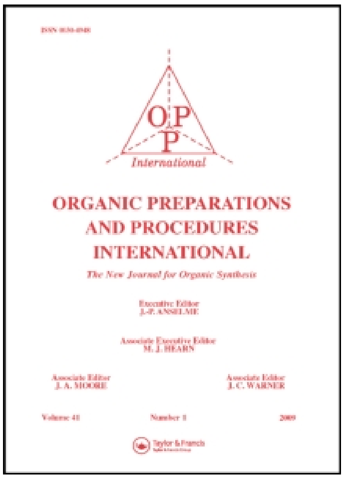

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF 1,6-DICARBOXYHEX-3-ENE

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF 1,6-DICARBOXYHEX-3-ENE

Submitted by (10/14/92)

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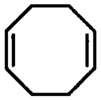
Generation of *cisoid* C=C bonds has been one of the crucial steps in the synthesis of many natural products.[1] The Z-olefinic diester **4c** has been employed as a suitable starting material in a few instances.[2] For the preparation of this diester, we previously reported a method using H_2WO_4-H_2O_2 for the vicinal hydroxylation of *cis,cis*-1,5-cyclooctadiene (**1**) to obtain the *trans*-diol **2** in 65% yield.[3] The *trans*-diol **2** was readily cleaved with sodium metaperiodate in moist ether to give the dialdehyde **4a** which, on oxidation with Jones' reagent,[4] furnished the diacid **4b** in 65% overall yield from the *trans*-diol **2**. The diacid **4b** was esterified with methanol in the presence of conc. H_2SO_4 to afford the diester **4c** in 64% yield. This method, though favorably comparable with others,[5] required large quantities of the expensive reagent, sodium metaperiodate. We now report a shorter and inexpensive method for the preparation of the Z-olefinic acid **4b** from the *trans*-diol **2**. Jones' reagent itself[6] can be used for the cleavage of the *trans*-diol **2** as well as for the oxidation of the dialdehyde **4a** formed *in situ*. The treatment of the *trans*-diol **2** with Jones' reagent at 5° furnished the diacid **4b** in one step directly in 70% yield.[7] This new method not only avoids the use of expensive oxidant but also gives better yields of the diacid **4b** by a shorter route. The Jones' reagent is also equally effective in cleaving *cis*-diol **3** to diacid **4b**.



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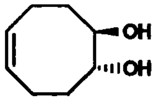

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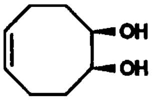

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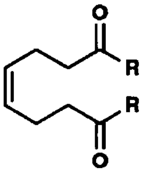

4

a) R = H
b) R = OH
c) R = OMe

EXPERIMENTAL SECTION

The melting point was determined on a Gallenkamp-350 micromelting point apparatus. The infrared spectrum was recorded on a Shimadzu IR 408. NMR Spectra (90 MHz) was obtained on a Perkin-Elmer R32 instrument using TMS as an internal standard. The UV spectrum was determined on a Shimadzu Graphicord UV 240.

Preparation of Diacid 4b.- To a cooled solution of *trans*-diol **2** (3.28 g, 0.023 mol) in acetone (freed from oxidizable impurities) was added freshly prepared Jones' reagent dropwise with stirring till the orange color persisted (8 mL, excess). After complete oxidation (tlc, 1 hr), acetone was removed *in vacuo* and the residue was dissolved in water (40 mL). The aqueous layer was then extracted with ethyl acetate (4 x 30 mL). The combined organic extracts were washed with water (2 x 15 mL) and brine (20 mL). Drying (Na_2SO_4) and removal of the solvent gave diacid **4b** which was recrystallized from ethyl acetate to give colorless prisms (2.8 g, 70%), mp. 102-104°. The diacid thus obtained was identical in all physical and spectral characteristics with the sample obtained by the previous method.[3]

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A FACILE SYNTHESIS OF bis(3-ARYL-3-OXO-1-PROPENYL)BENZENES

Submitted by (12/11/92)

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bis(3-Aryl-3-oxo-1-propenyl)benzenes are important intermediates in organic synthesis,[1] which are usually obtained by the condensation of benzenedicarboxaldehyde and substituted acetophenones in the presence of sodium hydroxide. If benzene ring of the acetophenone bears an electron-withdrawing group (such as nitro group) however, the yields of the bis(3-aryl-3-oxo-1-propenyl)benzenes are poor under these conditions. Recently, we obtained α,β-unsaturated ketones, nitriles, cyanoesters, cyanoamides and α-cyano-α,β-unsaturated sulfones under neutral conditions[2] by using *bis*(4-methoxyphenyl)telluroxide (BMPTO)[3] as catalyst. The present communication reports the synthesis of *bis*(3-aryl-3-oxo-1-propenyl)benzenes catalyzed by BMPTO.

The polarity of solvent has a remarkable effect on the reaction; for example, the yield of **5a** from the reaction of **2** with acetophenone for 2 hrs at 80° was 77%, 21%, and 0% in DMSO, acetonitrile and benzene, respectively. The temperature and amount of BMPTO also have a significant effect on the reaction. The best reaction conditions for each case studied is given in the Table. Since the condensation proceeds under neutral conditions, the reaction can be applied to the olefination of aldehydes sensitive to alkali.