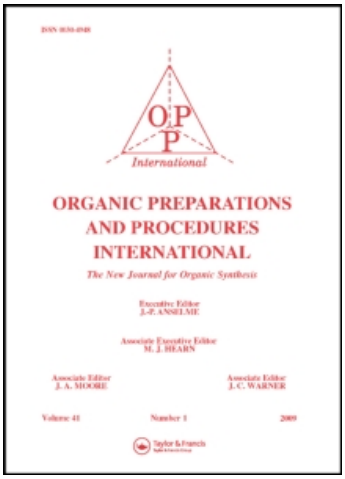

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A RAPID, CONVENIENT, HIGH YIELD PROCEDURE FOR THE REGENERATION OF 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ) FROM THE CORRESPONDING HYDROQUINONE (DDHQ)

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OPPI BRIEFS

(By James A. Moore, Associate Editor)

A RAPID, CONVENIENT, HIGH YIELD PROCEDURE FOR THE REGENERATION OF 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ) FROM THE CORRESPONDING HYDROQUINONE (DDHQ)[1]

Submitted by (3/29/76)

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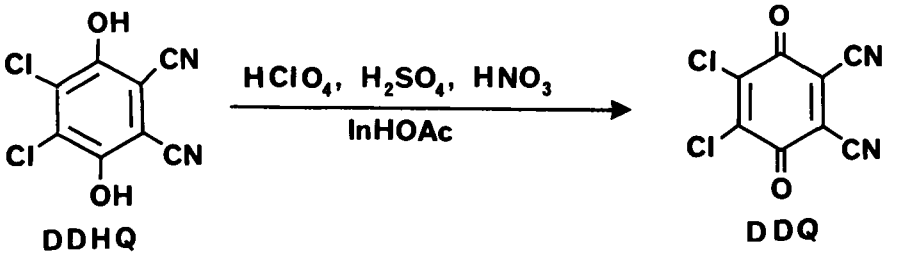
The use of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as an oxidizing agent and as an analytical tool is well established.[2-5] The use of large quantities of DDQ is relatively expensive and is practical only if the 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ) produced in the dehydrogenation reaction is recovered and re-oxidized to DDQ. The nitric acid



oxidation procedure of Walker and Waugh[6] is generally used. Although this method works well to regenerate a few grams of DDHQ, considerable foaming occurs in the vigorous nitric acid procedure with large quantities.

We report here simple, rapid and high yield oxidation procedure employing a mixed mineral acid oxidant consisting of perchloric acid, sulfuric acid and nitric acid in the ratio of 1:4:2.5 in glacial acetic acid as solvent. The average yield of three reactions with 32.4 g of DDHQ was 95%.

EXPERIMENTAL

The mps. were determined on a Thomas-Hoover apparatus and are uncorrected. Ir spectra were recorded on a Beckman Model IR-33 grating spectrometer. The elemental analysis was performed on a Hewlett-Packard Model 185B C,H,N Analyzer.

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ). - In 60 ml of glacial acetic acid in a 250 ml Erlenmeyer flask was suspended 34.2 g (0.149 mole) of DDHQ. In succession, 1.8 ml of $HClO_4$ (70-72% w/w) and 7.7 ml of H_2SO_4 (96.5% w/w) were added slowly to the suspension. Then 4.5 ml of HNO_3 (70.4% w/w) was added over a period of several seconds with magnetic stirring. After one minute, a mixture of 30 ml of carbon tetrachloride (cooled by the addition of solid CO_2 to ca. -25°) and 30 ml of cold water were added. The precipitate was collected by suction filtration and was washed with 30 ml of cold carbon tetrachloride followed by 30 ml of cold water (0-5°). Recrystallization from a mixture of dichloromethane and ethyl acetate afforded 32.8 g (96%) of pure DDQ, mp. 210-211°, lit.[6] 212-213° with an ir spectrum identical to that of authentic[7] DDQ (KBr disc).

Anal. Calcd. for $C_8Cl_2N_2O_2$: C, 12.34; N, 42.40
Found: C, 12.44; N, 42.29

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A SIMPLIFIED PROCEDURE FOR THE SYNTHESIS OF THE 6,7-BENZOMORPHAN NUCLEUS

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Benzomorphan derivatives such as phenazocine (IIIa),[1] cyclazocine (IIIb),[2] and pentazocine (IIIc)[3] have proved to be potent analgesics. The latter compound in particular which is commercially available, has been found to be an effective, non-addictive analgesic. The synthesis of the basic nucleus according to the Grewe method,[4,5] although modified by several authors,[6,7] still suffers from serious disadvantages.[8,9]