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The Synthesis and Reactions of 2,6-Dimethyl-4-silaspiro[3.4]oct-6-ene

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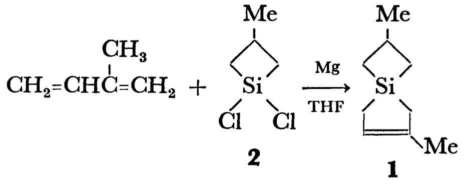
Synopsis. A new silaspiro compound, *i.e.*, 2,6-dimethyl-4-silaspiro[3.4]oct-6-ene, was synthesized by treating 1,1-dichloro-3-methyl-1-silacyclobutane with isoprene in the presence of magnesium in tetrahydrofuran. The reactions of the silaspiro compound with $LiAlH_4$, H_2PtCl_6, dimethyl acetylenedicarboxylate in the presence of $PdCl_2(PPh_3)_2$, and the Simmons-Smith agent were investigated.

A number of reports on the preparations and the reactions of silacyclobutanes have appeared.[1] However, a little work has been done on the synthesis of four-membered spiro compound which contains silicon atom in the ring.[2]

In the course of our studies of the synthesis and reactions of silacyclic compounds,[3b] a new silaspiro compound, *i.e.*, 2,6-dimethyl-4-silaspiro[3.4]oct-6-ene (**1**), was obtained. Being interested in the point that **1** contains two kinds of functional groups, double bond and silicon containing four-membered ring, in the molecule, we carried out some investigations concerning the reactivity of **1**.

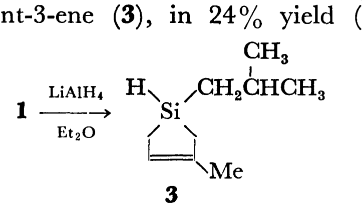
Results and Discussion

2,6-Dimethyl-4-silaspiro[3.4]oct-6-ene (**1**) was obtained in 59% yield by treating 1,1-dichloro-3-methyl-1-silacyclobutane (**2**) with an equimolar amount of isoprene in the presence of Mg in THF[3a] (Scheme 1).



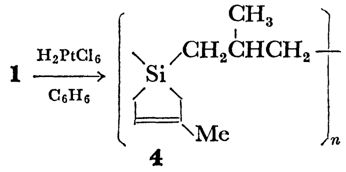
Scheme 1.

The reaction of **1** with $LiAlH_4$ gave the four-membered ring opening product, *i.e.*, 1-isobutyl-3-methyl-1-silacyclopent-3-ene (**3**), in 24% yield (Scheme 2).



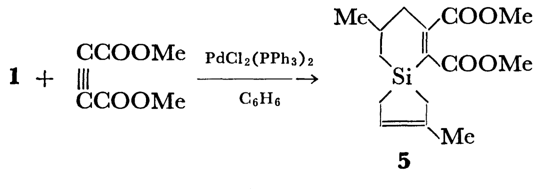
Scheme 2.

Polymerization of **1** was carried out in the presence of a small amount of H_2PtCl_6 in benzene. A solid polymer (**4**) ([η]=0.26 in benzene at 25 °C) was obtained in 74% yield. It was found that only the four-membered ring opening polymerization occurred and the five membered ring remained intact in the polymer, by comparing the IR and NMR spectra of **4** with those of **3**, and with those of the polymer obtained from 1,1,3-trimethyl-1-silacyclobutane (Scheme 3).



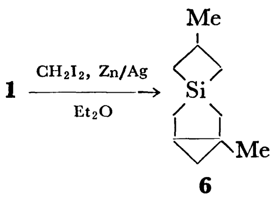
Scheme 3.

In the presence of a catalytic amount of $PdCl_2(PPh_3)_2$, the reaction of **1** with dimethyl acetylenedicarboxylate in benzene was carried out.[4] Another spiro compound, *i.e.*, 2,9-dimethyl-6,7-bis(methoxycarbonyl)-5-silaspiro[4.5]deca-2,6-diene (**5**), was obtained in 85% yield (Scheme 4).



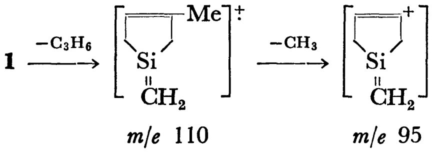
Scheme 4.

The reaction of **1** with the Simmons-Smith reagent in ether gave 1,3′-dimethylspiro[3-silabicyclo[3.1.0]hexane-3,1′-silacyclobutane] (**6**) in 47% yield. No methylene insertion product to the silicon-carbon or carbon-hydrogen bond of the four-membered ring was found in the reaction mixture (Scheme 5).



Scheme 5.

It is interesting that the silylene type fragment appears as the base peak in the case of 5-silaspiro[4.4]nona-2,7-diene,[5] whereas the silaethylene type fragment (*m*/*e* 110) is the base peak in the mass spectrum of **1**. Another silaethylene type fragment (*m*/*e* 95, relative intensity 71%) is also found in the spectrum of **1** (Scheme 6).



Scheme 6.

Experimental

The IR spectra were determined with a JASCO IR-A2 spectrometer. The NMR spectra were determined at 60

MHz with a Varian A-60D spectrometer in CCl_4 using TMS as the internal standard. Mass spectra were recorded on a JEOL-01SG instrument. The analytical GLC was carried out with a Shimadzu GC-5A chromatograph[1.5 m, 5% OV-1 on Chromosorb W(80—100 mesh)].

*Preparation of 2,6-Dimethyl-4-silaspiro[3.4]oct-6-ene (**1**).* In a flask Mg(5.5 g, 0.26 mol) was placed. A solution of isoprene (14.4 g, 0.21 mol) and **2**(29.5 g, 0.19 mol) in THF(85 ml) was added to the flask. The mixture was refluxed for 27 h with stirring. Water(150 ml) was added to the reaction mixture at 0 °C. The organic layer was washed three times with water, dried with Na_2SO_4. Subsequent evaporation and distillation gave **1** in 59%(17.1 g) yield. Bp 91—92 °C/38 Torr(1 Torr=133.322 Pa). n_D^{20} 1.5011. IR(neat) 1640, 1150, 1130, 950 cm^{-1}. NMR (δ) 0.6—1.2(m, 4, Si-CH_2), 1.16(d, 3, CH_3), 1.3—1.65(m, 4, Si-CH_2-C=), 1.75(broad s, 3, =C-CH_3), 2.1—2.8(m, 1, CH), 5.5(broad s, 1, =CH). Mass(*m*/*e*) 152(M$^+$), 124, 111, 110(base peak), 109, 96, 95, 83, 82, 81, 74, 69, 68, 67, 59, 55, 53, 31, 29. Found: C, 70.59; H, 10.61%. Calcd for $C_8H_{16}Si$: C, 70.97; H, 10.59%.

*Reaction of **1** with $LiAlH_4$.* A solution of **1**(1.0 g, 6.6 mmol) in ether(5 ml) was added to a suspension of $LiAlH_4$ (1.0 g, 0.026 mol) in ether(7 ml) with stirring. The reaction mixture was refluxed for 4 h. Saturated aqueous Na_2SO_4(about 20 ml) was added to the mixture with external cooling. Usual workup of the solution gave **3** in 24% (0.24 g) yield. Bp 90—92 °C/25 Torr. IR(neat) 2100, 1640 cm^{-1}. NMR(δ) 0.52(m, 2, Si-CH_2), 0.97(d, 6, C-CH_3), 1.3—1.6(m, 4, Si-CH_2-C=), 1.6—1.8(m, 3, CH_3), 2.1—2.3 (m, 1, CH), 4.2(m, 1, Si-H), 5.46(m, 1, =CH). Mass(*m*/*e*) 154(M$^+$), 149, 126, 112, 98, 97(base peak), 83, 71, 70, 69, 67, 59, 55, 45, 43, 31. Found: C, 69.70; H, 11.55%. Calcd for $C_9H_{18}Si$: C, 70.05; H, 11.76%.

*Polymerization of **1**.* A solution of **1**(0.50 g, 3.3 mmol) in benzene(10 ml) was refluxed for 3 h in the presence of a small amount of H_2PtCl_6. The mixture was poured into methanol(250 ml). The polymer precipitated was collected, dried in a desiccator. Thus, **4** was obtained in 74%(0.37 g) yield. IR(KBr) 1640 cm^{-1}. NMR(δ) 0.5—0.7(m, 4, Si-CH_2), 0.97(d, 3, CH_3), 1.3—1.6(m, 4, Si-CH_2-C=), 1.6—1.8(m, 3, CH_3), 2.0—2.9(m, 1, CH), 5.5(m, 1, =CH).

*Reaction of **1** with Dimethyl Acetylenedicarboxylate in the Presence of $PdCl_2(PPh_3)_2$.* A solution of **1** (1.0 g, 6.6 mmol), $PdCl_2(PPh_3)_2$ (0.063 g, 0.065 mmol), and dimethyl acetylenedicarboxylate (1.0 g, 7.0 mmol) in benzene(16 ml) was refluxed for 2 h with stirring. Water was added to the reaction mixture. Usual workup of the organic layer gave **5** in 83%(1.6 g) yield. Bp 144—147 °C/3 Torr. n_D^{20} 1.5153. IR(neat) 1720, 1640, 1600 cm^{-1}. NMR(δ) 0.8—1.2(m, 2, Si-CH_2), 1.1(d, 3, CH_3), 1.25—1.6(m, 4, Si-CH_2-C=), 1.75 (m, 3, =C-CH_3), 1.9—2.2(m, 2, CH_2), 2.3—2.5(m, 1, CH), 3.62, 3.70(two singlets, 6, $COOCH_3$), 5.45(broad s, 1, =CH). Mass(*m*/*e*) 294(M$^+$), 279, 263, 262(base peak), 245, 228, 219, 218, 204, 190, 182, 162, 152, 126, 125, 57. Found: C, 61.06; H, 7.99%. Calcd for $C_{15}H_{22}O_4Si$: C, 61.20; H, 7.53%.

*Reaction of **1** with the Simmons-Smith Reagent.* Diiodomethane (4.0 g, 0.015 mol) was added slowly to the suspension of Zn-Ag couple(0.98 g, 0.015 mol) in dry ether (9 ml) at room temperature. The mixture was stirred for 1 h, and then **1**(1.0 g, 6.6 mmol) was added to the mixture. After the mixture was refluxed for 20 h with stirring, dil HCl was added to the mixture with cooling. Usual workup of the organic solution, gave **6** in 47%(0.52 g) yield. Bp 98—100 °C/20 Torr. IR(neat) 1130, 950 cm^{-1}. NMR(δ) −0.23(t, 1, C-H in cyclopropane ring), 0.2—0.45(m, 1, C-H in cyclopropane ring), 0.5—1.25(m, 8, Si-CH_2), 1.12 (d, 3, CH_3), 1.18(s, 3, CH_3), 1.2—1.4(m, 1, CH), 2.0—2.8 (m, 1, C-H in cyclobutane). Mass(*m*/*e*) 166(M$^+$), 138, 124, 109, 96(base peak), 83, 69, 55, 43. Found: C, 72.01; H, 10.80%. Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91%.

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