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Structure of silylation products of acetohydroxamic acid

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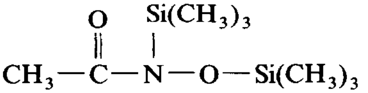
Abstract

The ^{29}Si, ^{13}C, and ^{15}N NMR spectra of the mixture of the two products of trimethylsilylation of acetohydroxamic acid show that the products are the (*E*)- and (*Z*)-isomers of *O*-trimethylsilyl ester of *O'*-trimethylsilylacetohydroximic acid.

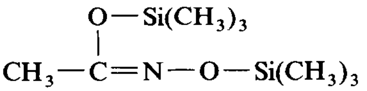
Introduction

Complete trimethylsilylation of acetohydroxamic acid by hexamethyldisilazane was reported [1] to produce a mixture of two doubly silylated isomers that were believed to have the structures I and II:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{N}-O-Si(CH_3)_3$$

(I)



$$CH_3-\overset{\overset{\displaystyle O-Si(CH_3)_3}{|}}{C}=N-O-Si(CH_3)_3$$

(II)

Since the isomers could not be isolated, they could not be completely characterized; only unassigned IR and ^{1}H NMR spectra of the mixture were reported. We decided to undertake a multinuclear NMR study of the mixture with the aim of assigning the spectra and determining the structures of the silylation products. The results are reported here.

Experimental

Preparation

The trimethylsilylation of commercial (Aldrich) acetohydroxamic acid was carried out exactly as described previously [1], that is, no catalyst or solvent was used

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for the reaction between equimolar amounts of the acid and hexamethyldisilazane (Fluka). (Anal. Found: C, 42.96; H, 9.39; N, 6.8; Si, 25.91. $C_8H_{21}NO_2Si_2$ calc.: C, 43.78; H, 9.66; N, 6.38; Si, 25.60%.)

NMR spectra

The spectra (^{1}H, ^{13}C, ^{29}Si, and ^{15}N) were recorded on a Varian UNITY-500 spectrometer operating at 500, 125, 99, and 50 MHz, respectively. Standard software (including pulse sequences) was employed throughout; ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded by use of a one pulse sequence; ^{29}Si spectra were recorded by the INEPT sequence; ^{13}C–^{13}C couplings were determined by onedimensional INADEQUATE experiments; lines in ^{13}C and ^{29}Si NMR spectra were assigned by heteronuclear COSY correlation with the lines in the ^{1}H NMR spectrum; ^{15}N NMR lines were assigned through a heteronuclear ^{15}N{^{1}H} selective decoupling of CH_3 protons (for explanation and description of all used NMR experimental techniques see ref. 2). The reported data were obtained with dilute (5% v/v) deuteriochloroform solutions (5 mm NMR tube) containing 1% (v/v) of hexamethyldisilane which served as a secondary reference for ^{1}H, ^{13}C, and ^{29}Si chemical shifts. Coupling constants ^{13}C–^{13}C and all ^{15}N NMR experiments were performed on a 90% solution in hexadeuteriobenzene (10 mm NMR tube), the ^{15}N chemical shifts were referenced to external nitromethane in the same solvent. For high temperature experiments deuterated toluene was used as solvent. No indication of exchange was noticed in ^{1}H NMR spectra at 90 °C.

Results and discussion

Quantitative ^{1}H, ^{13}C, and ^{29}Si NMR spectra confirmed that the product mixture contained two compounds, labeled here as compounds **A** and **B**, in an approximate ratio of 1.5/1.0. The lines in the spectra of the mixture could be assigned to the compounds **A** and **B**; the number and relative intensities of the NMR for each compound were consistent with both structures I and II. The NMR data are summarized in Table 1.

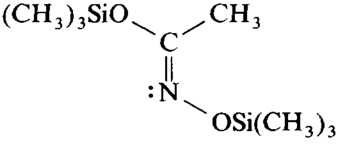
Table 1

NMR data for compounds **A** and **B** in the product mixture [a]

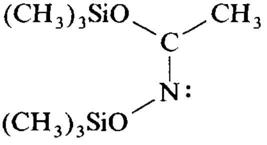
Group	Compound **A**				Compound **B**			
	δ(Si)	δ(C)	δ(H)	δ(N)	δ(Si)	δ(C)	δ(H)	δ(N)
$>C=$	–	163.72 [b]	–	–	–	154.80 [c]	–	–
CH_3	–	14.15 [b]	1.936 [d]	–	–	18.81 [d]	1.827 [e]	–
$(CH_3)_3Si$ [f]	20.69	0.08	0.251	–	19.33	1.68	0.231	–
$(CH_3)_3Si$ [f]	23.26	−0.76	0.170	–	23.84	−0.65	0.197	–
N	–	–	–	−73.2 [d]	–	–	–	−87.9 [e]

[a] All the chemical shifts are in δ scale, i.e. chemical shifts to higher frequency (lover magnetic field) of the reference are positive; ^{1}H, ^{13}C, and ^{29}Si chemical shifts are relative to that for tetramethylsilane, the ^{15}N lines are relative to that for nitromethane (external). Approximate error in chemical shifts are: for ^{13}C and ^{29}Si ±0.02 ppm, for ^{1}H ±0.002 ppm, and for ^{15}N ±0.2 ppm, errors in coupling constants are ±0.02 Hz for ^{13}C–^{13}C and ±0.2 Hz for ^{15}N–^{1}H couplings. [b] Coupling constant $^1J(^{13}C–^{13}C) = 53.36$ Hz. [c] Coupling constant $^1J(^{13}C–^{13}C) = 61.29$ Hz. [d] No coupling with CH_3 or any other proton observed, apparently $J < 0.5$ Hz. [e] Coupling constant $^3J(^1H_3–C–C=^{15}N) = 3.3$ Hz. [f] The two trimethylsilyl groups were not assigned further.

The observed ^{29}Si and ^{15}N chemical shifts in compounds **A** and **B** exclude the possibility of structure I. For this structure one of the trimethylsilyl groups would be attached to a nitrogen atom and hence should have $\delta(^{29}\mathrm{Si})$ either in the range -2–0 or 0–10 ppm, depending on whether the nitrogen is or is not doubly bonded to the rest of the molecule [3,4]. All the observed ^{29}Si chemical shifts are in the range 19–24 ppm in which signals of trimethylsiloxy groups are found [5]. Further, in the light of the available data for similar compounds, the ^{15}N chemical shifts of the two isomers I and II would be expected to differ by much more than is observed ("tautomeric shifts" of 100 ppm or more would be expected an going from structure I to II [6]). Since rotamers (around the N–O bond) of the parent acetoxyhydroxamic acid give ^{15}N signals at -207 and -209 ppm [7], the shift in the case of acetohydroximic acid (the parent acid for the structure II) would be expected to be near -100 ppm or an even lower negative value. The values found for the bis(trimethylsilyl) derivatives **A** and **B** are close to this expected value. Comparison of the ^{15}N chemical shifts for **A** and **B** with those found for the (*E*)- and (*Z*)-isomers of *O*-trimethylsilyl-*N′*,*N′*-dimethylacetohydrazide, (III), $(\mathrm{CH_3})_2$-NN=C(CH$_3$)OSi(CH$_3$)$_3$ (-81.5 and -93.7 ppm, respectively [8]), suggested that the compounds **A** and **B** are (*E*)- and (*Z*)-isomers of II, i.e. *O,O′*-bis(trimethylsilyl) derivatives of acetohydroximic acid IIA and IIB, respectively.



(IIA (*E*))



(IIB (*Z*))

This suggestion is supported by other observations. Thus the coupling constant $^{3}J(^{1}\mathrm{H}-^{15}\mathrm{N})$ is larger in **B** than in **A**, in agreement with the general rule that such couplings are larger for protons that are spatially near the nitrogen lone electron pair [9] (for examples see ref. 6). The ^{13}C chemical shifts for the C= carbons in **A** and **B** match those found for the (*E*)- and (*Z*)-isomers of III (165.0 and 155.7 ppm, respectively [8]). Finally, the coupling constant $^{1}J(^{13}\mathrm{C}-^{13}\mathrm{C})$ in **B** is about 8 Hz larger than that is in **A** which is in agreement with the generalisation that such coupling constants are 7–11 Hz larger for oximes with the nitrogen lone pair close to the coupled carbon nuclei [10,11].

Conclusion

The NMR spectra show that trimethylsilylation of acetohydroxamic acid by hexamethyldisilazane leads to a mixture of (*E*)- and (*Z*)-derivatives of acetohydroximic acid. The data obtained for these compounds will assist in the determination of the structures of more complicated silylated hydroxamic acids.

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