Heteroorganic betaines
6.* Structure and reactivity of silicon-containing organophosphorus betaines with the $^{-}$S—Si—C—P^{+} fragment: a DFT study

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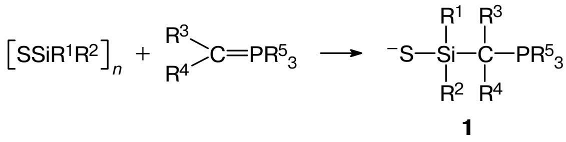
The structures of silicon-containing organophosphorus betaines $^{-}S—SiR^1{}_2—CR^2{}_2—P^+R^3{}_3$ and their ylide isomers were calculated using the density functional approach with the gradient-corrected PBE functional and extended TZ2P basis set. Three possible pathways of thermal decomposition of these betaines were analyzed. These are (i) cleavage of the central C—Si bond with the formation of a Wittig ylide and silanethione, (ii) intramolecular nucleophilic S_N-substitution with elimination of phosphine $PR^3{}_3$ and the formation of silathiirane (the Corey—Chaikovscky transformation), and (iii) a Wittig-type decomposition followed by the formation of substituted silaethylene.

The structures of products and transition states of these reactions were calculated. The *cis-gauche* conformation of the $^{-}$S—Si—C—P^{+} fragment of betaines was found to be the most stable. This is in agreement with the results of X-ray diffraction study and can be rationalized by strong Coulomb attraction between the cationic and anionic centers. The betaines are stable toward retro-Wittig thermal decomposition. The Corey—Chaikovscky formation of thiirane is preferable under conditions of thermal decomposition. Retro-Wittig-type decomposition of betaines followed by the formation of silanethione is favored by intra- and intermolecular coordination of donor ligands.

Key words: silene, silanethione, silathiirane, betaine, phosphorus ylides, nonempirical quantum-chemical calculations, density functional theory, molecular structure, reactivity.

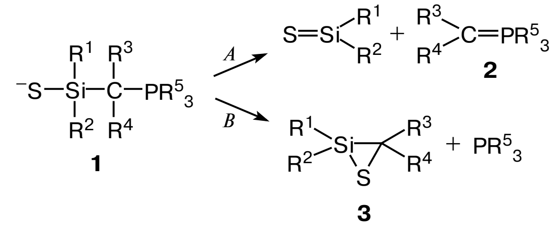
Recently,[2—5] we have reported the results of our studies of silicon-containing organophosphorus betaines **1** with the $^{-}$S—Si—C—P^{+} fragment. These compounds were obtained in the reactions of nonstabilized phosphorus ylides with organocyclosilathianes (Eq. (1)).



$$[SSiR^1R^2]_n + R^3R^4C{=}PR^5{}_3 \longrightarrow {}^{-}S{-}SiR^1R^2{-}CR^3R^4{-}PR^5{}_3 \quad (1)$$

R^1, R^2, R^5 = Alk, Ar; R^3, R^4 = H, Alk, Ar;
n = 2, 3

Betaines **1** appeared to be rather stable, which made possible detailed characterization of these compounds by different methods including X-ray diffraction analysis.[3] They were found to have a number of remarkable structural features and to possess some unusual chemical properties. For instance, kinetically unstable silanethiones **2** and silathiacyclopropanes **3** can be generated *in situ* from betaines **1** in solutions under conditions of thermal or photoinduced decomposition (Eq. (2)) and introduced then into various chemical reactions.



(2)

R^1, R^2, R^5 = Alk, Ar; R^3, R^4 = H, Alk, Ar

Controlling the reactivity of compounds **1—3** requires knowledge of the main determining factors. To this end, we carried out a DFT study of these compounds. The results obtained are presented in this work.

Calculation Procedure

The computational procedure and software[6] used in this work were the same as those employed previously in our studies

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Table 1. Energies of compounds under study obtained from DFT calculations

Molecule	E	E_0	ZPE /kcal mol^{-1}
	au		
$^{-}$S—SiMe$_2$—CH$_2$—P$^+$Me$_3$ (**1a**)	−1267.29968	−1267.08866	132.4
$^{-}$S—SiMe$_2$—CMe$_2$—P$^+$Ph$_3$ (**1b**)	−1920.48446	−1920.06266	264.7
$^{-}$S—SiPh$_2$—CHMe—P$^+$Et$_3$ (**1c**)	−1807.48887	−1807.06089	268.6
$^{-}$S—SiMe$_2$—S—SiMe$_2$—CH$_2$—P$^+$Me$_3$ (**1d**)	−2034.53546	−2034.24880	179.9
Me$_2$Si=S (**2a**)	−767.18015	−767.10602	46.5
Me$_2$Si(S)CH$_2$ (**3a**)	−806.44168	−806.34180	62.7
(Me$_2$SiS)$_3$ (**4**)	−2301.68777	−2301.46283	141.1
(Me$_2$SiS)$_2$ (**5**)	−1534.46820	−1534.31895	93.7
EtS—SiMe$_2$—CMe$_2$—P$^+$Ph$_3$ (**6**)	−1999.44351	1998.95508	306.5
Me$_3$P=CH$_2$ (**7**)	−500.04717	−499.91361	83.8
$^{-}$S—SiMe$_2$—CH$_2$—P$^+$Me$_3$ (**9**)*	−1267.24558	−1267.03694	130.3
(Me$_2$Si(S)CH$_2$)$_2$ (**10**)	−1612.94734	−1612.74575	126.5
Me$_2$SiS · Py (**11**)	−1015.27609	−1015.11413	101.6
Me$_2$Si=CH$_2$ (**12**)	−408.33498	−408.23943	60.0
Me$_2$Si=CH$_2$ · Py (**13**)	−656.40652	−656.22390	114.6
HS—SiMe$_2$—CH$_2$=PMe$_3$ (**14**)	−1267.27674	−1267.06922	130.2
HS—SiPh$_2$—CMe=PEt$_3$ (**15**)	−1807.45878	−1807.03535	265.7
PMe$_3$	−460.82466	−460.71546	68.5
C$_5$H$_5$N	−248.05956	−247.97353	53.9
Me$_3$P=S	−858.90741	−858.79493	70.5

Note. E is the total energy; $E_0 = E + ZPE$ is the total energy calculated with inclusion of zero-point energy correction, and ZPE is the zero-point energy correction.

* Transition state.

of the mechanisms of haptotropic rearrangements in transition-metal complexes with polycyclic ligands,[7] activation of C—H bonds in alkanes by cationic complexes of Ti and Zr,[8] as well as the structure of betaines with the general formula R$_3$P$^+$—CH$_2$—SiR$'_2$—C$_5$H$_4$$^-$ (R, R$'$ = Alk, Ar).[1]

The exchange-correlation energy was calculated using the generalized gradient approximation and the PBE hybrid functional.[9] One-electron wave functions were expanded using extended basis sets of contracted Gaussian functions of size {311/1} for H, {611111/411/11} for C and N, and

Table 2. Energies of the simplest unsaturated silicon compounds obtained from DFT and MP4SDTQ/6-31G* calculations

Molecule	State	$E_{\rm DFT}$ /au	$E_{\rm rel}$^{a} /kcal mol^{-1}	$E_{ab\ initio}$ /au	$E_{\rm rel}$^{a} /kcal mol^{-1}
H$_2$CSiH$_2$	^{1}A$_1$	−329.75830	0.0	−329.28639^b	0.0
H$_3$CSiH	^{1}A$'$	−329.75370	2.9	−329.28508^b	2.2
H$_3$CSiH	^{3}A$''$	−329.72467	22.4	−329.25420^b	22.0
H$_2$CSiH$_2$	^{3}A$''$	−329.70216	34.0	−329.22969^b	33.7
HSiNH$_2$	^{1}A$'$	−345.84933	0.0	−345.35715^b	0.0
H$_2$SiNH	^{1}A$_1$	−345.82299	14.0	−345.32007^b	20.6
HSiNH$_2$	^{3}A$''$	−345.77508	44.9	−345.29156^b	40.3
H$_2$SiNH	^{3}A$''$	−345.75629	54.5	−345.25961^b	56.4
H$_2$SiO	^{1}A$_1$	−365.71838	0.0	−365.20411^b	0.0
trans-HSiOH	^{1}A$'$	−365.72100	0.0	−365.19883^b	4.6
cis-HSiOH	^{1}A$'$	−365.72059	0.0	−365.19763^b	5.1
HSiOH	^{3}A	−365.66430	34.9	−365.13736^b	42.6
H$_2$SiO	^{3}A$''$	−365.62921	54.0	−365.09105^b	69.3
H$_2$SiS	^{1}A$_1$	−688.59462	0.0	−687.82984^c	0.0
trans-HSiSH	^{1}A$'$	−688.58065	8.8	−687.81499^c	8.9
cis-HSiSH	^{1}A$'$	−688.57623	11.3	−687.81075^c	11.4
HSiSH	^{3}A	−688.52820	41.0		
H$_2$SiS	^{3}A$''$	−688.52843	40.4		

^{a} The relative energies obtained from DFT and *ab initio* calculations with inclusion of *ZPE.*

^{b} Calculated at the MP4SDTQ/6-31G* level of theory.[10]

^{c} The energies calculated by the CI(S+D+QC)/6-31G** method for the structures optimized by the HF/6-31G* method.[11]

{6111111111/5111111/11} for Si and P (figures in braces indicate the contraction patterns for the s-, p-, and d-AOs, respectively). According to the algorithm proposed earlier,[9] the matrix elements of the Coulomb and exchange-correlation potentials were calculated using the electron density expansion over an auxiliary basis set. In this work, the auxiliary basis set comprised sets of uncontracted atom-centered Gaussian functions of dimensions (5s1p) for H, (10s3p3d1f) for C and N, and (14s7p7d1f1g) for Si and P. Stationary points on the potential energy surfaces (PES) of the systems under study were located by analyzing the Hesse matrices. The second derivatives of energy with respect to coordinates were calculated analytically. Zero-point vibrational energy corrections (*ZPE*) were calculated in the harmonic approximation (Table 1).

To check the adequacy of the approach employed, we carried out preliminary calculations of the geometries of some simplest X=Si molecules containing double bonds, *viz*., silaethylene $H_2C=SiH_2$, silanone $O=SiH_2$, silanethione $S=SiH_2$, and silaneimine $HN=SiH_2$, as well as isomeric silylenes H_3C-SiH, $HO-Si-H$, $HS-Si-H$, and $H_2N-Si-H$. Recently,[10–14] MO LCAO SCF calculations of all these molecules with inclusion of electron correlation and extended and split-valence basis sets have been carried out. The results of our DFT calculations are compared with the best results available in the literature in Tables 2 and 3. Our DFT-based computational method correctly reproduces the results of *ab initio* calculations of the geometries and relative energies of isomeric structures, in particular, a decrease in the relative stability of singlet silylenes (relative to the isomers with multiple bonds) in the order $HSi-NH_2 > HSi-OH > HSi-CH_3 > HSi-SH$. Previously,[1] we have shown that DFT calculations allow a correct reproduction of the geometry of phosphorus ylides and adequate description of their properties.

Table 3. Comparison of geometric parameters of several simplest unsaturated silicon compounds obtained from DFT calculations (this work, first line) with the experimental data and results of *ab initio* calculations (second line)

Molecule	Bond length/Å			Bond angle/deg	
	Si—X	Si—H	X—H	X—Si—H	Si—X—H
H_2SiCH_2	1.721	1.491	1.089	122.5	122.0
H_2SiCH_2[a]	1.704	1.467	1.082	122.4	122.0
H_2SiCH_2[b]	1.704	1.467	1.082	122.5	122.1
HSiMe	1.914	1.549	1.101	93.9	111.1
HSiMe[c]	1.903	1.513	1.090	94.3	111.2
H_2SiNH	1.625	1.506 (1.490)[d]	1.023	129.9 (117.4)[d]	117.2
H_2SiNH[e]	1.616	1.490 (1.474)[d]	1.018	130.6 (117.0)[d]	121.6
$HSiNH_2$	1.734	1.549	1.016	93.7	126.5 (121.5)[d]
$HSiNH_2$[e]	1.719	1.524	1.012	94.1	126.1 (121.6)[d]
H_2SiO	1.546	1.501		124.0	
H_2SiO[f]	1.521	1.476		124.1	
trans-HSiOH	1.692	1.548	0.972	93.8	112.4
trans-HSiOH[f]	1.662	1.521	0.958	94.8	114.3
cis-HSiOH	1.687	1.567	0.971	97.7	117.0
cis-HSiOH[f]	1.658	1.536	0.957	98.0	118.2
H_2SiS	1.968	1.500		124.8	
H_2SiS[g]	1.936	1.469		125.5	
trans-HSiSH	2.150	1.543	1.361	88.9	97.4
trans-HSiSH[g]	2.133	1.503	1.327	91.6	99.3
cis-HSiSH	2.164	1.543	1.359	94.4	101.7
cis-HSiSH[g]	2.143	1.506	1.328	95.8	103.3

[a] Microwave spectroscopy data.[12a]

[b] Calculated by the CCSD(T)/cc-pV(Q,T)Z method.[12a]

[c] Calculated at the MP2/6-31G** level of theory.[12b]

[d] Figures in parentheses refer to the *trans*-H atom with respect to the N—H fragment.

[e] Calculated at the MP2/6-31G(d′) level of theory.[13]

[f] Results of microwave spectroscopy studies and calculations by the CCSD/TZ2P(f,d) method.[14]

[g] Calculated by the HF/6-31G* method.[11]

Results and Discussion

Geometric parameters, dipole moments, and properties of betaines 1 and organocyclosilathianes. The molecular structures of 1,1,3,3,5,5-hexamethylcyclotrisilatrithiane (**4**) and 1,1,3,3-tetramethylcyclodisiladithiane (**5**) are shown in Figs. 1 and 2 and the geometric parameters of molecules **4** and **5** obtained from DFT calculations are listed in Table 4. It is of interest to compare the geometries of structure **4** and the trisilatrithiane fragment of tetrakis(methylsila)hexasulfide molecule, which is an analog of adamantane. Characteristic of tetrakis(methylsila)hexasulfide are the Si—S (2.129 Å) and Si—C (1.836 Å) bond lengths. The trisilatrithiane fragment adopts a "chair" conformation (the Si—S—Si—S dihedral angle is 56.8°), which is in agreement with the results of our calculations. The bond angles at the Si and S atoms (Si—S—Si = 104.6° and S—Si—S = 111.8°)[15] differ slightly from ideal tetrahedral angle (109°28′). Compound **5** was studied by X-ray

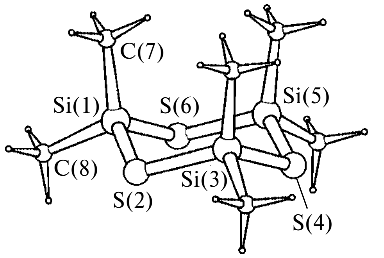


Fig. 1. Molecular structure of 1,1,3,3,5,5-hexamethyltrisilatrithiane (**4**) (C_{3v} symmetry group).

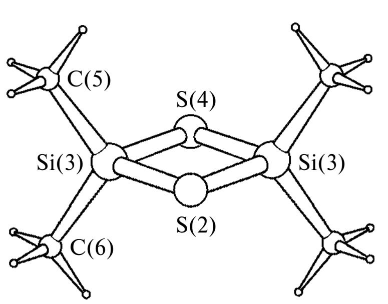


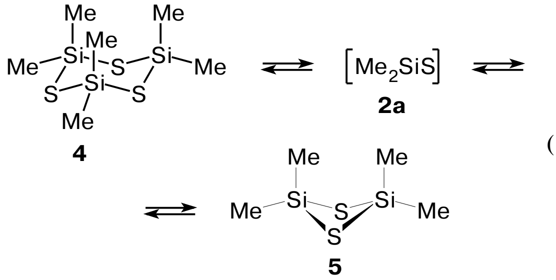
Fig. 2. Molecular structure of 1,1,3,3-tetramethyldisiladithiane (**5**) (D_{2h} symmetry group).

Table 4. Geometric parameters of structures **4** and **5**

Parameter	4	5
Bond	*d*/Å	
Si(1)—S(2)	2.177	2.185
Si(1)—C(7)	1.889	—
Si(1)—C(8)	1.885	—
Si(1)—C(5)/C(6)	—	1.884
C(5)—H	—	1.100
Bond angle	ω/deg	
Si(1)—S(2)—Si(3)	107.4	81.4
S(6)—Si(1)—S(2)	113.6	—
C(7)—Si(1)—S(2)	111.9	—
C(8)—Si(1)—S(2)	104.2	—
S(4)—Si(1)—S(2)	—	98.6
S(2)—Si(1)—C(5)/C(6)	—	111.7
Dihedral angle	φ/deg	
Si(1)—S(2)—Si(3)—S(4)	57.5	0
C(7)—Si(1)—S(2)—Si(3)	70.6	—
C(8)—Si(1)—S(2)—Si(3)	170.2	—
Si(3)—S(2)—Si(1)—C(5)/C(6)	—	±117.6

diffraction analysis.[16] The bond lengths calculated in this work insignificantly differ from the experimental values (2.152 Å for Si—S and 1.846 Å for Si—C). Our calculations correctly reproduced the conformation of the cyclic Si—S—Si—S fragment (the Si—S—Si and S—Si—S bond angles are 82.4° and 97.6°, respectively, and the Si—S—Si—S dihedral angle is 0°).[16]

The molecules **4** and **5** are respectively a trimer and a dimer of the molecule of dimethylsilanethione **2a** ($R^3 = R^4 = Me$). In solutions, these compounds undergo an interconversion (Eq. (3)) on heating and coexist as equilibrium mixtures.[17] This implies the formation of dimethylsilanethione as intermediate.



(3)

According to calculations, the energies of decomposition of **4** and **5** into monomers in the gas phase are 90.9 and 67.1 kcal mol^{-1}, respectively. These values should be regarded as the upper bounds for the reactions in solutions, since, as will be shown below, the molecule of dimethylsilanethione **2a** has a large dipole moment (μ = 4.14 D) and forms strong complexes with donor molecules. Because of this, the medium should have a pronounced effect on the activation energy of reaction (3) and on position of the dimer-trimer equilibrium in this reaction.

In Fig. 3, *a—d*, we present the calculated molecular structures of model betaine **1a** (R, R^3, R^4 = Me; R^1, R^2 = H), betaines **1b** (R = Ph; R^1—R^4 = Me) and **1c** (R = Et; R^1 = H; R^2 = Me, R^3; R^4 = Ph) and the cation of phosphonium salt Ph_3P^+—CMe_2—$SiMe_2$—SEtBr$^-$ (**6**) obtained by ethylation of **1b**. Previously,[3] the structures of compounds **1b,c** and salt **6** were characterized by X-ray diffraction analysis. Selected geometric parameters of these molecules obtained from DFT calculations are compared with the experimental data in Table 5. As can be seen, the most stable conformations of all three betaines are *cis-gauche* ones in which the phosphonium cationic and thiolate anionic centers approach each other owing to strong Coulomb interaction. This is in excellent agreement with the results of X-ray diffraction study. In compound **1a**, the P—S interatomic distance (3.583 Å) is close to the sum of the van der Waals radii of P and S (3.6 Å). Despite the fact that calculations were carried out for isolated molecules in the gas phase, the differences between the calculated and experimental values are, as a rule, no larger than 0.04 Å for the bond lengths and no greater than 4° for the bond angles (for the three molecules). The effect of the crystal packing on the dihedral angles in the S—Si—C—P fragment is much more pronounced. As should be expected, for all the three compounds the

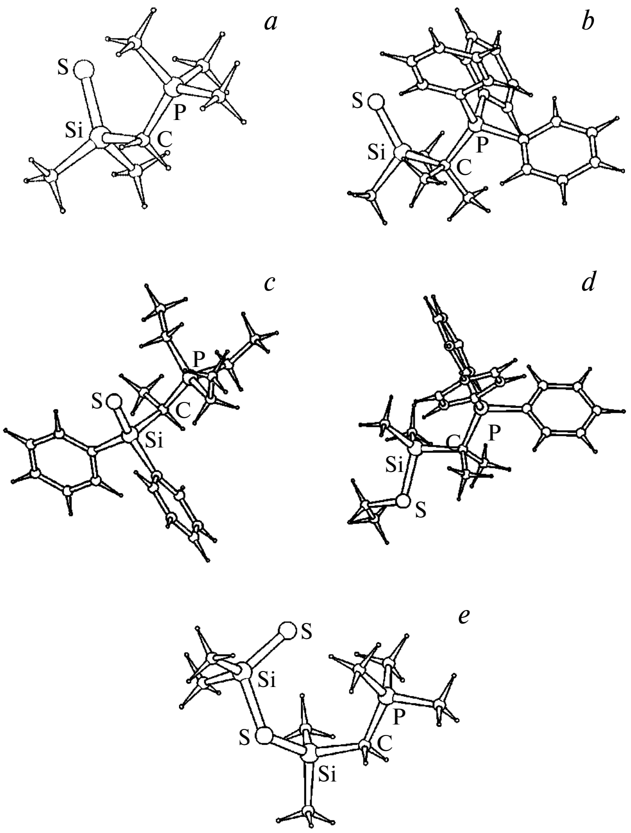


Fig. 3. Molecular structures of betaines **1a—d** and cation of phosphonium salt **6**: ^-S—$SiMe_2$—CH_2—P^+Me_3 (**1a**) (*a*), ^-S—$SiMe_2$—CMe_2—P^+Ph_3 (**1b**) (*b*), ^-S—$SiPh_2$—CHMe—P^+Et_3 (**1c**) (*c*), Ph_3P^+—CMe_2—$SiMe_2$—SEt (**6**) (*d*), and ^-S—$SiMe_2$—S—$SiMe_2$—CH_2—P^+Me_3 (**1d**) (*e*).

Table 5. Selected geometric parameters of compounds $^-S—SiR^1R^2—CR^3R^4—P^+R^5{}_3$

Compound	Bond length/Å				Angle/deg		
	P—C	C—Si	Si—S	P—S	Si—C—P*	S—Si—C*	S—Si—C—P**
$^-S—SiMe_2—CH_2—P^+Me_3$ (**1a**)	1.794	2.002	2.065	3.584	114.6	111.8	20.8
$^-S—SiMe_2—CMe_2—P^+Ph_3$ (**1b**)	1.865	2.037	2.064	3.687	111.7	111.9	36.7
	(1.825)	(1.986)	(2.048)	(3.988)	(115.60)	(114.6)	(56.1)
$^-S—SiPh_2—CHMe—P^+Ph_3$ (**1c**)	1.827	1.993	2.063	3.527	110.1	110.9	32.9
	(1.811)	(1.934)	(2.044)	(3.681)	(112.8)	(114.7)	(38.2)
$EtS—SiMe_2—CMe_2—P^+Ph_3$ (**6**)	1.891	1.989	2.176	5.093	112.5	113.7	187.2
	(1.839)	(1.939)	(2.141)	(5.011)	(166.6)	(107.3)	(177.1)

Note. The results of X-ray diffraction study[3] are given in parentheses.

* Bond angle.

** Dihedral angle.

calculated dihedral angles are systematically underestimated.

Salt **6** is characterized by the absence of intramolecular Coulomb interaction between the cationic center and S atom, which is no longer negatively charged. Therefore, the S—Si—C—P fragment adopts the *anti-trans* conformation, which corresponds to minimum steric strain in the molecule.

Our experiments showed that reaction (1) occurs stepwise. Initially, the first phosphorane molecule cleaves one of the ring Si—S bonds. We succeeded in isolating betaine **1d** with the $^-S—Si—S—Si—C—P^+$ structural fragment, which was characterized by X-ray diffraction analysis.[3] Figure 3, *e* the molecular structure of compound **1d** formed in the reaction of tetramethyldisiladithiane **5** with methylenetrimethylphosphorane **7**, obtained from DFT calculations. Similarly to all compounds **1**, the cationic and anionic centers in this molecule also approach each other (the $S^-—P^+$ interatomic distance is 3.971 Å). The molecule adopts a folded conformation. The formation of **1d** from compounds **5** and **7** in the gas phase occurs exothermically ($\Delta E = -10.2$ kcal mol^{-1}), while its decomposition into **1a** and dimethylsilanethione **2** is an endothermic process ($\Delta E = 33.9$ kcal mol^{-1}).

Reactivity of betaine 1a. The structure and reactivity of a model betaine **1a** were studied in more detail. Rotation about the central C—Si bond in this molecule is hindered. Analysis of the curve of changes in the energy of the system (Fig. 4) suggests that the *anti-trans* conformation of molecule **1a** corresponds to a shallow minimum separated from the global minimum by a barrier of 12 kcal mol^{-1}. A salient feature of molecule **1a** is that its dipole moment changes with variation of the S—Si—C—P dihedral angle (Fig. 5). The dipole moment is 9.71 D for the most stable *cis-gauche* conformer of **1a** and increases up to 14.19 D for the *anti-trans* conformer of this molecule. Hence it follows that the solvent will have a pronounced effect on the position of the conformational equilibrium in solution and that an increase in the solvent polarity will favor a decrease in the energy barrier and an increase in the fraction of the *anti-trans* conformer of molecule **1a**.

The formation of **1a** from dimethylsilanethione **2** and **7** in the gas phase occurs barrierlessly and exothermically ($\Delta E_0 = -43.3$ kcal mol^{-1}). In order to locate a cyclic isomer of betaine **1a**, silathiaphosphetane **8**, we carried out a point-by-point scanning of the corresponding PES region; however, our attempts to find local minima failed. This suggests that no equilibrium occurs between the open betaine and cyclic silathiaphosphetane forms (Eq. (4)) and compound **8** cannot act as intermediate in the gas-phase chemical reactions of **1a**.

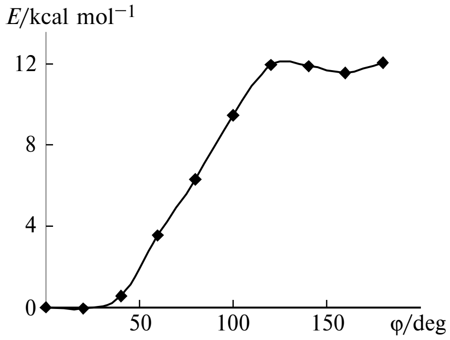


Fig. 4. Energy (E) of molecule **1a** as function of the S—Si—C—P dihedral angle (φ).

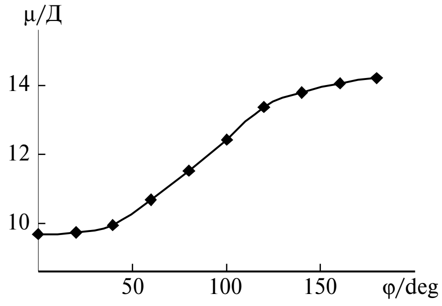
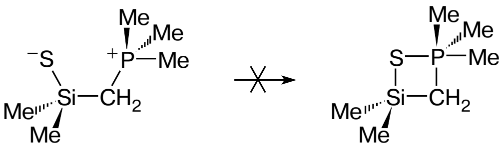


Fig. 5. Dipole moment (μ) of betaine **1a** as function of the S—Si—C—P dihedral angle (φ).



1a **8**

(4)

Earlier,[5] we have experimentally shown that the main channel of photodecomposition of betaines **1** is elimination of PR^5_3 to give silathiacyclopropanes **3** (Eq. (2), route ***B***) and that this route competes with decomposition into compound **2** (Fig. 6) and corresponding phosphorus ylide (route ***A***) under conditions of thermal decomposition. The ratio of the two processes is determined by the betaine structure and to a great extent by the reaction conditions. Elimination of phosphine in the thermolysis proceeds by the mechanism of intramolecular nucleophilic substitution with an activation energy of 32.5 kcal mol^{-1} *via* a "late" transition state **9** and is endothermic (ΔE_0 = 19.7 kcal mol^{-1}). The molecular structures of compounds **2**, 1,1-di-

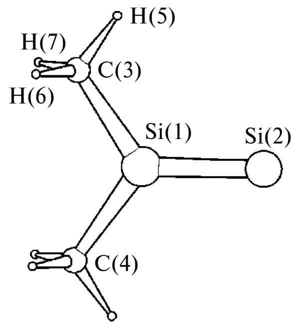


Fig. 6. Molecular structure of dimethylsilanethione **2a** (C_{2v} symmetry group).

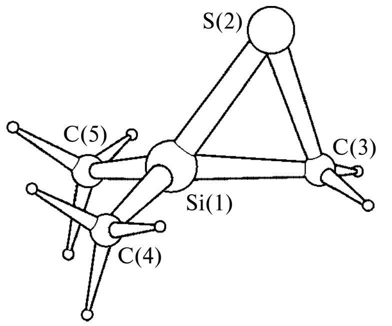


Fig. 7. Molecular structure of 1,1-dimethyl-1-sila-2-thiacyclopropane $Me_2Si(S)CH_2$ (**3a**) (C_s symmetry group).

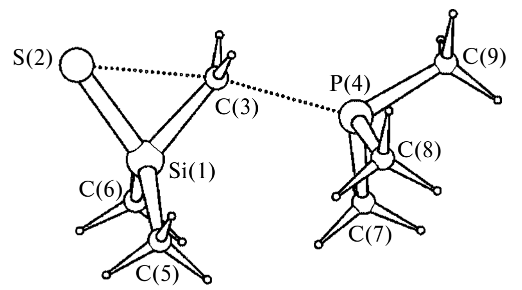


Fig. 8. Structure of transition state $^-S—SiMe_2—CH_2—P^+Me_3$ (**9**) (C_1 symmetry group).

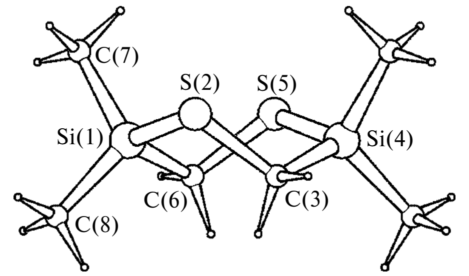


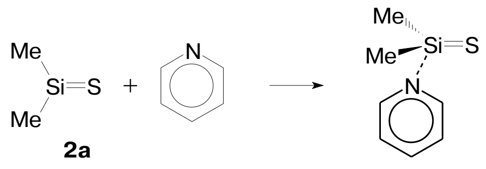
Fig. 9. Molecular structure of 1,1,4,4-tetramethyl-1,4-disila-2,5-dithiocyclohexane (**10**) (C_2 symmetry group).

Table 6. Geometric parameters of structures **2**, **3a**, **9**, and **10**

Parameter	2	3a	9	10
Bond length		*d*/Å		
Si(1)—S(2)	1.978	2.135	2.080	2.182
Si(1)—C(3)/C(4)	1.882	1.860	1.875	—
C(3)—H(5)	1.095	—	—	—
C(3)—H(6)/H(7)	1.100	—	—	—
Si(1)—C(4)/C(5)	—	1.881	1.875	—
S(2)—C(3)	—	1.903	2.446	1.853
Si(1)—C(6)	—	—	1.893	1.907
C(3)—P(4)	—	—	2.507	—
P(4)—C(7)	—	—	1.851	—
P(4)—C(8)	—	—	1.852	—
P(4)—C(9)	—	—	1.861	—
Si(1)—C(7)	—	—	—	1.886
Si(1)—C(8)	—	—	—	1.896
Bond angle		ω/deg		
S(2)—Si(1)—C(3)/C(4)	124.5	56.4	76.2	—
Si(1)—C(3)—H(5)	110.4	—	—	—
Si(1)—C(3)—H(6)/H(7)	110.2	—	—	—
Si(1)—S(2)—C(3)	—	54.5	—	100.4
Si(1)—C(3)—S(2)	—	69.1	—	—
C(3)—Si(1)—C(4)/C(5)	—	119.0	114.2	—
C(3)—Si(1)—C(6)	—	—	114.6	—
Si(1)—C(3)—P(4)	—	—	114.5	—
C(3)—P(4)—C(7)	—	—	103.8	—
C(3)—P(4)—C(8)	—	—	110.5	—
C(3)—P(4)—C(9)	—	—	133.7	—
C(6)—Si(1)—S(2)	—	—	—	108.7
Si(1)—C(6)—S(5)	—	—	—	112.8
S(2)—Si(1)—C(7)	—	—	—	106.9
S(2)—Si(1)—C(8)	—	—	—	110.6
C(7)—Si(1)—C(8)	—	—	—	110.9
Dihedral angle		φ/deg		
C(3)—Si(1)—S(2)—C(4)	180	—	—	—
S(2)—C(3)—Si(1)—C(4)/C(5)	—	73.7	—	—
S(2)—Si(1)—C(3)—P(4)	—	—	175.3	—
S(2)—Si(1)—C(3)—C(5)	—	—	115.2	—
S(2)—Si(1)—C(3)—C(6)	—	—	115.8	—
Si(1)—S(2)—C(3)—Si(4)	—	—	—	74.2
C(6)—Si(1)—S(2)—C(3)	—	—	—	25.0
S(5)—C(6)—Si(1)—S(2)	—	—	—	49.8
C(3)—S(2)—Si(1)—C(7)	—	—	—	35.0
C(3)—S(2)—Si(1)—C(8)	—	—	—	−85.8

methyl-1-sila-2-thiacyclopropane (**3a**), and **9** are presented in Figs. 7 and 8 and the geometric parameters of these molecules are listed in Table 6. The three-membered ring in molecule **3** is highly strained. This compound is unstable and undergoes an exothermic dimerization (ΔE_0 = −38.9 kcal mol^{-1}), which was observed experimentally.[5] The molecular structure of dimer **10** is presented in Fig. 9 and its geometric parameters are listed in Table 6.

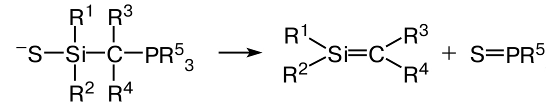
From the aforesaid it follows that gas-phase (in the absence of intermolecular interactions) decomposition of betaine **1a** with elimination of phosphine is much more energetically favorable than its decomposition into **2a** and **7**. However, the situation can change essentially in solvents in the presence of donor molecules. In most cases, we studied thermal decomposition of betaines **1** in pyridine solutions. According to calculations, dimethylsilanethione can form a strong complex **11** with pyridine (ΔE_0 = −21.7 kcal mol^{-1}, Eq. (5)).



2a **11** (5)

The molecular geometry changes dramatically upon coordination (Fig. 10). The Si atom becomes "pyramidal" and the Si—S bond length increases. Thus, decomposition following route *A* becomes quite competitive with elimination of phosphine in this solvent.

It was of interest to study yet another decomposition channel of betaines **1**, namely, a Wittig-type reaction with the formation of silaethylenes and phosphine thiooxide (Eq. (6)), which is observed for carbon analogs of **1**.[18,19]



1 (6)

R^1, R^2, R^5 = Alk, Ar; R^3, R^4 = H, Alk, Ar

This process is less energetically favorable than the decomposition with elimination of phosphine (ΔE_0 = 34.7 kcal mol^{-1}). 1,1-Dimethylsilaethylene **12** (R^1 = R^2 = H, R^3 = R^4 = Me) thus formed can also form a complex **13** with pyridine (ΔE_0 = −6.8 kcal mol^{-1}).

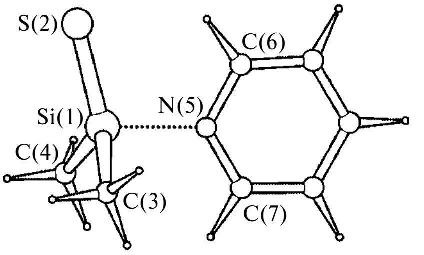


Fig. 10. Structure of complex $Me_2SiS \cdot Py$ (**11**) (C_s symmetry group).

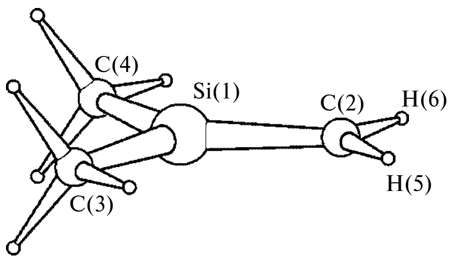


Fig. 11. Molecular structure of $Me_2Si{=}CH_2$ (**12**) (C_{2v} symmetry group).

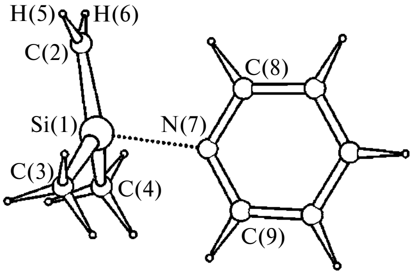


Fig. 12. Structure of complex $Me_2Si{=}CH_2 \cdot Py$ (**13**) (C_s symmetry group).

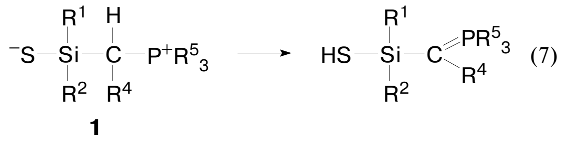
Table 7. Geometric parameters of structures **11—13**

Parameter	11	12	13
Bond length		d/Å	
Si(1)—S(2)	2.022	—	—
Si(1)—C(3)	1.899	1.884	1.896
Si(1)—C(4)	1.899	1.884	1.896
Si(1)—N(5)	2.011	—	—
N(5)—C(6)/C(7)	1.349	—	—
Si(1)—C(2)	—	1.722	1.738
C(2)—H(5)/H(6)	—	1.090	1.090
C(3)—H	—	1.099	—
Si(1)—N(7)	—	—	2.195
N(7)—C(8)	—	—	1.343
N(7)—C(9)	—	—	1.346
Bond angle		ω/deg	
S(2)—Si(1)—C(3)/C(4)	119.8	—	—
C(3)—Si(1)—C(4)	109.2	—	113.0
S(2)—Si(1)—N(5)	106.3	—	—
C(6)—N(5)—C(7)	119.9	—	—
Si(1)—N(5)—C(6)	117.6	—	—
Si(1)—N(5)—C(7)	122.6	—	—
C(2)—Si(1)—C(3)/C(4)	—	122.7	119.8
Si(1)—C(2)—H(5)/H(6)	—	122.2	122.1
C(2)—Si(1)—N(7)	—	—	107.8
Si(1)—N(7)—C(8)	—	—	144.0
Si(1)—N(7)—C(9)	—	—	126.6
H(5)—C(2)—H(6)	—	—	115.6
Dihedral angle		φ/deg	
C(2)—Si(1)—N(5)—C(6)	0	—	—
C(4)—Si(1)—S(2)—C(3)	40.4	—	—
H(5)—C(2)—Si(1)—C(3)	—	0	—
C(2)—Si(1)—N(7)—C(8)	—	—	0

The molecular structures of compounds **11**—**13** are shown in Figs. 10—12 and their geometric parameters are listed in Table 7.

Comparison of the calculated free energies for three channels of thermal decomposition of betaine **1a** suggests that two of them are more probable (previously,[5] these two routes were observed experimentally). However, our calculations were carried out ignoring solvation effects and taking into account complexation effects only in the framework of approximate model of complexes with pyridine (1 : 1). In real situations, these effects will undoubtedly have a pronounced effect on the ratio of thermal decomposition products.

Tautomeric equilibrium of betaines with H atoms in α-position relative to phosphonium center and of ylides containing sulfhydryl groups. Previously,[5] we have shown that particular representatives of betaines **1** with H atoms in α-position relative to the phosphonium center can readily undergo rearrangements into isomeric ylides containing sulfhydryl groups (Eq. (7)).



$$^{-}S{-}Si(R^1)(R^2){-}C(H)(R^4){-}P^{+}R^5_3 \longrightarrow HS{-}Si(R^1)(R^2){-}C(R^4){=}PR^5_3 \qquad (7)$$

1

R^1, R^2, R^5 = Alk, Ar; R^4 = H, Alk, Ar

In this work, we obtained theoretical estimates of position of this equilibrium for betaines **1a** and **1c**. The structures of the corresponding isomeric ylides **14** and **15** are shown in Figs. 13 and 14 and their geometric parameters are listed in Table 8. In both cases, betaines were found to be more thermodynamically stable (ΔE_0 = 12.2 kcal mol^{-1} for **1a** and 16.0 kcal mol^{-1} for **1c**). Substantial difference between the dipole moments of the tautomers (μ(**14**) = 4.04 D) should favor a shift of position of the tautomeric equilibrium with a decrease in polarity of the medium toward the ylide forms, which is also confirmed by our experimental data[4].

The results of our theoretical analysis show that silicon-containing organophosphorus betaines **1** with phosphonium cationic and thiolate anionic centers exist in zwitterionic form and their molecules adopt the *cis-gauche* conformation due to the strong Coulomb interaction between the charged centers. Betaines **1** do not tend to form four-membered cyclic silathiaphosphetane-like structures. In this regard, they behave similarly to the carbon analogs which act as true intermediates of the Wittig reactions of thiocarbonyl compounds.[18,19] Recent experimental studies[20,21] and high-level calculations[22—24] have shown that the Wittig reaction of carbonyl compounds can proceed *via* both a betaine-like intermediate and a cyclic phosphetane in the absence of Li salts. It seems likely that the structure of the true intermediate can be intermediate between these two forms. In this connection, theoretical investigation of silicon-containing organophosphorus betaines with oxide anionic center acquires a great importance.

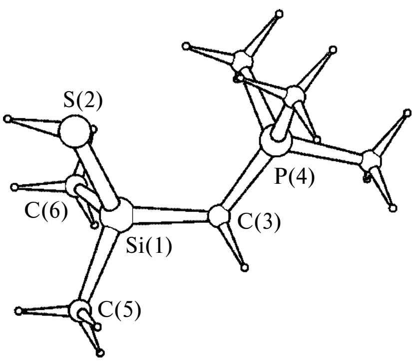


Fig. 13. Structure of ylide form of betaine **1a** HS—SiMe$_2$—CH$_2$=PMe$_3$ (**14**) (C_1 symmetry group).

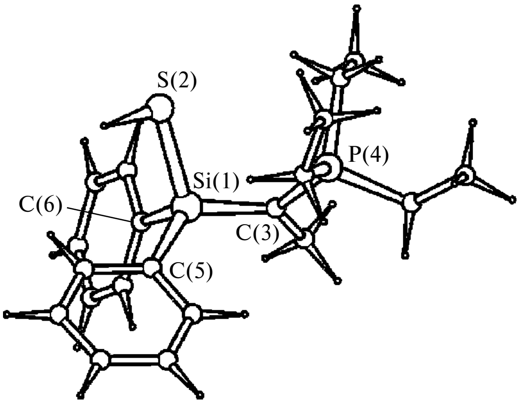


Fig. 14. Structure of ylide form of betaine **1c** HS—SiPh$_2$—CHMe=PEt$_3$ (**15**) (C_1 symmetry group).

According to our calculations, out of the three possible channels of gas-phase thermal decomposition of betaines **1** the most energetically favorable is route ***B*** (Eq. (2)) which involves elimination of phosphine and formation of silathiacyclopropane. However, in real situations (in polar solvents in the presence of donor molecules capable of forming strong complexes with silanethiones **2** and silaethylenes (*e.g.*, **12**)) the ratio of

Table 8. Geometric parameters of structures **14** and **15**

Parameter	14	15
Bond length	*d*/Å	
Si(1)—S(2)	2.228	2.221
Si(1)—C(3)	1.825	1.828
C(3)—P(4)	1.701	1.723
Si(1)—C(5)	1.902	1.916
Si(1)—C(6)	1.895	1.906
Bond angle	ω/deg	
C(3)—Si(1)—S(2)	108.4	107.9
Si(1)—C(3)—P(4)	126.5	121.7
C(3)—Si(1)—C(5)	116.1	117.3
C(3)—Si(1)—C(6)	109.4	108.9
Dihedral angle	φ/deg	
S(2)—Si(1)—C(3)—P(4)	43.9	35.9

products will be equally determined by both the structure of particular betaine and the properties of the medium. Thus, choosing an appropriate solvent and introduction of additives with donor properties can be useful for controlling the reactivity of betaines **1** in solutions.

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