

ORGANOGERMANIUM COMPOUNDS. XIII.*
 THE PREPARATION AND RELATIVE BASICITY
 OF (DIALKYLAMINO)CHLOROGERMANES

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(Dialkylamino)chlorogermanes of the type $(R_2N)_4-nGeCl_n$ ($n = 1-3$; $R = CH_3$ or C_2H_5) were prepared by the reaction of $GeCl_4$ with appropriate secondary amines. The relative basicity of the dimethylamino derivatives was determined by IR spectroscopy and discussed in terms of structural effects.

In connection with the study of basicity of some (amino)alkyl derivatives of germanium¹ in the present work we have been interested in the preparation and properties of (dialkylamino)chlorogermanes. To our knowledge the only method so far used to prepare these compounds was the redistribution reaction between $GeCl_4$ and $(R_2N)_4Ge^{2,3}$. Although the reaction itself proceeds almost quantitatively², overall yields are substantially smaller, since the starting tetrakis-amino derivatives can usually be obtained only in moderate yields ($[(CH_3)_2N]_4Ge$ 58% (lit.¹), $[(C_2H_5)_2N]_4Ge$ 45% (lit.⁴)). The higher yield was achieved only by reacting the dipyrindine complex, $GeCl_4 \cdot 2 C_5H_5N$, with diethylamine at 120°C for 30 h (69%)⁵.

For this reason we attempted at preparing these compounds by the reaction of $GeCl_4$ with appropriate secondary amines. This simple reaction has not yet been used in this case, perhaps due to the fact that the reaction of diethylamine with $GeCl_4$ has been reported⁶ to yield germanium-diimide hydrochloride, $Ge[N(C_2H_5)_2]_2 \cdot HCl$. We have found that at the conditions described in Experimental (dialkylamino)chlorogermanes can be obtained by this reaction in yields which are comparable with the overall yields of redistribution reaction (Table I). The obtained products were not contaminated by the hydrochlorides of corresponding secondary amines in amounts detectable by IR spectroscopy.

The reaction of $GeCl_4$ with diethylamine in excess (carried out at the conditions used to prepare the (dimethylamino)chloro derivatives, did not afford tetrakis(diethylamino)germane (VIII), but led selectively to tris(diethylamino)chlorogermane (III). A similar situation has already been observed by us¹ in the preparation of tetrakis(dimethylamino)germane, where the reaction was accomplished only with the use of the higher boiling solvent, cyclohexane, and at more drastic conditions (heating

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to 100–110°C for 8 h). Even at these conditions the attempt to transform tris(diethylamino)chlorogermane to tetrakis(diethylamino)germane has failed. In this case we have isolated from the reaction mixture only the starting tris(diethylamino) derivative. The low reactivity of this compound can obviously be attributed to greater steric screening of the central atom, due to the presence of three bulky diethylamino groups. Similarly, when attempting to prepare substance VIII according to Anderson⁴, *i.e.* by the reaction of GeBr₄ with diethylamine in cyclohexane, we have obtained tris(diethylamino)bromogermane as the sole product. Even by heating this substance with three-fold molar excess of diethylamine in cyclohexane at 100°C for 36 h, we were unable to convert it to tetrakis(diethylamino)germane. We have found that the exchange of bromine can be accomplished by the reaction of the tris(diethylamino) derivative with lithium diethylamide. The product formed was contaminated however with small amount of the starting bromogermane which could not be removed by repeated distillation.

For this reason we have studied systematically the change of relative basicity of nitrogen in dependence on structure only in the series of the dimethylamino derivatives. As the measure of the relative basicity we have taken the difference between the positions of the maxima of the absorption bands corresponding to stretching vibrations of the free C–D bond of deuteriochloroform and the associated

TABLE I
(Dialkylamino)chlorogermanes Prepared

Compound b.p., °C/Torr	Molar ratio GeCl ₄ : amine Yield, %	Formula (m.w.)	Calc./Found %C
(CH ₃) ₂ NGeCl ₃ (I) 57.5/42	1 : 2 47	Ge ₁ C ₂ H ₆ Cl ₃ N (223.1)	47.70 47.65
[(CH ₃) ₂ N] ₂ GeCl ₂ (II) 44–45/7	1 : 4.2 53	Ge ₁ C ₄ H ₁₂ Cl ₂ N ₂ (231.7)	30.60 30.30
[(CH ₃) ₂ N] ₃ GeCl (III) 59–60/8	1 : 6.3 56	Ge ₁ C ₆ H ₁₈ ClN ₃ (240.3)	14.75 14.65
(C ₂ H ₅) ₂ NGeCl ₃ (IV) 52–53/8	1 : 2 46	Ge ₁ C ₄ H ₁₀ Cl ₃ N (251.2)	42.36 42.05
[(C ₂ H ₅) ₂ N] ₂ GeCl ₂ (V) 97–99/7	1 : 4 51	Ge ₁ C ₈ H ₂₀ Cl ₂ N ₂ (287.1)	24.70 25.04
[(C ₂ H ₅) ₂ N]G ₃ Cl (VII) 106–107/26	1 : 6.5 71.5	Ge ₁ C ₁₂ H ₃₀ ClN ₃ (323.0)	10.98 11.28

C—D...N bond formed by interaction of deuteriochloroform with the corresponding amino derivative ($\Delta\nu = \nu(\text{C—D})_{\text{free}} - \nu(\text{C—D})_{\text{assoc}}$). As it is seen from Fig. 1, the intensity of the $\nu(\text{C—D})_{\text{assoc}}$ absorption band as well as the frequency shift $\Delta\nu$ decreases with increasing number of chlorine atoms in the molecule of studied compounds. For tetrakis(dimethylamino)germane (curve 1) this difference amounts to 41 cm^{-1} (1), for tris(dimethylamino)chlorogermane it is 29 cm^{-1} , and for bis(dimethylamino)dichlorogermane it equals to 16 cm^{-1} . The trichloro derivative 1 exhibits only one absorption band with apparent asymmetry on the lower frequency side, which is caused by the overlap of $\nu(\text{C—D})_{\text{assoc}}$ and $\nu(\text{C—D})_{\text{free}}$ bands. As follows from these results the relative basicity of (dimethylamino)chlorogermanes decreases with increasing number of chlorine atoms in their molecule. The substitution of dimethylamino group for more electronegative chlorine atom brings about a decrease of electron density on the nitrogen of the remaining amino groups, decreasing thus its proton acceptor ability. This is in harmony with the observation made earlier in our laboratory¹ that the gradual substitution of dimethylamino groups for more electropositive ethyl groups in a series of the ethyl(diethylamino)germanes $(\text{C}_2\text{H}_5)_n \cdot \text{Ge}[\text{N}(\text{CH}_3)_2]_{4-n}$ leads on the contrary to progressive increase of the basicity of these compounds. Almost linear decrease of $\Delta\nu$ also indicates that the interaction of deuteriochloroform with these derivatives is not substantially influenced by steric factors. Their role increases, however, when dimethylamino groups are replaced by bulkier diethylamino groups. So, for instance, in the spectrum of binary mixtures of deuteriochloroform with tris(diethylamino)chlorogermane we have not been able to detect the band corresponding to $\nu(\text{C—D})_{\text{assoc}}$.

A comparison of relative basicities of (dimethylamino)chlorogermanes with those of analogous series of silicon derivatives is also of interest. While in the case of (dimethylamino)chlorosilanes the substitution of one dimethylamino group in tetrakis(dimethylamino) derivative for chlorine has already reduced the basicity to negligible

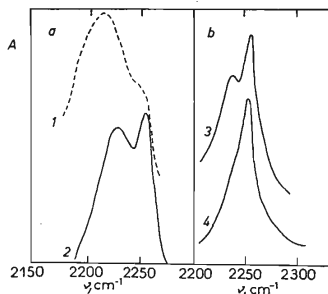


FIG. 1

IR Spectra, in the Region of $\nu(\text{C—D})$, of Binary Mixtures of Deuteriochloroform with $[(\text{CH}_3)_2\text{N}]_{4-n}\text{GeCl}_n$
 $n: 1\ 0, 2\ 1, 3\ 2, 4\ 3.$

value, with (dimethylamino)chlorogermanes such an effect can be observed only for the trichloro derivative. Furthermore, the decrease of relative basicity is steeper in the series of the silicon analogues. These results can be taken as further support for our opinion^{1,9} that the increased relative basicity of the amino derivatives of germanium, relative to analogous silicon compounds, is caused — besides the different electronegativity of both elements — also by the lesser ability of germanium to form ($p - d$) π bonds with nitrogen.

EXPERIMENTAL

Temperature data are uncorrected. The content of chlorine (bromine) was determined argentometrically with the use of potentiometric indication. The nitrogen was determined by alkalimetric titration after mineralization of a compound by Kjeldahl method.

(Dimethylamino)chlorogermanes I—III were prepared in the following manner. To a solution of 10.2 ml (0.09 mol) of GeCl_4 in 100 ml of dry redistilled ether cooled to -25°C , the appropriate amount of dimethylamine (Table I), cooled to -20°C , was added with stirring over the period of 1 h. The reaction mixture was then refluxed for 3 h, the dimethylamine hydrochloride was removed by filtration through a fine glass frit under nitrogen pressure, and the residue was distilled at reduced pressure under nitrogen. The purity of the so prepared aminochlorogermanes was checked by chlorine content determination, the presence of dimethylamine hydrochloride was checked by IR spectroscopy. *Tetrakis(dimethylamino)germane (IV)* was prepared according to the reported procedure¹. B.p. $82-84^\circ\text{C}/13$ Torr, n_D^{20} 1.4590 (lit.¹ b.p. $82-82.5^\circ\text{C}/12$ Torr, n_D^{20} 1.4588). (Diethylamino)chlorogermanes V—VII were prepared in the same way as were prepared dimethylamino derivatives I—III.

Tetrakis(diethylamino)germane (VIII). A) Attempted preparation by the reaction of tris(diethylamino)chlorogermane with diethylamine. A mixture of 23 ml (0.23 mol) of dry diethylamine, 18 g (0.06 mol) of $[(\text{C}_2\text{H}_5)_3\text{N}]_3\text{GeCl}$, and 25 ml of cyclohexane was heated in sealed ampoule at 100°C for 6 h. After removal of the unreacted diethylamine and the solvent, a distillation afforded a compound boiling $90-92^\circ\text{C}/4$ Torr, which, according to the chlorine content (10.73%), has turned out to be slightly impure starting chloro derivative VII (72% of the amount used). B) Attempted preparation by the reaction of GeBr_4 with diethylamine⁴. A total of 103 ml (1.0 mol) of dry diethylamine were added at room temperature to a solution of 20 g (0.05 mol) of GeBr_4 (prepared by bromination of 7 g of Ge powder) in 90 ml of dry cyclohexane with stirring over the period of 1 h. The reaction mixture was then refluxed for 3 h. The usual work-up afforded 11.2 g of the product, b.p. $86.5-88^\circ\text{C}/2$ Torr, which contained 12.00% N and 21.50% Br (for $[(\text{C}_2\text{H}_5)_3\text{N}]_3\text{GeBr}$ ($\text{Ge}_1\text{C}_{12}\text{H}_{30}\text{BrN}_3$, 369.2) calculated: 11.37% N and 21.64% Br). A mixture of 6 g of the so obtained impure tris(diethylamino)bromogermane, 16.8 ml (0.15 mol) of dry diethylamine and 30 ml of cyclohexane was heated in sealed ampoule at 100°C for 36 h. The reaction product, collected as the fraction boiling $86-89^\circ\text{C}/2$ Torr, contained 18.2% Br. C) Preparation by the reaction of tris(diethylamino)bromogermane with lithium diethylamide. To stirred ethereal solution of lithium diethylamide⁸ (0.04 mol), 15.0 g (0.04 mol) of tris(diethylamino)bromogermane were added at room temperature under nitrogen. The mixture was refluxed for 3 h. The organic layer was separated from the salts by decantation and then distilled, giving 5.4 g of the desired product, b.p. $160-163^\circ\text{C}/20$ Torr, which was contaminated by small amount of the starting bromo derivative (1.4% Br). For $[(\text{C}_2\text{H}_5)_3\text{N}]_4\text{Ge}$ ($\text{Ge}_1\text{C}_{16}\text{H}_{40}\text{N}_4$, 361.4) calculated: 15.51% N; found: 14.79% N. This admixture could not be removed by repeated distillation.

IR spectra of prepared substances were measured on a double-beam Zeiss, Model UR-20, spectrophotometer (Jena) in the $850-400\text{ cm}^{-1}$ (KBr prism), $1650-650\text{ cm}^{-1}$ (NaCl prism) and $1600-400\text{ cm}^{-1}$ (LiF prism) regions, using the procedure described in a previous work¹. The spectra of liquid films of the compounds were measured in composed KBr cell, the spectra of solutions of the compounds in CCl_4 were measured in NaCl cell (0.04 cm thick). The values of $\Delta\nu$ of deuteriochloroform were determined from the spectra of binary mixtures of studied compounds with the proton donor (conc. 3M) measured in the $2350-2100\text{ cm}^{-1}$ region. The NaCl cells used were 0.04 and 0.01 cm thick. The preparation of samples was carried out in a dry box under nitrogen atmosphere.

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