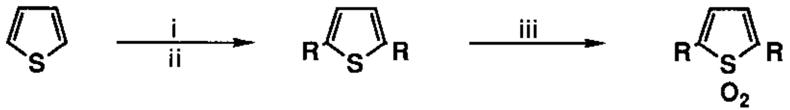
PREPARATION OF 2,5-DISILYLATED THIOPHENE DERIVATIVES AND THEIR CONVERSION TO 2,5-DIHALO DERIVATIVES

Naomichi Furukawa,* Hiroki Hoshiai, Tadao Shibutani, Masato Higaki,
Fujiko Iwasaki,[§] and Hisashi Fujihara
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
[§]Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Abstract - 2,5-Disilylated thiophenes were prepared and readily oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding 1,1-dioxides. The thiophene dioxide was converted to 2,5-dihalogenothiophene dioxides with halogenating agents.

A few thiophene monooxides have been successfully isolated,[1] while dioxides bearing suitable substituents are isolated as stable compounds.[2] We have intended to explore the utilization of thiophene derivatives for organic synthesis and found that 2,5-bistrimethylsilyl and the related silyl derivatives were oxidized readily to give the corresponding sulfones. This paper reports the preparation and reactions of several silylated thiophene derivatives including silicon-bridged macrocycles.

2,5-Disilylthiophenes (**1a-c**) were prepared by the known method[3] using 2 equivalents of BuLi and subsequent treatment of the dilithiothiophene with 2 equivalents of silyl chlorides. Then these were treated with *m*-CPBA to afford the corresponding sulfones (**2a-c**) in good yields (Scheme 1).[4]



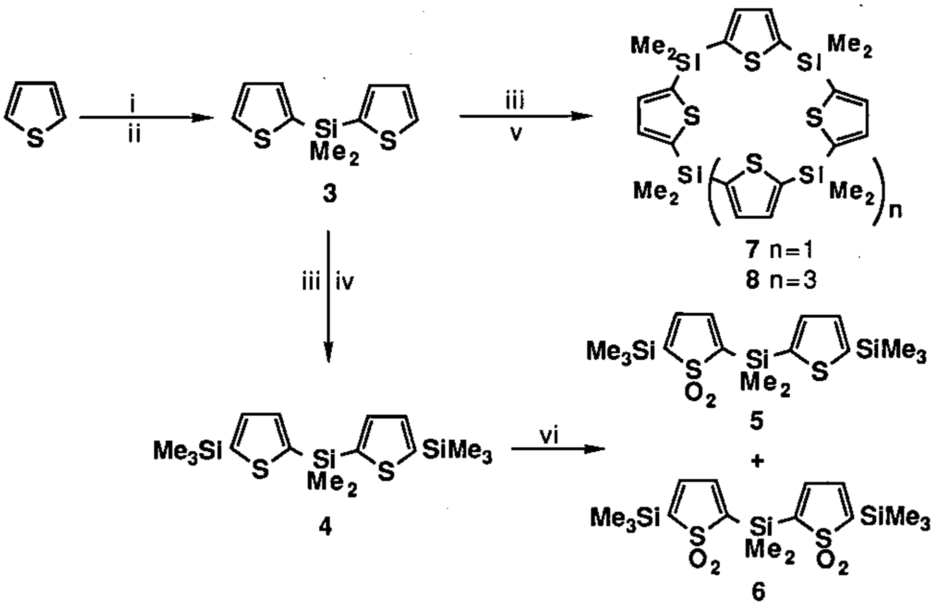
1 a R=Me_3Si
b $PhMe_2Si$
c *t*-$BuMe_2Si$

2a-c

Scheme 1. i. 2 eq. BuLi/THF/N_2/-20°C/1 h; ii. RCl/-20°C/1 h; iii. *m*-CPBA/CH_2Cl_2/room temperature/1 day

In a typical experiment, 2,5-bis(trimethylsilyl)thiophene (1a) (2.32 g, 10 mmol) was oxidized with *m*-CPBA (6.16 g, 25 mmol) in CH_2Cl_2 (200 ml) for 24 h at room temperature. After usual work-up and column chromatography using silica gel and hexane-CH_2Cl_2 (1:1) as an eluent, the crude crystals separated were recrystallized from hexane. 2,5-Bis(trimethylsilyl)thiophene 1,1-dioxide (2a) was obtained in 91% yield (Scheme 1). X-ray crystallographic analysis of **2a** reveals that it is a nearly planar molecule having a C_{2v} symmetry bisecting the SO_2 and the C_3-C_4 bond.[5]

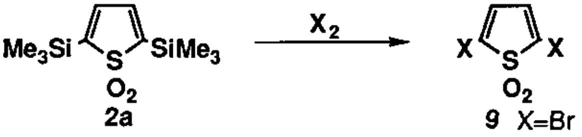
When thiophene was treated with 1 equivalent of BuLi and then with 0.5 equivalent of dichlorodimethylsilane, dimethyldi(2-thienyl)silane (**3**) was obtained in 74% yield. **3** was treated with 2 equivalents of lithium diisopropylamide (LDA) and then with trimethylsilyl chloride affording dimethyl-bis-(5-trimethylsilyl-2-thienyl)silane (**4**) in 76% yield. In the oxidation of **4** with 1 equivalent of *m*-CPBA, one thiophene ring was preferentially oxidized to afford only the mono-sulfone (**5**) in 36% yield. For further addition of *m*-CPBA, the corresponding mono-sulfone (**5**) and bis-sulfone (**6**) were obtained in 21% and 41% yields, respectively.



Scheme 2. i. 1 eq. BuLi/THF/N_2/-20°C/1 h; ii. 0.5 eq. Me_2SiCl_2/-20°C/1 h;
iii. 2 eq. LDA/THF/N_2/-20°C/1 h; iv. 2 eq. Me_3SiCl/-20°C/1 h;
v. 1 eq. Me_2SiCl_2/-20°C/1 h;
vi. *m*-CPBA/CH_2Cl_2/room temperature/1 day

When the reaction of **3** was conducted by using 2 equivalents of LDA and 1 equivalent of dichlorodimethylsilane at -20 °C in THF for 2 h, macrocyclic compounds (**7**) and (**8**) were obtained without using high dilution technique. The products were separated by column chromatography (silica gel) and then purified by preparative liquid chromatography affording **7** and **8** in 17 and 15% yields, respectively.[6] Kauffman *et al.* reported the preparation of **7** in 16 % yield by similar procedure but using BuLi instead of LDA as a base.[7] However, judging from the physical and spectroscopic evidence, their product seems to be a mixture of **7** and **8**.

In order to convert these 1,1-dioxides to other thiophene derivatives, **2a** was treated with bromine or iodine in the presence of $AgBF_4$ in CH_2Cl_2 at 0 °C for 1 h to afford the corresponding bromo (**9**) and iodo (**10**) derivatives in 72 and 97 % yields, respectively.[8,9] When the reaction was carried out in the absence of $AgBF_4$, iodine did not react at all even changing the reaction conditions while bromine reacted with **2a** to give **9** in 47 % yield. But the reaction required high temperature (50 °C) and longer reaction time (72 h). The results are shown in Table 1.


2a

9 X=Br

10 X= I

Table 1. Preparation of 2,5-Dihalogenated Thiophene 1,1-Dioxides

Run	X_2	Equiv.	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	Br_2,$AgBF_4$[a)]	2	CH_2Cl_2	0	1	72
2	I_2,$AgBF_4$[a)]	2	CH_2Cl_2	0	1	97
3	Br_2	3	CCl_4	50	72	47
4	I_2	3	CCl_4	reflux	168	0

a) 3 eq. of $AgBF_4$ was used.

Introduction of silyl groups at the 2,5-positions in thiophene provides advantages not only for protection of the sulfonyl group from dimerization but also masking of the 2,5-positions of the thiophene ring to which halogen atoms can readily be introduced and hence promises to be a convenient method for preparation of various thiophene derivatives.

Further investigations on these thiophene dioxides and their derivatives are in progress.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority area of Organic Unusual Valency No. 03233101 from Ministry of Education, Science and Culture, Japan.

REFERENCES AND NOTES

1. W. L. Mock, J. Am. Chem. Soc., 1970, 92, 7610; P. J. Fagan and W. A. Nugent, J. Am. Chem. Soc., 1988, 110, 2310; A. E. Skaugset, T. B. Rauchfuss, and C. L. Stern, J. Am. Chem. Soc., 1990, 112, 2432.
2. (a). M. S. Raasch, J. Org. Chem., 1980, 45, 856, 867; (b). J. Nakayama, S. Yamaoka, T. Nakanishi, and M. Hoshino, J. Am. Chem. Soc., 1988, 110, 6598; (c). Y. Miyahara and T. Inazu, Tetrahedron Lett., 1990, 31, 5955.
3. (a). H. Sakurai, S. Hoshi, A. Kamiya, A. Hosomi, and C. Kabuto, Chem. Lett., 1986, 1781; (b). For review, E. Block and M. Aslam, Tetrahedron, 1988, 44, 281.
4. **2a**: Yield, 91%; mp 153-154 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 6.74 (s, 2H, ThH), 0.34 (s, 18H, Me); ^{13}C-nmr ($CDCl_3$) δ 150.6, 135.9, -1.74; FT-ir (KBr) 1282, 1129 cm^{-1} (SO_2). Anal. Calcd for $C_{10}H_{20}O_2SSi_2$: C, 46.11; H, 7.74. Found: C, 46.05; H, 7.58; **2b**: Yield, 84%; mp 62-64 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 7.57-7.25 (m, 10H, ArH), 6.54 (s, 2H, ThH), 0.63 (s, 12H, Me); ^{13}C-nmr ($CDCl_3$) δ 149.6, 137.5, 134.5 134.0, 130.1, 128.1, -3.29; FT-ir (KBr) 1284, 1131 cm^{-1} (SO_2). Anal. Calcd for $C_{20}H_{24}O_2SSi_2$: C, 62.50; H, 6.25. Found: C, 62.41; H,6.24; **2c**: Yield, 80%; mp 154-155 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 6.80 (s, 2H, ThH), 0.99 (s, 18H, *t*-Bu), 0.31(s, 12H, Me); ^{13}C-nmr ($CDCl_3$) δ 149.1, 137.2, 26.3, 17.2, -6.02; FT-ir (KBr) 1284, 1127 cm^{-1} (SO_2). Anal. Calcd for $C_{16}H_{32}O_2SSi_2$: C, 61.54; H, 10.09. Found: C, 61.35; H, 10.18.
5. X-ray crystallographic analysis: bond lengths (Å); C-S:1.761, C_2-C_3(C_4-C_5):1.323, C_3-C_4:1.480. bond angles; O-S-O:113.4°, C_2-S-C_5:96.1°, C_2-S-O:111.5°.
6. **7**: mp 278-279 °C (lit.[8] 224-226 °C); ^{1}H-nmr ($CDCl_3$) δ 7.39 (s, 8H, ThH), 0.63 (s, 24H, Me); ^{13}C-nmr ($CDCl_3$) δ 144.8, 135.5, -0.34; ms (m/z) 560 (M^+). Anal. Calcd for $C_{24}H_{32}S_4Si_4$: C, 51.38; H, 5.71. Found: C, 51.38; H, 5.61; **8**: mp 252-253 °C (benzene-hexane); ^{1}H-nmr ($CDCl_3$) δ 7.34(s, 12H, ThH), 0.63 (s, 36H, Me); ^{13}C-nmr ($CDCl_3$) δ 143.8, 136.6, -0.02; ms (m/z) 840 (M^+). Anal. Calcd for $C_{36}H_{48}S_6Si_6$: C, 51.38; H, 5.71. Found: C, 51.41; H, 5.73.
7. T. Kauffman and H. H. Kniese, Tetrahedron Lett., 1973, 4043.
8. The compound (**9**) has been synthesized by the oxidation of 2,5-dibromothiophene.[2c]
9. **10**: mp 147 -150 °C (decomp.) (dichloromethane-hexane); ^{1}H-nmr ($CDCl_3$) δ 6.87(s, 2H); ^{13}C-nmr ($CDCl_3$) δ 128.3, 119.3; ms (m/z) 368 (M^+); FT-ir (KBr) 1303, 1147 cm^{-1}(SO_2). Anal. Calcd for $C_4H_2O_2I_2S$: C, 13.04; H, 0.74. Found: C, 13.37; H, 0.74.

Received, 18th February, 1992