EXCLUSIVE *CIS*-1,4-ADDITION REACTION IN THE BROMINATION OF 2,5-BIS(TRIMETHYLSILYL)THIOPHENE MONOOXIDE

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Abstract 2,5-Bis(trimethylsilyl)thiophene monooxide (**1**) underwent a 1,4-addition reaction with Br_2 to give stereospecifically 2,5-bis(trimethylsilyl)-2,5-*cis*-dibromothiolene monooxide (**2**) in quantitative yield.

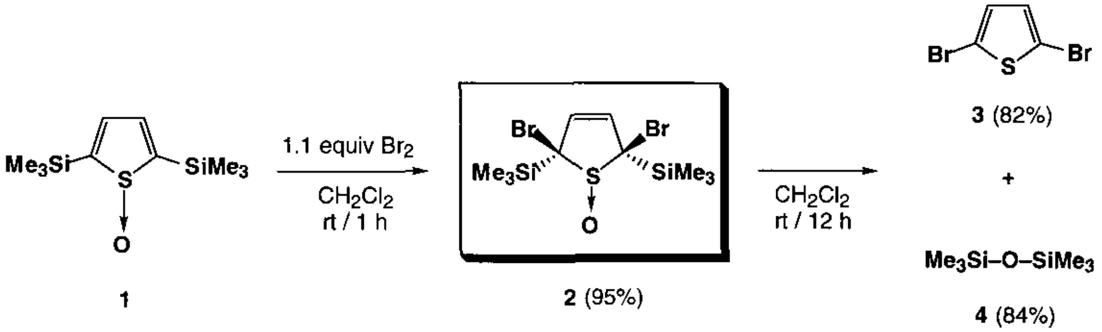
Recently, we have reported a simple and convenient method for the preparation of 2,5-bissilylated thiophene monooxides using *m*-chloroperbenzoic acid (*m*-CPBA) in the presence of BF_3•OEt_2.[1] X-Ray crystallographic analyses of the 2,5-bis(diphenylmethylsilyl)thiophene monooxide[2] and also the 2,5-bisdiphenylthiophene monooxide[3] revealed that the thiophene ring is not a planar structure and hence it should behave as a diene and not as an aromatic compound. In fact, the thiophene monooxide underwent a Diels-Alder [4 + 2] cycloaddition reaction with *p*-benzoquinone.[4] Similar [4 + 2] cycloadditions of other thiophene monooxides were reported by Tashiro *et al.*[5] We have manipulated the roles of the thiophene monooxides as the starting materials for organic synthesis. As an initial trial, 2,5-bis(trimethylsilyl)-thiophene monooxide (**1**) was treated with bromine.

Normally, when thiophene monooxide (**1**) was treated with 1.1 molar equivalent of bromine for 12 h, the substitution product, 2,5-dibromothiophene (**3**) was obtained in high yield together with hexamethyl disiloxane (**4**). However, when the reaction was conducted using CH_2Cl_2 as a solvent, then after 1 h the

1,4-bisdibromo-adduct, 2,5-bis(trimethylsilyl)-2,5-*cis*-dibromothiolene monooxide (**2**), was obtained quantitatively in high stereo- and regio-selectivity. This article describes this new *cis*-1,4-addition reaction of the thiophene monooxide (**1**) with Br_2, together with the structure determinations of the products.

The bromination of the monooxide (**1**) was carried out as follows: **1** was dissolved in dry CH_2Cl_2 and to this solution a 1.1 molar equivalent of bromine was added in dry CH_2Cl_2 at room temperature for 12 h. After evaporating the solvent, the products were separated and purified by liq. chromatography to give two products as shown in Scheme 1. The products were identified by ^1H, ^{13}C, and ^{29}Si NMR spectroscopies by comparing the spectra with those of the known compounds in the literatures.[6] These results indicate that bromine behaves as an electrophile and replaces the silyl groups affording the final products, (**3**) and (**4**).

Scheme 1



This reaction mode is similar to the reactions of 2,5-bis(trimethylsilyl)thiophene and -thiophene dioxide with bromine which give the substituted 2,5-dibromothiophene derivatives as reported previously.[7] However, the reaction monitored by ^1H NMR was interrupted after 1 h at which time the monooxide (**1**) was completely consumed. The solvent was removed by evaporation to produce only one crystalline compound (**2**) in more than 95% yield. The ^1H, ^{13}C, and ^{29}Si NMR spectral results and the molecular structure (Figure 1) demonstrate that the product obtained was in fact the 1,4-dibromo-adduct to the monooxide (**1**) and that the expected 2,5-dibromothiophene (**3**) had not formed at all. Recrystallization of **2** from hexane/dichloromethane produced colorless crystals with a mp 98 °C.

The structure of this compound (**2**) was subsequently determined by X-Ray crystallographic analysis. Monitoring the reaction in an NMR tube in situ also indicated the formation of only one stereoisomer. The

ORTEP drawing of **2** is shown in Figure 1 and the representative bond distances and bond angles of **2** are summarized in Table 2.

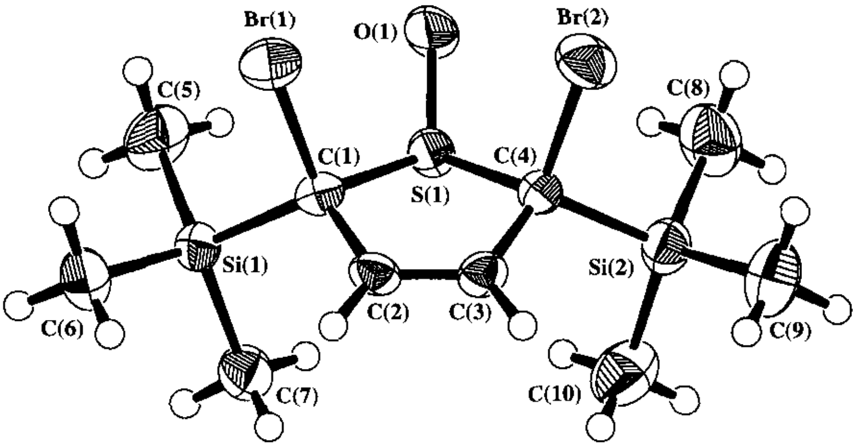


Figure 1. An ORTEP (30% probability ellipsoids) view of **2**.

Interestingly, the compound (**2**) has a C_s symmetry and the two bromine atoms are attached at the 2 and 5 positions of **1** and are *syn* to the S–O bond. This stereospecific addition mode of bromine to the 1,4-diene is identical to that observed in the Diels-Alder addition products of **1** using electrophilic olefins such as *p*-benzoquinone.[2] The obvious explanation for this unusually high stereo- and regio-selectivity is that the bromine approaches to the 2,5-positions in the thiophene monooxide (1) from the *syn*-side with respect to the S–O bond in a concerted manner avoiding the lone pair electrons at the sulfur atom as shown in Figure 2. The electron density distribution of the 2,5-bis(diphenylmethylsilyl)thiophene monooxide was

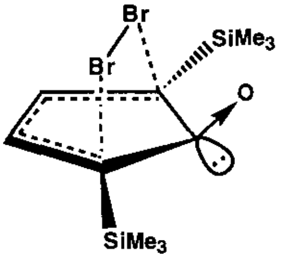
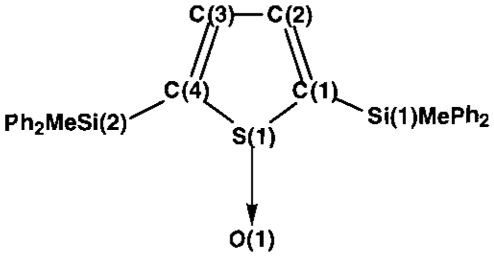


Figure 2. Intermediate in the bromination of **1**

calculated by a single point *ab initio* RHF method using STO-3G$^{(*)}$ as a basis set on the basis of its crystal structure[8] and the results are summarized in Table 1. Atomic charges were calculated by the natural population analysis.[9] The result suggests that the negative charges are accumulated at the 2,5-positions and hence Br_2 attacks preferentially at these positions.

Table 1. The charge distribution (natural population analysis) of 2,5-bis(diphenylmethylsilyl)thiophene *S*-oxide.



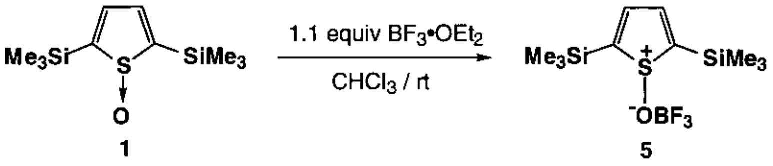
atoms	charges
S(1)	+1.429
C(1)	–0.799
C(2)	–0.162
C(3)	–0.171
C(4)	–0.809
O(1)	–0.990
Si(1)	+1.968
Si(2)	+1.957

The isolation of 1,4-adduct clearly indicates that the reaction of **1** with Br_2 proceeds via 2 steps involving initially the concerted 1,4-addition to the diene part in the thiophene monooxide followed by the substitution of the silyl groups and oxygen. Indeed, when **2** was dissolved in CH_2Cl_2 and the solution was stirred for 12 h, the elimination products, namely a mixture of 2,5-dibromothiophene (**3**) and $Me_3SiOSiMe_3$ (**4**), were obtained in around 80% yields. Although the reaction was carried out with an excess amount of Br_2 under the same conditions, further addition or substitution products were not observed probably due to the steric hindrance of the bulky substituents at the 2,5-positions in **2**.

The iodination of **1** with I_2 did not proceed at room temperature or refluxing temperature in CH_2Cl_2 for 24 h, but only proceeded after refluxing in THF for 24 h. In contrast to the bromination reaction, iodination of the monooxide (**1**) did not give the corresponding addition product at all, but 2,5-diiodothiophene was obtained in 70% yield together with hexamethyl disiloxane (**4**) only by refluxing in THF with excess I_2. Therefore, we tried to accelerate the iodination reaction in CH_2Cl_2 by adding $BF_3 \bullet OEt_2$.

However, neither an addition nor a substitution reaction occurred, instead **1** was converted to the stable BF_3 adduct, 2,5-bis(trimethylsilyl)thiophene monooxide(*O*–*B*)-trifluoroborane (**5**), in a quantitative yield and with a mp 96 – 98 °C. This reaction proceeds without I_2. The complex (**5**) was analyzed by X-Ray crystallographic analysis revealing that the structure of **5** is a BF_3-adduct at the sulfinyl oxygen atom as shown in Equation 1 and Figure 3. The representative bond distances and bond angles of **5** are summarized in Table 2.

Equation 1



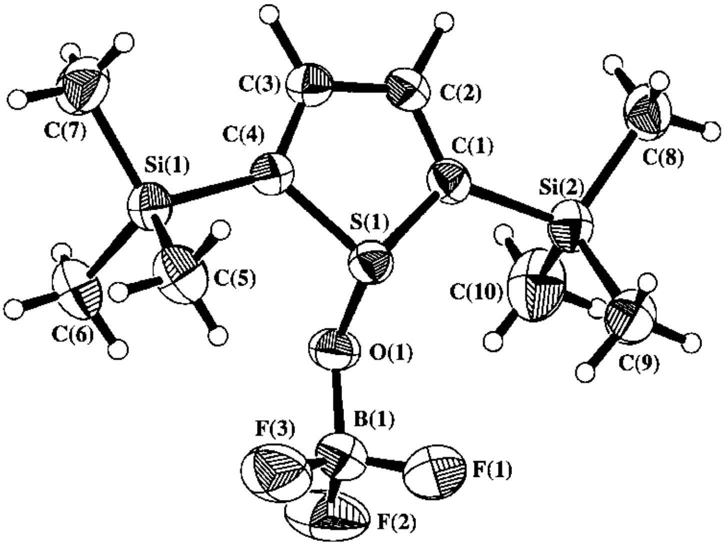


Figure 3. An ORTEP (30% probability ellipsoids) view of **5**.

The halogenation of thiophene monooxide (**1**) results in two different modes of addition depending on the reaction conditions and halogenating reagents. Particularly, bromination gives initially the 1,4-adduct exclusively which can be used for further conversion of the thiophene ring as functionallized materials. On this aspect, detailed mechanistic investigations on the stereospecific addition of Br_2 to **1** are currently underway in this laboratory.

2,5-bis(trimethylsilyl)-2,5-dibromo thiolene monooxide (**2**): mp 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 0.28 (s, 18H, Me), 6.14 (s, 2H, olefin-H); ^{13}C NMR (100 MHz, $CDCl_3$, rt) δ –2.9, 73.4, 131.3; ^{29}Si NMR (80 MHz, $CDCl_3$, rt) δ 8.9 (relative to Me_4Si); IR (KBr, cm^{-1}) 1050 (S–O); MS m/z 324 (M^+ – 80); Anal. Calcd for $C_{10}H_{20}OBr_2SSi_2$, C; 29.71, H; 4.99; Found C; 29.76, H; 5.07. **Crystal data for 2**: $C_{10}H_{20}OBr_2SSi_2$, M = 404.31, monoclinic, space group $P2_1/n$, a = 6.777(1) Å, b = 12.292(8) Å, c = 20.117(3) Å, β = 93.85(1)°, V = 1672.0(8) Å^3, D_c = 1.606 g/cm^3, Z = 4, $F(000)$ = 808, μ = 51.13 cm^{-1}. A colorless crystal of dimensions 0.50 x 0.70 x 0.80 mm was used for measurements at 296 K on an Enraf-Nonius CAD4-FR four-circle diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) using the $\omega/2\theta$ scan technique. A total of 4200 unique reflections were corrected for Lorentz and polarization effects, secondary extinction (coefficient = 8.0470e-07), and crystal absorption (DIFABS[10]: transmission = 0.58–1.00). The structure was solved by direct methods. The final full-matrix least-squares refinement, based on F using 1844 reflections ($I > 3.00\sigma(I)$) and 146 parameters, converged with R = 0.042 and R_w = 0.046.

2,5-bis(trimethylsilyl)thiophene monooxide(*O–B*)trifluoroborane (**5**): mp 96 – 98 °C; ^{1}H NMR (270 MHz, $CDCl_3$, rt) δ 0.41 (s, 18H, Me), 7.13 (s, 2H, Th-H); ^{13}C NMR (68 MHz, $CDCl_3$, rt) δ –1.29, 143.3, 154.2; ^{19}F NMR (254 MHz, $CDCl_3$, room temperature) δ –149.0 (relative to $CFCl_3$); ^{11}B NMR (87 MHz, $CDCl_3$, rt) δ –19.1 (relative to $(CH_3O)_3B$); ^{29}Si NMR (54 MHz, $CDCl_3$, rt) δ –2.5 (relative to $(CH_3)_4Si$); MS m/z 244 (M^+ – 68); Anal. Calcd for $C_{10}H_{20}OBF_3SSi_2$, C; 38.46, H; 6.45; Found C; 38.43, H; 6.62. **Crystal data for 5**: $C_{10}H_{20}OBF_3SSi_2$, M = 312.30, monoclinic, space group $P2_1/c$, a = 11.666(2) Å, b = 10.821(2) Å, c = 13.887(2) Å, β = 106.71(1)°, V = 1679.0(5) Å^3, D_c = 1.235 g/cm^3, Z = 4, $F(000)$ = 656, μ = 3.51 cm^{-1}. A colorless crystal of dimensions 0.60 x 0.90 x 1.00 mm was used for measurements at 296 K on an Enraf-Nonius CAD4-FR four-circle diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) using the $\omega/2\theta$ scan technique. The structure was solved by direct methods. The 4357 unique reflections were corrected for Lorentz and polarization effects, a linear decay (8.7%), and crystal absorption (DIFABS[10]: transmission = 0.46–1.00). The structure was solved by direct methods. The final full-matrix least-squares refinement, based on F using 1657 reflections ($I > 3.00\sigma(I)$) and 163 parameters, converged with R = 0.056 and R_w = 0.056. All calculations were performed on a SGI-Indy workstation using the teXsan crystallographic software package from Molecular Structure Corp. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

Table 2. The bond distances (Å) and a selected list of angles (°) for the non-hydrogen atoms are given below (e.s.d.'s in parenthesis) of **2** and **5**.

2		**5**	
Br(1)–C(1) = 1.979(7)	Br(2)–C(4) = 1.977(7)	S(1)–O(1) = 1.522(4)	S(1)–C(1) = 1.770(6)
S(1)–O(1) = 1.479(5)	S(1)–C(1) = 1.841(7)	S(1)–C(4) = 1.759(5)	Si(1)–C(4) = 1.877(6)
S(1)–C(4) = 1.846(7)	Si(1)–C(1) = 1.915(8)	Si(2)–C(1) = 1.890(6)	O(1)–B(1) = 1.491(10)
Si(2)–C(4) = 1.906(8)	C(1)–C(2) = 1.484(10)	C(1)–C(2) = 1.336(7)	C(2)–C(3) = 1.447(8)
C(2)–C(3) = 1.32(1)	C(3)–C(4) = 1.497(10)	C(3)–C(4) = 1.351(7)	F(1)–B(1) = 1.36(1)
O(1)–S(1)–C(1) = 111.5(3)		O(1)–S(1)–C(1) = 107.7(3)	
C(1)–S(1)–C(4) = 93.8(3)		C(1)–S(1)–C(4) = 108.1(3)	
Br(1)–C(1)–S(1) = 109.9(3)		C(1)–S(1)–C(4) = 96.5(3)	
Br(1)–C(1)–Si(1) = 107.8(4)		S(1)–O(1)–B(1) = 119.3(6)	
Br(1)–C(1)–C(2) = 109.9(5)		S(1)–C(1)–Si(2) = 123.3(3)	
S(1)–C(1)–Si(1) = 110.5(4)		S(1)–C(4)–Si(1) = 123.6(3)	
S(1)–C(1)–C(2) = 102.4(5)		S(1)–C(1)–C(2) = 104.9(4)	
Si(1)–C(1)–C(2) = 116.2(5)		S(1)–C(4)–C(3) = 104.6(4)	
C(1)–C(2)–C(3) = 117.5(6)		C(1)–C(2)–C(3) = 116.2(5)	
C(2)–C(3)–C(4) = 117.4(6)		C(2)–C(3)–C(4) = 116.2(5)	
S(1)–C(4)–C(3) = 101.8(5)		F(1)–B(1)–O(1) = 108.5(7)	

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