NMR SPECTRA (^{29}Si AND ^{13}C) OF TRIMETHYLSILYLATED CYCLIC ACYLOINS AND KETONES

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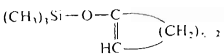
^{13}C and ^{29}Si NMR chemical shifts are reported for several 1-trimethylsiloxycycloalkenes and 1,2-bis(trimethylsiloxy)cycloalkenes, $(CH_3)_3SiO)_xC_nH_{2n-2-x}$ ($x = 1, 2$), dissolved in hexadeuterioacetone. Several correlations of the chemical shifts with structural parameters (ring size, interatomic distances *etc.*) are noted and an attempt is made to explain the found strong dependence of the ^{29}Si chemical shifts on the ring size. Steric crowding with the nearest CH_2 group drives the trimethylsilyl group out of the double bond plane and thus causes steric inhibition of the resonance of unshered oxygen electron pairs with electrons of the double bond. Since the crowding becomes more accute with increasing ring size, the ring size is in this way projected into the chemical shifts of silicon and olefinic carbons.This mechanism provides a united interpretation of all observed NMR chemical shifts.

The very first investigation of ^{29}Si NMR spectra[1] has revealed considerable sensitivity of the silicon chemical shift to the structure of siloxanes, namely to the ring size of cyclosiloxanes. Subsequent studies[2-4] have shown that high structural sensitivity is not limited to siloxanes but it is found in a general class of $(CH_3)_3SiOR$ compounds. This finding has led to analytical applications of ^{29}Si NMR spectroscopy to trimethylsilylated derivatives of carbohydrates[2,5,6] and other polyfunctional compounds[7].

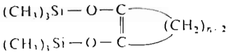
In the course of our investigation of limits of possible analytical utilization of ^{29}Si NMR we have investigated a series of trimethylsilyl derivatives of cyclic enols and endiols with different ring sizes. The found (see the preliminary communication[8]) strong dependence of the chemical shift of the exocyclic silicon on the ring size is not only of analytical importance but has some interesting consequences for the theory of ^{29}Si chemical shift. These aspects and ^{13}C NMR spectra of title compounds are discussed in the present paper.

RESULTS AND DISCUSSION

The experimental results for 1-trimethylsiloxycycloalkenes (*I*) and 1,2-bis(trimethylsiloxy)cycloalkenes (*II*) are summarized in Tables I and II.



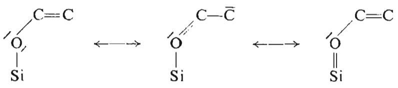
I



II

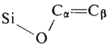
The strong dependence of ^{29}Si chemical shifts on *n* in the compounds *I* and *II* was already reported and its potential analytical applications discussed[8,10]. When looking for possible explanation of this dependence we noted several interesting facts and correlations. A similar dependence (though not so strong) exists for ^{13}C chemical shifts of methyl carbons in 1-methoxycycloalkenes (n = 5, 6 and 8)[11]. Our ^{29}Si chemical shifts can be linearly correlated with ^{13}C chemical shifts of $C_{(4)}$ and $C_{(5)}$ aromatic carbons in benzocycloalkenes (data of ref.[12]), but while the shielding of the carbons decreases with increasing *n* the shielding of the silicon increases (both nuclei are in a β position to the branching carbon atoms). The ^{29}Si chemical shifts in *I* and *II* do not show any obvious relation to the ring strain in cycloalkenes (using the data of ref.[13]). They exhibit, however, an acceptable linear correlation with Taft's E_S values of the corresponding cycloalkyls[14] and a good linear correlation with the calculated non-bonding distances between *cis* olefinic protons in the parent cycloalkenes. The last two mentioned correlations suggest steric origin of the observed dependence.

All these observations and ^{13}C chemical shifts in compounds *I* and *II* can be explained if the interpretation of NMR chemical shifts[15], in trimethylsiloxy derivatives of acyclic alkenes is extended to cyclic compounds. This interpretation places the origin of the observed effects into steric interactions but the mechanim by which they affect the chemical shifts is not a direct steric (through-space) interaction with the observed atoms. The chemical shifts, or the electron density distribution, are the results of competing mechanism which can be conventiently described by resonance scheme:

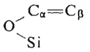


III *IV* *V*

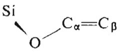
Contribution of structure *IV* which is responsible for deshielding of the silicon atom and for the shielding of β olefinic carbon, strongly depends on rotamer population.



s-trans



s-cis



s-gauche

Because of steric inhibition of resonance, structure *IV* is unimportant if the molecule is predominantly in a pure *s-gauche* conformation. In such a conformation

TABLE I

^{29}Si and ^{13}C NMR chemical shifts in 1-trimethylsiloxycycloalkenes[a]

Cycloalkene[b] n	$\delta(^{29}Si)$	$\delta(^{13}C)$								
		$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	CH_3
4[c]	—	148·48	102·15	20·01	34·39	—	—	—	—	0·10
5	17·82	155·26	101·55	28·67	21·25	33·49	—	—	—	−0·57
5[c]	—	155·26	101·39	29·08	21·57	33·89	—	—	—	0·00
6	15·22	150·56	103·56	23·79[d]	23·22[d]	22·46[d]	29·98[e]	—	—	−0·21
6[c]	—	150·61	103·27	24·16	23·50	22·79	30·31	—	—	0·43
7	14·87	156·46	107·85	28·03[d]	25·42[d]	25·24[d]	31·69[d]	35·62	—	−0·24
8	14·74	153·20	104·72	30·96[d]	26·39[d]	25·47[d]	26·39[d]	27·80[d]	31·10	−0·11
8[c]	—	153·19	104·63	28·05	26·60	25·87	31·25	25·65	31·39	0·47

[a] Chemical shifts in δ-scale, approximate error ± 0·02 ppm. [b] n is the number of carbon atoms in the cycloalkene ring. [c] Taken from ref.[9]. Measured in C_6D_6, ^{29}Si chemical shifts not given. [d] Assignment of the lines with the same index in the raw is not determined experimentally. [e] The line coincides with one of hexadeuterioacetone lines.

TABLE II

^{29}Si and ^{13}C NMR chemical shifts in 1,2-bis(trimethylsiloxy)cycloalkenes[a]

Cycloalkene[b] n	$\delta(^{29}Si)$	$\delta(^{13}C)$						
		$C_{(1,2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	CH_3
4	19·48	120·11	25·86	25·86	—	—	—	−0·17
5	17·60	130·47	30·32	16·81	30·32	—	—	0·31
6	16·15	132·25	29·87	23·45	23·45	29·87	—	0·39
7	15·92	136·72	33·12	25·70[c]	30·55[c]	25·70	33·12	0·26
8	14·88	133·11	31·26	28·90	26·44	26·44	28·90	0·72
9	17·72	134·15	30·95	25·26[c]	24·88	26·41	24·88	0·74
10	14·62	133·56	29·14	26·48	24·94[c]	20·82[c]	20·82[c]	0·97
12	15·56	134·75	28·00	24·92[c]	24·47[c]	24·18[c]	22·34[c]	0·70
13	15·62	134·46	29·97	26·84[c]	26·43[c]	26·33[c]	25·49[c]	0·63

[a] Chemical shifts in δ-scale, precission ±0·02 ppm. [b] n is the number of carbon atoms in the cycloalkene ring. [c] Assignment of the lines with the same index in the raw is uncertain.

the role of structures *III* and *V* increases with concomitant increase in ^{29}Si shielding (lower δ values) and decrease of C_β shielding.

In cycloalkenes the C=C—C bond angle increases with *n* increasing from 4 to 6 (in cyclobutene 94·0°, ref.[16], in cyclopentene 111·5°, ref.[17], in cyclohexene 123·3°, ref.[18]). Larger C=C—C bond angle leeds to more accute steric interaction between the trimethylsilyl group and the nearest CH_2 group (*i.e.* the interaction with $C_{(n)}$ carbon in *I* and with $C_{(3)}$ or $C_{(n)}$ carbons in *II*). The interaction is, of course, relieved by conformational motion of the trimethylsilyl group around the C_α—O bond. The more accute is the interaction, the farther is the trimethylsilyl group driven out of the double bond plane. As the stable conformation approaches that of *s-gauche* rotamer, the silicon becomes more shielded for reasons described above. In cycloalkenes with larger rings ($n < 7$), the changes in the steric conditions are not so drastic and the steric interactions can be also relieved through the ring flexibility. For that reason the dependence levels-off for larger *n* values and the chemical shifts are close to those in acyclic derivatives[15]. Small dip on the dependence observable for the cycloheptene derivative might be related to the fact that a "normal" 120° bond angle is assumed[19] for this compound (*i.e.* a smaller angle than observed in cyclohexene[18]).

This interpretation not only provides a satisfactorily account for the trend in ^{29}Si shieldings but it also explains adequately the ^{13}C chemical shifts and ^{13}C substituent chemical shifts (SCS) induced by the trimethylsiloxy group (Table III).

In monotrimethylsiloxy derivatives *I* the trimethylsiloxy group causes shielding of the olefinic β carbon $C_{(2)}$. Only in cyclobutene derivative the SCS($C_{(2)}$) value approaches the values usually encountered in strain free vinyl ethers (approx. −36 ppm, ref.[11]). In this derivative the small C=C—C bond angle allows the bulky trimethylsilyl group to assume conformation with dihedral angle φ between the C=C and O—Si bonds close to 180° (*s-trans*) and hence structure *IV* is important with increased electron density on $C_{(2)}$ carbon atom. With increasing *n* this structure becomes less important and the SCS values algebraically decrease; for $n = 7$ they reach the values found in acyclic derivatives. Varying values of SCS($C_{(n)}$) reflect variations in geometry in the fragment CH_2—C—O—Si. Comparison with the chemical shifts in 1-methoxycycloalkenes indicates almost constant difference in the corresponding shifts in the two classes of compounds suggesting that already methoxy derivatives assume very similar conformations as the much bulkier trimethylsiloxy derivatives (constant SCS($C_{(n)}$) values). Positive SCS($C_{(2)}$) values can be caused by a contribution of structure *V*.

In bis(trimethylsiloxy) derivatives *II* the substituent chemical shifts of CH_2 carbons adjacent to the double bond show again large variations irrespective whether evaluated for both trimethylsiloxy groups combined or for the "second" group only. This variation in SCS values reflects similar changes in local geometry in the fragment CH_2—C—O—Si as in compounds *I*. The substituent chemical shifts of olefinic carbons show also similar trends as in compounds *I* (because of numbering system, $C_{(1)}$ carbon in *II* should be compared with $C_{(2)}$ carbon in *I* and *vice versa*). Similar interpretation of these shifts can be offered but as both olefinic carbon atoms are at the same time α and β carbons to the "first" and "second" trimethylsiloxy groups, the interpretation is complicated by other factors which affect the shifts of α carbons and which are not yet fully understood.

The above interpretation considers the dependence of ^{29}Si chemical shifts on the ring size to be in fact a conformational dependence. If so, ^{29}Si NMR could be used in conformational studies of similar systems.

EXPERIMENTAL

Preparation of trimethylsilylated enols (I) *and endiols* (II). All 1-trimethylsiloxycycloalkenes(*I*) were prepared by trimethylsilylation of the corresponding ketones with chlorotrimethylsilane in dimethylformamide[21]). Acyloin condensation[22] of ethyl alkanedioates in the presence of chlorotrimethylsilane afforded derivatives *II*. Purity of the prepared compounds was checked by gas chromatography and their identity varified by ^{1}H and ^{13}C NMR spectroscopy.

Sample preparation. The samples were measured as 20–30% (V/V) solutions in hexadeuterioacetone (Merck, Uvasol) with 5% (v/v) of hexamethyldisilane (HMDSS) added to serve as

TABLE III

^{13}C Substituent chemical shifts (SCS) induced by trimethylsiloxy and trimethylsilyl groups[a]

n Compounds	4	5	6	7	8
I SCS($C_{(1)}$)[b]	12·5[c]	25·7	24·4	25·0	24·0
SCS($C_{(2)}$)[b]	−33·8[c]	−28·0	−22·6	−23·6	−24·5
SCS($C_{(n)}$)[b]	4·2[c]	1·9	5·5	7·2	6·2
SCS($C_{(1)}$)[d]	—	− 5·8	− 4·9	− 5·1	—
SCS($C_{(2)}$)[d]	—	9·2	11·6	11·2	—
SCS($C_{(n)}$)[d]	—	2·1	3·1	2·8	—
II SCS($C_{(1)}$)[c]	−28·4[c]	−24·8	−18·3	−19·7	−20·1
SCS($C_{(2)}$)[c]	18·0[c]	28·9	28·7	28·9	28·4
SCS($C_{(3)}$)[e]	5·8[d]	1·6	6·1	5·1	—[f]
CSCS($C_{(1)}$)[g]	−15·9	0·9	6·0	5·2	3·9
CSCS($C_{(3)}$)[g]	− 4·3	− 1·3	5·4	4·7	—

[a] SCS values in ppm given as the chemical shift relative to the corresponding shift in the parent compound. [b] Relative to the shifts in cycloalkenes given in ref.[20], precission ±0·5 ppm. [c] Data taken from ref.[9]. [d] Relative to the shifts in 1-methoxycycloalkenes, ref.[11]. [e] SCS of the second $(CH_3)_3SiO$ group relative to compound *I*. [f] Assignment uncertain. [g] Combined SCS of two $(CH_3)_3SiO$ groups relative to parent cycloalkene, ref.[20].

secondary reference. Precautions were made to prevent decomposition of the samples by moisture, the solvents were dried over activated molecular sieve (Fisher Scientific, 4A grade), 5 mm NMR tubes were either sealed or closed by septum caps.

Spectral measurements. ^{29}Si and ^{13}C NMR spectra were measured on a Varian XL-200 spectrometer operating at 39·7 and 50·3 MHz, respectively. The probe temperature was 23–25°C. ^{29}Si FIDs were recorded using a flip angle of 30°, an acquisition time of 1 s, a delay of 5 s between the pulses, and the gated incoherent (Chirp) proton decoupling in order to suppress the negative Overhauser effect. Typically 300 scans provided sufficient signal/noice ration with no need for exponential weighting. The spectra were referrenced to the line of HMDSS with δ (HMDSS) = $-19·75$. With a spectral width of 4 kHz and zero filling of the data points to 16*K*, the chemical shifts were accurate within 0·02 ppm. ^{13}C NMR spectra were measured both with noice decoupling and single frequency off-resonance decoupling of protons. The spectra were referenced to the line of the acetone methyl carbon with the chemical shift $\delta((CD_3)_2CO) = 29·20$ (in this scale the line of HMDSS occurs at δ(HMDSS) = $-2·91$). A flip angle of 30° was employed together with acquisition time of 1 s and a 1 s delay between the pulses. Using a spectral width of 14 kHz and zero filling of the FID data points to 32*K* the chemical shifts were reported with an approximate error of ±0·02 ppm.

The carbon chemical shifts were assigned according to their value (sp^2 *versus* sp^3 carbons) and multiplicity in the off-resonance decoupled spectra (substituted *versus* unsubstituted carbons). The sp^3 carbon line with the largest shift value was assigned to the carbon adjacent to the double bond; the remaining sp^3 carbon-lines were assigned on the basis of intensity and symmetry consideration and comparison with the spectra of unsubstituted cyclcalkanes[20]. In the monosiloxy derivatives (*I*) the carbon attached to the substituted olefinic carbon was assumed to be the least shielded sp^3 carbon.

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