

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/dl in water. In a neutral salt solution (NaCl, 5%) the reduced viscosity retained normal behavior¹⁵.

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

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

References

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

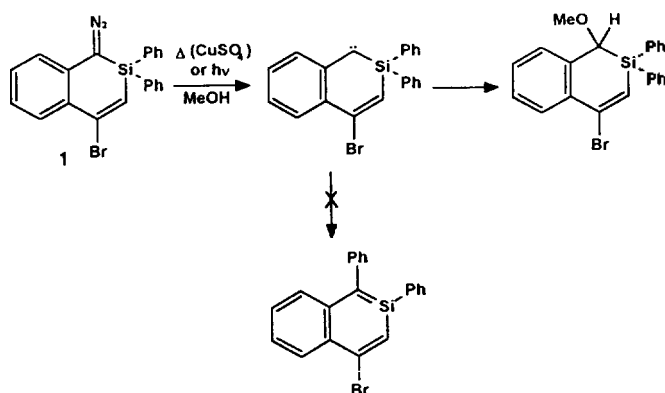
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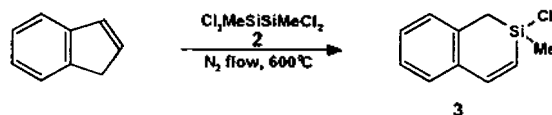
Received December 11, 1993

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.^{1c} 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 retroene 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 sila-aromatic 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 coprolysis of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (**2**)^{4,5} and indene at 600°C with a 55 ml/min flow of the nitrogen gas.^{1a,6}

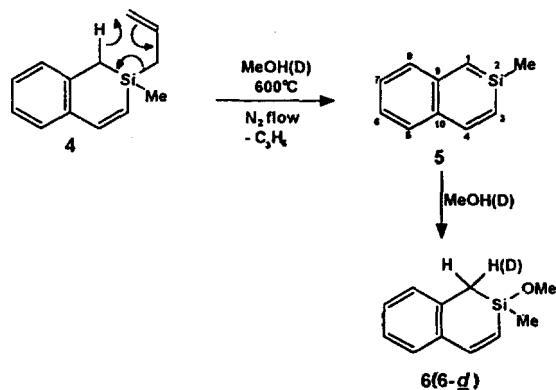


The compound **4**, the possible precursor of the 2-methyl-2-silanaphthalene (**5**), was prepared with a yield of 65% by the reaction of 2-chloro-2-methyl-2-sila-1,2-dihydronaphthalene (**3**) with an allylmagnesium bromide in dry ether.⁷ We copolymerized the 2-methyl-2-silanaphthalene precursor **4**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

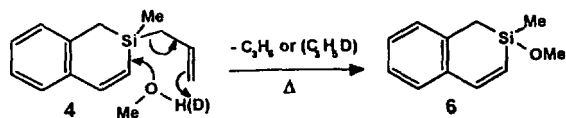
Table 1. Calculated Geometrical Parameters of the 2-Methyl-2-silanaphthalene 5

	Bond length (Å)				Bond angle (deg)		
	AM 1	MNDO	MINDO/3		AM 1	MNDO	MINDO/3
C ₁ Si	1.657	1.655	1.730	C ₁ SiC ₃	110.9	111.0	105.8
SiC ₃	1.720	1.705	1.784	SiC ₃ C ₄	118.0	118.9	119.8
C ₃ C ₄	1.357	1.371	1.378	C ₃ C ₄ C ₁₀	125.2	125.0	127.7
C ₄ C ₁₀	1.431	1.447	1.454	C ₄ C ₁₀ C ₉	123.2	122.6	121.4
C ₅ C ₁₀	1.423	1.440	1.451	C ₇ C ₉ C ₁₀	122.8	121.9	121.5
C ₅ C ₆	1.373	1.381	1.369	SiC ₁ C ₃	119.9	120.8	123.8
C ₆ C ₇	1.414	1.427	1.429	C ₅ C ₁₀ C ₃	119.0	118.5	117.4
C ₇ C ₈	1.370	1.380	1.379	C ₆ C ₅ C ₁₀	121.6	122.0	122.8
C ₈ C ₉	1.431	1.447	1.456	C ₅ C ₆ C ₇	119.6	117.7	120.4
C ₉ C ₁₀	1.425	1.381	1.466	C ₆ C ₇ C ₈	120.2	120.1	119.2
SiC ₁₁	1.800	1.782	1.836	C ₇ C ₈ C ₉	121.7	121.9	123.1
				C ₉ C ₉ C ₁₀	117.9	117.9	117.0
				C ₁ SiC ₁₁	126.0	125.2	127.4
				C ₃ SiC 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°C with the flow of nitrogen gas (55 ml/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 employing a methanol-*d*₁ may help identification of the reaction pathway for the methanol addition. The coprolysis of 4 with MeOD at 600°C (N₂ 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 AM¹⁸, MNDO⁹, and MINDO/3¹⁰ 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 C₁-Si is appreciably shorter than that of Si-C₃ and is much shorter than that of the Si-C₁₁ single bond. This indicates that the C₁-Si bond has a double bond character more than the Si-C₃ 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 CDCl₃ 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-dimethyltetraphenyldisilane⁴ dissolved in 200 ml of dry benzene and 0.2 g of sublimed AlCl₃ was placed in a 250 ml 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°C. The pyrolysate was swept through the reaction chamber with N₂ (55 ml/min) into 100 ml 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. ¹H-NMR (CDCl₃) δ 0.26 (s, 3H, SiCH₃), 2.01 (m, 2H, SiCH₂C=), 5.80 (d, 1H, SiCH=C, *J*=14.1 Hz), 6.71-6.88 (m, 4H, C₆H₄), 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). ¹H-NMR (CDCl₃) δ 0.19 (s, 3H, SiCH₃), 1.66 (d, 2H, allyl, *J*=8.1 Hz), 2.09 (d, 1H, SiCH₂C=, *J*=16.5 Hz), 2.22 (d, 1H, SiCH₂C=, *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, C₆H₄), 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 C₁₃H₁₆Si 200.1022, measured *m/z* 200.1022.

2-Methoxy-2-methyl-2-sila-1,2-dihydronaphthalene (6). ¹H-NMR (CDCl₃) δ 0.25 (s, 3H, SiCH₃), 2.05 (m, 2H, SiCH₂=), 3.30 (s, 3H, OCH₃), 5.99 (d, 1H, SiCH=C, *J*=14.3 Hz), 7.09-7.22 (m, 4H, C₆H₄), 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 C₁₁H₁₄SiO 190.0814, measured *m/z* 190.0817.

1-Deuterio-2-methoxy-2-methyl-2-sila-1,2-dihydronaphthalene (6-d). ¹H-NMR (CDCl₃) δ 0.27 (s, 3H, SiCH₃), 1.96 (m, 1H, SiCHD=C), 3.29 (s, 3H, OCH₃), 6.03 (d, 1H, SiCH=C, *J*=14.4 Hz), 7.04-7.20 (m, 4H, C₆H₄), 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 C₁₁H₁₃DSiO 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, Ministry of Education of Korea, 1993. We wish to express our appreciation to Mr. Byung Kag Ahn for his help of the semiempirical calculations.

References

- (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.
- (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.
- (a) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics* 1985, 4, 584; (b) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* 1981, 103, 3579.
- Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* 1960, 82, 6129.
- (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.
- (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.
- Rabjohn, N. *Organic Synthesis*; John Wiley and Sons, Inc.; 1963, Vol. 4, p 749.
- Dewar, M. J. S.; Jie, C. *Organometallics* 1987, 6, 1486.
- (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.
- (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.