

SILANE ADDITION REACTIONS—THEIR SYNTHETIC UTILITY AND MECHANISM

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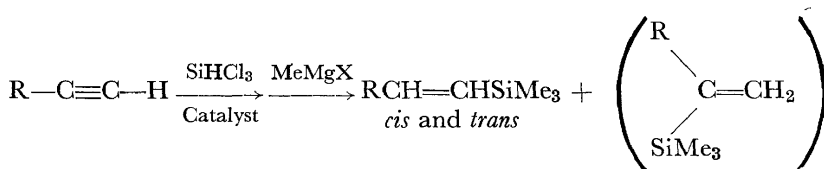
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The addition of silanes (compounds containing the $\equiv\text{SiH}$ group) to unsaturated organic compounds (olefins and acetylenes) is a reaction of tremendous importance in the field of organosilicon chemistry. The reaction can be effected thermally¹, by peroxides or u.v. light², or by a variety of catalytic³ agents. It is my purpose to review our research efforts in this area of Chemistry. Some of the material I will present has already been published, but a considerable portion of the work remains to be published.

For purposes of clarity my talk will be divided into three parts: (1) Stereochemistry of silane additions, (2) Synthetic utility of silane additions as derived from a knowledge of their stereochemistry, and (3) Mechanisms of silane additions catalyzed by *tertiary* amines and chloroplatinic acid.

I. STEREOCHEMISTRY OF SILANE ADDITION REACTIONS

Before any final judgement could be made about the mechanism of these addition reactions we considered it essential that the stereochemistry of the process be established. Toward this end, we chose five different acetylenes, viz. 1-pentyne, 1-hexyne, 1-heptyne, 3-methyl-1-butyne and 3,3-dimethyl-1-butyne, and added trichlorosilane to each of these under a variety of catalytic conditions. The trichlorosilyl adducts obtained as products were methylated with methylmagnesium halide prior to analysis by vapour phase chromatography (v.p.c.).



The results of this study are given in *Table 1*.

The results^{4,5} of these experiments can be summarized as follows: the silane additions which were catalyzed by platinized charcoal or chloroplatinic acid gave almost exclusive *trans* products arising from *cis* additions of the elements of H and SiCl_3 , whereas the reactions catalyzed by benzoyl peroxide, gave predominantly *cis* products (from *trans* addition) except for 3,3-dimethyl-1-butyne which produced almost all *trans* product after a 20-hour reaction time.

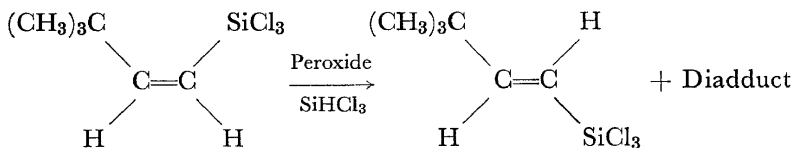
With regard to 3,3-dimethyl-1-butyne, it was found that the highly hindered *cis* adduct was isomerized to *trans* product in the presence of benzoyl

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Table 1. Methylated adducts [RCH=CHSi(CH₃)₃]

Sl. No.	Alkyne	Catalyst	Isomer Distribution (%)	
			Cis	Trans
1	1-Pentyne	Peroxide	79	21
2	1-Pentyne	Pt/C		~100
3	1-Pentyne	H ₂ PtCl ₆ ·6H ₂ O		~100
4	1-Hexyne	Peroxide	77	23
5	1-Hexyne	Pt/C		~100
6	1-Hexyne	H ₂ PtCl ₆ ·6H ₂ O		~100
7	1-Heptyne	Peroxide	75	25
8	1-Heptyne	Pt/C		~100
9	1-Heptyne	H ₂ PtCl ₆ ·6H ₂ O		~100
10	3-Methyl-1-butyne	Peroxide	72	28
11	3-Methyl-1-butyne	H ₂ PtCl ₆ ·6H ₂ O		~100
12	3,3-Dimethyl-1-butyne	Peroxide		~100
13	3,3-Dimethyl-1-butyne	H ₂ PtCl ₆ ·6H ₂ O		~100

peroxide and trichlorosilane. In addition to the isomerization, a considerable amount of diadduct formation



also occurred. The structure of the diadduct was not determined. It was of considerable interest that this diadduct was formed *only* from the *cis* monoadduct and not from the *trans* isomer. When an authentic sample of *trans*-1-trichlorosilyl-3,3-dimethyl-1-butene was treated with trichlorosilane and peroxide, no reaction occurred. However, *cis*-1-trichlorosilyl-3,3-dimethyl-1-butene, treated under identical conditions, formed considerable amounts of the *trans* isomer along with the diadduct. Hence, it is probable that the peroxide catalyzed addition to 3,3-dimethyl-1-butyne (Sl. No. 12, Table 1) is no exception to the stereochemical rule of *trans* addition leading to *cis* products in the presence of peroxides. All *cis* product may form initially but some of this is isomerized to *trans* while the rest adds trichlorosilane to give a diadduct.

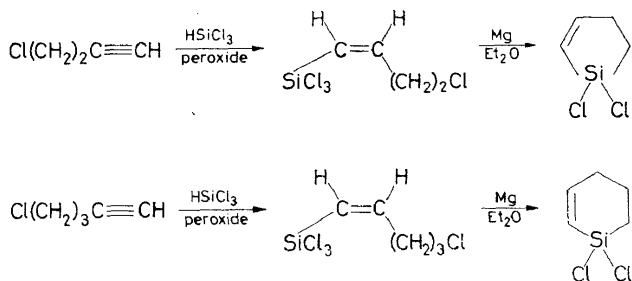
Recent work by Skell⁶, involving the gas phase addition of hydrogen bromide to propyne, assigns an energy of activation for the isomerization of vinyl radical of over 17 kcal/mole*. If one may extrapolate from this work to our own, it is likely that the addition of trichlorosilane to acetylenes in the presence of peroxides is completely stereospecific leading initially only to *cis* products. The minor amounts of *trans* products obtained would then arise from an isomerization of the *cis* olefin product. This could be determined by analyzing the reaction mixture at extremely short reaction times (for example at 0.15 per cent conversion as Skell⁶ did) and observing whether the *cis/trans* isomer ratio diminishes with time. Such an experiment remains to be done.

* The accuracy of this calculation has recently been challenged. It is possible that the actual value is considerably lower, thus allowing for a rather facile *cis* → *trans* isomerization of a vinyl radical intermediate. We are indebted to Dr Alexis A. Oswald for drawing our attention to this fact.

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2. SYNTHETIC UTILITY OF SILANE ADDITIONS IN RING SYNTHESIS

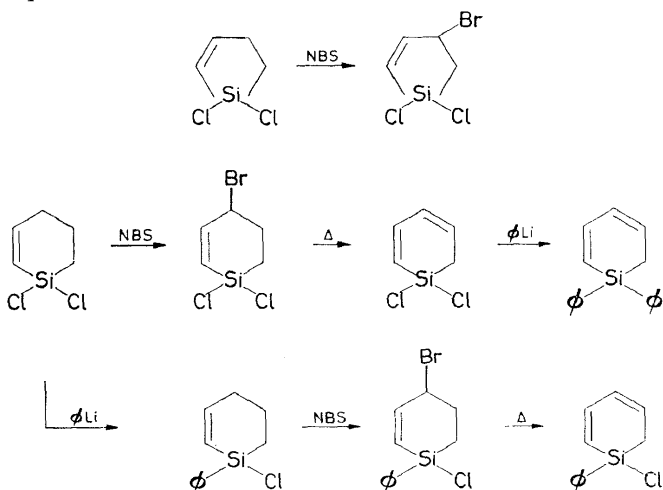
We have found the information regarding the stereochemistry of silane additions of extreme value in working out the synthesis of certain silicon ring systems⁷⁻⁹. Thus, the following reaction sequences have been successfully carried out:



As might be expected, the yield of cyclic material was poor when the *trans* olefin was used rather than the *cis*.

It is of interest that attempts to prepare the 7-membered cyclic silicon olefin by a similar reaction sequence have so far met with failure¹⁰. Only polymeric material has been obtained from these reactions.

The chemistry of these cyclic olefin systems, while not the direct subject matter of this presentation, promises to be of interest. Outlined below are some of the reactions which we have already carried out successfully on some of the compounds.



NBS = N-Bromosuccinimide

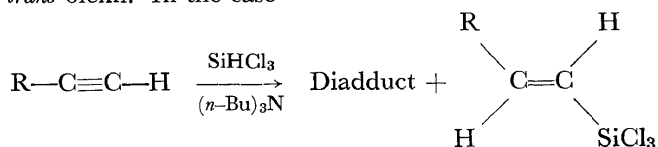
3. MECHANISMS OF SILANE ADDITIONS

Amine-Catalyzed Additions of Trichorosilane

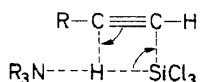
In the course of our investigations on silane additions, we noted that

relatively little attention has been given to base-catalyzed reactions. Accordingly, we undertook a study of base-catalyzed silane additions to alkynes with the object of elucidating the general mechanism of such reactions.

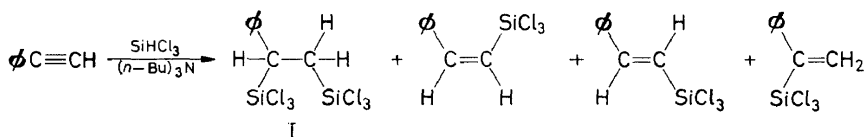
The most definitive mechanistic work on such reactions was that of Pike¹¹. He reported that, when trichlorosilane was added to phenylacetylene and 1-hexyne in the presence of tri-*n*-butylamine as catalyst, a considerable amount of a diadduct (structure not determined) was produced in addition to the *trans* olefin. In the case



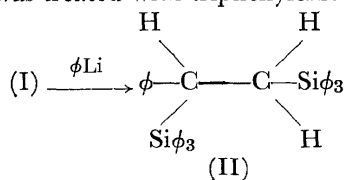
of 1-hexyne, some non-terminal adduct was also detected. Based upon these findings, as well as the observation that polar solvents like acetonitrile favour the reaction, it was proposed¹¹ that the reaction proceeds through a solvated four-centred transition state.



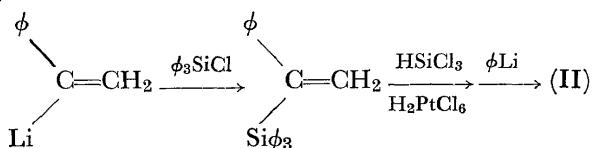
We have reinvestigated the reaction with phenylacetylene and have confirmed that a considerable amount of diadduct is produced. We have established conclusively¹² that this diadduct is α,β -bis(trichlorosilyl)-ethylbenzene. In addition, we have identified the monoadducts of the reaction to be α -trichlorosilylstyrene and *cis*- and *trans*- β -trichlorosilylstyrene.



The structure of the diadduct was established unequivocally by chemical methods. Treatment of compound (I) with excess phenyllithium produced α,β -bis(triphenylsilyl)ethylbenzene (II). Compound (II) was also produced when α -styryllithium was treated with triphenylchlorosilane followed by the

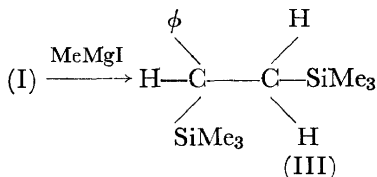


addition of trichlorosilane (catalyzed by chloroplatinic acid) and then phenylation.

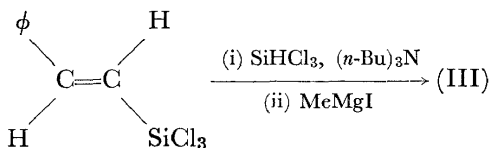


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This reaction sequence eliminates the β,β structure as a possibility for (I). Treatment of (I) with excess methylmagnesium iodide produced α,β -bis-(trimethylsilyl)ethylbenzene (III).



Compound (III) was also produced by methylation of the product obtained by treating *trans*- β -trichlorosilylstyrene with trichlorosilane and tri-*n*-butylamine.



This reaction sequence of necessity eliminates the α,α structure as a possibility for (I). The only remaining possibility, then, is the α,β structure shown above for compound (I).

The n.m.r. spectrum of (III) also bears out the proposed α,β structure since it shows two singlets at 9.78 and 9.88 τ units for the trimethylsilyl protons. The presence of two distinct singlets is indicative of the different environment of the two trimethylsilyl groups—a situation not compatible with either a di- α or a di- β structure.

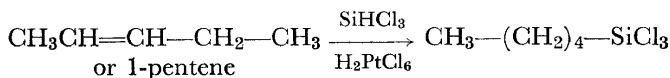
It becomes apparent immediately that our discovery of *cis*- β -trichlorosilylstyrene among the monoadduct products of this reaction is potentially significant since it is not congruous with the mechanisms which have been suggested^{11, 13}. It also becomes imperative to determine from which monoadduct the diadduct (which is formed in significant quantities) is produced. It is not inconceivable that one of the three monoadducts detected adds trichlorosilane much more rapidly than the other two and that the diadduct is formed preferentially from just this one monoadduct. It will be recalled that this was exactly the situation which prevailed in the peroxide catalyzed additions to 3,3-dimethyl-1-butyne (see above). At any rate, valid conclusions concerning the stereochemistry of the initial addition cannot be drawn safely from the small quantity of a particular monoadduct (in this instance, *trans*) which might be detected in the reaction products.

Further experiments designed to shed light on the mechanism and stereochemistry of the addition and source of the diadduct are being carried out in our laboratory.

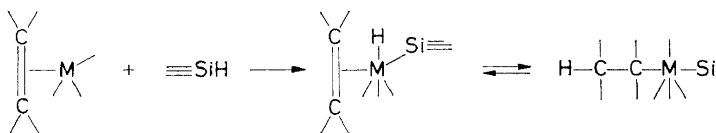
Chloroplatinic Acid-Catalyzed Additions of Trichlorosilane

A considerable amount of information has been published on the scope and mechanism of silane addition reactions catalyzed by chloroplatinic acid³. One of the most intriguing aspects of this reaction is the tendency for internal olefins to react so as to produce terminal addition products. Thus,

either 1- or 2-pentene will add trichlorosilane in the presence of chloroplatinic acid to produce *n*-amyltrichlorosilane¹⁴.

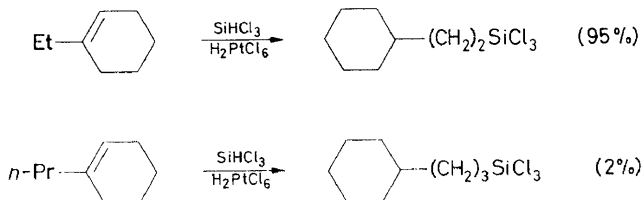


Recently¹⁵ it was proposed that the mechanism for such reactions is similar to that for the "oxo" process. Indeed, "oxo" catalysts like dicobalt octacarbonyl were shown¹⁶ to be effective substitutes for the chloroplatinic acid catalyst. It was suggested that the double bond migrates from an internal to a terminal position *via* a series of π and σ -bonded metal complexes.

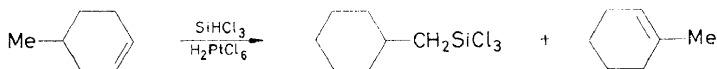


This rather attractive mechanism would seemingly require some type of progressive double bond shift down a carbon chain resulting from 1,2-hydrogen shifts *via* the metal atom.

It came to our attention that there was at least one report in the literature which suggested that the double bond shifts in such silane additions were occurring by some 1,3-type hydrogen transfer. Thus it was reported¹⁷ that 1-ethylcyclohexene reacts with trichlorosilane and chloroplatinic acid to form terminal adduct as shown, but that 1-*n*-propylcyclohexene was essentially unreactive under the same reaction conditions.



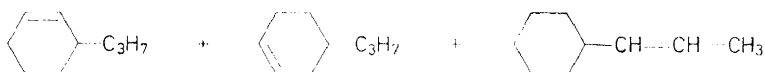
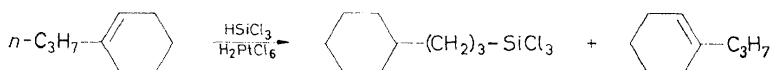
Likewise, when 4-methylcyclohexene was subjected to the same reaction conditions, terminal adduct and some 1-methylcyclohexene (but not 3-methylcyclohexene) were produced.



These results were rationalized in terms of a 1,3-type hydride shift.

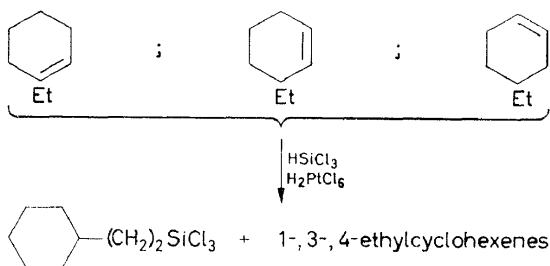
In a re-examination of this work, we found that 1-*n*-propylcyclohexene would add trichlorosilane in the presence of chloroplatinic acid although at a somewhat slower rate than 1-ethylcyclohexene. In addition to terminal adduct, all possible mono-olefin isomers could be detected in the reaction product except propylidenecyclohexane and allylcyclohexane.

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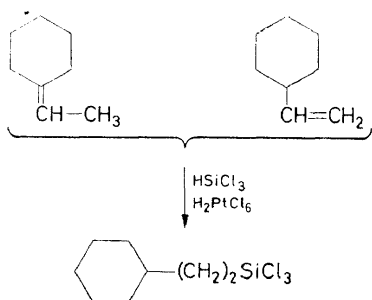


We discovered that if a large excess of trichlorosilane were used in the reaction, poor yields of addition products were obtained. When only a slight excess of trichlorosilane¹⁸ was used, the temperature of the refluxing reaction mixture was higher and addition occurred. This may account for the difficulty of earlier workers¹⁷ with this reaction.

We next turned our attention to trichlorosilane additions to the ethylcyclohexenes¹⁸. Using pure samples of 1-, 3- and 4-ethylcyclohexenes we found that in each case terminal adduct was obtained. But again we could detect, by employing the proper conditions, all of the other isomeric ethylcyclohexenes except vinyl- and vinylidenecyclohexane.



On the other hand, we synthesized the latter two isomers and found that they readily added trichlorosilane.



While these results are suggestive of 1,2-hydride shifts as proposed by Chalk and Harrod¹⁵, our inability to detect vinylidene-, propylidene-, vinyl- and allylcyclohexane in the reaction products* does not enable us to give un-

* The problem here is an analytical one. If they form at all, these four compounds are present in small quantities and their retention times are quite close to other components in the mixture. We have not yet found v.p.c. conditions for their adequate separation and identification.

equivocal support of this view. In addition, it must be conceded that the mere presence of all the isomeric olefins in the reaction product, while perhaps suggestive of a 1,2-hydride shift, does not preclude the possibility that 1,3-type shifts can occur in these systems.

Several miscellaneous observations were made during the course of the above experiments which tend to shed some light on the nature of the catalyst in these reactions.

When a mixture of ethylcyclohexane, trichlorosilane and chloroplatinic acid was heated without an olefin present, a precipitate formed on the walls of the flask within one hour. The liquid was decanted from the precipitate and the latter (grey in colour) was washed several times with anhydrous ether. This precipitate was shown by the appropriate qualitative tests to contain platinum metal. The clear filtrate (but not the precipitate) would catalyze the addition of trichlorosilane to 1-ethylcyclohexene. The precipitate, on the other hand, did catalyze the addition of trichlorosilane to allylcyclohexane. These results would tend to indicate that the active catalyst in these reactions is not platinum metal, but rather some soluble platinum compound¹⁹.

Finally, we synthesized¹⁸ dichlorobis(1-ethylcyclohexene)- μ , μ' -dichlorodiplatinum (II), a new compound, by the general method described by Kharasch²⁰. Its molecular weight and analysis indicated its dimeric nature. This platinum complex effectively catalyzed the addition of trichlorosilane to both 1-ethylcyclohexene and allylcyclohexane. Hence, the active catalyst in these systems might well be platinum-olefin complexes of this type as proposed¹⁵.

I would like to pay tribute to the graduate students and postdoctoral associates who have worked with me, particularly Drs M. L. Burrous, R. F. Cunico, R. A. Hickner, Y. Nagai, P. G. Nerlekar, J. V. Swisher, S. D. Work and Messrs. S. Dunny and P. R. Jones.

References

- ¹ A. J. Barry, L. DePree, J. W. Gilkey, and D. E. Hook. *J. Am. chem. Soc.* **69**, 2916 (1947).
- ² L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore. *J. Am. chem. Soc.* **69**, 188 (1947).
- ³ J. L. Speier, R. Zimmerman, and J. Webster. *J. Am. chem. Soc.* **78**, 2278 (1956) and later papers in this series.
- ⁴ R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher. *J. Am. chem. Soc.* **83**, 4385 (1962).
- ⁵ R. A. Benkeser and R. A. Hickner. *J. Am. chem. Soc.* **80**, 5298 (1958).
- ⁶ P. S. Skell and R. G. Allen. *J. Am. chem. Soc.* **86**, 1559 (1964).
- ⁷ R. A. Benkeser and R. F. Cunico. *J. organometal. Chem.* 284 (1965).
- ⁸ R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund. *J. Am. chem. Soc.* **86**, 2446 (1964).
- ⁹ R. A. Benkeser, J. L. Noe, and Y. Nagai. *J. org. Chem.* **30**, 378 (1965).
- ¹⁰ R. A. Benkeser and R. F. Cunico. Unpublished work.
- ¹¹ R. A. Pike. *J. org. Chem.* **27**, 2186 (1962).
- ¹² R. A. Benkeser, S. Dunny, and Paul R. Jones. *J. organometal. Chem.* 338 (1965).
- ¹³ J. C. Saam and J. L. Speier. *J. org. Chem.* **24**, 427 (1959).
- ¹⁴ J. L. Speier, J. A. Webster and G. H. Barnes. *J. Am. chem. Soc.* **79**, 974 (1957).
- ¹⁵ A. J. Chalk and J. F. Harrod. *J. Am. chem. Soc.* **87**, 16 (1965).
- ¹⁶ A. J. Chalk and J. F. Harrod. *J. Am. chem. Soc.* **87**, 1133 (1965).
- ¹⁷ T. J. Selin and R. West. *J. Am. chem. Soc.* **84**, 1863 (1962).
- ¹⁸ R. A. Benkeser and P. G. Nerlekar. Unpublished work.
- ¹⁹ R. A. Benkeser and S. D. Work. Unpublished work.
- ²⁰ M. Kharasch and T. A. Ashford. *J. Am. chem. Soc.* **58**, 1733 (1936)