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Solvent- and base-free synthesis of 1,3-bis(2,6-disilaalkyl)-2-methylimidazolium iodides

Nina O. Yarosh,* Larisa V. Zhilitskaya, Lyudmila G. Shagun, Ivan A. Dorofeev, Lyudmila I. Larina and Lyudmila V. Klyba

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 419 346; e-mail: yarosh.nina@irioch.irk.ru

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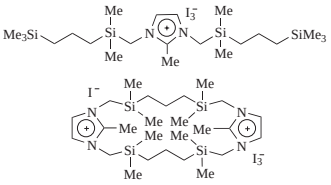
New organosilicon ionic liquids and cyclophanes were synthesized in a one stage by the solvent- and base-free reaction of 2-methylimidazole with 1-iodo- or 1,7-diiodo-2,2,6,6-tetramethyl-2,6-disilaheptanes.



Organosilicon imidazolium iodides, owing to their practically valuable properties, are promising building blocks, which can be employed as key components of electrolytes in dyes-sensibilized solar cells,[1,2] nano-structured composite materials and heterogeneous catalysts.[3] The diazole derivatives, bearing silicon atom in the N-alkyl chain, find application in the design of physiologically active compounds, efficient against viral diseases and cancer.[4] All this has awakened fresh interest onto new representatives of these compounds.

Organosilicon diazolium salts are generally synthesized in two stages. Initially, the reaction of azoles with halo derivatives of alkyl(alkoxy)-, alkylarylsilanes in the presence of KOH in EtOH[5] or with 3-(alkoxysilyl)alkyl isocyanates in THF[6] affords N^1-substituted azoles. The latter are further subjected to N^3-alkylation with various alkylating agents in DMF,[7] or without solvent in autoclave.[2]

We have previously shown that alkylation of 2-methylimidazole with 1-(iodomethyl)-1,1,3,3,3-pentamethyldisiloxane proceeds at 180 °C with cleavage of the siloxane bonds of $N^{1,3}$-alkylation adduct to afford cyclic silicone iodides.[8] In the case of 1,3-bis-(iodomethyl)-1,1,3,3-tetramethyldisiloxane, N^3-alkylation adduct is formed at 150 °C. Further this adduct undergoes autoalkylation to deliver imidazolophane with dimethylene(tetramethyl)-disiloxane bridges.[9] This work was aimed at studying the reaction of 2-methylimidazole with 1-iodo- or 1,7-diiodo-2,2,6,6-tetramethyl-2,6-disilaheptanes in the absence of solvents and base. We believed that the replacement of the oxygen atoms in the molecules of mono- and bis(iodomethyl)disiloxanes by the $(CH_2)_3$ moiety would allow new types of linear and cyclic silicone iodides to be synthesized under milder conditions.

The reaction of 2-methylimidazole **1** with 1-iodo-2,2,6,6-tetramethyl-2,6-disilaheptane **2** proceeds at 90 °C without solvents, bases and phase-transfer catalysts to deliver a novel type of linear organosilicon 1,3-bis(2,2,6,6-tetramethyl-2,6-disilaheptyl)-2-methyl-1*H*-imidazolium iodide **3** and triiodide **4** in 28 and 22% yields, respectively (Scheme 1).†

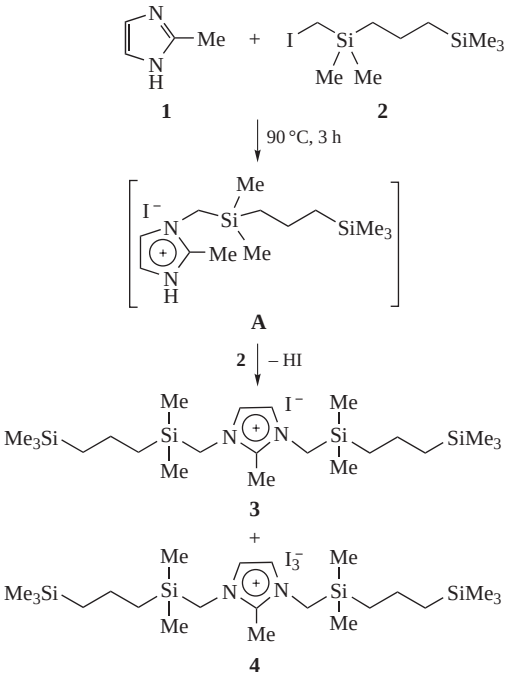
^{1}H, ^{13}C, ^{15}N NMR monitoring of the reaction course evidences that the process is triggered by quaternization of the N^3-atom of 2-methylimidazole **1** giving rise to intermediate **A**, which further undergoes N^1-alkylation with **2** to form monoiodide **3**. Hydrogen iodide, which is released in the course of the alkylation, partially

† ^{1}H, ^{13}C, ^{15}N and ^{29}Si spectra were run on a Bruker DPX-400 instrument at 400.13, 100.61, 40.56 and 79.5 MHz, respectively. Residual protons of deuterated solvents were used as references. The UV spectra were recorded on a UV-VIS Lambda 35 spectrometer in MeCN. The elemental composition was determined on a Thermo Scientific Flash 2000 automatic CHNS analyzer. The iodine content was determined by mercurimetric titration, silicon was determined by dry combustion method. Melting points were measured on a PolyTherm A Micro-Hot-Stage apparatus. Laser desorption ionization MS/MS mass spectra were recorded on a Bruker Daltonics UltrafleXtreme III TOF/TOF instrument equipped with a pulse nitrogen laser (337 nm) using Bruker Daltonics FlexControl software (version 3.3) in LIFT mode. The spectra were analyzed by Bruker Daltonics FlexFnalysis 3.3 software. Samples were prepared by 'Dried-Drop Method' on the target NALDI^{TM} with nanostructured surface and dried at room temperature for several minutes. The reaction course and the compounds purity were monitored by TLC (Silufol UV-254, acetone as an eluent).

The reaction of compounds **1** *and* **2**, **5** *(general procedure)*. A mixture of 2-methylimidazole **1 (**0.17 g, 2.02 mmol) and iodomethylsilane **2** (1.26 g, 4.04 mmol) or **5** (0.89 g, 2.02 mmol) was stirred at 90 °C for 3 h until the consumption of **2** (or **5**) (^{1}H, ^{13}C NMR monitoring), and then was cooled to room temperature. Then acetone (20 ml) was added, the precipitate of corresponding product **3** or **6** was filtered off, washed with acetone and diethyl ether, and dried. The filtrates containing polyiodides **4**, **7** were evaporated, and the residue was subjected to column (10×900 mm) chromatography [silica gel MN Kieselgel 60 (0.063–0.2 mm)]. Acetone was used as an eluent.

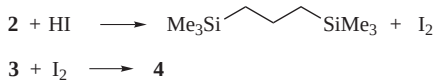
The reaction of compounds **1** *and* **2** *in the presence of elemental iodine*. Equimolar amounts of 2-methylimidazole **1** and elemental iodine were added to heated (90 °C) iodomethylsilane **2**. Further the reaction was carried out as described above.

*1,3-Bis(2,2,6,6-tetramethyl-2,6-disilaheptyl)-2-methyl-1*H*-imidazolium iodide* **3**. Yield 0.33 g (28%), white powder, mp 174–175 °C. ^{1}H NMR (DMSO-d_6) δ: –0.04 (s, 18 H, Me), 0.05 (s, 12 H, Me), 0.52 (t, 4 H, CH_2, $^3J_{HH}$ 7.92 Hz), 0.62 (t, 4 H, CH_2, $^3J_{HH}$ 7.96 Hz), 1.29 (m, 4 H, CH_2), 2.52 (s, 3 H, Me), 3.85 (s, 4 H, CH_2N), 7.53 (s, 2 H, $H^{4,5}$). ^{13}C NMR (DMSO-d_6) δ: –4.24 (Me_2Si), –1.49 (Me_3Si), 9.82 (Me), 17.50, 17.58, 20.66 (CH_2), 38.80 (CH_2N), 121.83 ($C^{4,5}$), 141.69 (C^2). ^{15}N NMR (DMSO-d_6) δ: –205.7. ^{29}Si NMR (DMSO-d_6) δ: 1.1 (Me_3Si), 4.1 (Me_2Si). Found (%): C, 45.05; H, 8.35; I, 21.54; N, 4.52; Si, 18.84. Calc. for $C_{22}H_{51}IN_2Si_4$ (%): C, 45.33; H, 8.82; I, 21.77; N, 4.81; Si, 19.27.



Scheme 1

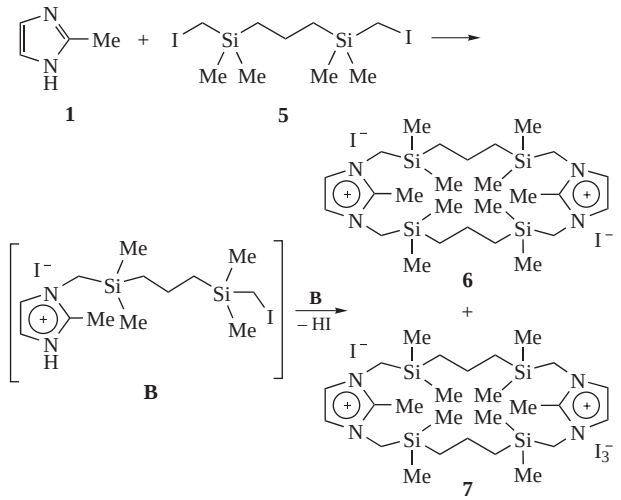
reduces the iodomethyl moiety of the starting silane **2** with elimination of elemental iodine. The latter further reacts with iodide anion of salt **3**. The formed triiodide **4** is red oil, which, upon the reaction progress, creates homogeneity of the medium and plays the role of solvent in this process (Scheme 2).



Scheme 2

When the **1** + **2** reaction is implemented in the presence of equimolar amounts of iodine, the yield of triiodide **4** augments up to 55%.

To develop an approach to the synthesis of cyclic organosilicon derivatives,[8] we have carried out for the first time the reaction between 2-methylimidazole **1** and hitherto unknown 1,7-diiodo-2,2,6,6-tetramethyl-2,6-disilaheptane **5**.‡ As expected, the alkylation involves both iodomethyl groups of compound **5** and likely proceeds *via* autoalkylation of the intermediate **B**, quaternization of 2-methylimidazole with the adduct **B** followed by cyclocondensation with the second molecule of **5**, or by intermolecular cyclization of $N^{1,3}$-dialkylation product with 2-methylimidazole **1**. This finally brings about imidazolophanes **6**, **7** of new type with silaalkylene bridges (Scheme 3).†,§



Scheme 3

The modest yields of compounds **6** and **7** (15 and 25%) are due to the parallel reduction of the iodomethyl fragments of silane **5** and adduct **B** with the released hydrogen iodide as well as to difficulties with purification of ionic liquid **7** from the side products.

Pairs of compounds **3** + **4** and **6** + **7** were separated based on their substantially different solubility in acetone.The further purification of ionic liquids **4** and **7** was performed by column chromatography.

The structures of earlier unknown compounds **3**, **4** and **6**, **7** have been proved by elemental analysis, mass specrometry, UV spectroscopy, 2D homo- and heteronuclear ^{1}H, ^{13}C, ^{15}N, ^{29}Si NMR technique. In the ^{1}H and ^{13}C NMR spectra of compounds **3**, **4**, signals of hydrogen and carbon of the terminal trimethylsilyl groups are observed. The ^{29}Si NMR spectrum shows two signals in the region of 1.1 and 4.8 ppm (**3**), and at 0.5 and 3.8 ppm (**4**) assigned to the $SiMe_3$ and CH_2SiMe_2 moieties, respectively. In the 2D ^{15}N NMR spectra of these compounds, a cross-peak between N^1 and N^3 atoms and protons of both the imidazole cycle and the methylene fragments appears. The ^{1}H and ^{13}C NMR spectra

*1,3-Bis(2,2,6,6-tetramethyl-2,6-disilaheptyl)-2-methyl-1*H*-imidazolium triiodide* **4**. Yield 0.25 g (22% based on **2**), red oil (R_f = 0.84, acetone). ^{1}H NMR (acetone-d_6) δ: –0.04 (s, 18H, Me), 0.16 (s, 12H, Me), 0.59 (t, 4H, CH_2, $^{3}J_{HH}$ 8.20 Hz), 0.77 (t, 4H, CH_2, $^{3}J_{HH}$ 8.20 Hz), 1.42 (m, 4H, CH_2), 2.75 (s, 3H, Me), 4.02 (s, 4H, CH_2N), 7.53 (s, 2H, $H^{4,5}$). ^{13}C NMR (acetone-d_6) δ: –4.02 (Me), –1.58 (Me_3Si), 11.37 (Me), 18.52, 18.71, 21.62 (CH_2), 40.28 (CH_2N), 123.77 ($C^{4,5}$), 144.09 (C^2). ^{15}N NMR (acetone-d_6) δ: –205.5. ^{29}Si NMR (acetone-d_6) δ: 0.5 (Me_3Si), 3.8 (Me_2Si). Found (%): C, 31.27; H, 5.72; I, 46.03; N, 3.45; Si, 13.02. Calc. for $C_{22}H_{51}I_3N_2Si_4$ (%): C, 31.58; H, 6.14; I, 45.50; N, 3.35; Si, 13.43.

In another run, from **1** (0.89 g, 2.02 mmol), **2** (0.51 g, 2.02 mmol) and molecular iodine (0.51 g, 2.02 mmol), 0.93 g (55%) of product **4** was obtained.

‡ *1,7-Diiodo-2,2,6,6-tetramethyl-2,6-disilaheptane* **5**. A mixture of 1.75 g (11.7 mmol) of sodium iodide and 1.2 g (4.7 mmol) of 1,7-dichloro-2,2,6,6-tetramethyl-2,6-disilaheptane in 30 ml of acetonitrile was stirred for 6 h at 81 °C. The precipitate was filtered off, the solvent was removed and the residue was distilled in vacuum to give 1.45 g (71%) of compound **5** as transparent liquid, bp 158 °C (2 Torr). ^{1}H NMR ($CDCl_3$) δ: 0.31 (s, 12H, Me), 0.91 (t, 4H, CH_2, ^{3}J 8.08 Hz), 1.58 (m, 2H, CH_2, ^{3}J 8.08 Hz), 2.13 (s, 4H, CH_2I). ^{13}C NMR ($CDCl_3$) δ: –14.19 (CH_2I), –2.47 (Me), 18.48, 19.69 (CH_2). ^{29}Si NMR ($CDCl_3$), δ: 4.3. Found (%): C, 24.75; H, 5.44; I, 57.17; Si, 12.22. Calc. for $C_9H_{22}I_2Si_2$ (%): C, 24.55; H, 5.04; I, 57.65; Si, 12.76.

§ *3,3,7,7,14,14,18,18,23,24-Decamethyl-12,20-diaza-1,9-diazonia-3,7,14,18-tetrasilatricyclo[18.2.1^{19,12}]tetracosa-1(23),9(24),10,21-tetraene diiodide* **6**. Yield 0.12 g (15%), white powder, mp 131–132 °C. ^{1}H NMR (DMSO-d_6) δ: 0.05 (s, 24H, Me), 0.66 (t, 8H, CH_2, $^{3}J_{HH}$ 8.21 Hz), 1.34 (t, 4H, CH_2, $^{3}J_{HH}$ 8.20 Hz), 2.56 (s, 6H, Me), 3.91 (s, 8H, CH_2N), 7.59 (s, 4H, $H^{4,5}$). ^{13}C NMR (DMSO-d_6) δ: –4.21 (Me), 10.15 (Me), 17.03, 17.61 (CH_2), 38.73 (CH_2N), 121.75 ($C^{4,5}$), 141.74 (C^2). ^{15}N NMR (DMSO-d_6) δ: –205.7. ^{29}Si NMR (DMSO-d_6) δ: 3.6. MS (MALDI), *m*/*z*: 660 $[M-HI]^{+\bullet}$. Found (%): C, 39.35; H, 6.65; I, 32.35; N, 7.78; Si, 14.47. Calc. for $C_{26}H_{54}I_2N_4Si_4$ (%): C, 39.58; H, 6.90; I, 32.17; N, 7.10; Si, 14.24.

3,3,7,7,14,14,18,18,23,24-Decamethyl-12,20-diaza-1,9-diazonia-3,7,14,18-tetrasilatricyclo[18.2.1^{19,12}]tetracosa-1(23),9(24),10,21-tetraene polyiodide **7**. Yield 0.18 g (25%), red oil (R_f 0.84, acetone). ^{1}H NMR (acetone-d_6) δ: 0.16 (s, 24H, Me), 0.81 (t, 8H, CH_2, $^{3}J_{HH}$ 8.21 Hz), 1.48 (t, 4H, CH_2, $^{3}J_{HH}$ 8.20 Hz), 2.79 (s, 6H, Me), 4.07 (s, 8H, CH_2N), 7.46 (s, 4H, $H^{4,5}$). ^{13}C NMR (acetone-d_6) δ: –4.84 (Me), 10.58 (Me), 17.28, 17.79 (CH_2), 39.24 (CH_2N), 121.75 ($C^{4,5}$), 142.89 (C^2). ^{15}N NMR (acetone-d_6) δ: –203.4. ^{29}Si NMR (acetone-d_6) δ: 4.6. Found (%): C, 30.23; H, 5.67; I, 48.03; N, 5.58; Si, 10.21. Calc. for $C_{26}H_{54}I_4N_4Si_4$ (%): C, 29.95; H, 5.22; I, 48.68; N, 5.37; Si, 10.77.

of imidazolophanes **6**, **7** contain no signals of the iodomethyl group. The ^{29}Si NMR spectra of compounds **6**, **7** exhibit one signal that supports their symmetry. In the UV spectra of triiodides **4**, **7**, the absorption bands, characteristic of the I_3^- anion,[7] are observed at 291–292 and 361–362 nm. The laser desorption/ionization MS/MS spectra of ion-precursor *m*/*z* 660 $[M-HI]^{+\bullet}$ of salt **6** contain the main characteristic ions with *m*/*z* 532 $[M-2HI]^{+\bullet}$, 446 $[M-2HI-C_2H_4SiMe_2]^{+\bullet}$, 266 $[M-HI-C_2H_3SiMe_2CH_2\text{-}imCH_2SiMe_2CH_2]^{+\bullet}$.

In conclusion, solvent- and base-free functionalization of 2-methylimidazole with mono- and bis(iodomethyl) silane derivatives proceeds in a one stage onto both nitrogen atoms to afford hitherto unknown ionic liquids and cyclophanes. The target products represent promising precursors in drug design and for the synthesis of electrolyte components and catalysts.

The main results were obtained using the equipment of Baikal Analytic Center of Collective Use of the Siberian Branch of the Russian Academy of Sciences.

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