9. M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternhell, and P. Y. Westerman, J. Am. Chem. Soc., 97, 1482 (1975).
10. R. Wasylishen and T. Schaefer, Can. J. Chem., 50, 2989 (1972).
11. J. E. Anderson and J. C. Brand, Trans. Faraday Soc., 6, 39 (1966).
12. P. Rademacher and B. Freckmann, Tetrahedron Lett., 1978, No. 9, 841.
13. J. M. Lehn, Topics in Current Chemistry, Vol. 15, Springer Verlag, Berlin—Heidelberg—New York (1970), p. 311.
14. R. G. Kostyanovskii (Kostyanovsky), V. F. Rudchenko, O. A. Dyachenko, I. I. Chervin, A. V. Zolotoi (Zolotoy), and L. O. Atovmyan, Tetrahedron, 35, 213 (1979).
15. V. F. Rudchenko, S. M. Ignatov, I. I. Chervin, V. S. Nosova, and R. G. Kostyanovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1986, No. 5, 1153.
16. V. F. Rudchenko, V. I. Shevchenko, and R. G. Kostyanovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1985, No. 7, 1685.

SYNTHESIS AND TRANSFORMATIONS OF SULFIDES OF THE THIOPHENE SERIES. 42.* SYNTHESIS AND PROPERTIES OF SOME 2-ALKYLTHIO(ALKYLSULFINYL, ALKYLSULFONYL)THIOPHENE-3-CARBONITRILE N-OXIDES

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Thiophene-3-carbonitrile N-oxides containing alkylthio, alkylsulfinyl, and alkysulfonyl groups in the 2-position, which readily undergo 1,3-dipolar cycloaddition to the C=C bond (styrene, N-phenylmaleinimide) to give the corresponding 3,5-disubstituted 2-isoxazolines, were obtained.

The use of organic nitrile oxides in 1,3-dipolar cycloaddition reactions with various dipolarophiles opens up extensive possibilities for the synthesis of the most diverse classes of mono- and polyheterocycles [2]. The number of stable nitrile oxides, particularly in the heterocyclic series, is extremely limited, since the overwhelming majority of them undergo spontaneous dimerization to furoxanes; they are therefore generally prepared in situ. The possibility of the formation of nitrile oxides of the thiophene series only as unstable intermediates was demonstrated in [3]. One of the necessary conditions for the stability of aromatic nitrile oxides is the presence in the ortho position relative to the nitrile oxide group of substituents that sterically hinder their dimerization [4].

In the present paper we describe the synthesis of some thiophene-3-carbonitrile N-oxides with methylthio, methylsulfinyl, or methylsulfonyl groups in the 2 position by two-phase oxidative dehydrogenation of 2-alkylthio(alkylsulfonyl)-5-alkylthiophene-3-aldoximes with sodium hypochlorite by the method in [5]. The starting 2-methylthio-5-methylthiophene-3-aldoxime (I) was obtained by the usual method from the corresponding aldehyde [6] and exists, according to the ^{15}N NMR spectral data ($J_{^{15}NH} = 3.4$ Hz), in the form of the syn isomer [7]. Since both of the oxime and methylthio groups may undergo changes during the reaction, we ascertained the sequence of their oxidation and the effect of the nature of the sulfur fraction on the properties and stabilities of the resulting nitrile oxides.

3-(2-Methylthio-5-methyl-3-thienyl)-5-phenyl-2-isoxazoline (II) was isolated in high yield when oxime I was added to a mixture containing one to two equivalents of NaOCl, styrene, and a small amount of Et_3N in CH_2Cl_2. Its structure was confirmed by data from the mass spectra and the PMR and ^{13}C NMR spectra: in particular, the chemical shifts for the $C_{(4)}$ – trip-

*See [1] for communication 41.

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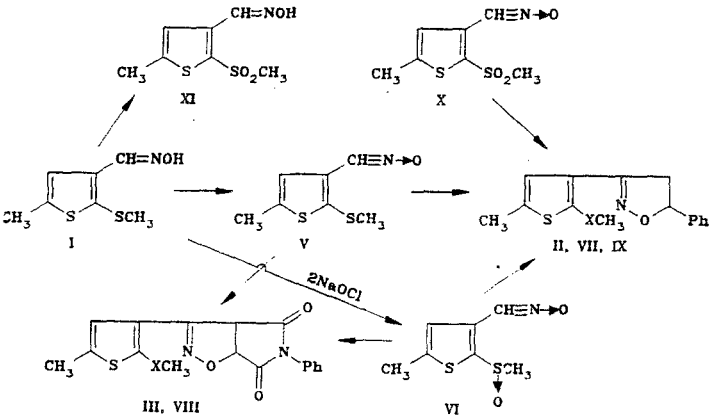
let at 44.3 ppm (J = 136.9 Hz) – and $C_{(5)}$ – doublet at 82.2 ppm (J = 150.7 Hz) – atoms constitutes evidence that the phenyl group is in the 5 position of the isoxazoline ring. Isoxazolinedicarboxylic acid N-phenylimide (III) and a small amount of amido acid IV, which is probably formed in the alkaline hydrolysis of N-phenylmaleinimide, were similarly obtained when N-phenylmaleinimide was used as the dipolarophile. This result indicates the formation of the highly reactive 2-methylthio-5-methylthiophene-3-carbonitrile N-oxide (V) as an intermediate and also constitutes evidence that only the aldoxime group undergoes oxidation under the conditions selected.

The reaction of oxime I with 1 mole of NaOCl in the absence of a dipolarophile leads to a mixture containing unchanged oxime I, nitrile oxide V, and sulfoxide VI in a ratio of 1:2:1 (according to the PMR spectral data). The yield of nitrile oxide V can be increased to 80-90% by reversing the order of mixing of the reagents, which virtually excludes the presence of excess oxidizing agent; in this case the purity of the product increases with an increase in the alkalinity of the hypochlorite solution used. Sulfide V is unstable in solutions and in the solid state at 20°C but can be stored for several days without changes in the IR and PMR spectra at −5°C to −10°C. Its IR spectrum contains intense bands at 2300 and 1370 cm^{-1}, which are characteristic for aromatic nitrile oxides.

The more stable 2-methylsulfinyl-5-methylthiophene-3-carbonitrile N-oxide (VI) is formed in good yield in the reaction of oxime I with 2 moles of NaOCl in the absence of a dipolarophile. It can be stored for a long time in the cold and at 20°C in the solid state and in solution in DMSO without a change in the PMR spectrum. The signal of the carbon atom of the CNO group with a characteristic strong-field shift of 31.2 ppm is present in the ^{13}C NMR spectrum of nitrile oxide VI; the signal of a nitrile oxide nitrogen atom at 174.3 ppm (as compared with 35.7 and 170.3 ppm, respectively, for mesitonitrile oxide [8]) is present in the ^{14}N NMR spectrum.



II, III X=S; VII, VIII X=SO; IX $X=SO_2$

The structure of nitrile oxide VI as a compound that bears a sulfoxide grouping is confirmed by synthesis from it of the corresponding derivatives with styrene (VII) and N-phenylmaleinimide (VIII), as well as by oxidation of its isoxazoline derivative VII to sulfone IX, which was obtained independently from sulfide II.

An attempt to obtain nitrile oxide containing a methylsulfonyl group in the 2 position by reaction of oxime I with 3 moles of NaOCl led to a difficult-to-separate mixture containing (according to the PMR spectrum) V, VI, and X. We were able to obtain 2-methylsulfonyl-5-methylthiophene-3-carbonitrile N-oxide (X), which is stable at 20°C, in 84% yield by oxidative dehydrogenation with NaOCl of 2-methylsulfonyl-5-methylthiophene-3-aldoxime (XI), which is formed in the oxidation of oxime I with excess H_2O_2 in AcOH. Like nitrile oxides V and VI, sulfone X reacts readily with styrene to give the corresponding isoxazoline IX.

Thus the stabilities of nitrile oxides V, VI, and X increase on passing from the sulfide to compounds that contain sulfur in higher oxidation states.

EXPERIMENTAL

The IR spectra were recorded with UR-20 and Specord IR-275 spectrometers. The PMR spectra of all of the compounds and the ^{13}C NMR spectra of isoxazolines II, VII, and IX (in $CDCl_3$)

TABLE 1. Characteristics of I-III and V-XI

Compound	IR spectrum ($CHCl_3$), ν, cm^{-1}	M_{calc}	Found, %				Empirical formula	Calc., %			
			C	H	N	S		C	H	N	S
II		289,4	62,1	5,2	4,8	21,8	$C_{15}H_{15}NOS_2$	62.2	5,2	4,8	22,2
VII	1050 (SO)	305,4	59,0	5,0	4,8	20,8	$C_{15}H_{15}NO_2S_2$	59,0	5,0	4,6	21,0
IX	1145, 1130, 1320 (SO_2)	321,4	55,9	4,9	4,3	19,9	$C_{15}H_{15}NO_3S_2$	56,0	4,7	4,4	20,0
III	1730 (CO)	358,4	57,0	3,9	7,6	18,0	$C_{17}H_{14}N_2O_2S_2$	57,0	3,9	7,8	17,9
VIII	1730 (CO), 1030—1040 (SO)	374,4	54,5	3,8	7,4	17,0	$C_{17}H_{14}N_2O_3S_2$	54,5	3,8	7,5	17,1
I	3580—3590 (N—OH)	187,3	44,7	4,8	7,6	34,2	$C_7H_9NOS_2$	44,9	4,8	7,5	34,2
XI	3580—3570 (N—OH), 1150, 1325 SO_2	219,3	38,4	4,5	6,5	29,1	$C_7H_9NO_3S_2$	38,3	4,1	6,4	29,2
V	2300 (C≡N), 1380 (N—O)	185,3					$C_7H_7NOS_2$				
VI	2300 (C≡N), 1380 (N—O), 1060 (SO)	201,3	41,7	3,5	6,7	31,8	$C_7H_7NO_2S_2$	41,8	3,5	7,0	31,9
X	2300 (C≡N), 1380 (N—O), 1150 br, 1330 SO_2	217.3	38,8	3,5	6,4	29,4	$C_7H_7NO_3S_2$	38,8	3,2	6,4	29,5

and oximes I and XI (in d_6-DMSO) were obtained with a Bruker WM-250 spectrometer; the ^{13}C and ^{14}N NMR spectra of nitrile oxides V, VI, and X ($CDCl_3$, −5°C) and the ^{15}N NMR spectra of oximes I and XI were recorded with a Bruker AM-300 spectrometer (75.47, 21.69, and 30.42 MHz, respectively). The ^{15}N and ^{14}N chemical shifts were measured relative to $MeNO_2$. The assignment of the signals in the ^{13}C spectra was made on the basis of experiments involving $^{13}C-\{^1H\}$ selective double heteronuclear resonance. The molecular masses were determined with a Varian MAT CH-6 mass spectrometer at an ionizing voltage of 70 eV with direct introduction of the substances into the ion source. The results of elementary analysis and the spectral characteristics of the synthesized compounds are presented in Tables 1 and 2.

2-Methylthio-5-methylthiophene-3-aldehyde Oxime (I). An aqueous solution (20 ml) of NH_2OH [obtained from 12.9 g (0.186 mole) of $NH_2OH \cdot HCl$ and 25.2 g (0.186 mole) of $AcONa \cdot 3H_2O$], was added to a solution of 23.6 g (0.166 mole) of 2-methylthio-5-methylthiophene-3-aldehyde [6] in 50 ml of EtOH, and the mixture was refluxed for 1.5 h. It was then cooled and poured into ice water, and the precipitate was removed by filtration, washed with water, and dried to give 30.76 g (99%) of a product with mp 77-79°C (from heptane).

2-Methylsulfonyl-5-methylthiophene-3-aldehyde Oxime (XI). A 2-g (10.5 mmole) sample of oxime I was heated in 15 ml of glacial AcOH and 11 ml (a tenfold excess) of 28% H_2O_2 at 30-40°C until the solid had dissolved completely, and the solution was allowed to stand at 20°C for 24 h. It was then poured into ice water, and the resulting precipitate was removed by filtration, washed with water, and dried to give 1.62 g (74%) of a product with mp 134-136°C (from $CHCl_3$).

3-(2-Methylthio-5-methyl-3-thienyl)-5-phenyl-2-isoxazoline (II). A solution of 0.94 g (5 mmole) of oxime I in 10 ml of CH_2Cl_2 was added dropwise at 0°C to −5°C to a vigorously stirred mixture of 0.55 g (5.3 mmole) of styrene, 0.05 ml (0.5 mmole) of Et_3N, 5 ml of CH_2Cl_2, and 3 ml of an aqueous solution of NaOCl (6 mmole, active Cl 14.93%, NaOH 4.1%), after which the mixture was stirred at −5°C for 1 h and without cooling for 1 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The extracts were combined, washed with water, and dried with $CaCl_2$. The solvent was removed by distillation, and the residue − 1.38 g of an oil − was chromatographed with a column packed with silica gel L 100/160 by elution with heptane and $CHCl_3$. Evaporation of the $CHCl_3$ gave 1.15 g (80%) of a product with mp 49-51°C (from heptane).

3-(2-Methylthio-5-methyl-3-thienyl)-4,5-dihydroisoxazole-4,5-dicarboxylic Acid N-Phenylmide (III). This compound was obtained from 1.87 g (10 mmole) of oxime I and 1.79 g (10.35 mmole) of N-phenylmaleinimide by a procedure similar to that used to prepare isoxazoline II. The product was obtained in 90% yield and had mp 148-150°C (from $CHCl_3$–EtOH).

TABLE 2. Spectral Characteristics of the Synthesized Compounds*[1]

Compound	PMR spectrum ($CDCl_3$), δ, ppm (J, Hz)*[2]	Mass spectrum, m/z (I, %)	^{13}C spectrum, δ, ppm (J_{C-H}, Hz)
II	2,44 (3H, d, CH_3); 2,48 (3H, s, SCH_3); 3,49 (1H, dd, 4-H, J=17,0 and 8,0); 3,94 (1H, dd, 4-H, J=17,0 and 0,5); 5,68 (1H, dd, 5-H, J=8,0 and 10,5); 7,00 (1H, q, 4′-H); 7,3—7,4 (5H, m, Ph)	289 (100), 274 (5,8), 272 (5), 257 (26), 256 (26), 242 (12), 224 (12), 215 (8), 212 (21)	15,0 (129,5 q.; d 2,8) Me; 21,3 (q 140,6) SMe: 44,3 (t 136,9) CH_2; 82,2 (d 150,7) CH; 152,5 (br.t 4,6) C=N; **Ph**: 125,7 (*o*-C); 127,8 (*p*-C); 128,4 (*m*-C); 140,9 ($C_{(1)}$); thienyl: 135,3 (m) $C_{(2)}$, 130,0 (m) $C_{(3)}$; 126,0 (d 168,0; q 5,0) $C_{(4)}$; 140,2 (d 5,5) $C_{(5)}$
VII	2,55 (3H, d, CH_3); 3,00 (3H, s, $SOCH_3$); 3,36 (1H, dd, 4-H, J=17,0 and 9,0); 3,68 (1H, dd, 4-H, J=17,0 and 10,5), 5,84 (1H, dd, 5-H, J=9,0 and 10,5); 6,82 (1H, d, 4′-H); 7,34—7,43 (5H, m, Ph)	305 (100), 304 (64), 290 (18), 288 (26), 242 (43), 228 (71), 225 (43), 170 (50)	15,9 (q 129,5; d 2,8) Me; 44,2 (q 139,6) SOMe; 44,0 (t 135,0) CH_2; 83,0 (d 152,6) CH; 151,7 (br.t 5,5) C=N; **Ph**: 125,9 (*o*-C); 128,4 (*p*-C), 128,9 (*m*-C); 140,3 ($C_{(1)}$); thienyl: 148,2 (m) $C_{(2)}$; 128,4 (m) $C_{(3)}$; 126,3 (d*[3]; q 4,7) $C_{(4)}$; 144,9 (dq 6,0) $C_{(5)}$
IX	2,55 (3H, d, CH_3); 3,42 (3H, s, SO_2CH_3), 3,25 (1H, dd, 4-H, J=17,0 and 8,5); 3,80 (1H, dd, 4-H, J=17,0 11,0); 5,77 (1H, dd, 4-H, J=11,0 and 8,5); 6,91 (1H, q, 4′-H); 7,33—7,42 (5H, Ph)	321 (100), 320 (57), 304 (9), 244 (80), 242 (29), 225 (40), 215 (29)	15,0 (q 132,2) Me; 45,5 (q 139,6) SO_2Me; 44,8 (t 135,9) CH_2, 83,0 (d 152,6) CH; 151,1 (br.t 5,5) C=N; **Ph**: 125,8 (*o*-C); 125,2 (*p*-C); 128,5 (*m*-C); 140,0 ($C_{(1)}$); thienyl: 137,2 (br.d 8,9) $C_{(2)}$; 132,9 (br.d 4,9) $C_{(3)}$; 128,1 (dq *[4]) $C_{(4)}$; 147,0 (dq 6,7) $C_{(5)}$
III	2,45 (3H, d, CH_3); 2,59 (3H, s, SCH_3); 5,24; 5,60 (1H, d 4-H, 1-H, 5-H, 2-H, J=10); 7,21 (1H, q, 4′-H); 7,41—7,52 (5H, m, Ph)	358 (100), 325 (15)	
VIII	2,58 (3H, d, CH_3); 2,90 (3H, s, $SOCH_3$); 4,86; 5,66 (2H, d, 4-H, 5-H, J=10,0); 7,29 (1H, q, 4′-H); 7,31—7,57 (5H, m, Ph)	374 (8), 358 (24), 284 (21), 283 (100)	
I	2,42 (3H, d, CH_3); 2,44 (3H, s, SCH_3); 6,99 (1H, q, 4-H); 8,38 (1H, s, CH=N); 8,66 (1H, s, OH)	187 (74), 170 (13,1), 169 (24), 156 (20), 155 (100), 154 (46)	15,1 (q 129,5; d 3,7) Me; 21,7 (q 140,6) SMe; 133,3 (br.s) $C_{(2)}$; 136,4 (dd 5,5) $C_{(3)}$; 123,5 (d 168,3, q 4,6) $C_{(4)}$; 141,9 (dq 6,5) $C_{(5)}$; 142,4 (d 164,6, d 9,2) CH=N
XI	2,50 (3H, d, CH_3); 3,13 (3H, s, SO_2CH_3); 7,18 (1H, q, 4-H); 7,85 (1H, br. s, OH); 8,63 (1H, s, CH=N)	219 (95), 202 (79), 189 (42), 170 (46), 140 (100)	15.1 (q 130,5; d 2,5) Me; 46,1 (q 139,0) SO_2Me; 135,1 (br.d 9,3) $C_{(2)}$; 138,1 (d 5,1; d 7,6) $C_{(3)}$; 125,1 (d 174,6; dq 5,1) $C_{(4)}$; 147,1 (dq 6,8) $C_{(5)}$; 141,6 (d 170,4; d 9,3) CH=N
V	2,44 (3H, d, CH_3); 2,51 (3H, s, SCH_3); 6,71 (1H, q, 4-H)		
VI	2,57 (3H, d, CH_3); 2,97 (3H, s, $SOCH_3$); 6,88 (1H, q, 4-H)	201 (8), 186 (18), 185 (25), 171 (100), 170 (27), 156 (36), 154 (15)	16,0 (q 131,8) Me; 44,1 (q 141,6) SOMe; 159,9 (d 9,8) $C_{(2)}$; 112,1 (s) $C_{(3)}$; 127,9 (d 173,3) $C_{(4)}$; 147,0 (dq 7,3) $C_{(5)}$; 31,2 (br.s) C≡NO
X	2,57 (3H, d, CH_3); 3,23 (3H, s, SO_2CH_3); 6,96 (1H, q, 4-H)	217 (53), 187 (100), 172 (65), 149 (76)	15,9 (q 129,4) Me; 45,6 (q 139,2) SO_2Me; 142,4 (d 9,8) $C_{(2)}$; 115,1 (d 4,8) $C_{(3)}$; 129,7 (d 173,8, q 4,9) $C_{(4)}$; 148,9 (dq 7,3) $C_{(5)}$; 29,7 (br.s) C≡NO

*[1] ^{15}N NMR spectra: for I δ −8.5 ppm (J_{NH} = 3.4 ± 0.8 Hz); for XI δ +2.8 ppm (J_{NH} = 3.0 ± 0.4 Hz); ^{14}N NMR spectra (widths of the lines at half the heights, Hz): for V −177.3 ppm (120); for VI −174.3 ppm (78); for X −173.6 (61).

*[2]For all of the compounds $J_{CH_3,4-H}$ = 1.2 Hz.

*[3]One of the components of the doublet is covered by signals of the Ph group.

*[4]Both components of the doublet are overlapped by signals of the Ph group.

2-Methylthio-5-methylthiophene-3-carbonitrile N-Oxide (V). A. A solution of 0.94 g (5 mmole) of oxime I in 10 ml of CH_2Cl_2 was added dropwise at −5°C to −8°C to 2.5 ml (5 mmole) of an aqueous solution of NaOCl (active Cl 14.93%, NaOH 4.1%), after which the mixture, which had turned yellow, was stirred for 15 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The extracts were combined, washed with water, and dried with $CaCl_2$.* The solvent was removed by distillation, and the residue was treated with dry ether. The ether solution was filtered and evaporated in vacuo to give 0.87 g of a mixture in the form of a red oil containing, according to PMR data (intensity ratio of the thiophene protons 4H in $CDCl_3$) 25% I, 50% V, and 25% VI.

B. A solution of NaOCl (5 mmole) was added dropwise at −5°C to −8°C to a solution of 5 mmole of oxime I in 10 ml of CH_2Cl_2. Workup as described in experiment A gave 0.93 g of a solid product with mp 30-40°C containing, according to the PMR spectrum, 7% I, 80% V, and 13% VI. A solution of 0.4 g of styrene in 3 ml of CH_2Cl_2 was added dropwise to 0.7 g of this product in 10 ml of anhydrous CH_2Cl_2, and the mixture was allowed to stand at 20°C for 12 h. The solvent was removed by distillation, and the residue − 1.0 g of an oil − was chromatographed with a column packed with silica gel L 100/160 to give 0.83 g (76%) of isoxazoline II, which, with respect to its melting point and PMR spectrum, was identical to the sample of II previously obtained.

C. The reaction of 0.94 g (5 mmole) of oxime I and 5 mmole of aqueous NaOCl (active Cl 10.6%, NaOH 16.4%) by method B gave 0.8 g (86%) of nitrile oxide V with mp 35-40°C, which was unstable at 20°C. A solution of 0.24 g (1.39 mmole) of N-phenylmaleinimide in 15 ml of anhydrous ether was added to 0.25 g (1.39 mmole) of this product in 5 ml of anhydrous ether. The precipitate that formed after 15 min was removed by filtration and washed with ether to give 0.45 g (93%) of derivative III, which, with respect to its melting point (148-150°C, from $CHCl_3$–EtOH) and PMR spectrum, was identical to the sample of III described above.

2-Methylsulfinyl-5-methylthiophene-3-carbonitrile N-Oxide (VI). This compound was obtained from 0.94 g (5 mmole) of oxime I and 5.5 ml (12.2 mmole) of an aqueous solution of NaOCl (active Cl 16.55%, NaOH 3.1%) after 10-15 min by a method similar to that used to obtain nitrile oxide V (method A). (At the end of the addition the yellow color of the mixture changed to light green.) After removal of the solvent by distillation, the residue − 0.94 g of a solid white substance with mp 76-77°C − was washed with cold dry ether with the addition of the minimal amount of EtOH to give 0.9 g (89%) of sulfoxide VI with mp 87-88°C (dec.).†

3-(2-Methylsulfinyl-5-methyl-3-thienyl)-5-phenyl-2-isoxazoline (VII). A solution of 0.15 g (1.44 mmole) of styrene in 1 ml of CH_2Cl_2 was added dropwise to a solution of 0.24 g (1.19 mmole) of nitrile oxide VI in 4 ml of dry CH_2Cl_2, after which the mixture was allowed to stand at 20°C for 12 h. The CH_2Cl_2 was removed by distillation, and the residue was recrystallized from EtOH to give 0.34 g (93.4%) of a product with mp 138-140°C.

3-(2-Methylsulfinyl-5-methyl-3-thienyl)-4,5-dihydroisoxazole-4,5-dicarboxylic Acid N-Phenylimide (VIII). A 1-g (5 mmole) sample of sulfoxide VI was added to a solution of 0.87 g (5 mmole) of N-phenylmaleinimide in 5 ml of EtOH and 15 ml of dry ether, and the mixture was stirred at 20°C for 15 min. The precipitate was removed by filtration and washed with ether to give 1.0 g of imide VIII. Treatment of this product with hot EtOH (40 ml) gave, after filtration and drying, a product with mp 218-219°C.

2-Methylsulfonyl-5-methylthiophene-3-carbonitrile N-Oxide (X). A 0.85-g (3.88 mmole) sample of oxime XI was added gradually at 0-3°C to a mixture of 15 ml of CH_2Cl_2 and 2.9 ml of a solution of NaOCl (active Cl 0.1471 g, 50% excess), and the mixture was stirred for 5-10 min until the solid vanished. Workup as described for oxide VI gave 0.7 g (83.5%) of oxide X with mp 111°C (dec.).

3-(2-Methylsulfonyl-5-methyl-3-thienyl)-5-phenyl-2-isoxazoline (IX). A. A mixture of 0.8 g (2.6 mmole) of sulfoxide VI and 3 ml of 28% H_2O_2 in 10 ml of glacial AcOH was allowed to stand at 20°C for 48 h, after which the AcOH was removed by distillation (with the addition of EtOH), and the residue was recrystallized from ethyl acetate–heptane to give 0.8 g (95%) of sulfone IX with mp 85-87°C.

*All of the operations were carried out in the cold at 0-5°C.
†The PMR spectrum in d_6-DMSO did not change after a month.

B. The compound was obtained in 97% yield as described above from 0.8 g of sulfide II and 5 ml of 28% H_2O_2. The product was identical with respect to its IR and PMR spectra and melting point to the sample of sulfone IX.

C. The compound was obtained in 94% yield as described above for isoxazoline VII from equivalent amounts of oxide X and styrene in solution in CH_2Cl_2. The product had mp 85-87°C; no melting-point depression was observed for a mixture of this product with the product obtained in experiment A.

LITERATURE CITED

1. Ya. L. Gol'dfarb, M. A. Kalik, V. K. Zav'yalova, Yu. S. Agarunova, and V. A. Kozlovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1620 (1986).
2. P. Caramella and P. Grünanger, in: 1,3-Dipolar Cycloaddition Chemistry, Vol. 1, A. Padwa (ed.), Interscience, New York–Chichester–Toronto (1985), p. 357.
3. Y. Iwakura, K. Uno, S. Shiraishi, and T. Hongu, Bull. Chem. Soc. Jpn., 41, 2954 (1968).
4. Ch. Grundman and J. M. Dean, J. Org. Chem., 30, 2809 (1965).
5. G. A. Lee, Synthesis, No. 4, 508 (1982).
6. Ya. L. Gol'dfarb, M. A. Kalik, and M. L. Kirmalova, Zh. Obshch. Khim., 30, No. 3, 1012 (1960).
7. D. Crepaux and J. M. Lehn, Org. Magn. Reson., 7, 524 (1975).
8. M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, J. Am. Chem. Soc., 95, 4392 (1973).

SPECTRAL INVESTIGATIONS OF THE TAUTOMERIC EQUILIBRIA OF THIOACYL DERIVATIVES OF 2-AMINOTHIAZOLE AND 2-AMINOBENZOTHIAZOLE

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The positions of the tautomeric equilibria for a number of thioacyl derivatives of 2-aminothiazole and 2-aminobenzothiazole were determined by UV and IR spectroscopy with the use of model compounds. Quantum-chemical calculations by the CNDO/2 method were made for some of the acyl and thioacyl derivatives of 2-aminothiazole and 2-iminothiazole.

It is known that the existence of amino derivatives of heterocyclic compounds in the amino or imino form depends to a substantial extent on the basicity of the exocyclic nitrogen atom [1, 2]. A decrease in the basicity of this nitrogen atom gives rise to a shift of the tautomeric equilibrium to favor the imino form [3, 4]. The available literature data from spectral investigations of amine-imine tautomeric equilibria in series of 2-aminothiazoles and 2-aminobenzothiazoles pertain to NH, N-alkyl, and N-acyl derivatives [5, 6]. The present paper is devoted to an investigation by means of UV and IR spectroscopy of such equilibria for thioacyl derivatives of 2-aminothiazole and its benzo analog, which can also exist in two tautomeric forms: amino (A) and imino (B).

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