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Methyltrioxorhenium catalyzed oxidation of 1,2-diols to 1,2-diketones using hydrogen peroxide as oxidant

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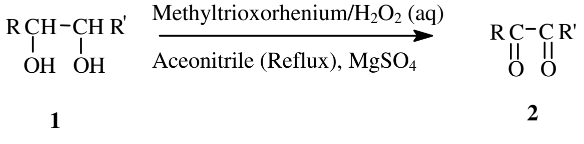
Abstract—A variety of 1,2-diols were oxidized selectively to the corresponding 1,2-diketones by the dropwise addition of 30% aqueous hydrogen peroxide using methyltrioxorhenium as catalyst.

The methyltrioxorhenium (MTO)/hydrogen peroxide oxidation system first reported by Herrmann and Kuhn[1] in 1991 for the epoxidation of olefins has proved to be an efficient and versatile system for various oxidation reactions.[2] The important features of the use of MTO as a catalyst are its ease of synthesis, commercial availability, stability in air and efficiency in acting as a homogeneous catalyst for oxidation using hydrogen peroxide in both aqueous and organic solvents. The oxidation of 1,2-diols is an important synthetic transformation as 1,2-diketones find wide applications as starting materials for the synthesis of heterocycles and are extensively used as substrates for benzilic acid rearrangements.[3] Although a variety of oxidants have been used to achieve this transformation, most are associated with drawbacks such as the use of stoichiometric amounts of corrosive acids or toxic metallic compounds that generate undesirable wastes.

In recent years the oxidation of 1,2-diols to 1,2-diketones has been reported using 4-MeO-TEMPO,[4] 4-PhCO$_2$-TEMPO-electrolysis,[5] (4-AcNH-TEMPO)-OTs-TsOH,[6] H_2O_2–[C_5H_5N–$(CH_2)_5$ $CH_3[PO_4(W(O)(O_2)_2]_4$],[7] O_2–Co(acac)$_3$-*N*-hydroxyphthalimide[8] and *N*-bromosuccinimide.[9] However these methods suffer from drawbacks such as the use of expensive reagents, difficult experimental conditions, long reaction times and low yields of products, leaving scope for further improvement in this area. In continuation of our studies on oxidation using eco-friendly oxidants[10] we report herein the first successful methyltrioxorhenium catalyzed oxidation of 1,2-diols to the corresponding 1,2-diketones using hydrogen peroxide as oxidant (Scheme 1). A variety of 1,2-diols were selectively oxidized to the corresponding 1,2-diketones by the dropwise addition of 30% aqueous hydrogen peroxide to their solution in refluxing acetonitrile using methyltrioxorhenium as catalyst and MgSO$_4$ as water trapping agent.[11] These results are presented in Table 1. Hydrobenzoins, in general, were found to be more reactive than aliphatic diols and required shorter reaction times for their oxidation. Hydrobenzoins containing electron-donating groups were found to be more reactive and could be oxidized more easily. It was interesting to note that the oxidation of hydrobenzoin with 5 equiv of 30% hydrogen peroxide, when added in one portion, gave a mixture of benzil and benzoic acid along with unreacted hydrobenzoin. In contrast, the same oxidation when carried out by the dropwise addition of the hydrogen peroxide afforded the benzil selectively in excellent yield. The oxidation of 1,2-diols was found to be highly dependent upon the reaction temperature, at room temperature these oxidations were found to be very slow and were not complete even after 20 h. Furthermore, the presence of a water trapping agent (MgSO$_4$) was found



Scheme 1.

Keywords: Methyltrioxorhenium; 1,2-Diols; 1,2-Diketones; Hydrogen peroxide; Oxidation.

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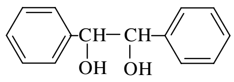
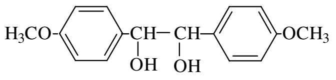
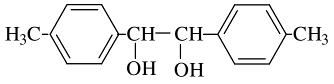
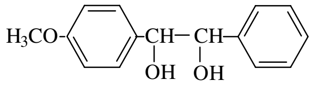
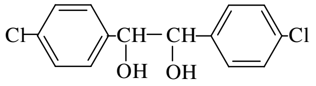
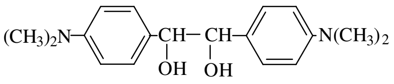
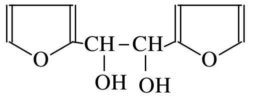
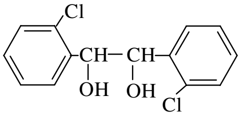
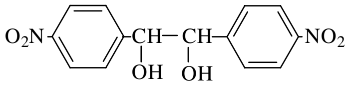
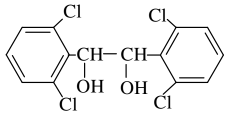
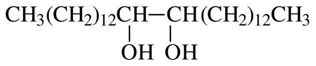
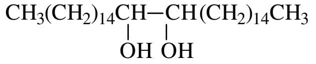
Table 1. Oxidation of 1,2-diols with the methyltrioxorhenium/H_2O_2 system[a]

Entry	Substrate	Reaction time (h)	Yield[b]
1		7.50	92
2		5.50	95
3		5.75	94
4		6.25	92
5		8.00	92
6		7.00	94
7		4.00	97
8		8.75	90
9		9.25	85
10		10	80
11	 $CH_3(CH_2)_{12}\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_{12}CH_3$	12.00	75
12	 $CH_3(CH_2)_{14}\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_{14}CH_3$	12.50	70

[a] Reaction conditions: substrate (1 mmol), catalyst (1 mol%), 30% aq. hydrogen peroxide (0.5 mL) in refluxing acetonitrile in the presence of $MgSO_4$ as water trapping agent.

[b] Isolated yields.

to be essential and in the absence of $MgSO_4$ only very low yields of the 1,2-diketones were obtained.

The reactions involve the formation of α-hydroxycarbonyl compounds followed by their oxidation into the corresponding diketones. The intermediacy of α-hydroxycarbonyl compounds was confirmed in the case of hydrobenzoin and hydroanisoin by quenching the reactions after 2 h and isolating benzoin and anisoin, respectively, from the reaction mixtures.

In conclusion, we have developed a very simple and efficient method for the selective oxidation of 1,2-diols to the corresponding diketones by 30% hydrogen peroxide using methyltrioxorhenium as a catalyst under mild reaction conditions.

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11. Typical experimental procedure: To a stirred and refluxing solution of hydrobenzoin (1 mmol, 214 mg) containing the drying agent $MgSO_4$ (100 mg) and methyltrioxorhenium (2.5 mg, 1 mol%) in acetonitrile (5 mL), 30% aqueous hydrogen peroxide (0.5 mL, 5 mmol) was added dropwise over a period of 7.5 h. The progress of the reaction was monitored by TLC (SiO_2) using benzene/ethyl acetate (9:1) as eluent. At the end of the reaction, the reaction mixture was treated with excess MnO_2 (for destruction of the excess H_2O_2) followed by filtration. The solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane. The dichloromethane layer was washed twice with water and dried over anhydrous sodium sulfate followed by evaporation of the solvent. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded benzil (190 mg, 92%), which was identified by comparing physical and spectral data with those of an authentic sample.