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INTRAMOLECULAR REACTIONS OF (ALKENYLDIMETHYLSILYL)-CARBENES

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SUMMARY

The reaction between compounds of the type $[CH_2{=}CH(CH_2)_n](CH_3)_2$-$SiCH_2Cl$ and sodium has been studied. Intermediacy of the corresponding carbene (or carbenoid reagent) is proposed and evidence for intramolecular carbene addition to the olefinic linkage is presented in the case where $n = 0$, 2 and 3.

INTRODUCTION

Investigation of the reaction between compounds of the type $R(CH_3)_2SiCH_2Cl$ and sodium have led us to postulate an α-silylcarbene (or carbenoid reagent) as an intermediate according to the following mechanism*[1,2] as shown by eqns. (1a) and (1b):

$$R(CH_3)_2SiCH_2Cl + 2\ Na \rightarrow R(CH_3)_2SiCH_2Na + NaCl \qquad (1a)$$

$$R(CH_3)_2SiCH_2Cl + R(CH_3)_2SiCH_2Na \rightarrow$$
$$\rightarrow [R(CH_3)_2SiCH{:}] + RSi(CH_3)_3 + NaCl \qquad (1b)$$

Thus far we have investigated the intramolecular rearrangements of the above carbene where R is saturated. In the present work we have examined the reaction between compounds of the type $R'(CH_3)_2SiCH_2Cl$ and sodium where R′ contains an olefinic linkage. We have observed, and report here, rearrangements of the type already known for alkenyl carbenes and carbenoid reagents[5].

RESULTS AND DISCUSSION

In examining the reaction between $R(CH_3)_2SiCH_2Cl$ and sodium the following R groups have been used: vinyl, allyl, 3-butenyl, 2,3-dimethyl-3-butenyl, 4-pentenyl, and 5-hexenyl. The following is a brief listing of the products in each case followed by a more detailed explanation of each reaction.

(*i*). R = vinyl: The products were vinyltrimethylsilane (22%), 1,2-bis(vinyldimethylsilyl)ethane (6%), and [(cyclopropyldimethylsilyl)methyl]vinyldimethylsilane (I) (6%).

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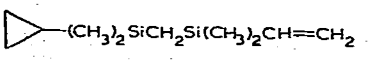
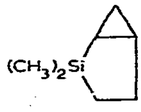
* This mechanism was shown to apply to the reaction between neopentyl chloride and sodium by earlier workers[3,4].



(I)



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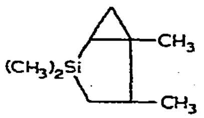


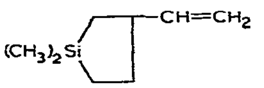
(III)

(*ii*). R=allyl: The only identified product was allyltrimethylsilane (22%). The "dimeric" product fraction contained seven components, none in greater than 0.5% yield.

(*iii*). R=3-butenyl: The products were 3-butenyltrimethylsilane (47%) and 2,2-dimethyl-2-silabicyclo[3.1.0]hexane (II) (27%).

(*iv*). R=2,3-dimethyl-3-butenyl: The products were (2,3-dimethyl-3-butenyl)-trimethylsilane (43%) and 2,2,4,5-tetramethyl-2-silabicyclo[3.1.0]hexane (III) (19%).

(*v*). R=4-pentenyl: The products were 4-pentenyltrimethylsilane (42%), unresolved *cis*- and *trans*-3-pentenyltrimethylsilane (9%), 1,1-dimethyl-3-vinyl-1-silacyclopentane (IV) (10%), and 2,2-dimethyl-2-silabicyclo[4.1.0]heptane (V) (7%).



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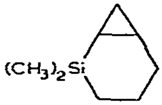

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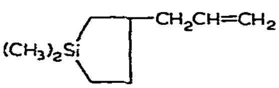
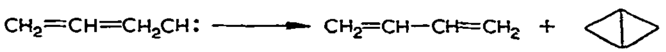


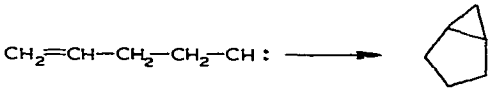
(VI)

(*vi*). R=5-hexenyl: The products were 5-hexenyltrimethylsilane (27%) and 1,1-dimethyl-3-allyl-1-silacyclopentane (VI) (15%).

Intramolecular rearrangements of alkenylcarbenes and carbenoid reagents have been investigated by several workers, and the subject has been reviewed recently[5]. It is known that allylcarbene produces 1,3-butadiene and bicyclobutane in a 5/1 ratio [eqn. (2)], 3-butenylcarbene does not undergo intramolecular addition, 4-pentenylcarbene yields bicyclo[3.1.0]hexane in 36% yield [eqn. (3)], and 5-hexenylcarbene yields bicyclo[4.1.0]heptane in 18% yield [eqn. (4)].



(2)



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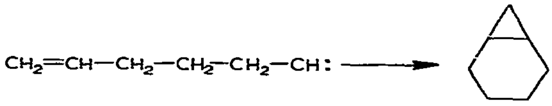
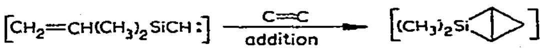
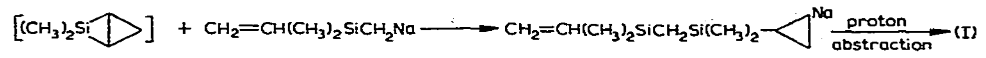


(4)

With regard to the position of the double bond relative to its carbene, the α-silylcarbenes generated in this work resemble the above-mentioned alkenyl carbenes. Thus in case (*i*) we suggest that (vinyldimethylsilyl)carbene is generated by a reaction sequence described by eqns. (1a) and (1b), and then rearranges to 2,2-dimethyl-2-silabicyclo[1.1.0]butane which subsequently undergoes ring opening as described by eqns. (5a) and (5b).



(5a)



(5b)

The ring opening reaction described by eqn. (5b) is consistent with the known chemistry of small ring silacycloalkanes[6].

The low yield of this ring-opened product could either be due to the relative unimportance of this carbene rearrangement or to the tendency of the ring opening reaction to proceed beyond one step to give higher molecular weight products.

The complexity of the product mixture in case (*ii*) prevented us from obtaining any information about the reaction, but it does not appear that intramolecular carbene rearrangement is an important reaction here.

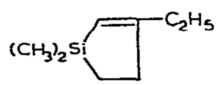
In case (*iii*) it appears that the carbene generated rearranges to (II), which is stable under the conditions of the reaction [eqn. (6)].

$$[CH_2{=}CHCH_2CH_2(CH_3)_2SiCH:] \xrightarrow[\text{Addition}]{C=C} (II) \qquad (6)$$

The stability of (II) is to be expected considering the known chemistry of silacyclopentanes[6]. The yield of this bicyclic product was 54% of theoretical, which is the highest of any of the cases studied here. This parallels the above-mentioned study of alkenylcarbenes of the type $CH_2{=}CH(CH_2)_nCH:$ in which the highest yield of bicyclic product was in the case where $n=3$.

In case (*iv*) the yield of bicyclic compound was diminished (38% of theoretical), suggesting that the methyl groups hold the carbene in an extended conformation more of the time, reducing the chance for intramolecular reaction.

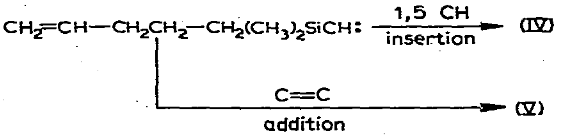
In case (*v*) the first time the Wurtz reaction was run, the pentenyltrimethylsilane fraction (34%) was found to be 80% unresolved *cis* and *trans* 3-pentenyltrimethylsilane with the other 20% being a complex mixture of isomers. The silacyclopentane fraction (17%) was found to be 70% 1,1-dimethyl-3-ethyl-1-sila-2-cyclopentene (VII)



(VII)

and 30% (IV). The yield of (V) was 10%. Subsequently the Wurtz reaction was run several times using identical reaction and workup conditions to those which gave the above results. One additional reaction was run using sodium sand to see if surface effects are involved. In these latter cases the product composition remained unchanged during the course of the reaction and the yields were consistently 42% 4-pentenyltrimethylsilane, 9% *cis*- and *trans*-3-pentenyltrimethylsilane, 10% (IV) and 7% (V). Also, heating the product mixture with sodium or n-butyllithium for prolonged periods did not change the composition of the mixture.

We assume that (IV) and (V) result from the rearrangement of (4-pentenyldimethylsilyl)carbene as shown in eqn. (7).



(7)

The 1,5 CH insertion process has been demonstrated in the case of saturated α-silylcarbenes[2] and the 1,6 C=C-addition process has been demonstrated in the case of alkenylcarbenes[5]. The origin of the other product(s) (aside from 4-pentenyltrimethylsilane) observed in this reaction is currently under study.

In case (*vi*) the double bond is in such a position that it is never close to the carbene and thus only 1,5 CH insertion is observed.

It appears then that aside from the complication of the reactivity of small ring silicon compounds the chemistry of the carbenes reported here is very similar to the analogous non-silicon-containing ones which have already been reported.

EXPERIMENTAL

All boiling points reported here are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Infrared spectra were determined with a Perkin–Elmer model 337 spectrophotometer. The NMR spectra reported here were obtained with a JEOL 4H 100, using benzene as an internal standard. All the compounds reported showed satisfactory proton integrations. The gas chromatographic analyses were done using a Varian aerograph model A-90 P chromatograph. The preparative work was carried out using a 20′ × $\frac{3}{8}$″ column packed with FFAP on Chromosorb P.

The sources of the specialized reagents were as follows: Lithium aluminum hydride, Alpha Chemical Co, 8 Congress St., Beverly, Mass. 01915; 4-chloro-1-butene, Aldrich Chemical Co., 2371 N. 30th St., Milwaukee, Wisconsin 53210; allylmagnesium chloride and the chlorosilanes and chloromethylsilanes, Pierce Chemical Co., P.O. Box 117, Rockford, Illinois 61105; the α,ω-dienes, chemical Samples Co., 4692 Kenney Road, Columbus, Ohio 43220. These reagents were used as received. The solvents used were dried over molecular sieves or calcium hydride.

Preparation of starting materials

Of the starting materials for the Wurtz reaction, only vinyldimethyl(chloromethyl)silane is commercially available. Of the remaining starting materials, allyldimethyl(chloromethyl)silane and 3-butenyldimethyl(chloromethyl)silane were prepared by Grignard reactions, and the others were prepared by addition of (chloromethyl)dimethylsilane to the appropriate diene. (Chloromethyl)dimethylsilane was prepared by the lithium aluminum hydride reduction of (chloromethyl)dimethylchlorosilane[7].

Allyldimethyl(chloromethyl)silane. A 2 l three-necked flask was equipped with an additional funnel, a reflux condenser and a paddle-type stirrer. Into this flask was put 1 mole of allylmagnesium chloride dissolved in 500 ml ether. (Chloromethyl)-dimethylchlorosilane (115 g, 0.85 mole) was added over a two-hour period, and the mixture was then refluxed for 12 h. Following hydrolysis, drying, and removal of the ether, the product was distilled with the fraction collected boiling at 42–47°/1 mm.

A 63% yield was obtained. (Found: C, 48.77; H, 8.95; Cl,24.20; Si, 18.51. $C_6H_{13}SiCl$ calcd.: C, 48.48; H, 8.75; Cl, 23.90; Si, 18.85%.)

The IR spectrum of the material showed absorptions at 3083 m and 3010 (sh) cm^{-1} (CH stretch); 1630 s (C=C stretch) and 901 s, 997 m cm^{-1} (C–H bend), all of which are characteristic of monosubstituted olefin.

The NMR data for this compound and all the others described here are included in Table 1.

3-Butenyldimethyl(chloromethyl)silane. Following a procedure similar to the above, with the exception that the 3-butenyl grignard was prepared in our laboratory and added to the chrorosilane, a 35% yield of 3-butenyldimethyl(chloromethyl)silane was obtained. The boiling point was 70–73°/17 mm. (Found: C, 51.64; H, 9.12; Cl, 21.53; Si, 17.27. $C_7H_{15}SiCl$ calcd.: C, 51.69; H, 9.23; Cl, 21.84; 17.23%.)

The IR spectrum included absorptions at 3085 m, 3000 (sh), 900–912 s and 997 s cm^{-1}, which are given the same assignments as above.

(2,3-Dimethyl-3-butenyl)(chloromethyl)dimethylsilane. Into a 250 ml, three-necked flask equipped with a stirrer, a reflux condenser and an addition funnel were added 2,3-dimethyl-1,3-butadiene (32 g, 0.40 mole) and 0.2 ml of Speier's catalyst*. The solution was heated to 75°, and (chloromethyl)dimethylsilane (32 g, 0.30 mole) was added dropwise over a one-hour period, during which the temperature did not exceed 120°. The product, (2,3-dimethyl-3-butenyl)(chloromethyl)dimethylsilane (36 g, 0.19 mole), was distilled from the reaction mixture at 80°/10 mm. The yield was 63%. (Found: C, 56.50; H, 10.16; Cl, 18.70; Si, 14.94. $C_9H_{19}SiCl$ calcd.: C, 56.64; H, 10.04; Cl, 18.59; Si, 14.73%.)

The IR spectrum of this material showed absorptions at 3070 m, 1642 m and 880–890 s cm^{-1}, to which are assigned the same modes as above. Each of these absorptions falls within the ranges assigned to geminally disubstituted alkenes[8]. No evidence was found in the gas chromatograph or IR and NMR spectra of this material for the 1,4 addition product.

4-Pentenyldimethyl(chloromethyl)silane. The same procedure was used here as with the preceding compound with the exception that a diluent was added to permit a sufficiently high temperature to allow the addition to begin. *Note: The reaction was attempted at the reflux temperature of the pentadiene; and after a considerable amount of silane had been added an explosion occurred.*

The product, which has a boiling point of 42°/0.5 mm, was obtained in 68% yield. (Found: C, 54.57; H, 9.97; Cl, 20.29; Si, 16.22. $C_8H_{17}SiCl$ calcd.: C, 54.36; H, 9.17; Cl, 20.05; Si, 15.89%.)

The IR spectrum of this material included absorptions at 3080 m, 3010 (sh), 1652 m, 915 s, and 990–1005 m cm^{-1}.

5-Hexenyl(chloromethyl)dimethylsilane. Using the same procedure as with the preceding compound, excluding the use of the diluent, the product, which boiled at 70°/0.4 mm, was obtained in 33% yield. (Found: C, 56.82; H, 10.30; Cl, 18.41; Si, 14.56. $C_9H_{19}SiCl$ calcd.: C, 56.64; H, 10.04; Cl, 18.59; Si, 14.73%.)

Reaction of vinyldimethyl(chloromethyl)silane with sodium. Into a 500 ml three-necked flask equipped with a stirrer and a reflux condenser were added 11.3 g (0.084 mole) of vinyldimethyl(chloromethyl)silane, 3.1 g (0.13 mole) of pentane-washed so-

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* See ref. 6, p. 233.

dium spheres and 300 ml of n-pentane. The reaction was monitored by gas chromatography, and after starting material was gone, ethanol was added. Subsequently water was added, and the organic layer was isolated and dried over sodium sulfate. The pentane was distilled off, and a fraction boiling from 40–70° containing vinyltrimethylsilane was collected. This mixture was weighed, and the amount of vinyltrimethylsilane (1.88 g, 0.0188 mole) was determined gas chromatographically. The residue was distilled using a microspinning ban column, and a fraction was collected at 41°/3.0 mm, which weighed 1.1 g. This fraction was analyzed gas chromatographically and shown to contain 0.5 g (2.5 mmole) 1,2-bis(vinyldimethylsilyl)ethane and 0.5 g (2.5 mmoles) (I). Both of these products were then isolated by preparative gas chromatography. Their characterization is described below.

The same general procedure was followed for the other Wurtz reactions. In the case of butenyldimethyl(chloromethyl)silane and higher homologs, only the fraction containing products with one silicon atom was isolated. The weighed fractions were analyzed gas chromatographically and subsequently pure samples of each product were isolated by preparative GLC. The characterization of the products is described below.

Identification of products

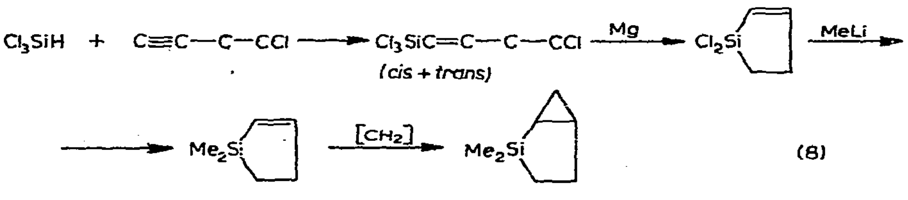
The elemental analyses of all new compounds are listed in Table 2.

(*a*). *Alkenylsilanes.* Vinyltrimethylsilane was identified on the basis of the weak IR absorption at 1590 cm^{-1} [ν(C=C)] (lit.[9] 1590 cm^{-1}) and the fact that its NMR spectrum coincides with that already reported[10]. Allyltrimethylsilane was identified on the basis of its terminal carbon–carbon stretching frequency at 1630 m cm^{-1} (lit.[9] 1633 cm^{-1}) and the facts that its NMR spectrum showed vinyl, allyl-CH_2 and $SiCH_3$ signals. Of the other terminally unsaturated alkenylsilanes reported here, 3-butenyltrimethylsilane, 4-pentenyltrimethylsilane, and 5-hexenyltrimethylsilane had IR absorptions at 3080 m, 3019 (sh), 1645 m (lit.[9] 1645–1648 cm^{-1}), 900 m and 910 s cm^{-1}. The IR spectrum of (2,3-dimethyl-3-butenyl)trimethylsilane had absorptions at 3070 m, 1642 m and 880–890 s cm^{-1}. The NMR spectra of these compounds (Table 1) are completely compatible with the assigned structures.

In the case of 3-pentenyltrimethylsilane the IR spectrum contained absorptions at 3020 w, 1650 w, 1640 w, 960 m, which are consistent with a *trans* disubstituted olefin. The two C=C stretching bands suggest that both the *cis* and *trans* isomers are present. The NMR assignments (Table 1) are based on the fact that when the allyl-CH_2 resonance was irradiated the α-(to silicon)-CH_2-signal collapsed to a singlet.

(*b*). *Bicyclohexanes and bicycloheptane*: The compound (II) was obtained by independent synthesis and shown to be identical (GLC retention time and NMR spectrum) to the material obtained in the Wurtz reaction. The independent synthesis was follows:

The procedure of Benkeser[11] was used to make 1,1-dichloro-1-silacyclo-2-pentene, which was methylated *in situ*. The resulting 1,1-dimethyl-1-silacyclopentene (VIII) was treated with methylene iodide and zinc-copper couple to yield the desired product. The reaction sequence is described by eqn. (8).



(VIII)

(8)

To 100 ml ether and 4 g (0.16 g atom) Mg were added 10 g (0.045 mole) of *cis*- and *trans*-1-trichlorosilyl-4-chloro-1-butene. After 48 h reflux 50 ml of 2 *M* methyllithium in ether was added and the mixture was refluxed for another 48 h. Hydrolysis and distillation gave 0.7 g (6 mmoles) of crude (VIII) boiling from 90–100° (lit.[12] 98–99°) (14% yield overall). Small portions of this material were purified by preparative GLC. The IR spectrum of it showed a strong absorption at 1570 cm^{-1} [ν(C=C)] (lit.[12] 1570 cm^{-1}. The NMR spectral data for this material is shown in Table 1.

Zinc–copper couple was prepared by the method of Le Gof[13]. Two grams of it (30 mmoles) were added to 15 ml diethyl ether and 13 mmoles methylene iodide was added subsequently. After the effervescence had subsided, 0.6 g (5 mmole) of crude (VIII) was added and the mixture was refluxed for 48 h. The mixture was then hydrolyzed and the ether layer separated and dried. Analytical GLC indicated that about one-third of the silacyclopentene had reacted during this time. Preparative GLC yielded enough product for elemental analysis and NMR spectral determination. The NMR spectrum and GLC retention time were identical to the material obtained from the Wurtz reaction.

The IR spectrum of (II) contained no absorption in the 1500–1700 region, indicating the absence of a carbon–carbon double bond. There were absorptions at 3050 m and 3000 m cm^{-1}, which are indicative of the CH_2 and CHR groups in cyclopropane respectively[14].

The structure of (III) was assigned on the basis of its IR and NMR spectra and its elemental analysis. The spectrum contained no absorption in the 1500–1700 region, and it contained absorptions at 3050 m and 2995 (sh) cm^{-1}. The NMR assignments (Table 1) were based on the facts that when the C-4 proton resonance is irradiated the C-4 methyl doublet collapses to a singlet and the C-3 proton doublet of doublets collapses to a single doublet. The remaining splitting of the C-3 proton is due to the geminal C-3 proton which has its signal in the silicon methyl region. Also when the 9.56 τ signal is irradiated the C-1 proton signal collapses to a singlet, indicating that both C-6 proton resonances are in the 9.56 τ envelop. It has not been determined whether this compound is a mixture of isomers or, if not, what the geometrical disposition of the 3-methyl group is.

The structure of (V) was assigned on the basis of its IR and NMR spectra and its elemental analysis. The IR spectrum has no absorptions in the 1500–1700 cm^{-1} region and has absorptions at 3060 m and 3000 m cm^{-1}. The NMR spectrum has a multiplet at 10.30 τ, which we assign to the C-1 proton by analogy with the above. The two silicon methyl groups are nonequivalent, suggesting α-(to silicon)-substitution (see below). Because of the potential nonequivalence of geminal protons in this cyclic structure, the rest of the spectrum cannot be assigned purely on the basis of integral values. The assignments in Table 1 are consistent with simple inductive effect arguments.

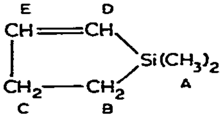
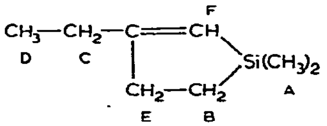
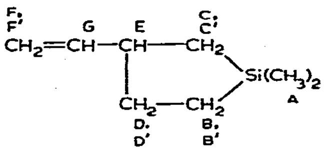
(continued on p. 325)

TABLE 1

NMR DATA[a]

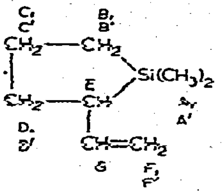
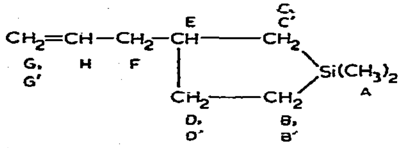
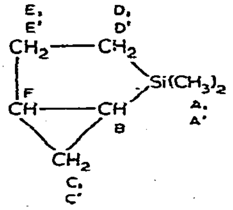
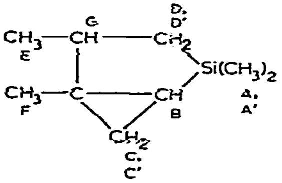
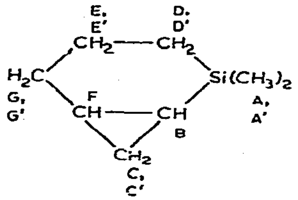
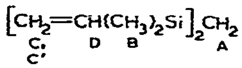
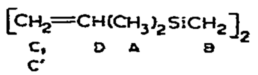
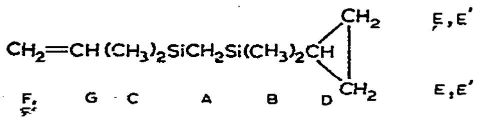
Compound	Signal (τ)	Assignment
$\mathrm{CH_2{=}CH{-}CH_2Si(CH_3)_2CH_2Cl}$	9.97 (1)	A
D, E B A C	8.44 (2)	B
D′	7.40 (1)	C
	5.06	D, D′
	4.20	E
$\mathrm{CH_2{=}CHCH_2CH_2(CH_3)_2SiCH_2Cl}$	9.94 (1)	A
E, F C B A D	9.30	B
E′	7.95	C
	7.39 (1)	D
	5.02	E, E′
	4.10	F
$\mathrm{CH_2{=}C(CH_3)CH(CH_3)CH_2(CH_3)_2SiCH_2Cl}$	9.87 (1)	A
G, D E C B A F	9.29	B
G′	8.93 (2)	C
	8.35 (1)	D
	7.61 (4)	E
	7.40 (1)	F
	5.07 (2)	G, G′
$\mathrm{CH_2{=}CHCH_2CH_2CH_2(CH_3)_2SiCH_2Cl}$	9.94 (1)	A
F, G D C B A E	9.41	B
F′	8.85	C
	7.94	D
	7.49 (1)	E
	5.00	F, F′
	4.17	G
$\mathrm{CH_2{=}CHCH_2CH_2CH_2CH_2(CH_3)_2SiCH_2Cl}$	9.93 (1)	A
G, H E D C B A F	9.39	B
G′	8.62	C
	7.94	D, E
	7.34 (1)	F
	5.00	G, G′
	4.19	H
$\mathrm{CH_2{=}CHCH_2Si(CH_3)_3}$	9.98 (1)	A
C, D B A	8.46 (2)	B
C′	5.04	C, C′
	4.22	D
$\mathrm{CH_2{=}CHCH_2CH_2Si(CH_3)}$	10.00 (1)	A
D, E C B A	9.35	B
D′	7.89	C
	4.95	D, D′
	4.00	E
$\mathrm{CH_2{=}C(CH_3)CH(CH_3)CH_2Si(CH_3)_3}$	9.88 (1)	A
F, D E C B A	9.24 (4)	B
F′	8.87 (2)	C
	8.27 (1)	D
	7.52 (4)	E
	5.07 (2)	F, F′

TABLE 1 *(continued)*

Compound		Signal (τ)	Assignment
$\underset{E,\ E'}{CH_2}{=}\underset{F}{CH}\underset{D}{CH_2}\underset{C}{CH_2}\underset{B}{CH_2}\underset{A}{Si(CH_3)}$		10.00 (1)	A
		9.50	B
		8.65	C
		8.00	D
		5.05	E, E′
		4.25	F
$\underset{C}{CH_3}\underset{E,\ E'}{CH{=}CH}\underset{D}{CH_2}\underset{B}{CH_2}\underset{A}{Si(CH_3)_3}$		9.83 (1)	A
		9.25 (3)	B
		8.22	C
		7.88	D
		4.28	E, E′
$\underset{F,\ F'}{CH_2}{=}\underset{G}{CH}\underset{E}{CH_2}\underset{D}{CH_2}\underset{C}{CH_2}\underset{B}{CH_2}\underset{A}{Si(CH_3)_3}$		9.91 (1)	A
		9.46	B
		8.49	C
		7.88	D, E
		4.95	F, F′
		4.08	G
$\underset{E}{BrCH_2}\underset{F,\ F'}{CH{=}CH}\underset{D}{CH_2}\underset{C}{CH_2}\underset{B}{CH_2}\underset{A}{(CH_3)_2SiCl}$	(X)	9.50 (1)	A
		9.10	B
		8.48	C
		7.85	D
		6.05	E
		4.25	F, F′
$\underset{H,\ H'}{CH_2}{=}CHCH_2BrCH_2CH_2CH_2\underset{G}{(CH_3)_2}SiCl$	(XI)	9.85 (1)	G
		4.95	H, H′
	(VIII)	9.65 (1)	A
		9.13 (3)	B
		7.45	C
		3.78	D
		3.03	E
	(VII)	9.76 (1)	A
		9.14 (3)	B
		8.81 (3)	C
		7.80 (4)	D
		7.50 (3)	E
		4.40 (1)	F
	(IV)	9.70 (1)	A
		7.6–9.6	B–E
		5.01	F, F′
		4.10	G

(Table continued)

TABLE 1 *(continued)*

Compound	Signal (τ)	Assignment
 (IX)	9.88, 9.78 (2) 9.23 7.8–8.8 5.10 4.13	A, A' B, B' C–E F, F' G
 (VI)	9.75 (1) 7.6–9.6 7.77 4.93 4.13	A B–E F G, G' H
 (II)	9.75, 9.70 (2) 9.97–9.63 8.44 (1 proton) 7.87 (2 protons)	A, A' B–D E, E', F
 (III)	10.17 9.81, 9.80 (2) 9.56 9.26 (4) 8.86 (2) 8.73 (1) 7.99	B A, A'+D C, C' D' E F G
 (V)	10.30 9.83, 9.73 (2) 9.06–9.70 (4 protons) 8.44 (2 protons 8.27 (1 proton) 8.17 (2 protons)	B A, A' C, C', D, D' E–G
 $[CH_2{=}CH(CH_3)_2Si]_2CH_2$	10.10 (1) 9.80 (1) 4.06	A B C, C', D
 $[CH_2{=}CH(CH_3)_2SiCH_2]_2$	9.75 (1) 9.35 (1) 4.00	A B C, C', D
 (I)	10.19 (1) 9.96 (1) 9.76 (1) 9.30–10.46 4.01	A B C D, E, E' F, F', G

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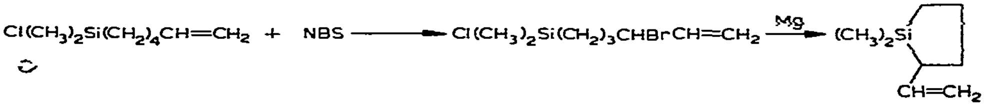
[a] The number in parentheses is the number of lines in the signal. If no number is given, the signal was complex. The proton integral values were consistent with the assignments in all cases; see the text for comments on the integral values of (X) and (XI).

(*c*). *Silacyclopentanes and silacyclopentenes.* The compound (VII) was identified by its IR and NMR spectra and elemental analysis. The IR spectrum contained strong absorption at 1590 cm^{-1}, indicating that the double bond is α-to silicon[12] and the NMR spectrum is a simple first order case.

The IR absorptions at 3080 m, 3010 (sh), 1640 m, 990 s and 910 s cm^{-1} and NMR spectrum of (IV) definitely establish that it contains a terminal double bond. The complexity of the α- and β-CH_2 portions of the NMR spectrum and the elemental analysis indicate that this is a ring compound. This being the case the only possibilities are the above-mentioned compound or 1-1-dimethyl-2-vinyl-1-silacyclopentane (IX). This latter compound was independently synthesized and shown to be different from the compound obtained in the Wurtz reaction.

The independent synthesis scheme was as described by eqn. (9).



(IX)

(9)

A mixture of 55 g 1-(chlorodimethylsilyl)-5-hexene (0.31 mole), 29 g *N*-bromosuccinimide (0.15 mole) and 300 ml carbon tetrachloride was refluxed overnight. Distillation yielded 17 g of crude product boiling at 102–115°/1 mm (44% yield).

Attempts at further purification by preparative GLC on several different columns led to substantial decomposition. Analytical GLC of this material indicated that it contained at least two components in approximately 4/1 ratio.

Interpretation of the NMR spectrum of this mixture suggests that it contains about 80% *cis*- and *trans*-1-(chlorodimethylsilyl)-6-bromo-4-hexene (X) and 20% 1-(chlorodimethylsilyl)-4-bromo-5-hexene (XI). The NMR spectrum contains signals at τ 9.50, 9.10, 8.48, 7.85, 6.05 and 4.25 (the latter pair are coupled) to which the assignments Si–CH_3, α-CH_2, β-CH_2, γ-CH_2, CH_2Br and CH=CH respectively for (X) are given. In addition there are signals at 9.85 τ and 4.95 τ which are assigned to $SiCH_3$ and *CH*=CH_2 for (XI). The integral ratio for these last two signals is 6/1, and the ratio of the 9.50 τ to 9.85 τ signal is about 4/1, which is consistent with the gas chromatographic analysis. The other integral values are non-whole numbers since both isomers give signals in the same regions.

Nine grams (36 mmoles) of the crude mixture were refluxed with 1 g Mg (0.040 g atom) in THF overnight. Subsequent hydrolysis and distillation (40–50°/50 mm) yielded 0.7 g (5 mmoles) crude (IX). Preparative GLC yielded a pure product which showed an IR absorption at 1660 m cm^{-1} [ν(C=C)]. The NMR spectrum (Table 1) shows a terminal olefinic group and two magnetically nonequivalent silyl–methyl groups. The C-2 proton is allylic and is shifted into the region of the C-3 and C-4 protons. The C-5 protons are distinguishable in the α-(to silicon)-CH_2 region. Alpha substitution on the silacyclopentane ring clearly gives rise to much simpler NMR spectra than does β-substitution.

The structure of (VI) was established on the basis of its IR and NMR spectra and its elemental analysis. The IR spectrum contained a band at 1650 m cm^{-1} [ν(C=C)]. The NMR spectrum (Table 1) shows a terminal vinyl group and has a single silicon–methyl signal and a complex envelope of lines from 7.6 τ to 9.6 τ, suggesting a β-substituted silacyclopentane. These plus the allyl-CH_2 signal at 7.77 τ

TABLE 2

ELEMENTAL ANALYTICAL DATA FOR PREVIOUSLY UNREPORTED REACTION PRODUCTS

Compound		Formula	Analysis, found (calcd.) (%)		
			C	H	Si
(2,3-Dimethyl-3-butenyl)trimethylsilane		$C_9H_{20}Si$	69.08 (69.12)	12.68 (12.90)	17.81 (17.98)
[(Cyclopropyldimethylsilyl)methyl]-vinyldimethylsilane	(I)	$C_{10}H_{22}Si_2$	60.38 60.45[a] (60.52)	11.34 11.26[a] (11.17)	28.66 28.50[a] (28.31)
2,2-Dimethyl-2-silabicyclo[3.1.0]hexane	(II)	$C_7H_{14}Si$	65.82 65.16[a] (65.62)	12.58 12.09[a] (12.50)	20.70 20.44[a] (21.88)
2,2,4,5-Tetramethyl-2-silabicyclo-[3.1.0]hexane	(III)	$C_9H_{18}Si$	70.46 (70.02)	12.20 (11.77)	17.58 (18.21)
1,1-Dimethyl-3-vinyl-1-silacyclopentane	(IV)	$C_8H_{16}Si$	68.66 (68.48)	11.61 (11.50)	19.70 (20.02)
2,2-Dimethyl-2-silabicyclo[4.1.0]heptane	(V)	$C_8H_{16}Si$	68.30 (68.48)	11.43 (11.50)	19.70 (20.02)
1,1-Dimethyl-3-allyl-1-silacyclopentane	(VI)	$C_9H_{18}Si$	70.32 (70.02)	11.92 (11.77)	18.04 (18.21)
1,1-Dimethyl-3-ethyl-1-sila-2-cyclopentene	(VII)	$C_8H_{16}Si$	68.66 (68.48)	11.61 (11.50)	19.70 (20.02)
1,1-Dimethyl-2-vinyl-1-silacyclopentane	(IX)	$C_8H_{16}Si$	68.52 (68.48)	11.71 (11.50)	19.55 (20.02)

[a] Analysis on independently synthesized sample.

superimposed on the ring proton signals are wholly consistent with the assigned structure.

(*d*). *Products containing two silicon atoms.* The compound 1,2-bis(vinyldimethylsilyl)ethane was identified on the basis of the weak carbon–carbon double bond stretching band at 1590 cm^{-1} characteristic of a vinylsilane and the fact that its NMR spectrum is completely consistent with the assigned structure.

The compound (I) was independently synthesized and shown to have the same IR and NMR spectrum and GLC retention time as the product of the Wurtz reaction. The preparation sequence was as described in eqn. (10).

$$CH_2{=}CH(CH_3)_2SiCH_2MgCl + CH_2{=}CH(CH_3)_2SiCl \rightarrow$$

$$[CH_2{=}CH(CH_3)_2Si]_2CH_2 \xrightarrow[CH_2I_2]{\text{Zn-Cu couple}} \text{(I)} \qquad (10)$$

Vinyldimethyl(chloromethyl)silane (25 g, 0.18 mole) was added dropwise to

4.8 g (0.2 mole) magnesium in THF. When this reaction was complete, 22 g of vinyl dimethylchlorosilane was added dropwise to the grignard solution. Overnight reflux followed by hydrolysis and distillation yielded an 11 g fraction boiling at 165–169° (30% yield). The IR spectrum of this material showed [ν(C=C)] at 1590 w cm^{-1}. The NMR spectral data is in Table 1.

Ten grams (0.6 mole) of the above-prepared bis(vinyldimethylsilyl)methane was added to 0.2 mole zinc-copper couple in ether along with 40 g (0.15 mole) methylene iodide. Overnight reflux followed by hydrolysis and evaporation of the ether yielded 9 g of residue. Gas chromatographic analysis of the residue showed that it contained two components in equal quantity, one of which was starting material. The other product was isolated by preparative GLC. Its IR spectrum contained absorptions at 3070 m, 3050 m, and 3000 m cm^{-1}, as compared to 3050 m and 3000 m cm^{-1} for 1,2-bis(vinyldimethylsilyl)ethane. Its NMR spectrum (Table 1) contains signals attributed to vinylsilane, two different silicon–methyl and Si–CH$_2$–Si groups. Part of the cyclopropyl ring proton spectrum overlaps with the silicon methyl signal.

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