Reduced viscosities of the sodium salt of polymer **11** exhibited typical polyelectrolyte behavior as a function of concentrations in water (Figure 3). By continuous dilution the reduced viscosity of polymer **11** decreased steadily and increased rapidly at the concentrations below 0.6 g/d*l* in water. In a neutral salt solution (NaCl, 5%) the reduced viscosity retained normal behavior[15].

Biological activities of the polymers **9**, **10**, and **11** and the sulfate of **11** as well as the body distribution of the polymer **11**-pharmacon conjugate are under investigation.

Acknowledgement. This work was supported by Ajou University and the Korea Science and Engineering Foundation.

References

1. Chiellini, E. In *Polymers in Medicine;* Giust, P., Ed.; Plenum Press: New York, U. S. A. 1983.
2. Donaruma, L. G.; Ottenbrite, R. M. In *Anionic Polymeric Drugs*; Vogl, O., Ed.; Wiley-Interscience Publication: New York, U. S. A. 1980.
3. Han, M. J.; Choi, K. B.; Chae, J. P.; Hahn, B. S.; Lee, W. Y. *J. of Bioactive and Compatible Polymers* **1990**, *5*, 80.
4. Han, M. J.; Choi, K. B.; Kim, K. H.; Cho, T. J.; Lee, W. Y.; Shin, W. N. *J. of Bioactive and Compatible Polymers* **1990**, *5*, 420.
5. Han, M. J.; Lee, D. H.; Lee, W. Y.; Hahn, B. S. *Bull. Korean Chem. Soc.* **1989**, *10*, 212.
6. Han, M. J.; Kang, S. D.; Lee, W. Y. *Bull. Korean Chem. Soc.* **1990**, *11*, 154.
7. Han, M. J.; Lee, C. W.; Kim, K. H.; Lee, W. Y. *Bull. Korean Chem. Soc.* **1991**, *12*, 85.
8. Duncan, R.; Lloyd, J. B.; Rejmanova, P.; Kopecek, J. *Macromol. Chem. Suppl.* **1985**, *9*, 3.
9. Duncan, R.; Hume, I. C.; Kopeckova, P.; Ulbrich, K.; Strohalm, J.; Kopecek, J. *J. Controlled Release* **1989**, *10*, 51.
10. Duncan, R.; Kopecek, J.; Rejmanova, P.; Lloyd, J. B. *Biochimica et Biophysica Acta* **1983**, *755*, 518.
11. Horton, D.; Turner, W. N. *Carbohyd. Res.* **1965-1966**, *1*, 444.
12. Whistler, R. L.; Wolfrom, M. L. In *Methods in Carbohydrate Chemistry;* Academic Press: New York, 1963 Vol. II, p 320-321.
13. Collins, P. M. In *Carbohydrates*; Chapman & Hall: London, 1987, p 197.
14. Fritz, J. S.; Lisiki, N. M. *Anal. Chem.* **1951**, *23*, 589.
15. Braun, D.; Chedron, H.; Kern, W. In *Praktikum der Makromolekulare Organischen Chemie;* Alfred Huthig Verlag: Heidelberg, 1966; p 65.

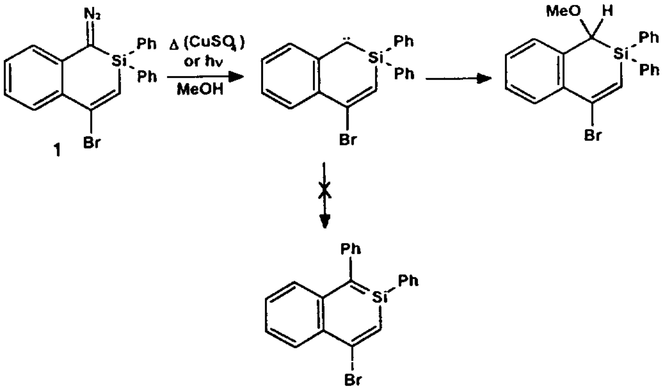
Generation and Trapping of 2-Methyl-2-sila-naphthalene

Young-Woo Kwak*, Jong-Bong Lee, Kyung-Koo Lee,
Seong-Su Kim, and Bong Hyun Boo†

Department of Chemistry, Kyungpook National University,
Taegu 702-701
†*Department of Chemistry, Chungnam National University,*
Taejon 305-764

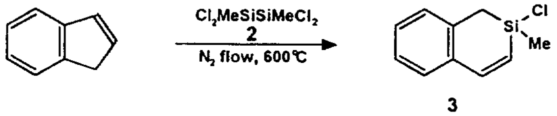
Received December 11, 1993

There has been many reports of the generation and their reactions of silabenzene intermediate from the readily available allyl or chloro precursors.[1] The intramolecular reaction of 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienylmethylene to give silatoluene was reported by Ando and Sekiguchi.[1e] West and coworkers reported the existence of the intermediacy of hexamethyl-1,4-disilabenzene.[1f] In 1978, Barton and Burns confirmed the first unambiguous generation and trapping of the silatoluene formed *via* a thermally induced retro-ene elimination of propene from the 1-allyl-1-methyl-1-silacyclohexa-2,4-diene.[2] There is precedent for the unsuccessful approach to produce 2-silanaphthalene intermediate from the thermolysis or photolysis of silyl diazo compound **1** in the presence of methanol.[3]



We now wish to report the first generation and its trapping of 2-methyl-2-silanaphthalene (**5**), a kind of new transient silaaromatic intermediate, which could arise from the thermolytic reaction of the 2-allyl-2-methyl-2-sila-1,2-dihydronaphthalene (**4**) with methanol or methanol-d_1.

The chlorosilane **3** was produced in 45% yield from the copyrolsis of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (**2**)[4,5] and indene at 600℃ with a 55 m*l*/min flow of the nitrogen gas.[1a,6]



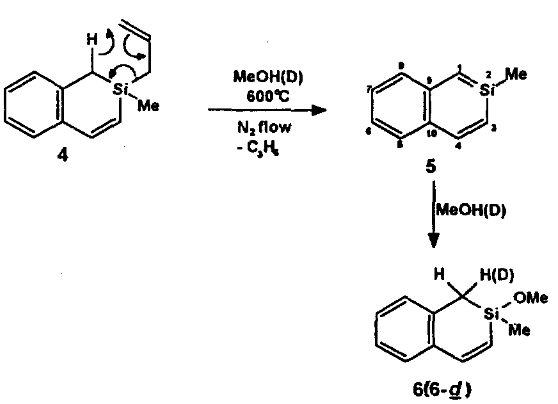
3

The compound **4**, the possible precursor of the 2-methyl-2-silanaphthalene (**5**), was prepared with a yield of 65% by the reaction of 2-chloro-2-methyl-2-sila-1,2-dihydronaphthalene (**3**) with an allylmagnesium bromide in dry ether.[7] We copyrolyzed the 2-methyl-2-silanaphthalene precursor **4** and

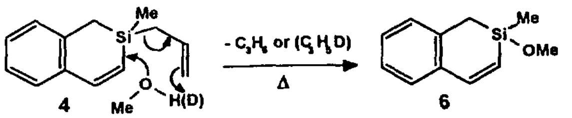
Table 1. Caculated Geometrical Parameters of the 2-Methyl-2-silanaphthalene 5

	Bond length (Å)				Bond angle (deg)		
	AM 1	MNDO	MINDO/3		AM 1	MNDO	MINDO/3
C_1Si	1.657	1.655	1.730	C_1SiC_3	110.9	111.0	105.8
SiC_3	1.720	1.705	1.784	SiC_3C_4	118.0	118.9	119.8
C_3C_4	1.357	1.371	1.378	$C_3C_4C_{10}$	125.2	125.0	127.7
C_4C_{10}	1.431	1.447	1.454	$C_4C_{10}C_9$	123.2	122.6	121.4
C_5C_{10}	1.423	1.440	1.451	$C_1C_9C_{10}$	122.8	121.9	121.5
C_5C_6	1.373	1.381	1.369	SiC_1C_9	119.9	120.8	123.8
C_6C_7	1.414	1.427	1.429	$C_5C_{10}C_9$	119.0	118.5	117.4
C_7C_8	1.370	1.380	1.379	$C_6C_5C_{10}$	121.6	122.0	122.8
C_8C_9	1.431	1.447	1.456	$C_5C_6C_7$	119.6	117.7	120.4
C_9C_{10}	1.425	1.381	1.466	$C_6C_7C_8$	120.2	120.1	119.2
SiC_{11}	1.800	1.782	1.836	$C_7C_8C_9$	121.7	121.9	123.1
				$C_8C_9C_{10}$	117.9	117.9	117.0
				C_1SiC_{11}	126.0	125.2	127.4
				C_3SiC_{11}	123.2	124.0	126.8

a 10-fold excess of methanol as a trapping agent in a vertical quartz tube packed with quartz chips heated to 600℃ with the flow of nitrogen gas (55 m*l*/min). The 2-methoxy-2-methyl-2-sila-1,2-dihydronaphthalene (**6**) was produced in 57% yield *via* a retro-ene elimination of propene. The observed product **6** or **6**-*d* can arise from the addition of methanol or methanol-d_1 into the 2-methyl-2-silanaphthalene intermediate (**5**).



An alternative pathway namely, the direct methanolysis, may lead to the formation of **6**. Note that in the latter mechanism shown below, the product **6** is formed without involving the 2-methyl-2-silanaphthalene (**5**).



A labelling experiment empolying a methanol-d_1 may help identification of the reaction pathway for the methanol addition. The copyrolysis of **4** with MeOD at 600℃ (N_2 flow) yielded a trapping adduct **6**-*d* arising from the replacement of the hydrogen atom attached to the methylene carbon atom by a deuterium atom. This observation may rule out the latter reaction pathway involving the direct methanolysis and support the existence of intermediacy of 2-methyl-2-silanaphthalene (**5**). We performed an AM 1[8], MNDO[9], and MINDO/3[10] semiempirical calculations to find the structure of the 2-methyl-2-silanaphthalene (**5**). The geometrical parameters derived from the AM 1 calculation are consistent with those from the MNDO calculation and little deviated from those from the MINDO/3 calculation. In all the calculations, the **5** is of the naphthalene-like coplanar structure. As shown in Table 1, the bond length of C_1-Si is appreciably shorter than that of Si-C_3 and is much shorter than that of the Si-C_{11} single bond. This indicates that the C_1-Si bond has a double bond character more than the Si-C_3 bond.

Experimental

All pyrolyses were carried out in a vertical hot zone consisting of a 10 mm i.d.×30 cm quartz tube packed with quartz chips under the flow of nitrogen. The pyrolysate was followed by GC analysis with a Hewlett Packard 5890 instrument on a HP-5 capillary column. Products yields were determined by GC(FID) with cyclohexane as an internal standard. Separation of the reaction mixtures was performed on a Varian model 920 GC using an 20% OV-17 column. Proton NMR spectra were recorded on a Bruker AMX 500 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained on a Hewlett Packard 5890 Series II coupled to a GC/5970 Series Mass Selective Detector. Exact mass measurements were performed on a VG 70 SEQ high resolution spectrometer.

1,1,2,2-Tetrachloro-1,2-dimethyldisilane (2). A mixture of 15 g (38 mmol) of 1,2-dimethyltetraphenyldisilane[4] dissolved in 200 m*l* of dry benzene and 0.2 g of sublimed $AlCl_3$ was placed in a 250 m*l* three-neck flask fitted with a stirrer, condenser and inlet tube for dry HCl gas.[5a] The b.p. of the tetrachlorodisilane was in agreement with literature value.[5b] MS m/z 230 (M^++4, 3), 228 (M^++2, 6), 226 (M^+, 4), 213 (2), 117 (9), 115 (53), 113 (79), 95 (4), 93 (11), 80 (34), 78 (100), 65 (30), 63 (83), 43 (13).

2-Chloro-2-methyl-2-sila-1,2-dihydronaphthalene

(3). A solution of 10.5 g (90 mmol) of indene and 5 g (22 mmol) of the tetrachlorodisilane 2 was added slowly to a vertical quartz tube packed with quartz chips and heated to 600℃. The pyrolysate was swept through the reaction chamber with N_2 (55 m*l*/min) into 100 m*l* flask cooled in a acetone/dry-ice bath. Fractional distillation of the dark tarry solution gave 1.9 g (10 mmol, 45%) of the chlorosilane 3. ^{1}H-NMR (CDCl$_3$) δ 0.26 (s, 3H, SiCH$_3$), 2.01 (m, 2H, SiCH$_2$C=), 5.80 (d, 1H, SiCH=C, J=14.1 Hz), 6.71-6.88 (m, 4H, C$_6$H$_4$), 6.99 (d, 1H, SiC=CH, J=14.1 Hz); MS m/z 196 (M^++2, 32), 194 (M^+, 86), 181 (26), 179 (73), 159 (13), 158 (67), 143 (26), 116 (100), 115 (68), 105 (5), 89 (21), 81 (4), 79 (15), 65 (42), 63 (92), 43 (4).

2-Allyl-2-methyl-2-sila-1,2-dihydronaphthlene (4). ^{1}H-NMR (CDCl$_3$) δ 0.19 (s, 3H, SiCH$_3$), 1.66 (d, 2H, allyl, J=8.1 Hz), 2.09 (d, 1H, SiCH$_2$C=, J=16.5 Hz), 2.22 (d, 1H, SiCH$_2$C=, J=16.5 Hz), 4.96 (d, 2H, allyl, J=11.0 Hz), 5.82 (m, 1H, allyl), 6.08 (d, 1H, SiCH=C, J=14.1 Hz), 7.04-7.13 (m, 4H, C$_6$H$_4$), 7.30 (d, 1H, SiC=CH, J=14.1 Hz); MS m/z 200 (M^+, 4), 185 (1), 159 (100), 143 (17), 131 (60), 115 (9), 105 (17), 43 (25); HRMS calcd for $C_{13}H_{16}Si$ 200.1022, measured m/z 200.1022.

2-Methoxy-2-methyl-2-sila-1,2-dihydronaphthalene (6). ^{1}H-NMR (CDCl$_3$) δ 0.25 (s, 3H, SiCH$_3$), 2.05 (m, 2H, SiCH$_2$=), 3.30 (s, 3H, OCH$_3$), 5.99 (d, 1H, SiCH=C, J=14.3 Hz), 7.09-7.22 (m, 4H, C$_6$H$_4$), 7.38 (d, 1H, SiC=CH, J=14.2 Hz); Mass m/z 190 (M^+, 21), 175 (36), 158 (13), 145 (15), 115 (10), 105 (4), 75 (29), 59 (100), 43 (10); HRMS calcd for $C_{11}H_{14}SiO$ 190.0814, measured m/z 190.0817.

1-Deuterio-2-methoxy-2-methyl-2-sila-1,2-dihydronaphthalene (6-*d*). ^{1}H-NMR (CDCl$_3$) δ 0.27 (s, 3H, SiCH$_3$), 1.96 (m, 1H, SiCHD=C), 3.29 (s, 3H, OCH$_3$), 6.03 (d, 1H, SiCH=C, J=14.4 Hz), 7.04-7.20 (m, 4H, C$_6$H$_4$), 7.32 (d, 1H, SiC=CH, J=14.4 Hz); Mass m/z 191 (M^+, 28), 176 (42), 159 (15), 146 (13), 116 (11), 105 (4), 75 (28), 59 (100), 43 (6); HRMS calcd for $C_{11}H_{13}DSiO$ 191.0877, measured m/z 191.0888.

Acknowledgement. We are grateful to the Korea Science and Engineering Foundation for financial support of this work. And, this was supported by the Basic Science Research Institute Program, Minsistry of Education of Korea, 1993. We wish to express our appreciation to Mr. Byung Kag Ahn for his help of the semiempirical calculations.

References

1. (a) Barton, T. J.; Banasiak, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5199; (b) Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788; (c) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 51; (d) Markl, G.; Hofmeister, P. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 789; (e) Ando, W.; Tanikawa, H.; Sekiguchi, A. *Tetrahedron Lett.* **1983**, *24*, 4245; (f) Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884; (g) Maier, G.; Mihm, G.; Baumgartner, R. O. W.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2337.
2. (a) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246; (b) Kreil, C. L.; Chapman, O. L.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 841.
3. (a) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics* **1985**, *4*, 584; (b) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1981**, *103*, 3579.
4. Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 6129.
5. (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organometal. Chem.* **1978**, *162*, 223; (b) Sakurai, H.; Watanabe, T.; Kumada, M. *J. Organometal. Chem.* **1967**, *7*, 14.
6. (a) Conlin, R. T.; Kwak, Y. W. *Organometallics* **1984**, *3*, 918; (b) Hwang, R. J.; Conlin, R. T.; Gaspar, P. P. *J. Organometal. Chem.* **1975**, *94*, C38.
7. Rabjohn, N. *Organic Synthesis;* John Wiley and Sons, Inc.; **1963**, Vol. 4, p 749.
8. Dewar, M. J. S.; Jie, C. *Organometallics* **1987**, *6*, 1486.
9. (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907; (b) Dewar, M. J. S.; Friedheim, J.; Grady, G.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375.
10. (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307; (b) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.