BISTRIFLUOROMETHYLKETENE AND PERFLUOROMETHACRYLIC ACID COMMUNICATION 4. PYROLYSIS OF SOME DERIVATIVES OF α -HYDROHEXAFLUOROISOBUTYRIC ACID

Yu. A. Cheburkov and I. L. Knunyants Institute of Heteroorganic Compounds, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya No. 9, pp. 1573-1576, September, 1963 Original article submitted July 13, 1962

In this work we investigated some pyrolytic reactions, as a result of which we developed a method of synthesizing methyl perfluoromethacrylate. In the investigation of the decarboxylation of potassium α -hydrohexafluoroisobutyrate it was noted that the composition of the mixture of products depends greatly on the reaction conditions. Thus, when the salt is, heated in ethyl acetate 2-hydropentafluoropropene is obtained in quantitative yield[1], when it is heated in water the only reaction product is 2,2-dihydrohexafluoropropane, and on pyrolysis of the dry salt α hydrohexafluoroisobutyryl fluoride and 2-hydropentafluoropropene are formed in approximately equal amounts.

$$(CF_3)_2 CHCOOK \xrightarrow{H_1O} CF_3CH = CF_2 > 90\%$$

$$(CF_3)_2 CHCOOK \xrightarrow{H_1O} CF_3CH_2CF_3 \sim 40\%$$

$$Dry salt \rightarrow CF_3CH = CF_2 (50\%) \approx nd(CF_3)_2CHCOF(50\%)$$

The alkali formed in the decarboxylation of the salt in water reacts with potassium hexafluoroisobutyrate with elimination of hydrogen fluoride, which leads ultimately to the mineralization of all the fluorine. This explains the low yield of hexafluoropropane*. Analysis of the impure α -hydrohexafluoroisobutyryl fluoride obtained in the pyrolysis of the dry salt with the aid of gas-liquid chromatography showed that it contained 10-15% perfluorometh-acryloyl fluoride impurity, which could be formed under the pyrolysis conditons from hexafluoroisobutyryl fluoride by the elimination of hydrogen fluoride. The correctness of this view was verified experimentally, and it was found that in the pyrolysis of the acid fluoride on glass wool at 400° perfluoromethacryloyl fluoride, bistrifluoromethylketene, α -hydrohexafluoroisobutyric acid, and 2-hydropentafluoropropene are formed.

$$(CF_3)_2 CHCOF \xrightarrow{400^\circ} CF_2 = C (CF_3) COF; \quad (CF_3)_2 C = CO; \quad (CF_3)_2 CHCOOH; \quad CF_3 CH = CF_2$$

The hydrogen fluoride liberated reacts with the glass with formation of water, which then adds to bistrifluoromethylketene and so reduces its yield at the expense of the formation of the acid.

$$HF + SiO_2 \rightarrow SiF_1 + H_2O$$
$$(CF_3)_2 C = CO + H_2O \rightarrow (CF_3)_2 CHCOOH$$

With rise in temperature the 2-hydropentafluoropropene content of the pyrolysis products increases as a result of the cleavage of a carbon-carbon bond and the elimination of carbonyl difluoride.

$$(CF_3)_2$$
 CHCOF $\xrightarrow{> 600^\circ}$ CF₃CII = CF₂ + COF₂

It is interesting to compare the result of the pyrolysis of α -hydrohexafluoroisobutyryl fluoride with the action of anhydrous potassium fluoride on this substance. Whereas in the first case the removal of a fluorine atom as hydrogen

^{*}A good yield of 2,2-dihydrohexafluoropropane is obtained by heating triethylamine α -hydorhexafluoroisobutyrate.

fluoride proceeds mainly from the trifluoromethyl group, in the second case the fluoride ion is eliminated exclusively from the fluorocarbonyl group with formation of bistrifluoromethylketene dimer.

$$(CF_3)_3 CHCOF + KF \rightarrow [(CF_3)_2 C = CO]_2 + KHF_2$$

In the reaction of perfluoromethacryloyl fluoride with methanol we were unable to arrest the reaction at the stage of the perfluoromethacrylic ester: a second molecule of alcohol added to the double bond of the latter with formation of methyl 3,3-difluoro-3-methoxy-2-(trifluoromethyl)propionate.

 $\mathbf{CF_3} = \mathbf{C} \ (\mathbf{CF_3}) \ \mathbf{COF} \xrightarrow{\mathbf{CH_3OH}} [\mathbf{CF_2} = \mathbf{C} \ (\mathbf{CF_3}) \ \mathbf{COOCH_3}] \rightarrow \mathbf{CH_3OCF_2CH} \ (\mathbf{CF_3}) \ \mathbf{COOCH_3}$

The possibility of the latter reaction is associated with the marked electrophilic character of the double bond of perfluoromethacrylic compounds. If we compare perfluoronsobutene with perfluoromethacryloyl fluoride it will be seen that in the latter compound the electronegative trifluoromethyl group is replaced by the still more electronegative fluorocarbonyl group.



It is known that the effect of the presence of two trifluoromethyl groups in perfluoroisobutene is manifested in the particular ease with which nucleophilic additions occur. In a homogeneous medium perfluoroisobutene reacts even with pure water [2]. These reactions should go just as readily with perfluoromethacrylic acid, which is indeed observed. After the protection of the double bend in perfluoromethacryloyl fluoride by the addition of chlorine no difficulty was experienced in obtaining the desired product, and methyl perfluoromethacrylate was synthesized from α , β -dichloropentafluoroisobutyryl fluoride after methanolysis and dehalogenation with zinc.

$$CF_{3} = C (CF_{3}) COF \xrightarrow{CI_{3}} CF_{2}CICCI (CF_{3}) COF \xrightarrow{CH_{3}OH} CF_{2}CICCI (CF_{3}) COOCH_{3} \xrightarrow{Zn} \\ \rightarrow CF_{2} = C (CF_{3}) COOCH_{3}$$

This ester did in fact react slowly with pure water in absence of catalyst and solvent, and a molecule of methanol added at the double bond with evolution of heat.

$$CF_3 = C(CF_3)COOCH_3 + CH_3OH \rightarrow CH_3OCF_2CH(CF_3)COOCH_3.$$

EXPERIMENTAL

Pyrolysis of Potassium α -Hydrohexa fluoroisobutyrate. 2 g of the dry salt was heated in a stream of nitrogen at 140-150° in a round-bottomed flask. The decomposition products were collected in a trap at - 75°. We obtained 1.4 g of liquid, which was analyzed on the chromatographic column described in Communication 2. Composition: 48% 2-hydropenta fluoropropene, 45% α -hydrohexa fluoroisobutyryl fluoride, and 7% perfluoromethacryloyl fluoride. At a temperature of not above 0° to 1.2 g of hexa fluoroisobutyric acid we added an equimolecular amount of triethylamine and stirred well. Liberation of gas began at room temperature and went briskly at 40°. In all 0.8 g of gas was condensed in the trap, and it was identified on the chromatographic column as 2,2-dihydrohexa fluoropropane; yield 85%.

An aqueous solution of 10.4 g of potassium α -hydrohexafluoroisobutyrate was boiled under reflux. The gas liberated was washed with water, dried with calcium chloride, and collected in a trap. We obtained 2.7 g (40%) of 2,2-dihydrohexafluoropropane, b.p. from - 1.8 to - 1.4°; mol.wt. found, 149; calculated, 152. Found: C 23.30; H 1.60; F 74.51%. C₃F₆H₂. Calculated: C 23.68; H 1.32; F 75.00%. The literature [3] gives b.p. - 0.7°.

Pyrolysis of α -Hydrohexa fluoroisobutyryl Fluoride. The pyrolysis of the acid fluoride was carried out in a glass tube, $\frac{4}{4}$ mm in diameter, filled with glass wool and heated over a length of 450 mm with an electric spiral.

The tube was heated to 400°, and 100 g of the acid fluoride was passed in dropwise in a stream of nitrogen over a period of two hours. The reaction products were collected in a trap containing roasted calcium chloride. We obtained 75 g of pyrolyzate, by the fractionation of which, first through a low-temperature column and then through an ordinary column, we obtained the following fractions: I (7.1 g), b.p. up to 4°; II (7.1 g), b.p. 5-30°; III (22.3 g) unchanged original acid fluoride, b.p. 31-33°; IV (25.0 g) perfluoromethacryloyl fluoride; b.p. 52° (760 mm); n_D^{20} 1.3025; d_2^{20} 1.4710. Found: C 26.96; F 62.37%. C₄F₆O. Calculated: C 26.97; F 64.04%.

Chromatographic analysis of Fractions I and II showed that Fraction I consisted mainly of 2-hydropentafluoropropene and Fraction II was bistrifluoromethylketene. On distillation of 8.5 g of the residue in the still from its mixture with concentrated sulfuric acid we obtained 5 g of α -hydrohexafluoroisobutyric acid, m.p. 52°.

Reaction of α -Hydrohexafluoroisobutyryl Fluoride with Potassium Fluoride. A mixture of 2.2 g of the acid fluoride and 0.7 g of anhydrous potassium fluoride was heated in a sealed tube at 100° for 16 hours. Distillation of the reaction mixture from an oil bath at 150° then gave a liquid, which was analyzed on a chromatographic column. It contained 65% unchanged original acid fluoride and 35% bistrifluoromethylketene dimer, identical with the compound described in Communication 2 of this series.

 α , B-Dichloropentafluoroisobutyryl Fluoride. This was prepared in 80% yield by the ultraviolet irradiation of an equimolecular mixture of perfluoromethacryloyl fluoride and chlorine in a sealed quartz tube; b.p. 68.5° (746 mm); n_D^{20} 1.3346; d_4^{20} 1.642. Found: C 19.17, F 45.01%. C₄F₆Cl₂O. Calculated: C 19.27; F 45.80%.

The NMR spectrum of the product[•] contains three lines having chemical shifts, measured relative to CF_2Cl_2 , of -42, + 48, and + 59, which can be assigned to the groups COF, CF_2Cl_1 and CF_3 , respectively [4]. The NMR spectrum of the isomeric α -chlorohexafluoroisobutyryl chloride, which has identical constants (b.p. 69.5°; n_D^{20} 1.3345; d_4^{20} 1.647), was determined for comparison purpose and contains only one line, which according to its intensity and shift (+ 59) is to attributed to two trifluoromethyl groups.

<u>Methyl</u> α , β -Dichloropentafluoroisobutyrate. This was prepared by the methanolysis of the corresponding acid fluoride; b.p. 134-135° (748 mm); n_D^{20} 1.3728; d_4^{20} 1.5721. Found: C 23.14; H 1.55%. C₅F₅H₃Cl₂O₂. Calculated: C 23.00; H 1.15%.

<u>Methyl Perfluoromethacrylate</u>. This was prepared in 77% yield by the dechlorination of methyl α , β -dichloropentafluoroisobutyrate with zinc in dry ether; b.p. 90-92°; n_D^{20} 1.3288; d_4^{20} 1.373 Found: C 30.85; H 2.11; F 49.34%. C₅F₅H₃O₂. Calculated: C 31.60; H 1.58; F 50.00%.

<u>Methyl 8,8-Difluoro-8-methoxy- α -(trifluoromethyl) propionate.</u> 7.3 g of perfluoromethacryloyl fluoride was added to cooled methanol, and when the exothermic reaction had stopped the mixture was refluxed for four hours and then diluted with water. The oil that separated was taken up in ether and dried with calcium chloride. After two vacuum distillations we isolated two fractions: I (6.1 g), b.p. 78-81° (60 mm); II (1.5 g), b.p. 100-102° (57 mm) and n_{20}^{20} 1.3708.

Fraction II was not investigated, but Fraction I was found to be methyl β , β -difluoro- β -methoxy- α -(trifluoro-methyl) propionate, n_D^{20} 1.3435; d_4^{20} 1.382; yield 67%. Found: C 32.60; H 3.40; F 42.92%. C₆F₅H₇O₃. Calculated: C 32.43; H 3.15; F 42.79%.

With the aid of gas-liquid chromatography the ester obtained was shown to be identical with the product of the reaction of methyl perfluoromethacrylate with absolute methanol. The yield in this case was more than 90%.

SUMMARY

1. In the pyrolysis of α -hydrohexafluoroisobutyryl fluoride fluorine atoms are eliminated as hydrogen fluoride both from the trifluoromethyl and from the fluorocarbonyl group, which leads to a mixture of bistrifluoromethylketene and perfluoromethacryloyl fluoride. On the other hand, under the action of potassium fluoride the elimination of a fluoride ion proceeds only from the fluorocarbonyl group.

2. It was shown that the double bond in perfluoromethacrylic compounds is highly active toward the addition of nucleophilic agents.

LITERATURE CITED

1. I. L. Knunyants and Yu. A. Cheburkov, Authors' Certificate, No. 130895, (1960).

2. I. L. Knunyants, M. P. Krasusskaya and Yu. A. Cheburkov, Authors' Certificate, No. 129653, (1960).

•NMR spectra were determined by Yu. S. Konstantinov at Moscow State University.

- 3. A. Henne and T. Waalkes, J. Amer. Chem. Soc. 68, 496 (1946).
- 4. Yu. S. Konstantinov, Dokl. AN SSSR 134, 868 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.