Novel epoxidation of perfluoroalkenes with *N,N*-diethylhydroxylamine

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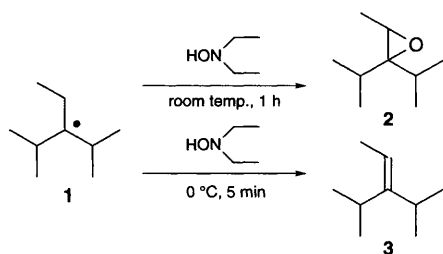[b] *Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA 18195-1501, USA*

N,N-Diethylhydroxylamine epoxidizes various kinds of perfluoroalkenes in good to excellent yields.

Epoxidation is a fundamental reaction both in hydrocarbon[1] and perfluorocarbon[2] chemistry. A wide range of reagents are available for the hydrocarbon epoxidation but few for the perfluorocarbon epoxidation. For example, epoxidation of perfluoroalkenes has been effected by aqueous sodium hypochlorite, ozone, oxygen or hydrogen peroxide. The reactivity of such inorganic reagents are not tunable unlike organic reagents. Here we describe the use of *N,N*-diethylhydroxylamine (DEHA) as a new epoxidation reagent for perfluoroalkenes.

During unrelated studies on the chemistry of the persistent perfluoroalkyl radical[3] **1**, we discovered a large excess of DEHA reacted with the radical to give the epoxide **2** (Scheme 1). When the reaction was conducted at 0 °C for 5 min. the perfluoroalkene **3** was obtained as a major product together with a small amount of epoxide **2**. This result suggested that the radical was converted first to **3** and then to the epoxide **2** by further reaction with excess DEHA. This was supported by the reaction of **3** directly with DEHA to give epoxide **2**. This unexpected ability of DEHA to epoxidize perfluoroalkenes prompted us to investigate this reaction further.

At first, the stoichiometry of the reaction was examined (Table 1), and it was confirmed that a large excess of DEHA is necessary for a good yield of the epoxide **2** (runs 1 and 2). Otherwise the yield of adduct **4** increased at the expense of the epoxide. Use of a commercially available aqueous DEHA

solution (85%) made the reaction sluggish and resulted in a lower yield of the epoxide while keeping the adduct yield unchanged (run 3).

The reactions of some other industrially important perfluoroalkenes with DEHA are summarized in Table 2. Perfluoroalkene **5**, the geometrical isomer of **3**, reacted with DEHA at a slower rate at room temperature giving the same epoxide product in high yield (run 4). It is known that the equilibrium between **3** and **5** is catalysed by the fluoride ion. A trace of fluoride ions is produced by an initial nucleophilic attack on **5** (Scheme 2). This type of nucleophile-initiated equilibration of **3** and **5** has previously been reported.[4] Since **5** is much less reactive than **3**, due to steric hindrance, only the isomer **3** is epoxidized. As **3** is consumed, the **3/5** equilibrium is shifted to **3** until all the starting perfluoroalkene is epoxidized. As a result **3** and **5** give the same product.

Highly branched trisubstituted perfluoroalkenes such as a *cis/trans* mixture of perfluoro-3-ethyl-4-methylpent-2-ene **6** and tetrafluoroethylene pentamer **8** gave corresponding epoxides **7** and **9** in good to excellent yields (runs 5 and 6), but less hindered

Scheme 1 Compounds 1-3 are perfluoro

Table 1 Epoxidation of **3** with *N,N*-diethylhydroxylamine

Run	Equiv. HONEt$_2$	Solvent	t	Yield (%)[a]	
				2	4
1	1.4	Neat	22 h	55	24
2	2.8	Neat	3 h	85	7
3	1.4	H$_2$O	2 h	35	27

[a] Isolated yields.

Table 2 Epoxidation of various perfluoroalkenes with *N,N*-diethylhydroxylamine

$$\text{Perfluoroalkenes} \xrightarrow[\text{RT}]{\text{HONEt}_2} \text{perfluoroepoxides}$$

Run[a]	Perfluoroalkene	t	Product	Yield (%)[b]
4	**5**	5 h	**2**	90
5	**6**	4 h	**7**	80
6	**8**	5 h	**9**	67
7	**10**	5 min	**11**	98
8	**12**	—	No reaction	—

[a] An excess of DEHA (1.3–1.9 equiv.) was used for runs 4–6 and 1.1 equiv. of DEHA was used for runs 7 and 8. [b] GC yield estimated by peak area ratios.

trisubstituted perfluoroalkene **10** gave only adduct **11** in almost quantitative yield (run 7). Disubstituted perfluoroalkene **12** did not react at all under the same reaction conditions (run 8); however, it is known that this perfluoroalkene is much less susceptible to nucleophilic attack than the trisubstituted per-fluoroalkene.[5]
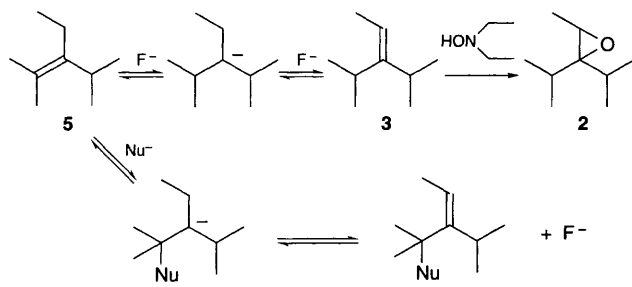
Scheme 2 All compounds are perfluoro
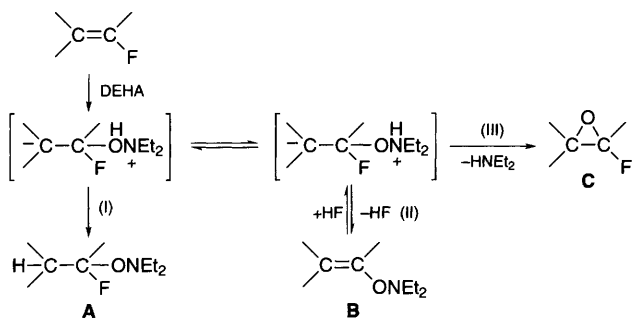
Scheme 3
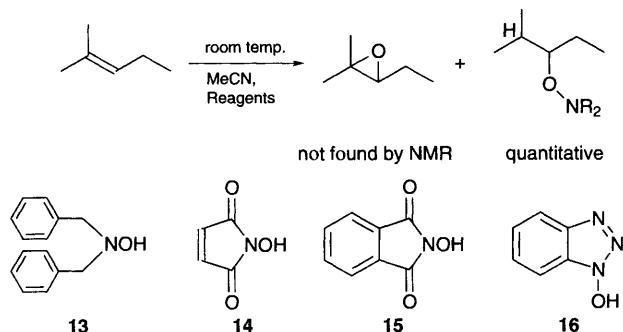
Scheme 4

There have been many reports dealing with the reaction of perfluoroalkenes with various kinds of nucleophiles *via* an addition–elimination mechanism.[6] In our proposed mechanism, Scheme 3, path (I) leads to addition product **A** and paths (II) and (III) lead to substitution products **B** and **C**. The probability of conversion from **A** to **C** is very low because the isolated addition product **4** did not give epoxide **2** by treating it under the same reaction conditions. Substitution product **B**, which is in equilibrium with the intermediates, is not observed in the product mixture. The data in Table 2 suggest that the competition between paths (I) and (III) in Scheme 3 is governed by steric hindrance. The more crowded alkenes in runs 4 and 5 in Table 2 give high yields of the epoxides **2** and **7**, whereas the less crowded tetrafluoroethylene pentamer in run 6 gives a lower yield of the epoxide **9**. The relatively unhindered **10** in run 7 yields only the addition product **11**.

In an attempt to form an epoxide from the hexafluoropropene dimer **10**, a series of hydroxylamine derivatives **13–16** in acetonitrile were used in place of DEHA. Despite the fact that **13–16** have an amine moiety which should lead to a better leaving group than DEHA and are bulkier than DEHA, epoxide formation was not observed (Scheme 4). There are two reasons why the epoxide was not formed. The unhindered hexa-fluoropropene dimer structure can accommodate even the relatively bulky diphenyl derivative **13** and the lower basicity of the nitrogen in compounds **13–16** *vs*. DEHA may have raised the energy barrier to the 1,2-proton shift necessary in the formation of the epoxide.

Thus, it appears that the epoxidation of perfluorinated alkenes with hydroxylamine derivatives is limited to rather bulky ones due to the competitive formation of the nucleophilic addition product in the less hindered alkene. Further investigations are necessary for an in-depth understanding of the reaction mechanism.

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