1,1-DIMETHYL-1-SILAETHYLENE IN THE REACTION OF CHLOROMETHYLPENTAMETHYLDISILANE WITH ALKALI METAL VAPORS

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The mechanism for the formation of 1,1-dimethyl-1-silaethylene (I) involves a step pyrolysis of hexamethyldisilane (II) at 500-600°C [1] involves a step featuring isomerization of pentamethyldisilanyl radical (III) to give dimethyl(trimethylsilylmethyl)silyl radical (IV), which was previously proposed for the thermal isomerization of (II) [2]

$$\underset{(III)}{Me_3SiSiMe_2\dot{C}H_2} \rightarrow \underset{(IV)}{Me_3SiCH_2\dot{S}iMe_2} \qquad (1)$$

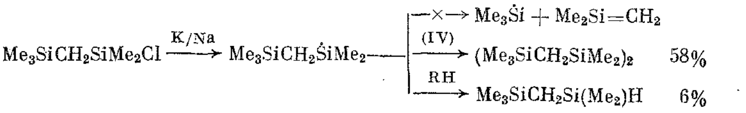
$$Me_3SiCH_2\dot{S}iMe_2 \rightarrow \underset{(I)}{Me_2Si{=}CH_2} + \underset{(V)}{Me_3\dot{S}i} \qquad (2)$$

We have obtained (III) in the gas-phase reaction of chloromethylpentamethyldisilane (VI) with K/Na vapor at 300°C and 0.1 torr and found that the formation of $Me_2Si{=}CH_2$ under these conditions is not related to reaction (1) but rather is the result of β-cleavage of primary radical (III)

$$ClCH_2Me_2SiSiMe_3 \xrightarrow{K/Na} Me_3SiSiMe_2\dot{C}H_2 \qquad (3)$$

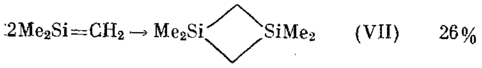
$$Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_3Si^{\cdot} + Me_2Si = CH_2 \qquad (4)$$

A special experiment showed that under conditions, under which the dehalogenation of (VI) was carried out, fragmentation (2) is not characteristic for radical (IV). Instead of products of the decomposition of radical (III), we find the products of its recombination and hydrogen abstraction



$$Me_3SiCH_2SiMe_2Cl \xrightarrow{K/Na} Me_3SiCH_2\dot{S}iMe_2 \begin{cases} \xrightarrow{\times} Me_3\dot{S}i + Me_2Si{=}CH_2 \\ \xrightarrow{(IV)} (Me_3SiCH_2SiMe_2)_2 \quad 58\% \\ \xrightarrow{RH} Me_3SiCH_2Si(Me_2)H \quad 6\% \end{cases}$$

The formation of the major stable products of the dehalogenation of (VI) with the participation of intermediates (I), (III), (IV), and (V) may be attributed to reactions (5)-(12)



(VII) 26% (5)

$$Me_3\dot{S}i + Me_2Si{=}CH_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2 \leftarrow (III) \qquad (6), (1)$$

$$Me_3SiCH_2\dot{S}iMe_2 \xrightarrow{RH} Me_3SiCH_2Si(Me_2)H \;\; (VIII) \;\; 19\% \qquad (7)$$

$$Me_3\dot{S}i \xrightarrow{RH} \underset{5\%}{Me_3SiH} \qquad (8)$$

$$2Me_3\dot{S}i \rightarrow \underset{17\%}{Me_3SiSiMe_3} \xleftarrow{RH} Me_3SiSiMe_2\dot{C}H_2 \qquad (9), (10)$$

$$(III) \xrightarrow{Me_3\dot{S}i} \underset{(5\%)}{Me_3SiSiMe_2CH_2SiMe_3} \xleftarrow{Me_3\dot{S}i} (IV) \qquad (11), (12)$$

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Reaction (4) is the first example of the β-fragmentation of disilanylmethyl radicals.

The reaction products were identified chromatographically on a Biokhrom chromatograph using a 50 m × 0.25 mm glass capillary column packed with OV-101 and an LKB 2091 chromato-mass spectrometer at 70 eV ionization energy. The mass spectra of the major reaction products, m/z (rel. intensity, %): (II) – 146 (6), $M^{+\cdot}$; 131 (20), $[M-15]^+$; 73 (100), $[Me_3Si]^+$; (VII) – 144 (23), $M^{+\cdot}$; 129 (100), $[M-15]^+$; 101 (11), $[M-43]^+$; 59 (15), $[Me_2SiH]^+$; (VIII) – 146 (1), $M^{+\cdot}$; 145 (4), $[M-1]^+$; 131 (100), $[M-15]^+$; 73 (62), $[Me_3Si]^+$; 59 (22), $[Me_2SiH]^+$.

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FORMATION OF THE BOND OF TETRAETHYNYLBORON(1-) ANION WITH NICKEL(II) SQUARE-PLANAR TETRAAMINE COMPLEXES

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The introduction of polydentate amines into the equatorial plane of Ni(II) complexes permits the formation of a weak (in the case of bidentate ethylenediamine) and strong (in the case of tetradentate 1,4,8,11-tetraazaudecane, 2,3,2-tet) bond of the tetraamine complex of Ni(II) with tetraethynylboron(1-) anion $[B(C \equiv CH)_4]^-$ (teb^-). Yellow-orange complex salts $[Ni(en)_2teb]teb$ (I) $[Ni(2,3,2\text{-}tet)teb]teb$ (II) were isolated. The product compositions were determined by chemical analysis. The molar electrical conductance of the aqueous solutions was 130-140 $\Omega^{-1}\cdot cm^2$/mole, which indicates dissociation of the salts into two ions. The electronic absorption spectra of (I) and (II) have strong bands at 22,500 and 21,500 cm^{-1}, respectively, characteristic for square-planar diamagnetic nickelous complexes, which was also confirmed by direct magnetic susceptibility measurements. The field desorption mass spectrum of (II) has a strong peak and 330 m/z which corresponds to the mass of the cation $[Ni(2,3,2\text{-}tet)teb]^+$. The IR spectrum has a $C \equiv C$ stretching band at 2060 cm^{-1} in addition to the band at 2060 cm^{-1} characteristic for ionic teb^-. The shift of the maximum of this band toward higher frequencies indicates an increase in electron density in the $C \equiv C$ bond upon coordination of teb^-. An x-ray diffraction structure analysis showed that the Ni^{2+} ion in the $[Ni(2,3,2\text{-}tet)teb]^+$ cation forms a tetraminic square-planar complex, above which teb^- is found such that the middle of the $C \equiv C$ bond is opposite nickel at a distance of 3.18 Å. Considering that the d_{z^2} orbital in diamagnetic nickelous complexes is occupied by two electrons and, therefore, cannot overlap with the occupied π_u orbital of the teb^- $C \equiv C$ bond, we may conclude that the bond of the teb^- anion with the Ni(II) complex is formed due to transfer of electron density from d_{xz} or d_{yz} metal orbitals to the teb^- orbitals.

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