Journal of Organometallic Chemistry, 299 (1986) 9–13
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF SOME TRIS(TRIMETHYLSILYL)GERMYL COMPOUNDS

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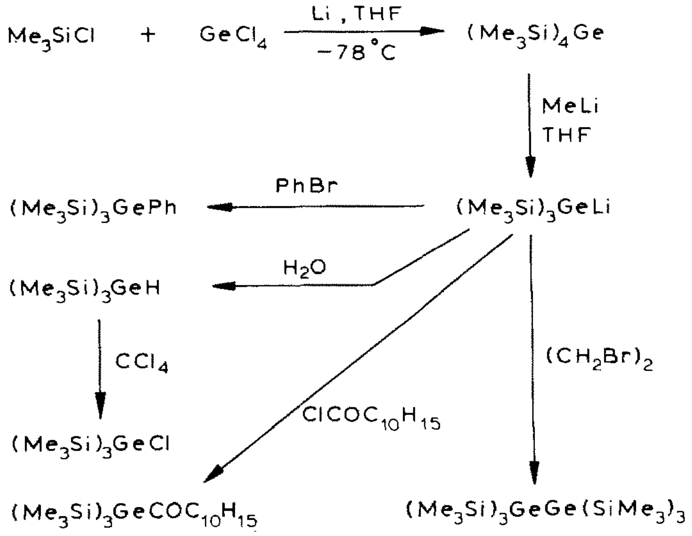
(Received July 11th, 1985)

Summary

A variety of compounds containing the tris(trimethylsilyl)germyl group were prepared and characterized spectroscopically. Photolysis of adamantoyltris(trimethylsilyl)germane failed to yield the isomeric germene: in CCl_4 the photolysis appeared to occur by a Norrish type 1 process.

We wish to describe briefly the synthesis of a variety of tris(trimethylsilyl)germyl compounds, outlined in Scheme 1, prepared in the course of an abortive attempt to



SCHEME 1

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synthesize a stable germene (Ge=C) by photolysis of a polysilylacylgermane, paralleling a known successful route to stable silenes [1] (eq. 1).

$$(Me_3Si)_3MCOC_{10}H_{15} \xrightarrow{h\nu} (Me_3Si)_2M{=}C(OSiMe_3)C_{10}H_{15} \qquad (1)$$

(M = Si, see ref. 1; M = Ge, this paper)

The compounds described in Scheme 1 all have related all-silicon analogs, and were prepared in most cases by analogous routes and were found to possess very similar properties.

The preparation of tetrakis(trimethylsilyl)germane, the key compound, has been described previously [2], and a serious drawback, the formation of a black precipitate (believed to be germanium from reduction of $GeCl_4$), was mentioned. It has now been found that if the coupling of trimethylchlorosilane with germanium tetrachloride using lithium in THF is conducted at −78°C, formation of the precipitate is largely avoided with a consequent improvement in yield of the tetrakis compound.

The germyllithium reagent was made in high yield by cleavage of the tetrakis compound using methyllithium in THF, and was readily purified and crystallized from pentane to give colourless material that was stable for months under argon. Between 2.5 and 3 mol of THF remained coordinated with the lithium reagent, the amount depending on the vigour of the pumping under reduced pressure. The germyllithium reagent, like its all-silicon analog [1,3], cleanly coupled with adamantoyl chloride in non-polar solvent to yield the acylgermane, and gave a modest yield of phenyltris(trimethylsilyl)germane when treated with bromobenzene. (Subsequent work with the all-silicon system suggests that coupling of phenylmagnesium bromide with tris(trimethylsilyl)germyl bromide would give better yields).

Tris(trimethylsilyl)germane was made by hydrolysis of the germyllithium reagent, and chlorination of the germane to tris(trimethylsilyl)chlorogermane was readily effected using CCl_4. Hexakis(trimethylsilyl)digermane, a possible coupling product of tris(trimethylsilyl)germyl radicals (see below) was made by reaction with ethylene dibromide following the procedure described for the fully silylated analog [4].

Whereas the photolysis of adamantoyltris(trimethylsilyl)silane in benzene cleanly gives rise to high yields of the isomeric silene [1], easily recognizable by its ^1H, ^{13}C, and ^{29}Si NMR spectra, and photolysis in benzene/methanol gives rise to near-quantitative yields of the methanol adduct of the silene [5], similar photolyses of the adamantoylgermane gave no evidence whatsoever of germene formation or of its methanol adduct. Complex mixtures of intractible insoluble polymeric material accompanied by a multitude of small fragments were observed. The ^{13}C NMR spectra showed no absorption downfield of benzene indicating the absence of sp^2-hybridized carbon of a germene, and the small benzene-soluble fraction of photolyses run in benzene/methanol had no strong methoxy signal characteristic of a germene-methanol adduct. The systems were not further studied. Photolyses in CCl_4 were much cleaner and, like the photolyses of simpler acylgermanes [6,7], resulted in Norrish type 1 cleavage leading to the formation of tris(trimethylsilyl)chlorogermane, adamantoyl chloride, hexachloroethane, a trace of chloroform, and a small amount of trimethylchlorosilane. No product from coupling of the germyl radicals was observed, presumably because of their efficiency in abstracting chlorine from the solvent. It is clear that the photochemistry of polysilylacylgermanes is quite different and very much more complex than that of its all-silicon analog and that photolysis of polysilylacylgermanes does not appear to be a promising route to relatively stable germenes.

Experimental section

Organometallic reagents were made and used under a dry argon atmosphere, using vacuum line techniques and sodium-dried solvents. NMR spectra were run on Varian T-60 or Bruker WP80 instruments using C_6D_6 as solvent unless noted otherwise. Analyses was performed by Galbraith Laboratories, Knoxville Tennessee.

Tetrakis(trimethylsilyl)germane

A mixture of 10 g (1.45 g atom) of chopped lithium wire, 69.4 g (0.64 mol) Me_3SiCl and 300 ml THF was cooled to −78°C, and 31.1 g (0.145 mol) of $GeCl_4$ in 75 ml of dry THF were slowly added over 1.5 h. The suspension turned dark red-brown immediately and the lithium wire was clean. On slowly warming to room temperature and stirring overnight the mixture became brown, with some black precipitate. The surface of the lithium turned black at that point in the reaction (25 h) when (as monitored by ^1H NMR) all the Me_3SiCl had been consumed. After filtration through Celite, and addition to 300 ml of 10% HCl, a voluminous brown precipitate formed which was removed by filtration. Extraction with ether, drying, and removal of the ether gave, after crystallization from acetonitrile, 22.2 g (42%) of $(Me_3Si)_4Ge$, m.p. 295°C, ref. 2: 295°C; NMR: $\delta(^1H)$ 0.40; $\delta(^{29}Si)$ −5.10 ppm.

Tris(trimethylsilyl)germyllithium

To a solution of 10 g (0.027 mmol) of $(Me_3Si)_4Ge$ in 100 ml of dry THF was added 18 ml of 1.5 *M* ethereal MeLi (0.027 mol). The solution immediately turned yellow, changing to amber. After 15 h, all the $(Me_3Si)_4Ge$ had reacted and only $(Me_3Si)_3GeLi$ (^1H NMR 0.12 ppm) and tetramethylsilane were present. The solvent was removed on a vacuum line and 150 ml of dry pentane was added to the yellowish residue. After stirring for 1 h, the precipitated LiBr was filtered off and on cooling, white needles of the germyllithium reagent precipitated from the pale yellow solution and were dried on the vacuum line to give 11.8 g (91%) of product. A ^1H NMR spectrum indicated that about 2.5 mol of THF were associated with each germyllithium molecule: NMR: $\delta(^1H)$ 0.75 (27H, s, Me_3Si), 1.42–1.74 (10H, m, CH_2), 3.54–3.86 (10H, m, CH_2O) ppm.

Adamantoyltris(trimethylsilyl)germane

A solution of 6.8 g (0.014 mol) of $(Me_3Si)_3GeLi \cdot 2.5THF$ in 125 ml pentane was added to 2.8 g (0.014 mol) of adamantoyl chloride in 50 ml pentane at −15°C over 1.5 h forming a pale yellow solution and a white precipitate. Filtration and removal of the solvent gave 6.0 g of yellow solid, which after recrystallization from methanol gave 2.75 g (50%) of acylgermane, m.p. 73–74°C: IR (KBr) 1640 cm^{-1} (C=O); NMR: $\delta(^1H)$ 0.45 (27H, s, Me_3Si), 1.6–2.1 (15H, m, $C_{10}H_{15}$); $\delta(^{13}C)$ 245.7 (C=O), 2.50 ($SiMe_3$), 52.1 (α), 37.6 (β), 28.5 (γ), 37.0 (δ) (adamantyl); $\delta(^{29}Si)$ − 5.24 ppm, $^1J(Si-CH_3)$ 44.5 Hz; UV (C_6H_{12}) λ_{max} 362 nm.

Anal. Found: C, 53.15; H, 9.52. $C_{20}H_{42}Si_3GeO$ calcd.: C, 52.76; H, 9.30%.

Tris(trimethylsilyl)germane

To an argon-saturated rapidly stirring emulsion of 5 ml of 10% aqueous HCl and 50 ml of pentane was added a solution of 3.9 g (8.2 mmol) of the above germyllithium reagent in 80 ml pentane over 0.5 h. A white precipitate formed. The aqueous layer was discarded and the pentane was evaporated under reduced pressure to give a mixture of oil and precipitate which was extracted with 80 ml of petroleum ether (b.p. 60–70%). The petroleum ether solution on evaporation yielded 2.1 g (89%) of the germane, b.p. 28–30°C/0.004 torr; ^{1}H NMR: δ 0.28 (Me_3Si), 2.13 (GeH) ppm; IR (neat) 1953 cm^{-1} (GeH).

Tris(trimethylsilyl)chlorogermane

A solution of 1.7 g (6.6 mmol) of the above germyl hydride in 65 ml petroleum ether was added slowly to 5 ml of CCl_4 in 30 ml of pentane at 0°C and was stirred overnight. Removal of the solvents under reduced pressure, followed by sublimation at 25°C/6 × 10^{-5} torr gave 1.3 g (60%) of pure compound, m.p. 45–46°C; NMR: $\delta(^1H)$ δ 0.27; $\delta(^{29}Si)$ −2.45 ppm.

Anal. Found: C, 32.70; H, 8.31. $C_9H_{27}ClGeSi_3$ calcd.: C, 33.00; H, 8.31%.

Tris(trimethylsilyl)phenylgermane

A solution of 4 g (10 mmol) of $(Me_3Si)_3GeLi \cdot 2.5THF$ in 100 ml of pentane was added over 1 h to 2.0 g (13 mmol) of bromobenzene in 50 ml pentane in the dark under reflux. On cooling after 2 h reflux, filtration of a white precipitate (LiBr) and removal of the solvent gave a yellow oil and more precipitate. After extraction with pentane followed by concentration to 10 ml volume, flash chromatography on silica gel using cyclohexane yielded 0.65 g (20%) of colourless product, m.p. 36°C; NMR: $\delta(^1H)$ (CCl_4) 0.25 (27H, s), 6.9–7.4 (5H, m); $\delta(^{29}Si)$ −6.66 ppm.

Anal. Found: C, 48.69; H, 8.83. $C_{15}H_{32}Si_3Ge$ calcd.: C, 48.79; H, 8.74%.

Hexakis(trimethylsilyl)digermane

A solution of $(Me_3Si)_3GeLi$ in THF, prepared as described above from 4.0 g (10.9 mmol) of $(Me_3Si)_4Ge$ was cooled to −78°C and 1 g (5.45 mmol) of $(CH_2Br)_2$ in 20 ml of THF was added slowly. A white precipitate formed immediately, and the brown colour of the germyllithium reagent disappeared. After stirring for 2 h at 20°C, the mixture was added to 100 ml of 10% aqueous HCl, and after ether extraction, drying, and removal of the ether, the residue was sublimed, initially with a 100°C bath at 9 × 10^{-4} torr, to yield a forerun of $(Me_3Si)_4Ge$, but subsequently to yield at 120°C the hexakis compound, m.p. 280°C (dec); NMR: $\delta(^1H)$ ($CDCl_3$) 0.32; $\delta(^{29}Si)$ ($CDCl_3/CCl_4$) −4.68 ppm.

Mass spectra

All of the above organogermanium compounds, run under EI conditions on a Dupont 21-490 mass spectrometer at 70 eV electron energy with source temperature about 160–170°C, had numerous similarities in their mass spectra. Thus signals for M^+, $(M - Me)^+$, and $(M - Me_3Si)^+$ were generally less than 10% of the base peak 73 [$(Me_3Si)^+$] in all cases, while peaks corresponding to $(Me_3Si)_3Ge^+$, (293), $((Me_3Si)_2Ge - H)^+$ (219), Me_3SiGe^+ (147), and $Me_3SiSiMe_2^+$ (131) were generally amongst the more intense (20–60%) peaks (masses calculated for Ge = 74). As expected no peak for $(Me_3Si)_3GeCO^+$ (321) was observed for the acylgermane [8].

Photolysis of acylgermane in CCl_4

NMR tubes containing degassed solutions of 250 mg of acylgermane in 0.5 ml CCl_4 were sealed under vacuum and irradiated with two 100-watt mercury flood lamps ($\lambda > 360$ nm) for up to 3 h at which time the starting material was completely consumed. The solution remained colourless. NMR spectra indicated the presence of $(Me_3Si)_3GeCl$ as the major silicon-containing species present ($> 65\%$), as well as some Me_3SiCl, based on comparisons with authentic samples. Cooling to $-15°C$ gave a near-quantitative yield of adamantoyl chloride, identified by m.p. and spectroscopic comparison with an authentic sample, and the filtrate contained a trace of chloroform (^1H NMR: δ 7.24 ppm) and an undetermined amount of hexachloroethane (^{13}C).

Photolysis under similar conditions in benzene gave coloured solutions (yellow-orange-amber) followed by the formation of a yellow precipitate. Proton or ^{29}Si NMR spectra showed more than 20 different Me-Si signals, but no ^{13}C absorption downfield of benzene. Photolyses in benzene/methanol behaved similarly, and after filtration of the precipitate, and removal of the solvents, the remaining benzene-soluble material contained only a very weak methoxy signal. The precipitate could not be recrystallized and changed colour and texture during the effort.

Acknowledgement

We are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this research.

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