Chromatomass-spectrometric analysis was performed on a Varian MAT-111 (Gnom) instrument with an ionizing energy of 80 eV and an emission current of 270 mA (column length 1.5 m, internal diameter 0.4 cm, 10% OV-1, temperature programing 80-220°C, 10 deg/min, helium, 20 ml/min).

The initial allylthiophenethiols were obtained by rearrangement of the isomeric allyl thienyl sulfides in m-xylene at 120°C with reaction times of 30-60 min. The physicochemical constants and PMR spectra are given in Table 3.

β-Methylallyl 3-Thienyl Sulfide (IX). Compound (IX) was obtained by the reaction of 3-thiophenethiol with β-methylallyl chloride in an aqueous alkaline solution. The yield was 54%; bp 61-62°C (2 mm Hg), n_D^{20} 1.5769. PMR spectrum, δ: 1.76 (CH_3, 3H, s), 3.23 ($-CH_2-$, 2H, s), 4.57 ($=CH_2$, 2H, m), 6.8-7.2 ppm (3H, m). The rearrangement of compound (IX) was realized at 120°C in an atmosphere of nitrogen, and 3-methylthieno[3,2-b]dihydrothiopyran (X) was isolated from the reaction products by vacuum distillation.

Cyclization of Allylthiophenethiols. The reaction was carried out in a thermostated flask with a stirrer and a reflux condenser in an atmosphere of nitrogen. At the end of the experiment the reaction mixture was dissolved in ether, washed three times with a 10% solution of potassium hydroxide and then to a neutral reaction with water, and dried with magnesium sulfate. The ether was distilled, and the residue was analyzed by GLC, PMR spectroscopy, and chromatomass spectrometry.

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MESOIONIC COMPOUNDS WITH A BRIDGING NITROGEN ATOM

1. INVESTIGATION OF THE PRODUCT FROM DEHYDRATING CYCLIZATION OF (2-PYRIDYLTHIO)ACETIC ACID

L. T. Gorb, E. D. Sych,
A. I. Tolmachev, and I. S. Shpileva

UDC 547.789.6'83

It has been considered [1, 2] that the product first obtained in 1924 by Koenigs [3] by heating (2-pyridylthio)acetic acid in acetic anhydride solution has the structure of thiazolo-[3,2-a]pyridinio-3-oxide (IIa), as proposed in 1951 by Duffin and Kendall [4].

In a development of investigations into polymethine dyes (derivatives of condensed heterocycles [5]), we decided to undertake the synthesis of compounds (IIb, c) in order to obtain the dyes (IId-f) from them. However, the elemental composition of the compound obtained by condensation of the substance with the supposed structure (IIb) with 1-ethyl-2-sulfo-6-methylquinolinium betaine differed greatly from that required for the structure (IIe). This prompted us to investigate the structure of the mesoionic compound formed from (2-pyridylthio)acetic acids [4, 6].

The molecular weight of the product with the supposed structure (IIa) was determined and was found to be twice the calculated value.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660.
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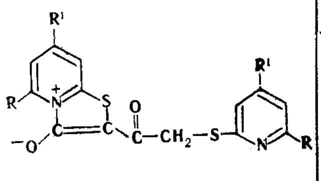
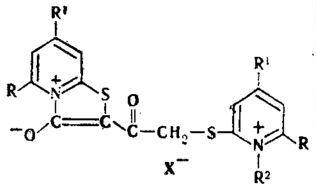
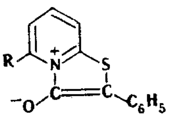
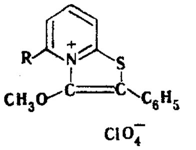
TABLE 1. UV Spectra of Methanol Solutions of the Dehydration Products from (2-Pyridylthio)acetic Acids

	Compound	R	R′	λ_1	lg ε	λ_2	lg ε	λ_3	lg ε	λ_4	lg ε
	IIIa	H	H	250	3,50	284	3,42	416 (443)[a]	3,55	—	—
	IIIa[b]	H	H	—	—	282	3,39	416	3,53	316	3,38
	IIIb	CH_3	H	248	3,40	290	3,49	429 (452)[a]	3,50	—	—
	IIIc	H	CH_3	250	3,33	280	3,29	406	3,44	—	—
	VIa,b[c]	H	H	251	3,9	284	3,9	416	4,2	316	4,0
	VIIIa	H	—	235	4,20	283	3,98	435	4,18	—	—
	VIIIb	CH_3	—	235	4,20	290	4,0	451	4,16		
	IXa	H	—	225	4,28	256	3,88	330	4,29	—	—
	IXb	CH_3	—	227	4,29	256	3,87	340	4,29		

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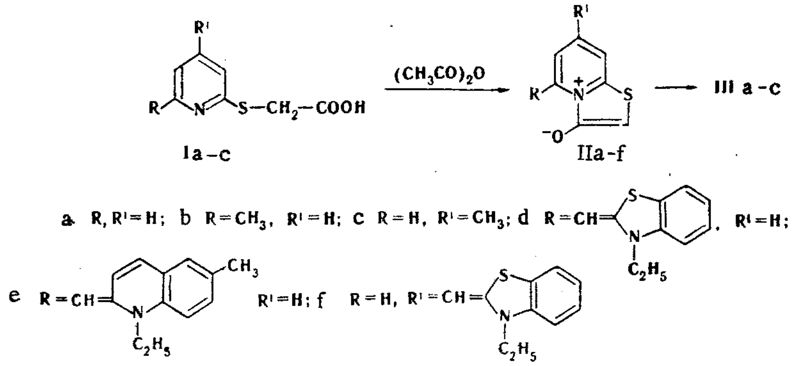
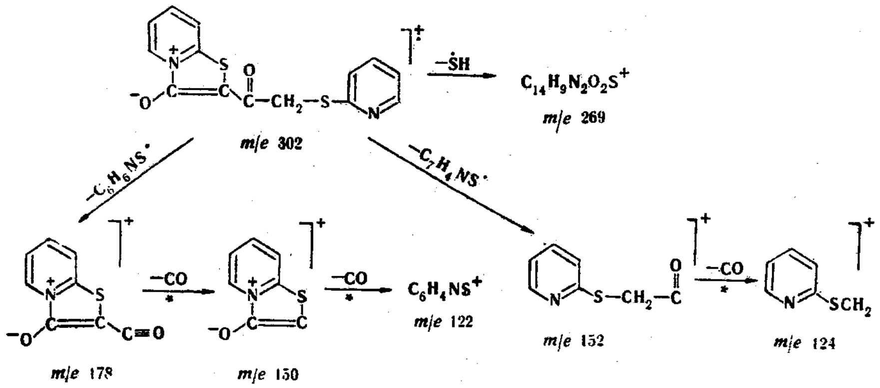
[a] For a benzene solution. [b] In a 1:1 mixture of methanol and trifluoroacetic acid. [c] a R^2=—CH_3, X=CH_3SO_4; b R^2=—C_2H_5, X=BF_4.

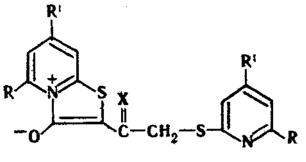


In the PMR spectra of this compound and its 5-methyl derivative [7], dissolved in trifluoroacetic acid, there are singlets at 4.70 and 4.63 ppm and multiplets for aromatic protons in the regions of 7.50-9.00 and 7.12-8.12 ppm respectively. The intensities of these signals are in a ratio of 1:4 for the first compound and 1:3 for the second. In addition, in the spectrum of the latter there are two signals at 3.05 and 2.68 ppm, indicating the presence not of one but of two nonequivalent methyl groups. When the spectra of solutions in deuterotrifluoroacetic acid were measured, the signals with chemical shifts of 4.70 and 4.63 ppm were not observed, and this indicates a high rate of exchange for the respective protons. It is significant also that in the PMR spectrum of the first product, dissolved in DMSO, the multiplet for the aromatic protons is observed in a wider range (7.05-9.00) than in trifluoroacetic acid solution. The upfield edge of this multiplet practically coincides with the corresponding edge of the multiplet for the aromatic protons in the spectrum of (2-pyridylthio)acetic acid (7.03-8.40 ppm). These data made it possible to suppose that the molecule contained a pyridine residue in addition to the mesoionic fragment. Investigation of the UV spectra showed that acidification of a methanol solution of the dehydration product from the acid (Ia) with trifluoroacetic acid led to the appearance of a new band at 316 nm (Table 1) identical with the absorption band of protonated pyridylthioacetic acid in addition to the bands with maxima at 250, 284, and 416 nm observed for a neutral solution (Table 1). These results not only confirm the presence of a pyridine residue in the molecule but also show that it is not conjugated with the mesoionic fragment. In the IR spectrum of the compound there is a strong band at 1650 cm^{-1}, corresponding to the C=O group. All the presented data make it possible to conclude that the mesoionic compounds (IIa-c) formed initially when the acids (Ia-c) are heated in acetic anhydride undergo dimerization to form the derivatives (IIIa-c) (Table 1). Additional information about the structure of compound (IIIa) was provided by its mass-spectrometric investigation. The scheme for the decomposition of (IIIa) can be represented as follows:



The molecular weight of the compound is confirmed by the presence of a high-intensity peak for the molecular ion with mass 302 (28%). As observed for other ketones, peaks due to α cleavage of the C–C bonds in relation to the carbonyl group predominate in the mass spectrum of (IIIa). The peaks for ions with m/e 178 (100%), 150 (10.3%), and 122 (19.6%) and with m/e 152 (32.7%) and 124 (17.7%) seem particularly characteristic of the structure of the compound. The ion with mass 269 (10.3%) is evidently due to skeletal rearrangement, accompanied by ejection of the ṠH particle from the molecular ion. Such a process is well known in the series of aryl sulfides [8]. The high-intensity peak for the ion with mass 78 (67%), corresponding to the pyridine fragment, should also be noted.

The structure (IIIa) explains the results in [4], according to which and contrary to data in [3] compound (IIIa) reacts with phenylhydrazine in a ratio of 2:1 with the loss of a molecule of water. In fact, the phenylhydrazone which forms has structure (IV). In the reaction of compounds (IIIa-c) with phosphorus pentasulfide only one oxygen atom is substituted with the formation, clearly, of the thioketones (Va-c). As seen from the presented data, these compounds have a somewhat deeper color than their oxygen analogs (IIIa-c) and, like the latter (Table 1), possess negative solvatochromism. In the case of the quaternary salts (VIa, b) (Table 1) it was shown that bases of type (III) only add one mole of alkylating agent, even if the latter is as active as Meerwein's salt.



IV, Va-c

IV R,R′= —H, X=N—NHC$_6$H$_5$; V a R,R′= —H, X=S, λ_{max} 470 (497)*nm; V b R= —CH$_3$, R′= —H, X=S, λ_{max} 488 (509)nm; V c R= —H, R′= —CH$_3$, X=S

The similarity of the UV spectra of the quaternary salts (VIa, b) and of the simple salt of the base (III) and also the absence of alkoxy groups in compounds (VIa, b), show that the addition of alkyl groups to (IIIa-c), like protonation, occurs at the nitrogen atom of the

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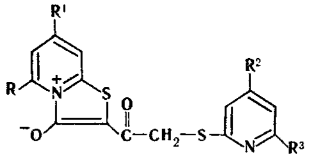
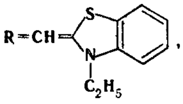
*For methanol solutions; for benzene solutions in parentheses.

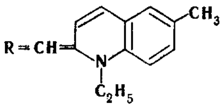
pyridine ring. The monomethinecyanines of our supposed initial structure (IId-f) do in fact correspond to formulas (VIIa-c).



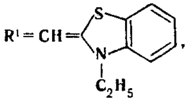
VIIa-c

VII a 

, $R^1, R^2=H$, $R^3=CH_3$, λ_{max} (lg ε) 532(4,41), 566(4,47) nm;

b 

$R^1, R^2=H$, $R^3=CH_3$, λ_{max} (lg ε) 582(4,58), 610(4,64) nm;

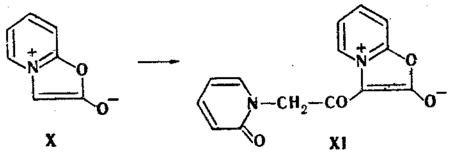
c $R, R^3=H$, 

, $R^2=CH_3$, λ_{max} (lg ε) 495(4,38), 522(4,48) nm

Compounds (VIIa, c) were synthesized similarly to (VIIb) by the reaction of the mesoionic compounds (IIIb, c) with 3-ethyl-3-sulfobenzothiazolium betaine. We note that the long-wave absorption maxima of the dyes (VIIa) and (VIIc) were shifted by 94 and 52 nm respectively toward the red part of the spectrum compared with the absorption maxima of the corresponding unsymmetrical thiamonomethinecyanines, containing thiazolo[3,2-a]pyridinium residues [5].

Dimerization is impossible for the mesoionic compounds formed from α-substituted (2-pyridylthio)acetic acids. In fact, determination of the molecular weight and the data from the PMR spectra for 2-phenylthiazolo[3,2-a]pyridinio-3-oxide (VIIIa) and its 5-methyl-substituted (VIIIb) (Table 1) confirm their monomeric structure. Compounds (VIII) also differ greatly from the dimers (III) in their chemical characteristics. They do not react either with phenylhydrazine or with phosphorus pentasulfide. The latter confirms, in particular, the direction of the reaction with phosphorus pentasulfide at the ketone group in the dimers (III). The addition of dimethylsulfate to compounds (VIII) leads to the formation of the colorless quaternary salts (IXa, b) (Table 1), which are readily dealkylated by heating with triethylamine.

The transformation of the thiazolo[3,2-a]pyridinio-3-oxides at the moment of their formation into dimers with the structure (IIIa-c) has an analogy in the transformation of the mesoionic 1,3-oxazole-5-one (X), during its isolation from the corresponding salt, into a product with twice the molecular weight (XI) [9].



X XI

The question as to whether the described reaction is specific for (2-pyridylthio)acetic acid or has more general character will form the subject of a subsequent investigation.

EXPERIMENTAL

The PMR spectra were measured on a Tesla BS478B spectrometer with HMDS as external standard. The mass spectra were obtained on a JMS-01-S62 mass spectrometer with a system for direct injection into the ion source at 200°C with an ionization potential of 75 eV and with the ionization chamber at 200°C. The electronic spectra were measured on an SF-8 spectrophotometer. The IR spectra were measured on a UR-20 spectrophotometer (for tablets with potassium bromide). The molecular weights were determined on an ÉP-68 ebulliograph in dichloroethane.

(4-Methyl-2-pyridylthiol)acetic Acid (Ic). Compound (Ic) was obtained similarly to (Ia)

TABLE 2. Derivatives of Thiazolo[3,2-a]pyridinio-3-oxide

Compound	mp, °C	Found, %	Molecular formula	Calculated, %	Yield, %
IIIc^a	193	S 19,2; N 8,5	$C_{16}H_{14}N_2O_2S_2$	S 19,4; N 8,5	74
IV^b	143	S 14,0; N 16,3	$C_{20}H_{16}N_4OS_2$	S 14,3; N 16,3	51
Va^c	164	S 29,9; N 8,9	$C_{14}H_{10}N_2OS_3$	S 30,2; N 8,8	50
Vb^b	152	C 55,7; H 4,0; S 27,6	$C_{16}H_{14}N_2OS_3$	C 55,5; H 4,0; S 27,7	39
Vc^b	180—182	S 28,1; N 7,9	$C_{16}H_{14}N_2OS_3$	S 27,7; N 8,0	52
VIa^b	194	C 45,1; H 3,8; S 22,6	$C_{16}H_{16}N_2O_6S_3$	C 44,8; H 3,7; S 22,4	74
VIb^b	201—202	S 15,4; F 18,3	$C_{16}H_{15}BF_4N_2O_2S_2$	S 15,3; F 18,2	91
VIIa^a	185—186	S 19,3; N 8,7	$C_{25}H_{21}N_3O_2S_3$	S 19,5; N 8,5	40
VIIb^d	197—198	S 12,6; N 8,4	$C_{28}H_{25}N_3O_2S_2$	S 12,8; N 8,4	37
VIIc^a	218—219	S 19,2; N 8,6	$C_{25}H_{21}N_3O_2S_3$	S 19,5; N 8,5	39
VIIIb^e	153	S 13,1; N 5,9	$C_{14}H_{11}NOS$	S 13,3; N 5,8	62
IXa^b	183	S 9,4; OCH_3 8,9	$C_{14}H_{12}ClNO_5S$	S 9,4; OCH_3 9,1	73
IXb^b	180—181	S 8,9; OCH_3 8,7	$C_{15}H_{14}ClNO_5S$	S 9,0; OCH_3 8,7	57

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[a] From acetic anhydride. [b] From alcohol. [c] From a mixture of DMFA and alcohol. [d] From pyridine. [e] From a mixture of benzene and petroleum ether.

[4]; mp 123°C (from isopropyl alcohol). The yield was 88%. Found, %: S 17.5; N 7.6. $C_8H_9NO_2S$. Calculated, %: S 17.5; N 7.6.

2-[(2'-pyridylthio)acetyl]thiazolo[3,2-a]pyridinio-3-oxide (IIIa). Compound (IIIa) was obtained by the method in [4]; mp 179-180°C. Found, %: C 55.7; H 3.3; N 9.2; S 21.1. Mol. wt. 302. $C_{14}H_{10}N_2O_2S_2$. Calculated, %: C 55.6; H 3.3; N 9.2; S 21.2. Mol.wt. 302.

7-Methyl-2-[(4'-methyl-2'-pyridylthio)acetyl]thiazolo[3,2-a]pyridinio-3-oxide (IIIc). Compound (IIIc) was obtained similarly to (IIIa). The characteristics of this compound and of the compounds described below are given in Table 2.

2-[(2'-Pyridylthio)acetyl]thiazolo[3,2-a]pyridinio-3-oxide Phenylhydrazone (IV). A mixture of 0.9 g (3 mmole) of (IIIa) and 0.44 g (4 mmole) of phenylhydrazine in 4 ml of acetic acid was heated for 2 min. The precipitate was filtered off; λ_{max} 489 nm (alcohol), log ε 4.24. Found: Mol.wt. 393. Calculated: Mol.wt. 392.

2-[(2'-Pyridylthio)thioacetyl]thiazolo[3,2-a]pyridinio-3-oxide (Va). Compound (IIIa) was heated with equal weight of phosphorus pentasulfide at 100°C for 50 min in pyridine. After cooling, the product was precipitated with ether.

The thioketones (Vb) were obtained similarly to (Va).

2-[(1'-Methyl-2'-pyridiniothio)acetyl]thiazolo[3,2-a]pyridinio-3-oxide Methyl Sulfate (VIa). A mixture of (IIIa) and dimethyl sulfate in a molar ratio of 1:2 was heated at 80°C for 30 min. After cooling, the salt was rubbed with ether. PMR spectrum, δ (in DMSO-d_6): 4.47 (s, $N-CH_3$), 5.22 (s, CH_2), 7.8-9.4 ppm (m, aromatic -H).

2-[(1'-Ethyl-2'-pyridiniothio)acetyl]thiazolo[3,2-a]pyridinio-3-oxide Tetrafluoroborate (VIb). A mixture of 0.3 g (1 mmole) of (IIIa) and 0.4 g (2 mmole) of Meerwein's salt in 20 ml of methylene chloride was shaken in a closed flask for 10 min. The precipitate was filtered off. PMR spectrum, δ (in DMSO-d_6): 1.75 and 4.9 (t, CH_3 and q, CH_2 with J = 7 Hz, $N-C_2H_5$), 5.30 (s, CH_2), 7.8-9.4 ppm (m, aromatic -H).

2-[(6'-Methyl-2'-pyridylthio)acetyl]-5-[(3-ethyl-2(3H)-benzothiazol-2-ylidene)methyl]-thiazolo[3,2-a]pyridinio-3-oxide (VIIa). Compound (VIIa) was obtained by heating equimolar amounts (1 mmole) of (IIIb), 3-ethyl-2-sulfobenzothiazolium betaine, and triethylamine in 2 ml of acetic anhydride at 100°C for 30 min.

2-[(4'-Methyl-2'-pyridylthio)acetyl]-7-[(3-ethyl-2(3H)-benzothiazol-2-ylidene)methyl]-thiazolo[3,2-a]pyridinio-3-oxide (VIIc). Compound (VIIc) was obtained similarly to (VIIa).

2-[(6'-Methyl-2'-pyridylthio)acetyl]-5-[(1-ethyl-6-methyl-1(2H)-quinolin-2-ylidene)-methyl]thiazolo[3,2-a]pyridinio-3-oxide (VIIb). To a mixture of 0.16 g (0.5 mmole) of (IIIb) and 0.12 g (0.5 mmole) of 1-ethyl-2-sulfo-6-methylquinolinium betaine in 4 ml of pyridine we added 0.5 mmole of triethylamine. The mixture was heated at 100°C for 15 min, and the dye was precipitated with water.

2-Phenyl-5-methylthiazolo[3,2-a]pyridinio-3-oxide (VIIIb). A 0.52-g sample (2 mmole) of α-(6-methyl-2-pyridylthiophenyl)acetic acid [obtained by analogy with α-(2-pyridylthiophenyl)acetic acid [10]] was boiled in 2 ml of acetic anhydride for 2 min. After cooling, the precipitate was filtered off. PMR spectrum, δ (in trifluoroacetic acid): 3.12 (s, CH_3), 7.15-8.1 ppm (m, aromatic —H). Found: Mol.wt. 240. Calculated: Mol.wt. 241.

2-Phenyl-3-methoxythiazolo[3,2-a]pyridinium Perchlorate (IXa). Compound (IXa) was obtained by heating (VIIIa) and dimethyl sulfate in a molar ratio of 1:2 to 80°C. The product was rubbed with ether and converted into the perchlorate from an alcohol solution. PMR spectrum, δ (in trifluoroacetic acid): 3.9 (s, OCH_3), 7.26-8.9 ppm (m, aromatic —H).

2-Phenyl-3-methoxy-5-methylthiazolo[3,2-a]pyridinium Perchlorate (IXb). Compound (IXb) was obtained similarly to (IXa). PMR spectrum, δ (in trifluoroacetic acid): 3.78 (s, OCH_3), 3.0 (s, CH_3), 7.27-8.07 ppm (m, aromatic —H).

Dealkylation of the Salts (IXa, b). A 1-mmole sample of the salt (IXa) or (IXb) was heated in 15 ml of absolute alcohol with 1 mmole of triethylamine for 1 h at 75°C. The precipitated ammonium salt was filtered off, and the mesoionic compounds (VIIIa, b) were precipitated from the filtrate with water.

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PRODUCTION OF 3-BROMOSELENOPHENO[2,3-b]SELENOPHENE

Ya. L. Gol'dfarb, V. P. Litvinov,
and I. P. Konyaeva

UDC 547.739.3:543.422.25

β-Monobromo-substituted condensed five-membered heterocycles are of considerable interest for the synthesis of various derivatives of this series. However, their production by traditional direct bromination involves a series of difficulties (bromination of the initial compound to the tribromide, debromination, purification) [1]. The synthesis of β-bromoselenophenoselenophenes in this way is also complicated by the absence of developed methods for the production of the starting compounds. The selenophenoselenophene system was first reported in 1928, when English investigators [2], in the reaction of acetylene and selenium, isolated in addition to other compounds, a compound boiling at 240-250°C and containing ∿ 20% of selenium, which in their opinion represented contaminated selenopheno[2,3-b]selenophene. More recently Umezawa et al. [3, 4] investigated the residue formed during the production of

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1072-1073, August, 1979. Original article submitted January 3, 1979.

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