SYNLETT Spotlight 189

m-Chloroperoxybenzoic Acid (MCPBA)

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

MCPBA is a strong electrophilic oxidising agent. It is a white powder (mp 90 °C), easy to handle, flammable, hygroscopic, soluble in less-polar solvents like CH₂Cl₂, CHCl₃, 1,2-DCE, EtOAc, EtOH, *t*-BuOH, Et₂O and some nonpolar solvents like benzene, it is slightly soluble in hexane, CCl₄ and insoluble in H₂O. Pure MCPBA is shock-sensitive and can deflagrate, it is potentially explosive beyond 85% purity. It shows 1% degradation per year at room temperature. It is widely used in organic chemistry to carry out a variety of chemical transformations such

as oxidation of carbonyl compounds, iminoindolines, olefins, imines, alkanes, silyl enol ethers, N- and S-heterocycles, active methylene groups, fluoromethylated allylic bromides, cyclic acetals and N-substituted phthalimidines, etc.^{1a} Besides these it also oxidises selenides, furans and phosphates to selenoxides, pyranones and phosphates, respectively. It is superior to H₂O₂ and other oxidising agents because of its reactivity, stereoselectivity, purity and yield of products.^{1b}

Preparation

It can be prepared by the reaction of *m*-chlorobenzoyl chloride with H₂O₂ in presence of MgSO₄·7H₂O, aqueous NaOH and dioxane in a polythene beaker.²

Abstracts

(A) MCPBA is a versatile reagent for the oxidation of 4-methoxyphenyl-substituted fluorinated carbonyl compounds to the corresponding esters using 1,1,1,3,3,3-hexafluoro-2-propanol as cosolvent with CH₂Cl₂ and aqueous buffer (KH₂PO₄/NaOH) as an additive base under mild conditions.³

(B) MCPBA is used along with phenyliodine(III) bis(trifluoroacetate) (PIFA) for the synthesis of dienone lactones from phenyl ether derivatives.⁶ Here MCPBA acts as a co-oxidant which regenerates the hypervalent iodine(III) species after each cycle, thus making the reaction catalytic.⁴

(C) Oxidation of cycloalkanes is carried out with MCPBA in MeCN catalyzed by Fe(III) chloride to form alkylhydroperoxide which partially decomposes to the corresponding more stable alcohol and ketone.⁵

(D) Trimethylsilyl enol ethers are oxidized to α -hydroxy ketones by MCPBA. This reaction involves regioselective and stereoselective α -hydroxylation of ketones via a trimethylsilyl enol ether derivative.⁶

(E) MCPBA provides an efficient conversion of cyclic acetals to respective hydroxyalkyl esters. This oxidation using MCPBA gives the product in good to excellent yields under moderate reaction conditions.⁷

(F) Amides are obtained in high yields from imines which are prepared from aldehydes by using one equivalent MCPBA along with a catalytic amount of $\text{BF}_3\cdot\text{Et}_2\text{O}$. In this reaction the product is strongly influenced by the electron-releasing capacity of aromatic substituents.⁸

(G) It is used for the synthesis of 3-substituted pyrrolidin-4-ones from 4-aryl-1,2,5,6-tetrahydro pyridines by iterative synthetic operations using the combination of MCPBA and $\text{BF}_3\cdot\text{OEt}_2$.⁹

(H) Fluoromethylated allenes can be synthesized from 2-phenylthioallylic bromide by treatment with 1.5 equivalents MCPBA in CH_2Cl_2 at reflux temperature for 1–2 h.¹⁰

References

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