Alkylation of 2-Methylimidazole with Iodomethylsilanes

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Abstract—2-Methyl-1,3-bis[(1-methylsilolan-1-yl)methyl]-1*H*-imidazolium triiodide, 1,3-bis{[dimethyl-(phenyl)silyl]methyl}-2-methyl-1*H*-imidazolium iodide and triiodide, and cyclic 3,3,5,5,10-pentamethyl-4-oxa-7-aza-1-azonia-3,5-disilabicyclo[5.2.1]deca-1(10),8-diene iodide were synthesized by solvent-free reactions of 2-methyl-1*H*-imidazole with 1-(iodomethyl)-1-methylsilolane, (iodomethyl)(dimethyl)phenylsilane, and ethynyl(iodomethyl)(dimethyl)silanes, respectively, in the absence of base catalyst.

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Nitrogen heterocycles with side alkyl chains containing a silicon atom are important compounds for organoelement chemistry due to broad spectrum of their useful properties. They are used as solvents and nanohybrid catalysts [1–10] and components of stable electrolytes [11] and photoelectric cells [1]. Therefore, there is increased interest in the synthesis of new compounds of this series and studying their properties.

According to published data, organosilicon diazolium salts can be synthesized in two steps. In the first step, diazoles react with chloro or bromo derivatives of alkyl(alkoxy)- or alkylarylsilanes in which the silicon atom is covalently bound to three sp^3 -hybridized carbon atoms. N-Substituted diazoles thus formed are then subjected to alkylation at the second nitrogen atom with various alkylating agents. The reactions are carried out in ethanol in the presence of potassium hydroxide [12], in the presence of 3-(alkoxysilyl)alkyl isocyanates in THF [2, 11] or DMF [13], or without a solvent under pressure [14]. Analogous solvent-free reactions with mono- and bis(iodomethyl)silanes in the absence of basic reagents involved both nitrogen atoms with formation of linear and cyclic products, respectively [15].

In this work we were the first to study how hybridization of carbon atoms attached to silicon affect the alkylating ability of iodomethylsilanes toward 2-methylimidazole. For this purpose, 2-methylimidazole (1) was brought into reactions with iodomethyl-silanes with sp^3 - [1-(iodomethyl)-1-methylsilolane (2a) and 1-(iodomethyl)-1-methylsiletane (2b)], sp^2 -[(iodomethyl)(dimethyl)phenylsilane (2c)], and sp-hybridized carbon atom linked to silicon [(iodomethyl)(dimethyl)ethynylsilane (2d)].



The reaction of 1 with 2a was carried out under solvent free-conditions in the absence of a base by heating for 3 h at 100-105°C until the initial silane disappeared (according to the NMR data). The major product was triiodide 4 (yield 66%; Scheme 1). According to the ¹H, ¹³C, and ¹⁵N NMR monitoring data, the reaction begins with quaternization of the N^3 atom of 1 with formation of intermediate A which then reacts through the second nitrogen atom with the second iodomethylsilane molecule. Hydrogen iodide liberated during the process partially reduces compound 2a, as follows from the appearance of a methyl proton signal at δ 0.20 ppm in the ¹H NMR spectrum of the reaction mixture. Iodine generated from HI adds to iodide ion of salt 3, yielding triiodide 4 (Scheme 2). Iodide 3 was isolated as a minor product (yield 3.5%).



We failed to obtain analogous compounds by reaction of 2-methylimidazole (1) with 1-(iodomethyl)-1methylsiletane (2b). Under the given conditions, opening of the four-membered ring in unstable siletane 2b led to the formation of oligomeric compounds.

2-Methylimidazole (1) reacted with (iodomethyl)-(dimethyl)phenylsilane (2c) to give a mixture of iodide 5 and triiodide 6 in 49 and 25% yield, respectively (Scheme 3). Our results indicated insufficiency of molecular iodine (generated *in situ* by reduction of the iodomethyl group of 2c) in the reaction mixture. This may be due to formation of a stable donor-acceptor π -complex with the aromatic substituent of the reagent. Mono- and triiodides 5 and 6 were separated on the basis of their considerably different solubilities in acetone and chromatographic mobilities.

Triiodides 4 and 6 were isolated as red-brown thick oily materials. As they accumulated during the alkylation process, the reaction mixtures became homogeneous. The physicochemical properties of 4 and 6 allow us to class them with a new type of ionic liquids which can be used as surfactants, catalysts in organic synthesis, and solvents for organic, bioorganic, and inorganic substances.

By alkylation of **1** with ethynyl(iodomethyl)(dimethyl)silane (**2d**) we obtained cyclic iodide **8** in 33% yield. Its formation may be rationalized by cleavage of the Si– C_{sp} bond in the 1,3-dialkyl derivative by the action of liberated hydrogen iodide. Labile iodosilane **7** thus formed undergoes hydrolysis during the isolation procedure with atmospheric moisture of traces of water present in the solvent, and the subsequent cyclization yields bicyclic structure **8** (Scheme 4). Analogous Si– C_{sp} bond cleavage with formation of labile iodosilane was observed by us previously in the alkylation of 2-methylimidazole (**1**) with bis[(iodomethyl)dimethylsilyl]ethyne [16].

The ¹H and ¹³C NMR spectra of **8** lacked signals assignable to terminal \equiv CH groups. The ²⁹Si NMR spectrum of **8** contained one signal at δ_{Si} 6.7 ppm, which is typical of siloxanes. The two-dimensional ¹H–¹⁵N NMR spectrum of **8** displayed cross-peaks of the N¹ and N³ atoms with protons of both imidazole ring and methylene protons, indicating that the reaction involved both nitrogen atoms. The physical constants and spectral parameters of compound **8** coincided with those reported by us previously for the product obtained by reaction of 2-methylimidazole (**1**) with 1-(iodomethyl)-1,1,3,3,3-pentamethyldisiloxane, 3,3,5,5,10-pentamethyl-4-oxa-7-aza-1-azonia-3,5-disilabicyclo[5.2.1]deca-1(10),8-diene iodide [17].



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The UV spectra of monoiodides **3**, **5**, and **8** were fairly similar; the absorption maxima were located at λ 244–246 nm. In the UV spectra of triiodides **4** and **6** we observed absorption maxima at λ 291–292 and 362–364 nm, which are typical of triiodide anion [18].

Thus, the alkylation of 2-methylimidiazole with iodomethylsilanes containing sp^3 -, sp^2 -, or *sp*-hybridized carbon atom on the silicon gives 1,3-dialkyl-imidazolium iodides and triiodides or organylcyclosiloxane iodide, respectively, in one preparative step.

EXPERIMENTAL

The ¹H, ¹³C, ¹⁵N, and ²⁹Si NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13, 100.61, 40.56, and 79.5 MHz, respectively. The chemical shifts were measured relative to tetra-methylsilane (¹H, ¹³C, ²⁹Si) or nitromethane (¹⁵N). The UV spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer from solutions in acetonitrile. The iodine content was determined by mercurimetry, and the silicon content, by dry combustion. The melting points were measured with a PolyTherm A micro hot stage. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using acetone as eluent. Compounds **2a** and **2c** were synthesized previously [19, 20], but their spectral parameters were not given.

Compounds 2a–2d (*general procedure*). A mixture of 14 mmol of sodium iodide and 11 mmol of the corresponding (chloromethyl)silane in 50 mL of acetonitrile was refluxed for 6 h with stirring. After cooling, the precipitate was filtered off, the solvent was distilled off, and the residue was distilled under reduced pressure.

1-(Iodomethyl)-1-methylsilolane (2a). Yield 2.05 g (78%), colorless liquid, bp 77–78°C (10 mm).

¹H NMR spectrum (CDCl₃), δ, ppm: 0.31 s (3H, CH₃), 0.66 m (2H, 2-H), 0.76 m (2H, 5-H), 1.67 m (4H, 3-H, 4-H), 2.05 s (2H, CH₂I). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: -15.17 (CH₂I), -2.77 (CH₃), 12.74 (CH₂Si), 27.26 (CH₂). ²⁹Si NMR spectrum (CDCl₃): δ_{Si} 21.2 ppm. Found, %: C 30.43; H 5.48; I 52.17; Si 11.22. C₆H₁₃ISi. Calculated, %: C 30.01; H 5.46; I 52.84; Si 11.69.

1-(Iodomethyl)-1-methylsiletane (2b). Yield 1.86 g (75%), colorless liquid, bp 59–60°C (10 mm). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.38 s (3H, CH₃), 1.08 m (4H, 2-H, 4-H), 2.00 m (2H, 3-H), 2.18 s (2H, CH₂I). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: -13.24 (CH₂I), -1.41 (CH₃), 15.40 (CH₂Si), 17.06 (CH₂). ²⁹Si NMR spectrum (CDCl₃): δ_{Si} 19.0 ppm. Found, %: C 26.63; H 5.04; I 55.87; Si 12.52. C₅H₁₁ISi. Calculated, %: C 26.56; H 4.90; I 56.12; Si 12.42.

(Iodomethyl)(dimethyl)phenylsilane (2c). Yield 1.91 g (63%), colorless liquid, bp 95–98°C (1 mm). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.29 s (6H, CH₃), 2.02 s (2H, CH₂I), 7.20–7.38 m (5H, C₆H₅). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: –13.09 (CH₂I), –2.39 (CH₃); 128.46, 130.09, 134.15, 137.28 (C₆H₅). ²⁹Si NMR spectrum (CDCl₃): $\delta_{\rm Si}$ –1.9 ppm. Found, %: C 30.73; H 4.87; I 45.68; Si 10.31. C₉H₁₃ISi. Calculated, %: C 39.14; H 4.74; I 45.95; Si 10.17.

Ethynyl(iodomethyl)(dimethyl)silane (2d). Yield 1.28 g (52%), colorless liquid, bp 64–68°C (10 mm). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.34 s (6H, CH₃), 2.10 s (2H, CH₂I), 2.48 s (1H, \equiv CH). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: -15.43 (CH₂I), -2.01 (CH₃), 86.72 (C \equiv), 94.43 (\equiv CH). ²⁹Si NMR spectrum (CDCl₃): δ_{Si} –15.9 ppm. Found, %: C 27.01; H 4.93; I 56.15; Si 12.68. C₅H₉ISi. Calculated, %: C 26.80; H 4.05; I 56.62; Si 12.53.

Imidazolium iodides 3, 5, and 8 and triiodides 4 and 6 (*general procedure*). A mixture of 2.02 mmol of

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2-methylimidazole (1) and 4.04 mmol of (iodomethyl)silane 2a, 2c, or 2d was stirred for 3 h at 100–120°C until the initial (iodomethyl)silane disappeared (according to the ¹H and ¹³C NMR data). The mixture was cooled to room temperature, 20 mL of acetone was added, and the precipitate was filtered off, washed with acetone and diethyl ether, and dried. The filtrate containing triiodide 4 or 6 was evaporated, and the residue was purified by chromatography in a 10×900 -mm column charged with silica gel (MN Kieselgel 60, 0.063-0.2 mm) using acetone as eluent.

2-Methyl-1,3-bis[(**1-methylsilolan-1-yl)methyl]**-**1***H***-imidazolium iodide** (**3**). Yield 0.03 g (3.5%), white powder, mp 285°C. ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 0.05 s (6H, MeSi), 0.51 m (4H, CH₂Si), 0.58 m (4H, CH₂), 1.66 m (8H, CH₂), 2.38 s (3H, Me), 4.05 s (4H, CH₂N), 7.60 s (2H, 4-H, 5-H). ¹³C NMR spectrum (DMSO-*d*₆), $\delta_{\rm C}$, ppm: -4.40 (MeSi), 10.64 (Me), 9.81, 26.41 (CH₂), 38.05 (CH₂N), 121.40 (C⁴, C⁵), 142.92 (C²). ¹⁵N NMR spectrum (DMSO-*d*₆): $\delta_{\rm N}$ –199.6 ppm. ²⁹Si NMR spectrum (DMSO-*d*₆): $\delta_{\rm Si}$ 19.6 ppm.

2-Methyl-1,3-bis[(**1-methylsilolan-1-yl)methyl**]-**1***H***-imidazolium triiodide** (**4**). Yield 0.91 g (66%), $R_{\rm f}$ 0.87 (acetone). ¹H NMR spectrum (acetone- d_6), δ, ppm: 0.27 s (6H, MeSi), 0.69 m (4H, CH₂Si), 0.79 m (4H, CH₂), 1.57 m (8H, CH₂), 2.81 s (3H, Me), 4.21 s (4H, CH₂N), 7.74 s (2H, 4-H, 5-H). ¹³C NMR spectrum (acetone- d_6), $\delta_{\rm C}$, ppm: -4.44 (MeSi), 11.35 (Me), 11.00, 27.14 (CH₂), 39.37 (CH₂N), 122.60 (C⁴, C⁵), 143.97 (C²). ¹⁵N NMR spectrum (acetone- d_6): $\delta_{\rm N}$ -205.3 ppm. ²⁹Si NMR spectrum (acetone- d_6): $\delta_{\rm Si}$ 19.8 ppm. Found, %: C 27.73; H 4.13; I 54.85; N 4.47; Si 7.86. C₁₆H₃₁I₃N₂Si₂. Calculated, %: C 27.92; H 4.54; I 55.31; N 4.07; Si 8.16.

1,3-Bis{[dimethyl(phenyl)silyl]methyl}-2-methyl-1*H***-imidazolium iodide (5). Yield 0.50 g (49%), white powder, mp 265–267°C. ¹H NMR spectrum (DMSO-***d***₆), \delta, ppm: 0.31 s (12H, MeSi), 2.02 s (3H, Me), 3.98 s (4H, CH₂N), 7.32 s (2H, 4-H, 5-H), 7.40 m (5H, Ph). ¹³C NMR spectrum (DMSO-***d***₆), \delta_{\rm C}, ppm: –3.67 (MeSi), 10.09 (Me), 39.84 (CH₂N), 122.46 (C⁴, C⁵); 128.91, 130.95, 134.63, 135.30 (Ph); 142.53 (C²). ¹⁵N NMR spectrum (DMSO-***d***₆): \delta_{\rm N} –206.2 ppm. ²⁹Si NMR spectrum (DMSO-***d***₆): \delta_{\rm Si} –2.5 ppm. Found, %: C 52.45; H 6.04; I 24.66; N 5.18; Si 11.63. C₂₂H₃₁IN₂Si₂. Calculated, %: C 52.16; H 6.17; I 25.05; N 5.53; Si 11.09.**

1,3-Bis{[dimethyl(phenyl)silyl]methyl}-2-methyl-1*H*-imidazolium triiodide (6). Yield 0.48 g (25%), *R*_f 0.87 (acetone). ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 0.51 s (12H, MeSi), 2.41 s (3H, Me), 4.17 s (4H, CH₂N), 7.38 s (2H, 4-H, 5-H), 7.59 m (5H, Ph). ¹³C NMR spectrum (acetone-*d*₆), $\delta_{\rm C}$, ppm: –4.34 (MeSi), 10.88 (Me), 39.69 (CH₂N), 118.49 (C⁴, C⁵); 123.14, 129.04, 131.03, 134.64 (Ph); 141.48 (C²). ¹⁵N NMR spectrum (acetone-*d*₆): $\delta_{\rm N}$ –204.8 ppm. ²⁹Si NMR spectrum (acetone-*d*₆): $\delta_{\rm Si}$ –1.9 ppm. Found, %: C 34.72; H 4.14; I 49.72; N 4.05; Si 6.91. C₂₂H₃₁I₃N₂Si₂. Calculated, %: C 34.75; H 4.11; I 50.07; N 3.68; Si 7.39.

3,3,5,5,10-Pentamethyl-4-oxa-7-aza-1-azonia-3,5disilabicyclo[5.2.1]deca-1(10),8-diene iodide (8). Yield 0.25 g (34%), light yellow powder. The physical constants and spectral characteristics of the product coincided with those reported in [17].

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