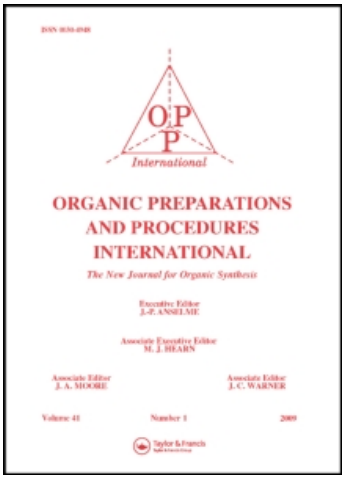

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A RAPID AND MILD PROCESS FOR THE OXIDATION OF 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ) FROM 2,3-DICHLORO-5,6-DICYANOHYDROQUINONE (DDHQ)

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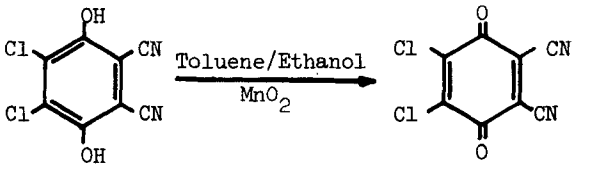
The potent, and often quite selective oxidizing power of 2,3-dichloro-5,6-dicyanoquinone (DDQ, II) has led to its extensive use[1,2] as a



I II

synthetic reagent. However, the cost of the reagent is such that its use on other than a millimole scale mandates that the by-product 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ, I) be recovered and reoxidized to DDQ. Typically, this oxidation has been accomplished by a mixture of nitric and hydrochloric acids.[3] As has been noted,[4,5] this procedure is often unsuitable for larger scale work. Recently, a modification[4] of the nitric acid procedure and an electrochemical oxidation[5] have been proposed as alternative oxidation methods. This note reports a method for the reconversion of DDHQ to DDQ which requires neither the corrosive reaction mixtures of the nitric acid method[3,4] nor the need for dilute solutions and an electrochemical apparatus.[5] Our work is based on that of Mitchell,[6] who reported the use of lead dioxide for preparation of DDQ. We have found that replacement of this reagent by activated manganese dioxide (and of benzene by the less toxic toluene as solvent) gave 82-86% yields of DDQ of excellent quality. Using this process we have prepared over 10 kg of DDQ in lots as large as 670 g without incident.[7]

EXPERIMENTAL

2,3-Dichloro-5,6-dicyanoquinone (DDQ, II).- A 63.4 g (0.20 mole) sample of 1:1 DDHQ/dioxane complex, obtained from the oxidation of a tetrahydrodibenzothiophene derivative to the corresponding dibenzothiophene,[7] was dried 16 hrs at 100°/0.1 mm to give 45.72 g of solvent-free compound. A suspension of this material in 550 ml of toluene, 550 ml of 2N HCl and 200 ml of ethanol was mechanically stirred in a flask surrounded by a 20° water bath. To the flask was added, in one portion, 39.15 g (0.288 mole) of 64% activated manganese dioxide.[8] The suspension gave an instantaneous red color which was accompanied by a 2-3° rise in temperature.[9] The suspension was stirred for 25 min[10] and filtered through Celite. The filter

cake was rinsed with 3 x 200 ml of toluene and 200 ml of ethyl acetate. The aqueous portion of the filtrate was extracted with 50 ml of toluene and the combined organic solutions were washed with 250 ml each of water and saturated brine and dried over Na_2SO_4. To this suspension was added 4 g of Norite A and the total was shaken briefly and filtered through Celite. Solvent removal gave 44.2 g of orange-tan solid which was suspended with warming in 200 ml of 30-60° petroleum ether. The suspension was stirred rapidly for ca. 30 min and filtered to give 42.0 g (91.7%) of crude DDQ as a yellow-orange powder, mp. 211-213°. This product was taken up in 500 ml of 1,2-dichloroethane at reflux to give a cloudy orange solution which was treated with 2 g of Celite and filtered through a preheated medium porosity sintered glass funnel. About 50 ml of hot 1,2-dichloroethane was used to wash the filter cake. The combined filtrates were stripped on a rotary evaporator to a volume of 100 ml. The resultant suspension was stirred with ice bath cooling for 1 hr and filtered. The solid was washed quickly with a total of 50 ml of cold (-20°) 2:3 1,2-dichloroethane/30-60° petroleum ether followed by 100 ml of 30-60° petroleum ether. Drying at 25°/70 mm gave 38.15 g (84%) of DDQ as small dark yellow needles, mp. 214.5-215.5°, lit.[3,4,5] mp. 212-213°, 210-211°, and 204-206°.

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8. Purchased from General Metallic Oxides Co., Jersey City, N. J. as "Manganese Hydrate 37."

9. In larger runs,[7] an ice-water bath was employed to control the exotherm.

10. This is a maximum reaction time (ca. 10 min after all the DDHQ has gone into solution). Our experience indicates that longer stirring times lead to lower yields of darker product and to more water-soluble by-products.

A BRIEF PREPARATION OF THIAN-4-CARBOXYLIC ACID 1,1-DIOXIDE

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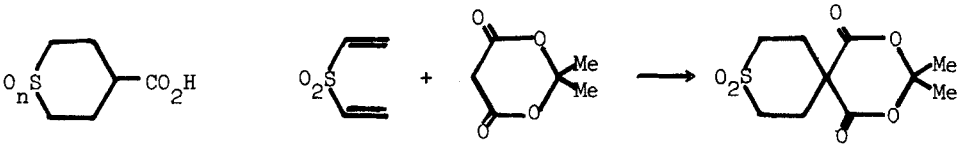
Thian-4-carboxylic acid 1,1-dioxide (I), which may be prepared by oxidation of thian-4-carboxylic acid (II), was needed for amidation of aromatic amines.[1] Since Prelog's seven-step synthesis of II was unduly long, a brief preparation of I or a suitable derivative was sought.[2-4]



I (n = 2) V III IV

II (n = 0)

By analogy to Meldrum's acid (III) which converts aniline to acetanilide, the spirocyclic compound IV expected from Michael reaction of III and divinyl sulfone (V), seemed a likely starting material for the required amidation.[5] When a solution of Meldrum's acid, divinyl sulfone, and a little potassium hydroxide in t-butyl alcohol was boiled, pure crystals of