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Synthesis and reactivity of the new digermaheterocycles $Me_2Ge(CH_2)_nGe(Me_2)NC(O)N(R)C(O)N$ ($n=0$, 1, 2; R=Ph, Me)

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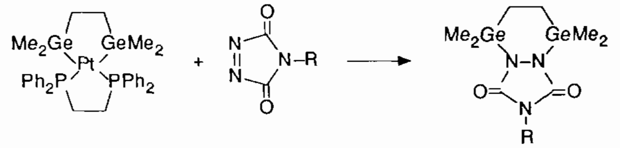
Abstract

The synthesis or attempted synthesis of the digermaheterocycles **1–6** is described, $Me_2Ge(CH_2)_n$-$Ge(Me_2)NC(O)N(R)C(O)N$ (R=Me, $n=1$ (**1**); R=Ph, $n=1$ (**2**); R=Me, $n=2$ (**3**); R=Ph, $n=2$ (**4**); R=Me, $n=0$ (**5**); R=Ph, $n=0$ (**6**)). Monomers **1–4** and dimers of **5** and **6** are isolated. **5** and **6** are obtained as intermediates. Addition of dimethylgermylene to triazolinedione is described.

We have recently reported the synthesis and different aspects of the reactivity of various digermylplatinum(II) complexes $Me_2Ge(CH_2)_nGe(Me_2)PtL_2$ ($n=0$, 1, 2; L=PPh_3, L_2=diphos, [1]. These polymetallic heterocyclic compounds have a high potential in organometallic synthesis; they can lead to new organogermanium heterocycles as well as to new complexes. Various cleavage reactions with halogens and organic halides were described. Reactions with various unsaturated systems afforded new heterocycles arising from the formal addition of these compounds across the Ge–Ge bond of $Me_2Ge(CH_2)_nGeMe_2$ ($n=0$, 1, 2) [1]. For example with *N*-phenyl and *N*-methyl triazolinediones $Me_2Ge(CH_2)_nGe(Me_2)Pt$(diphos) reacts according to:



Germylated heterocycles being the subject of considerable scrutiny in our laboratory [2–4], we sought to explore the potential of this kind of new germylated heterocycle with Ge–N–N–Ge linkages. Thus we report herein the direct syntheses and some of the properties of the digermaheterocycles **1–6**: $Me_2Ge(CH_2)_n$-$Ge(Me_2)NC(O)N(R)C(O)N$, R=Me, $n=1$ (**1**); R=Ph, $n=1$ (**2**); R=Me, $n=2$ (**3**); R=Ph, $n=2$ (**4**); R=Me, $n=0$ (**5**); R=Ph, $n=0$ (**6**).

Experimental

Procedures follow those described in ref. 5 for reactions of dehydrochlorination. All products gave satisfactory combustion analyses.

$Me_2GeCH_2Ge(Me_2)NC(O)N(Me)C(O)N$ (**1**), m.p. 163–166 °C. MS (70 eV) *m/z* 333 (M^+). ^1H NMR (C_6D_6, ppm): $\delta=0.48$ (s, 12H, CH_3), 0.14 (s, 2H, CH_2), 2.9 (s, 3H, N-CH_3). IR ($CDCl_3$, cm^{-1}): 1651, 1712 (νCO).

$Me_2GeCH_2Ge(Me_2)NC(O)N(Ph)C(O)N$ (**2**), m.p. 173–176 °C. MS (70 eV) *m/z* 395 (M^+). ^1H NMR (C_6D_6, ppm): $\delta=0.42$ (s, 12H, CH_3), 0.14 (s, 2H, CH_2), 6.8–7.25 (m, 5H, C_6H_5). IR ($CDCl_3$, cm^{-1}): 1676, 1718 (νCO).

$Me_2GeCH_2CH_2Ge(Me_2)NC(O)N(Me)C(O)N$ (**3**), m.p. 145–148 °C. MS (70 eV) *m/z* 347 (M^+). ^1H NMR (C_6D_6, ppm): $\delta=0.48$ (s, 12H, CH_3), 0.80 (s, 4H, CH_2), 2.9 (s, 3H, N-CH_3). IR ($CDCl_3$, cm^{-1}): 1651, 1717 (νCO).

$Me_2GeCH_2CH_2Ge(Me_2)NC(O)N(Ph)C(O)N$ (**4**), m.p. 154–158 °C. MS (70 eV) *m/z* 409 (M^+). ^1H NMR (C_6D_6, ppm): $\delta=0.49$ (s, 12H, CH_3), 0.81 (s, 4H, CH_2), 6.9–7.3 (m, 5H, C_6H_5). IR (C_6D_6, cm^{-1}): 1676, 1728 (νCO).

$(Me_2GeGe(Me_2)NC(O)N(Me)C(O)N)_2$ (**7**), m.p. 247–249 °C (dec.). MS (70 eV) *m/z* 638 (M^+). ^1H NMR ($CDCl_3$, ppm): $\delta=0.84$ (s, 24H, CH_3), 3.02 (s, 6H, N-CH_3). IR ($CDCl_3$, cm^{-1}): 1664, 1709 (νCO).

$(Me_2GeGe(Me_2)NC(O)N(Ph)C(O)N)_2$ (**8**), m.p. 250–252 °C (dec.). MS (70 eV) *m/z* 762 (M^+). ^1H NMR ($CDCl_3$, ppm): $\delta=0.9$ (s, 24H, CH_3), 6.85–7.07 (m, 10H, C_6H_5). IR ($CDCl_3$, cm^{-1}): 1658, 1729 (νCO).

Results and discussion

Dehydrochlorination, one of the most convenient routes to germylated heterocycles with N–Ge–N linkages [5], applied to the dihalodigermanes

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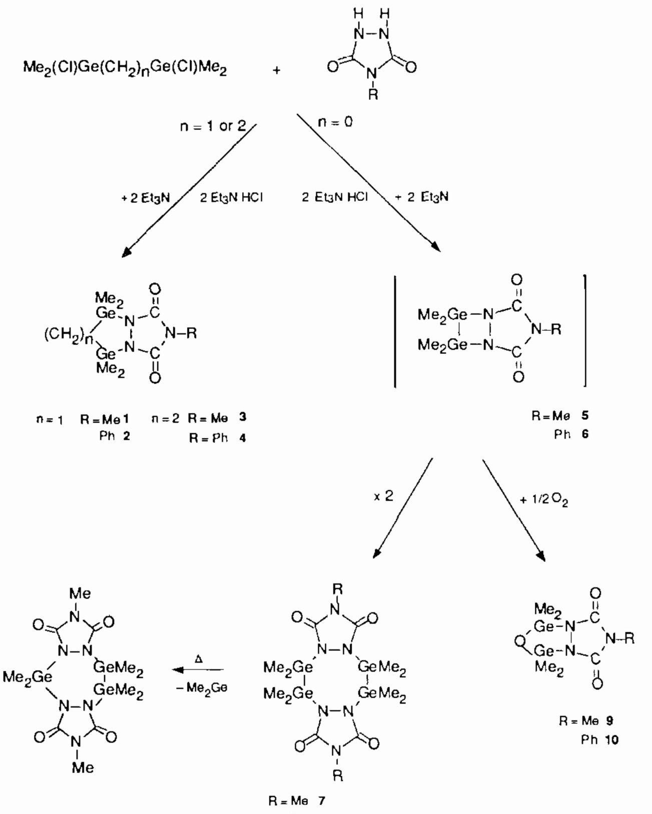
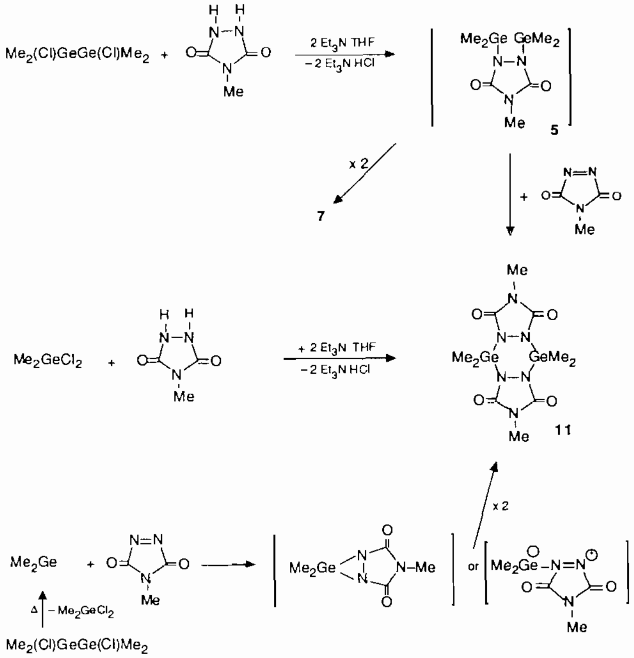


Scheme 1.

$Me_2(Cl)Ge(CH_2)_nGe(Cl)Me_2$ ($n=1$, 2) and the 4-substituted urazols $\overline{NH-C(O)-N(R)-C(O)-NH}$ (R = Me, Ph) in the presence of triethylamine in THF solution lead to the expected heterocycles **1**–**4**. In the attempted synthesis of **5**, **6** we only isolated the corresponding dimers **7** and **8**, respectively, and the oxides **9** and **10** suggestive of the formation of the intermediate four-membered heterocycles **5** and **6** (Scheme 1).

Similarities in the reaction of triazolinedione and singlet oxygen have been reported [6], so to provide some evidence for the intervention of strained heterocycles **5** or **6** in these reactions we carried out the synthesis of **7** in the presence of *N*-methyltriazolinedione. As expected, in addition to the dimer **7** we



Scheme 2.

observed substantial formation of **11** by triazolinedione insertion reaction in the Ge–Ge bond of **5** (Scheme 2). **11** is also accessible by direct synthesis from the dichloride Me_2GeCl_2, or by addition of dimethylgermylene to triazolinedione from $Me_2(Cl)GeGe(Cl)Me_2$ as thermochemical precursor to Me_2Ge (Scheme 2).

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