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PRELIMINARY NOTE

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Novel Synthesis and Properties of N-Bis(trifluoromethyl)nitroso-Germaine,  
(CF<sub>3</sub>)<sub>2</sub>NON=GeH<sub>2</sub>

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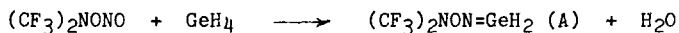
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SUMMARY

(CF<sub>3</sub>)<sub>2</sub>NON=GeH<sub>2</sub>, synthesized by a novel method involving the reactions of (CF<sub>3</sub>)<sub>2</sub>NONO and GeH<sub>4</sub>, underwent addition reactions with HI to give (CF<sub>3</sub>)<sub>2</sub>NONHGeH<sub>2</sub>I and substitution reactions to afford a number of derivatives, (CF<sub>3</sub>)<sub>2</sub>NON=GeRR' [where R, R' = H, Cl and ON(CF<sub>3</sub>)<sub>2</sub>].

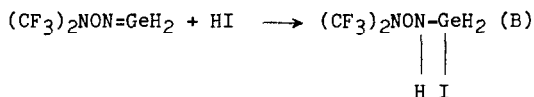
In recent years, there has been a growing interest in the chemistry of germaines of the type R<sub>2</sub>Ge=NR', where the Ge=N double bond has been shown to be reactive and that it can be detected by the so-called trapping experiments [1]. Thus far, only one such compound has been isolated, namely [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Ge=N-N=C(COOMe)<sub>2</sub>, whose stability has been attributed to mesomeric effects [2, 3]. We now report a number of new stable germaine derivatives, namely (CF<sub>3</sub>)<sub>2</sub>NON=GeRR' (where R, R' = H, Cl, ON(CF<sub>3</sub>)<sub>2</sub>), whose stability can be attributed to the presence of highly electronegative (CF<sub>3</sub>)<sub>2</sub>NO groups(s).

The reactions of N-nitrosobis(trifluoromethyl)hydroxylamine with germane in a 1:1 molar ratio in an evacuated glass ampoule afforded N-bis(trifluoromethyl)nitroso-germainime,  $(CF_3)_2NON=GeH_2$  in 35% yield, according to the equation:



A hygroscopic yellow solid was also formed in the reaction ampoule. The germainime (A) was isolated as a white solid at  $-96^\circ C$  on vacuum trap-to-trap fractionation. Its infrared spectrum gave the following peaks:  $2261\text{ cm}^{-1}$ , ( $\nu$  Ge-H);  $890\text{ cm}^{-1}$ , ( $\delta$  Ge-H);  $1324, 1271, 1243\text{ cm}^{-1}$ , ( $\nu$  C-F);  $1050\text{ cm}^{-1}$ , ( $\nu$  N-O); and  $720\text{ cm}^{-1}$ , ( $\delta$  C-F). The peak located at  $1002\text{ cm}^{-1}$  can be attributed to the Ge=N stretching vibration, which is slightly higher than the band at  $970\text{ cm}^{-1}$  reported for  $F_2Ge=NPh$  [1]. Molecular weight determination by Regnault's method gave  $255\text{ g mol}^{-1}$ ; (compound (A) requires  $256\text{ g mol}^{-1}$ ).

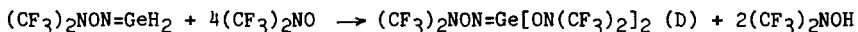
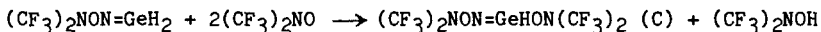
The presence of the Ge=N double bond in the germainime (A) was chemically confirmed by the addition reactions with hydrogen iodide to give  $(CF_3)_2NONHGeH_2I$ , as shown below:



The addition compound (B) was isolated at  $-60^\circ C$  trap on vacuum fractionation as a pale yellow liquid. The following peaks were shown in its infrared spectrum:  $3419\text{ cm}^{-1}$ , ( $\nu$  N-H);  $2232\text{ cm}^{-1}$ , ( $\nu$  Ge-H);  $822\text{ cm}^{-1}$ , ( $\delta$  Ge-H);  $1497, 1324, 1270, 1243\text{ cm}^{-1}$ , ( $\nu$  C-F); and  $1050\text{ cm}^{-1}$ , ( $\nu$  N-O). The Ge=N stretching vibration at  $1002\text{ cm}^{-1}$  disappeared. The spectral data indicate that addition across the double bond occurred with the migration of hydrogen to the nitrogen atom and iodine to the germanium atom.

$^1H$  NMR of the compound (B) consists of 2 peaks of 1:2 intensity: one ( $\delta$  NH) located at 11.6 ppm and the other ( $\delta$   $GeH_2$ ) at 2.1 ppm, both downfield w.r.t. TMS. The  $^{19}F$  NMR shows a singlet ( $\delta$   $CF_3$ ) at 17.6 ppm downfield w.r.t.  $CF_3COOH$ . Analysis of iodine gave 32.67%; (compound (B) requires 33.02%).

The presence of the  $\text{GeH}_2$  moiety was chemically confirmed by the reactions between the germainine (A) and bis(trifluoromethyl)nitroxyl which is a powerful hydrogen abstractor and a radical scavenger [4]. Their reactions in 1:2 and 1:4 ratio afforded N-bis(trifluoromethyl)nitroso derivatives (C) and (D) in 62% and 64% yields respectively:

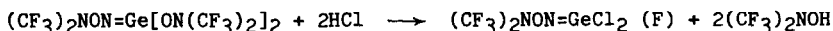


Both the reactions gave quantitative amounts of bis(trifluoromethyl)-hydroxylamine. The germainines (C) and (D) were isolated at  $-40^\circ\text{C}$  and  $-20^\circ\text{C}$  traps respectively as colourless liquids.

The infrared spectrum of compound (C) shows peaks located at 1393, 1290, 1243 1050, 995, 721  $\text{cm}^{-1}$  due to the presence of  $(\text{CF}_3)_2\text{NO}$  groups; as well as 2271 and 1001  $\text{cm}^{-1}$  due to Ge-H and Ge=N stretching vibrations respectively. Molecular weight determination of the germainine (C) gave 420  $\text{g mol}^{-1}$  (calcd. 423  $\text{g mol}^{-1}$ ).

The infrared spectrum of the germainine (D) shows characteristic peaks due to the  $(\text{CF}_3)_2\text{NO}$  group located at 1313, 1271, 1243 and 721  $\text{cm}^{-1}$ , and the Ge=N stretching at 1001  $\text{cm}^{-1}$ .

Compounds C and D underwent cleavage at the Ge-ON bonds when reacted with excess anhydrous hydrogen chloride to give the corresponding chloro derivatives, according to the equations:



In both the reactions, quantitative yields of bis(trifluoromethyl)-hydroxylamine were obtained.

Compound (E) shows peaks due to  $(CF_3)_2NO$  group at 1286, 1214, 1148, 900 and  $720\text{ cm}^{-1}$ , and the Ge=N stretching vibration at  $1022\text{ cm}^{-1}$ . Analysis for chlorine gave 11.34%, (compound (E) requires 12.19%). Similarly, compound (F) shows peaks due to  $(CF_3)_2NO$  group located at 1352, 1214, 1194 and  $720\text{ cm}^{-1}$ , and Ge=N group at  $1022\text{ cm}^{-1}$ . Analysis for chlorine gave 20.83%; (compound (F) requires 21.80%).

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