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THE SYNTHESIS OF SF_5-EPOXIDES

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SUMMARY

The epoxidation of two fluorinated pentafluorothio olefins, $F_5SCH{=}CF_2$ and $F_5SCF{=}CF_2$, was achieved by treatment with NaOCl under phase transfer catalytic conditions at lowered temperatures. Some reactions were run and it was found that in anionic reactions loss of the SF_5 group generally occurred.

INTRODUCTION

Fluorinated epoxides have been obtained by several different methods. For partially fluorinated olefins, halohydrins are often employed in the synthesis of oxiranes of the type $R_fCH_2\overline{CHCH_2O}$, $R_f\overline{CHCH(R)O}$ (R = alkyl), and $R_f\overline{CHCH_2O}$ [1,2]. Carbene addition to ketones or aldehydes leads also to epoxides. Perfluoroepoxides are accessible from olefins ($R_fCF{=}CF_2$), H_2O_2 and KOH, oxygen and a catalyst or light, or ozone itself. Likewise, addition of CF_2 has been employed in their synthesis. A more comprehensive overview is given in

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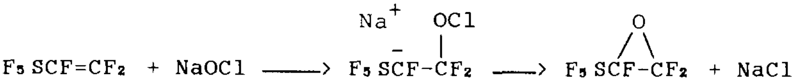
ref. 1. A newer method employs treatment of olefins $R_fCF{=}CFR_f$ with NaOCl in a CH_3CN and H_2O mixture [3]. This method can be suitably accomodated to phase transfer catalysis-conditions.

Previously, it was found that treatment of $F_5SCF{=}CF_2$ with oxygen or ozone under pressure failed to give the epoxide, but resulted in the compound $F_5SOCF_2C(O)F$ [4],

RESULTS AND DISCUSSION

Fluorinated olefins exhibit a proclivity towards nucleophilic addition with the ensuing formation of anion intermediates; $F_5SCF{=}CF_2$, when treated with COF_2 in CH_3CN and in the presence of CsF forms $F_5SCF(CF_3)COF$ [5]. As the epoxidation of fluorocarbons with hypochlorite passes through an anion intermediate, and the SF_5 group can stabilize negative charges better than a CF_3 group it seemed a promising pathway for the preparation of pentafluorothio epoxides [6]. We have found this route, with a phase-transfer catalyst, to be effective:



$$F_5SCF{=}CF_2 + NaOCl \longrightarrow F_5S\overset{Na^+}{\overset{-}{C}}F-\overset{OCl}{\overset{|}{C}}F_2 \longrightarrow F_5S\overset{O}{\overbrace{CF-C}}F_2 + NaCl \qquad (1)$$

1,1,2-Trifluorotrichloro ethane ("Freon-113") was chosen as the solvent for the reaction with $F_5SCF{=}CF_2$ and CCl_4 for $F_5SCH{=}CF_2$. In the latter case it was easier to isolate the product by distillation, because with $SF_5CF{=}CF_2$, CCl_2FCClF_2 boils in the same region as the resulting epoxide. The phase transfer catalyst $N(n\text{-}C_8H_{17})_3CH_3^+\ Cl^-$ was used in a concentration of 10-20 mol %. Temperature control (<-6°C) and slow addition of the olefin to the cold two-phase system consisting of the phase-transfer catalyst, solvent and basic NaOCl solution, were especially important. Too fast addition led to temperature rise and the solution turned acidic. In these cases no fluorinated products were found. The reactions were monitored by ^{19}F n.m.r. and terminated with the disappearance of the olefin. In the case of the perfluoroolefin a by-product was observed which according to its appearance and chemical shift is S_2F_{10}.

$F_5S\overline{CFCF_2O}$ is an analogue to hexafluoropropylene epoxide and should exhibit similar reaction behavior [7]. We find, however, that bases even as weak as $(C_2H_5)_2O$ will lead to loss of SF_4. In the reaction with CsF in CH_3CN in a thick-walled glass vessel, CF_3COF and SF_4 could be identified as major reaction products; the SF_4 was converted to SOF_2 and SiF_4 upon prolonged storage in glass. While antimony pentafluoride converts perfluoro epoxides either to ketones or acyl fluorides [8], the infrared spectrum of the product mixture of the reaction of SbF_5 with $F_5S\overline{CFCF_2O}$ indicates again formation of $CF_3C(O)F$. A conversion into the isomers $F_5SCF_2C(O)F$ [9] or $F_5SC(O)CF_3$ was not possible by this route. This loss of SF_5 was also observed with $F_5SC(O)CF_3$ [10] and bases, and is also similar to the observation made by DesMarteau and Sekiya with $F_5S\overline{NCF_2O}$ [11]. In the infrared spectra, the epoxide ring band is seen at 1530 ($SF_5\overline{CFCF_2O}$) and ~1500 cm^{-1} ($SF_5\overline{CHCF_2O}$), respectively, and are at the upper limit of the values observed for other fluorinated epoxides.

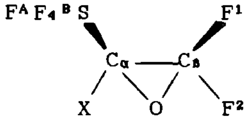
The ^{19}F n.m.r. spectra of the two epoxides show the typical AB_4 spectra of the SF_5 group. The SF_5 resonances in the epoxides have moved upfield, as compared to the olefins, by 6-10 ppm.

The CF_2 groups in $F_5S\overline{CFCF_2O}$ and in $F_5S\overline{CHCF_2O}$ appeared as AB and MX systems, respectively; in the case of the perfluoro compound this system was rather complicated due to extensive overlap. There was also a dependence on the solvent. For example, the two fluorines in the CF_2 group of $SF_5\overline{CFCF_2O}$ had a very small chemical shift difference as a pure sample and appeared as an incomprehensible multiplet, but in Freon-113 a complicated, partially overlapped, although interpretable, AB system was observed; in $CDCl_3$ the two resonances were clearly separated. It was possible to reproduce the CF_2 resonances (see Figure 1) with an n.m.r. simulation program [12]. The coupling within the CF_2 group in hexafluoropropylene oxide is 43.5 Hz [13], considerably larger than in $SF_5\overline{CFCF_2O}$, but comparable to the value in $SF_5\overline{CHCF_2O}$. The F-α,ß-trans coupling in fluoro olefins and in other fluorinated epoxides is found to be negative [13]. Most likely, J_{XF^1} is also negative in the present case, but only the absolute value is given.

In the ^{13}C n.m.r. spectra of both epoxides, no unusual shifts are observed; the resonances and coupling constants for both carbons appear in the expected regions, and are comparable with the shifts and couplings in the ß-sultone $F_5S\overline{CHCF_2OSO_2}$ [14] and other (partially) fluorinated oxiranes [15] with the exception of the C_α-F_α coupling in $SF_5\overline{CFCF_2O}$.

TABLE I

^{19}F and ^{13}C n.m.r. data+



X = H or F

X	F		H	
ϕ_A	60.3 ppm	(0.95)	68.1	(1.00)
ϕ_B	46.2	(4.33)	53.0	(3.90)
ϕ_{F^1}	-110.5 (m)	(2.06)	-119.3 (d-d)	(0.90)
ϕ_{F^2}	-110.5 (m)		-105.2 (d-d-p)	(1.00)
$(\phi, \delta)_X$	-129.0 (d-septet)	(1.00)	5.30 (m)	
J_{AB}	152.3 Hz		153.3	
J_{AX}	5.6		0.0	
J_{BX}	14.4		-	
J_{BF^1}	0.0		0.0	
J_{BF^2}	12.4		13.6	
J_{XF^1}	$\lvert 16.3 \rvert$		2.9	
J_{XF^2}	$\lvert 17.2 \rvert$		4.1	
$J_{F^1F^2}$	32.2		44.0	
$\delta_{C\alpha}$*	107.4 (d-m)		81.4≈(d-p)**	
$\delta_{C\beta}$	107.7 (d-t)		108.4 (t)	
$J_{BC\alpha}$	-		≈29 Hz	
$J_{XC\alpha}$	≈337 Hz		205.7	
$J_{XC\beta}$	18.0		0.0	
$J_{CF_2C\beta}$	344.6		295.6	
$J_{CF_2C\alpha}$	-		-	

+For ^{19}F and ^1H n.m.r. spectra samples were determined neat with external references (CCl_3F for ^{19}F and $Si(CH_3)_4$ for ^1H). Coupling measurements of the CF_2 group to other fluorines were determined in $CDCl_3$ solution. *^{13}C spectra are run in $CDCl_3$ solution. **The individual bands show further poorly resolved structure.

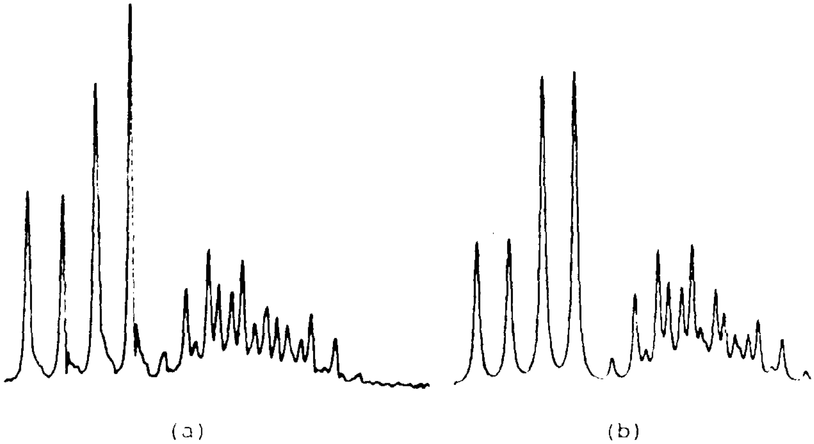


Fig. 1. Recorded (a) in CDCl$_3$ and simulated (b) AB part of the ^{19}F n.m.r. spectrum of $SF_5\overline{CFCF_2O}$. Linewidth = 2.6 Hz. $\phi^1-\phi^2$ = 1.02 ppm.

EXPERIMENTAL

$F_5SCH=CF_2$ was obtained via a modified literature [16] procedure as described by us [17], and $F_5SCF=CF_2$ was made by a similar procedure from $F_5SCHFCF_2Br$ [18]. Gases were manipulated in a conventional Pyrex-glass vacuum line, equipped with a mercury manometer and a Televac thermocouple gauge. Infrared spectra were obtained on a Nicolet 20 DX spectrometer. ^{19}F and ^{1}H n.m.r. spectra were recorded on a Varian EM-390 spectrometer (84.67 MHz for ^{19}F and 90.00 MHz for H), using either $Si(CH_3)_4$ or $CFCl_3$ as external references. The ^{13}C n.m.r. spectra were obtained with a Bruker AMX-400 spectrometer, at 100.6 MHz, with an internal deuterium lock.

Mass spectra were obtained on a VG 7070 HS mass spectrometer at 70 eV. Gas chromatograms were run with a Varian Aerograph and elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany.

Synthesis of $F_5S\overline{C(H,F)CF_2O}$

Methyl-tri-n-octylammonium chloride (1.50 g, 3.7 mmol, TCI) and 41.0 g of freshly prepared NaOCl+NaOH solution (calc. 11.8 % in NaOCl, 5 % in NaOH) were cooled in a 100 ml round-bottomed flask with stirring in an ice-salt bath to -12°C. Then, 4.72 g of $F_5SCF{=}CF_2$ (22.7 mmol) in 20 ml of CCl_2FCClF_2, precooled to -10°C, were added in three portions, with vigorous stirring. After each addition, 2 minutes elapsed before the next addition. The temperature had risen to -6°C after the third addition and had dropped to -10°C three minutes later; a ^{19}F n.m.r. spectrum indicated that all starting olefin was gone. The mixture was poured into a separatory funnel and the lower layer was transfered and dried at -5°C (Na_2SO_4, 16 h). The liquid was vacuum-transferred and distilled with a spinning band column; the product was removed from the head of the column and condensed in a -78°C trap; access of moisture to the cold-trap was prevented with a Drierite tube. After 5 h, 2.67 g (53 %) of product was collected. This material was virtually pure and contained only a trace of Freon 113 (g.c.). The infrared spectrum was identical with that of a sample of $F_5S\overline{CFCF_2O}$, purified by gas chromatography.

Infrared spectrum: (gas phase, 10 cm path length, KBr, 20 torr): (cm^{-1}); 1585 (m); 1530 (s); 1274 (vs); 1193 (s); 1133 (s); 1031 (m-s); 960 (w); 936 (m-s); 905 (vs); 863 (vs); 824 (m); 795 (w); 724 (m-w); 696 (m); 622 (m); 599 (m-s); 581 (m); 544 (w); 418 (w).

Mass spectrum (chemical ionization, mass, fragment, %): 209, $(M+H-O)^+$, 0.9; 127, SF_5^+, 9.1; 108, SF_4^+, 6.5; 98, $(M+H-SF_5)^+$, 3.4; 97, $(M-SF_5)^+$, 72.2; 89, SF_3^+, 43.8; 70, SF_2^+, 5.6; 59, C_2FO^+, 4.1; 51, SF^+, 12.1; 50, CF_2^+, 2.9.

<u>Anal.calcd.:</u> for C_2F_8OS: C, 10.72; F, 67,8; S, 14.31. Found, C, 10.54; F, 68.2; S, 14.37 %.

$F_5S\overline{CHCF_2O}$ was obtained in a similar fashion with CCl_4 at -10°C. The dried CCl_4 layer was distilled twice and gave a fraction with a boiling range 42.4-46.0 °C that consisted of $SF_5\overline{CHCF_2O}$ (87 % by g.c.) and CCl_4 (13 %). Further purification was achieved with preparative gas chromatography (30 % SE-30, 3m, 95 °C). Yield ≈ 30 %.

<u>Anal.Calcd.:</u> for C_2HF_7OS: C, 11.66; H, 0.49; F, 64.5; S, 15.56. Found: C, 11.76; H, 0.56; F, 63.7; S, 15.65 %.

The samples were generally stored at -196°C, but for $F_5S\overline{CFCF_2O}$ the observation was made that storage at room-temperature in glass vessels resulted in the formation of COF_2.

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