

CuCl₂, and CrCl₂ it is to be expected that interactions between chains are more likely to be a factor, thus adding another dimension to the problem.

The magnetic susceptibilities of several of the RMX₃ complexes have been measured to liquid nitrogen temperatures by Asmussen and Soling¹⁴ and some of their data are reproduced in Table IV. Inasmuch as the Curie-Weiss constant increases¹⁴ with the metal-metal distance as one goes from CsNiCl₃ to CsNiBr₃, indicating larger antiferromagnetic interactions, it would appear that in agreement with the discussion of Schlueter, *et al.*,⁸ the important factor is not the metal-metal overlap. Stout and Chisholm¹⁵ have pointed out that in the interlinked chain structures of CuCl₂ and CrCl₂ one would expect Kramers¹⁶ superexchange to be much greater within the chain than between chains and were able to explain the heat capacity maximum (23.91°K for CuCl₂) and magnetic susceptibility maximum (70°K for CuCl₂) on this basis using an Ising model. The antiferromagnetic ordering in CrCl₂ within a chain has been verified by neutron diffraction studies.¹⁷ Since exchange *via* the bridging halogens depends rather critically on the metal-halogen distance, the differences in the magnetic properties of tetramethylammonium¹⁸ ($\theta = 0^\circ\text{K}$) and cesium¹⁴ ($\theta = -75^\circ\text{K}$) salts of NiCl₃⁻ might be explained to a large extent by distortions of the type found in tetramethylammonium tribromonickelate. We are currently examining the crystal structures and magnetic properties of several MX₃⁻ salts with different cations and transition metals to further correlate the magnetic and structural properties of these compounds. Neutron diffraction studies are being carried out at Argonne National Laboratories.

(15) J. W. Stout and R. C. Chisholm, *J. Phys. Soc. Japan, Suppl. B-1*, 522 (1962).

(16) H. A. Kramers, *Physica*, **1**, 182 (1934).

(17) J. W. Cable, M. K. Wilkinson, and E. O. Wollon, *Phys. Rev.*, **118**, 950 (1960).

(18) See footnote *a*, Table IV.

Table IV. Magnetic and Structural Data for RNiX₃ Compounds

Compound	Curie-Weiss constant		μ_{eff}	Ni-Ni distance, Å
	$-\theta$, °K	Ref		
RbNiCl ₃	112	14	2.95; 20°	...
CsNiCl ₃	76	14	3.01; 21°	2.97
RbNiBr ₃	156	14	2.84; 21°	3.09
CsNiBr ₃	101	14	2.94; 22°	3.12
(CH ₃) ₄ NNiCl ₃	0	<i>a</i>	3.20; 20°	3.08

^a D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

The absorption spectra of some of the compounds MNiX₃ have been reported by Asmussen,¹⁹ Cotton,²⁰ and Goodgame.¹⁸ The absorption spectrum of (CH₃)₄NNiBr₃ shows the following spin-allowed bands: ³A_{2g} → ³T_{2g} at 6300 cm⁻¹, ³A_{2g} → ³T_{1g}(F) at 10,400 cm⁻¹, and ³A_{2g} → ³T_{1g}(P) at 19,700 cm⁻¹. In addition the following spin-forbidden bands are observed: ³A_{2g} → ¹E_g(¹D) at ~11,400 cm⁻¹ and ³A_{2g} → ¹T_{2g}(¹D) at 17,500 cm⁻¹ (s). There is no evidence of the trigonal distortion in the absorption spectra. Using the same method as Goodgame,¹⁸ the value of Δ is 6300 cm⁻¹ and B' is approximately 750 cm⁻¹. Goodgame reports values of Δ and B' as 6600 and 840 cm⁻¹, respectively, for (CH₃)₄NNiCl₃. Preliminary X-ray data show that (CH₃)₄NNiCl₃, $a = 7.85$, $c = 6.16$ Å, has a similar structure to that of (CH₃)₄NNiBr₃, but is not isomorphous; for example, using the same fractional position coordinates found in (CH₃)₄NNiBr₃ with the above experimental lattice parameters for (CH₃)₄NNiCl₃ results in a N-C distance of 1.22 Å. The complete three-dimensional structure of this compound will be reported in a subsequent paper.

(19) R. W. Asmussen and O. Bootrup, *Acta Chem. Scand.*, **11**, 745 (1957).

(20) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 349 (1961).

Amination and Transamination as Routes to Fourth Group Diamines¹

C. H. Yoder and J. J. Zuckerman

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. Received March 30, 1966

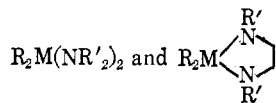
Abstract: Preparation and properties of some examples of *gem*-diamines of carbon, silicon, germanium, and tin are presented. These bis(dialkylamino) compounds were used in transamination reactions with N,N'-disubstituted ethylenediamines to yield monomeric imidazolidine derivatives, with piperazine to yield analogs of 1,4-diazabicyclo-[2.2.1]heptane (germanium) or its dimer (silicon) and polymers, and with ethylenediamine to yield polymers. Backbone structures for the polymers are assigned on the basis of nmr and infrared spectra and analytical data. Mechanistic implications of the observed group IV reactivities toward amination (Si > Ge > Sn) and transamination (Sn > Ge > Si) are discussed.

This publication reports the results of our investigations on the synthesis and relative reactivities of organometallic diamines of carbon, silicon, germanium,

(1) Portions of this investigation were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, and

and tin. We were interested in the comparative aspects of the chemistry of the *gem*-diamines of these elements, especially the dialkyldiamines of the type

at the Second International Symposium on Organometallic Compounds, Madison, Wis., Sept 1965.



where M = C, Si, Ge, Sn.

Syntheses

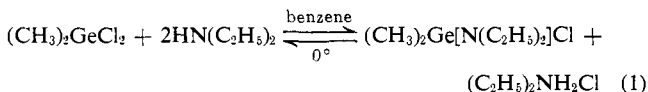
Silicon, germanium, and tin amines are commonly prepared by one of two general synthetic routes: amination (reaction of an amine or its alkali metal derivative with a fourth group halide) or transamination (exchange of amino groups on a group IV element). Organic amines are frequently obtained by amination procedures, but transamination² is very rarely encountered. Another common route to organic amines, condensation of amines with carbonyl groups, is not available to the other members of the group.

I. Bis(dialkylamino) Compounds. Bis(dialkylamino)methane derivatives can be conveniently prepared by a method first examined by Henry³ in 1893 which utilizes the simple condensation of aqueous formaldehyde with diethylamine to produce bis(diethylamino)methane in good yield. The physical properties of the liquid we obtained agreed with that reported, and the nmr and infrared spectral evidence was consistent with the formulation proposed by Henry.

Numerous bis(amino)silanes have been prepared by direct amination of chlorosilanes and the interested reader is referred to pertinent review articles for details.⁴ Dimethylbis(diethylamino)silane was obtained following the method of Henglein and Lienhard.⁵

Three examples of bis(dialkylamino)germanium compounds have been reported: one [dibutylbis(dimethylamino)germane] was from direct amination of the chlorogermane in petroleum ether at -70° ,⁶ but in the other preparations alkali metal salts of pyrrole⁷ and bis(trimethylsilyl)amine⁸ were employed.

We have found that the direct amination of dimethylchlorogermane with diethylamine replaces only one chlorine atom on germanium to produce dimethylchlorodiethylaminogermane as the sole product.



The proton nmr spectrum of this compound showed a ratio of peak areas consistent with the monosubstituted derivative. Analogous reaction with dimethylamine at -60° resulted in a mixture of dimethylchlorodimethylaminogermane and the disubstituted bis(dimethylamino)dimethylgermane. The two aminogermanes distill together at 144° (745 mm) and were not separated. They could be distinguished by nmr, however, since resonances in the spectrum of the mixture are easily assignable to each compound, and gas chromatographic analysis using a Carbowax column showed two peaks with equal areas.

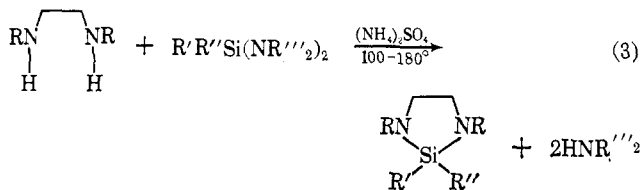
Dimethylbis(diethylamino)germane itself can be obtained by amination of the dichlorogermane with the lithium salt of diethylamine,⁹ and diphenylbis(dimethylamino)germane was prepared by the same route.¹⁰



The reaction of organotin halides with amines is exactly analogous to the reaction with alcohols and phenols;¹¹ only stable complexes are formed. Amination can be effected, however, by the use of lithium salts of amines.¹²⁻¹⁴

II. Imidazolidines. The synthesis of N,N'-dimethylimidazolidine from N,N'-dimethylethylenediamine and paraformaldehyde in dimethylformamide has been described by Krässig, who also reviewed previous syntheses from the diamine and formaldehyde.¹⁵ We obtained the N,N'-dimethyl, diethyl, and diphenyl derivatives by suitable modifications of this method.^{16,17}

We have already reported on the synthesis of silaimidazolidines which can be obtained in fair yields by direct amination of dichlorosilanes by N,N'-disubstituted ethylenediamines. Alternatively, an amine exchange reaction utilizing a silanediamine as precursor can be employed.

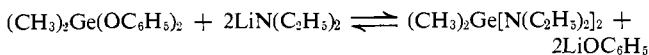


This method, although requiring preliminary preparation of the silanediamine, produces the silaimidazolidine in good yield after removal of the displaced organic amine. Ammonium sulfate serves as a catalyst and transaminations at silicon do not proceed at a reasonable rate without it.¹⁸

The reluctance of dichlorogermanes to part with both of their chlorine atoms is once again demonstrated in our attempt to apply the direct amination method in the preparation of germainimidazolidines; N,N'-bis(dimethylchlorogermyl)-N,N'-dimethylethylenediamine

(9) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966).

(10) A. Köster-Pflugmacher and E. Termin [*Naturwiss.*, **23**, 554 (1964)] adapted the interesting route



to the preparation of bis(diethylamino)dimethylgermane. Their product (no analytical data are given) is a liquid, bp $106-108^\circ$ (2 mm), but differs from ours in being stable to aqueous acetone and boiling 3 N sodium hydroxide.

(11) H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, **1**, 328 (1964).

(12) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1962); *J. Chem. Soc.*, 1944 (1965).

(13) K. Jones and M. F. Lappert, *J. Organometal. Chem.*, **3**, 295 (1965).

(14) We have elsewhere pointed out the danger of explosion during distillation of bis(dialkylamino)stannanes from large-scale reaction mixtures; see E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Nucl. Chem. Letters*, **1**, 105 (1966).

(15) H. Krässig, *Makromol. Chem.*, **17**, 77 (1955), and references therein.

(16) R. A. Donia, J. A. Shotton, L. O. Bentz, and G. E. P. Smith, Jr., *J. Org. Chem.*, **14**, 952 (1949).

(17) H. Wanzlich and W. Löchel, *Chem. Ber.*, **86**, 1463 (1953).

(18) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).

(2) Not to be confused with biochemical NH_2 exchange between amino acids.

(3) L. Henry, *Bull. Acad. Roy. Med. Belg.*, **8**, 200 (1893).

(4) (a) U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964);

(b) R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

(5) F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959).

(6) H. H. Anderson, *J. Am. Chem. Soc.*, **83**, 547 (1961).

(7) F. Rijkens and G. J. M. van der Kerk, "Organogermanium Chemistry," Germanium Research Committee, Utrecht, 1964.

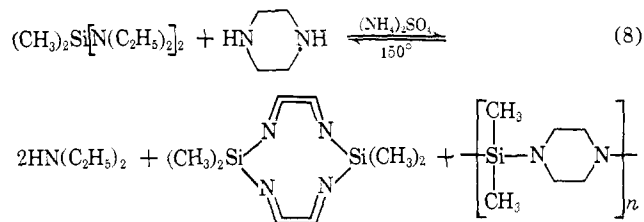
(8) O. Scherer and M. Schmidt, *Angew. Chem.*, **75**, 642 (1963).

tives which lack substituents at nitrogen are apparently stable.²⁴

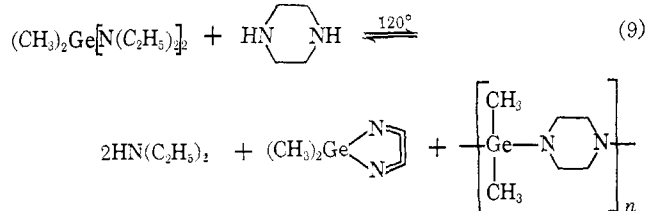
The simple bis(diethylamino) derivatives hydrolyze to diethylamine in less than 1 min (as can be observed by nmr) after addition of an equimolar amount of water to a dioxane solution of the compound. The hydrolysis of bisdiethylaminomethane, however, appears to reach an equilibrium rapidly, where an approximately 1:2 ratio of diamine to hydrolysis product is present. Quantitative hydrolysis of this diamine takes place upon addition of ammonium sulfate.

III. Other Imidazolidine Derivatives. A particular advantage of the transamination route is the great variety of amines which can be used to exchange with the organometallic amines. We have investigated the preparation of bicyclic imidazolidine-type ring systems which might result from the use of piperazine and ethylenediamine itself in transamination with organosilicon and germanium diamines.

Transaminations with Piperazine. Transamination of dimethylbis(diethylamino)silane with piperazine in the presence of ammonium sulfate as a catalyst at 150° produced a white solid. Purification by recrystallization from carbon tetrachloride or chloroform and sublimation gave a material whose analytical data, molecular weight (see Table I), and nmr spectrum [Si-methyl at τ 9.97 \pm 0.03, methylene bridge at τ 7.28 \pm 0.03] are consistent with a dimer as the predominant product, although the nmr spectrum indicates that other compounds including higher homologs and polymers (not isolated) may constitute as much as 20–30% of the original reaction mixture. The transamination can be summarized by the following formulation.



Purification of the product of transamination of dimethylbis(diethylamino)germane with piperazine was more difficult, but we are able to assign the monomer shown below as the predominant product on the basis of analytical data, molecular weight determinations (see Table I), and nmr spectra [Ge-methyl at τ 9.69 \pm 0.03, methylene bridge at τ 7.17 \pm 0.03].



Transaminations with Ethylenediamine. Action of dimethylbis(diethylamino)silane on ethylenediamine at 125° in the presence of a small amount of ammonium sulfate as a catalyst gave a white solid (slightly soluble in halocarbon solvents) which was crushed to a powder

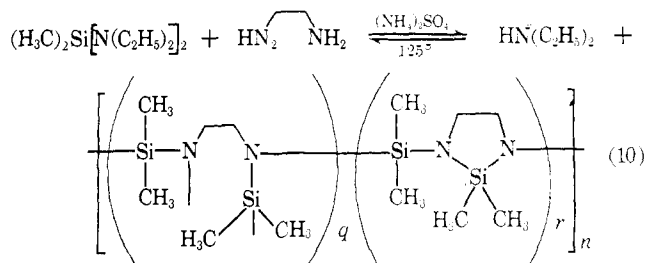
(24) D. Kummer and E. G. Rochow, *Angew. Chem.*, **75**, 207 (1963); M. Wieber and M. Schmidt, *Z. Naturforsch.*, **18b**, 849 (1963).

Table I. Products from Transamination with Piperazine

Compound	C	H	N	M	Mol wt
M = Si					
Found 1	49.77	11.18	16.98	17.39	331 ^a
2	51.43	10.12	18.71	18.19	300 \pm 30 ^b
Calcd for C ₆ H ₁₄ N ₂ Si	50.64	9.91	19.69	19.74	142
M = Ge					
Found	37.25	7.71	12.52	40.11	205 ^c
Calcd for C ₆ H ₁₄ N ₂ Ge	38.58	7.55	14.99	38.86	186.5

^a By vapor phase osmometry. ^b Ebullioscopic in benzene. ^c Ebullioscopic in chloroform.

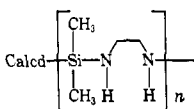
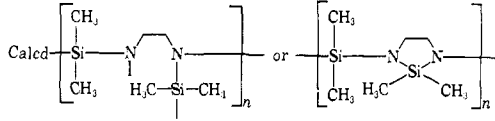
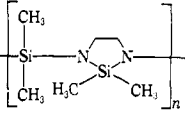
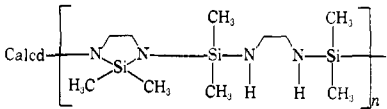
and dried *in vacuo*. An nmr spectrum in dibromomethane showed a broad resonance in the region associated with Si-methyl. No nmr resonance or infrared absorption which could be attributed to an N-H function was observed. A sharp infrared absorption was found at 1330 cm⁻¹ which is observed in similar silaimidazolidines and has been assigned to a ring motion.⁵ In simple N-alkyl derivatives we find this absorption at 1330 cm⁻¹ to be of the same order of intensity as the C-H or Si-N stretches. Analytical data for two samples of polymer from separate preparations as well as theoretical values calculated for linear, cross-linked, or pure ring, and ring-plus-chain backbone structures are given in Table II. These values serve to eliminate the pure linear polymer, and absence of evidence for N-H bonds in nmr or infrared spectra supports this. Distinguishing between the pure ring or cross-linked and ring-plus-chain structures is more difficult on the basis of the analytical data alone, but spectral evidence would again suggest that structures containing N-H bonds cannot constitute the predominant product. The polymer can then take a pure ring, a pure cross-linked structure, or some structure which is a combination of the two. The physical properties (white resinous solid) and low solubility of our materials differ markedly from those of the mixed ring and chain polymers (viscous oils) and pure ring polymers (viscous resins) obtained by Kummer and Rochow,²³ and from our apparently predominantly ring germanium polymer discussed below. On this basis we assign the structure shown in the following formulation



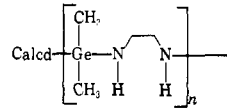
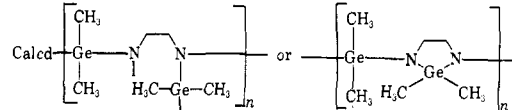
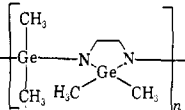
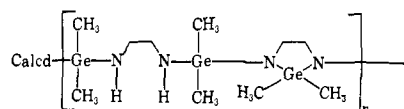
where the ratio q to r of cross linking to ring units must be high on the basis of the weak infrared absorption at 1330 cm⁻¹ (*ca.* two-fifths the intensity of the C-H or Si-N absorption) and resin-like physical properties. Identical analytical data are to be expected from pure ring and pure cross-linked structures.

Reaction of dimethylbis(diethylamino)germane with ethylenediamine at 120° released diethylamine quantitatively and produced a paste which was dried *in vacuo*. The nmr spectrum of this material in carbon tetrachloride showed resonances associated with Ge-methyl protons at τ 9.71 \pm 0.03 and two overlapped signals

Table II. Products from Silicon Transaminations with Ethylenediamine

Polymer	C	H	N	Si	Mol wt
Found 1	40.56	9.45	15.15	28.94	5200 ^a
2	42.74	9.56	16.67	30.43	
Calcd 	41.34	10.41	24.11	24.17	
Calcd  or 	41.80	9.36	16.25	32.59	
Calcd 	41.60	9.78	19.42	29.20	

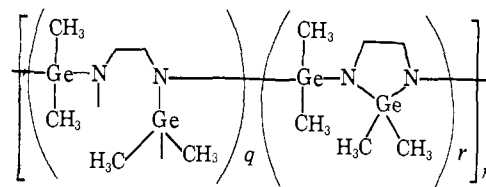
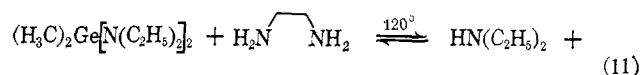
^a By vapor phase osmometry.**Table III.** Products from Germanium Transaminations with Ethylenediamine

Polymer	C	H	N	Ge	Mol wt
Found	27.19	6.42	9.00	50.88	>1000 ^a
Calcd 	29.89	7.53	17.38	45.17	
Calcd  or 	27.57	6.17	10.71	55.55	
Calcd 	28.45	6.68	13.28	51.60	

^a Ebullioscopic in benzene.

centered at τ 9.66 \pm 0.03 (integrated area ratios of 2:3). A broad resonance was found in the region associated with methylene bridge protons (τ 7.01 \pm 0.03). An infrared spectrum of the paste as a Nujol mull showed a sharp absorption at 1330 cm^{-1} . We have found previously that germanium imidazolidines exhibit a sharp absorption around 1333 cm^{-1} whereas the bis(dialkyl-amino) derivatives⁹ do not. In the simple N-alkyl germainimidazolidines this absorption is about two-thirds the intensity of the C-H absorption, and we assign this absorption, like the similar one in the silaimidazolidines,⁵ to a ring motion. In our polymer this absorption is *ca.* one-half as intense as the C-H stretching frequency. No evidence for the N-H function was found in either nmr or infrared spectra. Table III lists analytical data for our material and theoretical values calculated for the various possible backbone structures. Kummer and Rochow, on the basis of model compounds, have been able to assign nmr resonances of polymeric systems in the Si-methyl region to dimethylsilyl groups acting as connection units between rings (τ 9.87), between rings and chains (τ 9.97), and dimethylsilyl units contained in imidazolidine rings (τ 9.91).^{22,23} In likewise fashion we can assign the three types of Ge-methyl groups in our polymer whose

structure is shown in the following mixed ring-chain formulation

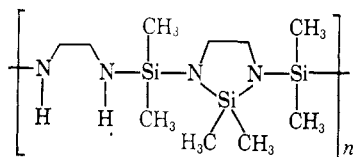


where the imidazolidine ring Ge-methyl resonance appears at τ 9.71 \pm 0.03 as in the parent N-methyl monomer and both the connecting Ge-methyl types appear near τ 9.66 \pm 0.03 with the integrated area ratios of these resonances and relative intensity of the characteristic infrared ring absorption consistent with the polymer repeating unit as shown. The ratio of q to r , then, is considerably greater for the silicon polymer than for the germanium polymer.

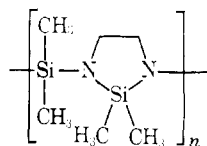
Apart from the usual factors which hamper unambiguous assignment of molecular structure from chemical and spectroscopic evidence, there exists in this instance

the more difficult considerations of the actual distribution of polymer units and variation of polymer composition and configuration with reaction conditions and time. Attempted extrapolation from macroscopic properties to a single unambiguous structure would be hazardous; the properties of our materials we have been able to measure are doubtless weighted averages of properties of several possible polymer types whose precise composition in the mixture remains unknown.

It is interesting to note briefly the polymer types obtained by other workers from similar reaction systems. Henglein and Lienhard assigned a cross-linked structure to the plastic resin of molecular weight 3100 which they obtained through transamination of dimethylbis(diethylamino)silane in the absence of solvent,⁵ but Kummer and Rochow obtained a waxy material (no molecular weight reported) from similar transaminations in mesitylene, which, on the basis of infrared and nmr evidence, they believe to consist of



units as the backbone structure.²³ These workers and others have investigated the various polymeric materials received from the reaction of dimethylchlorosilane with ethylenediamine carried out under a variety of conditions.^{5, 23, 25} Differences in the transamination products obtained by these two groups is ascribed to the use of solvent by Kummer and Rochow. These workers also showed that the chain-ring backbone polymer can be converted to a pure cyclic polymer (viscous resin) of the structure



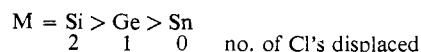
by heating to 370° at low pressure.²³ Transamination in the absence of solvent might also result in higher temperatures and the possibility of more ring formation. The production of higher molecular weight materials from our silylamine transaminations as compared with previously reported syntheses^{5, 23} is probably associated with (i) the presence in our systems of small amounts of ammonium sulfate as a catalyst which seems to promote the fuller utilization of active amine sites in forming Si-N links, and (ii) a mole ratio of silylamine to ethylenediamine of 2:1. It is clear that the gross compositions of the polymers obtained from these reactions are strongly dependent upon such variables as temperature of synthesis, route (whether amination or transamination), starting mole ratios, presence or absence of a solvent or catalyst, and history of the isolated polymer.

Discussion

I. Relative Reactivities. Amination of dimethylchlorosilane by diethylamine displaces two chlorine

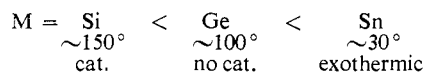
(25) R. Minné and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 5625, 5628 (1960).

atoms easily. In dimethyldichlorogermane only one chlorine atom is replaced. No chlorine is lost in the action of diethylamine on dimethyltin dichloride which forms a donor-acceptor complex instead. Thus, ease of amination of $(\text{CH}_3)_2\text{MCl}_2$ by diethylamine varies.



Analogous esterification reactions exhibit the same pattern: organodichlorosilanes react vigorously, dichlorogermanes sluggishly, and organotin dichlorides react not at all (or form donor-acceptor adducts). Synthesis of organogermanium esters is facilitated by the presence of base;²⁶ for organotin esters strong base is demanded.¹¹

Transamination of the easily formed organosilyl diamines with various ethylenediamines requires moderately strong heating (to *ca.* 150°) and ammonium sulfate as a catalyst, without which the conversion does not proceed at a reasonable rate. With bis(diethylamino)-organogermanes transamination proceeds at *ca.* 100° in the absence of a catalyst. Tin diamines undergo transamination at room temperature, even exothermically.²⁷ Thus, ease of transamination of $(\text{CH}_3)_2\text{M}[\text{N}(\text{C}_2\text{H}_5)_2]_2$ by ethylenediamines varies.



Not enough is known concerning transesterifications in the germanium and tin series to draw meaningful analogies. In the reaction of dimethylchlorodiethylamino-germane with *N,N'*-dimethylethylenediamine we have a competition between amination and transamination at the same germanium atom; only the transamination proceeds.

II. Mechanistic Considerations. Explanation for these striking trends must lie in mechanistic considerations. Several types of reaction mechanism are available to silicon, but the SN_2 type appears to be general, especially in the presence of a suitable nucleophile.²⁸ Studies of the amination of optically active organochlorosilanes containing asymmetric silicon indicate that amination by the amines themselves as well as their lithium salt derivatives proceeds through inversion of configuration consistent with the SN_2 reaction mechanism.^{29, 30}

SN_2 reactions at silicon, germanium, and tin may differ considerably in mechanistic detail from those at carbon because of the stabilization of penta- or hexacoordinated transition states by use of low-lying d orbitals.³¹ Not only can the energy of the penta-coordinated Walden inversion transition state for these elements be lowered by this interaction, but it is possible for the transition state to become an unstable intermediate in the reaction process. It is to be expected

(26) D. C. Bradley, L. Kay and W. Wardlaw, *Chem. Ind.* (London), 746 (1953).

(27) This has been observed in numerous stannylamine exchange reactions: K. Jones, personal communication, 1964.

(28) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(29) L. H. Sommer, J. D. Citron, and C. L. Frye, *J. Am. Chem. Soc.*, **86**, 5684 (1964).

(30) K. Rühlmann and G. Tuchtenhagen, *Z. Chem.*, **5**, 107 (1965); K. D. Kaufmann, U. Mann, and K. Rühlmann, *ibid.*, **5**, 188 (1965).

(31) For a discussion of this point with reference to silicon, see C. Eaborn, "Organosilicon Compounds," Butterworth & Co., Ltd., London, 1960, p 103.

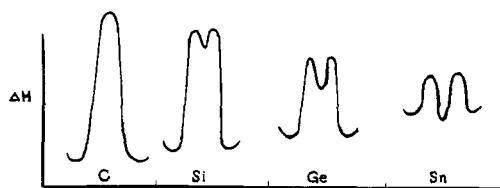
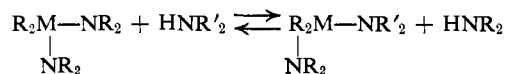
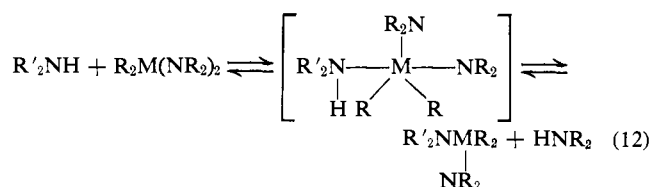


Figure 1. Reaction profiles for transamination.



that the stabilities of these intermediates for silicon and its lower congeners in group IV should parallel the stabilities of their donor-acceptor adducts even though the intermediate may not itself be a normal adduct.³²

Consider a possible SN2 reaction mechanism for transamination



The symmetrical nature of the reaction allows us to assume the over-all enthalpy and entropy changes to be close to zero, where R and R' are similar organic groupings. If we also assume similar reaction mechanisms for silicon, germanium, and tin,³³ and that stability of the intermediate goes as adduct stability, then we can draw enthalpy profiles as in Figure 1. The position of the curves along the energy axis in the figure is dictated by the general trend of decreasing element-nitrogen bond energies on descending a normal group. Increasing stability of the reaction intermediate or decreasing energy of the transition state (the validity of our discussion is independent of whether the reaction proceeds through an intermediate or not) with attendant adjustment of activation energy can thus serve in the approach due to Hammett to rationalize the observed trends in transamination. The exothermic nature of transaminations at tin²⁷ (provided this is not a heat of mixing) dictates the profile for tin with the placement of the intermediate as drawn.

The effectiveness of ammonium salts as catalysts in the silicon transaminations can be discussed with reference to their effect on the reaction intermediate or transition state as in (12). Protonation of the leaving diethylamino moiety in (12) would enhance the displacement of this group. In addition protonation would be expected to stabilize the intermediate by strengthening the bond being formed (by essentially making the silicon center more electron deficient).

The observed amination pattern is more difficult to rationalize, if only because the reaction is no longer symmetrical. Thus the heat of reaction will change from silicon to tin and the symmetry of the enthalpy

(32) Stabilities of these adducts (which have been exhaustively studied) are in the order: Sn >> Ge > Si; see I. R. Beattie, *Quart. Rev.* (London), 17, 382 (1963).

(33) Studies of optically active organogermanes reported to date indicate that silicon and germanium follow similar reaction mechanisms; see A. G. Brook and G. Peddle, *J. Am. Chem. Soc.*, 85, 2338 (1963). Unfortunately no stereochemical studies of transaminations or germanium aminations are available. Organotin compounds are apparently too labile to resolve.

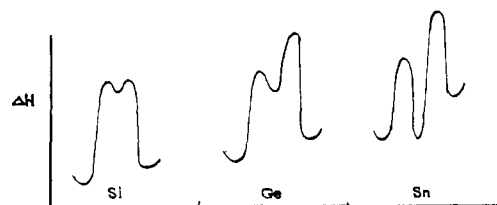
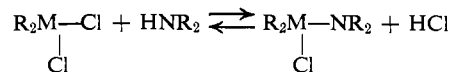
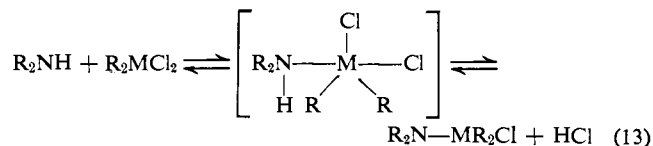


Figure 2. Reaction profiles for amination.



profile at the intermediate may be destroyed. Assuming again the SN2-type mechanism established for silicon^{28,29} is also followed by germanium and tin,³³ we write



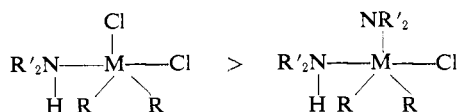
Intermediates of this general type in the tin series have been isolated. The entropy difference between aminations on changing M from silicon to tin should be small, and trends in reactivity can be discussed in terms of changes in the relative M-Cl and M-N bond energies and the stability of the intermediates (again our discussion is equally valid for a transition state). Relevant M-Cl bond energies are 91 (M = Si in SiCl₄), 81 (M = Ge in GeCl₄), and 76 kcal/mole (M = Sn in SnCl₄);³⁴ bond-energy data for the M-N systems are confined to silicon (three values in the range 77-83 kcal/mole)^{4a} and tin (ca. 40 kcal/mole).¹³ Thus the decrease in energy silicon to tin for the bonds to chlorine is much smaller than the same decrease for the nitrogen bonds (approximately 15 vs. 40 kcal/mole). It is apparent that the observed heat liberated in the aminations must be mainly the result of acid-base reactions between hydrogen chloride and excess amine.

Clearly in the amination series silicon to tin the relative stabilities of the reactants decrease while those of the intermediates increase. Were the energy profiles symmetric as in the transamination case, the activation energy would decrease from silicon to tin, and this is contrary to our observation. If the conversion of intermediate to products is rate determining, then the relative energy profiles as drawn in Figure 2 show the activation energies in the series to be dependent upon relative intermediate and product energies and the position of the rate-determining transition state along the reaction coordinate. Assuming this last factor remains constant silicon to tin, a delicate adjustment of intermediate and product energies can bring about the parallel adjustment in activation energy necessary to obtain a trend of reactivity in agreement with experiment.³⁵ The energy of the tin intermediate in Figure 1 is again placed at such a level as to indicate exothermic formation of this species.

(34) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, London, 1963.

(35) A rapid equilibrium step prior to formation of the intermediate (an SN2* mechanism in Sommer's notation) is expected to lead to extensive racemization.²⁸

Transaminations with ethylenediamines from which the relative reaction tendencies were derived are assumed to be stepwise processes in which each step involves a simple energy profile as shown in Figure 1, or may involve chelated six-coordinated intermediates depending on the central atom. If the amination process proceeds stepwise as well, then it is clear from existing evidence³² that the second intermediate should be less stable than the first



and this difference is particularly important where M = germanium. In this case the steric requirements of the amination agent determine whether the second process is to proceed at all. Mixed chloroamines are now available for silicon, germanium, and tin,³⁶ but it is possible that aminations of difunctional organohalo derivatives of the fourth group may proceed in one step in certain cases.³⁷

Experimental Section

All commercial starting materials were redistilled before use. N,N'-Dimethylethylenediamine and diethylamine were stored over molecular sieves (Linde Type 4A), while ether was dried over sodium wire. Dimethyldichlorogermane (bp 119–123°) was obtained by direct reaction of methyl chloride with 20% copper germanium metal.³⁸ The infrared and nmr spectra and properties of this material were consistent with those reported. All operations were carried out under nitrogen.

Physical properties and analytical data for bis(dialkylamino)silanes and silaimidazolidines¹⁸ have been listed in previous publications. Literature procedures were followed for the carbon and tin compounds and these references are in the text. Experimental details listed below will be limited primarily to the germanium derivatives³⁹ and modifications of literature procedures, although we will also present general procedures which we have found useful for aminations and transaminations.

Amination of Dihalide Derivatives of Group IV. A solution of the dihalide (0.1 mole) in an equal volume of benzene or ether is added dropwise to a stirred solution of amine (0.5 mole) in about 200 ml of benzene or ether at -20 to 0° under nitrogen. In some instances, e.g., because of the cost or low basicity of the amine, it is helpful to use triethylamine rather than excess starting material to take up the HCl produced. A simple and convenient apparatus for inert atmosphere reactions, described by Cason and Rapoport,⁴⁰ was used to exclude atmospheric moisture. Addition is accomplished in about an hour, accompanied by precipitation of the amine hydrochloride. After an additional hour or two of stirring at -20 to 0°, the reaction mixture is allowed to warm to room temperature (in some instances even refluxed for an hour) and then filtered. Filtration can be accomplished in the air without appreciable hydrolysis if done rapidly by suction through a glass frit funnel. Solvent is removed by vacuum distillation (atmospheric distillation if product bp is low) and liquid products are purified by distillation. Hydrolytically sensitive products are collected in glass pigs which can be sealed off without exposure to air. Solid products can generally be recrystallized from benzene or benzene-hexane mixtures. Lithioamination procedures can be found elsewhere.⁹

Transamination of Bis(diethylamino) Derivatives of the Fourth Group. Equimolar quantities (0.05 mole) of the diamine and the

bis(dialkylamino) derivative are placed in a reaction unit equipped with thermometer, nitrogen inlet, stirrer, and reflux condenser. A small amount (ca. 0.01 g) of ammonium sulfate is added as a catalyst for silicon transaminations. The reactants are heated (oil bath) with stirring under nitrogen to 100–160°. The amine is liberated and begins to reflux; the oil bath temperature is maintained constant. As the amine continues to be liberated the temperature of the reaction mixture decreases until an equilibrium is reached. Usually the liberated amine is swept out of the system on a nitrogen stream and can be trapped at -196° if desired. Products are purified as above.

Dimethylchlorodiethylaminogermane. Dimethyldichlorogermane (0.1 mole) in 50 ml of diethyl ether was added dropwise to a stirred solution of diethylamine (0.5 mole) in 300 ml of ether at 0°. After addition, the reaction mixture was allowed to stand at room temperature for 16 hr. The white precipitate which had formed during the addition was then filtered (0.12 mole). Ether was removed from the filtrate by distillation at atmospheric pressure, leaving a liquid residue which distilled at 177° (743 mm) to give ca. 10 g (50% yield based on germane) of product. A yield of 65% was obtained in another preparation. Samples of the product sealed in glass vials at atmospheric pressure developed a brown-red discoloration and precipitated a small amount of solid material on standing. *Anal.* Calcd for C₆H₁₆NClGe: C, 34.28; H, 7.67; N, 6.66; Ge, 34.53, mol wt, 210. Found: C, 34.23; H, 7.79; N, 7.10; Ge, 18.96;⁴¹ mol wt (ebullioscopic in benzene), 232.

Diphenylbis(dimethylamino)germane. A hexane solution of butyllithium, 1.6 M (0.16 mole), was added dropwise to a stirred solution of dimethylamine (0.16 mole) in 100 ml of ether at ca. -70°. After the addition, the mixture was allowed to warm to room temperature, and then diphenyldichlorogermane (0.08 mole) in 100 ml of benzene was added at room temperature. Several hours of reflux was followed by *in vacuo* solvent removal, decantation of the liquid residue from the precipitate, and distillation of the residue to give the desired product (41% yield) at 181–182° (13 mm). *Anal.* Calcd for C₁₆H₂₂N₂Ge: C, 61.03; H, 7.04; N, 8.90; Ge, 23.05. Found: C, 60.51; H, 6.96; N, 9.09; Ge, 23.20.

N,N'-Bis(dimethylchlorogermyl)-N,N'-dimethylethylenediamine. An attempt to prepare the imidazolidine by amination of dimethyldichlorogermane with N,N'-dimethylethylenediamine in the presence of triethylamine produced the compound above along with other minor products which were not identified. Dimethyldichlorogermane (0.075 mole) in 15 ml of benzene was added to a stirred solution of N,N'-dimethylethylenediamine (0.073 mole) and triethylamine (0.16 mole) in 100 ml of benzene. The addition was begun at room temperature, but the reaction mixture was heated to 80° halfway through the addition and maintained at this temperature for 10 hr. After filtration of the cool mixture and washing of the white precipitate with benzene, the filtrate was distilled at atmospheric pressure to remove solvents. A liquid, bp ca. 90° (9 mm) (which solidified in the distillation head), was obtained by reduced pressure distillation of the residue.

This compound was also formed in the reaction between dimethylchlorodiethylaminogermane (0.064 mole) and N,N'-dimethylethylenediamine (0.055 mole). Immediate formation of a white solid with evolution of heat occurred upon mixing. A small amount of ammonium sulfate was then added and the mixture heated to 170° for 6 hr. The solid melted or dissolved at 80–90° during the heating. Some material sublimed to the cooler parts of the apparatus and the remaining liquid distilled at 97° (10 mm). An infrared spectrum of the product showed it to be identical with the product obtained above. *Anal.* Calcd for C₅H₂₂N₂Cl₂Ge₂: C, 26.51; H, 6.12; N, 7.73; Ge, 40.07; mol wt, 362. Found: C, 25.74; H, 6.02; N, 7.32; Ge, 39.00; mol wt (cryoscopic in cyclohexane), 454.

2,2-Diphenyl-1,3-dimethylgermimimidazolidine. Diphenylbis(dimethylamino)germane (0.023 mole) reacted with N,N'-dimethylethylenediamine (0.029 mole) at 100° to give a material which partially solidified on standing. The liquid portion distilled at 172° (13 mm) and was identified as the imidazolidine. *Anal.* Calcd for C₁₆H₂₀N₂Ge: C, 61.41; H, 6.44; N, 8.95; Ge, 23.20; mol wt, 313. Found: C, 61.04; H, 6.59; N, 9.36; Ge, 22.92; mol wt (osmometry in benzene), 326.

Bis(diethylamino)methane. An aqueous solution (ca. 37%) of formaldehyde (0.27 mole) was added dropwise to diethylamine (0.55 mole) with stirring. The temperature of the exothermic

(36) C. H. Yoder and J. J. Zuckerman, unpublished results; U. Wannagat and G. S. Schreiner, *Monatsh. Chem.*, **96**, 1889 (1965).

(37) It appears that the tendency for 1:1 adduct formation decreases relative to 1:2 formation as the fourth group is descended.³²

(38) E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947); **70**, 436 (1948); M. Schmidt and I. Rudisch, *Z. Anorg. Allgem. Chem.*, **311**, 331 (1961); J. J. Zuckerman, *Advan. Inorg. Chem. Radiochem.*, **6**, 383 (1964).

(39) See ref 9 for the preparation of dimethylbis(diethylamino)germane and 1,2,2,3-tetramethylgermimimidazolidine.

(40) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1962, p 452.

(41) Analysis for germanium in compounds with both nitrogen and chlorine present on germanium often produces a low value for germanium in our experience.

reaction was kept below 45° by external cooling. Two layers formed and the top organic layer was removed and dried over CaSO₄. The product (ca. 25 g, 60% yield based on formaldehyde) distilled at 162.5–165° (743 mm). Henry reported a boiling point of 168°.³

N,N'-Dimethylimidazolidine. An aqueous (ca. 37%) formaldehyde solution (0.19 mole) was added slowly to a solution of N,N'-dimethylethylenediamine (0.19 mole) in 200 ml of chloroform. After stirring for several hours, the water layer was removed and the chloroform layer was dried over MgSO₄. Atmospheric pressure distillation served to remove the solvent; the product (26% yield) distilled at 110–112° (collected as a cloudy material). After several days a red oil separated and the clear liquid was distilled trap to trap *in vacuo*. The product must be refrigerated to prevent decomposition. Krässig reports a boiling point of 114°.¹⁵

N,N'-Diethylimidazolidine. The procedure of Donia, *et al.*,¹⁶ was followed except that the reaction mixture were merely dried thoroughly over CaSO₄ and then distilled at atmospheric pressure to give the product boiling at 152–155° in 35% yield. Donia, *et al.*, report a boiling point of 65.6° (35 mm).¹⁶

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The Reaction between Metal Carbonyls and Amines. II. Iron Carbonyl with Pyrrolidine. Initial Stages of the Reaction¹⁻³

Walter F. Edgell and Bernard J. Bulkin

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. Received May 16, 1966

Abstract: The reaction between Fe(CO)₅ and pyrrolidine has been investigated, using infrared and nmr spectra, conductance measurements, and stoichiometry; attention is focused on the first species (I) formed in this reaction. The over-all reaction path is similar to that of the reaction between Fe(CO)₅ and piperidine or *n*-butylamine; however, certain differences occur which have permitted further elucidation of the structure and nature of I. Additional conductance data on Fe(CO)₅-piperidine reactions are also presented. The data reported here put the more tentative proposals of the earlier paper regarding the nature of I on a firmer basis.

When iron pentacarbonyl, Fe(CO)₅, and piperidine or *n*-butylamine are mixed at room temperature, a reaction ensues at once which yields a compound (I) in which considerable modification of the metal carbonyl and amine moieties has taken place.³ In water, this compound hydrolyzes to form HFe(CO)₄⁻ (II) and the carbamate of the amine, >NCOO⁻, both as the >NH₂⁺ salts. After some time at room temperature, but more rapidly at 60°, I reacts to form another metal carbonyl containing species III in which there is evidence for formylation of the amine at the nitrogen, *i.e.*, a carbon monoxide insertion reaction has taken place. We have now investigated the reaction of Fe(CO)₅ with pyrrolidine, and extended the studies of the reaction between Fe(CO)₅ and piperidine. These investigations have yielded a body of evidence concerning the structure and nature of I, a compound which is the important first intermediate in the CO insertion reaction which has taken place.

The general reaction path in the pyrrolidine case parallels that of piperidine and *n*-butylamine,³ but certain differences in I for pyrrolidine allow more detailed structural and chemical evidence to be obtained.

The hydrolysis products of I in pyrrolidine reaction mixtures were again found to be HFe(CO)₄⁻ and pyr-

rolidine carbamate. It was these hydrolysis products in the other amines which first led to a proposed structure for I containing the linkage >NCOFe⁻.

Although spectral evidence was interpreted to mean that I was probably an LFe(CO)₄ compound with the amide ligand, L, located at the axial position of a trigonal bipyramid, two other structures were also possible.³ These were both trigonal bipyramidal L₂Fe(CO)₃ compounds, either with both ligands on planar sites or with one axial and one planar. Each of these could give the observed 5-μ region CO stretching frequency pattern of 2010 (w-m), 1918 (m), and 1895 (s) which I shows, when the amine is piperidine or *n*-butylamine. The 5-μ region spectrum of an Fe(CO)₅-pyrrolidine reaction mixture taken within 2 min after mixing is shown in Figure 1. This spectrum shows the same basic pattern found in the piperidine and *n*-butylamine cases. As can be seen in the pyrrolidine case, however, the strong band is split into a doublet with components at 1898 and 1885 cm⁻¹. These bands are due to C≡O stretching vibrations of the metal carbonyl moiety in I. Since the number of metal carbonyl CO groups in the molecule must be equal or greater than the number of bands due to fundamental modes in the 5-μ region (C≡O stretching vibrations), the presence of four fundamental bands for I in pyrrolidine solutions clearly eliminates the L₂Fe(CO)₃ structures as possibilities for I.

The spectrum of I in the pyrrolidine case is readily understood in terms of the proposed LFe(CO)₄ struc-

(1) Abstracted in part from the Ph.D. Thesis of B. J. Bulkin, Purdue University, June 1966.

(2) Supported by a contract with the Atomic Energy Commission.

(3) Paper I of this series: W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 3080 (1965).