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EPOXIDATION AND TRANS-HYDROXYLATION OF OLEFINS WITH o-SULPHOPERBENZOIC ACID.

J.M. Bachhawat and N.K. Mathur
Department of Chemistry, University of Jodhpur,
Jodhpur (Rajasthan) INDIA.

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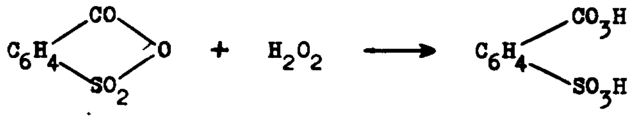
Reaction between o-sulphobenzoic anhydride (1.0 mole) and hydrogen peroxide (30%, 1.3 mole) in acetone solution at -4 to 0°C produces o-sulphoperbenzoic acid in 65-75% yield.



This new peracid is freely soluble in water and water-organic solvent mixtures. An attempt to isolate the free peracid by evaporation of the solvents under reduced pressure results in a considerable loss of active oxygen, but the aqueous-acetone solutions of the peracid can be used directly for epoxidation or trans-hydroxylation of double bonds. The aqueous acetone solution of the peracid is quite stable at room temperature and the loss of active oxygen amounts to 1-2% per week. o-Sulphoperbenzoic acid contains a weakly acidic peracid group and strongly acidic sulphonic acid group. Hence, during oxidation, an acid catalysed cleavage of the initially formed epoxide takes place resulting in the formation of a trans-diol.

Unlike certain other peracids, no esterification of the diol has been observed, whereas during the cleavage of the epoxide the esterification of a diol has been reported in case of perbenzoic, pertrifluoroacetic and performic acids(1).

If it is desired to isolate the epoxide, then the reaction can be carried out in presence of a solid buffer such as sodium carbonate *cf.* epoxidation with pertrifluoroacetic acid(2).

Oxidation of Olefins : 0.1 mole olefin is dissolved in a minimum amount of acetone and 0.11 mole of the aqueous acetone peracid solution is added. The mixture is set aside for 0.5 to 1.5 hrs. The progress of the reaction may be followed iodometrically. Most of the acetone is removed under reduced pressure, and the diol or epoxide is extracted with ether. The o-sulphobenzoic acid formed is insoluble in ether.

Table I

Epoxidation or trans-hydroxylation of olefins with o-sulphoperbenzoic acid in acetone at 25°C

Compound	Product	Yield (%)
Cyclohexene	Trans-1,2-cyclohexanediol	88[a]
α-Terpineol	α-Terpineol oxide	82[b]
Cholesterol	5,6-Cholesterol epoxide	89[a]
Oleic Acid	8,10-Dihydroxy stearic acid	86[a]
Cinnammic Acid	α-Phenylglyceric acid	78[b]
Maleic Acid	Tartaric acid	80[b]
Styrene	Styrene	80[b]
Allyl alcohol	Glycerol	79[b]

(a) based on isolation; (b) based on hydrogen peroxide used.

Other oxidations with o-sulphoperbenzoic acid : Baeyer - Villiger oxidation of cyclic ketones e.g. cyclopentanone and cyclohexanone takes place smoothly at 0°C with o-sulphoperbenzoic acid over 4-6 hrs. to give corresponding lactones (80%). Oxidation of heterocyclic tert-amines gives the corresponding N-oxides (75-80% yield at 60-65°C after 1 hr.).

References :

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