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Poly(per)fluoroalkanesulfonyl fluoride promoted olefin epoxidation with 30% aqueous hydrogen peroxide

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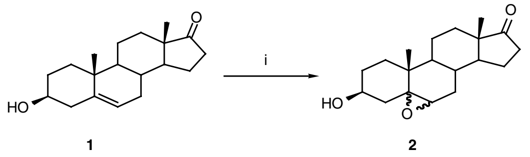
Abstract—Epoxidation of various electron rich olefins with a novel oxidation system of poly(per)fluoroalkanesulfonyl fluoride/hydrogen peroxide/base is reported.

Due to the importance of epoxides in organic synthesis, a variety of reagents for epoxidation of olefins have been developed to date. Among them, peracids are most widely used. Organo persulfonic acids, studied until recently and which served as alternative oxidants, cannot be isolated in pure form because of their instability. Their in situ generation from the reaction of arylsulfonyl imidazolides with hydrogen peroxide (H_2O_2) in the presence of a base (NaOH or K_2CO_3) and chemical behaviour towards epoxidation of olefins were reported by Schulz.[1] The treatment of sulfonyl chlorides with H_2O_2 did not result in the formation of persulfonic acids. Whereas the reaction of sulfonyl chlorides with KO_2 was proven to produce sulfonyl peroxy radicals instead of the anions of persulfonic acids.[2] In addition, trifluoromethanesulfonic acid was presumed to form when concentrated H_2O_2 (90–98%) and excess CF_3SO_3H were mixed.[3] However this method suffers from the use of strong acidic media and the extremely dangerous concentrated H_2O_2, which limited its extensive application as strong oxidant.

As a part of our program of the reactions of polyfluoroalkanesulfonyl fluorides[4] and their application of R_fSO_2F in synthetic organic chemistry,[5] we for the first time found the system consisting of R_fSO_2F and H_2O_2/NaOH can efficiently epoxidize a wide range of electron rich olefins co-existed in solution. In this communication, we would like to report the results of our study.

In an initial experiment, a steroidal homoallylic alcohol **1** was treated with the system $HCF_2CF_2OCF_2CF_2SO_2F$/H_2O_2/NaOH (30% H_2O_2 aqueous solution and 4 N NaOH aqueous solution were used in our experiments) in MeOH at room temperature. After 10 min, epoxide **2** was obtained in 95% yield (α-epoxide:β-epoxide = 2.0:1). The system of $HCF_2CF_2OCF_2CF_2SO_2F$ and NaOH without H_2O_2 did not oxidize **1** to **2**. It is well known that electron rich olefins cannot be epoxidized by H_2O_2/NaOH. Without exception, **1** was totally recovered when treated solely with H_2O_2 and NaOH in solution in absence of $HCF_2CF_2OCF_2CF_2SO_2F$. From these observations and in combination with the result reported previously in Refs. 1 and 2 we reached the conclusion: (1) a new persulfonic acid ($HCF_2CF_2OCF_2CF_2SO_2OOH$) was generated in situ in the reaction of $HCF_2CF_2OCF_2CF_2SO_2F$ with H_2O_2 in the presence of NaOH; (2) the generated persulfonic acid in situ is an excellent epoxidant, which resulted in



Scheme 1. Reagents and conditions: (i) $HCF_2CF_2OCF_2CF_2SO_2F$ (4 equiv), H_2O_2 (8 equiv), 4 N NaOH aqueous solution (8 equiv), MeOH, rt, 10 min, 95%.

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Table 1. Effects of R_fSO_2F[a]

Entry	R_fSO_2F	Time (min)	Yield (%)
1	$I(CF_2)_2O(CF_2)_2SO_2F$	1440	0[b]
2	n-$C_8H_{17}SO_2F$	10	96[c]
3	$MeO_2CCF_2SO_2F$	10	93[d]

[a] **1**:R_fSO_2F:H_2O_2:NaOH = 1:4:8:8 (equiv).

[b] No reaction.

[c] α:β Isomer = 2.0:1.

[d] α:β Isomer = 2.1:1.

the epoxidation of **1**. In the course of our investigation on effects of base and solvent, NaOH (or KOH) and MeOH were, respectively, proven to be the best choice (Scheme 1).

Following the above findings, several poly(per)fluoroalkanesulfonyl fluorides were tested for the epoxidation of **1** (see Table 1). 5-Iodo-3-oxa-octafluoropentanesulfonyl fluoride ($ICF_2CF_2OCF_2CF_2SO_2F$) was found to be unreactive (entry 1 in Table 1). This could be due to the existence of iodine at C-5 position. Perfluorooctanesulfonyl fluoride (n-$C_8F_{17}SO_2F$) and Methyl fluorosulfonyldifluoroacetate ($MeOOCCF_2SO_2F$) all displayed high reactivity for the epoxidation of **1** affording **2** in 96% and 93% yields, respectively, in 10 min (entries 2 and 3). However it should be mentioned that, using the present oxidation system, no significant α:β selectivity for epoxidation of **1** was obtained (α-epoxide:β-epoxide = 2.0–2.3:1).

To further demonstrate the application of the above methodology, various electron rich olefins were subjected to $HCF_2CF_2OCF_2CF_2SO_2F/H_2O_2/NaOH$ system in MeOH at room temperature. Results were summarized in Table 2.

The reaction of terminal olefin **3** with oxidant generated in situ can proceed readily, offering epoxide **4** in 93% yield (entry 1 in Table 2). Excellent yields were also obtained for allylic and homoallylic alcohols (entries 2, 3 and 5). At the same time, the complete retention of the stereochemistry was observed as expected for the epox-

Table 2. Results of epoxidation of various electron rich olefins[a]

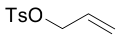
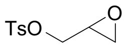
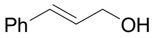
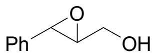
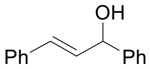
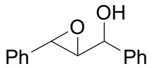
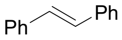
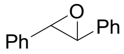
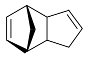
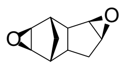
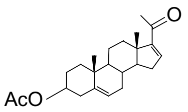
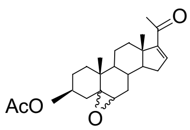
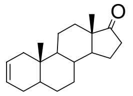
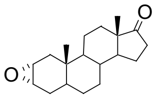
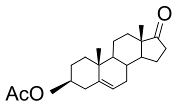
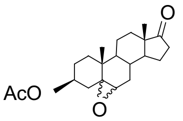
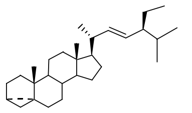
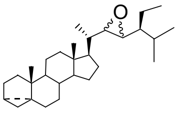
Entry	Substrate	Time (min)	Product	Yield (%)[b]
1	 **3**	10	 **4**	93
2	 **5**	10	 **6**	95
3	 **7**	480	 **8**	76
4	 **9**	1440	 **10**	84
5	 **11**	10	 **12**	80
6	 **13**	10	 **14**	76[c]
7	 **15**	10	 **16**	99
8	 **17**	10	 **18**	99[d]

Table 2 (*continued*)

Entry	Substrate	Time (min)	Product	Yield (%)[b]
9	 **19**	2400	 **20**	53[e]

[a] Substrate:R_fSO_2F:H_2O_2:OH^- = 1:4:8:8 (equiv).

[b] Isolated yields.

[c] Trace of 5(6),16(17)bis-epoxide of 19 was also found in this reaction.

[d] α:β Isomer = 2.2:1.

[e] α:β Isomer = 1:1.

idation of *trans*-olefins (entries 2–4). In the case of **11** (entry 5), two isolated electron rich double bonds were both epoxidized simultaneously. It was reported that the epoxidation of **15** using peracetic acid as oxidant provided **16** in 94% yield after 17 h.[6] For comparison, the same reaction employing our present method occurred with the formation of **16** in nearly quantitative yield within only 10 min (entry 7). On the other hand, although 4 N NaOH aqueous solution was used as base in the reaction, ester group in substrates **13** and **17** (entries 6 and 8) was not hydrolyzed under this conditions even after leaving the reaction mixture stirred for an additional 24 h. Furthermore, no formation of Baeyer–Villiger oxidation products was observed for substrates bearing ketone group (entries 6–8). In entry 6, the reaction selectivity between 5(6) and 16(17) double bonds has further proved that true epoxidation reagent is persulfonic acid generated from polyfluoroalkanesulfonyl fluorides and H_2O_2 rather than H_2O_2 itself. Finally for the highly sterically hindered olefin, such as substrate **19** (entry 9), a moderate isolated yield (53%) of product was still acquired by increasing reaction time to 48 h along with the recovery of 44% of starting material.

In conclusion, we have developed a novel oxidation system $R_fSO_2F/H_2O_2/NaOH$ for the epoxidation of a variety of electron rich olefins. The corresponding persulfonic acid was generated in situ in the reaction and acted as the oxidizing species in the epoxidation of olefins. High efficiency and mild reaction conditions are the main advantages for this novel oxidation system, particularly suitable for the epoxidation of acid-sensitive olefins. Therefore, it is recommended as an alternative oxidation method in synthetic organic chemistry.

A typical experimental procedure is as follows: To a stirred solution of 107 mg (0.37 mmol) of **1** in 10 mL of MeOH were added 0.28 mL (1.50 mmol) of $HCF_2CF_2OCF_2CF_2SO_2F$ and 0.30 mL (3.00 mmol) of 30% H_2O_2 aqueous solution at room temperature. An aqueous solution of 4 N NaOH (0.75 mL, 3.00 mmol) was slowly added to the above obtained solution over a period of 5–10 min. The resulting mixture was stirred for an additional 10 min at room temperature. Crude product obtained after usual work-up procedure was further purified through flash chromatography affording 108 mg of corresponding epoxide **2** (yield 95%).

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