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The Synthesis of the First Acetylenic Silyl Derivatives of 2-Methylimidazole and Benzimidazole

N. O. Yarosh, L. V. Zhilitskaya, L. G. Shagun, L. I. Larina, and I. A. Dorofeev

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk 664033 Russia
e-mail: yarosh.nina@irioch.irk.ru

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Abstract—The earlier unknown acetylenic silyl iodides of linear and cyclic structure form in the reaction of 2-methylimidazole and benzimidazole with bis[dimethyl(iodomethyl)silyl]ethyne. The synthesized compounds are characterized by the data of elemental analysis, ^{1}H, ^{13}C, ^{15}N, ^{29}Si NMR, IR, Raman and UV spectroscopy.

Keywords: 1,3-bis(iodomethyl)tetramethyldisilylethyne, 2-methylimidazole, benzimidazole, alkylation, iodides

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Nitrogen-containing products of linear and cyclic structure attract the attention of researchers due to valuable practical properties. They are a part of numerous drugs [1–6], ecologically pure fertilizers [7], basic media and catalysts in organic synthesis [8], components of hardeners of epoxide resins [9], and electrochemically stable electrolytes [10].

Principal methods of preparation of organic and organosilicon derivatives of azoles are based on their reaction with alkyl halides, α-chloro(bromo)ketones, chloroalkyl formats, and chloro(iodomethyl)siloxanes [2–5, 11–15]. The reaction proceeds successfully without catalysts if the molecules of the alkylating reagents contain iodomethyl groups [10, 16, 17].

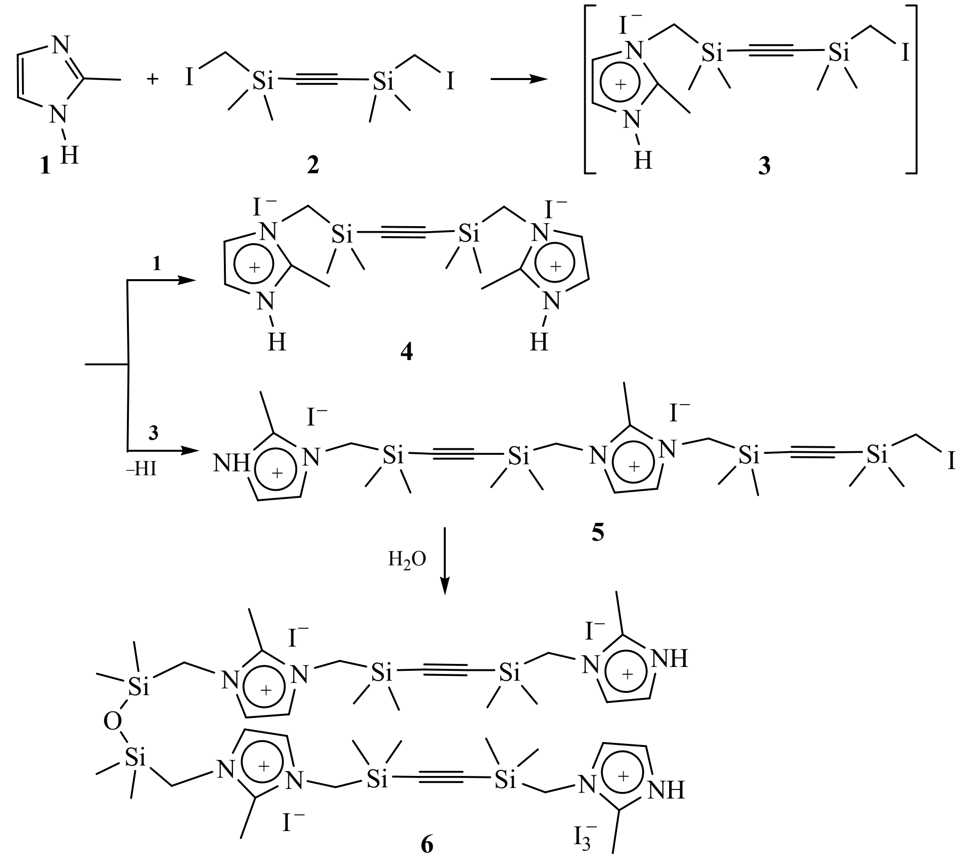
Earlier, we studied the alkylating ability of 1,3-bis-(iodomethyl)-1,1,3,3-tetramethyldisiloxane in the reaction of unsubstituted derivatives of imidazole and triazole [18–20]. It was found that the presence of two iodomethyl groups resulted in the involvement of the pyridine and pyrrole nitrogen atoms in the reaction, while a high flexibility of the siloxane bond in the molecule of the alkylating agent favors the formation of cyclic polyiodides in one preparative step. Continuing these studies, we suggested that replacement of the oxygen atom in 1,3-bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane by the acetylene fragment can lead to acyclic acetylenic silyl derivatives of azoles, which prompted us to examine the reaction of the earlier unknown bis[dimethyl(iodomethyl)silyl]ethyne with 2-methyl- and benzimidazoles.

The reaction of 2-methylimidazole **1** with bis-[dimethyl(iodomethyl)silyl]ethyne **2** proceeds in melt (175°C, 5 h) and apparently includes the formation of the key product **3**, which further enters the reaction of quaternization with 2-methylimidazole **1** and auto-alkylation leading to diiodides **4** and **5** respectively. Hydrogen iodide evolved during autoalkylation participates in the Si–C$_{sp}$ bond splitting in product **5** with the formation of the labile iodosilane, which further suffers hydrolysis with the air or solvent moisture resulting in polyiodide **6**. No splitting of the Si–C$_{sp}$ bond in diiodide **4** occurs, since the latter sediments from the reaction mixture as a light-yellow precipitate (Scheme 1).

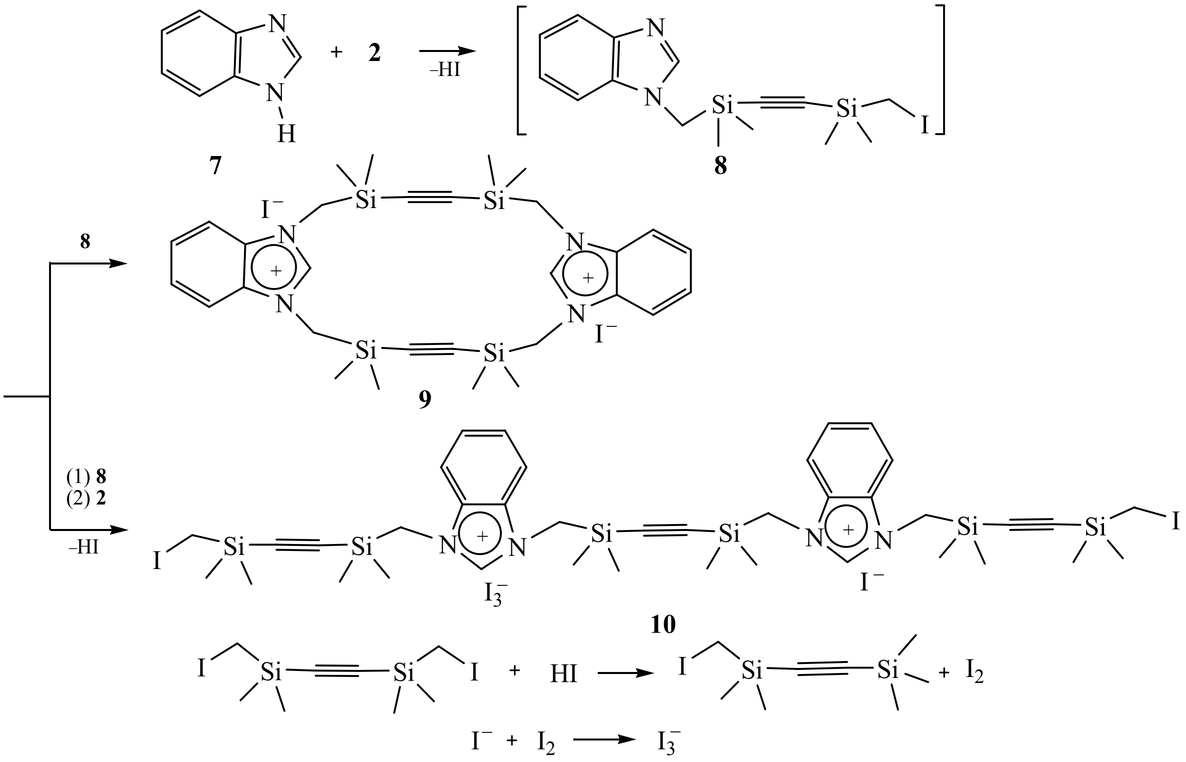
The formation of acetylenic silyl derivatives of benzimidazole **7** occurs, apparently, via the stage of N^1-alkylation with the formation of adduct **8**, which also enters the autoquaternization and alkylation reactions with bis[dimethyl(iodomethyl)silyl]ethyne **2** leading, respectively, to benzimidazolophane with dimethylene(tetramethyl)disilylethyne spacers **9** and poliiodide **10** (Scheme 2).

Hydrogen iodide formed in the reaction of N^1-alkylation is partially consumed in the reduction of the starting bis(iodomethyl)tetramethyldisilylethyne **2** to (iodomethyl)tetramethyldisilylethyne with the elimina-

Scheme 1.



Scheme 2.



tion of elemental iodine, which participates in the formation of triiodide anions of salts **6** and **10**.

The composition and structure of polyiodides **4**, **6**, **9**, **10** is proved by the methods of elemental analysis, ^{1}H, ^{13}C, ^{15}N, ^{29}Si, NMR, IR, Raman and UV spectroscopy. In the ^{1}H, ^{13}C NMR spectra of compounds **4**, **6,** and **9** the signals of carbon atoms of the terminal iodomethyl groups are lacking. The ^{29}Si NMR spectra of compounds **6** and **10** contain three signals corresponding to different silicon atoms in the molecule. In the two-dimensional ^{15}N NMR spectra of compounds **4**, **6**, **10** cross-peaks of the nitrogen atoms are present both with the protons of the azole cycle and with the protons of the methylene fragments of the ethyne molecule. The ^{29}Si NMR spectrum of compound **9** contains one signal proving the equivalence of the silicon atoms in the ring. The cyclic structure of benzimidazolophane **9** is also confirmed by the presence of cross-peak of the methylene groups with the equivalent nitrogen atoms of benzimidazole in its two-dimensional ^{15}N NMR spectrum.

Therefore, the studied reactions demonstrate the possibilities of the use of bis(iodomethyl)tetramethyldisilylethyne as an N-alkylating reagent for the preparation of earlier unknown linear and cyclic acetylenic silyl iodides, which are of interest from both theoretical and practical point of view.

EXPERIMENTAL

IR and Raman spectra were taken on a Vertex 70 Bruker instrument, UV spectra were recorded on a UV-Vis Lambda 35 spectrometer in MeCN. ^{1}H, ^{13}C, ^{29}Si, and ^{15}N NMR spectra were registered on Bruker DPX-400 and Bruker AV-400 at 400.13, 100.61, 161.98, and 40.56 MHz, respectively. Chemical shifts are measured relative to TMS (^{1}H, ^{13}C, ^{29}Si) and ^{15}N chemical shifts are given relative to nitromethane. Two-dimentional ^{1}H–^{15}N NMR spectra were registered using the HMBC-gp ^{1}H–^{15}N procedure. Elemental analysis was performed on a CHNS-analyzer Thermo Scientific Flash 2000. Iodine content was determined by mercurymetry, the content of silicon was determined by the method of dry burning. Melting points were determined on a Micro-Hot-Stage PolyTherm A apparatus. The reactions were monitored by ^{1}H, ^{13}C, ^{29}Si, ^{15}N NMR spectroscopy and by TLC on Silufol UV-254 plates (eluent acetone, visualization of chromatograms by iodine vapors).

Bis[dimethyl(iodomethyl)silyl]ethyne (2). The solution of 9.3 g (0.062 mol) of NaI and 6.09 g (0.025 mol) of bis(chloromethyl)tetramethyldisilylethyne in 80 mL of acetonitrile was stirred for 6 ч at reflux. The formed precipitate was filtered off, the solvent was removed, and the residue was distilled in a vacuum. Yield 7.44 g (70%), colorless crystals, mp 27–28°C, bp 134°C (2 mmHg). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 0.41 s (12H, CH$_3$), 2.15 s (4H, CH$_2$). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: –1.61 ($\underline{C}H_3$), –15.45 ($\underline{C}H_2I$), 112.39 (C≡). ^{29}Si NMR spectrum (CDCl$_3$), δ_{Si}: –17.62 ppm. Found, %: C 22.97; H 3.95; I 59.94; Si 13.47. $C_8H_{16}I_2Si_2$. Calculated, %: C 22.76; H 3.82; I 60.12; Si 13.30.

Reaction of imidazoles 1 and 7 with bis[dimethyl(iodomethyl)silyl]ethyne 2 *(general procedure).* The mixture of 2.4 mmol of the imidazole derivative **1** or **7** and 2.4 mmol of compound **2** was dissolved in 3 mL of acetonitrile at stirring in an argon flow. The solvent was removed by gradually increasing the temperature to 80°C. The formed homogeneous mass was stirred for 5 h at 175°C till disappearance of the imidazole derivative. The reaction mixture was dissolved in 15 mL of acetone, the formed precipitate was filtered off, dried in a vacuum, the filtrate was evaporated. The formed red oil was thrice sedimented from acetone with ether (acetone – ether, 1 : 6).

3-{Dimethyl[(2-methyl-1*H*-imidazolium-3-yl)methyl(dimethyl)silylethynyl]silylmethyl}-2-methyl-1*H*-imidazolium diiodide (4). Yield 0.14 g (20%), light-yellow powder, mp 255°C. Raman spectrum, ν, cm^{-1}: 2103 (SiC≡CSi). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.19 s (12H, CH$_3$), 2.5 s (6H, CH_{3imid}), 3.91 s (4H, CH$_2$), 7.44 s (H, CH_{arom}), 7.55 s (H, CH_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: –3.22 (CH$_3$), 10.98 (CH_{3imid}), 37.20 (CH$_2$), 113.00 (C≡C), 118.14, 122.21, 143.16 (CH_{arom}). ^{15}N NMR spectrum (DMSO-d_6), δ_N, ppm: –206.1. ^{29}Si NMR spectrum (DMSO-d_6), δ_{Si}, ppm: –17.44. UV spectrum, λ_{max}, nm, CH$_3$CN: 246 (I^-). Found, %: C 32.35; H 5.01; I 43.61; N 9.63; Si 10.03. $C_{16}H_{28}I_2N_4Si_2$. Calculated, %: C 32.77; H 4.81; I 43.28; N 9.55; Si 9.58.

Polyiodide (6). Yield 0.45 g (47%), red oil. IR spectrum, ν, cm^{-1}: 2108 (SiC≡CSi), 1064 (SiOSi). ^{1}H NMR spectrum (acetone-d_6) δ, ppm: 0.29 s (12H, 4CH$_3$), 0.37 s (12H, 4CH$_3$), 0.39 s (12H, 4CH$_3$), 2.17 s (6H, CH_{3imid}), 2.20 s (6H, CH_{3imid}), 4.17 s (4H, 2CH$_2$), 4.25 s (4H, 2CH$_2$), 4.37 s (4H, 2CH$_2$), 7.53 s (4H, $H^{4,5}$), 7.64 s (2H, H^4), 7.80 s (2H, H^5). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: –3.52, –3.43, –0.87 ($Si\underline{C}H_3$), 10.94, 11.03 ($\underline{C}H_3$), 37.95, 39.15, 39.73 ($\underline{C}H_2N$), 115.15, 117.61 (C≡), 121.98, 122.35, 122.21 ($C^{4,5}$), 143.12, 143.79 (C^2). ^{15}N NMR spectrum (acetone-d_6), δ_N, ppm: –206.6, –203.1 (N-1,3). ^{29}Si NMR spectrum (acetone-d_6), δ_{Si}, ppm: –17.38 (SiC≡), –15.68 (≡CSi), 6.66 (SiO). UV spectrum, λ_{max}, nm, CH_3CN: 245 (I^-); 292, 361 (I_3^-). Found, %: C 28.87; H 4.67; I 48.28; N 6.94; Si 10.52. $C_{38}H_{70}I_6N_8OSi_6$. Calculated, %: C 28.79; H 4.45; I 48.04; N 7.07; Si 10.63.

3,3,6,6,17,17,20,20-Octamethyl-15,22-diaza-1,8-diazonium-3,6,17,20-tetrasilapentacyclo-[20.6.1.1^{8,15}.0^{9,14}.0^{23,28}]triaconta-1(29),8(30),9(14),10,12,-23(28),24,26-octaene-4,18-diyn (9). Yield 0.23 g (23%), light-yellow powder, mp 254–258°C. Raman spectrum, ν, cm^{-1}: 2110 (SiC≡CSi). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.14 s (24H, CH_3), 4.38 s (8H, CH_2), 7.60 d (4H, $CH^{5,6}$), 7.99 d (4H, $CH^{4,7}$, ^3J 7.1 Hz), 9.52 s (2H, CH^2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: –2.38 (CH_3), 37.43 (CH_2), 111.44 (C≡), 114.67 ($C^{4,7}$), 126.80 ($C^{5,6}$), 131.95 ($C^{8,9}$), 142.16 (C^2). ^{15}N NMR spectrum (DMSO-d_6), δ_N: –221.5 ppm. ^{29}Si NMR spectrum (DMSO-d_6), δ_{Si}: –17.7 ppm. UV spectrum, λ_{max}, nm, CH_3CN: 246 (I^-). Found, %: C 39.05; H 5.03; I 31.71; N 7.02; Si 13.77. $C_{13}H_{21}IN_2OSi_2$. Calculated, %: C 38.61; H 5.23; I 31.38; N 6.93; Si 13.89.

Polyiodide (10). Yield 0.44 g (43%), red oil. IR spectrum, ν, cm^{-1}: 2029 (SiC≡CSi). ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.20 s (12H, $4CH_3$), 0.33 s (12H, $4CH_3$), 0.40 s (12H, $4CH_3$), 2.08 s (4H, CH_2I), 4.69 s (4H, $2CH_2$), 4.72 s (4H, $2CH_2$), 7.59 d (4H, $H^{5,6}$), 8.05 d (4H, $H^{4,7}$, ^3J 7.3 Hz), 9.77 s (2H, H^2). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: –15.85 ($\underline{C}H_2I$), –3.57, –3.49, –2.78 ($Si\underline{C}H_3$), 36.94, 37.42 ($\underline{C}H_2N$), 110.06, 110.43 (C≡), 114.37 ($C^{4,7}$), 126.04 ($C^{5,6}$), 130.52 ($C^{8,9}$), 131.67 (C^2). ^{15}N NMR spectrum (acetone-d_6), δ_N, ppm: –221.7. ^{29}Si NMR spectrum (acetone-d_6), δ_{Si}, ppm: –16.70 ($SiCH_2I$), –15.09 (SiC≡), –14.97 (≡CSi). UV spectrum, λ_{max}, nm, CH_3CN: 246 (I^-); 291, 361 (I_3^-). Found, %: C 30.87; H 4.07; I 50.58; N 3.44; Si 10.98. $C_{38}H_{58}I_6N_4Si_6$. Calculated, %: C 30.41; H 3.90; I 50.73; N 3.73; Si 11.23.

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