

DUAL BEHAVIOUR OF $(\text{CH}_3)_3\text{SiCH}_2$ AND $(\text{CH}_3)_3\text{GeCH}_2$ GROUPS IN OXYGEN-CONTAINING α -CARBOFUNCTIONAL COMPOUNDS*

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The influencing of reactivity of the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{M} = \text{Si}, \text{Ge}$; $\text{X} = \text{H}$, alkyl, $\text{C}(\text{O})\text{CH}_3$, $\text{Si}(\text{CH}_3)_3$) by the electronic effect of $(\text{CH}_3)_3\text{MCH}_2$ groups depends on the nature of the second reactant. $(\text{CH}_3)_3\text{MCH}_2$ -groups are weakly electron-accepting in reactions with nucleophiles ($\text{X} = \text{Si}(\text{CH}_3)_3$, base-catalysed methanolysis; $\text{X} = \text{C}(\text{O})\text{CH}_3$, alkaline hydrolysis) while strongly electron-donating in interactions with electrophiles (inter action with proton donors; $\text{X} = \text{C}(\text{O})\text{CH}_3$, interaction with ZnCl_2 ; $\text{X} = \text{H}$, addition to CH_2CO , $\text{C}_6\text{H}_5\text{NCO}$). These facts are in agreement with the electron back donation from the oxygen to the atom M in the ground state of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ compounds (proved by NMR and IR spectroscopy), which is not reduced by interaction with nucleophiles, but it is fully suppressed by interaction with electrophiles.

The suitable geometry and energetic proximity of molecular orbitals enables their mutual (through space or through bond)¹ interaction, which in the case of full and empty molecular orbitals localised at separated centers leads to electron distribution different from that resulting from operation of inductive and/or mesomeric effects only. The extent of such non-inductive and/or non-mesomeric electron transfer between two centers (*i.e.* a substituent and the rest of the molecule or another group) depends on the structure of the rest of the molecule (of another group) and makes for the variance of the polar effect of the substituent in a series of similar compounds. Such a substituent has then amphoteric behaviour²⁻⁹, which can be invoked not only by structural changes in the rest of the molecule, but also in transition state (TS), a complex or an intermediate occurring during interaction of the molecule with another partner. Deviation of the polar effect of the substituent during such interaction from that exerted in the ground state (GS) of molecules is classified as the anchimeric assistance^{10,11}. As for organic compounds of Group IVb elements, terms amphoteric behaviour and anchimeric assistance have been used to explain the behaviour of trialkylsilyl^{12,13} and poly(alkylsilyl)¹⁴ groups attached to an aromatic system and to account for the reactivity of trialkylchloromethylsilanes¹⁵ toward nucleophiles.

This paper deals with behaviour of $(\text{CH}_3)_3\text{MCH}_2$ groups ($\text{M} = \text{Si}, \text{Ge}$) in oxygen-containing α -carbofunctional compounds. Our earlier reported results concerning the ground state properties and reactivity of oxygen-containing α -carbofunctional compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{M} = \text{Si}, \text{Ge}$; $\text{X} = \text{H}$, alkyl, $\text{C}(\text{O})\text{CH}_3$, $\text{Si}(\text{CH}_3)_3$) toward nucleophiles and electrophiles have shown that in the ground state of the above

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compounds the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups is reduced. This fact together with the finding that these groups do not influence the reactivity of compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ in reactions with electrophiles and nucleophiles in the same way compelled us to carry out some additional measurements and to interpret all the data at our disposal on compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ with the aim to clarify the behaviour of $(\text{CH}_3)_3\text{MCH}_2$ groups in these substances.

Since 1949, when Taft σ^* substituent constant for $(\text{CH}_3)_3\text{SiCH}_2$ group -0.26 was calculated from the ionisation constant of trimethylsilylacetic acid¹⁶ and from the rate of hydrolysis of its methyl ester¹⁷, this group — in agreement with another numerous evaluations of its substituent effect in the compounds $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ ($\text{Y} = \text{functional group}$) (see ref.¹⁸ and refs therein) — is considered to be strong electron donor. As to $(\text{CH}_3)_3\text{GeCH}_2$ group, its electron donor effect was shown to be somewhat higher than that of $(\text{CH}_3)_3\text{SiCH}_2$ group when this group is attached to the *ortho* position of the benzoic acid or trimethylsilylbenzene¹⁹. The lower pK_a value for $(\text{CH}_3)_3\text{GeCH}_2\text{CO}_2\text{H}$ compared to $(\text{CH}_3)_3\text{SiCH}_2\text{CO}_2\text{H}$ was ascribed¹⁹ to different steric hindrance to solvation of the anion formed in both cases on dissociation.

RESULTS AND DISCUSSION

REACTIONS OF $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{M} = \text{Si, Ge}$) WITH NUCLEOPHILES

It has been reported that $(\text{CH}_3)_3\text{MCH}_2$ groups ($\text{M} = \text{Si, Ge}$) influence in the same way (by strong electron-donating effect) also O-functional groups in the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{X} = \text{H, C(O)CH}_3, \text{alkyl, Si(CH}_3)_3$) when these react with electrophiles. Thus, the reactivity of the alcohols $(\text{CH}_3)_3\text{M(CH}_2)_n\text{OH}$ ($\text{M} = \text{Si}$ (ref.^{20,21}); $\text{M} = \text{Ge}$ (ref.²²); $n = 1-4$) toward ketone or phenyl isocyanate is the highest for the α -homologues ($n = 1$). The rate-determining step of both reactions is nucleophilic attack of the alcohol oxygen on the electron-deficient carbon of ketene or $\text{C}_6\text{H}_5\text{NCO}$ (structure I). The highest reactivity of the α -homologues thus proves that in these compounds the oxygen displays the highest nucleophilicity. Another evidence for electron-donating effect of these groups in the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ follows from the IR measurements of the ability of $(\text{CH}_3)_3\text{M(CH}_2)_n\text{OC(O)CH}_3$ compounds to interact with ZnCl_2 (ref.²³). The highest $\nu \text{C—O—(C)}$ wavenumber shifts for the α -homologues ($\text{M} = \text{Si, Ge}$) when going from the esters of this series to their corresponding complexes with ZnCl_2 can be ascribed to the highest electron-donating effect of the $(\text{CH}_3)_3\text{MCH}_2$ groups.

Strong electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups controls also protonation equilibrium. Changes of the $\nu(\text{OH})$ of phenol on its interaction with $(\text{CH}_3)_3\text{M(CH}_2)_n\text{OX}$ were reported earlier (for $\text{M} = \text{Si, X} = \text{H}$ (ref.²¹), a more detailed discussion of these values is presented in the work²⁴, $(\text{CH}_2)_n\text{Si(CH}_3)_3$ (ref.²⁵),

$\text{Si}(\text{CH}_3)_3$ (ref.²⁶); for $\text{M} = \text{Ge}$, $\text{X} = \text{H}$ (ref.²²), $\text{Si}(\text{CH}_3)_3$ (ref.²⁷)) those for the compounds with $\text{M} = \text{Si}$, $\text{X} = \text{CH}_3$ are reported in this work. Basicity of the oxygen is the highest for the α -homologues of all the series studied (Fig. 1). Moreover, the $\Delta\nu(\text{OH})$ values for the compounds $\text{X} = \text{H}$ (ref.²⁷), $\text{Si}(\text{CH}_3)_3$ (ref.²⁸), CH_3 (Fig. 2) correlate well with Taft σ^* constants of groups R and the point for $\text{R} = (\text{CH}_3)_3\text{SiCH}_2$ does not deviate from the line if its σ^* constant is considered to be -0.26 .* As to the $(\text{CH}_3)_3\text{GeCH}_2$ group, the basicity of the compounds $(\text{CH}_3)_3\text{GeCH}_2\text{OX}$ is comparable to that of the β -homologues, but higher than the basicity of γ - or δ -homologues²⁷.**

In addition, the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups ($\text{M} = \text{Si}$, Ge) influences also the reactivity of $(\text{CH}_3)_3\text{MCH}_2\text{OC}(\text{O})\text{CH}_3$ in acid-catalysed hydrolysis³².

Information about the Ground State of the Compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{M} = \text{Si}$, Ge)

The ability of α -carbofunctional compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{M} = \text{Si}$, Ge) to interact with electrophiles is in sharp contrast to their spectral properties which provide information about ground states of these molecules. Not all of the data reflect electronic effect of $(\text{CH}_3)_3\text{MCH}_2$ groups solely, but some are influenced also by steric effect and conformational population. However, most of them were analyzed in more detail and they do show that the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups is strongly reduced in the ground state of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ molecules.

Thus from ¹³C-NMR spectra of the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ and $(\text{CH}_3)_3\text{CCH}_2\text{OX}$ (Table I) it follows that the $\text{CH}_2(\text{O})$ group in the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ with $n = 1$ is shielded more than in analogous carbon compounds or β - or γ -homologues. However, shielding of the atom of the functional group attached to the oxygen is smaller in $(\text{CH}_3)_3\text{SiCH}_2\text{OX}$ (with respect to the same types of compared compounds). It is worthy of note that shielding of the silicon atom of the $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n$ group is greater in the α -homologues than in the β - or γ -homologues.

* The lesser increase of $\Delta\nu(\text{OH})$ values when going from the β - to α -homologues, compared to analogous increase from the γ - to β -homologues (Fig. 1), was considered^{25,26} earlier as not being in harmony with the polar effect of the electron-donating $(\text{CH}_3)_3\text{Si}$ group³⁰, keeping in mind the ability of the CH_2 - group to attenuate³¹ substituent polar effects. It was supposed that the highest basicity for the α -homologues in the $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ series is still lower than one would expect from the electron-donating properties of the $(\text{CH}_3)_3\text{Si}$ group alone. In the light of the above correlations $\Delta\nu(\text{OH})$ vs σ^* for ROX and the fact that the point for $\text{R} = (\text{CH}_3)_3\text{SiCH}_2$ lies on the line it follows that the slopes of the $\Delta\nu(\text{OH})$ vs n plots (Fig. 1) can be rationalized in terms of either strong electron-donating effect of the $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2$ group, or (more likely), its high polarizability.

** Comparable basicities of the α - and β -homologues of the series $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ could be explained similarly as in the case of analogous organosilicon compounds.

Also influenced similarly are functional group atoms more distant from the oxygen. Deshielding of $\text{CH}_3\text{-C(O)}$ protons in $(\text{CH}_3)_3\text{SiCH}_2\text{OC(O)CH}_3$ is illustrated in Table II. Substituent chemical shifts of the acetates R'OC(O)CH_3 relative to methyl acetate have been found to be controlled mainly by polar effect of the R' group and also by six number effect³⁶, and the above δH value for trimethylsilylmethyl acetate can be therefore attributed to reduced electron-donating effect of $(\text{CH}_3)_3\text{SiCH}_2$ group in this compound. Additional evidence for such a reverse effect of the $(\text{CH}_3)_3\text{SiCH}_2$ group in this compound is provided by trend in the absorptivity of the $\nu(\text{C}=\text{O})$ band for the series of acetoxyalkyltrimethylsilanes (Table II).

The IR evidence for reduced or reverse electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ -groups in $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{X} = \text{H}$ (ref.^{27,37}), C(O)CH_3 (ref.²³)) was reported earlier. With the alcohols $(\text{CH}_3)_3\text{MCH}_2\text{OH}$, the $\nu(\text{OH})$ wavenumber is lower compared to the higher homologues and the absorptivity of the $\nu(\text{OH})$ band is comparable to that found for neopentanol. With regard to the value of σ^* $(\text{CH}_3)_3\text{SiCH}_2 - 0.26$, small $\text{C}=\text{O}$ bond weakening and small $\text{C}-\text{O}$ bond strengthening in $(\text{CH}_3)_3\text{MCH}_2\text{O} \cdot \text{C(O)CH}_3$ ($\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O}-\text{C})$) vs σ_{R}^* plots for various acetates R'OC(O) .

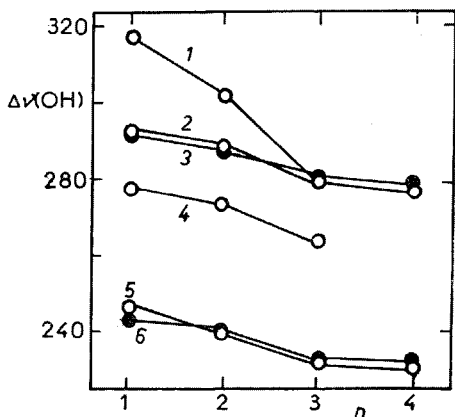


FIG. 1

Basicity ($\Delta\nu(\text{OH})$ Values) of the Compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$; $\text{M} = \text{Si}$ (\circ), Ge (\bullet); $\text{X} = (\text{CH}_2)_n\text{Si}(\text{CH}_3)$ (1), $\text{Si}(\text{CH}_3)_3$ (2, 3), CH_3 (4), H (5, 6)

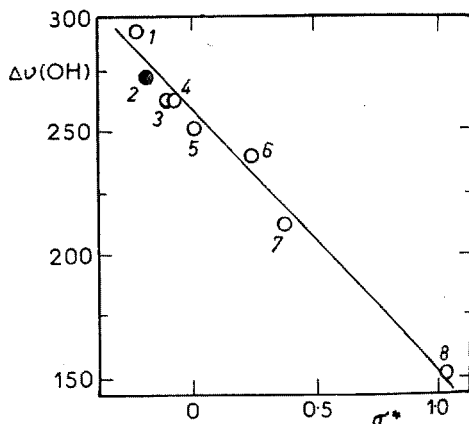


FIG. 2

Correlation of Basicity ($\Delta\nu(\text{OH})$ Values) of the Compounds $\text{R}-\text{OCH}_3$ with Taft σ^* Constant of Group R

$\Delta\nu(\text{OH})$ values for the compounds ROCH_3 with $\text{R} = (\text{CH}_3)_3\text{C}-$ (1), $n\text{-C}_5\text{H}_{11}-$ (3), $n\text{-C}_4\text{H}_9-$ (4), CH_3- (5), $\text{CH}_2\text{CH}=\text{CH}-$ (6), $\text{Cl}(\text{CH}_2)_2-$ (7), ClCH_2- (8), were taken from ref.²⁹, point 2 corresponds to the $(\text{CH}_3)_3\text{SiCH}_2$ group.

CH_3 were considered²³) seems to be real since mass effect can not be responsible for this result³⁸. The authors suppose that the reduction or reversal of the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups is also responsible for general decrease of $\nu(\text{C}-\text{O})$ wavenumbers observed in all series of $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ for $n = 1$ (ref.^{27,36}).

To estimate the polar effect of $(\text{CH}_3)_3\text{SiCH}_2$ and $(\text{CH}_3)_3\text{GeCH}_2$ groups in GS of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ we made use of satisfactory correlation of chemical shifts $\delta(\text{Si})$ with σ^* constant of R in the silane $\text{ROSi}(\text{CH}_3)_3$ (ref.³⁹). By using this correlation $(\text{CH}_3)_3\text{SiCH}_2$ group was found to be weakly electron-accepting (with $\sigma^* = \pm 0.15 \pm \pm 0.05$). The same correlation allowed to establish analogous decrease of the electron-donating effect of the $(\text{CH}_3)_3\text{GeCH}_2$ group ($\sigma = +0.18 \pm 0.05$) (ref.⁴⁰).

Decrease of the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ groups was termed the α -effect, ascribed to electron transfer from the functional group to the silicon (structure II) and interpreted in various ways ($n \rightarrow d$ (ref.²⁵), $n \rightarrow \sigma_{\text{Si}-\text{C}}^*$ (ref.^{41,42}), $\sigma_{\text{C}-\text{X}} \rightarrow d$ (ref.⁴³) interactions).

Interpretation of the Reactivity of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ Toward Electrophiles

Let us turn again to the reactivity of the alcohols $(\text{CH}_3)_3\text{MCH}_2\text{OH}$ toward electrophiles (CH_2CO , $\text{C}_6\text{H}_5\text{NCO}$), basicity of the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\Delta\nu(\text{OH})$ of phenol) and the ability of the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OC}(\text{O})\text{CH}_3$ to interact with ZnCl_2 . In the light of the GS properties of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$, the ability of these compounds to interact with electrophiles can be explained by change of substituent effects of $(\text{CH}_3)_3\text{MCH}_2$ groups, this change being induced by interaction of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ with electron acceptors, *i.e.* by cancellation of the α -effect due to electronic demands of the attacking electrophile (structure III).

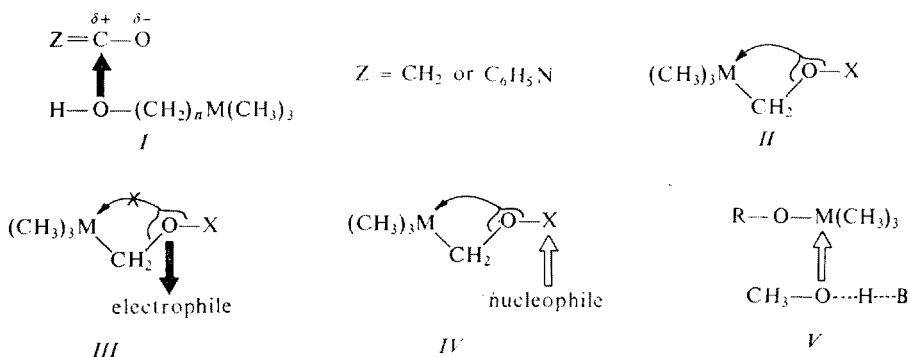
REACTIONS OF $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ WITH NUCLEOPHILES

From the above standpoint it was of interest to examine the behaviour of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ during their interaction with nucleophiles. These reactions (structure IV) do not include such polarisability of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ molecules as during their interactions with electrophiles (structure III). Moreover, they could provide information about how the α -effect is influenced by interaction with electron donors. Two reactions in which rate-determining step is nucleophilic attack at the functional group X were studied: alkaline hydrolysis of the acetate⁴⁴ and base-catalysed methanolysis of $(\text{CH}_3)_3\text{SiO}$ derivative⁴⁵. In both cases the ease of formation of TS depends not only on the electron deficiency of the reaction centre but also on its steric shielding.

As to the alkaline hydrolysis, we compared⁴⁴ reactivities of the individual series $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OC}(\text{O})\text{CH}_3$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}$). Steric shielding of all the $(\text{CH}_3)_3\text{M}$ groups in the γ -position (carboxylic carbon) should be very similar and electronic

effect of $(\text{CH}_3)_3\text{MCH}_2$ groups would play predominant role, since the alkoxy group oxygen transfers electronic effect of substituent R rather well⁴⁶. About the same decrease in the rate when going from γ - to α - via β -homologues in all the series and the lower reactivity for organosilicon and organogermanium derivatives were explained by decreased electron-donor ability of $(\text{CH}_3)_3\text{MCH}_2$ groups and by the fact that the carboxylic carbon is more sterically hindered in organosilicon and organogermanium compounds.

The other reaction, methanolysis of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ ($\text{X} = \text{Si}(\text{CH}_3)_3$), was examined in more detail⁴⁵. TS of this reaction can be depicted by structure V. Relative importance of steric and electronic effects of group R in $\text{RO-Si}(\text{CH}_3)_3$ was estimated by using the Taft equation. Providing that $(\text{CH}_3)_3\text{SiCH}_2$ and $(\text{CH}_3)_3\text{GeCH}_2$ groups exhibit the same inductive effect expressed as $\sigma^* = -0.26$, the E_s constant for these groups acquires unlikely high value of -0.09 and $+0.40$, respectively.^{***} The re-



activity of the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OSi}(\text{CH}_3)_3$ ($\text{M} = \text{Si}, \text{Ge}$) is therefore attributable to the fact that the electron acceptor ability of the Si and Ge atom of $(\text{CH}_3)_3\text{M}$ groups is higher than one would expect on the ground of $\sigma^*(\text{CH}_3)_3\text{MCH}_2$ being about -0.26 .

Reactivity data for reactions of $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ with nucleophiles thus speak for preserving the ground state α -interaction in transition states of reactions of these compounds with electron donors.

EXPERIMENTAL

Trimethylsilylmethyl methyl ether was prepared⁴⁹ by reaction of sodium methylate with (chloromethyl)trimethylsilane in methanol (71% yield, b.p. 85°C , n_D^{20} 1.3879, d_4^{25} 0.7576; ref.⁵⁰: b.p. $83^\circ\text{C}/740$ Torr, n_D^{20} 1.3878, d_4^{25} 0.7576).

^{***} This statement is in harmony with the observation that Taft E_s values are linear function of van der Waals radii⁴⁷ and also with the value of the steric constant ν for $(\text{CH}_3)_3\text{Si}$ group introduced by Charton⁴⁸.

TABLE I
Some Carbon-13, $\delta(\text{C})$, and Silicon-29, $\delta(\text{Si})$, Chemical Shifts for the Compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ and $(\text{CH}_3)_3\text{CCH}_2\text{OX}$ ^{3,3}

<i>n</i>	XSi = $(\text{CH}_3)_3$		X = H		X = OC(O)CH ₃		X = $(\text{CH}_2)_n\text{Si}(\text{CH}_3)_3$		X = CH ₃				
	$\delta(\text{Si})^a$	$\delta(\text{C})^b$	$\delta(\text{Si})^a$	$\delta(\text{C})^b$	$\delta(\text{Si})^a$	$\delta(\text{C})^b$	$\delta(\text{Si})^a$	$\delta(\text{C})^b$	$\delta(\text{Si})^a$	$\delta(\text{C})^b$			
1	-2.0	53.8	16.1	-2.5	54.2	-2.5	47.0	169.9	-4.7	68.7	-3.5	66.9	62.7
2	-1.3	57.7	13.1	-2.6	57.3	-2.6	60.8	168.4	-1.3	66.6	-1.4	69.4	57.3
3	—	—	13.3	-1.3	64.9	-2.3	66.1	168.5	-2.4	72.5	—	—	—
1 ^f	—	71.9	14.1	—	—	—	73.4	169.4	—	—	—	—	—

^a $(\text{CH}_3)_3\text{Si}(\text{C})$, ^b $\text{CH}_2(\text{O})$, ^c $(\text{CH}_3)_3\text{Si}(\text{O})$, ^d $\text{C}=\text{O}$, ^e $\text{CH}_3(\text{O})$, ^f $(\text{CH}_3)_3\text{CCH}_2\text{OX}$.

TABLE II

Proton Chemical Shift, δH (Hz), of the $\text{CH}_3\text{C}(\text{O})$ -Group and the Absorptivity, A ($1 \text{ mol}^{-1} \text{ cm}^{-1}$), of the $\nu(\text{C}=\text{O})$ Band in the Compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OC}(\text{O})\text{CH}_3$

n	δH	A^a	n	δH	A^a
1	116.84	500	4	116.10	560 ^b
2	115.20	650	5	116.00	575 ^b
3	116.19	650			

^a Ref.³⁴. ^b These lower values can be interpreted similarly as those for $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n$ - ($n = 4, 5$) groups (see ref.³⁵).

2-Trimethylsilylethyl methyl ether was obtained⁴⁹ by reaction of trimethylsilylmethylmagnesium chloride with chloromethyl methyl ether in ether (43% yield, b.p. 80–82°C/168 Torr, n_D^{20} 1.4001, d_4^{25} 0.7682; ref.⁵¹ b.p. 112.5°C, n_D^{20} 1.4037, n_D^{20} 0.7809).

3-Trimethylsilylpropyl methyl ether was prepared by reaction of 3-trimethylsilylpropyl chloride with sodium methylate in methanol (85% yield, b.p. 142°C, n_D^{25} 1.4095; ref.⁵² b.p. 140°C/764 Torr, n_D^{20} 1.4102).

Relative basicity of the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCH}_3$ ($n = 1-3$) was determined from the spectra of hydrogen bonds in the region of LiF prism in NaCl cells (0.1 cm thickness) with a double-beam Zeiss, Model UR-20, spectrophotometer. Phenol (0.02M) was used as a proton donor; the concentration of studied compounds in pure CCl_4 was 0.1–0.2M. Wavenumbers of absorption band maxima were obtained as an average of three measurements. For $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCH}_3$ (n , $\Delta\nu(\text{OH})$ in cm^{-1}): 1,278; 2,274; 3,264.

Absorptivity of the sample at wavenumber of the $\text{C}=\text{O}$ stretching vibration (around 1700 cm^{-1} , LiF prism) was measured for 0.1M solutions of the compounds in CCl_4 (spectrograde) in 0.01 cm-cells. The values presented are the average of six times recorded maxima for twice prepared 0.1M solutions. Relative experimental error did not exceed 3%.

Chemical shifts of the $\text{CH}_3\text{C}(\text{O})$ group of the acetates $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OC}(\text{O})\text{CH}_3$ in CCl_4 were recorded on a modified Tesla BS-477 spectrometer (60 MHz), using TMS as internal reference compound; the accuracy was ± 0.2 Hz. All esters were used in concentrations of 100 mg of the ester per 1 ml of CCl_4 .

REFERENCES

- Hoffmann R.: *Accounts Chem. Res.* 4, 1 (1971).
- Exner O. in the book: *Advances in Linear Free Energy Relationships* (N. B. Chappman, J. Shorter, Eds), Chapter 1, p. 34 and 50. Plenum Press, London—New York 1972.
- Volger H. C., Arens J. F.: *Rec. Trav. Chim. Pays-Bas* 77, 1170 (1958).
- Wels P. R., Adcock W.: *Aust. J. Chem.* 18, 1365 (1965).
- Golden R., Stock L. M.: *J. Amer. Chem. Soc.* 88, 5928 (1966).
- Bowden K., Parkin D. C.: *J. Chem. Soc., Chem. Commun.* 1968, 75.
- Bowden K., Parkin D. C.: *Can. J. Chem.* 47, 185 (1969).
- Bowden K., Price M. J., Taylor R. G.: *J. Chem. Soc. (B)* 1970, 1022.
- Hajo M., Katsurakawa K., Yoshida Z.: *Tetrahedron Lett.* 1968, 1497.

10. Capon B.: *Quart. Rev., Chem. Soc.* 18, 45 (1964).
11. Streitwieser A.: *J. Amer. Chem. Soc.* 78, 4935 (1956).
12. Soffer H., de Vries T.: *J. Amer. Chem. Soc.* 73, 5817 (1951).
13. Chernyshev E. A., Tolstikova M. G.: *Izv. Akad. Nauk SSSR* 1961, 455.
14. Traven V. F., Korolev B. A., Pyatkina T. V., Stepanov B. I.: *Zh. Obshch. Khim.* 45, 954 (1975).
15. Bott R. W., Eaborn C., Swaddle T. W.: *J. Organometal. Chem.* 5, 233 (1966).
16. Sommer L. H., Gold J. R., Goldberg G. M., Marans M. S.: *J. Amer. Chem. Soc.* 71, 1509 (1949).
17. Taft R. W. in the book: *Steric Effects in Organic Chemistry*. (M. S. Newman, Ed.). Wiley, New York 1956.
18. Jarvie A. W. P.: *Organometal. Chem. Rev. A*, 6, 153 (1970).
19. Bott R. W., Eaborn C., Pande K. C., Swaddle T. W.: *J. Chem. Soc.* 1962, 1217.
20. Speier J. L., Daubert B. F., McGregor R. R.: *J. Amer. Chem. Soc.* 70, 1117 (1948).
21. Pola J., Bažant V., Chvalovský V.: *This Journal* 37, 3885 (1972).
22. Krumpolc M., Bažant V., Chvalovský V.: *This Journal* 37, 711 (1972).
23. Pola J., Papoušková Z., Chvalovský V.: *This Journal* 40, 2487 (1975).
24. Pola J., Jakoubková M., Chvalovský V.: *This Journal* 40, 2063 (1975).
25. Pola J., Schraml J., Chvalovský V.: *This Journal* 38, 3158 (1973).
26. Pola J., Chvalovský V.: *This Journal* 38, 1674 (1973).
27. Pola J., Jakoubková M., Chvalovský V.: *This Journal* 39, 2651 (1974).
28. Pola J., Papoušková Z., Chvalovský V.: *This Journal* 41, 239 (1976).
29. Trofimov B. A., Shergina N. I., Korostova S. E., Kositsyna E. I., Vyletzhnin O. N., Nedolya N. A., Voronkov M. G.: *Org. Reactivity* 8, 1047 (1971).
30. Zhdanov Y. A., Minkin V. I.: *Korelatsionnyi Analiz v Organicheskoi Khimii*, p. 376. Ed. House of the Rostov Univ., Rostov 1966.
31. Bowden K.: *Can. J. Chem.* 41, 2781 (1963).
32. Pola J., Chvalovský V.: *This Journal* 39, 2637 (1974).
33. Pola J., Schraml J., Lippmaa E.: Unpublished results.
34. Pola J., Jakoubková M.: Unpublished results.
35. Pola J., Jakoubková M., Chvalovský V.: *This Journal* 41, 374 (1976).
36. Rosado-Lojo O., Hancock C., Danti A.: *J. Org. Chem.* 31, 1899 (1966).
37. Pola J., Papoušková Z., Chvalovský V.: *This Journal* 38, 3163 (1973).
38. Nolin B., Jones R. N.: *Can. J. Chem.* 34, 1382, 1392 (1956).
39. Pola J., Papoušková Z., Chvalovský V.: *This Journal*. in press.
40. Pola J., Lippmaa E.: Unpublished results.
41. Ponec R., Chvalovský V.: *This Journal* 40, 2309 (1975).
42. Ponec R., Beck H., Chvalovský V.: *J. Organometal. Chem.*, in press.
43. Feshin V. P., Voronkov M. G.: *Dokl. Akad. Nauk SSSR* 209, 400 (1973).
44. Pola J., Chvalovský V.: *This Journal* 39, 2247 (1974).
45. Pola J., Bellama J. M., Chvalovský V.: *This Journal* 39, 3705 (1973).
46. Tommila E., Hinshelwood C. N.: *J. Chem. Soc.* 1938, 1801.
47. Charton M.: *J. Amer. Chem. Soc.* 91, 615 (1969).
48. Charton M.: *J. Amer. Chem. Soc.* 97, 1552 (1975).
49. Novák P.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1973.
50. Speier J. L.: *J. Amer. Chem. Soc.* 70, 4142 (1948).
51. Calas R., Valade J., Josien M. L.: *C. R. Acad. Sci., Ser. C* 249, 826 (1954).
52. Mironov V. F., Pogonkina N. A.: *Izv. Akad. Nauk SSSR* 1957, 1199.

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