SYNTHESIS OF SOME PENTACOORDINATED GERMANIUM COMPOUNDS

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ABSTRACT: The 1,1-dichloro-1,2-germathia-3-cyclopentanones react with diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate in the presence of triethylamine to afford the pentacoordinated germanium compounds. The reaction of dimethylgermanium dibromide with the sodium salt of phenyl bis-(2-hydroxyethyl) phosphine produced a novel type of pentacoordinated germanium compound. The transannular interaction in these compounds is discussed in terms of acidity of the germanium and basicity of the nitrogen or phosphorus.

INTRODUCTION

The synthesis of pentacoordinated germanium compounds featuring a N→Ge linkage has recently attracted particular attention, not only owing to their specific biological activity, but also because of their unique structures and chemical properties^[1]. Of interest in systems of these compounds is the characterization of the transannular interaction between germanium and nitrogen. However, which factor influences the transannulation is less well-understood. Generally, the degree of transannular interaction depends on the basicity of nitrogen and the acidity of germanium. Thus the donor-acceptor relationship will merit further investigation.

RESULTS AND DISCUSSION

We have previously reported ^[2] that the reaction of germanium sesquioxides **1** with diethyl N,N-bis-(2-hydroxyethyl)aminomethylphosphonate **2** afforded the pentacoordinated germanium compounds **3**, characterized by the presence of a N→Ge bond.

It should also be recognized that the electrophilic phosphoryl group, which is directly bonded to the nitrogen in the compounds **3**, decreases the basicity of the nitrogen so that it inhibits the formation of N→Ge bond^[2]. To explore further the influence of the acidity of germanium on the transannulation, we synthesized the following compounds, **5** and **6**.

After work-up, the reaction mixture must be stored in the refrigerator over a period of weeks to give a solid, compounds **6**. This contrasts with the rapid and excellent transannulation of the compounds **3**. Moreover, the compounds **6** exhibit less thermal and hydrolytic stabilities in comparison with the compounds **3**. The difference could be attributed to the stronger acidity of the germanium in **3** than in **6**. The reaction of **5** with diethoxy N,N-bis(2-hydroxyethyl)phosphamide **7** also has not been successful. If the alkyl groups bonded to the germanium, it might be expected that the reaction of **7** with **8** will be realized^[3].

We also obtained an interesting result in studying the reactivity of **10** with **8**. As might be expected, the germanium in **11** is sufficiently acidic to induce the transannulation between germanium and phosphorus to form a P→Ge bond.

Although the compound **11** is too unstable to perform an X-ray diffraction analysis, its structure has been characterized by NMR criteria. The ³¹P chemical shift for **11**(43.34 ppm) is considerably lower than that of **10**(-39.57 ppm) and this shift moves downfield to 82.91 ppm, implying the presence of

transannular P→Ge interaction. In contrast, when **10** reacts with **5**, ^{31}P NMR spectroscopy reveals no evidence for any transannular P→Ge interaction.

EXPERIMENTAL

Preparation of **5**

To a stirred solution of trichlorogermyl propionyl chlorides **4**^[4] (40 mmol) in absolute acetonitrile (80 mL) was added anhydrous sodium sulfide (50 mmol) at room temperature. The reaction mixture was allowed to stir for 14 hours at 30°C. The sodium chloride that had formed was removed by filtration, and the filtrate was concentrated at reduced pressure to give a viscous liquid, which then was distilled in vacuum to yield **5**.

5a: b.p 118-120°C/10mmg, yield 66%. ^1H NMR(CDCl_3): 2.21(t, 2H, $^3J_{\text{HH}}$ 7.2Hz), 3.35(t, 2H, $^3J_{\text{HH}}$ 7.2Hz). Anal. Calcd. for $\text{C}_3\text{H}_4\text{Cl}_2\text{GeOS}$: C, 15.54; H, 1.73. Found: C, 15.46; H, 1.84.

5b: b.p 134-136/4mmg, yield 59%. ^1H NMR(CDCl_3): 1.40(d, 3H, $^3J_{\text{HH}}$ 7.2Hz), 1.96-2.64(m, 2H), 2.94-3.28(m, 1H). Anal. Calcd. for $\text{C}_4\text{H}_6\text{Cl}_2\text{GeOS}$: C, 19.54; H, 2.44. Found: C, 19.48; H, 2.46.

Preparation of **6**

To a stirred solution of diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate **2**^[2] (2.5 mmol) and triethylamine (5 mmol) in absolute THF (20 mL) was added dropwise a solution of **5** (2.5 mmol) in THF (5 mL) at -10°C. After addition, the reaction mixture was allowed to warm up to room temperature and stirred for 8-12 additional hours. The triethylamine hydrochloride that had formed was filtered out, and the filtrate was concentrated in vacuum to give a sticky material, which was washed with petroleum ether to isolate a solid. The solid was recrystallized from dichloromethane-petroleum ether (4:1), then kept in refrigerator for several weeks to yield the desired products **6**.

6a: m.p 121-122°C, yield 72.1%. ^1H NMR(CDCl_3): 1.31(t, 6H, $^3J_{\text{HH}}$ 7.2Hz), 1.60(t, 2H, $^3J_{\text{HH}}$ 7.0Hz), 2.56(t, 2H, $^3J_{\text{HH}}$ 7.0Hz), 2.94(d, 2H, $^2J_{\text{HP}}$ 10.8Hz), 3.04-3.24(m, 4H), 3.74-4.01(m, 4H), 3.96-4.24(m, 4H). ^{31}P NMR(CDCl_3): 20.05. Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{NGeO}_6\text{PS}$: C, 34.82; H, 5.80; N, 3.38. Found: C, 34.71; H, 5.98; N, 3.59.

6b: m.p 100-101°C, yield 69.1%. ^1H NMR(CDCl_3): 1.14(d, 3H, $^3J_{\text{HH}}$ 7.2Hz), 1.33(t, 6H, $^3J_{\text{HH}}$ 7.2Hz), 1.56-1.72(m, 2H), 2.00-2.17(m, 1H), 2.80-3.00(m, 4H), 3.24(d, 2H, $^2J_{\text{HH}}$ 10.8Hz), 3.80-3.90(m, 4H), 4.12-4.19(m, 4H). ^{31}P NMR(CDCl_3): 21.66. Anal. Calcd. for $\text{C}_{13}\text{H}_{26}\text{NGeO}_6\text{PS}$: C, 36.48; H, 6.08; N, 3.27. Found: C, 36.52; H, 6.18; N, 3.41.

Preparation of **11**

To a suspension of the sodium salt of phenyl bis(2-hydroxyethyl)phosphine^[5] (2.5 mmol) in DMF (30 mL) was added a solution of dimethylgermanium dibromide^[6] (2.5 mmol) in DMF (5 mL) at room temperature in a nitrogen atmosphere. After addition, the reaction mixture was stirred for 24 hours. The solvent was removed in vacuum to give a solid, which was dissolved in trichloromethane (30 mL), and filtered. The filtrate was concentrated in vacuum, and the residue was purified by column chromatography on silica gel using ethyl acetate as the eluent to give a white solid, i.e. compound **11**. Immediately, the compound **11** was detected by NMR spectroscopy and elemental analysis, because the compound **11** in solid state is unstable. Yield 58%. ^{31}P NMR(CDCl_3): 43.34. ^1H NMR(CDCl_3): 0.045(s, 6H), 2.15(t, 4H, $^3J_{\text{HH}}$ 6.5Hz), 3.78(dt, 4H, $^3J_{\text{HH}}$ 6.2Hz,

$^2J_{HP}$ 11.00Hz), 7.35(m,5H). Anal. calcd. for $C_{12}H_{19}GeO_2P$: C, 48.23; H, 6.36. Found: C, 48.18; H, 6.48.

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