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We had earlier reported on the production of perfluorodimethylketene (I) by the dehalogenation of α -haloperfluoroisobutyryl halides [1]; however, the question of the influence of the solvent upon the yield of bis-tri-fluoromethylketene was not considered. In the production of the ketene (I) in large quantities by the dehalogenation of α -bromoperfluoroisobutyryl chloride with zinc in dibutyl ether, it was found that the yield of the ketene (I) does not exceed 40%. If the dehalogenation is conducted in diethyl ether, the yield of the ketene (I) is negligible, and the main reaction product is the ethyl ester of hexafluoroisobutyryl chloride in the presence of zinc chlorobromide, followed by reduction of the ethyl ester of α -bromoper-fluoroisobutyryl chloride in the presence of zinc chlorobromide, followed by reduction of the ethyl ester of α -bromoper-fluoroisobutyric acid with zinc in ether

$$(CF_3)_2CBr - COCl \xrightarrow{Zn} (CF_3)_2C = C = O + ZnBrCl$$

$$(I)$$

$$(CF_3)_2CBr - COCl + C_2H_5OC_2H_5 \xrightarrow{ZnBrCl} (CF_3)_2CBr - COOC_2H_5 + C_2H_5Cl$$

$$(CF_3)_2CBr - COOC_2H_5 \xrightarrow{Zn,RH} (CF_3)_2CH - COOC_2H_5$$

$$(II)$$

An analogous conversion also occurs in the dehalogenation of monofluorochloroacetyl chloride (III) by zinc in ether

$$\begin{array}{c} \text{CFHCl} - \text{COCl} \xrightarrow{\text{Zn/Et}_2\text{O}} \text{CHFClCO}_2\text{Et} + \text{CH}_2\text{F} - \text{CO}_2\text{Et} \\ (\text{III}) \end{array}$$

Such cleavage of ethers by acid halides has been described in the literature [2] and is a side reaction in dehalogenation. We found that this reaction can also occur without zinc salts. Thus α -bromoperfluoroisobutyryl chloride and diethyl ether react upon simple mixing and evidently give first the ethyl ester of α -bromoperfluoroisobutyric acid, which then brominates the solvent, being converted to the ethyl ester of hexafluoroisobutyric acid. The bromination of the solvent by the α -bromoperfluoroisobutyric ester is evidence of a polarization of the C-Br bond in derivatives of this acid such that the positive end of the dipole is situated on the bromine atom.

If the reaction of dehalogenation is conducted in a solvent less basic than diethyl ether, for example, in ether acetate, then the yield of perfluorodimethylketene rises to 70%. We attempted to extend the method of producing ketenes by dehalogenation to other halides of α -haloperfluorinated acids, primarily to α -chloro- and α -bromoperfluoropropionyl chlorides [3]. It may be assumed that trifluoromethylfluoro-ketene, which could be formed in the dehalogenation of the acid halides indicated above, will boil lower than perfluorodimethylketene. Therefore in these reactions we searched for volatile products. No low-boiling substances are formed from α -bromoperfluoropropionyl chloride, and the only reaction product is a resin, which cannot be redistilled under vacuum and could not be purified. The IR spectrum of this resin is very simple and contains bands belonging to the vibrations of the C-F bonds and the carbonyl group, from which it can be concluded that the polymerization of the intermediate ketene proceeds at the C = C double bonds.

In the dehalogenation of α -chloroperfluoropropionyl chloride, of course, a fraction boiling within the range 9-36°, representing a mixture of perfluoroacrylyl (IV) and tetrafluoropropionyl chlorides (V), can be isolated in a low yield:

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$$CF_3CFClCOCl \rightarrow CF_2 = CF - COF$$
 and $CF_3CFHCOF$
(IV) (V)

Perfluoroacrylyl fluoride was synthesized by identification in the following way. From α,β -dibromoperfluoropropionitrile, α,β -dibromoperfluoropropionic acid (VI) was obtained; when treated with phosphorus pentachloride, this product gives the acid chloride (VII). Under the action of antimony trifluoride on the acid chloride (VII), α,β -dibromoperfluoropropionyl fluoride (VIII) was obtained; dehalogenation of this compound led to perfluoroacrylyl fluoride

$$\begin{array}{ccc} CF_2BrCFBrCN \xrightarrow{H_{2}O} CF_2BrCFBrCOOH \xrightarrow{PCl_s} CF_2BrCFBrCOCl \xrightarrow{SbF_3} CF_2BrCFBrCOF \\ (VI) & (VII) & (VIII_1 \searrow \mathbb{Z}n \\ CF_2=CF-COF & (IV) \end{array}$$

The hydrolysis of α , β -dibromoperfluoropropionitrile with 85% H₂SO₄ was described in [4]; the yield of the acid (VI) is 40%. We somewhat modified this procedure, conducting the hydrolysis with conc. H₂SO₄ and distilling off the α , β -dibromoperfluoropropionic acid under vacuum from the mixture with H₂SO₄. The yield of the acid (VI) was practically quantitative. The formation of the acid fluoride (IV) in the dehalogenation of α -chloroperfluoropropionyl chloride can be explained by rearrangement of the intermediate trifluoromethylfluoroketene in the presence of zinc salts

$$\mathrm{CF_3CFClCOCl} \xrightarrow{\mathrm{Zn}} [\mathrm{CF_3} - \mathrm{CF} = \mathrm{CO}] \xrightarrow{\mathrm{ZnCl_2}} \mathrm{CF_2} = \mathrm{CF} - \mathrm{COF}$$

We had demonstrated a similar isomerization previously for the example of bis-trifluoromethylketene [5]. However, the possibility of splitting out of fluorine atoms from the trifluoromethyl group and of chlorine, which might lead to perfluoroacrylyl fluoride after exchange of the chlorine atoms for fluorine by zinc chlorofluoride, is not excluded:

$$CF_3CFClCOCl \xrightarrow{Z_n} CF_2 = CF - COCl \xrightarrow{Z_nFCl} CF_2 = CF - COF$$

Tetrafluoropropionyl fluoride (V) is evidently a reaction product of the exchange of a chlorine atom for fluorine in the chlorocarbonyl group of α -chloroperfluoropropionyl chloride, followed by reduction of the α -chlorine atom with zinc in ether

$$CF_{3}CFClCOCl \xrightarrow{Zn+RH} CF_{3}CFClCOF \xrightarrow{Zn+RH} CF_{3}CFClCOF \xrightarrow{Zn+RH} CF_{3}CFHCOF \xrightarrow{(V)} (V)$$

The exchange of a chlorine atom for fluorine can be accomplished both on account of the zinc fluoride and on account of perfluoroacrylyl fluoride; in the latter case, such exchange is facilitated by the increase in the mobility of the fluorine atom in the fluorocarbonyl group of perfluoroacrylyl fluoride as a result of conjugation with the double bond. Since we had at our disposal α , β -dibromoperfluoropropionyl halides, we were interested in producing from them the previously undescribed perfluoroacrylyl bromide and chloride.* Perfluoroacrylyl bromide (IX) was produced in the dehalogenation of α , β -dibromoperfluoropropionyl bromide with zinc in dibutyl ether, in a yield of ~14% of the theoretical (the cause of the low yield will be discussed below)

$$CF_2BrCFBrCOBr \rightarrow CF_2 = CF - COBr$$
 (IX)

Dehalogenation of α , β -dibromoperfluoropropionyl chloride is a more complex process, since two reaction pathways are possible here: the first is a splitting out of two bromine atoms, forming perfluoroacrylyl chloride (X), and the second is a splitting out of bromine and chlorine atoms, leading to difluorobromomethylfluoroketene (XI), followed by its isomerization to perfluoroacrylyl bromide. In this reaction we actually succeeded in isolating perfluoroacrylyl chloride and bromide:



*A communication on the synthesis of perfluoroacrylyl chloride [6] appeared while this work was being prepared for publication.

In the case considered, there is also a possibility of formation of the acid bromide (IX) on account of an exchange reaction of the acid chloride (X) with zinc bromide. The possibility of such an exchange was confirmed by a special experiment. The known acid chloride (X) was synthesized for identification from perfluoroacrylic acid and phosphorus pentachloride.

In the dehalogenation of α , β -dibromoperfluoropropionyl chloride and bromide, a common side reaction is the cleavage of the ethers (solvents), which was mentioned above. This side reaction substantially lowers the yield of perfluoroacrylyl halides. Thus, in the dehalogenation of α , β -dibromoperfluoropropionyl chloride in dibutyl ether, we succeeded in isolating butyl chloride and bromide — products of the cleavage of dibutyl ether by α , β -dibromoperfluoropropionyl chloride or perfluoroacrylyl halides from the reaction mixture

$$CF_{2}BrCFBrCOCl + C_{4}H_{9}OC_{4}H_{9} \xrightarrow{Zn+ZnX_{2}} \xrightarrow{CF_{2}=CF-COX} \xrightarrow{} \rightarrow CF_{2}BrCFBrCOOC_{4}H_{9} \xrightarrow{} \rightarrow CF_{2}BrCFBrCO$$

Another reaction product should have been the butyl ester of perfluoroacrylic acid, which was not isolated on account of the difficulty of separating it from large quantities of dibutyl ether; however, in an analogous case, in the dehalogenation of α , β -dibromoperfluoropropionyl bromide in diethyl ether, ethyl trifluoroacrylate was obtained in addition to ethyl bromide.

Known ethyl trifluoroacrylate (XII) was synthesized for identification from the ethyl ester of α , β -dibromoperfluoropropionic acid (XIII) in ~90% yield

$$\begin{array}{c} CF_2BrCFBrCOOC_2H_5 \xrightarrow{Zn} CF_2 = CF - COOC_2H_5 \\ (XIII) & \text{ether} & (XII) \end{array}$$

An analogous process — the dehalogenation of the ethyl ester of β -bromo- α -chloroperfluoropropionic acid was described earlier by Yakubovich and Rozenshtein [7]; together with ethyl trifluoroacrylate, they obtained the ethyl ester of β -ethoxy- α -ethylperfluoropropionic acid (XIV)

 $\begin{array}{c} \mathrm{CF_2BrCFClCOOC_2H_5} \xrightarrow{\mathrm{Zn}} \mathrm{CF_2} = \mathrm{CF} - \mathrm{COOC_2H_5} \text{ and} \\ & \overset{\mathrm{ether}}{\overset{\mathrm{ether}}{\phantom{\mathrm{cher}}}} (\mathrm{XII}) \\ & \mathrm{C_2H_5OCF_2CF}(\mathrm{C_2H_5})\mathrm{COOC_2H_5} \quad (\mathrm{XIV}) \end{array}$

The authors considered that the formation of ethyl- β -ethoxy- α -ethyltrifluoropropionate is the result of addition of diethyl ether to acrylic ester.

We did not observe the formation of $ethyl-\beta-ethoxy-\alpha-ethyltrifluoropropionate$ in the dehalogenation of the ester of α , β -dibromoperfluoropropionic acid; when ethyl trifluoroacrylate is heated with $ZnCl_2$ in ether, the ester (XIV) also is not formed. Moreover, when perfluoroacrylyl chloride is heated with diethyl ether in the presence of $ZnCl_2$, ethyl trifluoroacrylate is obtained in good yield; it is known that this product could not be obtained on the basis of perfluoroacrylic acid itself or its derivatives, as a result of further addition of alcohol at the double bond [7, 8].

Thus, the cleavage of ethers by the acid chloride can be used as a convenient preparative method for obtaining esters in cases when this reaction is complicated by side processes.

EXPERIMENTAL

All the substances described in the literature and obtained in this work were identified with known samples by gas-liquid chromatography. Bis-trifluoromethylketene, and the acid bromides and chlorides were identified on a column in which Kel-F was used as the solid phase; the acid fluorides were identified on a column filled with diatomite brick with brand 1 thiokol rubber, produced by the Kazan' Synthetic Rubber Plant, applied on it; and the esters were identified on a column with thiokol and an analogous column in which the liquid phase was heated oil (All-Union Technical Specifications No. 285-72-61).

<u>Perfluorodimethylketene</u> (I). In a three-necked flask, equipped with a dropping funnel, mixer, and reflux condenser, connected to a trap cooled to -78° , we placed 6 g of activated zinc dust and 50 ml abs. ethyl acetate. The mixture was heated to boiling, and 10.9 g of α -bromoperfluoroisobutyryl

chloride was added dropwise. The liquid condensed in the trap was distilled off. Yield 4.7 g (77%) perfluorodimethylketene with b.p. 3-7°. According to the data of [9]: b.p. 5-6°.

Analogously, 77.24 g α -bromoperfluoroisobutyryl chloride in 70 ml diethyl ether was added dropwise to abs. diethyl ether (300 ml), containing 26 g of zinc dust activated with copper, and heated to boiling. The mixture was mixed for 1 h and distilled. The following fractions were collected: I - 3.5 g (7.4%) perfluorodimethylketene with b.p. 4-6°; II - 30.5 g (51%) ethyl ester of hexafluoroisobutyric acid (II) with b.p. 100-110°. According to the data of [10]: b.p. 102.5°.

In a control experiment, equimolar amounts of α -bromoperfluoroisobutyryl chloride and abs. diethyl ether were heated without zinc dust in a sealed ampule at 100° for 1 h. In addition to diethyl ether, the ethyl ester of α -bromoperfluoroisobutyric acid and the ethyl ester of hexafluoroisobutyric acid in a 1:9 ratio were detected in the reaction mixture by chromatography.

Dehalogenation of Monofluorochloroacetyl Chloride. In the instrument described above we placed 11.83 g activated zinc dust and 50 ml abs. diethyl ether. The mixture was heated to 40° , and 16.15 g of monotrifluorochloroacetyl chloride in 20 ml of abs. ether was added dropwise over a period of 30 min. The reaction mass was boiled with a reflux condenser for another 2 h, then filtered, and the ether distilled off on a column,* while 5.75 g of liquid was distilled off from the residue (24.04 g) on a boiling water bath under vacuum (1 mm). When the liquid obtained was redistilled, a fraction with b.p. $123-132^{\circ}$ (3.28 g), representing a mixture of 30% of the ethyl ester of monofluorochloroacetic acid (yield 8% of the theoretical) and 70% ethyl ester of monofluoroacetic acid (13%) was isolated. The residue, after vacuum distillation of the esters, was a mixture of zinc chloride and nondistillable resins. After treatment of this mixture with hot water, the residue comprised 13 g of a solid black mass.

Interaction of α -Bromoperfluoropropionyl Chloride with Zinc. In the instrument described above we placed 7 g of copper-activated zinc dust and 50 ml abs. diethyl ether. The mixture was heated to 40° and 15.64 g of α -bromoperfluoropropionyl chloride in 20 ml of ether was added dropwise over 30 min. Heating was continued at 40° for another 10 h; then the solution was filtered off, the ether distilled off, and the residue (19.82 g) washed with water and dried. The oil that separated, 4.95 g (60%), could not be redistilled under vacuum without distillation. IR spectrum (ν_{max} , cm⁻¹): 1135-1360 s (C-F), 1780 s (C=O).

Interaction of α -Chloroperfluoropropionyl Chloride with Zinc. Analogously to the preceding experiment, 33.79 g of α -chloroperfluoropropionyl chloride was added dropwise to abs. dibutyl ether, containing 23 g of activated zinc dust and heated to boiling. After the end of the reaction, a fraction with b.p. 9-36°, 8 g, representing a mixture of tetrafluoropropionyl (V) and perfluoroacrylyl fluorides (IV), was distilled off from the solution. The acid fluoride (IV) was identical with that obtained below. After the acid fluorides were distilled off from the reaction mixture, nothing distilled off up to the beginning of the boiling of dibutyl ether (130°). The yields of the acid fluorides were calculated chromatographically and were equal to 14% for perfluoroacrylic acid and 20% for tetrafluoropropionic acid.

 α , β -Dibromoperfluoropropionic Acid (VI). A mixture of 92.5 g of α , β -dibromoperfluoropropionitrile and 100 ml of conc. H₂SO₄ was left overnight in a flask with a reflux condenser, after which the solution was heated on a boiling water bath for 2 h, 10 ml of water was added, and the mixture was heated for another 6 h. Vacuum distillation of the reaction mixture yielded 98 g of a fraction with b.p. 85-97° (2 mm), repeated distillation of which yielded 86.8 g of the acid (VI) with b.p. 76-78° (2 mm); nD²⁰ 1.4472; yield 88% of the theoretical. According to the data of [4] b.p. 72-73° (2.5 mm); nD²⁰ 1.4458.

 $\frac{\alpha,\beta-\text{Dibromoperfluoropropionyl Chloride (VII).}{\alpha}$ Produced in the usual way from 86.07 g of the acid (VI) and 77 g PCl₅. After the end of the reaction, the mixture was poured out into crushed ice, the oil that separated was washed with water, dried, and distilled. We obtained 71 g of the acid chloride (VII) with b.p. 126.5-127° (758 mm); n_D²⁰ 1.4382; yield 77%. Found %: Cl 11.09. C₃F₃Br₂. ClO. Calculated %: Cl 11.51. IR spectrum (ν_{max} , cm⁻¹): 740-800 m, doublet 850, 870 m, 980 s, 1050-1220 s (C-F), 1300 m, 1780 s (C=O).

 α,β -Dibromoperfluoropropionyl Bromide. Produced analogously from 70 g of the acid (VI) and 135 g Pbr₅. Yield of α,β -dibromoperfluoropropionyl bromide with b.p. 55.5° (20 mm) and

*The ether distillate contained ethyl chloride, which was identified chromatographically, by analysis of a gas sample taken above the surface of the ether. The amount of ethyl chloride was not determined.

 n_D^{20} 1.4704, 76%. Found %: Br 16.05. C₃F₃Br₃O. Calculated %: Br 16.31. IR spectrum (ν_{max} , cm⁻¹): 732 s, 760 s, 818 w, 860 m, 975 m, 1046 w, 1070 m, 1155-1215 s (C-F), 1780 (C=O).

 α, β -Dibromoperfluoropropionyl Fluoride (VIII). A 71-g portion of the acid chloride (VII) and 147 g of an equimolar mixture of antimony trifluoride and pentachloride were mixed. When the reaction mass was heated, at first on a boiling water bath for 2 h, then on an oil bath at 110-130°, 58.1 g of a red liquid distilled off; distillation of this liquid on a column yielded 55 g (82%) of the acid fluoride (VIII) with b.p. 89.5° (754 mm); n_D²⁰ 1.3980. Found %: C 13.12; F 26.35. C₃F₄Br₂O. Calculated %: C 12.56; F 26.41. IR spectrum (ν_{max} , cm⁻¹): 720 m, 780 s, 825 w, 850 w, 930 m, 1025 m, 1100-1250 s (C-F), 1860 s (C=O).

<u>Perfluoroacrylyl Fluoride (IV)</u>. In the instrument described above we placed 10 g of zinc dust and 70 ml abs. dioxane. The mixture was heated to boiling, and 21.33 g of the acid fluoride (VIII) in 20 ml of dioxane was added dropwise over a period of 2 h. The solution was heated for 2 h on a boiling water bath. The liquid condensed in the trap (6 g) was redistilled on a column. Yield 5.1 g (54%) of the acid fluoride (IV) with b.p. 23-24° (736 mm); n_D^{20} 1.3140. Found %: C 27.52; F 59.50. C₃F₄O. Calculated %: C 28.12; F 59.43. According to the data of [11]: b.p. 25.5°.

<u>Perfluoroacrylyl Bromide (IX)</u>. To dibutyl ether (80 ml), containing 18 g of zinc dust, 64 g of α,β -dibromoperfluoropropionyl bromide was added dropwise over a period of 20 min with mixing while heating on a boiling water bath. The mixture was heated for 1-5 h, after which a liquid was distilled off under vacuum at 30 mm and at room temperature into a trap cooled to -78°. The following fractions were isolated when this liquid was distilled on a column: I - 5 g (14.5%) of the acid bromide (IX) with b.p. 74.5° (751 mm); n_D²⁰ 1.4195. Found %: Br 41.73. C₃F₃OBr. Calculated %: Br 42.32. II - 4 g of a mixture with b.p. 75-101°, consisting of 90% butyl bromide and 10% perfluoroacrylyl bromide. The mixture was analyzed chromatographically. IR spectrum of the acid bromide (IX) (ν_{max} , cm⁻¹): 460 m, 555 m, 650 m, 670 m, 810 s, 880 m, 940 w, 1050 w, 1140 m, 1240 w, 1300 s, 1360 s, unresolved doublet 1700 and 1725 s (C=C), 1780 (C=O).

<u>Perfluoroacrylyl Chloride (X)</u>. To 60 ml of abs. dibutyl ether, containing 10 g of zinc dust and heated to 100°, 33 g of the acid chloride (VII) was heated dropwise over a period of 20 min. The mixture was heated with mixing for 1 h at 100°, after which a liquid with b.p. up to 65° (20 mm) was distilled off under vacuum into a trap cooled to -78° . Fractionation of this liquid on a column yielded the fractions: I - 7.8 g (50%) of the acid chloride (X) with b.p. 54.2° (750 mm); n_D²⁰ 1.3760 (according to the data of [6]: b.p. 49-51°). Found %: Cl 24.22. C₃F₃OCl. Calculated %: Cl 24.59. II - 3.9 g of a mixture with b.p. 55-110°, consisting of 9.5% of the acid chloride (X), 28% butyl chloride, 8.7% of the acid bromide (IX), identical with that obtained above, and 53.8% butyl bromide. The composition of this fraction was calculated on the basis of a chromatogram. IR spectrum of the acid chloride (X) (ν_{max} , cm⁻¹): 850 s, 920 m, 1150 m, 1270 w, 1300 s, 1370 s, unresolved doublet 1720 and 1740 s (C=C), 1780 s (C=O).

(X) was produced in the usual way from perfluoroacrylic acid and PCl_5 in a yield of 58% of the theoretical.

Equimolar amounts of the acid bromide (IX) and zinc chloride in 1 g of abs. diethyl ether were heated at 100° in a sealed ampule for 30 min. Chromatographic analysis of the reaction mixture demonstrated that the acid bromide (IX) was 33% converted to the acid chloride (X) in this case.

<u>Ethyl Trifluoroacrylate</u>. To 70 ml of diethyl ether, containing 20 g copper-activated zinc dust, and heated to 40° , 29 g of the ethyl ester (XIII) was added dropwise over a period of 30 min. The mixture was heated at 40° and mixed for 2 h, then filtered, the ether distilled off on a column, and all the liquid distilled off to dryness from the residue under a vacuum of 2 mm. Redistillation of the liquid yielded 12.45 g (XII) with b.p. $100-103^{\circ}$, yield 88%. According to the data of [7]: b.p. $100-101^{\circ}$ (750 mm). A mixture of 2.08 g of the acid bromide (IX), 0.8 g ZnCl₂, and 2.07 g abs. diethyl ether was heated to a sealed ampule at 100° for 6 h. After the ampule was opened, 1.68 g of diethyl ether was distilled off at a still temperature of 100° , and the residue was recondensed under vacuum (0.01 mm) into a receiver cooled with liquid nitrogen. We obtained 1.64 g of a liquid, with chromatographic composition 60% ethyl trifluoroacrylate and 40% diethyl ether. According to these data, we calculated the yield of the ethyl ester of perfluoroacrylic acid, equal to 58% of the theoretical.

A mixture of 3.14 g α , β -dibromoperfluoropropionyl bromide, 1 g copper-activated zinc dust, and 4 g abs. diethyl ether was heated in a sealed ampule at 100° for 2 h. Then all the liquid was distilled off

from the ampule under vacuum to dryness. Distillation of this liquid yielded a fraction with b.p. $99-104^{\circ}$, 0.3 g (21%), representing ethyl trifluoroacrylate (XII).

CONCLUSIONS

1. Conditions were found for the production of perfluorodimethylketene in good yields by the dehalogenation of α -haloperfluoroisobutyryl halides with zinc in ethyl acetate.

2. The interaction of α -chloroperfluoropropionyl chloride with zinc, leading to the production of a low yield of a mixture of perfluoroacrylyl and tetrafluoropropionyl fluorides, was investigated.

3. Perfluoroacrylyl halides were produced by dehalogenation of α,β -dibromoperfluoropropionyl halides. In this case there is a side reaction of cleavage of the ethers by the acid halides, leading to esters of fluorinated acids.

4. The cleavage of ethers by perfluoroacrylyl halides in the presence of zinc salts can be used as a preparative method for obtaining alkyl perfluoroacrylates.

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