Chemistry of Heterocyclic Compounds, Vol. 42, No. 10, 2006

SULFENYL HALIDES IN THE SYNTHESIS OF HETEROCYCLES. 3*. INTERACTION OF PERFLUORO-1-ETHYL-2-METHYL–1-PROPENYL-IMINOCHLOROMETHANESULFENYL CHLORIDE WITH 1-ALLYL-2-METHOXYBENZENE

A. V. Borisov, V. K. Belsky, V. K. Osmanov, G. N. Borisova, and Zh. V. Matsulevich

Reaction of perfluoro-1-ethyl-2-methyl-1-propenyliminochloromethanesulfenyl chloride with 1-allyl-2-methoxybenzene in methylene chloride and nitromethane gives as the main products β- and γ-chloro sulfides plus derivative of 2,3-dihydrobenzofuran. The reaction in nitromethane in the presence of lithium perchlorate gave a product of addition of sulfur-containing electrophiles to the double bond – a derivative of 1,3-thiazolidin-2-one – in preference to the cycloaddition product.

Keywords: alkenes, sulfenyl chlorides, heterocyclization.

Iminochloromethanesulfenyl chlorides are very promising synthons for the synthesis of heterocycles [2-10], however only N-phenyliminochloromethanesulfenyl chloride was used, as a rule, in the investigation of reactions of this class of compounds with alkenes.

In the present work we have produced the first example of a perfluorinated α,β-unsaturated N-substituted iminochloromethanesulfenyl chlorides – perfluoro-1-ethyl-2-methyl-1-propenyliminochloro-methanesulfenyl chloride (**1**) and have studied its reaction with 1-allyl-2-methoxybenzene (**2**).

We have established that when the sulfenyl chloride **1** reacted with allylanisole **2** at 20°C a number of products were formed, the ratio of which depended of the reaction conditions. For example, in methylene chloride products of 1,2-addition of the sulfenyl chloride both according to Markovinkov's rule and contrary to it are formed – β-chloro sulfides **3** and **4** respectively, addition with a 1,2-shift of the aryl group – the γ-chloro sulfide **5**, and cyclization brought about by the nucleophilic part of the substrate, *o*-methoxyanisole – derivatives of 2,3-dihydrobenzofuran **6**. In nitromethane products of cyclization with ring closure at nitrogen atom of the sulfenyl fragment – derivatives of 1,3-thiazolidin-2-one (**7**) – were formed along with the products mentioned above. The formation the heterocycle **7** is the main direction of the reaction of sulfenyl chloride **1** with allylanisole **2** in nitromethane in the presence of lithium perchlorate. The composition of the reaction mixtures produced determined by ^{1}H NMR spectroscopy and the yields of isolated products are cited in Table 1.

* For paper 2 see [1].

Nizhni Novgorod Technical University, Nizhni Novgorod 603606, Russia; e-mail: ifxf@nntu.nnov.ru.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, 1558-1564, October, 2006. Original article submitted November 11, 2004; revision submitted March 24, 2006.

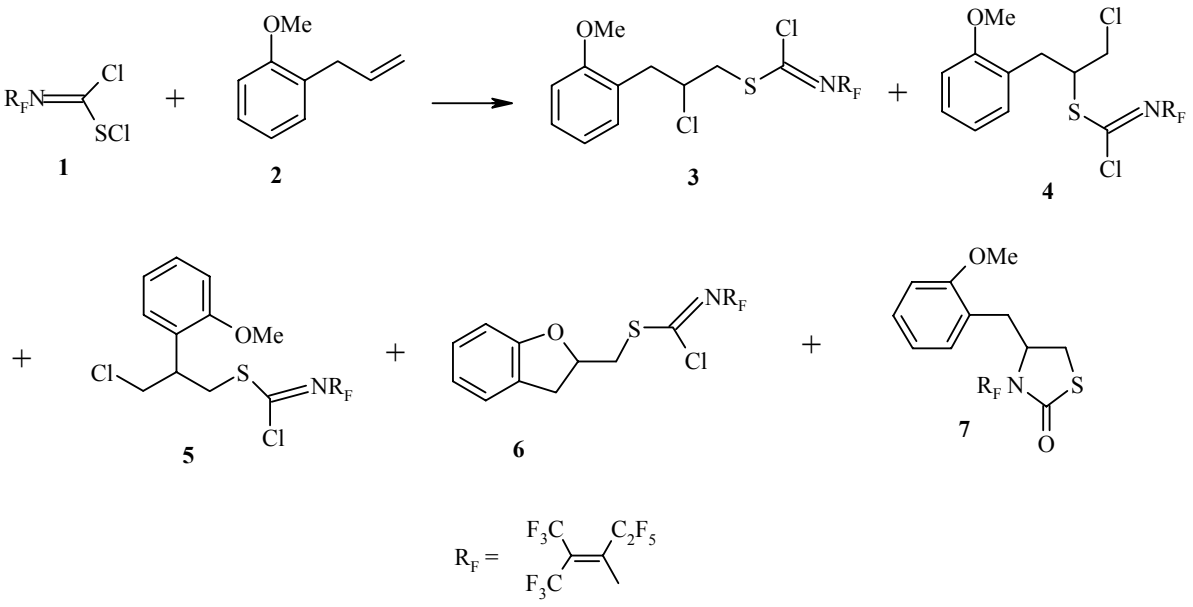

TABLE 1. Results of the Reaction of the Sulfenyl Chloride **1** with 1-Allyl-2-methoxybenzene **2** (20°C)

Medium	Composition of the reaction mixture (yield, %)				
	3	**4**	**5**	**6**	**7**
CH_2Cl_2	22 (12)	9 (3)	60 (38)	9 (5)	—
$MeNO_2$	20	18	49	10	3
$MeNO_2$–$LiClO_4$	13 (5)	15 (9)	5	5	62 (47)

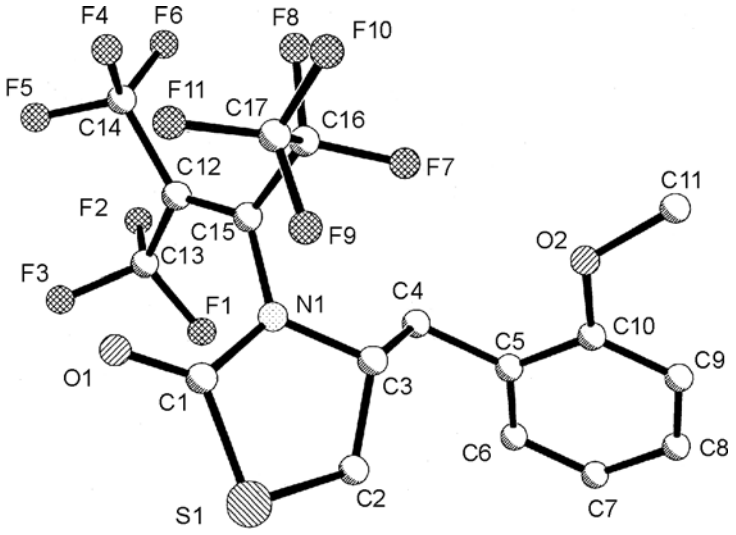

Fig. 1. General view of the molecule of compound **7**.

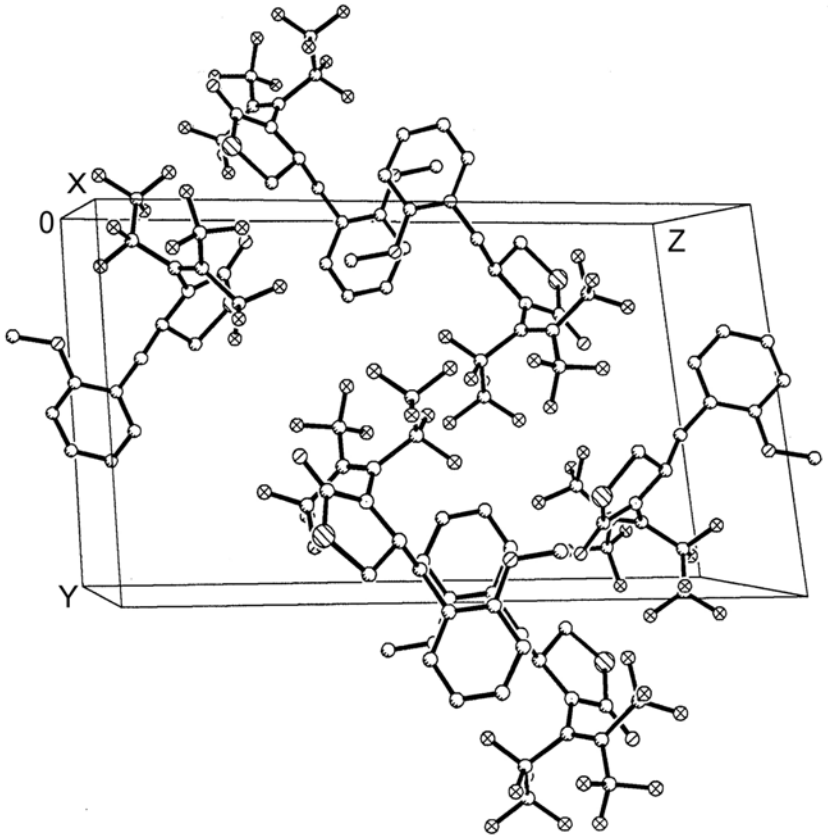

Fig. 2. Packing of compound **7** in the crystal structure viewed along the 0Y axis (H atoms are not shown).

In the reactions of sulfenyl chlorides, products of rearrangement and cyclization can be obtained either directly in the Ad_E reactions or as a result of conversions of the products of 1,2-addition – β-chlorosulfides [1, 9-12]. In this connection the stability of the products **3** and **4** under the reaction conditions was investigated and it was established they underwent no appreciable conversions. Consequently all of the products obtained were formed by the Ad_E process.

The composition and structure of the compounds synthesized were confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR, and mass spectra. The spatial and molecular structure of the heterocycle were established by X-ray crystallography (Tables 2 and 3).

Two symmetrically independent molecules of compound **7** occupy the unit cell in the crystalline state. The general view of one of the independent molecules is shown in Fig. 1. Packing of the molecules in the crystal is shown in Fig. 2. The assignment of the signals in the NMR spectra of the synthesized compounds agrees with literature characteristics of allylbenzenes with sulfenyl substituents in the ring [13-15].

TABLE 2. Bond Lengths (*d*) in the Molecule of Compound **7**

Bond	*d*, Å	Bond	*d*, Å
S(1)–C(1)	1.750(5)	F(10)–C(17)	1.322(6)
S(1)–C(2)	1.805(5)	F(11)–C(17)	1.303(6)
O(1)–C(1)	1.207(5)	C(2)–C(3)	1.512(6)
O(2)–C(10)	1.358(5)	C(3)–C(4)	1.517(5)
O(2)–C(11)	1.415(6)	C(4)–C(5)	1.509(6)
N(1)–C(1)	1.397(5)	C(5)–C(10)	1.384(6)
N(1)–C(15)	1.415(5)	C(5)–C(6)	1.379(6)
N(1)–C(3)	1.492(5)	C(6)–C(7)	1.399(7)
F(1)–C(13)	1.319(6)	C(7)–C(8)	1.359(8)
F(2)–C(13)	1.332(5)	C(8)–C(9)	1.347(7)
F(3)–C(13)	1.329(6)	C(9)–C(10)	1.399(6)
F(4)–C(14)	1.311(6)	C(12)–C(15)	1.334(6)
F(5)–C(14)	1.328(6)	C(12)–C(13)	1.504(7)
F(6)–C(14)	1.313(6)	C(12)–C(14)	1.540(7)
F(7)–C(16)	1.340(5)	C(15)–C(16)	1.529(6)
F(8)–C(16)	1.341(5)	C(16)–C(17)	1.522(7)
F(9)–C(17)	1.324(6)		

TABLE 3. Bond Angles (ω) in the Molecule of Compound **7**

Angle	ω,deg.	Angle	ω,deg.
C(1)–S(1)–C(2)	92.1(2)	F(1)–C(13)–F(2)	105.0(5)
C(10)–O(2)–C(11)	118.2(4)	F(3)–C(13)–F(2)	106.0(4)
C(1)–N(1)–C(15)	116.7(3)	F(1)–C(13)–C(12)	115.6(4)
C(1)–N(1)–C(3)	115.8(3)	F(3)–C(13)–C(12)	113.4(5)
C(15)–N(1)–C(3)	126.4(3)	F(2)–C(13)–C(12)	109.0(5)
O(1)–C(1)–N(1)	124.6(4)	F(4)–C(14)–F(6)	108.6(6)
O(1)–C(1)–S(1)	125.0(3)	F(4)–C(14)–F(5)	106.1(4)
N(1)–C(1)–S(1)	110.4(3)	F(6)–C(14)–F(5)	107.4(4)
C(3)–C(2)–S(1)	107.4(3)	F(4)–C(14)–C(12)	113.7(4)
N(1)–C(3)–C(2)	104.4(3)	F(6)–C(14)–C(12)	112.2(4)
N(1)–C(3)–C(4)	112.7(3)	F(5)–C(14)–C(12)	108.4(5)
C(2)–C(3)–C(4)	112.1(3)	F(1)–C(13)–F(3)	107.2(5)
C(5)–C(4)–C(3)	111.9(3)	C(12)–C(15)–N(1)	119.8(4)
C(10)–C(5)–C(6)	118.2(4)	C(12)–C(15)–C(16)	125.8(4)
C(10)–C(5)–C(4)	120.2(4)	N(1)–C(15)–C(16)	114.1(4)
C(6)–C(5)–C(4)	121.6(4)	F(8)–C(16)–F(7)	105.9(4)
C(5)–C(6)–C(7)	120.8(5)	F(8)–C(16)–C(17)	108.3(4)
C(8)–C(7)–C(6)	119.4(5)	F(7)–C(16)–C(17)	106.4(4)
C(9)–C(8)–C(7)	121.2(5)	F(8)–C(16)–C(15)	111.3(4)
C(8)–C(9)–C(10)	120.0(5)	F(7)–C(16)–C(15)	109.3(4)
O(2)–C(10)–C(5)	115.8(4)	C(17)–C(16)–C(15)	115.0(4)
O(2)–C(10)–C(9)	123.8(4)	F(11)–C(17)–F(10)	108.9(4)
C(5)–C(10)–C(9)	120.4(4)	F(11)–C(17)–F(9)	107.9(5)
C(15)–C(12)–C(13)	122.2(4)	F(10)–C(17)–F(9)	106.9(5)
C(15)–C(12)–C(14)	125.1(5)	F(11)–C(17)–C(16)	112.7(4)
C(13)–C(12)–C(14)	112.7(4)	F(10)–C(17)–C(16)	110.3(4)
F(1)–C(13)–F(3)	107.2(5)	F(9)–C(17)–C(16)	109.9(4)

EXPERIMENTAL

IR spectra of KBr disks or thin films were recorded on a Specord M-80 instrument. ^{1}H NMR spectra were recorded with Bruker WM-250 (250 MHz), ^{13}C NMR spectra with a AM-300 (75 MHz), and ^{19}F NMR spectra with a Bruker WP-200 SY (188 MHz) in $CDCl_3$ solution with TMS (^{1}H and ^{13}C NMR spectra) and CF_3COOH (^{19}F NMR spectra) internal standards.

Perfluoro-1-ethyl-2-methyl-1-propenyliminochloromethanesulfenyl Chloride (1). Liquid chlorine (2 ml, 44 mmol) and a catalytic amount iron powder were added to perfluoro-1-ethyl-2-methylpropenyl isothiocyanate (13.6 g, 40 mmol) (prepared by method [16]) cooled to -78°C in an ampule. The ampule was sealed and heated for 4 h in a water bath at 70°C. The excess chlorine was removed on a rotary evaporator. The residue was distilled in vacuum to give sulfenyl chloride **1** (11.8 g, 72%); bp 90-93°C (1 mm Hg). IR spectrum (film), ν, cm^{-1}: 1660 (C=C, C=N). ^{19}F NMR spectrum, δ, ppm: -23.2 (m, CF_3C=C); -19.6 (m, CF_3C=C); 2.3 (m, CF_3CF_2); 33.2 (m, CF_2). Found, %: C 19.88; F 49.94; N 3.25; S 7.51. $C_7Cl_2F_{11}NS$. Calculated, %: C 20.50; F 50.97; N 3.42; S 7.82.

Reactions of 1 and 2. A. In methylene chloride or nitromethane. A solution of the unsaturated compound **2** (0.74 g, 5 mmol) in 30 ml of solvent was added to the sulfenyl chloride **1** (2.05 g, 5 mmol) in 30 ml of solvent at 20°C. The solvent was removed in vacuum after 15 h. The residue was chromatographed on an L40/100 silica gel column (40 × 2 cm) with a 10:1 mixture of hexane–methylene chloride.

B. In a nitromethane–lithium perchlorate system. A solution of $LiClO_4$ (2.12 g, 20 mmol) in nitromethane (50 ml) and a solution of compound **2** (0.74 g, 5 mmol) in nitromethane (10 ml) were added to a solution of sulfenyl chloride **1** (2.95 g, 5 mmol) in nitromethane (15 ml) at 20°C. The solvent was removed in vacuum after 3 h. Methylene chloride (50 ml) was added to the reaction mixture, the residue of LiCl and $LiClO_4$ was filtered off and washed many times on the filter with methylene chloride. The filtrate was evaporated and the residue was chromatographed as in method A.

N-(Perfluoro-1-ethyl-2-methylpropen-1-yl)-2-chloro-3-(2-methoxyphenyl)propylsulfanylchloromethanimine (3). Oil, R_f 0.62. IR spectrum (film), ν, cm^{-1}: 1660 (C=C, C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.34-6.84 (4H, m, Ar); 4.40 (1H, m, CHCl); 3.82 (3H, s, CH_3O); 3.48 (1H, dd, ^3J = 5.5, ^2J = 14.5, CH_2S); 3.31 (1H, m, CH_2S); 3.17 (2H, d, ^2J = 7.0, CH_2Ar). ^{19}F NMR spectrum, δ, ppm: -23.6 (m, CF_3C=C), -19.9 (m, CF_3C=C); 1.9 (m, $\underline{CF_3}CF_2$); 32.6 (m, CF_2). Found, %: C 35.88; H 2.05; F 36.79; N 2.35; S 5.87. Calculated $C_{17}H_{12}Cl_2F_{11}NOS$. Calculated, %: C 36.58; H 2.17; F 37.44; N 2.51; S 5.74.

N-(Perfluoro-1-ethyl-2-methylpropen-1-yl)-2-chloro-1-(2-methoxybenzyl)ethylsulfanylchloromethanimine (4). Oil, R_f 0.66. IR spectrum (film), ν, cm^{-1}: 1660 (C=C, C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.35-6.87 (4H, m, Ar); 4.28 (1H, m, CHS); 3.81 (3H, s, CH_3O); 3.73 and 3.68 (2H, both dd, ^3J = 5.5, ^3J = 3.8, ^2J = 11.5, CH_2Cl); 3.18 and 3.10 (2H, both dd, ^3J = 8.0, ^3J = 7.0, ^2J = 14.0, CH_2Ar). ^{19}F NMR spectrum, δ, ppm: -23.6 (m, CF_3C=C); -19.9 (m, CF_3C=C); 1.8 (m, $\underline{CF_3}CF_2$); 32.3 (m, CF_2). Found, %: C 36.12; H 2.09; F 37.15; N 2.39; S 5.51. $C_{17}H_{12}Cl_2F_{11}NOS$. Calculated, %: C 36.58; H 2.17; F 37.44; N 2.51; S 5.74.

N-(Perfluoro-1-ethyl-2-methylpropen-1-yl)-3-chloro-2-(2-methoxyphenyl)propylsulfanylchloromethanimine (5). Oil, R_f 0.54. IR spectrum (film), ν, cm^{-1}: 1660 (C=C, C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.37-6.90 (4H, m, Ar); 3.90 (1H, m, CH_2Cl); 3.84 (3H, s, CH_3O); 3.55 (2H, m, CH_2S); 3.20 (1H, m, CHAr). ^{13}C NMR spectrum, δ, ppm: 157.34, 129.25, 128.88, 126.50, 120.63 (Ar), 55.19 (CH_3O), 46.54 (CH_2Cl), 41.09 (CHAr), 36.29 (CH_2S). ^{19}F NMR spectrum, δ, ppm: -23.7 (m, CF_3C=C); -20.1 (m, CF_3C=C); 1.7 (m, $\underline{CF_3}CF_2$); 32.5 (m, CF_2). Found, %: C 35.98; H 2.07; F 37.20; N 2.42; S 5.45. $C_{17}H_{12}Cl_2F_{11}NOS$. Calculated, %: C 36.58; H 2.17; F 37.44; N 2.51; S 5.74.

N-(Perfluoro-1-ethyl-2-methylpropen-1-yl)-2,3-dihydrobenzo[*b*]furan-2-ylmethylsulfanylchloromethanimine (6). Oil, R_f 0.44. IR spectrum (film), ν, cm^{-1}: 1660 (C=C, C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.25-6.80 (4H, m, Ar); 5.01 (1H, m, CHO); 3.43 and 3.01 (2H, both dd, ^3J = 7.0, ^3J = 7.0, ^2J = 16.0, CH_2Ar); 3.38 (2H, m, CH_2S). ^{13}C NMR spectrum, δ, ppm: 158.95, 128.53, 125.36, 125.10, 121.19, 109.79 (Ar); 79.32 (CHO); 39.33 (CH_2S), 34.84 (CH_2Ar). ^{19}F NMR spectrum, δ, ppm: -23.6 (m, CF_3C=C); -20.0

(m, CF_3C=C); 1.8 (m, $\underline{CF_3}CF_2$); 32.5 (m, CF_2). Mass spectrum, *m/z* (I_{rel}, %): 507 $[M]^+$ (4), 472 $[M - Cl]^+$ (12), 132 (100), 69 (10). Found, %: C 37.27; H 1.65; F 40.91; N 2.55; S 6.50. $C_{16}H_9ClF_{11}NOS$. Calculated, %: C 37.85; H 1.79; F 41.16; N 2.76; S 6.31.

4-(2-Methoxybenzyl)-3-(perfluoro-1-ethyl-2-methylpropen-1-yl)-1,3-thiazolidin-2-one (7). Mp 65-66°C (hexane). IR spectrum (KBr), ν, cm^{-1}: 1730 (C=O), 1640 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.35-6.87 (4H, m, Ar); 4.69 (1H, m, CHN); 3.88 (3H, s, CH_3O); 3.25 (2H, m, CH_2S); 3.11 (1H, dd, ^3J = 6.8, ^2J = 11.2, CH_2Ar); 2.88 (1H, t, ^2J = 11.2, CH_2Ar). ^{13}C NMR spectrum, δ, ppm: 171.43 (C=O), 157.74, 131.15, 129.25, 123.14, 120.95, 110.86 (Ar), 61.81 (CHN), 55.14 (CH_3O), 34.14 (CH_2S), 32.25 (CH_2Ar).^{19}F NMR spectrum, δ, ppm: -23.4 (m, CF_3C=C); -17.6 (m, CF_3C=C); 1.8 (m, $\underline{CF_3}CF_2$); 29.3 and 31.8 (both br. d, *J* = 286.6, CF_2). Mass spectrum, *m/z* (I_{rel}, %): 503 $[M]^+$ (12), 362 (7), 121 (100), 91 (36). Found, %: C 40.25; H 2.30; F 41.05; N 2.59; S 6.19. $C_{17}H_{12}F_{11}NO_2S$. Calculated, %: C 40.57; H 2.40; F 41.52; N 2.78; S 6.37.

X-ray Structural Analysis of Compound 7. Crystals of **7**, obtained from hexane were triclinic. At 293 K: *a* = 8.861(2), *b* = 12.164(2), *c* = 19.784(4) Å; α = 87.16, β = 85.17, γ = 71.65°; *V* = 2016.2(7) $Å^3$; d_{calc} = 1.658 g/cm^3; space group $P\bar{1}$; *Z* = 4; *F*(000) = 1008 (there are two symmetrically independent molecules in the unit cell). Analysis was carried with an Enraf-Nonius CAD-4 automatic diffractometer (Mo*K*α-radiation, θ/2θ scanning, $2\theta_{max}$ = 50°). The structure was solved by direct methods using the SHELXTL programme. The number of experimental reflexion was 3011. In the calculations 2840 reflexions with $I > 3\sigma(I)$ were used in the calculations. Refinement was carried using full matrix least squares in the anisotropic approximation. The final value of the residual factor *R* = 0.29. The complete X-ray data have been deposited in the Cambridge Structural Data Bank (deposit number CCDC 299726).

REFERENCES

1. A. V. Borisov, V. K. Belsky, T. V. Goncharova, G. N. Borisova, V. K. Osmanov, Zh. V. Matsulevich, N. G. Frolova, and E. D. Savin, *Khim. Geterotsikl. Soedinen.,* 893 (2005). [*Chem. Heterocycl. Comp.,* **41**, 771 (2005)].
2. G. Ottmann and H. Hooks, *Angew. Chem.,* **78**, 210 (1966).
3. E. Kuhle, B. Anders, and G. Zumach, *Angew. Chem.,* **79**, 663 (1967).
4. G. Ottmann, H. Hoberecht, and H. Hooks, *Angew. Chem.,* **79**, 1063 (1967).
5. E. Kuhle and G. Zumach, *Angew. Chem.,* **82**, 63 (1970).
6. E. Kuhle, *The Chemistry of the Sulfenic Acids*, Thieme Verlag, Stuttgart (1973). p. 163.
7. I. V. Koval', *Usp. Khim*., **64**, 781 (1995).
8. A. V.Borisov, I. V. Bodrikov, G. N. Borisova, V. K. Belsky, W. A. Smit, and A. I. Lutsenko, *Mendeleev Commun.,* 52 (1996).
9. G. N. Borisova, A. V. Borisov, I. V. Bodrikov, V. K. Belsky, A. I. Lutsenko, V. A. Smit, and G. A. Kutyrev, *Zh. Org. Khim.,* **30**, 760 (1994).
10. A. V. Borisov, V. K. Osmanov, I. G. Sokolov, G. N. Borisova, and Zh. V. Matsulevich, *Khim. Geterotsikl. Soedinen.,* 1307 (2002). [*Chem. Heterocycl. Comp.,* **38**, 1150 (2002)].
11. A. V. Borisov, I. V. Bodrikov, G. N. Borisova, V. A. Smit, A. I. Lutsenko, and V. K. Belsky, *Zh. Org. Khim.,* **31**, 1018 (1995).
12. A. V. Borisov, V. K. Belsky, G. N. Borisova, V. K. Osmanov, Zh. V. Matsulevich, *Khim. Geterotsikl. Soedinen.,* 763 (2001). [*Chem. Heterocycl. Comp.,* **37**, 702 (2001)].
13. H. Kwart and D. Drayer, *J. Org. Chem.,* **39**, 2157 (1974).
14. G. Capozzi, V. Lucchini, F. Macuzzi, and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 3106 (1981).
15. M. Tiecco, M. Tingoli, L. Testaferri, and R. Balducci, *J. Org. Chem.,* **57**, 4025 (1992).
16. V. Ya. Popkova, E. I. Mysov, M. V. Galakhov, V. K. Osmanov, and L. S. German. *Izv. AN, Ser. Khim.,* 2861 (1990).