Chemistry of Heterocyclic Compounds, Vol. 37, No. 6, 2001

SULFENYL HALIDES IN THE SYNTHESIS OF HETEROCYCLES. 1. HETEROCYCLIZATION IN REACTIONS OF 1-PHENYL-5-TETRAZOLESULFENYL CHLORIDE WITH ARYLOLEFINS

A. V. Borisov, V. K. Bel'skii, G. N. Borisova, V. K. Osmanov, Zh. V. Matsulevich, and T. V. Goncharova

2,3-Dihydrothiazolo[3,2-d]tetrazolium perchlorates have been synthesized by the interaction of 1-phenyl-5-tetrazolesulfenyl chloride with styrene and with (E)-1-phenylpropene in nitromethane in the presence of lithium perchlorate.

Keywords: alkenes, 2,3-dihydrothiazolo[3,2-*d*]tetrazolium perchlorates, 1-phenyl-5-tetrazolesulfenyl chloride, heterocyclization.

A widely used method of synthesizing heterocycles is cyclization in the reaction of an unsaturated compound with an electrophilic reagent with ring closure by a nucleophilic group contained in the substrate molecule [1]. However another type of ring formation in Ad_E reactions of alkenes by the principle of polar cycloaddition [2] with completion of cyclization from nucleophilic participation of fragments of the reactant has received comparatively little development, and is probably linked with the fairly limited assortment of suitable electrophilic reagents used in the practice of organic synthesis. The sulfenyl chlorides are of significant interest in this respect, since the cationoid portion may be varied widely. Various potentially nucleophilically reactive fragments may also be introduced into them [3-5]. These would be capable of closing the ring on interaction of these reactants with unsaturated compounds. At the same time the formation of 1,2-addition products is a characteristic reaction for such typically weak electrophiles as sulfenyl chlorides with alkenes under the usual conditions [6,7]. Previously developed methods for stimulating conjugated addition, rearrangement, and cyclization in reactions of sulfenyl chlorides with alkenes are linked with the action of external factors on the initial reactants (reactant transformation) [8] or intermediates (intermediate transformation) [9], while the indicated action is directed mainly to the nucleophilic portion of the reactant. It was recently shown by us that an increase in the electronegativity of the cationoid portion of the reactant, due to the accumulation of the effects of strongly accepting substituents and/or coordination of them with metal cations, also provides the development of reaction directions which are mainly uncharacteristic for sulfenyl chlorides with alkenes [10-14], including cyclization completed due to participation of the electron-donating center of the sulfenyl

---

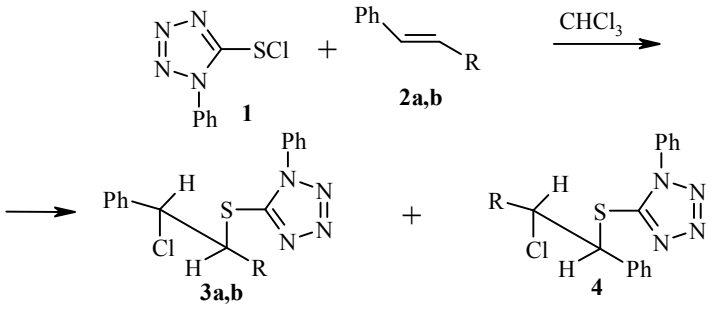
Nizhnii Novgorod State Technical University, Nizhnii Novgorod 603600, Russia; e-mail: ifxf@nntu.nnov.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 763-767, June, 2001. Original article submitted June 22, 2000.

 0009-3122/01/3706-0702$25.00

fragment. In view of the real possibilities of varying the structure of sulfenyl chlorides and unsaturated compounds it may be assumed that the approach considered to the synthesis of sulfur-containing heterocycles is extremely promising.

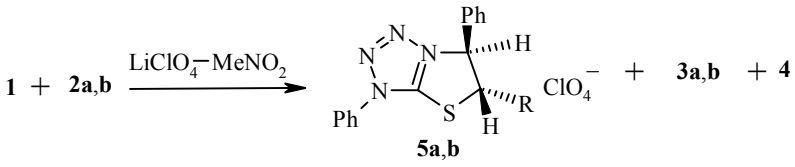
In the present work the interaction has been studied of 1-phenyl-5-tetrazolesulfenyl chloride (**1**), containing potentially nucleophilic centers in the sulfenyl fragment, with styrene **2a** and (*E*)-1-phenylpropene **2b**. Reactions were carried out in chloroform and in a lithium perchlorate–nitromethane system which, as was shown previously by us [10-12], provides stimulation of different directions on sulfenyl chlorination of alkenes.

It was established by us that products of 1,2-addition at the multiple bond are formed on reaction of sulfenyl chloride **1** with the unsaturated compounds **2a,b** in chloroform, in yields close to quantitative. With alkene **2a** the addition product is formed according to the Markownikoff rule and with alkene **2b** a mixture of products is formed with addition according to Markownikoff (**3b**) and against the rule (**4**) in a ratio of 3 : 2.



2a, **3a** R = H; **2b**, **3b**, **4** R = Me

Heterocyclization takes place in reactions of sulfenyl chloride **1** with alkenes **2a,b** in nitromethane in the presence of lithium perchlorate with the formation of 2,3-dihydrothiazolo[3,2-*d*]tetrazolium perchlorates **5a,b** in yields of 47 and 52% respectively. In addition the β-chlorosulfides, viz. the adduct **3a** (38% yield) and the regioisomers **3b** and **4** in a 1 : 1 ratio (total yield 35%), were formed, since, as was shown, these compounds are unchanged under the reaction conditions.



5 a R = H, **b** R = Me

The structures of the compounds synthesized were proved by IR, ^{1}H, and ^{13}C NMR spectroscopy, by data of elemental analysis, and by X-ray structural analysis (for compound **5b**).

A spatial model of the cation of salt **5b** is shown in Fig. 1. Bond lengths and valence angles for this structure are given in Table 1. Atomic coordinates and thermal parameters are given in Table 2. The $N_{(1)}$, $N_{(2)}$, $N_{(3)}$, $N_{(4)}$, S, $C_{(16)}$, and $C_{(17)}$ atoms are coplanar within 0.08 Å, the $C_{(18)}$ atom emerges from this plane by 0.43 Å. The $C_{(1)}$–$C_{(6)}$ bond forms an angle of 17.1° from the plane of the ring, but the $C_{(9)}$–$C_{(14)}$ bond forms an angle of 80.1°. A broad intense absorption band was observed in the IR spectra of compounds **5a,b** at 1100 cm^{-1} corresponding to the vibrations of the Cl–O bond. Assignment of the signals in the NMR spectra of the compounds obtained was carried out in accordance with the data of [15,16].

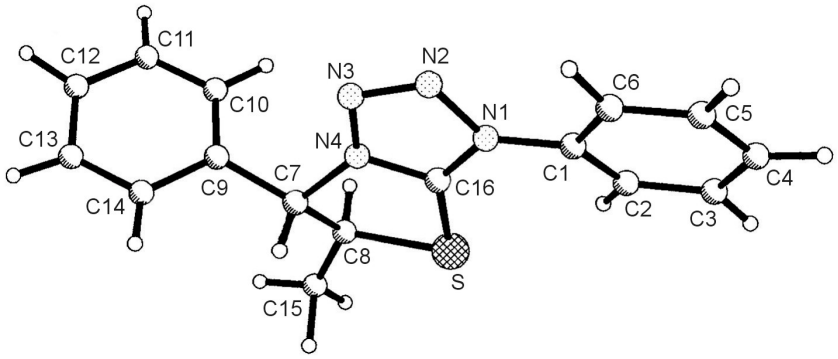


Fig. 1. Structure of the *trans*-2-methyl-3,7-diphenyl-2,3-dihydrothiazolo[3,2-*d*]tetrazolium ion **5b**.

It has therefore been shown by us that a new reaction direction for sulfenyl chloride **1** is developed in nitromethane in the presence of lithium perchlorate. The reaction in chloroform may be described within the framework of an Ad_E process, including cyclic intermediates of the episulfurane type or a tight ion-pair: ion of episulfonium–chloride anion [8,9]. In reactions in the nitromethane–lithium perchlorate system, in addition to the particles responsible for the formation of β-chloro sulfides, probably because of coordination of the reagent with lithium cations [10-14], intermediates may arise in which the reverse transfer of electrons from the sulfur atom to the carbon atoms of the multiple bond is not brought about. This also causes nucleophilic participation of a nitrogen atom of the tetrazole ring in binding the nascent electron-deficient center. The stereospecificity of ring formation revealed by us indicates a more or less coordinated process of formation of the sulfur–carbon and nitrogen–carbon bonds.

TABLE 1. Bond Lengths and Valence Angles in the Molecule of Compound **5b**

Bond	*d*, Å	Angle	ω, deg.	Angle	ω, deg.
$S–C_{(16)}$	1.71(2)	$C_{(16)}–S–C_{(18)}$	88.5(9)	$C_{(10)}–C_{(9)}–C_{(14)}$	119(2)
$S–C_{(18)}$	1.87(2)	$C_{(16)}–N_{(1)}–N_{(2)}$	106.2(14)	$C_{(10)}–C_{(9)}–C_{(17)}$	124(2)
$N_{(1)}–C_{(16)}$	1.32(2)	$C_{(16)}–N_{(1)}–C_{(1)}$	131(2)	$C_{(14)}–C_{(9)}–C_{(17)}$	117(2)
$N_{(1)}–N_{(2)}$	1.38(2)	$N_{(2)}–N_{(1)}–C_{(1)}$	123(2)	$C_{(9)}–C_{(10)}–C_{(11)}$	121(3)
$N_{(1)}–C_{(1)}$	1.39(2)	$N_{(3)}–N_{(2)}–N_{(1)}$	110(2)	$C_{(12)}–C_{(11)}–C_{(10)}$	120(3)
$N_{(2)}–N_{(3)}$	1.29(2)	$N_{(2)}–N_{(3)}–N_{(4)}$	107.4(14)	$C_{(13)}–C_{(12)}–C_{(11)}$	121(3)
$N_{(3)}–N_{(4)}$	1.36(2)	$N_{(3)}–N_{(4)}–C_{(16)}$	107.8(14)	$C_{(12)}–C_{(13)}–C_{(14)}$	121(3)
$N_{(4)}–C_{(16)}$	1.34(2)	$N_{(3)}–N_{(4)}–C_{(17)}$	133(2)	$C_{(13)}–C_{(14)}–C_{(9)}$	117(2)
$N_{(4)}–C_{(17)}$	1.45(2)	$C_{(16)}–N_{(4)}–C_{(17)}$	118(2)	$N_{(1)}–C_{(16)}–N_{(4)}$	109(2)
$C_{(1)}–C_{(6)}$	1.37(2)	$C_{(6)}–C_{(1)}–C_{(2)}$	119(2)	$N_{(1)}–C_{(16)}–S$	138(2)
$C_{(1)}–C_{(2)}$	1.36(2)	$C_{(6)}–C_{(1)}–N_{(1)}$	119(2)	$N_{(4)}–C_{(16)}–S$	113(2)
$C_{(2)}–C_{(3)}$	1.36(2)	$C_{(2)}–C_{(1)}–N_{(1)}$	122(2)	$N_{(4)}–C_{(17)}–C_{(18)}$	102(2)
$C_{(3)}–C_{(4)}$	1.37(3)	$C_{(1)}–C_{(2)}–C_{(3)}$	120(2)	$N_{(4)}–C_{(17)}–C_{(9)}$	114(2)
$C_{(4)}–C_{(5)}$	1.37(3)	$C_{(2)}–C_{(3)}–C_{(4)}$	121(2)	$C_{(18)}–C_{(17)}–C_{(9)}$	118(2)
$C_{(5)}–C_{(6)}$	1.33(2)	$C_{(5)}–C_{(4)}–C_{(3)}$	118(2)	$C_{(15)}–C_{(18)}–C_{(17)}$	121(2)
$C_{(9)}–C_{(10)}$	1.34(3)	$C_{(6)}–C_{(5)}–C_{(4)}$	120(2)	$C_{(15)}–C_{(18)}–S$	116(2)
$C_{(9)}–C_{(14)}$	1.42(3)	$C_{(5)}–C_{(6)}–C_{(1)}$	121(2)	$C_{(17)}–C_{(18)}–S$	107.4(13)
$C_{(9)}–C_{(17)}$	1.49(2)				
$C_{(10)}–C_{(11)}$	1.36(4)				
$C_{(11)}–C_{(12)}$	1.32(4)				
$C_{(12)}–C_{(13)}$	1.34(4)				
$C_{(13)}–C_{(14)}$	1.37(3)				
$C_{(15)}–C_{(18)}$	1.36(3)				
$C_{(17)}–C_{(18)}$	1.47(3)				

TABLE 2. Coordinates ($\times 10^4$) of Non-hydrogen Atoms and Coefficients of Equivalent Isotropic Displacement (Å $\times 10^3$) of Compound **5b**

Atom	*x*	*y*	*z*	$U_{(eq)}$
S	6385(5)	-3364(5)	642	103(2)
$N_{(1)}$	4175(14)	-355(11)	626(2)	76(4)
$N_{(2)}$	3644(15)	10(14)	796(3)	99(5)
$N_{(3)}$	4311(19)	359(16)	984(3)	113(5)
$N_{(4)}$	5286(14)	228(13)	942(3)	88(4)
$C_{(1)}$	3722(16)	-687(14)	397(3)	72(4)
$C_{(2)}$	4106(19)	-1264(17)	249(3)	103(6)
$C_{(3)}$	3654(23)	-1545(19)	24(4)	113(6)
$C_{(4)}$	2740(22)	-1347(19)	-49(4)	112(7)
$C_{(5)}$	2355(20)	-775(19)	105(4)	111(6)
$C_{(6)}$	2807(20)	-494(16)	324(3)	98(5)
$C_{(9)}$	6337(19)	690(25)	1328(3)	95(6)
$C_{(10)}$	5679(22)	-300(24)	1469(5)	130(8)
$C_{(11)}$	5725(34)	-228(39)	1702(7)	178(12)
$C_{(12)}$	6364(41)	829(49)	1808(5)	157(12)
$C_{(13)}$	7096(29)	1829(33)	1685(7)	164(11)
$C_{(14)}$	7052(23)	1825(24)	1441(5)	131(8)
$C_{(15)}$	8059(27)	205(31)	997(4)	173(11)
$C_{(16)}$	5189(16)	-191(15)	720(4)	82(5)
$C_{(17)}$	6427(20)	669(22)	1065(3)	125(8)
$C_{(18)}$	6902(22)	-64(25)	959(3)	136(10)

EXPERIMENTAL

The IR spectra were recorded on a UR 20 instrument in nujol. The ^{1}H NMR spectra were recorded on a Bruker WM 250 (250 MHz) spectrometer, and the ^{13}C NMR spectra on a Bruker AM 300 (75.47 MHz) instrument in $CDCl_3$, CD_3CN, and DMSO-d_6.

X-Ray Structural Analysis of Compound 5b. The crystals of compound **5b** obtained from dichloromethane were hexagonal. At 293 K a = 12.766(2), b = 12.766(2), c = 56.280(11) Å; α = 90, β = 90, γ = 120°; V = 7943(2) Å^3; d_{calc} = 1.342 g/cm^3; space group R-3; Z = 18; F(000) = 3297. The analysis was carried out on a Syntex P-1 automatic diffractometer (MoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, θ_{max} = 49.90°). The structure was solved by the direct method with the SHELXTL programs. In the calculation 978 reflections with $I > 3\sigma(I)$ were used. Refinement was carried out with the full-matrix least squares method. The final value of the divergence factor was R = 0.11 (destruction of the crystal occurs during analysis).

1-Phenyl-5-tetrazolyl 2-Chloroethyl Sulfides 3a,b, and 4. A solution of alkene (10 mmol) in chloroform (10 ml) was added with stirring to a solution of sulfenyl chloride **1** (10 mmol) in chloroform (15 ml) at 20°C. After 30 min the solvent was distilled off in vacuum. The β-chlorosulfides were obtained in quantitative yield.

Compound 3a. Mp 101-103°C (hexane). ^{1}H NMR spectrum ($CDCl_3$): 7.75-7.30 (10H, m, 2Ph); 5.40 (1H, t, CHCl); 3.98 ppm (2H, ddd, J_{AX} = 5.7, J_{BX} = 7.7, J_{AB} = 14.0 Hz, CH_2S). ^{13}C NMR spectrum ($CDCl_3$): 138.87 (C_{Het}); 133.33, 130.20, 129.78, 128.99, 128.79, 127.10, 123.71 (C_{Ph}); 60.55 (CHCl); 41.88 ppm (CH_2S). Found, %: C 56.71; H 4.08; S 10.16. $C_{15}H_{13}ClN_4S$. Calculated, %: C 56.87; H 4.14; S 10.12.

Compounds 3b and 4. Oil. ^{1}H NMR spectrum ($CDCl_3$): 7.65-7.32 (10H, m, 2Ph); 5.63 (0.6H, d, J = 6.4 Hz, PhCHCl); 4.55 (0.4H, m, CH_3CHCl), 3.75 (0.4H, d, J = 7.0 Hz, PhCHS); 3.48 (0.6H, m, CH_3CHS), 1.54 (1.2H, d, J = 6.9 Hz, CH_3CHCl); 1.40 ppm (1.8H, d, J = 6.2 Hz, CH_3CHS). Found, %: C 57.89; H 4.47; S 9.78. $C_{16}H_{15}ClN_4S$. Calculated, %: C 58.09; H 4.57; S 9.69.

2,3-Dihydrothiazolo[3,2-*d*]tetrazolium Perchlorates 5a,b. Lithium perchlorate (30 mmol) in nitromethane (40 ml) and a solution of alkene (10 mmol) in nitromethane (10 ml) were added with stirring to a solution of sulfenyl chloride (10 mmol) in nitromethane (10 ml) at 20°C. After 15 min dichloromethane (100 ml) was added, the precipitate of LiCl and $LiClO_4$ was filtered off and washed several times on the filter with dichloromethane. The filtrate was evaporated in vacuum. The products were separated by fractional crystallization from a hexane–dichloromethane mixture.

Compound 5a. Mp 220-221°C (chloroform). ^{1}H NMR spectrum (DMSO-d_6): 7.83-7.57 (10H, m, 2Ph); 6.37 (1H, q, J_{AX} = 8.3, J_{BX} = 9.9 Hz, CHN); 4.98 and 4.73 ppm (2H, both dd, J_{AB} = 11.8 Hz, CH_2S). ^{13}C NMR spectrum (DMSO-d_6): 160.06 (C_{Het}); 132.53, 131.95, 131.70, 130.73, 130.26, 129.24, 128.18, 121.41 (C_{Ph}), 64.79 (CHN), 49.67 (CH_2S). Found, %: C 47.12; H 3.47; S 8.34. $C_{15}H_{13}ClN_4O_4S$. Calculated, %: C 47.31; H 3.44; S 8.42.

Compound 5b. Mp 205-207°C (dichloromethane). ^{1}H NMR spectrum (CD_3CN): 7.82-7.54 (10H, m, 2Ph); 5.99 (1H, d, J = 9.9 Hz, CHN); 5.38 (1H, m, CHS); 1.84 ppm (3H, d, J = 6.6 Hz, CH_3). Found, %: C 48.50; H 3.78; S 8.15. $C_{16}H_{15}ClN_4O_4S$. Calculated, %: C 48.67; H 3.83; S 8.12.

The work was carried out with the financial support of the Ministry of Education of the Russian Federation (grant 97-9.4-28).

REFERENCES

1. Yu. I. Gevaza, V. I. Staninets, and N. S. Zefirov, *Electrophilic Intramolecular Cyclization of Olefins* [in Russian], Naukova Dumka, Kiev (1990), p. 156.
2. R. R. Schmidt, *Angew. Chem. Intern. Edit.*, **12**, 212 (1973).
3. E. Kuhle, *The Chemistry of the Sulfenic Acids*, Thieme Verlag, Stuttgart (1973), p. 163.
4. Yu. G. Gololobov and N. I. Gusar', *Sulfenyl Chlorides* [in Russian], Nauka, Moscow (1989), p. 177.
5. I. V. Koval', *Usp. Khim.*, **64**, 781 (1995).
6. G. H. Schmid and D. G. Garratt in S. Patai (editor), *The Chemistry of Double Bonded Functional Groups*, Wiley, New York (1977), Chap. 9, p. 725.
7. L. P. Rasteikene, D. I. Greichute, M. T. Lin'kova, and I. L. Knunyants, *Usp. Khim.*, **46**, 1041 (1977).
8. W. A. Smit*, Sov. Sci. Rev. B. Chem.*, Harwood, Amsterdam, **7**, 155 (1985).
9. N. S. Zefirov and A. S. Kozmin, *Sov. Sci. Rev. B. Chem.*, Harwood, Amsterdam, **7**, 297 (1985).
10. G. N. Borisova, A. V. Borisov, I. V. Bodrikov, V. K. Bel'skii, A. I. Lutsenko, W. A. Smit, and G. A. Kutyrev, *Zh. Org. Khim.*, **30**, 760 (1994).
11. A. V. Borisov, I. V. Bodrikov, G. N. Borisova, W. A. Smit, A. I. Lutsenko, and V. K. Bel'skii, *Zh. Org. Khim.*, **31**, 1018 (1995).
12. A. V. Borisov, I. V. Bodrikov, G. N. Borisova, V. K. Belsky, W. A. Smit, and A. I. Lutsenko, *Mendeleev Commun.*, 52 (1996).
13. V. Ya. Popkova, V. K. Osmanov, A. V. Borisov, B. I. Ugrak, and I. V. Bodrikov, *J. Fluorine Chem.*, **77**, 183 (1996).
14. A. V. Borisov, I. V. Bodrikov, A. Yu. Subbotin, G. N. Borisova, and V. K. Osmanov, *Zh. Org. Khim.*, **33**, 469 (1997).
15. G. H. Schmid and V. J. Nowlan, *Can. J. Chem.*, **54**, 695 (1976).
16. A. V. Borisov, A. I. Lutsenko, L. V. Chumakov, W. A. Smit, and I. V. Bodrikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2346 (1983).