REACTION OF PERFLUORO-2-METHYL-2-PENTENE WITH THIOUREA

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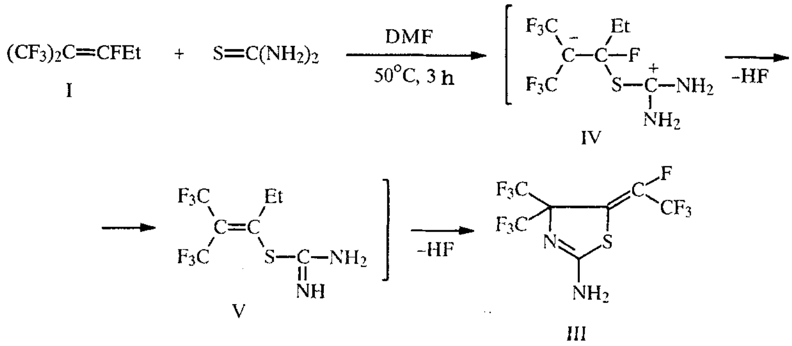
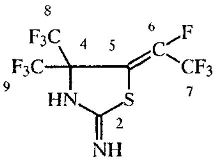
The reaction of perfluoro-2-methyl-2-pentene with thiourea in aprotic bipolar solvents gives 4,4-bis(trifluoromethyl-5-(tetrafluoroethylidene)-2-aminodihydrothiazole, the structure of which was confirmed by ^{19}F *and* ^{13}C *NMR and x-ray structural analyses. The mechanism of the reaction is discussed.*

Perfluoro-2-methyl- and 4-methyl-2-pentene are versatile starting materials which produce diverse substances upon reaction with nucleophilic reagents [1]. Studies of their reactions with S-containing nucleophiles include the following: mercaptans, thiophenols [2-5], and the sodium salts of N,N-dialkyldithiocarbamates [6], which lead to the corresponding perfluoroalkenylalkyl- or perfluoroarylsulfides. The goal of this work is a study of the reaction of dimeric hexafluoropropylenes [perfluoro-2-methyl-2-pentene (I) and perfluoro-4-methyl-2-pentene (II)] with thiourea.

We found that perfluoro-2-methyl-2-pentene (I) easily reacts with thiourea in dimethylformamide (CH_3CN, DMSO, sulfolane) at 50°C to form not the perfluorodialkenylsulfides but 4,4-bis(trifluoromethyl)-5-(tetrafluoroethyliden)-2-aminodihydrothiazole (III). The reaction did not proceed in ethanol, tetrahydrofuran, monoglyme, or acetone. The structure of compound III was established by x-ray structural analysis and confirmed by elemental analysis and by ^{19}F and ^{13}C NMR. The structure of the thiazole molecule in crystals is indicated in Fig. 1, and the coordinates of the atoms of the molecule are given in Table 1.



However, in organic solvents the possibility of finding compound III in its tautomeric form IIIa is not excluded.



IIIa

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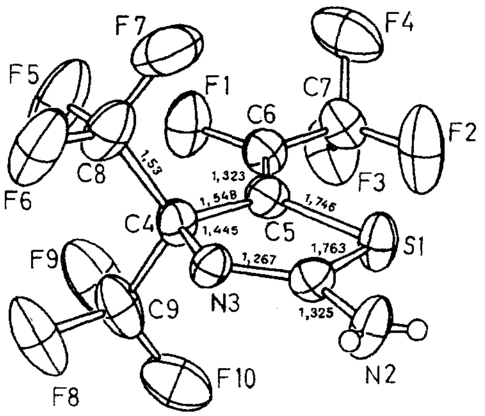

Fig. 1. Molecular structure of compound III with 30% probability ellipsoids of thermal oscillations. Maximum error of determination of bond length ±0.002 Å; for valence angles, ±0.159°.

It is recorded that the first representative of this class with perfluoroalkyl substituents was noted by the authors of [7], who obtained 5-trifluoromethyl-5-fluoro-2-amino-4-oxothiazoline by reaction of decafluoropropylene with thiourea.

The compound III molecule is almost flat: the $S_{(1)}$, $C_{(2)}$, $N_{(3)}$, $C_{(4)}$, $C_{(7)}$, and $F_{(1)}$ atoms lie in a plane with an accuracy of ±0.159°, and the $C_{(5)}$ atom is deflected from the plane by 0.145(7)°. The dihedral angle between the planar thiazole ring and the plane formed by the atoms of the double bond and the carbon of the CF_3 group equals 8.7°. The length of the $S_{(1)}-C_{(2)}$ and $S_{(1)}-C_{(5)}$ bonds are similar and their value corresponds to the 1.751(17) Å length of the single $C_{sp^2}-S_{(2)}$ bond in a $C{=}C{-}S{-}C^*$ fragment [8]. MNDO calculations of the π-region of these bonds from the experimental geometry gives 0.05-0.06. The lengths of the $C_{(2)}{=}N_{(3)}$ and $C_{(2)}-N_{(2)}$ bonds are close to the corresponding values for the bonds in the $C_{Ar}-C_{sp2}{=}N_{(2)}-C\#$ [1.279(8) Å] and the $C{=}C{-}N_{sp^2}H_2$ [1.336(17) Å] fragments [6]. Thus, the $N{=}C{-}NH_2$ system is conjugated and the π-region of these bonds according to the MNDO data equals 0.71 and 0.28. The sulfur atom, in agreement with the Zefirov radius [9, 10], exhibits only intramolecular coordination of $-S_{(1)}...F_{(2)}$ 2.752 Å and $-S_{(1)}...H_{(2)}$ 2.58 Å. The compound III molecules are connected in centrosymmetrical dimers by means of the hydrogen bonding $N_{(2)}-H_{(1)}...N_{(3)}$ (0.66:2.35 Å:165°).

The formation of compound III possibly proceeds by the following scheme. Initial attack of a nucleophilic atom on the sulfur of thiourea [7] occurs on the carbon atom of the double bond connected with the fluorine atom, in conformity with steric and electronic effects in the starting olefin (I) and the electronic effects in the forming intermediate carbanion IV [1]. Subsequent elimination of a fluorine anion is more favorable from the C–F fragment, not from the CF_3 groups and leads to compound V. The latter undergoes intramolecular nucleophilic cyclization, leading to compound III, in which the fluorine atom is found on the single bond in the trans-position relative to the sulfur substituent.

In attempts to introduce perfluoro-4-methyl-2-pentene into reaction with thiourea, a mixture of trimers of hexafluoropropylene and the olefins $CF_3CF{=}CF(CF_2)_7H$ and $CF_3CF_2CF{=}CF(CF_2)_4H$ was not separated. It is recorded that reaction of trimers of hexafluoroproplyene with mercaptans goes smoothly with the formation of the corresponding dialkylsulfides [11].

EXPERIMENTAL

The ^{13}C and ^{19}F NMR spectra were recorded on a Bruker WP-200 SY spectrometer at frequencies of 50.1 (^{13}C) and 188.28 (^{19}F) MHz with internal standards of TMS and C_6F_6, respectively. The mass spectra were obtained with a VG-7070E instrument, with electron ionization energy of 70 eV [336 (M^+), 317 (M – F), 267 (M – CF_3), 220, 217, 175, 150, 131]. X-ray structural studies were accomplished with a Syntex P21 diffractometer.

Elemental analysis data for C, H, N, F, and S agreed with the calculated values.

TABLE 1. Atom Coordinates in the Thiazoline III Molecule (in fractions of nuclei, multiplied by 10^4)

Atom	x	y	z	U Eq $Å^2 \times 10^3$	Atom	x	y	z	U Eq $Å^2 \times 10^3$
$S_{(1)}$	423(2)	895(2)	3920(1)	72,2(8)	$F_{(2)}$	-2836(5)	1367(8)	2446(5)	155(4)
$C_{(2)}$	2515(7)	482(5)	4433(5)	52(2)	$F_{(3)}$	-3471(6)	2723(5)	1150(6)	120(3)
$N_{(3)}$	3216(6)	697(4)	3788(4)	47(2)	$F_{(4)}$	-3637(7)	883(5)	713(8)	148(4)
$C_{(4)}$	2143(6)	1275(6)	2701(4)	54(2)	$F_{(5)}$	1626(8)	1039(7)	708(4)	143(3)
$C_{(5)}$	371(7)	1335(5)	2596(5)	55(2)	$F_{(6)}$	3770(6)	205(7)	1990(4)	119(3)
$C_{(6)}$	-992(7)	1674(6)	1679(5)	63(2)	$F_{(7)}$	1380(8)	-482(6)	1579(5)	125(3)
$C_{(7)}$	-2726(8)	1689(7)	1530(7)	77(3)	$F_{(8)}$	4352(6)	2572(6)	2902(6)	130(3)
$C_{(8)}$	2229(10)	514(10)	1732(6)	89(4)	$F_{(9)}$	1888(7)	3253(5)	1840(6)	142(4)
$C_{(9)}$	2817(8)	2600(8)	2772(8)	87(4)	$F_{(10)}$	2827(8)	3170(4)	3670(6)	121(3)
$N_{(2)}$	3259(10)	-6(7)	5486(5)	69(3)	$H_{(1)}$	4003(95)	-242(73)	5710(68)	64(25)
$F_{(1)}$	-964(5)	2045(5)	701(4)	102(2)	$H_{(2)}$	2818(112)	-61(85)	5714(82)	78(31)

X-Ray Structural Studies of Compound III. Basic crystallographic data: modified monoclinic, $C_7H_2N_2F_1OS$, M^+ 336, space group $P2_1/C$, $z = 4$, $d_{calc} = 1.96$ g/cm^3, μCuKα (graphite monochromator), $\mu = 38.3$ cm^{-1}, sample dimensions = $0.5 \times 0.5 \times 0.2$ mm^3: $a = 9.041(2)$, $b = 10.975(2)$, $c = 12.828(3)$ Å, $\beta = 116.41(2)°$, $V = 1140.0(4)$ Å^2. Because of the high volatility of the crystals, they were covered with Apiezon lubricant. The intensity of 1886 independent reflections with $2\Theta < 120°$ was measured according to the usual ω-scanning method (interval = 1°, variable rate of 5-30°/min). The intensity of three control reflections at the end of the experiment decreased by 1%. The calculations used 1298 observed ($F_0 > 4\sigma$) reflections without correction for absorption (calculation of absorption according to the experimental transmission curve resulted in a higher value of the R-factor). The structure was interpreted by the direct method and refined by the method of least squares in full matrix anisotropic approximation according to the SHELX76 program with $R = 0.078$, $R_W = 0.095$, $S = 0.93$, $W^{-1} = \sigma_{F2} + 0.0177F^2$. Coordinates of the hydrogen atoms were found from a different synthesis. The refined structural parameters are presented in Table 1.

4,4-Bis(trifluoromethyl)-5-(tetrafluoroethylidine)-2-aminodihydrothiazole (III, $C_7H_2N_2F_{10}S$). Into a three-necked, 150-ml flask supplied with stirrer, reflux condenser, and thermometer was charged 30 g of perfluoro-2-methyl-2-pentene, 15.2 g of thiourea and 80 ml of dry dimethylformamide. The mixture was stirred for 30 min and heated to 50°C for 3 h. The reaction mixture was diluted with water and the resulting precipitate of compound III was filtered off, washed with water, dried in air and recrystallized from hexane (sublimes at 100°C/3 mm Hg). mp 109-110°C, yield 26.9 g (80%). Calculated: M^+ 336. Found, M^+ 336. ^{19}F NMR (C_6F_6): 48.8 (3F, F^7, $J_{F^7-F^6} = 12$ Hz), 91.7 (6F, $F^{8(9)}$, $J_{F^9-F^6} = 28$ Hz), 94.6 ppm (1F, F^6, $J_{F^6-F^7} = 12$ Hz, $J_{F^6-F^{8(9)}} = 28$ Hz). ^{13}C NMR (TMS): 87.0 (C^4, $^1J_{C-F} = 10.2$ Hz), 119.9 (C^7, $^1J_{C-F} = 273.2$ Hz, $^2J_{C-F} = 41.7$ Hz), 121.4 ($C^{8(9)}$, $^1J_{C-F} = 41.7$ Hz), 121.4 ($C^{8(9),}$ $^1J_{C-F} = 286.4$ Hz), 121.9 (C^5, $^2J_{C-F} = 22.1$ Hz), 137.3 (C^6, $^1J_{C-F} = 266.9$ Hz, $^2J_{C-F} = 266.9$ Hz, $^2J_{C-F} = 41.7$ Hz) and 161.2 m.d (C^2).

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