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REACTIONS OF PERCHLOROFLUORO COMPOUNDS

VI. REARRANGEMENT OF HIGHER PERCHLOROFLUOROOLEFINS AND THEIR REACTIONS WITH NUCLEOPHILES AND ELECTROPHILES

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SUMMARY

The fluoride ion induced isomerization of $CFCl_2CF_2CFClCF_2CF{=}CF_2$ (1) gave only trans isomer $CFCl_2CF_2CFClCF{=}CFCF_3$ (2), then trans $CFCl_2CF_2CCl{=}CFCF_2CF_3$ (3) and trans $CFCl_2CF_2CF{=}CFCF_2CF_3$ (4), with the latter in predominance, while $AlCl_3$-catalyzed isomerization of 1 gave only 2 and then 3. No cis isomer could be detected. Such isomerization was terminated once a chlorine atom was linked to the double bond.

Reactions of perchlorofluoroolefins 1, 2 and 3 with various nucleophiles have been studied. With terminal olefin 1, C-1 was exclusively attacked by nucleophiles with the formation of three kinds of products[1]. In 2, merely C-2 was attacked and as a chlorine atom was just located at the allylic position, the reaction only proceeded through a S_N2' mechanism. In 3, only C-4 was attacked and no protonation product could be found. Competitive reaction showed the reactivity of these three perchlorofluoroolefins decreased in this order: $1 > 3 > 2$, which was directly related to the polarity of double bond. Only 1 reacted with electrophiles under normal conditions.

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INTRODUCTION

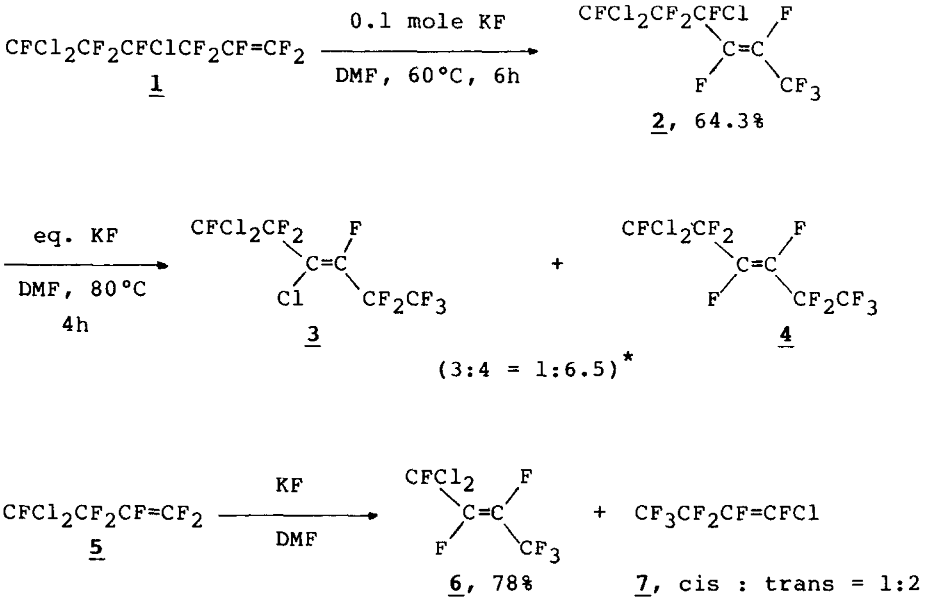
The chemistry of fluoroolefins is one of the most fundamental parts of organofluorine chemistry[2]. In recent years the reactivity and the direction of addition of higher fluoroolefins particularly their internal isomers still attract the attention of fluorine scientists[3].

The components separated from the pyrolyzate of polytrifluorochloroethylene provide a variety of perchlorofluoro compounds. The chlorine atom possesses less electronegativity and $+I_{\pi}$ effect than fluorine, but has a better leaving ability and spare 3d orbitals. Such perchlorofluoroolefins offer a possibility of studying the effect of chlorine atoms at different positions on the chemical behaviour of fluoroolefins[4,5]. Here mainly the reactions of perchlorofluorohexenes with various nucleophiles and electrophiles are studied.

RESULTS AND DISCUSSION

Rearrangement

The fluoride induced isomerization of terminal perfluoroolefins results in the thermodynamically more stable internal isomers [6]. Battais et al.[7] reported that the isomers formed in this way were all cis in configuration. On the contrary, isomerization of perchlorofluoroolefins all results in trans derivatives. For example, 4,6,6-trichloroperfluorohexene-1 (**1**), isolated from the pyrolyzate of polytrifluorochloroethylene[8], in the presence of KF at about 60°C produced only trans isomer **2** (SCHEME 1), as characterized by ^{19}F NMR (TABLE 1). Even at 15 °C, no cis isomer has been observed by ^{19}F NMR within the limits of detection. Under more severe conditions, **2** gave a mixture of two trans isomers **3** and **4** with the latter predominant. This is attributed to the better leaving ability of chlorine atom as compared with fluorine atom. A similar result was observed from the isomerization of 4,4-dichlorohexafluorobutene-1 (**5**) (SCHEME 1). Such products implied that instead of a cyclic intermediate[7], the isomerization of terminal fluoroolefins probably passes through an anionic intermediate or a S_N2' mechanism.



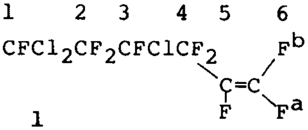
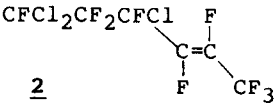
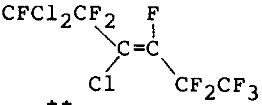
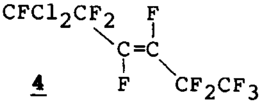
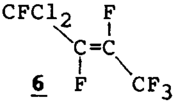
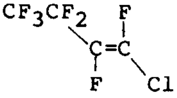
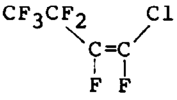
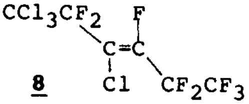
* Unless otherwise stated, all the ratios were determined by ^{19}F NMR at 56.4 MHz and the percentage yields were isolated ones.

SCHEME 1

In the presence of a Lewis acid like $AlCl_3$, SbF_5 or even FSO_3H, a terminal double bond also migrates successively into the internal positions[9,10]. Thus trans isomer 2 or 3 was formed when 1 was treated with $AlCl_3$ under different conditions. Under more drastic conditions instead of further rearrangement of 3, displacement of -F by Cl occurred and 8 was formed. It seems true that the rearrangement of a double bond catalyzed by $AlCl_3$ is terminated once a chlorine atom is located at the double bond(SCHEME 2). That no 4 was formed in this case implied that different mechanisms were involved when F^- or $AlCl_3$ was used as catalyst in such isomerizations.

TABLE 1

^{19}F NMR of rearranged products*

Compound.	ppm and J (Hz)					
	1	2	3	4	5	6
 1	-9.9	38.6	65.6	42.5	127	a. 15.5 b. 34.2
	$J_{5,6a}$=47.0, $J_{5,6b}$=142.0, $J_{6a,6b}$=63.0,					
 2	-8.7	30.3 34.5 (AB type)	51.9	69.4	79.3	-8.7
	$J_{3,5}$=50.8, $J_{4,5}$=135.4, J_{AB}=270.7					
 3**	-5.9	25.9	----	26.7	40.0	6.4
	$J_{1,2}$=8.8, $J_{1,4}$=21.4, $J_{2,4}$=28.8					
 4	-3.0	35.2	72.5	76.5	44.4	7.7
	$J_{1,2}$=9.4, $J_{2,4}$=23.5, $J_{3,4}$=124.8, $J_{3,5}$=22.5					
 6	-10.5	68.7	82.2	-8.2	----	---
	$J_{1,2}$=22.6, $J_{1,3}$=56.4, $J_{2,3}$=139.1, $J_{2,4}$=22.6 $J_{3,4}$=9.4					
 7, trans	8.5	43.7	83.3	31.0	----	---
	$J_{1,2}$=1.9, $J_{2,3}$=13.2, $J_{2,4}$=27.3, $J_{3,4}$=131.6					
 7, cis	8.3	42.5	70.6	11.0	----	---
	$J_{2,3}$=13.2, $J_{3,4}$=26.3					
 8	---	20.9	----	23.4	39.7	5.7
	$J_{2,4}$=30.4					

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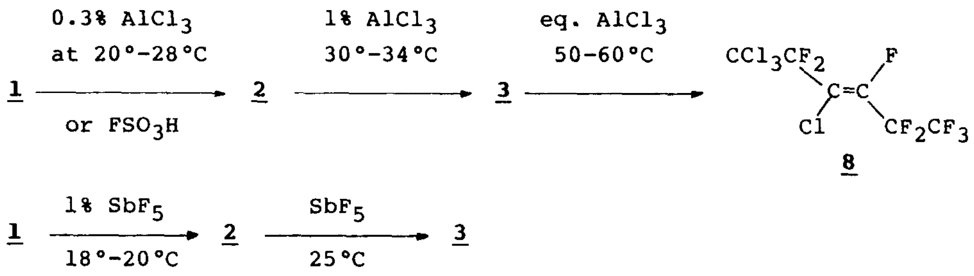
* See experimental section for details. ** Measured at 188.3MHz.

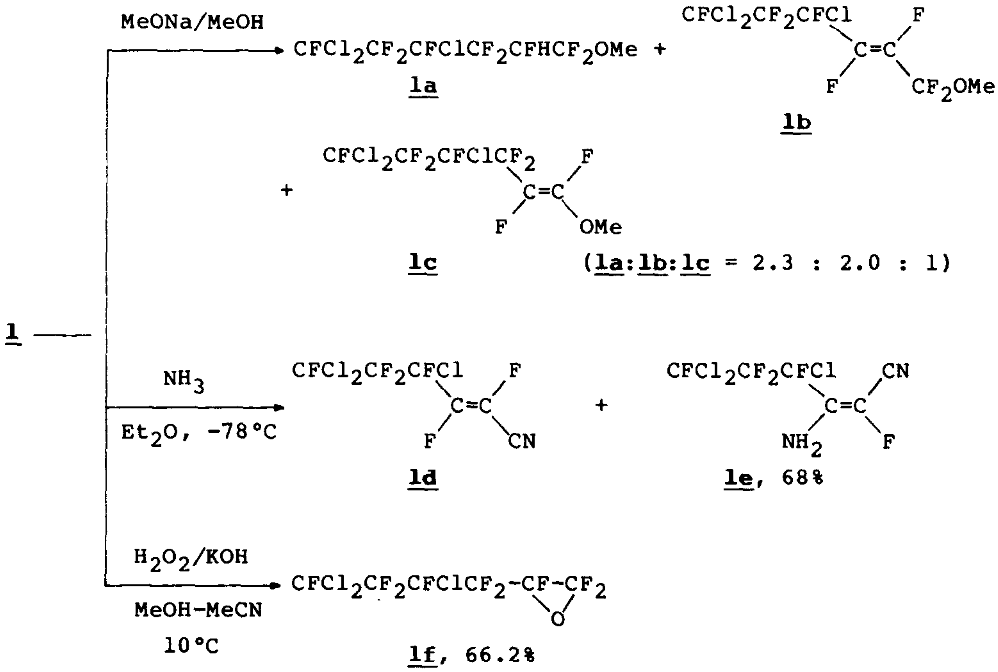


SCHEME 2

The reactions of perchlorofluoroolefins 1, 2 and 3 with other nucleophiles and electrophiles were studied as follows.

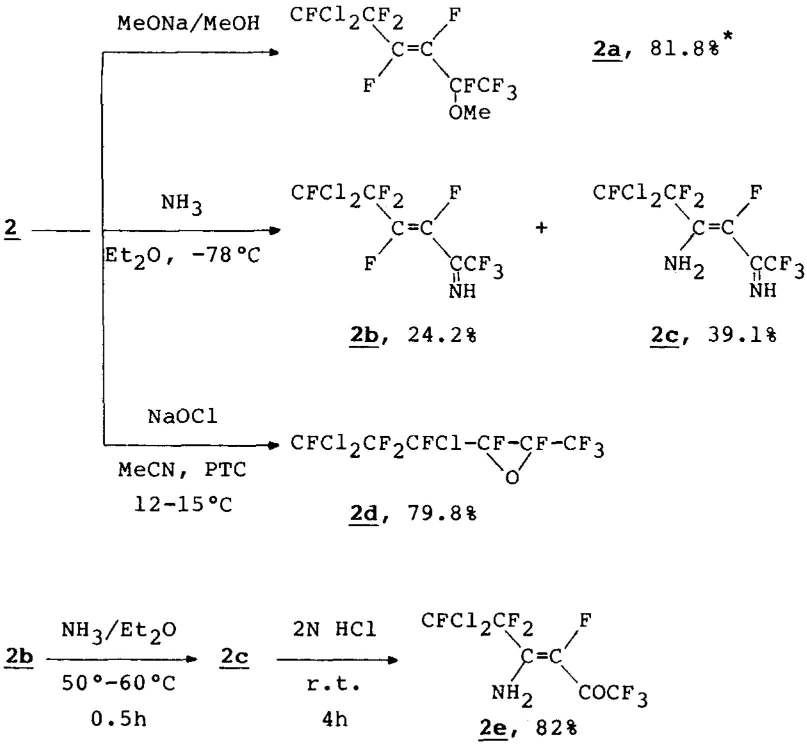
Reactions of olefin 1, 2 and 3 with nucleophiles

C-1 of terminal olefin 1 was exclusively attacked by MeO^- and **1a**-**1c** were formed (SCHEME 3). This indicated that a typical carbanionic intermediate was involved[1]. The reactions with NH_3 and H_2O_2 proceeded presumably through the same type of intermediate.



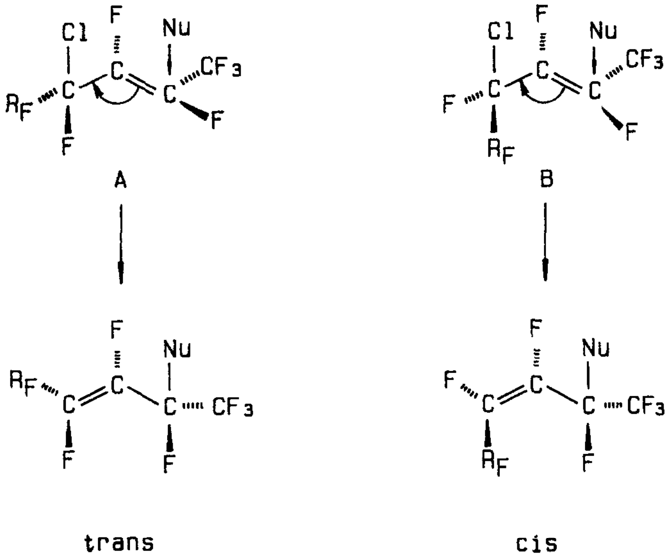
SCHEME 3

C-2 of olefin **2** was exclusively attacked by nucleophiles and only unsaturated compounds formed through an S_N2' mechanism together with their further reaction products were found (SCHEME 4). Under very mild conditions, **2** reacted with ammonia giving a mixture of **2b** and **2c** while only **2c** was formed at elevated temperature. Hydrolysis of **2c** with 2N HCl at 20°C led to ketoenamine **2e**.



SCHEME 4

The formation of trans isomers **2a** and **2b** could be explained by the S_N2' mechanism[5] which requires the nucleophile to enter syn to the leaving group[11], that is, the less hindered conformation **A** led to the most stable trans isomer (SCHEME 5).

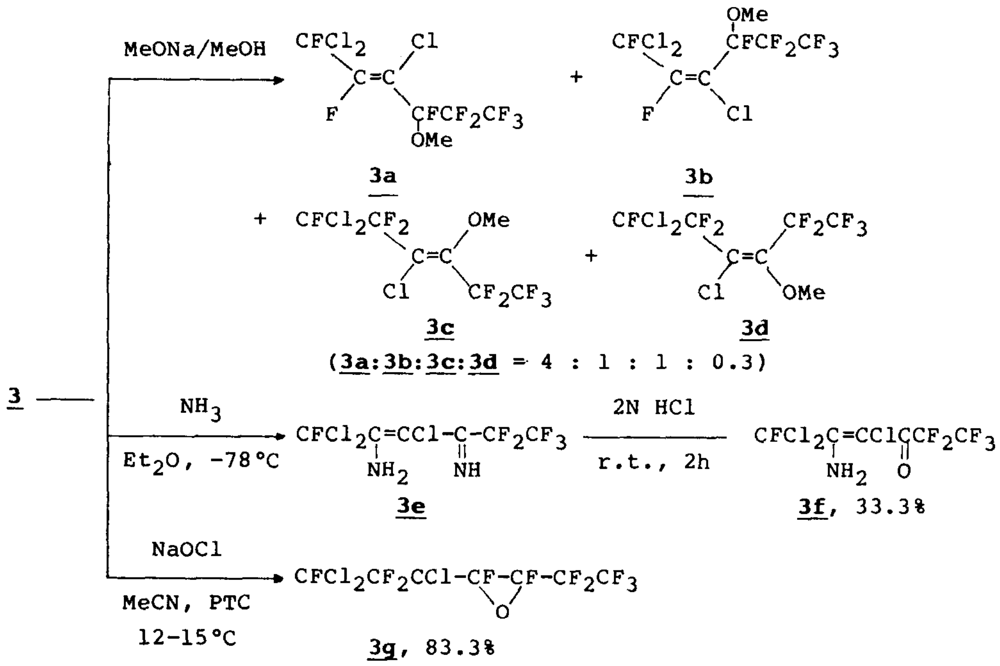


SCHEME 5

In the reaction of MeOH with olefin **3**, only C-4 was attacked and monosubstitution products **3a** - **3d** were formed (SCHEME 6), suggesting an anionic intermediate $[CFCl_2CF_2\overset{\ominus}{C}Cl\text{-}CFNu\text{-}CF_2CF_3]$ was involved. Such orientation is in accord with the polarity of the double bond and the stability of anion formed[4]. Lack of $CFCl_2CF_2CClH\text{-}CFNu\text{-}CF_2CF_3$ suggested that the intermediate carbanion would rather eliminate F^- than abstract a proton. **3e** was converted directly to **3f** by acid hydrolysis.

Only **1** could be epoxidized by H_2O_2. However, olefin **2** and **3** reacted with NaOCl in the presence of a phase transfer catalyst furnishing the corresponding epoxide in good yield.

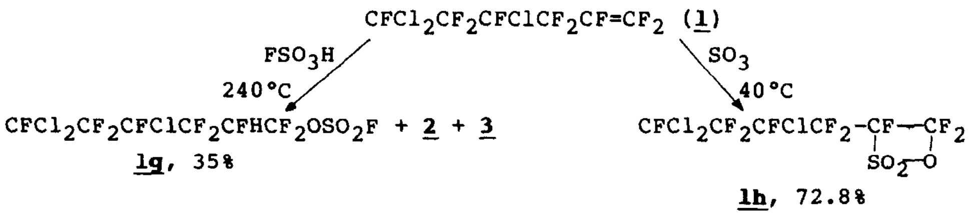
Competitive reaction of a mixture of equivalent mole of **1**, **2** and **3** with a deficiency of MeONa/MeOH showed the reactivity of olefins decreased in this order: **1** $>$ **3** $>$ **2**, which was related to the combined effects of the polarity and the steric hinderance of double bond.



SCHEME 6

Reactions with Electrophiles

1 reacted with FSO_3H at high temprature giving the adduct 1g and rearranged products 2 and 3 as well; 2 and 3, however, were stable to FSO_3H at even higher temperature (SCHEME 7). Sultone 1h was obtained from the reaction of 1 with SO_3 while no reaction was observed when 2 or 3 reacted with SO_3 even at 120°C for 48h. Such results showed that the internal perchlorofluoroolefins 2 and 3 are less reactive not only to nucleophiles but also to electrophiles than terminal isomer 1.



SCHEME 7

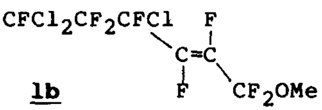
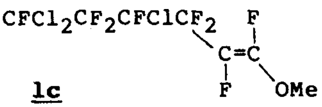
EXPERIMENTAL

Boiling points and melting points were uncorrected. A Shimadzu IR-440 was used to record infrared spectra. ^1H NMR spectra (with chemical shifts in ppm from external TMS) were measured at 60MHz on a Varian EM-360A Spectrometer. ^{19}F NMR spectra (with chemical shifts in ppm from external TFA and positive for upfield shifts) were determined at 56.4MHz on a Varian EM-360L or at 188.3MHz on a Varian XL-200 Spectrometer. Mass spectra were recorded with a Finnigan GC -MS 4021 Mass Spectrometer. The GLC analysis were performed with a 102G (Shanghai Analytical Factory) using 3-6m long columns packed with DNP(dinoyl phthalate,15%), APZ(Apiezon, saturated hydrocarbon, 15%), or SE-30(methyl siloxane polymer, 15%).

The chemical reagents used were A.R. grade. DMF was dried over 4A molecular sieve and freshly distilled under vacuum. Et_2O was treated with $LiAlH_4$ and freshly distilled as well. Spray dried KF was used. Olefin <u>1</u> was isolated from the pyrolyzate of polytrifluorochloroethylene with b.p. 140-1°C. All products described below are <u>new</u> and their ^{19}F NMR data are shown in TABLE 2.

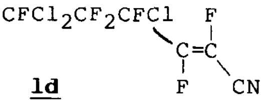
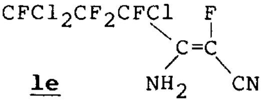
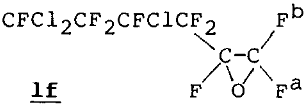
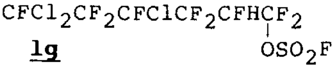
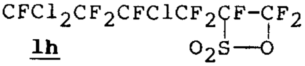
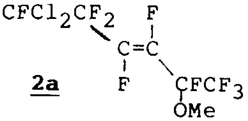
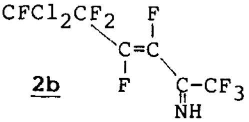
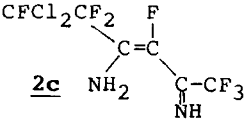
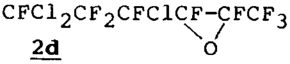
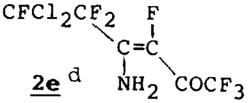
TABLE 2

^{19}F NMR of compounds formed from reactions with nucleophiles and electrophiles

Compound	ppm and J(Hz)					
	1	2	3	4	5	6
1 2 3 4 5 6 $CFCl_2CF_2CFClCF_2CFHCF_2OMe$ <u>**1a**</u>	-9.4	30.8	53.6	a	130.6	4.1, 7.1 (AB type)
	J_{AB}=130.6, J_{HF}=56.5					
 $CFCl_2CF_2CFClCF{=}CFCF_2OMe$ <u>**1b**</u>	-8.3	29.7, 33.9	50.8	70.8	74.8	-0.9
	$J_{3,5}$=50.8, $J_{4,5}$=126.4, $J_{4,6}$=18.6, J_{AB}=267.3					
 $CFCl_2CF_2CFClCF_2CF{=}CFOMe$ <u>**1c**</u>	-9.4	31.1	52.8	33	109.0	33
	$J_{5,6}$=131.6					

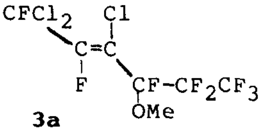
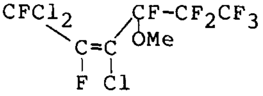
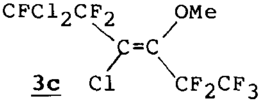
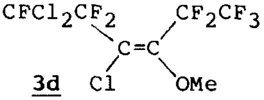
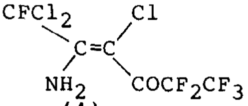
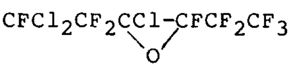
(continued)

TABLE 2 (Cont.)

 **1d**	-8.4	29.5, 33.3	52.2	60.2	72.8	---
	$J_{3,5}$=47.0, $J_{4,5}$=141.0, J_{AB}=259.0					
 **1e**	-9.3	28.7, 32.3	46.7	----	80.6	---
	$J_{1,2}$=6.6, $J_{1,3}$=11.3, $J_{2,3}$=9.4, J_{AB}=276.4					
 **1f**	-9.2	31.2	52.3	41.2	73.0	a.35.0 b.31.2
	$J_{5,6a}$=19.5, $J_{5,6b}$=18.8, $J_{6a,6b}$=41.3					
 $CFCl_2CF_2CFClCF_2CFH\underset{OSO_2F}{C}F_2$ **1g** [c]	-10.8	29.1	51.7	[b]	126.9	-1.6
	J_{HF}=45.0					
 **1h**	-10.5	30.1	49.3	30.1	69.8	4.7
	$J_{3,5}$=22.6					
 **2a**	-3.2	35.5	75.3	71.3	59.1	6.4
	$J_{1,2}$=9.4, $J_{2,3}$=6.2, $J_{2,4}$=23.5, $J_{3,4}$=141.0, $J_{3,5}$=31.0, $J_{4,6}$=4.2					
 **2b**	-5.0	32.4	70.0	73.7	----	-5.0
	$J_{2,4}$=22.6, $J_{3,4}$=141.0					
 **2c**	-6.2	32.4	----	90.9	----	-6.2
	$J_{1,2}$=9.4, $J_{1,4}$=24.2, $J_{2,4}$=28.2, $J_{4,6}$=16.9					
 **2d**	-6.5	29.1, 31.9	50.1	65.0	77.3	-1.1
	$J_{3,5}$=37.6, $J_{4,6}$=12.2, J_{AB}=259.4					
 **2e** [d]	-6.7	31.2	----	93.7	----	-3.5
	$J_{1,2}$=9.0, $J_{1,4}$=25.4, $J_{2,4}$=28.2, $J_{4,6}$=17.4					

(continued)

TABLE 2 (Cont.)

 **3a**	-18.5	21.4	----	45.3	47.1	2.7
	$J_{1,2}$=12.2, $J_{2,4}$=37.8, $J_{2,5}$=12.2, $J_{4,6}$=10.3					
 **3b**	-16.7	3.7	----	41.0	44.8	2.2
	$J_{1,2}$=22.6, $J_{1,4}$=83.5, $J_{1,5}$=22.6, $J_{4,6}$=11.3					
 **3c**	-8.3	24.6	----	----	36.7	5.2
	$J_{1,2}$=9.4					
 **3d**	-9.6	21.0	----	----	33.9	5.1
	$J_{2,5}$=33.9					
 **3f**(4)	-17.9	---	----	----	37.5	2.8
 **3g**	-11.3	28.8, 31.7	----	69.1	44.4	4.8
	$J_{1,A}$=5.6, $J_{1,B}$=9.0, $J_{3,A}$=30.5, $J_{3,B}$=21.4, $J_{4,6}$=11.2, J_{AB}=251.0					

[a] Two AB types were observed at 37.2, 42.8 and 39.2, 44.8ppm with J_{AB}=276.2Hz.

[b] Two AB types were observed at 35.7, 39.8 and 37.5, 41.6ppm with J_{AB}=282.0Hz.

[c] ^{19}F NMR of $-OSO_2F$ group was found at -126.0ppm.

[d] ^{19}F NMR was measured in CCl_4.

Rearrangement

1. Fluoride ion induced isomerization

A. 7.0g(20.0mmol) **1**, 0.12g(2.0mmol) KF in 5ml DMF were mixed in a 50ml three-necked flask equipped with mechanical stirrer, thermometer and a condenser with a $CaCl_2$ tube. The mixture was stirred at 60°C for 6h and poured into water. The separated organic layer was washed with H_2O and dried. Distillation gave 4.5g 2 (yield 64.3%) with b.p. 132-134°C. Elem. Anal. for 2 $C_6Cl_3F_9$: C,20.52; F,48.53; Cl,30.86 (required: C,20.62; F,48.92; Cl,30.47). MS m/e (intens., assign.): 197(100, M-CF_2CFCl_2), 348(0.8, M).

B. 7.0g(20.0mmol) 2 and 1.2g(20.7mmol) KF in 5ml DMF were stirred at 80°C for 4h. After work-up, 3.5g 4 (yield 52.5%) with b.p. 99°-102°C and 0.7g 3 (yield 10.0%) with b.p. 125°-128°C were obtained. Elem. Anal. for 3 $C_6Cl_3F_9$: C,20.19; F,49.96; Cl,30.59 (required: C,20.62; F,48.92; Cl,30.47). IR (cm^{-1}): 1661w (C=C). MS: 101(100, $CFCl_2$), 348(3.3, M). Elem. Anal. for 4 $C_6Cl_2F_{10}$: C,21.31; F,56.94; Cl,21.54 (required: C, 21.64; F, 57.05; Cl,21.32). MS: 101(100, $CFCl_2$), 231(11.5, M-$CFCl_2$).

C. 60.0g (0.26mol) 5 and 9g (0.15mol) KF in 30ml DMF were stirred at 85°C for 8h. 7 was separated by semipreparative GLC (Column: DNP; Temp.: 50°C) from the fraction which boiled below 55°C. Then 46g pure 6 (yield 77%) with b.p.62-64°C was obtained.

2. $AlCl_3$ induced isomerization

A. 60.0g (0.172mol) 1 and 0.7g (5.0mmol) $AlCl_3$ reacted at 20°C for 4h, and then at 26°C for 2h. The mixture was cooled to below 5°C and 100ml dil.HCl was added slowly. The organic matter was separated, washed with H_2O and dried over Na_2SO_4. Distillation gave 53.0g 2 (yield 88.3%).

B. 68.0g (0.195mol) 2 and 1.5g (11.3mmol) $AlCl_3$ reacted at 32°C for 4h. After work-up, 57g 3 (yield 84.0%) was obtained.

C. 7.0g (20.0mmol) 1 and 2.66g (20.0mmol) $AlCl_3$ were mixed at 0°C, while stirring. The reaction temperature was raised gradually to 50°C within 1h and maintained at that temperature for another hour. 4.1g 8 (yield 56.3%) with b.p. 87-9.5°C/40mmHg was obtained. Elem. Anal. for 8 $C_6Cl_4F_8$: C, 19.38; F, 41.57; Cl, 38.87(required: C, 19.69; F,41.52; Cl,38.79). IR: 1660W (C=C). MS: 117(100,CCl_3), 364(0.4, M).

Reactions With Nucleophiles

1. Reaction with MeONa/MeOH

A. To 7.0g (20.0mmol) 1 at 5°C a solution of 20mmol MeONa in 4ml MeOH was added dropwise while stirring. After that the mixture was stirred at 25°C for 2 more hours and poured into 40ml ice-water. The separated organic layer was washed with H_2O and dried. Distillation gave 6.3g products at 86-94°C/15mmHg. 1a, 1b and 1c were isolated by semipreparative GLC (Column: SE-30; Temp.: 110°C). Elem. Anal. for 1a $C_7H_4Cl_3F_9O$: C,21.86; H,0.97; F, 45.42; Cl,27.75 (required: C,22.03; H,1.06; F,44.81; Cl,27.91). ^1H NMR: 3.85(3H, s, OCH_3), 5.30(1H, d-m, J=56.5Hz, CFH). Elem. Anal. for 1b $C_7H_3Cl_3F_8O$: C,23.04; H,0.76; F, 41.44; Cl, 29.56 (required: C,23.25; H,0.84; F, 42.04; Cl,29.45). ^1H NMR: 3.53(s). Elem. Anal. for 1c $C_7H_3Cl_3F_8O$: C,23.38; H, 0.79; F,42.60; Cl, 29.73 (required: C,23.25; H,0.84; F, 42.04; Cl,29.45). ^1H NMR: 4.10(s).

B. To 5.0g (14.3mmol) 2 at 15°C, a solution of 14.4mmol MeONa in 3ml MeOH was added dropwise in 10min. while stirring. Then the mixture was kept at 50°C for 1h. 4.2g 2a (yield 81.8%) was obtained. Elem. Anal. for 2a $C_7H_3Cl_2F_9O$: C,23.83; H,0.71; F,50.42; Cl, 21.23 (required: C, 24.36; H, 0.88; F, 49.55; Cl,20.57). ^1H NMR: 3.62(s, OCH_3).

C. The reaction of 7.0g (20.0mmol) 3 with 20.0mmol MeONa in 4ml MeOH proceeded under the same conditions as that of 2. 5.8g 3a-3d (yield 80.2%) with b.p. 87-91°C/12mmHg was obtained and a mixture of 3a and 3b, 3c and 3d were separated by semipreparative GLC (Column: APZ; Temp.: 150°C). Elem. Anal. for 3a and 3b $C_7H_3Cl_3F_8O$: C,23.08; H,0.79; F,42.78; Cl,29.23 and for 3c and 3d: C, 23.23; H, 0.75; F,42.13; Cl,29.82 (required for 3a-3d: C, 23.25; H, 0.84; F, 42.05; Cl,29.45).

2. Reaction with NH_3

A. To 7.0g (20.0mmol) 1 in 30ml Et_2O at -78°C, NH_3 was bubbled in excess. The temperature was then allowed to rise to r.t. The deposit was filtered off and the ethereal solution was washed with H_2O and dried over Na_2SO_4. Distillation gave 0.5g 1d at 50-53°C/12mmHg which was purified further by semipreparative GLC

(Column: SE-30; Temp.: 120°C) and 4.2g **1e** (yield 68.8%) with b.p. 121-122.5°C/6mmHg. Elem. Anal. for **1d** $C_6Cl_3F_6N$: C, 23.83; N,5.48; F,36.40; Cl, 33.62 (required: C,23.51; N,4.57; F,37.19; Cl,34.71). IR: 2245m (CN), 1696m (C=C). MS: 154(100,M-CF_2CFCl_2), 305(2.6, M), 306(8.9, M+1). Elem. Anal. for **1e** $C_6H_2Cl_3F_5N_2$: C, 23.60; H, 0.67; N,9.43; F, 30.86; Cl, 34.84 (required: C,23.74; H,0.66; N,9.22; F, 31.29; Cl, 35.08). IR: 3530m (NH), 3395s (NH), 2250s (CN), 1664s (NH_2 bending vibration), 1618m (C=C). MS: 151(100, M-CF_2CFCl_2), 302(43.0, M), 303(65.7, M+1). ^1H NMR: 5.15 (s, NH_2).

B. Treated as in the previous experiment, 7.0g (20.0mmol) **2** gave after fractional distillation 1.5g **2b** at 48-50°C/15mmHg (yield 24.2%) and 2.4g **2c** at 84.5-85°C/15mmHg (yield 39.1%). Elem. Anal. for **2b** $C_6HCl_2F_8N$: C, 23.02; H, 0.30; N, 4.53; F, 48.78; Cl, 23.18 (required: C, 23.24; H, 0.33; N, 4.52; F, 49.02; Cl, 22.90). IR: 3320m (NH), 1633w (C=C). MS: 101(100,$CFCl_2$), 309(4.1, M),310(40.3, M+1). ^1H NMR: 11.6 (s, NH). Elem. Anal. for **2c** $C_6H_3Cl_2F_7N_2$: C, 23.48; H,0.91; N,9.11; F,42.81; Cl, 23.52 (required: C, 23.47; H, 0.98; N, 9.12; F, 43.31; Cl, 23.12). IR: 3525s (NH), 3360s (NH), 1659s (NH_2 bending vibration), 1600s (-C=C-C=N). MS: 155(100, M-CF_2CFCl_2), 306(33.7, M), 307(21.5, M+1). ^1H NMR: 7.89(s, NH_2 and NH).

C. 14.0g (40.0mmol) **2** and about 25ml liquid NH_3 were sealed in a 200ml stainless steel bomb at -78°C, and then shaken at 50-60°C for 0.5h. 8.0g pure **2c** (yield 65.1%) was obtained.
2.0g **2c** and 60ml 2N HCl were stirred at 20°C for 12h. The residue was washed with H_2O and dried under vacuum. 1.64g **2e** (yield 82%) was obtained with m.p. 42-3.5°C after recrystallization from CCl_4. Elem.Anal. for **2e** $C_6H_2Cl_2F_7NO$: C,23.93; H,0.62; N,4.32; F,43.31; Cl,22.91 (required: C, 23.39; H, 0.65; N, 4.54; F,43.17; Cl,23.05). IR: 3540s (NH), 3340m (NH), 1681m (NH_2 bending vibration), 1617s(-C=C-C=O). MS: 307(40.7,M), 308(100, M+1). ^1H NMR (in CCl_4): 6.75 (broad, NH_2).

D. To 7.0g(20.0mmol) **3** in 30ml Et_2O at -78°C, NH_3 was bubbled in for 2h giving 3.0g product at 49-53.5°C/1.5mmHg. ^{19}F NMR showed the main component was **3e**. 1.0g of the crude product was hydrolyzed with 30ml 2N HCl at 25°C for 2h and 0.72g **3f** (yield

33.3%) was obtained with m.p. 102.5-104°C after recrystallization from CCl_4. Elem. Anal. for **3f** $C_6H_2Cl_3F_6NO$: C,22.09; H, 0.50; N,4.55, F,35.84; Cl,32.80 (required: C,22.20; H,0.62; N, 4.31, F, 35.12, Cl, 32.81). IR: 3470s (NH), 3245m (NH), 1626s (NH_2 bending vibration), 1602s(-C=C-C=O). MS: 222(100,M-$CFCl_2$), 323(4.6, M), 324(7.6,M+1). ^1H NMR (in CCl_4): 7.86 (broad, NH_2).

3. Epoxidation

A. To a mixture of 14.0g (40.0mmol) **1**, 16ml 30% aq. H_2O_2 and 7.5ml MeOH at below 8°C, a solution of 5.9g KOH in 2.4ml H_2O and 7ml MeOH was added dropwise during a period of 50min. while stirring. After that the solution was stirred at below 15°C for another 0.5h, and then 100ml ice-water was poured in. 9.8g **1f** (yield 66.3%) at 130-5°C was collected and purified by semipreparative GLC (Column: DNP; Temp.: 100°C). Elem. Anal. for **1f** $C_6Cl_3F_9O$: C, 19.50; F, 47.22; Cl, 29.03 (required: C, 19.71; F, 46.78; Cl,29.13). IR: 1540m.

B. 7.0g(20.0mmol) **2** was added dropwise into a solution of 40ml 14% aq.NaOCl, 4ml MeCN and one drop of $MeN(C_8H_{17})_3Cl$ at 8°C during a period of 15min. The mixture was allowed to react at 12-16°C for 2h. 5.84g **2d** (yield 79.8%) at 120-125°C was obtained and purified by semipreparative GLC (Column: DNP; Temp.: 100 °C). Elem. Anal. for **2d** $C_6Cl_3F_9O$: C,19.73; F, 45.70; Cl,28.43 (required: C,19.71; F,46.78; Cl,29.13). IR: 1490m.

C. 7.0g(20.0mmol) **3** was epoxidized by 32ml 14% aq.NaOCl in 4ml MeCN in the presence of $MeN(C_8H_{17})_3Cl$. 6.1g **3g** (yield 83.8%) at 125-130°C was purified by semipreparative GLC (Column: DNP; Temp.: 100°C). Elem. Anal. for **3g** $C_6Cl_3F_9O$: C,19.48; F, 45.74; Cl,29.41 (required: C,19.71; F,46.78; Cl,29.13). IR: 1440m.

Reactions with Electrophiles

1. 14.0g (40.0mmol) **1** and 4.3g (43.0mmol) FSO_3H was placed in a 70ml stainless steel bomb and reacted at 220-240°C for 12h. The cooled content was poured carefully into ice-water and

13.3g crude products were separated. Distillation gave 6.7g rearrangement products 2 and 3, and 6.3g 1g (yield 35.0%) at 167-8.5°C/270mmHg which was purified by semipreparative GLC (Column: SE-30; Temp.: 144°C). Elem. Anal. for 1g $C_6HCl_3F_{10}O_3S$: C,16.05; H,0.18; F,41.50; Cl,23.17; S,7.51 (required: C, 16.03; H, 0.22; F,42.26; Cl,23.68; S,7.12). ^1H NMR: 5.65(d-m, J_{HF}=45.0Hz).

2. 7.0g(20.0mmol) 1 and 2.4g (30.0mmol) freshly distilled SO_3 were stirred at 40°C for 24h. After distillation 0.97g 1 was recovered and 5.4g 1h (yield 72.8%) at 35-36°C/2mmHg was obtained. Elem. Anal. for 1h $C_6Cl_3F_9O_3S$: C,16.72; F,39.15; Cl, 25.01; S, 7.54 (required: C,16.78; F,39.81; Cl,24.78; S,7.45)

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