

## ORGANOGERMANIUM COMPOUNDS. X.\*

THE EFFECT OF STRUCTURE  
ON THE BASICITY OF ETHYL(DIMETHYLAMINO)GERMANES

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A series of ethyl(dimethylamino)germanes of type  $(C_2H_5)_4-nGe[N(CH_3)_2]_n$  was prepared. By means of  $\Delta\nu$  of hydrogen bonds between deuteriochloroform (or pyrrole) and these nitrogen-containing compounds their relative basicities were determined. The basicities were found to decrease with increasing number of the dimethylamino groups in the molecule of these compounds. The inductive effect of the dimethylamino groups is discussed, along with a possible ( $p \rightarrow d$ )  $\pi$  interaction in the germanium-nitrogen bond.

To date, the effect of the two or more nitrogen-containing groups attached to the central germanium atom on the physical and chemical properties of organogermanium compounds has not been investigated. We therefore decided to prepare some model organogermanium compounds with the aim to examine to what extent the properties of these compounds are affected both by the inductive effects of substituents attached to the central atom and by a possible ( $p \rightarrow d$ )  $\pi$  interaction of vacant  $d$ -orbitals of the central atom with unshared electron pairs of the nitrogen. This work is a continuation of our study on the relative basicities of some dimethylaminosilanes<sup>1</sup>.

## EXPERIMENTAL

## Compounds Used

*Germanium tetrachloride* (Lachema, Kaznějov), b.p. 83°C, was distilled before use. *Ethyltrichlorogermane* and *diethyldichlorogermane* were prepared by a direct synthesis from germanium

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(Lachema, Kaznějov; zone-melted, maximal grain size 10  $\mu\text{m}$ ) and ethyl chloride in the presence of a copper powder (Safina, Potštejn; 96% Cu, 0.26% Co, 0.14% Sn, 0.1% Ni, 0.05% Pb, 0.04% Si, 0.03% Zn, trace amount of Fe and oxygen; maximal grain size 10  $\mu\text{m}$ ) as the catalyst<sup>2</sup>. The reaction was carried out in a flow reactor for 80 hours at 360°C (the ratio of the copper to the germanium was 1 : 4). The product contained 11% of ethyl chloride, 72% of ethyltrichlorogermane and 17% of diethyldichlorogermane. Overall yield of the direct synthesis amounted to 85% (based on the germanium).

*Diethyldichlorogermane* was prepared also by the redistribution reaction of germanium tetrachloride and tetraethylgermane<sup>3</sup>. A mixture of 25.2 g (117.6 mmol) of germanium tetrachloride, 26.8 g (142 mmol) of tetraethylgermane and 3.2 g (24 mmol) of aluminium chloride was heated in a sealed glass ampule to 200°C for 30 hours. After cooling to room temperature, the reaction mixture was fractionated on a column packed with Raschig rings under reduced pressure. The main fraction containing diethyldichlorogermane distilled at 75–76°C/30 Torr.

*Triethylchlorogermane* was prepared by the redistribution reaction of tetraethylgermane and germanium tetrachloride<sup>3</sup>. A mixture of 16.8 g (77.8 mmol) of germanium tetrachloride, 47.4 g (251 mmol) of tetraethylgermane and 2 g (15 mmol) of aluminium chloride was heated in a sealed glass ampule to 210°C for 20 hours. The reaction mixture was fractionated under reduced pressure, yielding the pure triethylchlorogermane (56–58°C/13 Torr).

*Tetraethylgermane* was prepared by the reaction of germanium tetrachloride with an excess of ethylmagnesium bromide in diethyl ether<sup>4</sup>.

The yields, analyses, boiling points and indices of refraction of all the starting germanium compounds are given in Table I.

*Ethyl(dimethylamino)germanes* were prepared by reactions of appropriate ethylchlorogermanes with an excess of dimethylamine (Fluka AG, Buchs SG) in cyclohexane (Lachema, Brno), using procedure described below.

*Diethylbis(dimethylamino)germane*. To a 500 ml three-necked flask fitted with a mechanical stirrer, a dropping funnel and a dry ice-ethanol condenser were placed 41 g (0.91 mol) of dimethylamine in 180 ml of cyclohexane. To the solution 25 g (0.22 mol) of diethyldichlorogermane in 50 ml of cyclohexane were gradually added with stirring over an 1-hour period. The reaction mixture was then heated for 5–6 hours under reflux. After cooling down to room temperature the precipitated dimethylamine hydrochloride was separated, then the solvent distilled off and a fraction boiling 100–102°C/35 Torr and containing 8.7% of chlorine was collected. A mixture of 20 g of this compound, 20 ml of dimethylamine and 30 ml of cyclohexane was heated in a sealed

TABLE I  
Physical Constants of the Starting Alkylchlorogermanes

Compound	M.w.	B.p., °C		$n_D^{20}$		% C		Yield %
		found	lit.	found	lit.	calc.	found	
Ethyltrichlorogermane	208.0	141	140 <sup>2</sup>	1.4742	1.4745 <sup>2</sup>	51.14	51.37	72
Diethyldichlorogermane	201.6	173–175	173 <sup>5</sup>	1.4700	1.4700 <sup>5</sup>	35.18	35.08	17–55
Triethylchlorogermane	195.2	173	175.9 <sup>3</sup>	1.4587	1.4596 <sup>3</sup>	18.17	18.24	63
Tetraethylgermane	188.8	162–163	164.7 <sup>6</sup>	1.4427	1.4430 <sup>6</sup>	—	—	32–45

TABLE II  
Physical Constants of Alkyl(dimethylamino)germanes

Compound	B.p., °C (Torr)		$n_D^{20}$		$d_4^{20}$		M.w.	Calculated/Found			Yield %
	found	lit.	found	lit.	found	lit.		% C	% H	% N	
Tetrakis(dimethylamino)- germane	82-82.5 (12)	87-89 <sup>7</sup> (15)	1.4588	1.068 <sup>a</sup>	1.069 <sup>7,b</sup>	—	248.9	38.57 38.06	9.72 9.28	22.51 22.8	58
Triethyl(dimethylamino)- germane	66 (15)	176 <sup>8</sup> (760)	1.4516 <sup>c</sup>	1.023 <sup>a</sup>	1.0235 <sup>8</sup>	—	203.8	47.08 46.69	10.38 10.06	6.89 7.0	90
Diethylbis(dimethylamino)- germane	81-82 (17)	—	1.4541	1.034 <sup>b</sup>	—	—	218.8	43.88 43.12	10.14 9.89	12.81 12.6	78
Ethyltris(dimethylamino)- germane	86-87 (19)	105-107 <sup>7</sup> (34)	1.4575	1.048 <sup>a</sup>	1.049 <sup>7,b</sup>	—	233.9	41.04 41.07	9.91 10.11	17.97 17.8	65

<sup>a</sup>  $d_4^{23}$ , <sup>b</sup>  $d_4^{22}$ , <sup>c</sup> lit.<sup>10</sup>  $n_D^{20}$  1.4498.

glass ampule to 100–120°C for 8 hours. Then the precipitated dimethylamine hydrochloride was filtered off and the excess dimethylamine and the solvent were removed by distillation. A fractional distillation afforded the pure diethylbis(dimethylamino)germane, b.p. 81–82°C/17 Torr.

*Tetrakis(dimethylamino)germane.* The reaction of 15 g (0.07 mol) of germanium tetrachloride with 37 g (0.83 mol) of dimethylamine in cyclohexane afforded a compound, b.p. 72°C/10 Torr, containing 14.3% of chlorine (likely tris(dimethylamino)chlorogermane). A mixture of 12 g of this compound, 20 ml of dimethylamine and 30 ml of cyclohexane was heated in a sealed glass ampule to 100–110°C for 7 hours. The usual work-up afforded tetrakis(dimethylamino)germane, b.p. 82–83°C/12 Torr.

The physical properties, elemental analyses and yields of the (dimethylamino)germanes prepared are given in Table II. The purity and structure of all the compounds prepared were confirmed by elemental analysis, glc analysis and IR and NMR spectroscopy.

### Infrared Spectra

The IR spectra of the (dimethylamino)germanes were taken on a Zeiss (Jena) UR-20 double-beam spectrophotometer in the 850–400  $\text{cm}^{-1}$  (KBr prism), 1650–650  $\text{cm}^{-1}$  (NaCl prism), and 4000–1600  $\text{cm}^{-1}$  (LiF prism) regions. The frequency scale of the instrument was calibrated in the usual way<sup>9</sup>. Wavenumbers were determined with the accuracy of  $\pm 2 \text{ cm}^{-1}$ . The IR spectra of liquid substances were measured in part in a KBr cell (0.003 cm thickness), in part in tetrachloromethane solutions (5%) in a KBr cell (0.01 cm thickness). The spectra of studied compounds could not be measured in carbon disulphide because of the insertion of the molecule of the solvent to a germanium–nitrogen bond, yielding dialkyldithiocarbamate<sup>8</sup>, e.g. of type  $(\text{C}_2\text{H}_5)_3\text{GeSC(S)N}(\text{CH}_3)_2$ . This was confirmed also in the case of the dimethylaminogermanes studied by disappearance of the absorption band of stretching vibration of the germanium–nitrogen bond and by the occurrence of a new absorption band of the stretching vibration of the C=S bond.

The  $\Delta\nu$  values were determined from the spectra of hydrogen bonds in the region of LiF prism either in binary mixtures (a proton acceptor serves as the solvent of a proton donor) or in ternary mixtures with the pure tetrachloromethane as the solvent. The following compounds were employed as proton donors: deuteriochloroform (2.5M), pyrrole (0.03M), indole (0.03M), and phenylacetylene (0.1M). The concentration of a proton acceptor, unless used as the solvent, was 1 mol/l. The wavenumbers of absorption maxima are expressed as the average values of three measurements. The reproducibility of the reading was  $\pm 2 \text{ cm}^{-1}$ . The thickness of NaCl cells was 0.04 and 0.01 cm, resp. The preparation of samples for the IR measurements was carried out in a dry box under the atmosphere of nitrogen.

### RESULTS

The IR spectra of the ethyl(dimethylamino)germanes<sup>10</sup> were interpreted in accordance with the literature<sup>11,12</sup>. As expected, the pattern of the spectra closely resembles that of the spectra of the analogical series of organosilicon compounds<sup>1</sup>. Absorption bands of the stretching vibrations of the germanium–nitrogen and germanium–carbon bonds are, however, located at lower wavenumbers (in the region near 580  $\text{cm}^{-1}$ ) relative to the analogical silicon bonds.

The relative basicities of the nitrogen atom (atoms) of the compounds studied were determined from the changes in the IR spectra in the region of the absorption

TABLE III

Values of  $\Delta\nu$  (in  $\text{cm}^{-1}$ ) of Deuteriochloroform and Pyrrole with Some Dimethylaminogermanes

Proton acceptor	$\Delta\nu$	
	$\text{CDCl}_3$	pyrrole
$(\text{C}_2\text{H}_5)_3\text{Ge}[\text{N}(\text{CH}_3)_2]$	70	320
$(\text{C}_2\text{H}_5)_2\text{Ge}[\text{N}(\text{CH}_3)_2]_2$	63	310
$(\text{C}_2\text{H}_5)\text{Ge}[\text{N}(\text{CH}_3)_2]_3$	52	296
$\text{Ge}[\text{N}(\text{CH}_3)_2]_4$	41	286

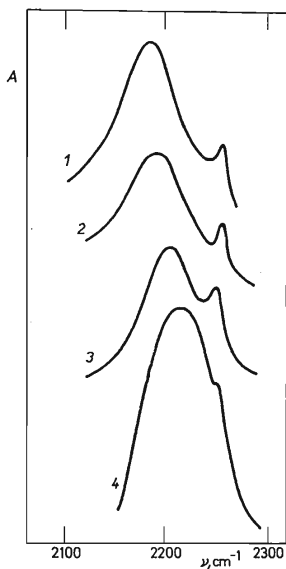


FIG. 1

The IR Spectra of Hydrogen Bonds of Deuteriochloroform with  $(\text{C}_2\text{H}_5)_{4-n}\text{Ge}[\text{N}(\text{CH}_3)_2]_n$   
 1  $n = 1$ , 2  $n = 2$ , 3  $n = 3$ , 4  $n = 4$ .

of hydrogen bond originated from the interaction of studied compounds with chosen proton donors in binary and ternary solutions. A rather low stability of the germanium–nitrogen bond sets limit to the selection of suitable proton donors. From these reasons we excluded in advance proton donors such as phenol, methanol and other hydroxy compounds, by the action of which an instantaneous cleavage of these bonds proceeds. Therefore, the compounds containing either the nitrogen–hydrogen bond (pyrrole, indole) or the carbon–hydrogen one (phenylacetylene, bromoform, deuteriochloroform) seemed to be suited for the above purpose. Of these compounds the N–H donors have not so far been employed, because of the possibility of reamination reactions<sup>13</sup>. We found that chloride ions (*e.g.* in the form of dimethylamine hydrochloride) exert catalytic effect on reamination reactions. The spectral changes in the  $3500\text{ cm}^{-1}$  region in the ternary system triethyl(dimethylamino)germane (containing 2% of chlorine)–pyrrole–carbon tetrachloride in dependence on time showed that the absorption band of stretching vibration of the nitrogen–hydrogen bond of the non-associated pyrrole disappears in a few minutes. On contrast, in the case of the pure (dimethylamino)germanes the above reactions proceed very slowly so that these proton donors may be used for the determination of relative basicities without difficulty. In spite of this finding we used only pyrrole as the proton donor. The hydrogen of the nitrogen–hydrogen bond of indole is more acidic than the hydrogen of pyrrole, due to the  $-M$  effect of benzene nucleus. As a result, the frequency shifts are larger, and in particular with more basic (dimethylamino)germanes the absorption bands of associated components lie in the region of stretching vibration of the carbon–hydrogen bonds, which results in an overlap of both bands.

Phenylacetylene<sup>14</sup>, too, could not be employed as the proton donor. In this case, the intensity of the absorption band of the non-associated phenylacetylene was observed to decrease with time, which seems to indicate that a reaction of the germanium–nitrogen bond with phenylacetylene occurred. This reaction has been already observed with tributyl(dimethylamino)germane, where the replacement of the dimethylamino groups by the phenylethynyl groups took place<sup>8</sup>.

Deuteriochloroform proved to be the most convenient proton donor for the determination of the basicity of the germanium–nitrogen bonds. Even that its hydrogen is weakly acid, the associated part of deuteriochloroform shows distinct absorption bands, the maxima of which can be accurately read. From this reason the values of the frequency shifts ( $\Delta\nu$ ) of deuteriochloroform were taken as the main criterion in the determination of the relative basicities of the compounds studied.

The  $\Delta\nu$  values obtained with deuteriochloroform and pyrrole are given in Table III. The spectra of hydrogen bonds of deuteriochloroform with the compounds studied are shown in Fig. 1.

## DISCUSSION

The relative basicity of triethyl(dimethylamino)germane is distinctly higher than that of triethyl(dimethylamino)silane ( $\Delta\nu(\text{C}-\text{D}) = 70 \text{ cm}^{-1}$  and  $\Delta\nu(\text{C}-\text{D}) = 40 \text{ cm}^{-1}$ , resp.), however, it still does not attain the basicity of tertiary amines. The  $\Delta\nu$  value for triethylamine was reported<sup>15</sup> to be  $84 \text{ cm}^{-1}$ ; in this work the value of  $80 \text{ cm}^{-1}$  was obtained for the same system. In spite of the fact that there is no general agreement in the literature as to the relative magnitude of the electronegativity of the Group IVB elements as well as the relative inductive effects of the  $\text{R}_3\text{M}$ -groups, it is evident that the  $(\text{C}_2\text{H}_5)_3\text{Ge}$  group should have a higher +I effect than the analogical carbon group. The data obtained thus speaks for a ( $p \rightarrow d$ )  $\pi$  bonding in the germanium-nitrogen bond, even that less distinct than in the case of the silicon-nitrogen bond; the concept of the ( $p \rightarrow d$ )  $\pi$  nature of the germanium-nitrogen bond is further supported by the decrease in the basicity of the nitrogen atom on its increasing substitution by the trimethylgermyl groups, i.e. on going from  $(\text{CH}_3)_3\text{GeN}(\text{C}_2\text{H}_5)_2$  to  $[(\text{CH}_3)_3\text{Ge}]_3\text{N}$ , observed by other authors<sup>15,16</sup>.

From Table III it follows that the relative basicity of the ethyl(dimethylamino)germanes decreases with the increasing number of the dimethylamino groups in the molecule of these compounds. This finding can be accounted for by the assumption that the +I effect of ethyl group decreases with the decreasing number of these groups in the molecule, or that the -I effect of the dimethylamino groups becomes gradually more important. If one compares the decrease in the relative basicity in dependence on the degree of substitution with the  $\Delta\nu(\text{C}-\text{D})$  values obtained for analogical organosilicon compounds<sup>1</sup>. ( $\Delta\nu(\text{C}-\text{D})$  for  $(\text{C}_2\text{H}_5)_{4-n}\text{Si}[\text{N}(\text{CH}_3)_2]_n$  was found to be 40, 38, 32, and  $28 \text{ cm}^{-1}$  for  $n = 1, 2, 3,$  and  $4,$  resp.) one finds that the decrease is larger for the germanium than the silicon compounds. The most distinct difference in the relative basicities is found for the mono(dimethylamino)derivatives of both series. The smaller difference in the basicities of the tetrakis(dimethylamino)-derivatives may be accounted for by the fact that with the increasing number of the dimethylamino groups bonded to the silicon, the interaction of each additional nitrogen with the silicon becomes less significant<sup>1</sup>.

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