Dialkylaminogermanes and Dialkylaminosilanes

By Herbert H. Anderson[1]

Dimethylamine or diethylamine react with certain germanium halides or chlorosilanes to yield dialkylaminogermanes or dialkylaminosilanes, including new $Si(NMe_2)_4$, $Si_2O(NEt_2)_6$, $MeSi(NMe_2)_3$, $Me_2Si(NMe_2)_2$, $Ge(NMe_2)_4$, $Ge(NEt_2)_4$, EtGe-$(NMe_2)_3$ and $EtGe(NEt_2)_3$. Dissolved dialkylammonium chloride contaminated some other preparations. Benzoyl chloride and a dialkylaminogermane or a dialkylaminosilane upon gentle reflux furnish the corresponding chloride C_6H_5COCl + $MeSi(NMe_2)_3 \rightarrow MeSiCl_3$. A modified method of changing a chloride into an iodide consists of treating $EtGeCl_3$ with Et_2NH to give soluble $EtGe(NEt_2)_3$, followed by conversion into $EtGeI_3$ using HI gas. There is a discussion of the tetrachlorides of carbon, silicon, germanium, tin and lead and their reactions with alkylamines, aniline and ammonia.

In the conversion of trialkyl- or dialkylgermanium chlorides into bromides or iodides there are several methods available, but the process for monoalkylgermanium halides uses the insoluble, polymeric $EtGeN$[2]; losses can be high both in time and in material. A single change, from $EtGeCl_3$ to $EtGe(NEt_2)_3$ to $EtGeI_3$, as reported herein, indicates a possible alternate method.

This paper fills some spaces vacant in earlier researches on silicon and germanium. The behavior toward ammonia is understood in halides of silicon and germanium; the behavior toward *dialkylamines* of halides of silicon and germanium is until now insufficiently known; the reaction of *aniline* with germanium halides needed clarification. (Other investigators in this Laboratory have just studied addition compounds which tertiary amines form with halides of germanium, and will report them separately.) The next paragraph lists some compounds essential to any description of tendencies in the fourth group of the periodic table.

The following are stable, known compounds: $Me_3Si(HNMe_2)$, Et_3SiNH_2, $Me_3Si(NEt_2)$[3]; $SiCl_3$-(NEt_2)[4]; $SiCl_2(HNC_6H_5)_2$[5]; $Si(HNC_6H_5)_4$[5a]; HSi-$(HNC_6H_5)_3$[6]; $Me_3Si(HNC_6H_5)$, $Me_2Si(HNC_6H_5)_2$ and $MeSi(HNC_6H_5)_3$[7]; $(Et_2GeNH)_3$[8]; $(Et_3Ge)_2NH$, possibly a trimer[9]; $(C_4H_4N_4)_4Ge$[10]; $(C_5H_{10}N)_4Ge$[11]; $SnCl_4·4NH_3$; $PbCl_4·4NH_3$ and $PbCl_4·3C_6H_5NH_2$ among others.[12] This list, not complete, serves only for illustration. Carbon tetrachloride reacts with aniline at elevated temperature, forming diphenylaminobenzamidine hydrochloride[13] and other substances.

Together with new results herein, the known information has been considered; the following conclusions apparently explain trends for the group IV elements carbon, silicon, germanium, tin and lead. Carbon tetrachloride, failing to react, does not fit in the series very well; silicon tetrachloride, germanium tetrachloride, stannic chloride and lead tetrachloride all react with ammonia, mono- and dialkylamines and aniline to form

primary "addition compounds," which are quite stable with the tin and lead tetrahalides, but which are not highly stable in the silicon and germanium cases. With tin and lead,[12] compounds such as $PbCl_4·3C_6H_5NH_2$ do not react further to yield an anilide; the Pb–Cl bond is too stable for rupture, and no HCl can form. With both $SiCl_4$ and $GeCl_4$ anilino derivatives form, undoubtedly derived from addition compounds; the Si–Cl bond and the Ge–Cl bond both are broken; alkylanilinosilanes, except for the tetraanilino derivative,[5] are quite stable when pure; anilinogermanes and alkylanilinogermanes exist, but evidently decompose too easily to permit isolation as pure compounds. The reaction of the silicon and germanium halides with ammonia is similar, except that the germanium derivatives are probably more stable; $(Et_2GeNH)_3$ boils at 100° under 0.01 mm. pressure,[8] the structure probably being a six-membered ring; $(Et_3Ge)_2$-NH boils at 100° under 0.1 mm. pressure,[9] and may be a cyclic trimer or a dimer. It is difficult to weigh the results of Thomas and Southwood[11]; their compound $(C_5H_{10}N)_4Ge$, prepared from piperidine and $GeCl_4$, is undoubtedly valid; little credence should be assigned to their reaction between Et_2NH and $GeCl_4$, most unfortunately performed in the absence of a solvent. All-in-all, the dialkylamino derivatives of silicon appear to be more stable than those of germanium, while $SnCl_4$ and $PbCl_4$ merely form "addition compounds"[12]; probably steric effects block preparation of $(Et_2N)_4$-Si (herein $Si_2O(NEt_2)_6$ is reported). Therefore, *as an over-all conclusion*, silicon tetrachloride and related chlorosilanes form stable amino, alkylamino and anilino compounds more easily than do chlorogermanes while tin and lead tetrahalides do not form such compounds at all; on the other hand, addition compounds of tin and lead tetrahalides are quite stable. Thus *basicity or acidity* appears to explain the trends: *neutral* CCl_4 reacts reluctantly with aniline[13]; *predominantly acidic* silicon halides react the most satisfactorily with aniline, alkylamines and ammonia, furnishing the most stable anilino, alkylamino and amino compounds (with the slightly basic Me_3SiCl the reaction with aniline requires forcing conditions, but the $Me_3Si(HNC_6H_5)$ forms); *transitional*, sometimes basic, sometimes acidic,[14] germanium halides react with aniline, alkylamines and ammonia, but the anilino compounds decompose easily (aniline is a bulky, very weak base); the *predominantly basic* elements tin and lead are represented as" addition compounds" only—no anilino, alkylamino or amino derivatives are formed.

(1) 1932 Commonwealth Ave., Auburndale 66, Mass.
(2) E. A. Flood, This Journal, 55, 4935 (1933).
(3) R. O. Sauer and R. H. Hasek, ibid., 68, 241 (1946).
(4) A. Michaelis and K. Luxembourg, Ber., 29, 711 (1896).
(5) A. Harden, J. Chem. Soc., 51, 40 (1897).
(5a) J. E. Reynolds, ibid., 474 (1889).
(6) O. Ruff, Ber., 41, 3738 (1908).
(7) H. H. Anderson, This Journal, 73, 5802 (1951).
(8) E. A. Flood, ibid., 54, 1663 (1932).
(9) C. A. Kraus and E. A. Flood, ibid., 54, 1635 (1932).
(10) R. Schwartz and W. Rinehardt, Ber., 65, 1743 (1932).
(11) J. S. Thomas and W. W. Southwood, J. Chem. Soc., 2083 (1931).
(12) J. M. Matthews, This Journal, 20, 815 (1898).
(13) E. J. Hartung, J. Chem. Soc., 113, 163 (1918).
(14) H. H. Anderson, This Journal, 72, 2089 (1950).

TABLE I

Compound	B.p., °C.	Mm.	M.p., °C.	d^{22}_4	Analyses Mol. wt. Calcd.	Found	Neut. equiv. Calcd.	Found
Si(NMe₂)₄	180	760	− 2	0.973	204.4	212	51.1	50.5
	74–75	19						
MeSi(NMe₂)₃[a]	161	760	−11	.850	175.3	173	58.4	58.5
	55–56	17						
Me₂Si(NMe₂)₂	128.4	760	−98	.809	146.3	...	73.1	74.7
Si₂O(NEt₂)₆	334	760	−16	1.022	504.9	530	84.1	..
	138–139	1						
Ge(NMe₂)₄	203	760	14	1.069	248.9	260	29.2	28.6
	87–89	15						
Ge(NEt₂)₄	266 dec.	760	None	1.215	361.1	...	20.1	19.7
	108–110	2						
EtGe(NMe₂)₃	191	760	−46	1.049	233.9	...	31.1	30.5
	105–107	34						
EtGe(NEt₂)₃	249	760	None	1.108	317.9	330	22.8	22.5
	117–118	12						

[a] For MeSi(NMe₂)₃, n^{22} is 1.4324 and R is 53.5; for Me₂Si(NMe₂)₃, n^{22} is 1.4169 and R is 45.5 . All distillations are at lowest pressures given.

Some reactions of alkylamines with chlorosilanes or chlorogermanes failed to yield pure compounds, mainly because some halide, probably alkylammonium halide, has remained in solution. Ammonium chloride and alkylammonium chlorides are not very soluble in pure benzene; undoubtedly the larger the alkyl group and also the greater the number of alkyl groups, the more soluble the alkylammonium halide is in pure benzene. A plot of the logarithm of solubility of Me₄NCl (in a mixture of benzene and ethylene dichloride) against the logarithm of the dielectric constant for the mixed solvent gave a straight line[15]; also, dialkylammonium halides were somewhat soluble in liquid H₂S.[16] In preparations described in this paper one does not have pure benzene; the actual mixtures, usually with excess amine, are sometimes evidently better solvents than pure benzene and thus retain enough alkylammonium halide to prevent purification of the desired alkylamino derivative. During the reaction of diphenylgermanium dichloride with ethylamine, a solid which precipitated at first later redissolved in the mixture.[17] Thus solubility remains a problem not to be overlooked. Steric factors may sometimes be involved.

Reactions such as that of benzoyl chloride with MeSi(NMe₂)₃ to give MeSiCl₃ indicate that the dimethylamino group is fairly mobile, both with the silanes and germanes.

Experimental

Preparation of New Compounds.—Aminosilanes were prepared by methods all essentially similar, and only the isolation of tetrakis-(dimethylamino)-silane is described in detail. Twenty grams of cold Me₂NH was added slowly, with shaking, to 9.5 g. of SiCl₄ in 100 ml. of (30–60°) petroleum ether at −40°; this is a moderate excess of amine. During the next hour, the mixture of solution and precipitated Me₂NH₂Cl warmed up slowly, accompanied by occasional agitation; then the pasty mass was filtered on a buchner funnel—and refiltered if necessary to get a clear solution—and washed with fresh petroleum ether; the precipitate was discarded. Distillation of the solution in equipment bearing all ground joints first removed the petroleum ether, leaving 7.4 g. of crude Si(NMe₂)₄; after transfer to smaller equipment the product was distilled at 74–75° under 19 mm. pressure. It was a clear, colorless liquid with the properties listed in Table I.

Twenty grams of Me₂NH and 7.5 g. of MeSiCl₃ in 100 ml. of petroleum ether furnished an immediate precipitate at −60°; after processing 7.3 g. of MeSi(NMe₂)₃, methyltris-(dimethylamino)-silane, was obtained, or 85% of the theoretical yield. Ten grams of Me₂NH and 6.2 g. of freshly-distilled Me₂SiCl₂ similarly yielded 5.9 g. of Me₂Si(NMe₂)₂ ultimately. Forty grams of Si₂OCl₆ in 250 ml. of dry, pure benzene reacted easily with Et₂NH at 0°; a definite excess of amine was added, and then the mixture filtered on a buchner funnel; the solution stood closed overnight at 0°. Thereupon, refiltration and distillation of solvent gave 54 g. of Si₂O(NEt₂)₆, hexakis-(diethylamino)-disiloxane; distillation of this as in Table I furnished a center fraction with the properties listed.

Alkylaminogermanes.—Twenty grams of Me₂NH and 14.4 g. of GeBr₄ in 100 ml. of cyclohexane at −60° reacted easily, with much precipitation; after four hours of occasional shaking, during which the mixture warmed to 25°, there followed the usual filtering, next a single wash of the solid, and then distillation of the solvent, leaving 7.2 g. of Ge(NMe₂)₄, tetrakis-(dimethylamino)-germane as product, or about 80% of the amount expected. Similarly, 4.4 g. of EtGeCl₃—Professor Eugene G. Rochow, of this Laboratory, kindly furnished pure EtGeCl₃—and 10 g. of Me₂NH in 40 ml. of cyclohexane at −50° finally yielded 4.5 g. of EtGe-(NMe₂)₃, ethyltris - (dimethylamino) - germane. Forty grams of Et₂NH and 11.0 g. of GeBr₄ in 50 ml. of cyclohexane reacted easily at 25°, with a temperature rise of over 30°; after three hours, the usual processing yielded only 4.3 g. of Ge(NEt₂)₄, tetrakis-(diethylamino)-germane, or a yield of 45%. Twenty grams of EtGeCl₃ and 70 g. of Et₂NH in 180 ml. of benzene reacted easily, with an immediate precipitate; the final amount of EtGe(NEt₂)₃ was 27 g., or a yield of 90%. Table I lists the properties of center fractions collected under the conditions specified, all distillations being at the lowest pressures given therein.

Physical Properties and Analysis; see Table I.—Eight new compounds occur in the table; they are not nice compounds to handle, and under ordinary cautions many etch glass easily. Except for Si₂O(NEt₂)₆ and Ge(NEt₂)₄, which are a bit more viscous than CCl₄, the compounds are colorless, mobile liquids. Their odors weakly resemble that of the free amine, although Si(NMe₂)₄ has very little odor. Their vapors are inflammable; Ge(NEt₂)₄ decomposes badly when boiled at 760 mm., turning a very dark red in a few minutes due to free germanium no doubt; Ge(NMe₂)₄ decomposes if heated slightly above the b.p. at 760 mm. All molecular weights employ the Dumas method, since the determination through lowering of the freezing point of camphor gives low answers due to attack on the amines. Analyses for amine rely on back-titration,[2] using excess acid in 65% ethanol, and then ethanolic sodium hydroxide solution—or on weighing GeO₂ after oxidation in solution. Table I lists the results.

(15) A. A. Vernon, G. M. Goldberg and J. H. LaRochelle, THIS JOURNAL, **73**, 2844 (1951).

(16) E. E. Lineken and J. A. Wilkinson, ibid., **62**, 251 (1940).

(17) C. A. Kraus and C. L. Brown, ibid., **52**, 4031 (1930).

Reaction of Dialkylaminogermanes and Dialkylaminosilanes with Benzoyl Chloride.—Reflux of 0.5 g. of Ge(NMe₂)₄ and 1.5 g. of benzoyl chloride (which spontaneously warmed on mixing) furnished a hydrolyzable compound boiling at about 86°, thus $GeCl_4$; this amino derivative also reacted vigorously with pure $CHCl_2COOH$. Similarly, $Si(NMe_2)_4$ and benzoyl chloride yielded $SiCl_4$, b.p. 57°; also the amine reacted with $CHCl_2COOH$ or even 40% aqueous formic acid; however, the amino compound apparently did not react readily with pure water, no heat being given off. Six grams of benzoyl chloride and 1.3 g. of $MeSi(NMe_2)_3$ upon gentle reflux in a distilling unit yielded 0.8 g. of $MeSiCl_3$, a hydrolyzable chloride boiling at 67°. Likewise, $Me_2Si(NMe_2)_2$ gave Me_2SiCl_2, boiling at 72°. When shaken with a twofold volume of water $Me_2Si(NMe_2)_2$ furnished a temperature rise of at least 20°, while free Me_2NH was detected easily by the odor.

Conversion of $EtGe(NEt_2)_3$ into $EtGeI_3$.—Twenty grams of the amino compound and an excess of anhydrous HI, in benzene solution, gave 35 g. of crude $EtGeI_3$ in the general Ruff method[6]; since the Et_2NH_2I precipitated a little slowly, the solution containing $EtGeI_3$ and excess HI was allowed to stand closed overnight in the dark before filtering the precipitate. $EtGe(NEt_2)_3 + 6HI \rightarrow EtGeI_3 + 3EtNH_2I$.

Unsuccessful Reactions.—Me_3SnCl_2 and aniline did not react in benzene solution; $EtGeCl_3$ or $GeCl_4$ and aniline in benzene solution gave anilinium chloride, but no definite germanium compound. Likewise $Si(NEt_2)_4$, $Et_2Si(NEt_2)_2$ and $Me_2Si(NEt_2)_2$ could not be isolated in the pure state, since halogen persisted in the filtrate obtained; Et_2NH_2Cl sublimed while the desired product distilled, even at low pressure. In a single try Me_3SiCl and Me_2NH gave no constant-boiling product.

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Metachromasy of Toluidine Blue Induced by Nucleic Acids[1]

BY N. WEISSMAN, WM. H. CARNES, P. S. RUBIN[2] AND JEAN FISHER

It has been shown that aqueous solutions of pentose and desoxypentose nucleic acid react metachromatically with the thiazine dye toluidine blue. Two types of linkage, polar and non-polar, are involved in the process. The parameters of hydrogen ion concentration and ionic strength affect the formation of the polar bonds. The parameters of concentration of reactants, type of solvent and temperature affect the formation of non-polar bonds. The conditions necessary for nucleic acids to induce metachromasy in toluidine blue solutions are: pH between 6 and 7; temperature less than 30°; ionic strength of solution less than 0.03; ratio of dye to nucleic acid phosphorus between 0.4 and 1.4.

Metachromasy is a term applied to that variation in the absorption spectrum of certain dyestuffs, which depends on the nature of the substrate with which the dye interacts.[3] Since Ehrlich first described metachromasy, it has been used as a valuable cytological tool for the identification of mast cells, cartilage and mucins.[4] Lison thought that the metachromatic reaction was specific for the sulfate esters of polysaccharides. Later work showed that, in general, polymerized molecules containing negatively charged groups such as sulfate, carboxylate, phosphate, oleate, metaphosphate and silicate could react with cationic dyes to yield metachromatic products.[5–8]

Although Bank and Bungenberg de Jong[5] had reported that yeast nucleic acid was a metachromatic substrate, both Michaelis[3] and Wiame[7] failed to confirm this finding. Michaelis chose nucleic acid as a model for a "normally" staining substrate while Wiame reported that nucleic acid (variety not specified) inhibited metachromasy.

Since we had observed that the nuclei of cells could be stained metachromatically,[9] we decided to investigate the *in vitro* relationships of the basic dye toluidine blue and both types of nucleic acid. In this paper, we will demonstrate that, under the proper physicochemical conditions, both pentose and desoxypentose nucleic acids react metachromatically with toluidine blue.

Materials and Methods

Desoxyribonucleic Acid.—The two samples $7W_7$ and $11W_{12}$ were prepared from calf thymus nucleoprotein according to the method of Mirsky.[10] Both were highly polymerized, yielding very viscous solutions at low concentrations. The nitrogen to phosphorus ratios were 1.70 and 1.89, respectively. Preparation $7W_7$ contained 13.7% N and 8.1% P; $11W_{12}$ contained 14.2% N and 7.5% P.

Ribosenucleic Acid.—A commercial preparation of yeast sodium nucleate (Schwarz) was used. This contained 8.5% P.

Toluidine Blue O (C.I. No. 925).—Two samples were used. One was a commercial certified stain (certification No. NU9) manufactured by the National Aniline Division of Allied Chemical and Dye Corp. and said to contain 67% dye. Kjeldahl analysis showed a dye content of 64% in the undried sample; after drying to constant weight *in vacuo* over P_2O_5 at 100°, there was a weight loss of 5.2%. The second sample was a specially purified preparation from the National Aniline Division said to contain 85% dye. Kjeldahl analysis showed a dye content of 76%.[11]

Spectrophotometric measurements were made at 10-mμ intervals in a Beckman model DU spectrophotometer. The cuvette chamber temperature was brought to a definite value by flowing tap water through a jacket on either side of the chamber. No effort was made to achieve constancy, the only consideration being the avoidance of over-heating. Corex cuvettes of 1-cm. light path were used for the dilute dye solutions. The most concentrated dye solutions were measured with 9-mm. quartz inserts which reduced the light path to 1 mm. All molar absorption coefficients are calculated on the basis of the Kjeldahl nitrogen determinations.[12]

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(2) National Research Council Senior Fellow in Orthopedic Surgery, aided by a grant from the National Foundation of Infantile Paralysis.

(3) L. Michaelis and S. Granick, THIS JOURNAL, **67**, 1212 (1945).

(4) L. Lison, "Histochimie Animale," Gauthier, Paris, 1936, p. 236.

(5) O. Bank and H. G. Bungenberg de Jong, *Protoplasma*, **32**, 489 (1939).

(6) L. Michaelis, *Cold Spring Harbor Symposia Quant. Biol.*, **12**, 131 (1947).

(7) J. M. Wiame, THIS JOURNAL, **69**, 3146 (1947).

(8) R. C. Merrill, R. W. Spencer and R. Getty, *ibid.*, **70**, 2460 (1948).

(9) W. H. Carnes, N. Weissman and P. S. Rubin, paper read March 21, 1951, before the second annual meeting of the Histochemical Society at Detroit, Michigan.

(10) A. E. Mirsky and A. W. Pollister, *J. Gen. Physiol.*, **30**, 117 (1946).

(11) W. M. Clark, B. Cohen and H. D. Gibbs, *Pub. Health Rep.*, **40**, 1131 (1925).

(12) That the Kjeldahl method is a valid one for the determination of dye content will be shown elsewhere in a study of toluidine blue perchlorate.