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REACTIONS OF ALKENYLPOLYSILANES CATALYZED BY SOME NOBLE METAL SALTS

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SUMMARY

Vinyl derivatives of disilane and trisilane were found to undergo nucleophilic cleavage of the silicon–silicon bond very easily in the presence of chlorides of certain noble metals. The ease of ethanolysis of the silicon–silicon bond and the course of the subsequent reactions of the cleavage fragments were dependent upon the nature of metals of catalysts. The ethanolysis of vinylpentamethyldisilane (I) in the presence of platinum salts mainly gave hydrosilation products ($Me_5Si_2CH_2CH_2SiMe_3$ and $EtOMe_2SiCH_2CH_2SiMe_3$), whilst hydrogenation products (Me_5Si_2Et and $EtOMe_2SiEt$) were formed as the main products, along with others, from the ethanolysis of (I) catalyzed by palladium(II) chloride. Allylpentamethyldisilane (XII) underwent chloroplatinic acid-catalyzed ethanolysis much slower than (I), while *cis*- and *trans*-propenylpentamethyldisilane, (XIII) and (XIV), did as easily as (I). With palladium(II) chloride as catalyst, (XII) also was cleaved very readily probably via its initial isomerization to (XIII) and (XIV). A mechanism is proposed for this type of facile nucleophilic cleavage of the silicon–silicon bond α to an olefinic linkage.

INTRODUCTION

During our studies on chloroplatinic acid-catalyzed hydrosilation reactions we found that the addition of methyldichlorosilane to vinylpentamethyldisilane (I) followed by treatment with methylmagnesium bromide produced a small amount of 1,2-bis(trimethylsilyl)ethane (II), in addition to the expected 1-(pentamethyldisilanyl)-2-(trimethylsilyl)ethane (III):

$$\underset{\text{(I)}}{\mathrm{Me_3SiSiMe_2CH{=}CH_2}} \xrightarrow[\mathrm{H_2PtCl_6\cdot 6\,H_2O}]{\mathrm{MeSiHCl_2}} \xrightarrow{\mathrm{MeMgBr}}$$

$$\underset{\text{(II)}}{\mathrm{Me_3SiCH_2CH_2SiMe_3}} + \underset{\text{(III)}}{\mathrm{Me_3SiSiMe_2CH_2CH_2SiMe_3}} \qquad (1)$$

This unexpected formation of (II) prompted us to investigate in some detail the behavior of certain alkenyl derivatives of disilane and trisilane under catalysis by some noble metal salts.

RESULTS AND DISCUSSION

Reactions of vinylpentamethyldisilane with various metal salts

In order to learn whether or not vinylpentamethyldisilane (I) undergoes cleavage by chloroplatinic acid in the absence of a hydrochlorosilane, and, if so, to identify the products, we stirred (I) with 5 mole per cent of $H_2PtCl_6 \cdot 6\ H_2O$ at room temperature and followed the progress of reaction by vapor phase chromatography (VPC). During the stirring, metallic platinum deposited as a black tarry precipitate. VPC analysis of the organic layer in the reaction vessel revealed that 1-(pentamethyldisilanyl)-2-(trimethylsilyl)ethane (III) was formed as the main product along with five ill-defined compounds with the siloxane linkage. After 10 h, no starting substance remained. The formation of (III) as the major product suggests that the vinyldisilane (I) underwent cleavage by hydrogen chloride and/or water, coming from the chloroplatinic acid, to lead to incipient formation of trimethylsilane [eqn. (2)] which added to the olefin (I) effectively [eqn. (3)]:

$$\underset{\text{(I)}}{Me_5Si_2CH{=}CH_2} + HX \xrightarrow{[Pt]} Me_3SiH + XMe_2SiCH{=}CH_2 \quad (X{=}Cl,\ OH) \tag{2}$$

$$Me_5Si_2CH{=}CH_2 + Me_3SiH \xrightarrow{[Pt]} \underset{\text{(III)}}{Me_5Si_2CH_2CH_2SiMe_3} \tag{3}$$

Trimethylsilane was in fact found to add to the vinyl disilane (I) in the presence of a platinum catalyst with great ease under relatively mild conditions (45°, 20 h) to give (III) in almost quantitative yield.

The observed formation of a small amount of compound (II) through the sequence of reactions (1), therefore, can be interpreted as a result of the addition of a silicon hydride (dimethylchlorosilane or trimethylsilane) to $ClMe_2SiCH{=}CH_2$ produced according to eqn. (2), followed by methylation of the silicon–chlorine bonds by the Grignard reagent.

The great ease with which the silicon–silicon bond of (I) is cleaved can best be understood if one considers that an olefin–metal π-complex is first formed between the vinyldisilane and chloroplatinic acid, and thus that there is a decrease in the electron density on the silicon atom α to the olefinic bond, so that this silicon atom becomes vulnerable to nucleophilic attack by chloride ions and/or water molecules.

As expected from such reasoning, vinyldisilane (I) underwent cleavage much more easily in ethanol in the presence of the same catalyst, giving 1-(ethoxydimethylsilyl)-2-(trimethylsilyl)ethane (IV) as well as (III) in very high yields on the basis of the trimethylsilyl group arising from cleavage. On the other hand, non-olefinic hexamethyldisilane and octamethyltrisilane were found to be completely inert under similar conditions.

$$Me_3SiSiMe_2CH{=}CH_2 + EtOH \xrightarrow{H_2PtCl_6 \cdot 6\ H_2O} \underset{\text{(III)}}{Me_5Si_2CH_2CH_2SiMe_3} + \underset{\text{(IV)}}{EtOMe_2SiCH_2CH_2SiMe_3}$$

$$\mathrm{Me(SiMe_2)_nMe + EtOH \xrightarrow{H_2PtCl_6 \cdot 6\,H_2O} no\ reaction}$$
$$(n=2 \text{ and } 3)$$

Since it has been well known that various compounds of noble metals are capable of coordinating to olefins, we examined also the reactions of vinyldisilane (I) with ethanol in the presence of several noble metal salts other than chloroplatinic acid.

When the vinyldisilane (I) was stirred with palladium(II) chloride at room temperature, no appreciable reaction took place although the chloride in part dissolved soon into the disilane to give a brown solution. However, the moment ethanol was introduced dropwise, strongly exothermic reaction was found to occur with precipitation of metallic palladium. The reaction of (I) with a catalytic amount of palladium(II) chloride in ethanol at a temperature near 0° was completed within a very short time, especially when excess ethanol was employed, and gave several products, among which trimethylethoxysilane, vinyldimethylethoxysilane (V), ethyldimethylethoxysilane (VI), and pentamethylethyldisilane (VII) were major products. In addition, sometimes a small amount of hexamethyldisiloxane also was obtained, probably arising from trimethylethoxysilane through a secondary reaction. However, neither trimethylsilane nor hydrosilation products were detected even by careful

$$\underset{\text{(I)}}{\mathrm{Me_3SiSiMe_2CH{=}CH_2}} \xrightarrow[\mathrm{EtOH}]{\mathrm{PdCl_2}} \mathrm{Me_3SiOEt} + \underset{\text{(V)}}{\mathrm{CH_2{=}CHSiMe_2OEt}}$$
$$+ \underset{\text{(VI)}}{\mathrm{EtOMe_2SiEt}} + \underset{\text{(VII)}}{\mathrm{Me_5Si_2Et}}$$

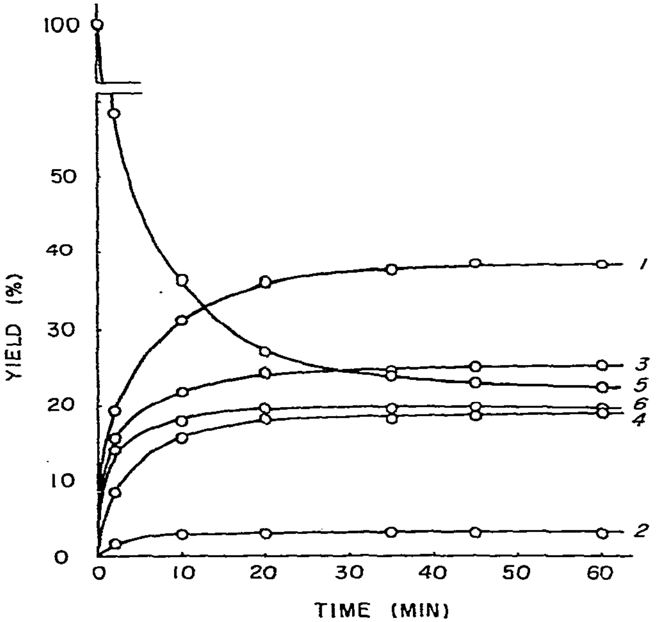


Fig. 1. Reaction of vinylpentamethyldisilane (I) with an equimolar quantity of ethanol in the presence of 5 mole per cent of palladium(II) chloride at 0°. 1, Me_3SiOEt; 2, $(Me_3Si)_2O$; 3, $EtOMe_2SiCH{=}CH_2$ (V); 4, $EtOMe_2SiEt$ (VI); 5, (I); 6, Me_5Si_2Et (VII).

VPC analysis. Fig. 1 illustrates an observed product distribution *vs.* time for the reaction involving the vinyldisilane (I) and ethanol in the molar ratio of 1 : 1 in the presence of 5 mole per cent of palladium(II) chloride.

Doubtless, the cleavage of the silicon–silicon bond in this case occurred in an analogous way to that discussed above, *i.e.*, by a mechanism involving initial formation of an olefin–metal π-complex and the nucleophilic attack of ethanol on the α-silicon atom, leading to production of vinyldimethylethoxysilane (V) and trimethylsilane. The absence of trimethylsilane in the products and production of two ethylsilicon derivatives, (VI) and (VII), as well as trimethylethoxysilane can be best understood if one assumes that the trimethylsilane immediately underwent ethanolysis catalyzed by palladium with liberation of hydrogen[1], which was efficiently transferred to the olefins (V) and (I) over this catalyst.

The ready cleavage of vinyldisilane (I) in ethanol could also be effected by using platinum (II) chloride, platinum (IV) chloride, rhodium (III) chloride, and ruthenium(III) chloride as catalysts. Table 1 lists the results obtained and eqns. (4)–(7) summarize the possible processes involved.

TABLE 1

REACTION OF VINYLPENTAMETHYLDISILANE (I) WITH ETHANOL CATALYZED BY NOBLE METAL SALTS

Catalyst	Type of Reaction[a]			
	Cleavage of Si–Si bond[b]	Cleavage of Si–H bond[c]	Hydrogenation[d]	Hydrosilation[e]
$H_2PtCl_6 \cdot 6\,H_2O$	◎	○	△	◎
$PtCl_2$	◎	○	△	◎
$PtCl_4$	◎	△	△	◎
$PdCl_2$	◎	◎	◎	×
$RhCl_3$	○	○	○	○
$RuCl_3 \cdot H_2O$	○	○	○	△

[a] The symboles indicate the extent to which the specified reactions took place: ◎, large; ○, some; △, small; ×, no. [b] An observed product is $EtOMe_2SiCH{=}CH_2$ (V) (see eqn. 4). [c] An observed product is Me_3SiOEt (see eqn. 5). [d] Products are $EtOMe_2SiEt$ (VI) and Me_5Si_2Et (VII) (see eqn. 6). [e] Products are $EtOMe_2SiCH_2CH_2SiMe_3$ (IV) and $Me_5Si_2CH_2CH_2SiMe_3$ (III) (see eqn. 7).

$$\underset{\text{(I)}}{Me_3SiSiMe_2CH{=}CH_2} + EtOH \xrightarrow{\text{catalyst}} Me_3SiH + \underset{\text{(V)}}{EtOMe_2SiCH{=}CH_2} \qquad (4)$$

$$Me_3SiH + EtOH \xrightarrow{\text{catalyst}} Me_3SiOEt + H_2 \qquad (5)$$

$$RMe_2SiCH{=}CH_2 + H_2 \xrightarrow{\text{catalyst}} \underset{\text{(VI, R=EtO; VII, R=Me}_3\text{Si)}}{RMe_2SiCH_2CH_3}$$

$$RMe_2SiCH{=}CH_2 + HSiMe_3 \xrightarrow{\text{catalyst}} \underset{\text{(IV, R=EtO; III, R=Me}_3\text{Si)}}{RMe_2SiCH_2CH_2SiMe_3} \qquad (7)$$

In no cases, however, traces of trimethylsilane and hydrogen in the free state were detected, the fact suggesting that these substances might undergo further reactions immediately after their formation, as mentioned above, or the two elements of each of these substances might add across the double bond over the catalyst before forming stable molecules.

Interestingly, the readiness of ethanolysis of the silicon–silicon bond and the direction of subsequent reactions of cleavage fragments are strongly dependent upon the nature of the metals used as catalysts. Qualitatively speaking, the catalytic activities of metals for reactions (4)–(7) decreased as follows: (*i*) for ethanolysis of the silicon–silicon bond [eqn. (4)], Pd, Pt > Rh ≫ Ru; (*ii*) for ethanolysis of the silicon–hydrogen bond[1] [eqn. (5)], Pd > Rh > Pt, Ru; (*iii*) for hydrogenation [eqn. (6)], Pd > Rh, Ru ≫ Pt; and (*iv*) for hydrosilation [eqn. (7)], Pt ≫ Rh > Ru. No essential difference in catalytic effectiveness was found among the platinum compounds. The findings that all the platinum salts catalyzed hydrosilation most specifically, rhodium and ruthenium compounds were also effective for hydrosilation, whereas palladium salts were completely ineffective, which, on the other hand, acted as the most active catalysts for hydrogenation, are quite in agreement with those made by Speier *et al.*[2], and by Chalk and Harrod[3] in their studies on hydrosilation.

Palladium(II) chloride-catalyzed ethanolysis of 1-*vinylheptamethyltrisilane*

1-Vinylheptamethyltrisilane (VIII) also was found to undergo cleavage very readily when stirred with a catalytic amount of palladium(II) chloride in ethanol at a temperature near 0° to give trimethylethoxysilane, dimethyldiethoxysilane, vinyldimethylethoxysilane (V), ethyldimethylethoxysilane (VI), pentamethylethoxydisilane (IX), and 1-ethylheptamethyltrisilane (X). An observed product distribution *vs.* time is illustrated in Fig. 2.

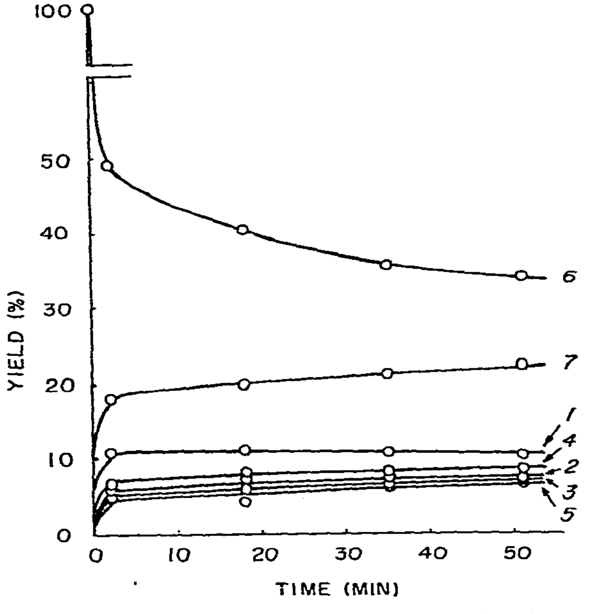


Fig. 2. Reaction of 1-vinylheptamethyltrisilane (VIII) with an equimolar quantity of ethanol in the presence of 5 mole per cent of palladium(II) chloride at 0°. 1, Me_3SiOEt; 2, $EtOMe_2SiCH{=}CH_2$ (V); 3, $EtOMe_2SiEt$ (VI); 4, $Me_2Si(OEt)_2$; 5, Me_5Si_2OEt (IX); 6, (VIII); 7, Me_7Si_3Et (X).

$$\underset{\text{(VIII)}}{Me_3SiSiMe_2SiMe_2CH{=}CH_2} \xrightarrow[EtOH]{PdCl_2} Me_3SiOEt + Me_2Si(OEt)_2 +$$

$$\underset{\text{(V)}}{CH_2{=}CHMe_2SiOEt} + \underset{\text{(VI)}}{EtMe_2SiOEt} + \underset{\text{(IX)}}{Me_5Si_2OEt} + \underset{\text{(X)}}{Me_5Si_2SiMe_2Et}$$

No products such as $CH_2{=}CHSiMe_2SiMe_2OEt$ and $EtMe_2SiSiMe_2OEt$ arising from the cleavage of the silicon–silicon bond β to the vinyl group, with the silicon–silicon bond in α position remaining intact, were formed. These results are consistent with the view mentioned above that the silicon atom adjacent to the olefinic bond becomes sensitive to nucleophilic attack upon complexation with metal. Here also, no traces of the silicon hydride, $Me_3SiSiMe_2H$ (XI), were detected in the product. This intermediate, immediately after its formation, must have undergone palladium-catalyzed ethanolysis proceeding concurrently in two different directions: (*a*) ethanolysis without silicon–silicon cleavage, leading to formation of ethoxypentamethyldisilane (IX); and (*b*) ethanolysis with cleavage of the silicon–silicon bond, leading to formation of dimethyldiethoxysilane and trimethylethoxysilane.

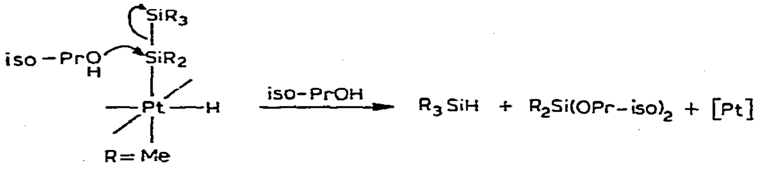
$$\underset{\text{(XI)}}{Me_3SiSiMe_2H} \xrightarrow[{[Pd]}]{EtOH} \begin{cases} \underset{\text{(IX)}}{Me_3SiSiMe_2OEt} + H_2 & \text{(8a)} \\ Me_3SiOEt + Me_2Si(OEt)_2 + 2\,H_2 & \text{(8b)} \end{cases}$$

In fact, pentamethyldisilane (XI), previously prepared, was found to undergo rapid cleavage in ethanol in the presence of catalytic amounts of palladium(II) chloride according to eqn. (8b), whereas ethoxypentamethyldisilane (IX), once formed, was completely inert under the same conditions.

The observed ethylsilicon derivatives (VI) and (X) again must have resulted from the palladium-catalyzed addition of hydrogen [produced incipiently during the ethanolysis, eqns. (8a) and (8b)] to the olefins present in the reaction system.

In connection with the facile cleavage of pentamethyldisilane (XI), it is of interest to refer to the observation by Urenovitch and West[4] that although this hydride underwent the addition to 1-octene under free radical conditions in the normal way to give n-octylpentamethyldisilane in 78% yield, it was only converted into trimethylsilane and isopropoxysilicon compounds and yielded only traces of the expected adduct under conditions of chloroplatinic acid-catalyzed hydrosilation. The mechanism for this cleavage, however, was not discussed by these authors.

According to the current mechanistic aspect of the platinum-catalyzed hydrosilation[3], it seems probable that an intermediate (or transition state) with a platinum–silicon bond is formed, with which the olefin and hydrogen may also be complexed. The cleavage of pentamethyldisilane (XI) may be rationalized by considering nucleophilic attack of isopropyl alcohol, which was used for preparing the catalyst solution, on the silicon atom that has become attached to platinum and thus susceptible to nucleophilic attack.



This proposed mechanism may, at least in part, be supported by demonstrating that pentamethyldisilane (XI) undergoes hydrosilation in the normal way in the presence of a certain platinum catalyst system free from any protic solvent. We could do this by accomplishing successful addition of the hydride (XI) to vinyltrimethylsilane in the presence of *trans*-dichloro(ethylene)(pyridine)platinum(II) as catalyst[5] in benzene. The expected 1-(pentamethyldisilanyl)-2-(trimethylsilyl)ethane (III) was isolated in 78% yield.

$$\underset{\text{(XI)}}{Me_3SiSiMe_2H} + CH_2{=}CHSiMe_3 \xrightarrow[\text{in } C_6H_6,\ 60°,\ 45\ h]{trans\text{-}[PtCl_2(C_2H_4)(C_5H_5N)]} \underset{\text{(III)}}{Me_5Si_2CH_2CH_2SiMe_3}$$

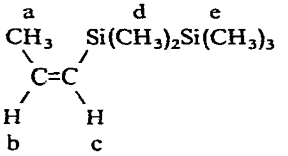
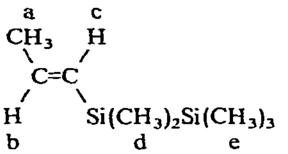
Reactions of allyl- and propenyldisilanes

In marked contrast to the vinyldisilane (I), allylpentamethyldisilane (XII) was found sluggish under the conditions of chloroplatinic acid-catalyzed ethanolysis. After 1-h reaction at room temperature, only 7.5 per cent cleavage of the silicon–silicon bond was observed to occur. On the other hand, an isomeric mixture of *cis*-propenylpentamethyldisilane (XIII) and *trans*-propenylpentamethyldisilane (XIV) underwent, after an about 5-min induction period, rapid and complete reaction under the same conditions. The observed lower reactivity of the allyldisilane, therefore, should be ascribed to its silicon–silicon linkage being located at the β, but not α, position to an olefinic bond, and is quite consistent with the above-mentioned view.

With palladium(II) chloride as the catalyst, the allyldisilane also was cleaved

TABLE 2

PHYSICAL PROPERTIES AND SPECTRAL DATA OF *cis*- AND *trans*-PROPENYLPENTAMETHYLDISILANE

		
B.p. (°C)	158–159	155–156
n_D^{20}	1.4512	1.4576
d_4^{20}	0.7703	0.7823
MR_D (calcd. 59.66)	59.77	60.04
NMR[a] [chemical shifts (δ ppm) and coupling constants (J, cps)]	a: a doublet ($J=7.2$) further split into a quartet with $J=1.4$ at 1.75 b: a sextet ($J=6.8$) at 6.36 c: a doublet ($J=13.9$) further split into quartets with $J=1.4$, respectively, at 5.42 d: a singlet at 0.18 e: a singlet at 0.09	a: a doublet ($J=4.8$) at 1.82 b: a pair of quartets ($J=4.8$) at 6.15 and 5.84 c: a doublet ($J=18.7$) at 5.53 d: a singlet at 0.09 e: a singlet at 0.06
UV[b] [λ_{max}(mμ) in n-hexane]	225 ($\varepsilon=6200$)	220 ($\varepsilon=7800$)

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[a] The NMR spectral data reported herein are very similar to those reported by Seyferth *et al.* for *cis*- and *trans*-propenyltrimethylsilane (ref. 6). [b] The authors are grateful to Mr. A. Hosomi of our laboratory for the measurement of the spectra.

very easily in excess ethanol. After 2-min reaction at room temperature, it was found that 40 per cent of (XII) was converted into the cleavage and hydrogenation products and the remaining into an isomeric mixture of (XII), (XIII) and (XIV) in the molar ratio of 50.2 : 7.6 : 42.2, respectively. Whithin less than a 15-min period, all the alkenyldisilanes disappeared completely. These findings suggested that the cleavage of (XII) was preceded by its isomerization to the isomeric propenyldisilanes, and so we studied in some detail the behavior of each of these alkenyldisilanes toward an equimolar amount of ethanol in the presence of palladium(II) chloride.

Pure samples of the *cis*- and *trans*-propenyldisilane were obtained by preparative VPC from a mixture of both compounds [(XIII) : (XIV) = 65 : 35)] prepared through the reaction of propenylmagnesium bromide with chloropentamethyldisilane. Some of their physical properties and NMR and UV spectral data are listed in Table 2.

The ethanolysis of the *trans* isomer (XIV) catalyzed by palladium(II) chloride proceeded as readily as that of the vinyldisilane (I) and yielded trimethylethoxysilane, propylpentamethyldisilane (XV), propenyldimethylethoxysilane (XVI), and propyldimethylethoxysilane (XVII). With excess ethanol, the reaction came to an end in a very short period of time at room temperature and none of the isomeric alkenyldisilanes was present at all in the product. However, when the reaction was carried out with an equimolar amount of ethanol, it was found that after one hour 83% of (XIV) was converted into the cleavage and hydrogenation products, and the remaining was composed of the allyldisilane (XII) and isomeric propenyldisilanes (XIII) and (XIV) in the molar ratio of approximately 11 : 2 : 87. Fig. 3a illustrates a profile for the conversion of (XIV) into cleavage and hydrogenation products and the composition of isomeric alkenyldisilanes *vs.* time.

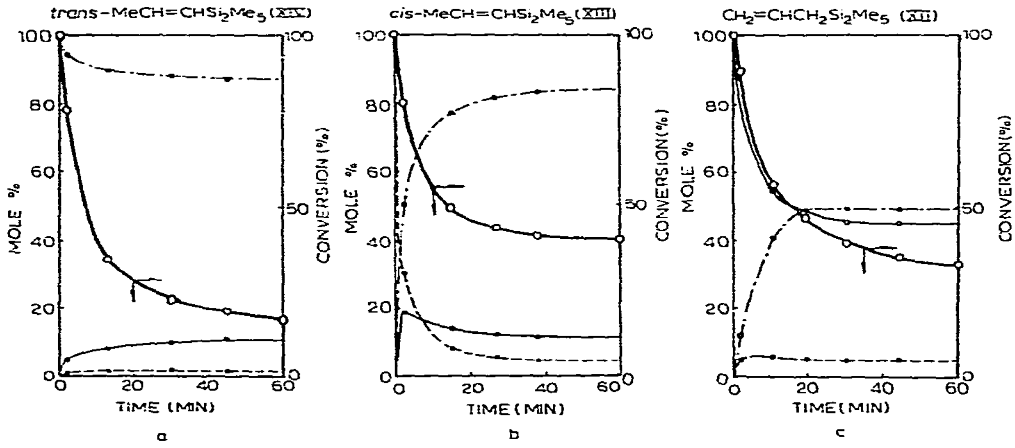

Fig. 3. Reaction of (a) *trans*-propenylpentamethyldisilane (XIV), (b) *cis*-propenylpentamethyldisilane (XIII), and (c) allylpentamethyldisilane (XII) with an equimolar quantity of ethanol in the presence of 5 mole per cent of palladium(II) chloride at room temperature: Conversion into cleavage and hydrogenation products, and isomerization of alkenyldisilanes. —o— Conversion; ——•——, (XII); ---•---, (XIII); —·—•—, (XIV).

The ethanolysis of *cis*-propenyldisilane (XIII) under the same conditions proceeded apparently slower than that of the *trans* isomer and after one hour only 60% of it was converted into the cleavage and hydrogenation products. In this case, as Fig. 3b shows, (XIII) underwent rapid isomerization at the early stages of reaction to give a mixture of three alkenyldisilanes (XII), (XIII) and (XIV), the molar ratio of which became approximately 11 : 5 : 84 after one hour. In view of this ratio being substantially identical with that observed with (XIV), it seems likely that both of the propenyldisilanes are converted fairly rapidly into an equilibrium mixture involving themselves and the allyldisilane during the ethanolysis reaction catalyzed by palladium(II) chloride. After 1-h reaction of (XIII), some amount of ethanol was still present unchanged in the reaction system. Nevertheless, the cleavage and hydrogenation did not proceed further. Only by introduction of an additional small amount of the catalyst it was possible to bring the reaction to completion. This deactivation of the catalyst during reactions, the cause of which is not fully understood at the present time, accounts for the observed lower conversion of (XIII) as compared to that obtained with (XIV).

The allyldisilane (XII) underwent very slow isomerization when it was stirred with a catalytic amount of palladium(II) chloride in the absence of any added protic solvent. VPC analysis, for example, after 40-h reaction at room temperature revealed that the reaction mixture was composed of allyldisilane (XII), *cis*-propenyldisilane (XIII) and *trans*-propenyldisilane (XIV) in the molar ratio of 63 : 7 : 30. Introduction of traces of water into the reaction system at this point accelerated the isomerization considerably to shift the above ratio to 38 : 11 : 51, at the same time causing the cleavage and hydrogenation to occur to some extent. Repeated additions of traces of water led at last to a mixture of (XII), (XIII) and (XIV) in the molar ratio of 13 : 5 : 82 (see Fig. 4), the value of which is nearly equal to the values obtained from both of the propenyldisilanes.

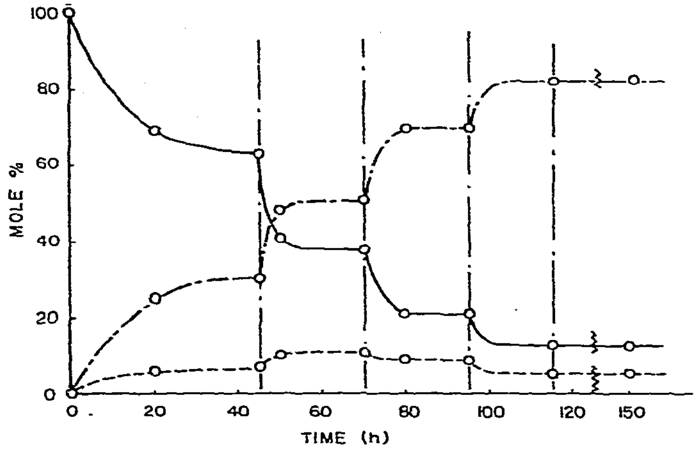

Fig. 4. Isomerization of allylpentamethyldisilane (XII) in the presence of 5 mole per cent of palladium(II) chloride at room temperature. Traces of water was added after 45, 70 and 95 hours. ———, (XII); -----, *cis*-propenylpentamethyldisilane (XIII); —·—·—, *trans*-propenylpentamethyldisilane (XIV).

Fig. 3c illustrates a profile for the progress of reaction of (XII) with an equimolar quantity of ethanol in the presence of palladium(II) chloride. By comparison of Figs. 3a–3c it will be seen that the isomerization of (XII) is slower than that of either of (XIV) and (XIII).

Preliminary observations that phenylpentamethyldisilane readily underwent cleavage of the silicon–silicon bond upon treatment with ethanol in the presence of palladium(II) chloride, whilst benzylpentamethyldisilane was completely inert under the same conditions, may be consistent with the view of initial isomerization of the allyldisilane to propenyldisilanes which undergo the ethanolysis.

EXPERIMENTAL

1. *Materials*

All the compounds listed below are known and were prepared by known methods. Physical constants for them were in good agreement with those reported in the literature except for Me_5Si_2Pr (XV), b.p. 155.5°, n_D^{20} 1.4390, d_4^{20} 0.7589 (lit.[7]: b.p. 147–148°, n_D^{20} 1.4378, d_4^{20} 0.7572). In the following list, the references given after the compounds are to the source or method of preparation: $Me_2EtSiOEt$ (VI)[8], Me_5Si_2OEt (IX)[7], $Me_5Si_2CH{=}CH_2$ (I)[9], $EtOMe_2SiCH{=}CH_2$ (V)[10], Me_5Si_2Et (VII)[11], $Me_7Si_3CH{=}CH_2$ (VIII)[9], $Me_5Si_2CH_2CH{=}CH_2$ (XII)[12], $EtOMe_2SiPr$ (XIV)[13], Me_5Si_2H (XI)[14], and $Me_3SiCH_2CH_2SiMe_3$ (II)[15].

Some new compounds were prepared as follows.

a. cis- and trans-Propenylpentamethyldisilane, (XIII) and (XIV) respectively. To a Grignard solution prepared from 40 g (0.33 mole) of 1-bromopropene and 7.5 g (0.33 g-atom) of magnesium in tetrahydrofuran was added 41.5 g (0.25 mole) of chloropentamethyldisilane. After the addition was completed, the reaction mixture was refluxed for 7 h. It was then hydrolyzed with saturated aqueous solution of ammonium chloride and worked up in the usual way. Distillation gave 23 g (53% yield) of a mixture of (XIII) and (XIV) in the ratio of 65:35, b.p. 155–159°. (Found: C, 55.75; H, 11.60. $C_8H_{20}Si_2$ calcd.: C, 55.69; H, 11.58%.) A pure sample of each isomer was obtained by preparative VPC, using a DOP column at 140°. Physical and spectral data are listed in Table 2.

b. 1-(Ethoxydimethylsilyl)-2-(trimethylsilyl)ethane (IV). In accordance with the procedure described recently[16], 1-(chlorodimethylsilyl)-2-(trimethylsilyl)ethane (VI'), b.p. 85°/41 mm, n_D^{20} 1.4350, d_4^{20} 0.8715 (Found: C, 43.79; H, 9.99; Cl, 18.42. $C_7H_{19}Si_2Cl$ calcd.: C, 43.15; H, 9.83; Cl, 18.19%), was prepared in 39% yield from the reaction involving 17.4 g (0.10 mole) of 1,2-bis(trimethylsilyl)ethane (II), 7.9 g (0.10 mole) of acetyl chloride, and 13.3 g (0.10 mole) of anhydrous aluminum chloride. Alternatively, (VI') was also prepared in 92% yield by heating a mixture of 3.0 g (0.03 mole) of vinyltrimethylsilane and 1.5 g (0.016 mole) of dimethylchlorosilane in the presence of *trans*-dichloro(ethylene)(pyridine)platinum(II)[17] (50 μl of 0.005 *M* benzene solution) in a sealed glass tube at 40° for 10 h. To a stirred ether solution of 3 g of absolute ethanol and 3 g of dry pyridine was added dropwise a solution of 6.8 g of (IV') in ether at room temperature. After an additional 4-h stirring, the resulting pyridine salt was separated by filtration, and the filtrate was distilled to give 6.2 g (81% yield) of (IV), b.p. 70.5–71.0°/18 mm, n_D^{20} 1.4209, d_4^{20} 0.8106, MR_D 63.95 (calcd. 63.83). (Found: C, 52.61; H, 11.74. $C_9H_{24}Si_2O$ calcd.: C, 52.87; H, 11.83%.)

c. 1-Ethylheptamethyltrisilane (X). To an excess of ethylmagnesium bromide in ether solution was added 3.0 g of 1-chloroheptamethyltrisilane[14]. The mixture was heated to reflux for 8 h and then worked up in the usual way to give 2.0 g (70% yield) of (X). b.p. 106.5–107.0°/45 mm, n_D^{20} 1.4684, d_4^{20} 0.7933, MR_D 76.64 (calcd. 76.73). (Found: C, 49.63; H, 12.06. $C_9H_{26}Si_3$ calcd.: C, 49.46; H, 11.99%.)

2. *Addition of methyldichlorosilane to vinylpentamethyldisilane (I)*

In a sealed glass tube, a mixture of 8.0 g (0.05 mole) of (I), 5.7 g (0.05 mole) of $MeSiHCl_2$ and 25 µl of 0.1 *M* chloroplatinic acid solution in isopropyl alcohol was heated at 60° for 10 h. At this point the contents of the tube were treated with excess methylmagnesium bromide in ether. After a work-up in the usual way, the resulting organic layer was fractionally distilled to give 6.0 g (60% yield) of 1-(pentamethyldisilanyl)-2-(trimethylsilyl)ethane (III), b.p. 102–103°/42 mm, n_D^{20} 1.4478, d_4^{20} 0.7815, MR_D 79.64 (calcd. 79.31) (Found: C, 51.70; H, 12.05. $C_{10}H_{28}Si_3$ calcd.: C, 51.64; H, 12.13%.) and 0.5 g of a liquid collected in the trap immersed in a Dry Ice-acetone mixture. VPC analysis of the latter product indicated that it was a mixture of five compounds, with the main product being 1,2-bis(trimethylsilyl)ethane (II) and the remaining four being all siloxane compounds (by their IR spectra).

3. *Reaction of vinylpentamethyldisilane (I) with chloroplatinic acid*

In a small Erlenmeyer flask, a mixture of 3.16 g (0.02 mole) of (I) and 0.518 g (0.001 mole) of $H_2PtCl_6 \cdot 6\,H_2O$ was magnetically stirred in a nitrogen stream. The reaction proceeded very slowly at 0°, but rapidly at room temperature to give a black tarry precipitate of platinum. After 4 h, the organic layer was analyzed by VPC to reveal that about 35% of (I) underwent cleavage and (III) was produced almost quantitatively on the basis of eqns. (2) and (3). After 10-h, reaction was completed. In addition to (III) as the main product, five compounds that were almost identical with those produced in Exp. 2 were formed.

4. *Addition of trimethylsilane to vinylpentamethyldisilane (I)*

A mixture of 3.95 g of (I), 2.5 ml of trimethylsilane, and 1 mg of *trans*-dichloro(ethylene)(pyridine)platinum(II)[17] dissolved in 2 ml of benzene was heated in a sealed glass tube at 45° for 20 h. Distillation of the contents of the tube gave 5.1 g (88% yield) of (III), b.p. 78–79°/12 mm, n_D^{20} 1.4483. No other products were detected.

5. *General procedures for ethanolysis of vinylpentamethyldisilane (I) catalyzed by Group VIII metal salts*

In a 50-ml Erlenmeyer flask, previously flushed with pure nitrogen and sealed with a serum cap, was placed a mixture of 1.58 g (0.01 mole) of (I) and 5×10^{-5} mole [corresponding to 0.5 mole per cent of (I)] of a salt of Group VIII metals, and stirred at room temperature. In all cases except for platinum(II) chloride, the salts in part dissolved in the olefin (I) to give colored solutions. To the solution was added dropwise 0.46 g (0.01 mole) of absolute ethanol through the serum cap with a hypodermic syringe over a period of 2 to 4 min. The instant ethanol was introduced, exothermic reaction took place with development of deep color. With platinum and palladium salts, after about 30 min all the salts were reduced to finely powdered precipitates of metals and the organic layer turned clear. The reaction was then completed. With rhodium and ruthenium salts, on the other hand, decoloration of the organic layer was incomplete; in such cases, significant amounts of the olefin (I) were detected unchanged. The organic layer was analyzed by VPC (over Silicone DC 550, Apiezon L, or DOP), quantitatively as well as qualitatively, and main products were isolated by preparative VPC and characterized. In a typical example using $H_2PtCl_6 \cdot 6\,H_2O$ as the catalyst, the following product distribution in mole per cent was obtained:

Me_3SiOEt 14, $EtOMe_2SiCH{=}CH_2$ (V) 33, $EtOMe_2SiCH_2CH_2SiMe_3$ (IV) 26, $Me_5Si_2CH_2CH_2SiMe_3$ (III) 22, $EtOMe_2SiEt$ (VI) 2, and Me_5Si_2Et (VII) 3. In Table 1 are summarized all the results obtained.

6. *Product distribution vs. time for palladium(II) chloride-catalyzed ethanolysis of vinylpentamethyldisilane (I) and 1-vinylheptamethyltrisilane (VIII)*

In a 50-ml flat-bottom vessel equipped with a reflux condenser leading to a mercury seal and short sidearm sealed with a serum cap there was placed a mixture of 1.58 g (0.01 mole) of (I), 0.09 g [5×10^{-4} mole, 5 mole per cent of (I)] of palladium(II) chloride, and 1.74 g (0.01 mole) of 1,2-bis(trimethylsilyl))ethane as an internal reference for VPC analysis. The mixture was magnetically stirred with external cooling to 0° over a 15-min period. Although the salt gradually dissolved to give a brown-red solution, no appreciable reaction occurred. At this point 0.46 g (0.01 mole) of absolute ethanol was added at a time to the mixture through the serum cap by means of a syringe. At suitable intervals 10-μl aliquots of the solution were extracted and analyzed by VPC (carried out at 120°, a helium flow rate of 40 ml/min, with 2.5 × 6 mm column packed with 30% DOP on celite). The result obtained is illustrated in Fig. 1. A change in amount of the catalyst over the range of 0.5–10 mole per cent did not affect essentially the product distribution.

The progress of ethanolysis of (VIII) was followed by VPC in essentially the same manner, except for the use of *p*-cymene as the internal reference and analysis temperature of 145°. The result is illustrated in Fig. 2.

7. *Ethanolysis of pentamethyldisilane (XI) catalyzed by palladium(II) chloride*

To a stirred and cooled mixture of 0.46 g (0.01 mole) of absolute ethanol and 0.089 g (5×10^{-5} mole) of palladium(II) chloride in the same reaction vessel as used in Exp. 5 was added at a time a mixture of 1.32 g (0.01 mole) of (XI) and 1.20 g (0.01 mole) of cumene, as the internal reference, through the serum cap by means of a syringe. Vigorous reaction set in with precipitation of metallic palladium and was completed within several minutes. VPC analysis showed that the product was composed of trimethylethoxysilane (25%), dimethyldiethoxysilane (28%), and recovered (XI) (44%).

8. *Addition of pentamethyldisilane (XI) to vinyltrimethylsilane*

A mixture of 1.33 g of (XI), 1.00 g of vinyltrimethylsilane, and 0.8 mg (2×10^{-4} mole/mole olefin) of *trans*-dichloro(ethylenepyridine)platinum(II) dissolved in 3 ml of benzene was heated in a glass tube at 60° for 45 h. Distillation of the reaction mixture gave 1.80 g (78% yield) of 1-(pentamethyldisilanyl)-2-(trimethylsilyl)ethane (III).

9. *Ethanolysis of allylpentamethyldisilane (XII), and cis- and trans-propenylpentamethyldisilane, (XIII) and (XIV) respectively, catalyzed by palladium(II) chloride*

By the same techniques as described in Exp. 6, a mixture of 0.35 g of each of the isomeric alkenyldisilanes, 0.018 g of palladium(II) chloride, 0.095 g of absolute ethanol, and 0.27 g of *p*-cymene, as the internal reference, was stirred near 0° and analyzed periodically by VPC (with a DOP column, at 140°). The results are illustrated in Fig. 3.

10. *Isomerization of allylpentamethyldisilane (XII)*

In the same reaction vessel as that used in Exp. 6, previously flushed with argon, was placed a mixture of 0.69 g of (XII) and 0.035 g of palladium (II) chloride. The mixture was stirred at room temperature and analyzed periodically by VPC. Traces of water were added to the mixture, 45, 70 and 95 h after the start. A profile for the progress of reaction is illustrated in Fig. 4.

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