

ORGANOSILICON COMPOUNDS. C.*

 α -EFFECT IN IR SPECTRA OF SOME OXYGEN CONTAINING CARBON-FUNCTIONAL SILANES

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Received November 29th, 1972

Wavenumbers of valence vibrations $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O}-\text{C})$, $\nu(\text{C}-\text{O}(\text{Si}))$ and $\nu(\text{O}-\text{H})$ have been measured in compounds of the type $\text{L}_n(\text{CH}_3)_{3-n}\text{Si}(\text{CH}_2)_m\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_2\text{L}, \text{C}(\text{O})\text{CH}_3, (\text{CH}_2)_m\text{OSi}(\text{CH}_3)_3$; $\text{L} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$; $m = 1-4$). Anomalously low values of the valence vibration wavenumbers in the compounds of $m = 1$ as compared with the corresponding values in the compounds of the same type but of $m = 2-4$ or their carbon analogues are discussed in terms of α -effect.

Infrared spectroscopy of oxygen containing carbon-functional compounds of silicon has so far been studied only by Calas and coworkers¹. These authors have described the dependence of the wavenumbers of valence vibration $\nu(\text{C}-\text{O}-\text{C})$ on the number m of methylene groups in trimethylsilylalkyl methyl ethers $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{OCH}_3$ ($m = 1-6$). The $\nu(\text{C}-\text{O}-\text{C})$ wavenumbers are 1105, 1107 cm^{-1} for the ethers of $m = 1$ and 2, resp. For $m = 3-6$ it is 1118 cm^{-1} . The lowering of $\nu(\text{C}-\text{O}-\text{C})$ observed for the first two compounds in the series was assigned to the inductive effect of the trimethylsilyl group. Such interpretation is unsatisfactory because the +I effect of $(\text{CH}_3)_3\text{Si}$ group cannot be the same in α and β positions (relatively to the silicon atom). Moreover, this interpretation neglects hyperconjugation of $\text{Si}-\text{C}$ bond which would cause a similar shift of electrons from silicon towards oxygen in fragments $\text{R}_3\text{Si}-\text{C}_m-\text{O}$ ($m = 1, 2$) and also it is possible that in these compounds a "back" electron shift from oxygen to silicon — the so-called α -effect is operating (see e.g.²⁻⁵).

The aim of the present work was to determine whether the lowering of $\nu(\text{C}-\text{O})$ is a general property of oxygenous carbon-functional silanes of the type $\text{R}_3\text{Si}-\text{C}_m-\text{O}$ with $m = 1, 2$ and, if so, to attempt to characterize it further. For this reason a study of IR spectra of an extensive series of oxygen containing carbon-functional silanes had been initiated. The series included the following type of compounds $\text{L}_n(\text{CH}_3)_{3-n}\text{Si}(\text{CH}_2)_m\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_2\text{L}, \text{C}(\text{O})\text{CH}_3, (\text{CH}_2)_m\text{Si}(\text{CH}_3)_3$; $\text{L} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$; $m = 1-4$).

* Part IC: This Journal 38, 3158 (1973).

EXPERIMENTAL

The IR spectra of the studied compounds were recorded with a double-beam Zeiss, Model UR 20 spectrometer (Jena) using KBr prism for $400\text{--}850\text{ cm}^{-1}$, NaCl prism for $650\text{--}1700\text{ cm}^{-1}$ and LiF prism for $1600\text{--}4000\text{ cm}^{-1}$ regions. Frequency scale was calibrated in a usual way⁶. The spectra were measured in approximately 5% solutions of the compounds in CCl_4 and CS_2 (spectrograde quality), except for silylalkanols which were measured in 0.05M solutions in order to avoid their self-association. Low absorption region of the spectra of some compounds were also measured in neat liquids. Absorption bands of O—H groups in trimethylsilylmethanol and neopentanol were recorded with a Beckman IR-7 spectrometer. Preparation of the studied compounds is described in our other papers⁷⁻¹¹.

RESULTS AND DISCUSSION

Spectra of all the compounds containing a methyl group on silicon show a group of absorption bands at $800\text{--}860\text{ cm}^{-1}$, $1250\text{--}1260\text{ cm}^{-1}$, $1410\text{--}1420\text{ cm}^{-1}$, 2900 cm^{-1} and 2960 cm^{-1} . Absorption bands due to methylene group intervening between the silicon and oxygen atoms are not characteristic. Their frequency is not constant and owing to their low intensity they are very often overlapped by other bands. Presence of phenyl groups on silicon is indicated *e.g.* by characteristic sharp bands at 1120 cm^{-1} , 1428 cm^{-1} , 1488 cm^{-1} , 1591 cm^{-1} and by a group of bands in $3000\text{--}3100\text{ cm}^{-1}$ range. Ethyl group on silicon can be identified from *e.g.* absorption bands at 958 cm^{-1} and 1112 cm^{-1} . Other bands of this group are overlapped by absorption bands due to methyl groups bonded to silicon. The assignment of these absorption bands is in accord with literature¹².

It is apparent from Table I that the wavenumbers of valence vibrations $\nu(\text{C—O—(X)})$ are in all compounds $\text{R}_3\text{Si}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_2\text{L}, \text{C}(\text{O})\text{CH}_3, (\text{CH}_2)_m\text{Si}(\text{CH}_3)_3, \text{L} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) of $n = 1$ considerably lower than the corresponding wavenumbers in C-analogs and in higher members of the series. The lowering may be due to $\sigma_{\text{CO}} \rightarrow d$ interaction or coordinative interaction of the type $(p \rightarrow d)_\sigma$ or $\sigma_{\text{OH}} \rightarrow d$. Low value of this wavenumber in all the compounds of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{OX}$ (except in acetate) is unlikely to be caused by a specific influence of silicon since relatively low value is observed also in C-analogs. The same is true for the wavenumber of valence vibration $\nu(\text{O—H})$.

Interpretation of wavenumbers of valence vibration $\nu(\text{O—H})$ can be based on the works of Ōki and coworkers¹³ and Dalton and coworkers¹⁴, who established how is this wavenumber affected by substituents and assigned wavenumbers to individual conformers. According to their results each periplanar (relatively to the hydrogen atom of the OH group) alkyl group influences the wavenumber $\nu(\text{O—H})$ by its inductive effect while *syn*-clinal alkyl substituents lower the wavenumber $\nu(\text{O—H})$ by their steric effects. We have found that the absorption band of O—H valence vibration is not symmetrical in trimethylsilylmethanol. In neopentanol no deviation from symmetry of the band could be detected. Large difference between the wave-

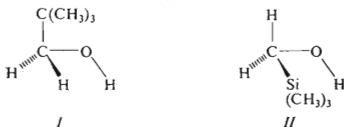
TABLE I

Wavenumbers (in cm^{-1}) of Characteristic Vibrations of Some Compounds of the Type $\text{L}_n(\text{CH}_3)_{3-n}\text{Si}(\text{CH}_2)_m\text{OX}$ (X = H, $(\text{CH}_3)_2\text{SiL}$, $\text{C}(\text{O})\text{CH}_3$, $(\text{CH}_2)_m\text{OSi}(\text{CH}_3)_3$; L = C_2H_5 , C_6H_5 ; $m = 1-4$) and of Some of Their C-Analogs

Compound	X = H		X = $\text{Si}(\text{CH}_3)_2\text{L}$		X = $\text{C}(\text{O})\text{CH}_3$		X = $(\text{CH}_2)_m\text{Si}(\text{CH}_3)_3^a$	
	$\nu(\text{OH})$	$\nu(\text{CO})$	$\nu(\text{C}-\text{O}-\text{Si})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O}-\text{C})$	$\nu(\text{C}-\text{O}-\text{C})$	$\nu(\text{C}-\text{O}-\text{C})$	
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{OX}$	3 626	995	1 065 ^b	1 740	1 222	—	—	
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{OX}$	3 624	999	1 059 ^c	1 744	1 220	—	—	
$(\text{C}_6\text{H}_5)_3\text{SiCH}_2\text{OX}$	3 618	999	—	1 745	1 216	—	—	
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{OX}$,	$m = 1$	3 627	996	1 063 ^d	1 740	1 224	1 090	
	$m = 2$	3 631	1 038	1 083 ^d	1 739	1 239	1 095	
	$m = 3$	3 636	1 049	1 094 ^d	1 740	1 237	1 118	
	$m = 4$	3 637	1 063	1 096 ^d	1 743	1 237	1 117	
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_m\text{OX}$,	$m = 1$	3 640	1 052	1 094 ^d	1 740	1 238	—	
	$m = 2$	3 633	1 036	—	1 738	1 240	—	
	$m = 3$	3 636	1 058	—	—	—	—	
	$m = 4$	3 637	1 063	1 099 ^d	—	—	—	

^a $(\text{CH}_3)_3\text{SiCH}_2\text{OC}_2\text{H}_5$; $\nu(\text{C}-\text{O}-\text{C})$ 1 100 cm^{-1} , $(n-\text{C}_4\text{H}_9)_2\text{O}$; $\nu(\text{C}-\text{O}-\text{C})$ 1 121 cm^{-1} ; ^b L = C_2H_5 ; ^c L = C_6H_5 ; ^d L = CH_3 .

numbers $\nu(\text{O—H})$ in trimethylsilylmethanol and neopentanol could therefore be caused by different conformer preference, in neopentanol conformer *I* and in trimethylsilylmethanol conformer *II* would be preferred. Increased conformer *II* population could be explained by a coordination of σ_{OH} bond into the vacant *d*-orbitals



of silicon. Occurrence of a conformation distribution in trimethylsilylmethanol would imply that $\sigma_{\text{CO}} \rightarrow d$ interaction cannot be effective.

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Translated by J. Schraml.