ORGANOSILICON COMPOUNDS. LXXXVII.*

THE NATURE OF THE SILICON–VINYL BOND IN METHYLVINYLFLUOROSILANES

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Methylvinylfluorosilanes of the type $CH_2=CHSi(CH_3)_{3-n}F_n$ ($n = 0-3$) were prepared and their dipole moments and relative rates of the addition of dichlorocarbene (with respect to 1-heptene) to these compounds, yielding methyl(2,2-dichlorocyclopropyl)fluorosilanes, were measured. The obtained results can be explained by formation of $(p \rightarrow d)\pi$ bond between silicon and vinyl group and by concurrent operation of the $-I$ effect of fluorine atom.

In the works devoted to the nature of the silicon–vinyl bond in methylsilyl(trimethyl-siloxy)silanes[1] and methylvinyl-tert-butoxysilanes[2] we have found that in these compounds π-electrons of the vinyl group compete with unshared electron pairs of the oxygen for $3d$ orbitals of silicon, forming concurrent $(p \rightarrow d)\pi$ dative bonds. Such a competition has not been observed, however, between the vinyl group and the chlorine atom in methylvinylchlorosilanes[3]. With the aim to study mutual influencing of silicon–vinyl and silicon–fluorine bonds in the present work we have prepared a series of methylvinylfluorosilanes of the type $CH_2=CHSi(CH_3)_{3-n}F_n$ ($n = 0-3$). In order to compare their reactivity with their properties in ground state, the relative rates of the addition of dichlorocarbene and the dipole moments of these compounds were measured.

From measurements of relative rates of electrophilic chlorination of phenylmethylfluorosilanes it was concluded[4] that the formation of dative bond takes place between phenyl group and silicon, not however between fluorine and silicon. On the other hand, $(p \rightarrow d)\pi$ character of the silicon–fluorine bond had to be taken into account in explaining the results obtained in an analogous study of electrophilic chlorination of benzylmethylfluorosilanes[5], the compounds in which the interaction of silicon with phenyl group does not occur. As follows from measurement of the chemical shifts of ^{19}F and ^1H in the series of alkylfluoro- and -chlorosilanes[6] fluorine atoms are expelled from their $(p \rightarrow d)\pi$ dative bonds with silicon by concurrent formation of dative bonds between silicon and vinyl or phenyl groups, which results in lesser shielding of fluorine atoms. On the basis of NMR study[7] of compounds of the type $(CH_3)_3SiX$, where $X = F, OCH_3$, Br, Cl, C_6H_5, the authors concluded that the ability of the atom or group X to form a $(p \rightarrow d)\pi$

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dative bond with silicon decreases in the order $F > OCH_3 > Cl > C_6H_5 > Br$. Also IR measurements of the Si—H stretching frequencies of substituted silicon hydrides[8] support the above order of halogens ($F > Cl > Br > I$). The calculation of group moments $CH_2=CH$—Si in vinylmethylchlorosilanes showed[9] that the moment decreases with increasing number of chlorine atoms in the molecule of these compounds, which indicates that chlorine atoms aid by their —I effect the formation of dative bond between vinyl group and silicon. By contrast, in phenylmethylfluorosilanes[10] fluorine atoms compete with phenyl group, most in the monofluoro derivative, the fluorine of which acts as electron donor in the $(p \rightarrow d) \pi$ dative bond with silicon. As the number of fluorine atoms increases their inductive effect becomes progressively more important, aiding thus interaction of phenyl group with silicon.

EXPERIMENTAL

Preparation of Compounds. Phenyl(bromodichloromethyl)mercury was prepared in 15% yield by reaction of phenylmercury chloride with bromodichloromethane and potassium tert-butylate[11] in ether at $-20°C$. The methylvinylfluorosilanes were obtained by a reaction of appropriate methylvinylchlorosilane with antimony trifluoride[12]. Their physical constants are given in Table I. A distillation flask equipped with a dropping funnel and a column filled with Raschig rings was charged with SbF_3 and then appropriate chlorosilane was slowly added. The desired fluorosilane was collected from the head of the column, cooled with dry ice–ethanol mixture. Trimethylvinylsilane and trimethylethylsilane were prepared by reaction of vinyltrichlorosilane or ethyltrichlorosilane with methylmagnesium chloride[13] in ether; b.p. 54°C and 64°C, respectively. Trimethyl(2,2-dichlorocyclopropyl)silane was prepared[2] by reaction of trimethylvinylsilane with the dichlorocarbene generated by thermal decomposition of phenyl(bromodichloromethyl)mercury in benzene. Dimethyl(2,2-dichlorocyclopropyl)-fluorosilane (n_D^{20} 1·4407, b.p. 155°C, for $SiC_5H_9Cl_2F$ (187·1) calculated: 32·10% C, 4·85% H; found: 32·42% C, 4·83% H) and methyl-(2,2-dichlorocyclopropyl)difluorosilane (n_D^{20} 1·4340, b.p. 130°C, for $SiC_4H_6F_2Cl_2$ (191·1) calculated: 25·15% C, 3·17% H; found: 25·01% C, 3·11% H) were prepared similarly.

Measurements of relative rates. Relative rates of the addition of the dichlorocarbene generated by Seyferth method[11] to dimethylvinylfluorosilane and trimethylvinylsilane were determined by the method of competition reactions[20]. Into a mixture of 249·0 mg of trimethylvinylsilane, 450·3 mg of dimethylvinylfluorosilane and 1 ml of benzene, placed in a 15 ml glass ampoule, were added 150 mg of phenyl(bromodichloromethyl)mercury. Sealed ampoule was placed in a bath warmed up to the reaction temperature and than shaken for 2 h. The temperature of the bath was kept constant within 0·1°C. The ampoule was then cooled to room temperature, opened, and the solid phenylmercury chloride was separated by centrifugation. The other couples of olefins were treated similarly. Reaction mixtures were analysed on a gas chromatograph made by Vývojové dílny ČSAV (Prague). The instrument was equipped with catharometer. The column was 300 cm long and 0·6 cm across and was filled with 5% silicone elastomer E 301 (Griffin and George, London) on a grinded unglazed tiles (0·2—0·3 mm particle size). The column temperature was 120°C and the flow rate of carrier gas (hydrogen) was 60 ml per min. The area of chromatographic peaks of corresponding dichlorocyclopropane derivatives were planimetred and converted by means of calibration graphs to relative amounts.

Dielectric measurements were carried out with solutions of the compounds in n-hexane, using resonance method at the frequency of 0·5 MHz with the accuracy of $\Delta\varepsilon/\varepsilon = \pm 1 . 10^{-4}$, at the temperature $-40·0 \pm 0·1°C$. The solutions were prepared in the following way. The compound measured was weighted in a small glass ball which was then crushed in the weighted amount of subcooled solvent. The trifluoro derivative was injected directly to the weighted amount of the

solvent and the solution reweighted. Dipole moments of the compounds under study were determined only from measurements of concentration dependence of dielectric constants of the solutions, using the method of Higashi[21], suggested by the author for the compounds unstable on air. This method was chosen because of impossibility of measuring densities and indices of refraction at the temperature $-40°C$ by the experimental equipment available in our laboratory. According to Higashi, dipole moments can be calculated from dielectric constants by means of equation

$$\mu = \beta \sqrt{(\mathrm{d}\varepsilon_{12}/\mathrm{d}x_2)}, \qquad (1)$$

where ε_{12} is the dielectric constant of the solution of measured compound in an appropriate solvent, x_2 the mole fraction of the measured compound, and β a constant which is characteristic of the solvent at the given temperature and is dimensionally identical with dipole moment. This constant is given by the expression[22]

$$\beta = \sqrt{\frac{27kT}{4\pi N} \frac{M_1}{\varrho_1(\varepsilon_1 + 2)^2}}, \qquad (2)$$

where M_1, ϱ_1 and ε_1 is respectively the molecular weight, density and dielectric constant of the solvent; the other symbols have usual meaning. In order to calculate the value of constant β for n-hexane we had to determine ε_1 and ϱ_1 for the temperature $-40°C$. The dielectric constant was obtained by extrapolation of temperature dependence of dielectric constant in the temperature range $-90°C$ to $+25°C$, using tabelated values[23,24] $\varepsilon_{(-40°C)} = 1·9765$. The density was determined from the critical values of n-hexane with the use of the theorem of corresponding states: $\varrho_{(-40°C)} = 0·7090$. The value of β for n-hexane is thus $0·937 . 10^{-18}$ oh. elst. The slope of concentration dependence of dielectric constants and the resultant dipole moments of studied methylvinylfluorosilanes and methylethylfluorosilanes are presented in Table II.

RESULTS AND DISCUSSION

In harmony with the results of studies of the reactivity of vinylsilanes[1-3] it can be expected that, as a result of $(p \to d) \pi$ character of the silicon–vinyl bond, all the methylvinylfluorosilanes studied will exhibit lower reactivity towards electrophilic reagents than carbon compounds. As expected we have found that 1-heptene reacts with dichlorosilane eight times faster than trimethylvinylsilane, the most reactive member of the series. The interpretation of the effect of substitution on the reactivity of the methylvinylfluorosilanes (Fig. 1) is complicated by the fact that we were unable to determine relative reactivity of vinyltrifluorosilane. This compound has very low boiling point $(-25°C)$, which presented difficulties already during its weighing. The additions of dichlorocarbene generated by Seyferth method[11] to other compounds were carried out in benzene. 2,2-Dichlorocyclopropyltrifluorosilane boils at the temperature which is close to the boiling point of benzene. For this reason we used toluene whose solvation properties can be compared, but not identified with those of benzene. Furthermore, the reaction mixture always contained a small amount of benzene which was probably formed by decomposition of phenyl-(bromodichloromethyl)mercury.

The low reactivity of methylvinylfluorosilanes (Fig. 1) cannot result from steric effects. The observed change of the reactivity of these compounds indicates that the $-I$ effect of fluorine atoms plays predominant role. From comparison of both dependences it is obvious that the $-I$ effect of fluorine atoms in methylvinylfluorosilanes is more important than the same effect of chlorine atoms in methylvinylchlorosilanes. It means that the $(p \rightarrow d)\pi$ dative interaction between unshared electron pairs of fluorine atom and vacant $3d$ orbitals of silicon is not strong enough so as to weaken the dative bond between vinyl group and silicon.

A reliable interpretation of dipole moments has to be based on comparability of the results of measurements carried out at $-40°C$ with those at which the temperature $+25°C$ was used. The latter temperature was chosen in measurements of all the series of compounds in our previous works. As found by Vij and Srivastava[25], the results obtained by Higashi method[21] deviate from those obtained by the method of Halverstadt and Kumler[26] by about 10%, this difference being dependent upon the indices of refraction of measured compound and solvent. This disagreement is caused by neglection of the excess of electron and atom polarisation of dissolved compound with respect to solvent. If the index of refraction of the solvent is under otherwise identical conditions lower, Higashi method yields lower dipole moments, and *vice versa*. In our case all the fluoro derivatives have lower indices of refraction (Table I) than n-hexane (n_D^{20} 1·3754), so that the values of dipole moments found in the present work are probably higher than those which would have been obtained by the method of Halverstadt and Kumler[26]. Another factor which should be taken into account is the effect of temperature. As far as dipole moments are temperature dependent, their values generally increase with increasing temperature, which is caused by decreasing energy barrier of less suitable conformations with increasing

TABLE I
Physical Constants of Methylvinylfluorosilanes and Methylethylfluorosilanes

Silane	Yield %	B.p., °C		n_D^{20}	
		found	lit.	found	lit.
Trimethylvinyl	62	55	54·4/745·4[14]	1·3921	1·3910[13]
Dimethylvinylfluoro	78	43[a]	—	1·3620	—
Methylvinyldifluoro	74	23	22/754[15]	1·3239	1·3250[15]
Vinyltrifluoro	70	−25	−25·5/760[16]	—	—
Trimethylethyl	68	64	62·7/63·2/736[17]	1·3818	1·3820[17]
Dimethylethylfluoro	75	49	49·8/742[18]	1·3560	1·3568[18]
Methylethyldifluoro	70	39	38/728[19]	1·3175	1·3181[19]

[a] Found: 18·23% F; calculated: 18·23% F.

dipole moment. Temperature effect could thus compensate, at least partially, the difference which results from the use of approximate Higashi method. We have already observed that chlorine atoms in vinylmethylchlorosilanes affect the properties of these compounds mainly by their inductive effect[9] whereas the vinyl group acts as electron donor in its $(p \rightarrow d) \pi$ dative bond with silicon. This character of the vinyl–silicon bond becomes more pronounced as the number of chlorine atoms in-
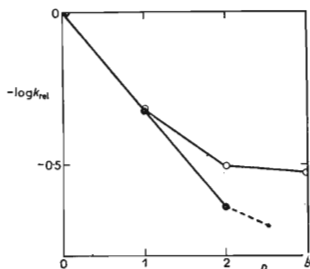

FIG. 1

Dependence of log k_{rel} of the Addition of Dichlorocarbene to Methylvinylfluorosilanes of the Type CH_2=CHSi$(CH_3)_{3-n}F_n$ (●) and Methylvinylchlorosilanes of the Type CH_2=CHSi$(CH_3)_{3-n}Cl_n$ (○) ($n = 0–3$) on Substitution
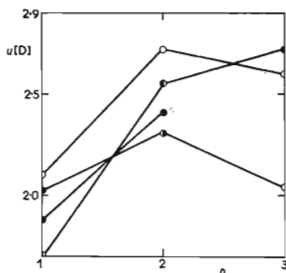
FIG. 2

Dependence of Dipole Moments (μ) of Methylvinylfluorosilanes of the Type CH_2=CHSi$(CH_3)_{3-n}F_n$ (○), Phenylmethylfluorosilanes of the Type $C_6H_5Si(CH_3)_{3-n}F_n$ (◐), Methylvinylchlorosilanes of the Type CH_2=CHSi$(CH_3)_{3-n}Cl$ (◑) and Methylethylfluorosilanes of the Type C_2H_5Si.$(CH_3)_{3-n}F_n$ (●) ($n = 1–3$) on the Number of Halogen Atoms

TABLE II

Slopes of Concentration Dependence of Dielectric Constants and Dipole Moments of Fluorosilanes

Silane	α	μ, D	Silane	α	μ, D
Trimethylvinyl	0·77	0·82	Trimethylethyl	0·17	0·38
Dimethylvinylfluoro	5·05	2·10	Dimethylethylfluoro	4·09	1·89
Methylvinylfluoro	8·40	2·71	Methylethyldifluoro	6·67	2·41
Vinyltrifluoro	7·70	2·60			

creases, which manifests itself in decreasing polarisation of the vinyl group with respect to the central atom.

From Fig. 2 it is seen that the form of the dependence of dipole moments on the number of halogen atoms is also in the series of vinylmethylfluorosilanes very similar. It is obvious that the vinyl group contributes to the total dipole moment of the molecule by its interaction with the central silicon atom and that this interaction becomes more important with increasing number of fluorine atoms, *i.e.* with increasing inductive effect of the fluorosilyl group. The difference between dipole moments of both series increases with increasing number of halogen atoms. This shows that, in harmony with expectation, fluorine atoms have greater inductive effect than chlorine atoms. Comparison of dipole moments of vinylmethylfluorosilanes and phenylmethylfluorosilanes (Fig. 2) allows to estimate the $(p \rightarrow d) \pi$ bonding ability of vinyl and phenyl groups. The dependence of dipole moments on the number of fluorine atoms is in the vinyl-substituted compounds less pronounced, which shows that vinyl group interacts with silicon more readily than phenyl group. As the result, the effect of increasing inductive effect of fluorosilyl group is not so strong as in the phenyl derivatives.

In the work[10] we pointed out that in phenyldimethylfluorosilane the bond between fluorine atom and silicon has very pronounced $(p \rightarrow d) \pi$ character. However, starting from the difluoro derivative the interaction of phenyl group becomes prevailing; as the inductive effect of fluorine atoms increases with their number this interaction becomes increasingly stronger. By contrast, the observed dependence of dipole moments of the vinyl derivatives on the number of fluorine atoms indicates that, in harmony with the already discussed results of the study of relative rates already the first fluorine atom acts predominantly by its $-I$ effect, so that the interaction of π-electrons of vinyl group with silicon systematically increases with increasing number of fluoro substituents along the whole series of vinylmethylfluorosilanes. Their dipole moments are even greater than the dipole moments of their ethyl analogues measured at the same experimental conditions.

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Translated by J. Hetflejš.