SYNLETT Spotlight 189

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

m-Chloroperoxybenzoic Acid (MCPBA)

Compiled by Rekha Tank

Rekha Tank was born in 1981. She received her B.Sc. (2002) and M.Sc. in Organic Chemistry (2004) from Rajasthan University, Jaipur, India. She passed the NET (National Eligibility Test) in Dec. 2004 and joined the Defence Research and Development Establishment, Gwalior in 2005 as a Junior Research Fellow where she currently pursues her Ph.D. under the tutelage of Dr. D. C. Gupta, Joint Director of DRDE. Her present research is focused on synthesis, characterization of polystyrene-based copolymers and their application as polymer-supported reagents in organic synthesis.

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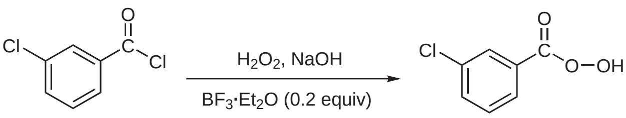
Introduction

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 CH_2Cl_2, $CHCl_3$, 1,2-DCE, EtOAc, EtOH, *t*-BuOH, Et_2O and some nonpolar solvents like benzene, it is slightly soluble in hexane, CCl_4 and insoluble in H_2O. 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 H_2O_2 and other oxidising agents because of its reactivity, stereoselectivity, purity and yield of products.[1b]

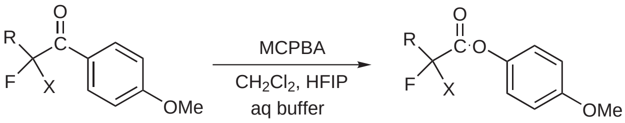
Preparation

It can be prepared by the reaction of *m*-chlorobenzoyl chloride with H_2O_2 in presence of $MgSO_4·7H_2O$, aqueous NaOH and dioxane in a polythene beaker.[2]

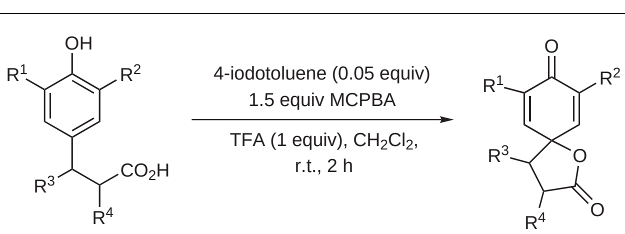


Abstracts

(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 CH_2Cl_2 and aqueous buffer (KH_2PO_4/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]



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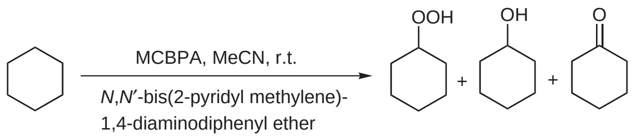
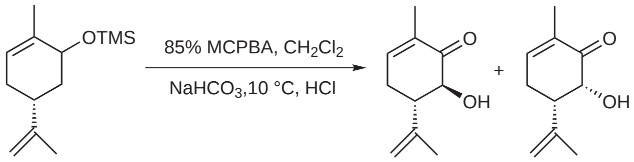
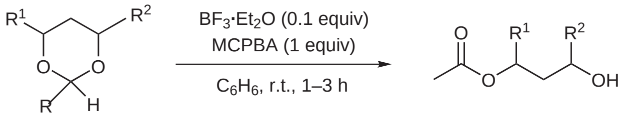
(C) Oxidation of cycloalkanes is carried out with MCPBA in MeCN catalyzed by Fe(III) chloride to form alkylhydroxyperoxide which partially decomposes to the corresponding more stable alcohol and ketone.[5]



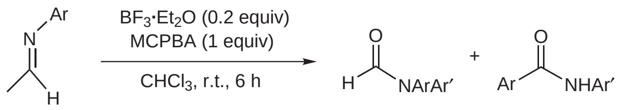
(D) Trimethylsilyl enol ethers are oxidized to α-hydroxy ketones by MCPBA. This reaction involves regioselective and stereoselective α-hydroxylation of ketones via a trimethylsilyl enol ether derivative.[6]



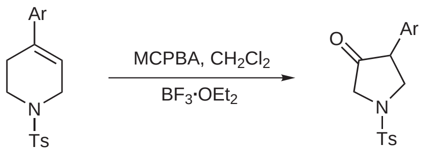
(E) MCPBA provides an efficient conversion of cyclic acetals to respective hydroxyalkyl esters. This oxidation using MCPBA gives the product in good to excellent yields under moderate reaction conditions.[7]



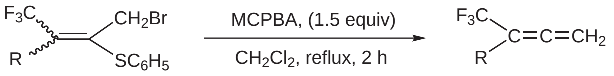
(F) Amides are obtained in high yields from imines which are prepared from aldehydes by using one equivalent MCPBA along with a catalytic amount of $BF_3·Et_2O$. In this reaction the product is strongly influenced by the electron-releasing capacity of aromatic substituents.[8]



(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 $BF_3·OEt_2$.[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]



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