Formation of Vicinal Diols by Re_2O_7-catalysed Hydroxylation of Alkenes with Hydrogen Peroxide

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Alkenes are hydroxylated to vicinal diols by H_2O_2 in 1,4-dioxane as solvent and using 1 mol% Re_2O_7 as catalyst, which can be easily separated from the products and recycled for several runs.

Oxidation of alkenes with H_2O_2 in the presence of transition metal oxides, such as WO_3, MoO_3 and OsO_4, yielding epoxides or vicinal diols is well known,[1] while rhenium compounds are considered to be poor catalysts.[2] Recently, Herrmann *et al.* demonstrated that CH_3ReO_3, prepared by reaction of Re_2O_7 with $Sn(CH_3)_4$, eqn. (1),[3] is an excellent

$$Re_2O_7 + Sn(CH_3)_4 \rightarrow CH_3ReO_3 + (CH_3)_3Sn\text{–}O\text{–}ReO_3 \quad (1)$$

catalyst for epoxidation and hydroxylation in the system H_2O_2–*tert*-butyl alcohol.[4,5] Also, in this context, Re_2O_7 itself is described to be ineffective.[5]

Nevertheless, we found that alkenes are converted to vicinal diols by Re_2O_7-catalysed hydroxylation with H_2O_2, if special solvents are applied, eqn. (2).

$$R^1\text{–CH=CH–}R^2 + H_2O_2 \xrightarrow[90\,°C,\ 1,4\text{-dioxane}]{[Re_2O_7]} R^1\text{–CH(OH)CH(OH)–}R^2 \quad (2)$$

The reaction is believed to proceed *via* epoxidation, followed by an acid-catalysed (pH value of the reaction mixture is *ca.* 1) opening of the oxirane-ring. This suggestion is supported by the fact that 1-epoxyoctene can be formed as a by-product in the oxidation of octene, which takes place with a yield of 40% of octane-1,2-diol under the same reaction conditions. Furthermore, *trans*-cyclohexane-1,2-diol was formed by the hydroxylation of cyclohexene.

The choice of solvent is the most critical reaction parameter. Of approximately thirty solvents (esters, alcohols, ethers, nitrogenous bases, aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, water) tested, only a very few, including trialkylphosphates (*e.g.* triethlyphosphate) and high-boiling ethers (*e.g.* 1,4-dioxane), are suitable for this reaction; otherwise the yields of diols are very poor, which is we believe the reason why the reaction has been neglected for so long.

α-Alkenes, internal alkenes and cyclic alkenes can be used as starting materials (see Table 1). Re_2O_7 does not cause decomposition of H_2O_2 therefore no greater an excess of H_2O_2 is necessary.

The reaction products are isolated by cooling the reaction mixture to 0 °C and separating the solid diols by filtration using a Büchner funnel. The filtrate, which contains the solvent, the catalyst and a little water, brought about by the

Table 1 Hydroxylation of alkenes by Re_2O_7/H_2O_2[a]

Alkene	Product[d]	Isolated yield (%)
Dodecene	Dodecane-1,2-diol	62
Hexadecene	Hexadecane-1,2-diol	80
Octadecene	Octadecane-1,2-diol	77
Oct-4-ene[b]	Octane-4,5-diol	60
Tetradec-7-ene[b]	Tetradecane-7,8-diol	71
Octadec-9-ene[b]	Octadecane-9,10-diol	80
Cyclohexene[c]	Cyclohexane-1,2-diol	74
Cyclododecene	Cyclododecane-1,2-diol[e]	68

[a] *Reaction conditions*: 0.036–0.06 mol H_2O_2 (aqueous solution, 60% by weight), 0.3–0.5 mmol Re_2O_7, 90 °C, 16 h, 20 ml 1,4-dioxane, 0.03–0.05 mol alkene; Re_2O_7 : alkene : H_2O_2 = 1 : 100 : 120. [b] Mixture of *cis*- and *trans*-isomers prepared by metathesis of α-alkenes.[6] [c] Reaction temperature 70 °C with respect to b.p.; the diol was identified as the *trans*-isomer. [d] Purity 93–96% (GC). [e] Purity 82% (GC), contains dodecane-1,12-dioic acid.

Table 2 Hydroxylation of octadec-9-ene by H_2O_2/Re_2O_7-catalyst recycling

Run	Yield of octadecane-9,10-diol (%)
1[a]	51
2[b]	78
3[b]	81
4[b]	71
5[b]	66
6[b]	91
Average	73

[a] 0.03 mol (7.6 g) octadec-9-ene, 0.036 mol (2.0 g) H_2O_2 (aqueous solution, 60% by weight), 0.3 mmol (0.14 g) Re_2O_7, 90 °C, 16 h, 20 ml 1,4-dioxane. [b] 0.03 mol (7.6 g) octadec-9-ene, 0.036 mol (2.0 g) H_2O_2 and 5 ml 1,4-dioxane for compensating losses of solvent occurring during the filtration.

use of an aqueous solution of H_2O_2, can be reused by simply adding new charges of alkene and H_2O_2. The results of the hydroxylation of octadec-9-ene with catalyst recycling are shown in Table 2.

The Re_2O_7-catalyst can be used six times without losing its activity. The slow decrease in yields of diol is considered to be caused by the growing proportion of water in the reaction mixture. In experiments, to be described elsewhere, water is shown to inhibit the reaction. After the sixth run a greater yield of octadecane-9,10-diol is achieved, based on a change in the work-up procedure (*i.e.* evaporating the solvent), which is only possible if further catalyst recovery is not intended.

In conclusion, we consider that rhenium compounds ought to be studied more carefully as oxidation catalysts for synthetic purposes than they have been so far.

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