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Multinuclear NMR study of compounds resulting from the silylation of indole; evidence for a 4,5-disilylation

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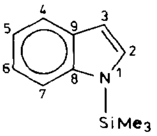
Abstract

Complete assignments of the ^{1}H, ^{13}C and ^{29}Si NMR data of 1-, 4- and 5-trimethylsilyl-, 1,4- and 1,5-bis(trimethylsilyl)- and 1,4,5-tris(trimethylsilyl)-indoles allowed unambiguous confirmation of the structures proposed for these products. For the trisilylated derivative it was found that silylation had occurred at the 1,4,5 and not at the 1,4,7 positions as previously suggested.

Introduction

In view of the importance of indole derivatives in chemistry and biochemistry and the potential use of organosilicon compounds for functionalization of organic



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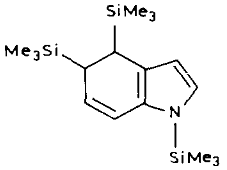

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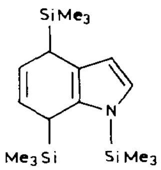

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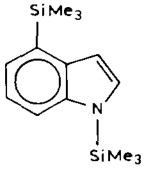

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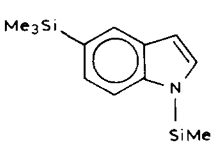

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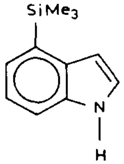

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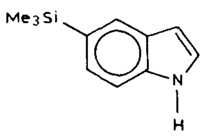

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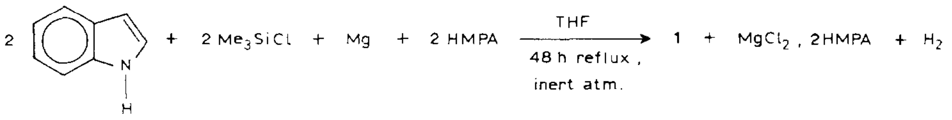
substrates we examined a few years ago the possibility of silylating indole or *N*-trimethylsilylindole and reported the preliminary results [1]. There was a problem of unambiguous identification of the formed products, and thus we postulated that the disilylation of *N*-trimethylsilyl indole **1** took place at the positions 4 and 5, (**2**), not 4 and 7 (**2a**) as previously suggested by Barrett et al. [1,2].

We present here the results of a study involving assignments of ^1H, ^{13}C and ^{29}Si NMR data for 1-trimethylsilyl indole (**1**), 1,4,5-tris(trimethylsilyl)[4*H*],[5*H*]indole (**2**), 1,4-bis(trimethylsilyl)indole (**3**), 1,5-bis(trimethylsilyl)indole (**4**), 4-trimethylsilyl indole (**5**) and 5-trimethylsilylindole (**6**); all these are attractive precursors for the functionalization of the indole system, silicon intermediates having already been used for that purpose [3]. Identification of **3**–**6** confirms the structure of **2**.

Experimental

(1) Syntheses

Compound **1** was obtained quantitatively by the following procedure [1]:



Compound **2** was made as described previously [1]:

$$\mathbf{1} \xrightarrow[\text{THF; 0–5 °C, inert atm.}]{\text{Me}_3\text{SiCl/Li (excess)}} \mathbf{2}$$

Compounds **3** and **4** were made from **2** by aromatization in the presence of benzoquinone (excess), and separated by HPLC (**3**/**4** ca. 70/30, 95% overall yield) [4].

Compounds **5** and **6** were made in almost quantitative yields by refluxing methanol solutions of **3** and **4** respectively.

(2) Identification of 1–6

Compound **1** was identified by comparison of its properties IR, NMR, and mass spectra, with those of an authentic sample [5], but in order to make available additional information to help in the characterization of the other products, a complete NMR study was carried out (see below and Tables 3–5).

Compound **2**, a new product (it was not isolated by Barrett et al. [2]) gave a satisfactory elemental analysis and mass spectrum (molecular peak at 335, signals at 262 ($[M - \text{SiMe}_3]^+$), 189 ($[M - 2\text{SiMe}_3]^+$), 174 ($[M - 2\text{SiMe}_3 - \text{Me}]^+$), 73 $[\text{Me}_3\text{Si}]^+$, etc., but its complete structure was assigned by multinuclear NMR spectroscopy.

Results

(1) NMR study of 2

The ^1H NMR spectra were recorded on a Bruker AM 360 apparatus (references: A 603006 H, A 603006 H and A 603 0008 C) (360 MHz) with $CDCl_3$ or C_6D_6 as solvent and Me_4Si as internal standard (δ(ppm); J (Hz); s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; dt, double triplet). $J \simeq 0$, after expansion

Table 1

Proton chemical shifts (δ,ppm) and coupling constants (Hz) for **2** [a]

Solvent	N-SiMe$_3$	C(4)-SiMe$_3$	C(5)-SiMe$_3$	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
CDCl$_3$	0.32 s	−0.09 s	−0.16 s	6.39 d J_{23} 2.5	5.73 d	2.05 ~ s $J_{45} \simeq 0$	1.71 d J_{56} 6.5	5.35 dd J_{67} 9.5	6.04 d
C$_6$D$_6$	0.14 s	0.15 s	0.03 s	6.47 d	6.00 d	2.30 s	1.87 d	5.44 dd	6.17 d

[a] Double resonance and differential NOE techniques were used for assignments.

at 10 Hz cm^{-1}, i.e. $J \ll 2$ Hz. Results are summarized in Table 1. In the case of **7** and **8** only one allylic proton is coupled (^2J) to an ethylenic one whereas in **9–11** the two allylic protons show similar coupling. Compound **2** behaves in this respect like **7** and **8** and so cannot be 1,4,7- (as assumed by Barrett et al. [2]) or 1,5,6-tris(trimethylsilyl)indole. Moreover application of the NOE technique to the Me$_3$SiN signal in the ^{1}H NMR spectrum produced response for positions 2 and 7, thus revealing the presence of a proton in position 7. Furthermore the identities of **3–6** formed from **2** by desilylation confirm the positions 1,4 and 5 for the silyl groups in **2**.

Further confirmation of the proposed structure of **2** is provided by the excellent ^{1}H/^{13}C 2D correlation (see Fig. 1).

The ^{13}C NMR spectra were recorded on the same spectrometer (90 MHz for the ^{13}C); the spectra were completely decoupled or gated-non decoupled (the ^{1}H/^{13}C 2D correlation was carried out with the Bruker AM 360 (δ(ppm); J (Hz); P, primary; S, secondary; T, tertiary; Q, quaternary carbon atom). The data are summarized in Table 2 and the ^{1}H/^{13}C NMR correlation is shown in Fig. 1, which confirms our assignments for C(2), C(3), C(6) and C(7). The ^{29}Si NMR spectra recorded on a Bruker AC 200 apparatus (39.76 MHz for ^{29}Si) (δ(ppm), CDCl$_3$ as solvent and TMS as internal standard). There were signals at δ 9.4 (SiN) and δ 2.6 and 1.3 (these were from SiC$_4$ and SiC$_5$, but could not be separately assigned).

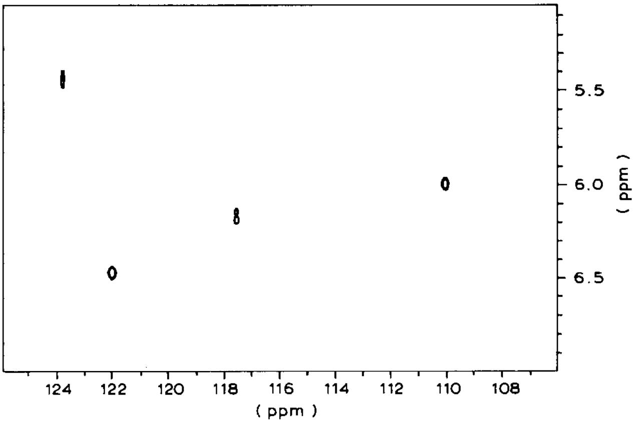


Fig. 1. ^{13}C-2D NMR/^{13}C-H correlation for compound **2**.

Table 2

^{13}C chemical shifts (δ,ppm) for **2** in C_6D_6 and $^1J(^1H^{13}C)$ coupling constants (Hz) for the olefinic carbons

N-SiMe$_3$	C(4)-SiMe$_3$	C(5)-SiMe$_3$	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
−0.2 [a]	2.5	−3.2	122.0	110	24.5	27.9	123.8	117.5	132.0	122.0
P	P	P	T	T	T	T	T	T	Q	Q
			d, *J* 181	m, *J* 166			m; *J* 157	d; *J* 157		

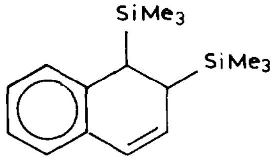
[a] Assigned by comparison with **1**.

Table 3

^1H NMR data for **1, 3, 4, 5, 6** (δ,ppm, *J*,Hz)

Products	N-SiMe$_3$ (9H)	C-SiMe$_3$ (9H)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	NH [b]
1	0.52								
	s	–	7.11	6.53	7.58	7.06	7.12	7.43	–
3 [a]	0.53	0.38	7.15	6.68		7.25	7.12	7.47	–
	s	s	d, (*J* 3.5)	d		dd, *J* 8.1	dd, *J* 9.8	dt, *J* 4.1	
4	0.53	0.30	7.14	6.59	7.84	–	7.34	7.50	–
	s	s	dd, *J* 3.2	dd	s		dd, *J* 9.2	dd, *J* 8.2	
5 [a]	–	0.41	7.23	6.68		7.29	7.20	7.40	8.0–8.3
		s	dd, *J* 3.2	m		dd, *J* 7.2	m	dt, *J* 1.5	broad
6		0.30	7.13	6.53	7.82	–	7.33	7.33	8.0–8.3
		s	dd, *J* 2.75	m	s		m	m	broad

[a] Previously reported by Barrett et al. [2]. [b] The chemical shift for this proton depends on the concentration.



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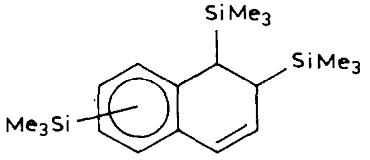

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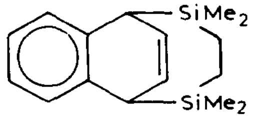

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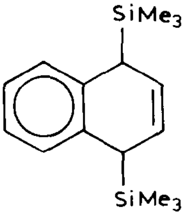

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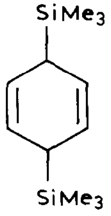

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From the data we identify the trisilylated derivative as **2** not as **2a** or any other isomer. We reached this conclusion because (a) no trimethylsilyl groups are bonded to C(sp^2) atoms, and for several reasons (involving comparison with the spectra of the *N*-silyl indole); (b) they cannot be in position 2 or 3, and (c) comparison of the ^{1}H NMR spectrum of **2** with those of **7** [6], **8** [7], **9** [8], **10** [6], and **11** [9], confirmed the proposed formulation.

As we showed previously for other cases, the ^2J coupling constants (^{1}H NMR) give useful information about the HC$_x$,C$_y$H dihedral angle in silylated cycloolefins [10]. Although the Karplus [11] or Teisseire [12] models have to be used with caution, when $^2J = 0$ the dihedral angle is near 90°. Since $J_{45} \approx 0$ we suggest that the two silyl groups are in a *trans*-pseudo-axial/pseudo-axial disposition, as depicted in Fig. 2.

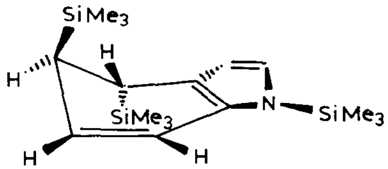


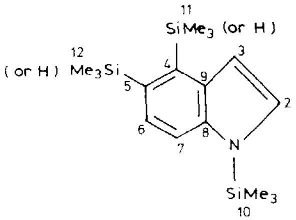
Fig. 2.

(2) NMR study of 3–6

The identities of compounds **3**,**4**,**5**,**6** were established by their elemental analysis, mass spectra, the molecular peak was present in each case, and their multi-nuclear NMR data. The ^{1}H NMR data were obtained for solutions in $CDCl_3$ (which served as lock and reference) on a Bruker WH90 spectrometer.

Table 4

^{13}C NMR data for **1**, **3**, **4**, **5**, **6** (δ,ppm)



Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10) [b]	C(11) [b]	C(12) [b]
1	129.7	104.5	120.8	121.0	119.8	112.8	140.0	131.5	−0.14	–	–
	T	T	T	T	T	T	Q	Q	P		
3	129.7	105.6	131.9	125.7	120.8	113.8	139.0	135.0	−0.05	−0.51	–
	T	T	Q	T	T	T	Q	Q	P	P	
4	129.6	104.4	126.0	129.9	126.3	112.4	140.6	131.3	−0.21	–	−0.77
			or		or						
			126.3		126.0						
	T	T	T	Q	T	T	Q	Q	P		P
5	123.8	103.6	131.7	125.6	121.8	112.0	134.5	131.5	–	−0.66	–
	T	T	Q	T	T	T	Q	Q		P	
6	123.9	102.5	126.1	129.9	126.6	110.5	134.6	128? [a]	–	–	−0.76
			or		or						
	T	T	126.6	Q	126.1	T	Q				P
			T		T						

[a] Very weak signal. [b] C(10): carbon atoms of eventual $SiMe_3$ bonded to N. C(11): carbon atoms of eventual $SiMe_3$ bonded to C(4). C(12): carbon atoms of eventual $SiMe_3$ bonded to C(5).

Table 5

^{29}Si NMR chemical shifts for **1, 3, 4, 5, 6**

Compounds	δ(N–Si) (ppm)	δ(C–Si) (ppm)
1	+10.8	–
3	+11.0	–4.9
4	+10.9	–4.0
5	–	–4.7
6	–	–4.0

The ^{13}C NMR spectra were determined on a Bruker AC 200 spectrometer (50.327 MHz) with freshly prepared $CDCl_3$ solutions containing TMS as internal standard (δ(ppm); P, primary; S, secondary; T, tertiary; Q, quaternary carbon atom).

The ^{1}H and ^{13}C NMR data are shown in Tables 3 and 4.

The ^{29}Si NMR spectra were recorded on a Bruker AC 200 spectrometer (39.76 MHz) with freshly prepared $CDCl_3$ solutions containing TMS as the internal standard.

The ^{29}Si chemical shifts are shown in Table 5.

Conclusion

Complete structures of the species under consideration have been assigned starting from data for the known compound species **1** and from the previously reported ^{1}H NMR data for **3** and **5** [2]; the latter data were not decisive by themselves but were important because the structure of **5** has been unambiguously established by X-ray diffraction [2]. All the signals have been attributed: in particular, the ^{1}H shift, known from study of compounds **1**, **9** and **5**, can be assigned in the cases of **4** and **6**. In the spectra of **4** and **6**, the singlets at 7.84 and 7.82 ppm (which is not from H(7)) show that the silicon is in the 5 position and rules out the isomer with silicon in the 6 position. The ^{13}C and ^{29}Si data are not decisive in themselves but they are consistent with the proposed structures.

The studies have established with certainty the structures of the new species **2**, **4** and **6**, and serve as a basis for interpretation of NMR data for further organosilicon derivatives of indole. This will be useful in studies of preparation of functional derivatives of indole at present under way.

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