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# An Effective and Selective Synthesis of Sterically Crowded Benzotrithioles from Benzodithiastannoles via Benzotrithiole 2-Oxides

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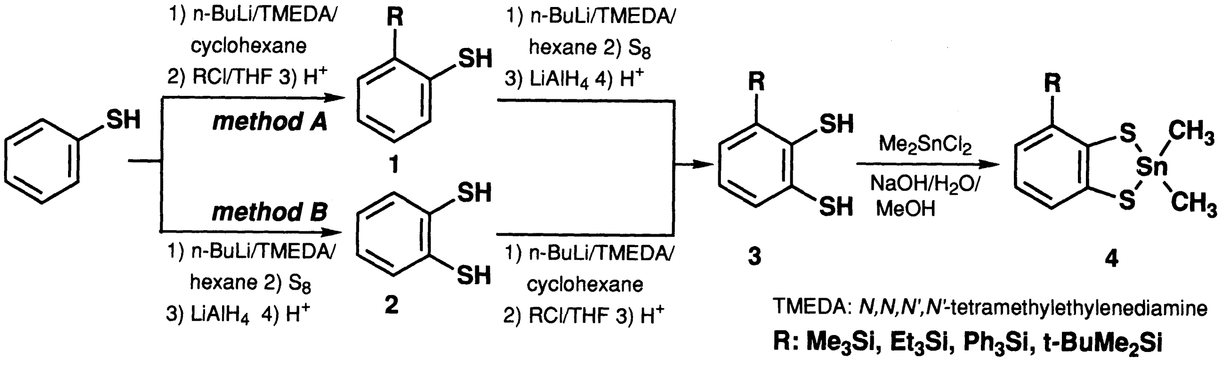
Sterically crowded benzotrithioles were efficiently and selectively prepared by the reduction of corresponding benzotrithiole 2-oxides which were readily obtained on treatment of benzodithiastannoles, synthetic equivalents of benzenedithiols, with thionyl chloride.

Considerable current interest has been focused on organic cyclic polysulfides because of their chemical reactivities,1) synthetic utility,2) and recent discovery in marine-natural products.3) Although there have been many reports on the synthesis of cyclic polysulfides containing linked five,4) seven,5) eight,6) and nine7) sulfur atoms, only a few examples of trithioles have been reported due to their less stability.8) Furthermore, it is well-known that trithiole framework is difficult to prepare selectively and generally obtained as a mixture together with other ring-sized cyclic polysulfides, which is hardly separated into each pure compound. As a part of our search for new stable benzotrithioles we report here a very efficient and useful method for the synthesis of stable trithioles fused to sterically crowded benzene ring.

To increase the stability of benzotrithioles, trialkylsilyl and triarylsilyl substituents were used as steric protection and/or electronic stabilization groups, because introductions of the silyl substituents onto benzene ring were easily achieved by treatment with the corresponding silyl chlorides as follows. 3-Trialkylsilyl or triarysilyl substituted 1,2-benzenedithiols **3** were prepared by the two methods (A and B) using stepwise ortho lithiations which were modified methods previously reported.9) Dithiols **3** were treated with dimethyltin dichloride under basic conditions to give the corresponding 4-substituted 2,2-dimethyl-1,3,2-benzodithiastannoles **4**10) in moderate yields, which were used as synthetic equivalents of dithiols **3** in the following reactions (Scheme 1, Table 1).



TMEDA: *N,N,N',N'*-tetramethylethylenediamine
**R: $Me_3Si$, $Et_3Si$, $Ph_3Si$, t-$BuMe_2Si$**

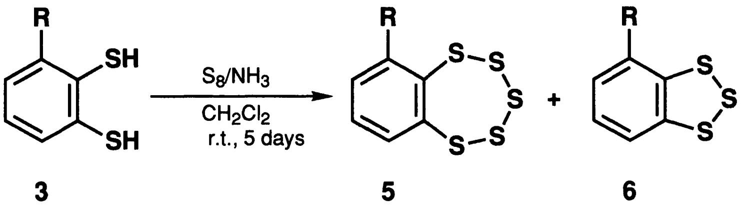
Scheme 1.

Table 1. Preparation of 4-Substituted 2,2-Dimethyl-1,3,2-benzodithiastannoles **4**

| R | Method | n-BuLi/TMEDA eq./eq. | Yield of **1** or **2** % | n-BuLi/TMEDA eq./eq. | Yield of **3**[a] % | Yield of **4**[a] % |
|---|---|---|---|---|---|---|
| $Me_3Si$ | A | 2.2/2.2 | 79 (**1a**) | 2.2/2.2 | 94 (**3a**) | 79 (**4a**) |
| $Et_3Si$ | A | 2.2/2.2 | 71 (**1b**) | 3.3/3.3 | 75 (**3b**) | 64 (**4b**) |
| $Ph_3Si$ | A | 2.2/2.2 | 58 (**1c**) | 3.3/3.3 | <5 (**3c**) | |
| | | | | 5.0/5.0 | <5 (**3c**) | |
| | B | 2.2/2.2 | 82 (**2**) | 3.3/3.3 | 48 (**3c**) | |
| | | | | 5.0/5.0 | 65 (**3c**) | 41 (**4c**) |
| t-$BuMe_2Si$ | A | 2.2/2.2 | 76 (**1d**) | 5.0/5.0 | <5 (**3d**) | |
| | B | 2.2/2.2 | 82 (**2**) | 3.3/3.3 | 40 (**3d**) | |
| | | | | 5.0/5.0 | 69 (**3d**) | 43 (**4d**) |

a) Based on **1** or **2**.

To examine the preferential ring size of the cyclic polysulfide in these substituted-benzene fused systems, several benzenedithiols **3** were allowed to react with elemental sulfur under bubbling of gaseous ammonia (Scheme 2, Table 2). These results suggest that pentathiepin structure **5**[11] may be a thermodynamically favored product as well as the case of unsubstituted benzenedithiol. Interestingly, more crowded benzene dithiols bearing triphenylsilyl or tert-butyldimethylsilyl group gave the corresponding trithioles **6** besides the pentathiepins **5** though it was a minor product.



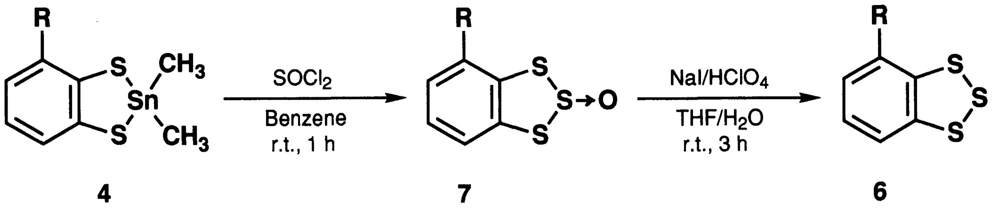
Scheme 2.

Table 2. Test of Preferential Ring Size

| R | | Ratio[a] **5** | Ratio[a] **6** |
|---|---|---|---|
| $Me_3Si$ | (**3a**) | 100 (**5a**) | 0 (**6a**) |
| $Et_3Si$ | (**3b**) | 100 (**5b**) | 0 (**6b**) |
| $Ph_3Si$ | (**3c**) | 80 (**5c**) | 20 (**6c**) |
| t-$BuMe_2Si$ | (**3d**) | 77 (**5d**) | 23 (**6d**) |

a) Determined by 400 MHz $^1H$ NMR.

We turned our attention to the selective synthesis of thermodynamically unfavored trithiole ring. We chose commercially available thionyl chloride ($SOCl_2$) as an S1 source, because sulfur dichloride ($SCl_2$) was generally supplied as a mixture of $SCl_2$ and sulfur monochloride ($S_2Cl_2$), which was hardly separated into each pure compound. Furthermore, it has been reported that ortho dithiols reacted with $S_2Cl_2$ to give the corresponding thermodynamically stable pentathiepin ring as a major product.[4,8d] When 4-substituted 2,2-dimethyl-1,3,2-benzodithiastannoles **4** were allowed to react with 1.2 equiv. of $SOCl_2$ in benzene at room temperature for 1 h under the dark conditions,[12] corresponding trithiole 2-oxides **7** were obtained in excellent yields. Subsequently, the solution of trithiole 2-oxides **7** in THF was treated with 5 equiv. of NaI in water and 65% $HClO_4$ at 0 °C.[13] Reduction on the sulfur atom was selectively performed without ring opening, and 4-substituted 1,2,3-benzotrithioles **6**[14] were obtained after usual work-up and purification by silica gel column chromatography (eluent, $CHCl_3$:$CCl_4$=1:1). Although relatively unhindered trithioles (**6a**, **6b**) could be detected only in solution, trithioles **6c** and **6d** having efficient stabilization group were isolated in moderate yields.



Scheme 3.

Table 3. Preparation of 4-Substituted 1,2,3-Benzotrithioles **6**

| R | | Yield of **7**/% | | Yield of **6**/%[a)] | |
|---|---|---|---|---|---|
| $Me_3Si$ | (**4a**) | 96 | (**7a**) | —[b)] | (**6a**) |
| $Et_3Si$ | (**4b**) | 94 | (**7b**) | —[b)] | (**6b**) |
| $Ph_3Si$ | (**4c**) | 90 | (**7c**) | 50 | (**6c**) |
| t-$BuMe_2Si$ | (**4d**) | 94 | (**7d**) | 62 | (**6d**) |

a) Based on **7**. b) Not isolated.

Consequently, our present method will provide us with a new preparative route for various substituted benzotrichalcogenoles. Further studies for the synthesis of other cyclic polychalcogenides are in progress.

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10) 4-Substituted 2,2-dimethyl-1,3,2-benzodithiastannoles **4** were characterized by physical and spectroscopic means. The data will be reported in full paper.

11) **5a**: yellow crystals; mp 74.0-74.5 °C; IR (KBr) 2948, 2891, 1407, 1360, 1245, 1148, 1079, 839, 789, and 756 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.85 (dd, J=7.8, 1.5 Hz, 1H, ArH), 7.51 (dd, J=7.4, 1.5 Hz, 1H, ArH), 7.28 (dd, J=7.8, 7.4 Hz, 1H, ArH), 0.39 (s, 9H, SiCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=150.1, 149.1, 144.7, 137.0, 136.3, 129.2, 1.0; MS m/z 308 (M$^+$). Found: C, 35.05; H, 3.92%. Calcd for $C_9H_{12}S_5Si$: C, 35.05; H, 3.96%. **5b**: yellow oil; IR (neat) 2953, 2873, 1457, 1417, 1361, 1238, 1127, 1004, 961, 765, and 727 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.86 (dd, J=7.7, 1.4 Hz, 1H, ArH), 7.47 (dd, J=7.4, 1.4 Hz, 1H, ArH), 7.28 (dd, J=7.7, 7.4 Hz, 1H, ArH), 0.96-0.91 (m, 15H, SiCH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=150.4, 146.2, 144.6, 137.4, 137.0, 129.0, 7.6, 4.8. Found: *m/z* 349.9813. Calcd for $C_{12}H_{18}S_5Si$: M, 349.9781. **5c**: yellow crystals; mp 197 °C (decomp); IR (KBr) 3067, 1542, 1484, 1428, 1364, 1110, 1082, 739, and 701 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.95 (dd, J=7.6, 1.5 Hz, 1H, ArH), 7.58-7.53 (m, 6H, ArH), 7.42-7.34 (m, 9H, ArH), 7.32 (dd, J=7.4, 1.5 Hz, 1H, ArH), 7.26 (dd, J=7.6, 7.4 Hz, 1H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=151.5, 144.7, 143.1, 139.6, 138.3, 136.1, 134.3, 129.7, 129.2, 128.1; MS m/z 494 (M$^+$). Found: C, 58.06; H, 3.67%. Calcd for $C_{24}H_{18}S_5Si$: C, 58.26; H, 3.67%. **5d**: yellow oil; IR (neat) 2952, 2927, 2879, 2855, 1468, 1360, 1249, 1128, 1078, 1007, 837, 823, and 774 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.87 (dd, J=7.7, 1.4 Hz, 1H, ArH), 7.52 (dd, J=7.5, 1.4 Hz, 1H, ArH), 6.85 (dd, J=7.7, 7.5 Hz, 1H, ArH), 0.91 (s, 9H, SiBu$^t$), 0.44 (s, 3H, SiCH$_3$), 0.39 (s, 3H, SiCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=150.3, 146.7, 144.9, 137.9, 137.1, 128.7, 27.3, 17.6, -1.5, -1.8. Found: *m/z* 349.9792. Calcd for $C_{12}H_{18}S_5Si$: M, 349.9781.

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14) **6c**: yellow crystals; mp 55.0 °C (decomp); IR (KBr) 3045, 2997, 1958, 1885, 1822, 1779, 1551, 1484, 1427, 1359, 1126, 1082, 783, 761, 742, 720, and 700 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.61-7.58 (m, 6H, ArH), 7.47 (dd, J=7.0, 1.7 Hz, 1H, ArH), 7.46-7.36 (m, 9H, ArH), 7.02 (dd, J=7.3, 1.7 Hz, 1H, ArH), 6.99 (dd, J=7.3, 7.0 Hz, 1H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=149.2, 142.0, 136.4, 135.6, 132.5, 131.6, 130.1, 128.2, 126.2, 125.2; MS m/z 430 (M$^+$). Found: C, 66.84; H, 4.33%. Calcd for $C_{24}H_{18}S_3Si$: C, 66.93; H, 4.21%. **6d**: yellow oil; IR (neat) 3039, 2955, 2852, 1915, 1854, 1800, 1548, 1464, 1356, 1250, 1127, 1080, 1034, 823, 769, and 671 cm$^{-1}$; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$=7.41 (dd, J=7.5, 1.2 Hz, 1H, ArH), 7.18 (dd, J=7.4, 1.2 Hz, 1H, ArH), 7.03 (dd, J=7.5, 7.4 Hz, 1H, ArH), 0.92 (s, 9H, SiBu$^t$), 0.37 (s, 6H, SiCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$=147.9, 140.7, 136.0, 134.1, 125.5, 124.3, 26.8, 18.1, -4.0. Found: *m/z* 286.0441. Calcd for $C_{12}H_{18}S_3Si$: M, 286.0339.

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