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Catalytic Oxidations in Aqueous Solution. III. Oxidation of Anthracene, Hydroquinone and Substituted Hydroquinones

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The induced oxidation of organic compounds by vanadium pentoxide with chlorates in dilute acid solution has been developed by Milas in the case of furfural[1] and some primary alcohols[2] with noteworthy success.

The material reported in the present paper resulted from an attempt to extend this method to the oxidation of other compounds. The proposed investigation unfortunately was terminated by the death of the senior author and the results thus far obtained are herein presented chiefly because of the marked advantages they offer in organic preparative work. In addition, the reaction has been extended to the oxidation of readily oxidized but water-insoluble compounds by the use of a solvent mixture containing about 80% acetic acid.

Many compounds, other than those discussed in the experimental part, were either unoxidized by the present method or did not yield results sufficiently different from those obtained with the more common oxidizing agents to warrant discussion here. Included among those which were apparently unaffected by prolonged heating with the reagents were toluene, phenanthrene, cyclohexanol, borneol and camphor. On the other hand, though many compounds such as aniline, *p*-aminophenol, *p*-phenylenediamine, and 1-amino, 4-hydroxynaphthalene yielded the expected oxidation products, the yields obtained were uniformly low. The failure of the reagents to oxidize some of the compounds employed may be attributed, at least in part, to the impossibility of accelerating the reaction by increasing the concentration of mineral acid in consequence of the danger of explosion.[3] In this connection it should be noted that while no explosion occurred in the course of the present work, the concentration of dilute sulfuric acid specified in the experimental part should be employed carefully, especially where heat is applied as in the oxidation of anthracene. Otherwise serious explosions due to evolution of chlorine dioxide may occur.

The present method offers the following practical advantages over the usual laboratory methods of oxidizing anthracene and hydroquinones to the corresponding quinones: greatly increased yields, extreme ease of manipulation, lower cost of materials and comparative purity of the crude products obtained. An additional advantage is the preparation of almost pure anthraquinone from a technical grade of anthracene by this mode of oxidation in which the dark-colored impurities are either completely oxidized to carbon dioxide and water or held in solution, yielding a product of light yellow color and of high degree of purity. This is in distinct contrast to the lower yields of dark-colored, rather impure anthraquinone obtained in the usual sodium dichromate–sulfuric acid oxidation of such material.

Experimental

Materials.—The catalyst employed was the C. P. grade of vanadium pentoxide furnished by the Vanadium Corporation of America. This was found to be as sufficiently active as that prepared by the usual method from ammonium metavanadate.[1] The sodium chlorate used was the U. S. P. grade furnished by Merck.

Oxidation of Anthracene.—Ninety grams (0.51 mole) of C. P. anthracene was finely ground in a mortar and added to a mixture of 76 g. of sodium chlorate (0.71 mole), 1 liter of glacial acetic acid, 200 cc. of 2% sulfuric acid and 0.5 g. of vanadium pentoxide in a 3-liter round-bottomed flask equipped with a long, efficient reflux condenser. The mixture was heated just to boiling, then the source of heat was removed; a vigorous reaction, lasting about twenty minutes, ensued, after which the mixture was refluxed for one hour. At the end of this time the flask was disconnected and cooled in an ice mixture. The yellow solid was brought upon a filter, washed with three 200-cc. portions of cold water and dried at 110°, yielding 103 g. of light yellow anthraquinone melting at 270–273°. On recrystallization from nitrobenzene a 90% yield (96 g.) of anthraquinone melting at 274–275° was obtained.

A technical grade of anthracene used in the above experiment gave 96 g. of light yellow crude anthraquinone melting at 265–270° and sufficiently pure for many purposes of synthesis. On recrystallization as above an 88% yield (77 g.) of pure anthraquinone was obtained, based upon an average content of 83% anthracene in the original product.

Oxidation of Hydroquinone.—One hundred and ten grams (1 mole) of hydroquinone, 60 g. (0.56 mole) of sodium chlorate and 0.5 g. of vanadium pentoxide were

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[1] Milas, THIS JOURNAL, **49**, 2005 (1927).

[2] Milas, *ibid.*, **50**, 493 (1928).

[3] Wagner, *ibid.*, **50**, 1233 (1928).

placed in a 2-liter flask with 1 liter of 2% sulfuric acid. The mixture was stirred by means of an electric motor for four hours, at the end of which time the hydroquinone had been completely converted to light yellow quinone. Because the temperature of the mixture rose to about 40° during the course of the reaction the flask was cooled in an ice mixture. The yellow solid was brought upon a filter, washed with 100 cc. of cold water and dried in a desiccator over calcium chloride yielding 90 g. of light yellow quinone melting at 110–112°. Extraction of the combined filtrate and washings with four 100-cc. portions of benzene gave an additional 14 g. of quinone. On recrystallization from ligroin (b. p. 90–120°) a 90% yield (97 g.) of pure quinone melting at 111–113° was obtained.

TABLE I

YIELDS AND MELTING POINTS OF SUBSTITUTED HYDROQUINONES

Quinone	Yield, %	M. p., °C. Crude	Recryst.
Methylbenzoquinone	90	66–68	68–69
Chlorobenzoquinone	92	52–54	53.5–64
Bromobenzoquinone	94	54–55	55–56
1,4-Naphthoquinone	93	123.5–125	124.5–125

Substituted hydroquinones are oxidized similarly with equally good results when amounts of materials proportional to those above are employed. In the table are shown the percentage yields of the quinones thus obtained from the corresponding hydroquinones together with the melting points of the crude and the purified products.

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Summary

Vanadium pentoxide in dilute sulfuric acid solution induces the oxidation of anthracene, hydroquinone and substituted hydroquinones with chlorates to give excellent yields of the corresponding quinones of a high degree of purity.

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The Isomerization of Certain Saturated and Unsaturated Hydantoins

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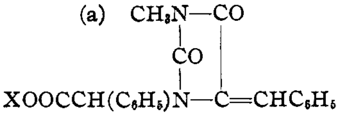
The present investigation deals with isomeric hydantoins of the types



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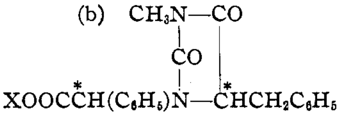
(b)



where X denotes H, C_2H_5, Na or Ba/2 and * denotes an asymmetric carbon. Four pairs of isomers have been isolated in each group (a) and (b). In the case of the unsaturated compounds (I to VIII) the isomers represent geometrical modifications since both VII and VIII on reduction yield the saturated acid IX.[1] The creation of a second asymmetric carbon accounts for the formation of racemic mixtures in the case of the saturated compounds (IX to XVI).

Mixtures of geometric isomers of type (a) can be resolved readily into their components through conversion to barium salts. These salts not only vary considerably in water solubility but separate from solution in well-defined crystalline forms. Transformations within each of the parallel series I, III, V, VII and II, IV, VI, VIII may be carried out quantitatively at low temperatures. Isomerization occurs at higher temperatures and notably in the presence of sodium hydroxide and hydrogen chloride. Partial and even complete hydrolysis may take place under the prolonged action of alkali. Considerable amounts of N-3-methylbenzalhydantoin and lesser amounts of N-3-methylbenzalhydantoin-N-1-phenylacetic acid along with benzaldehyde result from hydrolysis at the N-1- and C-5-positions.

Saturated hydantoins of the structure (b) may be obtained by heating compounds of the type (a) with hydrogen iodide and red phosphorus. As shown in the experimental part, ester I passes readily into the hydrate of the acid IX. The latter may be converted quantitatively into the sodium salt XIII and this into the products XI and XV. When heated with alcoholic hydrochloric acid, however, the hydrate of the acid IX yields a mixture of the esters XI and XII, which can be separated by recrystallization from alcohol.

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[1] Additional evidence was furnished by the fact that the absorption curves of the esters I and II agree closely, and are in all respects analogous to those observed in the case of other pairs of geometrical isomers having an ethylene bond in the C-5-position and substitutents in the N-1-N-3-positions. Compare Hahn and Evans, THIS JOURNAL, 50, 810 (1928); Hahn and Dyer, *ibid.*, 52, 2505, 2507 (1930).