<u>Monocrystals of Dimethyl N-Phthaloyl-threo-4-bromo-DL-glutamate (Ia)</u>. The crystalline isomer (Ia), mp 84-87°C (0.5 g), was dissolved in 8 ml of dry methanol. A firmly closed weighing bottle was placed in a reservoir contained in a thermostat heated at 65°C. As the solution cooled to  $\sim 20$ °C, after approximately one day, crystals were formed in the form of conjoined needles. The crystals were separated, dissolved in 15 ml of dry methanol, and kept for 24 h in order to crystallize slowly. The resulting crystals were carefully filtered off, washed with cold methanol, and dried in vacuo over  $P_2O_5$ .

Monocrystals of (Id) were obtained similarly.

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## SYNTHESIS OF STABLE o-SULFONYLBENZONITRILE OXIDES

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The use of the o-orienting effect of the sulfonyl group during metallation with BuLi made possible the synthesis of o-sulfonylbenzaldehydes. Oxidation of their oximes with hypochlorite gave o-sulfonylbenzonitrile oxides, stable at 20°C, which are compounds not obtained previously. They form normal 1,3-dipolar cycloaddition products with styrene, and on heating, they dimerize into furoxanes. o-Sulfonylbisbenzonitrile oxide cyclizes into dibenzo[b,f]furazano[3,4-d]thiepin 1(3),8,8trioxide. 2- and 2,2'-Bistrimethylsilyldiphenyl sulfones were also synthesized, and their metallation was investigated.

The stability of aromatic nitrile oxides is largely determined by steric factors, and compounds in which the nitrile oxide group is screened by o- and o'-substituents are stable for a long time, while the presence of one substituent in the o-position is in general still insufficient for the stabilization of the nitrile oxide group [1]. It was, however, recently shown [2] that the introduction of the sulfonyl group into the o-position of the thiophene ring makes it possible to obtain stable nitrile oxides even in the absence of another screening substituent. Analogous compounds in the benzene series have not yet been described.

Bearing in mind that stable carbonitrile oxides can serve as intermediates in the synthesis of various heterocyclic compounds, while bisnitrile oxides may find use as crosslinking agents for rubbers [1], it was desirable to develop methods for their synthesis. The o-metallation of aromatic sulfones may be a convenient path for the synthesis of o-sulfonylsubstituted benzaldehydes, the starting materials for the preparation of o-sulfonylbenzonitrile oxides. It has earlier been shown [3] that tert-burtyl phenyl sulfone (Ia) is metallated in the o-position in good yield. Through the substitution of lithium with an aldehyde

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	*	x	13,92	14,10	13,29	12,88 13,02	<u>12,27</u> 12,27	(	10,61	11,69	9,89 10,23	9,21 9,25	7,92	8,30 8,21	7,90
	culated,	z	1	6,00	5,81	1	5,08	1	9.39	1	8,78 8,69	J	7.70		3,58
	ound/Calc	11	6,33	0,23 6.58	6,27	4,09	4,42	I	6,18	3,61	4,12	5,34 5,23	5,88 5,88	6,71	6,75
	β <b>έ</b> ι	υ	58,22	58,38 54 71	54,75	63,75 63,40	59,87 59,75	ł	52,08 52,08	61,23 61,30	53,66 53,66	58,98 58,93	54,22	58,32 58,32 58,41	56,25
~		Empirical formula	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub> S	C., H., NO.S		C <sub>13</sub> H <sub>10</sub> O <sub>3</sub> S	CtaH11NO3S	C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> S	Ctall18N2QtS	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> S	$C_{11}H_{12}N_2O_1S - \frac{1}{2} - H_2O_1$	C <sub>17</sub> II <sub>18</sub> O <sub>4</sub> SSi	C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> SSi	$C_{19}H_{26}O_3SSi_2$	C <sub>10</sub> H <sub>27</sub> NO <sub>3</sub> SSi <sub>2</sub>
ydes R <sup>n</sup> CHC		Mp, °C	125.5~126	(ethanol)	(aq. ethanol)	92,593 (CCI4)	98-99 (aq. ethanol)	100,5-101,5	(heptane/benzene) 151-152 (22 2+banc1)	(aq. ethaliot) 116-117 (CCLA)	198-199 (aq. ethanol)	175,5-178 (hexane)	20/1-208,5	(aq. ethanol) 89-90 (hexane)	139,5-140 (aq. ethanol)
aldeh	1.2.7.4	niar I	63	ÿÖ	3	32	83	30	70	58	85	50	75	31,5	85
Benz		R″	II I			11 }		l CII3		I II		II I		11	
ubstituted		ж —	II		xıme	11 1	Oxime		Oxime	h H	Oxime	Si(CH <sub>3</sub> ) <sub>3</sub>	Oxime	Si (CH <sub>3</sub> ) 3	Oxime
l. Sulfonyl S		ä	C(CII <sub>3</sub> ) 3		<u> </u>	$G_6 H_5$		(C(CII <sub>3</sub> ) <sub>3</sub>	_	o-CHO-C <sub>6</sub> JI <sub>4</sub>		0-CHO-C6H4		a-Si (CH <sub>3</sub> ) 3-CaH <sub>4</sub>	
TABLE 1	Com-	punod	(11a)		(1113)	(411)	(9111)	Ś	(IA)	(NII)	(XX)	(XIV)	(XXV)	(XV)	(IVXX)

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group by the action of DMF, we obtained o-tert-butylsulfonylbenzaldehyde (IIa) in 63% yield. o-Phenylsulfonylbenzaldehyde (IIb) was synthesized in a similar way from sulfone (Ib).



When bromine is exchanged by lithium in tert-butyl-(2,6-dibromo-4-tolyl)sulfone (IV), followed by the action of DMF, a mixture of approximately equal amounts of mono- and diformyl derivatives is obtained, although, as has been shown previously by carboxylation results [4], the corresponding dilithium derivative predominates in the mixture. 2-tert-Butylsul-fonyl-5-methylisophthaldehyde (V) was isolated from the mixture in the form of a bisoxime (VI).

We converted the o,o-dilithium derivative of diphenyl sulfone (Ib), obtained under the previously described [5] conditions, into o-sulfonylbisbenzaldehyde (VII) by the action of DMF in 58% yield.

To obtain substituted bisaldehydes, which are derivatives of diphenyl sulfone, we studied the metallation of readily available 2,2',5,5'- and 3,3',4,4'tetramethoxydiphenyl sulfones (VIII) and (IX) and trimethylsilyl derivatives of diphenyl sulfone. Action of 4 equivalents of BuLi on (VIII) and subsequent carboxylation led to a mixture of mono- and dicaboxylic acids (X) and (XI) in a 1:1 ratio. However, when a mixture of Li-derivatives was treatedwith DMF, the initial sulfone was recovered only. Attempts to carry out the functionalization by using ethyl formate instead of DMF also were not successful. A similar pattern is also observed with sulfone (IX), after the metallation of which by the action of DMF no formyl derivatives were detected, while during carboxylation a mixture of mono- and dicarboxylic acids was obtained in low yield, which could not be separated. The difficulties in the functionalization of Li derivatives are probably caused by steric effects.



 $R = R^2 = OMe, R^1 = H(VIII), (X), (XI); R = H, R^1 = R^2 = OMe(IX).$ 

2-Trimethylsilyl- and 2,2'-bistrimethylsilyldiphenyl sulfones (XII) and (XIII) were obtained in a yield of 49 and 30%, respectively, by the action of trimethylchlorosilane on mono- and dilithium derivatives of sulfone (Ib). The metallation of (XII) proceeds in o- and o'-position to sulfonyl. Dialdehyde (XIV) was obtained in 50% yield by the action of DMF. Its structure follows from the PMR spectrum, in which together with proton singlets of the two aldehyde groups (10.40 and 10.66 ppm), a doublet of triplets is observed in a weak field of two protons, neighboring with the aldehyde groups (8.12 ppm) and doublet of doublets of one proton adjacent to the sulfonyl group (7.97 ppm).

Metallation of sulfone (XIII) even with an excess (4 equivalents) of BuLi proceeds only into one o-position to the sulfonyl group, which was confirmed by the isolation of

s punc				Sec. 10	Jide Lee	1 3 T 4						
	 			Chem	cal shif	ts of be	nzene rin	lg proton:	s			Chemical shifts of
	io (vent	112	H <sup>2′</sup>	113	H3′	Ĥ	HV,	115	H <sup>5'</sup>	116	H <sup>6'</sup>	other protons
a)	cDCl <sup>3</sup>	1		8,10- 8,10-		7,76-		7,76-	1	-66'2	I	10,90s (CHO), 1,38s (3CH <sub>3</sub> )
	* r.	11	1 1	7,47 d 7,47 d 1-9,0	7,05 d J=9,0	7,18 d J=9,0	7,34d.d	7,91s	11		7,78d J=3,2	10,82 s(2CH0), 2,51 s (CH <sub>3</sub> ) 4,00 s(0CH <sub>3</sub> ), 4,10 s(0CH <sub>3</sub> ), 3,61 s(0CH <sub>3</sub> ), 4,22 s(0CH <sub>3</sub> )
 (1	<u> </u>	1	1	7,56		7,23	d d	1	1	I	ι	3,86 s (20CH <sub>3</sub> );
) (II	(CD <sub>3</sub> ) <sub>2</sub> CO	7,62– 7,92 m	1	7.62- 7,92 m	7,50d.d		-	7,62-7,	Э2 m -	-		0,45 s (Si(CH <sub>3</sub> ) 3)
(111	*	1	1	7,60–7,	c,1=7		7,46–7,	55 m		7,91 J=	d.d 7,5	0,38 s (2Si(CH <sub>3</sub> ) <sub>3</sub> )
, ( <b>N</b> 1	CDC) <sub>3</sub>	1	7,97 d.d J=7,5	7,59 d.d <i>J</i> =7,5	7,66 d.t <i>j</i> =7,5	7,79t J=7,5	7,75 d.t J=7,5	8,12 (	d.d	ll	2	0,40 s (Si(CH <sub>3</sub> ) 3), 10,40 s (CHO), 10,66 s (CHO)
 (^	(CD <sub>3</sub> ) <sub>2</sub> CO	ł	J=1,5 -	7=1,5 7,96 d.d 7=7,5	7=1,5 7,35, d.d J=7,5	7,90t J=7.5	7,400.t	8,21 d.d	7,63d.t	I	7,96d.đ	0,38s (Si(CH <sub>3</sub> ) <sub>3</sub> ), 0,52 s(Si(CH <sub>3</sub> ) <sub>3</sub> ),
(1)	*	I	1	J=1,5 7,77d.d	J=1,5 7,32d.d J=7,5	J=1,5 7,8/tt J=7,5	J = 1.5 7,365d.t	8,07 d.d	7,53 <b>d.</b> t	1	7.77d.đ	10,22 \$ (CHO) 0,22 \$ (Si (CH <sub>3</sub> ) 3), 0,48 \$ (Si (CH <sub>3</sub> ) 3)
	CDCl <sub>3</sub> (CD <sub>3</sub> ) 2CO	1 1	1 1	/=1.5 7,63s 7,61 d.d /=7.5	/=1,5 7,61d.d	1,67-1	/=1,5 7,82m	7,63s	1	8,12	ថំ ៨	2,50 s (CH <sub>3</sub> ) 3,38 d.d 3,82 d.db 5,70 d.dc <i>l</i> =17,0, <i>l</i> =10,8,
(VX	\$	1	7.95 d.d J=7,5 J=1,5	7,65 d.d 7,65 d.d 1=7,5	7,90 d.t J=7,5 J=1,5	7,76 t J=7,5	7,70 d.t <i>j=</i> 7,5 <i>j=</i> 1,5	8,04	с. д	I	I	[7,30-7,50 m (2C <sub>6</sub> H <sub>3</sub> ) 0,465 (Si (CH <sub>3</sub> ) <sub>3</sub> ), 8,455 (CH), 8,50 s (CH), 10,68 s (OH), 10,85 s (OH)

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

a)Solvent C<sub>5</sub>D<sub>5</sub>N:D<sub>2</sub>O = 1:1
b)4H Of isoxazoline rings.
c)2H Of isoxazoline rings.

aldehyde (XV) and carboxylic acid (XVI) in approximately the same yields ( $\sqrt{30\%}$ ) by treating the Li-derivatives with DMF and CO<sub>2</sub>, respectively. The bulk Me<sub>3</sub>Si groups possibly cause serious steric hindrances for the metallation into the second o-position to the sulfonyl



Y = CHO (XV), COOH (XVI).

The above-described aldehydes were converted into nitrile oxides by oxidation of the corresponding oximes with NaOC1. Thus, oxime (IIIa) of o-tert-butylsulfonylbenzaldehyde (IIa) gave benzonitrile oxide (XVIIa) in 89% yield, which is stable at 20°C. Its structure was confirmed by the spectral data. In the IR spectrum, there is, in particular, a characteristic strong band at 2310 cm<sup>-1</sup> (C=N), and also a band at 1370 cm<sup>-1</sup> (NO). Its structure is chemically confirmed by its transformation on heating in benzene into furoxane (XVIIIa) and the formation of 'a product of 1,3-dipolar cycloaddition with styrene, the isoxazoline (XIXa)



By a similar oxidation of oxime (IIIb), nitrile oxide (XVIIb) was obtained in good yield, which withstands boiling in benzene, and from bisoximes (VI) and (XX) - bisnitrile oxides (XXI) and (XXII). The latter forms with styrene a bisadduct (XXIII). Heating in a solvent (benzene) and even an attempt of chromatography on silica gel cause rapid cyclization of nitrile oxide (XXII) into furoxane (XXIV), which is probably due to the steric distribution of the nitrile oxide groups and the ready formation of condensed five- and seven-membered rings



The half-conversion period of nitrile oxide (XXII) on storage at 20°C, determined from the decrease in the intensity of the 2310 cm<sup>-1</sup> band and increase in the intensity of the 1610 cm<sup>-1</sup> band in the IR spectrum, is  $\sim$ 1 year.

Aldehydes (XIV) and (XV), containing a  $Me_3Si$  group in the o-position to the sulfonyl, were converted into the corresponding oximes (XXV) and (XXVI) (Table 1), during the oxidation of which difficultly separable mixtures are formed, containing, according to the spectral data, not only the nitrile oxides but also other products including those corresponding to the elimination of the  $Me_3Si$  group.

	ted, %	8	9,27 9,48	2 5	7,92 8,09	1	<u>6,88</u> 7,05	1	8,67 8,84	8,12 7,88
	calcula	Π	5,86		5,10	I	4,97	I	7,23	6,46 6,45
	Found	σ	56,89		54,58 54,54	I	52,36 52,85	1	<u>59,74</u> 59,61	56,04
		Empirical-formula	C <sub>18</sub> H <sub>18</sub> O <sub>6</sub> S	C <sub>17</sub> H <sub>18</sub> O <sub>8</sub> S	C <sub>18</sub> H <sub>20</sub> O <sub>6</sub> S	C18H18O10S	C <sub>20</sub> H <sub>22</sub> O <sub>10</sub> S	C <sub>15</sub> H <sub>18</sub> O <sub>2</sub> SSi	$C_{18}H_{26}O_2SSi_2$	$C_{i_9}II_{2_0}O_4SSI_2 b$
502 R	Mp, °C, bp, °C	(p, mm Hg)	157-158 (athanol /hourano)	272,5-274	193-194	328330	283-284	179-181 (0,3)	138-139,5 (methanol)	191–192,5 (hexane/CHCl <sub>3</sub> )
	Yield.	%	28	10,5		21		r 49 a	30	28
enyl Sulfones <sup>R</sup> .		R	3'-0CH <sub>3</sub> , 4'-0CH <sub>3</sub>	2'-0CH <sub>3</sub> , 5'-0CH <sub>a</sub>	ester	2'-0CH <sub>3</sub> , 5'-0CH <sub>3</sub> 6'-COOH	yl ester		2'Si (CH <sub>3</sub> ) 3	2'-Si(CH <sub>3</sub> ) <sub>3</sub>
Substituted Diph		и	3-0CH <sub>3</sub> , 4-0CH <sub>3</sub>	2-0CH <sub>3</sub> , 5-0CH <sub>3</sub> , 6-C0011	Methyl	2-0CH <sub>3</sub> , 5-0CH <sub>3</sub> , 6-COOH	Dimeth	2-Si(CH <sub>3</sub> ) <sub>3</sub>	2-Si (CH <sub>3</sub> ) 3	2-Si(CII <sub>3</sub> ) <sub>3</sub> , 6-COOH
TABLE 3.	Com-	punod	(XI)	(X)		(IX)		(IIIX)	(XIII)	(IVX)

a)Composition according to the GLC data: 4% of (Ib), 85% of (XII), 11% of (XIII). b)Found Si 13.47%. Calculated 13.81%.

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## EXPERIMENTAL

The melting points were determined on a Boetius stage. The mass spectra were run on a Varian MAT CH-6 spectrometer (ionizing voltage 60 eV, temperature of the ionization chamber 50-150°C). The PMR spectra were obtained on a Bruker WM-250 (250 MHz) spectrometer, relative to TMS. The IR spectra were recorded on a UR-20 spectrophotometer in the 400-4000  $\rm cm^{-1}$  region.

<u>o-tert-Butylsulfonylbenzaldehyde (IIa)</u>. A 32.6 ml portion (80 mmoles) of an ethereal solution of n-BuLi was added at  $-30^{\circ}$ C, in the course of 30 min, to a solution of 14.85 g (75 mmoles) of sulfone (Ia) [3] in 250 ml of absolute ether, stirred in an Ar atmosphere. The mixture was stirred at  $-30^{\circ}$ C for 40 min, and at 20°C for 1 h. A 9 ml portion (120 mmoles) of DMF in 40 ml of ether was added to the cooled mixture ( $-40^{\circ}$ C). The mixture was then heated to 20°C and stirred for an additional hour, and poured at 0°C into 600 ml of 10% HCl. The precipitate was filtered, washed with water and ether, and dried. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1695 (C=O), 1280, 1135 (SO<sub>2</sub>). Mass spectrum: 226 (M<sup>+</sup>). The yield, physical constants and analyses of (IIa) and oxime (IIIa) are given in Table 1, and the PMR spectrum in Table 2.

<u>o-Phenylsulfonylbenzaldehyde (IIb)</u>. A 15.2 ml portion (50 mmoles) of an ethereal solution of EtLi was added at 0°C in the course of 20 min to a suspension of 10.9 g (50 mmoles) of diphenyl sulfone (Ib) in 100 ml of absolute ether and 25 ml of absolute benzene. The mixture was stirred at 0°C for 1.5 h, and then 7.5 ml (100 mmoles) of DMF in 40 ml of absolute ether was added at -60°C. The mixutre was stirred for 3 h at 20°C, poured into 400 ml of 10% HCl, and 1.49 g of precipitate of (Ib) was separated. The organic layer of the filtrate was separated, washed with water, dried, and the solvent was removed under vacuum. Compound (IIb) obtained was separated from the residues of the initial (Ib) via the bisulfite compound, and was crystallized from CCl<sub>4</sub>. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1700 (C=O), 1310, 1150 (SO<sub>2</sub>). Mass spectrum: 246 (M<sup>+</sup>). The yield, the constants and analyses of (IIb) and its oxime (IIIb) are given in Table 1.

<u>2-tert-Butylsulfonyl-5-methylisophthaldehyde (V)</u>. A 45.3 ml portion (80 mmoles) of an ethereal solution of BuLi was added under Ar to a cooled ( $-70^{\circ}$ C) suspension of 7.4 g (20 mmoles) of tert-butyl (2,6-dibromo-4-methylphenyl) sulfone (IV) [4] in 120 ml of absolute ether. The mixture was stirred at  $-70^{\circ}$ C for 1 h, and 9 ml (120 mmoles) of DMF in 20 ml of ether was added. The mixture was stirred for 1 h, heated to 20°C and stirred for another hour; it was then poured into 250 ml of a 10% HC1. The organic part was extracted with ether, the extract was dried and evaporated. Yield, 3.2 g of a mixture of approximately equal amounts (GLC) of monoaldehyde and (V). After multiple crystallization from a heptane-benzene mixture, the product still contained  $\sim 10\%$  of an admixture of monoaldehyde. It was purified in the form of oxime (VI) (Table 1). The PMR spectrum, see Table 2.

<u>2,2'-Bisformyldiphenyl Sulfone (VII)</u>. A 36 ml portion (60 mmoles) of BuLi was added tat 0°C to a suspension of 4.36 g (20 mmoles) of diphenyl sulfone (Ib) in 40 ml of absolute ether and 10 ml of absolute benzene, and the mixture was stirred at 0°C for 1.5 h. After cooling to -60°C, 6 ml (80 mmoles) of DMF in 40 ml of ether was added, and after reaching 20°C the mixture was poured into 250 ml of ice-cooled 10% HCl. The precipitate that separated out was filtered off, washed with water and ether, and dried. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1700, 1720 (C=0), 1315, 1155 (SO<sub>2</sub>). Mass spectrum: 304 (M<sup>+</sup>). The yield, physical constants and analyses of (VII) and its oxime (XX) are given in Table 1, the PMR spectrum, in Table 2.

2.2',5,5'-Tetramethoxydiphenyl Sulfone (VIII). A 40 ml portion (0.4 mmole) of dimethyl sulfate was gradually added to a solution of 14.2 g (50 mmoles) of 2,2',5,5'-tetrahydroxydiphenyl sulfone [6] in 100 ml of a 20% solution of NaOH, and the mixture was heated for 4 h at 90°C. The solution was cooled, the precipitate was filtered, washed with water, a 10% NaOH solution, and dried. Yield, 13.94 g (84%), mp 170°C (ethanol/benzene) [7].

2,2',5,5'-Tetramethoxy-6-carboxy- and 2,2',5,5'-tetramethoxy-6,6'-dicarboxydiphenyl Sulfones (X) and (XI). A 280 ml portion (0.42 mole) of an ethereal solution of Buli was added to -20°C to a suspension of 35.5 g (0.105 mole) of sulfone (VIII) in 600 ml of absolute ether and 800 ml of absolute benzene, and the mixture was stirred at 0°C for 5 h, and then poured onto dry ice in ether. Water was added at 20°C, and the precipitate of the initial (VIII) was filtered off (3.25 g). The aqueous layer was separated, washed with ether, and acidified. The mixture of acids was filtered off. The dry product was boiled in glacial AcOH. The part that was insoluble during hot filtration was dicarboxylic acid

Products	
Conversion	
Their	
and	
Oxides	
Nitrile	
TABLE 4.	

$\frac{10000}{70,85}$	C <sub>14</sub> 11 <sub>8</sub> C <sub>30</sub> 11 <sub>2</sub>	$\begin{array}{c c} 188-196^{a} & C_{13}H_{1} \\ 250 & C_{14}H_{8} \\ (dec.) & C_{14}H_{8} \\ 148-149 & C_{30}H_{2} \\ ethyl \ acetate \end{array}$	96 188-196 a C <sub>13</sub> H <sub>1</sub> 71 (dec.) C <sub>14</sub> H <sub>8</sub> 67 148-149 C <sub>30</sub> H <sub>2</sub> 67 (ethyl acetate)
.S 10,85 55,90 55,99	C <sub>14</sub> II <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	(ethyl acetate) $298-300$ $C_{14}H_8N_2O_1$ (benzene)	$\begin{array}{c c} (e \operatorname{Cn} y_1 \ a \operatorname{cecate}) \\ 90 \ 298 - 300 \ C_{14} \operatorname{H}_8 \operatorname{N}_2 \operatorname{O}_1 \\ (b \operatorname{enzene}) \end{array}$
2,4bis-()-pnenyl - 1490-149     0/     1490-149       3-yl)diphenyl sulfone     (ethyl acetate)       Dibenzo[b,f]furazano[3,4-d]-     90     298-300       thiepin I(3),8,8-trioxide     (benzene)	phthalonitrile trioxide Diphenylsulfone-2,2'dicarboni- trile oxide 2,2'-Bis-(5-phenyl-2-isoxazolin- 3-y1)diphenyl sulfone Dibenzo[b,f]furazano[3,4-d]- thiepin I(3),8,8-trioxide	<pre>2-tert-Butylsulfonyl-5-methyl1so- phthalonitrile trioxide Diphenylsulfone-2,2'dicarboni- trile oxide 2,2'-Bis-(5-phenyl-2-isoxazolin- 3-yl)diphenyl sulfone Dibenzo[b,f]furazano[3,4-d]- thiepin I(3),8,8-trioxide</pre>	

aPurified by reprecipitation by hexane from a methylene chloride solution.

(XI). The precipitate of acid (X) that separated out from the filtrate on cooling was filtered and dried. The yields, physical constants, analyses and PMR spectra are given in Tables 2 and 3.

In the treatment of Li-derivatives of sulfone (VIII) with DMF, followed by the usual isolation treatment, 93% of the initial sulfone (VIII) was recovered.

<u>3,3',4',4'-Tetramethoxydiphenyl Sulfone (IX) [6].</u> A solution of 60 g of  $K_3[Fe(CN)_6]$ and 36 g AcONa in 250 ml of water was rapidly added at 20°C to a stirred solution of 11 g (0.1 mole) of pyrocatechol and 11.7 g (0.062 mole) of rongalite in 63 ml of water. The mixture was stirred for 3 h at 30°C, then cooled to 20°C, and a solution of 16 g (0.4 mole) of NaOH in 20 ml of water was added, followed by 38 ml (0.4 mole) of dimethyl sulfate. Stirring was carried out for 1.5 h at 20°C and 2 h at 95°C, and 50 ml of 10% NaOH was added. The mixture was cooled and the precipitate that formed was filtered off (Table 3). By metallation of (IX) with subsequent carboxylation as described above for (VIII), 8% of a mixture of mono- and dicarboxylix acids was obtained, while by the action of DMF no formyl derivatives were observed.

<u>2-Trimethylsilyldiphenyl Sulfone (XII)</u>. A 15 ml portion (0.12 mole) of Me<sub>3</sub>SiCl in 15 ml of ether was added at  $-50^{\circ}$ C to a solution of an o-Li derivative of dimethyl sulfone, prepared from 21.8 g (0.1 mole) of (Ib) and 0.09 mole of BuLi in a similar way as described for the preparation of (IIb). The mixture was stirred for 15 min at  $-50^{\circ}$ C, 3 h at 20°C, and 1 h at 40°C, and then poured into ice-cooled 10% H<sub>2</sub>SO<sub>4</sub>. The ether layer was separated, washed with water, and dried. The residue after the removal of the solvent was treated with hexane, the precipitate of (Ib) (6.1 g) was filtered, the solution was evaporated, and the mixture obtained, which according to the GLC data consisted of 5% of (Ib), 77% of (XII) and 18% of (XIII) was separated by distillation under vacuum (Tables 2 and 3).

<u>2,2'-Bis(trimethylsilyl)diphenyl Sulfone (XIII)</u>. A 15 ml portion (0.12 mmole) of Me<sub>3</sub>. SiCl in 15 ml of ether was added at -50°C to a solution of dilithium derivative of diphenyl sulfone, prepared from 8.72 g (40 mmoles) of sulfone (Ib) and 100 mmoles of BuLi, as described above during the preparation of (VII). The mixture was stirred for 15 min at -50°C and for 3 h at 40°C, and was then poured into cold 10% H<sub>2</sub>SO<sub>4</sub>. The ether layer was separated and dried. The solvent was removed under vacuum (Tables 2 and 3). Mass spectrum: 346 (M<sup>+</sup> - 15).

<u>2-Trimethylsilyl-6,6'-bisformyldiphenyl Sulfone (XIV)</u>. A 58.2 ml portion (0.105 mole) of an ethereal solution of BuLi was added to a stirred (at 0°C) solution of 10.1 g (35 mmoles) of (XII) in 40 ml of absolute ether. The mixture was stirred for 1 h, and then 10.5 ml (0.14 mole) of DMF in 30 ml of ether was added at -70°C. After standing for 3 h at 20°C, the mixture was poured into cold 10% H<sub>2</sub>SO<sub>4</sub>. The precipitate that separated out was filtered off. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1700 (C=O), 1310, 1160 (SO<sub>2</sub>). Mass spectrum: 311 (M<sup>+</sup> - 15). The yield, physical constants and analyses of (XIV) and oxime (XXV) are given in Table 1, the PMR spectrum in Table 2.

<u>2,2'-Bistrimethylsilyl-6-formyldiphenyl Sulfone (XV)</u>. A 22 ml portion (36 mmoles) of an ethereal solution of BuLi was added at 0°C to a stirred solution of 3.2 g (9 mmoles) of (XIII) in 30 ml of absolute ether and 10 ml of absolute benzene. The mixture was stirred for 1.5 h, and then 3 ml (40 mmoles) of DMF in 20 ml of ether was added at -50°C. After standing for 2.5 h at 20°C, the mixture was poured into cold  $H_2SO_4$ . After the extraction of the organic part with ether, drying, and evaporation of the solvent, compound (XV) was obtained. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1690 (C=O), 1310, 1165 (SO<sub>2</sub>). Mass spectrum: 375 (M<sup>+</sup> - 15). The yield, physical constants, and analyses of (XV) and oxime (XXVI) are given in Table 1 and the PMR spectrum in Table 2.

<u>2,2'-Bis(trimethylsilyl)-6-carboxydiphenyl Sulfone (XVI)</u>. The Li derivative prepared from 1.28 g (3.6 mmoles) of (XIII) and 14.4 mmoles of BuLi, similarly as described above, was poured onto dry ice in ether. On reaching 20°C, water was added, the aqueous layer was separated, washed with ether, and acidified. Compound (XVI) that separated out was filtered off. Mass spectrum 391 ( $M^+ - 15$ ) (Tables 2 and 3).

<u>o-tert-Butylsulfonylbenzonitrile Oxide (XVIIa)</u>. A 1 g portion (4 mmoles) of oxime (IIIa) was gradually added to a mixture of 20 ml of  $CH_2Cl_2$  and 4.5 ml of NaOCl solution (12 mmoles, the active chlorine content 0.18 g/ml), and the mixture was stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic layer was washed with water and dried. After removal of the solvent, com-

pound (XVIIa) was obtained. IR spectrum (v, cm<sup>-1</sup>): 2310 (C=N), 1360 (NO), 1310, 1145 (SO<sub>2</sub>). Mass spectrum: 239 (M<sup>+</sup>) (Table 4).

<u>o-Phenylsulfonylbenzonitrile Oxide (XVIIb)</u> was obtained in a similar way as (XVIIa). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2320 (C=N), 1370 (NO), 1320, 1160 (SO<sub>2</sub>). Mass spectrum: 259 (M<sup>+</sup>) (Table 4).

<u>3,4-Di(o-tert-butylsulfonylphenyl)</u> Furoxane (XVIIIa). A 0.3 g portion (1.2 mmoles) of (XVIIa) was boiled in toluene for 7 h. The precipitate was filtered off (Table 4). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1610 (C=N), 1410 (NO), 1300, 1140 (SO<sub>2</sub>). Mass spectrum: 478 (M<sup>+</sup>).

<u>3-(o-tert-Butylsulfonyl)phenyl-5-phenyl-2-isoxazoline (XIXa)</u>. A 1 g portion (4 mmoles) of oxime (IIIa) was added at 0°C to a stirred solution of 5 ml of NaOCl of the above-indicated concentration and 1 ml of sytrene in 20 ml of  $CH_2Cl_2$ , and the mixture was stirred for 1 h at 20°C. The organic layer was separated, washed with water, and dried. The residue remaining after the separation of the solvent was treated with hexane. The solid product was filtered (Table 4). Mass spectrum: 343 (M<sup>+</sup>).

 $\frac{2-\text{tert-Butylsulfonyl-5-methylisophtalonitrile Oxide (XXI)}{\text{was obtained in a similar way as (XVIIa). IR spectrum (v, cm<sup>-1</sup>): 2300 (C=N), 1340 (NO), 1310, 1125 (SO<sub>2</sub>). Mass spectrum: 294 (M<sup>+</sup>) (Tables 2 and 4).$ 

Diphenylsulfone-2,2'-dicarbonitrile Oxide (XXII) was obtained in a similar way as (XVIIa). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2310 (C=N), 1310 (NO), 1340, 1165 (SO<sub>2</sub>). Mass spectrum: 300 (M<sup>+</sup>) (Table 4). In an attempt to carry out chromatography and recrystallization (XXII) cyclizes into furoxane (XXIV) (Table 4). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1610 (C=N), 1420 (NO), 1320, 1165 (SO<sub>2</sub>). Mass spectrum: 300 (M<sup>+</sup>).

<u>2,2'-Bis-(5-phenyl-2-isoxazolin-3-yl)diphenyl Sulfone (XXIII)</u>. A 1 g portion (3 mmoles) of oxime (XX) was added at 0°C to a stirred solution of 7.7 ml of NaOCl and 1.5 ml of styrene in 20 ml of  $CH_2Cl_2$ , and the mixture was stirred for 1 h at 20°C. The organic layer was separated, washed with water, and dried. The solvent was evaporated, the residue was treated with hexane, and compound (XXIII) was filtered off (Tables 2 and 4). Mass spectrum: 508 (M<sup>+</sup>).

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