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THE PYROLYSIS OF 3-OXA-11-CHLORO-EICOSAFLUOROUNDECANE SULFINATE AND SULFONATE SALTS

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SUMMARY

The thermal decomposition of sodium 3-oxa-11-chloro-eicosafluoroundecane sulfinate **(1)** and potassium 3-oxa-11-chloro-eicosafluoroundecane sulfonate **(2)** were studied. 7- Chloro-tridecafluoroheptene-1 **(3)** , 1-hydro-7-chloro-tetradecafluoroheptane **(4)**, 1-hydro-3-oxa-11-chloro-eicosafluoroundecane **(5)**, methyl 8-chloro-tetradecafluorooctanate **(6)**, and methyl 3-oxa-11 - chloro - octadecafluoroundecanate **(7)** were isolated and characterized when compound **1** was pyrolyzed and then reacted with methanol. However, only 8-chloro-tetradecafluorooctanoic acid and its methyl ester were obtained in high yield when compound **2** was subjected to pyrolysis. A possible mechanism was proposed.

INTRODUCTION

Previous workers have shown that thermal decompositions of the alkali metal salts of perfluoroalkane sulfinates produced perfluoroolefins [1] in high yield. In this paper the pyrolysis of sodium 3-oxa-11-chloro-eicosafluoroundecane sulfinate **(1)** was studied in an attempt to get a perhalovinyl ether. Experimental results, however, showed that the carbon-oxygen bond in such a compound was cleaved following the fission of carbon-sulfur bond in a stepwise manner. Thus, a mixture of at least five compounds was obtained.

The above result prompted us to study the thermolysis of potassium 3-oxa-11- chloro-eicosafluoroundecane sulfonate (**2**), and it was found that this latter reaction furnished an effective method of preparing 8-chloro-tetradecafluorooctanoic acid and its derivatives.

RESULTS

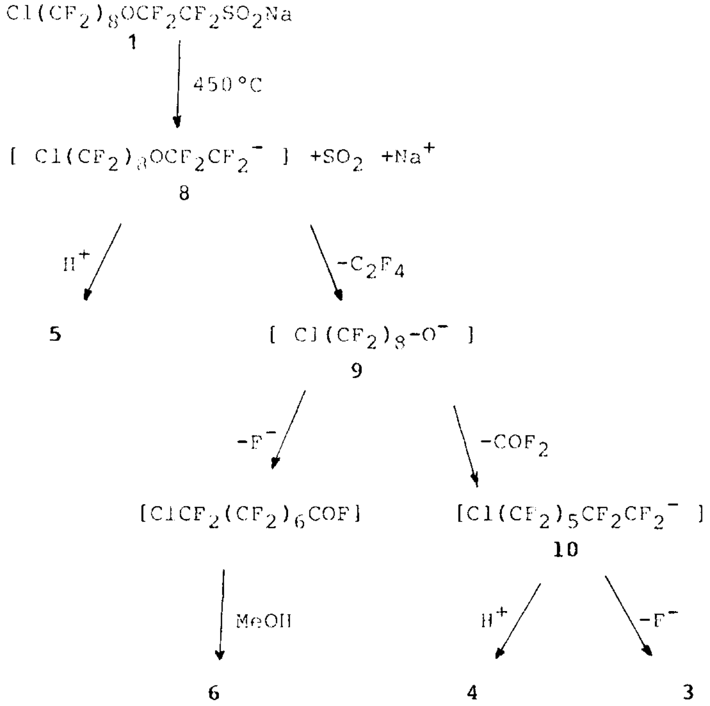
Compound **1** was pyrolyzed at about 450°C. From the methanolic solution of such a pyrolyzate, five components **3** - **7** were separated by semipreparative glc and identified spectroscopically. The result is shown in Table 1.

TABLE 1

Compound		%
$ClCF_2(CF_2)_4CF{=}CF_2$	(3)	22.6
$ClCF_2(CF_2)_5CF_2H$	(4)	6.8
$ClCF_2(CF_2)_6CF_2OCF_2CF_2H$	(5)	28.4
$ClCF_2(CF_2)_6COOCH_3$	(6)	28.2
$ClCF_2(CF_2)_6CF_2OCF_2COOCH_3$	(7)	2.9

*The percentage yield of these compounds were estimated by glc analysis of the crude products with 11.1% of them unidentified.

The formation of such compounds could be explained as follows:



Analogously to decarboxylation [2], sulfur dioxide was evolved from the sulfinate in the initial step of thermolysis to form carbanion **8**. Compound **5** was formed from such a carbanion by protonation . Further fission produced both alkoxide **9** and carbanion **10** which reacted further to give compounds **3**,**4** and **6** .

As the resulting mixture was strongly acidic, so compound **7** could be formed directly from compound **1** by acidic hydrolysis [3] [4].

The loss of SO_3 from the sulfonate was much more difficult than that of SO_2 from the sulfinate. Thus, the cleavage of the C-O bond took place simultaneously with that of C-S to give 8-chloroperfluorooctanoic acid in 93.0% yield when compound **2** was pyrolyzed.

EXPERIMENTAL

Melting and boiling points were uncorrected. ^1H and ^{19}F spectra were taken on a Varian EM-360L spectrometer at 60Hz using TMS and TFA (positive up field) as external standards respectively. The MS was measured with a Finnigan GC-MS 4021 Spectrometer. The IR spectra were recorded on IR-400 spectrometer. Product mixtures were separated by Shanghai Analytical Factory Model 102 glc with column packed with 15% oxaperfluoroalkylene triazine polymer.

The pyrolysis of compound 1

A mixture of 62g 3-oxa-11-chloro-eicosafluoroundecane sulfonyl fluoride [5] and 40g Na_2SO_3 was heated at 75-80°C for 8 hr. with vigorous stirring under N_2. The solution was then evaporated to dryness, extracted with ethyl acetate , and dried over Na_2SO_4. After the removal of solvent, 59g compound 2 was obtained, yield 92.3%. ^{19}F nmr (in i-PrOH) -9.0 (2F, s, $ClCF_2$); 4.7 (4F, s CF_2OCF_2) 42.5-47.3 (12F, m, $6\times CF_2$); 55.4 (2F, s, CF_2SO_2Na).

8g compound **1** was placed in a nickel tube heated at 450°C for 2-2.5 hr. using N_2 as carrier gas. The gas evoluted was absorbed by methanol. The methanolic solution was then refluxed for 4 hr., washed with water, 6.5g organic compound were separated. Pure compounds **3** - **7** were obtained by semi-preparative glc and characterized.

Compound **(3)**,[6] (Found: C, 22.59; F, 67.80; Cl, 9.63. Calc. for ClC_7F_{13}: C, 22.93; F, 67.39; Cl, 9.67); ir: 1792,(s) ($CF=CF_2$); ^{19}F nmr: -9.3 (2F, s, $ClCF_2$) 12.6 (1F, d,d,t, J=52.4, 40.6, 5.6Hz, C=CF); 28.5 (1F, d,d,t, J=115.0, 52.4, 25.3Hz; $R_fC=CF$) 40.3-45.6 (8F, m, 4xCF_2); 111.0 (1F, d,d,t, J=115.0, 40.6, 3.2Hz, $R_fFC=$) ;m/e: 366 [M^+] 347[M^+-F], 331 [M^+-Cl].

Compound **(4)**,nc,(Found: C,21.55; F, 68.78; Cl 9.12; Calc . for C_7HClF_{14}: C, 21.74, F, 68.82; Cl 9.17); ir: 1230.6 (s) (C-F); ^1H nmr: 6,00 (1H, t,t, 51.0, 5.4, Hz, HCF_2); ^{19}F nmr: -8.5 (2F, s, $ClCF_2$); 42.6-45.6 (8F, m, 4xCF_2); 52.0 (2F, s, CF_2CF_2H); 60.0 (2F, d, J=50.8Hz, HCF_2); m/e: 367 [M^+-F]; 351 [M^+-Cl].

Compound **(5)**,nc,(Found: C, 21.38; F, 68.67; Cl,6.76; Calc. for $C_{10}HClF_{20}O$: C, 21.74; F, 68.77; Cl, 6.41); ir: 1230.6 (s) (C-F); ^1H nmr: 5.83 (1H, t,t, J=51.0, 18Hz, HCF_2); ^{19}F nmr: -8.8 (2F, s, $ClCF_2$), 5.5 (2F,s, CF_2O); 11.5 (2F,s, OCF_2CF_2H ; 42.8-47.5 (12F, m, 6xCF_2); 60.0 (2F, d, J=50.7, HCF_2); m/e: 533 [M^+-F].

Compound **(6)**,nc, (Found: C, 23.94; H, 0.35; F, 59.93; Calc. for $C_9H_3ClF_{14}O_2$: C,24.31; H, 0.68; F, 59.83); ir 1797.0 (s) (C=O); ^1H nmr: 3.93(3H, s, OCH_3); ^{19}F nmr: -9.2 (2F, s, $ClCF_2$) 40.7-43.2 (12F, m, 6xCF_2); m/e: 459 [M^++15]; 445 [M^++1].

Compound **(7)** , nc, (Found C, 21.79; H, 0.29; F, 62.40; Cl, 6.27; Calc. for $C_{11}H_3ClF_{18}O_3$: C, 21.88; H, 0.55; F, 62.35; Cl, 6.46); ir: 1805.4 (s), (C=O); ^1H nmr: 3.90 (3H, s, OCH_3); ^{19}F nmr: -9.5 (2F, s, $ClCF_2$) 0.3 (2F, s, OCF_2COOMe) , 5.0 (2F, s, CF_2O), 43.3-47.3 (12F, m, 6xCF_2); m/e: 575 [M^++15]; 561 [M^++1].

Preparation of potassium 3-oxa-11-chloro-eicosafluoroundecane sulfonate (2)

38g 3- oxa - 11 - chloro - eicosafluoroundecane sulfonyl fluoride, 5g KOH, 50ml water and 6ml ethanol were refluxed for 8 hr. The sulfonate was filtered, dried to give 33g compound **2**, yield 83.3%, crystallized from acetone- chloroform, (Found: C ,17.84; F, 56.52; Calc. for $C_{10}ClF_{20}SO_3K$: C, 17.90; F, 56.66); ^{19}F nmr (in i-PrOH): -12.1 (2F, s, $ClCF_2$), 1.7,2.5 (4F, s, CF_2OCF_2); 39.6 (2F, s, CF_2SO_3K), 40.7-44.9 (12F, m, $6xCF_2$).

The Pyrolysis of Compound 2:

In a similar way , 5g compound 2 was pyrolyzed at 550°C to yield 1.5g white solid, 8-chlorotetradecafluorooctanoic acid,m.p 49-50°C(Lit. 50°C[7]). ^1H nmr (in i-PrOH): 5.55 (1H, s, COOH), ^{19}F nmr : -9.3 (2F, s, $ClCF_2$), 41.0-44.0 (12F, m ,$6xCF_2$); m/e: 431 $[M^+ +1]$.

From the methanolic solution, 1.5g methyl 8-chlorotetradecafluorooctanate was separated and identified by comparison of the spectra with those of an authentic sample. Total yield 93.0%.

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