



## NOTE

Novel Epoxidation Reaction of Perfluoroalkenes with Triethylamine *N*-oxide

XINGWEI CAI, MIN SHA and REN MING PAN\*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, P.R. China

\*Corresponding author: E-mail: xin883@163.com

(Received: 6 August 2011;

Accepted: 26 December 2011)

AJC-10903

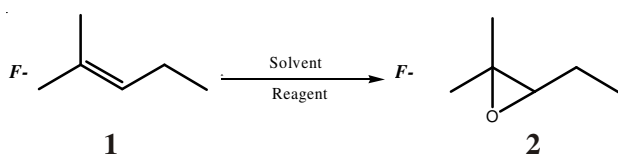
Triethylamine *N*-oxide was found to be nice reagent for the epoxidation of *tri*- and *tetra*-substituted perfluoroalkenes in good to excellent yields. By coupling this reaction with the *N*-oxidation of triethylamine by hydrogen peroxide, a novel catalytic epoxidation method was developed.

**Key Words:** Perfluoroalkenes, Triethylamine *N*-oxide, Catalytic.

Epoxides play an important role in fluorocarbon chemistry<sup>1</sup>. The methods for preparing the oxides of perfluoroolefins are extremely scanty<sup>2</sup>. In the present investigation, it has been established that when aqueous solutions of alkali or alkaline-earth hypohalites in alkaline solutions are used in the presence of aprotic solvents one succeeds in achieving the epoxidation of both the terminal and the internal fluoroolefins<sup>3-5</sup>. It is found that triethylamine *N*-oxide epoxidize *tri*- and *tetra*-substituted perfluoroalkenes in good to excellent yields.

**Preparation of Et<sub>3</sub>NO<sup>6</sup>:** To a mixture of Et<sub>3</sub>N (2 mmol), Na<sub>2</sub>WO<sub>4</sub> (200 mg), water (10 mL) and H<sub>2</sub>O<sub>2</sub> (30 % w/w, 6 mmol), dodecylbenzenesulfonic acid sodium (6 mg) was added. The mixture was stirred for 3.5 h at room temperature, standing, isolated, get 1.5 mmol Et<sub>3</sub>NO, yield 75 %.

**Preparation of epoxide 2:** To a mixture of Et<sub>3</sub>NO (1 mmol) and acetonitrile (2 mL), perfluoroalkene **1** (1 mmol) was added. The mixture was stirred for 20 min at room temperature, distillation gave 0.97 mmol of epoxide (**2**), yield 97 % (Scheme-I).



Scheme-I F-denotes all unmarked bonds are to fluorines

The epoxidation of perfluoroalkene (**1**) was tested using a variety of reagents and conditions summarized in Table-1.

TABLE-1  
EPOXIDATION OF PERFLUOROALKENE **1** WITH  
VARIOUS REAGENTS AND CONDITIONS

Run	Reagent	Quantity used	Solvent	Temp.	Time	Yield <sup>a</sup> (%)
1	30 % H <sub>2</sub> O <sub>2</sub>	Large excess	H <sub>2</sub> O	rt	1 day	N.R. <sup>b</sup>
2	MCPBA	1.0 equiv.	CH <sub>3</sub> CN	rt	1 day	N.R.
3	CH <sub>3</sub> CO <sub>2</sub> H	Large excess	H <sub>2</sub> O	rt	1 day	N.R.
4		Large excess	CH <sub>3</sub> CN	rt	1 day	N.R.
5	Et <sub>3</sub> NO	1.0 equiv.	CH <sub>3</sub> CN	rt	20 min	97
6		1.0 equiv.	DMF	rt	-	-
7		1.0 equiv.	DMF	-20 °C	40 min	95
8		1.0 equiv.	H <sub>2</sub> O	70 °C	2 day	85
9	NaClO	2.0 equiv.	CH <sub>3</sub> CN	rt	3 h	95
10	Ca(ClO) <sub>2</sub>	2.0 equiv.	CH <sub>3</sub> CN	rt	10 h	47

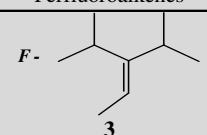
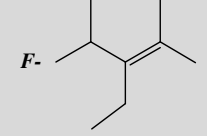
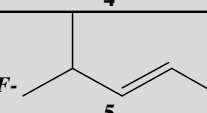
a. GC yield based on **1** used; b N.R.= no reaction; rt = Room temperature; MCPBA = *m*-Chloroperbenzoic acid

As expected, electrophilic reagents such as hydrogen peroxide, ethaneperoxoic acid, *meta*-chloroperbenzoic acid (MCPBA) and 2-carboperoxybenzoic acid, which are commonly used for epoxidation in hydrocarbon chemistry, gave no reaction with the electrophilic perfluoroalkene **1** (runs 1-4). However, the nucleophilic Et<sub>3</sub>NO was able to epoxidize (**1**) to give a corresponding epoxide (**2**) in excellent yields. For example, a 97 % yield was achieved in CH<sub>3</sub>CN under mild conditions (just 20 min stirring at room temperature, run 5) and only 85 % yield was obtained in water under more forcing conditions (2 days stirring at 70 °C, run 8). The reaction with Et<sub>3</sub>NO in DMF was interesting, for at room temperature no

product **2** was detected (run 6) while 95 % yield was obtained after 40 min stirring at  $-20\text{ }^{\circ}\text{C}$  (run 7). Reaction results using NaClO and  $\text{Ca}(\text{ClO})_2$  as oxidizing agents were also listed in Table-1 (runs 9 and 10).

$\text{Et}_3\text{NO}$  was studied further with other perfluoroalkenes, results were summarized in Table-2. Perfluoroalkenes **3** and **4** both reacted with  $\text{Et}_3\text{NO}$  in  $\text{CH}_3\text{CN}$  to give their corresponding epoxides in good yields under mild conditions (stirring at room temperature), but compound **4** reacted at a slower rate than **3** (runs 1 and 2). This probably dues to a fluorine atom directly connected to the double bond carbon atom of perfluoroalkene **3**, thus making the double bond more actively. Disubstituted perfluoroalkene **5** hardly reacted with  $\text{Et}_3\text{NO}$  under the same conditions of **1** although they are isomers (run 3). Thus, we have found that  $\text{Et}_3\text{NO}$  is a good epoxidation reagent for tri- and tetra-substituted perfluoroalkenes. Disubstituted perfluoroalkenes apparently are not sufficiently electrophilic for attack by  $\text{Et}_3\text{NO}$ .

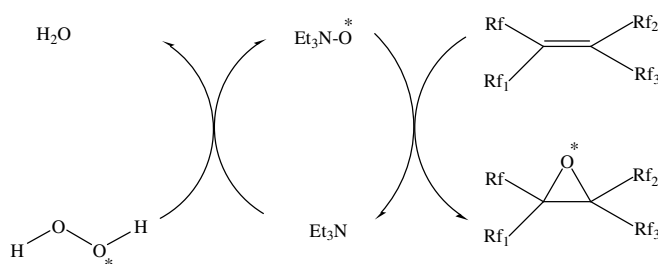
TABLE-2  
EPOXIDATION OF VARIOUS PERFLUOROALKENES  
WITH 1.1 EQUIV. OF TRIETHYLAMINE N-OXIDE

Run	Perfluoroalkenes	Solvent	Temp.	Time	Yield
1		$\text{CH}_3\text{CN}$	rt	40 min	96 %
2		$\text{CH}_3\text{CN}$	rt	2 h	94 %
3		$\text{CH}_3\text{CN}$	rt	5 h	N.R.

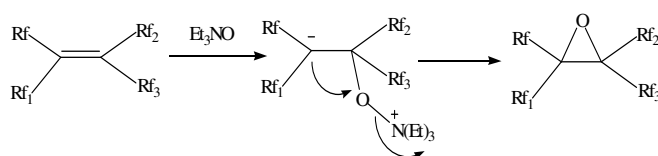
Since  $\text{Et}_3\text{NO}$  can be synthesized by triethylamine and hydrogen peroxide<sup>6,7</sup>, but epoxidation by sole  $\text{H}_2\text{O}_2$  cannot be done (Table-1, run 1). So electrophilic epoxidation  $\text{H}_2\text{O}_2$  can be used for the reaction by using triethylamine as a catalyst,

with  $\text{Et}_3\text{NO}$  formed as an intermediate nucleophilic oxygen carrier.

The reaction mechanism for this nucleophilic epoxidation is well established as shown in **Scheme-II** and **III**.



**Scheme-II** A catalytic cycle for the epoxidation of perfluoroalkene



**Scheme-III** Reaction mechanism of epoxidation of perfluoroalkenes with triethylamine N-oxide

## Conclusion

In present studies, it is found that triethylamine N-oxide ( $\text{Et}_3\text{NO}$ ) is a good epoxidation reagent for tri- and tetra-substituted perfluoroalkenes. Other tertiary amine N-oxides are under studying.

## REFERENCES

1. P. Tarrant, C.G. Allison, K.P. Barthold and E.C. Stump, *Fluorine Chem. Rev.*, **5**, 77 (1971).
2. P.L. Coe, A. Sellars and J.C. Tatlow, *J. Fluorine Chem.*, **23**, 102 (1983).
3. A. Ya Zapevalov and E.P. Lulie, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11**, 2509 (1979).
4. A. Ya Zapevalov, T.I. Filyakova and I.P. Kolenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2812 (1979).
5. A. Ya Zapevalov, T.I. Filyakova, I.P. Kolenko and M.I. Kodess, *Zh. Org. Khim.*, **22**, 93 (1986).
6. B.M. Choudary, B. Bharathi, Ch. Venkat Reddy, M. Lakshmi Kantam and K.V. Raghavan, *Chem. Commun.*, 1737, (2001).
7. K. Bergstad and J.-E. Backvall, *J. Org. Chem.*, **63**, 6652 (1998).