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## FLUORINATED MONOCARBOXYLIC ACIDS

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It has been shown previously [1] that 1,1-dichloro-2-iodotrifluoroethane reacts with oleum to give dichlorofluoroacetyl fluoride. By extending this reaction to the higher iodofluoroalkanes, which are obtained by the telomerization of tetrafluoroethylene with iododichlorotrifluoroethane [3], we have obtained the dichloroperfluormonocarboxylic acid fluorides

$$CF_2CICFCI_1 + CF_2 = CF_2 \rightarrow CF_2CICFCI(CF_2)_n CF_2 = \xrightarrow{SO_3} CF_2CICFCI(CF_2)_n COF$$

with n = 1, 3, 5.

As the chain lengthens so the reaction becomes more difficult; thus dichloroiodotrifluoroethane reacts with 10% oleum at 100°, 1,2-dichloro-4-iodoperfluorobutane at 150-160°, whereas 1,2-dichloro-6-iodoperfluorohexane and 1,2-dichloro-8-iodoperfluoroctane react only with 45% oleum in an autoclave at 200-250°. The acyl fluorides obtained were converted into anilides and acids.

#### EXPERIMENTAL PART

<u>3,4-Dichloroperfluorobutyryl fluoride</u>. Into a two-necked flask, fitted with a stirrer and a reflux condenser connected with a descending condenser, were placed 57 g (0.15 M) 1,2-dichloro-4-iodoperfluorobutane and 150 ml 10% oleum (s.g. 1.86). The mixture was stirred and heated on an oil bath at 150-160° for 1 hr. 33.6 g of liquid were collected in the trap. On redistilling this liquid 25 g of dichloroperfluorobutyric acid was obtained, 67.7% yield; b.p. 73-74°. Found: C 19.28; F 44.97%. C<sub>4</sub>F<sub>6</sub>Cl<sub>2</sub>O. Calculated: C 19.28; F 45.78%.

The first fraction (3.9 g, b.p. 40.73°) consisted of a mixture of 1,2-dichloro-4-iodoperfluorobutane and 3,4dichloroperfluorobutyryl fluoride. Unreacted dichloroiodoperfluorobutane remained in the residue. The anilide of 3,4-dichloroperfluorobutyric acid has m.p. 64-65° (from pentane). Found: C 37.23; H 1.94; F 28.69; N 4.63%.  $C_{10}H_{6}F_{5}Cl_{2}NO$ . Calculated: C 37.27; H 1.86; F 29.50; N 4.35%.

<u>3,4-Dichloroperfluorobutyric acid.</u> 7.5 g (0.03 M) 3,4-dichloroperfluorobutyryl fluoride was added gradually with stirring to 20 ml 20% potassium hydroxide. The solution was acidified with 50% sulfuric acid, the layers separated and dried over magnesium sulfate. The aqueous acidic solution was extracted with ether. On distillation 6.1 g 3,4-dichloroperfluorobutyric acid was obtained: yield 83.4%; b.p. 178-179°;  $N_D^{20}$  1.3470;  $d_4^{20}$  1.710; found MR 32.98; calculated for C<sub>4</sub>HF<sub>5</sub>Cl<sub>2</sub>O<sub>2</sub>, MR 32.65; neutralization equivalent found 246.3, calculated 247.0. Found: C 19.14; 19.19; H 0.33; 0.32%. C<sub>4</sub>HF<sub>5</sub>Cl<sub>2</sub>O<sub>2</sub>. Calculated: C 19.43; H 0.40%. The an ilinium salt has m.p. 108-109° (from dichloroethane). Found: C 35.43; H 2.33; F 28.38; N 4.20%. C<sub>10</sub>HgF<sub>5</sub>Cl<sub>2</sub>NO<sub>2</sub>. Calculated: C 35.29; H 2.35; F 27.94; N 4.12%.

<u>Methyl 3,4-dichloroperfluorobutyrate</u>  $3.7 \text{ g}(0.015 \text{ M})^3$ ,4-Dichloroperfluorobutyryl fluoride was added to 10 ml absolute methanol. The reaction mixture was heated for 2 hr on a water bath and then diluted with water. The lower

layer was separated, washed with water, sodium bicarbonate soltuion, and again with water, dried over calcium chloride, and distilled. 3.1 g Methyl 3,4-dichloroperfluorobutyrate was obtained; yield 80%, b.p. 143°;  $n_D^{20}$  1.3692;  $d_4^{20}$  1.585. Found: C 23.50; 23.36; H 1.22; 1.16%; MR 37.07. C<sub>5</sub>H<sub>3</sub>F<sub>5</sub>Cl<sub>2</sub>O<sub>2</sub>. Calculated: C 23.00; H 1.15%; MR 37.37.

5,6-Dichloroperfluorocaproic acid. 16 g 5,6-dichloro-1-iodoperfluorohexane and 10 ml 45% oleum (s.g. 1.98) were placed in a 50 ml steel ampoule. The ampoule was sealed and heated at 100° for 7 hr. The contents of the ampoule were emptied into a separating funnel, the upper light layer separated, and distilled. A fraction was separated with b.p. 115-130°. A second distillation gave 5,6-dichloroperfluorocaproyl chloride, b.p. 117-118°. Neutralization equivalent; found 181; calculated for  $C_6F_{10}Cl_2O$  174.5. Ionic fluorine; 4.47%. The anilide has m.p. 84° (from heptane). Found: C 34.19; 33.91; H 1.90; 1.96; F 40.11; 40.36%.  $C_{12}H_6F_9Cl_2NO$ . Calculated: C 34.12; H 1.42; F 40.52%.

In another similar experiment the product was separated, washed with water, and treated with sodium bicarbonate solution. The unreacted dichloroiodoperfluorohexane (2 g), which did not dissolve in the sodium bicarbonate, was separated. The bicarbonate solution was acidified with 50% sulfuric acid and extracted with ether. The ether extract was dried with magnesium sulfate, the ether evaporated, and the residue distilled in vacuum. 6.6 g 5.6-dichloroperfluorocaproic acid was obtained; yield 65%, based on dichloroiodoperfluorohexane consumed; b.p. 138° (63 mm); m.p. ~10°; n<sub>D</sub><sup>20</sup> 1.3612; d<sup>20</sup><sub>4</sub> 1.814; found MR 42.34; calculated for C<sub>6</sub>HF<sub>9</sub>Cl<sub>2</sub>O<sub>2</sub> MR 42.43; neutralization equivalent found 343.4; calculated 347.0. Found: C 20.80; 21.27; H 0.70; 0.44; F 50.69; 50.30% C<sub>6</sub>HF<sub>9</sub>Cl<sub>2</sub>O<sub>2</sub>. Calculated C 20.75; H 0.29; F 49.28%. The anilinium salt has m.p. 84° (from dichloroethane). Found: C 32.91; 32.88; H1.76; 1.96; F 37.88; 37.95%. C<sub>12</sub>H<sub>8</sub>F<sub>9</sub>Cl<sub>2</sub>NO<sub>2</sub>. Calculated C 32.73; H 1.82; F 38.86%

<u>7,8-Dichloroperfluorocaprylic acid</u>. In a similar way 7,8-dichchloroperfluorocapryloyl fluoride, b.p. 160-161°, was obtained by heating 22 g (0.037 M) 7,8-dichloro-1-iodoperfluorooctane with 15 ml 45% oleum at 250° for 16 hr. Found: C 20.99; 21.00; F 58.37; 57.07%. C<sub>8</sub>F<sub>14</sub>Cl<sub>2</sub>O. Calculated: C 21.38; F 59.24%.

The acyl fluoride was hydrolyzed and the ionic fluoride determined thoriometrically; found 3.45%; calculated for CF<sub>2</sub>ClCFCl(CF<sub>2</sub>)<sub>5</sub>COF 4.23%. The anilide has m.p. 114° (from dichloroethane). Found: C 33.01; 32.85; H 1.12; 1.13; F 46.19; 45.65% C<sub>14</sub>H<sub>6</sub>F<sub>13</sub>Cl<sub>2</sub>NO. Calculated: C 32.19; H 1.15; F 47.32%.

7,8-Dichloroperfluorocaprylic acid was obtained in 65.5% yield, calculated on 7,8-dichloro-1-iodoperfluoroctane consumed; b.p. 155° (58 mm); m.p. 51°. Neutralization equivalent found 449.9, 451.2; calculated 447. Found: C 21.09; 21.19; H 0.36; 0.34; F 53.12; 53.96%.  $C_8HF_{13}Cl_2O_2$ . Calculated: C 21.47; H 0.23; F 55.26%. The anilinium salt has m.p. 109° (from benzene). Found C 31.77; 31.93; H 1.17; 1.32; F 44.88; 45.36; N 2.56; 2.57%  $C_{14}H_8F_{13}Cl_2NO_2$ . Calculated: C 31.11; H 1.48; F 45.74; N 2.59%.

### SUMMARY

1. Fluorinated aliphatic acid fluorides have been formed by the action of oleum on iodofluoroalkanes having a  $CF_2I$  end group.

2. Dichloroperfluoro-butyric, -caproic, and -caprylic acids have been prepared.

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