α, β -UNSATURATED FLUORINE-CONTAINING THIOCYANATES*

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A new method has been developed for the synthesis of perfluorinated α,β -unsaturated thiocyanates by the reaction of the corresponding sulfenyl chlorides with KCN in water. The thiocyanate form of perfluoro-2-methyl-2-pentene-3-thiocyanate was isomerized to the isothiocyanate form. This rearrangement is initiated by both fluoride and thiocyanate anions.

Both saturated and α,β -unsaturated organic thiocyanates are common and extensively studied compounds [2,3].

In contrast, only a few perfluorinated saturated thiocyanates have been described by Igumnov [4] and Emeléus [5], while their α,β -unsaturated analogs have remained virtually unknown.

It might appear that the simple substitution of the fluorine atom at a vinyl carbon atom in perfluoroolefins by an SCN group would provide a synthesis for α,β -unsaturated perfluorothiocyanates. However, as shown in the case of perfluoroisobutylene, such a reaction leads to the isomeric isothiocyanate (I) and to a dimer, namely, bis(trifluoromethyl)thioketene (II). In the opinion of Knunyants [6,7], this dimer is formed due to decomposition of thiocyanate (II) under the reaction conditions.



The only α,β -unsaturated perfluorothiocyanate described in the literature, 1,2-dithiocyano-3,3-difluoro-1-cyclopropene (III), contains an electron-deficient small ring [8].



An attempt to expand this reaction to large-ring polyfluorocycloolefins did not lead to the expected results [8].

In the present work, we showed that both linear and cyclic α,β -unsaturated perfluorothiocyanates may be obtained by the replacement of the halogen at the sulfur atom by a nitrile group in readily available α,β -unsaturated perfluorinated sulfenyl chlorides [9,10].

*For previous communication, see [1].

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This reaction is carried out under phase transfer conditions at 5-10°C and leads to the desired products in 50-80% yield.

 α,β -Unsaturated thiodynates (II), (IV), and (V) are stable, highly mobile, colorless liquids, which do not spontaneously rearrange to the corresponding isothiodynates either at -20°C or upon heating in an autoclave at 150°C for 6-7 h. Isomerization is also not observed in polar solvents such as sulfolane and benzonitrile at room temperature as indicated by gas-liquid chromatography and IR and ¹⁹F NMR spectroscopy.

This behavior distinguishes these compounds from their hydrocarbon analogs, which are relatively unstable and undergo thermal isomerization to isothiocyanates readily and often during distillation [2].

Such isomerization is initiated by weak aprotic bases such as N-methylpyrrolidone (NMP) at 20°C and EIO_2 at 230°C in an autoclave.

Thus, thiocyanate (IV) isomerizes to the corresponding isothiocyanate (VI) in NMP over 30 h.



Perfluoro-2-methyl-2-pentene (VII) and 2-hydroperfluoro-2-methylpentane (VIII)^{*} were also isolated in the reaction products along with (VI).

One may expect that in the reaction medium in the above-indicated conditions fluoride ion is formed, which also intiates the isomerization process. The scheme of the conversion may be shown in the following way



Thiocyanate (IV) is converted to olefin (VII) as a result of nucleophilic attack by fluoride ion. The liberated thiocyanate anion, which is ambident, attacks olefin (VII) at the nitrogen atom, which leads to the formation of isothiocyanate (VI). The direct attack of the thiocyanate anion on (IV) also leads to (VI).

These hypotheses were demonstrated experimentally. Thus, under conditions excluding isomerization, the addition of either CsF or KSCN to thiocyanate (IV) in benzonitrile at 20°C gives isomerization to (VI) as indicated by gas-liquid chromatography and ¹⁹F NMR spectroscopy. The direct reaction of olefin (VII) with KSCN in benzonitrile at 10-20°C also leads to isothiocyanate (VI), which indicates that the isothiocyanate anion attacks olefin (VII) by means of the nitrogen atom.

Cyclic α,β -unsaturated thiocyanate (V) gives a complex mixture of unidentified products under analogous conditions in NMP at 20°C over seven days. The corresponding isothiocyanate was not found in the product mixture by IR spectroscopy.

The finding of (VIII) is readily explained by the addition of HF to (VII) as reported by Haszeldine et al. [11].

EXPERIMENTAL

The ¹⁹F NMR spectra (δ , ppm, J, Hz) were obtained on a Bruker WP-200SY spectrometer at 200 MHz, while (V) was obtained on a Perkin-Elmer R-32 spectrometer at 84.6 MHz with CF₃CO₂H. The IR spectra were taken on a UR-20 spectrometer. The purity of the compounds was monitored by gas-liquid chromatography on an LKhM-8MD model 3 chromatograph on a column packed with 20% QF on Chromaton. The mass spectra were taken on a VG 70/70 chromato-mass spectrometer at 70 eV. The m/z values and relative intensity in % for ³²S isotopes are given along with the proposed assignment.

Perfluoro-2-methyl-1-propene-1-thiocyanate (II). A solution of 1.0 g KCN in 5 ml water was added dropwise with stirring to 3.28 g perfluoro-2-methyl-1-propene-1-sulfenyl chloride [9] maintaining the temperature at 5-10°C. After the addition, the mixture was stirred for 15 min, warmed to ~20°C, and poured into water. The organic layer was separated, dried over MgSO₄, and distilled to give 1.7 g (53.9%) (II), bp 70°C (90 mm). Found: C, 25.21; F, 55.85; N, 5.73; S, 13.41%. Calculated for C_5F_7NS : C, 25.11; F, 55.62; N, 5.86; S, 13.41%. Mass spectrum: 239 (45.3) M⁺, 220 (13.9) [M - F]⁺, 108 (29.8) CF_2SCN⁺, 93 (22.5) $C_3F_3^+$, 69 (100) CF_3^+ , 63 (78.7) CFS⁺, 58 (4.3) SCN⁺. IR spectrum (ν , cm⁻¹): 1660 s (C=C), 2170 m (SCN). ¹⁹F NMR spectrum in CCl₄: -24.1 d.q (CF₃¹), -23.4 d.q (CF₃²), -19.3 q.q (F); $J_{CF_3}^{1}r_F = J_{CF_3}^{1}r_{CF_3}^{2} = 9.0$, $J_{CF_3}^{2}r_F = 24.0$ Hz.

Perfluoro-2-methyl-2-pentene-3-thiocyanate (IV). By analogy to the previous procedure, 10.3 g perfluoro-2-methyl-2-pentene-3-sulfenyl chloride [10] and 2.00 g KCN in 8 ml water gave 8.07 g (80.5%) (IV), bp 73-75°C (65 mm). Found: C, 24.44; F, 61.07; S, 9.71%. Calculated for $C_7F_{11}NS$: C, 24.79; F, 61.63; S, 9.45%. Mass spectrum: 339 (25.5) M⁺, 320 (19.9) [M - F]⁺, 220 (56.5) [M - C_2F_5]⁺, 175 (10.6) $C_4F_5S^+$, 163 (21.2) $C_3F_5S^+$, 143 (12.8) $C_4F_5^+$, 132 (9.6) $C_2F_4S^+$, 108 (46.1) CF_2SCN^+ , 93 (9.0) $C_3F_3^+$, 69 (100) CF_3^+ , 63 (8.7) CFS^+ , 58 (7.4) SCN⁺. IR spectrum (ν , cm⁻¹): 1620 s (C=C), 2160 m (SCN). ¹⁹F NMR spectrum in CCl₄: -23.2 t:q.q (CF₃²), -22.0 (q (CF₃¹), -3.5 q (CF₃³), 22.0 q (CF₂); $J_{CF_3}^{1}-CF_3^{2}} = J_{CF_3}^{2}-CF_3^{3}} = 11.0,$ $J_{CF_3}^{2}-CF_2 = 20.0$ Hz.

2-Chloroperfluoro-1-cyclohexene-1-thiocyanate (V). By analogy to the preceding procedure, 6.03 g chloroperfluoro-1-cyclohexene-1-sulfenyl chloride [9] and 1.5 g KCN in 5 ml water gave after distillation 3.02 g (52.0%) (V), bp 65-66°C (10 mm). Found: C, 26.56; F, 48.07; N, 4.74; S, 10.21%. Calculated for C_7F_8CINS : C, 26.47; F, 47.86; N, 4.41; S, 10.10%. IR spectrum (ν , cm⁻¹): 1610 s (C=C), 2160 m (SCN). ¹⁹F NMR spectrum: 29.1 m (CF₂⁻¹), 33.3 m (CF₂⁴), 56.9 m (CF₂², CF₂³).

Perfluoro-2-methyl-2-pentene-3-isothiocyanate (VI). a. A sample of 7.88 g (VII) was added dropwise with vigorous stirring to 4.42 g KSCN in 20 ml abs. PhCN at about 10°C. After completion of the addition, the mixture was brought to ~20°C and maintained for 1 h. Then, the volatile products were evacuated at 1 mm, initially at ~20°C and then at ~50°C into a trap at -78°C. The lower layer in the trap was isolated and distilled to give 4.86 g (VI) [40.3% based on reacted (VII)], bp 56-57°C (69 mm); that remaining in the trap (-78°C) was 1.27 g (VII). Found: C, 24.83; F, 61.76; S, 9.46%. Calculated for C₇F₁₁NS: C, 24.79; F, 61.63; S, 9.45%. Mass spectrum: 339 (100) M⁺, 320 (35.1) [M - F]⁺, 220 (59.3) [M - C₂F₅]⁺, 143 (7.0) C₄F₅⁺, 132 (12.3) (C₂F₄S⁺), 108 (90.0) CF₂NCS⁺, 93 (7.3) C₃F₃⁺; 69 (44.6) CF₃⁺, 63 (6.2) CFS⁺, 58 (2.3) SCN⁺. IR spectrum (ν , cm⁻¹): 1630 s (C=C), 2025, 2080 sh.v.s.br (N=C=S). ¹⁹F NMR spectrum: -21.3 t.q.q (CF₃¹), -17.7 q (CF₃²), 3.6 q (CF₃³), 33.3 q (CF₂); J_{CF3}¹-CF₂ = 21.0; J_{CF3}¹-CF₃² = 11.0; J_{CF3}¹-CF₃³ = 8.0 Hz.

b. A sample of 2 ml abs. N-methylpyrrolidone was added to 2.24 g (IV), maintaining the temperature at about 0°C. Then, the mixture was brought to ~20°C and maintained at this temperature for 30 h. The reaction endpoint was monitored relative to the disappearance of the starting reagent by gas-liquid chromatography. Then, the volatile products were pumped at 1 mm into a trap at -78°C, initially at ~20°C and then at 70°C to give 1.01 g product. Gas-liquid chromatography, ¹⁹F NMR spectroscopy, and chromato-mass spectrometry revealed 62% (VI), 10% (VII), and 28% (VIII). Distillation gave virtually pure (VI), which was identical to the sample obtained in procedure a as indicated by gas-liquid chromatography, IR and ¹⁹F NMR spectroscopy. Products (VII) and (VIII) were collected in the trap at -78°C (the ¹⁹F NMR spectrum coincides with that published by Yanagida [12]).

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CRYSTAL PACKING OF "STRAINED" ORGANIC MOLECULES

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Comparison of the energy of nonbonding interactions in the molecules of a series of conformers and isomers showed that a looser molecular crystal packing corresponds to the conformer or isomer with greater U_{nb} . Analysis of the distribution of the packing coefficients (K_p) for 159 medium and high density organic crystalline structures indicates that the fraction of structures with low K_p is greater for the high density crystals. The minimal K_p (0.612) is close to the value predicted by Kitaigorodskii in the dense packing theory (0.60). A tendency was noted to decreasing K_p with increasing molecular density.

In a search for a correlation between crystal structure and molecular properties, Atovmyan et al. [1] showed that the conformer with shorter intramolecular contacts has longer intermolecular distances in the case of bis(2-fluoro-2,2-dinitroethyl)nitramine and formulated a hypothesis concerning the saturability of van der Waals bonds. The essence of this hypothesis is that strained molecules have loose crystal packing. This interesting hypothesis was tested by Ammon et al. [2] using a geometrical analysis as in the work of Atovmyan [1] in correlating the intra- and intermolecular distances in the structure of the same aliphatic nitramine. Ammon et al. [2] concluded that this crystal structure cannot be used as evidence for the hypothesis of van der Waals bond saturability.

We attempted to find evidence for the saturability hypothesis of Ammon et al. [1] by a) comparison of the nonbonding interaction energies in conformer and isomer molecules (U_{nb}) , whose crystals have different densities (energy approach) and b) statistical analysis of the packing coefficient (K_p) for crystals of medium and high density compounds assuming that the high density crystals are formed mainly by "strained" molecules (statistical approach).

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