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Reaction of Iodo(trimethyl)silane with *N*,*N*-Dimethyl Carboxylic Acid Amides

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Abstract—The reactions of iodo(trimethyl)silane with *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide Me_2NCOR (R = H, Me) at a molar ratio of 1 : 2 involved mainly cleavage of the N–C(=O) bond with formation of up to 80% of *N*,*N*-dimethyltrimethylsilylamine Me_3SiNMe_2 and the corresponding acyl iodide RCOI. In the reaction with *N*,*N*-dimethylformamide, formyl iodide HCOI was detected for the first time by gas chromatography–mass spectrometry. The contribution of Me–N bond cleavage, leading to *N*-methyl-*N*-trimethylsilyl derivative $Me(Me_3Si)NCOR$ and methyl iodide was considerably smaller. Another by-product was the corresponding *N*-methyl imide $MeN(COR)_2$ formed by reaction of the initial amide with acyl iodide. The primary intermediate in the reaction of iodo(trimethyl)silane with DMF and DMA is quaternary ammonium salt $[Me_2(Me_3Si)N^+COR]I^-$ which decomposes via dissociation of the N–CO and N–Me bonds.

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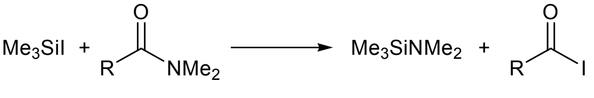
We previously noted similarity in the reactivities of acyl iodides and iodo(trimethyl)silane [1] which was introduced by us for the first time into organic and organometallic synthetic practice [2–6]. We recently showed that reactions of acyl iodides RCOI (R = Me, Ph) with *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) involve elimination of one methyl group from the nitrogen atom with formation of the corresponding *N*-methyl dicarboximide (including mixed one). The process is accompanied by transacylation, i.e., acyl group exchange between the reagents [7].

We now report that iodo(trimethyl)silane reacts with excess DMF or DMA (molar ratio 1 : 2) under mild conditions (boiling methylene chloride, 5 h) to give *N*,*N*-dimethyltrimethylsilylamine as a result of cleavage of the N–(C=O) bond (Scheme 1).

Scheme 1.

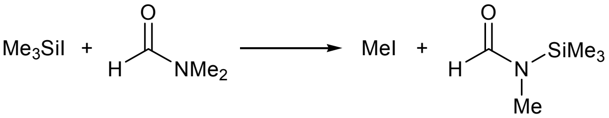


R = H, Me.

This reaction is reversible, but the equilibrium can be displaced almost completely toward the products using a considerable excess of the initial *N*,*N*-dimethyl carboxamide. *N*,*N*-Dimethyltrimethylsilylamine was isolated by distillation of the reaction mixture in 32 (R = H) or 25% yield (R = Me). Subsequent distillation of the residue was not performed to avoid thermolysis. However, by gas chromatography–mass spectrometry we identified 61% of Me_3SiNMe_2, 11% of MeI, 5% of HCOI, 1% of $MeN(CHO)_2$, and 11% of $Me(Me_3Si)NCHO$ (R = H) and 76% of Me_3SiNMe_2, 3% of MeI, and 5% $MeN(COMe)_2$ (R = Me). In both cases, the still residue contained ~40% of unreacted initial amide which was taken in excess. No iodo(trimethyl)silane (expected product of the reverse reaction) was detected. Thus the overall yield of Me_3SiNMe_2 was 83% for R = H and 77% for R = Me.

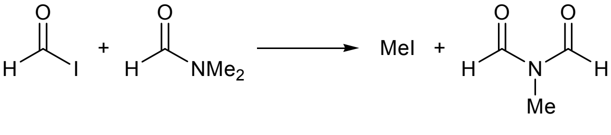
Interestingly, the reaction of Me_3SiI with DMF afforded *N*-methyl-*N*-trimethylsilylformamide as a result of cleavage of the Me–N bond (Scheme 2).

Scheme 2.



In this case iodo(trimethyl)silane reacts with DMF in a way similar to acyl iodides [7]. It was even more surprising that we detected formyl iodide HCOI among the products by GC–MS. The possibility for the existence of formyl iodide was so far doubtful. The formation of HCOI was also confirmed by the presence of *N*-formyl-*N*-methylformamide among the products (Scheme 3). Analogous elimination of one methyl group from DMF by the action of acyl iodides was described by us previously [7].

Scheme 3.



The reaction of Me_3SiI with DMA involves only processes shown in Schemes 1 and 3, which lead to formation of Me_3SiNMe_2 and $MeN(COMe)_2$, respectively. The primary intermediate in the reactions of iodo(trimethyl)silane with DMF and DMA is the adduct $[Me_2(Me_3Si)N^+COR]\ I^-$ (Schemes 1, 2). This labile quaternary ammonium salt readily undergoes decomposition via cleavage of the N–C=O and $N–CH_3$ bonds as a result of attack by iodide ion on the most electrophilic carbonyl carbon atom and (to a lesser extent) on the carbon atom in the *N*-methyl group. The decomposition products are, respectively, *N*,*N*-dimethyltrimethylsilylamine and *N*-methyl-*N*-trimethylsilylcarboxamide. Cleavage of the most reactive N–Si bond, which should lead to the initial reactants, does not occur due to the presence of excess initial *N*,*N*-dimethyl carboxamide.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.1, 100.61, and 79.5 MHz, respectively, using $CDCl_3$ as solvent and cyclohexane as internal reference. Gas chromatographic–mass spectrometric analysis was performed on a Hewlett–Packard HP 5890 gas chromatograph coupled with an HP 5971A mass-selective detector (electron impact, 70 eV; Ultra-2 column, stationary phase 5% of phenylmethylsilicone; injector temperature 250°C, oven temperature programming from 70 to 280°C at a rate of 20 deg/min). Gas chromatographic analysis was performed on a Tsvet-500 chromatograph equipped with a thermal conductivity detector and a glass column, 3 m × 4 mm, packed with 10% of PSM-1000 on Inerton-Super (0.125–0.150 mm); carrier gas helium.

Reaction of iodo(trimethyl)silane with *N*,*N*-dimethylformamide. Iodo(trimethyl)silane, 7.25 g (0.036 mol), was added dropwise to a solution of 5.29 g (0.072 mol) of *N*,*N*-dimethylformamide in 10 ml of methylene chloride, and the mixture was stirred for 5 h at 40°C. Distillation gave 1.35 g (32%) of Me_3SiNMe_2, bp 80–112°C; published data [8]: bp 86°C, $n_D^{20} = 1.3950$. Mass spectrum, m/z (I_{rel}, %): 117 (40) $[M]^+$, 73 (100), 61 (5), 45 (20), 15 (9); and 1.44 g (40%) of initial DMF, bp 150–160°C; published data [9]: bp 153°C, $n_D^{20} = 1.4305$. Mass spectrum, m/z (I_{rel}, %): 73 (100) $[M]^+$, 58 (30), 44 (90), 15 (45). According to the GC–MS data, the still residue, 3.49 g, contained [fraction, %; mass spectrum, m/z (I_{rel}, %)]: 11% (0.47 g) of MeI, 142 (100) $[M]^+$, 127 (40), 15 (86); 5% (0.22 g) of HCOI, 156 (15) $[M]^+$, 127 (35), 29 (80); 61% (2.14 g) of Me_3SiNMe_2, 117 (40) $[M]^+$, 73 (100), 57 (5), 45 (20), 15 (10); 11% (0.49 g) of Me_2NCHO, 73 (100) $[M]^+$, 58 (30), 44 (90), 15 (45); 1% (0.06 g) of $MeN(CHO)_2$, 87 (30) $[M]^+$, 72 (24), 57 (35), 29 (72), 15 (40); and 11% (0.49 g) of $MeN(SiMe_3)CHO$, 131 (40) $[M]^+$, 116 (17), 102 (35), 73 (60) 58 (25), 29 (7), 15 (10).

Reaction of iodo(trimethyl)silane with *N*,*N*-dimethylacetamide. Iodo(trimethyl)silane, 12.4 g (0.062 mol), was added dropwise under stirring to 10.8 g (0.124 mol) of *N*,*N*-dimethylacetamide in 10 ml of methylene chloride, and the mixture was stirred for 5 h at 35°C. Distillation gave 2.13 g (29%) of Me_3SiNMe_2, bp 80–120°C. Mass spectrum, m/z (I_{rel}, %): 117 (10) $[M]^+$, 102 (70), 87 (12), 73 (59), 58 (15), 44 (12), 15 (3); and 4.03 g (40%) of initial DMA, bp 160–168°C; published data [10]: bp 165°C, n_D^{20} = 1.4380. Mass spectrum, m/z (I_{rel}, %): 87 (50) $[M]^+$, 72 (20), 58 (5), 44 (100), 30 (15), 15 (30). According to the GC–MS data, the still residue, 4.5 g, contained [fraction, %; mass spectrum, m/z (I_{rel}, %)]: 3% (0.16 g) of MeI, 142 (100) $[M]^+$,127 (40), 15 (86); 76% (3.44 g) of Me_3SiNMe_2, 117 (40) $[M]^+$, 73 (100), 57 (5), 45 (20), 15 (10); 15% (0.79 g) of Me_2NCOMe, 87 (60) $[M]^+$, 72 (20), 57 (35), 44 (100), 15 (40); 5% (0.24 g) of $MeN(COMe)_2$, 115 (10) $[M]^+$, 100 (35), 72 (34), 57 (15), 4 (100), 29 (22), 15 (30); and 1% (0.07 g) of $MeN(SiMe_3)_2$, 175 (2), 87 (20), 73 (100), 44 (35).

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