ChemComm

Dealkylation of a 1,2-bis(benzylthio)benzene derivative: generation of benzodithiete or its equivalent *via* a dithia dication†

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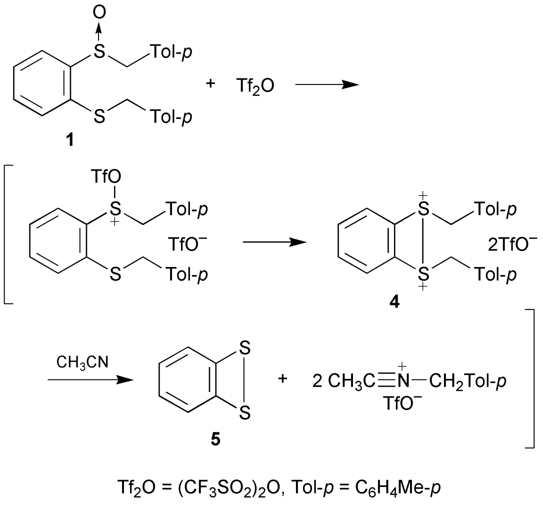
Received (in Cambridge, UK) 20th June 2000, Accepted 21st July 2000

The reaction of 1,2-bis(4-methylbenzylthio)benzene *s*-oxide with triflic anhydride in CH_3CN–CH_2Cl_2 in the presence of alkynes affords 1,4-benzodithiin derivatives and *N*-(4-methylbenzyl)acetamide after quenching with H_2O; this suggests the generation of benzodithiete or its equivalent.

The development of new methodologies for the generation of reactive species is an important goal in organic chemistry. Benzodithiete **5** is a highly reactive transient species, which occurs in thermolysis[1–3] and photolysis[4–6] of appropriate precursors, and is trapped by alkynes to form 1,4-benzodithiin derivatives.[7,8] Benzodithiete **5** is estimated to be 17 kcal mol^{-1} more stable than *o*-dithiobenzoquinone by calculations at the MP2 level[9] and decomposed at more than −90 °C.[1] σ-Bonded dithia dications have attracted considerable attention in heteroatom chemistry from the viewpoint of structural interests.[10] The strained dication of 1,4-dithiane reacts with alkynes to give dithiabicyclo[2.2.2]octene derivatives.[11] Recently, we have demonstrated the facile dealkylation of dithia dications with a flexible conformation to afford thiasulfonium salts;[12] in particular, the dithia dication obtained from the reaction of 2,2′-bis(benzylthio)biphenyl *s*-oxide with triflic anhydride (Tf_2O) is decomposed even at −20 °C to afford biphenyl disulfide and a benzyl cation.[13] Herein we report the reactions of 1,2-bis(4-methylbenzylthio)benzene mono-*s*-oxide **1** with Tf_2O in the presence of alkynes **2** and alkenes **3**, which produce 1,4-benzodithiins **6** and 2,3-dihydro-1,4-benzodithins **7**, respectively. The key reaction for the generation of benzodithiete **5** or its equivalent is based on the dealkylation of **1** *via* a dithia dication **4** (Scheme 1).

The substrate **1** was prepared by the reaction of benzene-1,2-dithiol with 4-methylbenzyl chloride in the presence of KOH (86% yield) followed by the oxidation of the resulting bis-sulfide with MCPBA (73% yield).



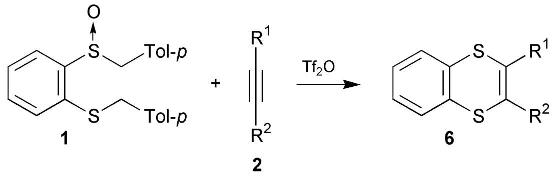
$Tf_2O = (CF_3SO_2)_2O$, Tol-*p* = C_6H_4Me-*p*

Scheme 1

The reaction of **1** with triflic anhydride (Tf_2O) was monitored by ^1H NMR spectroscopy. When 1 eq. of Tf_2O was added to a solution of **1** in CD_3CN-CD_2Cl_2 (v/v 1:1) at −75 °C, **1** immediately disappeared and a sole peak due to the *N*-benzyl–acetonitrile adduct appeared at δ 5.21 in the region of benzyl groups.[13] This result indicates that both benzyl groups of **1** are completely eliminated at −60 °C within a minute, although we have no direct evidence for the generation of dithia dication **4** and benzodithiete **5**. After warming up to rt, the reaction mixture gave a white precipitate. Treatment of the supernatant with H_2O afforded *N*-(4-methylbenzyl)acetamide (57% yield), and treatment of the white precipitate with $NaBH_4$ in THF followed by addition of iodomethane gave 1,2-bis(methylthio)-benzene (42% yield).

In order to elucidate the generation of benzodithiete **5** indirectly, the reaction of **1** with Tf_2O was carried out in the presence of alkynes **2** as a trapping reagent (Scheme 2).§¶ After complete dealkylation of **1** with Tf_2O in CH_3CN–CH_2Cl_2 (v/v 1:1) at −60 °C, **2** was added to the reaction mixture. From diarylacetylenes **2a–c**, 2,3-diaryl-1,4-benzodithiins **6a–c** were obtained in 44, 64, and 20% respective yields, and from arylacetylenes **2d–e**, 2-aryl-1,4-benzodithiins **6d–e** were produced in 18 and 21% respective yields. Thus, the formation of **6** strongly suggests the generation of **5** or its equivalent in the course of the reaction of **1** with Tf_2O. Diarylacetylenes serve as a more effective trapping reagent of **5** than arylacetylenes. However, dimethyl acetylenedicarboxylate[2,5] did not give 2,3-bis(methoxycarbonyl)-1,4-benzodithiin, although *N*-(4-methylbenzyl)acetamide and 1,2-bis(methylthio)benzene were obtained in 59 and 20% yields, respectively, after as treatment mentioned above. This result implies that a concerted mechanism may not be involved in the reaction of **5** or its equivalent with alkynes.

The reaction of **1** with Tf_2O in the presence of alkenes **3** was also conducted under the same conditions (Scheme 3).§¶ The stereochemistry of the product reflects the reaction mechanism. *trans*-Stilbene (*trans*-**3a**) gave *trans*-2,3-diphenyl-2,3-dihydro-1,4-benzodithiine (*trans*-**7a**) (29% yield), whereas *cis*-stilbene (*cis*)-**3a**) afforded a mixture of *trans*-**7a** (17% yield) and (*cis*)-**7a** (10% yield). The formation of two stereoisomers (*trans*)- and



2a: $R^1 = R^2 = C_6H_5$ **6a** (44%)
2b: $R^1 = R^2 = C_6H_4Me$-*p* **6b** (64%)
2c: $R^1 = R^2 = C_6H_4OMe$-*p* **6c** (20%)
2d: $R^1 = C_6H_5$, R^2 = H **6d** (18%)
2e: $R^1 = C_6H_4Me$-*p*, R^2 = H **6e** (21%)

Scheme 2

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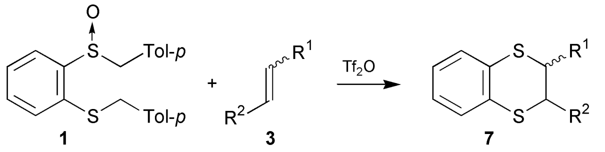
† Electronic supplementary information (ESI) available: spectral data of compounds. See http://www.rsc.org/suppdata/cc/b0/b004940i/

DOI: 10.1039/b004940i



(*trans*)-**3a**: $R^1 = R^2 = C_6H_5$	(*trans*)-**7a** (29%)
(*cis*)-**3a**: $R^1 = R^2 = C_6H_5$	(*trans*)-**7a** (17%), (*cis*)-**7a** (10%)
(*trans*)-**3b**: $R^1 = C_6H_5$, $R^2 = CO_2Et$	(*trans*)-**7b** (19%)
3c: $R^1 = C_6H_4Me$-*p*, $R^2 = H$	**7c** (32%)

Scheme 3

(*cis*)-**7a**) from *cis*-**3a**, but not from (*trans*)-**3a**, suggests a stepwise addition mechanism of benzodithiete **5** or its equivalent to carbon–carbon multiple bonds such as an Ad_E path. Ethyl (*E*)-cinnamate (*trans*-**3b**) and 4-methylstyrene **3c** gave the corresponding (*trans*)-**7b** and **7c** in 19 and 32% yields, respectively.

The redox behavior of 1,4-benzodithiin derivatives has been studied extensively from the viewpoint of cationic π-conjugated systems.[7,14] Cyclic voltammetry of 1,4-benzodithiins **6** in CH_3CN with Bu_4NClO_4 (0.1 M) at rt showed two oxidation waves, where, in all cases, the first ones are reversible and the second ones are irreversible. The redox potentials of **6a**–**e** obtained here are summarized in Table 1. The first half-wave potentials are in the range of $E^1_{1/2}$ = +0.93– +1.02 V and the second oxidation potentials are in the range of E^2_{pa} = +1.26– +1.53 V *vs*. Fc/Fc+. The first oxidation potentials of 1,4-benzodithiin derivatives are heightened with increasing the number of aromatic groups at the 2- and 3-positions owing to a π-conjugative effect: unsubstituted 1,4-benzodithiin[15] < **6d** (**6e**) < **6a** (**6b**). The oxidation potentials are lowered as the electron-donating ability of a substituent at the *para*-position of the aromatic ring is increased: **6a** > **6b** > **6c**. A good linear relationship between the first half-wave potentials and their σ_p^+ values was obtained with $\rho = 0.12$ and a correlation coefficient $r = 0.98$.

In conclusion, we have demonstrated the generation of benzodithiete **5** or its equivalent through the facile dealkylation of a 1,2-bis(benzylthio)benzene derivative **1** *via* a dithia dication **4**. The present study opens the way to the synthetic application of dithia dications.

Table 1 Redox potentials of 1,4-benzodithiin derivatives **6**[a]

Compound	E^1_{pa} [b]	$E^1_{1/2}$ [b]	E^2_{pa} [b]
6a	1.06	1.02	1.52
6b	1.04	1.00	1.47
6c	0.96	0.93	1.26
6d	1.03	1.00	1.53
6e	0.99	0.96	1.53

[a] In CH_3CN with Bu_4NClO_4 (0.1 M) at rt. [b] V *vs*. Fc/Fc+; scan rate, 0.1 V s^{-1}.

This work was supported in part by grants-in-aid from the Ministry of Education, Science, Sports and Culture, Japan (No. 11440186) and University of Tsukuba (TARA project fund).

Notes and references

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§ To a solution of **1** in $CH_3CN–CH_2Cl_2$ (v/v 1:1) at −60 °C under Ar were added 1 eq. of Tf_2O and, after about 30 s, 2 eq. of **2** or **3**. The mixture was stirred at −60 °C for 10 min and then at rt for 1 h, and quenched with aqueous $NaHCO_3$. Extraction with CH_2Cl_2 followed by purification with silica gel chromatography gave 1,4-benzodithiin derivatives **6** from **2** or 2,3-dihydro-1,4-benzodithiin derivatives **7** from **3** and *N*-(4-methylbenzyl)-acetamide in modest yields.

¶ Representative data for **6b**: wax; ^1H NMR (270 MHz, $CDCl_3$) δ 2.26 (s, 6H), 6.96 (d, *J* = 7.8 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 4H), 7.25 (dd, *J* = 3.5 and 5.7 Hz, 2H), 7.46 (dd, *J* = 3.5 and 5.7 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.2, 127.6, 127.9, 128.8, 129.6, 133.8, 135.5, 136.1, 137.5; EI-MS *m*/*z* 346 (M^+); Calc. for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24. Found: C, 76.02; H, 5.49%. For *trans*-**7a**: mp 120–121 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 4.67 (s, 2H), 7.10 (dd, *J* = 3.8 and 5.9 Hz, 2H), 7.14–7.19 (m, 10H), 7.33 (dd, *J* = 3.8 and 5.9 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 54.6, 125.4, 127.8, 128.0, 128.1, 128.4, 134.2, 138.3; EI-MS *m*/*z* 320 (M^+); Calc. for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03. Found: C, 74.84; H, 5.19%.

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