

Acyl Iodides in Organic Synthesis: XII.* Reactions with Organosilicon Amines

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Abstract—Reactions were investigated between acyl iodides RCOI (R = Me, Ph) and organosilicon amines of two classes: trimethyl(diethylamino)silane, dimethyl-bis(diethylamino)silane, and hexamethyldisilazane on the one hand, and 3-aminopropyl(triorganyl)silanes $H_2N(CH_2)_3SiX_3$ (X = Et, EtO) on the other hand. The reaction of RCOI with trimethyl(diethylamino)silane Me_3SiNEt_2 occurred with a cleavage of the Si–N bond and the formation of N,N-diethylacet- or -benzamides and trimethyliodosilane separated in a mixture with hexamethyldisiloxane. At the reaction of acyl iodides RCOI (R = Me, Ph) with dimethyl-bis(diethylamino)silane in the ratio 2:1 in benzene solution both Si–N were ruptured leading to the diethylamide of the corresponding acid and dimethyldiiodosilane. The main product of the reaction of acetyl iodide with hexamethyldisilazane at the molar ratio 2:1 was diacetyl-imide $(MeCO)_2NH$. This reaction can be recommended as a simple and convenient preparation procedure for diacylimides. The exothermal reaction of the acetyl iodide with 3-aminopropyl(triethyl)- and -(triethoxy)silanes at the molar ratio of the reagents 1:1 without solvent resulted in quaternary ammonium salts, hydroiodides of the corresponding acetyl-amides $I-MeCON^+H_2(CH_2)_3SiX_3$ (X = Et, OEt).

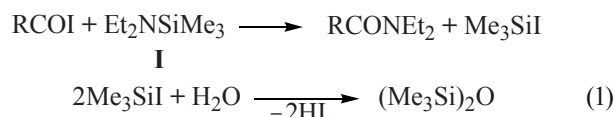
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The exothermal reaction of acyl chlorides with primary and secondary amines is known to lead to the formation of quaternary ammonium salts. Later in the presence of excess amine, alkali metal hydroxides or carbonates etc. these salts were converted into the corresponding acetyl-amides [2]. Therewith the secondary amines considerably more difficult undergo the dehydrochlorination than the primary analogs. The reaction of aliphatic acyl chlorides with tertiary amines takes two routes: either salt adducts form or the initial tertiary amine effects the dehydrochlorination of the acyl chloride into ketene [2].

The data on the reactions of acyl iodides with organic nitrogen-containing compounds is limited by their reactions with ammonia, 2,4-dichloropyridine, 2-bromopyridine, and 2-chloromorpholine [3]. The reaction of acyl iodides with organosilicon amines containing N–C or N–Si bonds has not been investigated up till now. In extension of research on the application of acyl iodides as reagents and synthons in organic and organoelemental synthesis we studied the

reactions of RCOI (R = Me, Ph) with organosilicon amines of two classes, namely, with trimethyl(diethylamino)silane (**I**), dimethyl-bis(diethylamino)silane (**II**), and hexamethyldisilazane (**III**) on the one hand, and 3-aminopropyl(triorganyl)silanes $H_2N(CH_2)_3SiX_3$ on the other hand.

The reaction of RCOI (R = Me, Ph) with trimethyl(diethylamino)silane Me_3SiNEt_2 (**I**) was carried out in benzene. The reaction with acetyl iodide (R = Me) is exothermal, does not require additional heating, and proceeds with the cleavage of the Si–N bond in silane **I** providing N,N-diethylacetamide and trimethyliodosilane. According to 1H and ^{29}Si NMR data alongside the trimethyliodosilane the reaction mixture contained also hexamethyldisiloxane in a ratio $Me_3SiI-(Me_3Si)_2O \approx 1:3$.



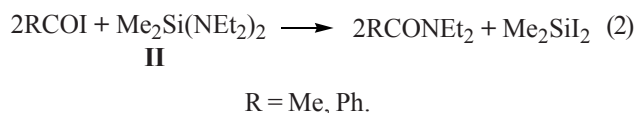
R = Me, Ph.

* For communication XI, see [1].

The reaction of benzoyl iodide with $\text{Me}_3\text{SiNEt}_2$ (**I**) in benzene was only slightly exothermal and required for its completion a heating at 70–80°C for 6 h. In this case alongside the formed according to equation (1) *N,N*-diethylbenzamide and trimethyliodosilane was also identified hexamethyldisiloxane in a similar ratio $\text{Me}_3\text{SiI}-(\text{Me}_3\text{Si})_2\text{O} \approx 1:3$. The formation of hexaalkyldisiloxanes from trialkyliodosilanes in glass reactors in the absence of moisture was also observed before [4, 5]. This may originate from the reaction of R_3SiI with water usually strongly adsorbed by the glass of the reaction vessels.

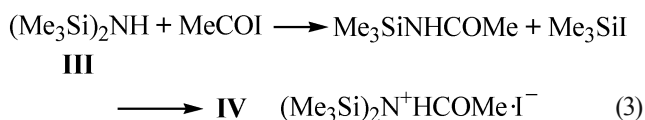
It cannot be excluded that in this event the formation of the hexamethyldisiloxane may originate from the reaction of trimethyliodosilane with initial acyl iodides.

In the course of the reaction of acyl iodides RCOI ($\text{R} = \text{Me}, \text{Ph}$) with dimethyl-bis(diethylamino)silane (**II**) in a ratio 2:1 in benzene solution both Si-N bonds suffered cleavage giving the diethylamide of the corresponding acid and dimethyldiiodosilane.

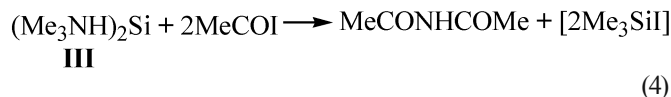


The exothermal reaction between acetyl iodide and hexamethyldisilazane (**III**) proceeded with the cleavage of one or two Si-N bonds depending on the reagents ratio. At their equimolar ratio the final product was a complex of trimethylsilylacetamide with trimethyliodosilane (main products of this reaction) corresponding to *N*-acetamidohexamethyldisilazane hydroiodide (**IV**).

Compound **IV** is amorphous yellow solid whose structure is proved by ^1H and IR spectra.



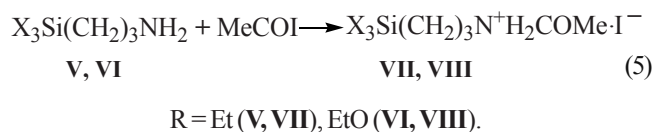
The main reaction product of the reaction between acetyl iodide and hexamethyldisilazane (**III**) in the molar ratio 2:1 was diacetyl imide $(\text{MeCO})_2\text{NH}$. Its formation originated from the secondary reaction of the Si-N bond cleavage in the intermediately arising *N*-trimethylsilylacetamide.



The main procedure for preparation of acyclic imides is based on the reaction of amides with acylating agents, in particular, with carboxylic acids chlorides. A selective proceeding of the reaction required its promotion, in particular, with such strong bases like sodium hydride and Grignard reagents [6].

We failed to identify the second product of reaction (4), trimethyliodosilane, for it was completely converted into hexamethyldisiloxane.

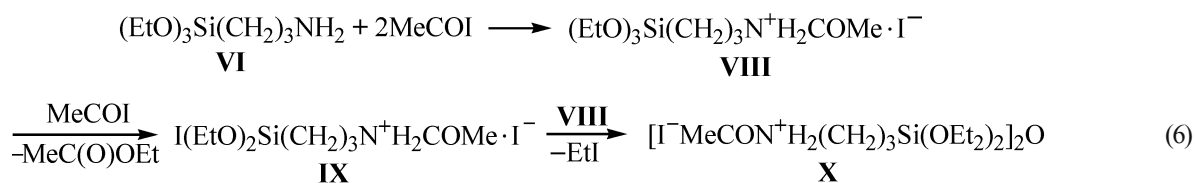
The exothermal reaction of acetyl iodide with 3-aminopropyl(triethyl)- and -(triethoxy)silanes (**V**) and (**VI**) at the molar reagents ratio 1:1 without solvent resulted in quaternary ammonium salts, hydroiodides of the corresponding acetamides $\text{I-MeCON}^+\text{H}_2(\text{CH}_2)_3\text{SiX}_3$ (equation 5).



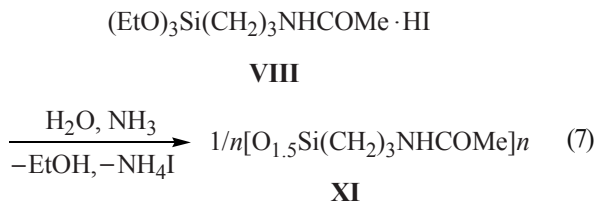
The obtained salt adducts **VII** and **VIII** are insoluble in organic solvents and are moderately hygroscopic. Their purification was performed by maintaining in a vacuum (residual pressure 1–0.1 mm Hg) to remove volatile compounds (initial acetyl iodide, iodine) from the salt.

In this case the ethoxy groups of organosilicon amine **VI** were not involved into the reaction with acetyl iodide. Yet we previously established that the Si-O bonds in alkoxy silanes quite easily were cleaved under the action of RCOI [7]. The observed direction of the reaction between MeCOI and $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ (**VI**) showed that the acyl iodides far easier reacted with the NH_2 group than with SiOEt .

However when an excess of the acetyl iodide is involved into the reaction with *N*-(3-triethoxysilylpropyl)amine (**VI**) the pattern changes. For instance, in the reaction of organosilicon amine **VI** with a double quantity of MeCOI we obtained disiloxane $[\text{I-MeCON}^+\text{H}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_2]_2\text{O}$ (**X**). Its formation showed that the reaction of amine **VI** with acetyl iodide in this event affected not only NH_2 group but also the Si-OEt moiety with the cleavage of the Si-O . The intermediate product of this process was a highly reactive iodosilane **IX**. The reaction of compound **IX** with preliminary formed salt **VIII** occurred with the characteristic for iodosilanes [8, 9] cleavage of the O-C bond in the Si-OEt moiety and resulted in disiloxane **X**.



3-Acetamidopropyl(triethoxy)silane hydroiodide (**VIII**) was tested as a monomer for obtaining on its basis of a cross-linked organosilicon polymer, poly[*N*-3-silsesquioxanylpropylacetamide] $1/n[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{NHC(O)Me}]_n$ (**XI**). Formerly we obtained this carbofunctionalized organosilicon polymer by the hydrolysis of *N*-(3-triethoxysilylpropyl)acetamide prepared by condensation of *N*-(3-triethoxysilylpropyl)amine with acetamide. This polymer exhibit the property of a highly efficient complexing sorbent for noble metals (Au, Pd, Pt) [9].



EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 from thin films. ^1H and ^{29}Si NMR spectra were registered on a spectrometer Bruker DPX-400 with operating frequency 400 MHz from solutions in CDCl_3 (internal references TMS and HMDS). GC-MS measurements were performed on an instrument Hewlett-Packard 5971 A (Electron impact, 70 eV, mass-selective detector), chromatograph HP-5890, column Ultra-2 (5% of phenylmethylsilicone), vaporizer temperature 250°C , oven ramp $70\text{--}280^\circ\text{C}$ at a rate 20 deg/min .

Initial acyl iodides were obtained by reaction of anhydrous sodium iodide with the corresponding acyl chlorides [8].

Reaction of acetyl iodide with trimethyl(diethylamino)silane (I). To a solution of 10.5 g (72 mmol) of trimethyl(diethylamino)silane in 10 ml of anhydrous benzene was added dropwise at stirring 12.29 g (72 mmol) of acetyl iodide. The reaction mixture was left standing for 72 h at room temperature, then by distillation under the atmospheric pressure was isolated a fraction weighing 15.1 g of bp $105\text{--}108^\circ\text{C}$ composed of trimethyliodosilane and hexamethyldisiloxane in a molar ratio 1:3. ^1H NMR spectrum, δ , ppm: 0.049 s (18H, 6CH_3), 0.76 s (9H,

3CH_3). ^{29}Si NMR spectrum, δ , ppm: 8.02 (Me_3SiI), 6.78 ($\text{Me}_3\text{SiOSiMe}_3$). By distillation of the residue in a vacuum was isolated 9.7 g (84%) of *N,N*-diethylacetamide, bp 63°C (9 mm Hg), n_D^{20} 1.4353 (bp $185\text{--}186^\circ\text{C}$, n_D^{20} 1.4374 [11]). Mass spectrum, m/z (I_{rel} , %): 115 (45) [M^+], 100 (10), 86 (5), 72 (22), 58 (100), 44 (32), 30 (15), 15 (6).

Reaction of benzoyl iodide with trimethyl(diethylamino)silane (I). To a solution of 1.16 g (80 mmol) of trimethyl(diethylamino)silane in 5 ml of anhydrous benzene was added at stirring 1.82 g (80 mmol) of benzoyl iodide. The reaction mixture was heated for 6 h at 78°C . By distillation of the mixture under the atmospheric pressure was isolated a fraction weighing 3.41 g, bp $105\text{--}108^\circ\text{C}$, composed of trimethyliodosilane and hexamethyldisiloxane in a ratio 1:3. ^1H NMR spectrum, δ , ppm: 0.06 s (18H, 6CH_3), 0.79 s (9H, 3CH_3). ^{29}Si NMR spectrum, δ , ppm: 8.02 (Me_3SiI), 6.78 ($\text{Me}_3\text{SiOSiMe}_3$).

By distillation of the residue in a vacuum was isolated 1.19 g (84%) of *N,N*-diethylbenzamide, bp 102°C (2 mm Hg) (bp $280\text{--}282^\circ\text{C}$ [12]). Mass spectrum, m/z (I_{rel} , %): 176 (25) [M^+], 162 (2), 148 (3), 134 (3), 105 (91), 91 (2), 58 (3), 42 (5).

Reaction of acetyl iodide with dimethylbis(diethylamino)silane (II). To a solution of 20.24 g (10 mmol) of dimethylbis(diethylamino)silane in 5 ml of benzene was added at stirring 4.25 g (25 mmol) of acetyl iodide. The reaction mixture was left standing for 3 h at room temperature, then by distillation under the atmospheric pressure was isolated 0.07 g (3%) of dimethyldiiodosilane, bp $160\text{--}162^\circ\text{C}$ (bp 167°C [13]). Mass spectrum, m/z (I_{rel} , %): 295 (5) [M^+], 281 (100), 59 (5).

By distillation of the residue in a vacuum was isolated 0.73 g (32%) of *N,N*-diethylacetamide, bp 61°C (8 mm Hg) (bp $185\text{--}186^\circ\text{C}$ [11]). Mass spectrum, m/z (I_{rel} , %): 115 (20) [M^+], 100 (5), 83 (5), 72 (10), 58 (100), 44 (45).

Reaction of benzoyl iodide with dimethyl-bis(diethylamino)silane (II). To 1.53 g (7.5 mmol) of dimethyl-bis(diethylamino)silane in 5 ml of benzene was added dropwise at stirring 3.51 g (15 mmol) of benzoyl iodide. The reaction mixture was left standing for 3 h at room temperature, then by distillation under the atmo-

spheric pressure was isolated 0.19 g (8%) dimethyl-diiodosilane, bp 160–162°C (bp 167°C [13]). Mass spectrum, m/z (I_{rel} , %): 295 (5) $[M]^+$, 281 (100), 59 (5).

By distillation of the residue in a vacuum was isolated 0.78 g (29%) of *N,N*-diethylbenzamide, bp 102°C (2 mm Hg) (bp 280–282°C [12]). Mass spectrum, m/z (I_{rel} , %): 176 (20) $[M]^+$, 162 (2), 148 (5), 105 (100), 77 (65), 51 (38), 42 (15).

Reaction of acetyl iodide with hexamethyldisilazane (III). *a.* To 1.6 g (10 mmol) of hexamethyldisilazane was slowly added at stirring 1.7 g (10 mmol) of acetyl iodide. The reaction mixture self-heated to 60°C. Its further heating at 60–80°C for 4 h furnished 3.0 g of crystalline *N*-acetamido-hexamethyldisilazane hydroiodide. IR spectrum, ν , cm^{-1} : 3420 (NH), 2960, 2900 (CH), 1720 (CO), 1150, 1120, 960 (MeSi). Found, %: C 29.42; H 6.72; I 39.29; N 4.21; Si 17.12. $\text{C}_8\text{H}_{22}\text{INSiO}$. Calculated, %: C 29.00; H 6.69; I 38.30; N 4.23; Si 16.95.

b. To 1.6 g (10 mmol) of hexamethyldisilazane was added at stirring 3.4 g (20 mmol) of acetyl iodide. The reaction mixture self-heated to 70°C. After its further keeping for 4–5 h without heating we separated by simple distillation 1.6 g (95%) of hexamethyldisiloxane, bp 98–100°C, n_D^{20} 1.3780 (bp 98–101°C, n_D^{20} 1.3774 [14]). The recrystallization of the residue provided 1.1 g (57%) of diacetyl-imide, mp 76–77°C (Et_2O) (mp 78°C [6]).

Reaction of acetyl iodide with *N*-(3-triethylsilylpropyl)amine (IV). To 6.7 g (40 mmol) of *N*-(3-triethylsilylpropyl)amine was added dropwise 6.5 g (40 mmol) of acetyl iodide. The reaction mixture self-heated to 50°C. On cooling to room temperature it was subjected to a vacuum (residual pressure 0–0.1 mm Hg). We obtained 7 g (53%) of *N*-(3-triethylsilylpropyl)-*N*-acetyl-**amide (VII)**. IR spectrum, cm^{-1} : 1675 (ν_{CO} in secondary amides, free), 1635 (ν_{CO} in secondary amides, associated), 1550 [δ_{NH} in secondary amides, (amide II band)], 1000 ($\nu_{\text{Si-Et}}$), 750–700 (ν_{NH}). Found, %: C 41.46; H 8.96; I 33.39; N 4.34; Si 8.25. $\text{C}_{11}\text{H}_{26}\text{INOSi}$. Calculated, %: C 38.48; H 7.58; I 37.02; N 4.08; Si 8.16.

Reaction of acetyl iodide with *N*-(3-triethoxysilylpropyl)amine (V). *a.* To 22.2 g (100 mmol) of amine **V** was added dropwise 17 g (100 mmol) of acetyl iodide. The reaction mixture self-heated to 60°C. On completion of acetyl iodide addition the reaction mixture was cooled to room temperature and was subjected to a vacuum (residual pressure 0–0.1 mm Hg). We obtained 20 g (52%) of *N*-(3-triethoxysilylpropyl)-*N*-acetyl-**amide hydroiodide (VIII)**. IR spectrum, cm^{-1} : 1680 (ν_{CO} in secondary amides, free), 1640 (ν_{CO} in secondary amides,

associated), 1530 [δ_{NH} in secondary amides, (amide II band)]. Found, %: C 31.13; H 6.60; I 33.75; N 4.04; Si 7.5. $\text{C}_{11}\text{H}_{26}\text{INO}_4\text{Si}$. Calculated, %: C 33.76; H 6.65; I 32.48; N 3.58; Si 7.16.

b. To a solution of 11.1 g (50 mmol) of amine **V** in 20 ml of octane was added 8.5 g (50 mmol) of acetyl iodide. The reaction mixture self-heated to 50°C. The reaction mixture was stirred for 0.5 h till its cooling. The reaction mixture divided in two layers that were separated on a separatory funnel. The bottom layer was kept in a vacuum to remove the volatile substances, and afterwards we isolated 12 g (61%) of *N*-(3-triethoxysilylpropyl)-*N*-acetyl-**amide hydroiodide (VIII)**. Found, %: C 33.43; H 6.80; I 34.18; N 4.43; Si 7.56. $\text{C}_{11}\text{H}_{26}\text{INO}_4\text{Si}$. Calculated, %: C 33.75; H 6.65; I 32.47; N 3.58; Si 7.16.

c. To 2.5 g (10 mmol) of amine **V** was slowly added dropwise at stirring on a magnetic stirrer 3.4 g (20 mmol) of acetyl iodide. The reaction mixture vigorously self-heated with HI liberation. Reaction time 40 min. On completion of the reaction the reaction mixture was kept in a vacuum to remove the volatile substances. We obtained 3.2 g (47%) of **[di(3-*N*-acetylaminopropyl)-tetraethoxy]disiloxane *N,N'*-dihydroiodide (X)**. IR spectrum, cm^{-1} : 1690 (ν_{CO} in secondary amides, free), 1650 (ν_{CO} in secondary amides, associated), 1520 [δ_{NH} in secondary amides (amide II band)], 1690 ($\nu_{\text{C=O}}$), 1100–1000 (ν_{SiOSi}). Found, %: C 28.06; H 5.28; I 40.00; N 3.95; Si 8.38. $\text{C}_{18}\text{H}_{42}\text{I}_2\text{N}_2\text{O}_7\text{Si}_2$. Calculated, %: C 31.95; H 6.21; I 37.57; N 4.14; Si 8.28.

Hydrolysis of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{Me}$ -HI (VIII). To 6 g of *N*-(3-triethoxysilylpropyl)-*N*-acetyl-**amide hydroiodide** was added 20 ml of NaOH solution to pH 8. The mixture was stirred for 3–4 h at room temperature, and thereafter through the reaction mixture a flow was passed of gaseous ammonia for 2 h. The separated precipitate was filtered off, washed with water, with acetone, ethyl ether, and dried over P_2O_5 . We isolated 2 g (80%) of polymer $1/n[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{NHCOMe}]_n$ insoluble and nonswelling in water and organic solvents. Found, %: C 38.44; H 6.76; N 9.20; Si 19.98. $\text{C}_5\text{H}_{10}\text{NO}_{2.5}\text{Si}$. Calculated, %: C 39.47; H 6.57; N 9.21; Si 18.42.

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