methylsilyldiethylamine and a catalytic amount of $(NH_4)_2SO_4$ were added, and the mixture was heated for 1-2 h at 130-160° until the liberation of diethylamine had ceased. The products were vacuum-distilled (see Table 1).

1-Phenyl-2-isopropoxy-2-thiono-1,3,2-diazaphospholane (X). A mixture of 4.08 g of N-phenylethylenediamine and 7.02 g of isopropyl tetraethyldiamidophosphite was heated for 1 h at 130-140°. When the liberation of diethylamine had ceased the mixture was treated with 0.96 g of sulfur and then heated for 15 min at 100°. Recrystallization from benzene gave 3.1 g (40%) of (X), mp 110°. ^{31}P NMR spectrum = −72 ppm; IR spectrum: ν 3290 cm^{-1} (NH). Found: N 10.96; P 11.76%. $C_{11}H_{17}N_2OP$. Calculated: N 10.94; P 12.21%.

CONCLUSIONS

1. The reaction of N-phenyl(benzyl)ethylenediamine with the full amides of phosphorous acid gave a number of N-phosphorylated 1,3,2-diazaphospholanes.

2. The reaction of alkanolamines with the diamides of alkylphosphorous acids, followed by treatment with trimethylsilyldiethylamine in the presence of catalytic amounts of ammonium sulfate, gave N-silylated 1,3,2-oxazaphospholanes and phosphorinanes.

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ELECTROPHILIC ISOMERIZATION OF FLUORO-CONTAINING OLEFINS

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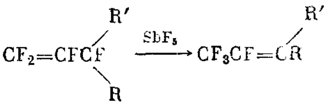
UDC 542.952.1:547.413

Previously we had shown that perfluoropropylene and 2-hydroperfluoropropylene react with fluoro-containing ethylenes in the presence of SbF_5 to give the corresponding pentenes with the multiple bond in the 2 position [1].

$$CF_3CF{=}CF_2 \xrightarrow{SbF_5} [CF_2{=}CFCF_2]^+ \xrightarrow{CF_2=CF_2,\ SbF_6^-}$$
$$[CF_2{=}CFCF_2CF_2CF_3] \xrightarrow{SbF_5} CF_3CF{=}CFCF_2CF_3$$

One of the steps of the proposed scheme includes rearrangement under the influence of SbF_5, with migration of the multiple bond from the 1 to the 2 position. A similar shift of the multiple bond was confirmed experimentally in the present paper. It proved that terminal fluoro-containing olefins when treated with catalytic amounts of SbF_5 are smoothly isomerized to the corresponding olefins with the multiple bond in the 2 position, in which connection the rearrangement is stereospecific and leads only to the trans isomers.



$$CF_2{=}CFCF(R')(R) \xrightarrow{SbF_5} CF_3CF{=}C(R')R$$

(Ia)—(IVa)

$R = C_2F_5$, $R' = F$ (I); $R = C_3F_7$, $R' = F$ (II); $R = CF_3CF_2CF_2H$, $R' = F$ (III);
$R = R' = CF_3$ (IV)

The sole exception is perfluoroallylbenzene, the rearrangement of which gives a mixture of the cis- and trans-perfluoropropenylbenzenes in a 1:1 ratio. Both isomers were isolated in the pure state by preparative GLC. The pure cis and trans isomers when treated with SbF_5 again form equivalent mixtures of the cis- and trans-perfluoropropenylbenzenes.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1640-1643, July, 1978. Original article submitted October 13, 1977.

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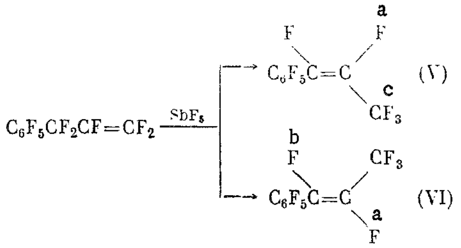
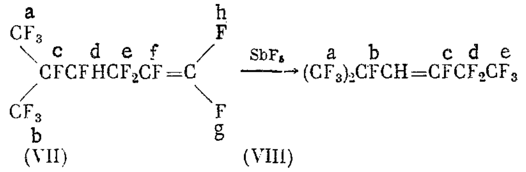
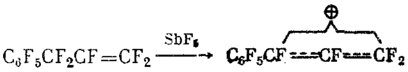


Previously we had postulated that under the influence of SbF_5 the multiple bond can shift not only to the 2 position, but also to the 3 position, provided the starting olefin has a CFH group β to the multiple bond [1]. This postulation was also confirmed experimentally.

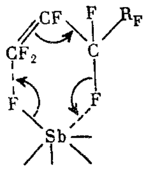


Migration of the multiple bond in fluoroolefins under the influence of alkali metal fluorides is known [2]. In this case the rearrangement is accomplished via the intermediate formation of the carbanion and naturally leads to a mixture of the cis and trans isomers. Since SbF_5 is one of the most powerful acceptors of fluoride ion, the migration of the multiple bond in our case bears a substantially different character. It may be assumed that the rearrangement of perfluoroallylbenzene is accomplished via the step of forming the carbcation. This assumption makes it possible to explain both the formation of equal amounts of the cis- and trans-perfluoropropenylbenzenes and the mutual transformations of the cis and trans isomers under the influence of SbF_5.



$$C_6F_5CF_2CF{=}CF_2 \xrightarrow{SbF_5} \overset{\oplus}{C_6F_5CF{\cdots}CF{\cdots}CF_2}$$

In the case of aliphatic perfluoroolefins the formation of the carbenium ion is less probable, and reaction is apparently accomplished via a six-membered transition complex, in which the bulky perfluoroalkyl group can occupy an equatorial position, which leads to the predominant formation of the trans-olefin.



EXPERIMENTAL

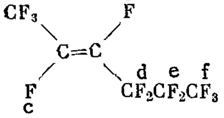
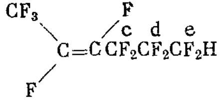
The ^1H and ^{19}F NMR spectra were recorded on a Hitachi–Perkin–Elmer R-20 instrument (60 and 56.4 MHz), using HMDS and CF_3COOH as the external standards. Both the GLC analysis and the preparative separation were run using a column packed with 20% SE-30 deposited on Chromosorb W. The ^{19}F NMR of (IIa) was recorded on a Perkin–Elmer R-32 instrument (86.4 MHz). The starting olefins, (I)-(III), were obtained by the pyrolysis of the Na salts of the corresponding acids as described in [3, 4], while olefins (IV) and (VII) were obtained by a modification of the method given in [5] for the radical telomerization of trifluoroethylene and perfluoroisopropyl iodide in the presence of benzoyl peroxide, with subsequent dehydrohalogenation of the adducts using solid KOH. Compound (VII), bp 68-70°C. ^{19}F NMR spectrum (δ, ppm): -3.4 (F_a), 0.2 (F_b), 111 (F_c), 133 (F_d), 30.4 (F_e), 114.2 (F_f), 15.5 (F_g), 37.9 (F_h); $J_{ab} = 10.5$, $J_{eh} = 27.4$, $J_{fh} = 116$, $J_{fg} = 39.4$, $J_{hg} = 56.5$ Hz. PMR spectrum: 5 ppm. $J_{HF_d} = 42.7$, $J_{HF_e} = 7.3$ Hz. Infrared spectrum: ν 1790 cm^{-1}. Mass spectrum, m/e: 332 (M^+, $C_7F_{13}H$), 313 ($C_7F_{12}H$), 121 (100%, $C_3F_5^+$).

The fluoroolefins were rearranged by a typical method. To the fluoroolefin at 0° was added several drops of SbF_5. After holding for 1 h the reaction mass was poured on ice and the organic layer was separated, dried, and distilled. The yield was 70-90%. The rearrangement of olefin (IV) was run in a sealed glass ampul at 30-40°.

TABLE 1

Compound	δF_o	δF_p	δF_m	δ_a	δ_b	δ_c	J_{bc}	J_{ac}	J_{c-F_o}
							Hz		
(V)	60,8	69,3	83,9	67,5	38,7	−7,2	7	11,8	2,4
(VI)	60,1	69,6	83,9	82,7	58,7	−8,5	21	10	141,5 *

* J_{ab}

Based on the IR, Raman, and ^{19}F NMR spectra, compound (Ia), bp 27-29°, is identical with the authentic compound [1].  (IIa), bp 52-53°. Raman spectrum: 1733 cm^{-1}. ^{19}F NMR spectrum (δ, ppm): −6.3 (F_a), 81.5 (F_b, F_c), 81.3 (F_b, F_c), 41 (F_d), 52.3 (F_e), 5.3 (F_f); J_{ab} = 13.6, J_{bc} = 139, J_{be} = J_{ce} = 6.5, J_{cd} = 18.2, J_{df} = 9.1 Hz. Mass spectrum, m/e: 300 (M^+, C_6F_{12}), 281 ($C_6F_{11}^+$), 181 (100%, $C_4F_7^+$).  (IIIa), bp 68-69°. Raman spectrum: 1733 cm^{-1}. ^{19}F NMR spectrum (δ, ppm): −6.6 (F_a), 81.6 (center of AB system, F_b), 43.7 (F_c), 59.6 (F_d), 61.4 (F_e). Mass spectrum, m/e: 282 (M^+, $C_6F_{11}H$), 263 ($C_6F_{10}H^+$), 181 ($C_4F_7^+$, 100%). (IVa), bp 28-30°. Infrared spectrum: 1700 cm^{-1}. The ^{19}F NMR spectrum is identical with that described in [6]. Mass spectrum, m/e: 250 (M^+, $C_5F_{10}^+$), 231 ($C_5F_9^+$), 181 (C_4F_7, 100%). For (V) and (VI) the IR spectra correspond to those described in [7]. The ^{19}F NMR spectrum (δ, ppm)* is given in Table 1. Compound (VIII), bp − 68 to −70°. ^{19}F NMR spectrum (δ, ppm): 1.6 (Fa), 110.2 (F_b), 35 (Fc), 46.4 (F_d) 8.2 (F_e); J_{ab} = 7.3, J_{bc} = 35, J_{cd} = 12.2, J_{ce} = 6.4, J_{de} = 1.4, J_{ac} = 5.2 Hz. PMR spectrum: δ5.5 ppm, J_{HFc} = 29.5 J_{HF_b} = 22.3 Hz. Mass spectrum, m/e: 332 (M^+, $C_7F_{13}H$), 313 ($C_7F_{12}H$), 263 (100%, $C_6F_{10}H$).

CONCLUSIONS

Antimony pentafluoride isomerizes terminal fluoroolefins to olefins with an internal multiple bond.

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*The ^{19}F NMR spectra of CCl_4 solutions of (V) and (VI) are described in [7].