

as well as subsequent reactions, and

c) by analogy with the method of *Ebsworth* and *Mays* [2] from disilver cyanamide and trimethylchlorosilane according to the equation:



The infrared spectrum supports the carbodiimide structure, since the symmetrical NCN- and the asymmetrical SiNSi vibrations, which should occur for the structural isomer bis(trimethylsilyl)cyanamide $(\text{R}_3\text{Si}\bar{\text{N}})_2\text{-C}\equiv\bar{\text{N}}$, are not present.

Received December 15, 1961 [Z 196/27 IE]

[1] 14th Communication on Si-N compounds.

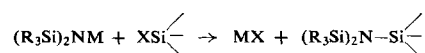
[2] *E. A. V. Ebsworth* and *M. J. Mays*, *Angew. Chem. internat. Edit.* 1, 113 (1962).

Silyl-Substituted Sulfur Amides and Imides

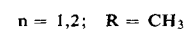
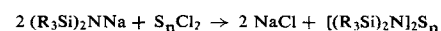
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Although silyl-substituted alkali amides (I) react almost quantitatively with halogenosilane derivatives according to [2]:

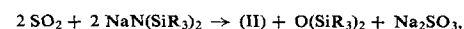


complicated sequences occur in the reaction of (I) with sulfur halides. The following compounds have so far been isolated from the reaction products of SCl_2 : sulfur(II)-tetrakis(trimethylsilyl)diimide, $[(\text{CH}_3)_3\text{Si}]_2\bar{\text{N}}-\bar{\text{S}}-\bar{\text{N}}[\text{Si}(\text{CH}_3)_3]_2$, m.p. 65°C, b.p. 142 to 143°C/15 mm., colorless needles (from methanol); sulfur(IV)-bis(trimethylsilylimide) (II), $(\text{CH}_3)_3\text{Si}-\bar{\text{N}}=\bar{\text{S}}-\bar{\text{N}}-\text{Si}(\text{CH}_3)_3$, yellow oil, b.p. 73 to 74°C/24 mm. Tris(trimethylsilyl)amine, $\text{N}[\text{Si}(\text{CH}_3)_3]_3$ was also formed, among other products. Disulfur(I)-tetrakis(trimethylsilyl)diimide, $[(\text{CH}_3)_3\text{Si}]_2\bar{\text{N}}-\bar{\text{S}}-\bar{\text{S}}-\bar{\text{N}}[\text{Si}(\text{CH}_3)_3]_2$, a yellowish oil, b.p. 115 to 116°C/0.5 mm. was separated from mixtures using S_2Cl_2 . However, the expected reactions:



only play a subordinate role (10%).

(II) was also formed by reacting SO_2 with (I); the reaction proceeded stoichiometrically, but here, too, the yields were low. In addition to the reaction



increased formation of hexamethyldisiloxane and reduction of SO_2 to sulfide occurred.

Received December 15, 1961 [Z 197/24 IE]

[1] 15th Communication on Si-N compounds.

[2] *U. Wannagat* and *H. Niederprüm*, *Chem. Ber.* 94, 1540 (1961).

The Reaction between Halosilanes and Silver Cyanamide

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The reaction between iodasilane and silver cyanamide yields the compound $(\text{SiH}_3)_2\text{CN}_2$, m.p. $-74.8 \pm 0.5^\circ\text{C}$., b.p. $84.7 \pm 0.5^\circ\text{C}$., $\log p_{\text{mm}} = -1761/T + 7800$ [1]. The infrared spectrum between 4000 and 400 cm^{-1} shows that there are only two strong bands at 2280 and 795 cm^{-1} which are associated

with skeletal stretching modes. They are either missing or very weak in the Raman spectrum. For a molecule of the cyanamide type, $\text{R}_2\text{N}-\text{C}\equiv\text{N}$, all four skeletal stretching modes should be both infrared and Raman active, and all are observed in the infrared [2] and Raman [3] spectra of dimethyl cyanamide. However, a molecule of the carbodiimide-type, will have a center of symmetry if the skeleton is linear (as in silyl isothiocyanate [4]); the mutual exclusion rule holds and the infrared active modes will be forbidden in the Raman. Even if the angles are not quite 180° , the *trans* form will still have a center of symmetry, while vibrations of the *cis* form, which are strong in the infrared, might well give very weak Raman lines. (Since only one peak appears in the proton resonance spectrum, it is unlikely that both *cis* and *trans* forms are present.) Moreover, if the skeleton is almost linear, the molecule approximates to a symmetric top, with one small moment of inertia; parallel and perpendicular bands should have characteristic and different contours, and rotational detail might be observed in the perpendicular bands. The observed gas-phase infrared band contours correspond closely with those expected for such a molecule. Rotational fine structure, with separation of the order of 2–3 cm^{-1} , has been observed in the bands associated with SiH-stretching and SiH₃-deformation modes. This would be difficult to understand if the molecule had the Si₂NCN-configuration. Thus the vibrational spectra, while hard to reconcile with the cyanamide form, are readily explained in terms of the carbodiimide structure.

Received December 15, 1961 [Z 195/21 IE]

[1] *E. A. V. Ebsworth* and *M. J. Mays*, *J. chem. Soc. (London)* 4879 (1959); see also *J. Pump* and *U. Wannagat*, *Angew. Chem. internat. Edit.* 1, 112 (1962).

[2] *M. Davies* and *W. J. Jones*, *Trans. Farad. Soc.* 54, 1454 (1958).

[3] *L. Kahovec* and *K. W. F. Kohrausch*, *Z. physik. Chem.* 37B, 421 (1937).

[4] *D. R. Jenkins*, *R. Kewley*, and *T. M. Sudgen*, *Proc. chem. Soc. (London)* 220 (1960).

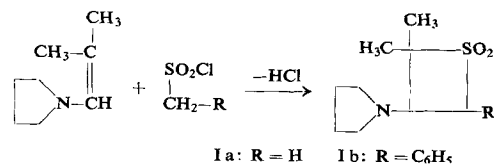
Cycloaddition of Sulfenes to Enamines

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A personal communication from *G. Stork* and *I. J. Borowitz* concerning the reaction of mesyl chloride with 1-morpholinocyclopentene, -cyclohexene, or -propene in the presence of triethylamine, leads us to report our own findings [1].

We have found that the sulfenes, R_2CSO_2 , which are formed primarily from aliphatic sulfochlorides $\text{R}_2\text{CHSO}_2\text{Cl}$ and triethylamine, will form substituted 3-aminotrimethylene sulfones with enamines by cycloaddition.



If mesyl chloride in ether is allowed to drop into a mixture of triethylamine and 1-pyrrolidinoisobutene at room temperature, triethylamine hydrochloride precipitates immediately. The filtrate yields 2,2-dimethyl-3-pyrrolidinotrimethylenesulfone (Ia, 80% yield, m.p. 68°C., mol. wt. calc. 203; found 199). In a similar way, the following trimethylene sulfone bases are obtained from 1-pyrrolidinoisobutene, 1-piperidinopropene, 1-morpholinobutene, or 1-piperidinopentene, and methane-, propane-, and toluene- ω -sulfochlorides.