The Wurtz Reaction of Chloromethyltrimethylsilane. A Classical Study

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The Wurtz reaction of chloromethyltrimethylsilane has been studied in a variety of solvents. In nonpolar solvents the products obtained indicate that both the SN2 displacement of chloride and the α-elimination of hydrogen chloride occur during the course of reaction. These products include tetramethylsilane, 2,2,4,4-tetramethyl-2,4-disilahexane, 2,2,5,5-tetramethyl-2,5-disilahexane, and two isomers of $C_{12}H_{32}Si_3$. When tetrahydrofuran is used as solvent the products formed can most readily be explained by assuming CH_2 carbene, formed by Si–C bond cleavage, as an intermediate. The products obtained in the latter case are ethylene, tetramethylsilane, ethyltrimethylsilane, 2,2,4,4-tetramethyl-2,4-disilapentane, 2,2,5,5-tetramethyl-2,5-disilahexane, and a third isomer of $C_{12}H_{32}Si_3$.

The Wurtz reaction between an alkyl halide and an alkali metal results in coupling, dehydrohalogenation, or reduction of the alkyl halide to the corresponding alkane. When a metal alkyl is treated with an alkyl halide the halide often is dehydrohalogenated to the corresponding olefin while the metal alkyl is converted to the corresponding alkane.[3,4]

Whitmore suggested that coupling occurred by an SN2 mechanism. The fact that inversion of the alkyl group occurs in the Wurtz coupling would support this point of view.[5]

More recently, studies of reactions of α,α-dideuterio alkyl halides with metal alkyls[6,7] have demonstrated the α-elimination of hydrogen halide to form a carbene intermediate. The mode of rearrangement of the carbene intermediate apparently depends upon its structure. Carbenes generated from normal alkyl halides rearrange to olefins. Isoalkyl halides give rise to carbenes which rearrange to olefins and cyclopropanes while carbenes resulting from the α-elimination of hydrogen halide from neoalkyl halides rearrange mainly to cyclopropanes.

The Wurtz reaction of bromomethyltrimethylsilane has been studied by Post and Noller.[8] The products reported were 2,2,5,5-tetramethyl-2,5-disilahexane and tetramethylsilane.

Results and Discussion

We have studied the reaction between chloromethyltrimethylsilane and alkali metals in hydrocarbons, tetraalkylsilanes, and tetrahydrofuran. In hydrocarbons and tetralkylsilanes the products are essentially the same as those obtained when no solvent is used. The products obtained in a typical reaction are shown in Table I.

TABLE I

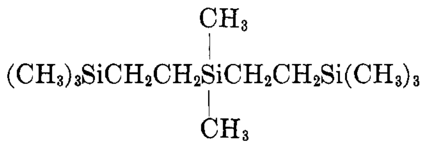
PRODUCTS OBTAINED FROM WURTZ REACTION IN INERT SOLVENTS

Products	Yield[a]
Methane	Trace
2,2,5,5-Tetramethyl-2,5-disilahexane (III)	40
Tetramethylsilane (IV)	18
$C_{12}H_{32}Si_3$ (two isomers, VIII and IX in approximately equal amounts)	20
2,2,4,4-Tetramethyl-2,4-disilahexane (X)	12

[a] The yields reported are weight % based on the total weight of products isolated from the reaction. Over 90% of the chloromethyltrimethylsilane consumed in the reaction is accounted for by these products.

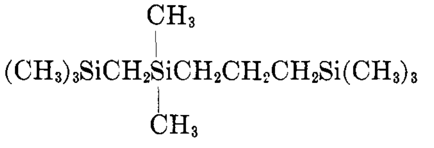
The isomers of $C_{12}H_{32}Si_3$ (VIII and IX) obtained in this reaction do not possess Si–Si bonds nor Si–H bonds, since treatment of each of these isomers with alcoholic potassium hydroxide produced no hydrogen. The n.m.r. spectra for these two isomers were complex and poorly resolved except for the following features common to both isomers: an intense peak assigned to the $-Si-(CH_3)_3$ proton which appears at the same position as the proton resonance in $Si(CH_3)_4$, a sharp peak one-third as intense at 0.1 p.p.m. to higher field which we assign to the $-Si(CH_3)_2-$ methyl proton. Absent from the spectrum of isomer VIII but present in the spectrum of isomer IX is a sharp, well-resolved singlet at 0.30 p.p.m. to higher field in the same position as that for the methylene protons in 2,2,4,4-tetramethyl-2,4-disilapentane. The intensity of this peak is one-tenth that of the major methyl proton peak. For both isomers the region from 0 to 1.0 p.p.m. to lower field consists of a series of poorly resolved peaks of relatively low individual intensity.

Possible structures for these isomers which are not in disagreement with the foregoing data are shown.



$$(CH_3)_3SiCH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}CH_2CH_2Si(CH_3)_3$$

the more volatile isomer (VIII)



$$(CH_3)_3SiCH_2\overset{CH_3}{\underset{CH_3}{Si}}CH_2CH_2CH_2Si(CH_3)_3$$

the less volatile isomer (IX)

The reaction of chloromethyltrimethylsilane with the alkali metals studied proceeds most rapidly for potassium, least rapidly for lithium, with the rate of the sodium reaction intermediate. The reaction of chloromethyltrimethylsilane with potassium produces smaller amounts of 2,2,4,4-tetramethyl-2,4-disilahexane than does the reaction with sodium. In the lithium reaction all of the products observed in the sodium and potassium reactions are formed along with a mixture of less volatile compounds. The reaction between lithium

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[1] The work herein reported fulfilled in part the requirements for the degree of Doctor of Philosophy for J. W. Connolly at Purdue University, 1963.

[2] To whom inquiries concerning this publication should be addressed.

[3] A. A. Morton, *J. Am. Chem. Soc.*, **64**, 2240 (1942).

[4] F. C. Whitmore and A. D. Zook, *ibid.*, **64**, 1783 (1942).

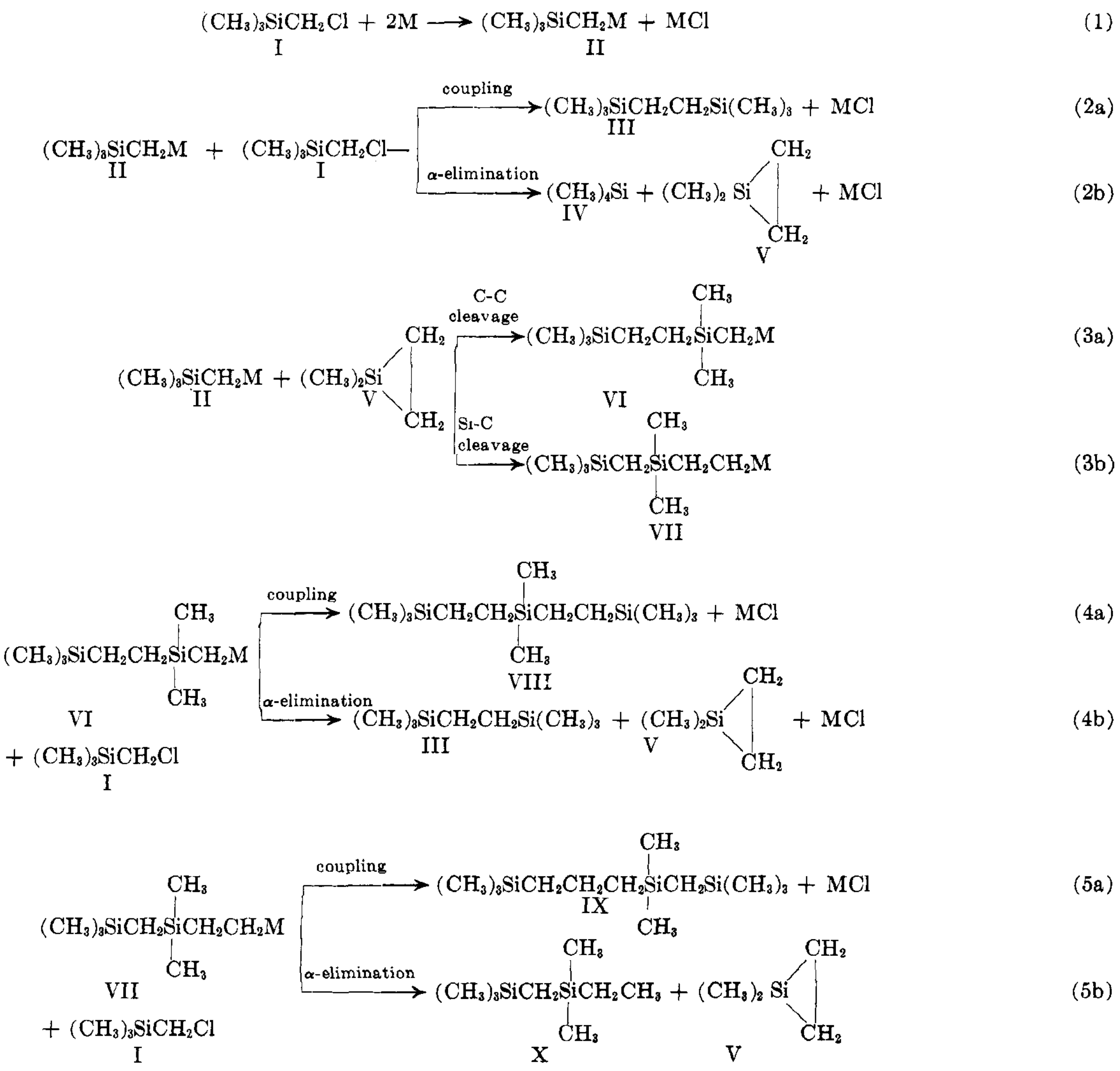
[5] E. LeGoff, S. E. Ulrich, and D. B. Denny, *ibid.*, **80**, 622 (1958).

[6] L. Friedman and J. Berger, *ibid.*, **83**, 492 (1961); **83**, 500 (1961).

[7] D. S. Skell and A. P. Krapcho, *ibid.*, **83**, 759 (1961).

[8] H. Post and D. W. Noller, *ibid.*, **74**, 1361 (1952).

CHART I



and chloromethyltrimethylsilane can be carried out in such a manner that lithiomethyltrimethylsilane is the major product.[9]

The reaction sequence in Chart I is suggested to account for the products observed.

According to the proposed scheme, 2,2,5,5-tetramethyl-2,5-disilahexane (III) is formed in two ways: one by a typical SN2 displacement by II on I, shown in reaction 2a, the other by the α-elimination reaction shown in reaction 4b. We can estimate the amount of III formed by each path as follows.

The isomers of $C_{12}H_{32}Si_3$ (VIII and IX) are formed in nearly equal amounts. Hence, if we assume that the reactivities of the precursor metal alkyls (VI and VII) are such that they will react in α-elimination in the same relative way that they react in the SN2 coupling, we would expect the amount of III formed in reaction 4b to be roughly equivalent to the amount of X formed in reaction 5b. We thus can estimate that of the 40% yield of 2,2,5,5-tetramethyl-2,5-disilahexane, 12% arises from reaction 4b and 28% by the SN2 coupling reaction 2a.

An intermolecular carbene insertion path is ruled out by the fact that no new products result when ethyltrimethylsilane is used as a solvent.

In the Wurtz reaction of neopentyl chloride less than 2% coupling was reported.[4] This has been attributed to steric hindrance of the SN2 reaction in the neopentyl group. It is well-known that chloromethyltrimethylsilane undergoes SN2 reactions more readily than neopentyl chloride[10]; it is reasonable that a higher yield of coupling product would be obtained in the case of the silane derivative.

Attempts to isolate the proposed intermediate, 1,1-dimethyl-1-silacyclopropane, produced only small amounts of impure material which exhibited an infrared absorption *at the same frequency and with the same shape* as the ring deformation mode of cyclopropane. Purification of the material exhibiting this absorption using vacuum line, gas chromatographic, and chemical separation techniques proved to be impossible.

The difficulty in isolating the proposed 1,1-dimethyl-1-silacyclopropane was presumably due to its susceptibility to nucleophilic attack and its lack of thermal stability.

An interesting solvent effect was observed in the reaction between sodium and chloromethyltrimethyl-

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(9) J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963).

(10) C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, pp. 130 and 431.

TABLE II

PRODUCTS FROM WURTZ REACTION IN TETRAHYDROFURAN

Products	Yield[a]
Hydrogen	Trace
Methane	Trace
Ethylene	1.6
2,2,5,5-Tetramethyl-2,5-disilahexane (III)	29
Tetramethylsilane (IV)	18
2,2,4,4-Tetramethyl-2,4-disilapentane (XI)	20
Ethyltrimethylsilane (XIII)	15
$C_{12}H_{32}Si_3$	20

[a] Weight % based on total weight of product isolated. The products account for all of the chloromethyltrimethylsilane consumed in the reaction.

silane carried out in tetrahydrofuran. The products and yields are listed in Table II.

The $C_{12}H_{32}Si_3$ produced in this case has no silicon–silicon or silicon–hydrogen bonds and is a different isomer from either of the isomers produced in the analogous reaction in hydrocarbon or tetraalkylsilane solvents. Apparently some tetrahydrofuran is consumed in the reaction, since in no case was all the solvent recovered.

It would appear that the reaction does not proceed through a cyclic intermediate in this case. One possibility is that 2,2,4,4-tetramethyl-2,4-disilapentane (XI) is formed by a cleavage of the silicon–carbon bond and that ethyltrimethylsilane (XIII) is produced from the resulting carbene as follows.

$$\underset{\text{II}}{(CH_3)_3SiCH_2Na} + \underset{\text{I}}{(CH_3)_3SiCH_2Cl} \longrightarrow \underset{\text{XI}}{(CH_3)_3SiCH_2Si(CH_3)} + [Na\ Cl\ CH_2] \qquad (6)$$

$$[Na\ Cl\ CH_2] \longrightarrow CH_2\colon\ + NaCl \qquad (7)$$

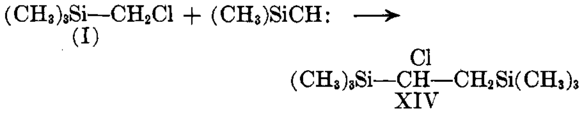
$$CH_2\colon\ + \underset{\text{II}}{(CH_3)_3SiCH_2Na} \longrightarrow \underset{\text{XII}}{(CH_3)_3SiCH_2CH_2Na} \qquad (8)$$

$$\underset{\text{XII}}{(CH_3)_3SiCH_2CH_2Na} \xrightarrow{\text{solvent}} \underset{\text{XIII}}{(CH_3)_3SiCH_2CH_3} \qquad (9)$$

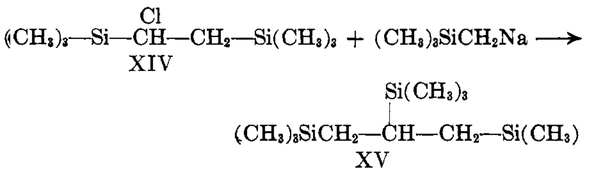
The fact that halogenated carbon atoms can be cleaved easily from silicon by nucleophilic reagents[10] would add support for the suggested mechanism. An addition of carbenes to metal alkyls similar to the one suggested here has been postulated by Closs.[11] The ethylene and methane produced as side products of the described reaction can be explained by assuming known hydrogen abstraction and dimerization reactions by the carbene intermediate.

The 2,2,5,5-tetramethyl-2,5-disilahexane (III) produced in this reaction presumably comes about as the result of SN2 displacement of chloride in chloromethyltrimethylsilane or by a reaction of XII with chloromethyltrimethylsilane (I) in a fashion analogous to that of II with I in reaction 6. It is interesting to note that the yield from this type of coupling in tetrahydrofuran is virtually identical with that estimated for the SN2 coupling in hydrocarbons and tetraalkylsilanes. This would indicate that in this solvent the carbene producing coupling does not contribute greatly to the yield of III.

An intermolecular carbene insertion reaction sequence as described in reactions 10 and 11, favored in



$$\underset{\text{(I)}}{(CH_3)_3Si{-}CH_2Cl} + (CH_3)SiCH\colon \longrightarrow \underset{\text{XIV}}{(CH_3)_3Si{-}\overset{Cl}{CH}{-}CH_2Si(CH_3)_3} \qquad (10)$$



$$\underset{\text{XIV}}{(CH_3)_3{-}Si{-}\overset{Cl}{CH}{-}CH_2{-}Si(CH_3)_3} + (CH_3)_3SiCH_2Na \longrightarrow \underset{\text{XV}}{(CH_3)_3SiCH_2{-}\overset{Si(CH_3)_3}{CH}{-}CH_2{-}Si(CH_3)} \qquad (11)$$

tetrahydrofuran over the intramolecular carbene insertion postulated in the case of nonpolar solvents, could account for the third isomer of $C_{12}H_{32}Si_3$ observed in this case.

Experimental

All vacuum line manipulations were carried out using standard techniques similar to those described in the literature.[12,13] Gas chromatographic analyses were effected using either an Aerograph analytical gas chromatograph or the Aerograph Auto-Prep Model 700 gas chromatograph. The separation conditions are given when appropriate.

Reagents.—Acetic anhydride, commercial grade, was distilled at atmospheric pressure before it was use. *n*-Butyllithium (1 *M* in hexane), obtained from the Foote Mineral Co., West Chester, Pa., was used as received. Chloromethyltrimethylsilane, received from the Anderson Chemical Co., Inc., Weston, Michigan, and Peninsular Chemresearch, Inc., Gainesville, Fla., was purified by atmospheric pressure distillation. Chloroplatinic acid obtained from the Eastman Chemical Co., Rochester, N. Y., was dehydrated *in vacuo* before use. Diethyl ether, obtained from the Mallinckrodt Chemical Works, St. Louis, Mo., was used as received. *n*-Heptane, pure grade, was obtained from the E. I. du Pont de Nemours and Co., Wilmington, Del. Lithium wire, commercial grade, was used as received. Phenylsodium (25% suspension in heptane) obtained from Orgmet Inc., Hampstead, N. H., was used as received. Potassium, commercial grade, was distilled *in vacuo*. Potassium *t*-butoxide, obtained from Orgmet Inc., Hampstead, N. H., was used as received. Sodium, commercial grade, was treated briefly with ethanol and was washed with *n*-heptane before use. Tetrahydrofuran, commercial grade, was dried by distillation from calcium hydride at atmospheric pressure. 2-Methylpentane, pure grade, obtained from the Phillips Petroleum Co., Bartlesville, Okla., was dried by distillation from calcium hydride at atmospheric pressure. Triphenylmethylsodium (25% suspension in heptane), obtained from Orgmet Inc., Hampstead, N. H., was used as received.

Reaction between Chloromethyltrimethylsilane and Sodium in Inert Solvents.—A mixture consisting of 5.676 g. of chloromethyltrimethylsilane and 4.620 g. of ethyltrimethylsilane was distilled into an evacuated 50-ml. round-bottomed flask which was attached to the vacuum apparatus and was equipped with a breakoff seal. The flask contained excess sodium. The flask was sealed off and then attached to the shaft of a stirring motor and rotated for 12 hr. After this time, the flask was attached to a preweighed tube, connected to the vacuum apparatus, and the volatile products removed through a −196° trap by means of a Toepler pump. The condensible material then was fractionated in a low temperature vacuum distillation column attached to the vacuum apparatus. Fractions were taken at −79°, from −79° to −35°, and from −35° to room temperature. These fractions were weighed and analyzed by gas chromatography on a 5 ft. × 0.5 in. column packed with Apiezon M on Chromosorb. A fourth fraction was obtained by distilling the residue of the reaction mixture into the preweighed U tube at 80°. This fraction was weighed and analyzed also.

The products, amount recovered, and yield were methane, 0.003 g., <1%; tetramethylsilane, 0.743 g., 18.3%; 2,2,5,5-tetramethyl-2,5-disilahexane, 1.651 g., 40.5%; 2,2,4,4-tetramethyl-2,4-disilahexane, 0.476 g., 11.8%; $C_{12}H_{32}Si_3$, 0.785 g.,

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(11) G. Closs, *J. Am. Chem. Soc.*, **84**, 809 (1962).

(12) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1949.

(13) A. Stock, "Hydrides of Boron and Silicon," The Cayuga Press, Ithaca, N. Y., 1933.

TABLE III

VAPOR PRESSURES OF 2,2,5,5-TETRAMETHYL-2,5-DISILAHEXANE

t, °C.	27.0	36.5	42.3	46.0	51.5	55.7	60.4	66.8	74.2	82.4
p_{obsd}, (mm. of Hg)	6.03	9.55	12.60	15.70	19.30	24.65	30.40	40.68	55.94	87.14
p_{calcd}[a]	5.80	9.71	12.60	15.15	20.55	25.12	30.75	41.70	53.90	76.50

[a] The calculated values were obtained using the equation $\log P$ (mm.) = $(-2.1978/T \times 10^3) + 8.0815$. Using this equation the extrapolated boiling point is 150°, lit.[8] 150°.

19.5%. Essentially all (4.558 g.) of the solvent ethyltrimethylsilane was recovered unchanged. The measured products account for 90% of the chloromethyltrimethylsilane consumed in the reaction.

In a similar experiment in which 2-methylpentane was the solvent the results were methane, 0.002 g., <1%; tetramethylsilane, 0.470 g. 17%; 2,2,5,5-tetramethyl-2,5-disilahexane, 1.120 g., 43%; 2,2,4,4-tetramethyl-2,4-disilahexane, 0.302 g., 11%; $C_{12}H_{32}Si_3$, unmeasured. This experiment was repeated on a larger scale in order to obtain sufficient quantities of all products for adequate characterization. The product mixture was crudely separated by fractional distillation and pure samples were obtained by preparative scale gas chromatography. Each product was identified with the corresponding product in the small scale experiment by gas chromatography.

The 2,2,5,5-tetramethyl-2,5-disilahexane was identified by its analysis.

Anal. Calcd.: C, 55.17; H, 12.78; mol. wt., 174. Found: C, 55.27; H, 12.44; mol. wt. (vapor density), 178.

Observed was m.p. −48°, lit.[8] −45°. The n.m.r. spectrum of this material consisted of two proton resonances in a ratio of 9:2 with an internal chemical shift of 0.35 p.p.m. The less intense peak is at lower field.

The vapor pressures of 2,2,5,5-tetramethyl-2,5-disilahexane are shown in Table III.

The 2,2,4,4-tetramethyl-2,4-disilahexane was characterized by its analysis.

Anal. Calcd.: C, 55.17; H, 12.78; mol. wt., 174. Found: C, 55.20; H, 12.80; mol. wt. (vapor density), 176.

To establish further the identity of this substance a different synthesis involving the reaction of lithiomethyltrimethylsilane and ethyldimethylchlorosilane gave an authentic sample which had an identical retention time in gas chromatography and exhibited the identical n.m.r. spectrum. The vapor pressures for 2,2,4,4-tetramethyl-2,4-disilahexane are shown in Table IV.

TABLE IV

VAPOR PRESSURES OF 2,2,4,4-TETRAMETHYL-2,4-DISILAHEXANE

t, °C.	43.2	54.0	62.0	75.0	80.7
p_{obsd}, (mm. of Hg)	10.10	18.12	26.20	46.6	59.100
p_{calcd}[a]	11.00	18.10	26.25	44.6	57.300

[a] The calculated values were obtained from the equation, $\log P$ (mm.) = $(-2.1704/T \times 10^3) + 7.900$, from which an extrapolated boiling point of 155° can be calculated. This is good agreement with the value of 158° found for an authentic sample.

The molecular formulas for the two isomers of $C_{12}H_{32}Si_3$ (VIII and IX) were established by analyses.

Anal. Calcd. for $C_{12}H_{32}Si_3$: C, 55.40; H, 12.32; mol. wt., 260. Found for isomer VIII: C, 55.55; H, 12.71; mol. wt. (vapor density), 255. Found for isomer IX: C, 55.83; H, 12.50; mol. wt., 256.

The vapor pressures for these compounds are shown in Table V. In a 5 ft. × 0.5 in. column packed with Apiezon M on Chromosorb, with the column maintained at 200° and the preheater at 230°, isomer VIII has a retention time of 13 min. and isomer IX a retention time of 16 min. when the helium flow rate is 10 ml./sec. The n.m.r. spectra for these two isomers were described in the discussion section of this paper.

Reaction between Chloromethyltrimethylsilane and Potassium in Inert Solvents.—The reaction between chloromethyltrimethylsilane and potassium was carried out in a manner identical with the reaction involving sodium. The products were worked up in the same way, but the various fractions were not weighed. Thus, only relative yields were obtained by gas chromatographic analysis. The same products were found but slightly less 2,2,4,4-tetramethyl-2,4-disilahexane and isomer IX were formed.

TABLE V

VAPOR PRESSURES FOR TWO ISOMERS OF $C_{12}H_{32}Si_3$

	t, °C.	100	105	112	116	125	131
VIII	p_{obsd}, (mm. of Hg)	9.90	12.25	16.67	19.80	27.60	33.10
	p_{calcd}[a]	10.01	12.01	16.30	19.70	27.90	33.30
IX	p_{obsd}, (mm of Hg)	7.85	9.43	13.40	14.70	22.35	27.40
	p_{calcd}[a]	8.04	9.56	13.45	15.50	22.30	26.35

[a] The calculated vapor pressures were obtained from the equation $\log P$ (mm.) = $(-2.5875/T \times 10^3) + 7.9403$ for VIII, and $\log P$ (mm.) = $(-2.6898/T \times 10^3) + 8.1081$ for IX.

Reaction between Chloromethyltrimethylsilane and Sodium in Tetrahydrofuran.—The reaction between chloromethyltrimethylsilane and sodium in tetrahydrofuran was carried out, using the vacuum apparatus, in a manner identical with the same reaction in inert solvents. The results obtained from the reaction of 30.9 mmoles chloromethyltrimethylsilane, dissolved in 90.0 mmoles of tetrahydrofuran, with an excess of sodium were (product, amount recovered, and yield) hydrogen, 0.06 mmole, <1%; methane, 0.27 mmole, <1%; ethylene, 0.58 mmole, 1.6%; tetramethylsilane, 5.36 mmoles, 17.5%; ethyltrimethylsilane, 4.94 mmoles, 15.9%; 2,2,4,4-tetramethyl-2,4-disilapentane, 2.66 mmoles, 17.2%; 2,2,5,5-tetramethyl-2,5-disilahexane, 4.48 mmoles, 29.0%; $C_{12}H_{32}Si_3$, 2.60 mmoles, 25.2%.

The 2,2,5,5-tetramethyl-2,5 disilahexane was identified by comparison of its gas chromatographic retention time with that of an authentic sample. The 2,2,4,4-tetramethyl-2,4-disilapentane was characterized by its analysis.

Anal. Calcd.: C, 52.50; H, 12.50; mol. wt., 160. Found: C, 52.98; H, 12.75; mol. wt. (vapor density), 156.

The g.c. retention time and the n.m.r. spectrum proved to be identical with those of authentic sample prepared by the reaction of lithiomethyltrimethylsilane with trimethylchlorosilane.

The n.m.r spectrum of 2,2,4,4-tetramethyl-2,4-disilapentane consists of two proton resonances in the ratio of 9:1 with an internal chemical shift of 0.30 p.p.m., the less intense peak lying at higher field. This spectrum is consistent with a structure containing 18 methyl protons and 2 methylene protons.

The $C_{12}H_{32}Si_3$ produced in this reaction was characterized by analysis.

Anal. Calcd. for $C_{12}H_{32}Si_3$: C, 55.40; H, 12.32; mol. wt., 260. Found: C, 55.83; H, 12.80; mol. wt. (vapor density), 258.

This substance was found to differ from both isomers prepared by the Wurtz reaction in inert solvents by its vapor tensions, shown in Table VI, and by a comparison of its n.m.r. spectrum with the spectra of the other two isomers.

TABLE VI

VAPOR PRESSURES OF $C_{12}H_{32}Si_3$ FROM REACTION IN TETRAHYDROFURAN

t, °C.	81	96	108	116	125	135
p_{obsd}, (mm. of Hg)	4.45	9.08	15.55	22.95	31.90	46.95
p_{calcd}[a]	4.85	9.35	15.20	21.65	32.00	46.50

[a] The calculated values were obtained from the equation $\log P$ (mm.) = $-2.6815/(T \times 10^3) + 8.2737$.

In this reaction the products isolated and characterized account for all of the chloromethyltrimethylsilane consumed.

Reaction between Chloromethyltrimethylsilane and Lithium in Inert Solvents.—In a three-necked flask, equipped with a stirrer and a reflux condenser, a mixture of 100 g. of chloromethyltrimethylsilane, 200 ml. of *n*-heptane, and 7 g. of lithium wire was refluxed with vigorous stirring. Under these conditions, the reaction began immediately. After 24 hr. the reaction mixture was hydrolyzed and the organic layer separated and dried. The product solution obtained in this way was pale yellow in color. Tetramethylsilane and the solvent were removed from the mixture by an atmospheric pressure distillation through a column packed with glass helices. After removal of the solvent the residual mixture was cooled and a fractionation was carried out under a pressure of 1 mm. The receiver was maintained at room temperature and a $-79°$ trap was placed between the collecting head of the fractionating column and the pump. The product mixture then was separated into the material collected in the $-79°$ trap, the material which remained in the receiver, and the residue remaining in the reaction (boiling) flask.

The products were identified by matching chromatograms with authentic samples. The material collected in the $-79°$ trap contained 2,2,5,5-tetramethyl-2,5-disilahexane and 2,2,4,4-tetramethyl-2,4-disilahexane, the mixture in the receiver contained isomers VIII and IX of molecular formula $C_{12}H_{32}Si_3$, and the residue in the boiling flask appeared to be a complex mixture of less volatile materials.

Attempted Preparation of 1,1-Dimethyl-1-silacyclopropane. A. 1. Reaction of Chloromethyltrimethylsilane with Lithium.—One hundred grams of chloromethyltrimethylsilane dissolved in 200 ml. of *n*-heptane was refluxed with 6 g. of lithium wire in a three-necked flask fitted with a glass helix packed distilling column equipped with a reflux head. The material boiling below 30° was removed continuously from the top of the column. The material, thus recovered, was introduced into the vacuum apparatus and fractionated in a low temperature vacuum distillation column at $-79°$. The infrared spectrum of the distillate showed a strong tetramethylsilane spectrum and a weak absorption at 1030 cm.$^{-1}$. Several subsequent distillations through the low temperature column at $-79°$ increased the concentration of the constituent exhibiting the infrared absorption with typical pqr structure at 1030 cm.$^{-1}$, but it proved impossible to obtain this substance in a pure form by this means. Passage of the mixture through a silicone rubber gas chromatography column also failed to effect a separation and apparently destroyed the substance responsible for the peak at 1030 cm.$^{-1}$.

2. Attempted Chemical Separation of the Volatile Product Mixture.—Treatment of 16 mmoles of the distillate, just described, with excess chloroplatinic acid in acetic anhydride in the vacuum apparatus produced a brown precipitate. Fifteen mmoles of volatile material was recovered from the treatment. The recovered material exhibited no infrared absorption at 1030 cm.$^{-1}$. Treatment of the brown precipitate with either potassium iodide in acetone or tributylphosphine failed to regenerate any material exhibiting an infrared absorption at 1030 cm.$^{-1}$.

Treatment of pure tetramethylsilane with chloroplatinic acid in acetic anhydride also produced a brown precipitate similar in appearance to that previously described.

B. Reaction of Chloromethyltrimethylsilane with Sodium.—A reaction between chloromethyltrimethylsilane and sodium, under conditions where the most volatile products could be removed continuously resulted in the removal only of tetramethylsilane.

C. Reaction of Previously Prepared Organometallic Compounds with Chloromethyltrimethylsilane.—In several different experiments, solutions of chloromethyltrimethylsilane in *n*-heptane were treated with various nucleophilic reagents dissolved in or suspended in hexane. The bases studied in this fashion were potassium *t*-butoxide, triphenylmethylsodium, phenylsodium, and lithiomethyltrimethylsilane. All of these reactions were carried out under an atmosphere of dry nitrogen. In most cases the reactions were effected at reflux temperature (about 100°) and the more volatile materials were removed as formed. In some cases the reaction mixture was stirred at room temperature and the volatile products removed by a nitrogen sweep into a $-79°$ trap. Only in the case of reactions involving *n*-butyllithium, carried out at elevated temperature, did the volatile product show an infrared absorption at 1030 cm.$^{-1}$. The fraction in which this absorption was found exhibited six peaks when samples of it were injected into a 20-ft. Apiezon M on Chromosorb gas chromatography column maintained at 60° or a 4-ft. silicone rubber column maintained at 25°. Isolation and examination of the materials corresponding to each of these peaks showed that none of them was the desired 1,1-dimethyl-1-silacyclopropane and none of these materials exhibited the infrared absorption at 1030 cm.$^{-1}$.

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Highly Branched Alkylphosphorus Compounds.
I. Synthesis of 2,3-Dimethylbutylphosphonyl Chloride[1,2]

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A number of unequivocal syntheses leading to 2,3-dimethylbutylphosphonyl chloride have been developed. This and related compounds have been characterized carefully. These syntheses have provided the opportunity to make a brief study of the chemical reactivity of alkyl halides, an alcohol derivative, and an ester of an alkylphosphonic acid, all of which contained the 2,3-dimethylbutyl group. As expected, these compounds were found to have low orders of reactivity in S$_N$2 type reactions.

During the study of the reaction of hydrocarbons with phosphorus trichloride and oxygen,[4] the hydrocarbon 2,3-dimethylbutane was employed. From this reaction, one might expect to obtain the two isomeric compounds, 2,3-dimethylbutylphosphonyl chloride (I) and 1,1,2-trimethylpropylphosphonyl chloride (II). In fact, Soborovskii, Zinov'ev, and Englin[5] claimed to have isolated these two products from the reaction in question and reported that the product contained 92 parts of II to 8 parts of I. Since this is a very important reaction in the study of the oxidative phosphonation of hydrocarbons, since Soborovskii and coworkers gave little evidence of the purity or even the identity of the two isomers, and since their analytical procedure seemed to be open to question, we have un-

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