydroxyhydrindene (VII).—A paste of 40 g. of potassium hydroxide and 7 cc. of water was heated to 250° in a nickel crucible. The 13 g. of dry powdered sodium hydrindene-4-sulfonate was added in portions over the course of forty-five minutes with stirring by means of a copper rod. During the course of the addition the temperature was allowed to increase to 280° and, after completion of the addition, to 305°. The mixture changed from an olive green

thick mass to a dark brown liquid in a few minutes. It was heated at 270–285° for one and one-half hours longer, during which a dark crust gradually formed on top. On cooling, the solid mass was ground up and dissolved in 200 cc. of water, acidified with concd. hydrochloric acid and extracted with several portions of ether. The extract was combined with 100 cc. of water and the ether was distilled off. The residual brown oil was then steam distilled. Treatment of the distillate in the usual way gave 6.35 g. (80%) of a yellow phenolic oil that solidified completely on cooling; m. p. 39–40°. Repeated crystallizations from low-boiling petroleum ether, however, raised the melting point only to 39.5–40.5°. Mixed with an authentic sample of 4-hydroxyhydrindene (m. p. 49–50°) prepared from the amine (VI), it gave a melting point of 49–50°. This has been found to be a case of dimorphism.¹⁰

4,7-Hydrindenequinone (II).—7-Amino-4-hydroxyhydrindene (VIII) was prepared exactly as described above in the preparation of 2,3-dimethyl-4-aminophenol; yield, 93%, m. p. about 205° with decomposition and with sublimation at 160°.

Anal. Calcd. for C_9H_9ON : C, 72.48; H, 7.44. Found: C, 72.60; H, 7.49.

From 4.75 g. of (VIII) there was obtained 3.36 g. of 4,7-hydrindenequinone (II) by the manganese dioxide oxidation procedure described above; yield, 66% from the 4-hydroxyhydrindene; yellow cubic prisms from petroleum ether, m. p. 41–42°. Oxidation of (VIII) with ferric chloride in hydrochloric acid solution gave highly colored by-products and reduced the over-all yield of quinone to 40%.

Anal. Calcd. for $C_9H_8O_2$: C, 73.03; H, 5.44. Found: C, 72.81; H, 5.42.

4,7-Hydrindenehydroquinone.—Reduction of the quinone with zinc and acetic acid proved unsatisfactory so the following procedure was finally adopted. The hydrindenequinone (1.5 g.) was dissolved in 30 cc. of ether and shaken in a separatory funnel with 15 cc. of water containing 3.0 g. of sodium hydrosulfite. The ether layer turned red and then became colorless. The water layer was extracted with an extra 80 cc. of ether in three portions. The combined extracts gave 1.21 g. (80%) of 4,7-hydrindenehydroquinones; m. p. 184–185° after recrystallization from acetone-petroleum ether.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.96; H, 6.71. Found: C, 71.99; H, 6.83.

Quinhydrone of 4,7-Hydrindenehydroquinone.—Equal weights (0.4 g.) of the 4,7-hydrindenequinone and hydroquinone were dissolved in 10 cc. of ether and evaporated to dryness under diminished pressure. The black residue was recrystallized several times from dilute ethanol. Jet black, flat needles were obtained which melted at 98–99° to a dark red viscous liquid.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.37; H, 6.03.

2,5-Dimethoxyhydrocinnamic Acid (XI).—2,5-Dimethoxyhydrocinnamic acid prepared according to J. S. Buck¹¹ was reduced catalytically with platinum oxide using glacial acetic acid in 95% ethanol as a solvent. The yield was

(8) Spilker, *Ber.*, **26**, 1540 (1893).

(9) J. Moschner, *ibid.*, **34**, 1258 (1901).

(10) Arnold, Klug, Sprung and Zaugg, *This Journal*, **63**, 1161 (1941).

(11) J. S. Buck, *ibid.*, **54**, 3663 (1932).

quantitative; m. p. 65–66° after recrystallization from ether-petroleum ether.

4,7-Dimethoxyhydrindone-1.—Ten grams of 2,5-dimethoxyhydrocinnamic acid dissolved in 250 cc. of dry benzene was treated with 40 g. of phosphorus pentoxide. The mixture was heated gently with good stirring for two and one-half hours on the steam-bath. After decomposition with water, the aqueous layer was extracted with 300 cc. of ether in small portions. The combined benzene and ether extracts were washed with sodium carbonate solution and water, clarified with charcoal, and evaporated to dryness. The light yellow solid residue weighed 7.5 g. Fractional crystallization from ether gave the pure 4,7-dimethoxyhydrindone-1; m. p. 124.5–125°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 68.71; H, 6.29. Found: C, 68.66; H, 6.50.

4,7-Dimethoxyhydrindene (XII).—The 4,7-dimethoxyhydrindone-1 (0.83 g.) was dissolved in 10 cc. of 95% ethanol and reduced with hydrogen and Raney nickel at 150° under a pressure of 1400 pounds for two hours. The solution was filtered and evaporated to 4 cc. Hot water was added to start crystallization and on cooling, 0.69 g. (90%) of 4,7-dimethoxyhydrindene (XII) was obtained; long white needles of m. p. 85–85.5°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.30; H, 7.96.

Methylation of 4,7-Hydrindenehydroquinone.—The hydroquinone (0.45 g.) was dissolved in 3 cc. of methanol and 2.9 cc. of dimethyl sulfate. The mixture was refluxed and a solution of potassium hydroxide (3.6 g. in 18 cc. methanol) was added dropwise with stirring. Refluxing was continued for thirty minutes and the mixture was poured into 80 cc. of ice water. The finely divided precipitate was filtered and recrystallized from dilute ethanol; yield, 0.36 g. An additional recrystallization gave a product melting at 85–85.5°, found by a mixed melting point to be identical

with the sample prepared by the reduction of 4,7-dimethoxyhydrindone-1.

Measurements.—The oxidation-reduction potential measurements were carried out by preparing standard 0.003 *M* solutions of the quinones and hydroquinones in a buffer solution consisting of 0.1 *N* acetic acid and 0.1 *N* sodium acetate in 50% aqueous ethanol. For the polarographic measurements, the hydroquinone solutions were diluted to 0.0015 *M* concentration by an equal volume of buffer. For the potentiometric measurements equal volumes of corresponding quinone and hydroquinone solutions were mixed and the potential measured by means of a bright platinum electrode against the same saturated calomel electrode that was used as the reference in the polarographic determinations. In this way, both the *pH* and the ionic strength of the solutions used in both methods of measurement were kept constant at 5.40 and 0.1, respectively.

The method of mixtures was found to be unsatisfactory in the potentiometric measurement of 4,7-hydrindenequinone, undoubtedly because of the noticeable instability of standard solutions of the quinone. Fortunately, however, the quinhydrone was readily accessible and measurement of it dissolved in the standard buffer gave the value (0.641 v.) reported in the table.

Summary

1. The oxidation-reduction potentials of *o*-xyloquinone, 4,7-hydrindenequinone, and 1,2,3,4-tetrahydronaphthoquinone-5,8 have been measured by two standard procedures.

2. The relatively high value found for the 4,7-hydrindenequinone has been attributed to a positive Mills-Nixon type of partial double bond stabilization.

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 24, 1941

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Catalytic Dehydrogenation of Hydroaromatic Compounds with Benzene¹

BY HOMER ADKINS, LAWRENCE M. RICHARDS AND JAMES W. DAVIS

Linstead and his associates have in recent years developed the catalytic method² for the dehydrogenation of hydroaromatic compounds so that it has been found useful in several laboratories, especially in structural studies. Linstead's method involves passing the vapors of the hydroaromatic compound over platinum or palladium at 300 to 350°. In most instances the compound to be dehydrogenated was passed over 2 g. of the metal on a suitable support, at the rate of about

0.3 g. per hour. It has been our objective to develop a method for catalytic dehydrogenation in the liquid phase that can be used for high molecular weight compounds and upon a scale suitable for preparational work.

A method for catalytic dehydrogenation in the liquid phase in a closed system necessitates a hydrogen acceptor to prevent the reverse reaction. Even in the vapor phase at one atmosphere pressure we have found that the dehydrogenation of tetradecahydrophenanthrene does not go completely to phenanthrene at 325°. At superatmospheric pressures of hydrogen, in the temperature range 300–350°, the equilibrium is far on the

(1) This investigation was supported by the Wisconsin Alumni Research Foundation.

(2) Linstead, Millidge, Thomas, Walpole and Michaelis, *J. Chem. Soc.*, 1146–1157 (1937), 1127–1147 (1940). References are given to earlier work by Ipatieff, Zelinski and others.