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# STRUCTURE OF DISILYLACETAMIDES

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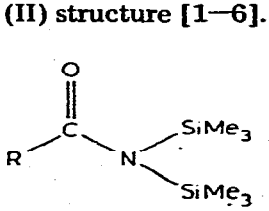
## Summary

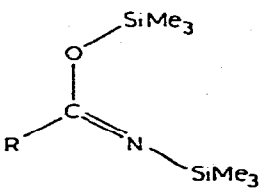
The structures of a series of bis(trialkylsilyl)acetamides and two bis(aryldimethylsilyl)acetamides have been investigated by IR and NMR spectroscopy. The IR and NMR characteristics of these compounds and the rate and activation data obtained from a study of temperature variable NMR spectra of the aryldimethylsilyl substituted amides provide evidence for a *N,O*-disilyliminoether structure for the compounds.

## Introduction

Several papers concerned with the chemistry of silylamides have considered the question of whether these compounds have the amide (I) or the iminoether (II) structure [1—6].




(I)




(II)

Most bis(trimethylsilyl)amides so far investigated have been assigned structure II. For example, the much used silylating agent bis(trimethylsiiyl)acetamide (BSA), whose structure had been a point of controversy for many years, was eventually shown to occur in the silyliminoether form II on the basis of NMR

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investigations of its $^{15}N$-substituted analogue [7]. An exception within this series is bis(trimethylsilyl) formamide, which was shown by the same method to have the amide structure I [8].

Most of the studies were concerned with trimethylsilyl derivatives of aliphatic and aromatic amides. We have recently presented evidence that two bis(halomethyldimethylsilyl)acetamides have the *N,N*-disilylamide structure [9], and it seemed of interest to ascertain how other substituents at silicon affect the structure of the disilylamide molecule. We report here the results of an investigation of disilylacetamides $CH_3CON(SiR^1R^2R^3)$ where $R^1$, $R^2$ and $R^3$ are alkyls, or where $R^1 = R^2 = CH_3$ and $R^3$ is an aryl group.

## Results and discussion

The disilylacetamides were prepared by treating appropriate chlorosilanes with acetamide in triethylamine. Their physical constants and analytical data are given in Table 3.

The infrared spectra of all compounds exhibit a strong absorption at about 1700 $cm^{-1}$ and medium intensity bands near 1040 $cm^{-1}$. The former band can be assigned either to C=O or to O—C=N in structures I or II, respectively. In the spectrum of BSA (structure II) there is an absorption at 1698 $cm^{-1}$ [7], while in bis(trimethylsilyl)formamide (structure I) there are bands at 1659 and 983 $cm^{-1}$. The latter were assigned to absorptions of the C=O and Si—N—Si groupings, respectively [8]. In the spectra of our compounds no absorption in the 980—990 $cm^{-1}$ region is observed. The 1040 $cm^{-1}$ band can be assigned to absorption of the Si—O—C grouping [10]; an absorption in this region was observed in the BSA spectrum [7] and is lacking in that of bis(trimethylsilyl) formamide. Close similarities between the IR spectrum of BSA and those of the silylamides reported here lead us to conclude that they have a similar, i.e. a silyliminoether, structure.

Chemical shifts in the NMR spectra of the disilylamides are listed in Table 1. For the methylsilyl protons in bis(trialkylsilyl)acetamides two closely spaced singlets of identical intensity were observed. The $CH_3Si$ groupings are thus magnetically nonequivalent, which may be due to their slow exchange between nitrogen and oxygen. In the spectra of bis(aryldimethylsilyl)acetamides at room temperature a broad signal in the methylsilyl region ($\delta$ = 0.35 ppm, $CHClCCl_2$) was observed, the peaks being sharp in the remainder of the spectrum. As the temperature was lowered the signal gradually broadend to split ultimately into two sharp peaks at —50°C ($\delta$ 0.45 and 0.26 ppm). The reverse process took place on raising the temperature (Fig. 1).

The first-order rate constant for this reaction is independent of the concentration of the silylamide: $k$ ($s^{-1}$) is 86.5, 85.1 and 87.2 at 20, 15 and 10% (v/v) respectively of bis(phenyldimethylsilyl)acetamide in trichloroethylene at 35°C. The process occurring is thus intramolecular.

The rate constants $k_c$ at the coalescence temperature $t_c$ were evaluated by the approximate method ($k_c = \pi\Delta\nu(\sqrt{2})$) [11]. The maximum difference ($\Delta\nu$) between the chemical shifts of the trimethylsilyl protons was determined at low temperature, when the rate constant was approaching zero. From the $k_c$ values using the Eyring equation, the free energies of activation $\Delta G_c^{\ddagger}$ for the reaction of bis(phenyldimethylsilyl)acetamide and bis(*p*-tolyldimethylsilyl)acetamide were

TABLE 1

NMR DATA FOR DISILYLACETAMIDES [a] $CH_3CON(SiR^1R^2R^3)_2$

| $R^1$ | $R^2$ | $R^3$ | δ values (ppm) | | | |
|---|---|---|---|---|---|---|
| | | | $CH_3Si$ | $C_2H_5Si$ | $CH_3C$ | X [b] |
| $CH_3$ | $CH_3$ | $C_2H_5$ | 0.09 and 0.14 | 0.87—0.97 | 1.92 | — |
| $CH_3$ | $C_2H_5$ | $C_2H_5$ | 0.09 and 0.13 | 0.85—0.93 | 1.92 | — |
| $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | — | 0.64—1.09 | 1.94 | — |
| $CH_3$ | $CH_3$ | $C_6H_5$ | 0.40 | — | 1.78 | — |
| $CH_3$ | $CH_3$ | $p$-$CH_3C_6H_4$ | 0.44 | — | 1.85 | 2.35 |
| $CH_3$ | $CH_3$ | $p$-$CH_3OC_6H_4$ [c] | 0.48 and 0.58 | — | 1.79 | 3.73 |

[a] About 20% solution in $CCl_4$; $(CH_3)_4Si$ as internal standard, room temperature. [b] Chemical shift of substituent in aromatic ring. [c] Solution in $CHClCCl_2$; purity about 75%.

calculated and are listed in Table 2, together with the data for BSA and *N,N*-bis-(trimethylsilyl) formamide. The complex pattern of the NMR spectra of trialkylsilylamides in the alkylsilyl region precluded studies of the temperature variability of the spectra of these compounds.

From Table 2 it is seen that the coalescence temperatures of the methylsilyl signals in bis(aryldimethylsilyl)acetamides and their free energies of activation are not solvent dependent. Neither are the chemical shifts of these protons affected by changing over from aliphatic to aromatic solvent. Different behaviour was previously observed for bis(halomethyldimethylsilyl)-acetamides [9] and some dialkylamides [13]. Both latter classes of compounds were shown to have the *N,N*-dialkylamide (or *N,N*-disilylamide) structure, and the magnetic non-equivalency of the alkyl (or silylmethyl) protons was interpreted in terms of hindered rotation around the carbon—nitrogen bond. If this is assumed for the disilylamides investigated in the present work, the barrier to rotation in them

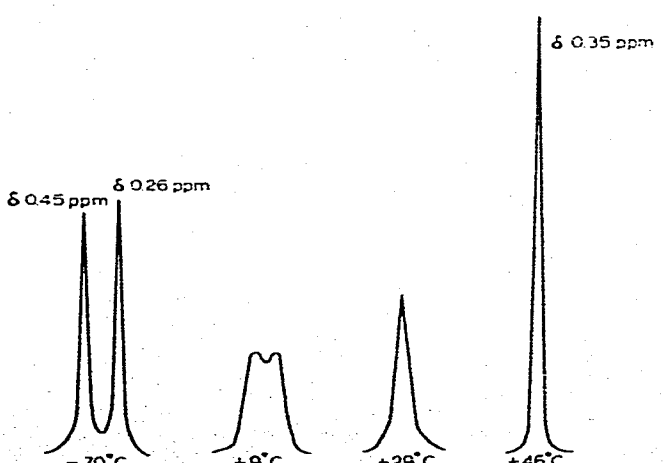



**Fig. 1. Variable temperature proton NMR spectra of bis(phenyldimethylsilyl)acetamide in chlorobenzene.**

TABLE 2

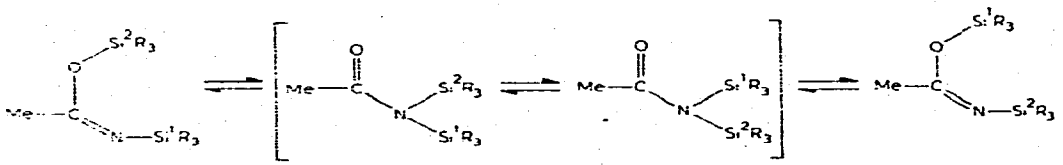
KINETIC AND THERMODYNAMIC PARAMETERS FOR DISILYLACETAMIDES

| Compound | Solvent | $t_c$ (°C) | $k_c$ ($s^{-1}$) | $\Delta\nu$ (Hz) | $\Delta G_c^{\ddagger}$ (kcal/mol) |
|---|---|---|---|---|---|
| $HCON[Si(CH_3)_3]_2$ [a] | $C_6H_5Cl$ | −46 | — | 12.1 | 11.6 |
| $CH_3CON[Si(CH_3)_3]_2$ [b] | $C_6H_5Cl$ | 11 | — | 8.1 | 15.3 |
| $CH_3CON[Si(CH_3)_2C_6H_5]_2$ | $CHClCCl_2$ | 12 | 33.2 | 14.9 | 14.7 |
| | $C_6H_5Cl$ | 15 | 36.4 | 16.4 | 14.8 |
| $CH_3CON[Si(CH_3)_2$-$p$-$CH_3C_6H_4]_2$ | $CHClCCl_2$ | 14 | 29.4 | 13.5 | 14.8 |
| | $C_6H_5Cl$ | 13 | 35.9 | 16.1 | 14.7 |

[a] See ref. 8. [b] See ref. 12.

would have to be comparable to or lower than that in *N,N*-bis(trimethylsilyl) formamide. It was found by Yoder et al. that the free energy of activation $\Delta G_c^{\ddagger}$ for rotation in a series of bis(trimethylsilyl)amides increased with increasing size of substituent at the carbonyl carbon [8]. On the other hand, larger substitents at nitrogen were found to decrease the rotation barrier in *N,N*-dialkylacetamides [14]. The bis(aryldimethylsilyl)acetamides, having $\Delta G_c^{\ddagger}$ values considerably higher than that of *N,N*-bis(trimethylsilyl) formamide (Table 2) do not fit into the pattern of structure-free energy of activation relationship in the *N,N*-disubstituted amides series. Therefore, evidence from both IR and NMR spectra strongly favours the *N,O*-disilyliminoether structure for our compounds.

It is interesting to note (Table 2) the closeness of the values of the coalescence temperature and free energy of activation of silyl exchange for the bis(aryldimethylsilyl)acetamides to those of BSA. It seems that replacing one methyl group at silicon by an aryl does not markedly affect the electronic structure of the molecule in spite of the fact that a phenyl substituent could be expected to enter into $d\pi$—$p\pi$ bonding with silicon, thus competing with the possible $d\pi$—$p\pi$ conjugation of the oxygen-bound silicon with the free electrons of nitrogen. The latter effect is thought to be decisive in determining the activation energy of the N—O—silyl exchange by the suggested mechanism [8,15]:



The silyl migration step is believed to be rate-determining, since the roatation around C—N would require a lower energy of activation (cf. 11.6 kcal/mol for bis(trimethylsilyl)formamide).

## Experimental

### *Synthesis of disilylacetamides*

The disilylacetamides were prepared by the procedure of Klebe et al. [16]. To

TABLE 3

PROPERTIES OF THE *N,O*-DISILYLACETAMIDES $CH_3CON(SiR^1R^2R^3)_2$

| $R^1$ | $R^2$ | $R^3$ | Yield (%) | B.p. (°C/mmHg) | $n_D^{25}$ | Analysis found (calcd.) (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Si | C | H | N |
| $CH_3$ | $CH_3$ | $C_2H_5$ | 78 | 84/17 | 1.4310 | 24.27 | 51.89 | 10.89 | 6.05 |
| | | | | | | (23.90) | (51.23) | (10.19) | (6.92) |
| $CH_3$ | $C_2H_5$ | $C_2H_5$ | 60 | 70—71/1.3 | 1.4412 | 21.64 | 55.53 | 11.26 | 5.39 |
| | | | | | | (21.53 | (55.80 | (11.39) | (4.96) |
| $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | 88 | 105/3 | 1.4518 | 19.53 | 58.47 | 11.57 | 4.87 |
| | | | | | | (20.01) | (58.53) | (11.60) | (5.27) |
| $CH_3$ | $CH_3$ | $C_6H_5$ | 69 | 110—113/0.11 | 1.5288 | 17.20 | 66.20 | 7.41 | 4.29 |
| | | | | | | (17.06) | (66.04) | (7.62) | (4.64) |
| $CH_3$ | $CH_3$ | $p$-$CH_3C_6H_4$ | 80 | 128—129/0.1 | 1.5257 | 15.79 | 67.54 | 8.22 | 3.94 |
| | | | | | | (15.60) | (68.07 | (8.30) | (4.21) |

a solution of acetamide (1 mol) in triethylamine (700 ml) the appropriate chlorosilane (2.2 mol) was slowly added at room temperature. The mixture was refluxed for 10—12 hours and filtered from the precipitated triethylamine hydrochloride. All operations were carried out under dry nitrogen. After evaporating volatile components in vacuo the residue was distilled at the lowest possible pressure in order to avoid thermal decomposition of the disilylamide. Because of its low thermal stability we could not obtain pure bis(*p*-methoxyphenyldimethylsilyl)acetamide (Table 1).

*IR and NMR measurements*

Infrared spectra of the neat compounds were obtained on a Pye Unicam SP 1200 spectometer. $^1$H NMR spectra were recorded on a JEOL C-60 HL spectometer equipped with a temperature controller. The temperatures of the samples were measured by using a capillary tube with acidified methanol and applying Van Geets equation [17]. The rate constants $k_c$ (Table 2) are average values from at least three measurements at appropriate temperature. They were used to evaluate the free energies of activation from the Eyring equation.

All solvents used in the syntheses and NMR measurements were purified and dried as described in ref. 18.

## Acknowledgment

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