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Perfluoro-2-azapropene (I) is a peculiar analog of the fluoroolefins, whose electrophilic properties are well known. Although the action of nucleophilic reagents on (I) was studied in a number of papers [1-5], a comparison of its reactivity with that of the fluoroolefins was not made.

The calculations of the atomic charges of (I) and fluoroolefins, made at our request by I. Ya. Aliev, who used the INDO method and a BÉSM-6 electronic computer, show that the electron density deficiency on the carbon of the difluoromethylene group in perfluoro-2-azapropane is greater than in perfluoroisobutylene ($Q_{CF_2} = 0.709$ and 0.645 for (I) and perfluoro-isobutylene, respectively). These data are found to agree with the results that were obtained by us when studying the action of trialkyl phosphites on (I). As it proved, the latter, similar to perfluoroisobutylene [6], reacts with trialkyl phosphites under mild conditions to give trialkoxyperfluoroazapropenylfluorophosphoranes (IIa, b), which are stable intermediate products of the Arbuzov reaction.

 $CF_{3}N = CF_{2} + P(OR)_{3} \rightarrow CF_{3}N = CF - PF(OR)_{3}$ (I)
(IIa, b) $R = CH_{3} (a), C_{2}H_{5} (b)$

The structure of (IIa, b), with a pentacoordination phosphorus atom, is confirmed by the ¹⁹F NMR spectra. Thus, signals were observed that correspond to a P-F group with a covalent bond bwtween the phosphorus and fluorine atoms (doublet with a spin-spin coupling constant of 825 Hz), and also signals from the CF₃ and CF groups ($J_{P-CF} = 110$ Hz).

As it proved, (I) is more active in the reaction with triethyl phosphite than perfluoroisobutylene: (IIb) was obtained in ~70% yield when (I), perfluoroisobutylene, and triethyl phosphite are mixed in equimolar amounts, and the perfluoroisobutylene was recovered almost completely unchanged. As a result, perfluoro-2-azapropene is more electrophilic than perfluoroisobutylene, which is the most electrophilic of the nonfunctional fluoroolefins.

Trialkoxyperfluoroazapropenylfluorophosphoranes (IIa, b) are stable at room temperature; (IIb) can even be vacuum-distilled without decomposition (bp 70°) (0.4 mm)). However, when heated above 120°C ((IIa) above 80°) they decompose.* Here it unexpectedly proved that, in contrast to triethoxyperfluoroisobutenylfluorophosphorane, which decomposes with the elimination of either ethyl fluoride or diethyl ether and gives the corresponding perfluoroisobutenylphosphonates (Arbuzov rearrangement) [6], phosphoranes (IIa, b) when pyrolyzed give the alkyl fluoride, dialkyl fluorophosphate, and trifluoromethylisonitrile (III).

Such a transformation can be either the result of the synchronous process (1) or the Arbuzov rearrangement, with subsequent decomposition of the formed perfluoroazapropenylphos-phonate.

*See [7] regarding the unusual cleavage displayed by the adducts of perfluoromethacrylates and trialkyl phosphites.

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The structure of trifluoromethylisonitrile (III) was proved by converting it to trifluoromethyldibromomethylenimine (IV).

EXPERIMENTAL

The ¹⁹F NMR spectra were taken on a Perkin-Elmer R-20 instrument (56.46 MHz), and the chemical shifts are given in parts per million (the standards were CF₃COOH and HMDS).

<u>Triethoxyperfluoroazapropenylfluorophosphorane (IIb).</u> With shaking, to 8.0 g of perfluoro-2-azapropene at -50° was added 8.3 g of triethylphosphite. The temperature of the mixture was brought up to 20° and then it was vacuum-distilled. We obtained 10.8 g (72.2%) of (IIb), bp 69-70° (0.4 mm); np^{2°} 1.3780; d₄^{2°} 1.2470. Found: C 32.15; H 5.22; N 4.66; P 10.52; F 31.48%. C₈H₁₅F₅NPO₃. Calculated: C 32.10; H 5.02; N 4.68; P 10.37; F 31.77%. ¹⁹F NMR spectrum: -2.8 br.d (PF); -68.9 d.q (CF); -22.6 d.d (CF₃); J_{F-P} = 825; J_{CF-P} = 6; J_{CF-CF₃} = 11; J_{CF-PF} = 110 Hz.

 $\frac{\text{Trimethoxyperfluoroazapropenylfluorophosphorane (IIa)}{\text{yield, mp 49-50°.}} \text{ obtained the same as (IIb) in 66.9% yield, mp 49-50°.} \text{ 19F NMR spectrum: 0.5 br.d (PF); -69.5 d.q. (CF); -22.5 d.d (CF_3);} J_{F-P} = 825; J_{CF-P} = 6; J_{CF-CF_3} = 11; J_{CF-PF} = 110 \text{ Hz.}}$

Reaction of Perfluoro-2-azapropene with Triethyl Phosphite in Presence of Perfluoroisobutylene. With shaking, to a mixture of 8.0 g of perfluoro-2-azapropene and 11.0 g of perfluoroisobutylene at -50° was added 8.3 g of triethyl phosphite. The temperature of the mixture was brought up to ~20° and then it was heated on the steam bath for 30 min, and here 9.8 g of perfluoroisobutylene (bp 6°, the ^{1°}F NMR spectrum was identical with the spectrum of an authentic specimen) was collected in a cooled trap (-78°). Vacuum-distillation of the residue gave 9.3 g (69%) of (IIb), which was identical with an authentic specimen.

Thermal Decomposition of Triethoxyperfluoroazapropenylfluorophosphorane (IIb). Here we heated 15.0 g of (IIb) to 120°, and then the temperature rose spontaneously to 150°. Using traps, immersed in a cooling mixture (-78 and -120°), we collected 5.6 g of gaseous products, which when distilled in a TsIATIM-52 apparatus gave 2.8 g (58.9%) of trifluoromethylisonitrile (III), bp -83 to -81° [8] (Found: mol. wt. 93.5. C_2F_3N . Calculated: mol. wt. 95.0), and 1.8 g (75.0%) of ethyl fluoride, bp -32°. The ¹H and ¹⁹F NMR spectra were identical with the spectra of authentic specimens.

Vacuum-distillation of the residue gave 5.8 g (74.3%) of diethyl fluorophosphate, bp 54° (9 mm); $n_D^{2°}$ 1.3729 [9]. The ¹⁹F NMR spectrum was identical with the spectrum of an authentic specimen.

<u>Thermal Decomposition of Trimethoxyazapropenylfluorophosphorane (IIa)</u>. Similar to the preceding, from 12.4 g of (IIa) we obtained 3.8 g of a mixture of gaseous trifluoromethyl-isonitrile (III) and methyl fluoride (GLC), and also 4.7 g (73.4%) of dimethylfluorophosphate, bp 48-50° (22 mm); n_D^{20} 1.3530 [9]. The ¹⁹F NMR spectrum was identical with the spectrum of an authentic specimen.

Trifluoromethyldibromomethylenimine (IV). The treatment of 1.9 g of (III) with bromine, followed by distillation, gave 2.9 g (56.8%) of (IV), bp 87-89° [8].

CONCLUSIONS

1. Perfluoro-2-azapropene is more electrophilic than perfluoroisobutylene, which is the most electrophilic of the nonfunctional fluoroolefins.

2. The reaction of perfluoro-2-azapropene with trialkyl phosphites gave trialkoxyperfluoroazapropenylfluorophosphoranes, which are stable intermediate products of the Arbuzov reaction.

3. The trialkoxyperfluoroazapropenylfluorophosphoranes when heated decompose to the alkyl fluoride, dialkyl fluorophosphate, and trifluoromethylisonitrile.

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REACTION OF PERFLUORO-2-AZAPROPENE WITH CARBOXYLIC ACIDS

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In a previous communication [1] it was shown that perfluoro-2-azapropene (I) is more electrophilic than perfluoroisobutylene. It seemed of interest to study the reaction of (I) with carboxylic acids.

As it proved, in contrast to perfluoroisobutylene [2], (I) reacts easily, without nucleophilic assistance, with carboxylic acids. In the case of weak acids (acetic, benzoic) the reaction proceeds in ether solution at low temperature (0 to -20° C). Less nucleophilic strong carboxylic acids (trifluoro- and trichloroacetic, perfluorobutyric) react without a solvent at room temperature. The addition products, the (trifluoromethylamino)difluoromethyl esters of the corresponding acids (IIa-e), are formed in all cases:

$$\begin{array}{c} CF_{3}N = CF_{2} + RCOOH \rightarrow CF_{3}N - CF_{2}OCOR \\ (I) & H & (II) \\ R = CH_{3}(a), C_{6}H_{5}(b), CCl_{3}(c), CF_{3}(d), C_{3}F_{7}(e) \end{array}$$
(1)

The structure of the (II) esters was confirmed by the ¹⁹F NMR and IR spectral data. The ¹⁹F NMR spectra displayed two multiplets at -17.3 to -21.5 and -19.6 to -22.5 ppm from the difluoromethyl and trifluoromethyl groups, respectively, with a 2:3 ratio of the integral intensities. The multiplet structure of the signals is evidently due to the additional splitting of the nuclei of the fluorine atoms on the proton of the NH group. Actually, the addition of D₂O to the sample transforms the multiplet structure to a triplet from the CF₃ group and a quartet from the CF₂ group. The IR spectra of all of the obtained compounds have a band in the 3300 cm⁻¹ region (NH). The (II) esters are heat unstable and, depending on the acyl radical, decompose in two directions. Whereas the esters of weak acids (IIa, b) when heated decompose to the corresponding acyl fluoride and trifluoromethylcarbamoyl fluoride,* the derivatives of strong acids decompose to the starting compounds. It is interesting that in the presence of catalytic amounts of triethylamine the reaction product of (I) with AcOH is not the ester (II), but rather a mixture of acetyl fluoride and N-trifluoromethylacetamide (III):

(I) + CH₃COOH
$$\xrightarrow{N(C_2H_3)_3}$$
 CF₃NH-C-CH₃ + CH₃COF + CO₂ (2)
(III)

Apparently, the initially formed addition product (II) is decomposed to acetyl fluoride and trifluoromethylcarbamoyl fluoride. The latter in the presence of triethylamine forms the mixed anhydride of trifluoromethylcarbamic and acetic acids (IV), the decarboxylation of which leads to amine (III):

*The reaction of (I) with AcOH, followed by treatment of the trifluoromethylcarbamoyl fluoride with KF, is a convenient method for the synthesis of trifluoromethyl isocyanate.

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