A Novel Synthesis and Properties of *N*-Trifluoromethylgermaimine, $CF_3N{=}GeH_2$

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$CF_3N{=}GeH_2$, synthesised by a novel method involving the reactions of CF_3NO and GeH_4, underwent addition reactions with HI to give CF_3NHGeH_2I and substitution reactions to afford a number of derivatives, $CF_3N{=}GeRR'$ [where R, R' = H, Cl and $ON(CF_3)_2$]

In recent years, increasing interests have been focussed on the chemistry of germaimines of the type $R_2Ge{=}NR'$, which are reported as reactive intermediates detected by trapping exeriments.[1] However, the stability of the compound $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(CO_2Me)_2$ isolated only recently is attributed to mesomeric factors.[2,3] We now report the first examples of stable *N*-trifluoromethylgermaimines of the type $CF_3N{=}GeRR'$ [where R, R' = H, Cl, $ON(CF_3)_2$] whose relative stability is conferred by the highly electronegative trifluoromethyl and bis(trifluoromethyl)-nitroxy groups.

The reactions of trifluoronitrosomethane with germane in a 1:1 molar ratio in an evacuated glass ampoule at 120 °C afforded *N*-trifluoromethylgermaimine, $CF_3N{=}GeH_2$ and water, according to equation (1).

$$CF_3NO + GeH_4 \rightarrow \underset{\textbf{(A)}}{CF_3N{=}GeH_2} + H_2O \qquad (1)$$

N-Trifluoromethylgermaimine was isolated at −96 °C trap in a trap-to-trap fractionation under high vacuum as a white solid in 25% yield. Water was isolated at −40 °C trap. At room temperature, the germaimine (**A**) became a colourless gas. Its i.r. spectrum gave the following peaks: 2099 cm^{-1}, (ν Ge–H); 805 cm^{-1}, (δ Ge–H); 1306, 1268, 1232 cm^{-1}, (ν C–F); 703 cm^{-1}, (δ C–F). The Ge=N stretching vibration appeared at 1030 cm^{-1}. Molecular weight determination using Regnault's method gave 158 g mol^{-1}, [compound (**A**) requires 158 g mol^{-1}]. On standing in an evacuated ampoule for 2 days at room temperature, the germaimine (**A**) underwent polymerisation to deposit a film of orange solid on the surface of the ampoule. The i.r. spectrum of the polymer in KBr gave the following peaks: 2087 cm^{-1}, (ν Ge–H); 821 cm^{-1}, (δ Ge–H); 1297, 1230, 1157 cm^{-1}, (ν C–F); 751 cm^{-1}, (δ C–F). Qualitative analysis gave a positive test for germanium.

The EI-MS (electron impact mass spectrometry) of the germaimine (**A**) gave three clusters of peaks at *m/z* 161, 160, 159, 158, 156, 155, 154, and 153 which are due to the presence of the parent ion $[CF_3NGeH_2]^{+\cdot}$ and fragment ions $[CF_3NGeH]^{+\cdot}$ and $[CF_3NGe]^{+\cdot}$. Moreover, numerous series of fragment ions are also observed in the mass spectrum. However, ^1H n.m.r. spectroscopy of the germaimine (**A**) gave a singlet δ 1.99 (GeH_2) ref. tetramethylsilane; and the ^{19}F n.m.r. spectrum also gave a singlet at δ 41.0 (CF_3) ref. trifluoroacetic acid.

The presence of the Ge=N double bond in the germaimine (**A**) was chemically confirmed by its reactions with hydrogen iodide which gave the addition product CF_3NHGeH_2I in 33% yield, as shown by equation (2).

$$CF_3N{=}GeH_2 + HI \rightarrow \underset{\textbf{(B)}}{CF_3NHGeH_2I} \qquad (2)$$

Compound (**B**) was isolated at −60 °C trap as a white solid. It is a volatile pale yellow liquid at room temperature. The presence of an N–H stretching vibration at 3432 cm^{-1} indicates that the addition of hydrogen iodide across the Ge=N double bond occurred with hydrogen migrating to the nitrogen atom and iodine to the more electropositive germanium atom. The other i.r. bands are: 2329 cm^{-1} (ν Ge–H); 830 cm^{-1} (δ Ge–H); 1375, 1353, 1200 cm^{-1}, (ν C–F); 720 cm^{-1} (δ C–F). The Ge=N stretching vibration at ~1030 cm^{-1} was absent. Analysis of iodine gave 45.07%; [compound (**B**) requires 44.56%].

The presence of the GeH_2 moiety in *N*-trifluoromethylgermaimine was further confirmed by its reactions with bis(trifluoromethyl)nitroxyl which is a powerful hydrogen abstractor and a radical scavenger. Reactions of the germaimine (**A**) with bis(trifluoromethyl)nitroxyl in the molar ratio of 1:2 and 1:4

gave the corresponding bis(trifluoromethyl)nitroxy derivatives (**C**) and (**D**) in 36% and 45% yields, respectively, as shown by equations (3) and (4).

$$CF_3N{=}GeH_2 + 2(CF_3)_2NO \rightarrow \underset{\textbf{(C)}}{CF_3N{=}GeHON(CF_3)_2} + (CF_3)_2NOH \quad (3)$$

$$CF_3N{=}GeH_2 + 4(CF_3)_2NO \rightarrow \underset{\textbf{(D)}}{CF_3N{=}Ge[ON(CF_3)_2]_2} + 2(CF_3)_2NOH \quad (4)$$

In both the reactions, bis(trifluoromethyl)hydroxylamine was eliminated almost quantitatively. On fractionation, the bis(trifluoromethyl)nitroxy derivatives (**C**) and (**D**) were isolated at −70 °C trap as white solids. On warming to room temperature in an evacuated ampoule, the solids melted and then vapourised. They are stable at room temperature.

Cleavage of the Ge–O bond of both the bis(trifluoromethyl)-nitroxy derivatives (**C**) and (**D**) by hydrogen chloride afforded the corresponding chloro-derivatives (**E**) and (**F**) in 53% and 57% yields respectively, together with an almost quantitative yield of bis(trifluoromethyl)hydroxylamine, according to equations 5 and 6. They are stable at −20 °C. On standing for a day at room temperature in evacuated ampoules, both the chloro-derivatives (**E**) and (**F**) deposited some non-volatile solids which consist of chlorine, germanium, the CF_3 and GeH groups. Analysis for chlorine gave: (**E**), 17.97%; (**F**), 30.82%; [calcd: (**E**), 18.53%; (**F**), 31.40%].

$$CF_3N{=}GeHON(CF_3)_2 + HCl \rightarrow \underset{\textbf{(E)}}{CF_3N{=}GeHCl} + (CF_3)_2NOH \quad (5)$$

$$CF_3N{=}Ge[ON(CF_3)_2]_2 + 2HCl \rightarrow \underset{\textbf{(F)}}{CF_3N{=}GeCl_2} + 2(CF_3)_2NOH \quad (6)$$

The presence of the Ge=N double bond in the new germaimines (**C**) to (**F**) was indicated by their i.r. spectra, which gave absorption peaks located at 1028, 1070, 1057, and 1076 cm^{-1} respectively, which are slightly higher than the band at 970 cm^{-1} reported for $F_2Ge{=}NPh$ double bond.[1] Where GeH, CF_3N and $(CF_3)_2NO$ groups are present, they were indicated by their i.r. spectra. Molecular weights of the germaimines determined by Regnault's method gave: (**C**), 323; (**D**), 492; (**E**), 191; (**F**), 224 g mol^{-1}; [calcd. values: (**C**), 324; (**D**), 492; (**E**), 192; (**F**), 225 g mol^{-1}].

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