Anal. Calcd. for $C_7H_{14}N_2O_3$: C, 48.3; H, 8.1; N, 16.1. Found: C, 48.6; H, 7.7; N, 16.1.

Infrared support for this structure is given by bands for NH at 3475 cm.$^{-1}$, carbonyl at 1735 cm.$^{-1}$, ether at 1095 cm.$^{-1}$, and CH_3 and CH_2 at 2995 cm.$^{-1}$ and 2875 cm.$^{-1}$.

General Procedure for the Chlorination of Glycolurils.—A stirred suspension of the glycoluril in water was treated with chlorine for 0.5 to 1.5 hr. while 1 or 3 *N* sodium hydroxide was added at such a rate as to maintain the mixture in the range pH 8–9. The resulting solid was filtered, washed with water, dried, and recrystallized. The experimental details used with this general procedure, melting points, yields, and analytical data observed are summarized in Table II.

Acknowledgment.—The authors wish to thank Mr. Henry A. McElravy, Jr., for his assistance in the preparation of many of the compounds reported in this study and Mr. John M. Sanders for the interpretation of the infrared data presented.

Addition of Silicon Hydrides to Olefinic Double Bonds. VII. Addition to Chloro- and Dichlorobutenes

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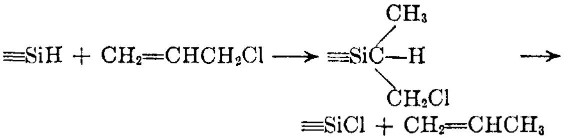
In the presence of platinum catalysts, silicon hydrides react with allylic chlorides in a highly complex way. The products obtained from 1-chlorobutene-2, 3-chlorobutene-1, 1,4-dichlorobutene-2, and 3,4-dichlorobutene-2 were found to include numerous compounds. The formation of the various compounds is explained as due to a series of allyl rearrangements, eliminations of chloride from allylic chlorides and double bond migrations during the reaction.

During the preparation of 3-chloropropylsilicon compounds by means of the addition of silicon hydrides (usually as chlorosilanes) to allyl chloride, propylene is formed in the presence of a platinum catalyst[2,3] or in the presence of palladium,[2–4] rhodium,[4] ruthenium,[4] or nickel.[4] The yield of propylene is dependent to some extent upon the structure of the silicon hydride[2] and to a far greater extent upon the catalyst.[2,4]

In an effort to increase our understanding of the reaction, this study was carried out with chloroplatinic acid with linear chloro- and dichlorobutenes as well as with allyl chloride.

The formation of propylene as outlined by equation I has been proposed.[2,4] β-Chloroisopropyltrichlorosilane was prepared by chlorination of isopropyltrichlorosilane and used as a solvent during the addition of trichlorosilane to allyl chloride. The reaction proceeded normally in every respect, and the solvent was recovered quantitatively and unchanged. The scheme of equation 1 may therefore be eliminated from further consideration because the last step did not occur under the conditions which form propylene.



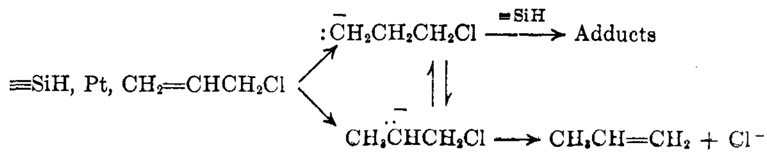
$$\equiv SiH + CH_2{=}CHCH_2Cl \longrightarrow \equiv Si\overset{CH_3}{\underset{CH_2Cl}{C}}{-}H \longrightarrow \equiv SiCl + CH_2{=}CHCH_3 \quad (1)$$

Methallyl chloride may be used instead of allyl chloride. It adds the hydride smoothly, but forms little or no isobutylene.[2] Methyldichlorosilane was added to allyl chloride dissolved in benzyl chloride and toluene was not found as a by-product. Because neither methallyl chloride nor benzyl chloride entered into metathetical reactions described by equation 2, it seems most unlikely that propylene from allyl chloride formed in this way.

$$\equiv SiH + ClCH_2CH{=}CH_2 \longrightarrow \equiv SiCl + CH_3CH{=}CH_2 \quad (2)$$

The hypothesis already advanced,[2] which assumes that the addition reaction may start by nucleophilic attack by a hydride ion upon the double bond of the olefin, therefore persists.

The hydride ion originates as a silane hydrogen. If completely ionized by the catalyst, it would give rise with allyl chloride to a carbanion which is thought to tautomerize according to the scheme:



$$\equiv SiH, Pt, CH_2{=}CHCH_2Cl \begin{array}{l} \nearrow \; \overset{-}{:}CH_2CH_2CH_2Cl \xrightarrow{\equiv SiH} \text{Adducts} \\ \qquad\qquad \uparrow\downarrow \\ \searrow \; CH_3\overset{..}{\underset{-}{C}}HCH_2Cl \longrightarrow CH_3CH{=}CH_2 + Cl^- \end{array} \quad (3)$$

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[1] Present address: Colgate-Rochester Divinity School, Rochester 20, N. Y.

[2] J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Am. Chem. Soc.*, **82**, 3601 (1960).

[3] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and G. V. Odabashyan, *Izvest. Akad. Nauk., S.S.S.R.*, **10**, 1206 (1957).

[4] A. D. Petrov, Kh. M. Minachev, V. A. Ponomarenko, B. A. Sokolov, and G. V. Odabashyan, *Doklady Akad. Nauk., S.S.S.R.*, **112** (2), 273 (1957).

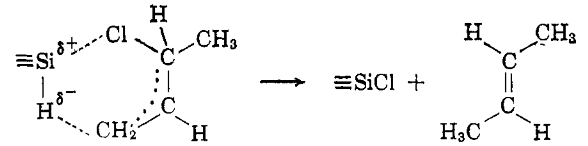
TABLE I

PRODUCTS FROM CH_3Cl_2SiH AND CHLORO- AND DICHLOROBUTENES

Olefin/CH_3Cl_2SiH: Products	$C{=}C{-}\overset{Cl}{C}{-}C$ (1)	$CC{=}CCCl$ (2)	(2 + 1)	$ClCC{=}CCCl$ (3)	$C{=}C\overset{Cl}{C}CCl$ (4)	(3 + 4)	$C{=}CCCCl$
	2/1	2/1	2/1	2/1	2/1		1/2[a]
Butene-1	1.3	0.8	2	1.8	0.7	0.5	
cis-Butene-2	5.7	1.2	4	2.9	1.3	1.2	
trans-Butene-2	3.8	2.4	7	2.5	1.3	1.2	
CH_3SiCl_3	19	22	22	15	15	17.8	9.3
$C{=}C{-}\overset{Cl}{C}{-}C$	18	14	18	7	4.4	3.1	1.6
$C{-}C{=}C{-}Cl$	23	24	21	11.3	9.4		0.4
$CH_3BuSiCl_2$	6.3	13	7		0.7		10
$CH_3Cl_2SiCC\overset{Cl}{C}C$	21	18	16				
$CH_3Cl_2SiCCCCCl$				20		1.4	39
$CH_3Cl_2SiCCCClCCl$					13.9	13.9	
$ClCC{=}CCCl$				31	9.9	30.9	
$C{=}CCClCCl$				6	40	4.3	0.8
$C{=}CCCCl$					4.4	1.8	0.8

[a] 39 area % CH_3HSiCl_2 was recovered.

Attack upon the olefin by a polarized silicon hydride in the presence of the catalyst could be visualized for 3-chloro-butene-1 in the form:



IV

Such a visualization is supported by the recent finding that with acetylenes *cis* addition does occur.[5] Either *cis*- or *trans*-butene-2 might be the predominant product in such a case. However, both *cis*- and *trans*-butene-2 as well as butene-1 were found. Further experiments revealed that both *cis*- and *trans*-butene-2 give rise to a mixture of butenes under the conditions employed. Therefore, even if one isomer of butene-2 is initially formed as suggested by equation 4, one cannot prove the point by this procedure.

Methyldichlorosilane and 3-chlorobutene-1 made 3-chlorobutylmethyldichlorosilane as expected, but this same product also was formed with 4-chlorobutene-2. This phenomenon may involve an allylic rearrangement followed by an addition reaction.

$$CH_3CH{=}CHCH_2Cl \rightleftharpoons CH_3{=}CHCHClCH_3 \xrightarrow{CH_3HSiCl_2} CH_3Cl_2SiCH_2CH_2CHClCH_3 \quad (5)$$

Methyldichlorosilane and 4-chlorobutene-1 formed 4-chlorobutylmethyldichlorosilane along with the by-products to be expected from 4-chlorobutene-2. The double bond in 4-chlorobutene-1, although not allylic, was capable of migrating to the 2- position during the reaction in the same manner observed with 1-olefins.[6] The formation of all the linear butenes starting with any linear butene also indicates that a rapid migration of double bonds occurred during these addition reactions in the presence of the catalyst.

1,4-Dichlorobutene-2 with methyldichlorosilane formed 4-chlorobutylmethyldichlorosilane as the chief adduct, with a smaller amount of 3-chlorobutylmethyldichlorosilane, 3,4-dichlorobutylmethyl dichlorosilane, and butylmethyldichlorosilane.

3,4-Dichlorobutene-1 gave chiefly 3,4-dichlorobutylmethyl-dichlorosilane, along with the usual mixture of other adducts. However, 4-chlorobutyl derivatives were absent.

A series of experiments were carried out in small sealed Pyrex tubes. The products in each were then estimated by vapor chromatography. The results of these experiments are in agreement with the data from larger scale preparations and are summarized in Table I. In Table I, all the values shown are area percentages as determined on vapor chromatographs.

All these data may be summarized as a complex series of reactions which occur during the addition of silicon hydrides to allylic chlorides. The overall effects can be systematized as a series of equilibria, eliminations, and additions outlined as follows:

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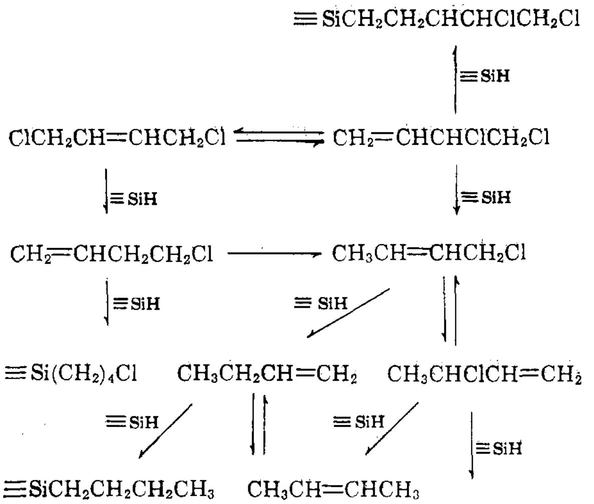
(5) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(6) J. Saam and J. Speier, *J. Am. Chem. Soc.*, **83**, 1351 (1961).



Experimental

The chlorosilanes were Dow Corning products whose purity had been checked by vapor phase chromatography and found to be at least 98%.

2-Chloroethyl-1-methyltrichlorosilane was prepared by the method of Sommer *et al.*,[7] using sulfuryl chloride with benzoyl peroxide as an initiator.

***cis*- and *trans*-butene-2** were more than 99% pure as obtained from the Phillips Petroleum Co., Special Products Division.

3-Chlorobutene-1 and 4-chlorobutene-2 were prepared from butadiene and hydrochloric acid by the method of Henne.[8] The former had b.p. 63°, $n^{25}{}_D$ 1.4224, $d^{25}{}_4$ 0.8929, and the latter had b.p. 84°, $n^{25}{}_D$ 1.4327, $d^{25}{}_4$ 0.9254.

4-Chlorobutene-1 was prepared from 1-buten-4-ol by the procedure of Roberts and Mazur.[9] Vapor chromatography led to an estimate of its purity as better than 93%. Its properties were: b.p. 75°, $n^{25}{}_D$ 1.4200, $d^{25}{}_4$ 0.916.

1,4-Dichlorobutene-2 was obtained from the E. I. du Pont de Nemours & Co. and seemed to be about 98% pure.

3,4-Dichlorobutene-1 was prepared from the 1,4-dichlorobutene-2 by heating the latter in the presence of cupric chloride as described by Otto.[10] It had b.p. 122°, $n^{25}{}_D$ 1.4620, $d^{25}{}_4$ 1.4291.

(2-Chloro-1-methylethyl)trichlorosilane as a Solvent.—A mixture of allyl chloride (76.5 g., 1.0 mole), trichlorosilane (203 g., 1.5 moles), and 2-chloro-1-methyltrichlorosilane (63.6 g., 0.25 mole) was added dropwise to 115 ml. of boiling benzene which contained 0.05 ml. of 0.2 *M* chloroplatinic acid solution in isopropyl alcohol. Heat of reaction maintained the mixture at reflux. When the reaction had subsided, the mixture was carefully fractionated. The recovered (2-chloro-1-methylethyl)trichlorosilane was estimated at 0.264 mole, b.p. 164–174°; neut. equiv. 56.0, calcd. neut. equiv. 53.0. The fraction contained a small amount of 3-chloropropyltrichlorosilane. As nearly as could be determined no 2-chloro-1-methylethyltrichlorosilane was lost nor made during the experiment. 3-Chloropropyltrichlorosilane was obtained in a typical[2] yield: 143 g., 67%.

Benzyl Chloride as a Solvent.—A mixture of methyldichloro-silane (115 g., 1.0 mole) and allyl chloride (76.5 g., 1.0 mole) was added to 253 g. of benzyl chloride which contained 0.05 ml. of 0.2 *M* chloroplatinic acid. The mixture was maintained at 114–129° by the heat of reaction. The mixture was carefully distilled in a search for toluene. None was apparent. A fraction (19 g.) boiling between 98 and 173° seemed most likely to contain toluene. It was examined further by a vapor chromatograph. Some toluene may have been present, but the amount would be less than a yield of 0.05%. This indicates that essentially no metathesis occurred between benzyl chloride and the silane under the conditions of these reactions.

Butene-2.—*cis*-Butene-2 (about 5 g.), methyldichlorosilane (5.8 g., 0.05 mole), and 0.02 ml. of 0.005 *M* chloroplatinic acid were sealed together into a glass tube and warmed to 70° when a sudden exothermic reaction occurred. The contents of the tube were analyzed by vapor phase chromatography and found to be in area percents: unknown, 0.7; butene-1, 0.7; *trans*-butene-2, 21; *cis*-butene-2, 14; two unknown components totalling 2.3%; and methylbutyldichlorosilane, 60%. The presence of all the possible butenes is of interest.

The experiment was repeated with about 5 g. of *trans*-butene-2. The results were essentially the same.

Addition of Methyldichlorosilane to Chloro- and Dichlorobutenes. 3-Chlorobutene-1.—Methyldichlorosilane (115 g., 1 mole) was added dropwise to 3-chlorobutene-1 (90.6 g., 1 mole) containing 0.05 ml. of 0.2 *M* chloroplatinic acid. The mixture was kept at reflux starting at 63° and rising steadily to 102°. A cold trap contained 10 g. of volatile liquid at the end of the reaction. The liquid was analyzed by vapor phase chromatography and found to be 14.5% butene-1, 50.2% *trans*-butene-2, 35.1% *cis*-butene-2, with a trace of two other compounds which were not identified.

The major portion of the products was distilled to give methyltrichlorosilane, 42.4 g., 0.28 mole, b.p. 65.5°, $n^{25}{}_D$ 1.4080; methylbutyldichlorosilane, 12.3 g., 0.07 mole; and 3-chlorobutylmethyldichlorosilane, 121 g., 0.59 mole, 59% yield, b.p. 99° at 32 mm., $n^{25}{}_D$ 1.4566, $d^{25}{}_4$ 1.158, R_D 0.2349, calcd. R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: Si, 13.7; neut. equiv., 102.8. Found: Si, 13.9; neut. equiv., 105.2, 105.8.

Treatment of a sample of this product with hot saturated potassium hydroxide caused the rapid formation of methylcyclopropane which was identified by its vapor pressure curve in a tensimeter and by its infrared spectrum. The formation of methylcyclopropane is good evidence for the identity of the adduct because as shown by Sommer and coworkers[11] only 3-chloroalkylsilanes make cyclopropanes when treated with caustic.

The above product was treated with excess methylmagnesium bromide in ether to form 3-chlorobutyltrimethylsilane in 61% yield, b.p. 69° at 30 mm., $n^{25}{}_D$ 1.4289, $d^{25}{}_4$ 0.8640, R_D 0.2983, calcd. R_D 0.2972.

Anal. Calcd. for $C_7H_{17}ClSi$: Si, 17.1; Cl, 21.5. Found: Si, 17.0, 17.1; Cl, 22.0.

4-Chlorobutene-2.—The experiment was repeated with 4-chlorobutene-2. The volatile liquid caught in a cold trap proved to be 12.9 g. made up of 26% butene-1, 54% *trans*-butene-2, and 20% *cis*-butene-2 with a trace of one of the same unknown compounds observed in the previous experiment.

The liquid products were methyltrichlorosilane, 65 g., 0.43 mole; methylbutyldichlorosilane, 18.6 g., 0.11 mole, yield, b.p. 57° at 28 mm., $n^{25}{}_D$ 1.4370, $d^{25}{}_4$ 1.0365, R_D 0.2527, calcd. R_D 0.2520.

Anal. Calcd. for $BuCH_3SiCl_2$: neut. equiv., 85.6. Found: neut. equiv., 86.6.

Following this in the distillation was 3-chlorobutylmethyldichlorosilane, 36.9 g., 0.18 mole, 18% yield, b.p. 95.2° at 27 mm., $n^{25}{}_D$ 1.4559, $d^{25}{}_4$ 1.170, R_D 0.2299, calcd. R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: neut. equiv., 102.8. Found: neut. equiv., 103.8, 104.4.

The experiment was repeated in a stainless steel vessel using 4-chlorobutene-2 (164 g., 1.8 moles), methyldichloro-

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(7) L. H. Sommer and F. J. Evans, *J. Am. Chem. Soc.*, **76**, 1186 (1954).

(8) A. L. Henne, H. Chanan, and A. Turk, *ibid.*, **63**, 3474 (1941).

(9) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(10) J. A. Otto, U. S. Patent 2,422,252, June 17, 1947.

(11) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 488 (1946).

silane (204 g., 1.8 moles), and 0.1 ml. of 0.2 *M* chloroplatinic acid. The vessel was closed and heated to 100° for 3 hr. The products were found to be methyltrichlorosilane (135.5 g., 0.91 mole), butylmethyldichlorosilane, 53 g., 0.31 mole, b.p. 57° at 29 mm., $n^{25}{}_D$ 1.4340, and 3-chlorobutylmethyldichlorosilane, 124 g., 0.60 mole, 33% yield, b.p. 96° at 30 mm., $n^{25}{}_D$ 1.4559, $d^{25}{}_4$ 1.1572, R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: Si, 13.7; neut. equiv., 102.8. Found: Si, 13.8; neut. equiv., 104.1, 103.3.

Part of the 3-chlorobutylmethyldichlorosilane obtained in the first experiment above was converted to 3-chlorobutyltrimethylsilane in 59% yield with excess methylmagnesium bromide. The sample had: b.p. 69° at 28 mm., $n^{25}{}_D$ 1.4289, $d^{25}{}_4$ 0.8654, R_D 0.2987, calcd. R_D 0.2972.

Part of the product from the second experiment was treated with hot saturated potassium hydroxide to form methylcyclopropane identified by infrared absorption spectrum.

These data all indicate that both 3-chlorobutene-1 and 4-chlorobutene-2 form the same adduct, *i.e.*, 3-chlorobutylmethyldichlorosilane. The chlorobutyltrimethylsilane prepared from the adducts of either reagent also had identical infrared spectra and identical retention times in vapor chromatograms.

3,4-Dichlorobutene-1 (105 g., 0.84 mole) and 0.08 ml. of 0.1 *M* chloroplatinic acid solution in isopropyl alcohol were heated to 120° and methyldichlorosilane (106 g., 0.92 mole) was added dropwise.

The liquid products were distilled to give: methyltrichlorosilane (67 g., 0.45 mole); 3,4-dichlorobutene-1 (28 g., 0.22 mole); butylmethyldichlorosilane (5 g., 0.03 mole); 1,4-dichlorobutene-2 (11.5 g., 0.09 mole); 3-chlorobutylmethyldichlorosilane (6.5 g., 0.03 mole); and 3,4-dichlorobutylmethyldichlorosilane (80 g., 0.33 mole, 59% yield), b.p. 131° at 30 mm., $n^{25}{}_D$ 1.4805, $d^{25}{}_4$ 1.2902, R_D 0.2204, calcd. R_D 0.2204.

Anal. Calcd. for $Cl_2CH_3SiC_4H_7Cl_2$: Si, 11.7; neut. equiv., 120.0. Found: Si, 12.1; neut. equiv., 121.5.

A portion of this product was methylated with methylmagnesium bromide to give 3,4-dichlorobutyltrimethylsilane in 63% yield, b.p. 101° at 31 mm., $n^{25}{}_D$ 1.4530, $d^{25}{}_4$ 1.026, R_D 0.2696, calcd. R_D 0.2701.

Anal. Calcd. for $C_7H_{16}Cl_2Si$: Si, 14.1; Cl, 35.6. Found: Si, 14.1; Cl, 35.4, 35.9.

The infrared spectra of these products is consistent with the assigned 3,4-dichlorobutyl structure which seems like the only likely one consistent with the properties and origin of the compounds.

1,4-Dichlorobutene-2 (876 g., 7 moles), methyldichlorosilane (1310 cc., 12.7 moles) containing 0.35 ml. of 0.2 *M* chloroplatinic acid were mixed in a stainless steel pressure vessel. The olefin was pumped into the chlorosilane maintained near 100° for several hours. Distillation of the products resulted in the following analysis: methyldichlorosilane (149 g., 10.2% of that charged); methyltrichlorosilane (883 g., 5.9 moles); 3,4-dichlorobutene-2 (68.7 g., 0.55 mole); butylmethyldichlorosilane (66.7 g., 0.39 mole); 1,4-dichlorobutene-2 (145 g., 1.16 moles); 3-chlorobutylmethyldichlorosilane (123 g., 0.60 mole, 8.6% yield); and 4-chlorobutylmethyldichlorosilane (697 g., 47.2 yield); b.p. 109° at 30 mm., $n^{25}{}_D$ 1.4608, $d^{25}{}_4$ 1.171, R_D 0.2343, calcd. R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: Si, 13.7; neut. equiv., 102.8. Found: Si, 14.3; neut. equiv., 102.7, 104.0.

The next fraction was identified as 3,4-dichlorobutylmethyldichlorosilane (96 g., 0.4 mole, 5.7% yield), b.p. 130° at 30 mm., $n^{25}{}_D$ 1.4799, $d^{25}{}_4$ 1.1287, R_D 0.2202, calcd. R_D 0.2204.

Anal. Calcd. for $Cl_2CH_3C_4H_7Cl_2$: Si, 11.7; neut. equiv., 120.0. Found: Si, 11.9, 120.0; neut. equiv., 121.

A portion of this compound was methylated with excess methylmagnesium bromide in ether to form 4-chlorobutyltrimethylsilane in 76% yield, b.p. 79° at 31 mm., $n^{25}{}_D$ 1.4314, $d^{25}{}_4$ 0.8715, R_D 0.2972, calcd. R_D 0.2972.

Anal. Calcd. for $C_7H_{17}ClSi$: Si, 17.1; Cl, 21.5. Found: Si, 17.2; Cl, 22.1.

These compounds have been assigned the structure of 4-chlorobutyl derivatives in view of their origin because they clearly are not 3-chlorobutylsilanes whose structures are thought to be quite certain. 2-Chloroalkylsilanes are so easily hydrolyzed as to be titratable.[12] 1-Chlorobutylsilanes cannot rigorously be said to be impossible, but they do seem extremely unlikely. The infrared spectra of the compounds are consistent with those expected of 4-chlorobutylsilanes.

A series of experiments were carried out in sealed Pyrex tubes with analyses accomplished by vapor phase chromatography. Data gathered in this way are compiled in Table I. These experiments all used 10^{-6} mole of chloroplatinic acid per mole of olefin and were heated to 135° overnight. The analyses in Table I are considered as approximations only. They are shown as area per cent as taken from the chromatograms, but area per cent is not synonymous with molar per cent in these mixtures.

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(12) L. H. Sommer and F. C. Whitmore, *J. Am. Chem Soc.*, **68**, 485 (1946).

Base-Catalyzed Additions of Trichlorosilane to Hydrocarbon Olefins

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Received November 16, 1961

Tertiary amines and tertiary phosphines catalyze the addition of trichlorosilane to hydrocarbon olefins in the presence of a nitrile solvent. Without solvent, or in less polar solvents such as benzene, little or no addition occurs. Trichlorosilane adds to terminal olefins using base–nitrile catalysts to give the same adducts obtained with platinum or peroxide. With nonterminal olefins such as pentene-2, branched chain alkyltrichlorosilanes similar to peroxide additions are obtained, in contrast to platinum-catalyzed additions which give straight chained adducts. Characterization of the chlorosilanes prepared by addition of trichlorosilane to hexyne-1 and phenylacetylene show that with the base–nitrile solvent system, trichlorosilane adds predominantly *cis* to give the corresponding *trans* adducts.

Preparation of organosilicon compounds by the peroxide[1b] or platinum[2,3] catalyzed addition of silicon-hydrogen bonds to unsaturated hydrocarbons is

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(1a) Present address: Norton Co., Worcester 6, Mass.

(1b) C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947); L. H. Sommer, F. W. Pietrusza, and F. A. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947); J. L. Speier, R. Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

(2) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).