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Epoxidation of Terminal or Electron-deficient Olefins with H_2O_2, catalysed by Mn-trimethyltriazacyclonane Complexes in the Presence of an Oxalate Buffer

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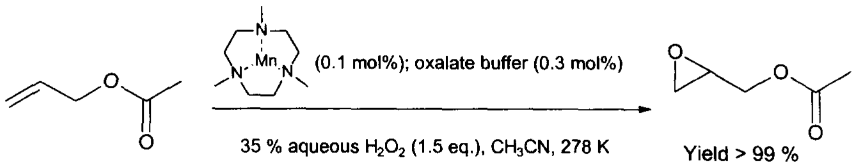
Abstract: A catalytic amount of an oxalate/oxalic acid buffer strongly enhances the catalytic properties of Mn-tmtacn complexes for epoxidation reactions with H_2O_2. Especially terminal olefins are easily epoxidized. Yields for *e.g.* allyl acetate or 1-hexene reach up to 99 % and 65 % on olefin and peroxide basis respectively. The reaction is stereospecific; there are no products of solvolysis.

1,2-Epoxides are valuable intermediates, especially when the molecule contains a second functional group. However, the low electron density of terminal olefins limits their reactivity for electrophilic oxygen transfer, and often the epoxidation is further retarded by nearby electron-withdrawing groups. Catalytic procedures for epoxidation of such deactivated olefins with hydrogen peroxide generally recur to Re or W.[1-2] In order to prevent solvolysis, these methods often employ a co-catalytic base (*e.g.* pyridine) or a biphasic reaction medium, which may limit the substrate choice to rather lipophilic molecules. In protic media, only the pertungstate-catalysed epoxidation of *e.g.* allylic alcohols is a well-established procedure.[3] We now report on an alternative catalytic system, comprising Mn, the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) and a catalytic amount of an oxalate buffer. With this catalyst and H_2O_2 as the oxidant, electron-deficient olefins (*e.g.* allyl acetate) are converted in high yields into the corresponding epoxides:



Previous catalytic work on Mn-tmtacn has shown that the complex as such mainly decomposes H_2O_2 into water and O_2, instead of using the peroxide for selective oxidation of olefins.[4] Peroxide disproportionation is suppressed in acetone;[5] but this procedure is unsuitable for the epoxidation of electron-deficient olefins because of competing solvent oxidation and the ensuing radical reactions.[6] An essential finding of the present work is that addition of catalytic amounts of ligands to Mn-tmtacn is an alternative way to favour epoxidation over disproportionation. In the experiments of Table 1, tmtacn (1.5 μmol) was reacted in CH_3CN (0.6 ml) with the Mn^{2+} salt of a weakly coordinating anion, namely $MnSO_4.H_2O$ (1 μmol in 0.1 ml H_2O). Next a co-catalyst (0.5-3 μmol), 1-hexene (0.666 mmol) and aqueous H_2O_2 (1 mmol) in CH_3CN (0.35

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ml) were added, and the 1,2-epoxyhexane yield (%) was measured until it no longer increased. Two major classes of effective co-catalysts were identified: *(i)* 1,3-diones, such as 1,3-indandione, and *(ii)* some dicarboxylic acids, such as oxalic and fumaric acid. These molecules are bi- or polydentate ligands; they may coordinate in bridging fashion to the Mn atoms in Mn-tmtacn complexes, and thus influence the nuclearity and the redox potential of the metal centers.[7] Remark that the effect depends on acid structure: for example, acetic acid does not promote the epoxidation. The epoxide yield is also low in the presence of trifluoroacetic acid, which excludes a simple peracid mechanism. The ionisation degree of the co-catalyst affects the catalyst performance. While rates are higher with Na oxalate, yields are better with oxalic acid. A 1:1 oxalic acid-oxalate buffer seems the optimum compromise between rate and efficiency: 1-hexene is converted for over 99 % into its epoxide within 20 minutes. This corresponds to a total of 650 catalytic cycles per Mn, and a 65 % yield on peroxide basis. Omission of Mn, tmtacn or co-catalyst leads to dramatic decreases of the epoxide yields, proving that all three components (Mn-tmtacn-oxalate) are essential for formation of the active species.

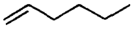
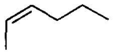
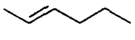
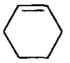
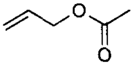
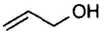
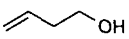
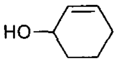
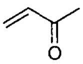
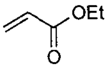
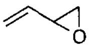
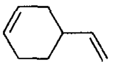
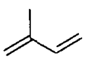
Table 1. 1,2-Epoxyhexane yields in the reaction of 0.666 mmol 1-hexene with 1 mmol H_2O_2, catalysed by Mn-tmtacn (1 μmol) and a co-catalyst.

Co-catalyst (μmol)	Yield (%), (*t*, h)	Co-catalyst (μmol)	Yield (%), (*t*, h)
-	1.5 (*10*)	fumaric acid (3)	57 (*10*)
1,3-cyclopentanedione (3)	25 (*10*)	$H_2C_2O_4$ (3)	94 (*10*)
1,3-indandione (2)	30 (*10*)	$Na_2C_2O_4$ (3)	70 (*1*)
acetic acid (3)	< 1 (*10*)	$H_2C_2O_4$ (1.5), $Na_2C_2O_4$ (1.5)	> 99 (*0.3*)
trifluoroacetic acid (3)	15 (*10*)		

In conjunction with the oxalate co-catalyst, Mn-tmtacn also effects the epoxidation of the isomeric hexenes and cyclohexene with H_2O_2. The epoxidation of the 2-hexenes is fully stereospecific (> 98 %). This is a significant improvement in comparison with the earlier procedure for Mn-tmtacn in acetone, which produced as much as 34 % of *trans* epoxide from *cis*-2-hexene. The chemoselectivity of the new Mn catalyst was evaluated from competitive oxidations of isomeric hexenes and cyclohexene. While most agents (*e.g.* *m*CPBA, or Mn-tmtacn in acetone) strongly discriminate against terminal, relatively electron-deficient double bonds, such distinctions are much less pronounced with Mn-tmtacn-oxalate. For instance, cyclohexene and *cis*-2-hexene are only 2.6 and 2 times more reactive than 1-hexene. In separate oxidations, the yields on peroxide basis are even better with 1-hexene than with the 2-hexenes or cyclohexene (Table 2, entries 1 and 3-5).

The Mn-tmtacn-oxalate/H_2O_2 system even forms epoxides when the olefin contains a second, deactivating function (-CH_2OH, -CH_2OCOR, -COR, -CO_2R and oxirane). As an example, allyl acetate is fully and selectively converted into its epoxide with only 1.5 equivalent of H_2O_2 (Table 2, entry 6). For other olefins, slightly more H_2O_2 may be required to obtain high epoxide yields. Remark that for allyl alcohol and 3-buten-1-ol, the epoxidation is strongly preferred over alcohol oxidation (entries 7-8).[8] Thus glycidol is obtained in over 90 % yield. Secondary alcohols, as in 2-cyclohexen-1-ol, are to some extent oxidized to the ketone (entry 9). Even double bonds conjugated to a carbonyl group are epoxidized, as in the case of methyl vinyl ketone or ethyl acrylate (entries 10-11). The reaction medium (acetonitrile, no pronounced acidity) shields the epoxides from solvolysis. Thus even a sensitive epoxide such as butadiene diepoxide can

Table 2. Epoxidation of terminal or electron-deficient olefins with Mn-tmtacn-oxalate and H_2O_2.[a]

Entry	Alkene	Stoichiometry olefin : H_2O_2 : oxalate : Mn	Time (*h*)	Epoxide Yield (%)[b]	Product Selectivity (%)[b]
1		666 : 1000 : 3 : 1	0.3	> 99	epoxide (> 99)
2		666 : 1333 : 3 : 1	0.6	95	epoxide (> 99)
3		666 : 1333 : 3 : 1	1	72	*cis* epoxide (> 98)
4		666 : 1333 : 3 : 1	1	35	*trans* epoxide (> 98)
5		666 : 1333 : 3 : 1	1	83	epoxide (92), allylic products (8)
6		666 : 1000 : 3 : 1	0.3	> 99	epoxide (> 99)
7		666 : 2000 : 3 : 1	1	92	glycidol (95)
8		666 : 1333 : 3 : 1	1	88	epoxide (91)
9		666 : 1333 : 3 : 1	0.3	63	epoxy-ol (66)[c], 2-en-1-one (16), epoxy-one (18)
10		666 : 1333 : 3 : 1	2	66	epoxide (96)
11		666 : 1333 : 3 : 1	2	55	epoxide (94)
12		666 : 2000 : 3 : 1	1	80	*meso* diepoxide (40), (±)-diepoxide (60)
13		166 : 2000 : 3 : 1	1	89	diepoxide (91), mono (8)
14		166 : 2000 : 3 : 1	1	91	diepoxide (92), mono (8)

[a] Procedure: 1μmol of $MnSO_4.H_2O$ (in 0.1 ml H_2O) and 1.5 μmol of tmtacn (in 0.1 ml CH_3CN) are mixed in 0.6 ml CH_3CN, and the co-catalyst (1.5 μmol of oxalic acid and 1.5 μmol of Na oxalate in 0.1 ml H_2O) is added. After addition of the olefin (typically 0.67 mmol), aqueous H_2O_2 (35 %, diluted in CH_3CN; between 1 and 2 mmol) is injected over 300 s into the reaction mixture (278 K). [b] determined by GC(MS). Olefin Conversion (%) = 100 x Epoxide Yield (%) / Epoxide Selectivity (%). [c] syn : anti epoxide = 30 : 70.

be obtained in 80 % yield from the monoxide, without formation of by-products.

The weak discrimination between terminal and more substituted double bonds suggests that this system is also suitable for direct, double oxidation of (non)-conjugated dienes. This is proven by the double epoxidation of isoprene or 4-vinylcyclohexene (entries 13-14).

Summarising, the addition of a simple oxalate co-catalyst to Mn-tmtacn is a major improvement in terms of (stereo)selectivity and peroxide efficiency. With only a slight H_2O_2 excess, high yields are obtained for a series of olefins. Suitable substrates are slightly polar or even water-soluble, and may contain electron-withdrawing groups. Importantly, the system is halide-free, and non-noxious solvents (acetonitrile, methanol) or even pure water can be used as a reaction medium. The substitution of the triazacyclononane core with other pendant arms may open perspectives for further catalyst refinement.[9-11] The precise role of the oxalate co-catalyst is currently investigated in more detail.

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6. In the absence of a suitable olefin substrate (*e.g.* styrene), the addition of H_2O_2 to Mn-tmtacn in acetone leads to oxidation of acetone to acetic acid, probably via homolysis of the perhemiketal and subsequent β-scission of $(CH_3)_2C(OH)O^*$ (De Vos *et al.*, unpublished results).
7. A Cu-tmtacn dimer with a μ-oxalato ligand, $[Cu_2tmtacn_2(C_2O_4)](ClO_4)_2$ has been described: Chaudhuri, P.; Oder, K. *J. Chem. Soc. Dalton Trans.*, **1990**, 1597.
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