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Simplified preparations of trialkylsilyl- and bis(trialkylsilyl)dihalomethanes via the deprotonation of dihalomethanes

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Abstract

Simple, high-yield routes to trialkylsilyl- and bis(trialkylsilyl)dihalomethanes are described. These compounds are prepared by the deprotonation of dibromomethane or dichloromethane by lithium diisopropylamide in the presence of a chlorosilane. The reactions are carried out at temperatures below −70°C in THF/hexane solvent mixtures. After aqueous workup, the air- and water-stable products are isolated by either distillation or crystallization. Further reactions on these compounds are possible, as illustrated by one example. © 1997 Elsevier Science S.A.

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1. Background

α,α'-Dihalomethyl-substituted silanes are useful compounds in both organic and organometallic synthesis. For example, they have been used as precursors to geminal Grignard and organolithium reagents [1,2], as intermediates to α,β-unsaturated ketones [3] and 1,1-bis(trimethylsilyl)alkenes [4], and as dihalomethyl dianionic synthons [5,6].

Synthetic routes to trialkylsilyl- and bis(trialkylsilyl)dihalomethanes have included the reaction of *n*-BuLi with dichloromethane in the presence of chlorosilanes at −120°C [7], the methylation of dimethyl(dichloromethyl)chlorosilane [8], the reaction of $CHBr_2MgCl$ with various chlorosilanes [9], and the reaction of $CHLiBr_2$ or Me_3SiCBr_2Li with chlorosilanes [9,10]. In most cases, the product yields were acceptable to good, but the procedures were not general to the syntheses of both trialkylsilyl- and bis(trialkylsilyl)dihalomethanes of either dichloro- or dibromo-substitution. In addition, the reaction of metal-alkyl reagents with dihalomethanes often leads to products resulting from both deprotonation *and* metal-halogen exchange of the dihalomethane [11]. In our search for a general synthesis of potentially reactive organosilicon monomers, we have explored the scope of these reactions and have found that an in situ reaction of chlorosilanes with lithiated halomethanes is a simple, effective, and general method of cleanly synthesizing both dibromo- and dichloro-substituted trialkylsilylmethanes and bis(trialkylsilyl)methanes. Furthermore, obtaining either trialkylsilylmethanes or bis(trialkylsilyl)methanes as the principal product is controlled by simply adjusting the stoichiometry of the starting reagents. The results of our work are presented in this report.

2. Results and discussion

The preparations of the trialkylsilyl- and bis(trialkylsilyl)dihalomethanes were carried out by adding a chilled solution of lithium diisopropylamide (LDA) in hexane/THF to a mixture of chlorosilane, dihalomethane, and THF cooled with a dry ice/acetone bath. Quenching with saturated aqueous ammonium chloride solution followed by a typical workup led to the isolation of the products. We have utilized various chlorosilanes in this reaction, and the results of our work are shown in Table 1. The products are all generally air- and water-stable, although the SiH-containing products slowly turn cloudy on prolonged storage under

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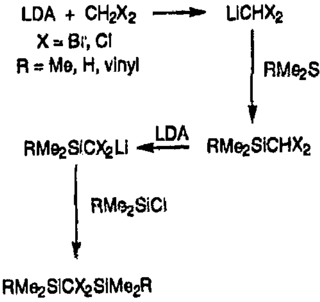
Table 1
Trialkylsilyl- and bis(trialkylsilyl)dihalomethanes (Vi = vinyl)

Compound	Yield[a] (%)
$Me_3SiCBr_2SiMe_3$ (**1a**)	85 (63[b])
$Me_3SiCCl_2SiMe_3$ (**1b**)	90 (82[d])
$HMe_2SiCBr_2SiMe_2H$[c] (**2a**)	62
$HMe_2SiCCl_2SiMe_2H$ (**2b**)	74 (74[d])
$ViMe_2SiCBr_2SiMe_2Vi$[c] (**3a**)	85
$ViMe_2SiCCl_2SiMe_2Vi$[c] (**3b**)	97 (91[d])
Me_3SiCBr_2H (**4a**)	62 (56[d])
Me_3SiCCl_2H (**4b**)	71
HMe_2SiCBr_2H (**5a**)	24 (19[d])
HMe_2SiCCl_2H (**5b**)	51

[a] NMR yield unless otherwise noted.
[b] Reaction cooled with water/ice bath.
[c] New compound.
[d] Isolated yield.

a normal room atmosphere. Particularly for the reactions with dibromomethane, we found that the order of addition was essential to obtain clean products in high yield. Reversing the order of addition, i.e. adding the dihalomethane to a mixture of LDA and chlorosilane, resulted in a lower yield of product accompanied with significant amounts of side products [1]. The reaction temperature was found to be important but not crucial to the success of the reactions. For the preparation of **1a**, carrying out the reaction with only ice water cooling resulted in an acceptable 63% yield of product. However, more impurities were present in the crude product. Reaction temperatures of −100°C or lower did not significantly improve the yields shown in Table 1, thus we used the more manageable dry ice/acetone cold baths for the reactions. These reactions are also tolerant of potentially reactive functionalities such as SiH and vinyl groups, although in general, the yields of the SiH-containing products were the lowest we observed. We also found that THF was superior to diethyl ether as a solvent for these reactions.

The products are presumably formed via the deprotonation reactions shown in Scheme 1. Using LDA instead of *n*-BuLi essentially makes the deprotonation steps unambiguous; no lithium–halogen exchange is possible. Lithium–halogen exchange between the intermediate lithiated dihalomethane species and dihalomethane is possible, but no products resulting from this interaction were observed. The advantage of deprotonating the dihalomethane in the presence of the chlorosilane is the relatively quick trapping of the intermediate lithiated dihalomethane before it can decompose to the carbene or other similar species [12].



Scheme 1.

For the preparation of the bis(trialkylsilyl)dihalomethanes we utilized the stoichiometrically correct molar ratio (LDA:dihalomethane:chlorosilane) of 2:1:2. For the preparation of trialkylsilyldihalomethanes we initially utilized a ratio of 1:1:1. However, this resulted in significant (up to 25%) formation of the bis-product, due to additional deprotonation of the initially formed trialkylsilyldihalomethane. Employing a LDA:dihalomethane:chlorosilane molar ratio of 1:2:1 alleviated this problem; a preparation of **4a** using this ratio resulted in only 5.8% formation of the bis-product. Thus, for all preparations of the trialkylsilyldihalomethanes, we utilized the 1:2:1 molar ratio. The desired products and excess dihalomethane are easily separated from the traces of bis-products by simple distillation [2].

One limitation of this reaction is that it could not be extended to the substitution of dichlorodialkylsilanes. Regardless of the molar ratio employed, reactions with dichlorodialkylsilanes only resulted in low mass recoveries of strongly colored oils. ^1H NMR spectroscopic and thin-layer chromatography analyses of these oils indicated highly complicated mixtures, and further investigations into these products were not carried out. The reasons for this anomalous behavior are unclear at this point, but it should be noted that similar difficulties were observed in the reaction of *n*-BuLi with CH_2Cl_2 and dichlorodialkylsilanes [7].

The halogenated products of these reactions show much promise for further modification. For example, treatment of bis(dimethylsilyl)dichloromethane **2b**, with dibenzoyl peroxide in refluxing carbon tetrachloride resulted in the isolation of bis(chlorodimethylsilyl)dichloromethane ($ClMe_2SiCCl_2SiMe_2Cl$) in 93% yield. We are currently exploring the possibilities of utilizing this compound in different polymerization processes.

In conclusion, the reaction of LDA with dihalomethanes and chlorotrialkylsilanes is a simple, effi-

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[1] Preparation of **1a** by adding CH_2Br_2 to a solution of $LDA/Me_3SiCl/THF$ at −100°C resulted in a 60% yield of product. See ref. [2].

[2] Oshima and co-workers report [6] the preparations of *t*-$BuMe_2SiCHBr_2$ and *t*-$BuMe_2SiCHCl_2$ in 89 and 85% yield, respectively, by the addition of LDA to a mixture of *t*-$BuMe_2SiCl$ and dihalomethane in THF at −78°C. No additional experimental details were given, however.

cient, and clean method of synthesizing both trialkylsilyl- and bis(trialkylsilyl)dihalomethanes. The reaction conditions require the use of easily managed dry ice/acetone baths, and the workup involves typical aqueous procedures. The halogenated products show much promise for further modification, and we are currently examining their potential as precursors to new organosilicon monomers.

3. Experimental section

3.1. General comments

All reactions were carried out under an atmosphere of dry nitrogen unless otherwise indicated. Solvents were dried by standard procedures. All reagents were of commercial origin. All NMR spectra were obtained on a 400 MHz Bruker AVANCE DRX multinuclear NMR spectrometer using $CDCl_3$ as solvent. ^1H NMR yields were obtained using dibromomethane as an internal reference (δ 4.9). All known products were verified by comparison of spectral or boiling point/melting point data with literature values. Elemental analyses were carried out by E + R Microanalytical Laboratory, Corona, NY.

3.2. Preparation of compounds *1a*, *1b*, *2a*, *2b*, *3a* and *3b*

These compounds were prepared using essentially the same procedure. In the syntheses of **2a** and **2b**, chlorodimethylsilane was used in place of chlorotrimethylsilane. In the syntheses of **3a** and **3b**, chlorodimethylvinylsilane was used in place of chlorotrimethylsilane. As an example, the preparation of bis(trimethylsilyl)dibromomethane (**1a**) is given in detail.

3.3. Bis(trimethylsilyl)dibromomethane (*1a*)

A 100-ml round-bottomed flask equipped with a stir bar, septum, and gas-inlet needle was charged with 4.7 ml of diisopropylamine (36 mmol) and 25 ml of THF. The flask was placed in a water/ice bath and then *n*-BuLi (14.4 ml of a 2.5 M solution in hexanes, 36 mmol) was added dropwise via syringe to make a clear yellow solution. This solution was stirred for an additional 10 minutes, after which it was added dropwise via cannula to a 100-ml round-bottomed flask containing dibromomethane (1.17 ml, 16.7 mmol), chlorotrimethylsilane (4.23 ml, 33.3 mmol), and 5 ml of THF cooled in a dry ice/acetone bath. The addition took 15–20 minutes. After addition, the pale yellow suspension was stirred cold for an additional 10 minutes, after which the cold bath was removed. After 1 hour of stirring, the pale yellow suspension was poured into an ice-cold solution of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted twice with ether. The organic layers were combined and washed twice with 2 N aqueous hydrochloric acid, twice with distilled water, and once with saturated aqueous sodium chloride solution. The clear yellow organic layer was dried over anhydrous magnesium sulfate and filtered. Removal of volatiles using a rotary evaporator left 4.70 g of a clear yellow oil. The NMR yield of product was determined to be 85%. Crystallization from methanol/water or vacuum distillation yielded spectroscopically pure **1a** as a white solid, mp 66–69°C (lit. [9] mp 68–69°C). ^1H NMR: δ 0.27 ($SiCH_3$). ^{13}C NMR: δ −0.99 ($SiCH_3$), 58.0 (CBr_2).

3.4. Bis(trimethylsilyl)dichloromethane (*1b*)

NMR yield: 90%. In a separate preparation, Kugelrohr distillation of the crude product yielded **1b** as a clear, colorless liquid in 82% isolated yield (bp 86–87°C/20 mm Hg; lit. [11] bp 204°C/760 mm Hg). ^1H NMR: δ 0.22 ($SiCH_3$). ^{13}C NMR: δ −2.22 ($SiCH_3$), 74.7 (CCl_2).

3.5. Bis(dimethylsilyl)dibromomethane (*2a*)

NMR yield: 62%. Vacuum distillation yielded spectroscopically pure **2a** as a clear, colorless liquid (bp 61.0–62.5°C/6 mm Hg). ^1H NMR: δ 0.34 (d, 12 H, $SiCH_3$, J = 3.4 Hz), 4.26 (sept, 2 H, SiH, J = 3.4 Hz). ^{13}C NMR: δ −4.2 ($SiCH_3$), 48.5 (CBr_2). IR (NaCl, neat): 2961 (m), 2904 (w), 2136 (s), 1418 (br w), 1251 (s), 881 (br s). Anal. Calcd for $C_5H_{14}Br_2Si_2$: C, 20.71; H, 4.83. Found: C, 20.95; H, 4.77.

3.6. Bis(dimethylsilyl)dichloromethane (*2b*)

NMR yield: 74%. In a separate large scale preparation, careful distillation through a Vigreaux column yielded spectroscopically pure **2b** as a clear, colorless liquid in 74% yield (bp 87.5–90.0°C/54 mm Hg). ^1H NMR: δ 0.31 (d, 12 H, $SiCH_3$, J = 3.5 Hz), 4.16 (sept, 2 H, SiH, J = 3.5 Hz). ^{13}C NMR: δ −5.8 ($SiCH_3$), 69.0 ($SiCCl_2$). The NMR data correlate with those reported in the literature [13].

3.7. Bis(dimethylvinylsilyl)dibromomethane (*3a*)

NMR yield: 85%. Vacuum distillation yielded spectroscopically pure **3a** as a clear, colorless liquid (bp 96–97°C/0.5 mm Hg). ^1H NMR: δ 0.35 (s, 12 H, $SiCH_3$), 5.81 (dd, 2 H, C=CHH, ^2J = 3.5 Hz, ^3J = 20

Hz), 6.08 (dd, 2 H, C=C*H*H, $^2J = 3.5$ Hz, $^3J = 15$ Hz), 6.27 (dd, 2 H, C*H*=CH$_2$, $^3J = 20$ Hz, $^3J = 15$ Hz). ^{13}C NMR: δ −2.9 (Si*C*H$_3$), 54.5 (*C*Br$_2$), 134 (*C*=C), 136 (*C*=C). IR (NaCl, neat): 3052 (m), 2960 (s), 1592 (w), 1406 (s), 1251 (s), 1006 (s), 955 (s), 848 (br s), 787 (br s), 701 (m). Anal. Calcd for $C_9H_{18}Br_2Si_2$: C, 31.60; H, 5.26. Found: C, 32.09; H, 5.22.

3.8. Bis(dimethylvinylsilyl)dichloromethane (3b)

NMR yield: 97%. Vacuum distillation yielded spectroscopically pure **3b** as a clear, colorless liquid (bp 104–105°C/18 mm Hg). Repeating this reaction yielded **3b** in 91% isolated yield. ^{1}H NMR: δ 0.29 (s, 12 H, SiC*H*$_3$), 5.81 (dd, 2 H, C=C*H*H, $^2J = 3.7$ Hz, $^3J = 20$ Hz), 6.07 (dd, 2 H, C=C*H*H, $^2J = 3.7$ Hz, $^3J = 15$ Hz), 6.22 (dd, 2 H, C*H*=CH$_2$, $^3J = 15$ Hz, $^3J = 20$ Hz). ^{13}C NMR: δ −4.2 (Si*C*H$_3$), 72.4 (*C*Cl$_2$), 134 (*C*=C), 135 (*C*=C). IR (NaCl, neat): 3053 (w), 2976 (m), 1593 (w), 1406 (m), 1251 (s), 1007 (m), 956 (m), 863 (s), 844 (s), 790 (m). Anal. Calcd for $C_9H_{18}Cl_2Si_2$: C, 42.67; H, 7.16. Found: C, 42.25; H, 6.87.

3.9. Preparation of compounds 4a, 4b, 5a and 5b

These compounds were prepared using essentially the same procedure used in the preparation of compounds **1–3**, the only difference being that the molar ratio of LDA to dihalomethane to chlorosilane was 1:2:1. In the syntheses of **5a** and **5b**, chlorodimethylsilane was used in place of chlorotrimethylsilane.

3.10. Dibromomethyltrimethylsilane (4a)

NMR yield: 62%. Careful distillation of a large-scale crude sample through a Vigreaux column gave spectroscopically pure **4a** as a clear, colorless liquid in 56% yield (bp 56–57°C/14 mm Hg; lit. [9] bp 49.5–51.5°C/12 mm Hg). ^{1}H NMR: δ 0.24 (9 H, SiC*H*$_3$), 5.13 (1 H, C*H*Br$_2$). ^{13}C NMR: δ −3.22 (Si*C*H$_3$), 36.8 (*C*HBr$_2$).

3.11. Dichloromethyltrimethylsilane (4b)

NMR yield: 71%. Vacuum distillation yielded spectroscopically pure **4b** as a clear, colorless liquid (bp 72.5–73.0°C/102 mm Hg; bp (commercial product) 134–5°C/760 mm Hg). ^{1}H NMR: δ 0.21 (9 H, SiC*H*$_3$), 5.25 (1 H, C*H*Cl$_2$). ^{13}C NMR: δ −4.2 (Si*C*H$_3$), 63.6 (*C*HCl$_2$).

3.12. Dibromomethyldimethylsilane (5a)

NMR yield: 24%. Vacuum distillation yielded spectroscopically pure **5a** as a clear, colorless liquid (bp 64–65°C/32 mm Hg; lit. [9] bp 67–68°C/40 mm Hg). A separate experiment yielded **5a** in 19% isolated yield after Kugelrohr distillation. ^{1}H NMR: δ 0.30 (d, 6 H, SiC*H*$_3$, $J = 3.5$ Hz), 4.24 (mult, 1 H, Si*H*), 5.17 (d, 1 H, C*H*Br$_2$, $J = 1.6$ Hz). ^{13}C NMR: δ −5.2 (Si*C*H$_3$), 32.9 (*C*HBr$_2$).

3.13. Dichloromethyldimethylsilane (5b)

NMR yield: 51%. Vacuum distillation yielded spectroscopically pure **5b** as a clear, colorless liquid (bp 61–62°C/144 mm Hg). ^{1}H NMR: δ 0.30 (d, 6 H, SiC*H*$_3$, $J = 3.5$ Hz), 4.14 (mult, 1 H, Si*H*), 5.35 (d, 1 H, C*H*Cl$_2$, $J = 1.5$ Hz). ^{13}C NMR: δ −6.6 (Si*C*H$_3$), 61.2 (*C*HCl$_2$). The NMR data correlate with those reported in the literature [13].

3.14. Bis(chlorodimethylsilyl)dichloromethane

A 250-ml round-bottomed flask equipped with a stir bar was charged with **2b** (6.68 g, 33.2 mmol), dibenzoyl peroxide (1.61 g, 20 mol %), and carbon tetrachloride (100 ml). A reflux condenser was attached to the flask, and the flask was heated in an oil bath maintained at 90–95°C for a period of 48 hours. Most of the carbon tetrachloride was removed at reduced pressure and the residue was distilled. Bis(chlorodimethylsilyl)dichloromethane was obtained as a clear, colorless liquid in 94% yield (bp 87–90°C/23 mm Hg). ^{1}H NMR: δ 0.70 (SiC*H*$_3$). ^{13}C NMR: δ 0.39 (Si*C*H$_3$), 69.3 (*C*Cl$_2$). The NMR data correlate with those reported in the literature [14].

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