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Organometallic Chemistry

Heteroorganic betaines

8.* Synthesis and structures of silicon- and germanium-containing organoarsenic betaines $R^1_3As^+—CR^2R^3—EMe_2—S^-$ (E = Si, Ge)

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The reactions of ylides $R^1_3As{=}CHR^2$ with hexamethyl-2,4,6-trisila- and hexamethyl-2,4,6-trigermatrithiacyclohexanes afforded betaines $R^1_3As^+—CHR^2—SiMe_2—S^-$ (**2**) (R^1 = Et; R^2 = Ph (**a**), Me_3Si (**b**); R^1 = R^2 = Ph (**c**)) and $Et_3As^+—CH(SiMe_3)—GeMe_2—S^-$ (**3**), respectively. Betaines **2a,b** and **3** were characterized by multinuclear NMR spectroscopy. According to the X-ray diffraction data, in the crystals the $As^+—C—E—S^-$ main chain (E = Si or Ge) of molecules **2a,b** and **3** adopts a twisted *cis* conformation due to strong intramolecular Coulomb interactions between the anionic and cationic centers. The equilibrium geometries of isolated molecules **2a** and **3**, which were calculated within the framework of the density functional theory (the PBE functional, the TZ2P basis set), are in qualitative agreement with the X-ray data. In solutions, betaines **2a** (in the absence of Li salts) and **2c** (in the presence of LiBr) selectively decomposed according to the Corey—Chaykovsky reaction, which was accompanied by elimination of R_3As and, probably, the intermediate formation of silathiirane. The subsequent transformation of the latter afforded 2,2,4,4-tetramethyl-5-phenyl-2,4-disila-1,3-dithiolane.

Key words: heteroorganic betaines, arsenic ylides, organosilicon and organogermanium compounds, X-ray diffraction analysis, NMR spectroscopy, density functional theory.

Heteroorganic betaines have been extensively investigated in recent years. Various types of these compounds were surveyed in reviews.[2—5] Previously, we have reported the synthesis of betaines $R^1_3P^+—CR^2R^3—ER^4R^5—S^-$ (**1**) (E = Si, Ge; $R^1—R^5$ = H, Alk, Ar) by the reactions of "nonstabilized" phosphorus ylides with organocyclo-

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silthianes (2,4,6-trisilatrithiacyclohexanes)[6] and hexamethylcyclotrigermathiane (2,4,6-trigermarithiacyclohexane).[1] The structures and major directions of decomposition of these betaines are similar to those observed in the reactions of phosphorus ylides with thiocarbonyl compounds.[7,8] The reactions of organocyclosilthianes and hexamethylcyclotrigermathianes with arsenic ylides whose reactivities are much higher than those of phosphorus ylides[9,10] allow one to prepare betaines bearing the arsonium cationic center $R^1_3As^+—CR^2R^3—ER^4R^5—S^-$ (E = Si (**2**) or Ge (**3**)). These compounds can be prepared with the use not only of "nonstabilized" but also of "semistabilized" arsenic ylides, which substantially extends the scope of the synthesis of heteroorganic betaines containing the pnictogen cationic center.

Previously,[11,12] it has been demonstrated that carbon-containing organophosphorus betaines bearing the thiolate center can form a continuum of structures intermediate between the open betaine and cyclic thiaphosphetane structures. The true structures of these compounds depend substantially on small structural variations and even the conditions in which these betaines are studied. Previously, we have noted[7] that the P—C—Si—S dihedral angles in betaines $R^1_3P^+—CR^2R^3—SiR^4R^5—S^-$ (**1**) vary essentially with the type of the substituents R^2–R^5, which enables one to extend the range of heteroorganic betaines. Investigations of betaines of the arsenic series are of obvious theoretical interest for the purpose of elucidating the effect of the type of the cationic center on the relative stabilities of the open and cyclic forms of theses compounds.

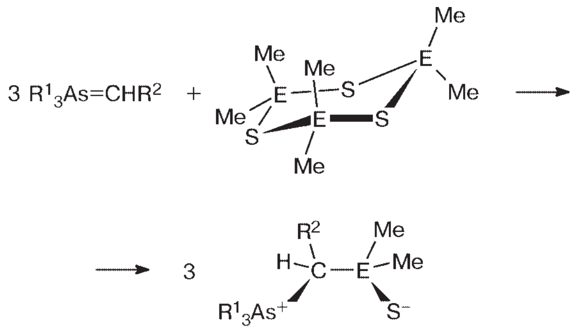
The present study was devoted to heteroorganic betaines **2** and **3** with the arsonium cationic center.

Results and Discussion

Compounds **2** and **3** were obtained in good yields by mixing stoichiometric amounts of hexamethylcyclotrisila- or hexamethylcyclotrigermatrithianes with arsenic ylides in THF or ether at ~20 °C (Scheme 1).

Betaines **2a,b** and **3** are crystalline white compounds, which are stable for ~1.5—6 months upon storage in the solid state under an atmosphere of argon or in solutions placed in a sealed vessel evacuated to ~10^{-3} Torr. In solution, betaine **2c** is unstable and readily eliminates Ph_3As.

Scheme 1



2, **3**

E = Si (**2a—c**), Ge (**3**)
R^1 = Et (**2a,b**, **3**), Ph (**2c**)
R^2 = Ph (**2a,c**), MeSi (**2b**, **3**)

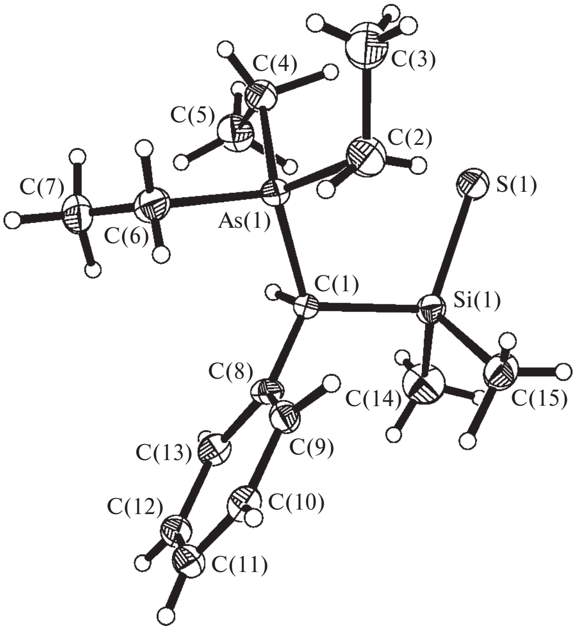


Fig. 1. Molecular structure of compound **2a** with thermal ellipsoids drawn at 50% probability level.

According to the X-ray diffraction data, the main chain $^+As—C—E—S^-$ (E = Si, Ge) of compounds **2a,b** and **3** (Figs. 1—3), like that in all their silicon- and germanium-containing organophosphorus analogs studied by us previously,[7] adopts a sterically hindered *gauche*-cisoid conformation due to the intramolecular Coulomb attractive $As^+.....S^-$ interactions between the cationic and anionic centers. The principal geometric parameters of the compounds under study are given in Table 1. The $As^+.....S^-$ distances in betaines **2a,b** and **3** (3.518, 3.497, and 3.565 Å, respectively) are substantially smaller than the sum of the van der Waals radii of the S and As atoms (~4.5 Å) and the P....S distances in P,E—S betaines (E = Si, Ge). At the same time, the $As^+.....S^-$ distance is essentially larger than the As—S single bond length (2.20—2.50 Å [13]). In betaines **2b** and **3**, the As—C—E—S dihedral angle (E = Si, Ge) in the main chain (22°) has the smallest value of all the known betaines (25—38°) studied by us previously.[1,7] The quantum-chemical DFT calculations for structures **2a** and **3** with the extended split-valence basis set (PBE/TZ2P),

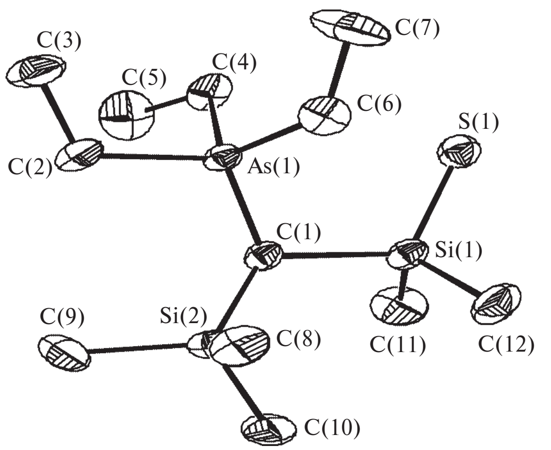


Fig. 2. Molecular structure of compound **2b** with thermal ellipsoids drawn at 50% probability level.

which were carried out analogously to those for betaines of the phosphorus series, adequately reproduced the geometry observed in the crystals.[1] The calculated geometric parameters and the X-ray diffraction data are given in Table 1. The maximum corresponding to the cyclic form is absent on the potential energy surface of **2a**. However, the results of calculations adequately reproduce the experimentally observed variations in the dihedral angle of the main chain as the type of the cationic center changes.

It should also be noted that X-ray diffraction analysis revealed the presence of a short nonbonded contact between the hydrogen atom in the *ortho* position of the phenyl ring and the As atom (As(1)...H(9), 3.23(1) Å) in compound **2a**. This contact was attributed to steric hindrances. Hence, the coordination polyhedron about the As atom in **2a** can be considered both as a distorted tetrahedron and a distorted trigonal bipyramid with the arsenic atom (0.655 Å) deviating substantially from the equatorial C(1)—C(2)—C(6) plane of the bipyramid. In solution, rotation about the CH—Ph bond is hindered due to steric factors. This is manifested in broadening both of the resonance signals for the C_o and C_m atoms of the phenyl ring in the ^{13}C NMR spectrum and of the signals for the H_o atoms in the ^{1}H NMR spectrum. The presence of the chiral carbon atom in molecule **2a**, as well as in betaines **2b,c** and **3**, causes diastereotopic doubling of the signals of the methyl groups at the silicon or germanium atom analogously to that observed previously for their Si,P-analogs containing the asymmetric carbon atom in the P—C—Si—S fragment.[6]

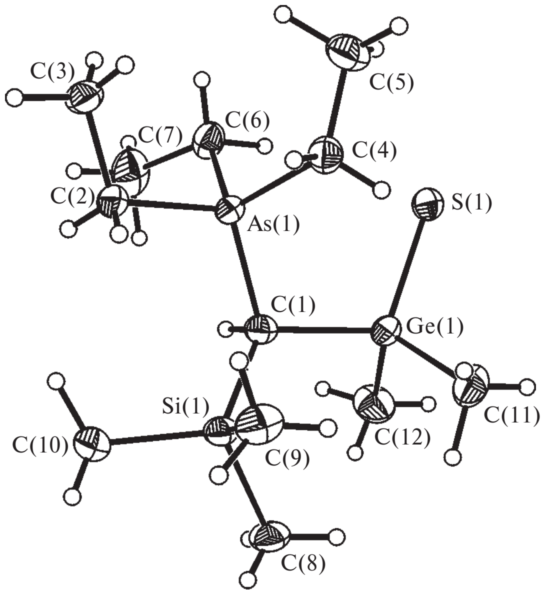


Fig. 3. Molecular structure of compound **3** with thermal ellipsoids drawn at 50% probability level.

Betaine **2a**, like its Si—P analog,[8] selectively decomposed according to the Corey—Chaykovsky reaction upon irradiation of its solution in pyridine-d$_5$ with UV light using a medium-pressure mercury lamp for 12 h (Scheme 2). This reaction afforded disiladithiolane (**5**), which was formed in virtually quantitative yield, and triethylarsine as the final products. The reaction proceeded analogously to photodecomposition of betaines of the phosphorus series, which we have studied previously.[8]

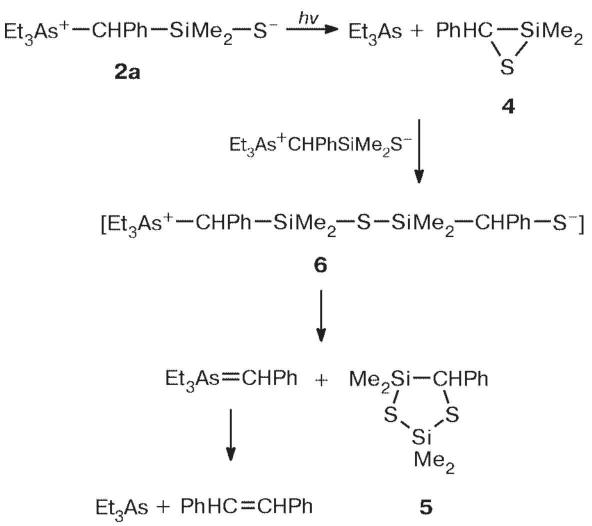
Highly reactive intermediate silathiirane **4** immediately reacted with the starting betaine **2a**, which served as a chemical scavenger. Subsequent elimination of

Table 1. Principal geometric parameters* of betaines **2a**,**b** and **3** containing the $^-$S—E—C—As$^+$ fragment accorring to the results of X-ray diffraction analysis and PBE/TZ2P calculations

Betaine	Method	E	d/Å				ω/deg		φ/deg
			S—E	E—C	C—As	S—As	S—E—C	E—C—As	S—E—C—As
2a	X-ray data	Si	2.0455(11)	1.946(4)	1.936(2)	3.518(2)	109.97(8)	111.44(17)	33.13(19)
	PBE/TZ2P		2.083	1.969	1.986	3.040	102.0	105.1	24.4
2b	PCA	Si	2.049(6)	1.956(13)	1.931(13)	3.497(2)	113.1(5)	110.0(7)	22.3(8)
3	PCA	Ge	2.1448(14)	2.032(3)	1.924(3)	3.565	111.68(9)	110.15(15)	21.74(16)
	PBE/TZ2P		2.164	2.103	1.944	3.441	108.7	1.944	21.0

* The distances (*d*), bond angles (ω), and torsion angles (φ).

Scheme 2



$Et_3As=CHPh$ from betaine **6** that formed afforded disiladithiolane (**5**). It is particularly remarkable that silathiirane **4** did not undergo dimerization, which was always observed for its analogs deprived of the phenyl group at the carbon atom.[7] Arsenic ylide, like other representatives of this class of compounds,[9,10] decomposed by the carbenoid mechanism to form Et_3As and stilbene. In a solution in pyridine-d_5, betaine **2c** produced compound **5** even in the absence of UV irradiation.

The results of the present study demonstrate that arsenic ylides are more reactive with respect to cyclotrisilatrithianes and cyclotrigermatrithianes, which allows one to carry out the reactions with semi-stabilized ylides. Studies of the chemical behavior of new betaines $R^1{}_3As^+—CR^2R^3—ER^4R^5—S^-$ (**2** and **3**) are being continued.

Experimental

The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AM-360 instrument in C_5D_5N. The chemical shifts in the ^1H and ^{13}C NMR spectra were measured relative to the signals of the solvent with an accuracy of ±0.01 and ±0.05 ppm, respectively, and were converted to the δ scale using standard formulas. The ^{29}Si NMR spectra were measured with respect to $SiMe_4$. The spin-spin coupling constants are given with an accuracy of ±0.1 Hz. The assignments of the signals of $SiMe_4$ in the ^{13}C NMR spectra were made using the APT procedure.

All operations were carried out under an atmosphere of dry oxygen-free argon using the standard Schlenk technique or *in vacuo* (10^{-3} Torr) in seamless-soldered apparatus with the use of a techniques of broken walls and tubes. Tetrahydrofuran and Et_2O were distilled over Na or $LiAlH_4$, stored over sodium benzophenone ketyl, and distilled over the latter into reaction vessels immediately before use. The hydrocarbon solvents were distilled over Na or $LiAlH_4$; C_5D_5N used in NMR spectroscopy was distilled over CaH_2 and recondensed with $LiAlH_4$ at 10^{-3} Torr immediately before use into an NMR tube containing the compound to be analyzed. Organochlorosilanes of reagent grade purity were purchased from the Redkinskii pilot-production plant.

Chloromethyltrimethylsilane,[14] tetramethyl-[15] and dimethyldichlorogermane,[16] hexamethyldisilthiane,[17] hexamethylcyclotrisila-[18] and hexamethylcyclotrigermatrithiane,[18] triethyl-[19] and triphenylarsine,[20] benzyl bromide,[21] arsonuim salts and arsenic ylides (except for benzylidenetriethylarsenic),[22,23] and sodium bis(trimethylsilyl)amide[24] were prepared according to procedures reported previously.

2-Methyl-3-phenyl-3-triethylarsonio-2-silapropane-2-thiolate, $Et_3As^+—CHPh—SiMe_2—S^-$ (2a). The starting arsenic ylide was prepared by the gradual addition of a solution of $NaN(SiMe_3)_2$ (1.91 g, 10.4 mmol) in THF (20 mL) to a stirred suspension of the salt $[Et_3As—CH_2Ph]^+ Br^-$ (3.39 g, 10.2 mmol) in THF (25 mL) at ~10 °C. The reaction mixture was refluxed for 10 min and then cooled. The precipitate of NaBr was filtered off and washed on a filter with THF (~20 mL). The bright-orange volatile products were removed from the solution at ~20 °C (1 Torr). The oily residue was washed with hexane, decanted, and kept at ~20 °C (1 Torr) for 30 min. A brown-red viscous oil was obtained in a yield of 2.11 g (82.3%). Immediately afterwards, its solution in THF (15 mL) was added portionwise to a solution of $(Me_2SiS)_3$ (0.82 g, 3 mmol) in THF (10 mL) at 15 °C (the solution of the ylide immediately turned colorless). The reaction mixture was kept at ~15 °C for 12 h and the solvent was removed *in vacuo* (1 Torr). The finely crystalline white precipitate that formed (2.78 g) was recrystallized from THF. A white compound was obtained in a yield of 1.31 g (45.8%) as large crystals, m.p. 125 °C (with decomp., sealed tube). ^1H NMR (C_5D_5N), δ: 0.41 and 0.57 (both s, 3 H each, nonequivalent Me_2Si groups); 1.17 (t, 9 H, $C\underline{H}_3CH_2As^+$, $^3J_{H,H}$ = 7.8 Hz); 2.63 and 2.93 (both dq, 3 H each, $CH_3C\underline{H}_2As^+$, AM portion of the AMX_3 spectrum, $^3J_{AM} \approx {}^3J_{XM}$ = 7.8 Hz, J_{AM} = 13.8 Hz); 3.69 (s, AsCHSi); 7.20—7.27 (m, 1 H, H_p); 7.36—7.39 (m, 2 H, H_m); 7.50—7.52 (br.m, 2 H, H_o). ^{13}C NMR (C_5D_5N), δ: 7.64, 8.79 (nonequivalent Me_2Si groups); 8.11 (CH_2As); 16.99 ($\underline{C}H_3CH_2As$); 39.52 (AsCHSi); 126.58 (C_p); 129.21 (C_m); 130.06 (br, C_o); 137.89 (C_i).

2,4,4-Trimethyl-3-triethylarsonio-2,4-disilapentane-2-thiolate, $Et_3As^+—CHSiMe_3—SiMe_2—S^-$ (2b). Ylide $Et_3As=CHSiMe_3$ (1.65 g, 6.7 mmol) was added portionwise with stirring to a solution of $(Me_2SiS)_3$ (0.70 g, 7.8 mmol) in ether (10 mL) at ~10 °C. After 15 min, the layers that formed were separated and the solvents were removed at 20—100 °C (0.1 Torr). A white powder was obtained from the residues of the lower (1.3 g) and upper (0.58 g) layers, decomposition temperature > 100 °C (in a sealed tube). According to the NMR spectra, the resulting compound was betaine **2b**. The total yield was 83.6%. ^1H NMR (C_5D_5N), δ: 0.32 (s, 9 H, Me_3Si); 0.60 and 0.66 (both s, 3 H each, nonequivalent Me_2Si groups); 1.26 (t, 9 H, $C\underline{H}_3CH_2As^+$, $^3J_{H,H}$ = 7.7 Hz); 1.41 (s, 1 H, AsCHSi); 2.61 and 3.05 (both dq, 3 H each, $CH_3C\underline{H}_2As^+$, AM portion of the AMX_3 spectrum, $^3J_{AM} \approx {}^3J_{XM}$ = 7.8 Hz, $^2J_{AM}$ = 13.6 Hz). ^{13}C NMR (C_5D_5N), δ: 3.19 (Me_3Si); 8.49 ($\underline{C}H_3CH_2As$); 11.33, 12.37 (nonequivalent Me_2Si groups); 16.06 (AsCHSi); 19.37 (CH_2As). ^{29}Si NMR (C_5D_5N), δ: +0.24 (Me_2Si); +1.88 (Me_3Si).

2,4,4-Trimethyl-3-triethylarsonio-2-germa-4-silapentane-2-thiolate, $Et_3As^+—CHSiMe_3—GeMe_2—S^-$ (3). Ylide

$Et_3As{=}CHSiMe_3$ (2.33 g, 9.4 mmol) was added portionwise with stirring to a solution of $(Me_2GeS)_3$ (1.27 g, 9.4 mmol) in ether (20 mL) at ~20 °C. After 2 h, the solvent was decanted from the precipitate that formed and the compound was dried *in vacuo* (1 Torr). A white crystalline compound was obtained in a yield of 2.73 g (75.6%). This compound deliquesced upon heating in a sealed tube at 71—72 °C and decomposed at 98—100 °C (the product turned green). ^1H NMR (C_5D_5N), δ: 0.30 (s, 9 H, Me_3Si); 0.77 and 0.82 (both s, 3 H each, nonequivalent Me_2Ge groups); 1.27 (t, 9 H, $C\underline{H}_3CH_2As^+$, $^3J_{H,H}$ = 7.7 Hz); 1.41 (br.s, 1 H, AsCHGe); 2.64 and 3.13 (both dq, 3 H each, $CH_3C\underline{H}_2As^+$, AM portion of the AMX_3 spectrum, $^3J_{AM} \approx {}^3J_{XM}$ = 7.7 Hz, $^2J_{AM}$ = 13.6 Hz). ^{13}C NMR (C_5D_5N), δ: 2.96 (Me_3Si); 8.35 ($\underline{C}H_3CH_2As$); 11.87 and 13.11 (nonequivalent Me_2Si groups); 14.47 (AsCHSi); 19.21 (CH_2As). ^{29}Si NMR (C_5D_5N), δ: + 0.59.

Reaction of benzylidenetriphenylarsorane with hexamethylcyclotrisilthiane. A solution of $Ph_3As{=}CHPh$, which was prepared from a solution of $[Ph_3As^+CH_2Ph]\ Br^-$ (7.91 g, 16.50 mmol) in ether (50 mL) and an ethereal 1 *N* solution of PhLi (16.2 mL), was added to a solution of $(Me_2SiS)_3$ (1.49 g, 16.5 mmol) in ether (20 mL). The mixture was stirred for 1 h, the solvents were decanted from the precipitate that formed, and the precipitate was washed with hexane and dried *in vacuo* (1 Torr). According to the NMR spectra, the resulting solid compound was a mixture of 2,2,4,4-tetramethyl-5-phenyl-2,4-disila-1,3-dithiolane (**5**), triphenylarsine, and 1,2-diphenylethylene. ^1H NMR of compound **5** (C_5D_5N), δ: 0.26, 0.48, 0.72, and 0.78 (all s, 3 H each, nonequivalent MeSi groups), 4.11 ($C\underline{H}Ph$); 7.09—8.81 (region of the Ar protons, overlapping of the signals of the Ph ring of disilolane **5** and isomers of *symm*-diphenylethylene). ^{13}C NMR of compound **5** (C_5D_5N), δ: 0.20, 1.33, 6.11, and 7.51 (nonequivalent MeSi groups); 41.26 (CH); 126.70, 128.05, 128.88, and 140.83 (C_{arom}). The ^{13}C NMR spectra of triphenylarsine correspond to the data published in the literature.[25]

Photolysis of betaine 2a (NMR control). According to the NMR spectroscopic data, irradiation of a solution of compound **2a** (0.23 g) in pyridine-d_5 (0.8 mL) in a sealed evacuated Pyrex-compatible NMR tube for 12 h (40—50 °C) afforded 2,2,4,4-tetramethyl-5-phenyl-2,4-disila-1,3-dithiolane **5** (the yield was ~96%), Et_3As (quantitative yield), and 1,2-diphenylethylene (quantitative yield).

NMR spectra of disiladithiolane 5 are identical with those given above.

^1H NMR of Et_3As (C_5D_5N), δ: 1.10 (t, 9 H, $C\underline{H}_3CH_2As$, $^3J_{H,H}$ = 7.7 Hz); 1.35 (quint, 6 H, $CH_3C\underline{H}_2As$), which corresponds to the data published in the literature.[25] ^{13}C NMR of Et_3As (C_5D_5N), δ: 11.04 ($\underline{C}H_3CH_2As$); 16.73 ($CH_3\underline{C}H_2As$).

X-ray diffraction study. Crystals of betaine **2a** ($C_{15}H_{27}AsSSi$, M = 342.44) are orthorhombic, space group $Pna2_1$, at T = 110 K a = 15.4114(18), b = 8.6658(10), c = 12.8394(15) Å, V = 1714.7(3) Å^3, Z = 4, d_{calc} = 1.326 mg cm^{-3}, $F(000)$ = 720, μ = 2.158 mm^{-1}.

The unit cell parameters and intensities of 19298 reflections were measured on an automated SMART CCD 1000 diffractometer (T = 110 K, λ-Mo-K_α, ω scanning technique, scan step was 0.3°, frames were exposed for 10 s, θ_{max} = 30°). The absorption correction was applied using the SADABS program.[26] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The absolute structure was determined by the refinement of Flack's parameter (0.00(1)). The final R factors were as follows: R_1 = 0.0383 for 4240 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.0932 for all 4979 independent reflections.

A single crystal of compound **2b** of dimensions 0.3×0.3×0.2 mm, which rapidly decomposed in air, was sealed in a glass capillary *in vacuo*.

Crystals of **2b** ($C_{12}H_{31}AsSSi_2$, M = 338.53) are monoclinic, space group $P2_1/n$, at T = 293 K a = 10.370(2), b = 12.681(3), c = 14.550(3) Å, β = 99.99(3)°, V = 1884.2(7) Å^3, Z = 4, d_{calc} = 1.193 mg cm^{-3}, $F(000)$ = 720, μ = 2.023 mm^{-1}.

The unit cell parameters and intensities of 2731 reflections were measured on an automated four-circle Siemens P3/PC diffractometer (T = 293 K, λ-Mo-K_α radiation, θ/2θ scanning technique, θ_{max} = 23°). The absorption was ignored. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were placed in geometrically calculated positions and refined isotropically with fixed positional (the riding model) and thermal parameters. The final R factors were as follows: R_1 = 0.1093 for 1611 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.2847 for all 2530 independent reflections. The rather high R factor was associated with the poor quality of the single crystal, the high background intensity of X-ray radiation, and the fact that it was impossible to correctly take into account absorption due to the glass capillary used.

Crystals of **3** ($C_{12}H_{31}AsGeSSi$, M = 383.03) are monoclinic, space group $P2_1/n$, at T = 120 K, a = 10.348(7), b = 12.307(8), c = 14.652(10) Å, β = 99.446(13)°, V = 1841(2) Å, Z = 4, d_{calc} = 1.382 mg cm^{-3}, $F(000)$ = 792, μ = 3.607 mm^{-1}. The unit cell parameters and intensities of 21309 reflections were measured on an automated SMART CCD 1000 diffractometer (T = 120 K, λ-Mo-Kα radiation, ω scanning technique, scan step was 0.3°, frames were exposed for 10 s, θ_{max} = 30°). The absorption correction was applied using the SADABS program.[26] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The final R factors were as follows: R_1 = 0.0366 for 3651 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.826 for all 5391 independent reflections. All calculations were carried out using the SHELXTL PLUS program package (Version 5.10).[27]

The tables of the atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic thermal parameters for compounds **2a,b** and **3** were deposited with the Cambridge Structural Database.

Calculation procedure. The calculations by the DFT method were carried out using the original program.[28] The exchange-correlation energy was calculated with the use of the generalized gradient approximation and the PBE hybrid functional.[29] The one-electron wave functions were expanded with the use of the extended three-exponential atomic TZ2P basis set of the grouped Gaussian functions containing the polarization functions. The stationary points were identified from the analysis of the Hessian matrix. The second derivatives of the energy with respect to the atomic coordinates were calculated analytically.

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