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Tetramethylsilane in Synthesis:[1] Selective Mono- and Polymethylations of Germanium Tetrachloride

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In the presence of catalytic amounts of aluminum bromide (or chloride), selective mono-, di-, tri-, or tetramethylation of germanium tetrachloride was effected in high yield with tetramethylsilane (Me_4Si) as the methylating reagent. According to the $Me_4Si/GeCl_4$ ratio, $MeGeCl_3$, Me_2GeCl_2, Me_3GeCl, and Me_4Ge were prepared in 66, 86, 100, and 91% maximum yields, respectively. In these reactions, Me_4Si was converted into Me_3SiCl and subsequently Me_2SiCl_2. A mechanism for methylation is proposed, involving the initial formation of Me_4Ge (observed regardless of the proportions of starting reagents) followed by disproportionation reactions, with methylchlorosilanes or -germanes present when the initial molecular ratio $Me_4Si/GeCl_4$ was lower than 4/1.

Introduction

During the course of the industrial preparation (direct synthesis) of Me_2SiCl_2, Me_4Si is formed in about 0.5% by weight relative to Me_2SiCl_2. The potentially utilizable four methyl groups attached to silicon have made this a compound of interest in our laboratory.[2-6] Thus, in the context of numerous studies concerning the electrophilic reactivity of the Si–Me bonds of Me_4Si, we have previously effected its conversion into Me_3SiCl either by the reaction with chlorine in the presence of catalytic amounts of iodine[3,4] or with other chlorosilanes such as $MeSiCl_3$, the main byproduct of direct synthesis,[5] or again with common polyhalo derivatives.[6] Moreover, some investigations in our laboratory were devoted to the use of Me_4Si as a methylating or silylating reagent for sulfonic moieties.[2] The useful and commercially available sulfonation reagent $ClSO_3SiMe_3$, for instance, was obtained from $ClSO_3H$ and Me_4Si.[2]

Methylchlorogermanes are important basic starting materials of organogermanium chemistry.[7,8] Consequently, we thought that Me_4Si could provide a convenient entry to methylchlorogermanes by methylation of germanium tetrachloride. We were encouraged by the Me/Cl exchange observed by Burch and Van Wazer[9] between germanium compounds at 300 °C in the presence of 0.1% $AlCl_3$ (eq 1–3).

$$Me_4Ge + GeCl_4 \rightleftharpoons Me_3GeCl + MeGeCl_3 \quad (1)$$

$$Me_3GeCl + MeGeCl_3 \rightleftharpoons 2Me_2GeCl_2 \quad (2)$$

$$Me_4Ge + MeGeCl_3 \rightleftharpoons Me_3GeCl + Me_2GeCl_2 \quad (3)$$

These disproportionation reactions, slow under these conditions (4–30 days[9]), allowed the synthesis of methylchlorogermanes from Me_4Ge and $GeCl_4$ even at 200 °C.[10] However, this route used as Me_4Ge a methyl source, which is only available from MeMgX and $GeCl_4$ (or $(Me_3Ge)_2O$, also obtained after previous methylation).[8]

Also, our proposed route seemed attractive to us in comparison to the other routes to alkylchlorogermanes.[7,8,11] R_3GeX and R_2GeX_2 (R = Bu, X = Cl; R = Et, X = Br) had been obtained from R_4Ge and GeX_4 in the presence of large amounts of $AlCl_3$.[7,11] R_3GeCl had been prepared previously from R_4Ge by R/Cl exchange with HCl, MeCOCl, or halo derivatives in the presence of $AlCl_3$ and with metal halides such as $SbCl_5$, $GaCl_3$, or $SnCl_4$.[8] R_3GeCl also was obtained from $(R_3Ge)_2O$ and HCl[8] or, by halogen exchange, from R_3GeX (X = Br, I) and AgCl,[8] but R_2GeCl_2 was not generally available from these methods since cleavage of a second R–Ge bond does not occur with HCl[7] and alkylation using organolithium or Grignard reagents generally affords a mixture of alkylchlorogermanes.[7] The direct synthesis of R_2GeCl_2 by the Rochow method (RCl and Ge catalyzed by copper derivatives) occurs in good yields with R = Me and Et[7,8] but is complicated by secondary reactions when larger alkyl halides are used.[7,8]

$RGeCl_3$ was previously difficult to obtain (as a byproduct in the direct synthesis of R_2GeCl_2,[7,8] by addition of $HGeCl_3$ to alkenes,[7,8] or by halogen exchange from $RGeX_3$ (X = Br, I)).[7,8]

This survey of the literature encouraged us to investigate the Me/Cl exchange, starting from $SiMe_4$ and $GeCl_4$.

Results

Reactions were carried out on a scale of 50 mmol of $GeCl_4$ in an autoclave at temperatures over 180 °C, generally 200 °C, in the presence of 3–5 mol % of $AlBr_3$. Organogermanium and silicon bromides were not detected in appreciable amounts after the reaction. Although $AlCl_3$ in similar proportions gave similar results, we are reporting only attempts with $AlBr_3$ as it led to a much faster reaction, perhaps because of its good solubility in the medium. By a judicious choice of the ratio of Me_4Si to $GeCl_4$ and a convenient reaction time, this versatile reaction provided selectively Me_4Ge, Me_3GeCl, Me_2GeCl_2, or $MeGeCl_3$ in high or quantitative yields.

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Table I. Selective Mono- or Polymethylation of $GeCl_4$

				conversion rate,[a] mol %		formed methylgermanes,[a] mol %				formed chlorosilanes,[a] mol %	
run	molar equiv $Me_4Si/GeCl_4$	time, h	temp, °C	Me_4Si, %	$GeCl_4$, %	Me_4Ge, %	Me_3GeCl, %	Me_2GeCl_2, %	$MeGeCl_3$, %	Me_3SiCl, %	Me_2SiCl_2, %
1	5/1	2.5	200	69[b]	53	83	16	0	traces	100	0
2	4-ϵ/1	8	200	77[b]	72	40	60	0	0	91	9
3	5/1	10	200	79[b]	73	60	40	0	0	100	0
4	4.5/1	22	200	69[b]	80	$\underline{91}$	9	0	0	100	0
5	3/1	21	200	92	77	20	80	0	0	80	20
6	2/1	2.75	180	50	30	82	18	0	0	100	0
7	2/1	3.5	200	53	43	87	13	0	0	100	0
8	2/1	4.5	180	53		77	23	0	0	100	0
9	2/1	6	200	100	100	0	71	29	0	85	15
10	2/1	15	200	100	100	0	$\underline{100}$	0	0	50	50
11	1/1	6	200	100	80	0	54	35	11	60	40
12	1/1	22	200	100	100	0	30	56	15	6	94
13	1/1	56	200	100	100	0	14	$\underline{86}$	0	0	100
14	0.5/1	6	200	100	66	0	33	37	30	26	74
15	0.5/1	28	200	100	90	0	0	36	$\underline{64}$	0	100
16	0.33/1	5	200	91		26	74	0	0	89	11
17	0.3/1	65	200	100	85.7	0	0	32	$\underline{68}$	0	70[c]

[a] Determined by ^1H NMR spectroscopy and GLC. Yields after distillation were ~10% lower. [b] Calculated in reference to the stoichiometric proportions $Me_4Si/GeCl_4 = 4/1$ (mol). [c] In this case $MeSiCl_3$ also was formed in 30% yield.

As specified below, the formation of Me_4Ge at the beginning of the reaction is observed regardless of the conditions used. It is for this reason that tetra-, tri-, di-, and finally monomethylations of $GeCl_4$ are successively described.

Tetramethylation of $GeCl_4$. Tetramethylation of $GeCl_4$ was performed according to eq 4.

$$\mathrm{GeCl_4 + 4Me_4Si \xrightarrow[200\ ^\circ C]{AlBr_3} Me_4Ge + 4Me_3SiCl} \tag{4}$$

With 4.5 molar equiv of Me_4Si and 3–5 mol % of $AlBr_3$ relative to $GeCl_4$ (run 4, Table I), the conversion rate of $GeCl_4$ was 80% and Me_4Ge was formed in 91% yield, together with Me_3GeCl (9%) after 22 h at 200 °C. Me_2SiCl_2 was not detected in any appreciable proportion, this likely being due to the equilibrium favoring Me_3SiCl (eq 5).[12,13]

$$\mathrm{Me_4Si + Me_2SiCl_2 \rightleftharpoons 2Me_3SiCl} \tag{5}$$

Trimethylation of $GeCl_4$. With 2 molar equiv of Me_4Si relative to $GeCl_4$, Me_3GeCl was quantitatively formed (cf. run 10) (eq 6).

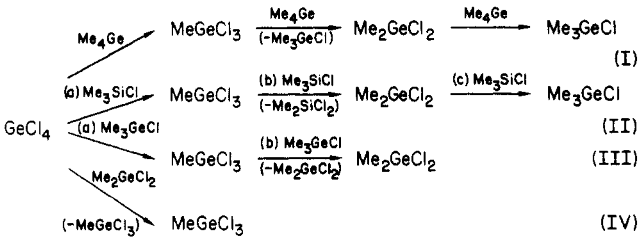
$$\begin{aligned} &\mathrm{GeCl_4 + 2Me_4Si \xrightarrow[15\ h,\ 200\ ^\circ C)]{AlBr_3\ (3\text{–}5\ mol\ \%)}} \\ &\qquad \mathrm{Me_3GeCl + Me_3SiCl + Me_2SiCl_2} \\ &\qquad \ \ 100\% \qquad\quad 50\% \qquad\quad 50\% \end{aligned} \tag{6}$$

It is worth noting that two methyl groups can be exchanged in Me_4Si; thus Me_3SiCl also acts as a methylating reagent. This result was corroborated by experiments in which the reaction conditions were varied. Thus with 3 molar equiv of Me_4Si relative to $GeCl_4$, Me_2SiCl_2 was formed as well as Me_3SiCl (20%), but Me_4Ge and Me_3GeCl (~20%) were still present when equilibrium was achieved (over 15 h) (run 5).

Dimethylation of $GeCl_4$. Optimum conditions required the use of $Me_4Si/GeCl_4$ (ca. 1/1 molar equiv) (cf. run 13) as expected from the stoichiometry in eq 7.

$$\mathrm{GeCl_4 + Me_4Si \xrightarrow[200\ ^\circ C]{AlBr_3} Me_2GeCl_2 + Me_2SiCl_2} \tag{7}$$

Scheme I



Even after prolonged reaction times, Me_3GeCl did not disappear completely (14% after 56 h). $GeCl_4$, however, reacted completely and, as previously observed, Me_3SiCl behaved as a methylating reagent and Me_2GeCl_2 was formed in 86% yield.

Monomethylation of $GeCl_4$. An excess of $GeCl_4$ is theoretically necessary to perform reaction 8.

$$\mathrm{2GeCl_4 + Me_4Si \xrightarrow[200\ ^\circ C]{AlBr_3} 2MeGeCl_3 + Me_2SiCl_2} \tag{8}$$

In fact only 90% of the $GeCl_4$ was converted after 28 h, whereas Me_4Si completely disappeared (cf. run 15). $MeGeCl_3$ and Me_2GeCl_2 were formed in 64% and 36% yields, respectively, and Me_2SiCl_2 was the only chlorosilane isolated (with $Me_4Si/GeCl_4$ = ca. 0.5/1). Under these conditions, $MeGeCl_3$ seems to be more difficult to obtain because it easily undergoes subsequent methylation. Consequently, it was not possible to isolate $MeGeCl_3$ when the $Me_4Si/GeCl_4$ ratio was greater than 2/1.

Discussion

The behavior of intermediate and final products was examined as a function of the parameters of reaction time and the proportion of unreacted starting materials (Table I). This would suggest the following mechanism.

(a) Tetramethylation of $GeCl_4$. This should be a fast reaction because Ge is large enough to undergo an easy tetramethylation despite the possible steric interactions among the four methyl groups (eq 9).

$$\mathrm{GeCl_4 \xrightarrow[-4Me_3SiCl]{4Me_4Si} Me_4Ge} \tag{9}$$

(b) Redistribution Reactions between $GeCl_4$ and the Products Formed during the Course of Methylation.

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Methylation was done by Me_4Si as previously observed during the synthesis of methylchlorogermanes from $GeCl_4$ and Me_4Ge (Scheme I).[10]

These reactions could occur simultaneously.

With a very large excess of Me_4Si ($Me_4Si/GeCl_4 \geq 4/1$), tetramethylation was almost the only reaction. Tetramethylation of $GeCl_4$ began relatively fast (53% conversion rate of $GeCl_4$ after 2.5 h (run 1, Table I)). $MeGeCl_3$ and Me_2GeCl_2 seem to react faster than $GeCl_4$ as they were not detected in appreciable amounts (previously observed during butylation of $GeCl_4$[8,11]). Then the reaction slowed down; the conversion ratio of $GeCl_4$ reached 72, 73, and 80% after 8, 10, and 22 h, respectively, while the percentage of Me_3GeCl present in the medium increased to 60% (after 8 h) and decreased between 8 and 22 h in favor of Me_4Ge (runs 2–4, Table I).

Working with $Me_4Si/GeCl_4 < 4/1$, the formation of Me_3GeCl and Me_4Ge was still observed at the beginning of the reaction regardless of the amount of Me_4Si lacking. Thus, with $Me_4Si/GeCl_4 = 2/1$ (reaction time between 2.75 and 4.5 h), only Me_3GeCl (~20%) and Me_4Ge (~80%) were formed (runs 6–8). Even with a large excess of $GeCl_4$ ($Me_4Si/GeCl_4 = 0.33/1$), we initially observed the formation of Me_3GeCl (74%) and Me_4Ge (26%, run 16).

However, once the Me_4Si had disappeared and the reaction time was prolonged, Me/Cl exchange between $GeCl_4$ or Me_nGeCl_{4-n} and Me_4Ge, Me_3SiCl, Me_3GeCl, and perhaps Me_2GeCl_2 was observed (reactions I–IV). Thus with $Me_4Si/GeCl_4 = 2/1$ and a reaction time of 4.5–6 h, Me_4Ge was observed to disappear, being progressively replaced by Me_3GeCl and Me_2GeCl_2 (reaction I), with Me_3SiCl being accompanied by Me_2SiCl_2 (runs 8 and 9, reaction II). After 6–15 h of reaction time, Me_2GeCl_2 was completely converted to Me_3GeCl (100%) by Me_3SiCl (which gave the corresponding amount of Me_2SiCl_2 (run 10, reaction IIc).

Methylation by Me_3SiCl after 6 h was confirmed by runs 11 and 14. With $Me_4Si/GeCl_4 = 1/1$, methylation from Me_3SiCl was achieved after 22 h, the percentage of Me_3GeCl decreasing because of its conversion into Me_2GeCl_2 (disproportionation with $MeGeCl_3$, reaction III, run 12). The yield of Me_2GeCl_2 was optimized by continuing the reaction for 56 h (run 13) (the decrease of Me_3GeCl and $MeGeCl_3$ was the same).

When $Me_4Si/GeCl_4$ was decreased to 0.5/1, Me_4Si, Me_4Ge, Me_3SiCl, and Me_3GeCl were completely consumed by $GeCl_4$ after 28 h and formation of $MeGeCl_3$ was largely favored (64% of the methylchlorogermanes, run 15). A comparison of runs 14 and 15 showed the disproportionation of $GeCl_4/Me_3GeCl$ as not being the only source of $MeGeCl_3$ as it also results from the redistribution between $GeCl_4$ and Me_2GeCl_2 according to reaction IV.

As the final point, we note that when a very large excess of $GeCl_4$ was used ($Me_4Si/GeCl_4 = 0.33/1$), the yield of $MeGeCl_3$ (68% of the formed methylgermanes) did not increase notably even after a 65-h reaction time (run 17). Quasi-equilibrium was reached after 28 h (run 15). It was observed, however, that because $MeSiCl_3$ was formed (run 17), Me_2SiCl_2 acts as a methylation reagent according to eq 10 and 11.

$$GeCl_4 + Me_2SiCl_2 \xrightleftharpoons{AlBr_3} MeGeCl_3 + MeSiCl_3 \quad (10)$$

$$MeGeCl_3 + Me_2SiCl_2 \xrightleftharpoons{AlBr_3} Me_2GeCl_2 + MeSiCl_3 \quad (11)$$

In conclusion, we note that the reaction between $GeCl_4$ and Me_4Si appears to be a versatile source of Me_4Ge, Me_3GeCl, Me_2GeCl_2, and even $MeGeCl_3$. The product obtained is a result of varying the respective ratios of starting reagents and the reaction time.

Experimental Section

Regardless of the proportions of $GeCl_4$ and Me_4Si, specified in Table I, we worked with 10.75 g of $GeCl_4$ (50 mmol). Similarly 3–5 mol % of $AlBr_3$ (0.4–0.67 g) or $AlCl_3$ (0.2–0.33 g) with respect to $GeCl_4$ were introduced. Results summarized in Table I were obtained with 5 mol % of $AlBr_3$; when 3 mol % was used, the reaction time was increased slightly to obtain the same yields.

Reagents were introduced with a syringe and weighed in an Erlenmeyer flask equipped with a sleeve stopper and previously cooled in an ice–water bath. In order to solubilize it and limit loss due to its volatility, Me_4Si always was introduced after $GeCl_4$ when the reagents were poured into an autoclave (125 mL) containing previously cooled dry argon. The autoclave was agitated at the temperature and time specified in Table I. After being cooled in an ice–water bath, the reaction mixture was analyzed by NMR, mass spectrometry, and gas chromatography (columns, Versilube F 50, 25% on Chromosorb P DMSCS, or QF_1 (2-m length, $^1/_8$-in. diameter); Me_2GeCl_2 and $MeGeCl_3$ not separable on Versilube thus were separated on QF_1 columns at 40 °C, whereas Me_2SiCl_2 and $GeCl_4$ not separable on QF_1 were separated on Versilube columns at 100 °C).

In order to avoid any modification of the reaction mixture during distillation, products were isolated upon distillation at temperatures lower than 100 °C after complexation of the Lewis acid with an excess of anhydrous NaCl. All products were identified by comparison of their NMR, mass spectra, or chromatography data with those of authentic samples.

Registry No. Me_4Si, 75-76-3; $GeCl_4$, 10038-98-9; Me_4Ge, 865-52-1; Me_3GeCl, 1529-47-1; Me_2GeCl_2, 1529-48-2; $MeGeCl_3$, 993-10-2; Me_3SiCl, 75-77-4; Me_2SiCl_2, 75-78-5; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0.