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The Synthesis of Silacyclopentane Derivatives

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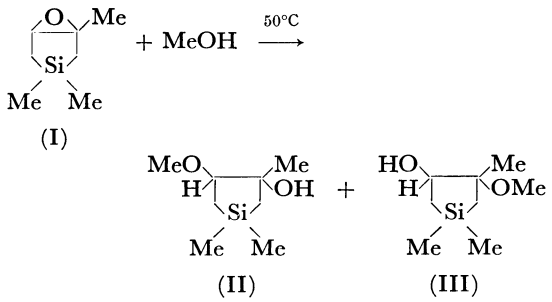
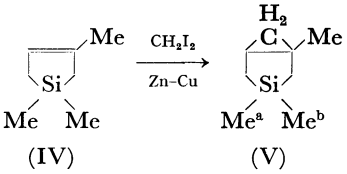
In the course of our studies of the reaction and polymerization of silacyclopentanes and -pentenes, 6-oxa-3-sila-1,3,3-trimethylbicyclo[3.1.0]hexane(I)[1], 1,3,3-trimethyl-3-silabicyclo[3.1.0]hexane(V), and 1,1,3-trimethyl-1-silacyclopentane(VI) were synthesized. Some of the reactions of I and the hydrogenation reaction of 1,1,3-trimethyl-1-silacyclopentene-3(IV)[2] were investigated.

Results and Discussion

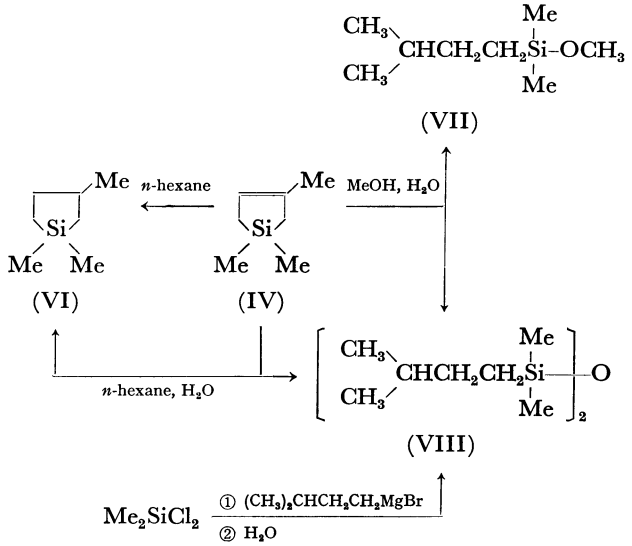
Because of its high strain in the epoxy ring, I was found to be very reactive; the addition of even a small amount of aluminum chloride to I caused a violent reaction, giving a solid polymer. Furthermore, I was found to react with methanol at 50°C giving a mixture of new compounds, 1,1,3-trimethyl-4-methoxy-1-silacyclopentane-3-ol(II) and its isomer, 1,1,3-trimethyl-3-methoxy-1-silacyclopentane-4-ol(III).



Under the same reaction conditions, other alcohols, such as ethanol, 1-propanol, and 1-butanol, and alkyl amines, such as methylamine and diethylamine, did not react with I. This lowering of the reactivity toward amines, in contrast with that of ordinary epoxy groups, may be explained in terms of the enhanced basisty of the carbon atomes next to oxygen caused by the electron-releasing effect of the CH_3Si- group. Now, we wish to report another successful synthesis of a new bicyclosilacyclopentane derivative, *i.e.*, 1,3,3-trimethyl-3-silabicyclo[3.1.0]hexane(V). This compound was synthesized by the method of carbene addition using the Simmons-Smith reagent.[3] The structural assignment was accomplished by the analysis of the IR and NMR spectra (IR spectrum; $-CH_2-$ in the cyclopropane ring, 3050 cm^{-1}; its skeletal vibration, 1010 cm^{-1}; NMR spectrum; the two singlets at $\tau=9.90$ and 9.95 for (CH_3^a) (CH_3^b)Si- show that the silacyclopentane ring remains intact).



Another new compound, 1,1,3-trimethyl-1-silacyclopentane(VI) was also synthesized by hydrogenating IV in the presence of the Pd–C catalyst. In this reaction, when *n*-hexane was used as the solvent hydrogenation proceeded successfully and VI was obtained, but when



Scheme 1. Hydrogenation of IV using a Pd-C catalyst.

1) G. Manuel, P. Mazerolles, and J. G. Florence, *C. R. Acad. Sci. Paris, Ser. C*, **269**, 1553 (1969).

2) D. R. Weyenberg, L. H. Toporcer, and L. E. Nelson, *J. Org. Chem.*, **33**, 1975 (1968).

3) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

methanol was used in place of *n*-hexane, only a ring-opening product, dimethylisopentylmethoxysilane(VII), was found in the reaction mixture. It was also observed that when a small amount of water was present in the solvent, diisopentyltetramethyldisiloxane(VIII) was formed as a by-product. The structural assignment for VIII was found by comparing its IR and NMR spectra with those of an authentic sample prepared from isopentylmagnesium bromide and dimethyldichlorosilane.

More detailed studies of the reaction of silacyclopentane derivatives are in progress.

Experimental

The NMR spectra were measured by means of a Varian A-60 spectrometer, using tetramethylsilane as the internal standard. The infrared spectra were obtained on a Shimadzu IR-27C spectrophotometer.

Preparation of 1,1,3-trimethyl-1-silacyclopentene-3(IV). A mixture of 34 g (0.5 mol) of isoprene and 64.5 g (0.5 mol) of dimethyldichlorosilane in 80 m*l* of tetrahydrofuran was added to 23 g (1 g atom) of a sodium dispersion in 120 m*l* of tetrahydrofuran over a 3-hr period at 30—35°C (external cooling) under a nitrogen atmosphere. After stirring for 20—25 hr at room temperature, filtration and distillation gave 18.0 g of IV; 28.5% yield; bp 123°C.

Epoxidation of IV. To a solution of 24 g (0.172 mol) of perbenzoic acid in 300 m*l* of chloroform, 20 g (0.157 mol) of IV was added over a 3-hr period at 5—7°C. After maintaining the reaction mixture at 5°C for 48 hr, benzoic acid and the excess perbenzoic acid were extracted with 200 m*l* of N sodium hydroxide. The chloroform solution was washed with two 100-m*l* portions of water and then dried. The removal of the solvent under reduced pressure at room temperature, followed by the frational distillation of the residue, gave 15.6 g of I; 64% yield; bp 60—62°C/34 mmHg, n_D^{25} 1.4442.

Reaction of I with Methanol. Five grams (35.2 mmol) of I and 5.5 g (171.9 mmol) of methanol were placed in a round-bottomed flask. The mixture was maintained for 5 hr at 50°C with stirring. The subsequent fractional distillation of the resulting mixture gave 3.7 g of the product; 60.7% yield; bp 85—90°C/20 mmHg. The H^1 NMR spectrum showed $SiCH_3$ singlets at τ 9.88 and 9.87, a complex multiplet for CH_2 at *ca.* 8.8—9.5, a singlet for C–CH_3 at 8.89, one for O–CH_3 at 6.89, and a quartet for C–H at 6.17. Two hydroxy H^1 peaks, at 7.1 and 8.3, indicate that *tert*-(II) and *sec*-(III) alcohols are present in the product.

Attempts to React I with Other Alcohols. I was reacted with ethanol, 1-propanol, and 1-butanol under the same reaction conditions as were used in the case of methanol. In every case, vapor-phase chromatographic analysis (3m, Thermal-3, 147°C) showed that I and the alcohol remained unchanged in the resulting mixture.

Attempts to React I with Amines. a) Methylamine was introduced into 1 g of I for 5 hr at 50°C. The vpc analysis of the resulting mixture indicated that the reaction did not occur.

b) A mixture of 1 g (7.0 mmol) of I and 2.5 g (34.2 mmol) of diethylamine was maintained for 5 hr at 50°C. The vpc analysis of the resulting mixture indicated that the reaction did not occur.

Preparation of 1,3,3-trimethyl-3-silabicyclo[3.1.0]hexane(V). A mixture of 8 g (0.0635 mol) of IV and 25 g (0.0933 mol) of methylene iodide in 50 m*l* of ethyl ether was refluxed in the presence of 6.5 g of Zinc-Copper couple for 24 hr with stirring. The ether solution was then decanted from the unreacted couple, washed with two 10 m*l* portions of a saturated aqueous ammonium chloride solution, and then dried over anhydrous magnesium sulfate. Fractional distillation gave 2.9 g of V; 33.1% yield; bp 35—36°C/17 mmHg. Found: Si, 20.4%. Calcd for $C_8H_{16}Si$: Si, 20.1%.

Hydrogenation of IV. General Procedure: Ten grams (0.0793 mol) of IV were hydrogenated in a catalytic hydrogenating apparatus in 50 m*l* of the four solvents described below using 0.5 g of palladium charcoal as the catalyst, at room temperature and under atmospheric pressure. The hydrogen uptake was almost theoretical in the case of each solvent. After the removal of the solvent, fractinal distillation gave the following compounds:

1) in the dry *n*-hexane solvent; 9.0 g of VI, bp 120—123°C, n_D^{20} 1.4345. Found: Si, 21.9%. Calcd for $C_7H_{16}Si$: Si, 22.0%.
2) in dry methanol: 10.2 g of VII, bp 60—62°C/80 mmHg, n_D^{20} 1.4120. Found: Si, 17.2%. Calcd for $C_8H_{20}OSi$: Si, 17.6%.
3) in *n*-hexane containing a small amount of water: VI and VIII (bp 120°C/20 mmHg, n_D^{20} 1.4282, Found: Si, 20.1%. Calcd for $C_{14}H_{34}OSi_2$: Si, 20.5%) were obtained. The yields of VI and VIII varied with the amount of water added.
4) in methanol containing a small amount of water: VII and VIII were obtained. The yields of VII and VIII varied with the amount of water added.

Preparation of an Authentic Sample of Diisopentyltetramethyldisiloxane. Isopentylmagnesium bromide prepared from 15.1 g (0.1 mol) of isopentyl bromide and 2.91 g (0.12 g atom) of magnesium in 50 m*l* of ether was stirred into 12.9 g (0.1 mol) of dimethyldichlorosilane in 20 m*l* of ether. The reaction mixture was heated at reflux for 2 hr, and then 30 m*l* of dilute hydrochloric acid were added. The ether layer was dried, subsequent distillation gave 4.8 g of diisopentyltetramethyldisiloxane; 35% yield. Its boiling point and IR and NMR spectra are consistent with those of VIII.

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