Inorganica Chimica Acta
LETTER

Synthesis of new germylated heterocyclic systems with bulky groups

J. Barrau*, G. Rima and **V. Cassano**
Laboratoire de Chimie des Organominéraux, U.R.A. 477 du C.N.R.S., Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, Cédex (France)

(Received April 2, 1991)

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**, [$>$Ge$=$X] potential precursors. $R_2Ge{-}X{-}Z{-}X$ **1**: R = Mes, X = O, Z = SO_2; **2**: R = Me, X = N-t-Bu, Z = CS; **3**: R = Mes, X = N-H, Z = CS; **4**: R = Mes, X = N-t-Bu, Z = CS.

Experimental

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

Mes_2GeOSO_2O(**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, pCH$_3$), 2.5 (s, 12H, oCH$_3$), 6,6 (s, 4H, C_6H_2).

$Mes_2GeOSO_2Ge(Mes_2)OSO_2O$(**5**). Cryometry ($C_6H_6$) *M* 850. MS (70 eV) *m/z* 814 (M^+). ^1H NMR (C_6D_6): $\delta = 2.15$ (s, 6H, pCH$_3$), 2.6 (s, 12H, oCH$_3$), 6.65 (4H, C_6H_2).

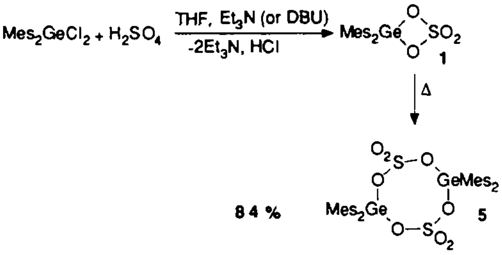
$Me_2GeN(tBu)CSN(tBu)Ge(Me_2)N(tBu)CSN(tBu)$ (**6**) m.p. 185–186 °C. MS (70 eV) *m/z* 578 (M^+). ^1H NMR (C_6H_6): $\delta = 0.83$ (s, 12H, CH$_3$), 1.2 (s, 36 H, tBu).

$Mes_2GeNHGe(Mes_2)S$ (**7**), m.p. 74–75 °C. IR (nujol) νNH = 3420 cm^{-1}. MS (70 eV) *m/z* 669 (M^+). ^1H NMR (C_6D_6): $\delta = 2.0$ (s, 6H, pCH$_3$), 2.5 (s, 12H, oCH$_3$), 3.80 (s, 1H, NH), 6.54 (4H, C_6H_2).

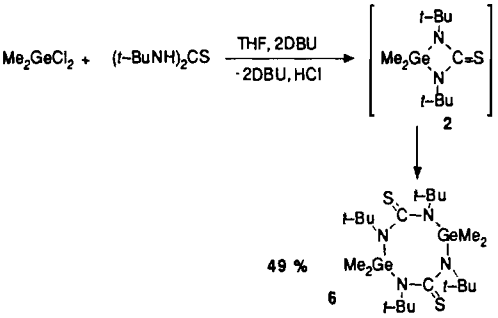
$(Mes_2GeNH)_2$ (**9**), m.p. 146–148 °C. IR (nujol): νNH = 3420 cm^{-1}. ^1H NMR (C_6D_6): $\delta = 1.97$ (s, 6H, pCH$_3$), 2.53 (s, 12H, oCH$_3$), 6.5 (4H, C_6H_2).

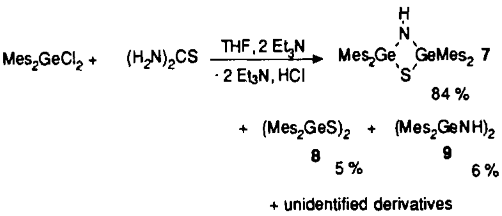
$Mes_2GeN(tBu)CSN(tBu)$ (**4**), m.p. 134–135 °C. MS (70 eV) *m/z* 498 (M^+). ^1H NMR (C_6D_6): $\delta = 1.16$ (s, 18H, tBu), 2.0 (s, 6H, pCH$_3$), 2.46 (s, 12H, oCH$_3$), 6.53 (4H, C_6H_2).

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 (R = Me, Mes) and thioureas H(R′)N–CS–N(R′)H (R′ = H, t-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.



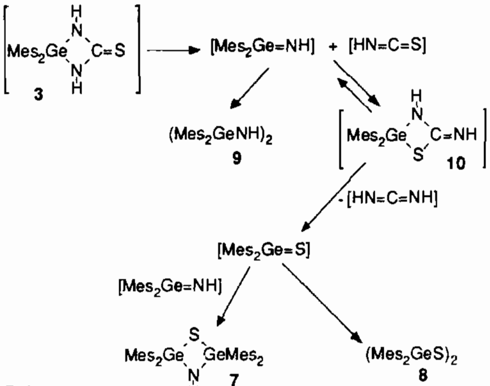


This decomposition leading to **7**–**9** is probably, in the first step, analogous to that observed for various four-membered heterocycles [1, 3–7] and probably involves, as previously postulated [12], the unsatu-

---

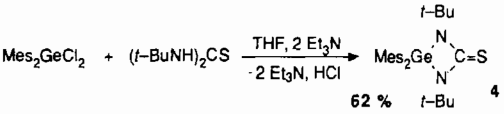
*Author to whom correspondence should be addressed.

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.



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.

References

1 J. Barrau, J. Escudié and J. Satgé, *Chem. Rev., 90* (1990) 283.
2 J. Barrau, M. Massol, D. Mesnard and J. Satgé, *J. Organomet. Chem., 30* (1971) C67.
3 J. Barrau, G. Rima and J. Satgé, *J. Organomet. Chem., 252* (1983) C73.
4 J. Barrau, G. Rima and J. Satgé, *J. Synth. React. Inorg. Met.-Org. Chem., 14* (1984) 21.
5 J. Barrau, G. Rima, M. El Amine and J. Satgé, *J. Chem. Res. S,* (1985) 30.
6 J. Barrau, M. El Amine, G. Rima and J. Satgé, *J. Organomet. Chem., 277* (1984) 323.
7 J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem., 282* (1985) 315.
8 J. Barrau, G. Rima, M. El Amine and J. Satgé, *J. Organomet. Chem., 345* (1988) 39.
9 C. Guimon, G. Pfister-Guillouzo, G. Rima, M. El Amine and J. Barrau, *Spectrosc. Lett., 18* (1985) 7.
10 P. Rivière, A. Castel, D. Guyot and J. Satgé, *J. Organomet. Chem., 290* (1985) C15.
11 P. Rivière and M. Rivière-Baudet, *Organomet. Synth., 4* (1988) 542.
12 G. Lacrampe, H. Lavayassière, M. Rivière-Baudet and J. Satgé, *Recl. Trav. Chim. Pays-Bas, 102* (1983) 21.
13 T. Tsumuraya, S. Sato and W. Ando, *Organometallics, 7* (1988) 2015.