A novel route to chlorodimethylsilane

Jerzy J. Chruściel

Abstract: A new efficient laboratory method of preparation of chlorodimethylsilane ($Cl(CH_3)_2SiH$) has been elaborated, which is a modification of the Eaborn et al. method (34) and is based on a *transsilylation reaction of substituted (amino)dimethylhydrosilanes, R_2NSiMe_2H* (R_2 = Me_2, Et_2, $(CH_2)_n$, etc.) with *dimethyldichlorosilane (Me_2SiCl_2)*. The reaction proceeds at reflux, at 70°C, preferably with an excess of Me_2SiCl_2. The most important feature of this novel method is a recovery of intermediate (amino)chlorodimethylsilanes (R_2NSiMe_2Cl), which can be again reduced to R_2NSiMe_2H. *The transsilylation mechanism* has been proven by reaction of (diethylamino)methylphenylsilane with Me_2SiCl_2. The products of this latter reaction are HMePhSiCl and R_2NSiMe_2Cl, thus a disproportionation mechanism has been excluded. New substituted bis(amino)dimethylsilanes ($(R_2N)_2SiMe_2$), (amino)dimethylchlorosilanes (R_2NSiMe_2Cl), and (amino)dimethylhydrosilanes (R_2NSiMe_2H) have been synthesized and characterized by NMR and IR.

Key words: chlorodimethylsilane, $(CH_3)_2SiHCl$, synthesis, new laboratory method, transsilylation mechanism.

Résumé : On a développé une nouvelle méthode de préparation du chlorodiméthylsilane, $Cl(CH_3)_2SiH$, efficace au niveau du laboratoire. Il s'agit d'une modification de la méthode de Eaborn et al. (34) et elle est basée sur une réaction de transsilylation de (amino)diméthylhydrosilanes substitués, R_2NSiMe_2H (R_2 = Me_2, Et_2, $(CH_2)_n$, etc.). Avec le diméthyldichlorosilane, Me_2SiCl_2. La réaction se produit à reflux, à 70°C, de préférence dans un excès de Me_2SiCl_2. La caractéristique la plus importante de cette nouvelle méthode est la récupération des intermédiaires (amino)chlorodiméthylsilanes, $R_2NSiMe_2Cl_2$, qui peuvent être soumis à une nouvelle réduction pour donner du R_2NSiMe_2H. On a démontré le mécanisme de transsilylation par la réaction du (diéthylamino)méthylphénylsilane avec le Me_2SiCl_2. Les produits de cette dernière réaction sont le HMePhSiCl et le R_2NSiMe_2Cl qui permettent d'exclure la possibilité d'une réaction de dismutation. On a synthétisé de nouveaux bis(amino)diméthylsilanes, $(R_2N)_2SiMe_2$, (amino)diméthylchlorosilanes, R_2NSiMe_2Cl, et (amino)diméthylhydrosilanes, R_2NSiMe_2H, que l'on a caractérisés par RMN et IR.

Mots clés : chlorodiméthylsilane, $(CH_3)_2SiHCl$, synthèse, nouvelle méthode de synthèse, mécanisme de transsilylation.

[Traduit par la Rédaction]

Introduction

Chlorodimethylsilane ($(H)Me_2SiCl$) (CDMS) is a very useful and valuable organosilicon monomer and reagent, bearing two different functional groups: ≡Si-Cl and ≡Si-H. The ≡Si-Cl bond can react with Grignard and organolithium reagents, or undergo alcoholysis and hydrolysis reactions. The ≡Si-H group enables preparation of complex derivatives, mainly through hydrosilylation reaction. HMe_2SiCl finds many synthetic applications in organosilicon synthesis and silicone technology (2–6), as well as in general polymer chemistry (7–12). Most often HMe_2SiCl is used in a preparation of 1,1,3,3-tetramethyldisiloxane ($HMe_2SiOSiMe_2H$), other Si-H terminated polysiloxanes (13–20), and multifunctional hydrosiloxanes (e.g., $Si(OSiMe_2H)_4$ (11), octa(hyridodimethylsiloxy)octasilsesquioxane $(HMe_2SiOSiO_{3/2})_8$ (21–23)), or hydropolysilanes (e.g., $Si(SiMe_2SiH)_4$ (24–27) and *o*-(bisdimethylsilyl)benzene (28)).

Yields of HMe_2SiCl in an industrial "direct process" (from elemental silicon and methyl chloride) are poor, usually 0.1–1% (29–31), although, when H_2 was added to the methyl chloride gas phase, yields can be significantly improved up to 8% (32), or 2.2–33% (33), depending on reaction conditions.

Many synthetic methods lead to chlorodimethylsilane, but some are unattractive due to expense and unavailability of intermediates. In the present paper a new laboratory procedure for preparation of HMe_2SiCl is described, which is a modification of the Eaborn et al. (34) method. The key of our method is a transsilylation of substituted (amino)dimethylhydrosilanes R_2NSiMe_2H with dimethyldichlorosilane Me_2SiCl_2.

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This paper is dedicated to Professor Adrian G. Brook, very distinguished organosilicon and organic chemist, and my briliant teacher, on the occasion of his 75th birthday. In 1982–83 Professor A.G. Brook gave me a chance to join his research group, at the Department of Chemistry of the University of Toronto. In the Lash Miller Chemical Laboratories I had the pleasure to continue studies on a very well known Brook rearrangement, work out some details of its mechanism, and discover a new silyl anion rearrangement (1). I have learned a lot from Professor Adrian G. Brook, who opened for me a world of international science, and I will be always grateful to him.

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Experimental

General procedures

All reactions were carried out under an atmosphere of dry nitrogen. Most of the substrates and reaction products were distilled through a Vigreux column (120 cm).

NMR spectra were determined with Tesla BS-487C (80 MHz) and Bruker MSL-300 (300 MHz); ~10% solutions of studied silanes in CCl_4, $CDCl_3$, or CD_2Cl_2 were used. Infrared spectra were recorded for neat samples on a Carl Zeiss Jena 75R spectrometer.

Reagents

Dimethyldichlorosilane (70.5–71.0°C) and methyltrichlorosilane (66°C) were purified by fractional distillation. Diethylamine (POCh, Gliwice, Poland), triethylamine (POCh), pyrrolidine (Aldrich), piperidine (Loba Chem.) were dried with KOH (POCh) and purified by distillation over small amounts of P_2O_5 (POCh). Dimethylamine (Fluka), magnesium (POCh), and lithium aluminium hydride (Aldrich) were used as received. Bromobenzene (POCh) was distilled over CaH_2 (Aldrich). Diethyl ether and tetrahydrofuran were dried with KOH and distilled over fresh sodium wire. Methylphenyldichlorosilane was prepared by a Grignard method (35), from $MeSiCl_3$ and PhMgBr, in ether, and fractionally distilled (bp 103–104°C/20 mmHg).

Bis(diethylamino)dimethylsilane

Bis(diethylamino)dimethylsilane (142.2 g, yield 85%) was prepared from 2.9 mol of diethylamine and 0.7 mol of Me_2SiCl_2, in dry ether (36, 37). Solution of Me_2SiCl_2 was added dropwise to a stirred solution of Et_2NH in 1300 mL of Et_2O, followed by reflux for 7 h. The reaction mixture was left overnight. A precipitate of diethylamine hydrochloride was filtered off and washed with dry ether. The product was fractionally distilled (bp 86°C/20 mmHg).

Preparation of (diethylamino)dimethylchlorosilane

Into a 500 mL four-neck flask, fitted with a condenser and a mechanical stirrer, was placed 116.3 g (0.575 mol) of bis(diethylamino)dimethylsilane. Stirring was turned on and the substrate was cooled down to –5°C. 70 mL (0.578 mol) of Me_2SiCl_2 was added dropwise from an addition funnel, at –5°C, within 2 h. The cooling bath was removed and stirring was continued at room temperature for 6 h. The products were fractionally distilled to give 152.4 g (80% yield) of Et_2NSiMe_2Cl (bp 152°C) (36, 37).

Preparation of (diethylamino)dimethylsilane

(*a*) Into a 500 mL four-neck flask, fitted with a condenser and a mechanical stirrer, was placed 10.63 g (0.28 mol) of $LiAlH_4$ and 250 mL of dry ether. 148.5 g (0.90 mol) of (diethylamino)dimethylchlorosilane in 80 mL of dry ether was added dropwise from an addition funnel, within 1.5 h. The reaction mixture was refluxed for 2.5 h, and cooled to room temperature. Solids were filtered off and washed with dry ether. Fractional distillation of the filtrate gave 94.0 g (80% yield) of Et_2NSiMe_2H (bp 110–111°C).

(*b*) Similarly, from 5.43 g (0.14 mol) of $LiAlH_4$ and 75.7 g (0.46 mol) of (diethylamino)dimethylchlorosilane, with 170 mL of dry ether, after 4 h of reflux and an identical work-up 37.9 g (63% yield) of Et_2NSiMe_2H was obtained.

Reaction of (diethylamino)dimethylsilane with dimethyldichlorosilane

(*a*) Into a 250 mL two-neck flask was placed 74.4 g (0.567 mol) of (diethylamino)dimethylsilane and 74.0 g (0.573 mol) of dimethyldichlorosilane. The reaction flask was connected to a Vigreux column and heated to reflux. A fraction of HMe_2SiCl (containing traces of Me_2SiCl_2) was continously distilled and collected to give 40.8 g (76% yield) of HMe_2SiCl (bp 36°C). Distillation of the reaction flask residue gave 74.8 g (80% yield) of Et_2NSiMe_2Cl (bp 152°C).

(*b*) A similar reaction of 33.0 g (0.252 mol) of (diethylamino)dimethylsilane was carried out with double excess of dimethyldichlorosilane (61 mL, 0.573 mol). 20 mL of Me_2SiCl_2 was added to a flask containing Et_2NSiMe_2H, the reagents were heated to reflux under Vigreux column, and the remaining amount of Me_2SiCl_2 was added dropwise at reflux. Products were recovered by distillation: (*i*) 20.7 g (87% yield) of HMe_2SiCl (bp 36°C); and (*ii*) 37.7 g (90% yield) of Et_2NSiMe_2Cl (bp 152°C) were obtained.

Preparation of bis(pyrrolidino)dimethylsilane

Into a four-neck 2.5 L sulphonation reactor, fitted with a condenser and a mechanical stirrer, was added 126 mL (1.04 mol) of Me_2SiCl_2, 309 mL (2.22 mol) of Et_3N, and 1800 mL of dry ether. 175 mL (2.10 mol) of dry pyrrolidine was added dropwise, within 2 h. A precipitate of triethylamine hydrochloride was filtered off and washed with dry ether (3 × 100 mL). The ether was distilled off and the residue was distilled to give $[(CH_2)_4N]_2SiMe_2$ (73% yield, bp 107–110°C/15 mmHg).

Preparation of (pyrrolidino)dimethylchlorosilane

(*a*) Into a 500 mL four-neck flask, fitted with a condenser and a mechanical stirrer, was placed 90.9 g (0.458 mol) of bis(pyrrolidino)dimethylsilane. The substrate was cooled to –10°C and 56 mL (2.10 mol) of Me_2SiCl_2 was added dropwise, within 2 h. Stirring was continued at –5°C for 4 h and reaction mixture was left overnight. Products were fractionally distilled to give 123.1 g (82% yield) of $(CH_2)_4NSiMe_2Cl$ (bp 80–81°C/40 mmHg).

(*b*) Into a four-neck 1.5 L sulphonation reactor, fitted with a condenser and mechanical stirrer, was added 124 mL (1.02 mol) of Me_2SiCl_2, 139 mL (1.00 mol) of Et_3N, and 900 mL of dry ether. 83.5 mL (1.00 mol) of dry pyrrolidine was added dropwise, within 2 h. Reaction mixture was stirred and refluxed for 2 h, and cooled to room temperature. Triethylamine hydrochloride was filtered off and washed with dry ether (2 × 150 mL). Ether was distilled off and a residue was distilled to give 72.8 g (44% yield) of $(CH_2)_4NSiMe_2Cl$ (bp 60–62°C/15 mmHg).

Preparation of (pyrrolidino)dimethylsilane

Into a 500 mL four-neck flask, fitted with a condenser and a mechanical stirrer, was placed 7.50 g (0.197 mol) of $LiAlH_4$ and 200 mL of dry ether. 64.3 g (0.393 mol) of $(CH_2)_4NSiMe_2Cl$ in 70 mL of dry ether was added dropwise, within 40 min. The reaction mixture was refluxed for 4 h,

cooled to room temperature, and left overnight. Solids were filtered off, washed with dry ether. The filtrate was fractionally distilled to give an ether fraction and 21.8 g (43% yield) of $(CH_2)_4NSiMe_2H$ (bp 47–48°C/40 mmHg).

Reaction of (pyrrolidino)dimethylsilane with dimethyldichlorosilane

Into a 250 mL two-neck flask was placed 18.1 g (0.14 mol) of (pyrrolidino)dimethylsilane and 34 mL (0.28 mol) of dimethyldichlorosilane. The reaction flask was heated to reflux, and HMe_2SiCl (with traces of Me_2SiCl_2) was continously distilled off through a Vigreux columnto give 9.0 g (68% yield) of HMe_2SiCl (bp 36°C). Distillation of the residue gave $(CH_2)_4NSiMe_2Cl$ (17.1 g, 74% yield; bp 80–81°C/40 mmHg).

Preparation of (diethylamino)methylphenylchlorosilane

Into a 1.5 L four-neck reactor, fitted with a condenser and a mechanical stirrer, was placed 116.3 mL (0.72 mol) of methylphenyldichlorosilane and 900 mL of dry ether. 151 mL (1.46 mol) of Et_2NH was added dropwise, within 5 h, followed by reflux for 2 h. On the next day a precipitate of $Et_2NH{\cdot}HCl$ was filtered off (under nitrogen) and washed three times with ether. After removal of ether, the liquid residue was distilled to give 130.2 g (79% yield) of $Et_2NSiMePhCl$ (bp 108–110°C/5 mmHg).

Preparation of (diethylamino)methylphenylsilane

Into a 0.5 L three-neck flask, fitted with a condenser and a mechanical stirrer, was placed 5.50 g (0.145 mol) of $LiAlH_4$ and 90 mL of dry THF. 65.8 g (0.289 mol) of (diethylamino)methylphenylchlorosilane in 70 mL of dry THF was added dropwise, within 30 min. The reaction mixture was refluxed for 4 h, and cooled to room temperature. Solids were filtered off and washed with dry pentane (3 × 30 mL). Solvents were removed and the residue fractionally distilled to give 7.5 g of $MePhSiH_2$ (bp 25–26°C/5 mmHg; n_D^{20} = 1.5051 (Lit. (38) value: 1.5058) and 52.2 g (58% yield) of $Et_2NSiMePhH$ (bp 87–90°C/5 mmHg).

Reaction of (diethylamino)methylphenylsilane with dimethyldichlorosilane

Into a 250 mL two-neck flask was added 13.75 g (0.071 mol) of (diethylamino)methylphenylsilane. 17 mL (0.140 mol) of Me_2SiCl_2 was added dropwise at ~30°C. Reaction mixture was heated to reflux and then fractionally distilled through a Vigreux column. Four fractions were collected and analyzed by means of ^1H NMR (and IR): (1) bp 69–72°C (11.5 g, Me_2SiCl_2); (2) bp 82–86°C/63 mmHg (4.9 g, ~95% of Et_2NSiMe_2Cl and ~5% of HMePhSiCl); (3) bp 97–115°C/65 mmHg (7.2 g, 35% of Et_2NSiMe_2Cl and 65% of HMePhSiCl); (4) bp 130–140°C/64 mmHg (7.0 g, 70% of $Et_2NSiMePhH$ (conversion 64.4%)); and 30% of HMePhSiCl). Contents of the above fractions are based on integrations of their ^1H NMR spectra (80 MHz, in CCl_4).

Analytical data for the products

HMe_2SiCl

Boiling point 36.0°C. IR (neat (cm^{-1})): 2170 (Si-H). ^1H NMR (80 MHz, δ (ppm)), in $CDCl_3$): 0.50 (d, 6H, $(CH_3)_2Si$), 4.88 (sept., 1H, Si-H); in CCl_4: 0.45 (d, J = 3.0 Hz, 6H, $(CH_3)_2Si$), 4.80 (sept., J = 3.0 Hz, 1H, Si-H).

Et_2NSiMe_2Cl

Boiling point 152–154°C. ^1H NMR: 0.38 (s, 6H, $(CH_3)_2Si$), 0.98 (t, J = 7 Hz, 6H, CH_3-C), 2.85 (q, J = 7 Hz, 4H, CH_2-N).

$Et_2NSiMe_2(H)$

Boiling point 111–112°C. IR (neat (cm^{-1})): 2120 (Si-H). ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.185 (d, 6H, J = 2.79 Hz, $(CH_3)_2Si$), 1.11 (t, 6H, J = 7.14 Hz, CH_3-C), 2.65 (q, 4H, J = 7.15 Hz, CH_2-N), 4.68 (sept., 1H, J = 2.78 Hz, Si-H). ^{13}C NMR: –1.49 (s, CH_3-Si), 15.63 (s, CH_3), 41.00 (s, CH_2-N). ^{29}Si NMR: –7.77 (s).

$Et_2NSiMePhCl$

Boiling point 136–140°C/25 mmHg, 108–110°C/5 mmHg. n_D^{20} 1.5073. IR (neat (cm^{-1})): 3068, 1800–2000, 1588 (Ph), 1426 (Si-Ph), 1253 (Si- CH_3), 2966, 2927, 2866 (C-H aliphat.), 1202, 1166, 1055 (C-N), 1028, 931 (Si-N), 640, 460, 413 (Si-Cl). ^1H NMR (80 MHz, CCl_4, δ (ppm)): 0.79 (s, 3H, CH_3-Si), 1.21 (t, J = 6.4 Hz, 6H, CH_3-C), 3.08 (q, J = 6.4 Hz, 4H, CH_2-N), 7.47–7.65 (m, 3H (Ph, *m*-, *p*-)), 7.8–8.0 (m, C-H (Ph, *o*-)). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 1.63 CH_3-Si, 15.12 CH_3-C, 39.37 CH_2-N, 128.06, 130.06, 134.32, 135.14 (Ph). Anal. calcd. (%): C 57.99, H 7.96, N 6.14, Cl 15.56; found (%): C 57.59, 57.59, H 8.02, 8.14, N 5.83, 5.63, Cl 15.16, 15.38.

$Et_2NSiMePh(H)$

Boiling point 115–117°C/21 mmHg, 86–89°C/5 Tr. n_D^{20} 1.4969. IR (neat (cm^{-1})): 3067, 1800–2000, 1591 (Ph), 1428 (Si-Ph), 1252 (Si- CH_3), 2965, 2927, 2864 (C-H aliphat.), 2126, 2085 (Si-H), 1211, 1180, 1065 (C-N), 1028, 931 (Si-N), 1030, 930 (Si-N). ^1H NMR (80 MHz, CCl_4, δ (ppm)): 0.33 (d, J = 3.2 Hz, 3H, CH_3-Si), 0.94 (t, J = 7 Hz, 6H, CH_3-C), 2.82 (q, J = 7 Hz, 4H, CH_2-N), 4.80 (q, J = 3.2 Hz, 1H, Si-H), 7.25 (m, 3H (Ph, *m*-, *p*-)), 7.50 (m, C-H (Ph, *o*-)). Anal. calcd. (%): C 68.33, H 9.90, N 7.24; found (%): C 67.63, 67.56, H 9.86, 9.89, N 6.67, 6.83.

HMePhSiCl

Boiling point 174–176°C, bp 92–95°C/65 mmHg. n_D^{20} 1.5073. IR (neat (cm^{-1})): 2170 (Si-H). ^1H NMR (80 MHz, $CDCl_3$, δ (ppm)): 0.65 (d, J = 3.4 Hz, 3H, CH_3-Si), 5.25 (q, J = 3.4 Hz, 1H, Si-H), 7.35 (m (t), 3H, Ph (*m*-, *p*-), 7.55 (m (d), 2H, Ph (*o*-)).

$[(CH_2)_4N]_2SiMe_2$

Boiling point 107–110°C/15 mmHg. n_D^{20} 1.4682. ^1H NMR (80 MHz, CCl_4, δ (ppm)): 0.24 (s, 6H, $(CH_3)_2Si$), 1.46 (m, 4H, $(CH_2)_2$), 2.73 (m, 4H, $(CH_2)_2N$). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): –3.33 CH_3-Si, 26.61 $(CH_2)_2$, 46.73 $(CH_2)_2N$. Anal. calcd. (%): C 60.54, H 11.18, N 14.12, Si 14.16; found (%): C 60.63, 60.71, H11.31, 11.31, N 13.54, 13.54, Si 14.10.

$(CH_2)_4NSiMe_2Cl$

Boiling point 80–81°C/40 mmHg, 60–62°C/15 mmHg. $n^{20}{}_D$ 1.4533. ^1H NMR (80 MHz, δ (ppm)) in CCl_4: 0.44 (s,

6H, $(CH_3)_2Si$), 1.75 (quintette, J = 3.6 Hz, 4H, $(CH_2)_2$), 3.01(m, J = 6.4 Hz, 4H, $(CH_2)_2N$); in $CDCl_2$: 0.44 (s, 6H, $(CH_3)_2Si$), 1.36 (quintette, J = 4.3 Hz, 4H, $(CH_2)_2$), 2.28 (m, J = 6.4 Hz, 4H, $(CH_2)_2N$).

$(CH_2)_4NSiMe_2(H)$

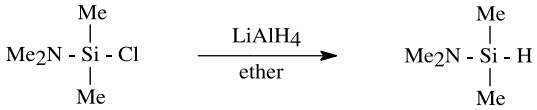
Boiling point 47–48°C/40 mmHg, 59–63°C/15 mmHg. IR (neat (cm^{-1})): 2960, 2869, 2820, 1591 (C-H), 2120, 2074 (Si-H), 1457, 1420, 1352 (C-H, CH_3), 1252 (Si- CH_3), 1125, 1200, 1080 (C-N), 896, 835 (Si-N), 764, 628 (Si-C). ^{1}H-NMR (80 MHz, $CDCl_2$, δ (ppm)): 0.07 (d, J = 4.6 Hz, 6H, $(CH_3)_2Si$), 1.22 (quintette, J = 4.6 Hz, 4H, $(CH_2)_2$), 2.11 (m, 4H, $(CH_2)_2N$), 3.14 (sept., J = 4.3 Hz, 1H, Si-H). Anal. calcd. (%): C 55.74, H 11.70, N 10.83; found (%): C 54.35, 54.21, H 11.33, 11.21, N 10.07, 9.95.

Results and discussion

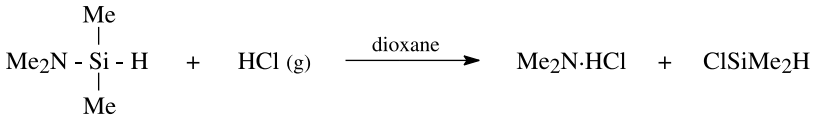
Since yields of chlorodimethylsilane obtained in a direct Rochow and Müller process are very low, many attempts have been made to find new efficient synthetic methods, especially useful on a laboratory scale. HMe_2SiCl has been prepared by the following methods: (*i*) the direct synthesis from elemental silicon and methyl chloride (29–33, 39–44); (*ii*) Grignard reaction between $MeHSiCl_2$ and MeMgBr (45); (*iii*) selective reduction of dimethyldichlorosilane Me_2SiCl_2 (DDS) with Na_3AlH_6, NaH, $NaBH_4$, $LiAlH_4$ (46–49), Et_3Al (50), or $Me_2SiCl(OMe)$ with i-Bu_2AlH (51), and Me_2NSiMe_2Cl with $LiAlH_4$ (followed by cleavage of the intermediate silane with HCl) (34); (*iv*) disproportionation of hydrochlorosilanes (52) or organohydrosilanes and -siloxanes with chlorosilanes (53–59); (*v*) cleavage of $HMe_2SiOSiMe_2H$ with HCl (60, 61), HCl and $AlCl_3$ (62), BCl_3 (63), and polymethylhydrolsiloxanes with Me_2SiCl_2, catalyzed by BF_3, n-Bu_4NCl, BCl_3 and HMPT (64); and with $MeSiCl_3$, Me_2SiCl_2, $PhSiCl_3$, catalyzed by HMPT and HCl (65); (*vi*) photolytic cleavage of polydimethylsilanes (66) and Me_3SiMe_2SiCl (67) with HCl; cleavage of disilanes with HCl towards phosphine–nickel complexes (68) and hydrogenation of chlorodisilanes obtained from the direct process, with copper catalysts (69) and phosphine–nickelocene (and nickel) complexes (70, 71); (*vi*) selective (and quantitative) chlorination of Me_2SiH_2 with $SnCl_4$ (72).

All of these procedures have limitations. Mainly due to safety precautions, the application of metal hydrides is limited to a relatively small scale. According to Eaborn (2) partial reduction of organohalogenosilanes with $LiAlH_4$ is not possible. Reductions of Me_2SiCl_2 with NaH afforded low yields of HMe_2SiCl: 11–17% (46) or 38% (at 150°C) (47). Reduction of Me_2SiCl_2 with Et_3Al, in c-C_6H_{12}, at 500°C, requires very short reaction time (1 s) and gives 17.7% of CDMS (50). Although reduction of DDS with i-Bu_2AlH, carried out at high temperature (at 330°C), gave 76% of CDMS (73). Also reaction of $Me_2Si(OMe)Cl$ with i-Bu_2AlH, at –23°C, gave good, 83% yield of CDMS. Similar reduction of DDS with $NaBH_4$ in HMPT, at 50°C, within 2 h, gave 71% yield of HMe_2SiCl (50). The symmetrical 1,1,3,3-tetramethyldisiloxane cannot be recommended as a substrate for the preparation of chlorodimethylsilane, and $HMe_2SiOSiMe_2H$ is synthesized from HMe_2SiCl. Synthesis of polydimethylsilanes is difficult, and the photolysis is limited to a small scale, requiring a special apparatus. The gaseous dimethylsilane and $SnCl_4$ are expensive substrates as well. The above reasons encouraged us to search for a new laboratory method of synthesis of HMe_2SiCl.

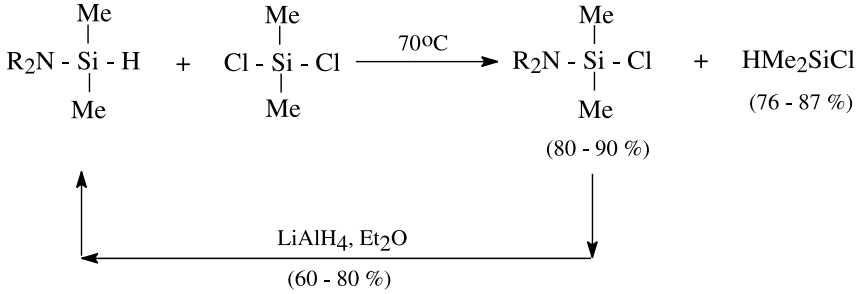
Our new method of preparation of Me_2SiHCl (74, 75) is a modification of the Eaborn et al. method (34), which involves the reduction of the Si—Cl bond to the Si—H bond, in the presence of the Si—N bond:

[1] 

and a subsequent cleavage of of the Si-N bond with gasous hydrogen chloride

[2] 

Our method is based on reaction of (dialkylamino)dimethylhydrosilanes (R_2NSiMe_2H) with dimethyldichlorosilane

[3] 

[4] $$2\,R_2NH + Me_2SiCl_2 + Et_3N \xrightarrow[25\text{ - }35^oC]{Et_2O} Me_2Si(NR_2)_2 + 2\,Et_3N{\cdot}HCl$$

As a single step, the yield of chlorodimethylsilane was in the range 76–87%, with respect to Et_2NSiMe_2H. The overall yield of four-step (or three-step) reaction, including synthesis of Et_2NSiMe_2Cl (see rxns. [4]–[6]), its reduction to (diethylamino)dimethylsilane, followed by reaction (3) with Me_2SiCl_2, ranged from 45 to 58%. However, intermediate Et_2NSiMe_2Cl and other (dialkylamino)dimethylchlorosilanes R_2NSiMe_2Cl were recovered, in a high yield (80–90%), and may be used again for synthesis of $HSiMe_2Cl$, after reduction with $LiAlH_4$. When we are considering the recovery of R_2NSiMe_2Cl, the overall yields of HMe_2SiCl are much higher (within the range of 150–240% (!!!)), than yields calculated for the single step reaction (3).

The starting (amino)chlorosilanes can be prepared either in two steps (36, 37)

[5] $$Me_2Si(NR_2)_2 + Me_2SiCl_2 \xrightarrow[-5\text{ - }0^oC]{Et_2O} \underset{\sim 85\ \%}{2\,R_2N\text{-}Me_2Si\text{-}Cl}$$

or in one step (36, 37)

[6] $$R_2NH + Me_2SiCl_2 + Et_3N \xrightarrow[-5\text{ - }0\ ^oC]{Et_2O} R_2N\text{-}Me_2Si\text{-}Cl$$

Alternatively a secondary amine can be used as an HCl acceptor.

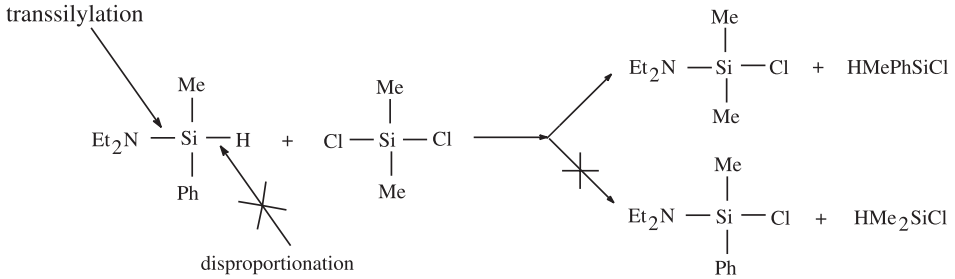
(Dialkylamino)chlorodimethylsilanes were reduced with excess $LiAlH_4$ in dry ether (or THF) at reflux. Yields of R_2NSiMe_2H depend on reaction time, and amount of reducing agent. Longer reaction times lead to lower yields, presumably due to reduction of Si—N bond; for Et_2NSiMe_2H: 80% after 2.5 h and 63% after 4 h (crude yields). Yields of reduction of $(CH_2)_4NSiMe_2Cl$ with $LiAlH_4$ were lower than in reduction of Et_2NSiMe_2Cl. Presumably a steric hinderance in this case diminishes the cleavage of the Si—N bond as a side reaction. In the case of reduction of $Et_2NSiMePh(Cl)$, small amounts of $MePhSiH_2$ were isolated. It has been reported (76), that (dimethylamino)trichlorosilane and bis(dimethylamino)dichlorosilane are reduced to monosilane SiH_4, as a result of the cleavage of Si—N bonds.

The final step of the synthesis of HMe_2SiCl, reaction of substituted (amino)dimethylchlorosilanes with Me_2SiCl_2, was carried out at reflux (~70°C), using a fractionation Vigreux column. During dropwise addition of Me_2SiCl_2 to Et_2NSiMe_2H, crude HMe_2SiCl was distilled off. When stoichiometric amounts of both substrates were used the reaction began at reflux and it was quite vigorous (a bleeding of the column appeared); thus 76% of CDMS was obtained. With excess Me_2SiCl_2, the yield of HMe_2SiCl reached 87%. Other substituted (amino)dimethylsilanes (R_2 = Me_2, n-Bu_2, $(CH_2)_5$), can be used for the synthesis of HMe_2SiCl, in the same manner.

Reaction mechanism

The Si—N bond (bond energy: 335 kJ/mol (77)) is slightly weaker than that of the Si—H bond (377 kJ/mole (78)). Thus it seems that reaction of (amino)dimethylsilanes ($R_2NSiMe_2(H)$) with Me_2SiCl_2 proceeds through a transsilylation mechanism, with a cleavage of the Si—N bond, rather than through a *disproportionation mechanism*, which would require breaking of the Si—H bond, in the aminosilane substrate. To prove this mechanism, $Et_2NSiMePhH$ was reacted with Me_2SiCl_2 to yield methylphenylchlorosilane (HMePhSiCl) and Et_2NSiMe_2Cl

[7]



The formation of HMePhSiCl confirms that the reaction of $Et_2NSiMePh(H)$ with Me_2SiCl_2 proceeds through the transsilylation mechanism, with the cleavage of the Si—N bond. The alternative disproportionation process, which would require breaking of the Si—H bond, would give $Et_2NSiMePhCl$ and $HSiMe_2Cl$, as reaction products. $HSiMe_2Cl$ was not detected in products of the above reaction. Moreover in disproportionation reactions of chlorosilanes with hydrosilanes the presence of various catalysts (e.g., $AlCl_3$ or H_2PtCl_6) is necessary. So far we have not conducted comprehensive mechanistic studies of reaction of (amino)hydrosilanes with chlorosilanes. It seems quite obvious, that this interesting and useful reaction is a next example of the nucleophilic displacement at silicon and may be catalyzed by traces of amine hydrochlorides or (amino)silanes hydrochlorides, which could be formed in the presence of traces of moisture, during the course of synthesis.

Conclusions

(1.) The new efficient laboratory method of the synthesis of HMe_2SiCl has been described, based on reaction of (dialkylamino)chlorodimethylsilanes (R_2NSiMe_2H) with dimethyldichlorosilane.

(2.) The main features of this novel method are as follows: (*a*) the intermediate products (dialkylamino)dimethylchlorosilanes (R_2NSiMe_2Cl) are recovered in high yields and are reused, in the synthesis cycle by reduction with $LiAlH_4$ to give R_2NSiMe_2H; (*b*) a very simple procedure and good yields of HMe_2SiCl are obtained (usually above 80%).

(3.) The reaction of substituted (amino)dimethylchlorosilanes with Me_2SiCl_2 proceeds through a nucleophilic substitution (transsilylation mechanism), and was confirmed by reaction of $Et_2NSiMePhH$ with Me_2SiCl_2. Products of this reaction are: HMePhSiCl and Et_2NSiMe_2Cl.

(4.) New compounds, not described in a literature, have been prepared: (*i*) bis(pyrrolidino)dimethylsilane $[(CH_2)_4N]_2SiMe_2$, from pyrrolidine and Me_2SiCl_2, in ether, in the presence of Et_3N; (*ii*) (pyrrolidino)dimethylchlorosilane $(CH_2)_4NSiMe_2Cl$, from reactions of bis(pyrrolidino)dimethylsilane or pyrrolidine with Me_2SiCl_2, in ether (in the presence of Et_3N, in the latter case); (*iii*) (diethylamino)methylphenylchlorosilane, from diethylamine and $MePhSiCl_2$, in ether; (*iv*) (diethylamino)methylphenylsilane, by reduction of $Et_2NSiMePh(Cl)$ with $LiAlH_4$, in THF.

(5.) (Pyrrolidino)dimethylsilane was synthesized by reduction of (pyrrolidino)dimethylchlorosilane $(CH_2)_4NSiMe_2Cl$ with $LiAlH_4$, in ether.

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