[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Preparation and Reactions of α-Halo Derivatives of Certain Tetra-substituted Hydrocarbon Silanes. Grignard Syntheses of Some Silyl Compounds[1]

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Certain tetrasubstituted hydrocarbon silanes were chlorinated and brominated to form α-halo derivatives which were converted to silyl acetates with potassium acetate and to displacement and cleavage products with potassium cyanide and sodium amide. The Grignard reagents of α-halosilanes were condensed with acetic anhydride to form the silyl ketone, with allyl bromide to form the silyl olefin, and with acetone and benzaldehyde to form silyl carbinols. The Grignard reagents were condensed with benzonitrile but cleavage products were obtained. The dimer of an α-halosilane was also prepared. The syntheses of a number of new silicon-containing compounds were realized.

This paper describes the preparation of α-chloro and α-bromo derivatives of certain tetrasubstituted hydrocarbon silanes, the types of reactions they exhibit with basic reagents, and their use in typical Grignard syntheses.

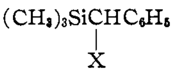
α-Halosilanes.—Hydrocarbon silanes I, II and III were converted by direct halogenation to mono, chloro or bromo derivatives IV, V and VI, respectively.

$(CH_3)_3SiCH_3$ I

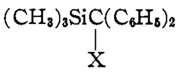
$(CH_3)_3SiCH_2C_6H_5$ II

$(CH_3)_3SiCH(C_6H_5)_2$ III

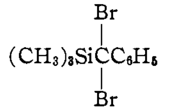
$(CH_3)_3SiCH_2X$ IV


$(CH_3)_3Si\underset{\underset{X}{|}}{C}HC_6H_5$

V


$(CH_3)_3Si\underset{\underset{X}{|}}{C}(C_6H_5)_2$

VI


$(CH_3)_3Si\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}C_6H_5$

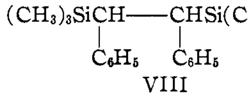
VII

Silane I was halogenated with a mixture of chlorine and bromine (bromine chloride) by the general method of Speier[2] to form a mixture of the bromo and chloro derivatives (in an estimated yield of 55%) from which the bromo derivative (IV, X = Br) was isolated in 36% yield, and the chloro derivative (IV, X = Cl), in 9% yield. A relatively better yield of the bromo derivative might have been obtained by controlling more carefully the rate of addition of the chlorine. Speier[2] apparently obtained only the bromo derivative, but no yield was reported. Silane I has previously been chlorinated with chlorine in the liquid phase[3] and vapor phase[4] to form the chloro derivative (IV, X = Cl), but this derivative appears to have been prepared more often indirectly, by the chlorination of trimethylchlorosilane followed by the reaction of the resulting chloromethyldimethylchlorosilane with methylmagnesium bromide.[5] The bromo derivative (IV, X = Br) has also been prepared indirectly,[2] and the iodo derivative (IV, X = iodine) has been obtained from the chloro derivative.[3] α-Halo derivatives of a few other tetrasubstituted hydrocarbon silanes are described in the literature,[6] but apparently no α-halo derivative of silane II or III has previously been prepared.

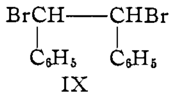
Silanes II and III were chlorinated by sulfuryl chloride in the presence of benzoyl peroxide to form the monochloro derivatives (V, X = Cl) and (VI, X = Cl) in yields of 52 and 74%, respectively. This method was originated by Kharasch and Brown[7] for chlorinating hydrocarbons and employed by Whitmore and co-workers with benzyltrichlorosilane and with other alkyl chlorosilanes.[6a,b,8]

Silanes II and III were brominated with N-bromosuccinimide in carbon tetrachloride to form the monobromo derivatives (V, X = Br) and (VI, X = Br) in yields of 60 and 89%, respectively. The reaction with II also gave some (21%) of the dibromo derivative (VII) which was readily separated from the mono derivative. In this elegant method, described by Wittig and Felletschin[9] for the bromination of fluorene, the by-product, succinimide, is easily removed. When silane II was brominated with bromine in carbon tetrachloride, the monobromo derivative (V, X = Br) was obtained in only 34% yield in a somewhat impure condition. When silane III was similarly brominated, only tars were produced.

Although cleavage was not observed in the brominations of silanes II and III with N-bromosuccinimide, this reagent brought about cleavage with ditrimethylsilane VIII from which dibromide IX was obtained.


$(CH_3)_3Si\underset{\underset{C_6H_5}{|}}{CH}—\underset{\underset{C_6H_5}{|}}{CH}Si(CH_3)_3$

VIII


$Br\underset{\underset{C_6H_5}{|}}{CH}—\underset{\underset{C_6H_5}{|}}{CH}Br$

IX

In addition to the trimethyl hydrocarbon silanes considered above, triphenylbenzylsilane (X) was brominated by the N-bromosuccinimide method to form monobromide XI in 52% yield. It has been

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[1] This work was carried out under Contract N7 onr-455 with the Office of Naval Research.

[2] J. L. Speier, THIS JOURNAL, **73**, 826 (1951).

[3] F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481 (1946).

[4] L. D. Roberts and S. Dev, *ibid.*, **73**, 1879 (1951). It was reported in this article that chlorination of tetramethylsilane with sulfuryl chloride and benzoyl peroxide in methylene chloride produced cleavage products. We have found that no appreciable chlorination occurs on refluxing the reaction mixture (without the methylene chloride) for 12 hours, most of the tetramethylsilane and sulfuryl chloride being recovered.

[5] F. C. Whitmore, L. H. Sommer and J. Gold, *ibid.*, **69**, 1976 (1947).

[6] See especially (a) L. H. Sommer, D. L. Bailey, W. A. Strong and F. C. Whitmore, *ibid.*, **68**, 1881 (1946); (b) L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946); (c) L. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948); (d) E. Larssen and L. O. Knopp, *Acta Chem. Scand.*, 1, 268 (1947); (e) S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem. U.S.S.R.*, **7**, 2495 (1937).

[7] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

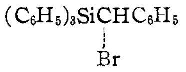
[8] (a) L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, *ibid.*, **68**, 488 (1946); (b) L. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2876 (1948).

[9] G. Wittig and G. Felletschin, *Ann.*, **555**, 133 (1943).

previously shown that cleavage occurs when phenyl substituted silanes such as phenyltrimethylsilane are treated with bromine.[10]

$(C_6H_5)_3SiCH_2C_6H_5$

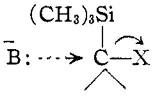
X



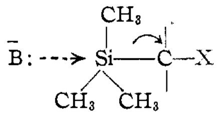
$$(C_6H_5)_3Si\underset{\underset{\displaystyle Br}{|}}{C}HC_6H_5$$

XI

Displacement and Cleavage Reactions.—An α-halosilane may be attacked by a base ($\bar{B}$) either at the α-carbon atom resulting in the displacement of the halide ion as indicated in (a) or at the silicon atom resulting in cleavage of the silicon–carbon bond as indicated in (b). The cleavage of the silicon–carbon bond is presumably also a displacement reaction.[11]



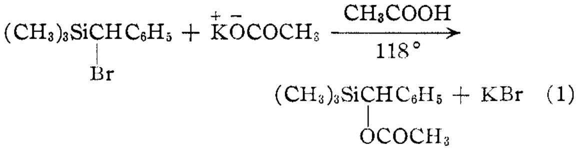
a



b

Earlier workers have shown already that chloromethyltrimethylsilane (IV, X = Cl) undergoes displacement on the α-carbon (a) with potassium acetate in glacial acetic acid at 190° and with ammonia at 60–120° to form trimethylsilylmethyl acetate[12] and trimethylsilylmethylamine,[13] respectively. Similar displacements have been realized with sodiomalonic ester and with sodioacetoacetic ester which have been alkylated with chloromethyltrimethylsilane[14] and iodomethyltrimethylsilane,[15] respectively. Chloromethyltrimethylsilane has also been found to exhibit exclusively displacement on the α-carbon (a) with sodium methoxide in refluxing methanol and mainly this type of displacement with sodium ethoxide in refluxing ethanol.[16] However, cleavage of the silicon–carbon bond (b) predominated with sodium *n*-butoxide in refluxing butanol.[16]

In the present investigation, bromomethyltrimethylsilane (IV, X = Br) and α-bromobenzyltrimethylsilane (V, X = Br) were found to undergo displacements on the α-carbon atom (a) with potassium acetate in refluxing acetic acid to form the corresponding acetates. Bromide V gave acetate XII in 84% yield (equation 1).

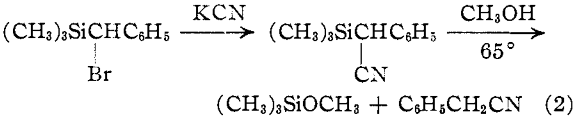


$$(CH_3)_3Si\underset{\underset{\displaystyle Br}{|}}{C}HC_6H_5 + \overset{+}{K}\overset{-}{O}COCH_3 \xrightarrow[118^\circ]{CH_3COOH} (CH_3)_3Si\underset{\underset{\displaystyle OCOCH_3}{|}}{C}HC_6H_5 + KBr \quad (1)$$

XII

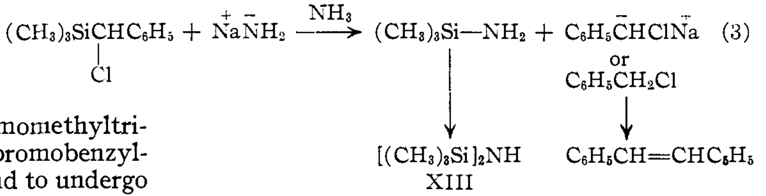
However, diphenyl-α-bromomethyltrimethylsilane (VI, X = Br) underwent with potassium acetate not only displacement at the α-carbon but also cleavage of the silicon–carbon bond since benzylhydryl acetate was mainly obtained.

Silyl bromides IV and V reacted with potassium cyanide in refluxing methanol to form displacement and cleavage products; trimethylmethoxysilane was obtained from bromide IV, and phenylacetonitrile, from bromide V. Presumably, acetonitrile was also produced from IV, and the methoxysilane from V. It seems likely that displacement on the α-carbon (a) occurred first to form the corresponding silyl nitrile which then underwent cleavage as represented, for example, by equation 2. Such intermediate silyl nitriles might be expected to be cleaved under the conditions employed, since the corresponding silyl ketones were found to cleave under similar conditions (see below). Bromide VI reacted with potassium cyanide in refluxing methanol, but only an unidentified product was isolated.



$$(CH_3)_3Si\underset{\underset{\displaystyle Br}{|}}{C}HC_6H_5 \xrightarrow{KCN} (CH_3)_3Si\underset{\underset{\displaystyle CN}{|}}{C}HC_6H_5 \xrightarrow[65^\circ]{CH_3OH} (CH_3)_3SiOCH_3 + C_6H_5CH_2CN \quad (2)$$

Silyl chloride V reacted with sodium amide in liquid ammonia to form decomposition products from which were isolated hexamethyldisilazane (XIII) and stilbene. These products seem best accounted for on the basis that cleavage at the silicon–carbon bond (b) occurred first, followed by the conversion of the resulting trimethylaminosilane to silazane XIII, and of the chlorobenzyl anion or benzyl chloride, to stilbene (equation 3).



$$(CH_3)_3Si\underset{\underset{\displaystyle Cl}{|}}{C}HC_6H_5 + \overset{+}{Na}\overset{-}{N}H_2 \xrightarrow{NH_3} (CH_3)_3Si{-}NH_2 + C_6H_5\overset{-}{C}HCl\overset{+}{Na} \text{ or } C_6H_5CH_2Cl \quad (3)$$

$$(CH_3)_3Si{-}NH_2 \longrightarrow [(CH_3)_3Si]_2NH \ (\text{XIII}) \qquad C_6H_5\overset{-}{C}HCl\overset{+}{Na} \text{ or } C_6H_5CH_2Cl \longrightarrow C_6H_5CH{=}CHC_6H_5$$

It was shown recently[11] that the parent hydrocarbon silane (II) undergoes an analogous cleavage to form silazane XIII and toluene, and evidence was presented that trimethylaminosilane was an intermediate in the formation of the silazane. Kharasch and co-workers[17] have shown that benzyl chloride is converted by sodium amide in liquid ammonia practically quantitatively to stilbene; this dimerization probably involves the intermediate formation of the chlorobenzyl anion. Had displacement at the α-carbon of silyl chloride V occurred first, some of the corresponding silylamine or benzylamine should have been formed; however, none was found. Silyl bromide V reacted only partly with lithium amide under similar conditions and no identifiable product was isolated.

Noll, Speier and Daubert[13] have shown that chloromethyltrimethylsilane (IV, X = Cl) reacts with sodium amide in liquid ammonia (the reaction

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[10] (a) B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. DiGiorgio and F. C. Whitmore, THIS JOURNAL, **70**, 433 (1948); (b) N. W. Cusa and F. S. Kipping, *J. Chem. Soc.*, 1040 (1933); (c) A. Ladenburg, *Ber.*, **40**, 2274 (1907); (d) G. Gruttner and M. Cauer, *ibid.*, **51**, 1283 (1918).

[11] C. R. Hauser and C. R. Hance, THIS JOURNAL, **73**, 5846 (1951).

[12] J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **70**, 1117 (1948).

[13] J. E. Noll, J. L. Speier and B. F. Daubert, *ibid.*, **73**, 3867 (1951).

[14] L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949).

[15] L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

[16] J. L. Speier, *ibid.*, **70**, 4142 (1948).

[17] M. S. Kharasch, W. Nudenberg and E. K. Fields, *ibid.*, **66**, 1276 (1944).

being completed under pressure) to form N-methyl-(trimethylsilyl)-amine, but the manner of formation of this product was not established.

On the basis of these results and those of earlier workers, it appears that at least with α-halosilanes IV and V, displacement at the α-carbon (a) is favored by weak bases and cleavage at the silicon atom (b), by strong bases such as sodium amide, although factors other than the basic strength also are undoubtedly important.

It should be mentioned that attempts to convert acetate XII and bromide V to the silylcarbinol without cleavage of the silicon–carbon bond were unsuccessful.

Whereas basic anions may attack either the silicon atom or the α-carbon atom of an α-halosilane, electrophilic reagents would presumably attack initially only the halogen atom. Although chloride IV (X = Cl) and iodide IV (X = iodine) were previously shown to be unreactive toward ethanolic silver nitrate, we have obtained immediate precipitates of silver halides on treatment of the more reactive bromides and chlorides V and VI with this reagent at room temperature. However, bromides IV and V were found to be unreactive toward silver cyanide in ether suspension, the original bromides being largely recovered after refluxing the mixtures 5 hours. Also, bromide V was largely recovered after refluxing an ether solution of it with silver oxide for 8 hours.

Whitmore, Sommer and Gold[5] have shown that chloride IV is rearranged by a catalytic amount of aluminum chloride to form ethyldimethylchlorosilane. We have found that chloride V reacts vigorously with a catalytic amount of aluminum chloride at room temperature, but under these conditions, such complete carbonization occurred that no product could be isolated.

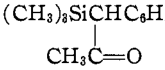
Syntheses with Grignard Reagents.—Earlier workers have shown that chloromethyltrimethylsilane (IV, X = Cl) reacts with magnesium to form, in 95% yield, the corresponding Grignard reagent[18] which may be carbonated to give the corresponding carboxylic acid[14] or condensed with acetaldehyde,[19] ethylene oxide,[20] phenyl isocyanate[21] or ethyl chlorocarbonate[22] to form the expected condensation products. However, the reaction of the Grignard reagent with acetyl chloride produced acetone and other decomposition products.[19]

In the present investigation, bromomethyltrimethylsilane (IV, X = Br), α-chlorobenzyltrimethylsilane (V, X = Cl) and α-bromobenzyltrimethylsilane (V, X = Br) were converted in high yield to the corresponding Grignard reagents. However, diphenyl-α-chloromethyltrimethylsilane (VI, X = Cl) and diphenyl-α-bromomethyltrimethylsilane (VI, X = Br) failed to form the Grignard reagent under similar conditions and were recovered. The Grignard reagent of bromide IV was acetylated with acetic anhydride to form trimethylsilylacetone (XIV) in 59% yield by an adaptation of the method of Newman and Smith[23] for preparing ketones from ordinary Grignard reagents and anhydrides. Less than an equivalent of the anhydride was employed and care was taken to avoid the cleavage of the silyl ketone (XIV) in working up the reaction mixture. The reaction may be represented by equation 4. On treatment of silyl ketone XIV with 2,4-dinitrophenylhydrazine in 85% ethanol containing sulfuric acid,[24] cleavage occurred and the 2,4-dinitrophenylhydrazone of acetone was obtained. The silyl ketone was found to be cleaved even in refluxing ethanol (equation 5), the trimethylethoxysilane being isolated as an azeotrope with ethanol. The corresponding silyl acid, trimethylsilylacetic acid,[14] and silyl ester, ethyl trimethylsilylacetate,[22] have previously been shown to cleave readily.

$$(CH_3)_3SiCH_2MgBr \xrightarrow[\text{at } -70°]{(CH_3CO)_2O} \xrightarrow[NH_4Cl]{H_2O} \underset{\text{XIV}}{(CH_3)_3SiCH_2COCH_3} \quad (4)$$

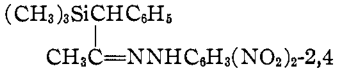
$$\underset{\text{XIV}}{(CH_3)_3SiCH_2COCH_3} \xrightarrow[\text{Reflux}]{C_2H_5OH} (CH_3)_3SiOC_2H_5 + CH_3COCH_3 \quad (5)$$

Similarly, the Grignard reagent of bromide IV was acetylated with acetic anhydride to form α-trimethylsilylbenzylmethyl ketone (XV) but the yield was rather low (19%). Although obtained in lower yield, this ketone is evidently more stable than ketone XIV, since on treatment with the 2,4-dinitrophenylhydrazine reagent, the corresponding 2,4-dinitrophenylhydrazone (XVI) was obtained.



$$\begin{array}{c}(CH_3)_3SiCHC_6H_5\\ |\\ CH_3C{=}O\end{array}$$

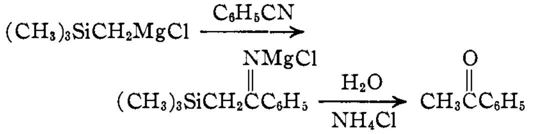
XV



$$\begin{array}{c}(CH_3)_3SiCHC_6H_5\\ |\\ CH_3C{=}NNHC_6H_3(NO_2)_2\text{-}2,4\end{array}$$

XVI

The Grignard reagents of both chlorides IV and V were evidently benzoylated with benzonitrile but cleavage occurred, presumably on working up the reaction mixtures,[25] and there was obtained acetophenone (64%) and desoxybenzoin (45%), respectively. The formation of acetophenone may be represented by equation 6.



$$(CH_3)_3SiCH_2MgCl \xrightarrow{C_6H_5CN} (CH_3)_3SiCH_2\overset{\overset{\displaystyle NMgCl}{\|}}{C}C_6H_5 \xrightarrow[NH_4Cl]{H_2O} CH_3\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 \quad (6)$$

An attempt to benzoylate the cadmium reagent of bromide IV[26] with benzoyl chloride failed, the benzoyl chloride being recovered.

The Grignard reagent of bromide IV condensed with acetone to form *t*-trimethylsilylmethyldi-

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[18] L. H. Sommer, G. M. Goldberg, J. Gold and F. C. Whitmore, THIS JOURNAL, **69**, 980 (1947).

[19] F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

[20] L. H. Sommer, R. E. Van Strien and F. C. Whitmore, *ibid.*, **71**, 3056 (1949).

[21] J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

[22] J. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

[23] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

[24] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[25] It seems entirely possible that the ketimine might be isolated under certain conditions; see G. A. Reynolds, W. J. Humphlett, F. W. Swamer and C. R. Hauser, *J. Org. Chem.*, **16**, 165 (1951).

[26] This reagent was prepared from the Grignard reagent; see H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

TABLE I

SYNTHESIS OF SILICON COMPOUNDS

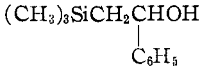
Starting compound	Mole	Reagent	Mole	Method	Product	Yield, %
Tetramethylsilane	2.83	Bromine (chlorine)	1.18	A	Bromomethyltrimethylsilane (IV, X = Br) Chloromethyltrimethylsilane (IV, X = Cl)	36[a] 9[b]
Benzyltrimethylsilane	0.55	Sulfuryl chloride	0.47	B	α-Chlorobenzyltrimethylsilane (V, X = Cl)	52[c,d]
Benzyltrimethylsilane	1.73	N-Bromosuccinimide	1.92	C	α-Bromobenzyltrimethylsilane (V, X = Br) α,α'-Dibromobenzyltrimethylsilane (VII)	60[c,e] 21[c,e]
Diphenylmethyltrimethylsilane	0.066	Sulfuryl chloride	0.105	B	Diphenyl-α-chloromethyltrimethylsilane (VI, X = Cl)	74[c]
Diphenylmethyltrimethylsilane	.13	N-Bromosuccinimide	.15	C	Diphenyl-α-bromomethyltrimethylsilane (VI, X = Br)	89[c]
Benzyltriphenylsilane	.023	N-Bromosuccinimide	.026	C	α-Bromobenzyltriphenylsilane (XI)	52[c]
Silane IV (X = Br)	.172	Potassium acetate	.20	D	Trimethylsilylmethyl acetate	37[f]
Silane V (X = Br)	.127	Potassium acetate	.22	D	α-Trimethylsilylbenzyl acetate (XII)	84[c]
$(CH_3)_3SiCH_2MgBr$	.16	Acetic anhydride	.139	E	Trimethylsilyl acetone (XIV)	59[c]
$(CH_3)_3SiCH(C_6H_5)MgBr$	.11	Acetic anhydride	.09	E	Trimethylsilylbenzyl methyl ketone (XV)	19[c]
Compound XV	...	2,4-Dinitrophenylhydrazine	...	Ref. 24	2,4-Dinitrophenylhydrazone (XVI)	...
$(CH_3)_3SiCH_2MgBr$	.10	Acetone	.096	F	Trimethylsilylmethyldimethylcarbinol (XVII)	52[c,g]
$(CH_3)_3SiCH_2MgBr$	.10	Benzaldehyde	.095	F	Trimethylsilylmethylphenylcarbinol (XVIII)	14[c]
$(CH_3)_3SiCH_2MgBr$	.10	Allyl bromide	.10	F	4-Trimethylsilyl-1-butene (XIX)	68[c]
$(CH_3)_3SiCH(C_6H_5)MgBr$	.09	Allyl bromide	.08	F	4-Trimethylsilyl-4-phenyl-1-butene (XX)[h]	74[c]
Silane V (X = Br)	.12	Magnesium	.06	H	1,2-Diphenyl-1,2-ditrimethylsilylethane (VIII)	35[c,i]

[a] B.p. 115–117°, n^{25}D 1.4421 (reported b.p. 115.5°, n^{25}D 1.4422) (ref. 2). [b] B.p. 96–97° (reported 97.1°) (ref. 3). [c] New compound; analysis and physical properties given in Table II. [d] The yield of chloride V was lowered to 44% when a 60% excess of sulfuryl chloride was used and to 23% when the sulfuryl chloride was not freshly distilled. [e] When the reaction was carried out on one-third the scale, the yield of bromide V was 55% and that of VII 13%. When the reaction was effected on one-sixth the scale, only bromide V was isolated. [f] B.p. 132–137°, n^{25}D 1.4118 (reported b.p. 136.8°, n^{25}D 1.4060) (ref. 12). [g] When the reaction was carried out using two equivalents of acetone to one of the Grignard reagent, there was obtained a mixture; b.p. 42–95° (3 mm.) which was not readily separated. [h] After refluxing this silyl olefin with 5% $KMnO_4$ for 8 hours, the only product isolated was benzoic acid. Treatment of the silyl olefin with concentrated sulfuric acid at 0° produced a vigorous reaction to give a non-silicon liquid, b.p. 156–158° (2 mm.) and a plastic solid. [i] When the reaction was carried out with equivalent amounts of the bromosilane and magnesium (a trace of solid silver bromide was also present), the yield of dimer VIII was 21%.

methylcarbinol (XVII) (52%) and with benzaldehyde to form apparently *s*-trimethylsilylmethylphenylcarbinol (XVIII) (14%), but the Grignard reagent of bromide V produced mixtures of products with these carbonyl compounds.

$(CH_3)_3SiCH_2C(CH_3)_2OH$

XVII

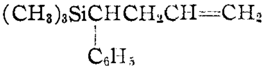

$(CH_3)_3SiCH_2\underset{C_6H_5}{\underset{|}{C}}HOH$

XVIII

The Grignard reagents of both bromides IV and V were alkylated with allyl bromide to form 4-trimethylsilyl-1-butene (XIX) (68%) and 4-trimethylsilyl-4-phenyl-1-butene (XX) (74%), respectively. Attempts to oxidize these silyl olefins with alkaline potassium permanganate to form carboxylic acids without cleaving the silicon–carbon bonds were unsuccessful. Benzoic acid was obtained from silyl olefin XX.

$(CH_3)_3SiCH_2CH_2CH{=}CH_2$

XIX


$(CH_3)_3Si\underset{C_6H_5}{\underset{|}{C}}HCH_2CH{=}CH_2$

XX

The Grignard reagent of bromide V was also alkylated with bromide V itself to form dimer VIII. In some of the reactions described above small amounts of this dimer were isolated as a by-product. It was obtained in 35% yield when bromide V was treated with one-half of an equivalent of magnesium.

Although the Grignard reagent from chloride IV has previously been converted in high yield to the corresponding silyl carboxylic acid, we were unable to isolate the analogous carboxylic acid after similar carbonation of the Grignard reagent of bromide V; instead, there was obtained the hydrocarbon silane, benzyltrimethylsilane (II). Apparently, the carboxylic acid was formed as an intermediate which underwent decarboxylation.

Experimental

Benzyltrimethylsilane[11] (II), diphenylmethyltrimethylsilane[11] (III) and triphenylbenzylsilane[27] (X) were prepared as described previously. Sulfuryl chloride (Eastman Kodak Co.) was freshly distilled (b.p. 68–69°) prior to use. National Aniline N-bromosuccinimide[28] and Anderson Laboratories, Inc., tetramethylsilane (I) were used without further purification.

Synthesis of Silicon Compounds (Table I). Method A.—Using the general method of Speier,[2] anhydrous bromine was added dropwise to tetramethylsilane while chlorine gas was added slowly. The reaction temperature was maintained at 25–35° and the product was distilled through a 30-cm. Vigreux column followed by fractionation of the distillate through a 30-cm. glass helices-packed column.

Method B.—Sulfuryl chloride, a catalytic amount of benzoyl peroxide and the appropriate silane were refluxed for 5 to 7 hours according to the method of Whitmore and co-workers.[6a] After removal of excess sulfuryl chloride under reduced pressure (water aspirator), the residue was fractionated *in vacuo*.

Method C.—Using the method of Wittig and Felletschin,[9] N-bromosuccinimide in carbon tetrachloride and the hydrocarbon silane were refluxed 7 to 10 hours. The mixture was cooled and filtered. The solid succinimide was washed twice with carbon tetrachloride, the washings being added to the filtrate. The solvent was removed from the filtrate under reduced pressure (water aspirator) and the residue fractionated *in vacuo*.

Method D.—Potassium acetate and the α-halosilane in 20 ml. of glacial acetic acid were refluxed 18–24 hours and allowed to stand 24–36 hours longer.[29] The mixture was poured onto 100–200 g. of ice and the resulting mixture extracted with ether. The ether phase was washed free of acetic acid with 10% sodium bicarbonate, dried over sodium

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(27) C. R. Hance and C. R. Hauser, THIS JOURNAL, **74**, 1856 (1952).

(28) We are indebted to the National Aniline Division of the Allied Chemical and Dye Corp. for a sample of this compound.

(29) When the reaction was carried out for only 5 to 7 hours, impure acetate XII was obtained, being contaminated apparently with some of the original halo silane.

TABLE II

ANALYSIS AND PHYSICAL PROPERTIES OF NEW COMPOUNDS

	Analyses,[b] %						B.p.,[c]					Molar refraction	
	Carbon		Hydrogen		Halogen								
Compound[a]	Calcd.	Found	Calcd.	Found	Calcd.	Found	°C.	Mm.	d^t_4	n^t_D	t, °C.	Calcd.[d]	Found
V (X = Cl)	60.44	60.67	7.61	7.51	17.84	17.80	100–101.3	6	0.9980	1.5132	25.0	59.51	59.82
V (X = Br)	49.38	49.53	6.19	5.90	32.86	32.73	98–99	4	1.2112	1.5389	20.0	62.35	62.89
VII	37.29	37.40	4.32	4.14	49.67	49.34	127–128	4	1.5074	1.5778	20.0	70.03	70.89
VI (X = Cl)	69.92	70.25	6.96	6.67	12.90	12.83	150–151.5	3	1.0940	1.5816	20.0	83.90	83.79
VI (X = Br)	60.18	60.36	6.00	5.91	25.03	25.11	166.5–167	4	1.2437	1.5986	20.0	86.74	87.66
XI	69.93	70.20	4.93	5.06	18.61	18.38	M. 144–145		....	....	..	...	...
XII	64.83	64.70	8.16	7.78	...	...	107.5	6	0.9780	1.4917	25.1	65.70	65.91
XIV	55.33	55.42	10.83	10.93	...	...	74	96	.8275	1.4188	26.0	39.54	38.72
XV	69.86	69.36	8.79	8.55	...	...	101–102	5	....	1.5242	20.8	....	...
XVI	55.94	55.96	5.74	5.30	14.49[e]	14.33[e]	M. 142–143		....	....	..	...	...
XVII	57.46	57.27	12.42	12.37	...	...	91–92	98	.8249	1.4284	27.0	45.72	45.57
XVIII	67.99	67.38	9.34	9.42	...	...	103–104	3	.9380	1.4984	27.0	60.85	60.76
XIX	65.52	65.34	12.56	12.11	...	...	112–113	760	.7294	1.4102	27.0	43.73	43.57
XX	76.42	76.23	9.87	10.03	...	...	91–92	5	.8805	1.5028	26.1	68.09	68.57
VIII	73.55	73.68	9.26	9.26	...	...	M. 151–152		....	....	..	...	...

[a] Compound numbers correspond to those in Table I. [b] Analyses are by Clark Microanalytical Laboratories, Urbana, Illinois. [c] All boiling points are uncorrected. [d] Molar refractivities were calculated using values reported by E. L. Warrick, THIS JOURNAL, 68, 2455 (1946). [e] Analysis for nitrogen.

TABLE III

CLEAVAGE OF α-HALOSILANES BY BASIC REAGENTS

α-Halosilane[a]	Mole	Reagent	Mole	Solvent	Ml.	Reflux, hr.	Product	Yield, %
VI (X = Br)	0.03	Potassium acetate	0.07	Acetic acid	20	7.5	Benzhydryl acetate	79[b]
IV (X = Br)	.2	Potassium cyanide	.3	Methanol	375	10	Trimethylmethoxysilane	77[c]
V (X = Br)	.12	Potassium cyanide	.23	Methanol	375	9	Phenylacetonitrile	64[d]
VI (X = Br)	.05	Potassium cyanide	.08	Methanol	400	7	Unidentified product[e]	...
V (X = Cl)	.135	Sodium amide[f]	.14	Ammonia	200	1.5	Hexamethyldisilazane	31[g]
						(−33°)	Stilbene	23[h]
V (X = Br)	.045	Sodium amide[f]	.065	Ethyl ether	200	2	V (recovered)	83
V (X = Br)	.041	Lithium amide	.048	Ammonia	200	1	V (recovered)	41
						(−33°)	Viscous tar	39 (by wt.)

[a] Compound numbers correspond to those in Table I. [b] B.p. 152–153° (4 mm.). Treatment with ethanolic potassium hydroxide at 50° gave benzhydrol, m.p. and mixed m.p. 65–66.5°. [c] B.p. 55–57, $n^{20.3}_D$ 1.3690 (reported b.p. 56–56.7°, n^{22}_D 1.3679, R. O. Sauer, THIS JOURNAL, 66, 1707 (1944)). Treatment with sulfuric acid gave hexamethyldisiloxane, b.p. 99°. [d] B.p. 100–101° (10 mm.), n^{26}_D 1.5210, d^{26}_4 1.0182. Treatment with phenylmagnesium bromide gave desoxybenzoin, m.p. and mixed m.p. 55–57°. [e] B.p. 147–149° (4 mm.), n^{26}_D 1.5626, d^{26}_4 1.0235 (*anal.* C, 75.92; H, 7.88; N, 0.5). [f] Prepared according to J. T. Adams and C. R. Hauser, THIS JOURNAL, 66, 1220 (1944). [g] B.p. 120–127°, n^{20}_D 1.4036. [h] M.p. and mixed m.p. 121–123° after one recrystallization from 90% ethanol.

sulfate and the solvent removed. The residue was distilled *in vacuo*.

Method E.—An ether solution of the silyl Grignard reagent[30] was added dropwise to a solution of freshly distilled acetic anhydride in 100 ml. of ether cooled to −70° by means of a Dry Ice–acetone-bath, the reaction being carried out under an atmosphere of nitrogen.[23] The Grignard solution was added at such a rate that the reaction temperature was maintained at −60° or below, and the reaction continued at these temperatures for 3.5 hours. The mixture was allowed to warm to −10° and 100 ml. of 10% ammonium chloride added slowly. The ether phase was separated, washed with water and 10% sodium bicarbonate, and dried over sodium sulfate. After removal of the solvent, the residue was fractionated under reduced pressure.

Method F.—A solution of freshly distilled aldehyde, ketone or allyl bromide in 50 ml. of ether was added to the silyl Grignard reagent in ether and the mixture refluxed for 4.5 hours. The mixture was then poured onto ice and ammonium chloride. The ether phase was treated essentially as described in method E and the product distilled under reduced pressure.

Method G.—One equivalent of the halo silane in ether was added to magnesium and refluxed until most of the magnesium was consumed. After a few minutes a second equivalent of the halosilane was added and the mixture refluxed for 8 hours and allowed to stand for 12 hours. The mixture was decomposed with ammonium chloride and the dimer isolated by evaporating the ether solution to dryness. The product was purified by recrystallization from methanol.

1,2-Diphenyl-1,2-ditrimethylsilyl Ethane (VIII) with N-Bromosuccimide.—On treating 4.34 g. (0.0133 mole) of this silane in 75 ml. of carbon tetrachloride with 5.6 g. (0.0316 mole) of N-bromosuccinimide according to method C, there was obtained a precipitate which, after two recrystallizations from hot benzene, gave 3.7 g. of stilbene dibromide (IX), m.p. 224–226° dec. (reported m.p. 226–229°).[31]

Silyl Grignard Reagents with Benzonitrile and Carbon Dioxide.—On treating 0.209 mole of trimethylsilylmethylmagnesium chloride in 115 ml. of ether with 19.5 g. (0.189 mole) of freshly distilled benzonitrile in 50 ml. of ether according to method F, there was obtained, on decomposing the reaction mixture and breaking the emulsion, 2.3 g. of forerun, b.p. 50–105° (51 mm.) and 14.5 g. (64%) of acetophenone (cleavage product), b.p. 105–107° (50 mm.), n^{21}_D 1.5280, d^{26}_4 1.000; semicarbazone, m.p. 196–197°; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 252–253°. The residue (4 g.) appeared to be a silicate.

Similarly, the reaction of 6.5 g. (0.063 mole) of benzonitrile in 50 ml. of ether with 0.06 mole of the Grignard re-

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(30) The formations of trimethylsilylmethylmagnesium bromide (obtained in 98% yield) and the corresponding chloride (obtained in 95% yield) were initiated by preheating the magnesium with a crystal of iodine. α-Trimethylsilylbenzylmagnesium bromide (obtained in 89% yield) and the corresponding chloride (obtained in 75% yield) were prepared in the usual manner. The reagents were analyzed by the method of H. Gilman, E. A. Zoellner and J. B. Dickey, THIS JOURNAL, 51, 1576 (1929).

(31) F. C. Whitmore and E. N. Thurman, *ibid.*, 51, 1502 (1929).

agent of V gave 5.5 g. (45%) of desoxybenzoin, b.p. 160–162° (3 mm.), m.p. 55–57° after one recrystallization from a mixture of benzene and ethanol. The desoxybenzoin was further identified by the mixed melting point method and by conversion to the 2,4-dinitrophenylhydrazone, m.p. 198–199°.

A solution of 0.06 mole of α-trimethylsilylbenzylmagnesium bromide in 200 ml. of ether was poured onto a large excess of Dry Ice and the reaction mixture worked up as usual, yielding 6.6 g. (58%) of benzyltrimethylsilane, b.p. 42–43° (1 mm.), n^{25}D 1.4912. The residue (3.2 g.) consisted of dimer VIII, m.p. 140–145°. No carboxylic acid was found.

In another experiment the ether phase was extracted with 10% sodium bicarbonate, but no acidic product was found.

Cleavage of α-Halosilanes with Basic Reagents.—In Table III are summarized the experimental conditions and results obtained on treating certain α-halosilanes with basic reagents.

Attempted Conversion of Acetate XII and Bromide V to the Carbinol.—Treatment of acetate XII with 12% ethanolic potassium hydroxide solution at 50° produced a vigorous reaction but no pure product could be isolated. Refluxing the methanolic solution of the acetate in the presence of a trace of sulfuric acid failed to produce any change within 6 hours, the acetate being recovered. After 16 hours under these conditions, about 25% of the acetate had been decomposed but the product, b.p. 80–82° (8 mm.), failed to analyze for the corresponding silyl alcohol.

Treatment of bromide V with equivalents of sodium hydroxide (in methanol at 50–55° for 10 hours) and of potassium hydroxide (in absolute ethanol at reflux temperature of one hour) caused decomposition, but the silyl alcohol could not be isolated. Bromide V was recovered (94%) after stirring an ether solution of it with 10% aqueous sodium hydroxide for 9 hours.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Reaction of Alkanes with Hydrogen and Deuterium. Racemization and Exchange

BY ROBERT L. BURWELL, JR., AND WARREN S. BRIGGS

RECEIVED MARCH 27, 1952

In the presence of a nickel–kieselguhr catalyst and at temperatures of about 90 to 130°, the hydrogen atoms of heptane, (+)3-methylhexane, 3,3-dimethylhexane and 2,2,3-trimethylbutane exchange with deuterium. The relative numbers of molecules exchanged under equivalent conditions decrease in the order listed with a factor of about seven separating the extremes. The relative abundance of the various exchanged species has been determined mass spectrographically. All possible exchanged species are present in the case of the first two hydrocarbons with the more exchanged species weighted much more heavily than corresponds to statistical equilibrium. A maximum of seven exchanged hydrogen atoms is found in the last two. Apparently, the exchange process cannot propagate past a quaternary carbon atom. (+)3-Methylhexane is racemized under the same conditions and at a rate substantially independent of whether hydrogen or deuterium is present. The ratio of the number of molecules which suffer exchange to that racemized is about 1.6. Within the range studied, the rate of racemization is representable by $k_0e^{-26,000/RT}\ p_{\mathrm{H}_2}{}^{-0.6}p_{3\mathrm{MH}}{}^{1/3}$. In the absence of hydrogen the catalyst becomes poisoned. Any mechanism must consider that exchange is apparently accompanied by racemization. Partial reversal of olefin hydrogenation seems a likely mechanism. It must involve, however, a symmetric intermediate.

The development of theories of mechanisms of organic reactions has been greatly facilitated by simultaneous study of the kinetics and the stereochemistry of reactions of optically active compounds. Little application of similar studies has appeared in heterogeneous catalytic processes.

Methane, ethane and propane have been shown to exchange with deuterium in the presence of nickel–kieselguhr catalysts.[1] Determination of whether racemization accompanies exchange when an optically active hydrocarbon is employed and, if so, determination of the relationship between the two reactions seemed of considerable potential value in extending our knowledge of the complex of reactions occurring between hydrogen and hydrocarbons. Accordingly, this paper presents the results of such an investigation employing (+)3-methylhexane and nickel–kieselguhr catalysts.

Experimental Techniques

Materials.—The preparation of (+)3-methylhexane has been described.[2] The heptylene was fractionated in a 50-plate Stedman column and hydrogenated at high pressure (about 100 atm.) at not over 70° with nickel–kieselguhr catalyst. Slight racemization results from this process but it is more convenient than the hydrogenation with platinum oxide formerly employed. In later stages of the present work, washing the resultant hydrocarbon with sulfuric acid before final fractionation was replaced by silica gel percolation. No difference in behavior of the product was observed. The infrared absorption spectrum of every batch was checked against a Bureau of Standards standard sample of 3-methylhexane on a Beckman IR2T infrared absorption spectrograph. Deviations were within 1% in transmission. However, traces of olefin were probably present since the product began to absorb in the ultraviolet at about 2200 Å.

Eastman Kodak Company synthetic n-heptane was refractionated and percolated through silica gel. High purity 2,2,3-trimethylbutane was supplied by the General Motors Corporation, Research Laboratories Division. It had been treated with silica gel before use. 3,3-Dimethylhexane was supplied by A.P.I. Research Project 45 at The Ohio State University. Its purity was reported to be 99.1 ± 0.3 mole %.

Nickel–kieselguhr catalyst (Universal Oil Products Company)[3] crushed and sieved to 20–40 mesh was reduced *in situ* with hydrogen. In the earlier experiments, a reduction temperature of 250° was employed. The catalytic activity varied considerably from sample to sample and was not stable for a given sample. After run 104, reduction at 300° was employed. Consistent and stable activity resulted.

Deuterium (99.5%) was obtained from the Stuart Oxygen Company under allocation from the Atomic Energy Commission.

Apparatus.—Tanks of electrolytic hydrogen, deuterium and helium were connected through capillary flow-meters to a manifold. Traps were provided between the flow-meters and the manifold. They were cooled with Dry Ice in the first two cases. With helium, activated charcoal cooled by liquid air was used. Effluent gas from the manifold was passed through a sintered glass bubbler immersed in hydrocarbon. The containing flask was thermostated

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[1] (a) K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1445 (1936); (b) **58**, 1795 (1936); (c) K. Morikawa, N. R. Trenner and H. S. Taylor, *ibid.*, **59**, 1103 (1937).

[2] G. S. Gordon, III, and R. L. Burwell, Jr., *ibid.*, **71**, 2355 (1949).

[3] Reported to contain, when reduced, about 65% nickel, V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).