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PREPARATION AND PROPERTIES OF SOME PENTAMETHYLDIGERMANYL COMPOUNDS*

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Summary

Compounds of the type $(CH_3)_3GeGe(CH_3)_2X$ have been prepared and investigated. They resemble their silicon analogs in many respects. The stability of the germanium—germanium bond does not seem to vary markedly with substituent.

Introduction

Many hexaorganodigermanes have been reported [1]. Digermane compounds having one or more organic groups replaced by inorganic ligands, however, are rather rare [2—4]. By contrast, there is an extensive chemistry of pentamethyldisilanyl compounds developed by Kumada and coworkers [5].

We report here concerning some new pentamethyldigermanyl derivatives.

Results and discussion

Preparation and physical properties

Chloropentamethyldigermane, prepared by the method of Bulten and Noltes [3, 4], served as a convenient synthetic starting point. The very facile hydrolysis of the halides made it necessary to work in a dry box under a protective atmosphere. The chlorodigermane could be converted to the bromo- or iodo-digermane by reaction with the appropriate potassium salt in acetone. Iodopentamethyldigermane could then be converted to the corresponding cyano, nitrato or isothiocyanato derivatives by reaction with the appropriate silver salts, analogously to the trimethylgermyl halides [6]. Cyanopentamethyldiger-

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mane will also react with AgNCS to form the isothiocyanate, or can be fused with sulfur to give this compound. In this respect it resembles $(CH_3)_3GeCN$ [7, 8].

Infrared spectra

Vibrations arising from the $(CH_3)_5Ge_2$ framework do not vary much among the different derivatives; this is also observed for pentamethyldisilanyl compounds [9]. The three halides show a band at 1070 cm^{-1}, probably from Ge—O bonds formed by hydrolysis. Nitratopentamethyldigermane shows two N—O stretching bands at positions expected for a singly-bonded covalent nitrate group [10]; a third expected band is probably masked by the strong Ge—O stretching peak at 1005 cm^{-1}. $(CH_3)_5Ge_2CN$ shows the "normal" $C{\equiv}N$ stretching band at 2177 cm^{-1}, along with a very weak band at 2080 cm^{-1} possibly due to $(CH_3)_5Ge_2NC$. This 2080 cm^{-1} band is appreciably weaker than the 2100 cm^{-1} band in cyanotrimethylgermane which has been attributed to $(CH_3)_3GeNC$ [7,8]. If the assignment is correct, then the "normal—iso" equilibrium lies more to the "normal" form in $(CH_3)_5Ge_2CN$ relative to $(CH_3)_3GeCN$. The Ge—Ge stretching mode appears between 275 and 280 cm^{-1} in these compounds. This compares favorably to the value of 273 cm^{-1} found for $(CH_3)_6Ge_2$ by Fontal and Spiro [11].

NMR spectra

Table 1 lists proton NMR peaks for various digermane compounds. These spectra strongly resemble those of silicon analogs, except that the peaks appear at lower field [5]. The chemical shifts of the α-methyl hydrogens vary as X changes. Both inductive and resonance effects seem to be operative. In the halide series there is a consistent downfield shift, indicating a predominance of inductive effect. Pentamethyldigermanyl cyanide and nitrate, by contrast, show a marked upfield shift for the α-methyl protons. This change is probably due to the presence of π-bonds in these groups, which create anisotropy in the magnetic field. The effect may also be augmented by interaction between the ligand π-bonds and *d*-orbitals on germanium. The change is so great in $(CH_3)_5Ge_2ONO_2$ that α-methyl hydrogens actually appear at higher field than the β-methyl hydrogens.

TABLE 1

PROTON NMR CHEMICAL SHIFTS[a]

	$(CH_3)_3Ge$	$Ge(CH_3)_2X$
$(CH_3)_6Ge_2$[b]	9.767	
$(CH_3)_5Ge_2Cl$	9.628	9.292
$(CH_3)_5Ge_2Br$	9.600	9.130
$(CH_3)_5Ge_2I$	9.600	8.933
$[(CH_3)_5Ge_2]_2O$	9.633	9.300
$(CH_3)_5Ge_2CN$	9.567	9.420
$(CH_3)_5Ge_2ONO_3$	9.700	9.937

[a] Tau units. [b] Lit. [12] 9.79.

TABLE 2

MASS SPECTRAL PEAKS[a]

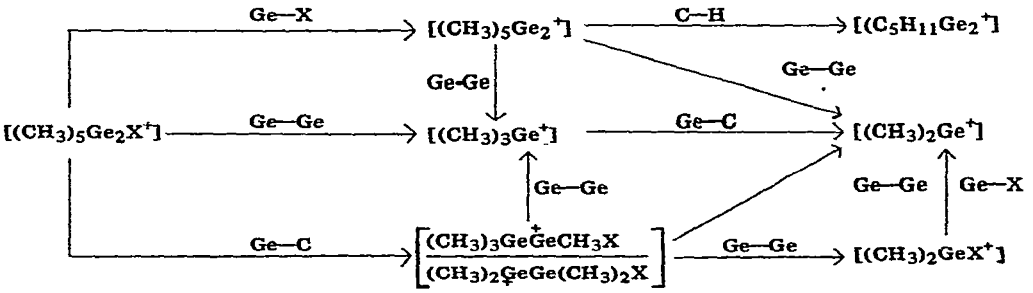
	$(CH_3)_5Ge_2Br$	$(CH_3)_5Ge_2I$	$(CH_3)_5Ge_2CN$	$[(CH_3)_5Ge_2]_2O$
$Me_5Ge_2X^+$	11.5	0.7	9.3	0.65
$Me_5Ge_2^+$	100	70.9	10.7	10.4
Me_3Ge^+	76	98.5	100	94
Me_2Ge^+	85	86.3	18.6	63.5
$C_5H_{11}Ge_2^+$	100	59.2	b	b
$Me_4Ge_2X^+$	10.9	b	49.2	26.8
H_3GeX^+	9.1	8.2	b	b
GeX^+	b	b	16.4	97.6
Other intense peaks		$CH_3GeH_2^+$ 100 $CH_3H_5Ge^+$ 99.5	$C_3H_5GeCN^+$ 100	Ge_4O^+ 100 $Me_5Ge_3O^+$ 100

[a] Relative intensities. [b] Not observed.

Mass spectra

Table 2 lists the major mass spectral peaks observed for pentamethyldigermanyl compounds. While the fragmentation patterns resemble those of hexaorganodigermanes to some extent [1], the presence of Ge—X bonds adds extra diversity. In all cases the molecule-ion peak is weak (Scheme 1).

SCHEME 1. INITIAL FRAGMENTATION PATTERNS OF PENTAMETHYLDIGERMANYL COMPOUNDS.



Germanium—halogen bond cleavage dominates in the halogens, whereas germanium—methyl bond cleavage is predominant in the oxide and cyanide. Carbon—hydrogen bond cleavage also occurs, and fragments containing Ge—H linkages are found in the spectra of the halides. While Ge—Ge cleavage is observed, fragments retaining the digermyl linkage are abundant, especially in the spectrum of the oxide.

Conclusion

The results so far available indicate that substituted derivatives of hexamethyldigermane strongly resemble the silicon analogs in their physical properties, and the trimethylgermyl derivatives in chemical properties. There does not seem to be any marked change in the germanium—germanium bond stability as different ligands are substituted, which suggests a chemistry comparable in extent to pentamethyldisilanyl compounds [5]. The bonding in pentamethyldigermanyl derivatives, especially as concerns interaction between germanium and the ligand, has special interest, since such interactions have been extensively studied for silicon [5]. We are currently investigating this aspect of organodigermane chemistry.

Experimental

General Comments

Trimethylbromogermane (Alfa Inorganics) and stannic chloride (Sargent Scientific Corp.) were used without further purification. The various solvents were dried over $CaSO_4$ (hexamethylphosphoric triamide, acetone, methanol, nitromethane), sodium (benzene, pentane) or $LiAlH_4$ (tetrahydrofuran) and distilled under nitrogen.

The infrared spectra were run on either Backman Model IR-12 or Perkin—Elmer Model 237 recording spectrophotometers. Infrared peak positions have an uncertainty of ± 2 cm^{-1}. Proton NMR spectra were obtained using Varian Model T-60 spectrophotometer, using CCl_4 solutions with tetramethylsilane as internal standard. The uncertainty was ± 0.003. Mass spectra were run on a Hitachi Perkin—Elmer RMU-7 Double Beam Spectrometer.

In order to minimize hydrolysis, all reported preparations were done in a dry box under nitrogen atmosphere. Certain compounds were purified by gas chromatography. The instrument used was a Hewlett—Packard 700 Laboratory Chromatograph. Two columns were generally used: a 6 foot stainless steel column, $\frac{3}{8}$ inch OD, with 10% SE 30 on 42/60 AW Chromosorb 22 silicone firebrick packing, or a 6 foot aluminum column, $\frac{3}{8}$ inch OD, with 25% Carbowax 20M on Chromosorb A packing. Helium was used as carrier gas, and the product trapped out in a dry ice—acetone bath.

Pentamethylbromodigermane

To 0.1911 g (0.747 mmol) of $(CH_3)_5Ge_2Cl$* in 10 ml of dry acetone was added 1.92 g (18.7 mmol) of dried NaBr over a 30 minute period. The mixture was refluxed overnight, cooled, extracted with 30 ml pentane, and filtered. The residue was washed with pentane, which was added to the filtrate. Distillation removed the solvents, leaving a liquid residue which was distilled to give 0.1062 g (47.4% yield) of bromopentamethyldigermane, b.p. 52°/0.08 mm. (Anal. Found: Br, 26.50. $C_5H_{15}Ge_2Br$ calcd.: Br, 26.63%.)

Iodopentamethyldigermane

To 0.8501 g (3.32 mmol) of $(CH_3)_5Ge_2Cl$ in 10 ml of dry acetone was added 4.98 g (0.033 mol) of dried NaI over a period of 30 min. The mixture was refluxed for 3.5 h, mixed with 30 ml of pentane, and filtered. Distillation of the filtrate gave 1.1539 g (90.0% yield) of iodopentamethyldigermane, b.p.

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* This compound was prepared by the method of Bulten and Noltes [3, 4], except that pentane was used instead of benzene.

58°/0.08 mm. The compound is photosensitive and rapidly turns yellow-brown upon exposure to light. (Anal. Found: I, 36.29. $C_5H_{15}Ge_2I$ calcd.: I, 36.56%.)

Cyanopentamethyldigermane

To 0.5017 g (1.44 mmol) of $(CH_3)_5Ge_2I$ in 20 ml of dry acetone was added 1.9273 g (14.4 mmol) of AgCN over a 30-minute period. Yellow silver iodide began to form immediately. The mixture was refluxed for 3.5 h, cooled, and filtered. The filtered solid was washed with 40 ml pentane, which was added to the filtrate. The solvents were boiled off, and the residue distilled under vacuum. The product crystallized in the receiver to give 0.2855 g (80.2% yield) of cyanopentamethyldigermane, m.p. 62—64°. (Anal. Found: C, 29.11; H, 6.09; N, 5.54. $C_6H_{15}NGe_2$ calcd.: C, 29.27; H, 6.14; N, 5.69%.)

Nitratopentamethyldigermane

This compound was synthesized in the same manner as the cyanide. Dried tetrahydrofuran, as well as acetone, could be used as solvent. In this preparation, 1.3715 g (5.32 mmol) of $(CH_3)_5Ge_2Cl$ was treated with 4.2438 g (25.0 mmol) of $AgNO_3$. When THF was used as solvent, the final product was purified by gas chromatography to give 0.7290 g (48.2% yield) of nitratopentamethyldigermane, b.p. 37°/0.08 mm.

Bis(pentamethyldigermanyl) oxide

To 0.4137 g (1.62 mmol) of $(CH_3)_5Ge_2Cl$ was added 10 ml of distilled water. This mixture was stirred overnight, after which the water was distilled off. The liquid residue was distilled under vacuum and purified by gas chromatography to give 0.4291 g (58.1% yield) of bis(pentamethyldigermanyl) oxide, b.p. 54°/0.3 mm. (Anal. Found: C, 26.52; H, 6.46. $C_{10}H_{30}OGe_4$ calcd.: C, 26.32; H, 6.63%.)

Isothiocyanatopentamethyldigermane

Approximately 50 mg of $(CH_3)_5Ge_2CN$ was placed in a glass tube with an excess of powdered sulfur. The tube was sealed and heated in an oil bath at 150° for 3 h to give a black residue and a clear liquid. This latter showed a strong infrared band at 2060 cm^{-1} and no sign of a band at 2177 cm^{-1}. Hydrolysis by an aqueous solution of ferric ion gave a deep blood-red color.

In another approach, 0.1023 g (0.420 mmol) of $(CH_3)_5Ge_2CN$ in 20 ml of anhydrous ether was refluxed for 2 h over excess AgNCS. The solution was decanted and the ether was removed by evaporation in a dry box. Distillation gave 0.0897 g (77.6% yield) of isothiocyanatopentamethyldigermane, b.p. 62°/0.08 mm Hg. (Anal. Found: C, 25.85; H, 5.39; N, 4.97. $C_6H_{15}NSGe$ calcd.: C, 25.90; H, 5.43; N, 5.03%.)

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