2. The fact that the corresponding 2-phenylazo and 2-aminomethyl derivatives were obtained shows that the electrophilic substitution of the β-hydroxypyrimidine ring is possible.

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ISOMERIC TRANSFORMATIONS OF POLYFLUOROBUTENES CAUSED BY SbF_5

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Previously it was shown [1] that the multiple bond is shifted from the 1 to the 2 position when terminally perfluorinated olefins are treated with SbF_5

$$R_fCF_2CF=CF_2 \xrightarrow{SbF_5} R_fCF=CFCF_3$$

A further shift occurs only if H or Cl atoms are present in the 4 position.

$$R_fCFXCF_2CF=CF_2 \xrightarrow{SbF_5} R_fCX=CFCF_2CF_3$$
$$X = H,\ Cl$$

As a rule, the rearrangement leads to the predominant formation of the trans isomers.

In the present paper it was established that migration of the multiple bond to an inner position in the chain is also observed when polyfluorobutenes are treated with SbF_5.

$$\underset{(I)}{CF_3CF_2CF=CF_2} \xrightarrow{SbF_5} \underset{(II)}{CF_3CF=CFCF_3} \quad (90\%\ \text{trans},\ 10\%\ \text{cis}).$$

$$\underset{(III)}{CF_3CF_2CCl=CF_2} \xrightarrow{SbF_5} \underset{(IV)}{CF_3CF=CClCF_3} \quad (80\%\ \text{trans},\ 20\%\ \text{cis}).$$

It is interesting to mention that the 4-H- and 4-Cl-perfluoro-1-butenes rearrange to terminal polyfluorobutenes that contain either H or Cl at the multiple bond.

Thus, only 1-H-perfluoro-1-butene (VII) is formed when 4-H-perfluoro-1-butene is treated with SbF_5. Olefin (VII) was also obtained by treating a mixture of the cis-trans isomers of 1-H-perfluoro-2-butene (VI) with SbF_5.

$$\left.\begin{array}{l} \underset{(V)}{HCF_2CF_2CF=CF_2} \\ \underset{(VI)}{HCF_2CF=CFCF_3} \end{array}\right| \xrightarrow{SbF_5} \underset{(VII)}{HCF=CFCF_2CF_3}\ (\text{cis})^*$$

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*The formation of the cis isomer of (VII), with a trans-orientation of the F atom and perfluoroalkyl group, is in agreement with the previously proposed mechanism of the isomerization [1].

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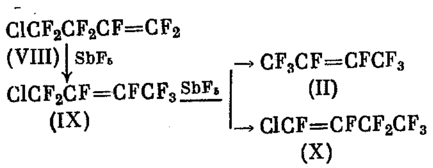
The treatment of 4-Cl-perfluoro-1-butene (VIII) with SbF_5 under analogous conditions gives a mixture of trans-1-Cl-perfluoro-2-butene (IX), trans- and cis-1-Cl-perfluoro-1-butenes (X), and perfluoro-2-butene (II). The composition and structure of products (IX), (X), and (II) were determined on the basis of the GLC, and the IR, ^{19}F NMR, and mass spectral data of the reaction mixture and standard samples. In this case the initially formed olefin (IX) then reacts with the SbF_5 in two directions: 1) replacement of the allylic Cl by F, which leads to (II), and 2) further rearrangement to (X).

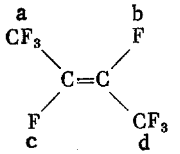


The obtained results confirm the previously proposed scheme for migration of the multiple bond in fluorine-containing olefins under the influence of SbF_5, which includes a cyclic transition state involving allylic fluorine [1]. In the initially formed 1-H- and 1-Cl-perfluoro-2-butenes the mobility of the allylic fluorine of the HCF_2 and $ClCF_2$ groups is higher than that of the CF_3 group, which is apparently the reason for their further rearrangement to olefins (VII) and (X).

EXPERIMENTAL

The ^{19}F NMR and PMR spectra were recorded on a Perkin—Elmer—Hitachi R-20 instrument (56.4 and 60 MHz) relative to CF_3COOH and HMDS (external standard). The mass spectra were taken on a Varian CH-8 instrument, and the IR spectra were taken on a UR-20 instrument. The GLC analysis was run on columns packed with Porapak Q and 15% SKTPT-50 deposited on Chromosorb W.

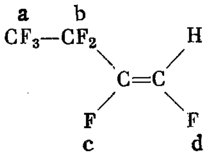
trans-Perfluoro-2-butene (II). In a flask, equipped with a reflux condenser, cooled to —78°C, and a gas-inlet tube, was placed 2 g of SbF_5, followed by the condensation of 16 g (10 ml, 0.08 mole) of (I). The reaction products were condensed in a trap (—78°). Distillation gave 15.4 g (96%) of (II), bp 0-1° (M^+, m/e 200). Infrared spectrum: 1740 cm^{-1}, weak. ^{19}F NMR spectrum



(δ, ppm): — 7,1 (F_a, F_d), 84,1 (F_b, F_c); $J_{ac} = J_{bd} = 8{,}5$; $J_{ab} = J_{cd} = 21{,}6$ Hz.

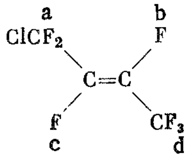
2-Chloro-perfluoro-2-butene (IV). In a flask, equipped with a reflux condenser (—78°) and a dropping funnel, was placed 18.5 g (0.085 mole) of (III), and then 1.5 g of SbF_5 was added in drops. We obtained 17 g (92%) of (IV), bp 31-32° (M^+, m/e 216). Infrared spectrum: 1680 cm^{-1}. The ^{19}F NMR spectrum coincides with that published in [2].

cis-1-Hydro-perfluoro-1-butene (VII). a) Similar to (IV), from 22 g (0.12 mole) of olefin (VIII) and 3 g of SbF_5 we obtained 19.8 g (90%) of (VII), bp 18° (M^+, m/e 182). Infrared spectrum: 1740 cm^{-1}. ^{19}F NMR spectrum

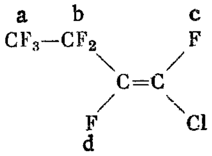


(δ, ppm): 9.1 (F_a), 47.6 (F_b), 78.7 (F_d), 80.8 (F_c); $J_{ab} = 1.9$, $J_{ac} = 6.6$, $J_{bc} = 16.8$, $J_{cd} = 5.5$ Hz. PMR spectrum (δ, ppm): 6.5; $J_{HF_c} = 13.3$, $J_{HF_d} = 68.6$ Hz. b) In a similar manner, from 8 g of (VI) and 1.5 g of SbF_5 we obtained 7.3 g (91%) of (VII).

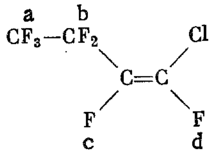
Reaction of SbF_5 with 4-Cl-Perfluoro-1-butene (VIII). In a similar manner, from 8.4 g (0.039 mole) of (VIII) and 1.5 g of SbF_5 we obtained 7.3 g of a mixture, bp 0-32°, which, based on the GLC data, contained 40% of (IX), 35.5% of trans-(X), 4.5% of cis-(X), and 20% of (II); bp of (IX) 28°, of (X) 31-32°, and of (II) 0°. Infrared spectrum: 1740 cm^{-1}. ^{19}F NMR spectrum of (IX)



(δ, ppm): −17.8 (F_a), −7.1 (F_d), 78.1 (F_c), 83.7 (F_b); $J_{ab} = 29.2$, $J_{ac} = 12.4$, $J_{bd} = 138$ Hz. ^{19}F NMR spectrum of trans-(X)



(δ, ppm): 8.86 (F_a), 44.2 (F_b), 32.9 (F_c), 86.5 (F_d); $J_{ab} = 2.4$, $J_{ac} = 4.7$, $J_{ad} = 5.7$, $J_{cb} = 27.5$, $J_{bd} = 13.2$, $J_{cd} = 135$ Hz. ^{19}F NMR spectrum of cis(X)



(δ, ppm): 8.51 (F_a), 11.2 (F_d), 43.0 (F_b), 73.8 (F_c); $J_{ab} = 2.4$, $J_{ac} = 6.8$, $J_{bc} = 11.6$, $J_{bd} = 5.1$, $J_{cd} = 21.2$ Hz. The mass spectra of (IX) and (X) are analogous to that of (IV). The ^{19}F NMR spectrum of (II) is given above.

CONCLUSIONS

The 4-H- and 4-Cl-perfluoro-1-butenes when treated with SbF_5 rearrange to terminal polyfluorobutenes that contain either H or Cl at the multiple bond.

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