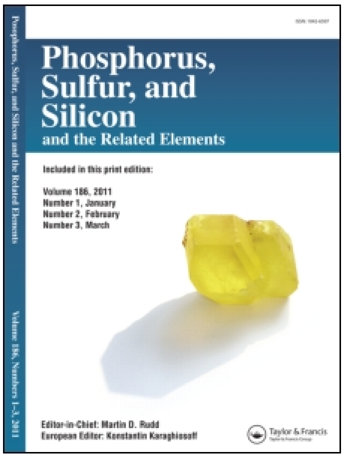

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Nucleophilic Addition of Secondary Amines to Bis[2-(5-trimethylsilyl-(germyl))thienyl]dimethylsilane(germane)-1,1,1',1'-tetroxides

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NUCLEOPHILIC ADDITION OF SECONDARY AMINES TO BIS[2-(5-TRIMETHYLSILYL-(GERMYL)) THIENYL]DIMETHYLSILANE(GERMANE)-1,1,1′,1′-TETROXIDES

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Lithiation of 2-trimethylsilyl- and 2-trimethylgermylthiophenes by n-*BuLi and subsequent silylation or germylation by dichlorodimethylsilane or dichlorodimethylgermane give bis[2-(5-trimethylsilyl-(germyl)thienyl]dimethylsilanes and -germanes (**1a–d**). Their oxidation with 4 equivalents of* m-*chloroperbenzoic acid leads to formation of corresponding thiophene-1,1,1′1′-tetroxides (**2a–d**). Nucleophilic addition of secondary amines to thiophene-1,1,1′1′-tetroxides (**2a–d**) has been studied. It has been shown that the basicity of amine and the nature of solvent determine the reaction pathway. In water, the addition of two dimethylamine or piperidine molecules and only one diethylamine or morpholine molecule to each thiophene-1,1,1′1′- tetroxide fragment of the sulfone was accompanied by complete desilylation and degermylation. In organic solvents (benzene, THF) the addition of two piperidine molecules to each thiophen-1,1-dioxide fragment of bis[2-(5-trimethylsilyl)thienyl]dimethylsilane was observed. In this case the desilylation of both trimethylsilyl and dimethylsilyl groups occurred.*

Keywords: Germane; nucleophylic addition; silane; thiophene; thiophene-1,1-dioxide

Substituted thiophene-1,1-dioxides have attracted much attention for the synthesis of different organic compounds. They serve as dienes,

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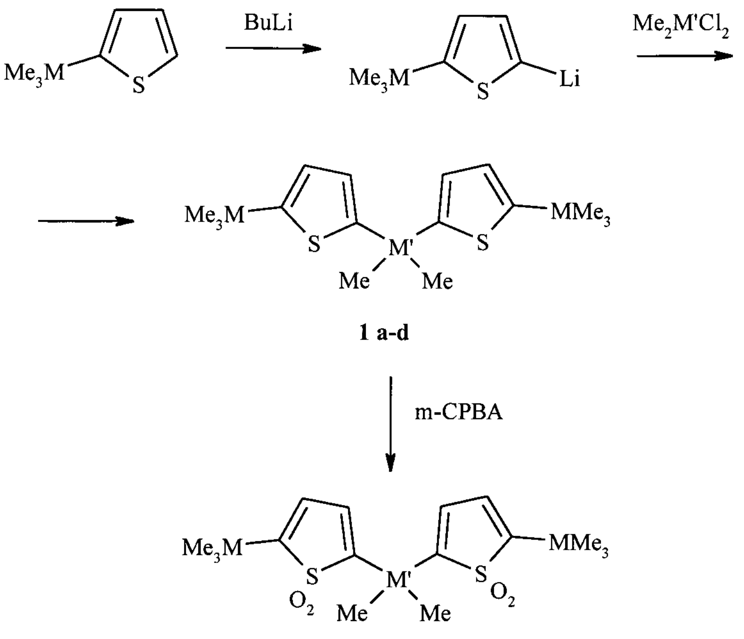
dienophiles[1,2] and 1,3-dipolarophiles[3–7] in numerous cycloaddition reactions due to presence of butadiene fragment. As typical α,β-unsaturated sulfones they enter into reactions of nucleophilic addition.[8] Amine-induced ring-opening reactions of thiophene-1,1-dioxides bearing methyl groups in position 2 of the heterocyclic system proceed with high regio- and stereoselectivity to yield transoid butadiene derivatives.[9–12] General methods for synthesis of thiophene-1,1-dioxides and their chemical transformations have been reviewed thoroughly.[13,14]

It has been shown[8] that the nucleophilic addition of secondary amines to the double C=C bonds of *tert*-butyl-, trimethylsilyl- and trimethylgermyl-substituted thiophene-1,1-dioxides depends on the substituent Me_3M (M=C, Si, Ge) character, the basicity of amine and the nature of solvent. Addition of amines to 2,5-bis(*tert*-butyl)thiophene-1,1-dioxide does not occur either in organic or in aqueous media. In organic solvents 2,5-bis(trimethylsilyl)-, 2-trimethylsilyl-5-trimethylgermyl- and 2,5-bis(trimethylgermyl)thiophene-1,1-dioxides add one piperidine molecule, the vinylsilane fragment being more active than vinylgermane one. In water the addition of diethylamine and morpholine (one molecule in each case) or dimethylamine and piperidine (two molecules in each case) was accompanied by complete demetallation. To study the influence of sulfone structure on amine addition bis[2-(5-trimethylsilyl(germyl)thienyl]dimethylsilane-1,1,1′1′-tetroxide and -germane-1,1,1′1′-tetroxide have been prepared by oxidation of corresponding thiophenes with *m*-chloroperbenzoic acid.

RESULTS AND DISCUSSION

Lithiation of 2-trimethylsilyl- and 2-trimethylgermylthiophenes by a solution of 2.5 *n*-BuLi in hexane and subsequent silylation or germylation of thienyllithium intermediates by dichlorodimethylsilane or dichlorodimethylgermane (Scheme 1) gave thiophene derivatives **1a–d**[15–17] in high yields (Table I). Metallation with *n*-BuLi was carried out at room temperature in inert atmosphere.

Different reagents have been used for oxidation of thiophenes to thiophene-1,1-dioxides, such as peracetic[1] and trifluoroperacetic[18] acids, dimethyldioxirane[2,19] and HOF·MeCN complex, obtained by passing F_2 through a mixture of acetonitrile and water.[20] This complex as well as trifluoroperacetic acid are excellent oxidants for thiophene derivatives containing several electron-withdrawing substituents. Electron-donor silyl- and germyl groups increase the reactivity of sulfur atom therefore, commonly used *m*-chloroperbenzoic acid



SCHEME 1

was applied for oxidation of thienylsilanes and thienylgermanes **1a–d** to corresponding sulfones **2a–d**. Oxidation was carried out in methylene chloride at room temperature to give thiophene-1,1-dioxides in 49–59% yields (Scheme 1, Table I).

The UV-visible absorption data for thiophene-1,1-dioxides **2a–d** and parent thiophenes **1a–d** are summarized in Table I. The maximum wavelength absorptions of the thiophene molecules **1a–f** are in the

TABLE I Yields and Characteristics of Thiophenes **1a–d** and Thiophene-1,1-dioxides **2a–d**

Compound	M	M′	Yield, %	m.p., °C	λ_{max}, (nm, CHCl$_3$)
1a	Si	Si	94	33–34	258
1b	Si	Ge	83	36–37	262
1c	Ge	Si	83	32–34	262
1d	Ge	Ge	75	35–36	264
2a	Si	Si	58	207–208	312
2b	Si	Ge	50	207–208	311
2c	Ge	Si	49	198–199	314
2d	Ge	Ge	59	206–207	310

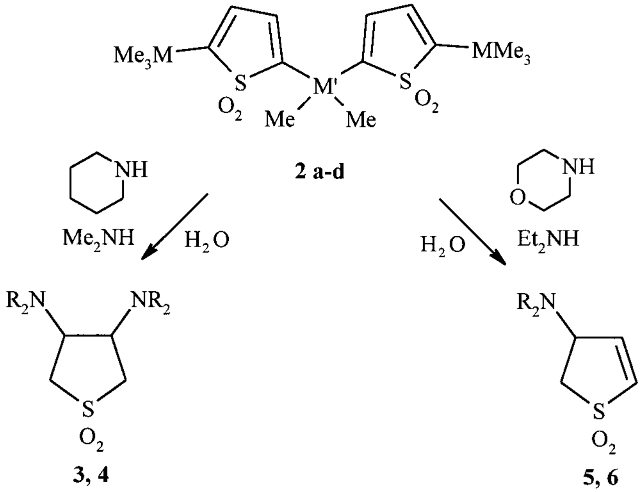
TABLE II ^{1}H and ^{13}C NMR-Spectroscopic Data for Thiophenes **1a–d** and Thiophene-1,1-dioxides **2a–d**

No.			δ ^{1}H ppm (J, Hz)				δ ^{13}C, ppm					
comp.	M	M′	H(3), d	H(4), d	Me_3M, s	Me_2M', s	C(2)	C(3)	C(4)	C(5)	Me_3M	Me_2M'
1a	Si	Si	7.39 (3.2)	7.33 (3.2)	0.33	0.66	146.9	136.4	135.1	143.1	0.1	0.2
1b	Si	Ge	7.37 (3.2)	7.36 (3.2)	0.36	0.81	145.7	134.9	134.9	143.7	0.1	−0.05
1c	Ge	Si	7.38 (3.2)	7.24 (3.2)	0.44	0.62	147.8	136.2	133.8	142.2	−0.3	0.2
1d	Ge	Ge	7.34 (3.2)	7.27 (3.2)	0.46	0.78	146.6	134.6	133.6	142.8	−0.3	−0.04
2a	Si	Si	7.06 (3.8)	6.76 (3.8)	0.34	0.68	151.4	139.2	135.9	145.6	−1.8	−3.7
2b	Si	Ge	6.97 (3.8)	6.76 (3.8)	0.33	0.87	150.6	137.1	134.6	146.7	−1.8	−2.9
2c	Ge	Si	7.05 (3.8)	6.69 (3.8)	0.50	0.67	152.7	139.4	134.3	145.1	−1.7	−3.7
2d	Ge	Ge	6.96 (3.8)	6.68 (3.8)	0.50	0.86	152.1	137.3	134.6	146.5	−1.7	−2.9

range 258–264 nm, their oxidation leads to the bathochromic effect, γ_{max} being red shifted by 46–54 nm as compared with thiophenes **1a–d**. The same effects were observed for transition from 2,5- and 2,4-substituted thiophenes to their sulfones.[7]

The NMR spectroscopy was used to study the influence of the oxidation of the sulfur atom on the ^1H and ^{13}C chemical shifts (Table II). The loss of aromatic character of the thiophene nucleus and the formation of the heterocyclic butadiene system leads to the high field shift of the ring protons and low field shift of the ring carbons in thiophene-1,1-dioxides as compared with parent thiophenes.

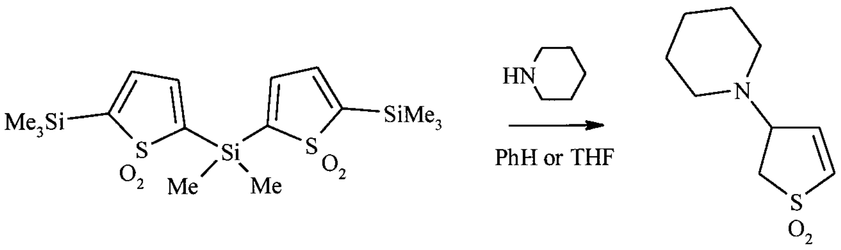
The nucleophilic addition of secondary amines to double C=C bonds of sulfones **2a–d** (the ratio of amine : sulfone is 10:1) in aqueous medium was determined by the basicity of amine used in the reaction. All thiophene-1,1-dioxides **2a–d** added four molecules (two for each thiophene-1,1-dioxide fragment) of dimethylamine or piperidine. The reaction was accompanied by demetallation of both trimethylsilyl (trimethylgermyl) and dimethylsilyl (dimethylgermyl) groups to give 3,4-bis(dimethylamino)sulfolane **3** and 3,4-bis(piperidino)sulfolane **4** in almost quantitative yields (Scheme 2).



SCHEME 2

The less basic diethylamine and morpholine also reacted with sulfones **2a–d** in water with complete demetallation, but, unlike with dimethylamine and piperidine, only one amine molecule added to each thiophene-1,1-dioxide fragment of molecules **2a–d** (Scheme 2). Yields of 3-diethylamino-2,3-dihydrothiophene-1,1-dioxide **5** and 3-piperidino-2,3-dihydrothiophene-1,1-dioxide **6** are more than 80%

The piperidine addition to bis[2-(5-trimethylsilyl)thienyl]dimethylsilane-1,1,1′,1′- tetroxide **2a** proceeded in THF or benzene leading to formation of 3-piperidino-2,3-dihydrothiophene-1,1-dioxide **7** in more than 70% yields (Scheme 3). The interaction occurred under the heating during 5–6 h. In spite of the piperidine excess (1:10) the second double bond in thiophene-1,1-dioxide units of sulfone **2a** did not add the molecule of amine. Contrary to 2,5-bis(trimethylsilyl)thiophene-1,1-dioxide[8] the addition of piperidine to thiophene-1,1-dioxide **2a** was accompanied by complete desilylation.



2 a **7**

SCHEME 3

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 spectrometer at 200.06 and 50.31 MHz correspondingly at 303 K. The chemical shifts are given relative to TMS from solvent ($CDCl_3$) signal ($\delta_H = 7.25$). Mass spectra were recorded on a Hewlett Packard apparatus (70 eV). UV-visible spectra were obtained on a Hitachi UV spectrometer U 3200. The melting points were determined on a “Digital Melting Point Analyser” (Fisher), the results are given without correction.

2-Trimethylsilylthiophene and 2-trimethylgermylthiophene were prepared by a literature method.[21]

General Method for Synthesis of Thienylsilanes and -germanes 1a–d

To a solution of 2-trimethylsilylthiophene (or 2-trimethylgermylthiophene) (0.02 mol) in dry ether (30 mL) was added 9 ml of

2.5 N *n*-BuLi in hexanes (0.0225 mol) at room temperature. After 1 h, dichlorodimethylsilane (or dichlorodimethylgermane) (0.01 mol) was added dropwise. The reaction mixture was refluxed for 1 h, hydrolyzed with a saturated solution of ammonium chloride, extracted with ether. The organic layer was separated, dried over Na_2SO_4, and evaporated. The residue was crystallized. Yields, melting points, UV- and $_1$H, $_{13}$C, and $_{29}$Si NMR spectroscopic data are presented in Tables I and II.

Bis[2-(5-trimethylsilyl)thienyl]dimethylsilane (1a). MS, *m/e* 368 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}S_2Si_3$: C, 52.11; H, 7.65; S, 17.39. Found: C, 51.87; H, 7.69; S, 17.48.

Bis[2-(5-trimethylsilyl)thienyl]dimethylgermane (1b). MS, *m/e* 414 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}GeS_2Si_2$: C, 46.50; H, 6.52; S, 15.52. Found: C, 46.21; H, 6.47; S, 15.43.

Bis[2-(5-trimethylgermyl)thienyl]dimethylsilane (1c). MS, *m/e* 460 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}Ge_2S_2Si$: C, 41.97; H, 6.16; S, 14.01. Found: C, 42.04; H, 6.23; S, 13.83.

Bis[2-(5-trimethylgermyl)thienyl]dimethylgermane (1d). MS, *m/e* 506 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}Ge_3S_2$: C, 38.25; H, 5.62; S, 12.77. Found: C, 38.06; H, 5.43; S, 12.84.

General Method for Synthesis of Thiophene-1,1-dioxides 2a-d

The solution of thiophene **1a–d** (0.005 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of 70% *m*-CPBA (0.02 mol) in CH_2Cl_2. After being stirred for 4 h at room temperature, the reaction mixture was cooled to −50°C, and the precipitate of m-chlorobenzoic acid was filtered off. After evaporation of the solvent, the residue was recrystallized from hexane-ether (2:1) mixture to yield thiophene-1,1 dioxide **2a–d**, as a white crystalline solid. Yields, melting points and spectroscopic data are presented in Tables I and II.

Bis[2-(5-trimethylsilyl)thienyl]dimethylsilane-1,1,1′1′-tetroxide (2a). MS, *m/e* 432 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}O_4S_2Si_3$: C, 44.40; H, 6.52; S, 14.82. Found: C, 44.19; H, 6.50; S, 14.89.

Bis[2-(5-trimethylsilyl)thienyl]dimethylgermane-1,1,1′1′-tetroxide (2b). MS, *m/e* 478 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}GeO_4S_2Si_2$: C, 40.26; H, 5.91; S, 13.44. Found: C, 40.11; H, 5.92; S, 13.33.

Bis[2-(5-trimethylgermyl)thienyl]dimethylsilane-1,1,1′1′-tetroxide (2c). MS, *m/e* 524 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}Ge_2O_4S_2Si$: C, 36.83; H, 5.41; S, 12.29. Found: C, 36.67; H, 5.22; S, 12.16.

Bis[2-(5-trimethylgermyl)thienyl]dimethylgermane-1,1,1′1′-tetroxide (2d). MS, *m/e* 570 ($M^{\bullet +}$). Anal. Calcd for $C_{16}H_{28}Ge_3O_4S_2$: C, 33.93; H, 4.98; S, 11.32. Found: C, 33.70; H, 5.11; S, 11.25.

3,4-Bis(dimethylamino)sulfolane (3)

To a 30% solution of dimethylamine in water (4 mL) thiophene-1,1-dioxide **2a–d** (0.5 mmol) was added. After 1 h sulfone was completely dissolved. The product was extracted with CH_2Cl_2. Organic layer was separated, dried by sodium sulfate. Pure product was obtained after solvent evaporation. Yields: 84% from **2a** and **2b**, 80% from **2c** and 82% from **2d**. Spectral characteristics of product **3** corresponded to literature data.[8]

3,4-Bis(piperidino)sulfolane (4)

To a mixture of thiophene-1,1-dioxide **2a–d** (0.5 mmol) and piperidine (5 mmol) water (5 mL) was added. Reaction is exothermic. After 2 h the precipitate was filtered, washed with cold water, and dried. Yields: 90% from **2a** and **2b**, 88% from **2c** and 82% from **2d**. Spectral characteristics of product **4** corresponded to literature data.[8]

Addition of dimethylamine and morpholine to sulfones ***2a–d***
General Procedure. To a mixture of thiophene-1,1-dioxide 2a–d (0.5 mmol) and amine (5 mmol) water (5 mL) was added. The reaction mixture was kept overnight, then the product was extracted with CH_2Cl_2. Organic layer was separated, dried by sodium sulfate. Pure products were obtained after solvent evaporation. Spectral characteristics of products **5** and **6** corresponded to literature data.[8]

3-Piperidino-2,3-dihydrothiophene-1,1-dioxide (7)

A mixture of sulfone **2** (0.4 mmol), piperidine (4 mmol), and 5 mL of benzene (or THF) was stirred under heating 6–8 h. Then solvent was evaporated and residue was chromatographed on silica gel with methylene chloride as eluent. Yields: 72% (benzene), 76% (THF). M.p. 90–92°C. MS, *m/e* 201 ($M^{\bullet+}$). ^1H NMR ($CDCl_3$, δ, ppm.): 6.70 (M, 2H), 4.28–4.32 (M, 1H), 3.21–3.27 (M, 2H), 2.42 (M, 4H), 1.43–1.60 (M, 6H). ^{13}C ($CDCl_3$, d, ppm): 141.1, 133.3, 64.3, 50.1, 47.1, 26.0, 25.8, 24.0. Anal. Calcd for $C_9H_{15}NO_2S$: C, 53.70; H, 7.51; N, 4.97; S, 15.93. Found: C, 53.86; H, 7.44; N 4.80; S, 15.75.

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