CONCLUSIONS

1. 1-(1,2-Dichlorotrifluoroethyl)- and 1,2-bis(1,2-dichlorotrifluoroethyl)perfluorobenzocyclobutenes were obtained by the reaction of perfluorobenzocyclobutene with 1,2-dichlorodifluoroethylene in the presence of SbF_5. In a similar reaction of perfluoro-1-methylbenzocyclobutene, 1-(1,2-dichlorotrifluoroethyl- and 2-(1,2-dichlorotrifluoroethyl)-perfluoro-1-methylbenzocyclobutenes are formed. The corresponding perfluorinated vinyl and divinylbenzocyclobutenes were synthesized by dechlorination of the compounds obtained.

2. Perfluorinated 1-vinyl-, 1,1-divinyl-, and 1,3-divinylindanes were obtained by dechlorination of the products of the reaction of perfluoroindane with 1,2-dichlorodifluoroethylene.

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SOME PROPERTIES OF POLYFLUOROACYL- AND POLYFLUOROACETONYL FLUOROSULFATES

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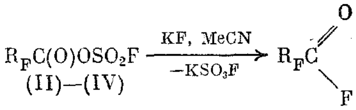
A. S. Tatarinov, and Yu. N. Studnev

UDC 542.92:547.299,
161:542.91:547.297

A large number of polyfluoroacyl fluorosulfates are known [1-8] as well as one representative of polyfluoroacetonyl fluorosulfates, pentafluoroacetonyl fluorosulfate (I) [9, 10]. However, the properties of these compounds have not been greatly investigated. Thermal decomposition of some polyfluoroacyl fluorosulfates [1, 3, 11], and reactions of 2-hydrotetrafluoropropionyl fluorosulfate with alcohols, esters and ethers [2] and also of (I) with nucleophilic reagents (methanol, water, fluoride ion) [9, 10] were described.

It was found in the present work that polyfluoroacyl fluorosulfates react with KF in polar aprotic solvents with a small exothermal effect to form the corresponding polyfluoroacyl fluorides. The liberation of SO_2F_2 thus was not observed.



$$R_FC(O)OSO_2F \xrightarrow[-KSO_3F]{KF,\ MeCN} R_FC(=O)F$$

(II)—(IV) (II a)—(IV a)

$R_F = (CF_3)_2CH$ (II), $(CF_3)_2CCl$ (III), n-C_4F_9 (IV).

The complete conversion of the starting fluorosulfates and a high yield of acid fluorides is observed when KF is used in close to equimolar amounts.

The result obtained indicates that the attack of the fluoride ion is directed exclusively to the C atom bound to the fluorosulfate group and not to the S atom, with the liberation of SO_2F_2, as in the case of polyfluoroalkyl fluorosulfates [12].

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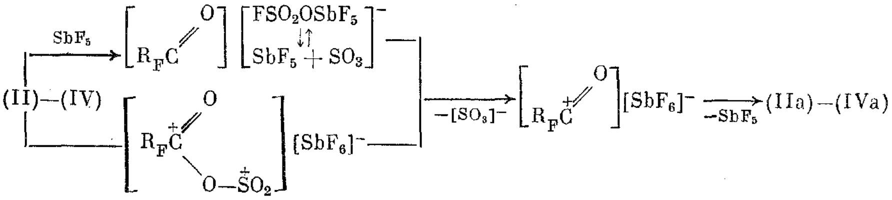
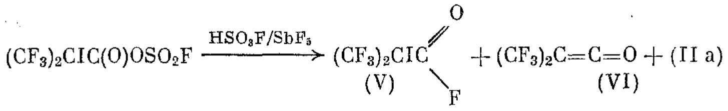
The action of an electrophilic reagent SbF_5 on polyfluoroacyl fluorosulfates leads also to formation in high yield of the corresponding polyfluoroacyl fluorides. The reaction is accompanied by a substantial exothermal effect, while the presence of HSO_3F markedly decreases the activity of SbF_5, and the decomposition of polyfluoroacyl fluorosulfates by mixtures of SbF_5 with HSO_3F begins on heating to 60°C. The following scheme including two paths of generation of the polyfluoroacyl carbocation, stabilizing further into a polyfluoroacyl fluoride, can be assumed

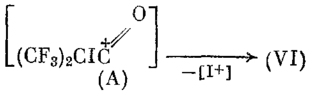


The action of HSO_3F/SbF_5 on α-iodohexafluoroisobutyryl fluorosulfate gives not only the expected α-iodohexafluoroisobutyryl fluoride (V), but also α-hydrohexafluoroisobutyryl fluoride (IIa) and bis(trifluoromethyl)ketene (VI)



$$(CF_3)_2CIC(O)OSO_2F \xrightarrow{HSO_3F/SbF_5} \underset{(V)}{(CF_3)_2CIC(O)F} + \underset{(VI)}{(CF_3)_2C{=}C{=}O} + (IIa)$$

The formation of (VI) is probably the result of stabilization of the intermediate carbocation (A) in HSO_3F/SbF_5 by elimination of an iodine cation



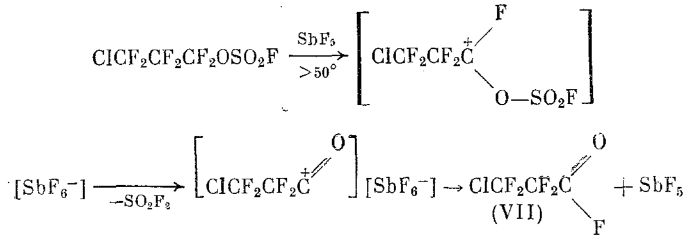
As known, iodine cations are readily formed and are stable in strongly acid media [13].

Ketene (VI) adds HSO_3F even under mild conditions

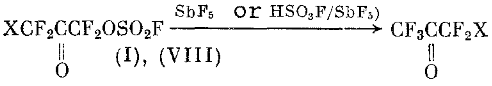
$$(VI) + HSO_3F \xrightarrow{0^\circ} (II)$$

Thus, in the above considered process, ketene (VI) becomes partially bound to HSO_3F and the polyfluoroacyl fluorosulfate (II) formed is decomposed by the HSO_3F/SbF_5 mixture to acid fluoride (IIa), as confirmed by an independent experiment.

It should be noted that polyfluoroalkyl fluorosulfates are more stable than polyfluoroacyl fluorosulfates to the action of SbF_5 or of its mixtures with HSO_3F. Thus 3-chlorohexafluoropropyl fluorosulfate, which is stable to the action of HSO_3F/SbF_5 up to 130°C, is decomposed by the action of SbF_3 at $\gtrsim 50$°C with the formation of 3-chlorotetrafluoropropionyl fluoride (VII) and SO_2F_2, possibly by the following scheme:



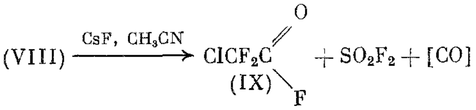
Polyfluoroacetonyl fluorosulfates (I) and (VIII) behave similarly to polyfluoroacyl fluorosulfates in the reaction with HSO_3F/SbF_5, which is possibly explainable from the formation of an intermediate carbocation due to elimination of the fluorosulfate group, and not because of splitting off of a fluorine atom in the α-position to it, as in the case of polyfluoroalkyl fluorosulfates



$$XCF_2\underset{\underset{O}{\|}}{C}CF_2OSO_2F \xrightarrow[(I),\ (VIII)]{SbF_5\ \text{or}\ HSO_3F/SbF_5)} CF_3\underset{\underset{O}{\|}}{C}CF_2X$$

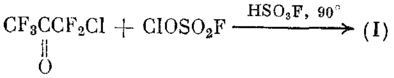
X = F (I), Cl (VIII).

However, as has already been shown in [9], compound (I) is decomposed by the action of the fluoride ion in a similar way as polyfluoroalkyl fluorosulfates. At the same time, 3-chlorotetrafluoroacetonyl fluorosulfate (VIII) in the presence of fluoride ion undergoes greater transformations

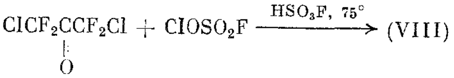


$$(\mathrm{VIII}) \xrightarrow{\mathrm{CsF,\ CH_3CN}} \underset{(\mathrm{IX})}{\mathrm{ClCF_2C}}\overset{\mathrm{O}}{\underset{\mathrm{F}}{}} + \mathrm{SO_2F_2} + [\mathrm{CO}]$$

In contrast to polyfluoroacyl fluorosulfates, fluorosulfates (I) and (VIII) are more stable in a HSO_3F/SbF_5 medium: their decomposition begins at >80°C. These compounds were obtained by the reaction of chlorofluoroacetones with chlorine fluorosulfate $ClOSO_2F$ in the presence of HSO_3F at 70-90°C. Hence, replacement of chlorine by a fluorosulfate group in chlorofluoroacetones proceeds under much milder conditions than the substitution of chlorine of the CF_2Cl group in perfluoroalkyl chlorides, for which a superacid HSO_3F/SbF_5 is necessary [14,15]

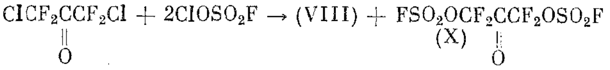


$$\mathrm{CF_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF_2Cl} + \mathrm{ClOSO_2F} \xrightarrow{\mathrm{HSO_3F,\ 90^\circ}} (\mathrm{I})$$



$$\mathrm{ClCF_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF_2Cl} + \mathrm{ClOSO_2F} \xrightarrow{\mathrm{HSO_3F,\ 75^\circ}} (\mathrm{VIII})$$

In a HSO_3F/SbF_5 medium, the above chlorofluoroacetones vigorously react with $ClOSO_2F$ to form (I) and (VIII). When 2 moles of $ClOSO_2F$ are used in the reaction with sym-dichlorotetrafluoroacetone, the main product is bis-(fluorosulfate) (X). In the presence of HSO_3F only, even at 70°C, it forms in a low yield (ratio (VIII):(X) = 1:9)



$$\mathrm{ClCF_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF_2Cl} + 2\mathrm{ClOSO_2F} \rightarrow (\mathrm{VIII}) + \underset{(\mathrm{X})}{\mathrm{FSO_2OCF_2}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CF_2OSO_2F}$$

EXPERIMENTAL

The NMR spectra were run on "Hitachi R-20" (60 and 56.45 MHz), and "Bruker WP-200SY" (188.31 MHz) spectrometers relative to HMDS and CF_3COOH (external standard) in $CHCl_3$.

Reaction of Polyfluoroacyl Fluorosulfates with KF. A 22 g portion (70.4 mmoles) of (III) was added dropwise, with stirring, to a mixture of 4.2 g (72.3 mmoles) of calcined KF and 5 ml of dry MeCN, and the mixture was stirred for 1 h at 20°C. Distillation from the mixture gave 13.7 g (84.3%) of (IIIa), bp 36-38°C, d_4^{20} 1.522. Found: C 20.39; Cl 15.45; F 57.01%. C_4ClF_7O. Calculated: C 20.64; Cl 15.27; F 57.20%. ^{19}F spectrum of (IIIa) δ_1 −6.2 d (CF_3), δ_2 −113.4 sept (COF), J_{12} = 9.9 Hz.

Compounds (IIa), yield 80.6%, and (IVa), yield 85.8%, were obtained in a similar way. Their constants and NMR spectra are identical with those given in [16].

Reaction of Polyfluoroacyl Fluorosulfates with SbF_5. A 5 g portion (23 mmoles) of SbF_5 was placed in a distillation flask, and 11.8 g (34.1 mmoles) of (IV) were added dropwise with simultaneous distillation of liquid products. Yield, 6.1 g (68.5%) of (IVa), bp 35-37°C, d_4^{20} 1.612. ^{19}F NMR spectrum of (IVa) is identical to that given in [16].

Compound (IIIa) was obtained in a similar way in a yield of 62.8%.

Reaction of Polyfluoroacyl Fluorosulfates with HSO_3F/SbF_5. A 13.9 g portion (50 mmoles) of (II) was added dropwise at 60°C to a solution of 1.5 g (6.9 mmoles) of SbF_5 in 4 g (40 mmoles) of HSO_3F, with simultaneous distillation of liquid products. Yield, 7.7 g (77.5%) of (IIa), bp 31-32°C, d_4^{20} 1.510 (cf. [16]).

Compounds (IIIa), yield 81.2%, and (IVa), yield 78%, were obtained in a similar way.

Reaction of α-Iodohexafluoroisobutyryl Fluorosulfate with HSO_3F/SbF_5. A 14 g portion (34.6 mmoles) of α-iodohexafluoroisobutyryl fluorosulfate was added dropwise, with stirring to a solution of 2 g (9.2 mmoles) of SbF_5 and 5 g (50 mmoles) of HSO_3F, with collection of the distilled liquid products in a receiver, and the gaseous products in a trap (−78°C). Thus, 1.7 g of (VI), bp 5-8°C were obtained in a trap and 5.5 g of (IIa), bp 31-32°C, in the receiver. Fractionation of the residue gave 2.8 g of (V), bp 72-74°C, d_4^{20} 1.996. Found: C 14.64; F 41.29%. C_4F_9IO. Calculated: C 14.82; F 41.06%. ^{19}F NMR spectrum of (V): δ_1 −13.2 d (CF_3), δ_2 −15.1 sept (COF), J_{12} = 12.9 Hz.

α-Hydrohexafluoroisobutyryl Fluorosulfate (II). A mixture of 19 g (106.7 mmoles) of (VI) and 7.5 g (75 mmoles) of HSO_3F was shaken for 30 min at 0°C in a sealed ampul. After the removal of excess of ketene, 19.8 g (95.2%) of (II) were obtained by fractionation, bp 63-64°C (160 mm), d_4^{20} 1.673, n_D^{22} 1.3120. ^{19}F NMR and PMR spectra: δ_1 −24.5 d (CF_3), δ_2 4.3 sept (CH), δ_3 −123.5 s (SF). J_{12} = 6.5 Hz (cf. [3]).

α-Hydrohexafluoroisobutyryl Fluoride (Ia). A mixture of 24.5 g (113 mmoles) of SbF_5, 22.6 g (226 mmoles) of HSO_3F and 23 g (129 mmoles) of (VI) was shaken in a sealed ampul for 3 h at 20°C. By fractionation, 17.2 g (83.8%) of (IIa), bp 31-32°C, were obtained (cf. [16]).

3-Chlorotetrafluoropropionyl Fluoride (VII). A mixture of 6 g (27.6 mmoles) of SbF_5 and 14.2 (50 mmoles) of 3-chlorotetrafluoropropionyl fluorosulfate was stirred for 3 h at 50-80°C with collection of the liquid products in a cooled receiver (−30°C), and the gaseous products in a trap (−78°C). Thus, 4.2 g (82.3%) of SO_2F_2, bp −54°C, and 7.1 g (77.8%) of (VIII), bp 21-23°C, were obtained. The constants and ^{19}F NMR spectrum of (VII) were identical with those given in [16].

Hexafluoroacetone. A 10.5 g portion (42.7 mmoles) of (I) was added dropwise, with stirring to 10 g (46.1 mmoles) of SbF_5 (the temperature rose to 35°C), with collection of the gaseous products in a trap (−78°C). After the addition of (I), the reaction mixture was heated for 30 min at 50°C. Fractionation of the trap contents gave 5.5 g (77.5%) of hexafluoroacetone, bp. −28 to −26°C. ^{19}F NMR spectrum: 0.8 s (CF_3), of hexafluoroacetone hydrate 5.1 s (cf. [9]).

Reaction of 3-chlorotetrafluoroacetonyl Fluorosulfate (VIII) with CsF. A 20.3 g portion (77.3 moles) of (VIII) was added dropwise, with stirring, to a mixture of 4 g (26.3 mmoles) of calcined CsF and 3 ml of dry MeCN, and the mixture was stirred for 1 h at 60°C, with collection of the gaseous products in a trap (−78°C). Fractionation of the trap contents gave 7.7 g (97.5%) of SO_2F_2, bp −54°C, and 6 g (58.5%) of chlorodifluoroacetyl fluoride (IX), bp −16 to −14°C. Found: C 18.32; Cl 26.56; F 43.18%. C_2ClF_3O. Calculated: C 18.11; Cl 26.79; F 43.02%. ^{19}F NMR spectrum: δ_1 −11.7 s ($ClCF_2$), δ_2 −87.3 s (COF).

Pentafluoroacetonyl Fluorosulfate (I). A mixture of 9.1 g (50 mmoles) of pentafluorochloroacetone, 6.7 g (50 mmoles) of chlorine fluorosulfate and 5 ml of HSO_3F was heated in a sealed ampul for 14 h at 90°C. After opening of the ampul and removal of Cl_2, 10.5 g (85.4%) of (I) was obtained by fractionation, bp 57-59°C. The ^{19}F NMR spectrum was identical with that given in [9].

3-Chlorotetrafluoroacetonyl Fluorosulfate (VIII). A mixture of 25 g (125.6 mmoles) of sym. dichlorotetrafluoroacetone, 13 g (96.6 mmoles) of chlorine fluorosulfate and 5 ml of HSO_3F was heated in a sealed ampul for 16 h at 75°C. Fractionation gave 20 g (78.8%) of (VIII), bp 92-94°C, d_4^{20} 1.684, n_D^{20} 1.3381. Found: C 13.62; Cl 13.75; F 36.28; S 12.32%. $C_3ClF_5O_4S$. Calculated: C 13.71; Cl 13.52; F 36.19; S 12.19%. ^{19}F NMR spectrum: δ_1 −11.4 t ($ClCF_2$), δ_2 −1.7 d.t (CF_2O), δ_3 −127.7 t (SF), J_{12} = 7.3, J_{23} = 6.4 Hz.

1,3-Bis(fluorosulfonyloxy)tetrafluoroacetone (X). A 14.5 g portion (72.9 mmoles) of sym. dichlorotetrafluoroacetone was added dropwise, with stirring, at 25-30°C to a mixture of 7.7 g of HSO_3F, 3 g of SbF_5 and 22 g (163.6 mmoles) of chlorine fluorosulfate (exothermal reaction), and the mixture was stirred for 2 h at 40°C. The volatile products were collected in a vacuum of 1 mm at 30°C in a trap (−78°C). Fractionation of the trap contents gave 1.8 g of (VIII), bp 92-94°C and 16.3 g (68.8%) of (X), bp 129-131°C, d_4^{20} 1.811, n_D^{20} 1.3291. Found: C 11.21; F 35.13; S 19.50%. $C_3F_6O_7S_2$. Calculated: C 11.04; F 34.97; S 19.63%. ^{19}F NMR spectrum of (X) corresponds to the $A_2A_2'XX'$ spin system and required a computerized calculation to obtain the SSCC: δ_1 −127.3 m (SF), δ_2 −0.1 m.

CONCLUSIONS

Polyfluoroacyl fluorosulfates are decomposed by the action of KF, SbF_5 and its mixtures with HSO_3F with the formation of the corresponding acyl fluorides. Pentafluoroacetonyl fluorosulfate reacts with SbF_5 to form hexafluoroacetone; the fluoride ion causes decomposition of 3-chlorotetrafluoroacetonyl fluorosulfate to chlorodifluoroacetyl fluoride.

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CYCLOADDITION OF 2-DIALKYLBORYLAMINO-N-HETEROCYCLES TO ETHOXYACETYLENE

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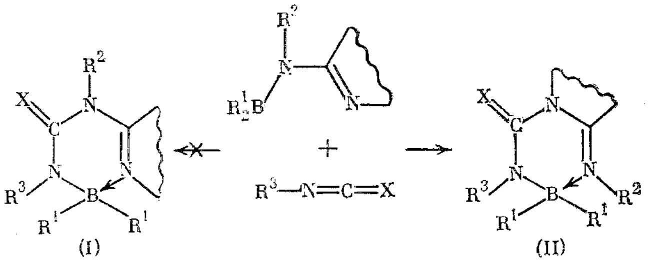
Reactions at the B—N bond in diorganylboryl derivatives of α-amino-N-heterocycles (DBAH) have been described with dicyclohexylcarbodiimide [1, 2], aldehydes and ketones [3, 4], and CO_2 [5]. The chelate structures of the cyclic products were established by a variety of methods, including X-ray crystallography (XRC) [6]. However, the reactions of DBAH with isocyanates and isothiocyanates give the (4+2) cycloadducts (II) rather than insertion products (I) [7-9].



X = O, S

In this case, attack by the reagent takes place at the nitrogen of the heterocycle and at boron, nucleophilic and electrophilic centers respectively, located in the 1,4-positions to each other. Hence, the reaction of DBAH with RCNX may be regarded as a unique (4+2) cycloaddition, as a result of which the B—N bond is not broken, but the valence of its constituent atoms changes.

We here show that the reaction of DBAH with ethoxyacetylene (EA) is also a (4+2) cycloaddition. Bicyclic compounds (Va-d) are formed when EA reacts with the dialkylborylaminopyridines (IIIa-c) or 2-diisopropylborylaminopyrimidine (IIId) in yields of 70-86%.

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