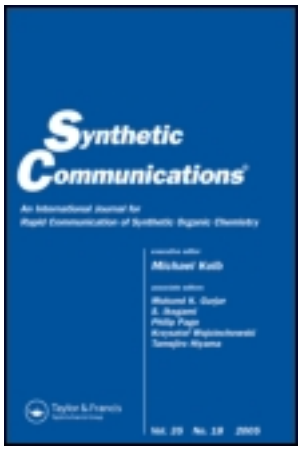

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EPOXIDATION OF OLEFINS AT LOW TEMPERATURE USING m-CHLOROPERBENZOIC ACID*

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EPOXIDATION OF OLEFINS AT LOW TEMPERATURE USING *m*-CHLOROPERBENZOIC ACID*

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ABSTRACT

Epoxidation of olefins using *m*-chloroperbenzoic acid in dichloromethane without catalyst at low temperature is described.

Key Words: Olefins; m-Chloroperbenzoic acid; Epoxides

Epoxides[1a] are important building blocks for the preparation of optically active diols[1b] and amino alcohols,[1c,d] aziridines,[1e] thieranes[1f] etc. The increasing attention has been paid to prepare volatile epoxides like 1,2- and *cis* & *trans* 2,3-butylene oxides apart from other epoxides, because of their commercial uses.[1g,h] The reports on epoxidation of alkenes using peracids with copper/vanadium/iron salts as catalyst at low temperature

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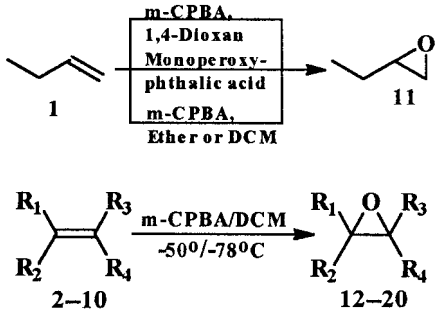


Scheme 1.

are known in literature.[1i,j] In this paper we report the epoxidation of variety of substrates at low temperature without using any catalyst.

Initially, we have done preliminary experiments on unsubstituted butylenes to convert to the corresponding volatile butyleneoxides. When epoxidation has been attempted using *m*-CPBA in 1,4-dioxane according to the reported procedure,[1k] the yield of product is not good. Monoperoxyphthalic acid in ether gave a poor yield of compound **2**. Although the same reaction was performed with *m*-CPBA in ether at −4–0°C, the yield was not improved. Then it was conducted in dichloromethane (DCM) at various temperatures i.e., 0–5°C, −4–0°C and −11–0°C and the optimum yields were obtained at −50–(−10)°C for 6 h (Scheme 1).

To generalize the above results, the similar study was conducted on functionalised acyclic, and cyclic olefins and the results are complied in Table 1. Analytical data of all compounds are matching with the literature report.[1k,2a–i]

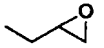
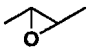
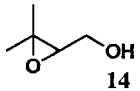
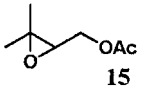
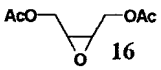
By considering the advantage of this reaction condition at low temperature, we prepared the volatile butyleneoxides from the butylenes, which are commercially important for drug intermediates. Also we have successfully utilized this condition for the conversion of other olefins with alcohol, and acetate groups to their corresponding epoxides.

EXPERIMENTAL

General Procedure for Epoxidation

Butylene (300 g, 5.357 mol) was collected in a precooled (−50°C) round bottom flask (10 L) fitted with overhead mechanical stirrer, a cold

Table 1.

S. No	Substrate	Product	Temp. (°C)	Time (h)	Ratio[a] Substrate : Product	Yield[b] (%)
1	1-Butene, **1**	 **11**	−50–(−10)	8	–[c]	71[2a]
2	*cis* 2-Butene, **2**	 **12**	−50–(−10)	6	–[c]	63[2b]
3	*trans* 2-Butene, **3**	 **13**	−50–(−10)	6	–[c]	60[2c]
4	Prenyl alcohol, **4**	 **14**	−78	6	0 : 1	65[2d]
5	Prenyl acetate, **5**	 **15**	−78	5	1 : 9	78[3]
6	1,4-Diacetoxy-2-butene, **6**	 **16**	−78	5	0 : 1	50[2e]

(*continued*)

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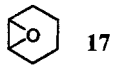
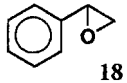
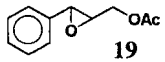
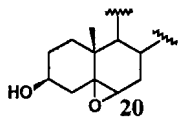
Table 1. Continued

S. No	Substrate	Product	Temp. (°C)	Time (h)	Ratio[a] Substrate : Product	Yield[b] (%)
7	Cyclo hexene, **7**	 **17**	−78	6	1 : 6	33[2f]
8	Styrene, **8**	 **18**	−78	6	1.0 : 1.5	60[2g]
9	Cinnamyl acetate, **9**	 **19**	−78	8	4.6 : 1.0	15[2h]
10	Cholesterol, **10**	 **20**	−78	7	1 : 6	53[2i]

[a]Based on ^{1}H NMR; [b]Isolated yields; [c]Gaseous starting material at room temperature.

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finger maintained at $-78^{\circ}C$ and diluted with cold DCM (0.5 L). *m*-CPBA (1347 g, 5.464 mol, 70%) in DCM (5.5 L) was added dropwise with stirring over a period of an hour. Stirring was continued at the same temperature for about 4 h and it was allowed to rise to $-10^{\circ}C$ during a period of 2 h. The insoluble material was filtered off and washed with cold DCM (3×0.3 L). The washings were combined and it was subsequently washed with 10% Na_2SO_3 solution (2×1 L), 5% NaOH solution (2×1 L), satd. NaCl solution (3×1 L) and dried over anhydrous Na_2SO_4. Removal of DCM and distillation of compounds **11**, **12** and **13** were carried out by using reflux divider with timer. All other compounds (**14**–**20**) were purified by silica gel column chromatography.

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Chem. Soc. **1959**, *81*, 3350–3356; (g) Fringvelli, F.; Pizzo, F. Org. Prep. Proced. Int. **1989**, *21*, 757–761; (h) Bohlmann, F.; Zdero, C. Chem. Ber. **1968**, *101*, 3243–3254; (i) Tohma, M.; Tomita, T.; Kimura, M. Tetrahedron Lett. **1973**, 4359–4362.

3. Compound **15**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 (s, 3H, CH_3); 1.31 (s, 3H, CH_3); 2.05 (s, 3H, $COCH_3$); 2.85 (dd, $J = 7.9$ & 4.7 Hz, 1H, O-CH); 3.95 (dd, $J = 12.6$ & 7.1 Hz, 1H, OOC-CH_2); 4.22 (dd, $J = 12.6$ & 4.7 Hz, 1H, OOC-CH_2).

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