

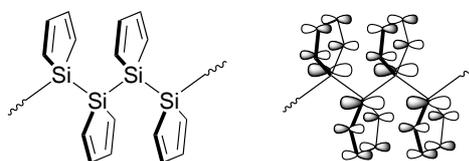
# Toward Silicon-Catenated Silole Polymers, Poly(1,1-silole)s: Syntheses and Structures of Oligo(1,1-silole)s

Shigehiro Yamaguchi, Ren-Zhi Jin, and Kohei Tamao

A series of 1,1-difunctionalized siloles have been synthesized from 1,1-diaminosiloles, which have been prepared via the intramolecular reductive cyclization of diaminobis(phenylethynyl)silane. With the 1,1-difunctionalized siloles in hand, oligo(1,1-silole)s, silole oligomers catenated through silicons, have been synthesized as model compounds of poly(1,1-silole)s. UV absorption spectra of the oligosiloles have been determined, in which tersilole and quatersilole have unique absorption maxima around 280-290 nm.

**Keywords:** Silole / Poly(1,1-silole) / Oligo(1,1-silole) /  $\sigma^*-\pi^*$  Conjugation / Polysilane / Intramolecular reductive cyclization / UV absorption spectra

Poly(1,1-silole)s, silole (silacyclopentadiene) polymers catenated through the ring-silicons, constitute a new class of polysilanes with  $\sigma^*-\pi^*$  conjugation, as shown in Figure 1. In the silole ring itself, there is a significant low-lying LUMO energy level due to the  $\sigma^*-\pi^*$  conjugation arising from the interaction of the  $\sigma^*$  orbital of the two exocyclic  $\sigma$  bonds on silicon with the  $\pi^*$  orbital of the *cisoid*-butadiene moiety [1]. This type of orbital interaction would also take place in the polymeric system, as schematically shown in Figure 1. Thus,  $\sigma^*-\pi^*$  conjugation between the  $\sigma^*$  orbital delocalized over the polysilane main chain and the  $\pi^*$ -orbital localized on the *cisoid*-butadiene moiety in every silole ring would lower the LUMO level. Poly(1,1-silole)s are thus interesting target molecules to synthesize, while only a few silole dimers have been



**Figure 1.** Schematic drawings of Poly(1,1-silole) and  $\sigma^*-\pi^*$  conjugation in the LUMO.

synthesized to date. Reported herein are our recent results toward the still veiled poly(1,1-silole)s.

## 1. A New Synthetic Route to 1,1-Difunctionalized Siloles [2]

For the synthesis of poly(1,1-silole)s, 1,1-functionalized siloles, especially 1,1-dichlorosiloles, are an important class of compounds as starting materials. However, their synthetic methodologies have been rather limited. We have now developed a new general

### SYNTHETIC ORGANIC CHEMISTRY –Synthetic Design–

#### Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel  $\pi$ -conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfonium and episelenonium ions.



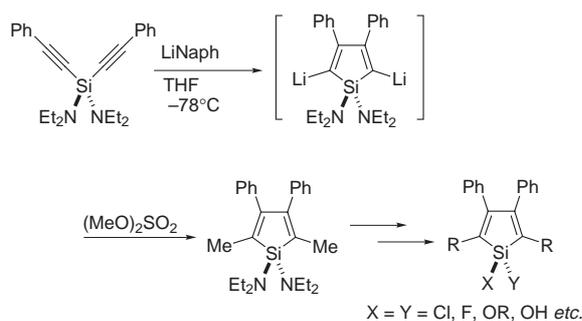
|                                    |  |   |   |
|------------------------------------|--|---|---|
| Prof<br>TAMAO,<br>Kohei<br>(D Eng) | Assoc Prof<br>TOSHIMITSU,<br>Akio<br>(D Eng) | Instr<br>KAWACHI,<br>Atsushi<br>(D Eng) | Instr<br>YAMAGUCHI,<br>Shigehiro<br>(D Eng) |
|------------------------------------|--|---|---|

KATKEVICS, Martins (Guest Res Scholar); JIN, Ren-Zhi (Guest Scholar); ASAHARA, Masahiro (DC); TANAKA, Yoko (DC); AKIYAMA, Seiji (DC); ISHII, Hiroyuki (MC); TERADA, Masayoshi (MC); ITAMI, Yujiro (MC); ENDO, Tomonori (MC); MITSUDO, Koichi (UG); GOTO, Tomoyuki (UG); SAEKI, Tomoyuki (UG); SANO, Atsushi (UG)

synthetic route to 1,1-functionalized siloles using 1,1-diaminosiloles as key compounds.

Our method is based on the intramolecular reductive cyclization of bis(phenylethynyl)silanes, which we have recently developed [3]. Thus, bis(diethylamino)bis(phenylethynyl)silane was added dropwise into an excess amount of lithium naphthalenide (4 molar amount) at  $-78\text{ }^{\circ}\text{C}$  to form 2,5-dilithio-1,1-diaminosilole cleanly. The dilithiosilole was successfully trapped with dimethyl sulfate to form 2,5-dimethyl-1,1-diaminosilole in good yield. A series of 1,1-difunctionalized siloles having alkoxy, Cl, and F functionalities were prepared by the conventional functional group transformation from 1,1-diaminosiloles (Scheme 1). The present methodology is also applicable to the synthesis of 1-monofunctionalized siloles.

### Scheme 1

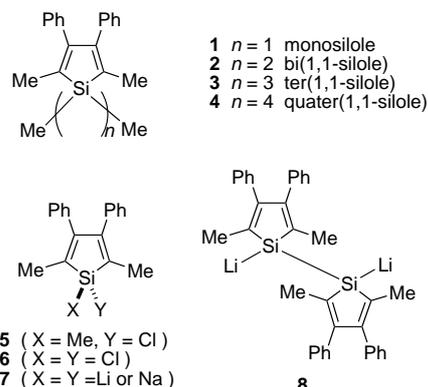


## 2. Oligo(1,1-silole)s as Models of Poly(1,1-silole)s [4]

With the silicon-chlorinated siloles **5** and **6** in hand, we have succeeded in the preparation of a series of oligo(1,1-silole)s from dimer **2** to tetramer **4** (Chart 1). Thus, silole trimer, tersilole **3**, has been obtained by the coupling of monochlorosilole **5** with silole dianion **7**, which was cleanly prepared from 1,1-dichlorosilole **6** with Li in THF. Quatersilole **4** has also been obtained by a similar coupling reaction. Thus, 1,1-dichlorosilole **6** was reduced with 3 molar amount of Na, resulting in the formation of a mixture of the bisilole dianion **8** and the silole dianion **7**. The mixture was treated with 1.5 molar amount of 1-chlorosilole to afford quatersilole **4** and tersilole **3** in 20% and 8% yields, respectively. These are the first examples of oligo(1,1-silole)s catenating more than three silole rings.

UV absorption data are summarized in Table 1, in which the data of the perphenyl- and permethyl-trisilanes and tetrasilanes are also given for comparison. The monosilole **1** has two absorption bands around 250 nm and 310 nm, assignable to the  $\pi-\pi^*$  transitions of the

### Chart 1



phenyl and silole moieties, respectively. In comparison with the monosilole **1**, the oligosiloles **2-4** show distinct spectra, where the absorption of the silole moieties is hidden by broad bands. Remarkably, tersilole **3** and quatersilole **4** have unique absorptions at around 280 and 290 nm, respectively. These absorption maxima are 50-60 nm longer than those of the permethyl oligosilanes. In comparison with the perphenyl counterparts, **3** has a 20 nm longer  $\lambda_{\text{max}}$  and **4** has a comparable  $\lambda_{\text{max}}$ . As mentioned previously, the unique absorptions of the oligo(1,1-silole)s would have arisen from the orbital interactions.

**Table 1.** UV Spectral Data for Oligo(1,1-silole)s<sup>a</sup>

| compound  | $\lambda_{\text{max}}$ / nm | loge |
|---|-----------------------------|------|
| monosilole <b>1</b>                                 | 307                         | 3.22 |
| bisilole <b>2</b>                                   | 255                         | 4.42 |
| tersilole <b>3</b>                                  | 279                         | 4.60 |
| quatersilole <b>4</b>                               | 289                         | 4.59 |
| Ph(Ph <sub>2</sub> Si) <sub>3</sub> Ph <sup>b</sup> | 255                         | 4.51 |
| Ph(Ph <sub>2</sub> Si) <sub>4</sub> Ph <sup>c</sup> | 288                         | 4.36 |
| Me(Me <sub>2</sub> Si) <sub>3</sub> Me <sup>d</sup> | 216                         | 3.96 |
| Me(Me <sub>2</sub> Si) <sub>4</sub> Me <sup>d</sup> | 235                         | 4.17 |

<sup>a</sup> In chloroform. <sup>b</sup> Gilman H, Atwell W. H, Sen P. K, and Smith C. L, *J. Organomet. Chem.*, **4**, 163 (1964). <sup>c</sup> Gilman H, and Atwell W. H, *J. Organomet. Chem.*, **4**, 176 (1964). <sup>d</sup> Gilman H, Atwell W. H, and Schwebke G. L, *J. Organomet. Chem.*, **2**, 369 (1964).

1. Yamaguchi S, and Tamao K, *Bull. Chem. Soc. Jpn.* **69**, 2327 (1996).
2. Yamaguchi S, Jin R.-Z, Tamao K, and Shiro M, *Organometallics*, **16**, 2230 (1997).
3. Tamao K, Yamaguchi S, and Shiro M, *J. Am. Chem. Soc.*, **116**, 11715 (1994).
4. Yamaguchi S, Jin R.-Z, Tamao K, and Shiro M, *Organometallics*, **16**, 2486 (1997).