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THE REACTION OF α-TRIALKYLSILYL CARBENES

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INTRODUCTION

Recently a report was published on the reaction between chloromethyltrimethylsilane and alkali metals[1]. It was shown that (trimethylsilyl)carbene is an important intermediate in this reaction and that it undergoes 1,3-insertion to form 1,1-dimethyl-1-silacyclopropane. The 1,1-dimethyl-1-silacyclopropane undergoes nucleophilic ring opening to produce higher molecular weight products.

In order to gain further information on the properties of (trialkylsilyl)carbenes we have studied the reaction of compounds of the type $R(CH_3)_2SiCH_2Cl$ with sodium where $R = C_2H_5$, n-C_3H_7, n-C_4H_9 and iso-C_4H_9. In addition to 1,3-insertion we have found 1,5-insertion to be an important reaction when it is possible. In all of the reactions reported here 1,3-insertion gives two different silacyclopropanes. From the two silacyclopropanes there are possible three isomeric cleavage products. The details and significance of three-ring formation and cleavage are presented in the Results and Discussion section.

RESULTS AND DISCUSSION

In general the results of the work reported here can be explained in terms of a three path mechanism, *i.e.*, (2a), (2a'), and (2b).

$$R(CH_3)_2SiCH_2Cl + Na \rightarrow R(CH_3)_2SiCH_2^- + NaCl \tag{1}$$

$$R(CH_3)_2SiCH_2^- + R(CH_3)_2SiCH_2Cl \begin{array}{ll} \xrightarrow{S_N2(C)} [R(CH_3)_2SiCH_2]_2 & (2a) \\ \xrightarrow{S_N2(Si)} [R(CH_3)_2Si]_2CH_2 & (2a') \\ \xrightarrow[\text{Elimination}]{\alpha} RSi(CH_3)_3 + R(CH_3)_2SiCH: & (2b) \end{array}$$

TABLE I

YIELD OF S_N2 PRODUCT *vs.* SIZE OF R IN THE REACTION BETWEEN $R(CH_3)_2SiCH_2Cl$ AND SODIUM

R	*Yield* $[R(CH_3)_2SiCH_2]_2$ (%)
C_2H_5	18
n-C_3H_7	15
n-C_4H_9	13

Product (III) (Table 2) is the result of path (2a') where $R = C_2H_5$. Since this material is formed in less than 1% yield this path is not an important one.

The data in Table 1 indicates that the relative importance of path (2a) decreases as R increases in size. This simply reflects the increasing difficulty of backside attack on the α-carbon as R increases in size. The identity of R determines the fate of the carbene formed in path (2b).

(*i*) $R = C_2H_5$

Table 2 shows the products of the reaction between ethyldimethyl(chloromethyl)silane and sodium. Ethyltrimethylsilane (I) is the result of proton abstraction by the (ethyldimethylsilyl)carbanion. Product (IV) is the result of (ethyldimethylsilyl)carbene insertion into the β-methyl group of (I) or into the β-methyl group of the starting material followed by reaction with sodium. It is possible that product (II) is one of the other isomers which could be produced by this type of intermolecular insertion reaction. The remainder of the products appear to be the result of intramolecular carbene insertion.

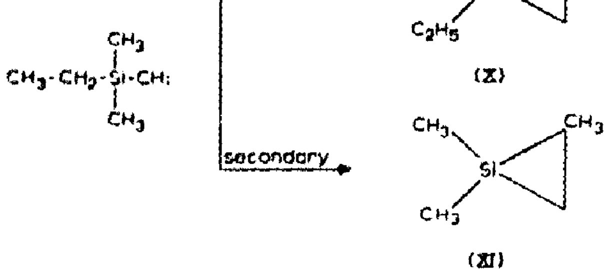
TABLE 2

PRODUCTS OF THE REACTION BETWEEN $C_2H_5(CH_3)_2SiCH_2Cl$ AND SODIUM

Product		*Yield* (%)	*Retention time* (*min*)[a]	*Mechanism*[b]
(I)	$C_2H_5Si(CH_3)_3$	21	3.3	A
(II)	[c]	3	13.6	
(III)	$C_2H_5(CH_3)_2SiCH_2Si(CH_3)_2C_2H_5$	< 1	14.9	B
(IV)	$(CH_3)_3Si(CH_2)_3Si(CH_3)_2C_2H_5$	< 1	16.7	C
(V)	$[C_2H_5(CH_3)_2SiCH_2]_2$	18	20.6	D
(VI)	$CH_3(C_2H_5)_2SiCH_2Si(CH_3)_2C_2H_5$	10	23.0	E
(VII)	$n\text{-}C_3H_7(CH_3)_2SiCH_2Si(CH_3)_2C_2H_5$	6	24.0	E
(VIII)	$iso\text{-}C_3H_7(CH_3)_2SiCH_2Si(CH_3)_2C_2H_5$	1.5	26.8	E
(IX)	$C_{15}H_{38}Si_3$[d]	[e]	7.5[f]	E

[a] 20' × ⅛" column packed with Apiezon L (20%) on 100–120 Chromosorb P; column temperature 190°, flow rate 24 ml/min. [b] A: proton abstraction; B: displacement on Si; C: intermolecular carbene insertion; D: displacement on C; E: intramolecular insertion. [c] Unidentified. [d] Several isomers. [e] Not measured. [f] 5' × ¼" column packed with SF 96 15% on Firebrick; column temperature 250°, pressure 20 psi.

(Ethyldimethylsilyl)carbene can undergo 1,3-insertion to give two silacyclopropanes as shown in equation (3). Compound (X) is the result of insertion into the

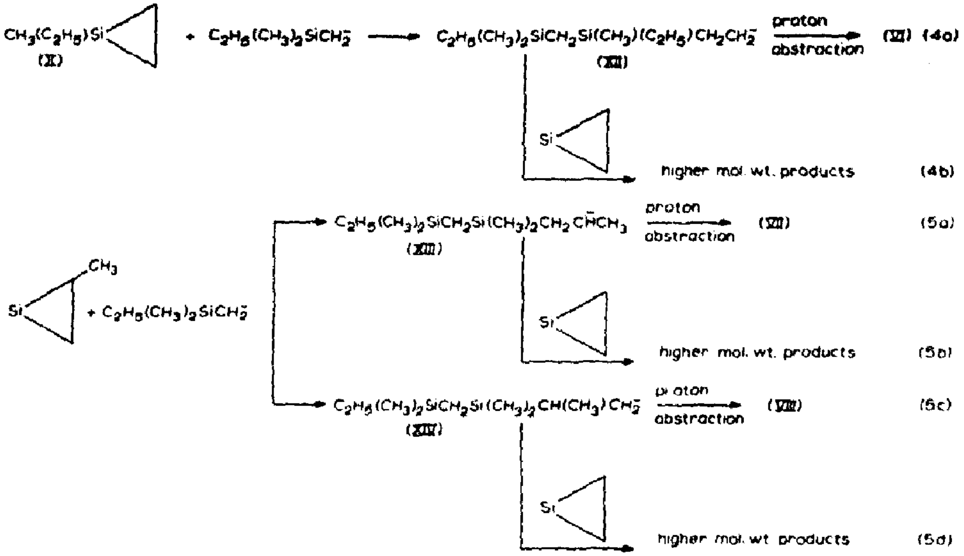


(X) (3a)

(XI) (3b)

CHART 1

MECHANISM OF SILACYCLOPROPANE CLEAVAGE BY $C_2H_5(CH_3)_2SiCH_2^-$ DURING THE REACTION BETWEEN $C_2H_5(CH_3)_2SiCH_2Cl$ AND SODIUM



primary C–H bond and (XI) is the result of insertion into the secondary C–H bond.

By reference to Chart 1 it can be seen that product (VI) is the result of cleavage of (X), and (VII) and (VIII) are the result of cleavage of (XI). Thus, measurement of the amount of (VI) relative to (VII) and (VIII) [assuming that paths (4b), (5b), and (5d) proceed at comparable rates] gives the relative reactivity of the silylcarbene to primary and secondary hydrogens. This ratio of reactivities is 1.0 : 2.5, respectively. This compares with the range 1.0 : 1.3–1.9 reported for sec-butylcarbene undergoing 1,3-insertion[2].

The cleavage of (XI) by the (ethyldimethylsilyl)carbanion produces (XIII) and (XIV) which are the anion precursors to (VII) and (VIII), respectively. On the basis of the stability of the anion intermediates more (VIII) than (VII) would be expected in the product mixture [assuming (5b) and (5d) proceed at comparable rates]. However, the ratio of (VII) to (VIII) is found to be 4 : 1 (Table 2). The best explanation of this seems to be in terms of steric hindrance in the transition state. Regardless of the direction from which the nucleophilic attack occurs on the silicon, cleavage of silicon–methine linkage will do more to alleviate ring methyl to *cis*-silyl methyl repulsion than will cleavage of the silicon–methylene bond.

This argument presumes that product (VII) does not come about by 1,4-insertion. This possibility can be ruled out on the basis of the results in section (ii). Isolation of (IX) is given as evidence for paths (4b), (5b), and (5d).

(ii) $R = n\text{-}C_3H_7$

Examination of Table 3 shows that in this reaction the 1,5-intramolecular insertion reaction occurs to a considerable extent, otherwise the results are quite analogous to those in section (i).

Comparison of the relative amounts of (XXIV) to (XXII) and (XXIII) shows that the relative reactivity of the silylcarbene to primary and secondary hydrogens is

TABLE 3

PRODUCTS OF THE REACTION BETWEEN $n\text{-}C_3H_7(CH_3)_2SiCH_2Cl$ AND SODIUM

Product		*Yield* (%)	*Retention time* (*min*)	*Mechanism*[a]
(XV)	$n\text{-}C_3H_7Si(CH_3)_3$	32	5.3[b]	A
(XVI)		18	9.3[b]	F
(XVII)[c]		4	29.0[d]	B, C
(XVIII)[c]			30.4[d]	B, C
(XIX)[c]			32.0[d]	B, C
(XX)[c]			34.2[d]	B, C
(XXI)	$[n\text{-}C_3H_7(CH_3)_2SiCH_2]_2$	15	40.2[d]	D
(XXII)	$n\text{-}C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$	6[e]	45.5[d]	E
(XXIII)	$sec\text{-}C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$		48.0[d]	E
(XXIV)	$n\text{-}C_3H_7(C_2H_5)(CH_3)SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$		49.3[d]	E
(XXV)[c]			51.0[d]	

[a] A: proton abstraction; B: intermolecular insertion; C: displacement on Si; D: displacement on C; E: 1,3-insertion; F: 1,5-insertion. [b] 20′ × ⅛″ column packed with Apiezon L (20%) on 100–120 Chromosorb P; column temperature 140°, flow rate 24 ml/mm. [c] Unidentified. [d] 40′ × 1/8″ column packed with Apiezon L (5%) on 100–120 Chromosorb P; column temperature 140°, pressure 40 psi. [e] The ratio of (XXII) and (XXIII) to (XXII) is 2:3; the ratio of (XXII) to (XXIII) is approximately 10:1.

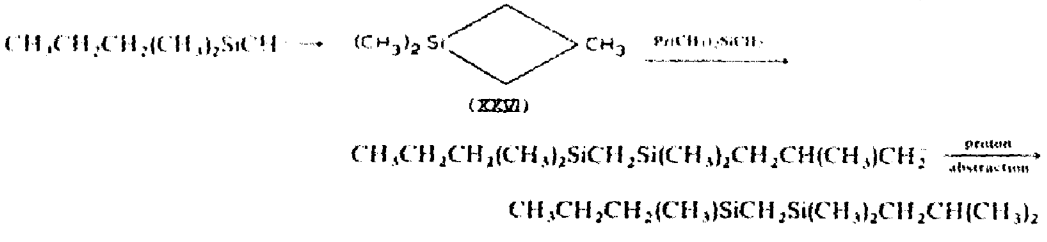
1:2. The ratio of (XXII) to (XXIII) is approximately 10:1 indicating that the steric effect in the ring cleavage is somewhat more pronounced in this case than in section (i).

It was not possible to identify (XXV) but it apparently is not a product of intramolecular insertion.

The compound iso-$C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2$-n-$C_3H_7$ was found not to be present among the products. Reference to Chart 2 shows that this material would result from 1,4-insertion. Thus the intramolecular insertion reaction is selectively 1,3 and 1,5.

CHART 2

RESULT OF HYPOTHETICAL 1,4-INSERTION IN THE REACTION BETWEEN $n\text{-}C_3H_7(CH_3)_2SiCH_2Cl$ AND SODIUM



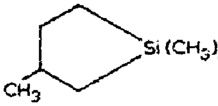
(XXVII)

(*iii*) $R = n\text{-}C_4H_9$

Reference to Table 4 shows that the results here are analogous to those in section (ii). No effort was made to identify products other than (XXVIII), (XXIX), and (XXXII), but the similarity of the chromatograms in this case to those of (i) and (ii) make it apparent that (XXXIII)–(XXXV) are the result of 1,3-insertion. It is pertinent that no 1,1-dimethyl-1-silacyclohexane was found in the reaction mixture. This finding makes it evident that 1,6-insertion does not occur.

TABLE 4

PRODUCTS OF THE REACTION BETWEEN n-$C_4H_9(CH_3)_2SiCH_2Cl$ AND SODIUM

Product		*Yield* (%)	*Retention time* (*min*)	*Mechanism*[a]
(XXVIII)	n-$C_4H_9Si(CH_3)_3$	33	10.2[b]	A
(XXIX)		17	14.5[b]	F
(XXX)[c]		2	19.0[d]	B, C
(XXXI)[c]			21.0[d]	B, C
(XXXII)	$[C_4H_9(CH_3)_2SiCH_2]_2$	13	24.8[d]	D
(XXXIII)[c]		3	28.7[d]	E
(XXXIV)[c]			30.0[d]	E
(XXXV)[c]			31.7[d]	E

[a] See Table 3. [b] $20' \times \frac{1}{8}''$ column packed with Apiezon L on Chromosorb P; column temperature 140°, flow rate 24 ml/min. [c] Unidentified. [d] Same column as above, column temperature 250°, flow rate 24 ml/min.

(iv) $R = iso$-C_4H_9

This reaction was run as a structure proof of (XXIX). No attempt was made to identify any products other than isobutyltrimethylsilane and (XXIX). The results are included in Table 5.

TABLE 5

RELATIVE AMOUNTS OF 1,3- AND 1,5-INSERTION PRODUCTS

R	*Yield $RSi(CH_3)_3$* (%)	*Yield 1,3-insertion product*[a] (%)	*Yield 1,5-insertion product* (%)
C_2H_5	21	18	
n-C_3H_7	34	6	18
n-C_4H_9	34	3	17
iso-C_4H_9	30	[b]	16

[a] The yields reported here are for the isolated 1,3-insertion products only. Higher molecular weight materials may result by 1,3-insertion so these figures do not represent the total amount of 1,3-insertion. [b] Not measured.

In each of the reactions studied here the product $RSi(CH_3)_3$ was formed. In every case the yield of it is too great to be consistent with the other products found. For example, when $R = C_2H_5$ a 21% yield of ethyltrimethylsilane was found. Further analysis of the products showed that a small amount of $C_{15}H_{38}Si_3$ was formed but no less volatile products. The analytical method did not rule out the presence of non-volatile polymers but they seem unlikely since no "tetramers", "pentamers" etc. were found.

The formation of 21% ethyltrimethylsilane would require a 63% yield of $C_{15}H_{38}Si_3$ if only intramolecular insertion occurred. Since this is obviously not the case and since there is evidence for intermolecular insertion [product(II)] it seems likely that some of the (ethyldimethylsilyl)carbene reacts with the solvent.

The data in Table 5 indicate that 1,5-insertion competes very favorably with 1,3-insertion. In each of the cases where 1,5-insertion is possible the product of this reaction occurs to the extent of approximately 17%. The data in Table 1 indicate that the α-elimination reaction occurs to the extent of approximately 85%. Half of this 85% goes to carbanion and half to carbene. Thus, 1,5-insertion occurs to at least the same extent as 1,3-insertion. If any appreciable amount of the carbene is involved in intermolecular reactions the ratio of 1,5/1,3-insertion would be even greater.

It is surprising that there is little difference in the absolute yields of 1,5-insertion products where R = n-C_3H_7, n-C_4H_9, and iso-C_4H_9. It would have been expected that the latter two would give more 1,5-insertion product than the former.

The results presented here indicate that (trialkylsilyl)carbenes are very similar to aliphatic carbenes. Their selectivity toward secondary hydrogens relative to primary hydrogens is very close to that reported for aliphatic carbenes. Neoheptyl- and neooctylcarbenes have not been reported yet so our results are directly comparable to wholly organic carbenes. However, photochemically generated aliphatic nitrenes undergo 1,2-, 1,3-, and 1,5-insertions exclusively[3]. It appears then that the selectivity observed here is purely a result of the geometry of the transition state and not due to the presence of the silicon atom.

EXPERIMENTAL

Preparation of starting materials

The compounds $R(CH_3)_2SiCH_2Cl$ were prepared from the appropriate Grignard reagent and (chloromethyl)dimethylchlorosilane. Isobutyldimethyl(chloromethyl)silane has not been previously reported. Its boiling point is 160–162°. Its NMR spectrum is in Table 7.

Wurtz reaction conditions

A 1.8 *M* solution of (chloromethyl)trialkylsilane in pentane, hexane, or heptane was put in an erlenmeyer flask. To this was added an excess of sodium. The vessel was stoppered and attached to the shaft of a stirring motor. The vessel was immersed in a tap water cooled water bath and rotated for 12–24 h. The excess sodium was then destroyed with ethanol and the mixture was washed with distilled water and aqueous washings were extracted with reaction solvent. The organic layer was dried and distilled in an annular spinning band still. Yields were obtained by weighing the fractions and analyzing them by gas chromatography.

In some cases the reaction was stopped before completion. In those cases chloride analyses were done and the yields based on the amount of chloride ion found. The results were the same whether the reaction went to completion or not.

Identification of products

In general identification of the products was done by NMR spectroscopy and/or matching chromatograms with authentic samples. This information is summarized in Table 6. The preparative gas chromatography used to isolate some of the Wurtz reaction products and the independently synthesized products was done with an Aerograph A 90 P3 chromatography unit containing a 20′ × ⅜th″ column packed with 20% Apiezon L on Chromosorb P. The elemental analyses and molecular weight were determined by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

To demonstrate that compound (XXVII) was not a product of the reaction

TABLE 6

METHOD OF IDENTIFICATION OF THE PRODUCTS OF THE WURTZ REACTION

R	*Product*	*Identification method*[a]	*Product isolated*	*Product analyzed*
C_2H_5	(I)	A	Yes	No
C_2H_5	(III)	B	No	No
C_2H_5	(IV)	B	No	No
C_2H_5	(V)	A	Yes	Yes
C_2H_5	(VI)	A, B	Yes	Yes
C_2H_5	(VII)	B	Yes[b]	Yes[b]
C_2H_5	(VIII)	B	Yes[b]	Yes[b]
C_2H_5	(IX)	C	Yes	Yes
n-C_3H_7	(XV)	A	Yes	No
n-C_3H_7	(XVI)	A	Yes	No
n-C_3H_7	(XXI)	A	Yes	No
n-C_3H_7	(XXII)	B	No	No
n-C_3H_7	(XXIII)	B	No	No
n-C_3H_7	(XXIV)	B	No	No
n-C_4H_9	(XXVIII)	A	Yes	No
n-C_4H_9	(XXIX)	B	Yes[c]	No
n-C_4H_9	(XXXII)	A	Yes	No
iso-C_4H_9	[d]	A	Yes	No
	(XXIX)	A	Yes	No

[a] A : identification by NMR spectra ; B : identification by matching chromatograms with authentic samples ; C : identification by analysis and molecular weight determination. [b] These two compounds were isolated and analyzed as a mixture. [c] It was not possible to isolate this material in a pure enough form to get a good NMR spectrum. [d] iso-$C_4H_9Si(CH_3)_3$.

between n-propyldimethyl(chloromethyl)silane and sodium a chromatogram was run on a mixture of (XXVII) and the Wurtz reaction product mixture. The retention time of (XXVII) was seen to be different from that of any of the products. The lower limit of detectability of (XXVII) corresponds to approximately 0.2% yield in this case.

In a similar way 1,1-dimethyl-1-silacyclohexane was shown not to be one of the products of the reaction between n-butyldimethyl(chloromethyl)silane and sodium. This material could not have been present in greater than 1% yield.

The preparative methods for the authentic samples which were synthesized are given below.

$CH_3(C_2H_5)_2SiCH_2Si(CH_3)_2C_2H_5$ (VI). The Grignard reagent from ethyldimethyl(chloromethyl)silane was prepared in diethyl ether. To this was added an equimolar amount of dimethyldichlorosilane. The ether was distilled off this mixture and the remaining mixture was refluxed overnight. An equimolar amount of methyllithium in ether was then added under nitrogen, the ether was distilled off and the mixture was refluxed under nitrogen overnight. After cooling to room temperature excess methanol was added to the reaction mixture followed by several washings with water. The product was isolated directly from the organic layer by preparative gas chromatography. It was characterized by its NMR spectrum (Table 7) and analysis. (Found: C, 59.41; H, 13.00; Si, 27.58. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94; Si, 27.74%.)

n-$C_3H_7(CH_3)_2SiCH_2Si(CH_3)_2C_2H_5$ (VII). Using the above procedure an equimolar amount of n-propylmethyldichlorosilane was added to the Grignard reagent from ethyldimethyl(chloromethyl)silane. This was followed by addition of an equimolar amount of methyllithium. The product was worked up and isolated as above. It was characterized by its NMR spectrum (Table 7) and analysis. (Found: C, 59.15; H, 12.96; Si, 27.69. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94; Si, 27.74%.)

$iso\text{-}C_3H_7(CH_3)_2SiCH_2Si(CH_3)_2C_2H_5$ *(VIII)*. Grignard couplings of isopropyl-Grignard with (chloromethyl)dimethylchlorosilane and dimethyldichlorosilane did not give the desired products*. Therefore isopropyltrichlorosilane was prepared from isopropyl-Grignard and silicon tetrachloride. An equimolar amount of this material was added to the Grignard from ethyldimethyl(chloromethyl)silane followed by the addition of two equivalents of methyllithium. The product was worked up and isolated as above. It was characterized by its NMR spectrum (Table 7) and analysis. (Found: C, 58.93; H, 12.93; Si, 27.04. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94; Si, 27.74%.)

$C_{15}H_{38}Si_3$ *(IX)*. The undistilled residue from the Wurtz reaction was analytically chromatographed under the conditions described in Table 2. There were several peaks from 6.5 to 8.5 min and no additional peaks up to 25 min. The mixture was then preparatively chromatographed on a $5' \times \frac{3}{8}$th″ column packed with Apiezon L (20%) on Chromosorb P. The mixture responsible for the several peaks mentioned above was collected. It was analyzed and its average molecular weight was determined by vapor phase osmometry. (Found: C, 59.31; H, 12.97; Si, 27.97; mol. wt., 290. $C_{15}H_{38}Si_3$ calcd.: C, 59.57; H, 12.58; Si, 27.81%; mol. wt., 302.)

$[(CH_3)_3Si(CH_2)_3Si(CH_3)_2C_2H_5$ *(IV)*. An equimolar amount of ethyldimethylchlorosilane was added to the Grignard from (γ-chloropropyl)trimethylsilane according to the above general procedure. The product was characterized by its NMR spectrum (Table 7).

$n\text{-}C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$ *(XXII)*. An equimolar amount of n-propylmethyldichlorosilane was added to a solution of the Grignard from n-butyldimethyl(chloromethyl)silane. To this mixture was added an equimolar amount of methyllithium. The mixture was worked up as above. The product was characterized by its NMR spectrum (Table 7).

$sec\text{-}C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$ *(XXIII)*: Several attempts were made to couple the sec-butyl group to silicon by Grignard reactions with dimethyldichlorosilane, methyltrichlorosilane and silicon tetrachloride. None of these reactions gave the desired product. Finally sec-butyltrichlorosilane was prepared by the γ-ray induced addition of trichlorosilane to 2-butene[5]. Product (XXIII) was prepared by the reaction of an equimolar amount of sec-butyltrichlorosilane and the Grignard from n-propyldimethyl(chloromethyl)silane followed by the addition of two equivalents of methyllithium. The product was characterized by its NMR spectrum (Table 7).

$n\text{-}C_3H_7(C_2H_5)(CH_3)SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$ *(XXIV)*. An equimolar amount of n-propylmethyldichlorosilane was added to a solution of the Grignard from n-propyldimethyl(chloromethyl)silane followed by addition of an equimolar amount of ethylmagnesium bromide. The product was characterized by its NMR spectrum (Table 7).

$iso\text{-}C_4H_9(CH_3)_2SiCH_2Si(CH_3)_2\text{-}n\text{-}C_3H_7$ *(XXVII)*. Equimolar amounts of n-propylmethyldichlorosilane and methyllithium were added in succession to the

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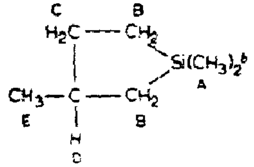
* Miller has reported similar difficulties[4]. The coupling of internal Grignards with chlorosilanes is not a facile reaction.

TABLE 7

NMR SPECTRA OF SOME PERTINENT ORGANOSILANES

Compound	Signal[a] (τ)	Assignment	Intensities Calcd.	Intensities Found
$CH_3CH_2Si(CH_3)_3$[b] C B A	10.0 (1)	A	9.0	9.4
	9.45 (m)	B	2.0	2.0
	9.00 (m)	C	3.0	2.9
$CH_3CH_2CH_2Si(CH_3)_3$[b] D C B A	10.0 (1)	A	9.0	9.0
	9.50 (m)	B		
	9.05 (m)	D	7.0	7.5
	8.73 (m)	C		
$CH_3CH_2CH_2CH_2Si(CH_3)_3$[c] E D C B A	10.0 (1)	A	9.0	9.0
	9.50 (m)	B	2.0	2.2
	9.10 (m)	E	3.0	3.3
	8.70 (m)	C + D	4.0	4.5
$(CH_3)_2CHCH_2Si(CH_3)_3$[b] D C B A	10.0 (1)	A	9.0	9.0
	9.50 (2)	B (J_{BC} = 6 cps)	2.0	2.2
	9.05 (2)	D (J_{DC} = 6 cps)	6.0	6.4
	8.40 (m)	C	1.0	1.6
$(CH_2CH_2)_2Si(CH_3)_2$[c] C B A	10.0 (1)	A	6.0	6.0
	9.55 (m)	B	4.0	4.4
	8.57 (m)	C	4.0	4.0
	10.0 (2)[d]	A	6.0	6.0
	9.45 (m)	B		
	9.10 (m)	C	10.0	9.0
	9.10 (2)	E (J_{DE} = 6 cps)		
	8.33 (m)	D		
$(CH_3)_2CHCH_2Si(CH_2Cl)(CH_3)_2$[b] D C B E A	10.0 (1)	A	6.0	5.8
	9.49 (2)	B (J_{BC} = 6 cps)	2.0	2.0
	9.10 (2)	D (J_{DC} = 6 cps)	6.0	6.0
	8.37 (m)	C	1.0	1.0
	7.48 (1)	E	2.0	1.9

(continued on next page)

TABLE 7 (continued)

Compound	Signal[a]	Assignment	Intensities		
	(τ)		Calcd.	Found	
$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2CH_3$[b] A B D B A' B' C	10.0 (2)[d]	A, A'	15.0	15.0	
	9.47 (m)	B, B'			
	9.10 (m)	C	11.0	12.1	
	8.77	D			
$[CH_3CH_2(CH_3)_2SiCH_2]_2$[c] D C A B	10.0 (1)	A	12.0	12.0	
	9.55 (1)	B	8.0	7.2	
	9.42 (m)	C			
	9.02 (3)	D (J_{DC} = 7 cps)	6.0	6.0	
$(CH_3CH_2)_2(CH_3)SiCH_2Si(CH_3)_2CH_2CH_3$[b] C B A D A' B C	10.0 (2)[d]	A, A'	9.0	9.0[e]	9.0[f]
	9.45 (m)	B	15.0	16.5[e]	15.0[f]
	9.03 (m)	C			
	10.31 (1)	D	2.0	1.9[e]	1.5[f]
$CH_3CH_2CH_2(CH_3)_2SiCH_2Si(CH_3)_2CH_2CH_3$[b] D C B A E A B D	10.0 (1)	A	12.0	12.0	
	9.55 (m)	B	12.0	12.8	
	9.10 (m)	D			
	8.71 (m)	C			
	10.31 (1)	E	2.0	2.1	
$(CH_3)_2CH(CH_3)_2SiCH_2Si(CH_3)_2CH_2CH_3$[b] C B A D A' B' C'	10.0 (1)	A, A'	12.0	12.0	
	9.42 (m)	B'	12.0	12.0	
	9.00 (m)	B, C, C'			
	10.30 (1)	D	2.0	1.5	
$[CH_3CH_2CH_2(CH_3)_2SiCH_2]_2$[c] D C B A E	10.0 (1)	A	12.0	12.0	
	9.58 (1)	E	8.0	8.7	
	9.47 (m)	B			
	9.02 (3)	D (J_{DC} = 6 cps)	6.0	6.0	
	8.65 (m)	C	4.0	4.5	
$CH_3CH_2CH_2(CH_3CH_2)(CH_3)SiCH_2Si(CH_3)_2CH_2CH_3$[b] C D B C B A E A' B' C'	10.0 (2)[d]	A	9.0	8.1	
	9.52 (m)	B, B, B'	17.0	17.0	
	9.08 (m)	C, C, C'			
	8.65 (m)	D			
	10.33 (1)	E	2.0	1.5	

$CH_3CH_2CH_2CH_2(CH_3)_2SiCH_2Si(CH_3)_2CH_2CH_2CH_3$[b] D C'' C B A E A B' C' D'	10.0 (1)	A	12.0	11.7
	9.52 (m)	B, B'	16.0	16.0
	9.07 (m)	D, D'		
	8.75 (m)	C, C', C''		
	10.30 (1)	E	2.0	2.0
$CH_3CH_2(CH_3)CH(CH_3)_2SiCH_2Si(CH_3)_2CH_2CH_2CH_3$[g] D'' C' D' B' A E A' B C D	10.0 (3)[d]	A, A'	12.0	12.0
	9.50 (m)	B	16.0	15.5
	9.00 (m)	B', D, D', D''		
	8.70 (m)	C, C'		
	10.33 (1)	E	2.0	2.3
$(CH_3)_2CHCH_2(CH_3)_2SiCH_2Si(CH_3)_2CH_2CH_2CH_3$[b] D' C' B' A' E A B C D	10.0 (3)[h]	A, A'	12.0	12.0
	9.50 (2)	B' ($J_{B'C'}$ = 6 cps)	4.0	4.9
	9.50 (m)	B		
	9.10 (2)	D' ($J_{D'C'}$ = 6 cps)	12.0	12.0
	9.10 (m)	D		
	8.74 (m)	C		
	8.25 (m)	C'		
	10.33 (1)	E	2.0	1.5
$[CH_3CH_2CH_2CH_2(CH_3)_2SiCH_2]_2$[e] E D C B A F	10.0 (1)	A	12.0	12.0
	9.60 (1)	F	8.0	8.3
	9.48 (m)	B		
	9.20 (m)	E	14.0	15.0
	8.67 (m)	C, D		

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[a] The numbers in parentheses are the number of lines in the given signal; the symbol m stands for many. [b] Varian A-60 NMR spectrometer. [c] Varian HA-100 NMR spectrometer. [d] Separation: 1.5 cps. [e] Material obtained by independent synthesis. [f] Material recovered from Wurtz reaction. [g] JEOL Co. NMR 4H-100 Spectrometer. [h] Separation: 6 cps.

Grignard from isobutyldimethyl(chloromethyl)silane. The product was characterized by its NMR spectrum (Table 7).

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SUMMARY

The reaction between a series of compounds $R(CH_3)_2SiCH_2Cl$ where R is aliphatic and sodium has been studied. The carbene $R(CH_3)_2SiCH:$ is an important intermediate and it undergoes 1,3- and 1,5-insertion exclusively. In each case the 1,3-insertion reaction produces two silacyclopropanes which undergo nucleophilic ring cleavage. The relative amount of cleavage products formed make it evident that steric hindrance is an important factor in the transition state.

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