HYDROSILATION IN THE SYNTHESIS OF ORGANOSILANES

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INTRODUCTION

The hydrosilation reactions, *i.e.* the addition of silanes to olefins (equation 1) emerged from about six separate laboratories in the United States[1–5] between 1945 and 1947.

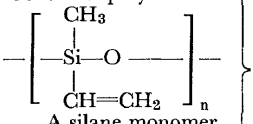
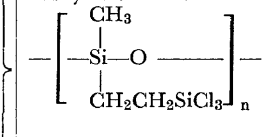
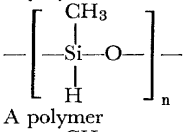
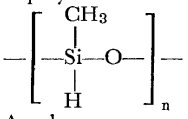
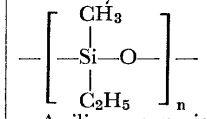
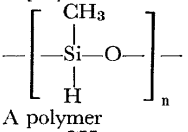
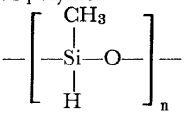
$$YCH{=}CH_2 + HSiX_3 \xrightarrow{\text{Catalyst}} \begin{cases} YCH_2CH_2SiX_3 \\ YCH(SiX_3){-}CH_3 \end{cases} \qquad (1)$$

A silane such as trichlorosilane adds to an olefin such as ethylene to give an organosilicon compound. The substituents X and Y can be varied rather widely, *e.g.* alkyl, aryl, halogen, alkoxy, and acyloxy for either X or Y. The reaction is very versatile. But changes in reaction rate and in the course of the reaction depend upon the substituents X and Y and the catalyst. The reaction is very complex and it is not a simple matter to make really effective use of it.

The usefulness of the reaction is limited by a number of things. There are some side reactions, including polymerization and isomerization of the olefin, and these cannot always be controlled. We do not know how to make all possible combinations of silanes and olefins react, let alone to make at will the upper or lower type product of equation (1). The silane we need may not be readily available. In the laboratory this is an inconvenience; on a larger scale it can make hydrosilation impracticable. There are other ways to synthesize silanes, and sometimes Grignard processes are attractive when the alternative involves making a silicon–hydrogen compound first. There are only a handful of hydrosilanes that we can get by direct means, for example as products or by-products of the direct process, and fewer still that are really abundant.

Hydrosilation is potentially useful for doing things besides the simple reaction illustrated in equation (1). A number of products have been obtained by the reaction of silanes with olefins. *Table 1* shows the products obtained when: (*i*) the silane is a monomer, and the olefinic group is attached to silicon, compounds with two silicon atoms are obtained; (*ii*) two (or more) silicon atoms are put on unsaturated polymers; (*iii*) substituted siloxanes are made by different routes; (*iv*) a siloxane containing SiH is alkylated to an alkylsiloxane. Silicone organic co–polymers can be made from unsaturated organic polymers. Siloxane polymers containing SiH combine with those containing vinyl groups to give cross-linked or cured

Table 1. Products obtained by the reaction of silanes with olefins

Silane	*Olefin*	*Product*
1. A monomer ($HSiCl_3$)	A monomer (C_2H_4)	An alkylsilane ($C_2H_5SiCl_3$)
2. A monomer ($HSiCl_3$)	An olefinic silane ($CH_2CHSiCl_3$)	A silethylene ($Cl_3SiCH_2CH_2SiCl_3$)
3. A monomer ($HSiCl_3$)	An organic polymer ($CH_2{=}CHRCH{=}CH_2$)	A silylated polymer $(Cl_3SiCH_2CH_2)_2R$
4. A monomer ($HSiCl_3$)	A siloxane polymer 	A silylated siloxane 
5. A polymer 	A silane monomer $CH_2{=}CHSiCl_3$	
6. A polymer 	A monomer (C_2H_4)	An alkylsiloxane 
7. A polymer 	An organic polymer	A silicone-organic copolymer
8. A polymer 	A siloxane polymer	A cross-linked or cured siloxane polymer

siloxanes. There are many reactions and environments implied in these different uses of hydrosilation. Control of the situation means one thing for monomer synthesis and quite another for polymer vulcanization. For today we can only consider the simplest cases which are complex enough.

GENERAL RELATIONSHIPS

The reactions described above do not take place spontaneously at room temperature. The mixtures have to be heated, and catalysts are often needed. We know that temperature, catalyst, and the groups on the olefin and silane affect the rate of the reaction. But quantitatively we know little about these things. Few rate constants are known, and few values for activation energy[6,7] are available in literature.

This situation is understandable, because during a synthesis one can adjust conditions to rate constants over a million-fold range. In the application of hydrosilation, we did not have to determine rate constants. However, in order to have a better grasp of mechanisms involved in hydrosilation data with regard to rate constants will be of considerable assistance.

Meanwhile most of the information we have on reaction rates has to be obtained from experiments not designed to measure rates at all. I have gone through some of the data and after making rough corrections for temperature have concluded that platinum catalysts, at concentrations as low as 10^{-6} molar can effect an increase in reaction rates from 10^4 to 10^6 times as compared to those of uncatalyzed thermal reactions. Bases are much less effective, requiring about 0·1 molar concentration for increases of a thousand or so in rate. Peroxides are perhaps a little more active than bases.

We have learnt a lot more about where the silicon becomes attached to the olefin than we have about rate. This is because the synthesis is not a success if the wrong isomer is produced. As shown in equation (1) and again in equation (3), addition may be

$$CH_2CH{=}CH{-}CH_2CH_3 + HSiCl_3 \longrightarrow Cl_3SiCH_2CH_2CH_2CH_2CH_3 \qquad (2)$$

$$CH_2{=}CHCN + HSiCl_3 \begin{cases} \longrightarrow Cl_3SiCH_2CH_2CN \\ \longrightarrow CH_3{-}CH(SiCl_3){-}CN \end{cases} \qquad (3)$$

Markownikoff or anti-Markownikoff. Ability to control the mode of addition can be a major problem. This was shown in the case of acrylonitrile[8-10]. Without catalyst, or with platinum or other metallic catalysts, the products were mixtures of β- and α-adducts. The β-isomer alone could be obtained by change to basic catalysts[11]. It was important to get the β-isomer because the silicon–carbon bond in the α-isomer cleaves under acid conditions, and products made from it are unstable.

The first sign that hydrosilation could involve something besides this conventional type of isomerism seems to have come from Speier *et al.*[12]. These workers noticed that pentene-2 gave 1-*n*-pentylsilanes (equation 2) when platinum-on-carbon, chloroplatinic acid, or ruthenium chloride was the catalyst. This shift in position towards the end of the carbon chain turned out to be very general. It is a complicated reaction and it has not been possible to separate its study from the study of hydrosilation itself. It does not occur with peroxide or base catalysts.

It is obvious that the yield of any one isomer will be affected by the proportions of the isomers obtained. This does not mean, necessarily, that the yield of useful product will be affected. For example, it would be expected to make little difference in the properties of a product whether a 1-pentyl- or a 2-pentylsilane is used in it. However, for acrylonitrile and other functional olefins this is not the case; the reaction has to be controlled to give the desired isomer.

The yield is also affected by the rate of the reaction. Low rates give more opportunity for the competing side-reactions. Two common side-reactions are telomerization and polymerization. These occur with certain combinations of olefins and catalysts. They are most serious in the presence of free radical initiators, and with active olefins such as acrylonitrile[13]. Free-radical inhibitors can be used to minimize their extent. However, peroxide-catalyzed hydrosilation is a special case of chain termination by transfer,

i.e. the removal of an atom from a neighbouring molecule by a radical. Telomerization and polymerization are also normal results of free radical reactions, and if we do not encounter them in hydrosilation it is simply due to the favourable reaction rates.

Another side-reaction causing low yields is given in equation (4) in which it is shown that during the addition of silanes to allyl compounds[12], three reactions occur.

$$CH_2{=}CH{-}CH_2Cl + HSiCl_3 \begin{cases} \longrightarrow Cl_3SiCH_2CH_2CH_2Cl \\ \longrightarrow Cl_3SiCH_2CH_2CH_3 \\ \longrightarrow Cl_4Si + CH_2{=}CHCH_3 \end{cases} \quad (4)$$

Thus allyl chloride gives chloropropylsilanes, propylsilanes, and propylene and chlorosilanes. Other allyl compounds such as allyl acetate also evolve propylene, and other allylic halides behave similarly. But methallyl chloride undergoes almost exclusively the first type of reaction[14]. This is explained by considering that the intermediate complex has to arrange itself in a different way because of the α-methyl group. Several factors are thus involved in determining how well a hydrosilation will proceed (*Table 2*).

Table 2. Effect of reaction conditions on hydrosilation

Condition	*Catalyst*	*Olefin*	*Silane*	*Solvent*	*Temperature*
Orientation	Very important	Very important	Moderate	Weak	?
Rate	Very important	Very important	Variable	Weak	Important
Side-reactions	May cause: isomerization polymerization redistribution	May cause: polymerization telomerization isomerization	Cause: isomerization Undergo: redistribution	Affects: polymerization	May cause: polymerization redistribution

The catalyst, the olefin, and the silane are important in determining the orientation of the product, *i.e.* the position of the silyl group. The solvent can have an effect, but it is usually not powerful. Similarly in the determination of reaction rate, the catalyst and olefin are very important; the silane used may or may not have an influence, depending on the catalyst–olefin combination; and the solvent used is not usually important. The catalyst may cause isomerization or polymerization of the olefin, but this can sometimes be controlled by inhibitors. It can also cause redistribution of the silane. The olefin undergoes several side-reactions, and the silane contributes to promoting isomerization.

DESCRIPTION BY CATALYST CLASSES

In any given synthesis there are a few degrees of freedom in the choice of silane and olefin. For example, amyltriethoxysilane can be made using trichlorosilane or triethoxysilane in the hydrosilation step. But the practical options are often rather few, and our principal freedom is in the choice of

reaction conditions. The most important of these is the catalyst. Because of this we must know what each type of catalyst can and cannot do. This aspect is of considerable consequence in understanding the science of hydrosilation.

Uncatalyzed thermal reactions are feasible, and are practical with simple olefins[1,15]. At 250–350°C for alkyl- or chlorosilanes, or at 120°C for silane itself[16] the reaction takes several hours; yields obtained are from 50 to 95 per cent. Addition is largely anti-Markownikoff, though substitution on secondary carbons has been reported[17]. Cracking and rearrangement lead to by-products. Telomerization can be a significant factor[3], as shown below:

$$HSiCl_3 + C_2H_4 \xrightarrow[35\text{–}85\ kg./cm^2]{300\text{–}320°C}$$

	mole %
$HSiCl_3$	6
$C_2H_5SiCl_3$	38
$C_4H_9SiCl_3$	20
$C_6H_{13}SiCl_3$	6
$C_8H_{17}SiCl_3$ and $C_{10}H_{21}SiCl_3$	3

Ethylene gives ethyl, butyl, hexyl, octyl and decylsilanes, and the total proportion of telomers is quite large.

Reversibility of a sort is indicated by the report that at 650° amyltrichlorosilane gives pentene-1 and trichlorosilane[18]. I do not know of any evidence that hydrosilation is a clearly reversible equilibrium.

Aluminium chloride added to the reaction mixture does not appear to speed up the reaction, but it does result in redistribution. Dialkyldichlorosilanes can be made from trichlorosilane under these conditions[19].

If a few mole per cent of acetyl or benzoyl peroxide is added to the reaction mixture, reaction occurs at about 100°C. Addition is anti-Markownikoff, as in the thermal reactions. Telomerization and polymerization are strong competitive reactions. The peroxide-initiated processes seem to be more influenced than the thermal reactions, as far as reaction rate is concerned, by the substituents on the silicon. Good yields are obtained with trichlorosilane, but not with methyldichlorosilane[20]. It was said, eight years ago, that trichlorosilane was the only abundant silane which gave good yields under these conditions[12], and I believe this statement still holds good.

Other free-radical initiators such as peresters[21], ultraviolet light[22], γ-rays[23] and azobisisobutyronitrile[24] produce similar effects. As a class, the free-radical initiators are useful for adding trichlorosilane to simple olefins when milder reaction conditions are required than are needed for thermal reactions. They are not satisfactory with easily polymerized olefins nor with highly alkylated silanes. Metals affect the creation of useful free radicals. Iron and lead have been reported to inhibit peroxide-catalyzed reactions[25]. Tin was found to be a promoter but there was some question about the reproducibility of this effect. It is claimed that the azo initiators are less affected by metals and so can be used in metallic containers[24].

The use of metallic catalysts goes back to the very early history of hydrosilation[3, 5]. The metals of Periodic Group 8 are especially useful[12, 26–28].

Each of the nine metals in this group, except osmium, has been shown to have some catalytic activity in hydrosilation. Platinum is active in many of its chemical compounds. Iron, cobalt, and nickel are most active as carbonyls. The activity of the catalyst varies widely. This applies both to rate, and to the position of attachment of silicon to the organic molecule. Palladium may behave entirely differently from platinum. A homogeneous catalyst such as a soluble complex platinum compound can behave differently from metallic platinum. In addition, platinum-on-charcoal does not act the same way as platinum-on-alumina. It could, therefore, be said that what is true about any specific catalyst is not necessarily true of any other in this group. Also, the differences are sometimes so great that they seem to be differences of kind rather than degree.

The platinum catalysts fill some of the needs left by the shortcomings of peroxides. They can be used with acrylates and other olefins that polymerize with peroxides. They can be used with alkylsilanes that do not react well with peroxides. Their cost is high, about $450/g mole but this is compensated by their great activity. It is sometimes cheaper to use platinum than peroxides or bases.

Platinum has faults, however. It tends to become fatigued and lose activity. Many things act as poisons. If the only remedy is to use more platinum the cost can get rather high. Platinum catalyzes side-reactions, and these can be troublesome. Induction periods are variable and unpredictable, and as the scale of operations gets larger, the hazards created by reactions that do not start in the expected way become greater.

Some rate studies were published by Grigor'eva and Reikhsfel'd[7] in 1964. These workers used siloxane polymers as the silanes and reported that the data fit into the first order kinetics. The rate constants for the addition to methyl methacrylate varied somewhat with the nature of the polymer, while those for α-methylstyrene did not. This was attributed to CO—SiH association. The reactions with α-methylstyrene had higher rate constants and lower activation energies than those with methyl methacrylate. Activation energies were 8 and 20 kcal, which are of the same order of magnitude as those found for base-catalyzed hydrolysis of trialkylsilanes[29].

So far as I know such data are not available for monomer–monomer additions. Chalk and Harrod[30] pointed out one reason for this lack of information. At the low concentration of catalyst (about 10^{-6} molar), at which rates become low enough to study isothermal reactions, impurity interference dominates the rate of reaction. Problems like this one can be solved. In the Russian work[7] the reactions were carried out in dilute solutions, which would dampen the thermal effect.

A well recognized way of avoiding problems due to inhibition by trace impurities is to run competitive reactions to compare rates[31]. Several investigators tried this, using one mole of each of two silanes and a total of one mole of the olefin[32–34]. Differences in reaction rates are reflected in differences in yields. Three things emerge from this work: (*i*) the differences were not large; yields were often nearly equal, and differed at most by a ratio of 5 to 2 in the series run; (*ii*) the order of reactivity of the silanes changed from one substrate-catalyst to another; and (*iii*) the silanes which had been unreactive when used separately became reactive in the presence

of the competing silane. This last point, of course, makes the whole approach hard to evaluate.

In one review of this situation it was concluded that the difference in activity of silanes could be explained on the basis of inductive and steric effects[35]. We usually try to relate rate to such effects by equations such as those suggested by Taft[36–38] (*Table 3*).

Table 3. Inductive and steric influences on reaction rate

$$X_3SiH + CH_2{=}CHR \xrightarrow{k} X_3SiCH_2CH_2R$$

$$\log (k/k_0) = \rho\sigma_I + \delta E_S$$

k_0 = rate constant for unsubstituted compound (X is H)
k = rate constant using substituted silane
σ_I = parameter representing polar effects of substituents
ρ = parameter representing sensitivity of ratio to polar effects
E_S = parameter representing steric effects
δ = parameter analogous to ρ.

According to these equations in a series of reactions involving different kinds of X, such as chlorine and methyl, the rate of each specific reaction can be predicted from the sigma value for X on the silane. These sigma values are typical of the substituent and are collected from various types of reactions[38]. For organic reactions in general there is a linear relationship between rate and sigma. The slope of the line for any particular olefin and catalyst is called rho. Until good values for rate constants (k) or ratios of these constants are known it will be hard to judge how well this type of relationship holds here.

In replacing the chlorines on trichlorosilane by methyl groups, sigma decreases by 0·52 units for each substitution. The differences in reaction rates appear to be of the order of 20 per cent for such a change. E_S varies in the same direction as σ_I here, so this cannot be looked to for a balancing effect. The sign of the rho changes from one olefin–catalyst combination to another. On the whole rho seems to have been small for the few series tried. This is another way of saying that the inductive effect does not have a major influence on the rate of platinum-catalyzed hydrosilation. Other factors have greater effects[39] such as the stability of intermediate complexes[30]; change from air to inert atmosphere can also be important[7].

The nature of the olefin also seems to have considerably more influence than that of the silane on reaction rate. Saam and Speier[40] ran a few competitive reactions, with pairs of olefins competing for insufficient silane. A change of only 0·07 units in the sigma values of the substituents on the olefin was associated with a tenfold change in the reaction rate. In the few examples we have, the value of rho for a series of substituted olefins appears to be about 60 times that of rho for a series of substituted silanes, using platinum catalysts.

This impression of the importance of substituents on the olefin is reinforced by a different type of experiment. Addition to allyl acrylate is reported to occur entirely on the allyl group, not on the acrylate[41] (equation 5).

$$HSi(OCH_3)_3 + CH_2{=}CH{-}CH_2OC(=O){-}CH{=}CH_2 \xrightarrow{Pt} (CH_3O)_3SiCH_2CH_2CH_2OC(=O)CH{=}CH_2 \quad (5)$$

The question as to where the silyl group becomes attached to the hydrocarbon chain is a complex one, much more so than in the case of peroxide or base-catalyzed additions. The principal reason for the complexity is that olefins can be isomerized in the presence of platinum catalysts and various promoters[42], which include silanes. The overall reaction thus involves shifting of the double bond along the carbon chain, and addition of the silane to the various isomeric olefins formed.

The result with simple alpha olefins is anti-Markownikoff addition to give exclusively terminal adducts. Olefins with internal double bonds also give only terminal addition with trichlorosilane[12] or dimethylfluorosilane[43], but with tetramethyldisiloxane addition occurs all along the chain. Thus hexene-3 gave mixtures of 1-, 2-, and 3- silylated hexanes[44, 45]. It is obvious that in this situation the relative rates of isomerization, and of the hydrosilation of each isomer, must control the composition of the product. It is the definition of the precise nature of this interaction that is troublesome. Chalk and Harrod[30] made some observations (*Table 4*) on the rates of

Table 4. Hydrosilation and isomerization of hexene-1[Pt (II) catalyst]

Silanes	*Rate of hydrosilation*	*Yield of hexylsilane* (%)	*Colour of solution*	*Isomerization of excess hexene*
$HSi(OCH)_3$ $HSi(OC_2H_5)_3$	Rapid	90	None	None
$HSiCl_3$ $C_2H_5SiHCl_2$ $C_6H_5SiHCl_2$	Slower	50 to 80	Darkened slowly	Extensive
$(C_2H_5)_3SiH$ $(C_6H_5CH_2)_3SiH$ $(C_6H_5)_3SiH$	Rapid then stopped	20	Dark brown at once	Rapid, then stopped

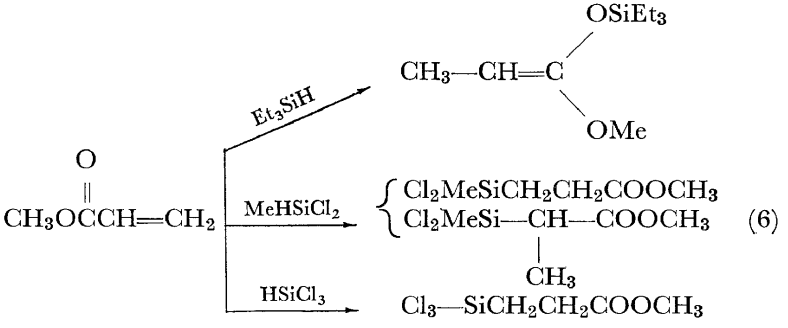
addition, isomerization, and catalyst deactivation that illustrate the point that the correlation between reaction rates and isomerization is not a close one. Rapid hydrosilation in one case was associated with isomerization, and in another not. Each class of silanes has its characteristic behaviour in this reaction, in terms of yield, colour, and degree of isomerization.

Phenylalkenes such as styrene or allylbenzene react to give only two products, one with silicon on the terminal carbon, the other with silicon on the benzylic carbon[43, 46–48]. The ratio of terminal to benzyl adduct depends

upon several factors: the nature of the substituents on the silane, the position of the double bond in the carbon chain, the substituents on the phenyl group, the presence or absence of certain solvents, and the ratio of silane to olefin in the mixture. It is strongly influenced toward terminal addition when tetrahydrofuran is used as solvent[49] and the silane is trichlorosilane, but with dimethylchlorosilane this effect is negligible[43].

Solvent effects have also been observed in the addition of methyldichlorosilane to ethyl acrylate[50]. Trichloroethylene reduced the ratio of α to β adduct. The greater the dilution, the greater was the effect. Tetrahydrofuran reduced the amount of α adduct, but only by leading to the production of polyacrylate, not by producing more β adduct. There was a surprisingly large proportion of α adduct observed when methyl acrylate was used in place of ethyl acrylate; this would not have been predicted from inductive effects, which do not change. It is much easier to rationalize the fact that methacrylates add silicon exclusively in the β position[51], for here the α methyl group exerts strong inductive and steric effects.

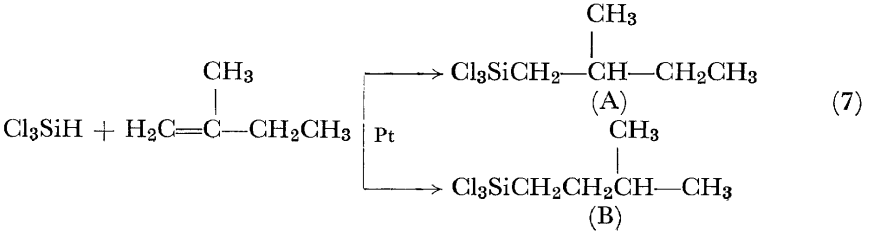
The composition of the silane also influences the mode of addition to methyl acrylate[52] (equation 6).



(6)

Here we can regard methyl acrylate as an oxygenated solvent, like tetrahydrofuran. We can then relate the exclusive formation of β-adduct with trichlorosilane, and the mixed α and β products with methyldichlorosilane, to parallel observations made with styrene and tetrahydrofuran.

Finally, changes in the catalyst support can influence orientation. Ponomarenko *et al.*[53] reported differences in orientation in addition to chlorotrifluorethylene using platinum-on-silica and platinum-on-carbon. In our laboratories some unpublished work by Ashby[54] better illustrates some differences between platinum-on-carbon and other platinum-type catalysts (equation 7):



(7)

The ratio B/A depends upon the olefin, catalyst, and silane as is clear from the data presented in *Table 5*.

Table 5. Effect of the nature and concentration of olefin, catalyst, and silane on the B/A ratio

Starting olefin	B/A Ratio			
	Silane: $HSiCl_3$ *Catalyst:* H_2PtCl_6 *Conc.* Pt: 5×10^{-5}	$HSiCl_3$ Pt/Al_2O_3 $2{\cdot}5\times10^{-4}$	$HSiCl_3$ Pt/C 7×10^{-4}	$MeHSiCl_2$ H_2PtCl_6 3×10^{-6}
C | C=C—C—C	1·04	1·62	0·01	0·0 fast 0·15 slow
C | C=C—C—C	7·33	13·3	∞	∞
C | C—C=C—C	1·62	1·62	0·06	2·33

Equation 7 illustrates the two types of terminal addition which occur when a silane is added to a methylbutene. The other two methylbutenes listed in *Table 5* give these two products, but in different ratios. Platinum-on-carbon gave addition without appreciable isomerization with the two terminal olefins. Use of the other two catalysts resulted in isomerization. The addition to the internal olefin, catalyzed by platinum on carbon, occurred almost entirely on the 14th day of refluxing, little reaction being observed in the first 13 days. It is also interesting that the ratio of adducts obtained from methyldichlorosilane and 2-methylbutene-1 changed slightly toward more isomerization, when the rate of addition of methyldichlorosilane to the reaction mixture was slowed down[40]. There are some indications in this group of experiments that are in agreement with the idea that slow hydrosilation is associated with isomerization. However, some of our data went counter to this trend. The overall relationships have been rationalized by Chalk and Harrod, as we shall see later.

Now let us turn to the base or complexing catalysts[55, 56]. These are principally useful for adding chlorosilanes to acrylonitrile to give beta cyanoethylchlorosilanes. They can also cause addition of trichlorosilane to isolated double and triple bonds[57]. They are much less active with alkylchlorosilanes, where special three-component basic catalysts are much more effective.

Yields in base-catalyzed cyanoethylation[8] are generally between 50 and 85 per cent. The reactions are, on the whole, rather slow, even with ten mole per cent catalyst. Not much has been published concerning by-products, but several reactions are known to occur, such as complex formation between chlorosilane and catalyst[55], and redistribution of the chlorosilane; telomerization[58] is to be expected.

No isothermal rate studies have been published, but many observations have been made on the effects of catalyst composition, silane, and olefin on yields. This is also true in the case of the three-component catalyst systems used by Bluestein. These are made of an amine, a diamine, and a copper

salt[59]. Bluestein[60] studied the effects of changing the amines, and the ratios of the catalyst components, on the yield of beta adduct obtained by refluxing acrylonitrile with methyldichlorosilane. The yields changed with the number and size of the alkyl groups on the amines, but not in any simple way. The yields also changed with the ratio of copper to nitrogen in the catalyst being good at ratios of 0·3 and 0·6, but negligible at ratios of 1 copper (or more) per nitrogen, as well as when copper was absent. No reasons have been advanced for the existence of an optimum ratio of copper to nitrogen in the catalyst.

Two other studies have been made of effects of changes in silane, olefin, and composition of Bluestein catalyst on yields of adducts in systems held at reflux[61, 62]. A typical reaction between acrylonitrile and methyldichlorosilane under these conditions starts at about 50°C. The temperature gradually increases to about 130°C over a period of 28 hours. With different silanes the starting and final reflux temperatures are different. Comparisons of yields of refluxed reaction mixtures are, therefore, not in any sense rate studies, though rate obviously is an important factor in determining the results. *Table 6* shows the results of one set of such experiments.

Table 6. Addition of chlorosilanes to acrylonitrile

Silane	DMF *Catalyst*	*Bluestein catalysts* (*Amines* + Cu_2Cl_2)					*Taft* $\Sigma\sigma_I$
		Using $(Et_2NCH_2)_2$		*Using* $(Me_2NCH_2)_2$			
	Yield after 72 h *reflux* (%)	h	*yield* (%)	h	*yield* (%)	*yield*/h (%)	
$HSiCl_3$	72	—	—	0·3	68	227	1·41
$\varphi HSiCl_2$	0	14·5	56	14·5	65·2	4·5	1·04
$MeHSiCl_2$	0	44	20	34·5	67	2·0	0·89
φ_2HSiCl	0	32	0	22	39·2	1·8	0·67
$Me\varphi HSiCl$	0	—	—	49	26·4	0·5	0·52
Me_2HSiCl	0	—	—	52	0	0	0·37

As can be seen from *Table 6* a simple base, dimethylformamide (DMF), catalyzes the addition of trichlorosilane to acrylonitrile. The alkyl and aryl silanes do not react using dimethylformamide, but do react, at varying rates, with Bluestein type catalysts. Tetramethylethylenediamine is superior to the corresponding tetraethylamine. This agrees with Bluestein's observations. The rate of reaction correlates with the inductive index. It was Chiang *et al.*[61] who pointed this out. The correlation may be fortuitous in part; for example the higher boiling point of phenyldichlorosilane would lead to apparent greater reactivity compared to methyldichlorosilane. In fact we have found that triethoxysilane, with a Taft index of 0·81, is not active under these conditions[54].

Chiang also varied the substituents on the olefin, using Bluestein type catalyst (*Table 7*).

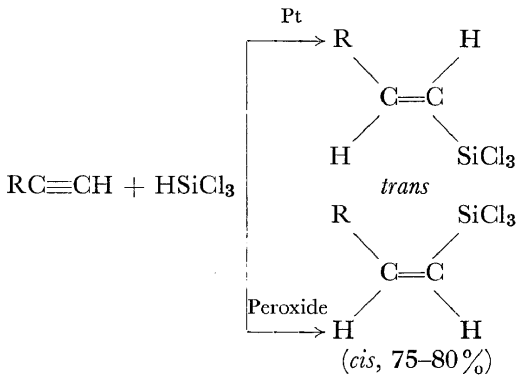
While differences in reactivity are certainly indicated, the suggested correlation of yield with inductive effect would require auxiliary explanations to be convincing.

Table 7. Addition of trichlorosilane to olefins $R_1R_2C{=}CH_2$

R_1	R_2	*Inductive index*	*Taft* $\Sigma\sigma_I$	*Yield* (%)
COOEt	CN	338·2	0·92	None
H	CN	169·1	0·58	80
CH_3	CN	160·1	0·53	15
C_2H_5	CN	156·8	0·53	12
H	CH_2CN	53·6	0·18	0

The addition of trichlorosilane to non-polar olefins in the presence of amines in nitrile solvents is reported to take place at the double bond, without isomerization[57]. In this respect the amines resemble peroxides more than they do platinum. This reaction is applicable to trichlorosilane, but not to alkylchlorosilanes. We have found that methyldichlorosilane does not add at all to hexene-1 in the presence of nitrile solvents, even when Bluestein catalyst is used[54].

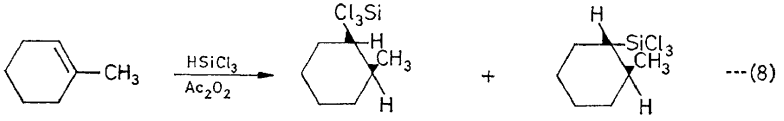
The stereochemistry of addition to acetylenes has been studied for each type of catalyst. Benkeser and his students developed most of the information we have on this[63, 64]. They found that peroxides induced largely *trans* addition to give *cis* adducts, while platinum or chloroplatinic acid induced *cis* addition to give *trans* products, as illustrated below:



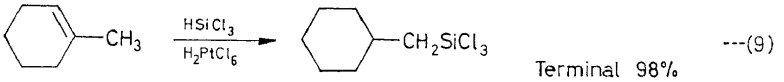
It was of particular interest that both heterogeneous and homogeneous platinum catalysts induced *cis* approach, resulting in the *trans* product. This could mean that both forms of platinum come to one common catalytic form. This is a plausible explanation but it not necessarily so. This difference between peroxide and platinum is one of the indications that platinum-catalyzed additions are not free-radical in nature, since peroxide initiated reactions are.

Pike[57] found that base-catalyzed addition of trichlorosilane to acetylenes gave mostly di-adducts, with some *trans* products. Dr. Benkeser has pointed out to us, however, that the presence of *trans* isomer in the system may actually be due to the rapid consumption of *cis* to form the disilylethane adduct[65]. If this is so, then the four-centre transition state invoked by Pike to explain the *cis* approach (*trans* product) is no longer helpful, and base-catalyzed addition again seems nearer to peroxide than to platinum in regard to orientation.

The stereochemistry of addition to methylcyclohexenes was studied by Ryan and Speier[66] and by Selin and West[67]. With peroxides, addition to the double bond occurs and gives two products (equations 8 and 9).



cis 85% *trans* 15% ---(8)



Terminal 98% ---(9)

Cis adduct with peroxide corresponds to that obtained with acetylenes. With platinum, isomerization and terminal addition take precedence over ring addition[68] thus obscuring the relationship. When this reaction was slowed down by the use of 1-methyl-d_3-cyclohexene, *trans* ring adduct was obtained. This is in agreement with acetylene results. Thermal reaction gave all three products[67]. Selin and West[67] inferred from this that both free-radical and ionic mechanisms were involved.

MECHANISMS

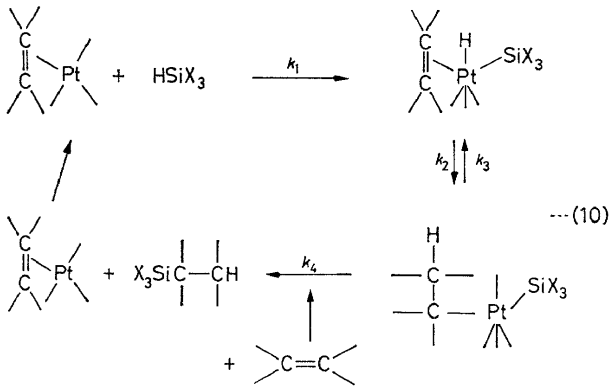
Concerning mechanisms, there is not much question about the additions initiated by peroxides or radiation. The facts seem to fit the free-radical mechanism proposed by Sommer *et al.*[2] in 1947.

Platinum-catalyzed reactions are quite a different matter. It is not even easy to decide whether these catalysts are really homogeneous, or really heterogeneous, or both. The systems are full of interactions among reagents, solvents, promoters, and poisons. Isomerization of the olefin is so entangled with addition that the two reactions cannot be treated separately. Traces of catalyst produce an enormous effect, so a chain mechanism must be involved. More catalyst increases the rate, but we do not know to what extent. The variable induction period indicates that addition is not a simple one-step process[69]. There is till some uncertainty about whether free radicals are involved[10,70].

It is difficult to explain some observations satisfactorily. An example is the exclusive formation of terminal and benzyl adducts[43] from 4-phenylbutene-1. There are many others, such as the rearrangements of allyl compounds[14].

Addition of hydride from the silane seems to precede the isomerization of the olefin[44]. Perhaps this takes place by actual addition and elimination of a metal hydride[30]. Chalk and Harrod suggested a sequence such as the one given in equation (10).

A platinum-olefin complex reacts with a silane, rearranges, and reacts with more olefin to give the alkyl silane and regenerate the complex. Chalk and Harrod pointed out that if $k_4 > k_3$ no isomerization would be expected, but if $k_3 > k_4$ isomerization will occur. Since platinum-olefin and other platinum-organic complexes are excellent catalysts for hydrosilation, this is a reasonable picture.

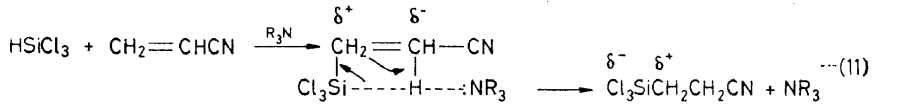


Ryan and Speier[66] on the other hand assumed formation of silane–platinum complexes to explain interchanges of hydrogen and deuterium. These complexes were then assumed to add to the olefin to form larger complexes not unlike those suggested by Chalk. Selin and West[67], and Benkeser and Hickner[63] also concluded that the addition occurred through olefin-catalyst or three-component intermediates.

More recent work by Harrod and Chalk with partly deuterated olefins showed that 1–3 shifts of hydrogen occur[71]. They find this hard to rationalize in terms of alkyl-hydride adducts. They therefore now lean toward the view that isomerization is intramolecular[72]. It certainly occurs with promoters other than silanes[73–76]. I think there should be some uncertainty in our minds about what part the silane plays here[40, 44, 66].

Base catalysis is not well understood, either. Here again we see a strange mixture of catalysts lumped into one class. Amines and amides which are extremely weak bases, as well as phosphines and other compounds of Group 5 are active[56]. The key to their activity is unknown. It does not seem to be base strength. The ability to complex with silanes may be involved[55]. However, we do not have enough information to judge. Certainly there are opportunities for the formation of complexes. This would be especially true of the three-component Bluestein catalysts. The formation and dissociation of complexes must somehow be involved in the addition reaction. It was originally suggested[8] that hydrogen acquires a partial positive charge and is attracted to the negative carbon next to the nitrile[77]. Pike and Schank[78] suggested a four-centre transition state (equation 11). This was to explain *cis* approach of the silane to acetylenes. As I mentioned before there is some doubt as to what really needs to be explained. However, as a whole this is representative of what is commonly accepted for this reaction. In equation (11) the silane is assumed to be polarized by the amine, with the hydrogen taking on a partial positive charge. There would be less tendency to do this with methylsilanes. The reduced activity of methyldichlorosilane is, therefore, compatible with this hypothesis. How diamine–copper salt mixtures compensate for this has not been explained.

It is interesting to note that when a Lewis acid, e.g. boron trichloride, is used instead of an amine, the reverse addition occurs and α-cyanoethyl-



methyldichlorosilane is obtained in good yield[62]. This indicates that polarizability of silicon–hydrogen bonds is the key to the situation.

In any or all of these addition reactions it is reasonable to look for analogies in other systems for help. For example it was pointed out several years ago that platinum-catalyzed hydrosilations resemble hydrogenation, the OXO reaction, and Ziegler catalysis[30,79]. Advances in these fields should, therefore, be looked up to.

We might also look at the addition of other hydrides to olefins. Unfortunately it seems that less is known about these than about silane additions. Hydrides of boron[80], germanium, tin[81, 82], and phosphorus[83] add more easily to olefins than the silanes. All tend to add anti-Markownikoff. Hydroboration and phosphination[84] are reversible, whereas hydrosilation in the ordinary sense is not. Addition of boranes to methylcyclohexene produces *trans* adducts, remindful of platinum-catalyzed hydrosilations. Addition to acetylenes gives *cis* adducts, as do peroxide-catalyzed hydrosilations. Since this group of hydrides includes those elements which are both more and less negative than silicon, it appears that neither rate nor orientation is simply related to the polarity of the metal–hydrogen bond.

An important consideration in summing up the overall situation is the reliability of the individual pieces of data. Several cases of conflicting evidence, or of correction of earlier work, are known. This is to be expected as procedures improve. However, several things contribute to make me question the firmness of our knowledge: (*i*) Many "facts" have been established on the basis of single runs; (*ii*) reproducibility is questionable and is affected by many factors; and (*iii*) the quality of raw materials is seldom defined accurately. Those workers who had the occasion to repeat hydrosilations would have realized the extent to which variations can occur. In spite of the excellent work already done, much careful work remains to be done before the factual bases for theories of hydrosilation can be established.

In summary, hydrosilation includes a group of reactions with a common feature—the addition of a silicon–hydrogen pair across an unsaturated carbon–carbon system. It appears that the easily polarizable silicon-hydrogen bond can be cleaved either homolytically, or heterolytically in either sense, depending on the catalyst used. The reagents involved are highly active, and numerous side-reactions occur. In spite of these side-reactions and other problems, this group of processes has become the method of choice for synthesizing organofunctional silicon compounds. It will take another great discovery to dislodge it from this position.

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