Methyltrioxorhenium: oxidative cleavage of CC-double bonds and its application in a highly efficient synthesis of vanillin from biological waste

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Abstract

An oxidation system consisting of methyltrioxorhenium and H_2O_2 catalyzes the cleavage of CC-double bonds. By varying the reaction conditions, it is possible to generate either the aldehyde or the carboxylic acid in reasonable-to-excellent yields and selectivities, depending on the starting material. The application of these findings to isoeugenol and *trans*-ferulic acid — both available from renewable resources — results in a highly efficient synthesis of vanillin. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Methyltrioxorhenium (MTO, CH_3ReO_3) has been proven to be an excellent catalyst in a variety of organic reactions [1]. In particular, the efficient catalytic oxidation system MTO/H_2O_2 is the subject of extensive studies. Whereas the epoxidation of alkenes by MTO/H_2O_2 has been known since 1991 [1], the selective cleavage of CC-double bonds leading to aldehydes, ketones or carboxylic acids, has never been observed. Herein, we describe reaction conditions for the MTO-catalyzed oxidation of different alkenes to aldehydes and carboxylic acids, respectively.

2. Results and discussion

2.1. Aldehydes from aliphatic olefins in organic solvents

The cleavage of CC-double bonds requires a significant increase in catalyst lifetime at temperatures up to 80°C, compared to the standard system $MTO/H_2O_2/tert$-butanol for olefin epoxidation, which occurs at room temperature or below [2]. The deactivation of the catalytically active bis(peroxo)rhenium complex in an aqueous solution is initiated by a nucleophilic

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Table 1
Oxidation of terminal olefins with MTO/H$_2$O$_2$[a,b]

Olefin	Drying agent	Solvent	GC yield of aldehyde (%)	GC yield of diol (%)
n-Hexene-1	MgSO$_4$	MTBE	68	32
	MgSO$_4$	*tert*-BuOH	58	42
n-Octene-1	MgSO$_4$	*tert*-BuOH	35	65
	MgSO$_4$	MTBE	65	35
	–	MTBE	58	42
	MgSO$_4$	*tert*-BuOH	48	52
	MgSO$_4$	*tert*-BuOH[c]	53	47
	–	*tert*-BuOH	0	70[d]
	MgSO$_4$	CH$_3$CN	32	68
	–	CH$_3$CN	0	41[e]
	MgSO$_4$	di-*n*-butyl ether	10	90
	Na$_2$SO$_4$	*tert*-BuOH	27	73
	HC(OEt)$_3$	*tert*-BuOH	23	77
n-Octadecene-1	MgSO$_4$	MTBE	54	46
	MgSO$_4$	*tert*-BuOH	42	58

[a]Reaction conditions: 10.0 mmol olefin, 0.10 mmol catalyst, 60.0 mmol H$_2$O$_2$ (30% in organic solvent), $T = 60°C$, $t = 7$ h.
[b]Conversion of olefin: 100%.
[c]120 mmol H$_2$O$_2$ (30% in organic solvent).
[d]Conversion of olefin: 70%.
[e]Conversion of olefin: 41%.

attack of water at the rhenium center [3]. Consequently, an exclusion of water generated during the reaction by adding water-trapping agents helps to increase the catalyst lifetime and allows the generation of aldehydes in reasonable yields. According to Table 1, methyl-*tert*-butyl ether (MTBE) and MgSO$_4$ represent an optimum in the match of drying agent and solvent.

Further, MTBE proves suitable for performing this reaction without any water trapping yielding comparable results to oxidations in the presence of MgSO$_4$. This is in sharp contrast to all the other solvents tested.

The limiting factor of all these systems is still the lifetime of the catalyst. Adding more of the catalyst after a 7-h reaction time results in higher yields. Mechanistically, the first step of the CC-bond cleavage is the epoxidation of the olefin. In the second step, two competitive pathways seem to be present: the CC-bond cleavage, and the hydrolysis of the epoxide leading to the diol. The latter is hardly accessible for further

oxidation under these conditions, explaining the high yields of diols at the end of the reaction.

2.2. Aldehydes from aliphatic olefins in a two-phase system

The insolubility of olefins and their oxidation products in water backs up a two-phase process. Of course, working in an olefin/aqueous H$_2$O$_2$ system increases the deactivation problems mentioned above. In order to accelerate the oxidation of the olefin, compared to the deactivation of the catalytically active species, the addition of Brønsted acids, such as HBF$_4$ or HClO$_4$ turned out to be very useful. Under these conditions, both the reaction rates and the yields of aldehyde are better than in the one-phase systems. Again, no carboxylic acid is detectable.

2.3. Carboxylic acids from aliphatic olefins

The only possibility of generating carboxylic acids close to the conditions of aldehyde generation, is by adding Brønsted acids to the MTBE system. With 300 mmol H$_2$O$_2$ and 1.0 mmol HBF$_4$, heptanoic acid is generated in 45% yield, starting at octene within 48 h under the reaction conditions given in Table 2. In the course of this oxidation process, a remarkable amount of

Table 2
Oxidation of *n*-octene-1 with MTO/H$_2$O$_2$ in a two-phase system[a,b]

Olefin	Catalyst	Acid	GC yield of aldehyde (%)	GC yield of diol (%)
n-Hexene-1	MTO	HBF$_4$	73	27
	MTO	HClO$_4$	68	32
	–	HBF$_4$	0	≤ 5[c]
	–	HClO$_4$	0	≤ 5[c]
n-Octene-1	MTO	HBF$_4$	75	25
	MTO	HClO$_4$	64	36

[a]Reaction conditions: 10.0 mmol n-octene-1, 0.10 mmol catalyst, 60.0 mmol H$_2$O$_2$ (30% in water), 1.0 mmol acid, $T = 60°C$, $t = 2$ h.
[b]Conversion of olefin: 100%.
[c]Conversion of olefin: ≤ 5%.
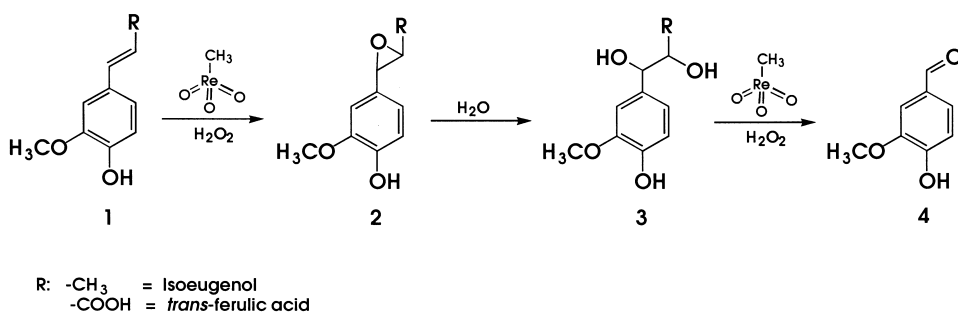
Scheme 1.

the MTBE is oxidized to the corresponding peroxide. This explains the high excess of H_2O_2 needed. Additionally, *tert*-butyl hydroperoxide — known as an oxidant by itself — can be detected in the reaction mixture. Thus, it seems likely that the oxidized solvent contributes to the aldehyde oxidation. A similar phenomenon regarding solvent oxidation is not observed in systems without Brønsted acids.

2.4. Aldehydes from styrene derivatives as a synthesis of vanillin

In contrast to the results above, the conditions for the selective oxidation of styrene derivatives to the corresponding aldehydes and benzylic acids are somewhat different. The aldehydes are formed by using a three-time excess of hydrogen peroxide without further additives except for the catalyst MTO itself. These results enable the oxidation of certain natural products, which are derived from styrene and its derivatives. We were able to apply this catalytic system on a new method for the synthesis of vanillin out of renewable resources such as isoeugenol and *trans*-ferulic acid. It is well known that both are available by extraction of sawdust (isoeugenol) [4] or agricultural waste (*trans*-ferulic acid) [5].

A proposal for the mechanism of the MTO-catalyzed oxidative cleavage of the CC-double bond is shown in Scheme 1.

Oxidation of **1** with MTO/H_2O_2 intermediately leads to the formation of the epoxide **2**, which reacts to the vicinal diol **3** in the presence of water. Finally, the corresponding aldehyde **4** is formed in an almost quantitative yield.

From an economical and ecological point of view, this efficient route to the highly precious vanillin, starting from biological waste, is extraordinarily attractive.

During the course of catalysis, the rhenium based catalyst is degraded to form perrhenate and oxidized derivatives (methanol) after 1000 to 2000 cycles [3]. To overcome this disadvantage and to bring the idea of 'green chemistry' of this synthetic cycle to completion, we developed an efficient way of catalyst recycling by recovering the rhenium as inorganic perrhenate, which is again transformed to catalytically active methyltrioxorhenium in a convenient one-pot-reaction [6].

3. Conclusion

CC-double bond cleavage is accessible with the MTO/H_2O_2 system in reasonable to excellent yields, depending on the reaction conditions and the starting material. In the case of aliphatic olefins, this extension of the applicability of MTO is effected by increasing the catalyst lifetime at elevated temperatures or increasing the reaction rates of the oxidation process by adding Brønsted acids. Both aldehydes and carboxylic acids are accessible with the help of various additives. In the case of styrene derivatives, we

succeeded in the selective oxidation to the corresponding aldehydes. This yields the access to vanillin out of cost-effective renewable resources. Considering our recent report about the selective oxidation of terminal alcohols [7], we now have established a concept for the oxidation of alkenes, alcohols and aldehydes to the corresponding products that is based solely on the catalytic use of MTO under the respective conditions.

4. Experimental

4.1. General

The synthesis of MTO and the preparation of oxidation solutions was carried out as described elsewhere [2,8]. A Hewlett-Packard 5890 gas chromatograph (capillary column: HP-1, 30 m, i.d. 0.25 mm: column head pressure 50 kPa) coupled with a HP5970 mass selective detector and a HP 5970 FT-IR detector was used for GC/MS-IR characterization of oxidation products.

4.2. Catalytic olefin oxidation

In a typical run, 10.0 mmol of olefin are dissolved in the oxidation solution (30% H_2O_2 in organic solvent or as an aqueous solution), mixed with drying agent or Brønsted acid if necessary and heated to the appropriate temperature. The reaction is started by adding 0.10 mmol of MTO (1.0 mol%) and stopped through the addition of MnO_2 (destruction of H_2O_2). Work-up consists in adding $MgSO_4$, filtration and removal of the solvent.

4.3. Catalytic oxidation as synthesis for vanillin

In a typical run, 5.0 g (4.7 ml, 30.5 mmol) of isoeugenol or 5.9 g (30.5 mmol) of *trans*-ferulic acid are dissolved in 40 ml of *tert*-butanol and treated with 3.1 g (91.5 mmol, 3.6 ml, 85% in H_2O) of hydrogen peroxide. The reaction solution is dried by $MgSO_4$. The addition of 8 mg (0.3 mmol, 1 mol%) of MTO starts the oxidation process. After 10 min, we obtained an almost complete conversion to vanillin in both cases. The reaction is stopped through the addition of MnO_2 (destruction of H_2O_2) to prevent further oxidation to the corresponding acid.

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