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Preliminary communication

A novel type of tautomerism in cyclic silylamides

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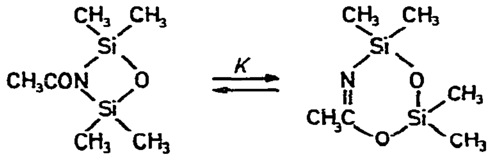
SUMMARY

N-Acetyltetramethylcyclodisiloxane, (I), co-exists in equilibrium with pentamethyldisiladioxazine, (II), in a novel type of tautomerism.

In a search for new examples of silyl tautomerism in cyclic silylamides[1], we have attempted to prepare pentamethyldisiladioxazine (II) from acetamide and 1,3-dichlorotetramethyldisiloxane. The structure of (II) presents the possibility of rearrangements analogous to those discovered by Klebe in disilaoxadiazines[1]. Unlike the latter, however, (II) lacks the exocyclic acyl group, which is thought to play a prominent role in both mechanisms proposed for the disilaoxadiazine tautomerizations[1,2].

We believe we have, in seeking to make (II), found a new type of tautomerization, involving formation of an equilibrium mixture of (II) with *N*-acetyltetramethylcyclodisilazoxane (I); the latter also being the first example of a stable four-membered silazoxane ring structure. The two components could be separated by a fast distillation of the reaction product obtained from equimolar quantities of starting materials; such distillation gave 60% of (I), b.p. 28–29°/6 mm, and 40% of (II), b.p. 34–35°/6 mm.



(I) (II)

The analyses and molecular weights of both products are in agreement with the empirical formula $C_6H_{15}NO_2Si_2$. Their IR spectra, however, show several differences. There is a broad absorption band in the 1000–1100 cm^{-1} region, characteristic of the

C–O–Si grouping, in the spectrum of (II), and two bands at 1230 cm^{-1} and 1720 cm^{-1} attributable to C=N stretching vibrations[3,4]. All these bands are absent in the spectrum of (I), in which a strong band is present at 955 cm^{-1}. This may be due to the Si–N–Si grouping, by analogy with the absorption which appears in the 912–990 cm^{-1} range in the case of cyclic disilazanes, and which is attributed to Si–N–Si asymmetric vibrations[4].

That (I) and (II) are, indeed, different compounds is further shown by differences in their solubility; (I) is readily miscible with CH_3CN and C_6H_5CN, while (II) dissolves in these solvents only on prolonged shaking,

Further evidence in support of the proposed structures for (I) and (II) is derived from NMR spectra. Both compounds undergo tautomerization in solution, and thus only the spectrum of the equilibrium mixture can be recorded. This shows (in benzonitrile) two singlets, at τ 7.90 and 8.00 ppm, attributable to acetyl protons, and three silicon methyl singlets at τ 9.65, 9.72 and 9.75 ppm. The relative intensities of signals at τ 7.90 and 9.65 ppm [set (a)] is 1/4, and that of the τ 8.00, 9.72 and 9.75 ppm signals [set (b)] are 1/2/2. These relative intensities do not change with changing temperature or solvent, but the value of the total intensity of set (a) relative to that of set (b) is strongly temperature-dependent, and at a given fixed temperature varies with the solvent.

Set (a) which is attributed to compound (I), in which all the silicon methyl protons are equivalent, diminishes in intensity with rising temperature, and has almost disappeared at 100° in benzonitrile. The equilibrium constant K [= (II)/(I)] can be derived from the appropriate intensities, and $\log K$ is linearly correlated to T^{-1}, the line having a negative, solvent-dependent, slope.

Compound (I) is stable at low temperatures, at which it becomes the predominant tautomer in polar solvents, *e.g.* $K = 0.26$ at –30° in pyridine. The tautomerization at this or even slightly higher temperatures is slow enough to allow separation of the isomers by fast distillation, thus showing that the equilibrium is a case of desmotropy.

Syntheses of a series of compounds expected to show the same kind of tautomerism, and kinetic studies of the isomerizations are in progress.

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