

## ORGANOSILICON COMPOUNDS. LXXVII.\*

NATURE OF THE SILICON-VINYL BOND  
IN METHYL-TERT-BUTOXYSILANES

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Synthesis and dipole moments of the methylvinyltert-butoxysilanes of type  $\text{CH}_2=\text{CHSi}(\text{CH}_3)_{3-n}(\text{OC}_4\text{H}_9\text{-t})_n$  ( $n = 0-3$ ) are reported. The relative rate constants (related to 1-heptene) of the addition of dichlorocarbene to these silanes, yielding methyl(2,2-dichlorocyclopropyl)tert-butoxysilanes, were determined. The obtained results were interpreted in terms of ( $p \rightarrow d$ )  $\pi$  bonding between silicon and  $\pi$ -electrons of vinyl group and of competitive ( $p \rightarrow d$ )  $\pi$  interaction between the silicon and the oxygen atoms of tert-butoxy groups.

In studying structure effects on the reactivity and physical properties of organosilicon compounds a tendency of silicon to formation of ( $p \rightarrow d$ ) $\pi$  dative bonds with vinyl<sup>1</sup> and phenyl groups, halogens, or oxygenous substituents should be considered. The aim of this work was to study the formation of competitive ( $p \rightarrow d$ )  $\pi$  dative bonds between silicon and  $\pi$ -electrons of vinyl group or unshared electron pairs of oxygen atom of an oxygenous substituent that takes place when these substituents are attached to a single silicon atom.

From the measurements of relative rate constants of the addition of dichlorocarbene to methyl(trimethylsiloxy)vinylsilanes<sup>2</sup> we concluded that in these derivatives the oxygen atoms of trimethylsiloxy groups can expel the double bond of vinyl group from ( $p \rightarrow d$ )  $\pi$  interaction with silicon.

The NMR spectra<sup>3</sup> and dipole moments<sup>4</sup> of methylvinylchlorosilanes and methylvinylalkoxysilanes showed that ( $p \rightarrow d$ )  $\pi$  bonding from chlorine to silicon in the chlorosilanes is not important, while in the alkoxysilanes the distinct formation of ( $p \rightarrow d$ )  $\pi$  dative bond between the silicon and the oxygen takes place, which may affect the nature of the silicon-vinyl bond.

In previous work<sup>2</sup> this problem was studied with trimethylsiloxy-substituted silanes where the oxygen atom of Si—O—Si bonds interacts with the two silicon atoms. Therefore, in the present paper we decided to use a series of vinylmethyl-tert-butoxysilanes of type  $\text{CH}_2=\text{CHSi}(\text{CH}_3)_{3-n}(\text{OC}_4\text{H}_9\text{-t})_n$  ( $n = 0-3$ ). The chemical reactivity

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of these compounds was determined by measuring the relative rate constants of the addition of dichlorocarbene generated either by thermal decomposition of phenyl-(bromodichloromethyl)mercury<sup>5</sup> or by reaction of chloroform with potassium tert-butylate. In order to compare the reactivity of these compounds with their properties in ground state we measured also the dipole moments of methyltert-butoxysilanes (denoted as series I) and methylvinyltert-butoxysilanes (denoted as series II) and calculated the differences<sup>4</sup>

$$\Delta\mu = \mu_I - \mu_{II} \quad (1)$$

Providing that the substitution of one methyl group in the series I for vinyl group (*i.e.* on going to the compound of series II having the same number of tert-butoxy groups) does not bring about any other change, the difference between dipole moments of the two compounds may be taken as the difference between dipole moments of the Si—CH<sub>3</sub> and Si—CH=CH<sub>2</sub> bonds.

## EXPERIMENTAL

*Phenyl(bromodichloromethyl)mercury* was prepared by reaction of phenylmercury chloride with bromodichloromethane and potassium tert-butylate<sup>6</sup> in ether at -20°C.

The *methylvinyltert-butoxysilanes* were prepared by reactions of appropriate methylvinylchlorosilanes with potassium tert-butylate.

*Dimethylvinyltert-butoxysilane* was obtained by reaction of 35 g of dimethylvinylchlorosilane dissolved in 200 ml of hexane with 35 g of potassium tert-butylate which was gradually added over a 2-hour period with cooling the reaction mixture. The precipitated potassium chloride was filtered off and the reaction mixture was distilled and then rectified to afford 25 g of dimethylvinyl-tert-butoxysilane (55% yield).

*Methylvinyl-ditert-butoxysilane* was prepared in a similar fashion (see Table I). In the preparation of *vinyl-tritert-butoxysilane* under the same experimental conditions *vinyl-ditert-butoxychlorosilane* was obtained in 10% yield as the only reaction product (for SiC<sub>10</sub>H<sub>21</sub>O<sub>2</sub>Cl (236.8) calculated: 50.72% C, 8.93% H; found: 50.63% C, 9.18% H). The desired product was obtained by reaction of the corresponding chlorosilane with potassium tert-butylate in octane at 125°C. The *methyltert-butoxysilanes*<sup>7</sup> were prepared in the similar way. Experimental conditions used in the preparation of *methyltert-butoxysilanes* and *methylvinyltert-butoxysilanes* are given in Table I. The physical properties of these compounds are summarized in Table II.

*Methyl(2,2-dichlorocyclopropyl)tert-butoxysilanes* were prepared by reactions of appropriate methylvinyltert-butoxysilanes with dichlorocarbene generated by thermal decomposition of phenyl(bromodichloromethyl)mercury in benzene<sup>5</sup>.

The structure of dimethyl(2,2-dichlorocyclopropyl)tert-butoxysilane ( $n_D^{20}$  1.4499, b.p. 208°C), methyl(2,2-dichlorocyclopropyl)ditert-butoxysilane ( $n_D^{20}$  1.4446, b.p. 237°C) and 2,2-dichlorocyclopropyltrtert-butoxysilane ( $n_D^{20}$  1.4353, b.p. 259°C) was proved by IR spectroscopy<sup>8</sup>.

The *relative rate constants* of the addition of dichlorocarbene to the vinylsilanes were determined by the method of competitive reactions<sup>9</sup>. The relative reactivity of trimethylvinylsilane with respect to 1-heptene (the reference compound) towards dichlorocarbene generated by Seyferth's method<sup>5</sup> was determined in the following way. Into a mixture of 89.9 mg of 1-heptene, 541.4 mg of trimethylvinylsilane and 3 ml of benzene placed in a 15 ml glass ampule were added 100 mg

TABLE I  
Preparation of Methyltert-butoxysilanes and Methylvinyltert-butoxysilanes

Compound	Solvent ml	Temperature °C	Starting chlorosilane g	Potassium tert-butylate g	Product g	Yield %
Dimethylvinyltert-butoxysilane	hexane 200	0	35	35	25	55
Methylvinyl-di-tert-butoxysilane	hexane 350	0	86	135	40	30
Vinyltri-tert-butoxysilane	octane 500	125	40	110	6.8	10
Trimethyltert-butoxysilane	hexane 200	0	30	30	25	65
Dimethyl-di-tert-butoxysilane	hexane 200	0	50	100	30	40
Methyltri-tert-butoxysilane	hexane 300	65	40	100	10	15

TABLE II  
Physical Constants of Methylvinyltert-butoxysilanes and Methyltert-butoxysilanes

Compound	B.p. °C/Torr	$n_D^{20}$	Dipole moment D <sup>e</sup>	$d_4^{20}$	% Si	
					calculated	found
Dimethylvinyltert-butoxysilane	122.5	1.4068	0.87	0.7962	16.50	16.70
Methylvinyl-di-tert-butoxysilane	94.5/60	1.4103	1.12	0.84272	12.97	12.55
Vinyltri-tert-butoxysilane	183 <sup>a</sup>	1.4090	1.08	0.86983	10.25	10.27
Trimethyltert-butoxysilane	101 <sup>b</sup>	1.3908 <sup>b</sup>	1.04	—	19.20	19.47
Dimethyl-di-tert-butoxysilane	85/100 <sup>c</sup>	1.3960 <sup>c</sup>	1.39	—	13.74	13.89
Methyltri-tert-butoxysilane	92/20 <sup>d</sup>	1.3980 <sup>d</sup>	1.55	—	10.70	10.92

<sup>a</sup>Determined by gas-liquid chromatography. <sup>b</sup>Reported<sup>15</sup> b.p. 101°C/754 Torr,  $n_D^{20}$  1.3913.

<sup>c</sup>Reported<sup>16</sup> b.p. 50.5°C/15 Torr,  $n_D^{20}$  1.3970. <sup>d</sup>Reported<sup>17</sup> b.p. 90–91°C/20 Torr,  $n_D^{25}$  1.3959.

<sup>e</sup>Dipole moment of trimethylvinylsilane 0.30D.

of phenyl(bromodichloromethyl) mercury. The sealed ampule was dipped into an oil bath kept at  $86 \pm 0.05^\circ\text{C}$  and then efficiently shaken for 2 hours. After cooling, the reaction mixture, freed of solid phenylmercury chloride by centrifugation, was analyzed by gas-liquid chromatography. The same procedure was employed in the determination of the relative rate constants for other couples of the olefins.

The relative reactivity of dimethylvinyltert-butoxysilane with respect to trimethylvinylsilane in the addition of dichlorocarbene generated by Doering-Hoffmann method<sup>10</sup> was determined at  $10^\circ\text{C}$  in benzene and at  $-30^\circ\text{C}$  in hexane. A 5 ml volumetric flask was charged with weighted amounts of the olefins (in ten-fold molar excess with respect to the dichlorocarbene generated), chloroform and the solvent and the solution was warmed to reaction temperature. Then potassium tert-butyrate was added and the content of the flask was shaken. After 1 hour standing, the reaction mixture was analyzed by gas-liquid chromatography.

The *gas-chromatography analyses* were carried out on a Griffin D 6 chromatograph (Griffin and George, London). The column (0.4 cm inside diameter, 200 cm length) was packed with 5% poly(dimethylsiloxane) elastomer of type E 301 (supported on a ground unglazed tile). The systems dimethylvinyl-tert-butoxysilane/trimethylvinylsilane, methylvinyl-di-tert-butoxysilane : dimethylvinyltert-butoxysilane, and methylvinyl-ditert-butoxysilane/vinyltriertert-butoxysilane were analyzed using 50 ml/min nitrogen flow rate and the oven temperature 120, 150, and  $180^\circ\text{C}$ , respectively.

The *dipole moments* of the methylvinyltert-butoxy- and methyltert-butoxysilanes were determined from concentration dependences of dielectric constants of diluted benzene solutions of the compounds. The dielectric constants were measured on the instrument designed after LeFèvre<sup>11</sup>. The dipole moments were calculated by Halverstadt-Kumler method<sup>12</sup>.

## RESULTS AND DISCUSSION

On the basis of the studies of the reactivity of vinylsilanes towards electrophilic agents<sup>2,13</sup> one can expect that also the methylvinyltert-butoxysilanes under study will be of markedly lower reactivity than the reference carbon compound, 1-heptene, due to the ( $p \rightarrow d$ )  $\pi$  nature of the silicon-vinyl bond in the former compounds. This assumption proved to be correct: the reactivity of 1-heptene towards dichlorocarbene generated by Seyferth method<sup>5</sup> is increased by a factor of eight over that of trimethylvinylsilane. The interpretation of the observed effect of substitution on the reactivity of the methylvinyltert-butoxysilanes (Fig. 1) is not simple. The lower reactivity exhibited by all the model silicon compounds towards dichlorocarbene generated by Seyferth method<sup>5</sup> (Fig. 1, curve 3) can be undoubtedly attributed to the ( $p \rightarrow d$ )  $\pi$  nature of the silicon-vinyl bond. This low reactivity cannot be caused predominantly by steric effects since in such a case the successive substitution of methyl groups in vinyltrimethylsilane for bulky tert-butoxy ones would have exerted more significant effect. The  $-I$  effect of tert-butoxy groups does not affect the reactivity of the methylvinyltert-butoxysilanes possessing one or two tert-butoxy groups. This fact may be accounted for by assumption that the competitive ( $p \rightarrow d$ )  $\pi$  dative bond between the silicon and the oxygen of tert-butoxy group reduces the ( $p \rightarrow d$ )  $\pi$  character of the silicon-vinyl bond, which makes  $\pi$ -electrons of the vinyl group more available. The operation of these two opposite effects might result in almost the same reactivity

of all the model compounds. The decreased reactivity of vinyl-*tert*-butoxysilane may be then attributed to the steric effect of the three bulky *tert*-butoxy groups.

The dependence of the rate of addition of dichlorocarbene generated by Doering-Hoffmann method<sup>10</sup> on substitution (Fig. 1, curves 1 and 2) is of little significance as well: the differences in the reactivity of individual members of the series are relatively small, and do not depend significantly on the experimental conditions employed in the generation of the carbene. When compared with the preceding case, the only difference can be seen in that here the decrease in reactivity is already observed with the second member of the series. It seems to us that this difference might be the result of greater importance of solvation effects in the case where dichlorocarbene is generated by Doering-Hoffmann method. In fact, the study of the selectivity<sup>14</sup> of the addition of dichlorocarbene generated by Seyferth method<sup>5</sup> showed that this reaction is little affected by solvent. It seems improbable that on generating dichlorocarbene by Doering-Hoffmann method<sup>10</sup> this would be the case, since strongly basic species, alcoholates, are present. Similar explanation has already been suggested in our previous paper.

The observed effect of the oxygenous substituents is smaller than it could be

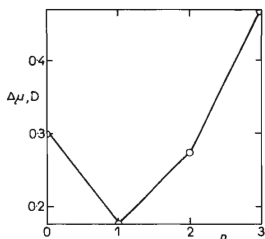


FIG. 1

Dependence of  $\log k_{rel}$  of the Addition of Dichlorocarbene to the Methylvinyl-*tert*-butoxysilanes  $\text{CH}_2=\text{CHSi}(\text{CH}_3)_{3-n}(\text{OC}_4\text{H}_9-t)_n$  ( $n = 0-3$ ) on  $n$

Dichlorocarbene generated by reaction of chloroform with potassium *tert*-butylate at 10°C in benzene (curve 1) and at -30°C in hexane (curve 2), and by thermal decomposition of phenyl(bromodichloromethyl)-mercury at 80°C in benzene (curve 3).

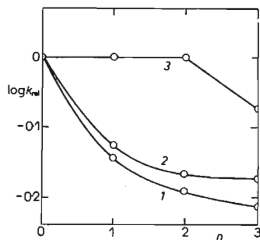


FIG. 2

Dependence of Differences in Absolute Values of Dipole Moments,  $\Delta\mu$  (Eq. (1)), of Methylvinyl-*tert*-butoxysilanes

$\text{CH}_2=\text{CHSi}(\text{CH}_3)_{3-n}(\text{OC}_4\text{H}_9-t)_n$  and Methyl-*tert*-butoxysilanes  $(\text{CH}_3)_{4-n}\text{Si}(\text{OC}_4\text{H}_9-t)_n$  on  $n$

expected under assumption that only the -I effect of tert-butoxy group is operative. It can be thus said that the ( $p \rightarrow d$ )  $\pi$  dative bond between the oxygen and silicon atom significantly participates in a small decrease of the reactivity of alkoxy-substituted derivatives. This competitive ( $p \rightarrow d$ )  $\pi$  interaction of the oxygenous groups, which affects the nature of the vinyl-silicon bond, seems to be proved by parallel measurements of dipole moments of the methylvinyltert-butoxy- and methyltert-butoxysilanes (Table II). The differences in absolute values of dipole moments for the corresponding members of both series were calculated from Eq. (1), where the methyltert-butoxysilanes and the methylvinyltert-butoxysilanes are denoted by index I and II, respectively. The values of  $\Delta\mu$  are graphically represented in Fig. 2.

The differences  $\Delta\mu$  between the vinylmethyltert-butoxysilanes and methyltert-butoxysilanes can be attributed to the substitution of methyl for vinyl groups<sup>4</sup>. It means that the change in the value of  $\Delta\mu$  corresponds to the change in the silicon-vinyl bond dipole moment.

From the dependence of  $\Delta\mu$  on the number of tert-butoxy-groups (Fig. 2) it follows that the introduction of the first tert-butoxy group brings about the decrease in the value of  $\Delta\mu$ , likely due to the -I effect of tert-butoxy group that intensifies the ( $p \rightarrow d$ )  $\pi$  interaction in the silicon-vinyl bond. The introduction of the second and the third tert-butoxy group is accompanied by the increase in the value of  $\Delta\mu$  and thus also in the silicon-vinyl bond dipole moment. This increase may be accounted for by the interaction of unshared electron pairs of the oxygen atom which competes with  $\pi$ -electrons of the vinyl group for vacant  $3d$  orbitals of the silicon atom. The result of such a competition is a partial expulsion of  $\pi$ -electrons of the vinyl group from the interaction. Therefore, the results of the measurements of the relative rate constants of the addition of dichlorocarbene to the methylvinyltert-butoxysilanes and those of the dipole moment measurements can be interpreted in the similar way. The interpretation suggested in the present paper is also in harmony with the results of NMR<sup>3</sup> and IR<sup>1</sup> spectra measurements, dipole moments<sup>4</sup> and the reactivity<sup>2</sup> of other methylvinylalkoxysilanes.

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