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HOMOGENEOUS PERMANGANATE OXIDATION IN NON-AQUEOUS ORGANIC SOLUTION. SELECTIVE OXIDATIONS OF OLEFINS INTO 1,2-DIOLS OR ALDEHYDES

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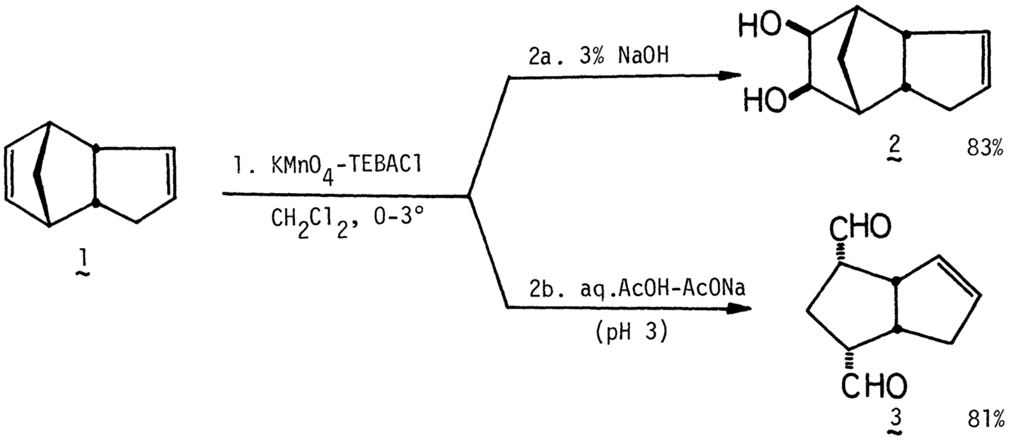
Potassium permanganate solubilized in dichloromethane by use of equimolar amount of triethylbenzylammonium chloride smoothly oxidized olefins to give homogeneous dark brown reaction mixtures, which were then selectively decomposed into either 1,2-diols or aldehydes in good yields by treatment with aqueous solutions depending upon pH.

The use of phase transfer catalysis (quarternary ammonium salts and crown ethers) has improved the permanganate oxidations of olefins into 1,2-diols or carboxylic acids.[1-6] However, most of the reactions so far reported were carried out in aqueous-organic two phase systems and few were reported about the reaction in homogeneous non-aqueous organic system.

We have found that potassium permanganate solubilized in dichloromethane by use of equimolar amount of a quarternary ammonium salt provides a convenient procedure for the oxidations of olefins. The reaction was conducted in an anhydrous condition and no precipitates of manganese dioxide were formed when permanganate ion had been consumed. Either 1,2-diols or aldehydes were obtained in good yields by quenching the resulting homogeneous reaction mixtures with an aqueous solution depending upon pH. It is notable that aldehydes were obtained as the bond cleavage product in place of carboxylic acids, the products of the earlier two phase procedures.[1,2,4-6]

In a typical example, *endo*-dicyclopentadiene (1) was converted to either an *exo,cis*-1,2-diol (2) or a dialdehyde (3) in more than 80% yield, respectively. The procedure is as follows: To a stirred solution of *endo*-dicyclopentadiene (2.27 mmol) in dichloromethane (20 ml) was added dropwise the oxidant solution freshly prepared with $KMnO_4$ (3.41 mmOl),[7] triethylbenzylammonium chloride(3.41 mmol) and dichloromethane (40 ml) at such a rate that the temperature was maintained at 0-3°C under cooling with an ice-bath (40-50 min). After addition was complete, stirring was continued until permanganate ion was completely consumed (30-40 min). The homogeneous dark brown solution was then treated with aqueous solutions of variant pH.



When the reaction mixture was treated with 3% NaOH solution (30 ml) under nitrogen atmosphere at room temperature for 18 hours, a crystalline product (2), mp 47-52° (lit. 48-51°),[8] was obtained in 83% yield from the organic layer upon usual work-up.[9] The product was identified as the *exo,cis*-diol (2) by its ir and nmr data, which was previously obtained in 28% yield by the oxidation of *endo*-dicyclopentadiene in EtOH with aqueous potassium permanganate.[8] No other products were detected on tlc and glc.

On the other hand, when the reaction mixture was treated with an acetate solution (30 ml) at pH 3, the dialdehyde (3), mp 42-44° (lit. 36-42°),[8] was obtained in 81% yield as the single product (tlc, glc). The compound (3) is known as a key intermediate for prostaglandin synthesis and has been synthesized indirectly through periodate oxidation of the diol (2).[8]

A mixture of (2) and (3) was obtained in a 5:1 ratio when the reaction mixture was decomposed by neutral water, while a mixture in a 3:2 ratio was obtained when decomposed by a buffer solution at pH 5. The results and further examples of the oxidation of olefins by this new procedure are summarized in Table 1.

The mechanism for the oxidations of olefins in non-aqueous organic solution is not known. However, it is apparent that stable organomanganese intermediates lasted in the non-aqueous solution until being quenched by aqueous solutions. The intermediates are probably cyclic hypomanganate esters as generally accepted for aqueous systems.[10-12] In aqueous solutions, these intermediates are known to be quite unstable and the transient existence has been detected only by tracing the rapid changes in uv-visible absorbance by stopped-flow techniques in the oxidation of crotonate anion[13] and cinnamic acid.[14] A longer-lived manganese intermediate has been also detected in the oxidation of thymine.[15]

This is the first example, we believe, that such long-lived organomanganese intermediates in permanganate oxidation have been noted in non-aqueous organic system.

Table 1. Oxidations by Potassium Permanganate in CH_2Cl_2 Using Triethylbenzylammonium Chloride

Starting material	Reaction time (min)	Quenching solution	Isolated yield (%) 1,2-Diol	Isolated yield (%) Aldehyde
endo-Dicyclopentadiene (1)	90	3% NaOH	83	0
		H_2O	71	15
		aq. AcOH-AcONa (pH 5)	51	36
		aq. AcOH-AcONa (pH 3)	0	81
Norbornene[16]	160	3% NaOH	69	0
		H_2O	41	34
		aq. AcOH-AcONa (pH 3)	0	63
cis-Cyclooctene[17]	90	H_2O	70	0
		aq. AcOH-AcONa (pH 3)	35	38
		1N $HClO_4$	0	74
trans-Stilbene[18]	120	3% NaOH	26*	26*
		aq. AcOH-AcONa (pH 5)	0**	79**
1-Octene[19]	520	3% NaOH	80***	0***

*Benzil (3%) and benzoic acid (9%) were also isolated. **Benzoic acid (11%) was also isolated. ***Heptanoic acid (10%) was also isolated.

The advantages of this procedure (high yield, selectivity) could be ascribed to the fact that the products are protected against secondary oxidations by MnO_4^- through the formation of stable organomanganese species in non-aqueous solutions.

As the quarternary ammonium salts are low-priced in comparison with crown ethers and can be simply removed by washing with water, this procedure will offer a versatile route for the conversion of olefins into 1,2-diols or aldehydes. Studies of further aspects of this oxidation reaction, especially on the nature of the intermediates, are in progress.

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18) For precedents of the oxidation of *trans*-stilbene by permanganate ion, see ref. 2 and 4.

19) For precedents of the oxidation of 1-octene by permanganate ion, see ref. 1 and 4.

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