^{29}Si, ^{13}C AND ^{1}H NMR SPECTRA OF SOME TRIMETHYLSILOXY- AND BIS(TRIMETHYLSILOXY)BUTENE ISOMERS

Jan SCHRAML[a], Ján ŠRAGA[b] and Pavel HRNČIAR[b]

[a] *Institute of Chemical Process Fundamentals,*
Czechoslovak Academy of Sciences, 165 02 Prague and
[b] *Department of Organic Chemistry*
Comenius University, 842 15 Bratislava

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Three isomers of trimethylsiloxybutene were prepared and identified by ^{1}H NMR spectroscopy to be 2-trimethylsiloxy-1-butene and *E* and *Z* 2-trimethylsiloxy-2-butenes. *E* and *Z* isomers of 2,3-bis(trimethylsiloxy)-2-butene were also prepared. ^{29}Si and ^{13}C chemical shifts in these compounds are interpreted. The shifts indicate that the spatial arrangements in the CH_3—C—O—Si$(CH_3)_3$ fragment is the same in all the pertinent compounds. Steric crowding forces the trimethylsilyl group to assume conformations in which conjugation between unshared electrons of oxygen atom and the electrons of the double bond is inhibited. As a result, olefinic β carbons are deshielded and the shielding of the silicon is increased.

In the course of our investigation of NMR spectra of cyclic acyloins and ketones (for a preliminary account see[1]) it has become necessary to study the spectra of acyclic analogues as limiting models for compounds with large rings. In the present paper we wish to report briefly preparation, NMR identification and spectral data of three isomers of trimethylsiloxybutene and two isomers of 2,3-bis(trimethylsiloxy)-2-butene.

RESULTS AND DISCUSSION

Trimethylsiloxybutenes were prepared according to ref.[2] by standard procedure (Et_3N method) from 2-butanone. Rectified reaction mixture (boiling at 116 – 122°C) was separated by gas chromatography (column filled with 13% of phenylmethylsilicon oil on Chemosorb W-AW, 52°C) into four components (9, 34, 43, and 14%) with retention ratios: 1·00, 1·82, 2·18, and 2·31. While the first component has not been identified, ^{1}H NMR spectroscopy established (see further) the last three components to be pure 2-trimethylsiloxy-1-butene (compound *1*), Z-2-trimethylsiloxy-2-butene (compound *2*) and E-2-trimethylsiloxy-2-butene (compound *3*), respectively.

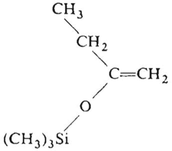
Identity of compound *1* followed directly from the presence of an *AB* pattern of geminal olefinic protons' signals and from a typical A_3M_2 pattern of the isolated ethyl group in ^{1}H NMR spectrum(for NMR data see Table I). This was further confirmed by the structure of the single frequency off-resonance proton decoupled ^{13}C NMR spectrum. In agreement with the structure of *E*/*Z* isomers *2* and *3* all their spectra have the same pattern and differ only by the values of NMR parameters. Comparison with available ^{1}H NMR and IR data[2] suggested isomer assignment which was later proved to be correct but because the numerical values differed markedly (*e.g.* CH_3 proton signals were reported[2] to be in *2* at $\delta = 1{\cdot}43$ and $1{\cdot}61$) the assignment was considered suspect. Our attempts to prove the *E*/*Z* assignment by measurements of the homonuclear Overhauser effects were also not conclusive. Since the isomers contain only one possible coordination site the assignment can be made from a shift reagent effects. The results are summarized in Fig. 1 1. In the *Z* isomer the coordination site (oxygen atom) is sterically shielded by the methyl group in *cis* position and coordination is small. Hence, all the observed

TABLE I

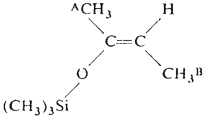
NMR Parameters of compounds *1*–*5*

Group	Parameter[a]	Compound				
		1	*2*	*3*	*4*	*5*
$(CH_3)_3Si$	δ(Si)	16·21	15·65	14·89	17·48	15·89
	δ(H)	0·19	0·17	0·14	[b]	[b]
	1(C)	−0·44	0·09	−0·26	0·04	0·32
A_{CH3}	δ(H)	0·99[c,d]	1·72	1·68	[b]	[b]
	$^{4}J^{e}$		1·1	1·0		
	$^{5}J^{f}$		1·5	1·0		
	δ(C)	28·05[c,d]	22·19	16·97	16·27	17·58
C=	δ(C)	161·05	147·56	148·28	133·79	129·89
= CH	δ(H)	4·03[g]	4·46	4·62		
	$^{4}J^{d}$	0·8[g]	1·1	1·0		
	^{3}J		6·6	6·9		
	δ(C)	88·52	102·15	101·24		
B_{CH3}	δ(H)		1·44	1·50		
	^{3}J		6·6	6·9		
	δ(C)		10·30[f]	11·58[g]		

[a] The chemical shifts are in δ scale. Nuclei are indicated by atomic symbol only, *i.e.* Si, H and C for ^{29}Si, ^{1}H and ^{13}C, resp. Coupling constants J are proton–proton coupling constants in Hz. Approximate errors in coupling constants $\pm 0{\cdot}1$ Hz, in chemical shifts $\pm 0{\cdot}01$ ppm (^{1}H), or $\pm 0{\cdot}02$ ppm (^{13}C, ^{29}Si). [b] Not measured. [c] CH_3 group from CH_3CH_2 group. [d] $^{3}J(H_3C—CH_2) = 7{\cdot}5$ Hz, $\delta(^{1}H_2C) = 2{\cdot}01$, $\delta(^{13}CH_2) = 11{\cdot}33$. [e] Coupling between $CH_3—C{=}C—H$ protons. [f] Coupling between $CH_3—C{=}C—CH_3$ protons. [g] Value for proton A; proton B: $\delta(H) = 4{\cdot}00$, $^{4}J = 0{\cdot}3$ Hz, $J_{AB} = 0{\cdot}9$ Hz



1



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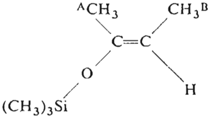


3

lanthanide induced shifts (LIS) are much smaller than in the other isomer with better coordination. According to the accepted dependence of LIS on the stereochemistry of the coordination complex[3], LIS of the olefinic proton in the *E* isomer should be the largest of all the observed shifts and LIS of $^{B}CH_3$ proton should be the largest among the small LISs observed in the *Z* isomer. This is in full agreement with experimental results and with the above isomer assignment. Small LISs of CH_3Si protons are in agreement with the shifts observed in other trimethylsiloxy derivatives[4], negligible effects observed on this proton in compound *2* are analogous to the effects observed in tert-butyldimethylsiloxy derivatives[5] in which methyl groups in γ-position to the oxygen atom block coordination in a similar way as the γ-methyl group in the compound *2*.

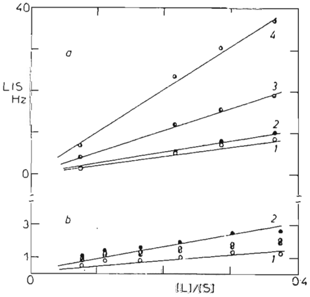


FIG. 1

Dependence of lanthanide induced shifts (LIS) on the lanthanide to substrate (L/S) molar ratio: *1* ○ CH_3Si, *2* ● $^{B}CH_3$, *3* ◐ $^{A}CH_3$, and *4* ◑ CH-proton chemical shifts. *a* Compound *3*. *b* Compound *2* (lanthanide: tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) europium(III), solvent: $CDCl_3$, substrate concentration: 0·07M)

As it is often the case the data in Table I demonstrate that ^{13}C and ^{29}Si chemical shifts are much more suitable for *E*/*Z* isomer determination than are ^{1}H NMR parameters. In future identifications chemical shifts of $^{A}CH_3$ carbons or $\delta(^{29}Si)$ values should give unambiguous *E*/*Z* isomer assignment as the difference between the corresponding values in the two isomers are sufficiently larger than any possible experimental error*.

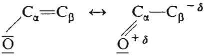
The *E* and *Z* isomers of 2,3-bis(trimethylsiloxy)-2-butene (compounds *4* and *5*) were prepared according to Schräpler and Rühlmann[6]. All the attempts to separate the isomers from the rectified mixture of reaction products (b.p. 75 – 82°C)1·6 kPa) by gas–liquid chromatography have yielded only pure *Z* isomer *5* (as determined from its Raman spectrum). Spectral data for the *E* isomer (*4*) are only tentative as they were obtained from the product mixture. The ^{13}C chemical shifts are in an acceptable agreement with those reported by Cookson and Whitham[7] for both isomers.

Comparison with the corresponding ^{13}C chemical shifts in *E* and *Z* 2-butene (ref.[8]) and 1-butene (ref.[9]) yields the following substituent chemical shifts (SCS) of the trimethylsiloxy group (in ppm; C-α and C-β denote olefinic carbons in α and β position to oxygen atom, resp.):

Compound	SCS($^{A}CH_3$)	SCS($^{B}CH_3$)	SCS(C-α)	SCS(3-β)
2	5·4	−6·5	22·1	−23·3
3	5·5	0·4	24·1	−23·0
4	5·9	—	31·6	−13·8
5	6·0	—	28·6	−18·4

(The values for *4* and *5* are relative to the shifts in *2* and *5*, resp.). Similar SCS values of trimethylsiloxy groups are also observed in cycloalkenes[10].

The ^{13}C chemical shifts in substituted alkyl vinyl ethers are considered[11–15] to be a result of an interplay of at least three factors (hyperconjugation has not been explicitely taken into account): nonbonded interactions, polarization of the double bond and conjugation. Conjugation, expressed as a contribution of structure *II* to the resonance hybrid, is the main factor



I *II*

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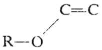
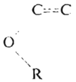
* *Note added in proof:* Similar shielding order was recently reported for *Z* and *E* isomers of $(CO)_5WC(OSiMe_3):CHP(CH_3)_5$ by Voran S., Blau H., Malisch W., Schubert U. (J. Organometal. Chem. 232, C33 (1982).

responsible for the increased shielding of β olefinic carbon in vinyl ethers. Of the possible rotamers,

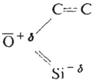

s-trans


s-gauche


s-cis

pure *s-trans* and *s-cis* rotomers cannot be populated in the compound *2* because of steric crowding. In the remaining *s-gauche* rotamer the role of the conjugating structure *II* is decreased because of steric inhibition of resonance (poor orbital overlap). (In a similarly hinderred Z 2-methoxy 2-butene SCS(C-β) = −22·8 ppm, which is practically the same value as in *2*, but in the *E* isomer, which can assume *s-cis* conformation, SCS(C-β) = −34·1 ppm: according to data of refs[7,15]). Following the line of thoughts of ref.[13], the similar and small SCS(C-β) values in *2* and *3* mean that conjugation *II* is similarly inhibited in both compounds. (The SCS values of olefinic carbons in *4* and *5* cannot be interpreted so simply. These carbon atoms are in α position to one of the substituents).

According to Stuart models, the large trimethylsilyl group cannot assume pure *s-cis* conformation (*i.e.* eclipsed with the double bond) even in the compounds *1* and *3* which do not possess substituents in *cis* position. However, the importance of structure *II* may be reduced also by competing back-bonding structure *III* in trimethylsilyl ethers which has no significant equivalent in alkyl vinyl ethers. Since


III

SCS($^{A}CH_3$) values are essentially the same in all the compounds *2*–*5*, the spatial arrangements in the fragment $^{A}C—C—O—Si(CH_3)_3$ should be the same in these compounds. Apparently both factors, structure *III* and *s-gauche* conformation, contribute to the observed SCS(C-β) and SCS($^{A}CH_3$) values. This conclussion seems to be generally valid for trimethylsiloxyalkenes since it is supported by our data on compound *1* and literature[16] data on *E* and *Z* isomers of 3-trimethylsiloxy-2-butene (compounds *6* and *7*, resp.).

Compound	SCS(CH_2)	SCS(C-α)	SCS(C-β)
1	−16·1	20·6	−25·0
6	4·1	21·1	−23·3
7	4·1	19·6	−22·9

The SCS(C-β) are also small and similar in *6* and *7*, the SCS(CH_2) values are the same. In the compound *1* the substantially different SCS(CH_2) value indicates different geometry permitted by absence of substituents on $C_β$. The SCS(C-β) value increases only little either because of contribution of structure *III* or because even this molecule cannot assume pure *s-cis* conformation.

The chemical shifts and SCS values of ${}^{B}CH_3$ carbons are practically the same as in analogous methoxy derivatives[15], ${}^{B}CH_3$ is not affected by the substituent in *trans* position but the shielding of *cis* ${}^{B}CH_3$ carbon is increased. Interpretation of olefinic α carbon chemical shifts is in general unclear, since the relative importance of the involved factors varies with the series of investgated compounds.

The ${}^{13}C$ chemical shifts in the alkyl part of alkyl vinyl ethers have been studied only little[15]. In agreement with the trend found for methyl carbon chemical shifts in substituted methyl vinyl ethers, all nuclei of the trimethylsilyl groups are shielde in the *E* isomer (compound *3*) more than in the *Z* isomer (compound *2*). This observation can be ascribed to direct (through-space) steric interaction of the trimethylsilyl group with the methyl groups in δ position relative to the silicon atom. In crowded situations (compounds *1* and *2*) this interaction causes deshielding of all nuclei of the trimethylsiloxy group. Mechanism of such interaction is not clear since somewhat different trend is apparent for *4* and *5* and since an oposite effect was noted for the ${}^{29}Si$ chemical shifts in alkoxytrimethylsilanes[17]. Hence it seems more likely that the chemical shifts of the trimethylsilyl group (${}^{29}Si$ and ${}^{13}C$) reflect varying contributions of structures *II* and *III* in dependence on the steric crowding and nature of other substituents.

EXPERIMENTAL

All the details of spectral measurements are the same as described in the forthcoming paper[10].

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