[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

Stereochemistry and Mechanism of Silane Addition to Olefins. I. Addition of Trichlorosilane to 1-Methylcyclohexene Under Free Radical and Thermal Conditions[1]

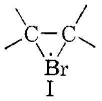
BY TERRY G. SELIN[2] AND ROBERT WEST

RECEIVED OCTOBER 19, 1961

The addition of trichlorosilane to 1-methylcyclohexene initiated with peroxides or ultraviolet light proceeds stereoselectively yielding principally *cis*-1-methyl-2-(trichlorosilyl)-cyclohexane. Thermal additions with and without free radical inhibitors were less selective and yielded some (cyclohexylmethyl)-trichlorosilane in addition to *cis*- and *trans*-1-methyl-2-(trichlorosilyl)-cyclohexane. Based on the observed stereochemistry, mechanisms are proposed for the various reactions.

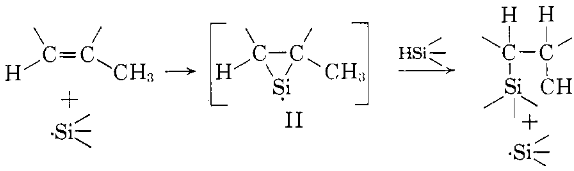
Recently the stereochemistry of trichlorosilane addition to acetylenes was studied by Benkeser and Hickner[3] for both peroxide-initiated and platinum-catalyzed additions. The resolution and characterization of the various *cis*- and *trans*-methylsilylcyclohexanes[4] have now made it possible to extend stereochemical studies to the addition of trichlorosilane to the olefin 1-methylcyclohexene. In these experiments trichlorosilane was allowed to react with 1-methylcyclohexene usually in the presence of a catalyst or a free radical initiator, and the resulting alkyltrichlorosilanes were reduced with lithium aluminum hydride to the methylsilylcyclohexanes. These alkylsilanes were then resolved and analyzed by vapor phase chromatography. Preparative vapor phase chromatography provided samples of the products for final characterization by comparison with known isomers.

Free Radical Additions.—Previously it has been shown that the free radical addition of hydrogen bromide to 1-methylcyclohexene proceeds with *trans* addition resulting in *cis*-1-bromo-2-methylcyclohexane.[5] This stereospecific *trans* addition is explained by assuming an intermediate (I) in which the bromine atom is centrally located between the ethylenic carbon atoms similar to the bromonium intermediates involved in ionic additions of bromine to olefins.[6] The second step would then involve abstraction of a hydrogen atom from hydrogen bromide from the opposite side of the bromine bridge.

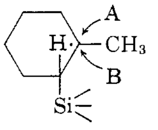


I

The addition of trichlorosilane to 1-methylcyclohexene in the presence of acetyl peroxide proceeded in quantitative yield. The product after reduction with lithium aluminum hydride was analyzed by vapor phase chromatography and found to consist of 15% *trans*-1-methyl-2-silylcyclohexane and 85% *cis*-1-methyl-2-silylcyclohexane. Since one might expect the *trans* isomer to predominate on purely thermodynamical grounds,[7] these results indicate that the mechanism involves a preferred *trans* stereochemical course as observed in hydrogen bromide additions. The preponderant formation of the *cis* isomer could be rationalized in terms of an analogous cyclic intermediate (II) followed by addition of silane hydrogen from the opposite side of the bridge.



However, unlike the additions of hydrogen bromide to 1-methylcyclohexene, a relatively large amount of the *trans* isomer resulting from *cis* addition was also obtained. To explain the presence of this isomer it is necessary to suppose the reaction can also proceed to a lesser degree through an open free radical intermediate such as III. The incoming trichlorosilyl group would be expected to assume the less hindered equatorial position making paths A and B equally likely for the chain propagation step. Path A would result in *cis* isomer, while path B would yield the observed *trans* isomer. The intermediate III would allow the bulky trichlorosilyl group to assume an equatorial configuration rather than one above or below the plane of the ring as in II. Since intermediate III would result in both *cis* and *trans* products, somewhat less than the observed 85% *cis*-1-methyl-2-(trichlorosilyl)-cyclohexane would be due to reaction by means of the cyclic intermediate II.



III

However, an alternate mechanistic interpretation is possible in which the cyclic intermediate II need not participate at all. In the chain propagation step hydrogen has to be abstracted from trichlorosilane. A possible transition state for this step is represented by IIIa in which the bulky trichlorosilyl group assumes an equatorial position

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] General Electric Co., Silicone Products Department, Waterford, N. Y.

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

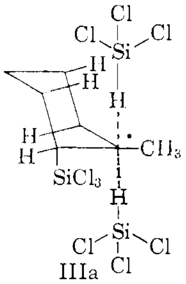
[4] T. G. Selin and R. West, *ibid.*, **84**, 1856 (1962).

[5] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

[6] I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

[7] The more thermodynamically stable isomer should be the one containing fewer skew interactions in the molecule. This stability could not be demonstrated experimentally for the methylsilylcyclohexanes for lack of a means for *cis–trans* equilibration. See reference 14 in preceding paper.[4]

and the free radical carbon becomes trigonal in structure.[8] Because of the size of the incoming trichlorosilane molecule, interactions with the axial 1,3-ring hydrogens may hinder approach from the top. The more facile approach of trichlorosilane from the bottom would give the observed higher yields of the *cis* isomer. In general, the observed ratio of *cis* to *trans* isomers would be a measure of the degree with which each approach is favored.



IIIa

Stereoselectivity has also been observed in the free radical addition of trichlorosilane to acetylenes.[3] Although a direct comparison between additions to olefins and acetylenes cannot be made, it is interesting that both proceed selectively, but not entirely, by *trans* addition. The free radical addition of trichlorosilane to 1-methylcyclohexene is somewhat more stereoselective (*cis–trans* ratios of 6:1) than additions to acetylenes (*cis–trans* ratios of 3:1).[9]

Similar stereoselective results were obtained when the reaction was initiated with ultraviolet light. The products from ultraviolet light-induced reactions consisted of 11% *trans*-1-methyl-2-(trichlorosilyl)-cyclohexane and 89% *cis*-1-methyl-2-(trichlorosilyl)-cyclohexane. However, the total yield of adducts was much less than for comparative reactions utilizing peroxides (*cf.* Table I).

TABLE I

YIELDS AND PRODUCTS OBTAINED FROM TRICHLOROSILANE ADDITIONS TO 1-METHYLCYCLOHEXENE

Conditions	Reaction time, hr.	Yield, %	Product composition, % 1,2-*cis*	1,2-*trans*	Terminal adduct
Acetyl peroxide	9	100	85	15	..
Ultraviolet light	44	49	89	11	..
Chloroplatinic acid	8	78	..	..	98[a]
Thermal[b]	24	100	58	23	19
Thermal, chloranil	36	100	57	25	18
Thermal, Fe and $FeCl_3$	36	93	44	35	21

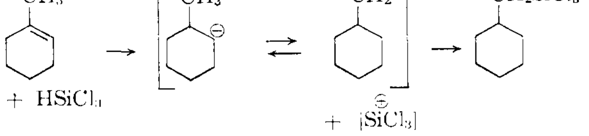
[a] In addition to the product listed, trace amounts of various methylsilylcyclohexane isomers were observed. [b] Thermal additions were carried out in sealed Pyrex tubes at a temperature of 300°.

Thermal Addition.—It is generally accepted[10] that thermal addition of silanes to olefins takes place through free radical processes. Such a view is consistent with the low energy of the silicon-hydrogen bond and is supported by the report that thermal cross-linking of vinyl siloxanes by disilylbenzene is inhibited in the presence of chloranil.[11] However, kinetic studies by Barry[12] indicate that these reactions are bimolecular suggesting an ionic mechanism as opposed to a radical chain process. The stereochemistry of the thermal addition of trichlorosilane to 1-methylcyclohexene was determined in an effort to shed further light on the mechanism.

Trichlorosilane added quantitatively to 1-methylcyclohexene at 300° (sealed tube) in the absence of added catalyst. After reduction, gas chromatographic and infrared analysis of the silane mixture indicated that three isomers were present. In addition to 23% *trans*-1-methyl-2-silylcyclohexane and 58% *cis*-1-methyl-2-silylcyclohexane, 19% (cyclohexylmethyl)-silane was also observed. This rearranged adduct is the principal product obtained from addition of trichlorosilane to 1-methylcyclohexene in the presence of chloroplatinic acid[13] (Table I). The presence of this terminal adduct as well as the higher proportion of *trans* isomer distinguish the thermal addition products from those of peroxide and light-induced reactions.

The increased amount of *trans* product could be rationalized in terms of a free radical mechanism. The possible bridged intermediate II might be thermally unstable, so that a greater proportion of the reaction would proceed through the open intermediate III at high temperature, leading to increased amounts of *trans* isomer. Alternatively, if an open intermediate such as IIIa were involved exclusively, the approach of trichlorosilane might be less selective at higher temperature. However, the presence of (cyclohexylmethyl)-silane is quite difficult to explain by a free-radical mechanism. This product does not appear to result from rearrangement followed by addition, because it was found that 1-methylcyclohexene underwent no isomerization to methylenecyclohexane when heated to 280° for comparable lengths of time.

It therefore seems probable that both free-radical and ionic mechanisms are operating simultaneously in thermal addition. If ionic addition of trichlorosilane to olefins exhibits the same stereochemistry as observed for acetylenes,[3] an increased amount of *cis* addition to give *trans* product would result if ionic catalysis took place. In fact, an ionic reaction involving carbanion intermediates would provide a pathway both to increased amounts of *trans* isomer and to terminal adduct.



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(8) There is some question as to the structure of carbon free radicals. A planar structure is assumed for simplicity.

(9) R. A. Benkeser, M. L. Burrous, L. E. Nelson and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385(1962).

(10) (a) C. L. Agre and W. Hilling, *ibid.*, **74**, 3895 (1952); (b) G. Fritz, *Z. Naturforsch.*, **7B**, 507 (1952); (c) R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 962 (1956); (d) M. G. Voronkov, N. G. Ramanova and L. G. Smirnova, *Chem. Listy*, **52**, 640 (1958); *C. A.*, **52**, 13615 (1958); (e) D. G. White and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 3897 (1954).

(11) C. L. Segal and J. B. Rust, "Abstracts of Papers of 137th Meeting, American Chemical Society," 1960, p. 37M.

(12) A. J. Barry, "Abstracts of Papers of 137th Meeting, American Chemical Society." 1960, p. 19M.

(13) The stereochemistry and mechanism of additions catalyzed by chloroplatinic acid will be the subject of the third paper in this series; T. G. Selin and R. West, *J. Am. Chem. Soc.*, **84**, 1863 (1962).

A similar mechanism has been proposed previously for platinum-catalyzed silane additions.[14,15]

In an attempt to check the duality of mechanism proposed for the thermal reactions, several thermal additions were carried out in which free radical inhibitors were added to the reaction mixture. This approach served a twofold purpose since it not only illustrated the presence of a free radical path but also indicated that the *trans* isomer was arising in part by a non-radical mechanism. Chloranil did not change the product composition, perhaps because it reacted with the trichlorosilane at the high reaction temperature. However, the use of iron and ferric chloride[16] as a free radical inhibitor did alter the isomeric composition of the product. From Table I it can be seen that increased amounts of both *trans*-1-methyl-2-silylcyclohexane and (cyclohexylmethyl)-silane were obtained at the expense of the *cis* isomer. This suggests that the free radical path is partially inhibited, allowing more efficient ionic competition for the olefin.

Other Catalysts.—Several other catalysts were used for the addition of trichlorosilane to 1-methylcyclohexene without success. Thus, while pyridine has been used successfully with simple olefins,[17] no reaction was observed between trichlorosilane and 1-methylcyclohexene at temperatures up to 180° in the presence of this amine. Similarly, the use of iron pentacarbonyl was fruitless at temperatures up to 120°. Triethoxysilane would not add to 1-methylcyclohexene under mild conditions in the presence of peroxides or chloroplatinic acid.

Experimental

All vapor phase chromatography was carried out in a 25 ft. × 0.25" copper column packed with 30% DC-550 Silicone oil on 30 mesh firebrick at 100° with a flow rate of 60 ml. of helium per minute. Pure samples of each of the silane products were obtained by preparative gas chromatography. These purified products were then characterized by comparison of their physical properties with those of authentic samples.[4]

Starting Materials.—The 1-methylcyclohexene was prepared according to the method of Bartlett and Rosenwald[18] in 51% yield. Gas chromatography showed that the product was contaminated by less than 1% of isomeric impurities. Trichlorosilane was purchased from Union Carbide Co., and redistilled prior to use. Triethoxysilane was prepared according to the method of Havill, Joffe and Post[19] in 46% yield and cyclohexylmethyl bromide was prepared from cyclohexylcarbinol and phosphorus tribromide in 53% yield. The properties of all of these compounds agreed with those reported in the literature.[5,19,20]

Preparation of Standards.—Both *cis*- and *trans*-1-methyl-2-silylcyclohexane were prepared by hydrogenation of *o*-tolyltriethoxysilane followed by lithium aluminum hydride reduction.[4]

Cyclohexylmethylsilane.—A Grignard reagent was prepared in ether from 18 g. (0.10 mole) of cyclohexylmethyl bromide. This reagent was added slowly with stirring to 51 g. (0.3 mole) of silicon tetrachloride dissolved in 300 ml. of ether. An exothermic reaction took place immediately. Upon completion of the addition the mixture was heated at reflux for an additional 18 hours. Magnesium salts were removed by filtration under a nitrogen atmosphere. The filtrate was fractionally distilled to give 15.2 g. (66%) of (cyclohexylmethyl)-trichlorosilane boiling at 68–69° at 1.5 mm.

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 46.4, 46.0.

The trichlorosilane was reduced by dropwise addition to an ethereal solution of lithium aluminum hydride. The excess lithium aluminum hydride was destroyed by adding the reaction mixture to a mixture of ether and crushed ice. The ether phase was separated, dried briefly over anhydrous sodium sulfate, and distilled. The desired (cyclohexylmethyl)silane was obtained in 56% yield with b.p. 144–145° and $n^{25}D$ 1.4540. Gas chromatography showed a single component with retention time 71.48 min.

Anal. Calcd. for $C_7H_{16}Si$: C, 65.53; H, 12.57. Found: C, 65.52, 65.33; H, 12.46, 12.49.

Addition Reactions. Peroxide-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene.—A 125-ml. three-necked flask was fitted with a reflux condenser, a pressure equalizing dropping funnel, and a thermometer which extended to the bottom of the flask. The fittings were wired in place and a nitrogen source was connected to the reflux condenser along with a mercury filled U-tube. By means of the U-tube, the system could be placed under an extra nitrogen pressure of 30 cm. After sweeping the system with nitrogen, 74 g. (0.55 mole) of trichlorosilane and 9.6 g. (0.1 mole) of 1-methylcyclohexene were charged to the flask. In the dropping funnel was placed 2 g. of acetyl peroxide (as a 25% solution in dimethyl phthalate) and 9.6 g. (0.1 mole) of 1-methylcyclohexene. Under an extra pressure of nitrogen (30 cm.), the trichlorosilane mixture was brought to reflux (45° pot temperature) while the contents of the dropping funnel were simultaneously added. The addition of the peroxide solution required 1 hour, and after an additional 8 hours the refluxing solution had reached a maximum temperature of 60°. The excess trichlorosilane was removed from the yellow solution by distillation and the adduct was obtained by fractional distillation through a glass helices packed column. A quantitative yield (47 g.) of 1-methyl-2-(trichlorosilyl)-cyclohexane was collected boiling at 96–97° at 11 mm.

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 46.7, 46.6.

The trichlorosilane was reduced with lithium aluminum hydride as described above for (cyclohexylmethyl)-trichlorosilane. There was obtained an 80% yield of a mixture of silanes boiling at 138–140°. Gas chromatographic purification and subsequent characterization[4] showed the mixture to consist of 85% *cis*-1-methyl-2-silylcyclohexane and 15% *trans*-1-methyl-2-silylcyclohexane.

Photoaddition of Trichlorosilane to 1-Methylcyclohexene.—Using the apparatus described above, 56 g. (0.41 mole) of trichlorosilane and 19.2 g. (0.2 mole) of 1-methylcyclohexene were heated to reflux under an extra nitrogen pressure of 30 cm. The flask was irradiated by means of an ultraviolet lamp for a period of 44 hours during which time the pot temperature rose from 49 to 59°. Distillation of the mixture gave 22.5 g. (49%) of 1-methyl-2-(trichlorosilyl)-cyclohexane boiling at 105–109° at 15 mm.

Lithium aluminum hydride reduction of the trichlorosilane yielded a mixture of silanes consisting of 89% *cis*-1-methyl-2-silylcyclohexane and 11% *trans*-1-methyl-2-silylcyclohexane. Identification was again made by comparison of retention times, infrared absorption spectra and refractive indices with those from characterized samples.

Thermal Addition of Trichlorosilane to 1-Methylcyclohexene.—In a Pyrex tube were sealed 19.2 g. (0.2 mole) of 1-methylcyclohexene and 27 g. (0.2 mole) of trichlorosilane. The tube and contents were placed in a hydrogenation bomb under helium pressure and agitated at 300° for 24 hours. After cooling and removal from the bomb, the tube was opened and the contents distilled to yield 46 g. (100%) of a mixture of alkyltrichlorosilanes with boiling point 93–96° at 10 mm.

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 46.4, 46.1.

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(14) J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **80**, 404 (1958).

(15) J. L. Speier, J. A. Webster and G. H. Barnes, *ibid.*, **79**, 974 (1957).

(16) J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

(17) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 322 (1956)

(18) P. D. Bartlett and R. H. Rosenwald, *J. Am. Chem. Soc.*, **56**, 1990 (1934).

(19) M. E. Havill, I. Joffe and H. W. Post, *J. Org. Chem.*, **13**, 280 (1948).

(20) G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 2385 (1926).

Lithium aluminum hydride reduction in the usual manner followed by fractional distillation of the resulting ether–silane mixture gave a 72% yield of silanes boiling at 141–143°. This silane mixture was analyzed by gas chromatography with two components being isolated for further characterization. The first component ($n^{25}\text{D}$ 1.4508) comprised 23% of the mixture and had an infrared spectrum and retention time corresponding to *trans*-1-methyl-2-silylcyclohexane. The second component ($n^{25}\text{D}$ 1.4580) was shown to be a mixture of (cyclohexylmethyl)-silane and *cis*-1-methyl-2-silylcyclohexane by means of its infrared spectrum. The infrared spectra and refractive indices of known mixtures of the pure isomers allowed accurate estimates of such silane mixtures. By comparison with these known samples, the product obtained by addition was shown to contain about 25% (cyclohexylmethyl)-silane. The over-all composition from thermal addition was 23% *trans*-1-methyl-2-silylcyclohexane, 19% (cyclohexylmethyl)-silane and 58% *cis*-1-methyl-2-silylcyclohexane. A trace of material corresponding to the *trans*-1,4- or *cis*-1,3-isomers was also observed.

Thermal Addition of Trichlorosilane to 1-Methylcyclohexene in the Presence of Iron and Iron Chloride.—Using a sealed Pyrex tube as above, 12 g. (0.125 mole) of 1-methylcyclohexene and 25 g. (0.18 mole) of trichlorosilane were allowed to react in the presence of 1 g. of steel wool and 0.1 g. of ferric chloride. Reaction at 300° for 36 hours yielded 27 g. (93%) of an alkyltrichlorosilane adduct. Reduction and analysis as above provided a mixture consisting of 35% *trans*-1-methyl-2-silylcyclohexane, 21% (cyclohexylmethyl)-silane and 44% *cis*-1-methyl-2-silylcyclohexane.

Thermal Addition of Trichlorosilane to 1-Methylcyclohexene in the Presence of Chloranil.—The above reaction was rerun in detail in the presence of 0.4 g. of chloranil as a free radical inhibitor. A theoretical yield of alkyltrichlorosilane was obtained which upon reduction with lithium aluminum hydride provided a mixture of silanes. The silane mixture showed the composition: 25% *trans*-1-methyl-2-silylcyclohexane, 18% (cyclohexylmethyl)-silane and 57% *cis*-1-methyl-2-silylcyclohexane.

Thermal Isomerization of 1-Methylcyclohexene.—In a Pyrex tube was sealed 9.6 g. (0.1 mole) of 1-methylcyclohexene. According to the above procedure, the olefin was agitated at 280° for a period of 36 hours. Upon gas chromatographic analysis, it was found that essentially no change had occurred.

Pyridine-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene (Attempted).—A Pyrex tube was charged with 19.2 g. (0.2 mole) of 1-methylcyclohexene, 30 g. (0.22 mole) of trichlorosilane and 0.3 g. (2 mole%) of pyridine. Upon the addition of the pyridine, a white precipitate was formed, probably a pyridine–trichlorosilane complex.[21] The tube was sealed, placed in a bomb, and agitated at 180° for 22 hours. Only unreacted trichlorosilane and 1-methylcyclohexene were obtained upon distillation of the reaction mixture.

Iron Carbonyl-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene (Attempted).—The reaction of 1-methylcyclohexene with an excess of trichlorosilane using iron pentacarbonyl as a catalyst did not take place. Upon mixing the reactants, the solution turned dark brown followed by the formation of a brown fluffy precipitate. After heating as usual at 50° or in a sealed tube at 120°, distillation gave only unreacted trichlorosilane and 1-methylcyclohexene.

Addition of Triethoxysilane to 1-Methylcyclohexene (Attempted).—In a 100-ml. three-necked flask was placed 33 g. (0.2 mole) of triethoxysilane and 0.05 g. (1×10^{-4} g. atom Pt) of chloroplatinic acid in 1 ml. of isopropyl alcohol. By means of a dropping funnel, 14.2 g. (0.15 mole) of 1-methylcyclohexene was added slowly while simultaneously bringing the silane to reflux. After approximately 10 minutes, the addition of olefin was complete and the mixture was heated at reflux for 120 hours. Fractional distillation of the reaction mixture resulted only in the isolation of unreacted starting materials.

The same reaction was repeated using acetyl peroxide as an initiator according to the methods described above. After 16 hours at reflux, the reaction mixture was distilled and shown to consist of only starting materials.

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[21] A. B. Burg, *J. Am. Chem. Soc.*, **76**, 2674 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

Stereochemistry and Mechanism of Silane Additions to Olefins. II. Chloroplatinic Acid-catalyzed Addition of Trichlorosilane to Alkylcyclohexenes[1]

BY TERRY G. SELIN[2] AND ROBERT WEST

RECEIVED OCTOBER 19, 1961

The addition of trichlorosilane to a number of alkylcyclohexenes was examined using chloroplatinic acid as a catalyst. Terminal adducts were obtained exclusively with 4-methylcyclohexene, 1-methylcyclohexene and 1-ethylcyclohexene. The addition to 4-methylcyclohexene proceeded through rearrangement to 1-methylcyclohexene. Both 1-*n*-propylcyclohexene and 1-*n*-octylcyclohexene were unreactive under the same conditions. A product resulting from addition to the ring was obtained from 4,4-dimethylcyclohexene. The reaction of trichlorosilane and 1-methyl-d_3-cyclohexene yielded (cyclohexylmethyl-d_3)-trichlorosilane and *trans*-1-methyl-d_3-2-(trichlorosilyl)-cyclohexane indicating that the addition proceeded with complete retention of deuterium and stereospecific *cis* addition of trichlorosilane to the ring. Mechanisms are proposed to account for the above observations.

Rearrangements occur when silicon hydrides are added to non-terminal olefins in the presence of platinum catalysts. These rearrangements were first recognized by Speier, Webster and Barnes[3] who obtained *n*-pentyldichloromethylsilane from the platinum-catalyzed addition of methyldichlorosilane to pentene-2. The rearrangement–addition reactions have been reasonably explained in terms of a carbanion intermediate arising from catalyzed attack on the double bond by hydride ion.[4,5] The resulting carbanion is then thought to rearrange by tautomerization to the more stable primary (terminal) carbanion. The next step in the mechanism is visualized as nucleophilic attack of the carbanion upon a silane which in the presence of another molecule of olefin produces the product and generates another carbanion. If formation of a complex involving platinum is required only to initiate the reaction, the process may be regarded as an ionic chain reaction.[5]

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] General Electric Co., Silicone Products Department, Waterford, N. Y.

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

[4] J. C. Saam and J. L. Speier, *ibid.*, **80**, 404 (1958).

[5] J. C. Saam and J. Speier, *ibid.*, **83**, 1351 (1961).