observed when it was warmed up to 0-10°, with the liberation of (I) and fluorosulfonic acid. ^{19}F NMR spectrum (δ, ppm): —107.5 s (NF_2); —129.0 s (OSO_2F); +62.5 s (NFH).

CONCLUSIONS

1. Pentafluoroguanidine reacts easily with electrophilic reagents: chlorine fluorosulfate, peroxydisulfuryl fluoride, and nitryl chloride.

2. In bis(difluoroamino)fluorochloroaminomethyl and bis(difluoroamino)fluorosulfatemethyl fluorosulfates the difluoroamino groups are easily replaced by fluorosulfate groups uncer the influence of either chlorine fluorosulfate or peroxydisulfuryl fluoride.

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DEDIMERIZATION OF PERFLUORODIMETHYLAZAPROPENYLAMINE

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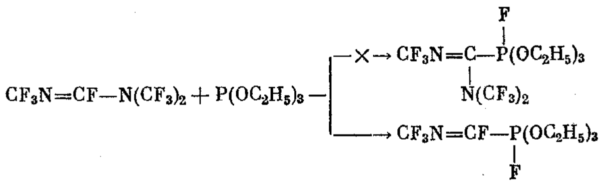
In contrast to the highly electrophilic perfluoro-2-azapropene (I), the chemical properties of its dimer, perfluorodimethylazapropenylamine (II), have received little study.

We found that the treatment of (II) with various nucleophilic reagents (triethyl phosphite, dialkylamines, fluoride ion) results in its dedimerization.* Thus, the reaction product from (II) and triethyl phosphite is not phosphorane (III), but instead triethoxyperfluoroazapropenylfluorophosphorane (IV), which we obtained earlier by reacting perfluoro-2-azapropene with triethyl phosphite [2], in which connection the yield of (IV) reaches 70% when a 1 : 2 mole ratio of (II) and the phosphite is used.



$$CF_3N{=}CF{-}N(CF_3)_2 + P(OC_2H_5)_3 \begin{cases} \xrightarrow{\times} CF_3N{=}\underset{N(CF_3)_2}{C}{-}\overset{F}{P}(OC_2H_5)_3 & \text{(III)} \\ \longrightarrow CF_3N{=}CF{-}\underset{F}{P}(OC_2H_5)_3 & \text{(IV)} \end{cases}$$

The decomposition of (II) that occurs here is explained by the presence of the easily leaving bis(trifluoromethyl)amino group in its molecule. The reaction apparently proceeds via a cyclic transition state; the (I) that is cleaved here reacts with a second triethyl phosphite molecule.

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* It was recently mentioned [1] that when (I) is reacted with aromatic amines to produce heterocyclic systems the dimer (II) can be used instead of (I).

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 488-490, February, 1978. Original article submitted July 8, 1977.

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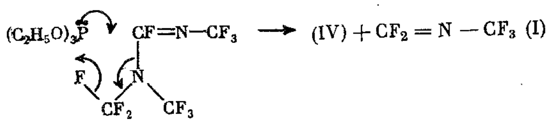
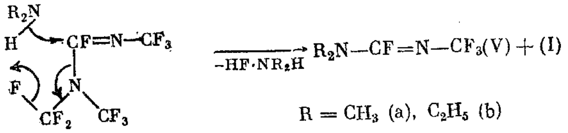
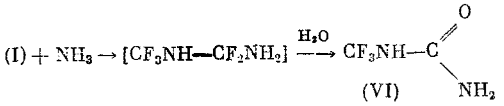


As it proved, the dedimerization of (II) is a quite general reaction, and is apparently explained by the low mobility of the vinyl fluorine atom. Thus, the previously unknown dialkylperfluoroazapropenylamines (Va, b) are formed when (II) is reacted with dialkylamines

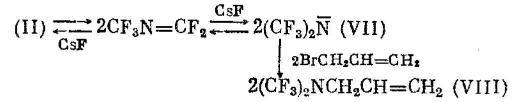


These compounds are also formed in quantitative yield by the direct reaction of dialkylamines with (I), while the reaction of (I) with NH_3, followed by hydrolysis of the reaction mixture, gave the amide of trifluoromethylcarbamic acid (VI)



In contrast to the dialkylperfluoroisobutenylamines [3], the (V) amines are hydrolytically stable (they remain unchanged when refluxed for a long time with excess water).

Previously we had found that the bis(trifluoromethyl)aza anion is generated when (I) reacts with CsF (KF) [4, 5]. As it proved, this same anion is also formed when CsF is reacted with (II), which is confirmed by the ^{19}F NMR spectrum, and also by fixing (VII) with allyl bromide



$$(II) \underset{CsF}{\rightleftarrows} 2CF_3N{=}CF_2 \overset{CsF}{\rightleftarrows} 2(CF_3)_2\bar{N}\ (VII) \xrightarrow{2BrCH_2CH=CH_2} 2(CF_3)_2NCH_2CH{=}CH_2\ (VIII)$$

In contrast to (I), dimer (II) does not react with carboxylic acids (acetic, trichloroacetic) and alcohols (CH_3OH, C_2H_5OH) [6].

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Hitachi – Perkin – Elmer R-20 instrument (56.46 MHz). The chemical shifts are given in parts per million relative to CF_3COOH (external standard). The IR spectra were taken on a Perkin – Elmer 225 spectrometer (as a thin layer).

Triethoxyperfluoroazapropenylfluorophosphorane (IV). With stirring, to 7.0 g of (II) at –30°C was added 8.3 g of triethyl phosphite. The temperature of the mixture was brought up to ~20° and then it was vacuum-distilled to give 10.5 g (70.5%) of (IV), bp 79° (2 mm); n_D^{20} 1.3780. The ^{19}F NMR spectrum was identical with the spectrum of an authentic specimen [2].

Diethylperfluoroazapropenylamine (Vb). a) With stirring, 3.6 g of diethylamine was added to a solution of 7.0 g of (II) in 25 ml of abs. ether. The reaction mixture was washed with water, dried over $MgSO_4$, and vacuum-distilled to give 6.0 g (65%) of (Va), bp 50° (6 mm); n_D^{20} 1.3830. Found: C 39.68; N 15.20; H 5.57%. $C_6H_{10}F_4N_2$. Calculated: C 39.71; N 15.05; H 5.38%. ^{19}F NMR spectrum: –25.56 q (CF); –29.41 d (CF_3); J_{CF_3-CF} = 11.2 Hz. Infrared spectrum: 1730 cm⁻¹ (C=N).

b) With stirring and cooling (–50°), 14.6 g of diethylamine was added to 13.3 g of (I) in 50 ml of abs. ether. The temperature of the mixture was brought up to ~20°, after which it was washed with water, dried over $MgSO_4$, and vacuum-distilled to give 18.0 g (96.7%) of (Vb), which was identical with that described above.

Dimethylperfluoroazapropenylamine (Va). With stirring and cooling (–30°), 2.2 g of dimethylamine was added to a solution of 7 g of (II) in 25 ml of abs. ether. The temperature of the mixture was brought up to ~20°, after which it was washed with water, dried over $MgSO_4$, and vacuum-distilled to give 4.8 g (60.8%) of (Va), bp 45° (10 mm); n_D^{20} 1.3690. Found: C 29.92; N 17.84; H 3.79%. $C_4H_6F_4N_2$. Calculated: C 30.30; N 17.72; H 3.79%. ^{19}F NMR spectrum: – 26.30 q (CF); –28.70 d (CF_3); J_{CF_3-CF} = 11.2 Hz. Infrared spectrum: 1730 cm⁻¹ (C = N).

Amide of Trifluoromethylcarbamic Acid (VI). With stirring and cooling (−60°), 2.3 g of dry NH_3 was added to a solution of 7 g of (I) in 30 ml of abs. ether. The temperature of the mixture was brought up to ~20°, after which it was washed with water, the aqueous layer was extracted with ether, the extract was dried over $MgSO_4$, the ether was distilled off, and the residue was recrystallized from benzene to give 4.2 g (65.6%) of (VI), mp 111° (sublimination). Found: 19.08; N 21.60; H 2.45%. $C_2F_3N_2H_3O$. Calculated: C 18.76; N 21.84; H 2.34%. ^{19}F NMR spectrum: −21.94 s (CF_3).

Bis(trifluoromethyl)allylamine (VIII). To a suspension of 15.2 g of CsF in 50 ml of abs. CH_3CN was added 7 g of (II). Exothermic reaction and transformation of the ^{19}F NMR spectrum of (II) were observed. Then, with stirring, 6.0 g of allyl bromide was added and the mixture was heated for 3 h at 50-60°. The products, collected in the trap (−70°), were distilled to give 3.5 g (39.3%) of (VIII), bp 42°; n_D^{20} 1.3100. ^{19}F NMR spectrum: = −18.7 s (CF_3) [4].

CONCLUSIONS

1. The reaction of nucleophilic reagents with perfluorodimethylazapropenylamine leads to its dedimerization.

2. The reaction of perfluoro-2-azapropene with dialkylamines and ammonia respectively gave dialkylperfluoroazapropenylamines and the amide of trifluoromethylcarbamic acid.

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