Journal of Organometallic Chemistry, 47 (1973) 331–336
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

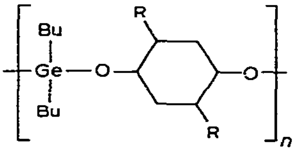
PREPARATION AND PROPERTIES OF SOME CYCLIC GERMANIUM 1,4-CYCLOHEXANEDIOLATES

A. N. SARA
Department of Chemistry, University of Oslo, Blindern (Norway)

(Received June 26th, 1972)

SUMMARY

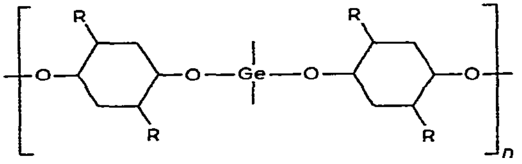
Colourless liquids of cyclic compounds of the type:



[$n = 2,4,6$ for R = H; $n = 1$ for R = t-Bu]

have been prepared by reactions of dibutylgermanium dichloride with *cis*-1,4-cyclohexanediol or *cis,cis,cis*-2,5-di-tert-butyl-1,4-cyclohexanediol, in benzene in the presence of a hydrogen halide acceptor.

Under similar conditions germanium tetrachloride gave solid products of the type:

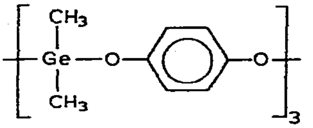


[$n=1$ for R=t-Bu; R=H gave a high polymeric product]

Physical and spectroscopic data (IR, Raman, and MS) are given and discussed.

INTRODUCTION

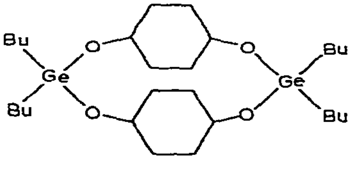
Cyclic germanium glycolates are usually described as monomeric compounds[1-4], but in a few cases larger ring compounds have been reported[5-7]. A cyclic compound derived from hydroquinone is reported to have a trimeric structure[5]:



The preparation of new cyclic organogermanium derivatives from *cis*-1,4-cyclohexanediol and *cis,cis,cis*-2,5-di-tert-butyl-1,4-cyclohexanediol is described below. The influence of substituents and reaction conditions on the ring size have been briefly examined.

RESULTS AND DISCUSSION

Cyclic organogermanium compounds of the type $[\mathrm{GeBu_2{-}O{-}(c\text{-}C_6H_{10}){-}O{-}}]_n$[*] were prepared by reaction in mole ratio 1/1 of dibutylgermanium dichloride with *cis*-1,4-cyclohexanediol in benzene in the presence of a hydrogen halide acceptor. The ring size was found to vary with concentration of the reaction solution and the temperature. In extremely dilute solution, the dimer ($n=2$) was isolated as a liquid in reasonably high yield (46–51%). The product, has been shown by elemental analysis, molecular weight determination, mass spectra and IR data, to have the structure (I).



(I)

Distillation of this compound (276°/0.05 mmHg) gave a viscous oil (II) of identical composition but higher molecular weight (1868), indicating that the ring size is increased by heating; this contrasts with the behaviour of the cyclic compounds, $\mathrm{-\!\![GeR_2{-}O{-}(CH_2)_x{-}O]\!\!-_n}$, for which depolymerization occurs on heating$^{5-7}$.

The same reaction at a higher concentration (0.17 mol/l) gave two products [(III) and (IV)] of identical composition having molecular weights of 1237 (III) and 1788 (IV), and believed to consist chiefly of the tetramer (Mol. wt. calcd.: 1203) and the hexamer (Mol. wt. calcd.: 1804.5), respectively, of the unit $\mathrm{{-}GeBu_2{-}O{-}(c\text{-}C_6H_{10}){-}O{-}}$. Attempts to distil these products were unsuccessful: a glassy material was formed and decomposition occurred above 350° on rapid heating at a pressure of 0.05 mmHg.

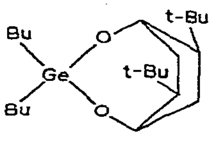
From the reaction in extremely dilute solution between germanium tetrachloride and *cis*-1,4-cyclohexanediol in mole ratio 1/2, a solid product (V) of the composition $\mathrm{-\!\![O{-}(c\text{-}C_6H_{10}){-}O{-}Ge{-}O{-}(c\text{-}C_6H_{10}){-}O]\!\!-_n}$ (yield 23%) was isolated; it was insoluble in benzene and several other solvents and so the molecular weight could not be determined. These observations, together with spectroscopic data indicate a polymeric compound. No change in composition and properties were observed on repeated sublimation.

In contrast, the reactions of dibutylgermanium dichloride and germanium tetrachloride with *cis,cis,cis*-2,5-di-tert-butyl-1,4-cyclohexanediol in mole ratios 1/1 (VI) and 1/2 (VII), respectively, gave only monomeric compounds. The products were

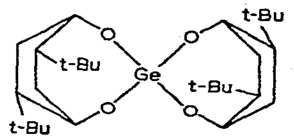
---

[*] c-C_6H_{10} = 

found to be stable to heat and could be distilled or sublimed under reduced pressure in high yields. The difference may be associated with the boat conformation of the diol favoured in this case[8]. The structures of the colourless liquid (VI) and of the white solid (VII), based on analytical and spectroscopic examination, are shown below.



(VI)



(VII)

Mass spectra

The molecular ions of compounds (I), (VI) and (VII) were found at *m/e* 602(0.5), 414(0.5) and 526(1.2), respectively, in agreement with the molecular weights found cryoscopically.

The fragmentation pattern of (I)–(IV) are mainly identical. The major peaks of high intensity at *m/e* 301 ($C_{14}H_{28}O_2Ge^+$), 245 ($C_{10}H_{19}O_2Ge^+$) and 188 ($C_6H_{10}O_2Ge^+$, $C_8H_{18}Ge^+$) are a good indication that the cyclic frameworks of the different products contain common $GeBu_2$–O–(c-C_6H_{10})–O ($C_{14}H_{28}O_2Ge$) units.

The mass spectrum of the polymeric compound (V) shows two interesting fragments at *m/e* 188 ($C_6H_{10}O_2Ge^+$) and 130 ($C_6H_{10}O_2Ge_2^{2+}$), consistent with the presence of the Ge–O–(c-C_6H_{10})–O–Ge ($C_6H_{10}O_2Ge_2$) skeleton.

TABLE 1

IR AND RAMAN SPECTRAL DATA

Compound		*Phase*	*C–O (cm^{-1})^a*	*Region 750–500 (cm^{-1})^a*
(I) (dimer)	IR	Pure liquid	1076 s	750 m, 679 s, 640 (sh), 585 m
(III) (tetramer)	IR	Pure liquid	1072 s	748 s, 700 s, 655 (sh), 584 m
(IV) (hexamer)	IR	Pure liquid	1070 s	750 m, 706 s, 666 m, 646 (sh), 590s
(V) (polymer)	IR	KBr	1075 s	734 m, 681 s
	Raman	Pure solid	1076 m	688 m, 642 w
(VI) (monomer)	IR	Pure liquid	1031 s	740 w, 694 s, 651 m, 610 m, 580 s
(VII) (monomer)	IR	KBr	1027 s	742 w, 700 s, 660 m, 640 s
	Raman	Pure solid	1018 w	697 m, 633 s

[a] s, Strong; m, medium; w, weak; (sh), shoulder.

IR and Raman spectra

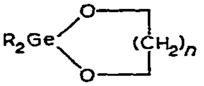
Only the characteristic bands assumed to involve C–O vibrations and the absorption bands in the region 750–500 cm^{-1} are discussed in this paper (Table 1). The Raman spectra were not obtainable for the liquids, however, because of fluorescence scattering.

The strong IR band in the region 1076–1027 cm^{-1}, which is present in all the spectra, is assigned to C–O vibrations. Raman lines for [(IV) and (VII)] were found for the solids close to the IR bands assigned to these C–O vibrations.

The strong band found between 706 and 679 cm^{-1} for each compound is assumed to involve the Ge–O vibrations. This is the only IR band (681) below 700 cm^{-1} found for the polymeric product (V). Raman lines were observed for the solids near these IR bands.

In the series, $[GeBu_2–O–(c-C_6H_{10})–O–]_n$ increasing ring size results in Ge–O band shifts to higher frequencies (dimer: 679, tetramer: 700, hexamer: 706 cm^{-1}). Only small displacements of the C–O band to lower frequencies are caused by ring expansion.

Butylgermanium compounds contain bands in the range 750–645 cm^{-1} [5,6,9]. The CH_2 rocking mode vibrations of hydrocarbons are also found in the region, usually between 750 and 720 cm^{-1} [10]. In addition, it has been shown that IR and Raman spectra of *cis*-1,4-dialkylcyclohexanes have intense bands near 630 cm^{-1} [11,12]. Marchand *et al.*[6] assigned the band near 580 cm^{-1} to vibrations in the C_2GeO_2 group of compounds of the general formula:



The IR results given in Table 1 show that the band at about 585 cm^{-1} is present only in compounds (I), (III), (IV) and (VI) having the Bu_2GeO_2 groups. This band is lacking in the IR and Raman spectra of compounds (V) and (VII) containing the GeO_4 groups. In view of this, the other bands observed in the region750–500 cm^{-1} are assigned to vibrations in (*i*), the butyl groups attached to germanium and (*ii*), the cyclohexane ring systems.

EXPERIMENTAL

Reagents

Cis,cis,cis-2,5-di-tert-butyl-1,4-cyclohexanediol was prepared as described earlier[8]. Solid compounds were recrystallized, and dried in vacuum over phosphorus pentoxide. Germanium halides were dried over phosphorus pentoxide and distilled in vacuum. Ammonia was dried by passing it through a mixture of calcium chloride and sodium hydroxide. Benzene was dried over sodium wire and distilled.

Analysis

Germanium was determined by atomic absorption spectroscopy and the other elements by combustion analysis. The molecular weights were obtained cryoscopically in benzene.

Reaction between dibutylgermanium dichloride and cis-1,4-cyclohexanediol in mole ratio 1/1

(*a*). 0.005 Moles of reactants were dissolved separately in 100 ml benzene and the solutions were added carefully at the same rate to 200 ml of benzene containing dissolved ammonia; the reaction temperatures were varied between 0 and 25°. After removal of the ammonium chloride by filtration, the benzene was removed by distillation under reduced pressure. The viscous residue was purified by gel filtration on a Sephadex LH-20 column using benzene as a solvent. A colourless liquid (I) was obtained. Yield 46–51%. (Found: C, 56.0; H, 9.2; Ge, 23.9; O, 10.5. Mol. wt., 602.5. Calcd.: C, 55.9; H, 9.3; Ge, 24.1; O, 10.6%. Mol. wt., 601.5.) MS: *m/e* (% abundance): molecular ion 602(0.5), 301(1.6), 245(100), 188(75).

Rapid distillation of the product (2 g) at 276/0.05 mmHg gave a viscous oil (II) (0.6 g). (Found: C, 55.6; H, 9.1; Ge, 23.1; O, 10.0%. Mol.wt. 1868.) MS: *m/e* (% abundance): 301(2.1), 245(97), 188(82). IR: C–O, 1070 cm^{-1} s(br); Ge–O, 710 cm^{-1} s(br).

(*b*). The same reaction was carried out by dissolving 0.05 moles of each reactant in 300 ml benzene and gaseous ammonia was passed in at 0°. Gel filtration gave two colourless liquids (III) and (IV): (III) (Found: C, 55.1; H, 9.0; Ge, 23.6; O, 11.1%. Mol. wt., 1237.) MS: *m/e* (% abundance): 301(0.9), 245(100), 188(90). (IV) (Found: C, 55.7; H, 9.5; Ge, 23.2; O, 11.4%. Mol. wt., 1788.) MS: *m/e* (% abundance): 301(1.8), 245(100), 188(72).

Reaction between germanium tetrachloride and cis*-1,4-cyclohexanediol in mole ratio* 1/2

0.001 Moles of germanium tetrachloride and 0.002 moles of diol were dissolved separately in 100 ml benzene. The solutions were added carefully at the same rate to 200 ml benzene at 0° containing dissolved ammonia. The white precipitate which formed was filtered off, and the product was extracted from this precipitate with nitromethane. Removal of the solvent and sublimation in vacuum at 120–140° gave a white solid (V), (yield 23%). (Found: C, 47.2; H, 7.1; Ge, 23.1 (by combustion analysis), O, 23.1%. Calcd.: C, 47.9; H, 6.7; Ge, 24.1; O, 21.3%.) MS: *m/e* (% abundance): 188(3.9), 130(3.1).

Reaction between dibutylgermanium dichloride and cis,cis,cis-2,5-di-tert-butyl-1,4-cyclohexanediol in mole ratio 1/1

0.02 Moles of each reactant were dissolved in benzene (300–200 ml), and ammonia was passed in at 25°. After filtration and removal of the benzene by distillation under reduced pressure a viscous residue remained. Distillation in vacuum gave a colourless liquid (VI), b.p. 317° (yield 49–53%). (Found: C, 64.1; H, 10.6; Ge, 17.2; O, 9.6. Mol. wt., 417.1. Calcd.: C, 64.0; H, 10.6; Ge, 17.6; O, 7.8%. Mol. wt., 413.2.) Molecular ion in MS was found at *m/e* 414(0.5).

The same reaction between 0.01 moles germanium tetrachloride and 0.02 moles diol (1/2) gave a white solid product (VII), which was isolated by removal of the benzene under reduced pressure and sublimation in vacuum. Subl. 129° (yield 50–51%). (Found: C, 63.2; H, 9.5; Ge, 14.5; O, 12.6. Mol. wt., 518.7. Calcd.: C, 64.1; H, 9.9; Ge, 13.8; O, 12.2%. Mol. wt., 524.9.) The mass spectrum showed the molecular ion at *m/e* 526(1.2).

REFERENCES

1 R. C. Mehrotra and S. Mathur, *J. Organometal. Chem.*, 6 (1966) 11; *ibid.*, 6 (1966) 425.
2 S. Mathur, G. Chandra, A. K. Rai and R. C. Mehrotra, *J. Organometal. Chem.*, 4 (1965) 371.
3 R. C. Mehrotra and G. Chandra, *J. Chem. Soc.*, (1963) 2804.
4 M. Lesbre and J. Satgé, *C.R. Acad. Sci.*, 254 (1926) 405.
5 G. Korb, G. Levy, M. Brine and A. Deluzarche, *J. Organometal. Chem.*, 23 (1970) 437.
6 M. Marchand, M.-T. Forel, M. Lebedeff and J. Valade, *J. Organometal. Chem.*, 26 (1971) 69.

7 M. Wieber and M. Schmidt, *Z. Naturforsch. B*, 18 (1963) 847.
8 R. D. Stolow, *J. Amer. Chem. Soc.*, 85 (1963) 3636.
9 R. J. Cross and F. Glocking, *J. Organometal. Chem.*, 3 (1965) 146.
10 L. J. Bellamy, *The infrared spectra of complex molecules*, Methuen & Co., London, 1966, p. 27.
11 B. A. Kasanski, A. L. Liberman and N. I. Tjunkina, *Dokl. Akad. Nauk SSSR*, 134 (1960) 93.
12 *Documentation of Molecular Spectroscopy*, Butterworths, Verlag Chemie.