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Methyltrioxorhenium Catalyzed Oxidative Cleavage of α-Hydroxycarbonyl Compounds to Carboxylic Acids with Hydrogen Peroxide

Suman L. Jain, Vishal B. Sharma, and Bir Sain*

Chemical and Biosciences Division,
Indian Institute of Petroleum, Dehradun, India

ABSTRACT

Methyltrioxorhenium catalyzed oxidative cleavage of a variety of α-hydroxycarbonyl compounds with hydrogen peroxide selectively yielded corresponding carboxylic acids in excellent yields.

Oxidative cleavage of α-hydroxycarbonyl compounds/α-diketones in a selective manner to the corresponding carboxylic acids or their derivatives is an important synthetic transformation[1] and apart from conventional stoichiometric oxidants like periodic acid,[2] calcium hypochlorite,[3] lead tetracetate[4] which generates undesirable waste, the use of molecular oxygen with dichloroethoxy-oxy-vanadium heteropoly acids as catalysts[5] and hydrogen peroxide with heteropoly acids as

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*Correspondence: Bir Sain, Chemical and Biosciences Division, Indian Institute of Petroleum, Dehradun 248005, India; E-mail: birsain@iip.res.in.

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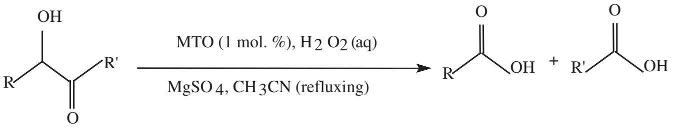
catalysts[6] has been reported in the literature for this transformation in pursuit to the development of eco-friendly synthetic methodologies.

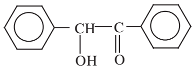
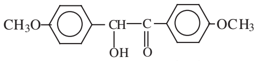
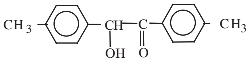
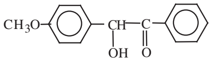
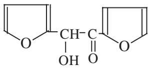
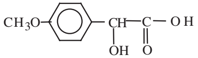
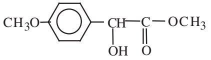
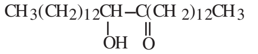
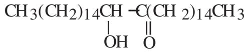
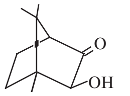
Methyltrioxorhenium (MTO)/hydrogen peroxide oxidation system first reported by Herrmann and Kuhn[7] in 1997 for epoxidation of olefins has proved to be an efficient and versatile system for various oxidation reactions.[8] The important features of MTO as catalyst are its ease of synthesis, commercial availability, stability in air, and efficiency to act as homogeneous oxidation catalyst for hydrogen peroxide in both aqueous and organic solvents. However, to the best of our knowledge there is no literature report on oxidative cleavage of α-hydroxycarbonyl compounds to carboxylic acid with MTO/hydrogen peroxide oxidation system. In continuation to our studies on transition metal catalyzed oxidations,[9] herein we report for the first time a simple and more convenient eco-friendly method for the oxidative cleavage of α-hydroxycarbonyl compounds to carboxylic acids with methyltrioxorhenium/hydrogen peroxide system (Sch. 1).

The oxidation of a variety of α-hydroxycarbonyl compounds[10] was carried out with 30% aqueous hydrogen peroxide using catalytic amount of methyltrioxorhenium in refluxing acetonitrile in the presence of dehydrating agent ($MgSO_4$).[12] All the substrates studied were smoothly and selectively converted to their corresponding acids in excellent yields. These results are presented in Table 1. In general aromatic α-hydroxycarbonyl compounds were found to be more reactive and required lesser reaction time for their oxidation. The oxidative cleavage of α-hydroxycarbonyl compounds was found to be highly dependent upon the reaction temperature and at room temperature these oxidations were found to be very slow and did not complete even after 20 h. Further the presence of water trapping agent ($MgSO_4$) was found to be vital in these reactions from yields point of view. The reaction involves the formation of α-dicarbonyl compounds followed by their oxidative cleavage to carboxylic acids. The intermediacy of α-dicarbonyl compounds was confirmed in case of benzoin and anisoin by quenching the reactions after 1 h and isolating benzil and anisil respectively from the reaction mixture. The α-dicarbonyl compounds separately prepared by oxidation



Scheme 1.

Table 1. The oxidative cleavage of α-hydroxycarbonyl compounds using MTO/H_2O_2 system.

Run	Substrate	Reaction time (h)	Yield (%)
1		6.00	96
2		3.50	97
3		3.00	97
4		4.50	94
5		1.50	96
6		5.00	90
7		6.00	85
8	 $CH_3(CH_2)_{12}\underset{OH}{CH}-\underset{O}{C}(CH_2)_{12}CH_3$	8.00	85
9	 $CH_3(CH_2)_{14}\underset{OH}{CH}-\underset{O}{C}(CH_2)_{14}CH_3$	10.00	80
10		12.00	75[11]

of α-hydroxylcarbonyl compounds[9c] could also easily be converted to the corresponding carboxylic acids under the similar reaction conditions.

In summary we have demonstrated for the first time, that methyltrioxorhenium catalyzed oxidative cleavage of a variety of α-hydroxycarbonyl compounds with hydrogen peroxide selectively yields corresponding carboxylic acids in excellent yields under mild conditions.

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12. Typical experimental procedure: To a stirred solution of benzoin (212 mg, 1 mmol) in acetonitrile (5 mL) was added 30% aqueous hydrogen peroxide (1 mL solution) mixed with drying agent followed by the addition of methyltrioxorhenium (0.01 mmol, 1.0 mol%) and the reaction mixture was refluxed for the 6 h. At the end of reaction, the reaction mixture was treated with excess MnO_2 (for destruction of H_2O_2) followed by filtration and passing through a short column of silica gel using dichloromethane as eluent, evaporation of the solvent gave benzoic acid (234 mg, 96%). Other α-hydroxycarbonyl compounds were oxidized using this procedure and their reaction times and yields are given in Table 1. The products were identified by comparing their physical and spectral data with those of authentic samples reported in literature. In case of asymmetric α-hydroxycarbonyl compounds the identity of the acids was established through GC by comparing the retention time of their methyl esters with those of authentic samples. Similarly α-dicarbonyl compounds (benzil and anisil) were oxidized to their corresponding acids.