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# Formation and Oxidation Reaction of Polychalcogenadisilabicyclo[k.l.m]alkanes and Their Germanium Analogues

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**Abstract:** Polychalcogenadisilabicyclo[k.l.m]alkanes and their germanium analogues were systematically synthesized by the reaction of tris(trimethylsilyl)methylsilane ($TsiSiH_3$) or tris(trimethylsilyl)methylgermane with elemental sulfur or selenium. Structures of the resulting bicyclo[k.l.m]alkanes were confirmed by X-ray diffraction analysis or $^{77}Se$ NMR spectroscopy. Oxidation of polythia-1,3-disilabicyclo-[k.l.m]alkanes with a peracid afforded the corresponding ring expansion products.

## INTRODUCTION

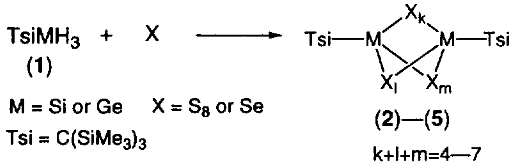
The chemistry of polychalcogenides has been widely studied during the past decade. Interest in polychalcogenides focuses not only on their structural features but also on synthetic and biological utilities.[1] Although polychalcogenides containing group 14 elements have been reported,[2] polychalcogena-disilabicycloalkanes and their germanium analogues have been little studied. We have already reported the synthesis of polychalcogena-1,3-disilabicyclo[k.l.m]alkanes which are good precursors of trichalcogena-1,3-disilabicyclo[1.1.1]pentanes.[3] We have succeeded in the synthesis and structural determineation of 1,3-bis-substituted 2,4,5-trichalcogena-1,3-disilabicyclo[1.1.1]pentane by taking advantage of an excellent steric protection group, tris(trimethylsilyl)methyl (denoted as Tsi hereafter) by means of photodechalcogenation of polychalcogenadisilabicyclo[k.l.m]alkanes.[3]

The most interesting structural features of trichalcogenadisilabicyclo[1.1.1]pentanes are to have remarkable short bridgehead distances without the formal Si-Si bond, which have been the focus of much attention for theoretical and practical chemists.[3,4] Herein we report detail accounts of the synthesis, structures and reactions of polythiadigermabicyclo[k.l.m]alkanes and the oxidation of polythiadisilabicyclo[k.l.m]alkanes.

## RESULTS AND DISCUSSION

### *Synthesis of Polychalcogenadisilabicyclo[k.l.m]alkanes and Their Germanium Analouges*

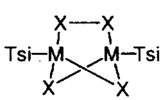
Polychalcogenadisilabicyclo[k.l.m]alkanes and their germanium analogues were prepared by the reaction of tris(trimethylsilyl)methylsilane ($TsiSiH_3$) or $TsiGeH_3$ with excess amount of elemental sulfur or selenium in the presence of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) as shown in equation 1 and Table 1.



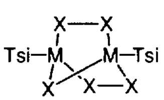
(1)

Table 1. Yields and Reaction Conditions in Equation 1.

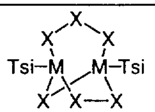
| | M | X | reaction conditions | [k.l.m] 5<br>[3.3.1] | Yield (%) 4<br>[3.2.1] | 3<br>[2.2.1] | 2<br>[2.1.1] | |
|---|---|---|---|---|---|---|---|---|
| a ) | Si | $S_8$ | 30 eq. decalin, 190—200°C | ------ | 12 | 12 | 22 | Reference 3c, d |
| b ) | Si | Se | 10 eq. decalin, DBU, 160°C | ------ | ------ | ------ | 19 | Reference 3a, b |
| c ) | Ge | $S_8$ | 30 eq. $Ph_2O$, 150—160°C | 9 | 26 | 8 | 8 | This work |
| d ) | Ge | Se | 10 eq. decalin, DBU, 160°C | ------ | 27 | 12 | 19 | Reference 5 |



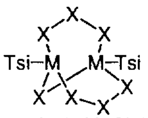
**(2a)** M=Si, X=S
**(2b)** M=Si, X=Se
**(2c)** M=Ge, X=S
**(2d)** M=Ge, X=Se



**(3a)** M=Si, X=S
**(3b)** M=Si, X=Se
**(3c)** M=Ge, X=S
**(3d)** M=Ge, X=Se

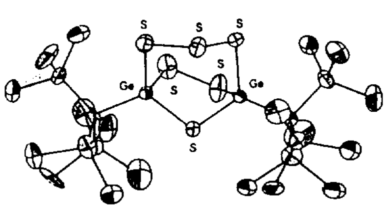


**(4a)** M=Si, X=S
**(4b)** M=Si, X=Se
**(4c)** M=Ge, X=S
**(4d)** M=Ge, X=Se



**(5a)** M=Si, X=S
**(5b)** M=Si, X=Se
**(5c)** M=Ge, X=S
**(5d)** M=Ge, X=Se

We could confirm the structures of tetraselenadigermabicyclo[2.1.1]hexane (**2d**), pentaselenadigermabicyclo[2.2.1]heptane (**3d**), and hexaselenadigermabicyclo[3.2.1]octane (**4d**) by $^{77}$Se NMR spectra.[5] Unfortunately, by means of NMR and other spectroscopic methods the structures of polythiadisilabicyclo-[k.l.m]alkanes could not be distinguished. Then, these structures of **2a**, **3a**, and **4a** are confirmed by X-ray structure analysis to be 2,4,5,6,7,8-hexathia-1,3-disilabicyclo[3.2.1]octane, 2,4,5,6,7-pentathia-1,3-disilabicyclo[2.2.1]heptane, and 2,4,5,6-tetrathia-1,3-disilabicyclo[2.1.1]hexane, respectively.[3d] In the case of polythiadigermabicyclo[k.l.m]alkanes, TsiGeH$_3$ was reacted with 30 equiv. of elemental sulfur at 160 °C for 48 h to give 2,4,5,6,7,8,9-heptathia-1,3-digermabicyclo[3.3.1]nonane (**5c**) in 9% yield along with 2,4,5,6,7,8-hexathia-1,3-digermabicyclo[3.2.1]octane (**4c**, 26%), 2,4,5,6,7-pentathia-1,3-digermabicyclo-[2.2.1]heptane (**3c**, 8%), and 2,4,5,6-tetrathia-1,3-digermabicyclo[2.1.1]hexane (**2c**, 8%), respectively.



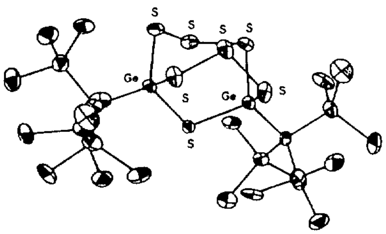
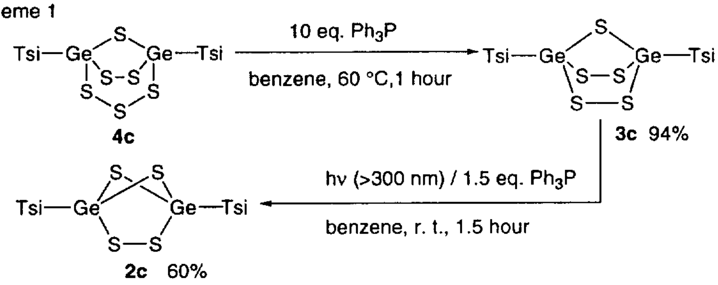


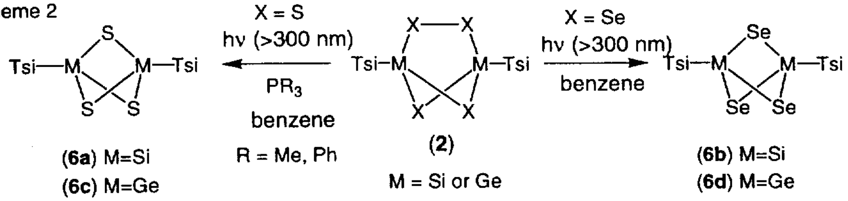
Figure 1. ORTEP Drawing of **4c**. Figure 2. ORTEP Drawing of **5c**.

The structures of **4c** and **5c** were unequivocally determined by single crystal X-ray diffraction analysis as depicted in Figures 1 and 2. Dechalcogenation reactions of polychalcogenadigermabicyclo[k.l.m]alkanes can be performed with triphenylphosphine in the presence or absence of irradiation by high pressure Hg lamp (hv>300 nm) as shown in Schemes 1 and 2. When reacted with 1 equiv. of triphenylphosphine at 60 °C after 12 h, **4c** was converted to **3c**. Using 10 equiv. of $PPh_3$, the desulfurization reaction of **4c** was completed during 1 h to afford **3c** in 94% yield. As for **4a**, the desulfurization with 1 equiv. of $PPh_3$ is completed during 30 min at room temperature, which is much faster than that of **4c**.[3d] Further desulfurization of **3c** was performed under irradiation with a high pressure Hg lamp (hv > 300 nm) in the presence of 1.5 equiv. of $PPh_3$ to give **2c** in 60% yield. This photodesulfurization reaction occurred via a thiyl radical intermediate.[6] We have already reported that syntheses and structure analysis of **6a**,[3c] **6b**,[3a] and **6d**[5]. Desulfurization of **2c** with triphenylphosphine under irradiation was monitored by $^{1}H$ and $^{13}C$ NMR spectra. After the irradiation for 55 min., **2c** was completely consumed and 2,4,5-trithia-1,3-digermabicyclo[1.1.1]pentane **6c** was yielded.

Scheme 1



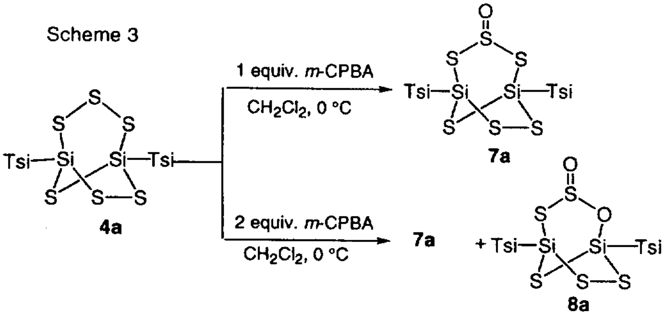
Scheme 2



## *Oxidation Reaction of Polythiadisilabicyclo[k.l.m]alkanes by m-Chloroperbenzoic Acid.*

The hexathiadisilabicyclo[3.2.1]octane **4a** reacted with 1 equiv. of *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane at 0° C to give 7-sulfoxy-2,4,5,6,8-pentathia-1,3-disilabicyclo[3.2.1]octane (**7a**) in 68% yield.

Scheme 3

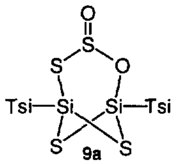


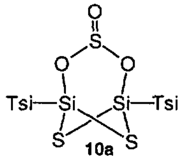
On the other hand, by using of 2 equiv. of *m*-CPBA, **8a** was yielded in 13% yield along with **7a** in 27% yield as shown in Scheme 3. Oxidation reactions of polythiadisilabicyclo[k.l.m]alkanes **2a**, **3a**, **4a**, and **6a** are summarized in Table 2. In the case of oxidation of **2a** and **3a** using 2 equiv. of *m*-CPBA, the ring expansion products **9a** and **8a** were yielded in 80% and 83% yields, respectively. Even using 1 equivalent of m-CPBA, pentathiadisilabicyclo[2.2.1]heptane-S-oxide and tetrathiadisilabicyclo[2.1.1]hexane-S-oxide could not be observed, but **9a** and **8a** were yielded along with the recovery **2a** and **3a**, respectively.

Table 2. Yields and Oxidation Conditions of Polythiadisilabicyclo[k.l.m]alkanes with *m*-CPBA.

| compounds | amt. of *m*-CPBA [a] | products (yields, %) |
|---|---|---|
| **2a** | 1 equiv. | **9a** (33) + **2a** (34) |
| | 2 equiv. | **9a** (80) |
| **3a** | 1 equiv. | **8a** (68) + **3a** (32) |
| | 2 equiv. | **8a** (83) |
| **4a** | 1 equiv. | **7a** (68) |
| | 2 equiv. | **7a** (27) + **8a** (13) |
| **6a** | 1 equiv. | **10a** (27) + **6a** (37) |
| | 2 equiv. | **10a** (62) |

a) Reaction conditions; $CH_2Cl_2$, 0 °C.


**9a**


**10a**

Interestingly, the oxidation of **6a** with 2 equivalent of *m*-CPBA gave the corresponding sulfite **10a** in 62% yield. This rearrangement was also observed when the reaction was carried out under -40°C and treated by $NH_3$ gas for the neutralization of the resulting *m*-chlorobenzoic acid. The structure of **10a** was confirmed by X-ray structure analysis as depicted in Figure 3.

The two possible machanisms are shown in Schemes 4 and 5. In the case of **2a** or **3a**, the disulfide moiety is easily oxidized by *m*-CPBA, then the following rearrangement smoothly takes place due to the strong affinity of silicon with oxygen. On the other hand, **6a** is oxidized with *m*-CPBA, then the following rearrangement and second oxidation occur twice to afford **10a**.

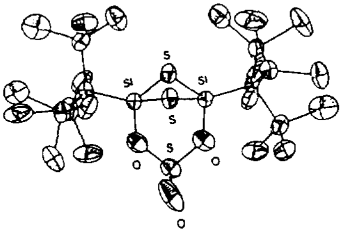
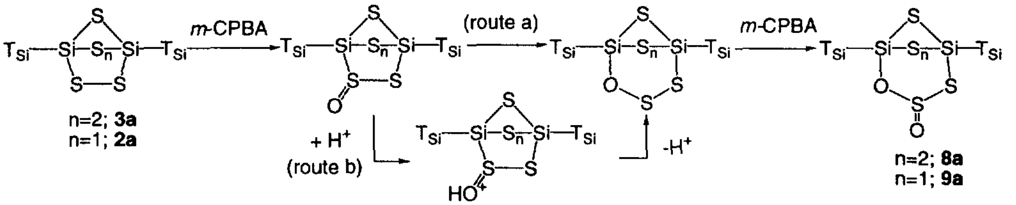
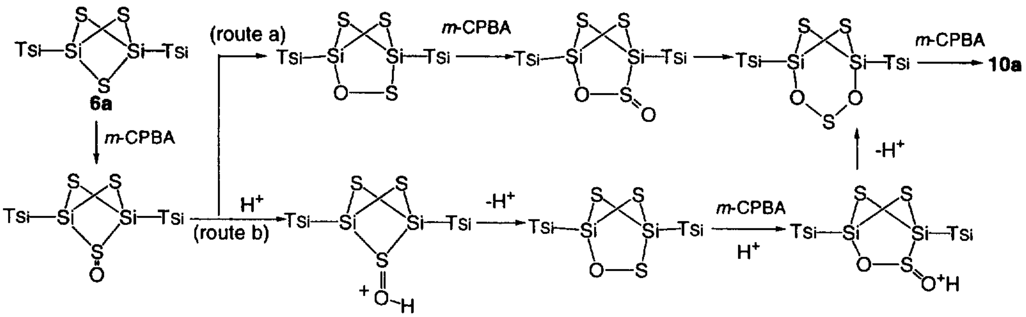


Figure 3. ORTEP Drawing of **10a**

Scheme 4



Scheme 5



These ring expansion reactions were never observed in the oxidation of bicyclo[2.1.1]thiahexane-*S*-oxide which is carbon analogue of **2a**-S-oxide.[7] Therefore, these rearrangements are not due to the ring strain of the corresponding bicyclic skeleton but the strong affinity of silicon to oxygen.

## EXPERIMENTAL

*General Considerations:*

All manipulations were performed using standard Schlenk technique under an argon atmosphere. Solvents were dried over sodium benzophenone ketyl, distilled, and degassed prior to use. The reagents used in this study were purchased from commercial sources and purified, dried and degassed as necessary. Preparative gel permeation liquid chromatography (GPC) was carried out on LC-908 on JAIGEL 1H and 2H columns (Japan Analytical Industry, styrene-divinylbenzene copolymer, pore size 25 Å) with toluene as solvent. NMR spectra were run on either a Bruker AC-400 or AC-300 spectrometer at 400 and 300 MHz, respectively. $^{1}$H and $^{13}$C NMR spectra were referenced to residual solvent resonances which were calibrated against tetramethylsilane. $^{29}$Si NMR spectra were referenced to external tetramethylsilane. Infrare spectra were recorded on a JASCO FT/IR-5000 using KBr tablet. UV spectra were carried out on a JASCO Ubest-55 spectrometer. Mass spectra (EI) and high-resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer. Elemental analyses were carried out on Perkin Elmer 2400 by the Chemical Analytical Center of the University of Tsukuba. All melting points are uncorrected.

**Preparation of TsiGeCl$_3$.**[8] To a THF (20 mL) solution of tetrachlorogermane (18.6 g, 86.0 mmol) which was charged to a three-necked round-bottomed flask prepared with a thermometer and a rubber septum, a THF (30 mL) solution of TsiLi (86 mmol) was added at 20 °C via a cannula. It was stirred at room temperature. After common work up procedure, the residue was recrystallized from ethanol to yield TsiGeCl$_3$ (9.5 g) as white crystals (mp > 300 °C) in 27% yield. $^{1}$H NMR (400 MHz, $C_6D_6$) δ 0.31 (s); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 0.0 (q), 1.2 (s); $^{29}$Si NMR (79.5 MHz, $C_6D_6$) δ 0.0 (SiMe$_3$); MS, m/z 395 ($M^+$-15). Anal. Calcd for $C_{10}H_{27}Cl_3GeSi_3$: C, 29.27; H, 6.59. Found: C, 29.72; H,6.61.

**Preparation of TsiGeH$_3$.** LiAlH$_4$ (1.1 g, 30 mmol) and 20 mL of THF were charged in a 200 mL round-bottomed flask prepared with a refluxing condenser and a dropping funnel. A THF (35 mL) solution of

TsiGeCl$_3$ (6.0 g, 15.0 mmol) was slowly dropped into a THF suspension of LiAlH$_4$ via a dropping funnel. After stirred for 1 h, the mixture was quenched by saturated aqueous ammonium chloride and inorganic salts were filtered off. The filtrate was extracted by Et$_2$O, then organic layers were combined and dried over Na$_2$SO$_4$. After removal of solvents, the residue was purified by silica-gel column chromatography (Eluent; hexane) to give 3.2 g of TsiGeH$_3$ as white crystals (mp. 257 °C) in 69% yield. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 0.19 (s), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 2.70 (q), 3.39 (s); MS, m/z 293 (M$^+$-15).

**Reaction of TsiGeH$_3$ with elemental sulfur.** A mixture of TsiGeH$_3$ (620 mg, 2.01 mmol), S$_8$ (3.5 g, 109 mmol), and 6.0 mL of Ph$_2$O was heated at 150-160 °C for 48 h. After removal of solvents in vacuo, the residue was dissolved in CH$_2$Cl$_2$. After filtration and removal of the solvent under reduced pressure, the residue was charged on silica-gel column chromatography (eluent; hexane-CH$_2$Cl$_2$). The resulting yellow solid was purified by GPC (eluent; toluene) and preparative TLC (hexane:CHCl$_3$ = 8 : 1) to give **2c**, **3c**, **4c**, and **5c** in 8 (57 mg), 8 (62 mg), 26 (209 mg) and 9% (75 mg) yields, respectively. **2c**: pale yellow crystals, mp 252 °C (decomp.). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 0.42 (s); $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 4.5 (q), 5.7 (s); UV (*n*-Hexane) $\lambda_{max}$/nm 295 (sh, $\varepsilon$ 510), 375 (sh, 50); MS, m/z 736 (M$^+$). Anal. Calcd for C$_{20}$H$_{54}$Ge$_2$Si$_6$S$_4$: C, 32.59; H, 7.33; S, 17.40. Found: C, 32.78; H, 7.41; S, 17.33. **3c**: yellow crystals, mp 286°C (decomp.). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 0.40 (s); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 4.7 (q), 5.2 (s); UV (*n*-Hexane) $\lambda_{max}$/nm 262 (sh, $\varepsilon$ 4400), 329 (sh, 610); MS, m/z 768 (M$^+$). Anal. Calcd for C$_{20}$H$_{54}$Ge$_2$Si$_6$S$_5$: C, 31.23; H, 7.08; S, 20.83. Found: C, 31.41; H, 7.06; S, 20.80. **4c**: yellow crystals, mp >300 °C. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 0.39 (s); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 1.4 (s), 5.1 (q); $^{29}$Si NMR (79.5 MHz, C$_6$D$_6$) $\delta$ -0.45 (SiMe$_3$); UV (*n*-Hexane) $\lambda_{max}$/nm 256 (sh, $\varepsilon$ 6850), 306 (sh, 1950); MS, m/z 768 (M$^+$-32). Anal. Calcd for C$_{20}$H$_{54}$Ge$_2$Si$_6$S$_6$: C, 29.98; H, 6.74; S, 24.01. Found: C, 30.07; H, 6.82; S, 23.39. **5c**: yellow crystals, mp 281 °C (decomp.). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 0.37 (s); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 1.9 (q), 5.4 (s); $^{29}$Si NMR (79.5 MHz, C$_6$D$_6$) $\delta$ -1.80 (SiMe$_3$); UV (*n*-Hexane) $\lambda_{max}$/nm 250 (sh, $\varepsilon$ 8800), 294 (sh, 2680); MS, m/z 768 (M$^+$-32x2). Anal. Calcd for C$_{20}$H$_{54}$Ge$_2$Si$_6$S$_7$: C, 28.83; H, 6.53; S, 26.93. Found: C, 28.77; H, 6.69; S, 26.62.

**Reaction of TsiGeH$_3$ with Elemental Selenium in the Presence of DBU.**[5] A mixture of TsiGeH$_3$ (1.0 g, 3.25 mmol), Se (2.5 g, 32.5 mmol), DBU (0.5 mL), and 20 mL of decalin was heated at 150-160 °C for 18 h. After filtration of selenium and removal of solvents in vacuo, the residue was dissolved in CH$_2$Cl$_2$. After filtration and removal of solvent under reduced pressure, the residue was charged on silica-gel column chromatography (eluent; hexane-CH$_2$Cl$_2$). The resulting yellow solid was purified by GPC (eluent; toluene) and preparative TLC (eluent; hexane) to give **2d**, **3d**, and **4d** in 19 (296 mg), 12 (198 mg), and 27% (450 mg) yields, respectively.

**Desulfurization of 4c with PPh$_3$.** (a) A benzene (2.4 mL) solution of **4c** (80.0 mg, 0.10 mmol) and triphenylphosphine (26.2 mg, 0.10 mmol, 1 eq.) was heated at 60 °C overnight. After removal of solvent, the residue was separated by silica-gel column chromatography (eluent; *n*-hexane-CH$_2$Cl$_2$) to give **3c** (70 mg, 92%). (b) A benzene (2.4 mL) solution of **4c** (80.0 mg, 0.10 mmol) and triphenylphosphine (262 mg, 1.0 mmol, 10 eq.) was heated at 60 °C for 1 h. After removal of solvent, the residue was separated by silica-gel column chromatography (eluent; *n*-hexane-CH$_2$Cl$_2$) to give **3c** (72 mg, 94%).

**Desulfurization of 3c with PPh$_3$.** A toluene (0.5 mL) solution of **3c** (15 mg, 0.020 mmol) and triphenylphosphine (52 mg, 0.198 mmol, 10 eq.) in a 20 mL round-bottomed flask was refluxed. After 24 h, **3c** was not changed by TLC and recovered by TLC.

**Desulfurization of 3c with PPh$_3$ under irradiation.** A benzene (4.0 mL) solution of **3c** (138 mg, 0.18 mmol) and triphenylphosphine (70 mg, 0.267 mmol, 1.5 eq.) in a Pyrex Schlenk tube was irradiated by a high-pressure Hg lamp at room temperature. After 1.5 h, **3c** was completely consumed by TLC. After removal of solvent, the residue was separated by preparative TLC to afford **2c** (79 mg, 60% yield).

**Desulfurization of 2c with PPh$_3$ under irradiation.** A benzene-d$_6$ (0.4 mL) solution of **2c** (10 mg, 1.36x10$^{-2}$ mmol) and triphenylphosphine (3.6 mg, 1.36x10$^{-2}$ mmol) in a NMR tube was irradiated by a high-pressure Hg lamp at room temperature. The reaction was monitored by $^{1}$H and $^{13}$C NMR spectroscopy. After 55 min, the signal of **2c** was completely consumed, and a new signal appeared at 0.13 ppm in $^{1}$H NMR, and at 3.4 ppm at $^{13}$C NMR spectroscopy. We could observe the molecular ion peak (m/z 704 (M$^+$)) stemmed from **6c** as well as that of hydrolyzed product of **6c** (i. e., 722 (M$^+$)).

**Deselenation of 4d with PPh$_3$.** A benzene (4.5 mL) solution of **4d** (10 mg, 9.21x10$^{-3}$ mmol) and triphenylphosphine (2.4 mg, 9.21x10$^{-3}$ mmol, 1.0 eq.) in a 20 mL round-bottomed flask was heated at 60°C for 3.5 h. After removal of the solvent, the residue was separated by TLC (eluent; hexane) to afford **3d** (7.7 mg) in 83% yield.

**Deselenation of 3d with PPh$_3$.** A benzene-*d*$_6$ (0.4 mL) solution of **3d** ( 7.0 mg, 6.96x10$^{-3}$ mmol) and triphenylphosphine (1.8 mg, 6.96x10$^{-3}$ mmol, 1.0 eq.) in an NMR tube was heated at 60°C. After 24 h, deselenation was not observed by $^{1}$H and $^{13}$C NMR spectroscopy and **3d** was recovered by TLC.

**Deselenation of 3d under irradiation.** A benzene-*d*$_6$ (0.4 mL) solution of **3d** (8.0 mg, 7.94x10$^{-3}$ mmol) in an NMR tube was irradiated by a high-pressure Hg lamp at room temperature. The reaction was monitored by $^{1}$H and $^{13}$C NMR spectra. After 60 min, **3d** was completely consumed, and **2d** and **6d** were formed in the ratio of 1 : 3 ($^{1}$H and $^{13}$C NMR).

**Deselenation of 2d under irradiation.** A benzene (30 mL) solution of **2d** (99.7 mg, 0.108 mmol) in a Pyrex Schlenk tube was irradiated by a high-pressure Hg lamp at room temperature. After irradiation for 70 min, **2d** was completely consumed (TLC). Liberated selenium was filtered off through celite and the solvent was removed in vacuo. The residue was separated by preparative HPLC (eluent; toluene) and recrystallization from benzene gave **6d**[3e] (65.4 mg) in 72% yield. A benzene solution of **6d** was hydrolyzed by moisture in air to yield **4**, quantitatively. **4**: white crystals, $^{1}$H NMR (300 MHz, C$_6$D$_6$) δ 0.42 (s, 27H), 0.44 (s, 27H), 2.87 (1H, s), 4.38 (s, 1H); MS, m/z 864 (M$^+$).

**Oxidation of polythiadisilabicyclo[k.l.m]alkanes with m-CPBA.**

**(a) Oxidation of 4a with 1 equiv. of *m*-CPBA.** A typical procedure of oxidation of polythiadisilabicyclo[k.l.m]alkane with m-CPBA is the following: To a dichloromethane (6 mL) solution of **4a** (29.8 mg) a dichloromethane (12 mL) solution of 1 equivalent of m-CPBA (14.5 mg) was added at 0. C. It was stirred for 1 h, and the resulting suspension was filtered. After removal of solvent, the residue was separated by TLC (eulent; *n*-Hexane : CH$_2$Cl$_2$ = 4 : 1) to give **7a** (20.5 mg) in 68% yield. **7**: pale yellow crystals, $^{1}$H-NMR (300 MHz, C$_6$D$_6$) δ 0.37 (s);$^{13}$C-NMR (75 MHz, C$_6$D$_6$) δ 5.5 (q), 6.6 (s); $^{29}$Si-NMR (59 MHz, C$_6$D$_6$) δ -0.3 (SiMe$_3$), 37.2 (Si-C); MS m/z 726 (M+); IR (KBr, cm$^{-1}$) ν 1131 (S=O).

**(b) Oxidation of 4a with 2 equiv. of *m*-CPBA.** By using 2 equiv. of *m*-CPBA for the oxidation of **4a**, **8a** was yielded in 13 % yield along with **7a** (27%). **8a**: pale yellow crystals, $^{1}$H-NMR (300 MHz, $C_6D_6$) $\delta$ 0.35 (27H, s), 0.37 (27H, s); $^{13}$C-NMR (75 MHz, $C_6D_6$) $\delta$ 4.7 (q), 5.4 (q), 8.3 (s), 14.3 (s); $^{29}$Si-NMR (59 MHz, $C_6D_6$) $\delta$ 0.1 ($SiMe_3$), 0.5 ($SiMe_3$), 17.6 (Si-C), 19.9 (Si-C); MS m/z 710 (M+); IR (KBr, $cm^{-1}$) $\nu$ 1195 (OS=O).

**(c) Oxidation of 3a with 1 equiv. of *m*-CPBA.** Using 1 equiv. of *m*-CPBA for the oxidation of **3a**, **8a** was afforded in 68% yield along with 32% of **3a** recovery.

**(d) Oxidation of 3a with 2 equiv. of *m*-CPBA.** Using 2 equiv. of *m*-CPBA for the oxidation of **3a**, **8a** was afforded in 83% yield.

**(e) Oxidation of 2a with 1 equiv. of *m*-CPBA.** Using 1 equiv. of *m*-CPBA for the oxidation of **2a**, **9a** was afforded in 33% yield along with 34% recovery of **2a**. **9a**: colorless crystals, decomp. > 288 °C; $^{1}$H-NMR (300 MHz, $C_6D_6$) $\delta$ 0.35 (27H, s), 0.38 (27H, s); $^{13}$C-NMR (75 MHz, $C_6D_6$) $\delta$ 4.6 (q), 5.3 (q), 11.4 (s), 15.5 (s); $^{29}$Si-NMR (79.5 MHz, $C_6D_6$) $\delta$ -1.5 (Si-C), -0.3 ($SiMe_3$), -0.3 ($SiMe_3$), 10.8 (Si-C); MS m/z 678 (M+); IR (KBr, $cm^{-1}$) $\nu$ 1190 (OS=O).

**(f) Oxidation of 2a with 2 equiv. of *m*-CPBA.** Using 2 equiv. of *m*-CPBA for the oxidation of **2a**, **9a** was afforded in 80% yield.

**(g) Oxidation of 6a with 1 equiv. of *m*-CPBA.** Using 1 equiv. of *m*-CPBA for the oxidation of **6a**, **10a** was afforded in 27% yield along with 37% recovery of **6a**. **10a**: pale orange crystals, decomp. > 273°C; $^{1}$H-NMR (300 MHz, $C_6D_6$) $\delta$ 0.38; $^{13}$C-NMR (75 MHz, $C_6D_6$) $\delta$ 4.5 (q), 9.0 (s); $^{29}$Si-NMR (59 MHz, $C_6D_6$) $\delta$ -0.1 ($SiMe_3$), -3.0 (Si-C); MS m/z 662 (M+); IR (KBr, $cm^{-1}$) $\nu$ 1230 (S=O).

**(h) Oxidation of 6a with 2 equiv. of *m*-CPBA.** Using 2 equiv. of *m*-CPBA for the oxidation of **6a**, **10a** was afforded in 62% yield.

**Crystal and Experimental Data for 4c, 5c, and 10a.**

Pale yellow crystals of **4c**, yellow crystals of **5c**, and colorless crystals of **10a** obtained from recrystallization from benzene, were used for X-ray analyses. Crystal data and data collection parameters and results of the analyses are listed in Table 2. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled Kappa axis diffractometer by using graphite monochromatized MoK$\alpha$ radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. All data processing was performed on a Micro VAX 3100 computer by using the MolEN structure-solving program obtained from Enraf-Nonius Corp., Delft, Netherlands. The $\omega$–2$\theta$ scan technique was adopted by varying the $\omega$ scan width as a function of $\theta$ ($\omega$ scan width, **4c**; 1.3 + 1.120 tan $\theta$, **5c**; 0.7 + 0.440 tan $\theta$, **10a**; 0.9 + 0.530 tan $\theta$). All intensities were corrected for Lorents and polarization factors as well as decay correction. An empirical absorption correction based on a series of $\psi$-scan was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[9] An anomalous dispersion correction was applied to all non-hydrogen atoms.[10] Full-matrix least-squares refinements minimized the function $\Sigma w(|F|o' - |F c|)^2$, w=1. **4c**: $C_{20}H_{54}Ge_2Si_6S_6$, FW=800.73, crystal size (mm) 0.50x0.50x0.50, monoclinic space group $P2_1/n$, a=15.714(3) Å, b=9.132(2) Å, c=27.296(5) Å, $\beta$=101.43(2)°, V=3839.5 Å$^3$, Z=4, $D_c$=1.39 g/cm$^3$, R=0.087 ($R_w$=0.107). Data collection were performed with MoK$_\alpha$ radiation ($\lambda$=0.71073 Å) on Enraf-Nonius CAD4, $\mu$= 20.6 $cm^{-1}$.

2140 unique reflections (|Fo|>3.0σ|Fc|) were observed (2θ < 50.0°). Empirical absorption correction was applied, and the structure was solved by a combination of direct methods (MULTAN 80) and difference fourier syntheses. Hydrogen atoms were not included in the calculation. **5c**: $C_{20}H_{54}Ge_2Si_6S_7$, FW=832.80, crystal size (mm) 0.80x0.50x0.30, monoclinic space group $P2_1$, a=15.663(2) Å, b=9.197(1) Å, c=15.791(2) Å, β=119.22(1)°, V=1985.3 $Å^3$, Z=2, $D_c$=1.39 g/cm$^3$, R=0.060 ($R_w$=0.082). Data collection were performed with MoK$_\alpha$ radiation (λ=0.71073 Å) on Enraf-Nonius CAD4, μ= 20.4 cm$^{-1}$. 3900 unique reflections (|Fo|>3.0σ|Fc|) were observed (2θ < 52.6°). Empirical absorption correction was applied, and the structure was solved by a combination of direct methods (SIR88) and difference fourier syntheses. Hydrogen atoms were not included in the calculation.

**10a**: $C_{20}H_{54}Si_8O_3S_3$, FW=663.53, crystal size (mm) 0.50x0.60x0.80, monoclinic space group $P2_1/a$, a=13.539(1) Å, b=17.830(2) Å, c=15.606(1) Å, β=102.93(1)°, V=3671.8 $Å^3$, Z=4, $D_c$=1.20 g/cm$^3$, R=0.061 ($R_w$=0.083). Data collection were performed with MoK$_\alpha$ radiation (λ=0.71073 Å) on Enraf-Nonius CAD4, μ= 4.7 cm$^{-1}$. 5172 unique reflections (|Fo|>3.0σ|Fc|) were observed (2θ < 52.6. ). Empirical absorption correction was applied, and the structure was solved by a combination of direct methods (MULTAN 80) and difference fourier syntheses. Hydrogen atoms were not included in the calculation. Refinement was performed by the full-matrix least-squares method with 315 (for **5c**), 406 (for **4c**), and 352 (for **10a**) variable parameters (anisotropic thermal parameters for non-hydrogen atoms, where the positions and thermal parameters for hydrogen atoms were not refined).

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