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Abstract

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ANIONOTROPIC REARRANGEMENT OF SUBSTITUTED PERFLUOROPROPENES

As we have shown ([1]), in the interaction of perfluoropropylene and perfluoroisobutylene with alcohols and amines, addition and vinylic substitution reactions compete. Allylic substitution is not observed, which indicates that in the molecules of these fluoroolefins the conjugation effect of the double bond with the C–F bond in the CF_3 group is weakly expressed. From this point of view, the reactions of chlorofluoropropenes and butenes, in particular perfluoroallyl chloride, $CF_2{=}CF{-}CF_2Cl$, are of great interest. There is an indication ([2]) that the action of nucleophilic reagents on perfluoroallyl chloride leads to replacement of chlorine by the corresponding anion, which, as may be supposed, is a consequence of conjugation of the C–Cl bond with the double bond.

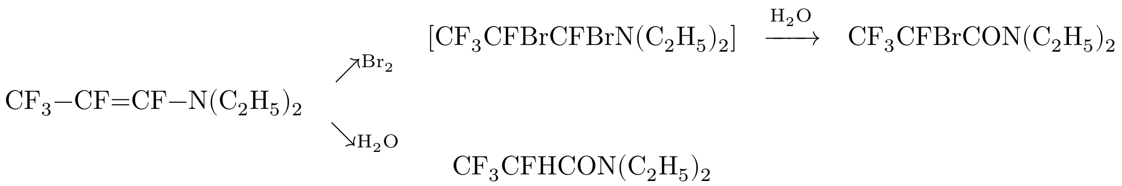
We investigated the reactions of perfluoroallyl chloride with sodium methylate and diethylamine. Interaction with sodium methylate leads to perfluoroallyl methyl ether, the structure of which we proved by bromination and subsequent hydrolysis to the methyl ester of α,β-dibromoperfluoropropionic acid. Thus, this reaction represents a new route to derivatives of perfluoroacrylic acid.

It turned out that perfluoroallyl methyl ether, on storage even at reduced temperature, isomerizes into perfluoropropenyl methyl ether; the structure of the latter was confirmed by bromination and then hydrolysis with formation of the methyl ester of α-bromoperfluoropropionic acid.

$$\begin{array}{ccc}
\mathrm{CF_2{=}CF{-}CF_2OCH_3} & \longrightarrow & \mathrm{CF_3{-}CF{=}CF{-}OCH_3} \\
\downarrow \mathrm{Br_2} & & \downarrow \mathrm{Br_2} \\
\mathrm{CF_2BrCFBrCF_2OCH_3} & & \mathrm{CF_3CFBrCFBrOCH_3} \\
\downarrow \mathrm{H_2SO_4} & & \downarrow \mathrm{H_2SO_4} \\
\mathrm{CF_2BrCFBrCOOCH_3} & & \mathrm{CF_3CFBrCOOCH_3}
\end{array}$$

Perfluoroallyl chloride readily reacts with diethylamine. The perfluoroallyldiethylamine formed in this process rearranges, already during the reaction, into perfluoropropenyldiethylamine, the hydrolysis of which leads to the diethylamide of α-hydroperfluoropropionic acid. Bromination of perfluoropropenyldiethylamine with subsequent hydrolysis gives the diethylamide of α-bromoperfluoropropionic acid.

$$CF_2{=}CF{-}CF_2Cl + HN(C_2H_5)_2 \longrightarrow [CF_2{=}CF{-}CF_2N(C_2H_5)_2] \longrightarrow$$



$$CF_3{-}CF{=}CF{-}N(C_2H_5)_2 \begin{cases} \xrightarrow{Br_2} [CF_3CFBrCFBrN(C_2H_5)_2] \xrightarrow{H_2O} CF_3CFBrCON(C_2H_5)_2 \\ \xrightarrow{H_2O} CF_3CFHCON(C_2H_5)_2 \end{cases}$$

The isomerization noted represents an allylic rearrangement and, apparently, is due to a tendency toward formation of a system,

more stable owing to conjugation of the double bond with the unshared electron pair of the substituent in the allylic position.

$$CF_2{=}CF{-}CF_2X \longrightarrow CF_3{-}CF{=}CFX$$

The rate of rearrangement depends on the degree of mobility of the electron pair:

$CF_2{=}CF{-}CF_2Cl$	most stable—rearrangement is not observed
$CF_2{=}CF{-}CF_2OCH_3$	relatively stable—rearranges on standing
$CF_2{=}CF{-}CF_2N(C_2H_5)_2$	completely unstable—rearranges immediately

Experimental Part

Perfluoroallyl methyl ether. To a solution of 59 g (0.35 mol) of perfluoroallyl chloride in 100 ml of abs. methanol containing phenolphthalein, cooled to −(10-15)° and stirred, there was added dropwise a solution of sodium methylate prepared from 4.6 g (0.20 g-atom) of sodium and 100 ml of abs. methanol, at such a rate that the alkali had time to react. After the addition was complete, the unreacted olefin was distilled off, and the reaction mixture was poured into water. The separated oil was dried over calcium chloride and distilled. After distilling off a small amount of the starting olefin (total weight 16 g), perfluoroallyl methyl ether was collected in the interval 30-41°/765 mm; the bulk distilled at 38-41°/765 mm. Yield 21.8 g (67% of theory, or 52% calculated on the olefin consumed). As a result of redistillation a substance was obtained with b.p. 38.5°, n_D^{20} 1.3000, d_4^{20} 1.3683. Found MR_D 21.91, calculated for $C_4F_5H_3OF$ MR_D 22.55. Literature data (2): b.p. 38.5°, n_D^{20} 1.296, d_{20} 1.358.

Found, %: C 29.55; H 1.87
$C_4F_5H_3O$. Calculated, %: C 29.64; H 1.86

β,γ-Dibromoperfluoropropyl methyl ether. Obtained in 82% of theory by the action of an excess of dry bromine on perfluoroallyl methyl ether with cooling by ice water. B.p. 136-138°/764 mm, after redistillation—136°, n_D^{20} 1.4090, d_4^{20} 2.1136. Found MR_D 37.36, calculated for $C_4F_5Br_2H_3O$ MR_D 38.54.

Found, %: C 14.45; H 0.93
$C_4F_5Br_2H_3O$. Calculated, %: C 14.92; H 0.94

Methyl ester of α,β-dibromoperfluoropropionic acid. A mixture of 10 g of dibromoperfluoropropyl methyl ether, 4 ml of conc. H_2SO_4, and 4 g of powdered glass was heated with stirring for 5 h at 100-105°. As a result of the usual work-up, 7.2 g (77% of theory) of methyl ester of α,β-dibromoperfluoropropionic acid was obtained, with b.p. 63-65°/22 mm. For determination of the constants and analysis the substance was distilled a second time: b.p. 70.5°/28 mm, n_D^{20} 1.4380, d_4^{20} 2.0598. Found MR_D 38.23, calculated for $C_4F_3Br_2H_3O_2$ MR_D 38.27.

Found, %: C 15.92; H 1.06
$C_4F_3Br_2H_3O$. Calculated, %: C 16.01; H 1.00

Amide of α,β-dibromoperfluoropropionic acid. The substance was obtained from the methyl ester of the acid by the action of an aqueous-alcoholic solution of ammonia. M.p. 61.5-62.5° (from *n*-hexane). Literature data (3)*: m.p. 60.6-61.6°.

Found, %: C 12.70; H 0.87; F 20.13; Br 56.11; N 5.06
$C_3F_3Br_2H_2ON$. Calculated, %: C 12.64; H 0.71; F 20.00; Br 56.10; N 4.91

* The substance was obtained by hydrolysis of $CF_2BrCFBrCN$.

Perfluoropropenyl methyl ether. This compound is formed as a result of the spontaneous isomerization of perfluoroallyl methyl ether, which occurs on storage for several days. B.p. 52.0-52.5°, n_D^{20} 1.3045, d_4^{20} 1.3605. Found MR_D 22.44; calculated for $C_4F_5H_3OF$, MR_D 22.55.

Found, %: C 29.29; H 1.97; F 58.92
$C_4F_5H_3O$. Calculated, %: C 29.64; H 1.86; F 58.61

α,β-Dibromoperfluoropropyl methyl ether. Obtained in 87% yield by the action of dry bromine on perfluoropropenyl methyl ether with cooling by ice water. B.p. 134°/736 mm, n_D^{20} 1.4040, d_4^{20} 2.0510. MR_D found 38.41; calculated for $C_4F_5Br_2H_3O$, MR_D 38.54. Literature data (1): b.p. 128-132°/732 mm.

Found, %: C 15.20; H 0.97
$C_4F_5Br_2H_3O$. Calculated, %: C 14.92; H 0.94

Methyl ester of α-bromoperfluoropropionic acid. The substance was obtained by hydrolysis of α,β-dibromoperfluoropropyl methyl ether as described by us previously (1). Yield 56%, b.p. 101-108°, n_D^{20} 1.3592. Literature data (1): b.p. 105-107°, n_D^{20} 1.3620.

Amide of α-bromoperfluoropropionic acid. Obtained from the methyl ester of the acid by the action of a concentrated aqueous solution of ammonia; m.p. 89.5-90.5° (from *n*-hexane). A mixed sample with an authentic specimen melted without depression. Literature data (1): m.p. 90.0-90.5°.

Perfluoropropenyldiethylamine. To a solution of 16.6 g (0.1 mole) of perfluoroallyl chloride in 50 ml of absolute ether at −(30-25)° and with vigorous stirring for 2 h was added a solution of 11 g (0.15 mole) of diethylamine in 30 ml of absolute ether. After 30 min, when the temperature of the mixture had risen to room temperature, the precipitate of diethylamine hydrochloride was filtered off, and the residue after distilling off the ether was distilled in vacuo in a stream of dry air. There was obtained 7.2 g (47% of theory) of perfluoropropenyldiethylamine as a mobile liquid with an unpleasant odor, very readily hydrolyzed in air. B.p. 56-59°/49 mm, n_D^{20} 1.3715. By hydrolysis of perfluoropropenyldiethylamine, diethylamide of α-hydroperfluoropropionic acid was obtained, with b.p. 67.5-68.0°/5 mm and n_D^{20} 1.3938. Literature data (1): b.p. 89°/22 mm, n_D^{20} 1.3910. The identity of the compound obtained with an authentic specimen was confirmed by the method of nuclear magnetic resonance.

Diethylamide of α-bromoperfluoropropionic acid. To a solution of 6.4 g of perfluoropropenyldiethylamine in 30 ml of dry methylene chloride was added an excess of dry bromine in the same solvent. After standing for half an hour at room temperature, the mixture was poured into water; the organic layer was washed with sodium bisulfite solution and with water and dried over calcium chloride. After removal of the solvent, the residue was distilled in vacuo. There was obtained 5.4 g (61% of theory) of diethylamide of α-bromoperfluoropropionic acid, having the following constants: b.p. 98-99°/23 mm, n_D^{20} 1.4200, d_4^{20} 1.5042. Found MR_D 47.12; calculated for $C_7F_4BrH_{10}ON$, MR_D 46.63.

Found, %: C 30.23; H 3.54; N 5.31; Br 28.53; F 27.72
$C_7F_4BrH_{10}NO$. Calculated, %: C 30.01; H 3.59; N 5.00; Br 28.53; F 27.13

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Note: Figure translations are in progress. See original paper for figures.

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