

Ultrasound Accelerated Permanganate Oxidation: An Improved Procedure for the Synthesis of 1,2-*Cis* diols from Olefins

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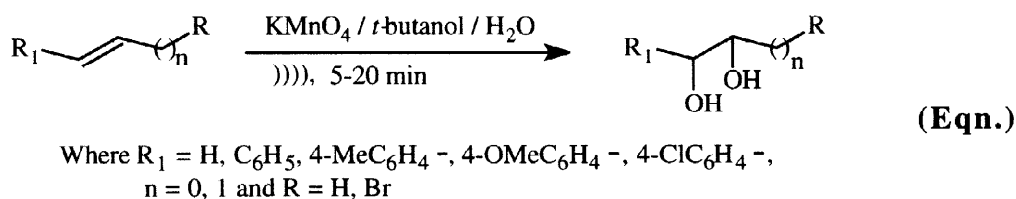
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Abstract: A simple and expeditious method for the preparation of 1,2-*cis* diols is described from olefins using an inexpensive oxidant potassium permanganate, KMnO_4 , *via* sonochemical activation in aqueous media. © 1998 Elsevier Science Ltd. All rights reserved.

A large number of permanganate reagents have been developed for the oxidation of organic molecules under heterogeneous conditions.¹ Potassium permanganate supported on silica gel² or molecular sieves³ has been used to oxidize alcohols to carbonyl compounds and for the cleavage^{4a} or oxidation^{4b} of carbon-carbon double bonds, permanganate supported on copper sulfate pentahydrate has been used for the oxidation of alcohols to the corresponding carbonyl compounds,⁵ diols to lactones,⁶ and sulfides to sulfones.⁷ Zinc permanganate supported on silica gel is utilized for the conversion of acetylenes to α -diketones and cyclic olefins to ketols.⁸ The dihydroxylation of olefins is generally accomplished by osmium tetroxide, OsO_4 ,⁹ and alkaline potassium permanganate, KMnO_4 , from the less-hindered side of the double bond.¹⁰ The main drawback of this reaction is that OsO_4 is expensive and highly toxic. Consequently, its use has been limited to small-scale preparations of scarce materials. Similar results are obtainable more economically by utilizing H_2O_2 ,¹¹ *t*-butylhydroperoxide in alkaline media¹² or *N*-methylmorpholine-*N*-oxide¹³ with judicious use of co-oxidant, OsO_4 in smaller amounts. Potassium permanganate, on the other hand, is a strong oxidizing agent that can readily oxidize glycols¹⁴ especially under acid and neutral conditions thus limiting its scope for the generation of glycols. Alkaline permanganate, however, can lead to glycol formation but the yields are seldom above 50%, although some improvement is feasible by employing phase transfer catalysis,¹⁵ or extensive stirring in dilute solution.¹⁶ We decided to explore the use of ultrasound irradiation in this oxidation protocol with KMnO_4 which has been successfully applied earlier to a number of heterogeneous reactions¹⁷ including the Baeyer's test for identifying the alkenes and alkynes.¹⁸

Herein, we report a facile oxidative conversion of olefins to 1,2-*cis* diols in aqueous media

using ultrasound activation and KMnO_4 under neutral conditions. The potential of conducting organic reactions in aqueous media is an emerging area of research¹⁹ with considerable pollution prevention advantages since the anhydrous and inflammable organic solvents can now be substituted by water. When olefins are subjected to ultrasound irradiation in the presence of powdered KMnO_4 in water and a small amount *t*-butanol for Ω -phase formation,^{4b} 1,2-*cis* diols are obtained in high yield (80-88%). In general, olefins are admixed with KMnO_4 , *t*-butanol and water are added and the reaction mixture is irradiated by inserting the sonic horn (probe) into the reaction mixture (Eqn.).

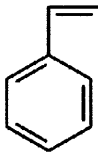
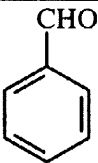
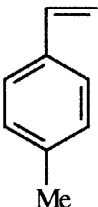
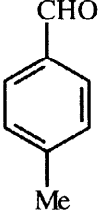
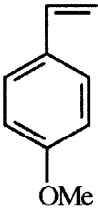
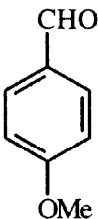
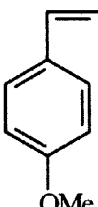
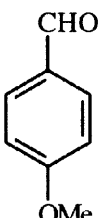
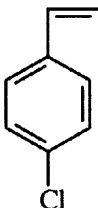
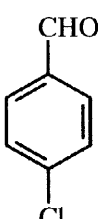




Our results for a variety of 1,2-*cis* diols are summarized in the Table and are exemplified by substrates such as styrene, substituted styrenes and allyl bromide. Styrene bearing an electron releasing substituents undergo the reaction at a much faster rates as compared to parent or styrene derivatives with electron withdrawing groups appended. This oxidation reaction is found to be very slow with styrene under classical conditions (stirring at room temperature without ultrasound), that requires nearly 30 h for completion of the reaction which affords diols in 55% yield contaminated with the corresponding carboxylic acid. Presumably, the ultrasound-promoted decomposition of the cyclic manganate(V) diester intermediate,^{14,20} formed as a result of [3+2] cycloaddition,¹ is responsible for the faster formation of diols. A disubstituted alkyne, diphenylacetylene, under similar reaction conditions rapidly affords benzil (entry 7) in good yields. In the case of terminal alkynes, however, the formation of carboxylic acids predominates.

We also have explored the applicability of this sonochemical approach to the oxidation of styrene using other benign oxidants such as NaIO_4 and H_2O_2 with the following results: (a) with NaIO_4 , 9h irradiation (reaction monitored intermittently by TLC), 95% benzaldehyde and 5% benzoic acid; whereas (b) with H_2O_2 , 10 h irradiation, 90% benzaldehyde, 7% 1,2-*cis* diol and 3% benzoic acid.

General procedure for the conversion of olefins to 1,2-cis diols:- In a typical experiment, styrene (208 mg, 2 mmol) was added to the finely powdered KMnO_4 (474 mg, 3 mmol). To this mixture, *t*-butanol (1 mL) was added followed by water (15-20 mL) and the reaction mixture was irradiated. On completion of the reaction, followed by TLC examination (hexane;EtOAc, 4:1, v/v), the product was extracted into dichloromethane (3 x 15 mL), the combined organic extract dried with anhydrous sodium sulfate and solvent removed under reduced pressure. In all cases the formation of the corresponding acids (3-5%) were determined by GC-MS analysis (Hewlett-Packard model 5890 gas chromatograph with a mass spectrometer). The NMR spectra were recorded on Jeol 300 MHz Spectrometer and IR spectra on a Perkin-Elmer 1310 spectrophotometer. Ultrasonic processor (Heat systems-Ultrasonics, Inc., W-380) was used for irradiation.

Table: Synthesis of 1,2-*cis* diols from olefins using KMnO₄ and ultrasound irradiation.^a

Entry	Starting material	Time	Product	% Yield	Starting material / oxidant ratio
1		15 min		80	(1:1.5)
2		5 min		85	(1:1.5)
3		5 min		80	(1:1.5)
4		30 h ^b		55	(1:7)
5		20 min		78	(1:1.5)
6		15 min		88	(1:1.5)
7	C ₆ H ₅ C≡CC ₆ H ₅	105 min	C ₆ H ₅ COCOC ₆ H ₅	86	(1:1.5)
8	C ₆ H ₅ C≡CC ₆ H ₅	24 h ^b	C ₆ H ₅ COCOC ₆ H ₅	85	(1:7)

^aYields refer to pure isolated products obtained that are characterized by IR and NMR spectra.

^bReaction under classical conditions with stirring at room temperature without ultrasound irradiation.

In conclusion, this ultrasound-accelerated oxidation reaction of olefins with potassium permanganate is a simple and facile method to produce 1,2-*cis* diols in high yields that uses relatively much reduced amount of the oxidant. The operational simplicity, the use of

inexpensive oxidizing agent, rapid reaction rates and high yields of pure product formation when compared to existing protocols makes this a useful procedure and an attractive alternative to the currently available methods.

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