^{29}Si (AND ^{13}C) NMR SPECTRA OF MODIFIED SILATRANYL DERIVATIVES OF SOME MONOSACCHARIDES

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Received April 25th, 1984

^{29}Si (and ^{13}C) NMR chemical shifts are reported for several 2-carba-3-oxahomosilatranyl (3,9,10-trioxa-6-aza-1-silabicyclo[3.3.4]dodecane-1-yl) and silatranyl (2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane-1-yl) derivatives of some monosaccharides and other alcohols. The limited data suggest somewhat larger sensitivy of the silicon chemical shifts to molecular structure in 2-carba-3-oxahomosilatranyl derivatives than in silatranyl derivatives. In comparison with trimethylsilyl derivatives homosilatranyl or silatranyl derivatives show lower structural sensitivity of the silicon chemical shift. In some cases, however, larger stability of the silatranyl or 2-carba-3-oxahomosilatranyl derivatives than that of trimethylsilyl derivatives might be a distinct advantage.

We are currently investigating the potential of analytical applications of ^{29}Si NMR spectroscopy in chemistry of polyfunctional organic compounds[1]. The applications are based on the enhanced sensitivity of the silicon chemical shift to molecular structure when the silicon atom of trimethylsiloxy group is attached to the rest of the molecule *via* an oxygen or nitrogen link[2]. For example, when a polyfunctional compound is trimethylsilylated the number of ^{29}Si lines present in the spectrum gives directly the number of silylated functional groups in the original sample. After such signals are assigned, further information can be derived from the values of the chemical shifts, *e.g.* the size of a ring[3], partial stereochemistry of a steroid[4] *etc.*

The range of possible applications can be extended if other silyl groups are found which would show even larger structural sensitivity or which could be employed for selective silylation of specific functional groups either because of their different reactivity or stereochemical requirements. An interesting possibility in this respect

is offered by silatranyl (*i.e.* 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane-1-yl) and 2-carba-3-oxahomosilatranyl (*i.e.* 3,9,10-trioxa-6-aza-1-silabicyclo[3.3.4]dodecane-1-yl) groups which are relatively easily introduced into organic functional compounds[5,6]. Substitution by silatranyl or 2-carba-3-oxahomosilatranyl group instead of trimethylsilyl group offers an additional bonus in higher stability of the product against moisture.

The available data about ^{29}Si NMR spectra of various silatrane derivatives indicate, however, that the specific bonding situation in this group renders the silicon only little sensitive to substituent effects in alkoxy silatranes[7]. Therefore we have chosen to measure the spectra of several 2-carba-3-oxahomosilatrane derivatives which were prepared earlier for other reasons[6] but which could serve the intended purpose. Since the results obtained for these compounds do not warant practical applicability of this approach the project was abandoned. However, the fragmentary results are reported here for future reference.

RESULTS

The studied series of compounds included the following 2-carba-3-oxahomosilatranyl derivatives: 2,3:4,6-di-O-isopropylidene-1-O-(2-carba-3-oxahomosilatrany)-α-L-sorbo furanose (*I*), 2,3:4,5-di-O-isopropylidene-1-O-(2-carba-3-oxahomosilatranyl)-β-D--fructopyranose (*II*), 3-O-(2-carba-3-oxahomosilatranyl)-3-hydroxytetrahydrofurane (*III*), 1,2:5,6-di-O-isopropylidene-3-O-(2-carba-3-oxahomosilatranyl)-α-D-glucofuranose (*IV*), 1,2:5,6-di-O-cyclohexylidene-3-O-(2-carba-3-oxahomosilatranyl)-α-D--glucofuranose (*V*), 1-O-(2-carba-3-oxahomosilatranyl)-1,1-dimethylethanol (*VI*) and silatranyl derivatives: 2,3:4,5-di-O-isopropylidene-1-O-silatranyl-β-D-fructopyranose (*VII*), 1,2:3,4-di-O-isopropylidene-6-O-silatranyl-α-D-galactopyranose (*VIII*), 2,3: :4,6-di-O-isopropylidene-1-O-silatranyl-α-L:sorbofuranose (*IX*), and 2,3:5,6-di-O-isopropylidene-1-O-silatranyl-α-D-manofuranose (*X*).

The ^{29}Si and ^{13}C NMR spectra of these compounds were measured in deuteriochloroform solutions on a Varian XL-200 spectrometer operating at 39·7 MHz and 50·3 MHz, respectively. The two spectra were measured in 8 kHz and 12 kHz spectral widths with noise decoupling of protons which was in the case of ^{29}Si NMR gated to suppress Overhauser effect. The lines of hexamethyldisilane (3% v/v) served as reference with δ (^{29}Si) = −19·79 and δ(^{13}C) = −2·48. ^{13}C NMR spectra were assigned with the aid of single-frequency off-resonance proton decoupling and by comparison with published data on related monosaccharides[8,9]. The results are summarized in Table I.

The ^{13}C NMR chemical shifts of compounds *I*–*X* do not show any remarkable features, they confirm to the trends established for monosaccharide derivatives[8,9] and to the earlier description of ^{13}C NMR spectra of silatranes[10,11]. Comparison of 2-carba-3-oxahomosilatranyl and silatranyl derivatives of the same monosaccha-

TABLE I

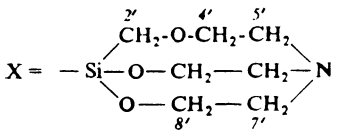
^{29}Si and ^{13}C NMR chemical shifts in $I-X$[a]

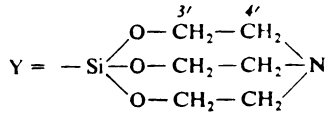
Comp.	$\delta(^{29}Si)$	$\delta(^{13}C)$											
		$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(2')}$	$C_{(4')}$	$C_{(5')}$	$C_{(7')}$	$C_{(8')}$	$C_{(3')}$
I	−77·75	62·07	96·99	71·83	73·43	83·59	60·41	57·99	66·03	65·56	52·86	59·30	—
II	−77·73	63·49	103·80	70·58	71·33	69·37	60·95	58·01	66·09	65·56	52·91	59·34	—
III	−77·89	—	75·28	71·02	35·39	66·60	—	57·48	66·45	65·67	52·37	59·07	—
IV	−79·45	105·27	74·91	81·73	85·55	73·78	65·39	57·82	66·21	65·71	52·78	59·21	—
V	−79·01	104·86	74·96	81·89	85·11	73·19	65·47	57·83	66·19	65·82	52·81	59·29	—
VI	−72·97	71·04	31·61	—	—	—	—	58·96	67·55	67·33	53·72	60·27	—
VII	−94·63	64·48	104·06	70·69	71·40	69·40	60·91	—	51·38	—	—	—	57·71
VIII	−94·58	96·42	67·79	70·48	70·55	71·33	61·26	—	51·23	—	—	—	57·65
IX	−94·61	63·10	96·99	71·76	73·61	83·74	60·49	—	51·40	—	—	—	57·72
X	−96·71	101·65	86·98	80·11	79·92	73·39	67·48	—	51·20	—	—	—	57·57

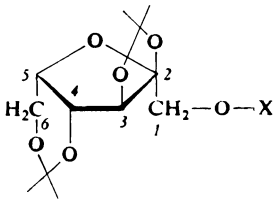
[a] For the numbering of carbon atoms see Scheme I. Assignment of carbon lines with the same multiplicity is only tentative.

ride (*e.g. I* and *IX* or *II* and *VII*) shows that the two groups differ in their ^{13}C substituent effects only very little, the difference is noticeable only on the substituted carbon atom where it amounts to 1 ppm.

In 2-carba-3-oxahomosilatranyl derivatives *I*–*VI* the ^{29}Si chemical shifts fall into three regions: around values $\delta = -77{\cdot}7$, $\delta = -79{\cdot}2$ and $\delta = -73$. With the







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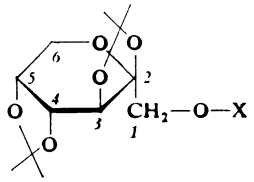
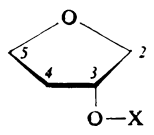


II



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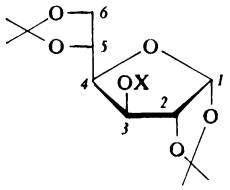

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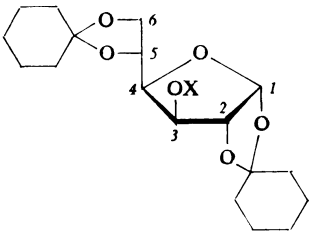

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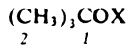
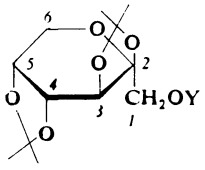
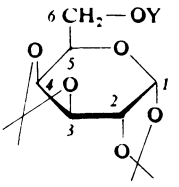


VI

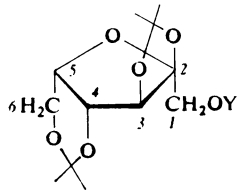


VII

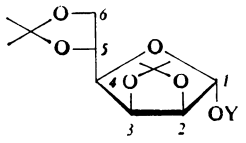


VIII

exception of compound *III*, the three regions correspond to 2-carba-3-oxahomosilatranyl groups being attached to oxygen atom on primary, secondary and tertiary carbon atoms, respectively. However, the exceptional ^{29}Si chemical shift in *III*



IX



X

suggests that other factors play also a role in determining the shift value. Comparison of the chemical shifts found in *I* and *II* indicates that the ring size or effects of remote substituents play only a minor role in determining the chemical shifts. Similarly, data for *IV* and *V* demonstrate larger effects caused by proximate substituents. The total range of ^{29}Si chemical shifts in 2-carba-3-oxahomosilatranyl derivatives is much larger than that reported for silatranyl derivatives of simple alcohols[7]. The chemical shifts found here for compounds *VII*–*X* indicate that the small range (1·5 ppm) found for silatranyl derivatives of alcohols[7] has to be somewhat extended (to 2·7 ppm) to include the derivatives of monosaccharides in which additional factors contribute to the observed chemical shift. Accordingly, it is reasonably safe to assume that the total range observed here for the chemical shifts in 2-carba-3-oxahomosilatranyl derivatives is a good approximation of the total range for all 2-carba-3-oxamohosilatranyl derivatives of alcohols. (In fact recent INDOR measurements gave the following ^{29}Si chemical shifts for 1-methoxy-, 1-ethoxy-, 1-isopropoxy-, and 1-tert-butoxy-2-carba-3-oxahomosilanes −77·0, −75·9, −74·4, and −72·8 ppm, respectively). Though this range, 6·5 ppm, is about three times larger than in silatranes it is only about half of the total range observed in trimethylsilyl derivatives of simple alcohols. The smaller range reflects lower sensitivity of silicon chemical shifts to substituent effects in 2-carba-3-oxahomosilatranyl (and silatranyl) than in trimethylsilyl derivatives.

From the practical point of view it is also noteworthy, that sensitivity of ^{29}Si NMR spectral measurements is also lower for homosilatranyl then for trimethylsilyl derivatives. ^{29}Si NMR spectra are now measured with very good effectiveness by polarization transfer techniques (INEPT (ref.[12]) or DEPT (ref.[13]) in which sensitivity enhancement increases with the number of equivalent protons coupled to the observed nucleus (*i.e.* 9 protons in trimethylsilyl derivatives as compared with two protons in 2-carba--3-oxahomosilatranyl and non in silatranyl derivatives).

Summarizing, low sensitivity of silicon in 2-carba-3-oxahomosilatranyl and silatranyl derivatives to substituent effects and to NMR detection does not make silatranylation or 2-carba-3-oxahomosilatranylation likely candidate for practical applications except for rare cases when their higher stability (against moisture) would be decisive.

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Translated by the author (J. S.).