ORGANOSILICON COMPOUNDS. LXXXVI.*

THE NATURE OF THE SILICON–VINYL BOND IN METHYLVINYLCHLOROSILANES

P.SVOBODA and V.CHVALOVSKÝ

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol

Received June 8th, 1971

Relative rates of the addition of dichlorocarbene to methylvinylchlorosilanes of the type $CH_2{=}CHSi(CH_3)_{3-n}Cl_n$ ($n = 0-3$), dipole moments of these compounds and of their carbon analogues, $CH_2{=}CHC(CH_3)_{3-n}Cl_n$ ($n = 0-3$), were measured. The obtained results were explained in terms of interaction of $3d$ orbitals of silicon with π-electrons of vinyl group and of the $-$I effect of chlorine atoms. It was found that chlorine atoms do not weaken π-interaction of the double bond by formation of concurrent $(p \rightarrow d)\,\pi$ bonds with silicon.

The aim of this work was to study the effect of chloro substituents on silicon on the $(p \rightarrow d)\,\pi$ bond between silicon and vinyl group. Our work[1] was devoted to an examination of the effect of substitution on the character of the vinyl–silicon bond in methylvinyl-tert-butoxysilanes.

The effect of different number of chlorine and oxygen atoms in vinyl- and allylsilicon compounds on the intensity of the absorption band of the C=C stretching vibration was already studied by IR spectroscopy[2]. In vinyl-substituted silanes this substitution leads to an increase in the intensity of the C=C stretching vibration. NMR spectra[3] and dipole moments[4] of methylvinylchlorosilanes have also been measured. As follows from these studies the $(p \rightarrow \mathrm{d})\,\pi$ interaction between electron pairs of chlorine and $3d$ orbitals of silicon does not take place to a significant extent. Group moment $Si{-}CH{=}CH_2$ decreases with progressive substitution of methyl groups for chlorine atoms, *i.e.* with decreasing +I effect of silyl groups, which creates better conditions for $(p \rightarrow d)\,\pi$ bond formation between silicon and vinyl group. Therefore, according to these results chlorine atom, even though being able to form $(p \rightarrow d)\,\pi$ dative bond with silicon, affects properties of the studied compounds predominantly by its $-$I effect and does not compete with π-electron system of vinyl group for $3d$ orbitals of silicon. Relative rates of the addition of dichlorocarbene to methylvinylchlorosilanes were also measured[5]. The dichlorocarbene was generated by thermal decomposition (250°C) of trichloromethyltrichlorosilane[6]. However, side reactions taking place at these conditions have made a detailed interpretation of the results impossible.

In the present work we therefore prepared a series of methylvinylchlorosilanes of the type $CH_2{=}CHSi(CH_3)_{3-n}Cl_n$ ($n = 0-3$) and determined relative rates of the

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* Part LXXXV: This Journal *37*, 2100 (1972).

addition of the dichlorocarbene generated under milder conditions, by thermal decomposition of phenyl(bromodichloromethyl)mercury[7]. In order to estimate specific effect of silicon atom in these compounds, we have also synthesized carbon analogues of the methylvinylchlorosilanes and compared their dipole moments with those of the chlorosilanes.

EXPERIMENTAL

Preparation of Methylvinylchlorosilanes and Their Carbon Analogues

Dimethylvinylchlorosilane was prepared by a reaction of dimethyldichlorosilane with vinylmagnesium bromide[5] in tetrahydrofuran; b.p. 82°C, 58% yield. *Trimethylvinylsilane* was prepared by methylation of vinyltrichlorosilane with methylmagnesium chloride[8] in ether; b.p. 54°C, 70% yield. *Methylvinylchlorosilane* and vinyltrichlorosilane (VCHZ Synthesia, Kolín) were purified only by distillation. 3,3-*Dimethyl*-1-*butene* was prepared by pyrolysis of 3,3-dimethyl-2-butyl acetate at 420°C[9] in 65% yield; b.p. 43°C, n_D^{20}, 1·3761 (lit.[9] gives b.p. 43°C, n_D^{20} 1·3765). 3-*Methyl*-3-*chloro*-1-*butene* was obtained by the addition of dry hydrogen chloride to isoprene[10] in ether at −15°C. As this compound decomposes on heating at 80°C for 2 h to give higher boiling compounds, chromatographic analysis of the purity of this compound was carried out at room temperature. B.p. 32°C/122 Torr, n_D^{20} 1·4189 (lit.[10] gives b.p. 32°C/120 Torr, n_D^{20} 1·4190). 3,3-*Dichloro*-1-*butene* was prepared by dehydrobromination of 1-bromo-3,3-dichlorobutane by potassium hydroxide[11] dissolved in 2-ethoxyethanol at 0°C in 40% yield. Because of decomposition of this compound on heating to 70°C, chromatographic analysis of its purity was carried out at room temperature. B.p. 44°C/15 Torr, n_D^{20} 1·4420 (lit.[11] gives 45°C/105 Torr, n_D^{20} 1·4460). 3,3,3-*Trichloro*-1-*propene*. The dehydration of methyl(trichloromethyl)carbinol by phosphorus pentoxide[12] afforded the fraction, b.p. 57°C/103 Torr (65%), which was identified by NMR as isomeric $Cl_2—C═CCl—CH_3$. The desired product was prepared by dehydrochlorination of 1,3,3,3-tetrachloropropane by solution of potassium hydroxide in 2-ethoxyethanol[13,14] in 45% yield. B.p. 60°C/175 Torr, n_D^{20} 1·4705 (lit.[12,13] gives b.p. 60°C/175 Torr, n_D^{20} 1·468). Rectification was carried out on a distillation column filled with Raschig rings (on distillation through a column filled with rings made from Kanthal wire 3,3,3-trichloro-1-propene was quantitatively converted into 1,1,3-trichloro-1-propene, as proved by NMR). Physical constants of the methylvinylchlorosilanes were reported elsewhere[5].

Preparation of Silyl-Substituted Dichlorocyclopropanes

Methyl(2,2-dichlorocyclopropyl)chlorosilanes were prepared by the reaction of methylvinylchlorosilanes with the dichlorocarbene generated by thermal decomposition of phenyl(bromodichloromethyl)mercury in benzene[7]. The procedure was described in detail in the work[1]. Their physical constants were reported in the work[5].

Measurement of Relative Rates

Relative rates of the addition of dichlorocarbene were deternined by the method of competition reactions; the dichlorocarbene was generated by Seyferth method[7]; the procedure used was described elsewhere[1]. The reaction mixtures were analysed on a gas chromatograph (Vývojové dílny, ČSAV). The instrument was equipped with catharometer; 140°C oven temperature, 60 ml : : min hydrogen flow rate. 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 grinded unglazed tiles. The area of chromatographic peaks corresponding to dichlorocyclopropane derivatives were planimetred and converted by means of calibration graphs to relative amounts. *Dipole moments* of carbon analogues of studied methylvinylchlorosilanes were determined by measurements of concentration dependence of the dielectric constants and specific volumes of dilute benzene solutions of the compounds, using the procedure described[1].

RESULTS AND DISCUSSION

As found earlier[5], in the addition of the dichlorocarbene generated by pyrolysis of trichloromethyltrichlorosilane at 200°C to trimethylvinylsilane and dimethylvinylchlorosilane the reaction components suffer decomposition[5]. In order to test their thermal stability at the conditions used to generate dichlorocarbene from phenyl(bromodichloromethyl)mercury (80°C) we have analysed corresponding reaction mixtures by gas chromatography. We have found that in this case no cleavage takes place.

As described, the carbon analogues of methylvinylchlorosilanes readily undergo rearrangement or decomposition reactions. 3-Methyl-3-chloro-1-butene, 3,3,-dichloro-1-butene and 3,3,3-trichloro-1-propene should be rectified under reduced pressure at temperatures below 60°C. Also their chromatographic analysis had to be carried out at the column temperature 25°C, since already at 50°C the above compounds undergo decomposition and oligomerization reactions, giving higher boiling substances. This fact rendered it impossible to carry out the addition of

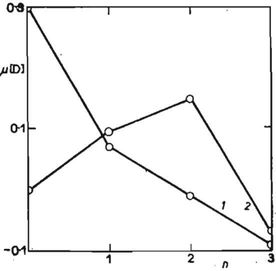

FIG. 1

Dependence of Differences of Absolute Values of Dipole Moments ($\Delta\mu$) of Compounds of the Type *1* $CH_2=CHSi(CH_3)_{3-n}Cl_n$ and *2* $CH_2=CHC(CH_3)_{3-n}Cl_n$ on the Number of Chlorine Atoms (n)

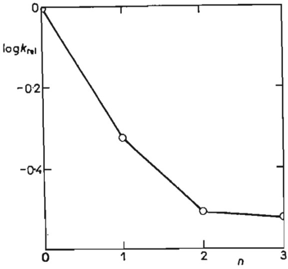

FIG. 2

Dependence of log k_{rel} of the Addition of Dichlorocarbene to Methylvinylchlorosilanes of the Type $CH_2=CHSi(CH_3)_{3-n}Cl_n$ on the Number of Chlorine Atoms (n) dichlorocarbene by Seyferth method[7] at 80°C; also Doering–Hoffmann method[15] could not be used in this case. For this reason with these compounds we restricted ourselves to determination of their dipole moments. From the obtained data and corresponding data for carbon analogues of methylchlorosilanes we calculated the difference of absolute values of dipole moments in the same way as in the case of $\Delta\mu$ calculated from data for methylvinylchlorosilanes and methylvinylchlorosilanes[4].

The dipole moments of methylvinylchloromethanes and methylchloromethanes ($\Delta\mu$, Fig. 1, curve *2*) do not deviate much from zero value and do not exceed significantly experimental error. Group moment $CH_2{=}CH{-}C$ is thus nearly constant. On going from the dichloro- to the trichloro-substituted derivative the difference of dipole moments attains negative value, which may be caused by a greater size of the vinyl group in 3,3,3-trichloro-1-propene, relative to the methyl group in 1,1,1-trichloroethane. The vinyl group can thus more efficiently reduce the mutual repulsion of chlorine atoms and aid in forming the arrangement closer to tetrahedral. The trend in differences of dipole moments for the first two members of the series of methylvinylchlorosilanes ($\Delta\mu$, Fig. 1, curve *1*) can be attributed to an increase in acceptive ability of silicon upon introducing chlorine atom into the molecule. This is demonstrated by progressive decrease in the vinyl–silicon bond moment. The chlorine atom, even though being able to form $(p \rightarrow d)\,\pi$ dative bond with silicon, affects physical properties of the studied compounds predominantly by its -I effect and does not compete with the π-electron system of vinyl group for $3d$ orbitals of silicon.

Based on the studies of the reactivity of vinylsilanes[5,16], it could be expected that, as the result of dative bond formation between vinyl group and silicon, the reactivity of all the methylvinylchlorosilanes towards electrophilic reagents would be lower than that of 1-heptene to which the relative reactivity of trimethylvinylsilane in the addition of dichlorocarbene was related[1]. The dependence of the reactivity on sub-

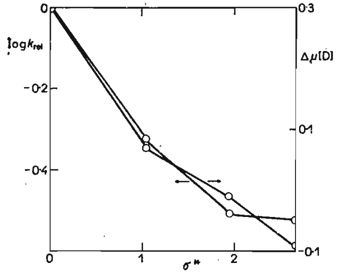

FIG. 3

Correlation of log k_{rel} and of Vinyl–Silicon Bond Moments on Taft Constants σ^* for Compounds of the Type $CH_2{=}CHSi(CH_3)_{3-n}.Cl_n$ (n = 0–3) stitution (Fig. 2) indicates that chlorine atoms affect the reactivity of studied compounds predominantly by their −I effect. The decrease of reactivity with increasing number of chlorine atoms is not however additive and, furthermore, it cannot be successfully correlated by Taft equation[17-20] with σ^* constants of corresponding chloro-substituted methyl groups. From Fig. 3 it is evident that increasing number of chlorine atoms does not bring about the expected change of inductive effect of chlorosilyl groups. Systematically decreasing effect of individual chlorine atoms, which reflects both in the difference of log k's and in the vinyl–silicon bond moments, can be explained by partial conjugation of chlorine which increases as the electron density on silicon decreases, as the result of progressive substitution of silicon by electron-withdrawing substituents.

Relative rate constants of the addition of dichlorocarbene to methylvinylchlorosilanes (Fig. 2) indicate that a concurrent formation of the $(p \rightarrow d)\,\pi$ dative bond between chlorine and silicon is not so important as to weaken back donation of π-electrons of vinyl group to silicon. The introduction of chlorine atom thus affects relative reactivity similarly as does chemical shifts of vinylic protons[3] and group moments[4] $Si{-}CH{=}CH_2$. When attached to silicon, chlorine atom decreases the reactivity much more than alkoxy[1] or trimethylsiloxy[16] groups, the oxygen atom of which is more engaged in concurrent dative bond formation with silicon.

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Translated by J. Hetflejš.