Tetrahedron Letters,Vol.30,No.11,pp 1427-1428,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

EPOXIDATION REACTION WITH m-CHLOROPEROXYBENZOIC ACID IN WATER

Francesco Fringuelli[a*], Raimondo Germani[b], Ferdinando Pizzo[a] and Gianfranco Savelli[b]

[a] Dipartimento di Chimica - Università di Perugia - Via Elce di Sotto, 06100 Perugia, Italy

[b] Dipartimento di Chimica, Ingegneria Chimica e Materiali - Università di L'Aquila - Via Assergi, 67100 L'Aquila, Italy

Summary: Epoxidation reaction of liquid alkenes with m-chloroperoxybenzoic acid in water at room temperature gives oxiranes in high yield.

In the realm of peroxy-acids, the m-chloroperoxybenzoic (MCPBA) is the most largely used to oxidize alkenes to epoxides[1] with reactions carried out in organic solvents[2] in biphasic[3] and emulsion systems[4]. To our knowledge no report details of using MCPBA in water solely. We wish to report our first results of epoxidation of a variety of alkenes by MCPBA in water.

The oxidation reaction is performed in an aqueous solution of $NaHCO_3$ (pH=8,3) where both reactants are insoluble. The reaction is fast[5], the epoxide is generally the sole reaction product isolated in high yield (Table). Opening reaction products sometimes contamine the epoxide in the absence of $NaHCO_3$. An exception is the reaction of 1-octene which, on the contrary, affords the epoxide in high yield in sole deionized water. The buffered aqueous medium seems especially suitable for acid-sensitive olefins and epoxides (entries 10 and 14).

The site selectivity (entries 6 and 13) and the face selectivity (entries 4, 6, 9, 13) in the heterogeneous aqueous system imitate those found in omogeneous media[6].

The solid-liquid reaction of MCPBA with high reactive liquid alkenes in the absence of water is strongly exothermic and difficult to control. When control of the temperature is possible (by using little amounts of reactants) the reaction time is considerably reduced and the epoxide is easily isolated in high yield (footnote d of table).

The epoxidation method[7] is illustrated in the following procedure for the synthesis of 1-methyl-1,2-epoxycyclohexane.

Pure[8] and powdered MCPBA ($2.2.10^{-2}$ mole) is added in ca. 10 min. to a stirred heterogeneous aqueous mixture of $NaHCO_3$ (0.3 N, 120 ml) and 1-methyl-1-cyclohexene ($2.0.10^{-2}$ mole) cooled at 0°C. The suspension is vigorously stirred at room temperature for 0.5 hrs and then extracted twice with ethyl ether. The organic phase is washed with a cooled solution of

10% NaOH, then with saturated brine and dried (Na_2SO_4). The solvent is removed at atmospheric pressure and the crude 1-methyl-1,2-epoxycyclohexane purified by distillation; b.p.137-138°C/760 mmHg, yield 95%.

Further work is in progress.

Table. Epoxidation Reactions Using m-Chloroperoxybenzoic Acid in Water at Room Temperature (ca. 20°C)

Entry	Substrate	Time(hr)	Yield(%)[a]	Entry	Substrate	Time(hr)	Yield(%)[a]
1.	Cyclopentene	0.5	90	8.	Cyclooctene	0.5	95
2.	Cyclohexene	0.5	95	9.	(+) 3-Carene	0.5	90
3.	1-Methyl-1--cyclohexene	0.5	95	10.	Styrene	1	95
				11.	1-Octene	8	95[d]
4.	3-Methyl-1--cyclohexene	1	88[b]	12.	2-Cyclohexen--1-one	7	60[e]
5.	Methylen-cyclohexane	0.5	90	13.	(-) Carvone	1	95[f]
6.	(+) Limonene	1	66[c]	14.	6-Methylhept--5-en-2-one	0.5	70[g]
7.	Cycloheptene	0.5	90				

[a] Yield of purified compound[8]. [b] Mixture (ca.1:1) of cis and trans-1,2-epoxy-3-methylcyclohexane. [c] Mixture (ca.1:1) of cis- and trans-1,2-epoxy-p-menth-8-ene; composition of reaction mixture: 1,2-epoxides (72%), 1,2,8,9-diepoxides (15%), (+)limonene (13%). [d] Reaction carried out in absence of $NaHCO_3$; the solid-liquid reaction (see text) is complete (95% yield) after 4 hrs at 0°C. [e] The remaining 40% is unreacted material. [f] Mixture (ca.1:1) of eritro- and treo-8,9-epoxy-p--menth-2-en-1-one. [g] Reaction temperature 0°C.

ACKNOWLEDGMENT: The Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione are gratefully acknowledged.

REFERENCES AND NOTES:

1. A.S.Rao, S.K.Paknikar and J.G.Kirtane, Tetrahedron 39, 2323 (1983).

2. [a] F.Camps, J.Coll, A.Messeguer and F.Pujol, J.Org.Chem., 47, 5402 (1982) [b] H.J.Schneider, N.Becker and K.Philippi, Chem.Ber., 114, 1562 (1981).

3. [b] M.Imuta and H.Ziffer, J.Org.Chem., 44, 1351 (1979).

4. M.Nakamura, N.Tsutsui, T.Takeda and T.Tokoroyama, Tetrahedron Lett., 25, 3231 (1984).

5. The epoxidation reactions of cyclohexene with MCPBA in homogeneous solutions of n-hexane and dichloromethane give quantitatively the epoxycyclohexane after 8 hrs and 0.5 hr respectively. In biphasic solvent system[3] the g.l.c. yield is 71% after 4 hrs.

6. G.Berti, Topics in Stereochemistry, 7, 93 (1973).

7. All the tested alkenes are liquid. The procedure for solid alkenes is under investigation. The structures of epoxides have been verified by comparison with authentic samples and/or by NMR and mass spectroscopy.

8. N.N.Schwartz and J.H.Blumbergs, J.Org.Chem., 29, 1976 (1964); identical results have been obtained by using commercial (85% purity) MCPBA.

(Received in UK 6 December 1988)