

MCPBA (*m*-Chloroperoxybenzoic Acid)

PRODUCT No.
C6,270-0

revised 4 / 96

6 pages

PROPERTIES:

White powder

F.W. 172.57

m.p. 92-94° (dec.)

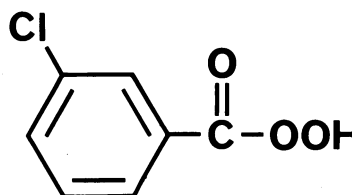
Contains up to 15% *m*-chlorobenzoic acid

Slight pungent odor

Bulk density 0.56g/cc.

pH of a saturated aqueous solution at 25°C: 4.5

pK_a (in water at 25°C): 7.57


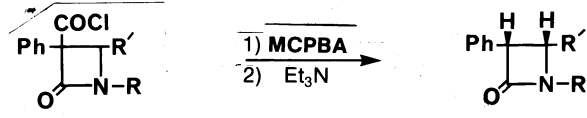
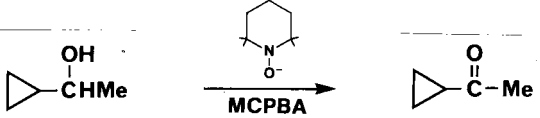
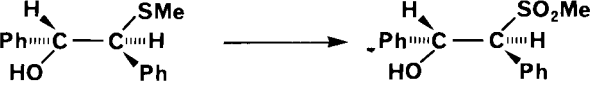
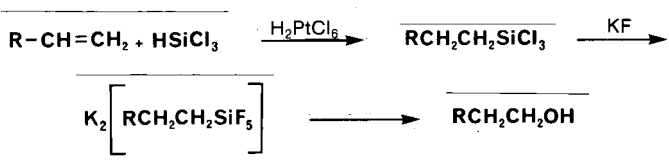



MCPBA (*m*-chloroperoxybenzoic acid), an oxidizing agent, is superior to hydrogen peroxide or other peracids in terms of reactivity, stereoselectivity, and in purity and yield of products. The scope of its reactivity is illustrated in the following table.

Reactant	Product	Example	Ref.
Olefins	Epoxides ^a	<p>Cholesterol $\xrightarrow{\text{MCPBA}}$ α-epoxide</p> <p>75% yield 95% yield</p>	1-7
Cyclopropenes	α,β -Unsaturated aldehydes and/or ketones		8,9
α,β -Unsaturated ketones and esters	Epoxides		10
Disubstituted acetylenes	Oxirenes ^b		11,12
Imines	Oxaziranes		13-16

Reactant	Product	Example	Ref.
Ketones (Baeyer-Villiger oxidation)	Esters		17-21
Acid Chlorides	Alcohols	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{Cl})\text{C}(=\text{O})\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3(\text{CH}_2)_3\text{CHOHCH}_2\text{CH}_3$	22
Acids	Alcohols		23
Primary alkyl amines	Nitro alkanes ^c		24
Primary aromatic amines	Aromatic nitroso compounds		25
Secondary amines	Nitroxide radicals	$\text{RNHR}' \longrightarrow \text{R}\ddot{\text{N}}(\text{R}')\text{O}$ <p>R, R' = aliphatic or aromatic</p>	26
Tertiary amines	N-oxides		27
Nucleic acid components	N-oxide ^d		28-31

Reactant	Product	Example	Ref.
<i>N</i> -substituted aziridines	Olefin ^e		17-21
2-Pyridine-acetates	Corresponding glycolates ^f		34
Sulfides	Sulfoxides or sulfones ^g		35-40
Carbodiimides	Diaziridinones		41
Ketals	Ortho esters		42
Trimethylsilyl vinyl and allyl systems	Trimethylsilyl epoxides (latent precursors to carbonyl groups)		43-46
Iminoethers	Esters and hydroxylamines		47
α -Hydroxy ketones	Aldehydes and acids		48
Mono-, di-, and trimethoxybenz aldehydes	Formate esters		49

Reactant	Product	Example	Ref.
α -Diazoketones	α -Diketones		50
β -Lactam acid chlorides	Aryl- β -lactam derivatives		51
Secondary alcohols	Ketones		52
Erythro thioether	Sulfone		53
Terminal olefines	Primary alcohols		54
Aromatics Hydrocarbons	Arene dioxides		55

- a In nonconjugated dienes the more substituted double bond is selectively epoxidized.
- b Oxirenes break down to ketones, carboxylic acids or esters depending on reaction conditions.
- c The yields of nitroalkanes decrease in the order: *tert*-alkyl > *sec*-alkyl > *n*-alkyl.
- d I.R. Subbaraman and co-workers²¹ reported that cytosine, adenine and their derivatives are oxidized to N-oxides while uracil, thymine, guanosine and their derivatives give ring-cleavage products. However, M.R. Harden *et al.*²² indicated that N(1)-oxides were obtained from adenine, cytosine and uracil derivatives while guanine derivatives yielded the N(3)-oxides.

- e N-substituted zairidines are presumably oxidized to the corresponding N-oxides. This reaction is successfully used in the stereospecific deamination of N-alkylzairidines to olefins.
- f the 3- and 4-pyridyl isomers gave the corresponding N-oxides in high yields.
- g Yields of sulfones or sulfoxides are excellent even in the presence of amino,²⁷ olefinic or acetylenic²⁸ moiety.

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SOLUBILITY, g / 100ml

Benzene	8.0	Diethyl ether	89.4
Hexane	1.4	Ethyl alcohol	113.0
Methylene chloride	11.2	tert-Butyl alcohol	69.0
Chloroform	9.8	Ethyl acetate	51.0
Carbon tetrachloride	2.1	Water	0.154
1,2-Dichloroethane	10.6		

HANDLING

m-Chloroperoxybenzoic acid irritates the mucous membranes and respiratory tract, eyes and skin. Skin contact with MCPBA results in burns and blisters similar to those cause by hydrogen peroxide. The material should be used only in a chemical fume hood. Safety goggles, rubber gloves, and a dust mask should be worn.

EMERGENCY PROCEDURES

FIRE

Extinguish with "alcohol" foam, dry powder, or carbon dioxide. Water may be ineffective. Fire conditions may cause explosions. Wear a self-contained breathing apparatus.

SPILL

Wear safety goggles and rubber gloves. Treat with excess sodium bisulfite solution. Test with acidic starch-iodide paper to ensure complete decomposition of the peracid. Wash down the drain.

SKIN CONTACT

Wash immediately with soap and water or sodium bicarbonate solution. Remove contaminated clothing.

EYE CONTACT

Flush immediately with large amounts of water and call a physician.

INGESTION

Take large quantities of milk or water immediately. Wash out mouth. Call a physician.

WASTE DISPOSAL

Treat with excess sodium bisulfite solution. Test with acidic starch-iodide paper to ensure complete decomposition. Dispose of properly. Observe all state, local and federal laws.

STORAGE AND STABILITY

Solid MCPBA shows less than 1% decomposition when stored at room temperature for 1 year. It has been determined that 95-100% material can be detonated by shock or sparks. 85% MCPBA is not shock-sensitive, but may be decomposed violently with heat. It should be stored in a refrigerator in tightly closed containers. MCPBA is a flammable solid and contact with heat or oxidizable material should be avoided.

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