Regio- and Stereo-Chemistry of Addition of Molecular Bromine to S-Oxidized Derivatives of 3,4-Di-*t*-butylthiophene: Exclusive 1,4-*Cis*-Additions

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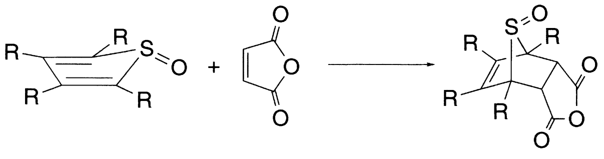
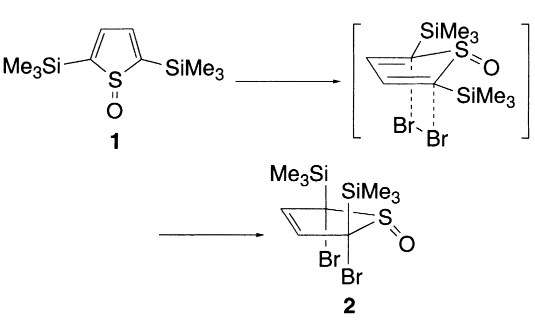
Bromine added to the 1-oxide, 1,1-dioxide, and sulfoximide derivatives of 3,4-di-*t*-butylthiophene exclusively in a 1,4-*cis*-addition mode. Thus, bromine added to 3,4-di-*t*-butylthiophene 1-oxide at room temperature in CH_2Cl_2 to give the 1,4-*cis*-adducts exclusively. The adducts are composed of two compounds in the ratio 57 : 43, where the major one is the *anti*-adduct respective to the S=O bond and the minor one is the *syn*-adduct. Addition of bromine to 3,4-di-*t*-butylthiophene 1,1-dioxide gave the 1,4-*cis*-adduct as the sole product. Addition of bromine to the *N*-tosyl substituted sulfoximide derivative of 3,4-di-*t*-butylthiophene afforded the single 1,4-*cis*-adduct in which two bromine atoms are *anti* to the *N*-tosyl group. Bromine added to the *N*-unsubstituted sulfoximide derivative of 3,4-di-*t*-butylthiophene to produce the 1,4-*cis*-addition products exclusively, which are a 67 : 33 mixture of the *anti*- and *syn*-adducts to the S=O bond.

Recently, considerable interest has been paid to the chemistry of thiophene 1-oxides from many viewpoints such as syntheses, structures, reactivities, applications to organic syntheses, and intermediates in the metabolism of thiophenes.[1] Thiophene 1-oxides act both as extremely reactive cyclic dienes and dienophiles, and are transient intermediates unless their double bonds are suitably deactivated either electronically or sterically. These compounds, which have the general structure shown in Fig. 1,[2,3] possess two π-faces for Diels–Alder reactions, i.e., *syn*-and *anti*-faces to the S=O bond. Therefore, one of the most interesting features in the chemistry of these compounds is the stereochemical course in Diels–Alder reactions. Recent reports described that the Diels–Alder reactions of thiophene 1-oxides take place exclusively at the *syn*-π-face to the S=O bond in an *endo*-mode (Scheme 1).[2e,4,5] It was also reported that even bromine addition to the thiophene 1-oxide **1** took place at the *syn*-face to the S=O bond and in a *cis*-1,4-addition mode to give the adduct **2** as the sole product.[6] A concerted mechanism was proposed to explain the observed stereochemistry (Scheme 2). Ab initio calculations also support the above mechanism. An important mechanistic problem which remains to be fully investigated is that of the stereochemistry of the 1,4-addition to 1,3-dienes. In this respect, the stereochemistry of bromine additions to cyclopentadiene and 1,3-cyclohexadiene has been investigated previously in some detail.[7]



Scheme 1. π-Face-selective Diels–Alder reaction (*syn* to the S=O bond).



Scheme 2. π-Face-selective 1,4-*cis*-addition of bromine.

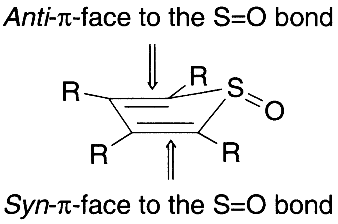


Fig. 1. General structure and two π-faces of thiophene 1-oxides.

Previously, we reported the synthesis of a series of S-oxidized species of 3,4-di-*t*-butylthiophene, such as 1-oxide **3**,[2d] 1,1-dioxide **4**,[8] 1-imide **5**,[9] and sulfoximides **6** and **7** (Chart 1).[10] Our recent study has also revealed that the Diels–Alder reactions of **3** and **5** also take place at the *syn*-π-face to the S=X (X = O or NTs) bond in an *endo*-mode.[11] Keeping these

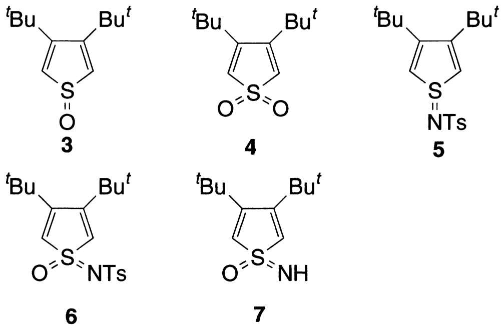


Chart 1. Structural formulas **3**–**7**.

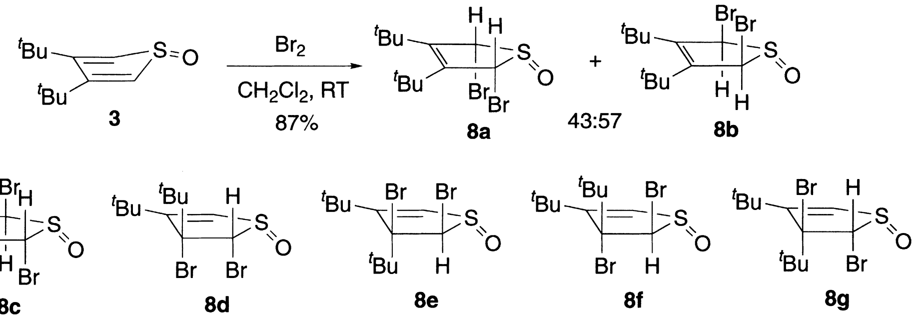
results in mind, we have now investigated the stereochemistry of the additions of bromine to **3**–**7**. Reactions of S-oxidized derivatives of thiophenes with bromine have hitherto not been reported except for the bromine addition to **1**.

Results

Product Analysis and Regio- and Stereo-Chemistry of Bromine Additions. Bromine added to **3** at room temperature to give the two 1,4-*cis*-adducts **8a** and **8b** in the ratio 43:57 in 87% combined yield (Scheme 3). Isomerization between **8a** and **8b** did not take place even when each of them was heated to its melting point. The observed ratio is therefore the kinetically controlled one. The two methine protons of both **8a** and **8b** are equivalent in the ^{1}H NMR spectra. Similarly, the two methine, vinyl, and *t*-butyl carbons of **8a** and **8b** are equivalent in the ^{13}C NMR spectra. These data rule out the 1,4-*trans*-adduct **8c**, the 1,2-*cis*-adducts **8d** and **8e**, and the 1,2-*trans*-adducts **8f** and **8g**, and shows unambiguously that the two compounds formed possess the structures described above.

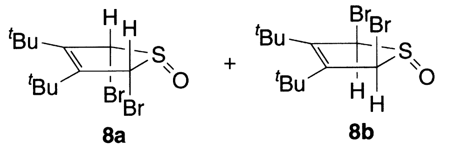
Discrimination of **8a** and **8b** was made based on the ^{1}H NMR chemical shift data (Table 1). The methine hydrogens of **8a** (δ 5.62) resonated at 0.27 ppm lower than those of **8b** (δ 5.35) in $CDCl_3$ as the solvent. The difference would be best explained as a result of anisotropic effect by the S=O group.[12] In order to obtain further support for the above assignment, DFT calculations were carried out.[13,14] The optimized structures of dibromides **8a** and **8b** are shown in Fig. 2. The dibromide **8b** is thermodynamically more stable by 1.66 kcal mol^{-1} than the other dibromide **8a**. As shown in Fig. 2, the methine protons of **8b** are located on the side of the S=O group so that they experience a high-field shift due to the anisotropic effect of the S=O group.[12] Calculations of the NMR shielding constants by the GIAO method[15] predicted that the methine protons of **8b** are more shielded than those of **8a**. Thus, the averaged shielding constants of those of **8b** are larger by 0.33 ppm than those of **8a**, and this value is in good agreement with the observed chemical shift difference of 0.27 ppm (δ 5.62 for **8a** and δ 5.35 for **8b**) and is no in contradiction with the structural assignment.

Furthermore, aromatic solvent-induced and [Eu(thd)$_3$]-induced shifts also support the above assignment (Table 1). In C_6D_6, the positive end (sulfur atom) of the S=O group of **8a** is expected to coordinate to the solvent molecule C_6D_6 to result in the aromatic solvent-induced shift.[16] Indeed, a larger down-



Scheme 3. Stereochemistry of bromine addition to **3**.

Table 1. Chemical Shift Data of the Methine Hydrogen of **8a** and **8b**: Aromatic Solvent- and [Eu(thd)$_3$]-Induced Shifts[a)]



	δ_H	δ_H	$\Delta\delta_H$	δ_H	$\Delta\delta_H$
	$CDCl_3$	C_6D_6	$CDCl_3 - C_6D_6$	$CDCl_3$ + [Eu(thd)$_3$]	$CDCl_3$ − [$CDCl_3$ + [Eu(thd)$_3$]]
8a	5.62	4.98	0.64	5.64[b)]	−0.02
8b	5.35	5.00	0.35	5.58[b)]	−0.23

a) [Eu(thd)$_3$] = Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium(III). b) 1.0 molar amount of [Eu(thd)$_3$] was used; δ 5.64 for **8a** and δ 5.47 for **8b** by use of 0.5 molar amount of Eu(thd)$_3$.

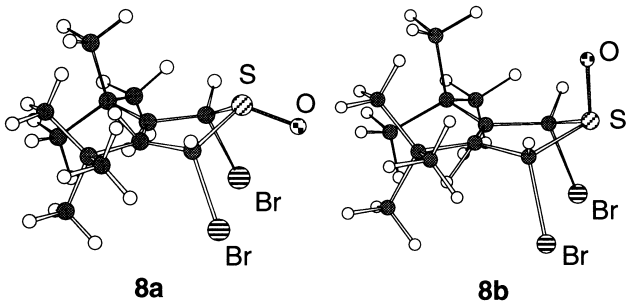
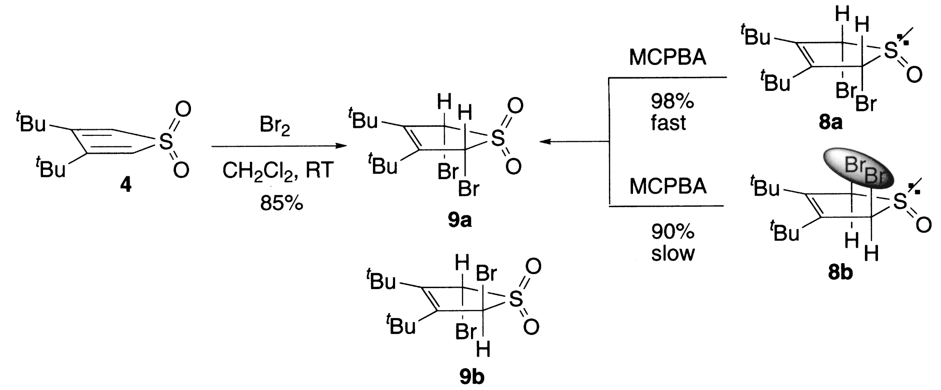


Fig. 2. Predicted optimized structures of **8a** and **8b**.

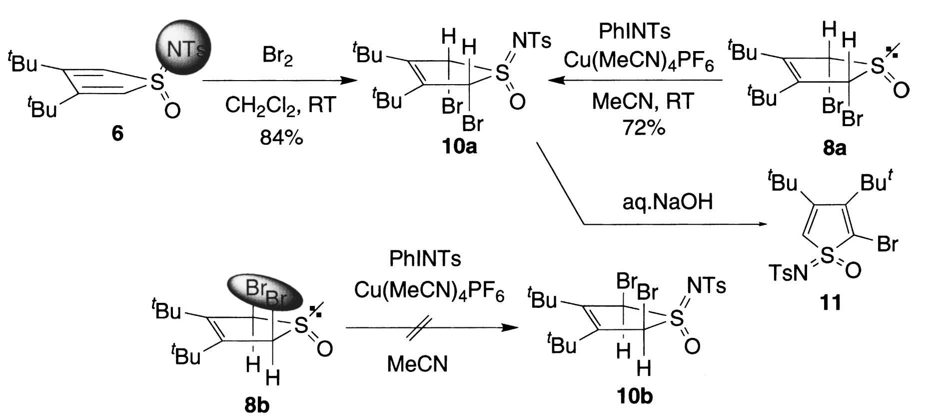
field shift of the methine hydrogen was observed for **8a** (0.64 ppm) than for **8b** (0.35 ppm). On the other hand, [Eu(thd)$_3$] coordinates to the negative end (oxygen atom) of the S=O group.[17] Thus the chemical shift value of the methine hydrogen of **8b** would be more influenced by [Eu(thd)$_3$] than that of **8a**. Actually, the methine proton of **8b** shifted up-field by 0.23 ppm in the presence of [Eu(thd)$_3$], whereas the up-field shift of **8a** is negligibly small (0.02 ppm).

Bromine added to the 1,1-dioxide **4** to furnish **9a** as a single diastereomer in 85% yield (Scheme 4). The *cis*-structure of **9a** was differentiated from the *trans*-structure **9b** by the experimental fact that **9a** was obtained both from **8a** and **8b** on oxidation. Thus, the oxidation of **8a** with 1.1 molar amounts of *m*-chloroperbenzoic acid (MCPBA) was completed in four days at room temperature to give **9a** in 98% yield, whereas that of **8b** was not completed even after a prolonged reaction of eight days and gave **9a** in 90% yield with 9% recovery of **8b**. The slower oxidation of **8b**, compared to **8a**, is ascribable to the steric hindrance due to the two bromine atoms which are *syn* to the lone pair of the sulfur atom. In other words, these findings support the structural assignment of **8a** and **8b**. 1,2-Adduct structures were ruled out unambiguously by ^{1}H and ^{13}C NMR spectra, which indicated a symmetrical structure of the product.

Addition of bromine to **6**, which was much slower than those to **3** and **4** probably because of steric and/or electronic effects, afforded the 1,4-adduct **10a** exclusively in 84% yield (Scheme 5). The diastereomeric adduct **10b** was not formed. The structure of **10a** was determined by an independent synthesis. Thus, treatment of **8a** with phenyl[(*p*-tolylsulfonyl)-imino]-λ^3-iodane (TsN=IPh)[18] in the presence of [Cu(MeCN)$_4$]PF$_6$ produced **10a** in 72% yield.[9c,10] The configuration at the sulfur atom of **8a** would be retained during this reaction since it is the mere addition of the tosyl nitrene or its equivalent to the lone pair of the sulfur atom.[19] When the crude mixture of the above reaction was washed with aqueous NaOH to remove *p*-toluenesulfonamide, formed from TsN=IPh, the dehydrobromination of **10a** took place to give a considerable amount of the sulfoximide **11**. Indeed, stirring a solution of **10a** with 1 M NaOH for 1 h gave **11** in 95% yield. The exclusive formation of **10a** suggests that bromine added to



Scheme 4. Stereochemistry of bromine addition to **4**.



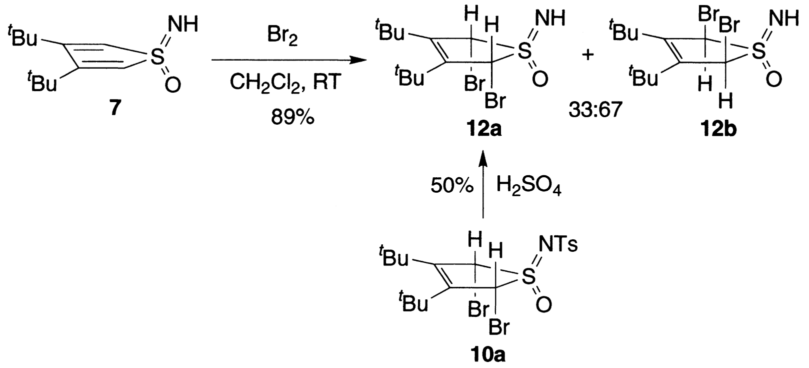
Scheme 5. Stereochemistry of bromine addition to **6**.

6 from the less hindered *anti*-side respective to the more bulky TsN group. Attempted preparation of **10b** by reaction of **8b** with TsN=IPh failed. No reaction took place even by use of excess TsN=IPh on a prolonged reaction time because of the steric hindrance of the two bromine atoms which are *syn* to the sulfur lone pair. In other words, these findings support again the validity of the structural assignment of **8a** and **8b**.

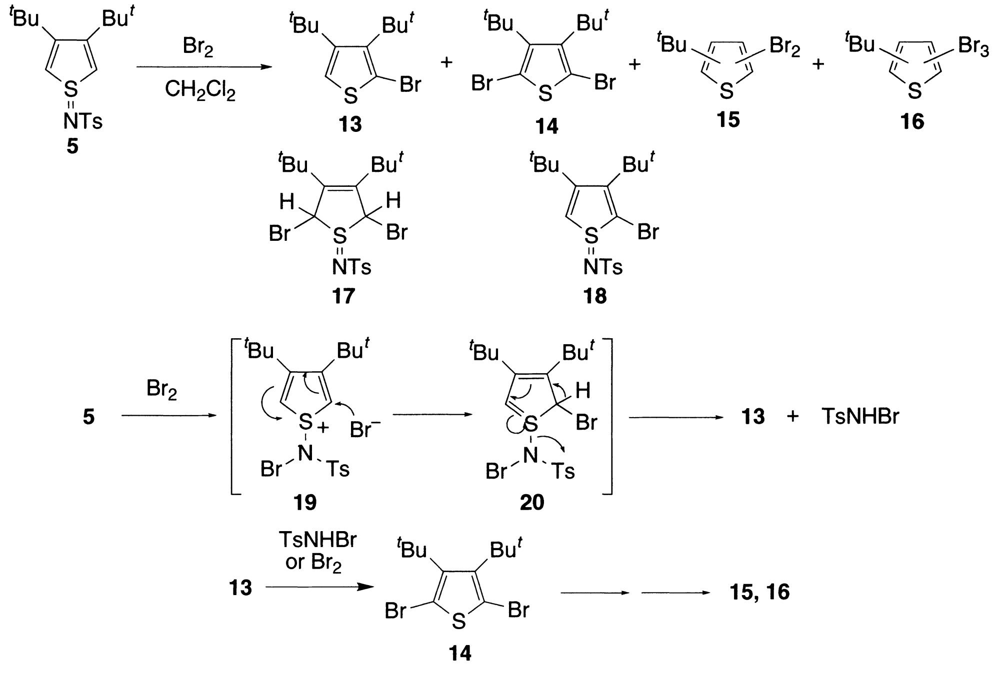
Addition of bromine to the *N*-unsubstituted sulfoximide **7** showed a small π-face selectivity (Scheme 6). Thus, bromine added to **7** from the NH side with a slight preference to produce **12a** and **12b** in the ratio 1:2 in a good combined yield. The reaction is again an exclusive 1,4-*cis*-addition. The discrimination of the structures **12a** and **12b** was made by the fact that **12a** was derived by treatment of **10a** with concentrated sulfuric acid.[9c,10,20]

Interestingly, the reaction of the 1-imide **5** with 1.1 molar amounts of bromine afforded **5**, **13**, **14**, **15**, and **16** in the ratio 26:17:7:25:24, in addition to *p*-toluenesulfonamide ($TsNH_2$) (Scheme 7). The product ratio was determined by ^1H NMR spectrum analysis. Structures of **13** and **14** were determined by comparison of spectral data with those of authentic samples, whereas the exact positions of the *t*-butyl group and the bromine atoms in **15** and **16** remained undetermined. The expected bromine adduct such as **17** might be formed in a small amount. Treatment of the reaction mixture by silica-gel column chromatography followed by aqueous NaOH resulted in the isolation of a compound whose structure is tentatively assigned as **18**, the dehydrobromination product of **17**.

The nitrogen atom of the imide **5** is expected to be more nucleophilic than is the oxygen atom of **3** and **4** or the nitrogen atom of **6** and **7**. Thus, the initial reaction would take place at the nitrogen atom to produce a sulfonium bromide **19**, although bromine addition may occur competitively as a minor path. The addition of bromide ion to **19** gives a sulfonium ylide **20**. Elimination of TsNHBr from **20** would produce **13** as one of the final products. The TsNHBr, thus formed, serves



Scheme 6. Stereochemistry of bromine addition to **7**.



Scheme 7. Reaction of **5** with bromine.

as a brominating agent of thiophenes, as does *N*-bromosuccinimide (NBS),[8a] and reacts with **13** to produce the dibromothiophene **14** (Br_2 used for the reaction also might be involved in this bromination, if it still exists). Further reactions of **14** with TsNHBr (Br_2) would result in the formation of **15** and **16** as observed when 3,4-di-*t*-butylthiophene was treated with excess NBS.[8a,21]

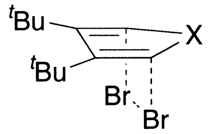
Discussion

The experimental findings, described above, raise two questions. The first question involves why bromine additions to **3**, **4**, **6**, and **7** take place exclusively in a 1,4-mode, and the second one involves why only *cis*-addition takes place. The simplest answer is to presume a concerted mechanism (Fig. 3) as was proposed for the bromine addition to **1**.[6]

Here, the third question arises why the bromine addition to **3** is not π-face selective, though that to **1** is π-face selective.[6] In other words, which is more general for bromine additions to thiophene 1-oxides? In order to answer this question, we need more experimental findings, although the study is hampered by the fact that only a few thiophene 1-oxides are stable enough to be handled under ordinary conditions.[1]

DFT MO calculations (B3LYP/6-31G* level) predicted that the lobe size of the π-HOMO at the α-carbon atoms of **3** is slightly greater at the *syn*-side than the *anti*-side respective to the S=O bond (Fig. 4).[14] Thus, the experimental findings suggest that nonequivalent orbital extension is not always a crucial factor to determine the π-face selectivity in additions that involve strong electrophiles such as bromine, even if the addition proceeds in a concerted mechanism.

In order to examine a possibility of mechanisms involving ionic intermediates in the bromine addition to the 1,1-dioxide **4**, calculation study (B3LYP/6-31G* level) was carried out.[14] The calculations were started by placing Br^+ above the center of the C2–C3 bond (**21**) and also above the center of the non-bonded C2–C5 bond (**22**) of the optimized structure of **4** (Chart 2). The calculations in both cases converged at the state of the open-chain carbonium intermediate **25**, thus predicting that **25** is more stable than are the 1,2-bridged bromonium ion intermediate **23** and 1,4-bridged intermediate **24**. This will explain why the 1,4-addition takes place in preference to the 1,2-addition; Br^- would add to the less crowded C5 of **25**, and not the sterically hindered C3, due to the contribution of the canonical structure **25b**. The question still remains, however, as to why *cis*-addition takes place exclusively.



X = SO, SO_2, S(O)NTs, S(O)NH

Fig. 3. Concerted bromine addition.

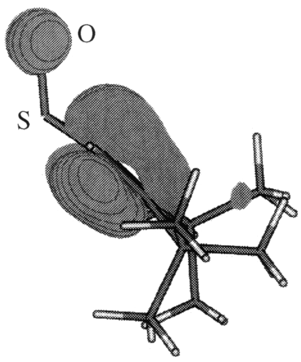


Fig. 4. Nonequivalent orbital extension of π-HOMO of **3**.

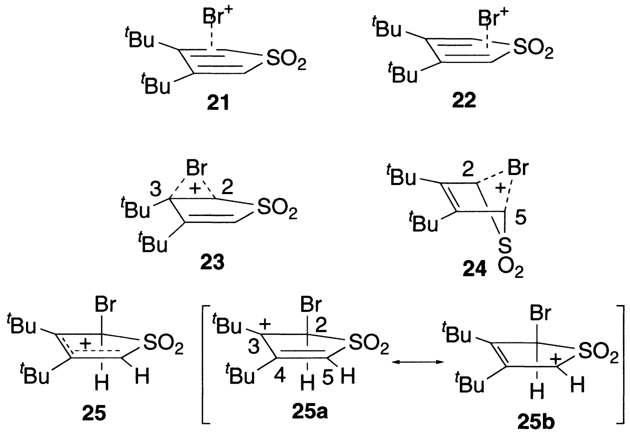


Chart 2. Intermediates of bromine addition to **4**.

In conclusion, we have presented interesting bromine additions to cyclic dienes which took place exclusively in a 1,4-*cis*-addition mode. Seemingly, the concerted mechanism would be best open to the above experimental findings, at least at the present stage of the investigation. However, we cannot present any direct evidence that rules out the ionic mechanism. Although bromine additions to cyclopentadiene and 1,3-cyclodiene were previously reported,[7] such exclusive 1,4-*cis*-additions are rather exceptional and would raise a new question for mechanistic organic chemistry.

Experimental

Solvents were purified and dried in the usual manner. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70–230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, a Bruker AC300P, or a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard. IR spectra were taken on a Hitachi 270-50 or a Perkin Elmer System 2000 FT-IR spectrometer. UV spectrum was determined on a JASCO V-560 spectrophotometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Addition of Bromine to Thiophene 1-Oxide 3. A solution of 352 mg (2.2 mmol) of bromine in 8 mL of CH_2Cl_2 was added slowly to a stirred solution of 426 mg (2.0 mmol) of **3** in 5 mL of CH_2Cl_2 at room temperature. The mixture was stirred for 1 h and then evaporated under reduced pressure. The resulting crystalline residue was chromatographed on a column of silica gel. The elution of the column by hexane/ether (3:2) as the eluent afforded 369 mg (50%) of **8b** and 273 mg (37%) of **8a** in this order. **8a**: mp 174–177 °C; colorless crystals (from hexane); ^1H NMR

(400 MHz) δ 1.48 (18H, s), 5.35 (2H, s); ^{13}C NMR (100.6 MHz) δ 32.0, 35.7, 66.3, 147.3; IR (KBr) 1115 cm^{-1} (S=O). Anal. Calcd for $C_{12}H_{20}Br_2OS$: C, 38.73; H, 5.42%. Found: C, 38.99; H, 5.43%. **8b**: mp 142.0–143.5 °C; colorless needles (from hexane); ^{1}H NMR (400 MHz) δ 1.45 (18H, s), 5.62 (2H, s); ^{13}C NMR (100.6 MHz) δ 32.3, 36.1, 68.2, 146.0; IR (KBr) 1060 cm^{-1} (S=O). Anal. Calcd for $C_{12}H_{20}Br_2OS$: C, 38.73; H, 5.42%. Found: C, 38.80; H, 5.41%.

Addition of Bromine to Thiophene 1,1-Dioxide 4. A mixture of 176 mg (1.1 mmol) of bromine and 228 mg (1.0 mmol) of **4** in 10 mL of CH_2Cl_2 was stirred at room temperature for 40 min; ^{1}H NMR analysis of an aliquot of the mixture showed that **9a** had been formed as the sole product with complete consumption of **4**. The reaction mixture was evaporated under reduced pressure. The resulting crystalline residue was crystallized from $CHCl_3$/hexane to give 328 mg (85%) of the adduct **9a** in analytically pure form: mp 179–181 °C; colorless crystals (from hexane); ^{1}H NMR (400 MHz) δ 1.48 (18H, s), 5.41 (2H, s); ^{13}C NMR (100.6 MHz) δ 32.1, 36.6, 59.0, 148.0. Anal. Calcd for $C_{12}H_{20}Br_2O_2S$: C, 37.13; H, 5.19%. Found: C, 36.85; H, 5.13%.

Oxidations of 8a and 8b to 9a. A mixture of 50 mg (0.13 mmol) of **8a** and 25 mg (0.14 mmol) of MCPBA in 5 mL of CH_2Cl_2 was stirred at room temperature for 4 days. The mixture was treated in a usual way and the resulting crude product was chromatographed on a column of silica gel to give 51 mg (98%) of **9a**. The oxidation of **8b** in the same scale was carried out at room temperature for 8 days to give 47 mg (90%) of **9a** with recovery of 5 mg (9%) of **8b**.

Addition of Bromine to Sulfoximide 6. A mixture of 46 mg (0.29 mmol) of bromine and 100 mg (0.26 mmol) of **10** in 10 mL of CH_2Cl_2 was stirred at room temperature. ^{1}H NMR analysis after 15 h showed the exclusive formation of **10a** with complete consumption of **6**. The mixture was evaporated under reduced pressure. The resulting crystalline residue was crystallized from ether/hexane to give 105 mg (74%) of **10a** in analytically pure form. The mother liquor of the crystallization was evaporated and the residue was purified by silica-gel column chromatography to give a further amount of **10a** (14 mg, 10%). **10a**: mp 154.0–157.5 °C; colorless crystals; ^{1}H NMR (400 MHz) δ 1.49 (18H, s), 2.41 (3H, s), 6.14 (2H, s), 7.28 (2H, J = 7.9 Hz, d); 7.83 (2H, J = 7.9 Hz, d); ^{13}C NMR (100.6 MHz) δ 21.5, 32.0, 36.7, 61.4, 126.7, 129.4, 139.6, 143.4, 147.5. Anal. Calcd for $C_{19}H_{27}Br_2NO_3S_2$: C, 42.15; H, 5.03; N, 2.59%. Found: C, 42.26; H, 4.95; N, 2.53%. Stirring a solution of **10a** (25 mg) in ether (10 mL) with 1 M NaOH (10 mL) for 1 h at room temperature gave 20 mg (95%) of **11**: mp 154.0–155 °C; colorless crystals; ^{1}H NMR (300 MHz) δ 1.46 (9H, s), 1.57 (9H, s), 2.42 (3H, s), 7.29 (2H, d, J = 8.3 Hz), 7.40 (1H, s), 7.89 (2H, d, J = 8.3 Hz); ^{13}C NMR (75.5 MHz) δ 21.5, 31.6, 32.0, 37.1, 37.3, 120.7, 125.2, 126.7, 129.3, 140.4, 143.0, 152.0, 160.8. Anal. Calcd for $C_{19}H_{26}BrNO_3S_2$: C, 49.56; H, 5.69; N, 3.04%. Found: C, 49.41; H, 5.60; N, 2.96%.

Conversion of 8a to 10a. A mixture of 50 mg (0.13 mmol) of **8a**, 150 mg (0.40 mmol) of TsN=IPh, and 7 mg of $[Cu(MeCN)_4]PF_6$ in 5 mL of MeCN was stirred at room temperature for 4 h. After the reaction had been quenched by addition of iced-water, the mixture was extracted with ether. The ether extracts were washed with water, dried over $MgSO_4$, and evaporated. The resulting crystalline residue was purified by silica-gel column chromatography with hexane/ether (3:1) as the eluent to give 53 mg (72%) of **10a**. Attempted conversion of **8b** to **10b** failed; no reaction took place on treatment of **8b** with excess TsN=IPh (12 molar amounts) for 10 h at room temperature.

Addition of Bromine to *N*-Unsubstituted Sulfoximide 7. A mixture of 35 mg (0.22 mmol) of bromine and 50 mg (0.22 mmol) of **7** in 5 mL of CH_2Cl_2 was stirred at room temperature for 1 h. The reaction mixture was evaporated under reduced pressure. The resulting crystalline residue was purified by silica-gel column chromatography with hexane/AcOEt (3:1) as the eluent to give 51 mg (60%) of **12b** and 25 mg (29%) of **12a** in this order. **12a**: mp 151–152 °C (dec); colorless crystals (from hexane); ^{1}H NMR (400 MHz) δ 1.48 (18H, s), 2.33 (1H, broad s), 5.41 (2H, s); ^{13}C NMR (100.6 MHz) δ 32.1, 36.4, 63.5, 148.2; IR (KBr) 3272 cm^{-1} (NH). Anal. Calcd for $C_{12}H_{21}Br_2NOS$: C, 37.23; H, 5.47; N, 3.62%. Found: C, 37.25; H, 5.45; N, 3.56%. **12b**: mp 160–162 °C (dec); colorless crystals (from hexane); ^{1}H NMR (400 MHz) δ 1.47 (18H, s), 4.14 (1H, broad s), 5.34 (2H, s); ^{13}C NMR (100.6 MHz) δ 32.1, 36.5, 64.7, 147.9; IR (KBr) 3284 cm^{-1} (NH). Anal. Calcd for $C_{12}H_{21}Br_2NOS$: C, 37.23; H, 5.47; N, 3.62%. Found: C, 37.18; H, 5.39; N, 3.45%.

Conversion of 10a to 12a. A mixture of 100 mg (0.18 mmol) of **10a** in 1 mL of concentrated H_2SO_4 was stirred at room temperature for 4 h. The resulting mixture was poured into an aqueous NaOH containing ice and was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography with hexane/ether (1:2) as the eluent to give 36 mg (50%) of **12a**.

Reaction of Imide 5 with Bromine. The imide **5** (100 mg, 0.27 mmol) and bromine (48 mg, 0.30 mmol) were dissolved in 10 mL of CH_2Cl_2 and the solution was stirred for 48 h at room temperature. ^{1}H NMR analysis of the resulting reaction mixture showed that **5**, **13**, **14**, **15**, and **16** were formed in the ratio 26:17:7:25:24. The resulting crude product was chromatographed on a column of silica gel. Elution of the column with hexane gave a mixture of **13**–**16**. Further elution of the column with ether gave a mixture of *p*-toluenesulfonamide and **17** (**18**). Removal of the *p*-toluenesulfonamide by washing the mixture with aqueous NaOH allowed the isolation of 5 mg (4%) of **18**. Purification of a mixture of **13**–**16** by silica-gel column chromatography and GPC allowed only isolation of **14** in pure form; the others were not isolated in pure form. **13**: ^{1}H NMR (200 MHz) δ 1.46 (s, 9H), 1.64 (s, 9H), 7.09 (s, 1H); ^{13}C NMR (50 MHz) δ 33.3, 33.7, 35.9, 36.3, 109.2, 122.0, 146.5, 151.6. **14**: mp 75.5–76.5 °C; ^{1}H NMR (200 MHz) δ 1.60 (s, 18H); ^{13}C NMR (50 MHz) δ 33.6, 37.9, 107.0, 149.2. **15**: ^{1}H NMR (200 MHz) δ 1.41 (s, 9H), 7.03 (s, 1H); ^{13}C NMR (50 MHz) δ 29.1, 34.9, 113.2, 114.3, 120.0, 149.2. **16**: ^{1}H NMR (200 MHz) δ 1.57 (s, 9H); ^{13}C NMR (50 MHz,) δ 30.6, 37.6, 104.7, 112.8, 114.3, 143.5. **18**: ^{1}H NMR (200 MHz) δ 1.42 (s, 9H), 1.56 (s, 9H), 2.40 (s, 3H), 6.87 (s, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H).

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