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APPENDIX III

Synthesis of 3-Methylene-1,1-dichlorosilacyclobutane and 1,1-Dichlorosilacyclopent-3-ene.

Robert Damrauer *,1 Andre Laporterie 2, Georges Manuel 2, Young Tae Park, Roger Simon 1 and William P. Weber *.

D. P. and K. B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA.

1. *Department of Chemistry, University of Colorado at Denver, 1200 Larimer St., Denver, CO 80204, USA.*

2. *Laboratoire des Organometalliques, Universite Paul Sabatier, Toulouse, 31062, France.*

Abstract

The preparation of 3-methylene-1,1-dichlorosilacyclobutane and 1,1-dichlorosilacyclopent-3-ene from readily available starting materials is reported.

Silacyclobutanes have played an important role in the development of modern silicon chemistry [1,2]. For example, silacyclobutanes serve as precursors to carbon-silicon double bonded intermediates silenes [3,4] as well as to pentacoordinate silicon anions in the gas phase [5,6]. Silacyclobutanes also undergo facile ring opening polymerization [1,7]. Despite the importance of this ring system surprisingly few functionalized silacyclobutanes and silacyclobutenes have been prepared. A recent exception is the reported isolation albeit in low yields of both 2-methylene-1,1-dimethylsilacyclobutane and 3-methylene-1,1-dimethylsilacyclobutane (I) from the co-pyrolysis of 1,1-dimethyl-1-silacyclobutane and allene [8].

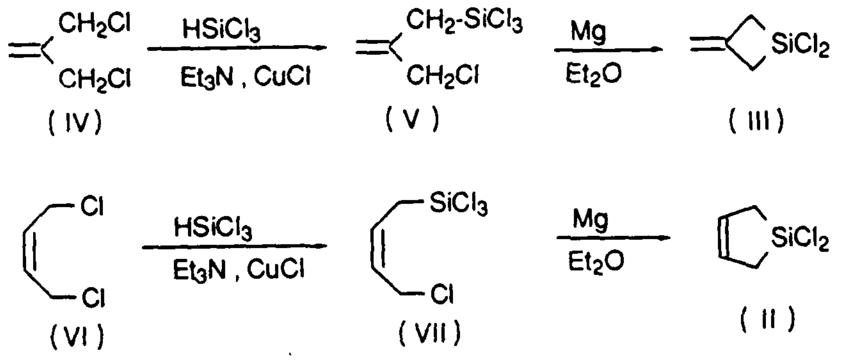
Similarly, there is considerable interest in 1-silacyclopent-3-enes due to their facile conversion into other functionalized silicon heterocycles [9] as well as due to their ability to undergo anionic ring opening polymerization [10]. These compounds have usually been prepared by reaction of a 1,3-diene with a dihalosilane under dissolving metal reduction conditions [9]. These conditions are not suitable for the preparation of silacyclopent-3-enes with reactive functional groups such as alkoxy, amino, chloride or fluoride bonded to silicon.

An alternate approach, utilized by Chernychev to prepare 1,1-dichlorosialcyclopent-3-ene (II) [11,12], involves the reaction of silylenes with 1,3-butadienes [11-14]. Unfortunately, the high cost and or lack of commercial availability of suitable silylene precursors such as hexachlorodisilane makes this route unattractive.

We would like to report new two step synthetic routes to prepare both 3-methylene-1,1-dichlorosilacyclobutane (III) and 1,1-dichlorosilacyclopent-3-ene (II) which utilizes readily available starting materials. Thus 3-chloro-2-chloromethyl-1-propene (IV) reacts with trichlorosilane, triethylamine and a catalytic amount of cuprous chloride to yield 2-chloromethyl-3-trichlorosilylpropene (V) [15]. This type of reaction has been previously utilized to prepare V and other allyltrichlorosilanes [16,17]. The equilibrium formation of a trichlorosilyl anion by reaction of triethylamine with trichlorosilane is probably critical to the success of this reaction [18-20]. The role of the cuprous chloride in the reaction is at present unclear. Trichlorosilyl cuprate reagents may in fact be involved. Of synthetic interest, V undergoes intramolecular Grignard ring closure to yield III (10%). While the yield of III is low, the ready availability of the starting materials make this a convenient procedure for the preparation of III.

In a similar manner, 1,4-dichloro-*cis*-2-butene (VI) reacts with trichlorosilane, triethylamine and a catalytic amount of cuprous chloride to yield 1-chloro-4-trichlorosilyl-*cis*-2-butene (VII) as the major product along with 1,4-*bis*(trichlorosilyl)-*cis*-2-butene (VIII). VII undergoes cyclization by an intramolecular Grignard ring closure to yield II in over 60% yield [21,22].

III has been converted to I by reaction with methylmagnesium iodide in diethyl ether. It is difficult to isolate I from this reaction. On the other hand, conversion of II to other functionalized silacyclopent-3-enes can easily achieved. For example, II has been reduced with $LiAlH_4$ to yield silacyclopent-3-ene [11]. 3-Methylene-silacyclobutanes are clearly more reactive than isomeric silacyclopent-3-enes and require significantly greater experimental care. We hope that the availability of these reactive silicon heterocycles will stimulate further interest in their chemistry.



Experimental

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on an IBM NR 80, IBM-Brucker-270-SY or Brucker AM-360 spectrometer operating in the Fourier Transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least one methylene groups bonded to them [23]. Identical ^{29}Si spectra could be obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 30 seconds [24]. Ten to fifteen percent solutions in chloroform-d were used to obtain ^{13}C and ^{29}Si NMR spectra. Five percent solutions were used to obtain ^{1}H NMR spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra were taken on neat films on NaCl plates.

Low resolution mass spectra were obtained on a Finnegan Mat Incos 50 GCMS or on a Hewlett Packard 5970 B Mass Selective Detector at an ionizing voltage of 70 eV. A 0.25 mm X 30 m fused silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Tetrahydrofuran (THF) and diethyl ether were distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Triethylamine was dried over potassium hydroxide pellets. Cuprous chloride, activated magnesium powder, trichlorosilane, IV and VI were purchased from Aldrich Chemical

Co. Inc.

All glassware was dried overnight in an oven at 120°C. It was assembled and was flame dried under an atmosphere of purified Argon. All reactions and transfers were conducted under an atmosphere of purified Argon.

4-Chloro-1-trichlorosilyl-cis-2-butene (VII)

In a 1-L three neck round bottom flask equipped with an efficient reflux condenser, a tru-bore mechanical stirrer equipped with a Teflon paddle and a pressure equalizing addition funnel was placed cuprous chloride (0.65 g, 6.5 mmol), triethylamine (73.9 g, 0.73 mol) and diethyl ether (500 mL). Trichlorosilane (98.2 g, 0.73 mol), VI (80.6 g, 0.65 mol) and diethyl ether (60 mL) was placed in the addition funnel. This solution was added to the vigorously stirred greenish suspension of cuprous chloride and triethylamine over a period of 4 h. The reaction mixture was stirred overnight. The triethylammonium hydrochloride salts were removed by filtration under Argon. These were washed several times with pentane. The solvents were removed from the combined filtrate by distillation through a 15 cm vacuum jacketed Vigreux column at atmospheric pressure. The residue was transferred to a 250 mL round bottom flask. The product was purified by fractional distillation under reduced pressure. A fraction bp 72-73°C/2.8 mm, 78.2 g, 54% yield was isolated. It had the following spectral properties. ^{1}H NMR : 2.43 (d of d,2H, J = 8.5 and 1.4 Hz), 4.08(d of d,2H, J = 7.7 and 1.0 Hz), 5.63(d of t of t,1H, J = 10.6, 8.5 and 1.0 Hz), 5.87(d of t of t, 1H, J = 10.6, 7.8 and 1.4 Hz). ^{13}C NMR : 25.17, 38.56, 123.12, 129.03. ^{29}Si

NMR : 6.70. IR : 3030, 2960, 2890, 1645, 1450, 1410, 1380, 1305, 1250, 1170, 1130, 1050, 945, 770, 730, 660 cm^{-1}. Elemental Anal. Calcd. for $C_4H_6SiCl_4$: C, 21.45; H, 2.70; Cl, 63.31. Found: C, 20.96; H, 2.71; Cl, 63.32.

1,4-bis(Trichlorosilyl)-cis-2-butene (VIII)

A fraction bp 93-94°C/3 mm, 10.7 g, 5.1 % yield was isolated. It had the following spectral properties. ^1H NMR : 2.37(d, 4H, J = 5.35 Hz), 5.66(t,2H, J = 5.33 Hz). ^{13}C NMR : 25.12, 122.20. ^{29}Si NMR : 7.08. IR : 3030, 2930, 2880, 1645, 1405, 1390, 1370, 1165 (s), 1110, 1095, 1050, 1020, 960, 925, 815, 750, 680 cm^{-1}. Elemental Anal. Calcd. for $C_4H_6Si_2Cl_6$: C, 14.88; H, 1.87; Cl, 65.86. Found: C, 15.12; H, 1.82; Cl, 66.03. ^1H NMR is in agreement with previously reported values [25].

1,1-Dichlorosilacyclopent-3-ene (II)

In a 1-L three neck round bottom flask equipped with an efficient reflux condenser, Teflon covered magnetic stirring bar and a pressure equalizing addition funnel was placed magnesium powder (18.3 g, 0.76 mol) and diethyl ether (400 mL). VII (73.0 g, 0.33 mol), diethyl ether (100 mL) and 1,2-dibromoethane (6.2 g, 33 mmol) was placed in the addition funnel. This solution was added to the well stirred magnesium suspension over 3 h. The reaction mixture was heated for 40 h with vigorous stirring. Magnesium chloride salts and excess magnesium were removed by filtration through a sintered glass filter. The salts were washed several times with pentane. The solvents were removed from the combined filtrate by distillation through a 15 cm vacuum jacketed Vigreux column at atmospheric pressure. The residue was transferred to a 100 mL round bottom flask. The product was purified by fractional distillation. A fraction bp 130-133°C (Lit. bp 134-135°C/750mm) [11] at atmospheric pressure, 30.6 g, 61% yield was isolated. It had the following properties. ^1H NMR : 1.86(d, 4H, J = 1.0 Hz), 5.99(t,2H, J =1.2 Hz). ^{13}C NMR : 21.89, 129.06. ^{29}Si NMR : 40.76. IR : 3020, 2915, 2885, 1600, 1390, 1200, 1190, 1095, 940, 810, 720, 640 cm^{-1}. The ^1H NMR is also in agreement with that previously reported [11].

2-Chloromethyl-3-trichlorosilylpropene (V)

V was prepared as above by reaction of trichlorosilane, IV, triethylamine and a catalytic amount of cuprous chloride in diethyl ether. V was purified by fractional distillation, bp 57-60°C/5 mm. ^1H NMR : 2.52(s,2H), 4.10(s,2H), 5.12(s,1H), 5.32(s,1H). ^{13}C NMR : 29.74, 48.67, 118.57, 136.38. GCMS m/e (rel. intensity): 228(1.0), 226(5.0), 224(9.0), 222 (7.0), 137(18.0), 135(37.0), 133(38.0), 54(100.0). The ^1H NMR is in agreement with that previously reported [15].

1,1-Dichloro-3-methylenesilacyclobutane (III).

A three-fold excess of powdered magnesium, activated by 1,2-dibromoethane in diethyl ether was reacted with V as above for three to five days. The progress of the reaction was monitored by gas chromatography. After bulb-to-bulb distillation a 10% yield of III contaminated with 3% diethyl ether and 12% 2-methyl-3-trichlorosilylpropene was obtained. Final purification was by fraction distillation. III had the following properties: bp 112-113°C/atm. ^1H NMR : 2.63(t,4H, J = 2.2 Hz), 5.13(q,2H, J = 2.2 Hz). ^{13}C NMR : 37.26, 114.26, 115.26. GCMS m/e (rel. intensity): 156(2.0), 154(11.0), 152(17.0) $M^{+\cdot}$, 118(18.0), 117(8.0), 116(61.0)(M-HCl)$^{+\cdot}$, 115(14.0), 114(33.0), 113(15.0), 112(43.0)(M-C_3H_4)$^{+\cdot}$, 65(19.0), 63(60.0)(SiH_2Cl)$^+$, 54(100.0)(M-$SiCl_2$)$^{+\cdot}$.

Silacyclopent-3-ene

In a 250 mL two neck round bottom flask equipped with a highly efficient reflux condenser, connected to a 0°C cooling bath, a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed $LiAlH_4$ (0.92 g, 24.2 mmol) and diethyl ether (100 mL). II (7.0 g, 46 mmol) and diethyl ether (30 mL) was placed in the addition funnel. This solution was added to the vigorously stirred suspension of $LiAlH_4$ over 2 h. The reaction mixture was stirred at rt overnight. Excess $LiAlH_4$ and salts were removed by filtration through a sintered glass filter. The salts were washed several times with pentane. The combined filtrate was fractionally distilled through a 30 cm vacuum jacketed Vigreux column. A fraction bp 65-66°C (Lit. bp 69-70°C) [11], 2.3 g, 60% yield was isolated. It had the following properties. ^1H NMR : 1.53(d of t,4H, J = 3.9 and 1.0 Hz), 3.97(q,2H, J = 3.8 Hz), 5.92(s,2H). ^{13}C NMR : 11.53, 130.92. ^{29}Si NMR : -27.70. IR : 3020, 2885, 2880, 2140, 1600, 1200, 1060, 940, 850, 725, 660, 620 cm^{-1}. Low resolution GC/MS m/e (rel. intensity): 86(3.6), 85(13.1), 84(79.5) M$^{+\cdot}$, 83(100.0)M-1$^+$, 82(41.4)M-2$^+$, 81(21.7), 80(3.4), 77(5.0), 70(2.0), 69(25.3), 68(2.2), 67(15.8), 66(6.2), 65(3.2), 58(29.7), 57(23.0), 56(83.8), 55(74.9), 54(24.5), 53(61.0), 51(5.7), 43(44.0), 42(14.4), 39(14.1). The ^1H NMR chemical shifts agree with those previously reported [11].

3-Methylene-1,1-dimethylsilacyclobutane (I)

I was prepared by addition of methyl Grignard to III. The ^1H

NMR chemical shifts of I in diethyl ether are consistently about 0.4 ppm downfield from those previously reported [8]. ^1H NMR : 0.30(s,6H), 1.76(t,4H), 4.65(m,2H).

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