

point of each ester agreed with the literature value,^{3,20} and the ratio of carbomethoxyferrocene (5.8 g.) to 1,1'-dicarbomethoxyferrocene (5.0 g.) was 59:41.

Metalation of Ferrocene with *n*-Amylsodium (1:1 Ratio).—The metalation of ferrocene with *n*-amylsodium (1:1 ratio) followed by carbonation and esterification with diazomethane showed a ratio of carbomethoxyferrocene to 1,1'-dicarbomethoxyferrocene of 30:70. Thus dimetalation was favored.

Homogeneous Metalation of Isopropylferrocene with *n*-Butyllithium and Coupling with Trimethylchlorosilane.—The metalation

(29) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

and coupling procedure with trimethylchlorosilane were identical with that described in (a) above for the metalation of ferrocene. Again the filtration technique followed by treatment of the solid residue with trimethylchlorosilane did not result in the isolation of any ferrocene derivative. When the ethereal solution was treated with trimethylchlorosilane, a v.p.c. analysis (16-ft. Apiezon L column, 240°, 60 cc./min. He) indicated a ratio 3-isopropyl- to 1'-isopropyl-1-trimethylsilylferrocene of 30:70. It also indicated a ratio of 3-isopropyl- to 2-isopropyl-1,1'-ditrimethylsilylferrocene of 97:3. The ratio of mono- to dimetalated products was 60:40. These results have been included in Table I and II.

[CONTRIBUTION FROM DOW CORNING CORPORATION, MIDLAND, MICH.]

The Addition of Silicon Hydrides to Olefinic Double Bonds. VIII. The Addition of Trichlorosilane-*d*

BY JOHN W. RYAN AND JOHN L. SPEIER

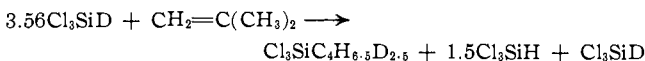
RECEIVED SEPTEMBER 12, 1963

The products formed by the addition of trichlorosilane-*d* (Cl₃SiD) to olefins are not usually monodeuterioalkylsilanes as might be expected. During the addition in the presence of a platinum catalyst extensive exchange occurs between the Si-D and C-H of the olefin. The adducts have deuterium distributed widely in their structures in a random manner. Certain olefins and diphenylacetylene add trichlorosilane-*d* without exchange and in an apparently simple manner. These exceptional compounds include allyl and methallyl chlorides and α -methylstyrene. Isomerization of olefins accompanies the exchange reaction. A mechanism to explain these data is postulated.

From the addition of silicon hydrides to olefins in the presence of platinum catalysts unexpected adducts were recognized¹ when methyl-*n*-pentylchlorosilane was the only adduct of methylchlorosilane to pentene-2. A tendency to form primary alkylsilanes from non-terminal olefins is common to a variety of silicon hydrides.² Isomerization of olefins occurred during these reactions. Each of the methylbutenes² and methylcyclohexenes^{3,4} form more than one adduct. Recent work⁵ indicates that olefins tend to form thermodynamic mixtures of isomers without change in their carbon skeletons during these addition reactions.

Benkeser⁶ and co-workers showed that the addition of trichlorosilane to acetylenes is a *cis* addition in the presence of either platinum-on-carbon or chloroplatinic acid, and more recently Selin and West⁴ found that addition of trichlorosilane to the ring of 1-methylcyclohexene proceeded in a stereospecific *cis* manner in the presence of chloroplatinic acid. In an effort to determine how these phenomena are the result of the catalyzed addition of silicon hydrides to olefins, a series of experiments was undertaken in which trichlorosilane-*d* was added to a variety of olefins in the presence of chloroplatinic acid.

Isobutylene was the chosen olefin because both it and isobutyltrichlorosilane have H¹ n.m.r. spectra that are easy to interpret. The reaction proceeded readily at room temperature and made no by-products. Excess trichlorosilane-*d*, with isobutylene and chloroplatinic acid, was sealed into a glass tube and held at 25° overnight. A noticeable shrinkage of the liquid volume in the tube indicated that the reaction was complete within an hour. Analysis indicated changes summed up by the equation



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

(2) J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) J. C. Saam and J. L. Speier, *ibid.*, **83**, 1351 (1961).

(4) T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

(5) M. C. Musolf, work to be forthcoming from this laboratory.

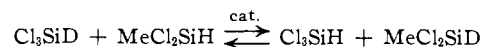
(6) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

The excess trichlorosilane was removed by distillation and analyzed by infrared. Both the Si-H and the Si-D bonds have very strong absorption maxima, the former at 2258 cm.⁻¹ and the latter at 1645 cm.⁻¹. The recovered silane was approximately 60% Cl₃SiH and 40% Cl₃SiD. The adduct was examined by comparison of its H¹ n.m.r. spectrum with that of undeuterated isobutyltrichlorosilane. The tertiary position in the isobutyl group was more than 70% deuterated and deuterium was also found in every other possible position so that an average of 2.5 D's per molecule was present.

This deuterated product was sealed into a tube with octene-1, excess trichlorosilane, and catalyst and heated 4 hr. at 100°. Octyltrichlorosilane was made as expected, but the recovered trichlorosilane was entirely free of deuterium. No Si-H, C-D exchange had occurred. From this we conclude that the result of the first experiment could not be due to exchange between trichlorosilane-*d* and isobutyltrichlorosilane, but that exchange occurred before the latter compound was made. Excess isobutylene, trichlorosilane-*d*, and catalyst were heated in a sealed tube. In this case isobutylene was recovered, passed through a tube of pellets of sodium hydroxide to remove traces of silanes, and analyzed by infrared, which revealed an absorption maximum at 2200 cm.⁻¹ assigned to a C-D bond.

A series of olefins was studied in the same manner and the results are found in Table I.







A separate experiment is of pertinence with these data. Chloroplatinic acid was found to be an efficient catalyst for exchange between trichlorosilane-*d* and methylchlorosilane.



In the absence of the catalyst there was no exchange during many hours at 100°, but a trace of chloroplatinic acid caused exchange at room temperature.

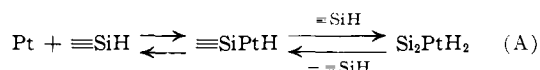
These data can be rationalized as being the results of a series of reactions differing somewhat from previous schemes^{3,6} but nevertheless having much in common with them. All of these reactions appear to be examples of homogeneous catalysis. No precipitates were observable. The catalyst responsible for the reactions may plausibly be a lower valence form of platinum

TABLE I
 Excess DSiCl_3 + olefins $\xrightarrow[100^\circ]{\text{H}_2\text{PtCl}_6}$ $\text{Cl}_3\text{SiR-d}$

Expt.	Olefin	Olefin, mmoles	Cl_3SiD , mmoles	D/H ratio mixt.	D/H ratio adducts	D/H ratio recovd. silane	Products
1	$\text{CH}_2=\text{C}(\text{CH}_3)_2^a$	5.53	19.6	0.44	0.39	0.67	$\text{Cl}_3\text{SiC}_4\text{H}_{6.5}\text{D}_{2.5} + \text{HSiCl}_3$
2	$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$	4.44	15.0	.28	.25	.50	$\text{Cl}_3\text{SiC}_6\text{H}_{10.4}\text{D}_{2.6} + \text{HSiCl}_3$
3	$\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$	5.89	15.2	.26	.20	.67	90% $\text{Cl}_3\text{SiCCCC} + \text{C}$ 10% $\text{Cl}_3\text{SiCCCC} + \text{HSiCl}_3$
4	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	5.66	12.3	.22	.20	.21	70% $\text{Cl}_3\text{SiCCCC} + \text{C}$ 30% $\text{Cl}_3\text{SiCCCC} + \text{HSiCl}_3$
5		2.1	9.4	.37	.28	.54	Cl_3SiC  + other adduct + HSiCl_3
6		8.57	31.00	.30	.31	.24	Cl_3SiC  + other adduct + HSiCl_3
7		4.64	13.5	.29	.23	.26	Cl_3Si  + HSiCl_3
8	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$	4.25	10.39	.24	.1	.32	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)\text{CH}_2\text{SiCl}_3^c$; no exchange
9	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	2.3	13.6	.84	.14	13.3	95% $\text{Cl}_3\text{SiCH}_2\text{CD}(\text{CH}_3)\text{CH}_2\text{Cl} +$ 5% $\text{Cl}_2\text{SiCH}_2\text{CH}(\text{CH}_3)_2$
10	$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$	2.1	9.4	.45	.1	.24	$\text{C}_6\text{H}_5\text{C}(\text{D})\text{C}(\text{SiCl}_3)\text{C}_6\text{H}_5^c$; no exchange
11	$\text{CH}_2=\text{CHCH}_2\text{Cl}^b$						$\text{Cl}_3\text{SiCH}_2\text{CHDCH}_2\text{Cl}$, $\text{DCH}_2\text{CH}=\text{CH}_2$, SiCl_4 ; no exchange

^a This reaction was carried out at 25°. ^b An excess of allyl chloride was used in this case (see Experimental part). ^c The structures of these adducts were not proved, but seem plausible as written.

made by reduction of chloroplatinic acid by the silicon hydride. This platinum may form a complex as in eq. A.



Such a scheme would readily explain the observed exchange between $\equiv\text{Si-D}$ and $\equiv\text{Si-H}$.

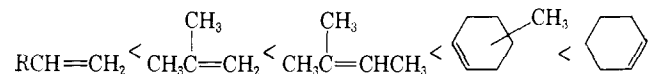
Either the first or the second product of (A) may be regarded as the catalyst during a typical addition reaction. Figure 1 illustrates a plausible scheme for the changes observed for trichlorosilane-*d* with 3-methyl-1-butene (expt. 3 of Table I). An olefin is thought to engage in a series of reversible reactions in which it adds the catalyst and eliminates it, by which process it becomes isomerized and deuterated.

The mechanism seems very like that shown by Smith and Burwell⁷ to explain the distribution of deuterium that resulted from the deuteration of olefins over a platinum catalyst. These authors found that olefins isomerized during the reaction and that they also took part in C-H, D-D exchanges.

It seems that processes occur involving the reversible formation of primary, secondary, and tertiary alkylplatinum intermediates from the appropriate olefins. Of these, the secondary and tertiary must form very rapidly and reversibly, leading to extensive exchange between C-H and Si-D. The secondary and tertiary alkylplatinum intermediates tend not to decompose by the irreversible formation of an alkylsilane. Thus isobutylene undergoes extensive exchange before making

isobutyltrichlorosilane. The primary alkylplatinum intermediates are the most likely to decompose irreversibly with the formation of a primary alkylsilane and the catalyst. Thus the primary alkylplatinum intermediates are thought to seldom, perhaps never, engage in exchange processes.

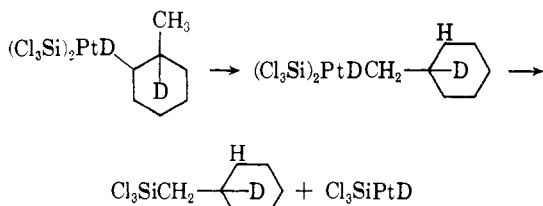
The extent of exchange seems to be inversely proportional to the ease of making alkylsilanes. In order of increasing extent of exchange, olefins may be arranged as



Selin and West⁴ found that 1-methyl-*d*₃-cyclohexene formed cyclohexylmethyltrichlorosilane-*d*₃ in a large excess of trichlorosilane. No exchange occurred. The adduct contained all of the deuterium, none being lost by exchange with the excess trichlorosilane. Their results led to the conclusion that "the rearrangement (of 1-methylcyclohexene) does not involve a simple hydride addition and elimination sequence but rather a single step intramolecular shift of hydrogen."

The data in Table I indicate that exchange indeed occurred and that hydride additions and eliminations are very likely the cause of the exchange. However, the formation of cyclohexylmethyltrichlorosilane must have been preceded by an intramolecular shift of hydrogen as shown by Selin and West. The illustrations of Fig. 1 would lead one to expect methylenecyclohexane as an intermediate leading to the observed product. This high energy olefin may be too difficult to form and

an intramolecular shift may in this case occur irreversibly.



A shift of this kind may also have occurred with some other olefins in Table I, but only in this example would such a shift lead to a detectable result.

Efforts were made to determine if the methylene group in the (cyclohexylmethyl)-trichlorosilane of expt. 5 and 6 of Table II contained any deuterium. The proton n.m.r. spectra of this trichlorosilane as well as of the corresponding trimethyl and trimethoxy derivatives were obtained. The absorptions due to protons in the methylene group could in no case be resolved from the absorptions of the protons in the cyclohexyl group. No conclusions were reached. Perhaps the spectra of other derivatives can be obtained which may resolve the problem.

TABLE II
PROTON N.M.R. SPECTRA OF PRODUCTS

Protons	τ	Type ^a	<i>J</i> , c.p.s.	Intensity, %
HSiCl ₃	3.847	S	...	100
CH ₃ SiHCl ₂	4.419	Quart.	~4 SiH	25
			CH	
CH ₃ SiHCl ₂	9.120	D	~4 SiH	75
			CH	
CH ₃ SiDCl ₂	9.120	T	~1 SiD	100
			CH	
CH ₃ CH=CH ₂	8.0	2T		50
CH ₃ CH=CH ₂	3.25	C		16.7
CH ₃ CH=CH ₂	4.0	C		33.3
DCH ₂ CH=CH ₂	8.0	C		40
DCH ₂ CH=CH ₂	3.25	C		20
DCH ₂ CH=CH ₂	4.0	C		40
Cl ₃ SiCH ₂ CHDCH ₂ Cl		D		40
Cl ₃ SiCH ₂ CHDCH ₂ Cl		C		20
Cl ₃ SiCH ₂ CHDCH ₂ Cl		D		40
Cl ₃ SiCH ₂ CH(CH ₃)CH ₂ Cl	8.45	Quart. ⁹		25
Cl ₃ SiCH ₂ CH(CH ₃)CH ₂ Cl	7.78	C		12.5
Cl ₃ SiCH ₂ CH(CH ₃)CH ₂ Cl	8.835	D	6.5	37.5
Cl ₃ SiCH ₂ CH(CH ₃)CH ₂ Cl	6.54	D	6.5	25
Cl ₃ SiCH ₂ CD(CH ₃)CH ₂ Cl	8.34	T, C ⁹		28.6
Cl ₃ SiCH ₂ CD(CH ₃)CH ₂ Cl	8.80	S		42.9
Cl ₃ SiCH ₂ CD(CH ₃)CH ₂ Cl	6.47	S		28.6
Cl ₃ SiCH ₂ CH(CH ₃) ₂	8.935	D	6.5	67
Cl ₃ SiCH ₂ CH(CH ₃) ₂	8.630	D	6.5	22
Cl ₃ SiCH ₂ CH(CH ₃) ₂	7.88	C		11
Deuterated sample				
Cl ₃ SiCH ₂ CH(CH ₃) ₂	8.942	D	6.4	...
	8.950	T	1.0	...
Cl ₂ SiCH ₂ CH(CH ₃) ₂	8.645	T	1.0	...
	8.642	D	6.4	...
Cl ₃ SiCH ₂ CH(CH ₃) ₂		C		Low

^a S, singlet; D, doublet; T, triplet; Quart., quartet; C, complex.

The behavior of allyl chloride may be explained as the result of two complexes, thus

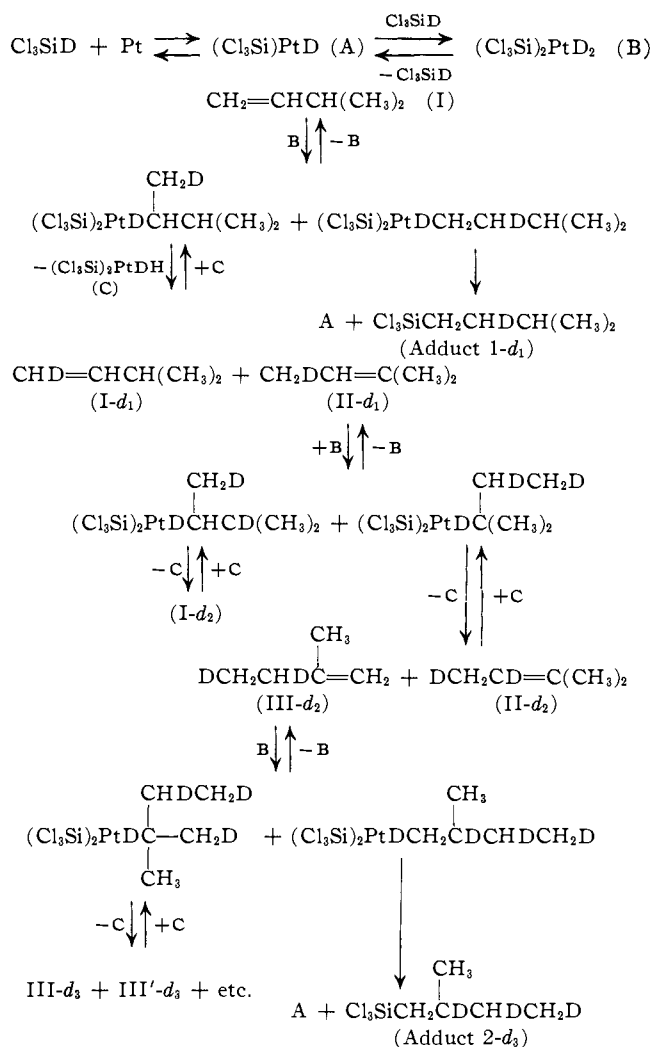
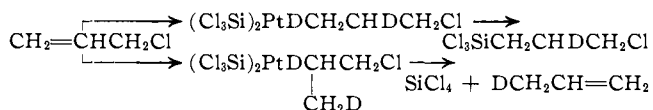


Figure 1.

In an earlier paper⁸ we visualized a similar scheme which permitted tautomerization between the two intermediate complexes above. The identity and purity of the two products preclude such tautomerization, however.

Methylal chloride and α -methylstyrene gave little or no exchange. This indicates that a strong orientation effect was operative to favor the formation of the primary alkyl-platinum complexes and thus lead to products without exchange. We also may conclude that hydrogen attached to an aromatic ring did not take part in exchange processes.

Experimental

Trichlorosilane-*d*.—Deuterium oxide (99.5% purity) was added in 0.25-ml. portions to a rapidly stirred mixture of equal volumes of silicon tetrachloride and tetrachloroethylene. The deuterium chloride formed in this process was passed through a trap cooled by Dry Ice and then through silicon powder mixed with 5% by weight copper powder held at 300° and agitated by an auger-type stirrer. The products were condensed in a trap cooled by Dry Ice and later distilled carefully to obtain a 44% yield of trichlorosilane-*d*, b.p. 32°, d^{25}_4 1.3429. The infrared spectrum of this material indicated that it contained 1.2% trichlorosilane.

Olefins with Excess Trichlorosilane-*d*.—Experiments 1-10 of Table I were carried out in 10 × 200 mm. Pyrex tubes. The olefin and trichlorosilane were carefully weighed into the tube and about 1 μ l. of a 0.1 *M* solution of chloroplatinic acid in isopropyl alcohol was added. The tube was then cooled by Dry Ice and sealed. Care was exercised while filling the tubes to minimize the introduction of moisture. The tubes were then heated overnight in a boiling water bath; v.p.c. analysis was then used

(8) A. G. Smith, J. W. Ryan, and J. L. Speier, *J. Org. Chem.*, **27**, 2183 (1962).

to ensure that the reaction had consumed all of the olefin. In all cases the v.p.c. analyses of the mixtures were identical with a mixture formed from trichlorosilane and the olefin.

The mixture was heated in a water bath and a sample of the excess trichlorosilane fraction was collected and an infrared spectrum obtained. The D/H ratio of the recovered silane was calculated from the relative intensities of the SiD and SiH absorption bands at 1645 and 2258 cm^{-1} , respectively. The over-all D/H ratio of the mixture and the D/H ratio of the adduct or adducts formed were then calculated from the stoichiometric equation for the reaction and the observed D/H ratio of the recovered silane. These values are shown in Table I.

The adducts were isolated by distillation or preparative v.p.c. methods, their purity was checked by v.p.c., and proton n.m.r. spectra were obtained. Comparison of the n.m.r. spectrum of the deuterated adduct with that of the corresponding nondeuterated adduct gave information concerning the position of deuterium in the adduct.

Trichlorosilane-*d* with Excess Isobutylene.—A mixture of trichlorosilane-*d* and isobutylene in a molar ratio of 1:3 was placed in a Pyrex tube with 1 μl . of 0.1 *M* chloroplatinic acid solution. The tube was sealed and heated at 100° for 1 hr. A decrease in volume indicated that addition had taken place. The tube was opened and the excess isobutylene was recovered by distillation. The isobutylene was passed over sodium hydroxide pellets to remove all traces of chlorosilanes. The infrared spectrum of the purified isobutylene showed an absorption band at 2200 cm^{-1} not present in normal isobutylene, indicative of a C-D bond. No Si-H was present in this sample. The experiment shows that exchange between Si-D and C-H in the olefin did take place.

Addition of Trichlorosilane to Octene-1 in the Presence of Isobutyltrichlorosilane-*d*_{2,5}.—Isobutyltrichlorosilane-*d*_{2,5} (Table I, expt. 1; 302 mg., 1.6 mmoles), octene-1 (109 mg., 1 mmole), and trichlorosilane (2.305 g., 17 mmoles) were sealed in a Pyrex tube with 1 μl . of 0.1 *M* chloroplatinic acid in isopropyl alcohol. After heating this mixture 4 hr. at 100°, v.p.c. analysis indicated that the octene had been completely converted to *n*-octyltrichlorosilane. The excess trichlorosilane was recovered by distillation and its infrared spectrum showed that it was pure trichlorosilane free of any trichlorosilane-*d* as indicated by the complete absence of absorption at 1645 cm^{-1} . This experiment indicates that no exchange of D and H takes place between an adduct and a silane under the conditions in which the silane added to an olefin.

Exchange of Hydrogen and Deuterium on Silicon. Into an n.m.r. sample tube were placed trichlorosilane-*d* (443 mg., 3.24 mmoles) and methylchlorosilane (323 mg., 2.81 mmoles). The tube was sealed and an n.m.r. spectrum obtained after 3 hr. and again after heating the tube 15 hr. in a boiling water bath. Each of these spectra showed only the characteristic spectrum of methylchlorosilane (Table II). The tube was then opened and 2 μl . of 0.1 *M* chloroplatinic acid in isopropyl alcohol was added. The tube was resealed and after 3 hr. at room temperature an n.m.r. spectrum was obtained. This spectrum showed the presence of HSiCl_3 by its absorption at 3.847 τ . Integration of the absorption bands for the protons attached to silicon indicated that the ratio of trichlorosilane to methylchlorosilane was approximately 1/3. After the tube had been kept 24 hr. at room temperature an n.m.r. spectrum showed that the concentrations of HSiCl_3 and MeHSiCl_2 were approximately equal. This latter spectrum also showed that the methyl group of methylchlorosilane-*d* was split to a triplet by the deuterium. This triplet appeared superimposed on the normal doublet for methylchlorosilane (see Table II).

Allyl Chloride and Trichlorosilane-*d*.—A mixture of allyl chloride (5 ml., 61 mmoles) and trichlorosilane-*d* (2 ml., 20 mmoles) containing 1 μl . of 0.1 *M* chloroplatinic acid solution in isopropyl alcohol was gently refluxed in a flask fitted with a water-cooled condenser. A Dry Ice trap was connected to the top of the condenser to collect propylene formed during the reaction. The

reaction was complete in 3 hr. The propylene was then passed over potassium hydroxide pellets to remove any chlorosilanes. An n.m.r. spectrum of this material showed that the propylene formed was essentially pure propylene-3-*d*₁. Integration of the proton absorptions showed that only two protons were located in the methyl group (see Table II).

The liquid product was carefully fractionated to give a sample of 3-chloropropyltrichlorosilane which appeared to be pure by v.p.c. analysis. An n.m.r. spectrum of this product (see Table II) indicated that it was 3-chloropropyl-2-*d*₁-trichlorosilane. The relative number of protons on the α -, β -, and γ -positions of the adduct were 2, 1, 2. A rather complex splitting pattern was observed in this compound because it contains an asymmetric center.⁹

3-Chloro-2-methylpropyl-2-*d*₁-trichlorosilane.—Careful distillation of the products from expt. 9, Table I, gave a fraction which by v.p.c. analysis was pure 3-chloro-2-methylpropyltrichlorosilane. The n.m.r. spectrum of this compound showed no hydrogen atom on the carbon atom β to silicon (Table II) but a complex triplet pattern for the $-\text{CH}_2-\text{Cl}$ group due to the presence of an adjacent deuterium atom complicated by the asymmetry of the molecule and possibly by restricted rotation.⁹ Splitting of the protons of the CH_3 - and SiCH_2 - by the adjacent deuterium atom was not observed; presumably the coupling in this case was low due to the molecules assuming a particular conformation in which spin-spin coupling is minimized.

2-Methylpropyl-*d*_{2,5}-trichlorosilane.—An n.m.r. spectrum was obtained on the adduct made from excess trichlorosilane-*d* and isobutylene (expt. 1, Table I). The stoichiometric equation calculated from the observed D to H ratio of the recovered silane indicated that the adduct contained an average of 2.5 deuterium atoms per molecule. The low intensity of absorption attributed to the tertiary proton indicated that the carbon atom β to silicon was highly deuterated. The complex spectrum also showed the expected triplets for the protons on the carbon α to silicon and for the protons of the CH_3 group caused by deuterium.

2-Methylbutyl- and 3-Methylbutyltrichlorosilane.—The products formed from 2-methylbutene-2 and trichlorosilane-*d* (Table I, expt. 4) were analyzed by v.p.c. The mixture contained two adducts. Treatment of these two adducts with excess methylmagnesium iodide formed a mixture of 2-methylbutyltrimethylsilane and 3-methylbutyltrimethylsilane. This mixture was qualitatively identical with the mixture of these same two compounds previously characterized and reported by Saam and Speier.² From the areas under the peaks it was estimated that the ratio of 2-methylbutyl- to 3-methylbutylsilanes formed was 30/70.

The product formed from trichlorosilane-*d* and 3-methylbutene-1 (Table I, expt. 3) contained the same two adducts, but in this case the ratio of 2-methylbutyl- to 3-methylbutyltrichlorosilane was 10/90.

N.m.r. Spectra of Randomly Deuterated Adducts.—Comparison of the n.m.r. spectrum of each of the adducts formed in experiments 2, 6, and 7 (Table I) with the n.m.r. spectrum of the corresponding nondeuterated adduct showed that in the cases where deuterium was present the spectra could generally not be resolved into distinct peaks but rather the absorption was spread over a broad band. Although all of these adducts show a complex pattern, the presence of deuterium greatly increases the complexity. Presumably the random nature of deuteration leads to such a mixture of species that resolution is not possible.

Acknowledgment.—The valuable aid of Dr. A. Lee Smith and Mr. N. C. Angelotti in obtaining and interpreting infrared and nuclear magnetic spectra was essential to this project and is appreciated by the authors.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., pp. 99-103.