ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 3, pp. 461–468. © Pleiades Publishing, Inc., 2006.
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Selenium- and Tellurium-containing Silatrane Derivatives Having an ECH_2Si Fragment (E = Se, Te)

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Received April 14, 2005

Abstract—Previously unknown 1-(methylselenomethyl)- and 1-(phenyltelluromethyl)silatrane, bis(silatranylmethyl) selenide, bis(silatranylmethyl) telluride, bis(silatranylmethyl) diselenide, and dimethyl(triethoxysilylmethyl)telluronium, phenyl(silatranylmethyl)telluronium, methylbis(silatranylmethyl)selenonium, methylbis(silatranylmethyl)telluronium, and tris(silatranylmethyl)selenonium iodides were synthesized. The NMR spectra of these compounds, as well as of isostructural (methylchalcogenomethyl)triethoxysilanes, 1-(methylchalcogenomethyl)silatranes, the corresponding methylchalcogenonium iodides, methylorganyl(silatranylmethyl)chalcogenonium iodides, bis(trialkoxysilylmethyl) chalcogenides, and bis(silatranylmethyl) chalcogenides, in $CDCl_3$, CD_3OH, CD_3CN, and DMSO-d_6 were studied.

DOI: 10.1134/S1070363206030170

We previously synthesized for the first time and studied numerous (organylchalcogenoalkyl)trialkoxysilanes $RE(CH_2)_nSi(OR')_3$ [1–3], the corresponding 1-(organylchalcogenoalkyl)silatranes $RE(CH_2)_nSi \cdot (OCH_2CH_2)_3N$ (E = S, n = 1–3; E = Se, n = 1, 2) [2–5], and their chalcogenonium derivatives, methylalkyl(trialkoxysilylalkyl)sulfonium iodides $MeRS^+ \cdot (CH_2)_nSi(OR')_3\ I^-$ (n = 1, 2) [6], dimethyl(triethoxysilylmethyl)selenonium iodides $Me_2Se^+CH_2Si(OEt)_3 \cdot I^-$ [7], and diorganyl(silatranylalkyl)chalcogenonium halides $[RR'E^+(CH_2)_nSi(OCH_2CH_2)_3N]\ X^-$ (X = Br, I; E = S, Se, $n \geq 1$) [3, 6]. 1-(Organylsulfanylalkyl)silatranes $RS(CH_2)_nSi(OCH_2CH_2)_3N$ (n = 1, 2) and 1-(phenylselanylmethyl)silatrane $PhSeCH_2Si(OCH_2 \cdot CH_2)_3N$ were oxidized with hydrogen peroxide to the corresponding organyl(silatranylalkyl)chalcogene oxides and dioxides $REO_m(CH_2)_nSi(OCH_2CH_2)_3N$ (R = Me, Et, Ph, $PhCH_2$, silatranyl, E = S, m, n = 1 or 2 [3]; R = Ph, E = Se, m = 1 or 2, n = 1 [8]).

(Organyltellanylalkyl)trialkoxysilanes $RTe(CH_2)_n \cdot Si(OR')_3$ and the corresponding silatranes $RTe(CH_2)_n \cdot Si(OCH_2CH_2)_3N$ ($n \geq 1$), as well as their derivatives, still remain difficultly accessible, especially when R = Alk {among these, only two (organylethynyltellanylmethyl)trimethoxysilanes $RC{=}CTeCH_2Si(OMe)_3$ and silatranes $RC{\equiv}CTeCH_2Si(OCH_2CH_2)_3N$ (R = Ph, Me_3Si) were synthesized by us previously [9, 10]}. Later on, we succeeded in developing procedures for the synthesis of (phenyltellanylmethyl)trimethoxysilane $PhTeCH_2Si(OMe)_3$, bis(trialkoxysilylmethyl) tellurides $[(RO)_3SiCH_2]_2Te$ (R = Me, Et,) [7, 11], and diorganylsilatranylmethyltelluronium iodides $R_2Te^+CH_2Si(OCH_2CH_2)_3N\ I^-$ (R = Me, Vin) [12, 13].

While continuing studies in this line, we synthesized previously unknown 1-(methylselanylmethyl)silatrane (**III**), 1-(phenyltellanylmethyl)silatrane (**IV**), bis(silatranylmethyl) selenide (**VII**), bis(silatranylmethyl) telluride (**VIII**), bis(silatranylmethyl) diselenide (**X**), phenyl(silatranylmethyl)telluronium iodide (**XII**), methylbis(silatranylmethyl)selenonium iodide (**XIII**), methylbis(silatranylmethyl)telluronium iodie (**XIV**), dimethyl(triethoxysilylmethyl)telluronium iodide (**XXII**), and tris(silatranylmethyl)selenonium iodide (**XXIV**). In addition, previously described dimethyl(silatranylmethyl)selenonium iodide (**XI**) [3] was synthesized by a different method, by reaction of 1-(methylselanylmethyl)silatrane (**III**) with methyl iodide. Compounds **III**, **IV**, **VII**, **VIII**, and **X** were prepared by transetherification of the corresponding trialkoxysilyl derivatives with tris(2-hydroxyethyl)amine [schemes (1–3)].

$$\underset{\textbf{I, II}}{RECH_2Si(OR')_3} + (HOCH_2CH_2)_3N \longrightarrow \underset{\textbf{III, IV}}{RECH_2Si(OCH_2CH_2)_3N} + 3R'OH, \qquad (1)$$

I, R = Me, R' = Et, E = Se; **II**, R = Ph, R' = Me, E = Te; **III**, R = Me, E = Se; **IV**, R = Ph, E = Te,

$$2N(CH_2CH_2OH)_3 + \underset{\textbf{V, VI}}{[(EtO)_3SiCH_2]_2E} \longrightarrow \underset{\textbf{VII, VIII}}{[N(CH_2CH_2O)_3SiCH_2]_2E} + 6MeOH, \qquad (2)$$

$$E = Se\ (\textbf{V, VII}),\ Te\ (\textbf{VI, VIII}).$$

$$2N(CH_2CH_2OH)_3 + \underset{\textbf{IX}}{[(MeO)_3SiCH_2]_2Se_2} \longrightarrow \underset{\textbf{X}}{[N(CH_2CH_2O)_3SiCH_2]_2Se_2} + 6MeOH. \qquad (3)$$

Transetherification of (methylselanylmethyl)triethoxysilane (**I**) and (phenyltellanylmethyl)trimethoxysilane (**II**) with tris(2-hydroxyethyl)amine [scheme (1)] was more difficult and less smooth than in the case of isostructural sulfur-containing compounds [6]. The reaction started only when the reactant mixture was heated to 120°C, and the yields of selenide **III** and telluride **IV** were relatively low (Table 1). Transetherification of bis(triethoxysilylmethyl) selenide (**V**) and bis(triethoxysilylmethyl) telluride (**VI**) with tris(2-hydroxyethyl)amine [scheme (2)] was even more difficult to effect. It occurred only at 150°C in the presence of base catalyst (a 10% solution of sodium methoxide in methanol), and the yields of selenide **VII** and telluride **VIII** were as poor as 23 and 19%, respectively (Table 1). By contrast, transetherification of bis(trimethoxysilylmethyl) diselenide (**IX**) with tris(2-hydroxyethyl)amine [scheme (3)] in the presence of the same catalyst occurred spontaneously after mixing the reactants, and diselenide **X** was obtained in more than 90% yield (Table 1).

Treatment of 1-(methylselanylmethyl)silatrane (**III**) and 1-(phenyltellanylmethyl)silatrane (**IV**) with methyl iodide afforded the corresponding methylorganyl(silatranylmethyl)chalcogenonium iodides **XI** and **XII** [(scheme 4)].

$$\textbf{III, IV} + MeI \longrightarrow \underset{\textbf{XI, XII}}{I^{-}RMe\overset{+}{E}CH_2Si(OCH_2CH_2)_3N}, \qquad (4)$$

$$\textbf{XI},\ R = Me,\ E = Se;\ \textbf{XII},\ R = Ph,\ E = Te.$$

When a small excess of methyl iodide was used as solvent, the reaction occurred too vigorously. Therefore, it was carried out methanol where initial compounds **III** and **IV** are considerably less soluble than the resulting iodides **XI** and **XII**. In 4–5 min after addition of methyl iodide to a suspension of silatrane **III** or **IV** in methanol, exothermic reaction started, and the reaction mixture warmed up from 20 to 40°C. In the reaction with selenide **III**, a solution of dimethyl(silatranylmethyl)selenonium iodide (**X**) in methanol was formed. Iodide **X** is readily soluble in methanol at 15–20°C as well. By contrast, methyl(phenyl)(silatranylmethyl)telluronium iodide (**XI**) is soluble only in boiling methanol, and it crystallizes from the solution almost completely on cooling to room temperature.

Bis(silatranylmethyl) selenide (**VII**) and bis(sila-

Table 1. Yields, melting points, and elemental analyses of compounds **III, IV, VII, VIII, X–XIV, XXI, XXII**, and **XXIV**

Comp. no.	Yield, %	mp, °C	Found, %					Formula	Calculated, %				
			C	H	N	Si	E		C	H	N	Si	E[a]
III	61.5	157–159	34.18	5.87	4.78	9.67	27.74	$C_8H_{17}NO_3SeSi$	34.03	6.07	4.96	9.95	27.96
IV	50	169–171	39.54	5.06	3.44	6.87	32.68	$C_{13}H_{19}NO_3SiTe$	39.73	4.87	3.56	7.15	32.47
VII	43	263 (decomp.)	36.73	6.37	6.03	12.16	17.33	$C_{14}H_{28}N_2O_6SeSi_2$	36.91	6.20	6.15	12.33	17.33
VIII	24	–	33.28	5.77	5.48	11.25	24.97	$C_{14}H_{28}N_2O_6Si_2Te$	33.35	5.60	5.56	11.14	25.31
X	90.3	275–277	32.35	5.56	5.39	10.68	30.56	$C_{14}H_{28}N_2O_6Se_2Si_2$	32.43	5.44	5.40	10.83	30.45
XI	89.5	175–177[b] (decomp.)	25.61	4.88	3.19	6.43	18.39	$C_9H_{20}INO_3SeSi$	25.47	4.75	3.30	6.62	18.61
XII	90.6	305 (decomp.)	31.28	4.23	2.69	4.97	23.52	$C_{14}H_{22}INO_3SiTe$	31.43	4.15	2.62	5.25	23.85
XIII	85 (*a*) 76 (*b*)	222–224 221–223	30.21	5.39	4.42	9.23	12.76	$C_{15}H_{31}IN_2O_6SeSi_2$	30.15	5.23	4.68	9.40	13.21
XIV	87	228	27.69	4.92	4.39	8.38	19.63	$C_{15}H_{31}IN_2O_6Si_2Te$	27.88	4.84	4.34	8.69	19.75
XXI	84	71–72[c]	26.38	5.54	–	5.63	18.86	$C_9H_{23}IO_3SeSi$	26.16	5.61	–	6.80	19.11
XXII	78	145–146	23.59	4.79	–	5.87	27.14	$C_9H_{23}O_3IO_3SiTe$	23.40	5.02	–	6.08	27.63
XXIV	88	318 (decomp.)	32.81	5.63	5.36	10.65	9.89	$C_{21}H_{42}IN_3O_9SeSi_3$	32.73	5.49	5.45	10.94	10.24

[a] E = S, Se, Te. [b] mp 176–177°C [3]. [c] mp 69–70°C [7].

tranylmethyl) telluride (**VIII**) reacted with excess methyl iodide (taken as solvent) without appreciable heat evolution, and the corresponding methylbis(silatranylmethyl)chalcogenonium iodides **XIII** and **XIV** were formed in 2 h in almost quantitative yield [scheme (5)].

$$\textbf{VII, III} + \mathrm{MeI} \longrightarrow \underset{\textbf{XIII, XIV}}{[\mathrm{N(CH_2CH_2O)_3SiCH_2}]_2\overset{+}{\mathrm{E}}\mathrm{MeI^-}}, \quad (5)$$

$$\mathrm{E} = \mathrm{Se}\ (\textbf{XIII}),\ \mathrm{Te}\ (\textbf{XIV}).$$

By heating telluride **VIII** in excess methyl iodide under reflux we obtained a mixture of products which (according to the NMR data) contained methylbis(silatranylmethyl)telluronium iodide (**XIV**), dimethyl(silatranylmethyl)telluronium iodide (**XV**), and 1-(iodomethyl)silatrane (**XVI**). Compounds **XV** and **XVI** were likely to be formed as a result of cleavage of the >$\mathrm{Te^+}$–$\mathrm{CH_2Si}$ bond in **XIV** by the action of methyl iodide [scheme (6)].

$$\textbf{XIV} + \mathrm{MeI} \longrightarrow \underset{\textbf{XV}}{\mathrm{N(CH_2CH_2O)_3SiCH_2}\overset{+}{\mathrm{Te}}\mathrm{Me_2I^-}} + \underset{\textbf{XVI}}{\mathrm{ICH_2Si(OCH_2CH_2)_3N}}. \quad (6)$$

Cleavage of the >$\mathrm{Se^+}$–$\mathrm{CH_2Si}$ in iodide **XIII** with methyl iodide also occurs under analogous conditions, but the contribution of this process is much smaller. The >$\mathrm{E^+}$–$\mathrm{CH_2Si}$ bond (E = Se, Te) in methylbis(triethoxysilylmethyl)chalcogenonium iodides $\mathrm{MeE^+\cdot[CH_2Si(OCH_2CH_2)_3N]_2\ I^-}$ (E = Te, Se) is cleaved with methyl iodide especially readily [scheme (7)].

$$\underset{\textbf{XVII, XVIII}}{\mathrm{[(EtO)_3SiCH_2]_2E}} + \mathrm{MeI} \longrightarrow \underset{\textbf{XIX, XX}}{\mathrm{[(EtO)_3SiCH_2]_2}\overset{+}{\mathrm{E}}\mathrm{Me_2I^-}}$$

$$\xrightarrow{\mathrm{MeI}} \underset{\textbf{XXI, XXII}}{\mathrm{(EtO)_3SiCH_2}\overset{+}{\mathrm{E}}\mathrm{Me_2I^-}} + \underset{\textbf{XXIII}}{\mathrm{ICH_2Si(OEt)_3}}, \quad (7)$$

$$\mathrm{E} = \mathrm{Se}\ (\textbf{XVII, XIX, XXI}),\ \mathrm{Te}\ (\textbf{XVIII, XX, XXII}).$$

Therefore, the reaction of bis(triethoxysilylmethyl) chalcogenide **XVII** or **XVIII** with excess methyl iodide gives rise to a mixture of the corresponding dimethyl(triethoxysilylmethyl)chalcogenonium iodide **XXI** or **XXII** and triethoxy(iodomethyl)silane (**XXIII**) rather than to expected bis(triethoxysilylmethyl)chalcogenonium iodide **XIX** or **XX**. The reson is the lower basicity of the chalcogen atom E in molecules **XVII** and **XVIII**, as compared to silatranyl analogs **XIII** and **XIV**.

Methylbis(silatranylmethyl)selenonium iodide (**XIII**) was also synthesized independently (yield 70%) by the reaction of 1-(methylselanylmethyl)silatrane (**III**) with 1-(iodomethyl)silatrane (**XVI**) at a molar ratio of 1 : 1 in boiling methanol [reaction time 4 h, scheme (8)].

$$\textbf{III} + \textbf{XVI} \longrightarrow \textbf{XIII}. \quad (8)$$

By analogous reaction of bis(silatranylmethyl) selenide (**VII**) with 1-(iodomethyl)silatrane (**XVI**) (reactant molar ratio 1 : 1; boiling methanol, 6 h) we obtained previously unknown tris(silatranylmethyl)selenonium iodide (**XXIV**) in ~90% yield [scheme (9)].

$$\textbf{VII} + \textbf{XVI} \longrightarrow \underset{\textbf{XXIV}}{[\mathrm{N(CH_2CH_2O)_3SiCH_2}]_3\overset{+}{\mathrm{Se}}\mathrm{I^-}}. \quad (9)$$

1-(Methylselanylmethyl)silatrane (**III**), 1-(phenyltellanylmethyl)silatrane (**IV**), bis(silatranylmethyl) chalcogenides **VII** and **VIII**, and bis(silatranylmethyl) diselenide (**X**) are colorless (**III, IV, VII**) or yellowish crystalline substances with a strong unpleasant odor. Compounds **III**, **IV**, and **X** are characterized by fairly sharp melting points (Table 1). Unlike bis(silatranylmethyl) telluride (**VIII**), silatranes **III**, **IV**, **VII**, and **X** are readily soluble in chloroform. All these compounds, including **VIII**, are soluble in acetonitrile, dimethylformamide, and dimethyl sulfoxide. Methylorganyl(silatranylmethyl)chalcogenonium iodides **XI**–**XIV**, tris(silatranylmethyl)selenonium iodide (**XXIV**), and dimethyl(triethoxysilylmethyl)chalcogenonium iodides **XXI** and **XXII** are finely crystalline powders. Among these, only iodides **XI**, **XIII**, **XXI**, and **XXII** melt without decomposition (Table 1). In contrast to silatranes **III**, **IV**, **VII**, **VIII**, and **X**, the above listed iodides are readily soluble in methanol, acetonotrile, DMSO, and DMF, but considerably less readily soluble in chloroform.

The structure of the newly sunthesized compounds was confirmed by the data of elemental analysis (Table 1) and ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se NMR (Table 2) and IR spectroscopy. Table 2 contains the ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se chemical shifts of compounds **III**, **IV**, **VII**, **VIII**, **X**–**XIV**, **XXI**, **XXII**, and **XXIV** in $\mathrm{CDCl_3}$. For comparison, we also recorded for the first time the ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se NMR spectra of structurally similar (methylchalcogenomethyl)triethoxysilanes, 1-(methylchalcogenomethyl)silatranes and the corresponding methylchalcogenonium iodides in $\mathrm{CDCl_3}$, $\mathrm{CD_3OD}$, $\mathrm{CD_3CN}$, and DMSO-d_6 (Table 3), of bis(trialkoxysilylmethyl) chalcogenides and bis(silatranylmethyl) chalcogenides in $\mathrm{CDCl_3}$ (Table 4), and of methylorganyl(silatranylmethyl)chalcogenonium iodides **XI**–**XIV** in $\mathrm{CDCl_3}$, $\mathrm{CD_3OD}$, $\mathrm{CD_3CN}$, and DMSO-d_6 (Table 5).

Table 2. NMR spectra of compounds **III, IV, VII, VIII, X–XIV, XXI, XXII**, and **XXIV** in $CDCl_3$

Comp. no.	δ, ppm	δ_C, ppm	δ_{Si}, ppm	δ_{Se}, ppm
III	1.68 s (2H, CH_2Si), 1.98 s (3H, CH_3Se), 2.83 t (6H, $3CH_2N$), 3.80 t (6H, $3CH_2O$)	7.44 (CH_3Se), 11.28 (CH_2Si), 51.10 (CH_2N), 57.60 (CH_2O)	–73.72	22.43
IV	2.08 s (2H, CH_2Si), 2.81 t (6H, $3CH_2N$), 3.79 t (6H, $3CH_2O$), 7.19–7.39 m (5H, Ph)	–8.98 (CSi), 50.99 (NC), 57.54 (OC), 116.27 (C_i), 125.96 (C_o), 128.57 (C_m), 135.61 (C_p)	–72.10	–
VII	1.72 s (4H, $2CH_2Si$), 2.80 t (12H, $6CH_2N$), 3.76 t (12H, $6CH_2O$)	12.46 (CSi), 51.30 (CN), 57.86 (CO)	–71.59	56.86
X	2.38 s (4H, $2CH_2Si$), 2.80 t (12H, $6CH_2N$), 3.78 t (12H, $6CH_2O$)	16.31 (CSi), 50.79 (CN), 57.27 (CO)	–73.72	–
XI	2.08 s (2H, CH_2Si), 2.91 s (3H, Me), 3.05 t (6H, $3NCH_2$), 3.85 (6H, $3CH_2O$)	–	–	–
XII	2.39 (*A*), 2.50 (*B*), q (2H, CH_2Si, *AB* system, $^2J_{AB}$ 12.13, $^2J_{\mathrm{H}^A\mathrm{C}-^{77}\mathrm{Se}}$ 12.8, $^2J_{\mathrm{H}^B\mathrm{C}-^{77}\mathrm{Se}}$ 4.9 Hz), 2.93 s (3H, Me), 2.96 t (6H, 3NCH2), 3.70 t (6H, $3CH_2O$), 7.60–7.90 m (5H, Ph)	24.55 (CSi), 29.49 (Me), 49.92 (CN), 56.72 (CO), 124.33 (C_i), 129.35 (C_o), 129.79 (C_m), 131.66 (C_p)	–82.95 –84.23[a]	–
XIII	1.87 (*A*), 2.07 (*B*) q (4H, $2CH_2Si$, *AB* system, $^2J_{AB}$ 12.7, $^2J_{\mathrm{H}^A\mathrm{C}-^{77}\mathrm{Se}}$ 6.6, $^2J_{\mathrm{H}^B\mathrm{C}-^{77}\mathrm{Se}}$ 5.4 Hz), 2.60 s (3H, Me, $^2J_{\mathrm{HC}-^{77}\mathrm{Se}}$ 9.0 Hz), 3.09 t (12H, $6NCH_2$), 3.83 t (12H, $6CH_2O$)	23.41 (Me), 29.75 (CSi), 50.84 (CN), 57.13 (CO)	–82.97	–
XIV	–	–	–80.34	–
XXI	1.26 t (9H, $3CH_3$), 2.95 s (9H, CH_2Si), 3.22 s (3H, CH_3Se^+), 3.95 s (6H, 3 CH_2O)	18.26 (CH_3C), 18.91 (CH_2Si), 24.60 (CSe), 59.75 (CH_2O)	–58.08	–
XXII	1.24 t (9H, MeC), 2.68 s (3H, MeTe), 2.42 s (2H, CH_2Si), 3.87 q (6H, $3OCH_2$)	0.45 (CSi), 6.51 (MeTe), 18.21 (MeC), 59.12 (OC)	–55.20	–
XXIV[b]	1.99 s (2H, CH_2Si), 2.98 t (6H, $3NCH_2$), 3.85 (6H, $3CH_2O$)	30.56 (CH_2Si), 52.39 (CH_2N), 58.72 (CH_2O)	–77.6	348.37

[a] In DMSO-d_6. [b] In CD_3OD.

The IR spectra of the obtained compounds contained a set of bands in the regions of 800 and 1050–1100 cm^{-1}, which are characteristic of 1-organylsilatranes, organylalkoxysilanes, and their derivatives (Si–O–C fragment). In addition, compounds **IV** and **XII** showed in the IR spectra absorption bands at 1590 and 3100 cm^{-1} due to stretching vibrations of aromatic C–H and C=C bonds (Ph).

EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord IR-75 spectrometer. The ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13, 100.61, and 79.49 MHz, respectively. The ^{77}Se NMR spectra were obtained on a Jeol FX-90Q instrument at 17.03 MHz. The ^{77}Se chemical shifts were measured relative to dimethyl selenide. The compounds were examined as 10–15% solutions in $CDCl_3$, CD_3OD, CD_3CN, and DMSO-d_6.

1-(Methylselanylmethyl)silatrane (III). A heterogeneous mixture of 5.0 g of (methylselanylmethyl)triethoxysilane (**I**), 2.7 g of tris(2-hydroxyethyl)amine, and 2–3 drops of a 10% solution of sodium methoxide in methanol was heated under stirring until it became homogeneous, and ~50% (of the theoretical amount) of the liberated ethanol was distilled off. The residue was cooled to room temperature, and the precipitate was filtered off through a Schott filter, washed with cold ethanol and diethyl ether, and dried under reduced pressure. Yield 2.7 g. The filtrate was evaporated and cooled to isolate an additional amount (0.5 g) of the product. Overall yield 3.2 g (62%), colorless thin needles.

1-(Phenyltellanylmethyl)silatrane (IV) was synthesized in a similar way from 7.0 g of trimethoxy(phenyltellanylmethyl)silane (**II**) and 3.0 g of tris(2-hydroxyethylamine). Yield 4.1 g (50%), colorless finely crystalline powder.

Bis(silatranylmethyl) selenide (VII) was synthesized in a similar way from 4.0 g of bis(triethoxy-

Table 3. ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se chemical shifts in the NMR spectra of isostructural (methylchalcogenomethyl)triethoxysilanes, 1-(methylchalcogenomethyl)silatranes, and the corresponding methylchalcogenonium iodides

E	Solvent	δ, ppm	δ_C, ppm	δ_{Si}, ppm	δ_{Se}, ppm
$CH_3ECH_2Si(OCH_2CH_3)_3$					
S	$CDCl_3$	1.26 t (9H, $3CH_3$), 1.86 s (2H, CH_2Si), 2.17 s (3H, CH_3S), 3.88 q (6H, $3CH_2O$)	7.42 (CH_3S), 11.60 (CH_2Si), 18.32 (CH_3C), 58.36 (CH_2O)	–52.70	–
Se	$CDCl_3$	1.24 t (9H, $3CH_3$), 1.73 s (9H, CH_2Si), 2.06 s (3H, CH_3Se), 3.88 s (6H, $3CH_2O$)	2.49 (CH_2Si), 7.21 (CH_3Se), 18.26 (CH_3C) 58.94 (CH_2O)	–51.70	18.57
$I^-(CH_3)_2E^+CH_2Si(OCH_2CH_3)_3$					
S	$CDCl_3$	1.26 t (9H, $3CH_3$), 3.16 s (2H, CH_2Si), 3.41 s (6H, $2CH_3S^+$), 3.96 s (6H, $3CH_2O$)	–	–60.9	–
Se	$CDCl_3$	1.26 t (9H, $3CH_3$), 2.95 s (9H, CH_2Si), 3.22 s (3H, CH_3Se^+), 3.95 s (6H, $3CH_2O$)	18.26 (CH_3C), 18.91 (CH_2Si), 24.60 (CSe), 59.75 (CH_2O)	–58.08	–
Te	$CDCl_3$	1.24 t (9H, $3CH_3$), 2.42 s (9H, CH_2Si), 2.68 s (3H, CH_3Se^+), 3.95 s (6H, $3CH_2O$)	0.45 (CH_2Si), 6.51 (CH_3Te+), 18.21 (CH_3C), 59.12 (CH_2O)	–55.20	–
$CH_3ECH_2Si(OCH_2CH_2)_3N$					
S	$CDCl_3$	1.74 s (2H, CH_2Si), 2.13 s (3H, CH_3S), 2.85 t (6H, $3CH_2N$), 3.83 t (6H, $3CH_2O$)	–	–75.3	–
Se	$CDCl_3$	1.68 s (2H, CH_2Si), 1.98 s (3H, CH_3Se), 2.83 t (6H, $3CH_2N$), 3.80 t (6H, $3CH_2O$)	7.44 (CH_3Se), 11.28 (CH_2Si), 51.10 (CH_2N), 57.60 (CH_2O)	–73.72	22.43
$I^-(CH_3)_2E^+CH_2Si(OCH_2CH_2)_3N$					
S	CD_3OD	2.14 s (2H, CH_2Si), 3.06 s (3H, Me), 3.09 t (6H, $3NCH_2$), 3.89 (6H, $3CH_2O$)	29.32 (CH_2), 30.92 (Me), 51.94 (CH_2N), 58.43 (CH_2O) in CD_3OD	–84.3	–
Se	$CDCI_3$	2.08 s (2H, CH_2Si), 2.91 s (3H, Me), 3.05 t (6H, $3NCH_2$), 3.85 (6H, $3CH_2O$)	–	–83.77[a]	–
Te	CD_3CN	1.78 s (2H, CH_2Si), 2.51 s (3H, Me), 2.93 t (6H, $3NCH_2$), 3.83 (6H, $3CH_2O$)	6.12 (CH_2), 11.73 (Me), 51.46 (CH_2N), 57.98 (CH_2O)	–81.0	–
$I^-E^+[CH_2Si(OCH_2CH_2)_3N]_3$					
S	CD_3OD	2.01 s (2H, CH_2Si), 2.97 t (6H, $3NCH_2$), 3.78 (6H, $3CH_2O$)	34.56 (CH_2Si), 30.92 (Me), 52.12 (CH_2N), 58.67 (CH_2O)	–77.5	–
Se	CD_3OD	1.99 s (2H, CH_2Si), 2.98 t (6H, $3NCH_2$), 3.85 (6H, $3CH_2O$)	30.56 (CH_2Si), 52.39 (CH_2N), 58.72 (CH_2O)	–77.6	348.37

[a] In DMSO-d_6.

Table 4. ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se chemical shifts in the NMR spectra of isostructural bis(trialkoxysilylmethyl)chalcogenides and bis(silatranylmethyl)chalcogenides $R_3SiCH_2ECH_2SiR_3$ in $CDCl_3$

R_3	E	δ, ppm	δ_C, ppm	δ_{Si}, ppm	δ_{Se}, ppm
$(CH_3CH_2O)_3$	S	1.23 t (18H, $6CH_3$), 1.95 s (4H, $2CH_2Si$), 3.86 q (12H, $6CH_2O$)	16.64 (CSi), 18.21 (CH_3), 58.84 (CH_2O)	–52.9	–
$(CH_3CH_2O)_3$	Se	1.24 t (18H, $6CH_3$), 1.87 s (4H, 2CH2Si), 3.89 q (12H, $6CH_2O$)	3.95 (CSi), 18.31 (CH_3), 58.89 (CH_2O)	–51.7	42.57
$(CH_3CH_2O)_3$	Te	1.22 t (18H, $6CH_3$), 1.84 s (4H, $2CH_2Si$), 3.85 q (12H, $6CH_2O$)	–22.98 (CSi), 18.12 (CH_3), 58.96 (CH_2O)	–49.03	–
$N(CH_2CH_2O)_3$	S	1.82 s (4H, $2CH_2Si$), 2.77 t (12H, $6CH_2N$), 3.76 t (12H, $6CH_2O$)		–73.04	–
$N(CH_2CH_2O)_3$	Se	1.72 s (4H, $2CH_2Si$), 2.80 t (12H, $6CH_2N$), 3.76 t (12H, $6CH_2O$)	12.46 (CSi), 51.30 (CN), 57.86 (CO)	–71.59	56.86

Table 5. ^1H, ^{13}C, and ^{29}Si NMR spectra of methylorganyl(silatranylmethyl)chalcogenonium iodides $I^{-}MeRE^{+}CH_2Si \cdot (OCH_2CH_2)_3N$

R	E	Solvent	δ, ppm	δ_C, ppm	δ_{Si}, ppm
Me	S	$CDCl_3$	2.14 s (2H, CH_2Si), 3.06 s (3H, Me), 3.09 t (6H, $3NCH_2$), 3.89 (6H, $3CH_2O$)	–	–84.30
Me	S	CD_3OD	2.10 s (2H, CH_2Si), 2.81 s (3H, Me), 3.06 t (6H, $3NCH_2$), 3.84 (6H, $3CH_2O$)	29.32 (CH2), 30.92 (Me), 51.94 (CN), 58.43 (CO)	–84.25
Me	S	DMSO-d_6	–	28.28 (CH_2), 29.36 (Me), 50.41 (CN), 57.19 (CO)	–85.23
Me	Se	$CDCl_3$	2.08 s (2H, CH_2Si), 2.91 s (3H, Me), 3.05 t (6H, $3NCH_2$), 3.85 (6H, $3CH_2O$)	–	–
Me	Se	CD_3OD	2.13 s (2H, CH_2Si), 2.65 s (3H, Me), 3.03 t (6H, $3NCH_2$), 3.83 (6H, $3CH_2O$)	–	–
Me	Se	DMSO-d_6	–	–	–83.77 [a]
Me	Te	$CDCl_3$	1.78 s (2H, CH_2Si), 2.51 s (3H, Me), 2.93 t (6H, $3NCH_2$), 3.83 (6H, $3CH_2O$)	11.49 (Me), 50.76 (CN), 57.15 (CO)	–80.3
Me	Te	CD_3OD	1.86 s (2H, CH_2Si), 2.28 s (3H, Me), 3.02 t (6H, $3NCH_2$), 3.83 (6H, $3CH_2O$)	5.74 (CH_2), 11.82 (Me), 51.75 (CN), 58.39 (CO)	–80.7
Me	Te	CD_3CN	1.86 s (2H, CH_2Si), 2.27 s (3H, Me), 2.95 t (6H, $3NCH_2$), 3.76 (6H, $3CH_2O$)	6.12 (CH_2), 11.73 (Me), 51.46 (CN), 57.98 (CO)	–81.0
Ph	S	DMSO-d_6	2.39 (*A*), 2.60 (*B*), q (2H, CH_2Si, *AB* system, $^2J_{AB}$ 12.85 Hz), 2.99 t (6H, $3NCH_2$), 3.16 s (3H, Me), 3.70 t (6H, $3CH_2O$), 7.63–8.00 m (5H, Ph)	29.51 (CSi), 30.58 (Me), 50.02 (CN), 56.77 (CO), 129.42 (C_o), 129.67 (C_i), 129.93 (C_m), 132.87 (C_p)	–85.67
Ph	Se	DMSO-d_6	2.39 (*A*), 2.50 (*B*), q (2H, CH_2Si, *AB* system, $^2J_{AB}$ 12.13, $^2J_{H^AC-{}^{77}Se}$ 12.8, $^2J_{H^BC-{}^{77}Se}$ 4.9 Hz), 2.93 s (3H, Me), 2.96 t (6H, $3NCH_2$), 3.70 t (6H, $3CH_2O$), 7.60–7.90 m (5H, Ph)	24.55 (CSi), 29.49 (Me), 49.92 (CN), 56.72 (CO), 124.33 (C_i), 129.35 (C_o), 129.79 (C_m), 131.66 (C_p)	–82.95 [b] –84.23 [a]
Ph	Te	DMSO-d_6	1.96 (*A*), 1.97 (*B*), q (2H, CH_2Si, *AB* system, $^2J_{AB}$ 12.23 Hz), 2.39 s (3H, Me, $^2J_{HC-{}^{125}Te}$ 23.74 Hz), 2.91 t (6H, $3NCH_2$), 3.65 t (6H, $3CH_2O$), 7.60–7.90 m (5H, Ph)	8.83 (CSi), 14.53 (Me), 49.79 (CN), 56.66 (CO), 123.14 (C_i), 129.26 (C_o), 130.65 (C_m), 133.56 (C_p)	–81.25
$N(CH_2CH_2O)_3SiCH_2$	S	$CDCl_3$	1.88 (*A*), 2.09 (*B*) q (4H, $2CH_2Si$, *AB* system, $^2J_{AB}$ 12.6 Hz), 2.74 s (3H, Me), 3.09 t (12H, $6NCH_2$), 3.86 t (12H, $6CH_2O$)	–	–84.25

Table 5. (Contd.)

R	E	Solvent	δ, ppm	δ_C, ppm	δ_{Si}, ppm
$N(CH_2CH_2O)_3SiCH_2$	Se	$CDCl_3$	1.87 (*A*), 2.07 (*B*) q (4H, $2CH_2Si$, *AB* system, $^2J_{AB}$ 12.7, $^2J_{H^AC-^{77}Se}$ 6.6, $^2J_{H^BC-^{77}Se}$ 5.4 Hz), 2.60 s (3H, Me, $^2J_{HC-^{77}Se}$ 9.0 Hz), 3.09 t (12H, $6NCH_2$), 3.83 t (12H, $6CH_2O$)	23.41 (Me), 29.75 (CSi), 50.84 (CN), 57.13 (CO)	–82.97
$N(CH_2CH_2O)_3SiCH_2$	Se	CD_3OD	1.93 (*A*), 2.08 (*B*), q (4H, $2CH_2Si$, *AB* system, $^2J_{AB}$ 12.7, $^2J_{H^AC-^{77}Se}$ 6.6, $^2J_{H^BC-^{77}Se}$ 5.4 Hz), 2.57 s (3H, Me, $^2J_{HC-^{77}Se}$ 9.2 Hz), 3.09 t (12H, $6NCH_2$), 3.83 t (12H, $6CH_2O$)	23.62 (Me), 30.29 (CH2), 51.88 (CN), 58.39 (CO)	–83.04
$N(CH_2CH_2O)_3SiCH_2$	Te	$CDCl_3$	–	–	–80.34
$N(CH_2CH_2O)_3SiCH_2$	Te	CD_3OD	–	–	–80.67
$N(CH_2CH_2O)_3SiCH_2$	Te	CD_3CN	–	–	–80.75

[a] In DMSO-d_6. [b] In $CDCl_3$.

silylmethyl) selenide (**V**) and 2.8 g of tris(2-hydroxyethyl)amine. Yield 0.96 g, colorless finely crystalline powder.

Bis(silatranylmethyl) telluride (VIII) was synthesized in a similar way from 3.0 g of bis(triethoxysilylmethyl) telluride (**VI**) and 1.8 g of tris(2-hydroxyethyl)amine. Yield 0.6 g, light yellow amorphous powder.

Bis(silatranylmethyl) diselenide (X). A heterogeneous mixture of 6.5 g of bis(trimethoxysilylmethyl) diselenide (**IX**), 4.5 g of tris(2-hydroxyethyl)amine, and 2–3 drops of a 10% solution of sodium methoxide in methanol was stirred for 5 min at 20°C. The mixture became homogeneous and warmed up to 40°C. It was cooled to room temperature, and the precipitate was filtered off through a Schott filter, washed with cold methanol (2×5 ml) and diethyl ether, and dried under reduced pressure. Yield 7.1 g, light yellow finely crystalline powder.

Dimethyl(silatranylmethyl)selenonium iodide (XI). Methyl iodide, 2 g, was added dropwise with stirring to a mixture of 2.5 g selenide **III** and 5 ml of methanol. When the addition was complete, the mixture became homogeneous, and its temperature rose from 22 to 40°C. The mixture was cooled to 20°C and kept for 12 h in a refrigerator. The precipitate was filtered off through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 2.9 g. An additional portion of the product (0.6 g) was isolated by evaporation of the filtrate. Overall yield 3.5 g, colorless fine crystals.

Methyl(phenyl)(silatranylmethyl)telluronium iodide (XII). Methyl iodide, 2.5 g, was added dropwise to a mixture of 4.7 g of telluride **IV** in 10 ml of methanol under stirring at 20°C. By the end of addition (~5 min), the mixture warmed up from 22 to 35°C. The mixture was heated to the boiling point, stirred for 5 min at that temperature, and cooled to 10–15°C. The precipitate was filtered off through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 5.8 g, colorless fine needles.

Methylbis(silatranylmethyl)selenonium iodide (XIII). *a* [scheme (4)]. Compound **XIII** was synthesized as described above for iodide **XI** from 1 g of bis(silatranylmethyl) selenide (**VII**) and 0.4 g of methyl iodide. Yield 1.1 g (85%), mp 222–224°C (from ethanol).

b [scheme (5)]. A heterogeneous mixture of 1.40 g of selenide **III** and 1.58 g of 1-(iodomethyl)silatrane (**XVI**) in 10 ml of ethanol was heated for 4 h under reflux. The resulting solution was evaporated by half, the residue was kept for 12 h in a refrigerator, and the precipitate of iodide **XIII** was separated through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 2.32 g.

Methylbis(silatranylmethyl)telluronium iodide (XIV) was synthesized as described above for compound **XIII** (method *a*) from 1.5 g of bis(silatranylmethyl) telluride (**VIII**) and 0.5 g of methyl iodide. Yield 1.7 g, grey finely crystalline powder.

Methyl(triethoxysilylmethyl)selenonium iodide

(XXI). Methyl iodide, 1.5 g, was added to 2 g of bis(triethoxysilylmethyl)selenide (**XVII**), the mixture was kept for 4 h in the dark, and the flaky crystals of iodide **XXI** were filtered off through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 1.2 g (84%), colorless flaky crystals, mp 71–72°C.

Methyl(triethoxysilylmethyl)telluronium iodide (XXII). Methyl iodide, 1.5 g, was added to 1.5 g of bis(triethoxysilylmethyl) telluride (**XVIII**). After ~1 min, the mixture spontaneously warmed up from 20 to 35°C. After cooling to 10–15°C, the mixture crystallized. The crystals were filtered off through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 1.6 g (78%), colorless finely crystalline powder, mp 146–147°C.

Tris(silatranylmethyl)selenonium iodide (XXIV). A mixture of 2.60 g of selenide **VII** and 1.92 g of 1-(iodomethyl)silatrane (**XVI**) in 10 ml of methanol was heated for 6 h under reflux. The resulting solution was evaporated by half under reduced pressure, and the residue was kept for 24 h in a refrigerator. The crystals of iodide **XXIV** were filtered through a Schott filter, washed with diethyl ether, and dried under reduced pressure. Yield 3.1 g. Evaporation of the filtrate under reduced pressure gave an additional 0.76 g of the product. Overall yield 3.86 g, colorless finely crystalline powder.

ACKNOWLEDGMENTS

This study was performed under financial support by the State contract no. 02.445.11.7209.

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