February, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 473—476 (1985)* 473

# *S*H2 Reactions of Triethylgermyl Radical with Thiosulfonic *S*-Esters and Selenosulfonic *Se*-Ester

Michio Kobayashi,* Masanori Kobayashi, and Masato Yoshida
*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158*

(Received June 25, 1984)

The triethylgermyl radical was found to react with thiosulfonic *S*-esters to generate sulfonyl radicals. The *S*H2 character of this new reaction was confirmed by a C-13 CIDNP study and products analysis. Selenosulfonic *Se*-ester reacts with germyl radical in a similar way.

Aryl areneselenosulfonates (**1**) are known to suffer a Se–S cleavage by attack of carbon radicals.[1] On the contrary, arenethiosulfonates (**2**), sulfur analogs of selenosulfonic *Se*-ester, are thermally highly stable and are not cleaved by the attack of carbon radicals. For instance, when *S*-*p*-tolyl *p*-toluenethiosulfonate (**2a**) was refluxed in benzene in the presence of phenylazotriphenylmethane (PAT) or azobisisobutyronitrile (AIBN), almost no decomposition of **2a** was observed.

We have found that thiosulfonic *S*-esters are easily attacked by germyl radical more nucleophilic than carbon radical, at the S–S bond. Although many investigations of the reaction of germyl radicals with olefins and organic halides have been reported,[2] very little is known about the reactivity of the germyl radical with sulfur bonding. We have established the *S*H2 character[3] of this new reaction and the results will be described in this paper.

## Results and Discussion

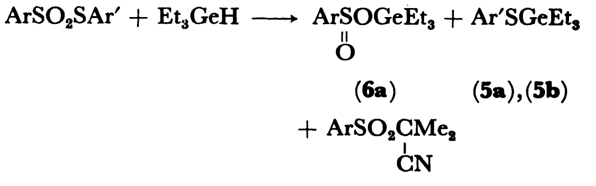
When solutions of thiosulfonic *S*-esters ArSO2SAr′ (**2**) are treated with 2 molar amounts of triethylgermane (**3**) in benzene in the presence of 0.2 molar equivalent of azobisisobutyronitrile for 17 h, thiosulfonic *S*-esters are decomposed completely and germyl esters of arenesulfonic acid (**4**) and thiogermane (**5**) are obtained in high yields.

$$\underset{(\mathbf{3})}{2\mathrm{Et_3GeH}} + \underset{(\mathbf{2})}{\mathrm{ArSO_2SAr'}} \xrightarrow{\mathrm{AIBN}} \underset{(\mathbf{4})}{\mathrm{ArSO_3GeEt_3}} + \underset{(\mathbf{5})}{\mathrm{Ar'SGeEt_3}}$$

|  | Yield/% | Yield/% |
|---|---|---|
| a: Ar = Ar′ = *p*-Tol |  |  |
| b: Ar = Ar′ = Ph | **4a** 96 | **5a** 92 |
|  | **4b** 82 | **5b** 82 |

Each product was identified by comparing its spectroscopic properties with those of the authentic samples prepared according to the literature.

Since thiosulfonic *S*-esters were found not to react with triethylgermane in the absence of AIBN, the above reaction was considered to be initiated by hydrogen abstraction from germane by a α-cyanoisopropyl radical and followed by radical chain reactions. The fact that germyl sulfonate (**4**), not germyl sulfinate (**6**), was isolated as the main product indicated the involvement of atmospheric oxygen. Therefore, the reaction of thiosulfonic *S*-esters with triethylgermane was carried out under deoxygenated conditions in the presence of AIBN. Under these conditions, the reactions proceeded only halfway and a part of **2** was recovered unchanged. No germyl sulfonate (**4**) but germyl sulfinate (**6**) and sulfone (**7**) were obtained as reaction products along with thiogermane (**5**).



$$\mathrm{ArSO_2SAr'} + \mathrm{Et_3GeH} \longrightarrow \underset{(\mathbf{6a})}{\mathrm{Ar\underset{\underset{O}{\|}}{S}OGeEt_3}} + \underset{(\mathbf{5a}),(\mathbf{5b})}{\mathrm{Ar'SGeEt_3}} + \underset{(\mathbf{7a})}{\mathrm{ArSO_2\underset{\underset{CN}{|}}{C}Me_2}}$$

(**6a**) (**5a**),(**5b**)

(**7a**)

| Substrate | AIBN/2 | Recovered (2)/% |
|---|---|---|
| **2a** | 0.2 | 65 |
| **2c** | 1.0 | 24 |

Products (Yield/mol%)

**6a** (9), **5a** (24), **7a** (9)

**6a** (10), **5b** (68), **7a** (37)

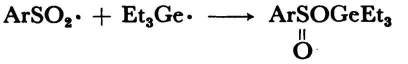
These findings suggest that the sulfonyl radical can not abstract a hydrogen atom from triethylgermane and combine with germyl radical and α-cyanoisopropyl radical to form **6** and **7** respectively. Assuming this inactivity of sulfonyl radical as hydrogen abstractor, it was possible to explain why the reaction was stopped halfway in the absence of oxygen.

The above reaction may be expressed in the following reaction sequences.

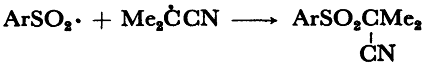
$$\mathrm{AIBN} \longrightarrow 2\mathrm{Me_2\dot{C}CN}$$

$$\mathrm{Me_2\dot{C}CN} + \mathrm{Et_3GeH} \longrightarrow \mathrm{Et_3Ge\cdot} + \mathrm{Me_2CHCN} \quad (1)$$

$$\mathrm{Et_3Ge\cdot} + \mathrm{ArSO_2SAr'} \longrightarrow \mathrm{Et_3GeSAr'} + \mathrm{ArSO_2\cdot} \quad (2)$$



$$\mathrm{ArSO_2\cdot} + \mathrm{Et_3Ge\cdot} \longrightarrow \mathrm{Ar\underset{\underset{O}{\|}}{S}OGeEt_3} \quad (3)$$



$$\mathrm{ArSO_2\cdot} + \mathrm{Me_2\dot{C}CN} \longrightarrow \mathrm{ArSO_2\underset{\underset{CN}{|}}{C}Me_2} \quad (4)$$

In the presence of atmospheric oxygen, the sulfonyl radical combines with oxygen to form a sulfonylperoxyl radical which can abstract a hydrogen atom from germane to regenerate germyl radical and thus start chain reaction.

$$\mathrm{ArSO_2\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ArSO_2OO\cdot} \quad (5)$$

$$\mathrm{ArSO_2OO\cdot} + \mathrm{Et_3GeH} \longrightarrow \mathrm{ArSO_2OOH} + \mathrm{Et_3Ge\cdot} \quad (6)$$

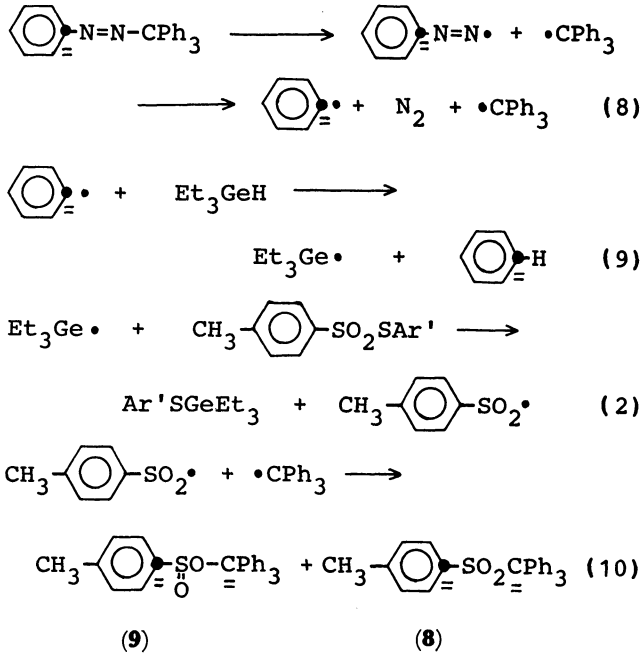
$$\mathrm{ArSO_2OOH} + \mathrm{Et_3GeH} \longrightarrow \mathrm{ArSO_2OGeEt_3} + \mathrm{H_2O} \quad (7)$$

Reaction (Eq. 2) is an $S_H2$ type reaction. To establish the $S_H2$ character for such a reaction shown below;

$$R\cdot + X\text{–}Y \longrightarrow RX + Y\cdot$$

it is essential to certify the formation of RX in high yield and also to verify that the expelled fragment Y is ejected from the solvent cage as a free radical unaccompanied by any radical partner.

We have confirmed the generation of free sulfonyl radicals in the reaction (Eq. 2) by C-13 CIDNP. When a sample tube containing a solution of **2a** and equimolecular PAT in nitrobenzene was inserted into the NMR probe previously heated at 90 °C, the CIDNP signals shown in Fig. 1a were observed. These signals were attributed to the phenyl carbon atom $C_1$ in the starting material PAT and also to the phenyl carbon atom $C_1$ in *o*- and *p*-nitrobiphenyl which were formed by the attack of the phenyl radical generated from PAT on the solvent nitrobenzene; same signals could also be observed in the decomposition of PAT alone in nitrobenzene. All the thiosulfonic *S*-ester (**2a**) was recovered unchanged after the complete consumption of PAT. On the other hand, when the reaction of **2a** and PAT was carried out in the presence of an equimolecular amount of triethylgermane at 90 °C, new CIDNP signals due to benzene (emission), *p*-tolyl triphenylmethyl sulfone (**8**), triphenylmethyl *p*-toluenesulfinate (**9**) were observed as shown in Fig. 1b. The latter reaction may be explained by the following reaction scheme.



(= denotes the nuclear polarized carbon atoms)

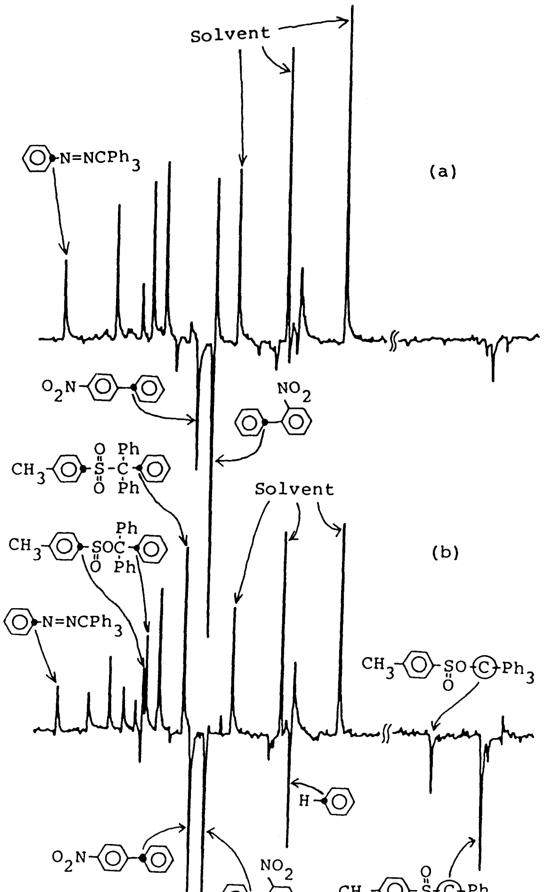


Fig. 1. $^{13}$C-CIDNP spectra in the reaction of PAT and *p*-$TolSO_2STol$-*p* (a), and PAT, $Et_3GeH$, and *p*-$TolSSO_2Tol$-*p* (b) at 90 °C in $PhNO_2$.

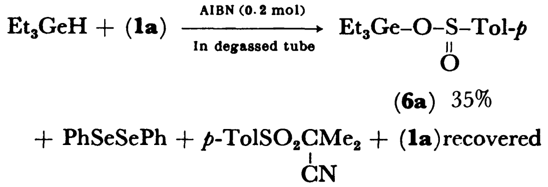
Since the nuclear spin of $C_1$ in the phenyl radical which diffused out of the solvent cage was polarized in $\beta$ state, the benzene molecule formed by hydrogen abstraction from **3** should exhibit an emission signal. The germyl radical generated in this reaction (Eq. 9) attacked the sulfur atom of **2** to form thiogerman (**5**) and expelled a sulfonyl radical. The latter radical came diffused out of the solvent cage and reacted with a triphenylmethyl radical to form a new radical pair. Spin selection occurred during this encounter of the radical pair to result in nuclear $\beta$ polarization at the tertiary carbon atom of the triphenylmethyl radical which had a smaller g value than the sulfonyl radical, thus causing an emission signal from the quarternary carbon atoms of **8** and **9**.

*Se*-Phenyl *p*-tolueneselenosulfonate (**1a**) is known to be decomposed easily by attack of carbon radicals on the selenium atom.[1] Reaction of **1a** with triethylgermane was also investigated.

Reaction between triethylgermane (**3**) and **1a** was found to proceed in the air without addition of any radical initiator, but in the presence of AIBN, the reaction was completed in a much shorter period. After the reaction, the triethylgermyl ester of *p*-toluenesulfonic acid (**4a**) and diphenyl diselenide (**10**) were obtained in almost quantitative yields.

$$\underset{}{Et_3GeH} + \underset{(\mathbf{1a})}{p\text{-}TolSO_2SePh} \xrightarrow[\text{air}]{\text{AIBN}} \underset{\substack{(\mathbf{4a})\\93\%}}{Et_3GeO\text{–}SO_2Tol\text{-}p} + \underset{\substack{(\mathbf{10})\\98\%}}{PhSeSePh}$$

When the reaction was carried out under deoxygenated conditions, triethylgermyl sulfinate (**6a**), sulfone (**7**), and diselenide (**10**) were obtained.



$$Et_3GeH + (\mathbf{1a}) \xrightarrow[\text{In degassed tube}]{\text{AIBN (0.2 mol)}} \underset{\substack{(\mathbf{6a})\ 35\%}}{Et_3Ge\text{–}O\text{–}\underset{\substack{\|\\O}}{S}\text{–}Tol\text{-}p}$$
$$+ \underset{(\mathbf{10})\ 58\%}{PhSeSePh} + \underset{\substack{|\\CN\\(\mathbf{7})\ 31\%}}{p\text{-}TolSO_2CMe_2} + \underset{23\%}{(\mathbf{1a})\text{recovered}}$$

The reaction of the germyl radical with selenosulfonic *Se*-ester was considered to proceed similarly to the reaction of germyl radical and thiosulfonic *S*-ester:

$$Et_3Ge\cdot + (\mathbf{1a}) \longrightarrow Et_3GeSePh + p\text{-}TolSO_2\cdot \qquad (11)$$

The fate of the sulfonyl radical expelled was the same as in the case of thiosulfonic *S*-ester. Instead of phenylselenogermane (**11**), diphenyl diselenide (**10**) was isolated in high yield. In a separate experiment, it was confirmed that phenylselenogermane (**11**) reacted with selenosulfonic *Se*-ester (**1a**) to give **4a** and **10** in almost quantitative yields under atmospheric conditions (Eq. 12).

$$Et_3GeSePh + (\mathbf{1a}) \xrightarrow[O_2]{} p\text{-}TolSO_2OGeEt_3 + PhSeSePh \qquad (12)$$

## Experimental

*Materials.* *Triethyl(*p*-tolylthio)germane (5a)*: To a solution of bromotriethylgermane (0.0209 mol) and *p*-toluenethiol (0.0209 mol) in 30 ml of benzene was added a solution of pyridine (0.0229 mol) in benzene (10 ml) at room temperature and stirred for 1.5 h. The precipitated pyridinium bromide was removed and the filtrate was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by redistillation; yield 85%. Bp 121—122 °C/2 mmHg (1 mmHg=133.322 pa). Mass, *m/z* 284 ($M^+$); $^1$H-NMR, 0.91—1.10 (m, 15H), 2.25 (s, 3H), 6.99, 7.26 (ABq, 4H, *J*=8.4 Hz); $^{13}$C-NMR, 7.6, 8.6, 21.0, 129.3, 129.8, 134.9, 136.0.

*Triethyl(phenylthio)germane (5b)*: This was prepared from bromotriethylgermane and benzenethiol in a similar way to **5a**; yield 66%. Bp 105—107 °C/2 mmHg (lit,[4] 112—113 °C/1 mmHg). Mass, *m/z* 270 ($M^+$); $^1$H-NMR, 0.90—1.07 (m, 15H), 7.05—7.47 (m, 5H); $^{13}$C-NMR, 7.7, 8.6, 126.2, 128.4, 133.3, 134.9.

*Triethyl(phenylseleno)germane (11)*: To a solution of bromotriethylgermane (0.0299 mol) and equimolar benzeneselenol in 20 ml of benzene was added pyridine (0.0328 mol) in 10 ml of benzene under nitrogen stream at room temperature, and stirred for 1.5 h. After similar workup of the reaction mixture as for **5a**, **11** was obtained in 87% yield. Bp 130—132 °C/2 mmHg. Mass, *m/z* 316 ($M^+$); $^1$H-NMR, 1.03 (s, 15H), 7.00—7.60 (m, 5H); $^{13}$C-NMR, 8.1, 9.0, 125.7, 126.5, 128.5, 136.6.

*Triethylgermyl* p-*Toluenesulfonate (4a)*: A solution of triethylgermane (2.04 mmol) and *p*-toluenesulfonic acid (2.04 mmol) in toluene was refluxed for 24 h. After the evaporation of the solvent, the residue was purified by recrystallization from ethanol. Mp 69.5—70.0 °C. $^1$H-NMR, 1.05—1.30 (m, 15H), 2.29 (s, 3H), 7.09, 7.56 (ABq, 4H, *J*=7.8 Hz); $^{13}$C-NMR, 7.4, 9.1, 21.5, 126.5, 129.3, 137.9, 142.6; IR, ($CCl_4$), 1330, 1172 cm$^{-1}$ ($SO_2$), 915 cm$^{-1}$ (Ge–O).

*Triethylgermyl Benzenesulfonate (4b)*: This was prepared in a similar way to **4a**. Bp 185 °C/5 mmHg (lit,[5] 160 °C/1.3 mmHg. $^1$H-NMR, 1.00—1.28 (m, 15H), 7.00—7.90 (m, 5H); $^{13}$C-NMR, 7.3, 9.2, 126.4, 128.7, 132.2, 140.6; IR, ($CCl_4$), 1325, 1175 cm$^{-1}$ ($SO_2$), 925 cm$^{-1}$ (Ge–O).

*Triethylgermyl* p-*Toluenesulfinate (6a)*: This was prepared according to the literature.[6] $^1$H-NMR, 1.08 (s, 15H), 2.31 (s, 3H), 7.22, 7.52 (ABq, 4H, *J*=7.8 Hz); $^{13}$C-NMR, 7.5, 8.9, 21.4, 124.5, 129.4, 141.3, 148.1; IR, neat, 1120 cm$^{-1}$ (S–O), 838 (Ge–O).

*Cyanoisopropyl* p-*Tolyl Sulfone (7)*: This was purified by recrystallization from methanol. Mp. 114—115 °C. $^1$H-NMR, 1.67 (s, 6H), 2.43 (s, 3H), 7.36, 7.81 (ABq, 4H, *J*=8.4 Hz); $^{13}$C-NMR, 21.1, 21.8, 57.5, 129.9, 130.4, 130.7, 146.5; IR, KBr, 1140, 1162, 1188, 1292, 1308, 1322 cm$^{-1}$ ($SO_2$), 2240 cm$^{-1}$ (CN); Anal. Found: C, 59.17; H, 5.95; N, 6.35%. Calcd for $C_{11}H_{13}NSO_2$: C, 59.17; H, 5.86; N, 6.27.

Thiosulfonic *S*-esters[7] and trietylgermane[8] were prepared according to the literature.

*Reaction Between Triethylgermane and Thiosulfonic* S*-ester. Reaction in Air*: A solution of triethylgermane (**3**) (1.0 mmol), thiosulfonic *S*-ester (**2a**) (0.5 mmol) and AIBN (0.2 mmol) in benzene (10 ml) was refluxed for 17 h. After the evaporation of the solvent under reduced pressure, the products were identified by $^1$H- and $^{13}$C-NMR.

*Reaction Under Degassed Conditions*: A solution of **2a** (0.622 mmol), **3** (0.622 mmol) and AIBN (0.124 mmol) in benzene (7 ml) was deoxygenated by a freeze-thaw cycle, sealed in an ampoule and heated at 80 °C for 38 h. The products were separated by column chromatography and identified by NMR.

*CIDNP Measurement.* Carbon 13 CIDNP was observed on JEOL FX-60 FT-NMR spectrometer at 90 °C; Ph–N=N–$CPh_3$ ($C_1$ of Ph: 152.1, A), Ph–$C_6H_4NO_2$-*p* ($C_1$ of Ph: 138.7, E), Ph–$C_6H_4NO_2$-*o* ($C_1$ of Ph: 137.3, E), *p*-$TolSO_2CPh_3$ ($C_1'$ of Ph: 139.8, A, $C_\alpha$: 87.3, E ), and *p*-Tol(SO)O$CPh_3$ ($C_1$ of *p*-Tol: 141.0, A, $C_\alpha$: 92.2, E, $C_1'$ of Ph: 142.5, A).

### References

1) T. Miura and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1982**, 438; T. G. Back, S. Collins, and R. G. Kerr, *J. Org. Chem.*, **48**, 3077 (1983); R. A. Gancarz and J. L. Kice, *J. Org. Chem.*, **46**, 4899 (1981).

2) M. Lesbre, P. Mazerolles, and J. Satgé, "The Organic Compounds of Germanium," Wiley-Interscience, New York (1971), Chap. 4.

3) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York (1971), Chap. 7.

4) H. H. Anderson, *J. Org. Chem.*, **21**, 869 (1956).

5) J. Satgé, *Ann. Chim. (paris)*, **6**, 519 (1961); J. Dubac, G. Manuel, and P. Mazerolles, *C. R. Acad. Sci., Ser. C*, **271**,

465 (1970).
6) E. Lindner and K. Schardt, *J. Organomet. Chem.*, **44**, 111 (1972).
7) S. Oae, T. Takata, and Y. H. Kim, *Tetrahedron*, **37**, 37 (1981).
8) H. H. Anderson, *J. Am. Chem. Soc.*, **79**, 326 (1957).