TABLE IV

MAGNETIC DATA FOR THE PHENANTHRENEQUINONE SERIES

Complex	$\mu_{\text{obs.}}$	$\mu_{\text{calcd.}}$	n	Reported range[a]
phenqu·MnBr$_2$	5.84	5.92	5	5.65–6.10
	5.85			
3phenqu·FeBr$_3$	5.83			
	6.16	5.92	5	5.70–6.0
	5.94			
phenqu·CoBr$_2$	4.71			
	4.74	3.88	3	4.30–5.20
2phenqu·NiBr$_2$	3.22			
	3.26	2.83	2	2.80–3.50

[a] J. Lewis and R. G. Wilkins, ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, pp. 400–454.

bonding, with the oxygen to metal bonds oriented in sterically favored directions. This orientation results in a tetrahedral configuration for the manganese(II) and cobalt(II) complexes, an octahedral configuration for iron(III), and either a tetrahedral or octahedral configuration for nickel(II).

The above results suggest an expanded classification of these complexes, as shown in Table V.

TABLE V

CLASSIFICATION OF THE COMPLEXES

Type	Empirical formula	Suggested formulation
I	phenqu·ZnBr$_2$	[Zn(phenqu)$_2$]ZnBr$_4$
II	phenqu·InBr$_3$	[In(phenqu)Br$_2$]Br
III	phenqu·SnBr$_4$	[Sn(phenqu)Br$_2$]Br[a] [Sn(phenqu)Br$_4$][b]
IV	2phenqu·NiBr$_2$	[Ni(phenqu)$_2$]Br$_2$[a] [Ni(phenqu)$_2$Br$_2$][b]
V	3phenqu·FeBr$_3$	[Fe(phenqu)$_3$]Br$_3$
VI	phenqu·MoO$_2$Cl$_2$	...

[a] If tetrahedral. [b] If octahedral.

The unique nature of the molybdenum complex probably results from the reductive action of MoCl$_5$ in the quinone, similar to the action of MoCl$_5$ on $(C_6H_5)_3PO$ reported by Horner and Tyree.[13]

[13] S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

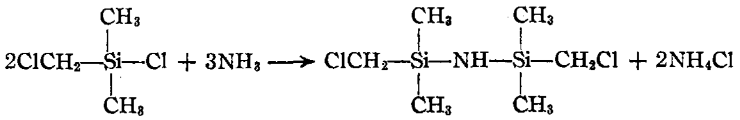
CONTRIBUTION FROM THE INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MARBURG, MARBURG, GERMANY

A New Heterocycle Containing Sulfur and Silicon

BY MAX SCHMIDT AND MARKUS WIEBER

Received October 9, 1961

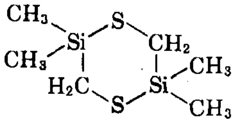
The reaction of chloromethyldimethylchlorosilane with ammonia yields the new 1,3-bis-(chloromethyl)-tetramethyldisilazane



$$2ClCH_2-\underset{CH_3}{\overset{CH_3}{Si}}-Cl + 3NH_3 \longrightarrow ClCH_2-\underset{CH_3}{\overset{CH_3}{Si}}-NH-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2Cl + 2NH_4Cl$$

Both the original chloromethyldimethylchlorosilane and the new 1,3-bis-(chloromethyl)-tetramethyldisilazane react with H$_2$S in the presence of triethylamine to give a new ring compound, 2,2,5,5-tetramethyl-1,4-dithia-2,5-disilacyclohexane.

$ClCH_2(CH_3)_2SiNHSi(CH_3)_2CH_2Cl + 2H_2S + (C_2H_5)_3N \longrightarrow$



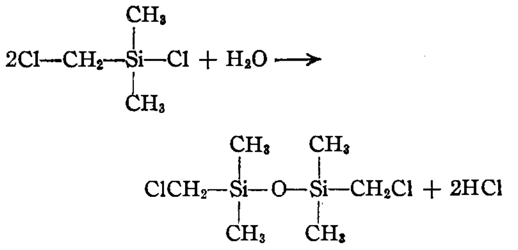
$+ (C_2H_5)_3N{\cdot}HCl + NH_4Cl$

The properties of the new compound are described. The reaction with water gives 1,3-bis-(mercaptomethyl)-tetramethyldisiloxane, which is converted into the corresponding silver mercaptide by silver nitrate. Dry hydrogen chloride converts the ring molecule into mercaptomethyldimethylchlorosilane, ethyl alcohol into mercaptomethyldimethylethoxysilane. The latter mercaptan reacts with disulfur dichloride in a condensation reaction and forms a sulfane derivative, 2,2′-bis-(ethoxydimethylsilane)-dimethyltetrasulfane.

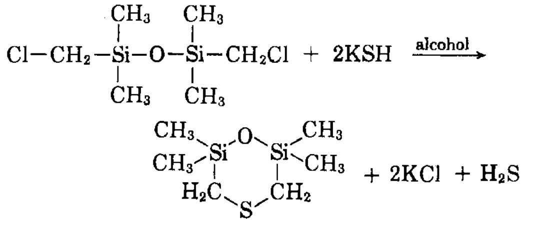
Introduction

The preparations of 2,2,6,6-tetramethyl-1-oxa-2,6-disila-4-thiacyclohexane and the corresponding selenium compound have been reported recently by members of this Laboratory.[1] The appropriate equations are

[1] M. Schmidt and M. Wieber, *Ber.*, **94**, 1426 (1961).



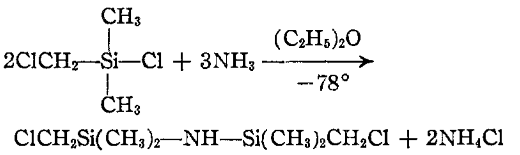
$$2\text{Cl—CH}_2\text{—Si(CH}_3)_2\text{—Cl} + \text{H}_2\text{O} \longrightarrow \text{ClCH}_2\text{—Si(CH}_3)_2\text{—O—Si(CH}_3)_2\text{—CH}_2\text{Cl} + 2\text{HCl} \quad (1)$$



(2)

The use of Na_2Se in place of KHS gave the corresponding selenium heterocycle.

The present paper reports an attempt to synthesize an analog of the above heterocycle, in which the oxygen of the ring is replaced by the isosteric N–H group. When ammonia is used in the first step in place of water, the reaction goes smoothly as anticipated to give the previously unreported disilazane



$$2\text{ClCH}_2\text{—Si(CH}_3)_2\text{—Cl} + 3\text{NH}_3 \xrightarrow[-78°]{(\text{C}_2\text{H}_5)_2\text{O}} \text{ClCH}_2\text{Si(CH}_3)_2\text{—NH—Si(CH}_3)_2\text{CH}_2\text{Cl} + 2\text{NH}_4\text{Cl} \quad (3)$$

The 1,3-bis-(chloromethyl)-tetramethyldisilazane is a colorless liquid which boils at 92–95°, under a pressure of 5 mm.

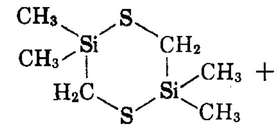
The reaction of the disilazane with H_2S differs in many ways from the corresponding reaction of the corresponding siloxane (equation 2 above). First, the known reactions of the non-chlorinated hexamethyldisilazane with water and alcohol[2,3] suggested that alcohol would not be an appropriate solvent for the reaction of the silazane with H_2S.

$$[(\text{CH}_3)_3\text{Si}]_2\text{NH} + 2\text{HOR} \longrightarrow 2(\text{CH}_3)_3\text{SiOR} + \text{NH}_3 \quad (4)$$

(R = H or alkyl group)

Furthermore, when H_2S was allowed to react with the dichlorinated silazane without a solvent, but in the presence of triethylamine, the NH of the ring was removed by further reaction with H_2S (compare reaction 2).

$[(\text{ClCH}_2)(\text{CH}_3)_2\text{Si}]_2\text{NH} + 2\text{H}_2\text{S} + (\text{C}_2\text{H}_5)_3\text{N} \longrightarrow$



$(\text{C}_2\text{H}_5)_3\text{N·HCl} + \text{NH}_4\text{Cl}$ (5)

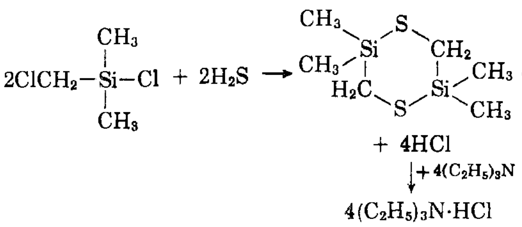
Based on the following reported reactions there is no doubt that the heterocycle, 2,2,5,5-tetramethyl-1,4-dithia-2,5-disilacyclohexane, is formed according to eq. 5.

The mechanism may be assumed to involve proton addition at the nitrogen of the silazane, thus polarizing the –Si–N– bond so that a nucleophilic SH^- attacks a silicon atom which results in a cleavage of the $>$Si–NH–Si$<$ bond

$$>\text{Si—NH}_2^{\oplus}\text{—Si}< + \text{SH}^{\ominus} \longrightarrow >\text{Si—NH}_2 + >\text{Si—SH} \quad (6)$$

The intermediate aminosilane thus formed would react easily with hydrogen sulfide to form the mercaptan which in turn would react in the usual way[1] with the chlorine atom bonded to the carbon.

On the basis of the results described above, we tried to synthesize the same compound directly from chloromethyldimethylchlorosilane and hydrogen sulfide with the addition of triethylamine as a hydrogen chloride acceptor



(7)

A stoichiometric mixture of the chlorinated chlorosilane, hydrogen sulfide, and triethylamine gave the desired compound after 3 days in a sealed tube, but only in a yield of 30%. The relatively small yield may be caused by the solidification of the liquid reaction mixture (formation of solid triethylammonium hydrochloride). Despite the low yield the data are consistent with the proposed mechanism for the formation of the heterocycle. The same hypothetical intermediate chloromethyldimethylmercaptosilane may be postulated. The intermediate then would react with a second molecule of the starting material with elimination of two moles of hydrogen chloride and resulting ring formation

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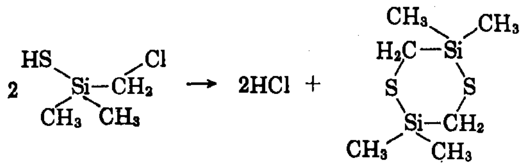
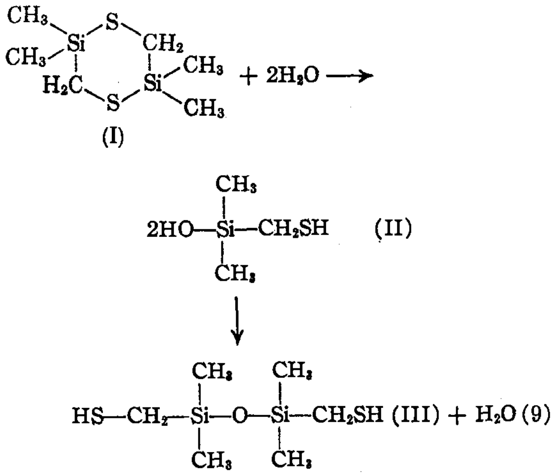
(2) R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

(3) S. H. Langer, S. Connell, and J. Wender, *J. Org. Chem.*, **23**, 50 (1958).



(8)

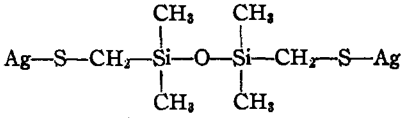
Properties of $[(CH_3)_2SiCH_2S]_2$ (I) and Structure Proof Reactions of 2,2,5,5-Tetramethyl-1,4-dithia-2,5-disilacyclohexane.—The hydrolysis of the new compound proceeded according to (9).



(I) (II) (III) (9)

Mercaptomethyldimethylsilanol and 1,3-bis-(methylmercapto)-tetramethyldisiloxane formed in this way could be isolated in good yield. On standing the silanol (II) changed slowly to siloxane (III) in a condensation reaction wherein drops of water were separated. This change was proved by the infrared spectrum as well as by other methods.

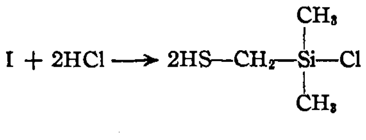
On addition of an aqueous silver nitrate solution to an acetone solution of 1,3-bis-(mercaptomethyl)-tetramethyldisiloxane, a yellow flocculent precipitate separated



$$Ag\text{—}S\text{—}CH_2\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}CH_2\text{—}S\text{—}Ag$$

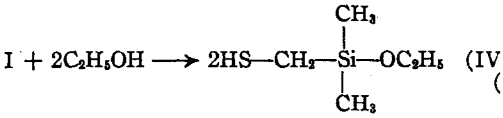
The silver salt darkened in the presence of light but was stable when light was absent.

The heterocycle was cleaved under the influence of dry hydrogen chloride and chlorosilane was formed according to eq. 10



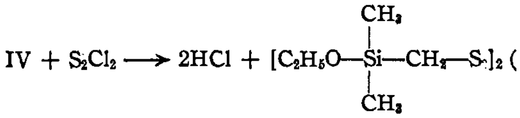
$$I + 2HCl \longrightarrow 2HS\text{—}CH_2\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}Cl \qquad (10)$$

Ethanol split the compound and formed mercaptomethyldimethylethoxysilane (IV)



$$I + 2C_2H_5OH \longrightarrow 2HS\text{—}CH_2\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}OC_2H_5 \quad (IV) \qquad (11)$$

The mercaptan, an oil with an aromatic odor, was isolated in an 80% yield. The mercaptan formed by alcoholysis of the new heterocycle could be condensed with sulfur dichloride according to the equation



$$IV + S_2Cl_2 \longrightarrow 2HCl + [C_2H_5O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}CH_2\text{—}S\text{—}]_2 \quad (12)$$

Experimental

1. **Preparation of 1,3-Bis-(chloromethyl)-tetramethyldisilazane (Equation 3.)**—A solution of 142 g. of chloromethyldimethylchlorosilane[1] in 200 ml. of ether was poured into a three-necked flask fitted with a stirrer, a drying tube, and a gas inlet tube. The reaction mixture was cooled to −78° and 32 ml. of liquid ammonia was condensed from a condensing tube during 1 hr. while the reaction mixture was stirred. During the operation the gas inlet tube was over the surface of the liquid so that the gas was evenly distributed and absorbed in the flask. The cooling bath was removed and the flask was allowed to warm up slowly. After 5 hr., the ammonium chloride could be filtered. Ether was removed and the remaining residue was distilled under a pressure of 5 mm. at a temperature of 90–95°. A clear colorless oil distilled which became cloudy after some time and which had to be distilled three times in order to obtain a clear product. 1,3-Bis-(chloromethyl)-tetramethyldisilazane thus was obtained in 70% yield (80 g.); b.p. 103–105° (10 mm.), $n^{25}{}_D$ 1.4671. (Chlorine and silicon analyses were obtained after fusion with sodium peroxide or evaporation with HCl, respectively.)

Anal. Calcd. for $C_6H_{17}NCl_2Si_2$: C, 31.4; H, 7.4; N, 6.2; Cl, 30.6; Si, 24.4; mol. wt., 230. Found: C, 30.80; H, 7.00; N, 6.11; Cl, 31.2; Si, 23.5; mol. wt. (f.p. in benzene), 227. Infrared peaks (cm.$^{-1}$) at: 3330 (s); 2920 (s); 1380 (s); 1250 (vs); 1190 (vs); 1100 (s); 945 (vs); 840 (vs); 815 (vs); 740 (s).

2. **Preparation of 2,2,5,5-Tetramethyl-1,4-dithia-2,5-disilacyclohexane (I).**—In a 2.5-cm. diameter sealed tube of Jena glass (length *ca.* 30 cm.), a 7 g. sample of dried H_2S was condensed by cooling the tube to −78°. The hydrogen sulfide was solidified by dipping the tube into liquid air and 22.9 g. of carefully cooled chlorinated silazane and 20.4 g. of triethylamine were added. The tube was sealed and stored in a steel cylinder for 3 or 4 days. After cooling with liquid air, the tube was opened to a Bunsen valve. As the temperature rose over a 2-hr. period, slow escape of H_2S occurred without air contacting the product. The white contents were rinsed with *ca.* 100 ml. of dry ether, the ether suspension was filtered, and the white residue was washed well with ether (21 g.; yield, 77%). After the ether was distilled, a yellow oil remained which could not be distilled up to a bath temperature of 170°. When the oil was cooled, it solidified to give white crystals. The

substance was recrystallized from boiling petroleum ether; white plates were obtained which were dried under high vacuum. Concentration of the mother liquor resulted in a second fraction. (If the petroleum ether were distilled off completely before the second crystallization, a yellow-brown non-distillable viscous oil remained (about 10%).) The white shiny plates, dried under vacuum, had a m.p. of 81–83°; yield, 13 g. (65%).

Anal. Calcd. for $C_6H_{16}S_2Si_2$: C, 34.6; H, 7.70; S, 30.70; Si, 26.80; mol. wt., 208. Found: C, 35.11; H, 7.73; S, 30.80; Si, 27.60; mol. wt. (f.p. in benzene), 186. Infrared peaks (cm.$^{-1}$) at: 2920 (s); 1410 (m); 1390 (s); 1250 (vs); 1190 (s); 1080 (s); 840 (vs); 785 (vs); 760 (s); 680 (vs).

3. **Hydrolysis of the 2,2,5,5-Tetramethyl-1,4-dithia-2,5-disilacyclohexane** (I) (**Equation 9**).—A 3-g. sample of compound I (2,2,5,5-tetramethyl-1,4-dithia-2,5-disilacyclohexane) was dissolved in 25 ml. of ethanol and a 10-ml. aliquot of water was added. The reaction mixture became moderately warm, and was refluxed for 0.5 hr. and then half of the alcohol was distilled off. Water and ether were added (*ca.* 40 ml. of each) and the ether layer separated. The ether extract was dried over $CaCl_2$ and the ether was removed. About 2 g. of an oily liquid remained which was distilled at 10 mm.

Fraction 1.—$HOSi(CH_3)_2CH_2SH$ (II) 1.2 g., b.p. 62–67° (10 mm.). *Anal.* Calcd.: C, 29.5; H, 8.2; S, 25.8; mol. wt., 122. Found: C, 31.4; H, 8.2; S, 25.3; mol. wt. (f.p. in benzene), 145.

Fraction 2.—$HS{-}CH_2{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2CH_2SH$ (III) 0.7 g.; b.p. 75–100° (10 mm.). *Anal.* Calcd.: S, 28.3; mol. wt., 226. Found: S, 27.9; mol. wt. (f.p. in benzene), 193; no OH band in the infrared.

4. **Preparation of the Silver Salt of the Hydrolysis Product.**—Water was added to a solution of 200 mg. of compound I in 10 ml. of acetone. The clear solution was boiled for 5 min.: then 2 drops of HNO_3 and aqueous $AgNO_3$ were added. No dark silver sulfide formed, but a flocculent precipitate separated which was filtered and washed with acetone. The substance was dried in a vacuum desiccator. The remaining yellow powder darkened after 8 days of exposure to light. After fusion with concentrated HNO_3, the substance showed 48.4% Ag (titration with 0.1 *N* NH_4CNS). (Calcd. for the Ag salt from compound III, 48.9%.) The color changes to red at 120° and to black at 160–180°, but no melting was observed.

5. **Reaction with Gaseous Hydrogen Chloride** (**Equation 10**).—A slow stream of HCl was led slowly into a reaction flask containing 2 g. of substance I. The white crystals melted and heat was evolved. The resulting liquid was freed of dissolved HCl by flushing with dry nitrogen; then the product was distilled. A 2-g. sample of a colorless liquid was obtained which boiled at 130° and fumed on contact with moist air. The chlorine analysis was carried out after fusion in the Wurzschmitt bomb. After direct hydrolysis, the addition of $AgNO_3$ resulted in the precipitation of yellow mercaptide in addition to AgCl.

Anal. Calcd. for $HSCH_2Si(CH_3)_2Cl$: C, 25.6; H, 6.42; Si, 19.9; S, 22.8; Cl, 25.2. Found: C, 26.1; H, 6.46; Si, 18.5; S, 24.0; Cl, 24.6.

6. **Alcoholysis** (**Equation 11**).—Five g. of the compound was refluxed for 0.5 hour in 20 ml. of absolute alcohol. After removal of the alcohol, the colorless residue was distilled. The resulting oil had an aromatic odor; b.p. 151°; 80% yield (6 g.).

Anal. Calcd. for $HSCH_2Si(CH_3)_2OC_2H_5$: C, 40.0; H, 9.3; S, 21.3. Found: C, 40.1; H, 9.34; S, 20.1.

7. **Reaction of the Alcoholysis Product with Disulfur Dichloride** (**Equation 12**).—The reaction product of the alcoholysis of mercaptomethyldimethylethoxysilane (IV) (1.2 g.) was dissolved in 20 ml. of dry petroleum ether. The stoichiometric amount of S_2Cl_2 (0.535 g.) was slowly dropped into the solution while the liquid was stirred with a magnetic stirrer. The reaction mixture became warm and HCl escaped through the reflux condenser, which was closed with a calcium chloride tube. The reaction mixture was refluxed until the evolution of gas stopped. Then petroleum ether was distilled off and a yellow viscous oil was obtained in quantitative yield. The distillation at 2 mm. produces decomposition (this explains the bad analyses and molecular weight data); b.p. 150–160° (2 mm.).

Anal. Calcd. for $C_2H_5OSi(CH_3)_2CH_2{-}S_4{-}CH_2Si(CH_3)_2{-}OC_2H_5$: C, 33.2; H, 7.2; Si, 15.4; S, 35.4; mol. wt., 362. Found: C, 29.3; H, 6.5; Si, 14.3; S, 32.0; mol. wt. (f.p. in benzene), 329.

8. **Preparation of the Heterocycle** (**I**) **from Chloromethyldimethylchlorosilane** (**Equation 7**).—Chloromethyldimethylchlorosilane[4] (28.4 g.), H_2S (6.8 g.), and triethylamine (40.8 g.) were allowed to react in a sealed tube. When the tube was opened after 3 days, the contents had solidified; the reaction tube was broken; then the reaction mixture was extracted with ether and filtered. An oily residue remained after removal of the solvent. Foaming was a problem during distillation. Fourteen g. (50%) of the starting material distilled at 80–85° under a pressure of 150 mm. Upon cooling, crystals separated out of the viscous residue. The crystals were recrystallized from petroleum ether; yield, 7 g. (30%); m.p. 81–83°. Infrared analysis shows that the recovered product is 2,2,5,5-tetramethyl-1,4-dithia-2,5-disilacyclohexane. When the petroleum ether was completely removed, a small amount of a viscous liquid (10%), which contained chlorine, remained.

Acknowledgment.—Very grateful acknowledgment is hereby made to Prof. Robert W. Parry for his help in preparing the English version of the manuscript.

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(4) F. Runge and W. Zimmermann, *Ber.*, **87**, 282 (1954).