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Abstract

Full Text

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α-Nitrosohexafluoroisobutyric Acid

Nitroso compounds of the aliphatic series are represented by a single type of substances, in which the nitroso group is located at a tertiary carbon atom; moreover, as is known, these latter are dimeric—they are, in the pure state, colorless, usually crystalline substances, which only in solutions and in vapors dissociate into blue or green monomers.

In recent years a series of ϕ-nitrosoalkanes has been obtained which, in contrast to their hydrocarbon analogs, are monomeric and therefore deeply colored; however, ϕ-nitrosoalkanes bearing functional groups in the α-position (apart from halogens) remained unknown. In the present work we have succeeded for the first time in synthesizing nitroso compounds containing carboxyl and fluorocarbonyl groups in the α-position.

These are the fluoroanhydride (I) and the ethyl ester (II) of α-nitrosohexafluoroisobutyric acid. The first of these compounds is readily obtained by addition of nitrosyl fluoride to the known [1] fluoroanhydride of perfluoromethacrylic acid, analogously to the procedure described for fluoroolefins [2,3]. Careful alcoholysis of fluoroanhydride I gives the nitroso ester II

$$CF_2{=}C(CF_3)-COF \xrightarrow{FNO} CF_3-C(CF_3)(NO)-COF \xrightarrow{C_2H_5OH} CF_3-C(CF_3)(NO)-COOC_2H_5.$$

(I) (II)

Derivatives of α-nitrosohexafluoroisobutyric acid constitute a new class of organofluorine compounds. They are dark blue in color, which indicates their existence in monomeric form (esters of the known α-nitrosoisobutyric acid [4] exist in the form of colorless dimers). On distillation, nitroso derivatives I and II become decolorized with evolution of nitrogen oxides, which is apparently connected with their facile oxidation by atmospheric oxygen and subsequent hydrolysis of the nitrites (III) formed

$$(CF_3)_2C(NO)-COX \xrightarrow{[O]} (CF_3)_2C(ONO)-COX \xrightarrow{H_2O} (CF_3)_2C(OH)-COX+HNO_2.$$

However, both the fluoroanhydride and the ester of α-nitrosohexafluoroisobutyric acid distil without decomposition in a stream of dry carbon dioxide.

The spectra in the visible region were measured in petroleum ether at room temperature on an SF-4A spectrophotometer. The blue coloration is due to weak absorption in the region 630-670 mμ. The spectra of derivatives of α-nitrosohexafluoroisobutyric acid are given below. For comparison we also recorded, in the visible region, the spectrum of the known tertiary nitrosoperfluorobutane

$$\begin{aligned} (CF_3)_3C-NO \quad & \lambda_{max}\ 663\ \text{m}\ ; \quad \varepsilon_{max}\ 8.8 \\ (CF_3)_2C(NO)-COOC_2H_5 \quad & \lambda_{max}\ 652\ \text{m}\ ; \quad \varepsilon_{max}\ 7.1 \\ (CF_3)_2C(NO)-COF \quad & \lambda_{max}\ 637\ \text{m}\ ; \quad \varepsilon_{max}\ 8.6 \end{aligned}$$

Monomeric nitroso compounds usually absorb in the region 670-690 mμ ([5–8]). There are a number of data indicating that, when an electronegative substituent is introduced into the α-position to the nitroso group, a hypsochromic shift of the absorption maximum occurs ([9]).

In the nitroso compounds we investigated, the trifluoromethyl, fluorocarbonyl, and carbethoxy groups, being strong electrophilic substituents, shift the absorption maximum of the nitroso group into the short-wavelength region; moreover, the maximum hypsochromic shift is observed for α-nitrosohexafluoroisobutyric acid fluoride, and the smallest for ethyl nitrosoperfluorobutyrate, in accordance with the electronegativities of the COF-, $COOC_2H_5$-, and CF_3-groups.

In the IR spectra of the nitroso derivatives of hexafluoroisobutyric acid obtained, interesting regularities are observed.* The vibrational frequencies of the carbonyl group are doublets: 1860, 1815 cm^{-1} for the acid fluoride and 1765, 1750 cm^{-1} for the ester. Splitting of the carbonyl frequency is a consequence of rotational isomerism, analogous to that observed for α-halocarbonyl compounds ([10]), with the role of the halogen in the case under consideration being played by the nitroso group. It may be assumed that the higher frequency, as usual, belongs to the more polar structure (IV)—the one in which the oxygen atom of the carbonyl group and the nitroso group are located closer to one another—the cis form

$$NO-C(CF_3)(C(=O)-X)-C(=O)-X \qquad \text{(IV)}$$

$$CF_3-C(NO)(CF_3)-C(=O)-X \qquad \text{(V)}$$

The correctness of this point of view is, on the one hand, indirectly confirmed by the fact that the intensity of the band under consideration is higher (approximately twofold). On the other hand, the reverse effect—the influence of the carbonyl on the nitroso group—is manifested in the appearance of doublets of absorption of the NO group: 1585, 1560 cm^{-1}, of equal intensity, for the acid fluoride, and 1585, 1545 cm^{-1} for the ester, with the intensity of the first band of the doublet in this case being 2.5 times greater. Splitting of the nitroso-group frequency is also apparently associated with hindered free rotation about the C—CO bond, analogous to what was observed earlier both for α-halonitroso compounds (doublet of NO-group absorption) ([11]) and for α-halocarbonyl compounds (splitting of the vibrational frequency of the carbon—halogen bond) ([12]).

Here it is necessary to note the interesting fact that the higher vibrational frequency in the nitroso-group doublet remains constant on going from the acid fluoride to the ester, whereas the lower one shifts into the long-wavelength region by 15 cm^{-1}, parallel to the shift of the carbonyl-group frequency. This fact can be satisfactorily explained by assuming that the frequency 1585 cm^{-1} belongs to the polar cis form of nitroso compounds IV, which is less sensitive to changes in the character of the group X than the trans form (V).

A doublet of low intensity in the spectrum of α-nitrosohexafluoroisobutyric acid fluoride at 1685 and 1720 cm^{-1} is due to an admixture of nitrite III (X-F), which is associated with the above-mentioned easy oxidation of the acid fluoride of the nitroso acid, occurring in this case during recording of the spectrum. Splitting of the nitrite-group frequency, however, cannot be unambiguously explained by field effects, since for nitrites cis-trans rotational isomerism is possible even in those cases when

* The IR spectra were recorded by Sh. Nadzhimutdinov at the Karpov Physicochemical Institute on an IKS-14.

the α-position relative to the nitrite group, for example, for methyl nitrite, is completely symmetrical (13, 14). Some indication that, in the case under consideration, the splitting of the frequency is nevertheless caused by the influence of the fluorocarbonyl group may be the equal intensity of the components of the doublet. Usually, in tertiary nitrites the intensity of the band of the cis form is many times weaker than the absorption intensity of the trans form.

The nitrite doublet cannot be clearly detected in the spectrum of the ethyl ester of nitrosohexafluoroisobutyric acid, since in this case it falls in the absorption region of the carbonyl group.

Experimental Part

Fluoroanhydride of α-nitrosohexafluoroisobutyric acid. Into a quartz flask equipped with a quartz bubbler, 6.2 g (0.035 mole) of the fluoroanhydride of perfluoromethacrylic acid was placed, and at −78° over the course of 30 min 1.89 g (0.039 mole) of nitrosyl fluoride was condensed. Nitrosyl fluoride can

be stored indefinitely long (but not more than 6 months) in a cylinder made of 1Kh18N9T steel passivated with elemental fluorine. A cylinder of 20 ml capacity was connected to the bubbler by means of a fluororubber tube. The mixture was kept at low temperature for 12 h, and then slowly warmed to 0°, passing a stream of dry carbon dioxide through it. By distillation at atmospheric pressure in a stream of CO_2, 3.83 g of the fluoroanhydride of α-nitrosohexafluoroisobutyric acid was obtained, b.p. 26-28°/730 mm, and 1.8 g of unreacted fluoroanhydride of perfluoromethacrylic acid, b.p. 48-52°. The latter was identified by gas-liquid chromatography. The yield of nitrosofluoroanhydride I was 56%, calculated on the unsaturated fluoroanhydride that entered into the reaction.

IR spectrum; ν_max (cm^{-1}): 670 m., 935 m., 960 m., 1100 m., 1140 m., 1205 v.s., 1245 s., 1300 m., 1560 m., 1585 m., 1685 w., 1720 w., 1815 m., 1860 v.s.

Found %: F 58.81; $C_4F_6O_2N$. Calculated %: F 58.65

Ethyl ester of α-nitrosohexafluoroisobutyric acid. To 2.72 g of the fluoroanhydride of α-nitrosohexafluoroisobutyric acid, on cooling to −78°, 10 ml of abs. ethanol was added. The mixture was warmed to 0°, diluted with ice water, and the precipitated blue oil was dried and distilled in an atmosphere of carbon dioxide. 1.54 g (51%) of the ethyl ester of α-nitrosohexafluoroisobutyric acid was obtained, b.p. 102-105°/740 mm; n_D^{20} 1.3260.

IR spectrum; ν_max (cm^{-1}): 680 m., 725 s., 825 m., 850 m., 900 w., 930 w., 990-1390 v.s., 1445 m., 1465 m., 1545 m., 1585 s., 1750 s., 1765 v.s.

Found %: C 28.35; H 2.13; F 45.14; N 5.75
$C_6H_5F_6O_3N$. Calculated %: C 28.45; H 1.98; F 45.07; N 5.41

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Note: Figure translations are in progress. See original paper for figures.