

## THE EXCHANGE OF CHLORO AND ETHOXY GROUPS UPON THE ADDITION OF DIMETHYLCHLOROSILANE TO VINYLDIMETHYLETHOXSILANE\*

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(Received October 26th, 1972)

### SUMMARY

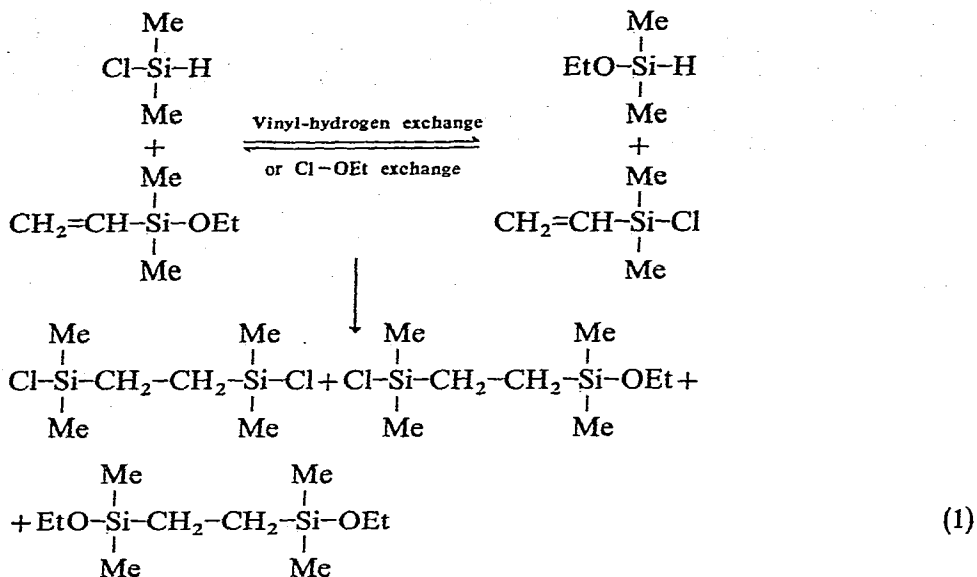
The addition of dimethylchlorosilane to vinyl dimethylethoxysilane in the presence of chloroplatinic acid yielded 1,2-bis(dimethylchlorosilyl)ethane, 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane. The formation of three products is explained on the basis of chloro-ethoxy exchange reactions. Equilibration of the dimethylchlorosilane-vinyldimethylethoxysilane system was investigated using  $^1\text{H}$  NMR and gas-liquid chromatography. The equilibrium constants indicated near random behavior for the substituent exchange.

### INTRODUCTION

The synthesis of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane  $(\text{Me})_2\text{-SiCH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{O}$  was previously carried out<sup>1</sup> by a chloroplatinic acid-catalyzed hydrosilation reaction between dimethylchlorosilane and vinyl dimethylchlorosilane followed by the hydrolysis of the adduct and subsequent pyrolysis of the hydrolysate in the presence of a base. We have utilized the more readily available vinyl dimethylethoxysilane in this synthesis, since the hydrolysis of the adduct and pyrolysis reaction yield the same cyclic compound. However the addition reaction yielded, in addition to the desired 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane, two other adducts which were identified as 1,2-bis(dimethylchlorosilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane.

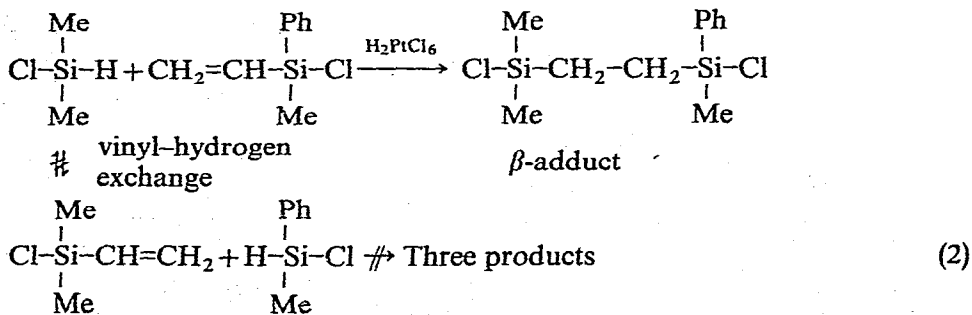
Redistribution reactions of organosilicon compounds are well known and have been the subject of several reviews<sup>2,3,4</sup>. Pitt and Skillern<sup>5</sup> first reported the exchange of vinyl groups and hydrogen on silicon atoms in the presence of chloroplatinic acid. The three products obtained in the present study can be explained by chloro-ethoxy exchange reactions among the reagents and products or by vinyl-hydrogen exchange (Eqns. 1 and 3). Therefore, a study was undertaken to determine the extent of these exchange reactions.

\* Contribution #173 from the Graduate Center for Materials Research.



## RESULTS AND DISCUSSION

Pitt and Skillern<sup>5</sup> carried out the addition of triethylsilane to vinyl dimethylchlorosilane catalyzed by chloroplatinic acid and isolated three adducts, 1,2-bis(dimethylchlorosilyl)ethane, 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane, and 1,2-bis(triethylsilyl)ethane. They explained the formation of the three products on the basis of vinyl-hydrogen ligand exchange between silicon atoms. In order to see if the vinyl-hydrogen exchange reaction is prevalent in our scheme, we carried out the addition of dimethylchlorosilane to phenylmethylvinylchlorosilane in the presence of chloroplatinic acid to obtain 1-(dimethylchlorosilyl)-2-(phenylmethylchlorosilyl)ethane in 90% yields. No other identifiable products were obtained. Had the vinyl-hydrogen exchange been occurring, we would have expected two other products, 1,2-bis(dimethylchlorosilyl)ethane, and 1,2-bis(phenylmethylchlorosilyl)ethane in addition to 1-(dimethylchlorosilyl)-2-(phenylmethylchlorosilyl)ethane (Eqn. 2).



Piccoli, *et al.*<sup>1</sup> reported that addition reactions of  $\text{ClSi}(\text{R})(\text{R}_1)\text{H}$  compounds to  $\text{CH}_2=\text{CHSi}(\text{R})(\text{R}_1)\text{Cl}$  compounds in the presence of chloroplatinic acid gave the  $\beta$ -adducts in high yields. These observations suggest that vinyl-hydrogen ligand exchange reac-

tion was not important for the formation of the products obtained in this study.

Unlike vinyl-hydrogen exchange, the chloro-ethoxy exchange reactions on silicon atoms do not require the presence of chloroplatinic acid. The chloro-ethoxy exchange reaction was independent of the presence or absence of chloroplatinic acid. Consequently, on mixing dimethylchlorosilane with vinyl dimethylethoxysilane, it was possible to study the exchange reaction in the absence of the hydrosilation addition reaction. The exchange was followed by  $^1\text{H}$  NMR, by observing the silyl proton signals of  $(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}$  and  $(\text{CH}_3)_2\text{Si}(\text{H})\text{OEt}$ , the chemical shifts for the lone protons being 294 and 282 Hz respectively, relative to  $\text{CHCl}_3$ . The relative amounts of dimethylchlorosilane and dimethylethoxysilane were measured by electronic integration of the two multiplets. Attempts to measure directly the amounts of all the components was not possible since the Si- $\text{CH}_3$  region of the spectra was too complex. Figure 1 shows the NMR pattern for the equilibration of 1/1 molar mixtures of dimethylchlorosilane and vinyl dimethylethoxysilane at  $28.5^\circ$ . From the relative ratios of dimethylchlorosilane and dimethylethoxysilane at equilibrium, and by a material balance the equilibrium constants were calculated according to the relationship:

$$K = \frac{[(\text{CH}_3)_2\text{Si}(\text{H})\text{OEt}][(\text{CH}_3)_2\text{Si}(\text{Cl})\text{CH}=\text{CH}_2]}{[(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}][(\text{CH}_3)_2\text{Si}(\text{OEt})\text{CH}=\text{CH}_2]}$$

and are presented in Table 1.

GLC analyses of equilibrated mixtures (Table 2) agree well with NMR deter-

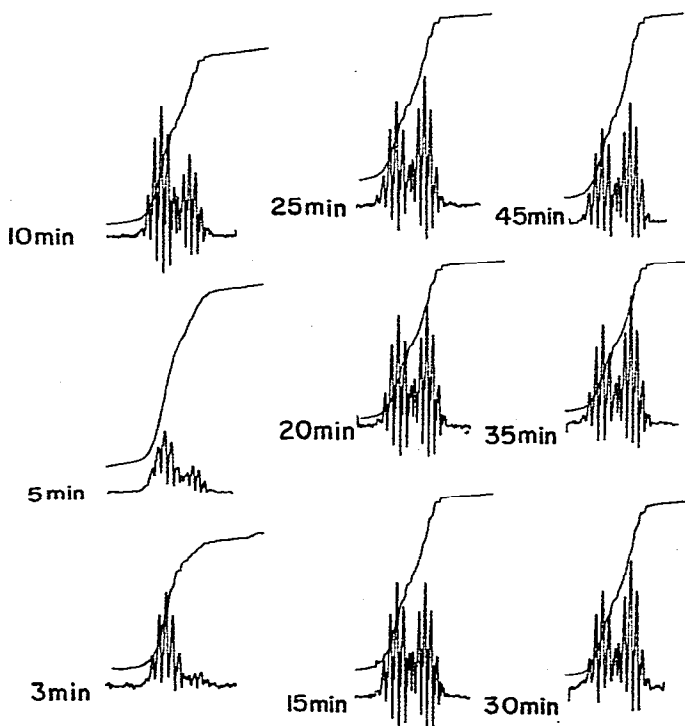


Fig. 1. NMR spectra of the equilibration of 1/1 molar mixture of  $(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}$  and  $(\text{CH}_3)_2\text{Si}(\text{OEt})\text{CH}=\text{CH}_2$  at  $28.5^\circ$  (270–310 Hz).

TABLE 1

EQUILIBRATION OF MIXTURES OF  $(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}$  AND  $(\text{CH}_3)_2\text{Si}(\text{OEt})\text{CH}=\text{CH}_2$  AT  $28.5^\circ\text{C}$ 

Mole ratio (EtO/Cl)	Exchange (%) at <sup>a</sup> equilibrium	Equilibrium constant <i>K</i>
1/1	55.3	1.53
3/2	63.0	1.33
2/3	42.0	1.23

<sup>a</sup> Duplicate measurement led to % exchange at equilibrium within 0.4%

TABLE 2

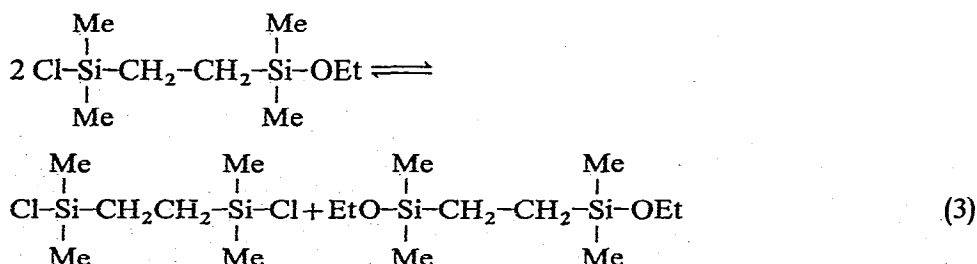
NMR AND GLC ANALYSES ON THE 1/1 MOLAR MIXTURE OF  $(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}$  AND  $(\text{CH}_3)_2\text{Si}(\text{OEt})\text{CH}=\text{CH}_2$  EQUILIBRATED AT  $28.5^\circ$ 

Component	Weight (%)	
	NMR	GLC
Dimethylchlorosilane	18.76	18.60
Dimethylethoxysilane	25.68	26.10
Vinyldimethylchlorosilane	29.60	30.20
Vinyldimethylethoxysilane	25.96	25.10

minations. Equilibrium constants obtained in this study are near unity as expected for random exchange.

The rate of exchange of chloro and ethoxy groups for the equilibration of 1/1, 3/2 and 2/3 molar mixtures of dimethylchlorosilane and vinyldimethylethoxysilane at  $28.5^\circ$  is shown in Fig. 2. The figure shows that the exchange is rapid near room temperatures. When precautions were not taken to exclude atmospheric moisture, equilibration was complete in less than two minutes. Trace amounts of HCl formed by hydrolysis of the chlorosilane are known<sup>6</sup> to exhibit catalytic activity. Figure 2 also shows that the rate of equilibration was faster as the amount of ethoxysilane was increased.

The formation of the two symmetrical products, 1,2-bis(dimethylchlorosilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane, may also be explained by means of Eqn. 3.



This possibility was investigated by mixing equimolar amounts of the two symmetrical

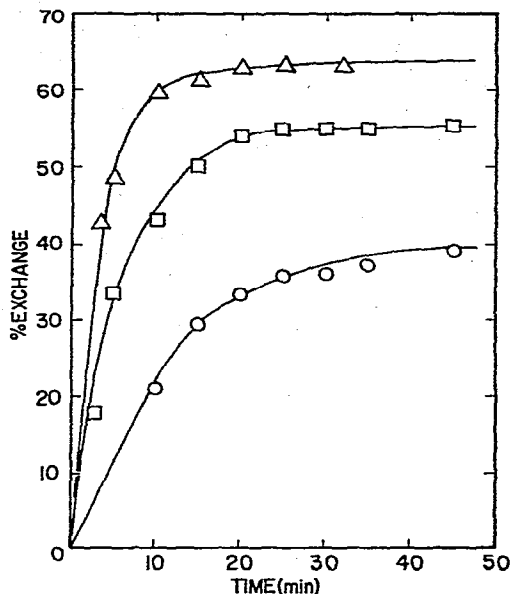


Fig. 2. Rate of equilibration of  $\circ$  3/2  $\square$  1/1 and  $\Delta$  2/3 molar mixtures of  $(\text{CH}_3)_2\text{Si}(\text{H})\text{Cl}$  and  $(\text{CH}_3)_2\text{Si}(\text{OEt})\text{CH}=\text{CH}_2$  at  $28.5^\circ$ .

compounds in an NMR tube, and heating to  $120^\circ$  for several hours. NMR Spectra showed the appearance of the multiplet due to  $-\text{CH}_2\text{CH}_2-$  of the unsymmetrical compound, indicating the reverse reaction. However, no quantitative data on this reaction was obtained.

It is thus evident that the chloro-ethoxy redistribution reactions before and after the hydrosilation addition reaction are responsible for the formation of the two symmetrical compounds in the preparative procedure.

#### EXPERIMENTAL

GLC analyses were performed with a Victoreen 4000 Series Chromatograph, equipped with a thermal conductivity detector and a 2 m column of 10% SE 30 on Chromosorb W. NMR spectra were obtained with a Varian EM-360 spectrometer. Melting and boiling points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

*Reagents.* Specially purified dimethylchlorosilane was purchased from Pierce Chemical Company, Rockford, Illinois. Vinyl dimethylethoxysilane was purchased from Alfa Inorganics, Cambridge, Massachusetts, and was purified by distillation. The catalyst for the addition reaction was prepared by dissolving 1.0 g of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in 19.3 g of isopropyl alcohol to give a 0.1 M solution. A  $10 \mu\text{l}$  sample of the catalyst solution was equivalent to  $10^{-6}$  mole Pt.

Phenylmethylvinylchlorosilane was prepared by a modification of the Grignard method employed by Curry<sup>7</sup>. The use of tetrahydrofuran as solvent increased the yield from 40 to 67%.

*Addition of dimethylchlorosilane to vinyl dimethylethoxysilane.* To 26.0 g (0.2 mole) of vinyl dimethylethoxysilane, 5  $\mu$ l of chloroplatinic acid solution was added and the mixture was heated to 75° under a nitrogen atmosphere. The mixture was stirred as 18.8 g (0.2 mole) of dimethylchlorosilane was added dropwise. The temperature rose to 120° and was maintained at that temperature by controlling the rate of addition. After the addition reaction was completed, the mixture was fractionated in a Nester-Faust auto annular still with a reflux ratio of 200/1 and the Teflon band spinning at 7200 rpm. 1,2-Bis(dimethylchlorosilyl)ethane was collected as a solid adduct at 109°/50 mmHg. Recrystallization from n-pentane yielded the pure compound melting at 36°. An NMR spectrum of the adduct using carbon tetrachloride as the solvent and chloroform as the internal standard\* showed the Si-CH<sub>3</sub> singlet at 24 Hz and the -CH<sub>2</sub>CH<sub>2</sub>- singlet at 50 Hz. The second fraction collected at 113°/50 mmHg was found by NMR analysis to be a mixture of 1,2-bis(dimethylchlorosilyl)ethane, 1,2-bis(dimethylethoxysilyl)ethane and 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane. Repeated fractionation gave the unsymmetrical adduct in 70% purity. The NMR spectrum of this fraction showed a multiplet due to -CH<sub>2</sub>CH<sub>2</sub>- group in the unsymmetrical adduct at 32 Hz. The third fraction, 1,2-bis(dimethylethoxysilyl)ethane, was collected at 116°/50 mmHg. ( $n_D^{20}$  1.4205, Found: C, 51.00; H, 11.08; Si, 23.97. Calcd.: C, 51.19; H, 11.18; Si, 23.97). The NMR spectrum of the compound showed the -CH<sub>2</sub>CH<sub>2</sub>- singlet at 25 Hz and the Si-CH<sub>3</sub> singlet at 0 Hz.

*Equilibration of dimethylchlorosilane with vinyl dimethylethoxysilane.* The exchange of chloro and ethoxy groups during the equilibration of dimethylchlorosilane with vinyl dimethylethoxysilane was determined as follows: measured amounts of the two reactants from previously calibrated syringes were transferred into an NMR tube in a polyethylene glove bag. A steady flow of purified inert gas (N<sub>2</sub> or Ar) was maintained inside the glove bag. The NMR tube was sealed and the reactants were mixed, the time of mixing being taken as zero time. The NMR tube was immediately transferred to the probe of the NMR spectrometer maintained at a constant temperature of 28.5°. The spectra between 270 and 310 Hz were scanned with respect to time. Electronic integration of the multiplets yielded the relative ratios of dimethylchlorosilane and dimethylethoxysilane.

GLC analyses on the equilibrated mixtures were performed on samples taken from the NMR tube. The elapsed time between NMR analysis and GLC analysis was usually about 3 h. GLC analysis showed four peaks corresponding to dimethylchlorosilane (b.p. 36°), dimethylethoxysilane (b.p. 54°), vinyl dimethylchlorosilane (b.p. 83-84°), and vinyl dimethylethoxysilane (b.p. 99°). The peaks due to dimethylchlorosilane and vinyl dimethylethoxysilane were identified by comparison with pure samples and assignments of the chromatographic peaks due to dimethylethoxysilane and vinyl dimethylchlorosilane were made from their boiling point sequence and were checked by material balance.

#### ACKNOWLEDGEMENTS

This work was supported in part by USPH-1-R01-HL-13999-01 and by the Graduate Center for Materials Research, University of Missouri-Rolla.

\* Chloroform was used as the internal standard rather than tetramethylsilane because of the extremely close chemical shifts of Si-CH<sub>3</sub> between these adducts and tetramethylsilane.

## REFERENCES

- 1 W. A. Piccoli, G. G. Haberland and R. L. Merker, *J. Amer. Chem. Soc.*, 82 (1960) 1883.
- 2 K. Moedritzer, *Organometal. Chem. Rev.*, 1 (1966) 179.
- 3 K. Moedritzer, *Advan. Organometal. Chem.*, 6 (1968) 171.
- 4 K. Moedritzer, *Organometal. Reactions, Vol. 2*, Wiley-Interscience, New York, 1971.
- 5 C. G. Pitt and K. R. Skillern, *J. Organometal. Chem.*, 7 (1967) 525.
- 6 H. Weingarten and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 88 (1966) 2700.
- 7 J. W. Curry, *J. Amer. Chem. Soc.*, 78 (1956) 1686.