A One-step Synthesis of 2,7-Dimethyl-5-silaspiro[4.4]nona-2,7-diene and the Synthesis of Its Derivatives

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The *in situ* reaction of dialkoxydichlorosilanes, such as dimethoxy-, diethoxy-, dipropoxy-, dibutoxy-, and diisobutoxydichlorosilane, with isoprene and magnesium in tetrahydrofuran (THF) was investigated. It was found that the double annelation product, *i.e.*, 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene (**1**), was obtained from diethoxy-, dipropoxy-, and dibutoxydichlorosilane in 87.0, 65.2, and 66.5% yields respectively. On the other hand, the reaction of dimethoxy- and diethoxydichlorosilane with butadiene and magnesium in THF gave 5-silaspiro[4.4]nona-2,7-diene (**7**) in 20.7 and 35.4% yields respectively. Several silaspirononane derivatives were synthesized from **1**.

Recently, Salomon reported on the synthesis of 5-silaspiro[4.4]nona-2,7-diene by a one-step reaction[1] from silicon tetrachloride and the butadiene–magnesium complex prepared from active-magnesium[2] and butadiene. Takase *et al.* reported independently on the preparation of silaspiro compounds by treating silicon tetrachloride with diene–magnesium compound in a step-by-step manner.[3] In a preliminary communication,[4] we have reported on a convenient method for the preparation of 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene (**1**). The double annelation product was obtained in a high yield when a mixture of diethoxydichlorosilane and isoprene in a molar ratio of 1/2 was refluxed in the presence of magnesium in THF. In this paper we wish to describe further details of the double annelation reaction and the synthesis of the derivatives of **1**.

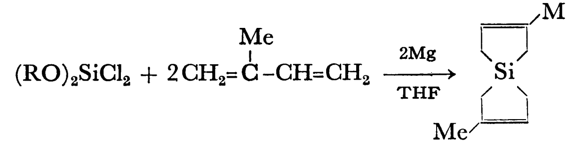
Results and Discussion

Reaction of Dialkoxydichlorosilanes with Isoprene and Magnesium. Dialkoxydichlorosilanes, such as dimethoxy-(**2**), diethoxy-(**3**), dipropoxy-(**4**), dibutoxy-(**5**), and diisobutoxydichlorosilane(**6**), were obtained by means of disproportionation reactions between the appropriate tetraalkoxysilane and silicon tetrachloride in a manner described by Kumada[5] [Table 1].

$$\mathrm{Si(OR)_4 + SiCl_4 \xrightarrow[30\,h]{160\,^\circ C} ROSiCl_3 + (RO)_2SiCl_2 + (RO)_3SiCl}$$

R=Me, Et, *n*-Pr, *n*-Bu, *i*-Bu

To investigate the effect of the varieties of alkoxyl groups of dialkoxydichlorosilanes in the preparation of **1**, the reactions of dialkoxydichlorosilanes (R=Me, Et, Pr, Bu) with two mole equivalents of isoprene and magnesium were carried out in THF [Table 2]. It was observed that the magnesium dichloride precipitated at the beginning of the exthothermic reaction dissolved gradually as the reaction proceeded. The reaction mixture became homogenous at the end of the reaction. These observations presumably indicate that the isoprene–magnesium complex reacts with dialkoxydichlorosilanes in 2 steps, *i.e.*, a first reaction with chloride groups, and a second reaction with alkoxide groups. In this reaction it was found that **3** was the best agent for the preparation of the double annelation product(**1**). In contrast, **2**, like silicon tetrachloride, was found to be less effective for the preparation of **1**. The predominance of the yield of **1** in the reaction using **3** as the starting material may be considered to be because **3** contains Si–Cl and Si–OR bonds which have a suitable reactivity difference from the isoprene–magnesium complex without decreasing the reactivity of the alkoxy group itself.



R=Me, Et, *n*-Pr, *n*-Bu **1**

The reactions of the dialkoxydichlorosilanes with equimolar amounts of isoprene and magnesium were then carried out. When such dialkoxydichlorosilanes as **3**, **4**, **5**, and **6** were employed in the reaction, it was found, by GLC analysis of the reaction mixture, that not only the mono annelation product, *i.e.*, 1,1-dialkoxy-

Table 1. The preparation of dialkoxydichlolorosilane

R	$\mathrm{Si(OR)_4}$ g(mol)	$\mathrm{SiCl_4}$ g(mol)	Temp °C	Time h	$\mathrm{(RO)_2SiCl_2}$ Bp °C/Torr	Yield, g(%)
Me	70.4(0.46)	78.7(0.46)	150	30	96—100	89.6(60.1)
Et	55.0(0.26)	44.9(0.26)	160	30	135—137	61.6(60.0)
n-Pr	156.6(0.59)	100.7(0.59)	160	30	173—175	151.1(58.7)
n-Bu	70.0(0.22)	37.2(0.22)	160	30	115/20	69.6(64.9)
i-Bu	64.0(0.20)	34.0(0.20)	160	30	119—198	53.4(54.5)

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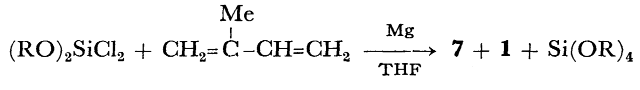
Table 2. Reaction of dialkoxydichlorosilanes with two mole equivalents of isoprene and magnesium

R	$(RO)_2SiCl_2$ g(mol)	Mg g(mol)	Isoprene g(mol)	Yield of **1** g(%)
Me	16.1(0.1)	5.3(0.22)	17.0(0.25)	0.8(5)
Et	75.5(0.4)	21.4(0.88)	68.0(1.0)	57.2(87.0)
n-Pr	21.7(0.1)	5.3(0.22)	17.0(0.25)	10.7(65.2)
n-Bu	24.5(0.1)	5.3(0.22)	17.0(0.25)	10.9(66.5)

3-methyl-1-sila-3-cyclopentene(**7**), but also the double annelation product(**1**) and tetraalkoxysilanes were formed [Table 3]. These results may support the above consideration that the 2-mole-equivalent reaction of isoprene-magnesium complex with unimolar dialkoxydichlorosilanes proceeds in 2 steps:



$$(RO)_2SiCl_2 + CH_2{=}\overset{\overset{\large Me}{|}}{C}{-}CH{=}CH_2 \xrightarrow[THF]{Mg} \mathbf{7} + \mathbf{1} + Si(OR)_4$$

R = Et, *n*-Pr, *n*-Bu, *i*-Bu

Table 3. Reaction of dialkoxydichlorosilanes with equimolar amounts of isoprene and magnesium

$(RO)_2SiCl_2$ R=	Yield[a] (%)		
	7	**1**	$Si(OR)_4$
Me	5	5	5
Et	32.5	23.2	23.1
n-Pr	40.0	20.1	25.0
n-Bu	49.4	18.9	18.4
i-Bu	36.5	10.1	15.4

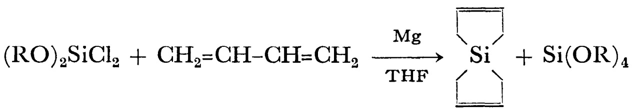
a) The yields were estimated by GLC.

It may be considered that the tetraalkoxysilanes found in the above experiment resulted from the reaction of magnesium dialkoxides with dialkoxydichlorosilanes as follows:

$$\mathbf{7} \xrightarrow[\text{isoprene}]{Mg} \mathbf{1} + Mg(OR)_2$$

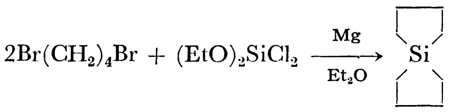
$$Mg(OR)_2 + (RO)_2SiCl_2 \longrightarrow Si(OR)_4 + MgCl_2$$

When butadiene was used as an annelating agent, **2** and **3** gave 5-silaspiro[4.4]nona-2,7-diene(**8**) in 20.7 and 35.4% yields respectively.



R = Me, Et **8**

On the other hand, when the reaction of **3** and the Grignard reagent prepared from 1,4-dibromobutane in a molar ratio of 1/2 was carried out, 5-silaspiro[4.4]nonane(**9**) was obtained in a 61.6% yield.



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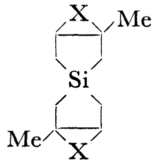
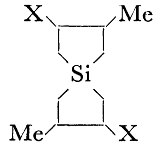
West[6)] obtained **9** in a 26.5% yield by the treatment of silicon tetrachloride with the same Grignard reagent, followed by treatment with the organolithium reagent prepared from 1,4-dibromobutane. These results indicate that **3** is also useful for the one-step synthesis of **9**.

*Preparation of the Derivatives of **1**.* The new derivatives of silaspirononane synthesized in the present work are 2,7-dimethyl-2,3: 7,8-dimethylene-5-silaspiro[4.4]nonane(**10**), 2,7-dimethyl-2,3: 7,8-diepoxy-5-silaspiro[4.4]nonane(**11**), 2,7-dimethyl-5-silaspiro[4.4]nonane(**12**), 2,7-dimethyl-5-silaspiro[4.4]nonane-3,8-diol(**13**), and 2,7-dimethyl-5-silaspiro[4.4]nonane-3,8-diamine (**14**). The silaspirononane **10** was obtained in a 54.9% yield by using the Simmons-Smith agent.[7)] The silaspirononane **11** was obtained in a 65.4% yield by the treatment of **1** with perbenzoic acid in chloroform.[8)] The structural assignment was done by the analysis of the IR and NMR spectra. (**10**, IR spectrum; -CH- in the cyclopropane ring, 3030 cm^{-1}; skeletal vibration, 1030, 1010 cm^{-1}: **11**, IR spectrum; skeletal vibration, 1040, 1005 cm^{-1}; NMR spectrum; (δ) 3.0—3.1 ∠O∖∕H).

The hydrogenation of **1** by using Pd–C catalyst in hexane gave **12** in a 78.8% yield. Although the hydrogenation of 1,1,3-trimethyl-1-sila-3-cyclopentene(**15**) using Pd–C catalyst in methanol afforded only a ring-opening product, *i.e.*, dimethylmethoxyisopentylsilane,[7b)] that of **1** in the presence of methanol gave **12** in a 64.4% yield. The hydroboration of **1**, followed by treatment with hydrogen peroxide in the presence of sodium hydroxide[8b),9)] or with hydroxylamine-*O*-sulfonic acid,[10)] gave **13** and **14** in 46.0 and 46.8% yields respectively. A large excess of diborane was required to attain the complete hydroboration of the bifunctional compound (**1**). The diol **13** and the diamine **14** were identified by the analysis of the IR and NMR spectra. (**13**, IR spectrum; skeletal vibration, 1075, 1040, 1030 cm^{-1}; NMR spectrum; (δ) 3.6 (CH–O): **14**, IR spectrum; skeletal vibration, 1075, 1040, 1030 cm^{-1}; NMR spectrum; (δ) 2.7 (CH–N)).

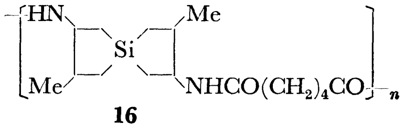


10: X = CH_2
11: X = O



12: X = H
13: X = OH
14: X = NH_2

The interfacial polycondensation reaction[11)] of the diamine(**14**) with adipoyl dichloride was carried out, and a white solid polymer (**16**) ([η] = 1.07) was thus obtained in a 69.8% yield. The polymer was soluble in methanol and ethanol, but insoluble in such solvents as ether, benzene, and acetone.



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Experimental

All the boiling and melting points are uncorrected. The IR and mass spectra were recorded on a JASCO IR-2A spectrometer and on a JEOL-01SG instrument respectively. The NMR spectra were recorded on a Varian A-60 spectrometer in CCl_4 using TMS as the internal standard. The analytical GLC was carried out with a Shimadzu GC-3A chromatograph [1.5 m, 15% SE-30 on Chromosorb W (60—80 mesh)].

Preparation of Dialkoxydichlorosilanes. A mixture consisting of the appropriate tetraalkoxysilane and silicon tetrachloride was placed into a sealed glass tube. The reaction tube was then maintained at 160 °C (at 150 °C for tetramethoxysilane) for 30 h. The fractional distillation of the reaction mixture by using a 1 × 60 cm column packed with Fenske ring gave the dialkoxydichlorosilanes in about a 60% yield. The results are shown in Table 1.

Reaction of 3 with Two Mole Equivalents of Isoprene and Mg. A mixture of **3** (75.5 g, 0.4 mol), isoprene (68.0 g, 1.0 mol), and Mg (21.4 g, 0.88 mol) in dry THF (300 ml) was refluxed with stirring for 30 h under a nitrogen atmosphere. During the reaction, the internal temperature gradually rose from 60 to 69 °C. After the removal of the solvent from the reaction mixture, dry hexane (150 ml) was added to the residue, and then the deposited magnesium salts was separated by filtration. The distillation of the mixture gave **1** in a 87.0% (57.2 g) yield. NMR: (δ) 1.1—1.4 (m, 8H, Si–CH_2) 1.5—1.7 (m, 6H, C–CH_3) 4.9—5.2 (m, 2H, =CH). IR (neat): 2900, 1640, 1450, 1430, 1400, 1220, 1160, 1100, 1030, 1010, 760 cm^{-1}. Mass, *m/e* 164 (M^+). Bp 140 °C/105 Torr, n_D^{20} 1.5062, d_4^{25} 0.9897. Found: Si, 17.1%. Calcd for $C_{10}H_{16}Si$: Si, 17.2%.

The reaction of **4** and **5** with isoprene and Mg was carried out in THF under the reaction conditions described above. These results are shown in Table 2.

Reaction of 3 with Equimolar Amounts of Isoprene and Mg. A mixture of **3** (25 g, 0.13 mol), isoprene (16.5 g, 0.24 mol), and Mg (3.2 g, 0.13 mol) in dry THF (160 ml) was refluxed with stirring for 30 h under a nitrogen atmosphere. After the removal of the solvent, dry hexane (150 ml) was added to the residue, and the deposited magnesium salts were filtered off. The resulting solution was evaporated to give 1,1-diethoxy-3-methyl-1-sila-3-cyclopentene (**17**), **1**, and tetraethoxysilane in 32.5, 23.2, and 23.1% yields respectively, as determined by GLC analysis. **17**, NMR: (δ) 1.1 (t, 6H, CH_3), 0.9—1.2 (m, 1H, Si–CH_2), 1.5—1.6 (m, 3H, =C–CH_3), 3.4 (q, 4H, O–CH_2), 5.0 (m, 1H, =CH). IR (neat): 2900, 1640, 1440, 1400, 1160, 1080, 1030, 1010, 780 cm^{-1}. Mass, *m/e* 172 (M^+). Bp 190 °C, n_D^{25}1.4389.

The reaction of **4**, **5**, and **6** with isoprene and Mg was carried out in THF under the reaction conditions described above, and the yields of the products were estimated by GLC. These results are shown in Table 3.

Reaction of 3 with Butadiene and Mg. A mixture of **3** (18.9 g, 0.1 mol), Mg (8.2 g, 0.3 mol), and dry THF (150 ml) was placed in a flask equipped with a magnetic stirrer and a Dry Ice trap. Butadiene was then introduced into the mixture at room temperature under a nitrogen atmosphere. After stirring for 30 h, saturated aq NH_4Cl (100 ml) was added to the mixture. The organic layer was separated and then treated with 4M NaOH at room temperature for 24 h in order to hydrolyze the side reaction product, *i.e.*, tetraethoxysilane. Then the mixture was washed with two 50 ml portions of water, and dried over Na_2SO_4. Evaporation and distillation gave **8** in a 35.4% (4.8 g) yield. Bp 102 °C/72 Torr (lit, 65—68 °C/13 Torr).[1] In a similar manner, when **2** was employed in place of **3**, **8** was obtained in a 20% yield.

Preparation of 9. A mixture of **3** (23.2 g, 0.12 mol) and 1,4-dibromobutane (53.0 g, 0.25 mol) in diethyl ether (100 ml) was added, over a 3-h period to magnesium (14.2 g, 0.58 mol) in diethyl ether (400 ml). After stirring had been continued for an additional 8 h, 150 ml of water was added to the mixture. The organic layer was separated, washed with water, and then dried over $CaCl_2$. Evaporation and distillation gave **9** in a 61.6% (10.6 g) yield. Bp 103 °C/90 Torr (lit, 178.5 °C).[6]

Preparation of 10. A mixture of **1** (3.3 g, 0.02 mol) and diiodomethane (26.8 g, 0.1 mol) in dry ether was refluxed in the presence of a Zinc–Copper couple (6.5 g) with stirring for 30 h. The ether slution was decanted from the unreacted couple, washed with two 30 ml portions of saturated aq NH_4Cl, and then dried over Na_2SO_4. Fractional distillation gave **10** in a 54.9% (2.1 g) yield. NMR: (δ) −0.2, 0.5 (m, 4H, $\underline{\diagup CH_2 \diagdown}$), 0.7—1.2 (m, 8H, Si–$CH_2$), 1.2—1.5 (m, 6H, C–$CH_3$). IR (neat): 3030, 2900, 1440, 1400, 1250, 1180, 1160, 1120, 1060, 1030, 1010, 930, 850, 750 cm^{-1}. Bp 110—112 °C/34 Torr, n_D^{20} 1.5033, d_4^{25} 0.9802. Found: Si, 14.6%. Calcd for $C_{12}H_{20}Si$: Si, 14.9%.

Preparation of 11. To a solution of perbenzoic acid (0.09 mol) in chloroform (157 ml), **1** (4.9 g, 0.03 mol) was added at 5 °C over 1 h. After the mixture had been maintained at 5 °C for two days, benzoic acid and excess perbenzoic acid were extracted with 1M NaOH (200 ml). The chloroform solution was washed with two 60 ml portions of water, and then dried. The removal of the solvent under reduced pressure at room temperature, followed by distillation, gave **11** in a 65.3% (3.8 g) yield. NMR: (δ) 0.7—1.3 (m, 8H, Si–CH_2), 1.2—1.5 (m, 6H, C–CH_3), 3.0—3.1 (m, 2H, $\overline{\diagdown O \diagup \diagdown} H$); IR (neat): 2950, 1450, 1390, 1260, 1180, 1040, 1005, 950, 900, 830, 780, 760 cm^{-1}. Bp 80 °C/0.45 Torr, n_D^{20} 1.4969, d_4^{25} 0.9974. Found: Si, 14.3%. Calcd for $C_{10}H_{16}O_2Si$: Si, 14.9%.

Preparation of 12. Compound **1** (6.6 g, 0.04 mol) was hydrogenated in a catalytic hydrogenating apparatus in hexane, using palladium charcoal (0.3 g) as the catalyst, at room temperature. The hydrogen up-take was almost theoretical. After the removal of the solvent, distillation gave **12** in a 78.7% (5.3 g) yield. NMR: (δ) 0.2—1.0 (m, 8H, Si–CH_2), 1.0 (d, 6H, –CH_3), 1.1—2.0 (m, 6H, –CH_2–CH–). IR (neat): 2940, 1450, 1405, 1370, 1180, 1080, 1040, 1030, 970, 840, 780, 750, 720 cm^{-1}. Bp 105—107 °C/45 Torr, n_D^{20} 1.4079, d_4^{20} 0.8682. Found: Si, 16.9%. Calcd for $C_{10}H_{20}Si$: Si, 16.7%.

Preparation of 13. Gaseous diborance generated from $NaBH_4$ (2.8 g) in diglyme and BF_3OEt_2 was added to a solution of **1** (8.2 g, 0.05 mol) in THF (125 ml) at 0 °C over a period of 2 h. After the mixture had then been stood for 2 h at room temperature, small chips of ice were added to hydrolyze the excess diborane. The solution was then immersed in an ice bath, and 3M NaOH (11 ml) was added, followed by 30% H_2O_2 (11 ml) over a period of 1 h. One hour later the organic layer was extracted with ether. The combined organic layer was dried and distilled to yield 4.6 g (46.0%) of **13**. NMR: (δ) 0.25—0.6 (m, 4H, Si–CH_2), 0.95 (d, 6H, C–CH_3), 0.7—1.3 (m, 4H, Si–CH_2–C–O), 1.5—2.1 (m, 2H, CH), 2.4 (s, 2H, OH), 3.6 (q, 2H, CH–O). IR (neat): 3300, 2900, 1450, 1400, 1330, 1250, 1190, 1130, 1075, 1040, 1030, 1000, 900, 840, 800, 780 cm^{-1}. Bp 122 °C/0.1 Torr. Found: Si, 14.9%. Calcd for $C_{10}H_{20}Si$: Si, 14.0%.

Preparation of 14. Gaseous diborane generated from $NaBH_4$ (4.5 g, 0.12 mol) in diglyme and BF_3OEt_2 was added to a solution of **1** (6.6 g, 0.04 mol) in diglyme (100 ml) at 0 °C over a period of 3 h. After the mixture was stood for 2 h at room temperature, a solution of NH_2OSO_3H (18.1 g, 0.16 mol) in diglyme (30 ml) was added. The solution was then refluxed for 4 h. The mixture was cooled, treated with concd HCl (32 ml), and poured into water (200 ml). The acidic solution was then made strongly alkaline with a concd NaOH solution, and the liberated amine was extracted with ether. The extracts was dried over KOH, and the solvent was evaporated. The residual solid product was distilled to yield 3.7 g (46.8%) of **14**. NMR: (δ) 0.25—0.7 (m, 4H, Si-CH_2), 0.95 (d, 6H, C-CH_3), 0.8—1.3 (m, 4H, Si-CH_2-CN), 1.0 (s, 4H, NH_2), 1.3—1.9 (m, 2H, CH), 2.7 (q, 2H, CH-N). IR (neat): 3350, 2900, 1560, 1450, 1360, 1100, 1075, 1040, 1030, 800, 760 cm^{-1}. Mass: *m/e* 198 (M^+). Mp 53 °C, Bp 79 °C/0.5 Torr. Found: N, 13.90, Si, 13.9%. Calcd for $C_{10}H_{22}N_2Si$: N, 14.11, Si, 14.2%.

Polycondensation of ***14*** *with Adipoyl Dichloride.* A solution of adipoyl dichloride (0.17 g, 0.93 mmol) in CCl_4 (7 ml) was placed in beaker. A solution of **14** (0.5 g, 2.5 mmol) in 3.3 ml of water was then carefully poured over the acid chloride solution. The polymeric film which formed at the interface of the two solutions was grasped with tweezers and raised from the beaker. Yield 0.2 g (69.8%). IR(KBr): 3250, 2950, 1640, 1540, 1460, 1400, 1280, 1160, 1075, 1010, 770 cm^{-1}. $[\eta]=1.07$ (MeOH). Found: N, 8.73%. Calcd for $C_{16}H_{28}N_2O_2Si$: N, 9.80%.

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