

A STUDY OF INTERMOLECULAR INTERACTION BETWEEN SILICON AND FUNCTIONAL GROUP IN (DIETHOXYMETHYLSILYL)ALKYL ACETATES*

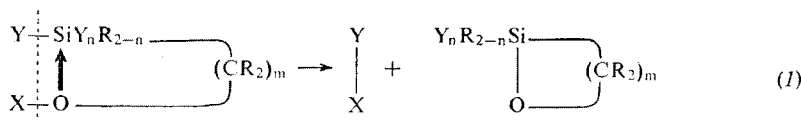
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The possibility of intramolecular interaction between the functional group and the silicon in the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) was studied by IR and NMR spectroscopy and by mass spectrometry, and the behaviour of these compounds at elevated temperatures and in the presence of acid-base catalysts was also examined. It was found that on electron impact silicon atom of all the compounds studied interacts with the ethereal oxygen of the acetoxy group and likely also with the carbonyl oxygen. The behaviour of the compounds $(C_2H_5O)_2 \cdot CH_3Si(CH_2)_nOC(O)CH_3$ at elevated temperatures and in the presence of acid-base catalysts was explained by redistribution reaction with participation of silicon atom which is intramolecular only in the base-catalysed reaction of the compound with $n = 4$. General character of this novel intramolecular redistribution of the type $R-C(O)OR^1 + R_3^2SiOR^3 \rightleftharpoons R-C(O)OR^3 + R_3^2 \cdot SiOR^1$ was demonstrated by the reaction of octyloxytrimethylsilane with methyl butyrate.

Oxygen-containing carbofunctional silicon compounds of the type $R_3Si(CR_2)_n-Y$ (Y is a functional group containing oxygen) are of interest with regard to the possible intramolecular interaction between the functional group and silicon atom which is usually interpreted in terms of a coordination $(p-d)_\sigma$ bond. The interaction of this type has been found to take place in the ground state of the ketones^{1,2} $R_3SiCH_2C(O)R$ and the esters $R_3Si(CH_2)_2CO_2R$ (ref.³) and $(CH_3)_3Si(CH_2)_nOC(O)CH_3$ (refs.^{4,5}) and can account for stabilisation of transition states of some reactions proceeding at elevated temperatures or in the presence of acid-base catalysts. Such reactions can be separately classified as rearrangement of a silyl fragment (ref.⁶ and references therein), elimination reactions with participation of a silyl fragment^{7,8} and intramolecular disproportionations with participation of silicon atom (equation (1)). In terms of this dispro-



portionation one can explain the thermal and acid-base catalysed decompositions of ω -hydroxy-alkyl-substituted siloxanes of the type $HO(CH_2)_nSi(CH_3)_2OSi(CH_3)_2R$ (ref.⁹⁻¹³), the compounds

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$X_nR_{3-n}Si(CH_2)_mOSiR_3$ (ref.¹⁴⁻¹⁶), carboxylic acids of the type $-(CH_3)_2SiOSi(CH_3)_2 \cdot (CH_2)_mCO_2H$ (ref.^{17,18}) and the esters $R_nCl_{3-n}Si(CH_2)_mCO_2R$ (ref.¹⁹). Some types of oxygen-containing carbofunctional silicon compounds have turned out to be so unstable due to intramolecular disproportionation that in some of their attempted syntheses they were formed only as unstable intermediates. These were the compounds $X_nR_{3-n}Si(CH_2)_nCO_2Si(CH_3)_3$ (refs^{20,21}) and $X_nR_{3-n}Si(CH_2)_nOSiR_3$ (refs^{22,23}). The esters $(RO)_nR_{3-n}Si(CH_2)_3OCOR'$ undergo base-catalysed reaction in alcohols as solvents, giving²⁴⁻²⁶ 1-oxa-2-silacyclopentanes and the esters $R'C(O)OR$. Whether in this case intramolecular disproportionation of the above esters or transiently formed alcohols of the type $(RO)_nR_{3-n}Si(CH_2)_3OH$ is taking place is not yet clear.

In the present work we have therefore studied the behaviour of the compounds of this type both at elevated temperatures and in the presence of base or acid catalysts, using the silanes $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) as model compounds. The possibility of intramolecular interaction between silicon and the functional group of these compounds during electron impact was examined by mass spectrometry. In this study the extent of this interaction in the ground state of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ was estimated from the values of the chemical shift $\delta CH_3(C)$ and the intensities of the $\nu(C=O)$ absorption band.

EXPERIMENTAL

Model Compounds

The preparation and physical constants of acetoxyethyl(methyl)diethoxysilane were reported elsewhere²⁷. 2-Acetoxyethyl(diethoxy)methylsilane and 3-acetoxypropyl(diethoxy)methylsilane were prepared by reaction of 2-acetoxyethyl(dichloro)methylsilane²⁸ or 3-acetoxy(dichloro)methylsilane²⁸ with ethanol in the presence of stoichiometric amount of pyridine in dry diethyl ether. The compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOCOCH_3$ ($n = 4-6$) were obtained by the addition of methyl-diethoxysilane to the appropriate alkenyl acetate such that stoichiometric amounts of both components were refluxed in the presence of hexachloroplatinic acid for 20 h. The purity of all the compounds was checked by gas chromatography and their identity was confirmed by elemental analysis and IR spectroscopy.

$(C_2H_5O)_2CH_3Si(CH_2)_nOCOCH_3$ (n , yield (%), b.p. ($^{\circ}C/Torr$), n_D^{20}): 2-46; 123/35; 1-4136; (ref.²⁹; b.p. 145 $^{\circ}C/49$ Torr, n_D^{25} 1-4163); 3-67; 122/20; 1-4168; 4-57; 133/20, 1-4199; 5-31, 121/10, 1-4230; 6-34, 126/5, 1-4258. The following derivatives are new compounds. $(C_2H_5O)_2CH_3Si(CH_2)_3 \cdot OCOCH_3$, for $C_{10}H_{22}O_4Si$ (234.4) calculated: 51.25% C, 9.46% H; found: 50.94% C, 9.33% H. $(C_2H_5O)_2CH_3Si(CH_2)_4OCOCH_3$, for $C_{11}H_{24}O_4Si$ (248.4) calculated: 53.18% C, 9.74% H; found: 52.99% C, 9.63% H. $(C_2H_5O)_2CH_3Si(CH_2)_5OCOCH_3$, for $C_{12}H_{26}O_4Si$ (262.4) calculated: 54.93% C, 9.99% H; found: 54.96% C, 9.88% H. $(C_2H_5O)_2CH_3Si(CH_2)_6OCOCH_3$, for $C_{13}H_{28}O_4Si$ (276.5) calculated: 56.48% C, 10.21% H; found: 56.55% C, 10.37% H.

Reactions Studied

Behaviour of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) at elevated temperature (160 $^{\circ}C$) and in the absence and presence of catalysts was followed by gas chromatography. Samples of the same relative amounts of acetoxyalkyl (diethoxy)methylsilane, an internal standard (tetradecane, hexadecane, octadecane) with and without a catalyst (1M-HCl or 1M- C_2H_5ONa)

in C_2H_5OH) were sealed in test tubes and heated at $160^\circ C$ for 2 and 4 h. The molar concentration of the catalysts was 10^{-2} -times lower than the concentration of the compounds $(C_2H_5O)_2 \cdot CH_3Si(CH_2)_nOC(O)CH_3$. The course of the reaction was evaluated from a decrease in the surface area of the elution peak of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOCOCH_3$ or from an increase in the surface area of the peak corresponding to ethyl acetate. Gas chromatographic analysis was also used to follow the course of the reaction of methyl butyrate with trimethyloxyloxy silane (see below).

Spectroscopic Measurements

IR absorption spectra ($4000-400\text{ cm}^{-1}$) were measured with a double-beam Zeiss, Model UR 20 spectrophotometer. The absorptivity of the sample at the wavenumber of the $C=O$ stretching vibration (around 1700 cm^{-1} , LiF prism) was determined for 0.1M solutions of the compounds in tetrachloromethane (spectrograde) using 0.01 cm cells. The values listed were determined as an average of six recorded maxima for two independently prepared 0.1M solutions. The relative experimental error did not exceed 3 per cent. Mass spectra of all the compounds were recorded with a LKB 8000 spectrometer (70 eV ionizing source energy). Chemical shifts of the methyl group of the acetates $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ in CCl_4 were measured with a modified Tesla BS-477 spectrometer (60 MHz), with an accuracy of ± 0.2 Hz using tetramethylsilane as an internal reference. Concentration of all the samples was 100 mg of the ester per 1 ml of tetrachloromethane.

RESULTS AND DISCUSSION

Acid-Base Catalysed Reactions

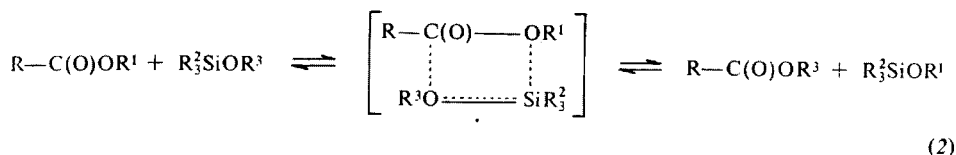
The compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) undergo condensation in the presence of catalytic amounts of hydrogen chloride at elevated temperature ($160^\circ C$) to form oligomers under the release of ethyl acetate. In the presence of hexachloroplatinic acid this reaction takes place already at room temperature. With the exception of the compound with $n = 4$, all the above compounds behave similarly also in the presence of catalytic amounts of sodium ethoxide at elevated temperatures. The rate of ethyl acetate formation was both for the base- (except $n = 4$) and acid-catalysed reaction approximately the same for all the derivatives ($n = 2-6$). The rate was faster than that for the reaction carried out in the absence of both types of catalysts and slower than the rate of the base-catalysed reaction of the compound $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ whose products were identified as ethyl acetate and 1-oxa-2-silacyclohexane, $(C_2H_5O)_2CH_3Si(CH_2)_nO$. From the above results it follows that the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) undergo acid-base catalysed condensation which is intermolecular with the exception of the base-catalysed reaction of the derivative with $n = 4$ (intramolecular cyclization).

On the basis of product analysis and the fact that decomposition of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ is acid-base catalysed the course of the above-

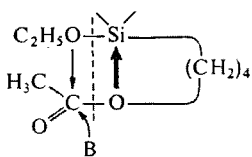
mentioned decomposition can be depicted by the transition states shown below which are formed by *a*) interaction of the $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ molecule with the catalyst (intramolecular route), *b*) interaction of the complex formed from the above acetate and the catalyst (further referred to as the complex) with another molecule of the silylalkyl acetates (intermolecular route).

β - or γ -oxygen-substituted carbofunctional compounds undergo under analogous conditions the β - or γ -elimination³⁰ to give alkenes or cyclopropane, respectively. This possibility has not to be considered in the case of the compounds $(C_2H_5O)_2CH_2Si(CH_2)_nOC(O)CH_3$ ($n = 2$ or 3) since the products of such decomposition have not been present in our case.

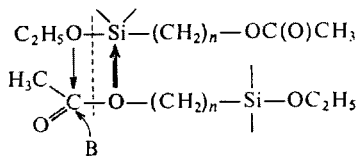
General character of this novel intramolecular redistribution reaction taking place between an ester of carboxylic acid and an alkoxy silane (equation (2)) was demonstrated by the reaction of octyloxytrimethylsilane and methyl butyrate catalysed with hexachloroplatinic acid.



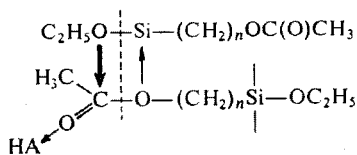
In the case of the base-catalysed reaction both types of transition states are represented by the structures *I* and *II* (B base). Intramolecular course of the base-catalysed disproportionation on silicon of the derivative with $n = 4$ has obviously its origin in the suitable distance between both primarily interacting centers in the complex, *i.e.* the ethereal oxygen of the acetoxy group and the silicon atom of the same molecule. From intermolecular character of the base-catalysed disproportionation of the other members of the series $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n \neq 4$) it can be concluded that the distance between the ethereal oxygen of the acetoxy group



B ... base *I*



II B ... base



III

and the silicon atom is great enough to prefer the intermolecular character of the $O \rightarrow Si$ interaction in the transition state of the condensation over the intramolecular interaction. (Reactions of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n \neq 4$) preserve intermolecular character even if the reaction is carried out in tenfold excess of dimethylformamide).

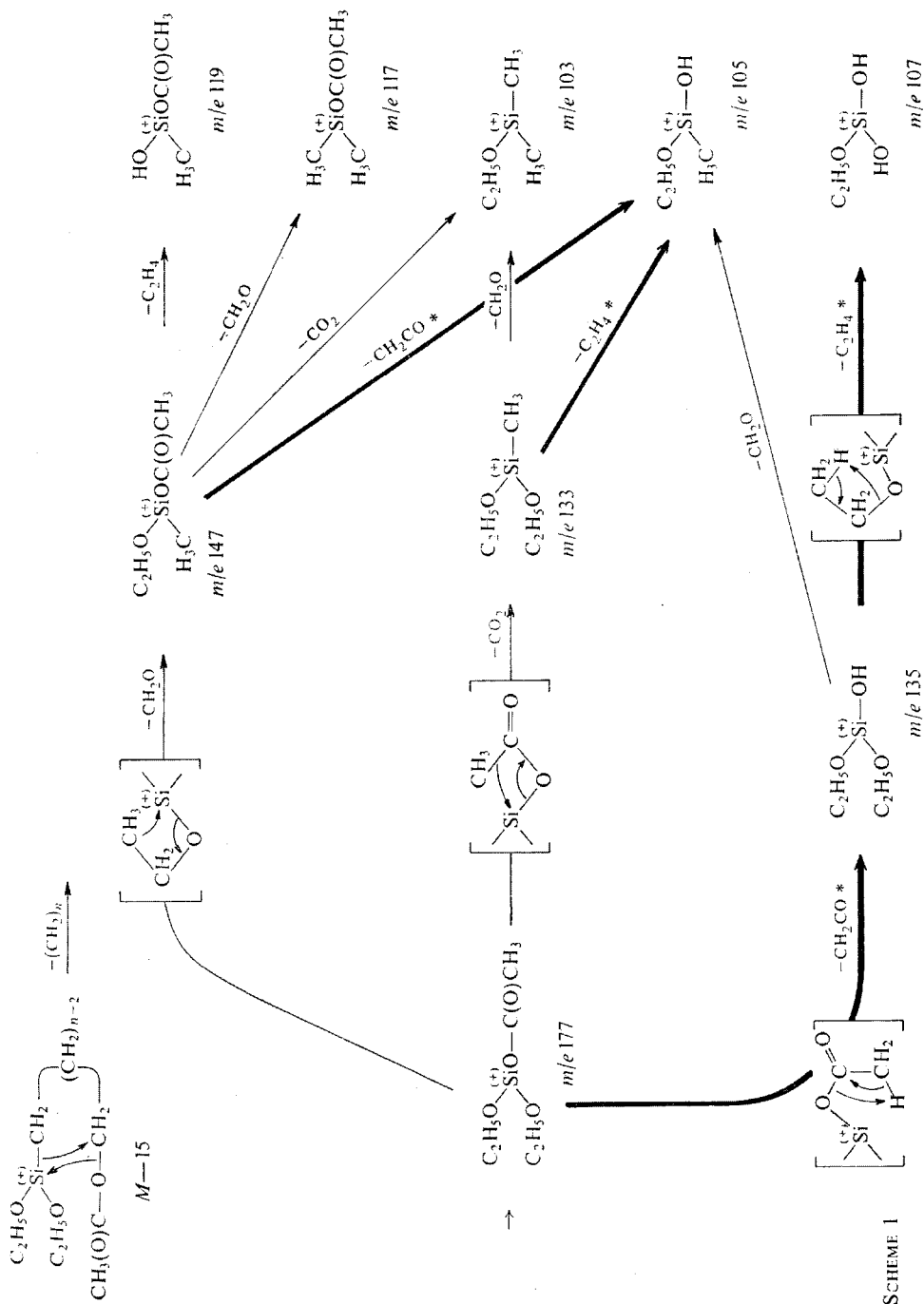
It can be assumed that the acid-catalysed disproportionation reaction of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ proceeds *via* transition state III (HA stands for an acid) whose formation is preceded by formation of the complex due to interaction of the Lewis acid with the oxygen atom of the carbonyl group of the silylalkyl acetate molecule. This interaction which reduced the ability of the ethereal oxygen of the acetoxy group to interact with the silicon atom would make initiation of the reaction by attack of the oxygen of the ethoxy group on the carbonyl carbon more favourable. Exclusively intermolecular character of the acid-catalysed disproportionation could then indicate how important has to be the $(p-d)_\sigma$ intramolecular $O \rightarrow Si$ interaction in the complex for initiation of the intramolecular disproportionation.

Thermal disproportionation, similarly as the acid-catalysed one, is exclusively intermolecular. This proves that a weak intramolecular $O \rightarrow Si$ interaction, taking place already in the ground state of some of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ (see later) is too weak to cause thermal cyclization of these compounds and must be further strengthened in the complex of the base-catalysed disproportionation of the derivative with $n = 4$.

Mass Spectra

Carbofunctional silicon compounds differ in their behaviour from carbon analogues during electron impact³¹⁻³³. The specific effect exerted by the silicon atom in the course of fragmentation of β -carbofunctional compounds of the type $(CH_3)_3Si(CH_2)_2.C(O)X$ ($X = OCH_3, OH, Cl$) results from interaction between the electron-deficient silicon atom and the part of the functional group X (ref.³²). In addition to this interaction, in the γ -carbofunctional compounds $(CH_3)_3Si(CH_2)_3C(O)OCH_3$ there is also migration of the trimethylsilyl group to the carbonyl oxygen³³. On the contrary, migration of the hetero atom to the silicon has been reported in the work³⁴.

Mass spectra of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ ($n = 2-6$) (Fig. 1) are all similar, *i.e.* on electron impact the same fragments are formed from all the members of the above series. Dominant peaks in all the spectra are at m/e 147 and 133, further intense peaks are at m/e 177, 161, 135, 105, 89, 77, 61, 45 and 43. Based on the same character of mass spectra of the derivatives with $n = 2-6$ and observed metastable ions (denoted by asterisks) one can assume that fragmentation of these compounds takes place according to Scheme 1 and involves specific rearrangements of the four types; rearrangement accompanied



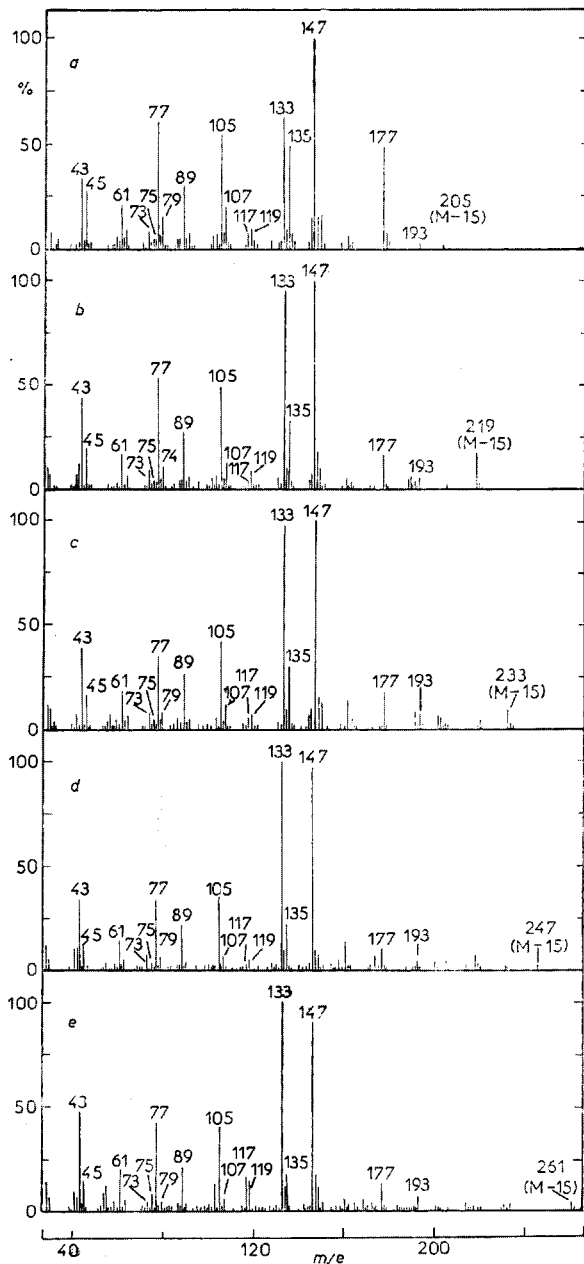
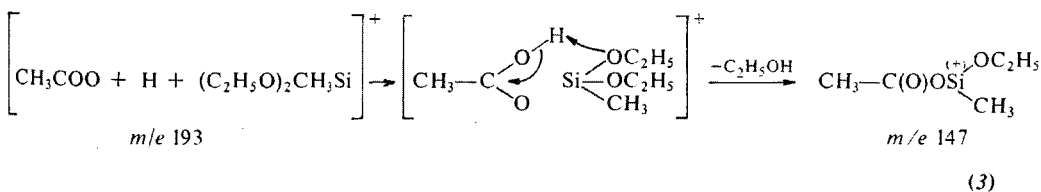


FIG. 1

Mass Spectra of the (Diethoxymethylsilyl)alkyl Acetates $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$
 $a n = 2, b n = 3, c n = 4, d n = 5, e n = 6$.

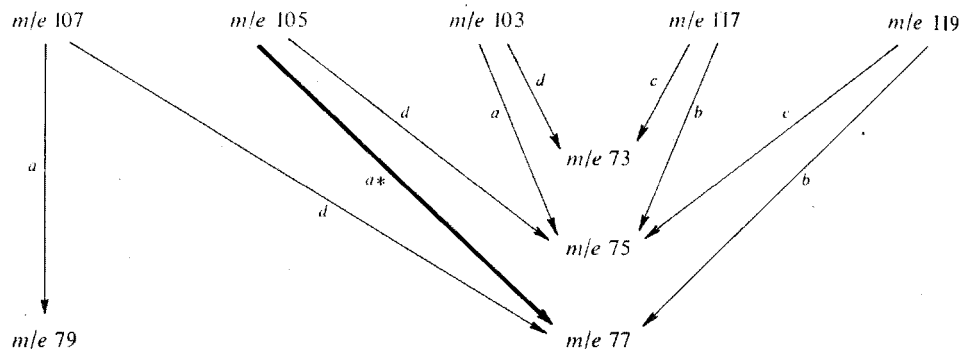
by elimination of the molecule of ethylene *a*), ketene *b*), carbon dioxide *c*) and formaldehyde *d*). The first type was already observed³⁵ with alkoxy silanes and in the present work it was proved together with the rearrangement *b*) by occurrence of the corresponding metastable ion. The other two types of rearrangement have their analogy in similar systems: trimethylsilyl esters of substituted benzoic acids³⁶ *c*) and benzyloxytrimethylsilanes³⁷ or aromatic ethers³⁸ *d*). The rearrangement *d*) was assumed to take place also during fragmentation of trimethylethoxysilane³⁹. On the basis of these interactions also further fragmentation of the ions with *m/e* 119, 117, 107, 105 and 103 (Scheme 2) can be explained and the corresponding fragments can be assigned the following structures: $(\text{OH})_3\text{Si}^+$ (*m/e* 79), $\text{CH}_3(\text{OH})_2\text{Si}^+$ (*m/e* 77), $(\text{CH}_3)_2(\text{OH})\text{Si}^+$ (*m/e* 75), $(\text{CH}_3)_3\text{Si}^+$ (*m/e* 73). The fragment with *m/e* 89 (intense peak) may arise from the fragment with *m/e* 107 by elimination of water molecule. Peaks at *m/e* 61 and 45 are characteristic of fragments formed by specific rearrangement of acetic acid esters and in agreement with the literature⁴⁰ they can be assigned the structure $[\text{CH}_3\text{COO} + 2\text{H}]^+$ and $[\text{CH}_3\text{CO} + 2\text{H}]^+$, respectively. The peak at *m/e* 43 can be ascribed to the fragment $[\text{CH}_3\text{CO}]^+$. Its height is 33–47% of the height of the base peak of the spectra (*m/e* 133 or 147) and is thus much smaller than that of the similar peak in the spectra of alkyl acetates (at least 75% of the height of the base peak of the spectrum⁴⁰). This fact could be explained provided that the $\text{M}^+ \rightarrow (\text{M}-15)^+$ fragmentation simultaneously taking place is preferred in our case. In all the spectra the peaks corresponding to the rearranged ions $[(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n-1]^+$ are practically absent (in the case of the esters $\text{RC}(\text{O})\text{OR}'$ the ions $(\text{R}'-1)^+$ are usually observed for R' greater than propyl⁴⁰) as well as the ions formed by their degradation. Of special interest is the peak at *m/e* 193 which occurs in all the spectra and which can be ascribed to the fragment $[\text{CH}_3\text{COO} + \text{H} + (\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}]^+$, since the presence of the corresponding metastable peak at $m = 112.0$ ($m_{\text{calc.}} = 111.96$) gives evidence for the fragmentation depicted by equation (3).



Formation of analogous ion $[\text{CH}_3\text{COO} + 2\text{H}]^+$ during fragmentation of the alkyl esters $\text{RC}(\text{O})\text{OR}'$ results from the cleavage of the $\text{O}-\text{C}_\text{R}$ bond and simultaneous migration of two hydrogens predominantly from γ - and δ -carbons of the group R' (ref.⁴¹). The presence of the fragment with *m/e* 193 speaks for a considerable migration ability of the bulky methyl diethoxysilyl group. Low intensity of this peak is

obviously due to the low stability of the corresponding fragment as a result of the decomposition according to equation (1).

The behaviour of the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ during electron impact can be thus characterized by the fragmentations $M^+ \rightarrow m/e$ 193



SCHEME 2

(Eq. (1)) and $(M-15)^+ \rightarrow m/e$ 177 (Scheme 1). Formation of the ion with m/e 193 is the evidence in support of the interaction of the silicon of the diethoxymethylsilyl group with the acetoxy oxygen in the molecular ion (the silicon atom may interact with both types of oxygen atoms and relative importance of each interaction may change with n). The mode of further cleavage of the fragment $(M-15)^+$ (Scheme 1) confirms the interaction of the etheral oxygen of the acetoxy group with the electron-deficient silicon atom. Both types of interaction of the silicon with the functional group ($M^+ \rightarrow m/e$ 193 and $(M-15)^+ \rightarrow m/e$ 177) "compete" with one another and their relative importance changes likely in dependence on the alkyl chain length. As follows from nearly identical relative intensity of the molecular ions for all the members of the series (from $n = 2$ to $n = 6$: 0.98, 0.20, 0.30, 0.07, 0.16) the ease with which the $-(CH_2)_n-$ chain is expelled does not practically depend on its length. A similar situation was observed (and discussed) in the case of the compounds $(CH_3)_3SiO(CH_2)_nOR$ ($R = (CH_3)_3Si$, alkyl, phenyl)^{42,43}.

NMR and IR Spectra

Chemical shift of the methyl group in 1H -NMR spectra of the acetates $CH_3C(O)OR$ is controlled above all by the polar effect of groups R and also by the effect of carbon atoms in the position 6 (ref.^{44,45}). The difference between the chemical shift of the $CH_3(C)$ group in the compounds $(C_2H_5O)_2CH_3Si(CH_2)_nOC(O)CH_3$ (the chemical shifts for $n = 2-6$: 115.54, 117.14, 116.52, 117.62 and 116.79 Hz) and tetramethyl-

silane is greater than the analogous difference for the alkyl acetates ROC(O)CH_3 (the chemical shift for $\text{R} = \text{CH}_3(\text{CH}_2)_n$, $n = 1-4$; 118.3 Hz)^{44,45}. The greater shielding of the $\text{CH}_3(\text{C})$ protons in the organosilicon acetates (perhaps with the exception of $n = 2$) can not be accounted for either by the inductive or steric effect (the steric effect of groups R is responsible for the shift of the signal of the methyl group down-field^{44,45}) of the $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}$ groups. The chemical shift $\delta(\text{CH}_3)$ of the acetates was interpreted by Kan⁴⁴ in terms of hybrid structures *IV* and *V*, assuming that steric inhibition of the form *V* decreases transmittance of the electron donor effect of the group R . The greater shielding of the methyl group in the compounds $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n\text{OC(O)CH}_3^*$ could be thus caused by the increased transmittance of the electron donor effect of the silylalkyl groups. Such permeability could – in agreement with the above-mentioned interpretation⁴⁴ – be ascribed to the greater contribution of the form *V* which could be justified by weak intramolecular interaction of the carbonyl oxygen with the silicon atom. This interpretation involving weak intramolecular interaction of the type $\text{C}=\text{O}\cdots\text{Si}$ is also consistent with the fact that the absorptivities of the compounds $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n\text{OC(O)CH}_3$ (and similarly also the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OC(O)CH}_3$ (ref.⁴⁷) with $n = 2-6$ (in $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 635, 625, 555, 585, 610 are as a rule higher than the same absorptivity of the alkyl acetates $\text{CH}_3(\text{CH}_2)_n\text{OC(O)CH}_3$ ($545 \pm 15 \text{ l mol}^{-1} \text{ cm}^{-1}$) with $n = 2-4$. The lowest values found for the silicon derivative with $n = 4$ may bear upon the ability of this compound to cyclize in an intramolecular fashion in the presence of bases (see preceding discussions) and can indicate that the importance of the $\text{C}=\text{O}\cdots\text{Si}$ interaction is decreased due to the shorter distance (and presumably also weak interaction) between the silicon and the ethereal oxygen.

The NMR and IR data just discussed thus support the assumption⁴⁵ about specific interaction between the acetoxy group and the silicon in the silylalkyl acetates. The character of this weak interaction (the wavenumber of the $\nu(\text{C}=\text{O})$ vibration of the compounds $\text{R}_3\text{Si}(\text{CH}_2)_n\text{OC(O)CH}_3$ ($\text{R}_3 = (\text{CH}_3)_3, (\text{C}_2\text{H}_5\text{O})_2\text{CH}_3$, $n = 2-6$) is the same as the wavenumber of the $\nu(\text{C}=\text{O})$ vibration of alkyl acetates⁴⁸) is not apparently the same in all the compounds studied, since both oxygens of the acetoxy group can interact with silicon (see also the mass spectra) and depends on the number of methylene groups separating the silyl group from the acetoxy group. The behaviour of the compounds $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n\text{OC(O)CH}_3$ under acid-base conditions indicates further that the relative importance of both of these interactions may be influenced also by weakening or strengthening of some of the interactions in the transition state⁴ of the reactions of these compounds, depending on the nature of the reactant.

* The $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n$ -group ($n = 2-6$) affects the chemical shift $\delta \text{CH}_3(\text{C})$ similarly as does the corresponding $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n$ -group⁴⁶.

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