

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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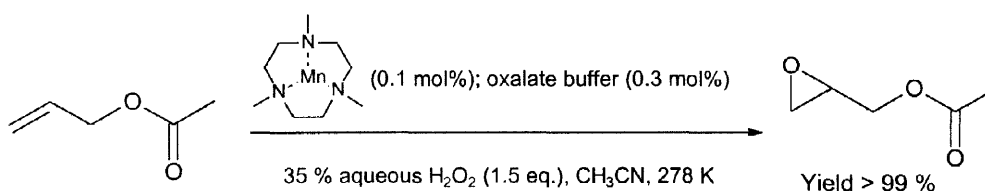
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Abstract: A catalytic amount of an oxalate/oxalic acid buffer strongly enhances the catalytic properties of Mn-tmtacn complexes for epoxidation reactions with H_2O_2 . Especially terminal olefins are easily epoxidized. Yields for *e.g.* allyl acetate 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.

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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 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (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

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.

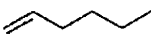

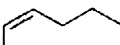
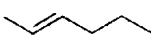

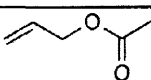
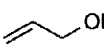
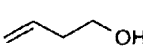
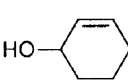

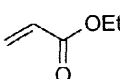
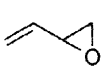


Table 1. 1,2-Epoxyhexane yields in the reaction of 0.666 mmol 1-hexene with 1 mmol H₂O₂, catalysed by Mn-tmtacn (1 μ mol) and a co-catalyst.

| Co-catalyst (μ mol) | Yield (%), (t, h) | Co-catalyst (μ mol) | Yield (%), (t, h) |
|---------------------------|-------------------|---|-------------------|
| - | 1.5 (10) | fumaric acid (3) | 57 (10) |
| 1,3-cyclopentanedione (3) | 25 (10) | H ₂ C ₂ O ₄ (3) | 94 (10) |
| 1,3-indandione (2) | 30 (10) | Na ₂ C ₂ O ₄ (3) | 70 (1) |
| acetic acid (3) | < 1 (10) | H ₂ C ₂ O ₄ (1.5), Na ₂ C ₂ O 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 H₂O₂. 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/H₂O₂ system even forms epoxides when the olefin contains a second, deactivating function (-CH₂OH, -CH₂OCOR, -COR, -CO₂R and oxirane). As an example, allyl acetate is fully and selectively converted into its epoxide with only 1.5 equivalent of H₂O₂ (Table 2, entry 6). For other olefins, slightly more H₂O₂ 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 H₂O₂.^a

| Entry | Alkene | Stoichiometry olefin : H ₂ O 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 | <i>cis</i> epoxide (> 98) |
| 4 |  | 666 : 1333 : 3 : 1 | 1 | 35 | <i>trans</i> 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 | <i>meso</i> 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: 1 μmol of MnSO₄·H₂O (in 0.1 ml H₂O) and 1.5 μmol of tmtacn (in 0.1 ml CH₃CN) are mixed in 0.6 ml CH₃CN, and the co-catalyst (1.5 μmol of oxalic acid and 1.5 μmol of Na oxalate in 0.1 ml H₂O) is added. After addition of the olefin (typically 0.67 mmol), aqueous H₂O₂ (35 %, diluted in CH₃CN; between 1 and 2 mmol) is injected over 300 s into the reaction mixture (278 K). ^b determined by GC(MS). Olefin Conversion (%) = 100 × 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 H₂O₂ 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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