New heterocyclic system based on vinylsulfonylfluorobenzene and X-ray structural study of this compound

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Oxidation of 1,2,4,5-tetrafluoro-3,6-bis(vinylthio)benzene (**1**) affords 1,2,4,5-tetrafluoro-3,6-bis(vinylsulfonyl)benzene (**2**) in 65 % yield. The reaction of compound **2** with allylamine gives a new heterocyclic compound, 5,6-difluorobenzo-[*a*,*d*]-bis(3,3′-dihydro-1,1′-sulfonylallyl-4,4′-perhydroazine) (**3**). This compound is the product of nucleophilic addition at the vinylsulfonyl group and intramolecular replacement of fluorine atoms of the benzene ring. The structure of compound **3** has been established by X-ray structural study.

Key words: 1,2,4,5-tetrafluoro-3,6-bis(vinylthio)benzene, 1,2,4,5-tetrafluoro-3,6-bis(vinylsulfonyl)benzene, 5,6-difluorobenzo-[*a*,*d*]-bis(3,3′-dihydro-1,1′-sulfonylallyl-4,4′-perhydroazine), oxidation, allylamine, X-ray structural study.

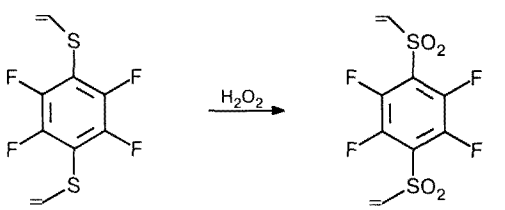
Nucleophilic replacement of fluorine atoms in hexafluorobenzene with sodium ethenethiolate, which was obtained by decomposition of divinyl sulfide with sodium in liquid ammonia, affords 1,2,4,5-tetrafluoro-3,6-bis(vinylthio)benzene (**1**).[1] When properties of compound **1** were studied, it was demonstrated that this compound is involved in reactions of both radical addition at the vinylthio groups and aryl nucleophilic replacement of fluorine atoms.[2]

As part of continuing studies of the reactivity of compound **1**, we have studied its oxidation, performed the reaction between the oxidation product 1,2,4,5-tetrafluoro-3,6-bis(vinylsulfonyl)benzene (**2**) and allylamine, and carried out an X-ray structural study of the cyclic compound formed, 5,6-difluorobenzo-[*a*,*d*]-bis(3,3′-dihydro-1,1′-sulfonylallyl-4,4′-perhydroazine) (**3**).

Oxidation of sulfur atoms in vinylthio groups of compound **1** changes the nature of the double bond, which makes it possible to perform reactions of nucleophilic addition.

Previously, the reactions of unsaturated sulfoxides and sulfones with amines[3—5] as well as the nucleophilic replacement of fluorine atoms in hexafluorobenzene with different nucleophiles[6—11] have been studied. We first described the capability of fluorine atoms to undergo nucleophilic replacement in vinylthiofluorobenzenes using its reaction with 2-aminoethanol.[2]

In this work, we have demonstrated that under the action of a ten-fold excess of hydrogen peroxide (30 %) in acetic anhydride at 20—25 °C for 14 days, compound **2** formed in 65 % yield.



1 **2**

The structure of compound **2** was established by IR and ^{1}H NMR spectroscopy and mass spectrometry.

The reaction of **2** with allylamine is of interest with respect to the synthesis of new potentially biologically active compounds.

Taking into account that this compound has several reaction centers with respect to nucleophilic reagents, one would expect either the addition of nucleophile at the activated double bonds or the replacement of fluorine atoms in the benzene ring. According to the data previously reported,[10] the occurrence of both pathways as well as intermolecular interactions are not excluded.

The reaction of compound **2** with allylamine affords tricyclic compound **3** in 40 % yield; this compound is the product of nucleophilic addition and intramolecular replacement.

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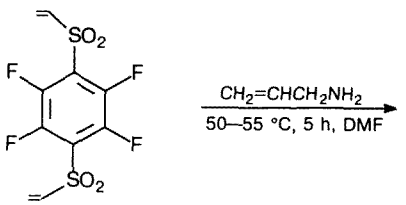
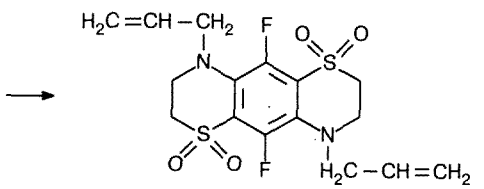


2



3

The addition of amine at vinyl groups of compound **2** occurs under conditions analogous to those previously described.[3] The replacement of fluorine atoms by the amino group in compound **2** occurs under milder conditions (50—55 °C) than those for vinylthiofluorobenzenes (100 °C).[2] Apparently, the reaction of nucleophilic replacement in compound **2** is promoted due to the presence of two vinylsulfonyl groups that exhibit stronger electron-withdrawing properties than vinylthio groups.

Compound **3**, which is a high-melting crystalline compound, has been studied by IR spectroscopy, ^1H and ^{19}F NMR spectroscopy, mass spectrometry, and elemental analysis.

The structure of compound **3** has been unambiguously established by X-ray structural study of a single crystal. The overall view of the centrosymmetric molecule and the bond lengths in the symmetrically independent part of the molecule are shown in Fig. 1; bond angles are given in Table 1.

In the molecule under consideration, the six-membered heterocycle has a half-chair conformation: the C(4) and C(5), C(4a) and C(5a) atoms deviate from the plane of the remaining four atoms (planar within ±0.006 Å) by 0.360 and −0.447 Å, −0.360 and 0.447 Å, respectively. As a whole, a nearly planar fragment, which involves the benzene ring and the S(1), N(1), and F(1) atoms as well as the S(1a), N(1a), and F(1a) atoms, can be separated. The allyl substituents are substantially twisted in opposite directions relative to the planar part of the molecule (the C(2)—N(1)—C(6)—C(7) and N(1)—C(6)—C(7)—C(8) torsion angles are −153.9° and −129.1°, respectively). Other geometric parameters of the molecule of compound **3** have normal values.[12]

Therefore, vinylsulfonylfluorobenzene **2** the molecule of which has several reaction centers is a promising precursor for constructing new heterocyclic systems based on reactions of nucleophilic addition and replacement.

Experimental

IR spectra were recorded on a Specord 75-IR spectrometer from cast films on KBr. NMR spectra were obtained on a JEOL FX 90Q instrument. Mass spectra were obtained on an LKB-2091 spectrometer; the energies of the ionizing electrons were 14 and 70 eV.

1,2,4,5-Tetrafluoro-3,6-bis(vinylsulfonyl)benzene (2). A cooled 30 % hydrogen peroxide solution (95 mmol) was added to a solution of 1,2,4,5-tetrafluoro-3,6-bis(vinylthio)benzene (**1**) (9.5 mmol) in 25 mL of acetic anhydride cooled to 8 °C. The reaction temperature was maintained in the range 8—10 °C in the course of addition of H_2O_2. Then the solution was kept at 20 °C for 14 days, white needle-like crystals of the product (1 g) were separated, the mother liquor was evaporated under reduced pressure, and an additional 0.6 g of compound **2** was obtained. The total yield of compound **2** was 65 %. M.p. 194—196 °C (from ethanol). Found (%): C, 36.08; H, 1.80; F, 22.89; S, 19.20. $C_{10}H_6F_4O_4S_2$. Calculated (%): C, 36.37; H, 1.83; F, 23.01; S, 19.41. IR, ν/cm^{-1}: 3100, 3060, 1620, 1605, 1480,

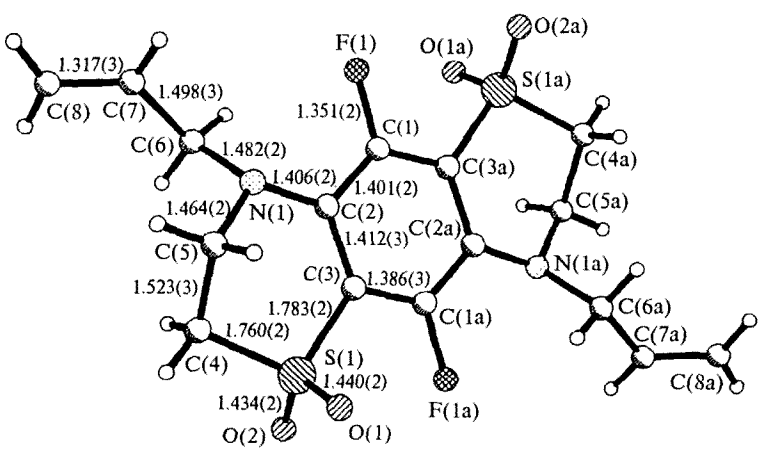


Fig. 1. Overall view of the centrosymmetric molecule of compound **3** and bond lengths in its symmetrically independent part.

Table 1. Bond angles (ω) in molecule **3**

Angle	ω/deg	Angle	ω/deg
O(1)—S(1)—O(2)	118.6(1)	C(2)—C(1)—C(3a)	124.1(2)
O(1)—S(1)—C(3)	106.3(1)	N(1)—C(2)—C(1)	120.0(2)
O(2)—S(1)—C(3)	109.8(1)	N(1)—C(2)—C(3)	125.0(2)
O(1)—S(1)—C(4)	109.4(1)	C(1)—C(2)—C(3)	114.9(2)
O(2)—S(1)—C(4)	109.4(1)	S(1)—C(3)—C(2)	121.6(1)
C(3)—S(1)—C(4)	102.0(1)	S(1)—C(3)—C(1a)	117.4(1)
C(2)—N(1)—C(5)	115.5(1)	C(2)—C(3)—C(1a)	121.0(2)
C(2)—N(1)—C(6)	115.5(1)	S(1)—C(4)—C(5)	109.0(1)
C(5)—N(1)—C(6)	114.4(1)	N(1)—C(5)—C(4)	113.1(2)
F(1)—C(1)—C(2)	117.9(2)	N(1)—C(6)—C(7)	111.9(2)
F(1)—C(1)—C(3a)	117.9(1)	C(6)—C(7)—C(8)	123.5(2)

1380, 1335, 1260, 1135, 980, 950, 795, 720, 640, 610, 530, 500. ^{1}H NMR (DMSO-d_6), δ: 6.57 and 6.64 (both d, CH_2=); 7.35 (q, —CH=). Mass spectrum, *m/z*: 330 $[M]^+$.

5,6-Difluorobenzo-[*a*,*d*]-bis(3,3′-dihydro-1,1′-sulfonylallyl-4,4′-perhydroazine) (3). A solution of allylamine (7.2 mmol) in 2 mL of DMF was added to a solution of compound **2** (2.4 mmol) in 15 mL of DMF heated to 50 °C. The reaction mixture was stirred at 50—55 °C for 5 h. The solvent was removed under reduced pressure; the remaining viscous mass was diluted with ether. Crystals were separated and recrystallized from ethanol. The yield of compound **3** was 0.4 g (40 %). M.p. 266 °C (from chloroform). Found (%): C, 47.52; H, 4.48; N, 6.87; F, 9.17; S, 15.90. $C_{16}H_{18}F_2N_2O_4S_2$. Calculated (%): C, 47.52; H, 4.48; N, 6.93; F, 9.39; S, 15.82. IR, ν/cm^{-1}: 1125, 1325 (SO_2). ^{1}H NMR ($CDCl_3$), δ: 5.23 and 5.27 (both d, $=CH_2$); 5.9 (q, —CH=); 3.40 (m, N—CH_2—CH=CH_2); 3.74—3.84 (w.m, N—CH_2—CH_2—SO_2). ^{19}F NMR ($CDCl_3$), δ_{CCl_3F}: −123.33 (s). Mass spectrum, *m/z*: 404 $[M]^+$.

Crystals of compound **3** are orthorhombic, at −125 °C a = 10.316 (2) Å, b = 18.484 (3) Å, c = 9.333 (4) Å, V = 1780 (1) Å^3, d_{calc} = 1.517 g cm^{-3}, space group *Pccn*, Z = 4; molecules of compound **3** occupy crystallographic symmetry centers. The unit cell parameters and intensities of 2369 independent reflections were measured using a four-circle automated Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique to θ_{max} = 28 °). The structure was solved by the direct method, which reveals all nonhydrogen atoms, and refined by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms using 1644 reflections with $I > 3\sigma(I)$. All hydrogen atoms were located from the difference syntheses and refined isotropically. The final value of the R factor was 0.032 (R_w = 0.032). All calculations were carried out using the SHELXTL PLUS program[13] (the PC version). Atomic coordinates are given in Table 2 (thermal parameters can be obtained from the authors).

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Table 2. Atomic coordinates (×10^4, ×10^3 for H) in molecule **3**

Atom	*x*	*y*	*z*
S(1)	1310(1)	3450(1)	−67(1)
F(1)	−1742(1)	5428(1)	−2000(1)
O(1)	663(2)	3034(1)	1025(2)
O(2)	2690(1)	3533(1)	19(2)
N(1)	−747(2)	4063(1)	−2285(2)
C(1)	−856(2)	5212(1)	−1023(2)
C(2)	−338(2)	4515(1)	−1161(2)
C(3)	553(2)	4317(1)	−82(2)
C(4)	892(2)	3109(1)	−1765(2)
C(5)	−521(2)	3289(1)	−2071(2)
C(6)	−447(2)	4327(1)	−3747(2)
C(7)	−1377(2)	4034(1)	−4836(2)
C(8)	−1010(3)	3716(1)	−6031(2)
H(41)	147(2)	330(1)	−245(3)
H(42)	103(2)	258(1)	−171(2)
H(51)	−80(2)	302(1)	−290(3)
H(52)	−106(2)	313(1)	−129(3)
H(61)	45(2)	421(1)	−397(2)
H(62)	−47(2)	485(1)	−369(2)
H(7)	−225(3)	410(1)	−461(3)
H(81)	−164(3)	358(2)	−665(3)
H(82)	−14(3)	364(1)	−619(3)

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