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TRIS(TRIMETHYLSILYL)METHYL GERMANIUM HALIDES *

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Summary

The sterically hindered organogermanium compounds $(Me_3Si)_3CGeR_2X$ (R = Me; X = Cl or I; R = Et, X = Br) have been prepared and their reactions examined. In contrast to the corresponding $(Me_3Si)_3CSiR_2X$ species, the germanium compounds undergo normal (though very slow) direct nucleophilic substitutions at germanium. Thus the iodide $(Me_3Si)_3CGeMe_2I$ reacts with boiling MeOH or, more rapidly, with $AgNO_3$—MeOH to give the methoxide $(Me_3Si)_3CGeMe_2OMe$. The compounds $(Me_3Si)_3CGeR_2X$ with R = Me, X = Cl or R = Et, X = Br do not react at a significant rate with boiling MeOH, but do react with NaOMe—MeOH or $AgNO_3$—MeOH to give the corresponding methoxides $(Me_3Si)_3CGeR_2OMe$.

Introduction

Tris(trimethylsilylmethyl)silicon compounds of the type $(Me_3Si)_3CSiR_2X$ have been shown to possess unusual properties, which can be attributed to the very large steric hindrance to nucleophilic attack at the silicon atom of the Si—X bond [1—8]. For the compounds with R = Me or Ph, X = F, Cl, Br or I, no reaction occurs with methanol alone, but with sodium methoxide in methanol fragmentation occurs (presumably driven by release of steric strain) to give products of the type $(Me_3Si)_2CHSiR_2OMe$, seemingly via the silaolefins $(Me_3Si)_2C{=}SiR_2$ [5]. For X = I, reaction occurs readily with silver or mercury(II) salts in methanol, and for R = Ph the products are of the type $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Y)$; (e.g., with $AgNO_3$, products with Y = OMe and NO_3 are formed), while with R = Et, mixtures of unrearranged and rearranged products, $(Me_3Si)_2CSiEt_2Y$ and $(Me_3Si)_2C(SiEt_2Me)(SiMe_2Y)$, are obtained [2,8]. These reactions are thought to proceed via bridged cations of type I.

Since the atomic radius of germanium (1.225 Å) is very close to that of silicon (1.176 Å), it seemed likely that comparable steric hindrance would be present in the germanium compounds $(Me_3Si)_3CGeR_2X$, so that these might also

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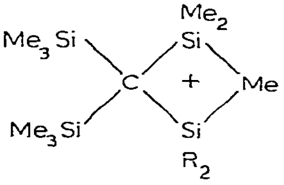
show unusual reactions, and, in particular, might give rearrangement products via a bridged ion of the type II, and so we made and examined some such compounds with R = Me and Et. The compound $(Me_3Si)_3CGeMe_3$ was prepared some years ago [9].

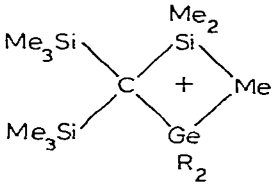
In the account below we shall, as usual, frequently denote the $(Me_3Si)_3C$ group (the 'trisyl' group) by the symbol Tsi.

Results and discussion

The chloride $TsiGeMe_2Cl$ was readily made from TsiLi and Me_2GeCl_2, and was reduced with $LiAlH_4$ in Et_2O to the hydride $TsiGeMe_2H$, which with iodine gave the iodide $TsiGeMe_2I$. (Treatment of the hydride with ICl, which with $TsiSiMe_2H$ gives the iodide, gave a 2 : 1 mixture of iodide $TsiGeMe_2I$ and chloride $TsiGeMe_2Cl$ even when a deficiency of the ICl was used.)



(I)



(II)

The chloride $TsiGeMe_2Cl$ did not react with PhLi in ether or NaI in acetone. It was recovered unchanged after 1 h of refluxing with methanol containing pyridine. It did, however, react, though fairly slowly, with 0.1 *M* NaOMe in MeOH under reflux. After 0.5 h a little of the methoxide, $TsiGeMe_2OMe$ had been formed, but the unchanged starting material greatly predominated. After 3.5 h only a little starting material remained, and this had almost disappeared after 4.5 h. The product was very largely $TsiGeMe_2OMe$, but small amounts of other compounds were also formed. In a similar reaction but with 0.5 *M* NaOMe, there was no starting material left after 2 h.

The chloride also reacted, again fairly slowly, with $AgNO_3$ in refluxing MeOH, reaction being about 50% complete after 1 h, and complete after about 13 h. The product was again the simple substitution product $TsiGeMe_2OMe$, and there was no indication from the ^1H NMR spectrum that any rearranged methoxide, $(Me_3Si)_2C(GeMe_3)(SiMe_2OMe)$, had been formed.

The iodide $TsiGeMe_2I$ was found to undergo essentially no reaction with NaO_2CCH_3 in CH_3CO_2H. It reacted with methanol alone, about 50% being converted into the methoxide $TsiGeMe_2OMe$ in 1 h at reflux, and 72% after 2 h. The methoxide was formed in about 90% yield after 1 h of reflux with $AgNO_3$ in MeOH (the reaction may have been complete in a shorter time), along with a small amount of another $TsiGeMe_2X$ product, possibly the nitrate. There was no indication of the formation of any $(Me_3Si)_2C(GeMe_3)(SiMe_2OMe)$.

The diethylgermanium bromide $TsiGeEt_2Br$ was made from TsiLi and Et_2GeBr_2. It did not react with refluxing methanol alone during 1 h, but underwent complete reaction with 0.5 *M* NaOMe in MeOH during 2.5 h under reflux. The main product was $TsiGeEt_2OMe$, but there were several minor products which were not identified. The methoxide $TsiGeEt_2OMe$ was also the main product from the reaction with $AgNO_3$ in MeOH, but there was about 10% of another $TsiGeEt_2Y$ product, perhaps the nitrate, and on work-up a little hydroxide $TsiGeEt_2OH$ was also isolated, possibly having been formed by hydrolysis of the nitrate. There was no evidence of any formation of the rearranged methoxide $(Me_3Si)_2C(GeEt_2Me)(SiMe_2OMe)$.

It is evident that the steric effects in $TsiGeR_2X$ compounds, while making the germanium halides very much less reactive than simple trialkylgermanium halides (e.g. the reaction of $i\text{-}Pr_3GeCl$ with 4 *M* H_2O in acetone has a half-life of <1 sec at 25°C [10]), are not so great as to divert reaction away from the normal direct nucleophilic substitution at germanium. Thus the $TsiGeR_2X$ systems seem to be less interesting in the respects examined than the corresponding silicon systems, and we have postponed further study of them.

In view of the very similar covalent radii of Si and Ge it is perhaps surprising that the steric effects are so much smaller in the $TsiGeR_2X$ than in the $TsiSiR_2X$ systems. Clearly the germanium compounds with R = Me or Et and X = Cl, Br, or I are markedly more reactive towards nucleophilic substitution than their silicon analogues. In contrast, the germanium compound Ph_3GeCl is some 80 times less reactive Ph_3SiCl towards water in acetone, though $i\text{-}Pr_3GeCl$ is at least 20 times as reactive as $i\text{-}Pr_3SiCl$ [10]. It is likely that this change in the reactivity order arises from the greater steric hindrance of the i-Pr groups when attached to silicon, though Chipperfield and Prince suggested that the greater effectiveness of π-bonding between the Ph groups and Si than between these groups and Ge was responsible for the higher reactivity of the Si compounds [10], with the implication that in the absence of such effects the germanium compounds would normally be the more reactive. However, it has been shown that in cleavage of $R_3M{-}R'$ bonds by base, which involves nucleophilic displacement at M, reaction is normally much faster for M = Si than for M = Ge [11,12], but with a large R′ group and with R = Et the germanium compounds become the more reactive [11], indicating clearly in this case that steric effects are smaller for Ge than for Si. Thus it seems probable that Me_3GeX would normally be less reactive than Me_3SiX species towards methanol or methoxide ion, and the greater ease of substitution in $TsiGeMe_2X$ than in $TsiSiMe_2X$ arises from the smaller steric hindrance caused by the Tsi group in the germanium compounds. The slightly larger covalent radius of Ge could account for some of this effect, but probably more important is that the generally lower strengths of bonds to Ge compared with those to Si allow greater deformation in the germanium compounds, both in bond lengths and bond angles, with reduction in the steric compression.

Experimental

General

The ^1H NMR spectral data reported were determined at 60 MHz and refer to solutions in CCl_4 containing CH_2Cl_2 as reference.

Preparations of $TsiGeMe_2Cl$ and $TsiGeEt_2Br$

(a) A solution of MeLi was made from MeCl and Li in THF, and to a portion of this (21 cm^3 of 1.44 *M* solution, 30 mmol) was added TsiH (5.8 g, 25 mmol) in THF (60 cm^3). The TsiLi was produced as previously described [4,9], and Me$_2$GeCl$_2$ (4.7 g, 27 mmol) was then added, giving an immediate precipitate of LiCl. The mixture was stirred at room temperature for 2 h, then the solvent was evaporated off under vacuum and the residue extracted with hexane. The combined hexane extracts were washed with water, dried (MgSO$_4$) and evaporated to leave a white solid, the ^{1}H NMR spectrum of which showed that there was one main product and about 10% of an impurity. Column chromatography (silica gel, with hexane as eluant) gave first a little TsiGeMe$_3$ [9] (probably formed from Me$_3$GeCl, itself produced from Me$_2$GeCl$_2$ and the residual MeLi in the TsiLi solution), and then (Me$_3$Si)$_3$CGeMe$_2$Cl (5.5 g, 60% m.p. >360°C; δ (ppm): 0.38 (s, 27 H) and 0.95 (s, 6 H) (Found: C, 39.0; H, 9.0; C$_{12}$H$_{33}$GeClSi$_3$ calcd.: C, 39.1; H, 9.0%). The mass spectrum (70 eV) gave the expected large peak at m/e 351 $[M - \text{Me}]^+$ and also a substantial peak at m/e 331 $[M - \text{Cl}]^+$.

(b) A similar procedure starting from Et$_2$GeBr$_2$ (11.7 g, 40.2 mmol) and TsiH (8.7 g, 37.5 mmol) and culminating in column chromatography gave white crystals of (Me$_3$Si)$_3$CGeEt$_2$Br (9.6 g, 58%); δ (ppm) 0.28 (s, 27 H), 1.06—1.50 (m, 10 H) (Found: C, 38.1; H, 8.4. C$_{14}$H$_{37}$BrGeSi$_3$ calcd.: C, 38.0, H. 8.4%).

Preparation of TsiGeMe$_2$H and TsiGeMe$_2$I

(a) A mixture of TsiGeMe$_2$Cl (0.5 g, 1.35 mmol) and LiAlH$_4$ (0.1 g, 2.7 mmol) in ether (100 cm^3) was refluxed for 4.5 h, then the ether was evaporated off and the residue extracted with hexane. The hexane extract was washed with water, dried (MgSO$_4$), and evaporated, to leave a white solid, which was shown by its ^{1}H NMR spectrum to contain about 10% of unchanged TsiGeMe$_2$Cl. Column chromatography (silica gel; hexane as eluant) gave, from the earlier fractions eluted, (Me$_3$Si)$_3$CGeMe$_2$H (3.2 g, 70%), m.p. 270—271°C (with sublimation); ν(Si—H) 2020 cm^{-1}; δ(ppm) 0.20 (s, 27 H), 0.45 (d, 6 H), and 4.23 (m, 1 H) (Found: C, 43.1; H, 10.0; C$_{12}$H$_{34}$GeSi$_3$ calcd.: C, 43.0; H, 10.2%).

(b) A solution of iodine (1.5 mmol) in CCl$_4$ (6 cm^3) was added to a solution of TsiGeMe$_2$H (0.25 g, 0.75 mmol) and the mixture was refluxed for 9 h. (This prolonged reflux may not be necessary.) Solvent and residual iodine were removed under reduced pressure, and the residue was recrystallized from ethanol-hexane. The recrystallized product was further purified by sublimation to give (Me$_3$Si)$_3$GeMe$_2$I (1.8 g, 52%), m.p. >360°C (sublimes); δ(ppm) 0.29 (s, 27 H), 1.25 (s, 6 H) (Found: C, 31.7; H, 7.3. C$_{12}$H$_{33}$GeISi$_3$ calcd.: C, 31.3; H, 7.2%).

Methanolysis of TsiGeMe$_2$Cl and TsiGeMe$_2$I

(a) A mixture of TsiGeMe$_2$Cl (0.25 g, 0.67 mmol), MeONa (1.35 g, 25 mmol) and anhydrous MeOH (25 cm^3) was refluxed for 2 h. The solvent was then removed under reduced pressure, and the residue was extracted with hexane. The hexane extracts were washed, dried (MgSO$_4$), and evaporated to leave a white solid, which was purified by column chromatography (silica gel; hexane as eluant) to give (Me$_3$Si)$_3$CGeMe$_2$OMe, m.p. 250—251°C; δ(ppm) 0.33 (s, 27 H), 0.64 (s, 6 H), and 3.43 (s, 3 H) (Found: C, 43.1; H, 9.9. C$_{13}$H$_{36}$GeOSi$_3$ calcd.: C, 42.8; H, 9.9%).

(b) A solution of TsiGeMe$_2$Cl (50 mg, 0.135 mmol) and NaOMe (54 mg, 1 mmol) in MeOH (10 cm^3) was refluxed for 0.5 h. The solvent was then removed under reduced pressure and the residue extracted with hexane. The hexane extract was washed, dried, and evaporated, and the ^{1}H NMR spectrum recorded. This showed that a little $TsiGeMe_2OMe$ had been formed, but that the $TsiGeMe_2Cl$ was mainly unchanged.

After a similar procedure but with 3 h reflux, mainly $TsiGeMe_2OMe$ was present but also some $TsiGeMe_2Cl$. Another similar experiment but with 4 h of reflux gave $TsiGeMe_2OMe$ containing only a little $TsiGeMe_2Cl$.

(c) A solution of $TsiGeMe_2Cl$ (40 mg, 0.11 mmol) in anhydrous MeOH (10 cm^3) containing pyridine (8 mg) was refluxed for 1 h. Work-up as described under (a) gave essentially unchanged $TsiGeMe_2Cl$, and there was no detectable OMe peak in the ^{1}H NMR spectrum.

(d) A solution of $TsiGeMe_2Cl$ (40 mg, 0.11 mmol) in anhydrous MeOH (10 cm^3) containing $AgNO_3$ (22 mg, 0.13 mmol) was refluxed for 1 h. Work-up as in (a) gave a solid which was shown by its ^{1}H NMR spectrum to contain about equal amounts of $TsiGeMe_2OMe$ and $TsiGeMe_2Cl$. A similar procedure with 6 h reflux gave these compounds in a ratio of ca. 78/22; with 9 h reflux, the ratio was ca. 90/10, and with 13 h reflux the product was essentially pure $TsiGeMe_2OMe$. Only one OMe peak was present in the ^{1}H NMR spectrum.

(e) A solution of $TsiGeMe_2I$ (40 mg) in MeOH (10 cm^3) was refluxed for 1 h. Work-up as in (a) gave a white solid which was indicated by its ^{1}H NMR spectrum to be an ca. 50/50 mixture of $TsiGeMe_2OMe$ and $TsiGeMe_2I$. A similar procedure but with reflux for 2 h gave these compounds in ca. 72/28 ratio.

(f) A solution of $TsiGeMe_2I$ (40 mg, 0.087 mmol) in MeOH (10 cm^3) containing $AgNO_3$ (20 mg, 0.12 mmol) was refluxed for 1 h. Work-up as in (a) gave a solid which was mainly $TsiGeMe_2OMe$ along with about 10% of another compound. These were separated by TLC (silica gel, with elution with hexane containing 10% $CHCl_3$), to give pure $TsiGeMe_2OMe$, and a compound with δ(ppm) 0.40 (2, 27 H) and 0.72 (s, 6 H), which was not further investigated.

Methanolysis of $TsiGeEt_2Br$

(a) A solution of $TsiGeEt_2Br$ (0.25 g) in MeOH (40 cm^3) containing $AgNO_3$ (0.125 g) was refluxed for 3 h. The solvent was then removed at reduced pressure and the residue was extracted with hexane. The hexane extract was washed, dried, and evaporated to give a white solid, the ^{1}H NMR spectrum of which indicated it to be $TsiGeEt_2OMe$ containing about 10% of another compound. (There was only one OMe peak.) Preparative TLC (silica gel; hexane) gave three products. The fastest moving spot was identified as $Tsi(GeEt_2OH$; ν(GeOH) 3640(sharp) and 3460(br); δ(ppm) 0.27 (s, 27 H) and 1.2—1.36 (m, 10 H). (Found: C, 44.6; H, 9.8. $C_{14}H_{37}GeOSi_3$ calcd.: C, 44.4; H, 10.0%.) The second, much the largest, band was shown to be $TsiGeEt_2OMe$; δ(ppm) 0.20 (s, 27 H), 1.04—1.45 (m, 10 H), and 3.53 (s, 3 H). The third band gave a very small amount of solid with δ(ppm) 0.23 (s, 27 H) and 0.93—1.33 (m, 10 H), which was not further investigated.

(b) A solution of $TsiGeEt_2Br$ (40 mg) in MeOH (10 cm^3) was refluxed for 1 h. The usual work-up gave essentially unchanged starting material.

(c) A solution of $TsiGeEt_2Br$ (0.50 g, 1.13 mmol) in MeOH (125 cm^3) containing MeONa (3.4 g, 63 mmol) was refluxed for 2.5 h. The usual work-up gave a solid, the ^{1}H NMR spectrum of which suggested that two major components and at least 2 minor components were present. The ratio of the integrated signal from the single OMe peak (at δ3.53 ppm) to that from all the Me_3Si peaks indicated that ca. 40% of $TsiGeEt_2OMe$ had been formed. The other major component could have been unchanged $TsiGeEt_2Br$. Preparative TLC (silica gel; hexane) gave, from the second fastest band, pure $TsiGeEt_2OMe$, identical with the sample described in (a).

Reaction of TsiGeMe$_2$H with ICl

A solution of $TsiGeMe_2H$ (50 mg, 0.15 mmol) in a little CCl_4 was treated with a solution of ICl (0.17 mmol) in CCl_4 (1 cm^3). The ^{1}H NMR spectrum indicated that $TsiGeMe_2I$ and $TsiGeMe_2Cl$ were present in ca. 60/40 ratio. The same ratio of products, along with unchanged $TsiGeMe_2H$, was formed when only 0.07 mmol of ICl was used.

Other attempted reactions

(a) A solution of PhLi (0.30 mmol) in THF (5 cm^3) was added to a solution of $TsiGeMe_2Cl$ (0.27 mmol) in THF (5 cm^3). The solution was set aside for 24 h then refluxed for 24 h. The usual work-up gave essentially unchanged $TsiGeMe_2Cl$.

(b) A mixture of $TsiGeMe_2Cl$ (50 mg, 0.135 mmol), NaI (50 mg) and acetone (10 cm^3) was refluxed for 1 h. The usual work-up gave essentially unchanged $TsiGeMe_2Cl$.

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