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}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}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.

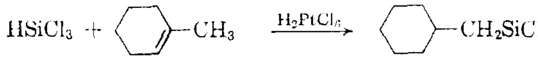
[2] General Electric Co., Silicone Products Department, Waterford, N. Y.

[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).

The addition of trichlorosilane to 1-methylcyclohexene takes place readily in the presence of chloroplatinic acid. Lithium aluminum hydride reduction of the adduct gave nearly pure (cyclohexylmethyl)-silane, along with traces of the isomeric 1,2- and 1,3-methylsilylcyclohexanes.[6] In accordance with earlier work[4] it was shown that this terminal adduct did not arise by rearrangement of 1-methyl-2-(trichlorosilyl)-cyclohexane as the latter was stable under the conditions of the reaction. Similarly, the olefin was stable toward the catalyst and chlorosilanes in the absence of silanic hydrogen. In addition, any tautomerization occurring in a carbanion intermediate is intramolecular since the use of *n*-hexane as a solvent did not yield any *n*-hexylsilanes.



When the addition of trichlorosilane to 1-methylcyclohexene was interrupted before completion of the reaction, the recovered olefin contained 5% 4-methylcyclohexene. The presence of this isomer suggested that addition to 4-methylcyclohexene might also produce the terminal adduct. Indeed, the addition to 4-methylcyclohexene produced (cyclohexylmethyl)-trichlorosilane in 73% yield. As in the addition to 1-methylcyclohexene, only trace amounts of other isomeric adducts were present. However, the addition to 4-methylcyclohexene was much slower than addition to 1-methylcyclohexene. This difference in rate was found to stem from an initial induction period in the case of 4-methylcyclohexene. After a reaction time of eight hours, only small amounts of adduct had formed, but half of the 4-methylcyclohexene had been isomerized to 1-methylcyclohexene. After sixteen hours, addition had begun to occur and the unreacted olefin mixture had the same composition as that observed in incomplete additions to 1-methylcyclohexene. Similar isomerization did not take place in the presence of chloroplatinic acid and silicon tetrachloride but rather required the presence of the silicon hydride. In addition, a mixture of 1,3- and 1,4-methyl-(trichlorosilyl)-cyclohexanes was not isomerized in the presence of trichlorosilane and chloroplatinic acid.

The reluctance of addition to occur in the ring provided a means for determining the extent of this "terminal migration effect." By increasing the length of the alkyl chain in a series of 1-alkylcyclohexenes, it was found that terminal addition did not take place when the double bond was further removed than two carbon atoms from the end of the chain (Table I). The infrared spectra of the unreacted olefins in each instance was virtually identical with the starting material indicating that little isomerization (less than 5%) occurred during reaction.

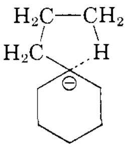
TABLE I

ADDITION OF TRICHLOROSILANE TO 1-ALKYLCYCLOHEXENES IN THE PRESENCE OF CHLOROPLATINIC ACID

Alkyl group	Time, hr.	Yield, %	Composition of adduct, % Terminal	Other
Methyl	20	78	98	2
Ethyl	96	95	95	5
n-Propyl	96	*ca.* 2	..	..
n-Octyl	70	*ca.* 2	..	..

When terminal addition did not take place, the olefin was essentially unreactive. This is interesting in view of the fact that cyclohexene added trichlorosilane in 88% yield after 42 hours under the same conditions.

It is difficult to rationalize all of the above observations by any simple mechanism. However, the fact that trichlorosilane does not add to 1-*n*-propylcyclohexene seems to exclude a cyclic intermediate involving a five- or six-membered ring as in I or II.[5] The rearrangement might result from an unlimited series of 1,2-proton shifts, and indeed this mechanism cannot be excluded. However, if this were the mechanism one might expect to observe intermediate olefins. It may be significant that the olefin methylenecyclohexane, which would lead directly to the terminal adduct, is not observed. The unreactivity of 1-*n*-propylcyclohexene also provides an argument against an unlimited series of 1,2-proton shifts. A gradual decrease of reactivity as the chain length increases might be expected on the basis of this mechanism, but the striking difference in reactivity between 1-ethylcyclohexene and 1-*n*-propylcyclohexene seems to require further explanation.



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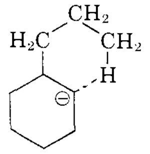
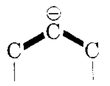
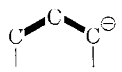


II

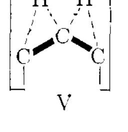
The above observations can be rationalized by considering a three-carbon atom reaction site which might exist on the surface of the catalyst or in a catalyst–olefin–silane complex. After addition of hydride ion to form a carbanion, the reaction site is utilized by the carbon atom bearing the negative charge and any other two carbon atoms such that a consecutive three-carbon chain is involved as in III or IV. The catalyst then provides a route by which a proton can be transferred over a two-carbon bond distance either as two 1,2-proton shifts (V) or a single 1,3-proton shift (VI).



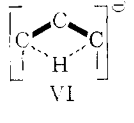
III



IV



V



VI

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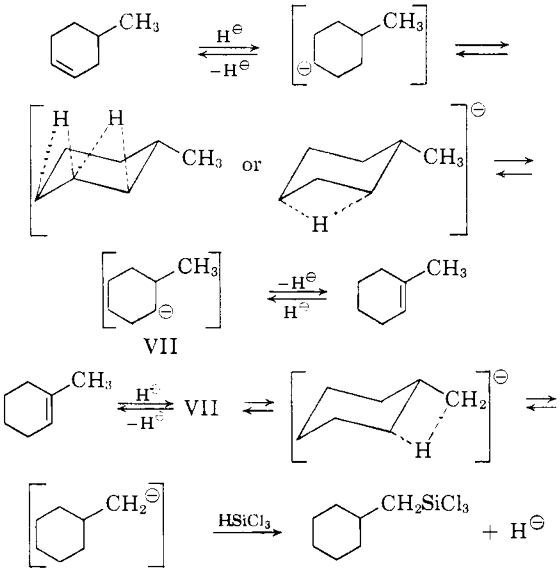
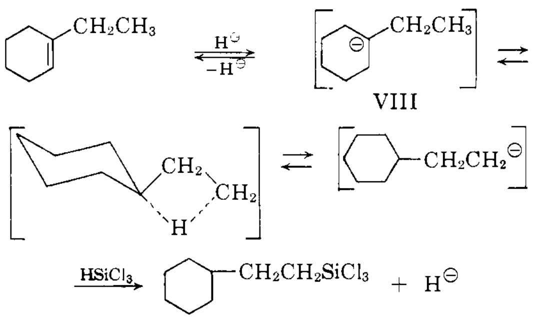
(6) Chloroplatinic acid-catalyzed additions of silanes to olefins appear to be markedly sensitive to the nature of the silane. Thus trichlorosilane adds to 1-methylcyclohexene in 80% yield in 8 hours. whereas the same reaction with methyldichlorosilane is only 56% complete after 48 hours.[5] This difference of rate in turn influences the product composition. Saam and Speier[5] report that the adducts of methyldichlorosilane with 1-methylcyclohexene consist of 84% (cyclohexylmethyl)-methyldichlorosilane and 16% 3-methylcyclohexylmethyldichlorosilane.

The fact that 4-methylcyclohexene yields 1-methylcyclohexene rather than terminal adduct directly suggests that only one such transfer is possible without reformation of olefin. Furthermore, there must be a preference for addition of hydride to 4-methylcyclohexene over 1-methylcyclohexene which prevents large amounts of terminal adduct from forming until nearly all of the 4-methylcyclohexene has been isomerized and a high concentration of 1-methylcyclohexene is present.

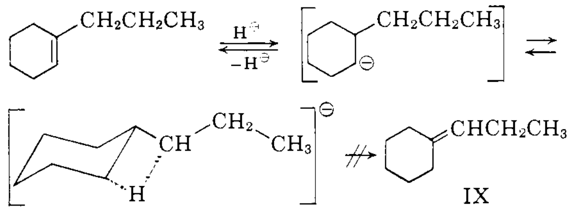
The addition of trichlorosilane to 4-methylcyclohexene and 1-methylcyclohexene can be written in terms of the following sequences.



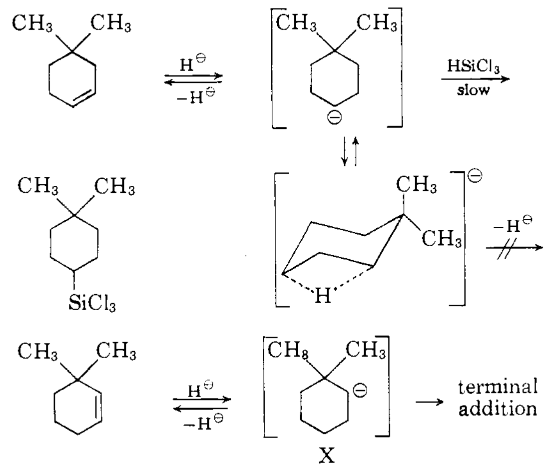
A similar scheme applies to the addition to 1-ethylcyclohexene. In order to include the terminal carbon atom in a three-carbon chain, it is necessary that the hydride ion add contrary to the polarization of the double bond (VIII). This is in agreement with the lower reactivity observed for 1-ethylcyclohexene compared to 1-methylcyclohexene.



As suggested in the above sequences, the carbanion intermediates must be capable either of producing a primary carbanion for the immediate reaction with silane or of reforming an olefin. The concentration of other isomeric cyclohexenes present during addition serves as an indication of the relative stability of each isomer under the conditions of the reaction. The evidence seems to indicate in the case of the 1-alkylcyclohexenes that if a primary carbanion cannot be formed in the alkyl chain, the more stable olefin is reformed. Thus, 1-*n*-propylcyclohexene does not meet the requirements for the formation of a system (such as IX) which would allow the formation of the primary carbanion.



Trichlorosilane was added to 4,4-dimethylcyclohexene in the presence of chloroplatinic acid to determine whether or not a quaternary carbon atom would prevent terminal addition. After a reaction time of 162 hours, an alkyltrichlorosilane was obtained in 39% yield. After reduction to the silane, gas chromatography showed the product to be a single isomer. This isomer was characterized as a product arising from addition to the ring by means of its infrared and proton magnetic resonance spectra. These results might suggest that the rearrangements proceed by two 1,2-proton shifts rather than a single 1,3-proton shift. However, the unreacted olefin was shown to be identical with the starting olefin and it is likely that the carbanion required for terminal addition (X) was never obtained.[7]



The observations described for the addition of trichlorosilane to 1-methylcyclohexene can also be rationalized by considering a catalyzed hydride addition and elimination sequence. It is only necessary to suppose that the methylenecyclohexane reacts so rapidly with trichlorosilane that it is not observed in the unreacted products. To test this hypothesis, trichlorosilane was allowed to react with 1-methyl-d_3-cyclohexene in the presence

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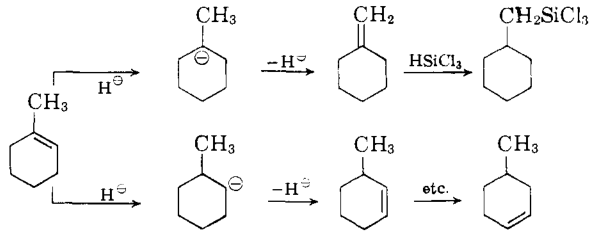
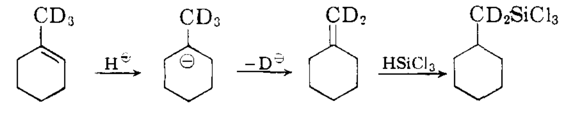
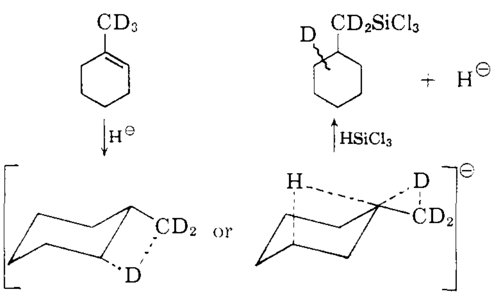
(7) No effort was made to determine which ring substituted adduct was formed in the addition to 4,4-dimethylcyclohexene. However, if the final step in the addition is nucleophilic attack of the carbanion upon the silane,[5] one might expect on steric grounds that the product is 4,4-dimethylcyclohexyltrichlorosilane. The two methyl groups would provide considerable steric complications in a nucleophilic attack of a carbanion located at the 2- or 3-position.



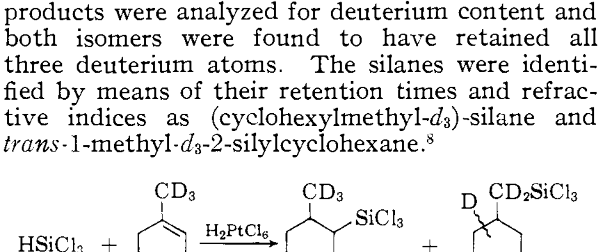
of chloroplatinic acid. A large excess of trichlorosilane was used so that if the reaction did involve an addition–elimination sequence, deuterium would be lost in the process. However, a single step



process would result in complete retention of deuterium.



The reaction was slow, providing only a 26% yield of adduct after forty-two hours. Gas chromatographic analysis of the silanes obtained by lithium aluminum hydride reduction indicated the presence of two isomers in approximately equal amounts. Samples of the pure isomers were obtained by preparative gas chromatography. These products were analyzed for deuterium content and both isomers were found to have retained all three deuterium atoms. The silanes were identified by means of their retention times and refractive indices as (cyclohexylmethyl-d_3)-silane and *trans*-1-methyl-d_3-2-silylcyclohexane.[8]



From these results a number of important conclusions can be drawn: (1) The rearrangement does not involve a simple hydride addition and elimination sequence but rather a single step intramolecular shift of hydrogen. (2) Deuterium substitution drastically decreases the rate of the addition reaction, allowing the slow addition to the ring to compete with the terminal addition process. The large observed kinetic isotope effect suggests that the rate-determining step occurs before or at the same time as the hydrogen shift. (3) Finally, ring addition of trichlorosilane to 1-methyl-d_3-cyclohexene proceeds in a stereospecific *cis* manner in the presence of chloroplatinic acid. This is consistent with the stereochemical findings of Benkeser and Hickner in trichlorosilane additions to acetylenes,[9] and indicates that the addition probably occurs through a specific olefin–catalyst[9] or olefin–catalyst–silane intermediate.

Experimental

Gas–liquid chromatography was carried out on a 25 ft. × 0.25″ copper column packed with 30% DC-550 silicone oil on 30-mesh firebrick at 100° and a flow rate of 60 ml. of helium per minute. In many instances pure samples of the silanes and unreacted olefins were obtained by preparative gas chromatography.[6]

In order to characterize the adduct from the reaction of trichlorosilane and 4,4-dimethylcyclohexene, the proton n.m.r. spectra of several standard compounds were recorded at 60 Mc. The samples employed were 20% solutions of silane in CCl_4 utilizing benzene as an internal standard. At medium low field[10] the proton resonance due to hydrogen bound to silicon was very prominent. In the spectrum of both silylcyclohexane and *cis*-1-methyl-2-silylcyclohexane this absorption appeared as a doublet, while in that of (cyclohexylmethyl)-silane the expected 1:2:1 triplet was observed.

Compounds were analyzed for deuterium content by oxidation in a stream of oxygen at 800° over platinized asbestos. The deuterium-containing water was collected and analyzed by means of a linear density gradient column. With this column, the deuterium content of water samples in the range of 10–30% D_2O could be determined with an accuracy of ±0.5%.

Starting Materials.—The 1-alkylcyclohexenes were prepared by the reaction of the appropriate Grignard reagent with cyclohexanone followed by iodine-catalyzed dehydration of the resulting alcohols.[11] The 4,4-dimethylcyclohexene was prepared by phosphoric acid cyclization of 4-pentenyldimethylcarbinol after the method of Hibbit and Linstead,[12] while the 4-methylcyclohexene was purchased from the Eastman Kodak Co. After purification by fractional distillation these products had physical constants agreeing with those reported in the literature.[11,13–16] They were also shown to be more than 99% pure by gas chromatography.

1-Methyl-d_3-cyclohexene was prepared from the Grignard reagent of methyl-d_3 bromide (Merck of Canada; 99.7% D) and cyclohexanone. Iodine-catalyzed dehydration of the resulting alcohol provided an 86% yield of 1-methyl-d_3-cyclohexene, b.p. 108–109.5°, $n^{25}\text{D}$ 1.4485. Gas chromatography indicated that the product was pure.

Anal. Calcd. for $C_7H_9D_3$: D, 6.1. Found: D, 6.0.

Trichlorosilane was obtained from Union Carbide Co. and redistilled before use.

Platinum-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene.—A mixture of 50 g. (0.37 mole) of trichlorosilane, 19.2 g. (0.2 mole) of 1-methylcyclohexene and 0.05 g. (1 × 10^{-4} g. atom of Pt) of chloroplatinic acid dissolved in 1 ml. of isopropyl alcohol was heated to reflux under an added pressure of nitrogen. After 8 hours, the temperature of the solution had risen from 49 to 65°. Additional heating did not cause further temperature increase so the mixture was worked up by distillation. An

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[8] T. G. Selin and R. West, *J. Am. Chem. Soc.*, **84**, 1856 (1962). The refractive indices were slightly greater than those of the corresponding non-deuterated compounds, as expected. Retention of three deuterium atoms by each isomer rules out the possibility that the reaction goes by means of a series of 1,2-shifts involving hydride transfer from a carbanion to an olefin. Such a mechanism would lead to retention of somewhat less than 3 atoms of deuterium in the terminal adduct and somewhat more than three atoms of deuterium in the ring adduct.

[9] R. A. Benkeser and R. A. Hickner *ibid.*, **80**, 5298 (1958).

[10] D. E. Webster and R. Okawara, *J. Phys. Chem.*, **64**, 701 (1960).

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

[12] D. C. Hibbit and R. P. Linstead, *J. Chem. Soc.*, 470 (1936).

[13] H. L. Goering, P. I. Abell and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

[14] O. Wallach, *Ann.*, **360**, 26 (1908).

[15] R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

[16] G. H. Elliott and R. P. Linstead, *J. Chem. Soc.*, 662 (1938).

alkyltrichlorosilane was obtained at 94–98° at 11 mm. in 78% yield (36.2 g.).

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 46.6, 46.8.

Reduction of the alkyltrichlorosilane with lithium aluminum hydride provided 14.5 g. (76% yield) of an alkylsilane. This product had a boiling point of 143–145° with $n^{25}D$ 1.4540 and was identified as (cyclohexylmethyl)-silane by comparing its physical properties with those of an authentic sample. Gas chromatography indicated the product was 98% pure with small amounts of isomeric methylsilylcyclohexanes as impurities.

Platinum-catalyzed Addition of Trichlorosilane to 4-Methylcyclohexene.—In a similar manner 19.2 g. (0.2 mole) of 4-methylcyclohexene was heated with 54 g. (0.4 mole) of trichlorosilane in the presence of 0.05 g. of chloroplatinic acid as catalyst. After 8 hours at reflux under an extra pressure of nitrogen, the reaction mixture was distilled yielding only unreacted olefins. Two components were isolated by preparative gas chromatography and shown by gas chromatography and infrared analyses to be 1:1 mixture of 4-methylcyclohexene, $n^{20}D$ 1.4420, and 1-methylcyclohexene, $n^{20}D$ 1.4500.

The reaction was repeated by the same procedure, but allowing 16 hours for reaction. Distillation yielded unreacted trichlorosilane and olefin and 2 g. (3%) of adduct distilling at 80–100° (11 mm.). Analysis of the recovered olefin indicated that more than 90% of the 4-methylcyclohexene had been isomerized to 1-methylcyclohexene.

A third experiment was allowed to react for 66 hours during which time the pot temperature slowly rose from 48° to 64°. Distillation afforded 33.5 g. (73%) of adduct boiling at 91–94° (8 mm.). Unreacted trichlorosilane and 7 g. of high boiling pot residue completed the material balance. Lithium aluminum hydride reduction of the alkyltrichlorosilane[4] followed by fractional distillation gave 81% (methylcyclohexyl)silane, b.p. 144–146°, $n^{25}D$ 1.4542. The infrared spectrum of a chromatographed sample was identical with that from a known sample. Small amounts of isomeric silanes were also observed in the gas chromatogram but amounted to only 2–3% of the total.

Platinum-catalyzed Addition of Trichlorosilane to Cyclohexene.—In the usual manner 16.4 g. (0.2 mole) of cyclohexene and 55 g. (0.4 mole) of trichlorosilane were heated at reflux in the presence of 0.05 g. of chloroplatinic acid. After 42 hours the temperature had gradually attained a maximum of 64°. Fractional distillation of the reaction mixture gave 38 g. (88%) of cyclohexyltrichlorosilane boiling at 202–204°, lit.[17] b.p. 199°.

Anal. Calcd. for $C_6H_{11}SiCl_3$: active Cl, 48.9. Found: active Cl, 48.4, 48.6.

Reduction of cyclohexyltrichlorosilane with excess lithium aluminum hydride followed by hydrolysis and distillation gave cyclohexylsilane in 82% yield, b.p. 115–116°, $n^{25}D$ 1.4472; lit.[18] b.p. 118°, $n^{25}D$ 1.4471.

Anal. Calcd. for $C_6H_{14}Si$: C, 63.07; H, 12.35. Found: C, 63.15; H, 12.40.

Addition of Trichlorosilane to 1-Ethylcyclohexene in the presence of Chloroplatinic Acid.—Using chloroplatinic acid as a catalyst, trichlorosilane was added to 1-ethylcyclohexene in quantitative yield. The reaction required 96 hours for completion, after which the adduct was isolated by distillation at reduced pressure. Fractional distillation yielded the desired adduct boiling at 56–60° (0.1 mm.).

Anal. Calcd. for $C_8H_{15}SiCl_3$: active Cl, 43.3. Found: active Cl, 43.7, 43.4.

Reduction of the above alkyltrichlorosilane with lithium aluminum hydride provided an 88% yield of silanes boiling at 166–167°. Gas chromatography showed only two components, a major component, $n^{25}D$ 1.4550, corresponding to 95% of the product, and a minor component which was not identified. The major component was isolated and purified by preparative gas chromatography and identified as (2-cyclohexylethyl)-silane resulting from terminal addition of trichlorosilane. The identification of this component was made by analysis of its infrared spectrum which showed no absorption in the region 1385–1370 cm.$^{-1}$. This region is considered diagnostic for the presence of a methyl group bound to carbon[19] and such absorption was observed in all the previously reported methylsilylcyclohexanes.[8] In addition, a band at 1408 cm.$^{-1}$ was observed which was not present in the methylsilylcyclohexane isomers. Similar bands have been observed in methyl- and ethylsiloxanes[20,21] at 1412 cm.$^{-1}$ and have been assigned to the C–H bending vibration of methylene groups bound to silicon. The spectrum of (cyclohexylmethyl)-silane also exhibits this band at 1401 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{18}Si$: C, 67.51; H, 12.75. Found: C, 67.68; H, 12.65.

Attempted Addition of Trichlorosilane to 1-*n*-Propyl- and 1-*n*-Octylcyclohexene. 1-*n*-Propylcyclohexene and 1-*n*-octylcyclohexene were refluxed in separate experiments with an excess of trichlorosilane in the presence of chloroplatinic acid according to the procedure used for addition to 1-ethylcyclohexene. After 96 hours and 70 hours, respectively, the mixtures were worked up by distillation. In both cases unreacted olefin was obtained along with small amounts of adducts. The infrared spectra of the recovered olefins were identical to those of the respective starting materials indicating that little isomerization had taken place during the reaction. The amount of adducts corresponded to yields of only 2 to 3% and were not characterized.

Platinum-catalyzed Addition of Trichlorosilane to 4,4-Dimethylcyclohexene.—Using the usual procedure, 16 g. (0.15 mole) of 4,4-dimethylcyclohexene and 66 g. (0.48 mole) of trichlorosilane were refluxed in the presence of chloroplatinic acid. Only a small rise in the pot temperature occurred over a period of 162 hours. However, distillation provided 14 g. (39%) of adduct boiling at 90–96° (9.5 mm.) in addition to unreacted olefin. Gas chromatography and infrared analyses showed that the recovered olefin was the same as the starting material.

Anal. Calcd. for $C_8H_{15}SiCl_3$: active Cl, 43.3. Found: active Cl, 43.3, 43.1.

A silane, b.p. 148–152°, was obtained by lithium aluminum hydride reduction of the above adduct. Gas chromatography indicated a single major component, $n^{25}D$ 1.4481, and several minor components which accounted for approximately 10% of the total product.[22] The infrared spectrum of the major component contained bands at 1381 and 1361 cm.$^{-1}$ of approximately the same intensity as did the starting material, 4,4-dimethylcyclohexene. These bands are characteristic of two methyl groups attached to the same carbon atom.[19] Another indication that the silyl group was not located terminally was the absence of a band in the region 1412–1400 cm.$^{-1}$ which again can be related to methylene groups bound to silicon. The proton magnetic resonance spectrum of this compound was obtained for further characterization. The proton resonance due to hydrogen bound to silicon appeared as a doublet as expected from spin–spin interactions if silicon is attached to the ring.

Anal. Calcd. for $CiH_{18}Si$: C, 67.51; H, 12.75. Found: C, 67.72; H, 12.87.

Free Radical Addition of Trichlorosilane to 4-Methylcyclohexene.—Using acetyl peroxide as a source of free radicals, trichlorosilane was added to 4-methylcyclohexene in 86% yield according to the method developed for addition to 1-methylcyclohexene.[4] Lithium aluminum hydride reduction of a portion of the adduct provided a mixture of the *cis* and *trans* isomers of 1,3- and 1,4-methylsilylcyclohexane boiling at 134–136°.

Attempted Isomerization of 1,3- and 1,4-Methyl-(trichlorosilyl)-cyclohexane in the Presence of Chloroplatinic Acid and Trichlorosilane.—A mixture of 1,3- and 1,4-methyl-(trichlorosilyl)-cyclohexanes (from free radical addition of trichlorosilane to 4-methylcyclohexene) was refluxed with trichlorosilane and chloroplatinic acid under the usual conditions employed for addition of trichlorosilane to 4-methylcyclohexene. After 70 hours the mixture was distilled

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[17] C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947).

[18] C. Eaborn, *J. Chem. Soc.*, 2047 (1955).

[19] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1958.

[20] N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 802 (1947).

[21] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

[22] The presence of several minor components was expected due to the presence of minor amounts of impurities in the starting olefin.

to recover the alkyltrichlorosilanes present. Reduction of the alkyltrichlorosilanes followed by distillation yielded a product with boiling point 134–136°. Gas chromatographic and infrared analyses indicated that the composition was identical to that obtained by reduction of the starting material.

Incomplete Addition of Trichlorosilane to 1-Methylcyclohexene.—The addition of trichlorosilane to 1-methylcyclohexene in the presence of chloroplatinic acid was interrupted after 4 hours and distilled to yield unreacted olefin and (cyclohexylmethyl)-trichlorosilane. On the basis of gas chromatography, the olefin was shown to be a mixture of 95% 1-methylcyclohexene and 5% 4-methylcyclohexene.

Attempted Isomerization of 1-Methylcyclohexene in the Presence of Chloroplatinic Acid.—In a 25-ml. flask was placed 5 g. (0.05 mole) of 1-methylcyclohexene and 0.02 g. of chloroplatinic acid as a solution in 0.5 ml. of isopropyl alcohol. The mixture was heated at 55° for a period of 48 hours then analyzed by gas chromatography. No isomerization had taken place.

Attempted Isomerization of 4-Methylcyclohexene in the Presence of Chloroplatinic Acid.—A mixture of 9.6 g. (0.1 mole) of 4-methylcyclohexene and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol was refluxed for 50 hours. Gas chromatographic and infrared analyses of the olefin showed that no isomerization had taken place. The attempt was repeated in the presence of $SiCl_4$ with the same result.

Platinum-catalyzed Addition of Trichlorosilane to 1-Methylcyclohexene Using *n*-Hexane as Solvent.—To a mixture of 51 g. (0.38 mole) of trichlorosilane and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol was added 19.2 g. (0.2 mole) of 1-methylcyclohexene and 17.2 g. (0.2 mole) of *n*-hexane (Phillips Petroleum). The mixture was refluxed for 26 hours during which time the pot temperature rose from 56° to 64°. Excess trichlorosilane and *n*-hexane were removed by distillation leaving 44 g. (78%) of adduct. Lithium aluminum hydride reduction of the adduct provided only (cyclohexylmethyl)-silane.

Platinum-catalyzed Addition of Trichlorosilane to 1-Methyl-d_3-cyclohexene.—In a 125-ml. three-necked flask was placed 5.0 g. (0.05 mole) of 1-methyl-d_3-cyclohexene, 91 g. (0.67 mole) of trichlorosilane and 0.05 g. of chloroplatinic acid in 0.5 ml. of isopropyl alcohol. The mixture was refluxed under an extra pressure of nitrogen for 42 hours to ensure complete reaction. The excess trichlorosilane was removed by distillation, but because only a small amount of adduct was obtained (5 g.) the reduction step was carried out without further purification. The reduction of the adduct was conducted in the usual manner with excess lithium aluminum hydride followed by hydrolysis and distillation. In addition to unreacted olefin, there was obtained 1.7 g. (26%) of silanes boiling at 140–145°. Gas chromatography showed that two isomeric silanes were present in a 1:1 ratio. The first component, $n^{25}D$ 1.4505, had a retention time corresponding to *trans*-1-methyl-2-silylcyclohexane.[8] The second component, $n^{25}D$ 1.4550, had a retention time corresponding to the terminal adduct (cyclohexylmethyl)-silane. These components were isolated by preparative gas chromatography and analyzed for deuterium content by the method described earlier in this section. The similarities of the retention times and refractive indices with the non-deuterated standards characterize these products as *trans*-1-methyl-d_3-2-silylcyclohexane and (cyclohexylmethyl-d_3)-silane.

Anal. Calcd. for $C_7H_{13}D_3Si$: D, 4.6. Found: *trans* isomer, D, 4.5, 4.5; terminal adduct, D, 4.4, 4.4.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, AGRICULTURAL CHEMICALS DIVISION, MONSANTO CHEMICAL CO., ST. LOUIS 66, MO.]

Reaction of Phosphorus Compounds. IV. Haloenamines and Imidoyl Chlorides from Reaction of Phosphines with Haloamides

BY A. J. SPEZIALE AND L. R. SMITH

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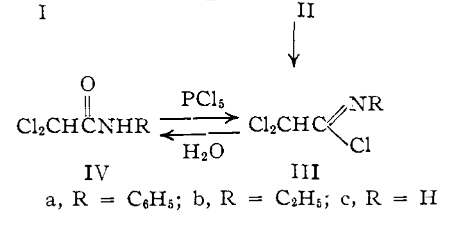
The reaction of trivalent phosphorus compounds with trichloroacetamides has been extended to N-monosubstituted trichloroacetamides and to trichloroacetamide. The products are imidoyl chlorides or dichloroacetonitrile, respectively. Extension of the reaction to α-substituted dichloroacetamides appears limited and depends on the electrical effects of the substituents on the α-carbon and the nitrogen atom. The reaction in one case led to a diphosphonium enamine. Reaction of α-chloroacetamides with phosphines leads to α-phosphonium salts. The mechanism of the reaction leading to haloenamines is discussed and generalized.

The reaction of trialkyl phosphites or tertiary phosphines with N,N-dialkyl or N,N-diaryl-2,2,2-trichloroacetamides has been shown to yield N,N-dialkyl or N,N-diaryl-1,2,2-trichlorovinylamines.[1] The reaction has now been extended to alkyl or aryl monosubstituted trichloroacetamides (I). The products in these cases are dichloroacetimidoyl chlorides (III). Treatment of 2,2,2-trichloroacetanilide (Ia) with tributylphosphine gave a 33% yield of N-phenyl-2,2-dichloroacetimidoyl chloride (IIIa). Similarly, reaction of N-ethyl-2,2,2-trichloroacetamide (Ib) with triphenylphosphine gave N-ethyl-2,2-dichloroacetimidoyl chloride (IIIb) in 46% yield. These imidoyl chlorides were identical with those obtained by the action of phosphorus pentachloride on the corresponding dichloroacetamides (IV). The N-phenyl- and N-ethylimidoyl chlorides (IIIa,b) were rapidly hydrolyzed to the corresponding dichloroacetamides (IVa,b) on treatment with water.

It is presumed that IIIa and IIIb are formed *via* a mechanistic route similar to that which produces the vinylamines in the case of disubstituted trichloroacetamides. However, in the monosubstituted case the supposed intermediate enamine II can tautomerize to the more stable imidoyl chloride III.



$$Cl_3C\overset{O}{\overset{\|}{C}}NHR + R_3'P \longrightarrow \left[Cl_2C{=}C\begin{smallmatrix}Cl\\NHR\end{smallmatrix}\right] + R_3'PO$$

$$Cl_2CH\overset{O}{\overset{\|}{C}}NHR \underset{H_2O}{\overset{PCl_5}{\rightleftarrows}} Cl_2CHC\begin{smallmatrix}{=}NR\\Cl\end{smallmatrix}$$

I, II, IV, III

a, R = C_6H_5; b, R = C_2H_5; c, R = H

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[1] A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).