aliquot of the reaction product in MeCN containing *ca.* 0.0216 g (3.3 mmol) of trioxane **3**, and the resulting mixture was heated for 15 min at 60 °C. An orange precipitate of methylglyoxal bis-2,4-dinitrophenylhydrazone **5** that formed was filtered off. Yield 0.037 g (86%). The precipitate was recrystallized from $C_6H_5NO_2$ to give a product with m.p. 296 °C that is consistent with the literature data.[13] A specimen prepared by mixing **5** with an authentic product obtained from methylglyoxal (Aldrich) gave no depression of m.p.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33132a).

References

1. M. F. Shostakovskii, N. A. Keiko, and A. Kh. Filippova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 392 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, **16** (Engl. Transl.)].
2. L. G. Egyud and A. Szent-Gyorgyi, *Science*, 1968, **160**, 1140.
3. V. S. Alekseev and N. V. Alekseeva, *Ukr. Biokhim. Zh.*, [*Ukrainian Biochemical Journal*], 1990, **62**, 13 (in Russian).
4. H. J. Sanders and A. W. Taff, *Ind. Eng. Chem.*, 1954, **46**, 414.
5. G. Leoncini, *Italian J. of Biochemistry*, 1979, **28**, 285.
6. M. Fedoronko, M. Petrusova, and I. Tvaroska, *Carbohydrate Rev.*, 1983, **115**, 85.
7. Sho-Chow Woo and Sze-Tseng Chang, *Trans. Faraday Soc.*, 1945, **41**, 157.
8. N. A. Keiko, T. N. Musorina, Yu. L. Frolov, A. M. Shulunova, Yu. A. Chuvashev, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1993 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
9. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Wiley, New York, 1963.
10. J. L. Jangnichel and C. A. Reilly, *J. Mol. Spectr.*, 1965, **16**, 135.
11. T. N. Mamashvili, N. A. Keiko, and M. G. Voronkov, *Zh. Org. Khim.*, 1995, **31**, 429 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
12. N. A. Keiko and M. F. Shostakovskii, *Dokl. Akad. Nauk SSSR*, 1965, **162**, 362 [*Dokl. Chem.*, 1965 (Engl. Transl.)].
13. N. A. Keiko, M. F. Shostakovskii, and A. P. Chichkarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2351 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, **16** (Engl. Transl.)].
14. Houben-Weyl, *Methoden der Organische Chemie*, Stuttgart, 1955, **3**, 2; 75.
15. *Beilstein Handbuch der Organische Chemie*, Berlin, 1942, **1**, **EII**, s. 822.

Received December 2, 1997;
in revised form June 8, 1998

Reaction of methyl iodide with organylethynyl silatranylmethyl chalcogenides

M. S. Sorokin, M. G. Voronkov, and V. A. Lopyrev*

Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 35 6046

The reactivity of organylethynyl silatranylmethyl chalcogenides $RC\equiv CYCH_2Si(OCH_2CH_2)_3N$ (R = Ph, Me_3Si; Y = S, Se, Te) in the reaction with methyl iodide depending on the nature of the chalcogen Y, the substituent R at the triple bond, and the reaction conditions was studied.

Key words: 1-organylethynyl silatranylmethyl chalcogenides, methyl organylethynyl silatranylmethyl telluronium iodide, dimethyl silatranylmethyl selenonium and telluronium iodides, ^1H NMR and IR spectra.

The extremely high electron-donor effect of silatranyl $-Si(OCH_2CH_2)_3N$ ($\sigma^* = -3.49$)[1] and silatranylmethyl $-CH_2Si(OCH_2CH_2)_3N$ ($\sigma^* = -2.24$)[1,2] groups ensures high nucleophilicity of the S and Se atoms in phenyl silatranylmethyl chalcogenides $PhYCH_2Si(OCH_2CH_2)_3N$ (Y = S, Se) in their reactions with MeI leading to the corresponding iodides $I^-(Me)PhY^+CH_2Si(OCH_2CH_2)_3N$.[3,4]

In a continuation of these studies, we investigated the reactivity of organylethynyl silatranylmethyl chalcogenides $RC\equiv CYCH_2Si(OCH_2CH_2)_3N$ (R = Ph, Y = S (**1**); R = Ph, Y = Se (**2**); R = Ph, Y = Te (**3**); R =

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2550—2551, December, 1998.

Scheme 1

$$\underset{\mathbf{3}\ (\mathbf{6})}{\mathrm{RC{\equiv}CTeCH_2Si(OCH_2CH_2)_3N}} \xrightarrow[-20\ ^\circ\mathrm{C}]{\mathrm{MeI}}$$

$$\longrightarrow \underset{\mathbf{7}\ (\mathbf{8})}{\mathrm{I^-(Me)(RC{\equiv}C)Te^+CH_2Si(OCH_2CH_2)_3N}}$$

R = Ph (**3**, **7**), Me_3Si (**6**, **8**)

$$\mathbf{3}\ (\mathbf{7}) \xrightarrow[\Delta]{\mathrm{MeI}} \underset{\mathbf{9}}{\mathrm{I^-(CH_3)_2Te^+CH_2Si(OCH_2CH_2)_3N}}$$

$$\underset{\mathbf{5}}{\mathrm{Me_3SiC{\equiv}CSeCH_2Si(OCH_2CH_2)_3N}} \xrightarrow[\Delta]{\mathrm{MeI}}$$

$$\longrightarrow \underset{\mathbf{10}}{\mathrm{I^-(CH_3)_2Se^+CH_2Si(OCH_2CH_2)_3N}} + \mathrm{PhC{\equiv}CI}$$

Me_3Si, Y = S (**4**); R = Me_3Si, Y = Se (**5**); R = Me_3Si, Y = Te (**6**)), which we had synthesized earlier,[5] in the reaction with MeI.

It turned out that sulfides **1** and **4** did not react with MeI even when they were refluxed with an excess of the reagent for 10 h. This indicates that the electron-acceptor properties of the RC≡C groups (R = Ph and Me_3Si) in compounds **1** and **4** prevent quarternization of the sulfur atom.

On the contrary, tellurides **3** and **6** reacted with MeI (Scheme 1) even at room temperature to give the corresponding methiodides **7** and **8** in almost quantitative yield. However, telluride **3** gave dimethyl silatranylmethyl telluronium iodide (**9**) upon reflux with an excess of MeI even for a short period of time (1 h). The same product was formed when methiodide **7** was refluxed with MeI.

Of the selenides studied (**2** and **5**), only compound **5** reacted with MeI to give dimethyl silatranylmethyl selenonium iodide (**10**) upon reflux with an excess of MeI (see Scheme 1).

The attempts to find conditions for the formation of methyl trimethylsilylethynyl silatranylmethyl selenonium iodide in the reaction with MeI failed.

The structures of the telluronium salts **7** and **8** synthesized were confirmed by ^{1}H NMR (recorded in CD_3OD) and IR spectra, and elemental analysis data. However, more detailed studies of the ^{1}H NMR spectra of these compounds in solvents, other than CD_3OD, indicate that they are unstable in $CDCl_3$ and CD_3CN solutions. Additional signals assigned for the protons of the corresponding tellurides (**3** and **6**) and MeI appeared in the ^{1}H NMR spectra of solutions of compounds **7** and **8** in these solvents. This indicates that an equilibrium shifted to the left is established in the solutions of telluronium salts **7** and **8** in the solvents studied (Scheme 2).

Scheme 2

$$\underset{\mathbf{7},\ \mathbf{8}}{\mathrm{I^-Me(RC{\equiv}C)Te^+CH_2Si(OCH_2CH_2)_3N}} \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{3},\ \mathbf{6}}{\mathrm{RC{\equiv}CTeCH_2Si(OCH_2CH_2)_3N}} + \mathrm{MeI}$$

The ^{1}H NMR and IR spectra of dimethyl silatranylmethyl selenonium (**10**) and telluronium (**9**) iodides are identical to the spectra of these compounds synthesized by us in another way.[4,6]

Experimental

^{1}H NMR spectra were recorded on a JEOL FX-90Q spectrometer (89.55 MHz) for 10—15% solutions in CD_3OD, $CDCl_3$, or CD_3CN (HMDS as the internal standard). IR spectra of the compounds synthesized were recorded on a Specord-75 IR instrument (in KBr pellets).

Methyl phenylethynyl silatranylmethyl telluronium iodide (7). Telluride **3** (2.08 g, 5 mmol) was dissolved in MeI (5 mL). In 1 min, a spontaneous warming up of the reaction mixture occurred and a finely crystalline precipitate of telluronium salt **7** formed. The precipitate was filtered off, washed with pentane, and dried *in vacuo* to give telluronium iodide **7** (2.70 g, 97%). M.p. 126—127 °C (from MeOH). Found (%): C, 34.4; H, 4.3; I, 23.1; N, 2.5; Si, 4.7; Te, 22.5. $C_{16}H_{22}INO_3SiTe$. Calculated (%): C, 34.4; H, 3.9; I, 22.7; N, 2.5; Si, 5.0; Te, 22.7. ^{1}H NMR, δ: 2.29 (A) and 2.41 (B) (q, 2 H, $SiCH_2$, $^2J_{AB}$ = 11.2 Hz); 2.63 (s, 3 H, CH_3Te^+); 3.16 (t, 6 H, NCH_2); 3.97 (t, 6 H, OCH_2); 7.57 (m (center), 5 H, C_6H_5). IR, ν/cm^{-1}: 1080, 1115 (Si—O—C); 1590 (C=C arom.); 2145 (C≡C); 3045 (C—H arom.).

Methyl trimethylsilylethynyl silatranylmethyl telluronium iodide (8). Telluride **6** (2.25 g, 5 mmol) was dissolved in MeI (5 mL) and kept at −20 °C for 1 h. Pentane (20 mL) was added to the resulting solution and stirred thoroughly. A yellowish solid of telluronium salt that precipitated was filtered off, washed with pentane on a filter, and recrystallized from MeOH to give iodide **8** (2.85 g, 94%), m.p. 110—112 °C. Found (%): C, 28.2; H, 4.6; I, 22.7; N, 2.4; Si, 9.1; Te, 22.7. $C_{13}H_{26}INO_3Si_2Te$. Calculated (%): C, 28.1; H, 4.7; I, 22.9; N, 2.5; Si, 9.4; Te, 23.0. ^{1}H NMR (CD_3OD), δ: 0.18 (s, 9 H, Me_3Si); 2.35 (A) and 2.47 (B) (q, 2 H, CH_2Si, $^2J_{AB}$ = 11.2 Hz); 2.68 (s, 3 H, CH_3Te^+); 3.08 (t, 6 H, NCH_2); 3.89 (t, 6 H, OCH_2). IR, ν/cm^{-1}: 1090, 1125 (Si—O—C); 2150 (C≡C).

Dimethyl silatranylmethyl telluronium iodide (9). *A.* A solution of telluride **3** (1.04 g (2.5 mmol) in MeI (3 mL) was refluxed for 1 h. The mixture was cooled to 20 °C and diluted with pentane (25 mL). The resulting precipitate of telluronium iodide was filtered off, washed, and dried *in vacuo* to give compound **9** (1.0 g, 84%), m.p. 210—212 °C (from MeOH) (*cf.* Ref. 6: m.p. 210—212 °C). Found (%): C, 22.7; H, 4.2; I, 26.5; N, 3.0; Si, 5.6; Te, 26.7. $C_9H_{20}INO_3SiTe$. Calculated (%): C, 22.9; H, 4.3; I, 26.8; N, 3.0; Si, 5.9; Te, 27.0. ^1H NMR (CD_3OD), δ: 2.18 (s, 6 H, $(CH_3)_2Te^+$); 1.81 (s, 2 H, $SiCH_2$); 3.00 (t, 6 H, NCH_2); 3.81 (t, 6 H, OCH_2).

B. A mixture of telluronium iodide **7** (1.4 g, 2.5 mmol) and MeI (2 mL) was refluxed for 1 h. The reaction mixture was cooled and pentane (20 mL) was added. The precipitate that formed was filtered off, washed with pentane and dried *in vacuo* to give telluronium iodide **9** (0.9 g, 81%), m.p. 209—211 °C (from MeOH).

Dimethyl silatranylmethyl selenonium iodide (10). Selenide **5** (2.55 g, 5 mmol) was refluxed in MeI (5 mL) for 3 h. The reaction mixture was cooled to −20 °C and diluted with pentane (30 mL). The precipitate that formed was filtered off, washed with pentane and dried *in vacuo* to give iodide **10** (1.8 g, 85%), m.p. 173—174 °C (from MeOH) (*cf.* Ref. 4: m.p. 178—180 °C). Found (%): C, 25.3; H, 4.7; I, 30.2; N, 3.4; Se, 18.3; Si, 6.7. $C_9H_{20}INO_3SeSi$. Calculated (%): C, 25.5; H, 4.8; I, 29.9; N, 3.3; Se, 18.6; Si, 6.6. ^1H NMR (CD_3OD), δ: 2.13 (s, 2 H, $SiCH_2$); 2.65 (s, 9 H, CH_3Se^+); 3.03 (t, 6 H, NCH_2); 3.83 (t, 6 H, OCH_2). Phenylethynyl iodide was identified by GLC in the filtrate after concentration.

References

1. M. G. Voronkov, E. N. Brodskaya, V. V. Belyaeva, T. V. Kashik, V. P. Baryshok, and O. G. Yarosh, *Zh. Obshch. Khim.*, 1986, **56**, 621 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
2. A. Daneshrad, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, 1975, **85**, 35.
3. M. G. Voronkov and M. S. Sorokin, *Zh. Obshch. Khim.*, 1979, **49**, 1671 [*J. Gen. Chem. USSR*, 1979, **49** (Engl. Transl.)].
4. M. G. Voronkov and M. S. Sorokin, *Zh. Obshch. Khim.*, 1986, **56**, 1818 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
5. M. G. Voronkov and M. S. Sorokin, *Zh. Obshch. Khim.*, 1990, **60**, 134 [*J. Gen. Chem. USSR*, 1990, **60** (Engl. Transl.)].
6. M. G. Voronkov and M. S. Sorokin, *Zh. Obshch. Khim.*, 1989, **59**, 590 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].

Received May 13, 1998

Recyclization of 5-allenyl-2,5-dichloro-3-*N*,*N*-dimethylamino-4,4-dimethoxycyclopent-2-enone under the action of SmI_2—$(Me_2N)_3P$. Functionalized *cis*-,*trans*-cycloocta-2,6-dienones

N. A. Ivanova, A. M. Shainurova, L. V. Spirikhin, and M. S. Miftakhov*

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Octyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

Reaction of 5-allenyl-2,5-dichloro-3-*N*,*N*-dimethylamino-4,4-dimethoxycyclopent-2-enone with SmI_2—$(Me_2N)_3P$ affords new functionalized *cis*-,*trans*-cycloocta-2,6-dienones.

Key words: allenylcyclopentenones, samarium diiodide, hexamethylphosphorous triamide, recyclization, functionalized *cis*-,*trans*-cycloocta-2,6-dienones.

Earlier,[1] we found that SmI_2, a one-electron reductive agent, which is widely used in organic synthesis,[2] is transformed in the presence of $(Me_2N)_3P$ into more reactive SmI intermediates (supposedly, Me_2NSmI). The latter generate ketyl-radicals from cyclopentenone (**1**), which undergoes a series of cascade transformations resulting in a tropone derivative. Note that compound **1** and a related compound (**2**)[3] are inert[4,5] with respect to SmI_2—$(Me_2N)_3PO$—THF under standard conditions. In the present work, we studied the reaction of allenyl-

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2552—2553, December, 1998.

1066-5285/98/4712-2469 $20.00 © 1999 Kluwer Academic/Plenum Publishers