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AN IMPROVED PROCEDURE FOR THE $KMnO_4$ OXIDATION OF OLEFINS TO CIS-1,2-GLYCOLS BY USE OF PHASE TRANSFER CATALYSIS

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Phase transfer catalysis (PTC) and crown ethers are two newer methods which have been utilized to make inorganic salts soluble in organic solvents. Starks has reported that terminal olefins can be oxidized by $KMnO_4$ using PTC to the one carbon shorter carboxylic acid.[1] Similarly, Sam and Simmons find that dicyclohexyl-18-crown-6 ether complex of $KMnO_4$ is effective in quantitatively oxidizing internal olefins to diacids.[2]

We should like to report that PTC can be used to oxidize internal olefins with basic $KMnO_4$ to the corresponding cis-1,2-glycols in 50% yield. While the oxidation of olefins to cis-1,2-glycols by basic $KMnO_4$ appears in many undergraduate organic textbooks, [3] it is with but a few exceptions (such as the oxidation of long chain mono unsaturated fatty acids)[4] a poor reaction. Cope, for example, reports that cis-cyclooctene is oxidized to the cis-1,2-cyclooctanediol by aqueous basic $KMnO_4$ - in only 7% yield. [5]

This led to other methods to achieve this transformation - such as osmium tetraoxide, which is both expensive and toxic[6,7,8] or Woodward's procedure which involves reaction of the olefin with iodine and silver acetate in moist acetic acid.[9,10]

The oxidation of cis-cyclooctene with basic $KMnO_4$ is an example of the new PTC method. cis-Cyclooctene (11 grams,0.1 mole) in 100 ml of CH_2Cl_2 was placed in a 1-ℓ three necked round bottom flask equipped with a mechanical stirrer. To this was added 100 ml of a 40% aqueous NaOH solution and 1 gram of benzyltriethylammonium chloride[11] (the PTC catalyst). The reaction was cooled to 0°C in an ice salt bath. Small portions of $KMnO_4$ (15.8 grams, 0.1 mole) were added over two hours with vigorous stirring and maintenance of the reaction temperature at 0°C. The reaction flask was packed in ice and let stir overnight. The

MnO_2 precipitate was dissolved by reaction with SO_2. Ether (500ml) was then added and the layers separated. The aqueous layer was then extracted three times with 150 ml portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and the solvent removed by evaporation under reduced pressure. The white solid thus isolated (9-9.5 grams) was recrystallized from ethyl acetate/n-heptane to yield 7.8 grams (50% yield) of cis-1,2-cyclooctanediol, mp 76-77°C.[5] Its spectral properties ir, and nmr were also consistent with the assigned structure.

Similar yields have been obtained in the oxidation of trans-cyclododecene to yield trans-1,2-cyclododecanediol, mp 98-99°C.[12] Lower yields are obtained, however, if the glycol product is highly soluble in the aqueous phase. Thus in the oxidation of cyclohexene in addition to a 15% yield of the desired cis-1,2-cyclohexanediol significant amounts of adipic acid are also obtained.

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