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LETTER

Synthesis of new germylated heterocyclic systems with bulky groups

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The production of transient low coordinated germanium species by thermolysis, pyrolysis or photolysis of germylated heterocycles has received considerable attention in our laboratory [1]. In particular several examples of decomposition of four-, five- or six-membered heterocycles have been reported [1–9]. However, quite a few four-membered rings are stable at room temperature [3–5]. We report herein our synthesis or attempted synthesis of the new four-membered heterocycles 1–4, [$\text{Ge}=\text{X}$] potential precursors. **1**: $\text{R}=\text{Mes}$, $\text{X}=\text{O}$, $\text{Z}=\text{SO}_2$; **2**: $\text{R}=\text{Me}$, $\text{X}=\text{N}-t\text{-Bu}$, $\text{Z}=\text{CS}$; **3**: $\text{R}=\text{Mes}$, $\text{X}=\text{N}-\text{H}$, $\text{Z}=\text{CS}$; **4**: $\text{R}=\text{Mes}$, $\text{X}=\text{N}-t\text{-Bu}$, $\text{Z}=\text{CS}$.

Experimental

Procedures follow those described in ref. 10 for reactions of dehydrochlorination. All products gave satisfactory combustion analyses.

$\text{Mes}_2\text{GeOSO}_2\text{O}$ (**1**), m.p. 176–178 °C. Cryometry (C_6H_6) M 440. MS (70 eV) m/z 408 (M^+). ^1H NMR (C_6D_6): $\delta=2.0$ (s, 6H, $p\text{CH}_3$), 2.5 (s, 12H, $o\text{CH}_3$), 6.6 (s, 4H, C_6H_2).

$\text{Mes}_2\text{GeOSO}_2\text{Ge}(\text{Mes}_2)\text{OSO}_2\text{O}$ (**5**). Cryometry (C_6H_6) M 850. MS (70 eV) m/z 814 (M^+). ^1H NMR (C_6D_6): $\delta=2.15$ (s, 6H, $p\text{CH}_3$), 2.6 (s, 12H, $o\text{CH}_3$), 6.65 (4H, C_6H_2).

$\text{Me}_2\text{GeN}(t\text{Bu})\text{CSN}(t\text{Bu})\text{Ge}(\text{Me}_2)\text{N}(t\text{Bu})\text{CSN}(t\text{Bu})$ (**6**) m.p. 185–186 °C. MS (70 eV) m/z 578 (M^+). ^1H NMR (C_6H_6): $\delta=0.83$ (s, 12H, CH_3), 1.2 (s, 36 H, $t\text{Bu}$).

$\text{Mes}_2\text{GeNHGe}(\text{Mes}_2)\text{S}$ (**7**), m.p. 74–75 °C. IR (nujol) $\nu\text{NH}=3420\text{ cm}^{-1}$. MS (70 eV) m/z 669 (M^+).

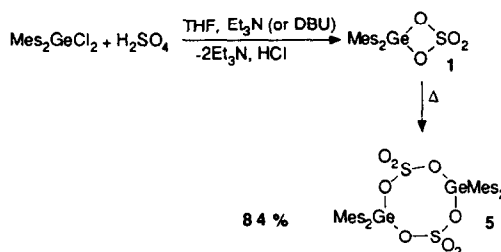
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^1H NMR (C_6D_6): $\delta=2.0$ (s, 6H, $p\text{CH}_3$), 2.5 (s, 12H, $o\text{CH}_3$), 3.80 (s, 1H, NH), 6.54 (4H, C_6H_2).

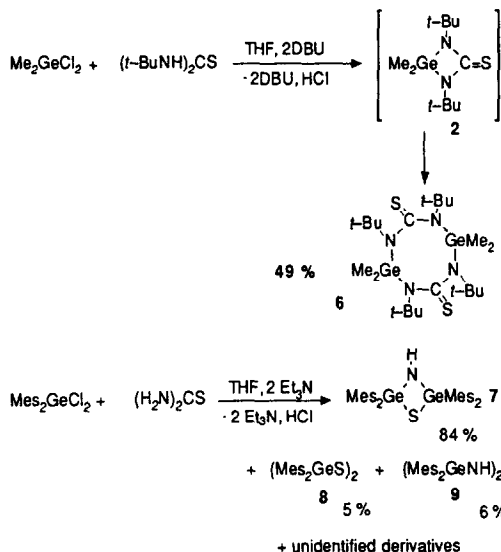
$(\text{Mes}_2\text{GeNH})_2$ (**9**), m.p. 146–148 °C. IR (nujol): $\nu\text{NH}=3420\text{ cm}^{-1}$. ^1H NMR (C_6D_6): $\delta=1.97$ (s, 6H, $p\text{CH}_3$), 2.53 (s, 12H, $o\text{CH}_3$), 6.5 (4H, C_6H_2).

$\text{Mes}_2\text{GeN}(t\text{Bu})\text{CSN}(t\text{Bu})$ (**4**), m.p. 134–135 °C. MS (70 eV) m/z 498 (M^+). ^1H NMR (C_6D_6): $\delta=1.16$ (s, 18H, $t\text{Bu}$), 2.0 (s, 6H, $p\text{CH}_3$), 2.46 (s, 12H, $o\text{CH}_3$), 6.53 (4H, C_6H_2).

Heterocycle **1** was prepared by dehydrochlorination reaction between sulfuric acid and dimesityldichlorogermane [11] by ethylamine in THF. **1** is stable at room temperature but under thermic effect it dimerizes to give the eight-membered ring **5**.

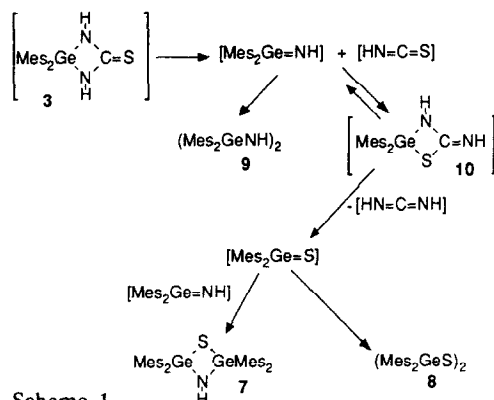


Dehydrochlorination, the classical route to germylated heterocycles with N–Ge–N linkages, was also applied to dihalogermanes R_2GeCl_2 ($\text{R}=\text{Me}$, Mes) and thioureas $\text{H}(\text{R}')\text{N}-\text{CS}-\text{N}(\text{R}')\text{H}$ ($\text{R}'=\text{H}$, $t\text{-Bu}$) with DBU or Et_3N in THF, with the aim of obtaining the compounds **2–4**. In the attempted syntheses of **2** and **3** we only isolated the corresponding dimer **6** of **2** and heterocyclic derivatives **7–9** suggestive of the formation and decomposition of the intermediate four-membered heterocycle **3**, respectively.

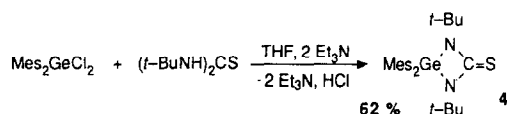


This decomposition leading to **7–9** is probably, in the first step, analogous to that observed for various four-membered heterocycles [1, 3–7] and probably involves, as previously postulated [12], the unsatu-

rated species $[S=C=NH]$ and $[Mes_2Ge=NH]$ which either dimerizes or reacts by $C=S$ addition with $[S=C=NH]$ producing the heterocycle **10**. In the same way this heterocycle **10** probably leads to the dimesitylgermanium sulfide dimer **8** [13] and the stable digermathiazetidine **7** by dimerization of the intermediate germanethione $[Mes_2Ge=S]$ and the pseudo-Wittig reaction with $[Mes_2Ge=NH]$, respectively. The postulated mechanism is summarized by Scheme 1.



It is noteworthy that the N-*t*-Bu, Ge-Mes heterocycle **4** is obtained stable at room temperature, probably due to steric hindrance.



All the stable compounds **1**, **4-9** were completely characterized by NMR, IR and mass spectroscopy analyses.

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