

## THE INSERTION OF PHENYL(BROMODICHLOROMETHYL)MERCURY-DERIVED DICHLOROCARBENE INTO THE Si-C(RING) AND $\beta$ C-H BONDS OF THE *cis* AND *trans* ISOMERS OF 1,3-DIMETHYL-1-n-BUTYL-1-SILACYCLOBUTANE

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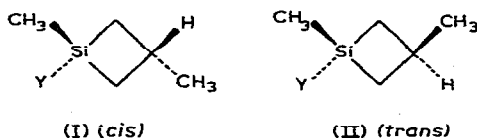
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### SUMMARY

Reaction of n-butylmagnesium bromide with a 1/1 *cis/trans* mixture of 1,3-dimethyl-1-chloro-1-silacyclobutane gave a 1/1 *cis/trans* mixture of 1,3-dimethyl-1-n-butyl-1-silacyclobutane and reaction of n-butyllithium with a 4/1 *cis/trans* mixture of 1,3-dimethyl-1-tert-butoxy-1-silacyclobutane resulted in a 4/1 mixture of the (presumed) *cis* and *trans* isomers of 1,3-dimethyl-1-n-butyl-1-silacyclobutane. Both of these isomer mixtures were treated with phenyl(bromodichloromethyl)mercury in benzene at 80° to give a mixture of the  $\beta$  C-H dichlorocarbene insertion product, 1,3-dimethyl-1-n-butyl-3-(dichloromethyl)-1-silacyclobutane (major product) and the Si-C insertion product, 2,2-dichloro-1,4-dimethyl-1-n-butyl-1-silacyclopentane. The NMR spectra of these products showed that both were formed as a mixture of *cis* and *trans* isomers, with the isomer ratios being very similar to those of the starting silacyclobutane. It was concluded that these stereoselective  $\text{CCl}_2$  insertion processes proceed with overall retention of configuration.

Recent work has made available the *cis* and *trans* isomers of various silacyclobutanes, (I) and (II) ( $\text{Y} = \text{RO}, \text{R}_2\text{N}$ )<sup>1\*</sup>. For instance, reaction of a 1/1 *cis,trans* isomer

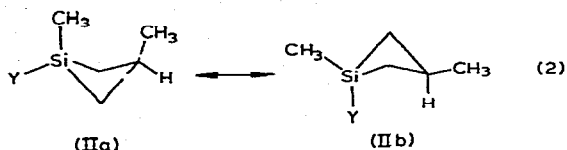
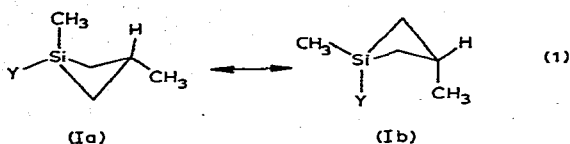


mixture of 1,3-dimethyl-1-chloro-1-silacyclobutane with tert-butanol and quinoline in pentane solution gave a 4/1 (I)/(II) mixture ( $\text{Y} = \text{Me}_3\text{CO}$ ).

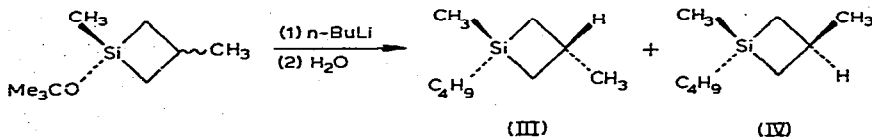
Studies using physical and spectroscopic methods<sup>2-4</sup> have shown that in the

\* In this paper we follow the definitions of "cis" and "trans" isomers used in ref. 1.

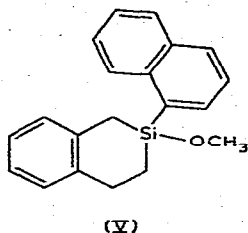
ground state the  $\text{SiC}_3$  ring of silacyclobutane is puckered, with an average dihedral angle of  $35.9 \pm 2^\circ$ . The barrier height,  $440 \pm 3 \text{ cm}^{-1}$ , is the largest found among four-membered ring molecules, but it still should allow the ready interconversion of (I) and of (II) as shown in eqns. (1) and (2). Since large substituents will prefer to occupy the equatorial positions in order to minimize 1,3 diaxial interactions<sup>5</sup>, these equilibria should favor (Ia) and (IIa).



Treatment of this 4/1 *cis/trans* mixture ( $\text{Y} = \text{Me}_3\text{CO}$ ) with *n*-butyllithium resulted in formation of the expected 1,3-dimethyl-1-*n*-butyl-1-silacyclobutane in 75% yield. Both geometric isomers of the product were formed, in a ratio of 4/1, which strongly suggests that the alkylation proceeded stereospecifically. Although an unambiguous assignment of structure to the isomers formed was not possible, it is reasonable to assume that the more abundant isomer is (III), the other (IV)\*. This assumption finds support in Sommer's demonstration that alkylation of optically



active alkoxy-silanes with alkyl-lithium reagents proceeds with retention of configuration<sup>7,8</sup>, and, more to the point, in the report by Corriu and Massé<sup>9</sup> that the same is true for the optically active cyclic methoxysilane (V) with alkyl-lithiums.



Although the  $\text{Si}-\text{CH}_3$  resonances of (I) and (II) ( $\text{Y} = \text{Cl}$  or  $\text{Me}_3\text{CO}$ ) were distinguishable in their 60 MHz NMR spectra, this was not the case for (III) and (IV). However, in the 100 MHz NMR spectrum of a (III)/(IV) mixture, their respective

\* The stereospecific synthesis of 1,2-dimethyl- and 1,3-dimethyl-1-silacyclobutanes with  $\text{Si}-\text{alkyl}$  and  $\text{Si}-\text{H}$  bonds has been reported<sup>6</sup>.

Si-CH<sub>3</sub> resonances were distinguishable, and, in fact, the composition of (III)/(IV) mixtures could be determined by integration of their respective Si-CH<sub>3</sub> signal areas (Fig. 1). The availability of isomerically enriched samples of such silacyclo-

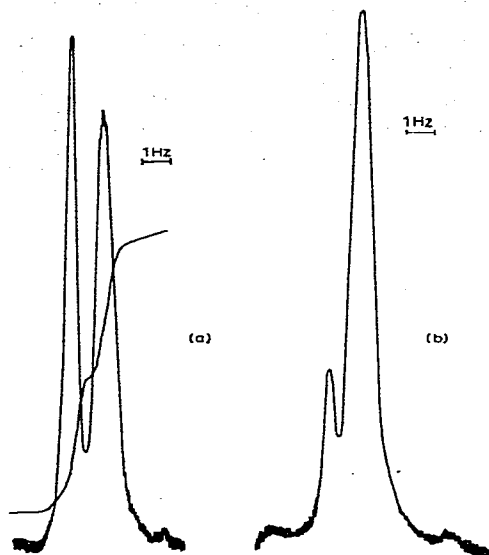
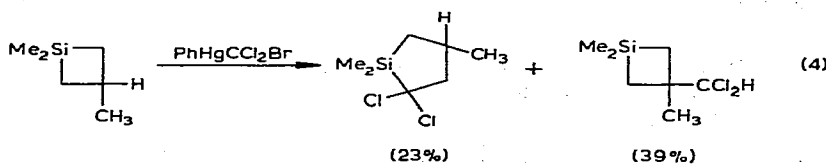
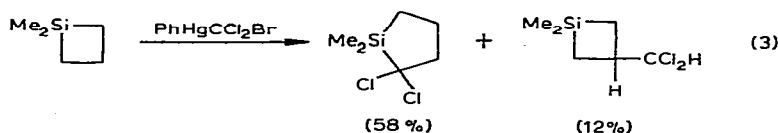


Fig. 1. 100 MHz NMR spectra of 1,3-dimethyl-1-n-butyl-1-silacyclobutane. (a) 1/1 *cis/trans* isomer mixture; (b) 4/1 *cis/trans* isomer mixture. (CH<sub>3</sub>-Si signals only).

butanes should allow the exploration of silacyclobutane chemistry in a more fundamental manner since stereochemical information now can be obtained. In the present report we address ourselves to the reaction of silacyclobutanes with dichlorocarbene.

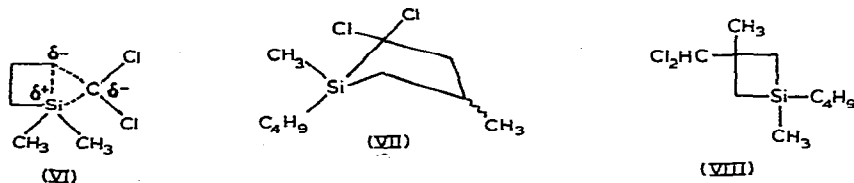
Previous studies have shown that dichlorocarbene [generated by thermolysis of phenyl(bromodichloromethyl)mercury] reacts with silacyclobutanes to insert CCl<sub>2</sub> into Si-C bonds of the SiC<sub>3</sub> ring and also into β C-H bonds of the ring [eqns. (3) and (4)]<sup>10,11</sup>.



It would be of interest to learn more about the mechanism of this novel ring expansion reaction for which a three-center mechanism [*i.e.*, transition state (VI)] was suggested<sup>10,11</sup>. Since this mechanism would predict that CCl<sub>2</sub> insertion into the

$\text{SiC}_3$  ring would occur with retention of configuration, the experimental determination of the steric course of this insertion process using (III) and (IV) as reactants seemed worth examining.

The insertion of dichlorocarbene into the benzylic C-H bond of optically active sec-butylbenzene occurs with retention of configuration<sup>12</sup>, but the stereochemistry of the Group IV element-activated insertion of  $\text{CCl}_2$  into  $\beta$  C-H bonds<sup>13-15</sup> has not yet been determined. Since such  $\beta$  C-H insertion also occurs in silacyclobutane systems as indicated in eqns. (3) and (4), reaction of (III) and (IV) with phenyl(bromodichloromethyl)mercury also should provide stereochemical information concerning this process.



The reaction of a 1/1 *cis/trans* mixture of 1,3-dimethyl-1-n-butyl-1-silacyclobutane [(III) and (IV)] with an equimolar quantity of  $\text{PhHgCCl}_2\text{Br}$  in benzene (2 h at  $80^\circ$ ) gave phenylmercuric bromide in 93% yield and two volatile products, the Si-C-(ring) insertion product (VII) and the  $\beta$  C-H insertion product (VIII), in yields of

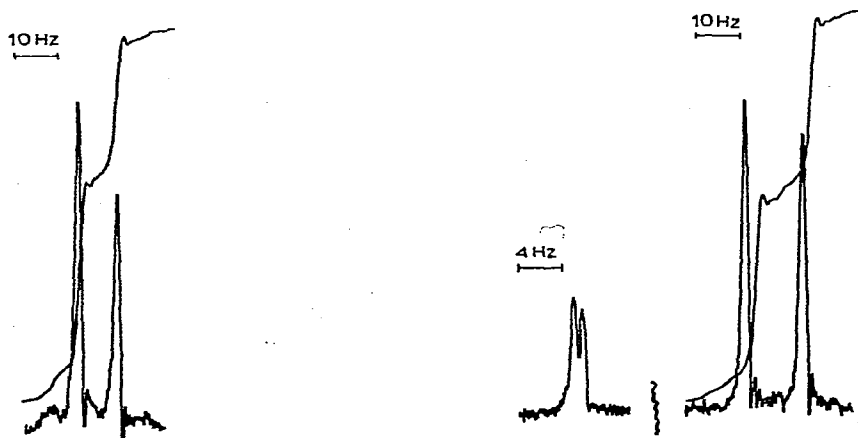


Fig. 2. 60 MHz NMR spectrum of 2,2-dichloro-1,4-dimethyl-1-n-butyl-1-silacyclopentane (1.3/1 isomer mixture). ( $\text{CH}_3$ -Si signals only).

Fig. 3. 60 MHz NMR spectrum of 1,3-dimethyl-1-n-butyl-3-(dichloromethyl)-1-silacyclobutane (1.1/1 isomer mixture). ( $\text{CH}_3$ -Si and  $\text{CCl}_2\text{H}$  signals).

18% and 47%, respectively. The 60 MHz NMR spectrum of (VII) (Fig. 2) showed Si- $\text{CH}_3$  resonances at  $\delta$  0.37 and 0.32 ppm with an area ratio of about 1.3/1. The NMR spectrum of (VIII) (Fig. 3) also showed two methyl-silicon signals at  $\delta$  0.52 and 0.42 ppm, with an area ratio of about 1.1/1. Two  $\text{CCl}_2\text{H}$  resonances also were seen for (VIII)

at 5.58 ppm, separated by 0.8 Hz, with a ca. 1/1 area ratio. In this reaction, as in the case of 1,1,3-trimethyl-1-silacyclobutane [eqn. (4)]<sup>11</sup>,  $\beta$  C-H insertion was the predominant process. This is in contrast to the observed modes of reaction with 1,1-dimethyl-1-silacyclobutane [eqn. (3)] and can be understood in terms of the extra activation provided for  $\beta$  C-H insertion into the 3-methyl substituted compounds by the fact that their  $\beta$  C-H bond is the more reactive tertiary type<sup>16</sup>. A similar reaction of the 1/1 (III)/(IV) mixture with a deficiency of  $\text{PhHgCCl}_2\text{Br}$  gave (VII) and (VIII) with about the same isomer ratios.

Reaction of phenyl(bromodichloromethyl)mercury with a 4/1 mixture of (III) and (IV) gave the two insertion products (VII) and (VIII) in yields of 22 and 50%, respectively. The NMR spectrum of the (VII) produced in this reaction indicated the presence of a 4.5/1 isomer mixture, while similar considerations implied that a 3.4/1 isomer mixture of (VIII) had been produced.

We cannot with any degree of confidence use the proton NMR spectra of these insertion products to determine the structures of the isomers involved. However, on the basis of the fact that the magnitude of the isomer ratios of the two insertion products [(VII) and (VIII)] does not differ greatly from the isomer ratio (III)/(IV) of the starting silacyclobutane, we suggest that both  $\text{CCl}_2$  insertion processes—into the Si-C bond and into the  $\beta$  C-H bond—occur largely with retention of configuration.

As mentioned above, dichlorocarbene insertion into the benzylic C-H bond of optically active *sec*-butylbenzene occurs with retention of configuration<sup>12</sup>, and  $\text{CCl}_2$  insertion into the  $\beta$  C-H bond of optically active bis[(*S*)-2-methylbutyl]mercury also proceeded with overall retention of configuration (23–50%)<sup>17</sup>. We therefore feel that the assumption that the highly stereoselective insertion of  $\text{CCl}_2$  into the  $\beta$  C-H bonds of (III) and (IV) proceeds with overall retention is a reasonable one.

A previous study by Landgrebe and Mathis<sup>18</sup> has shown that dichlorocarbene inserts into the carbon-mercury bond of optically active di-*sec*-butylmercury with complete retention of configuration. This finding and the fact that it is difficult to visualize a stereo-specific  $\text{CCl}_2$  insertion into the Si-C(ring) bonds of (III) and (IV) that occurs with inversion of configuration at either atom leads us to suggest that the insertion process proceeds with retention. Transition state (VI) thus remains an acceptable possibility.

## EXPERIMENTAL

### *General comments*

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All solvents used were dried with care. 60 MHz NMR spectra were obtained using a Hitachi-Perkin Elmer R20B, 100 MHz NMR spectra with a Varian HA-100 NMR spectrometer. Chemical shifts are given in  $\delta$  units ppm downfield from tetramethylsilane.

### *Preparation of 1,3-dimethyl-1-n-butyl-1-silacyclobutane*

(a). *The 1/1 cis/trans mixture from 1,3-dimethyl-1-chloro-1-silacyclobutane.* A 250 ml, two-necked flask equipped with a reflux condenser, a dropping funnel and a magnetic stirring unit was charged with 0.05 mol of *n*-butylmagnesium bromide in diethyl ether. To this solution was added slowly with stirring 3.0 g (22.3 mmol) of 1,3-dimethyl-1-chloro-1-silacyclobutane in 50 ml of ether. The reaction mixture was

heated at reflux for 24 h, cooled and hydrolyzed. The aqueous layer was extracted with ether and the combined organic phase was dried. Fractional distillation gave 2.8 g (80%) of the title compound, b.p. 93–94°/63 mmHg. Its IR spectrum showed a strong band at 1250  $\text{cm}^{-1}$  (Si–CH<sub>3</sub>) and a band at 1130  $\text{cm}^{-1}$  which is characteristic of the silacyclobutane system<sup>19</sup>. The NMR spectrum (100 MHz, CCl<sub>4</sub>; Fig. 1a) showed two singlets at  $\delta$  0.21 and 0.22 ppm in 1/1 ratio.

(b). *The 4/1 cis/trans mixture from 1,3-dimethyl-1-tert-butoxy-1-silacyclobutane.* The reaction was carried out using the procedure described in (a) with 76.6 mmol of *n*-butyllithium in hexane and 13.2 g (76.6 mmol) of 1,3-dimethyl-1-tert-butoxy-1-silacyclobutane (*cis/trans* ratio of 4/1)<sup>1</sup> in diethyl ether at room temperature for 24 h. Fractional distillation of the organic layer gave 8.9 g (75%) of the title compound. The NMR spectrum (100 MHz, CCl<sub>4</sub>; Fig. 1b) showed two singlets at  $\delta$  0.21 and 0.22 ppm in 4/1 ratio.

*Reaction of 1,3-dimethyl-1-*n*-butyl-1-silacyclobutane with phenyl(bromodichloromethyl)mercury*

(a). *The 1/1 cis/trans mixture.* A 50 ml, three-necked flask equipped with a reflux condenser, a magnetic stirring unit and a nitrogen inlet tube was charged with 1.0 g (6.4 mmol) of the silacyclobutane isomer mixture, 2.85 g (6.30 mmol) of phenyl(bromodichloromethyl)mercury<sup>20</sup> and 5 ml of dry benzene. The mixture was stirred and heated at reflux for 2 h. Filtration of 2.10 g (93%) of phenylmercuric bromide was followed by trap-to-trap distillation of the filtrate at 0.01 mmHg (pot temperature to 80°). GLC analysis of the distillate (F & M 5750, 6 ft.  $\times$   $\frac{1}{4}$  in. 20% Carbowax 20 M column at 145°) showed the presence of two products. The one with the shorter GLC retention time was present in 18% yield, the other in 47% yield. Analysis of a mixture of both products showed them to be CCl<sub>2</sub> insertion products. (Found: C, 50.33; H, 8.30; Cl, 29.44. C<sub>10</sub>H<sub>20</sub>Cl<sub>2</sub>Si calcd.: C, 50.19; H, 8.43; Cl, 29.64%.)

The less abundant product was assigned structure (VII) on the basis of its NMR spectrum, which further indicated that a mixture of geometric isomers was present:  $\delta$  0.32 (s, 1.3 H, Me–Si of one isomer), 0.37 (s, 1.7 H, Me–Si of the other isomer), 1.02 (d,  $J = 7.0$  Hz, 3 H, C–CH<sub>3</sub>) and 0.60–2.70 ppm (m, 14 H, C<sub>4</sub>H<sub>9</sub> and ring protons).

The other product was assigned structure (VIII); a mixture of isomers also was present:  $\delta$  0.42 (s, 1.45 H, Me–Si of one isomer), 0.52 (s, 1.55 H, Me–Si of the other isomer), 1.45 (s, 3 H, C–CH<sub>3</sub>), 0.80–1.70 (m, 13 H, C<sub>4</sub>H<sub>9</sub> and ring protons) and 5.58 and 5.59 ppm (s, of about equal intensity, 1 H total, CCl<sub>2</sub>H of each isomer).

A reaction of 0.54 g (3.50 mmol) of 1/1 (III) and (IV) mixture with 0.44 g (1.0 mmol) of PhHgCCl<sub>2</sub>Br in 1.5 ml of benzene at 80° for 2 h gave PhHgBr in 92% yield and (VII) and (VIII) in 22 and 55% yield, respectively. For (VII), the NMR spectrum showed the 0.32 and 0.37 ppm CH<sub>3</sub>–Si signals in 1/1.2 ratio. For (VIII), the 0.42 and 0.52 ppm CH<sub>3</sub>–Si resonances in the NMR spectrum were observed in a ratio of 1/1.2.

(b). *The 4/1 cis/trans mixture.* A similar procedure was used in the reaction of 7.50 g (17 mmol) of PhHgCCl<sub>2</sub>Br and 2.70 g (17.3 mmol) of the silacyclobutane isomer mixture in 8 ml of benzene. Phenylmercuric bromide was obtained in 99% yield. The yield of (VII) was 22%. In its NMR spectrum, the CH<sub>3</sub>–Si signals at 0.32 and 0.37 ppm were observed with relative intensity ratio of 1/4.5, respectively. The  $\beta$  C–H insertion product (VIII) was formed in 50% yield. In its NMR spectrum, the CH<sub>3</sub>–Si signals at 0.42 and 0.52 ppm were observed with relative intensity ratio of 3.4/1.

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