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A NEW CONDENSED SYSTEM, BENZOTHIENOFURAZANOTHIEPINE TRIOXIDE

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The dimetallation of phenyl thienyl sulfones was used to obtain derivatives of benzo[b]thieno[3,2-f]furazano[3,4-d]thiepine-1(3),7,7-trioxide, which is a new condensed system.

We have already shown that the diphenyl sulfone derivative, containing nitrile oxide groups in the o,o' positions, readily undergo intramolecular cyclization to give the condensed four-membered dibenzofuroxanothiepine system [1].

In the present work, the synthesis of condensed heterocyclic systems was extended to nitrile oxides of phenyl 2-thienyl sulfones.



Aldehydes (IIa) and (IIb) were obtained by the action of two equivalents of BuLi and DMF on sulfones (Ia) and (Ib). We should note that the consecutive action of one and two equivalents of BuLi leads to selective replacement of the hydrogens, initially at the β -position of the thiophene ring and in the ortho position of the benzene ring. The order of replacement in the exhaustive metallation of sulfone (Ia), leading to the trilithium derivative [2], was thereby established.

The structure of aldehydes (IIa) and (IIb) was confirmed by spectral data and further transformations. Oximes (IIIa) and (IIIb) derived from these aldehydes are readily oxidized to the corresponding nitrile oxides (IVa) and (IVb). The oxidation of oximes in the presence of styrene in situ leads to the formation of adducts (Va) and (Vb).

Nitrile oxides (IVa) and (IVb) proved much less stable than their analog, diphenyl sulfone 2,2'-dicarbonitrile oxide [1]. Both (IVa) and (IVb) are converted upon heating in

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Come			Chemical	Found	/Calcula	ted, %	
pound	Yield, %	Mp, °C	formula	С	H	N	S
(IIa)	34	118,5−120 (CCl₄)	$\mathrm{C_{12}H_8O_4S_2}$	<u>51,70</u> 51,42	$\frac{2,90}{2,88}$	-	$\tfrac{22,76}{22,87}$
(IIIa)	92	164,5-165 (aq. ethanol)	$C_{12}H_{10}N_2O_4S_2$	$\frac{46,74}{46,49}$	$\frac{3,19}{3,24}$	9,03	$\tfrac{20,29}{20,66}$
(IIH)	60	127,5-128,5 (CCl ₄)	$C_{13}H_{10}O_4S_2$	52,89 53,04	$\frac{3,21}{3,42}$	-	21,59 21,78
(IIIb)	93	174-175 (ag. ethanol)	$C_{13}H_{12}N_2O_4S_2$	<u>48,18</u> 48,13	<u>3,79</u> 3,73	8,38 8,63	<u>19,54</u> 19,76
(IVa)	80	150 (dec.)	$C_{12}H_6N_2O_4S_2$	$\frac{46,89}{47,05}$	<u>1,77</u> 1,97	8,98 9,15	$\frac{20,83}{20,93}$
(VIa)	76	160 (dec.)	$C_{12}H_6N_2O_4S_2$	47.17	1,88	8,91 9,15	$\tfrac{20,79}{20,93}$
(IVb)	74	200 (dec.)	$C_{13}H_8N_2O_4S_2$	$\frac{48.82}{48.74}$	$\frac{2,38}{2,52}$	8,91 8,75	$\frac{20,00}{20,02}$
(VIB)	72	210 (dec.)	$\mathrm{C_{13}H_8N_2O_4S_2}$	<u>48,71</u> <u>48,74</u>	2,30 2,52	8,84 8,75	20,07 20,02

TABLE 1. Phenyl Thienyl Sulfone Aldehydes and Their Transformation Products

benzene at reflux to benzothienofurazanothiepine trioxides (VIa) and (VIb), which are representatives of a new condensed heterocyclic system.

EXPERIMENTAL

The melting points were determined on a Boetius table. The mass spectra were taken on a Varian MAT CH-6 spectrometer. The PMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz. The IR spectra were taken on a Perkin-Elmer 577 spectrometer at 400-4000 cm⁻¹.

2,3'-Bisformylphenyl-2'-thienyl Sulfone (IIa). A sample of 28 ml (0.044 mole) *n*-BuLi was added to a suspension of 4.48 g (0.02 mole) (Ia) in 50 ml dry ether at -30° C under argon. The mixture was stirred for 5 h and cooled to -70° C. Then, 6.2 ml (0.08 mole) DMF in 15 ml dry ether was added. The mixture was stirred for 1 h at 20°C and poured into 10% hydrochloric acid. (IIa) was filtered off and washed on the filter with water. IR spectrum (ν , cm⁻¹): 1700 (C=0), 1320, 1160 (SO₂). Mass spectrum: 280 (M⁺). The yields, analyses, and PMR spectra of (IIa) and oxime (IIIa) are given in Tables 1 and 2. During the crystallization of (IIa), we also obtained 0.30 g 2,3',5'-trisformylphenyl-2'-thienyl sulfone, mp 122-123°C. Found: C, 50.72; H, 2.71; S, 20.76%. Calculated for $C_{13}H_8O_5S_2$: C, 50.64; H, 2.62; S, 20.79%. IR spectrum (ν , cm⁻¹): 1700 (C=0), 1330, 1160 (SO₂). Mass spectrum: 250 (M⁺ - 58). PMR spectrum in CDCl₃ (δ , ppm): 7.86-7.92 m (2H, H⁴, H⁵), 8.06-8.12 m (1H, H⁶), 8.12-8.26 m (1H, H³), 8.12 s (1H, H^{4'}), 9.98 s (1H, CHO), 10.45 s (1H, CHO), 10.78 s (1H, CHO).

2,3'-Bisformylphenyl-5'-methyl-2'-thienyl Sulfone (IIb). A sample of 25 ml (0.04 mole) n-BuLi was added to a suspension of 2.30 g (0.01 mole) (Ib) in 20 ml dry ether at -50°C under argon. The mixture was stirred for 1 h at -50°C and for 3 h at 0°C. Then, the mixture was cooled to -70°C and 4.7 ml (0.06 mole) DMF in 10 ml dry ether was added. The mixture was stirred for 1 h at 20°C and poured into 10% hydrochloric acid. (IIb) was filtered off and washed on the filter with water. IR spectrum (ν , cm⁻¹): 1680, 1700 (C=O), 1320, 1160 (SO₂). Mass spectrum: 294 (M⁺). The yields, analyses, and PMR spectra of (IIb) and (IIIb) are given in Tables 1 and 2.

2,3'-Difulmidophenyl-2'-thienyl Sulfone (IVa). A sample of 0.77 g (2.5 mmoles) oxime (IIIa) was added gradually to a mixture of 30 ml CH_2Cl_2 and 4 ml NaOCl (12.4 mmoles containing 0.18 g/ml active chlorine) at 0°C and stirred for 2 h. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 . The combined organic extract was washed with water and dried. The solvent was evaporated. (IVa) was purified by reprecipitation from CH_2Cl_2 by the addition of hexane. IR spectrum (ν , cm⁻¹): 2305 (C=N), 1590 (C=N), 1370 (NO), 1160, 1340 (SO₂). Mass spectrum: 306 (M⁺). The yield and analysis data are given in Table 1.

2-(5-Phenylisoxazolin-2-yl-3)phenyl-3'-(5-phenylisoxazolin-2-yl-3)-2'-thienyl Sulfone (Va). A sample of 0.7 g (2.3 mmoles) oxime (IIIa) was added to a stirred solution of 5.6 ml NaOCl and 1.03 ml styrene in 25 ml CH₂Cl₂ at 0°C and stirred for 2 h at 20°C. The organic layer

Com-	, , ,	Benze	ene ring protor	IS	Thiophene protons	ring	-
þunod	Solvent	Ε	H' H	Ħ	H4'	Πť	Other protons
(IIa)	cDCI3	8,15-8,23 m	7,78–7,86 m	8,04-8,10 m	7,58(7,70) d. d (5,0)	7,70(7,58) d.d	10,38 s (CHO) 10,93 s (CHO)
(111a)	(CD ₃) 2CO	8,128,20 m	7,68–7,76 m	7,98-8,04 m	7,50(7,95) d.d (5,1)	7,95(7,50) d.d	8,52 s (CH), 9,03 s (CH), 11,00 s (OH), 11,04 s (OH)
(911)	CDCI ₅	·8,108,18 m	7,75-7,82 ш	8,02-8,08 m	7,22 q (1,0)	I	10,30 s (CHO) 10,90 s (CHO), 2,50 d (Me)
(1111)	(CD ₃) 2CO	8,08-8,15 m	7,63–7,72 m	7,98–8,04 m	7,22 q. (1,0)	1	3,42 ^d (Me), 8,50 ^s (CH), 9,02 ^s (CH), 11,00 ^s (OH), 11,02 ^s (OH)
(Va)	CDC1 _s		7,20-7,90 m		7,20-	7,90 m	3,25 d.d, 3,40 d.d, 3,70 d.d 3,90 d.d,* 5,66 d.d, 5,82 d.d, ** 7,20-7,90 m (2C,H ₅)
(Ab)	CDCI.		7,30-8,00 m		6,98 q (1,0)	1	2,50 d (Me), 3,25 d d, 3,40 d d,3,70 d.d, 3,90 d d * 5,62 d d, 5,80 d d, ** 7,30-8,00 m (2C6Hs)

TABLE 2. PMR Spectral Data (6, ppm, J, Hz)

*4H-isoxazoline rings. **2H-isoxazoline rings. was separated, washed with water, and dried. The residue after evaporation of the solvent was treated with hexane and purified chromatographically. The PMR spectrum of this product is given in Table 2.

Benzo[b]thieno[3,2-f]furazano[3,4-d]thiepine-1(3),7,7-trioxide (VIa). This product was obtained by heating (IVa) in benzene at reflux. IR spectrum (ν , cm⁻¹): 1600 (C=N), 1420 (NO), 1320, 1150 (SO₂). Mass spectrum: 306 (M⁺). The yield and analysis are given in Table 1.

2,3'-Difulmidophenyl-5'-methyl-2'-thienyl Sulfone (IVb) was obtained by analogy to (IVa) from (IIIb). IR spectrum (ν , cm⁻¹): 2310 (C=N), 1600 (C=N), 1330, 1160 (SO₂), 1370 (NO): Mass spectrum: 320 (M⁺). The yield and analysis data are given in Table 1.

2-(5-Phenylisoxazolin-2-yl-3)phenyl-5'-methyl-3'-(5-phenylisoxazolin-2-yl-3)-2'-thienyl sulfone (Vb) was obtained by analogy to (Va) from (IIIb). The PMR spectrum of (Vb) is given in Table 2.

5-Methylbenzo[b]thieno[3,2-f]furazano[3,4-d]thiepine-1(3),7,7-trioxide (VIb) was obtained upon heating (IVb) in benzene at reflux. IR spectrum (ν , cm⁻¹): 1600 (C=N), 1420 (N0), 1325, 1160 (SO₂). Mass spectrum: 320 (M⁺). The yield and analysis data are given in Table 1.

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THE COMPLEXING PROPERTIES OF 1,4,7-TRIS(DIHYDROXY-

PHOSPHORYLMETHYL) - 1, 4, 7 - TRIAZACYCLONONANE

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The complexation of 1,4,7-tris(dihydroxyphosphorylmethyl)-1,4,7-triazacyclononane with metal ions, differing in both charge and ionic radius, was studied. This complexing agent is selective relative to cations of a given ionic radius. The stability of the complex increases with increasing charge and polarizability of the cation.

The complexing properties of 1,4,7-tris(dihydroxyphosphorylmethyl)-1,4,7-triazacyclononane (I) have been studied relative to a large number of cations [1]. This complexing agent displays high selectivity related to the ionic radius of the cation.



Thus, a large difference is noted in the stability constants of complexes of cations with similar properties but differing in size: Mg^{2+} (r = 0.66 Å) and Ca^{2+} (r = 0.99 Å), Zn^{2+}

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