VI

Thermodynamic Constants.—The energies and entropies of activation for a number of the dichloride dissociation reactions (Table III) have been calculated in

TABLE III

THERMODYNAMIC CONSTANTS FOR DISSOCIATION OF $XC_6H_4ICl_2$
IN ACETIC ACID

X	o-Derivative		p-Derivative	
	E_1, kcal./mole	$\Delta S_1^{\ddagger}$, e.u.	E_1, kcal./mole	$\Delta S_1^{\ddagger}$, e.u.
$CH_2OC_6H_5$	17.4 ± 1.0	-14 ± 3	20.2 ± 0.6	-10 ± 2
$CH_2OC_6H_5$	15.9 ± 0.3	-24 ± 1	$14.6 \pm .5$	-29 ± 2
CH_2COOCH_3	23.0 ± 1.1	$+3 \pm 4$	$23.0 \pm .2$	-1 ± 1

cases in which appropriate data (Table II) are available. As can be expected when the *ortho* located substituent participates in the reactions, the E_1 and $\Delta S^{\ddagger}$ values for o-CH_2OCH_3 substituted iodobenzene dichloride are less (less positive or more negative) then those for the

p-isomer. In the case of the corresponding phenyl ethers this situation is reversed. For reasons which are not obvious at this point, the entropies and energies of activation for o- and p-$CH_3OOCCH_2C_6H_4ICl_2$ are larger than those for any of the other substituted dichlorides which have been investigated currently or previously.

Comparative values of E_1 and $\Delta S_1^{\ddagger}$ are not reported for the o- and p-$COCH_3$ and o- and p-COC_6H_5 derivatives. Because of the rapidity of the reactions at temperatures much above 25°, k_1 values for the o-isomers cannot be determined at sufficiently widely varying temperatures so that thermodynamic constants can be reported with reasonable confidence. While check rate runs on the o-isomers were in exceptionally good agreement, it was not possible for technological reasons to vary starting concentrations of reactants sufficiently so that the limits of error reported for the k_1 values (Table II) can be accepted with certainty. The two o-isomers and also the two p-isomers show very similar rate responses to temperature changes.

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[CONTRIBUTION FROM THE PARMA RESEARCH LABORATORY, UNION CARBIDE CORP., PARMA 30, OHIO]

# Condensation of B-Aminoborazines with Dimethylformamide and Amine Hydrochlorides

BY R. H. TOENISKOETTER* AND K. A. KILLIP

B-Aminoborazines condense with dimethylformamide and amine hydrochlorides to yield borazyl oxides. Amidine hydrochlorides and amines are by-products in the reaction. The stoichiometry of the reaction has been established and a reaction mechanism proposed. Some observations relating to the effect of changing amino groups of the reactants on the composition of the amines and amidine salts formed are recorded and discussed in terms of the proposed mechanism.

Introduction

Mono- and dichloroborazines do not form stable complexes with dimethylformamide (DMF).[1] Nevertheless, when solutions of these borazines in DMF are treated with primary or secondary amines, borazyl oxides, rather than aminoborazines, are produced. For example, the reaction of dimethylamine with B-chloro-B-dimethyl-N-trimethylborazine (I) in DMF produces bis-(pentamethylborazyl) oxide (II), rather than B-dimethylamino-B-dimethyl-N-trimethylborazine (III); poly-(tetramethylborazylene) oxide (IV) is obtained similarly from B-dichloro-B-methyl-N-trimethylborazine.

I

II

III

IV
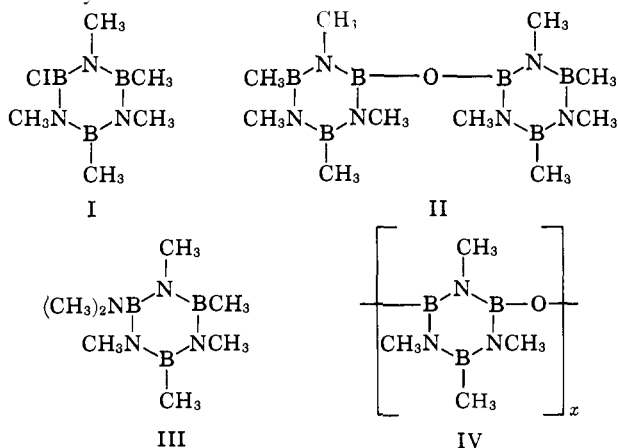
Superficially, these reactions appeared to be analogous to those between amines and phosphorus oxychloride–DMF[2] or cyanuric chloride–2DMF.[3] However, further investigation showed that aminoborazines condense with DMF in the presence of amine hydrochloride, thereby producing borazyl oxides. Since the reaction of a chloroborazine with an amine in inert medium produces an aminoborazine and amine hydrochloride,[1,4] it appeared likely that the same reaction took place in DMF medium, and that borazyl oxide formation resulted from the subsequent condensation of aminoborazine with DMF and amine hydrochloride. We wish to report here the initial observations with the chloroborazines, and the more definitive experiments with aminoborazines which have led to a workable hypothesis regarding the reaction mechanism.

Results and Discussion

I. Reaction of Amines with Chloroborazines in Dimethylformamide.—The reaction of a chloroborazine with dimethylamine and DMF is essentially quantitative according to the equation

$$2{>}BCl + (CH_3)_2NC(H)O + 2(CH_3)_2NH \longrightarrow$$
$$>BOB< + (CH_3)_2NH_2Cl + [(CH_3)_2NC(H)N(CH_3)_2]Cl \quad (1)$$
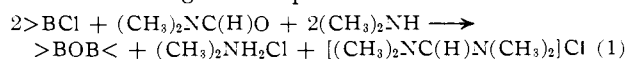
Observed ratios were: $(CH_3)_2NH/{>}BCl = 0.96$ and $DMF/{>}BCl = 0.50$. Yields of borazyl oxides were usually above 90%. Dimethylamine or monomethylamine were employed in this reaction for conversion of

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(1) R. H. Toeniskoetter and F. R. Hall, *Inorg. Chem.*, **2**, 29 (1963).

(2) H. Brederick, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).

(3) H. Gold, *Angew. Chem.*, **72**, 956 (1960).

(4) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 356 (1959).

B-chloro-B-dimethyl-, B-dichloro-B-methyl-, and B-dichloro-B-n-butyl-N-trimethylborazine to the corresponding borazyl oxides. Dibutylamine proved to be a suitable, although less reactive, substitute for dimethylamine, but no reaction took place with trimethylamine. When dimethylacetamide was substituted for DMF no compounds containing borazyl oxide structures were isolated; amination of the chloroborazine appeared to be the only reaction occurring.

The borazyl oxides were characterized through elemental analysis (Table III), molecular weight data, and infrared spectra. Characterization of bis-(pentamethylborazyl) oxide and polytetramethylborazylene oxide confirmed previous studies of these compounds by Wagner and Bradford.[5]

Weak DMF–chloroborazine complexes analogous to $POCl_3 \cdot DMF^2$ and cyanuric chloride–$2DMF^3$ are not unreasonable intermediates in the condensation of chloroborazines with DMF and amines. Nevertheless, the ease of amination of chloroborazines[1,4,6] in inert solvents raises serious doubt that reactions of complexes could efficiently compete with the rapid and exothermic formation of aminoborazines. The results presented in the following section, moreover, demonstrate that borazyl oxide formation readily occurs in aminoborazine–DMF–amine hydrochloride systems. It therefore appears likely that in DMF–chloroborazine–amine systems, the most probable sequence of events is *in situ* formation of an aminoborazine and amine hydrochloride followed by condensation with DMF.

II. Reaction of Aminoborazines with Dimethylformamide and Amine Hydrochlorides.—Solutions of aminoborazines in DMF appeared to be stable at temperatures below 100°. Addition of amine hydrochloride to a solution of an aminoborazine in DMF at 25°, however, initiated a reaction with evolution of amine and formation of the corresponding borazyl oxide. The aminoborazines investigated, together with the corresponding borazyl oxides obtained, are listed in Table I.

TABLE I

Reactants and Products in the Systems: Aminoborazine–$(CH_3)_2NH_2Cl$–DMF

Aminoborazine	Borazyl oxide
$(CH_3)_2N(CH_3)_2[BN]_3(CH_3)_3$	$O\{(CH_3)_2[BN]_3(CH_3)_3\}_2$
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	$\{O(CH_3)[BN]_3(CH_3)_3\}_x$
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	$O\{(CH_3)_2[BN]_3(CH_3)_3\}_2$
$(CH_3)_2N(CH_3)_2[BN]_3(C_2H_5)_3$	$O\{(CH_3)_2[BN]_3(C_2H_5)_3\}_2$
$[(CH_3)_2N]_2(CH_3)[BN]_3(C_2H_5)_3$	$\{O(CH_3)[BN]_3(C_2H_5)_3\}_x$
$[(CH_3)_2N]_2C_4H_9[BN]_3(CH_3)_3$	$-\{O(C_4H_9)[BN]_3(CH_3)_3\}_x$
$[(C_4H_9)_2N](CH_3)_2[BN]_3(CH_3)_3$	$O\{(CH_3)_2[BN]_3(CH_3)_3\}_2$

The stoichiometry of the reaction of either B-bis-(dimethylamino)-B-methyl- or B-dimethylamino-B-dimethyl-N-trimethylborazine with DMF and dimethylamine hydrochloride is given by the equation

$$2>BN(CH_3)_2 + (CH_3)_2NC(H)O + (CH_3)_2NH_2Cl \longrightarrow$$
$$>BOB< + [(CH_3)_2NC(H)N(CH_3)_2]Cl + 2(CH_3)_2NH \quad (2)$$
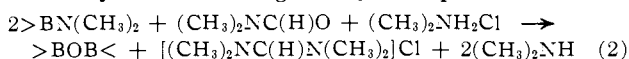
Pertinent data obtained included dimethylamine evolution, dimethylformamide consumption, and yield of borazyl oxide. Tetramethylformamidinium chloride was isolated as the benzene-insoluble product from reactions employing a slight deficiency of dimethylamine hydrochloride. Yield data were not obtained for the amidine salt, but its identification as a product, together with the other stoichiometric data, adequately support eq. 2. When an excess of amine hydrochloride was employed, the observed ratios were: DMF/$>BN(CH_3)_2 = 0.49$ and $(CH_3)_2NH/>BN(CH_3)_2 =$

(5) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962).
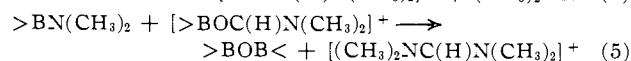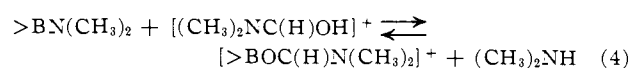(6) J. R. Gould, U. S. Patent 2,754,177 (July 10, 1956).

1.04 (line 1, Table II). Use of a deficiency of amine hydrochloride with DMF and the bis-aminoborazine resulted in control of the polymer molecular weight which could be calculated using the standard formulas of polymer chemistry. That the reaction in this case, nevertheless, followed the stoichiometry of eq. 2 was shown by the observed ratios: $(CH_3)_2NH/(CH_3)_2NH_2Cl = 2.02$ and $DMF/(CH_3)_2NH_2Cl = 1.03$ (line 2, Table II). Data from reactions of three other dimethylaminoborazines (lines 3, 4, and 5, Table II) also were in essential agreement with the stoichiometry of eq. 2. Stoichiometric data for all the systems investigated are summarized in Table II.

In searching for a plausible mechanism for the condensation reaction, two considerations seem to provide certain limitations. First, since solutions of aminoborazines in DMF appear to be stable indefinitely at 25°, and are readily separated into their component parts, it is unlikely that DMF–aminoborazine complexes are precursors to the formation of the borazyl oxides. Second, it can be argued that the preparative methods developed for aminoborazine synthesis provide convincing evidence that amine hydrochlorides and aminoborazines do not interact. One must, therefore, turn to the DMF–amine hydrochloride system in search of reactive species capable of initiating the reaction.
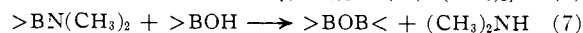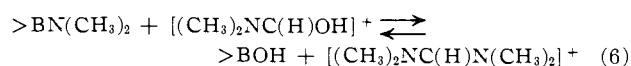
In view of the general utility of DMF as a nonaqueous solvent for weak acid titrations[7,8] and its solvent power for amines and their hydrochlorides,[9] proton transfer from substituted ammonium ions to solvent molecules is quite probable

$$(CH_3)_2NH_2^+ + (CH_3)_2NC(H)O \rightleftharpoons$$
$$(CH_3)_2NH + [(CH_3)_2NC(H)OH]^+ \quad (3)$$
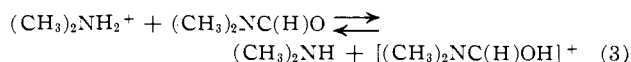
Recent evidence based on nitrogen nuclear resonance[10] and proton magnetic resonance[11] favor protonation on oxygen rather than nitrogen in amide-acid mixtures. However, in aqueous systems or in the presence of weak acids or bases, rapid proton exchange on nitrogen appears possible although the concentration of N-protonated species remains low.[11] In the amine hydrochloride–DMF systems, no clear choice between N- or O-protonation can be made based on our present knowledge of these systems. We assume the O-protonation and propose that the reaction proceeds through the interaction of protonated solvent species with the aminoboron group, followed by condensation of the intermediates to the borazyl oxide structure, which may be formulated according to either eq. 4 and 5

$$>BN(CH_3)_2 + [(CH_3)_2NC(H)OH]^+ \rightleftharpoons$$
$$[>BOC(H)N(CH_3)_2]^+ + (CH_3)_2NH \quad (4)$$
$$>BN(CH_3)_2 + [>BOC(H)N(CH_3)_2]^+ \longrightarrow$$
$$>BOB< + [(CH_3)_2NC(H)N(CH_3)_2]^+ \quad (5)$$

or 6 and 7

$$>BN(CH_3)_2 + [(CH_3)_2NC(H)OH]^+ \rightleftharpoons$$
$$>BOH + [(CH_3)_2NC(H)N(CH_3)_2]^+ \quad (6)$$
$$>BN(CH_3)_2 + >BOH \longrightarrow >BOB< + (CH_3)_2NH \quad (7)$$

Both reaction routes are in accord with the general experimental results and account for the observed stoichiometry of $(CH_3)_2NB<-DMF-(CH_3)_2NH_2Cl$ systems. Moreover, the important observation that trimethylammonium ion gives rise to trimethylamine

(7) J. S. Fritz, *Anal. Chem.*, **24**, 306 (1952).
(8) V. Z. Deal and G. E. A. Wyld, *ibid.*, **27**, 47 (1955).
(9) DMF Product Information Bulletin, Grasselli Chemicals Dept., E. I. du Pont de Nemours and Co.
(10) D. Herbison-Evans and R. E. Richards, *Trans. Faraday Soc.*, **58**, 845 (1962).
(11) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

TABLE II

STOICHIOMETRIC DATA FOR AMINOBORAZINE–DMF–AMINE HYDROCHLORIDE REACTION

Borazine	mmoles	Amine hydrochloride	mmoles	DMF consumed, mmoles	Amine obtained, mmoles	Yield of borazyl oxide, %
$(CH_3)_2N(CH_3)_2[BN]_3(CH_3)_3$	5.28	$(CH_3)_2NH_2Cl$	2.80	2.61	5.49[a]	100
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.58	$(CH_3)_2NH_2Cl$	3.53	3.65	7.15[a]	100
$[(CH_3)_2N]_2(C_4H_9)[BN]_3(CH_3)_3$	3.49	$(CH_3)_2NH_2Cl$	3.33	3.43	6.69[a]	100
$(CH_3)_2N(CH_3)_2[BN]_3(C_2H_5)_3$	8.15	$(CH_3)_2NH_2Cl$	5.72	4.90	8.71[a]	50
$[(CH_3)_2N]_2(CH_3)[BN]_3(C_2H_5)_3$	8.04	$(CH_3)_2NH_2Cl$	8.13	8.87	17.02[a]	100
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.83	$(CH_3)_3NHCl$	4.88	4.89	9.02[b]	100
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.76	CH_3NH_3Cl	4.49	5.11	8.32[a]	97
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.75	CH_3NH_3Cl	4.30	4.57	8.54[a]	98
$(CH_3)_2N(CH_3)_2[BN]_3(CH_3)_3$	6.31	CH_3NH_3Cl	3.06	2.46	6.01[a]	97
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	6.44	CH_3NH_3Cl	4.03	5.38[c]	6.03[d]	88
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	5.56	CH_3NH_3Cl	3.78	7.06[e]	5.63[e]	88
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	5.76	$(CH_3)_2NH_2Cl$	5.31	3.42	4.79[f]	87
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	8.71	$(CH_3)_2NH_2Cl$	4.75	6.63	6.95[g]	77
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.65	NH_4Cl	4.63	3.50	7.69[a]	82
$[(CH_3)_2N]_2(CH_3)[BN]_3(CH_3)_3$	4.72	$C_6H_5NH_3Cl$	3.71	4.15	6.95[a]	100

[a] 100% $(CH_3)_2NH$. [b] 4.90 $(CH_3)_3N$ + 4.12 $(CH_3)_2NH$. [c] High value due to MMF formation which was not separated with DMF. [d] 5.34 $(CH_3)_2NH$ + 0.69 CH_3NH_2. [e] 4.79 $(CH_3)_2NH$ + 0.84 CH_3CH_2. [f] 4.71 $(CH_3)_2NH$ + 0.08 CH_3NH_2. [g] 6.93 $(CH_3)_2NH$ + 0.02 CH_3NH_2.

TABLE III

ANALYTICAL DATA FOR BORAZYL OXIDES

Compound	M.p., °C	Found, %				Calculated, %			
		B	N	C	H	B	N	C	H
$O[(CH_3)_2[BN]_3(CH_3)_3]_2$	134	20.7	26.4	38.2	9.46	20.5	26.7	38.2	9.53
$[O(CH_3)[BN]_3(CH_3)_3]_x$	160	21.4	27.4	31.8	8.19	21.5	27.9	31.9	7.99
$O[(CH_3)_2[BN]_3(C_2H_5)_3]_2$	150[a]	16.1	20.3	48.1	11.2	16.2	21.0	48.1	10.6
$[O(CH_3)[BN]_3(C_2H_5)_3]_x$	112	15.7	20.0	42.1	9.74	16.8	21.8	43.7	9.41
$[O(C_4H_9)[BN]_3(CH_3)_3]_x$	80	15.9	21.4	44.5	9.69	16.8	21.8	43.7	9.41

[a] B.p. at 10^{-4} mm.

which constitutes approximately one-half of the total amine produced (line 6, Table II) follows directly from eq. 3.

Equation 3 also predicts that methylamine hydrochloride should lead to the formation of methylamine. This was not observed, however, for in the systems dimethylaminoborazine–DMF–methylamine hydrochloride (lines 7, 8, and 9, Table II), essentially pure dimethylamine was obtained as the gaseous product. Moreover, N,N,N'-trimethylformamidinium chloride, rather than tetramethylformamidinium chloride, was isolated from the reaction products. In all other respects, however, the stoichiometries of these reactions were consistent with eq. 2.

Although these results appear to invalidate eq. 3 as a reaction step, this is not substantiated by other observations; instead, complicating reactions tend to mask the true nature of the reaction system. It has been observed, for instance, that exchange reactions involving both protons and amino groups take place in amine–amine hydrochloride–DMF systems.[12] Hence, exchange reactions could account for the predominance of dimethylamine as the gaseous product in the methylamine hydrochloride–DMF–dimethylaminoborazine system. Furthermore, the isolation of N,N,N'-tri-

(12) Various mixtures of methyl- and dimethylamine and their hydrochlorides in DMF and MMF were prepared, allowed to equilibrate for 24–48 hr., and analyzed. In the absence of amine hydrochloride, solutions of methylamine in DMF, or dimethylamine in MMF, appeared to be quite stable. However, addition of either methyl- or dimethylamine hydrochloride initiates exchange reactions which apparently involve both protons and amino groups. Furthermore, in the absence of added amine, solutions of amine hydrochlorides in either DMF or MMF showed no detectable exchange of amino groups. The results of these experiments could be satisfactorily accounted for in terms of the equilibria

$$MeNH_2 + Me_2NH_2^+ \rightleftharpoons$$
$$Me_2NH + MeNH_3^+ \text{ (in amide solution)}$$
$$MeNH_3^+ + DMF \longrightarrow$$
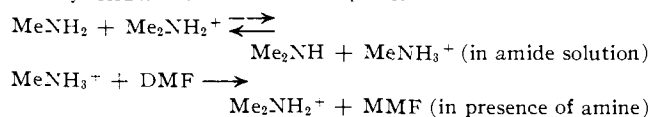$$Me_2NH_2^+ + MMF \text{ (in presence of amine)}$$

methylformamidinium chloride from this system makes the exchange hypothesis more tenable, for that salt may be thought of as derived from monomethylformamide (MMF) which is formed in the exchange between methylamine, methylamine hydrochloride, and DMF. Further support comes from the observation that monomethylformamide, if kept at low concentration, successfully competes with DMF in the condensation reaction.[13] Hence, a satisfactory explanation of the behavior of dimethylaminoborazine–DMF methylamine hydrochloride systems can be based on eq. 3 and exchange reactions generating dimethylamine and MMF, followed by condensation of MMF[14] according to eq. 4 and 5 at a much faster rate than DMF. This reaction scheme leads directly to formation of N,N,N'-trimethylformamidinium chloride.

The mechanism proposed above applies equally well to methylaminoborazine–DMF–methylamine hydrochloride systems (lines 10 and 11, Table II). In this system, however, the amount of MMF which can be produced via the exchange reaction exceeds that re-

(13) The competitive behavior of small amounts of MMF in DMF was briefly investigated. In a typical case, MMF equal to one-half the stoichiometric amount of amide was employed in the reaction of B-dimethylamino-B-dimethyl-N-trimethylborazine with dimethylamine hydrochloride and an excess of DMF. The gaseous product consisted of pure dimethylamine; no MMF was detected among the reaction products. The amount of DMF consumed plus the quantity of MMF taken gave a ratio of total amide consumed to >BN(CH₃)₂ of 0.49. An essentially quantitative yield of bis-borazyl oxide confirmed the validity of eq. 2 for the reaction.

(14) Under other conditions, the reaction of MMF with an aminoborazine follows a different course not requiring added amine hydrochloride. For example, when MMF and B-dimethylamino-B-dimethyl-N-trimethylborazine are mixed at 25°, a fairly vigorous reaction occurs with evolution of approximately 1 mole of amine (consisting of about 75% dimethylamine and 25% methylamine) per >BN(CH₃)₂ group. The nonvolatile products may be separated by extraction with n-heptane to give bis-(pentamethylborazyl) oxide (soluble) and a borazyl amide (insoluble) $(CH_3)_2[C(H)\cdot ON(CH_3)][BN]_3(CH_3)_3$, m.p. 111°, $\nu_{C=O} = 1710$ cm.⁻¹. Anal. Calcd.: B, 15.6; N, 27.1; mol. wt., 207. Found: B, 14.2; N, 26.9; mol. wt., 211. Reactions with bis-aminoborazines appeared to proceed directly to low molecular weight polyborazylene oxides with amide end groups.

quired for the condensation reactions 4 and 5. Accordingly, methylamine and MMF were expected among the reaction products; these anticipations were confirmed experimentally (footnote c, Table II).

Dimethylamine was also the sole gaseous product from reactions between dimethylaminoborazines and DMF with either ammonium chloride or aniline hydrochloride. In the latter case, N,N-dimethyl-N'-phenylformamidinium chloride was isolated, suggesting formation of benzamide as a reaction intermediate. Hence, it may be tentatively suggested that novel exchange reactions occur in these systems also.

Experimental

The unsymmetrical chloro- and aminoborazines were prepared by the methods reported[1] previously. Since B-dimethylamino-B-dimethyl-N-triethylborazine, B-bis-(dimethylamino)-B-methyl-N-triethylborazine, and B-bis-(dimethylamino)-B-n-butyl-N-trimethylborazine have not been described previously, their synthesis and characterization are included. The methylamine hydrochlorides (Matheson Coleman and Bell) were dried at 110°. Aniline hydrochloride (Matheson Coleman and Bell) was recrystallized from acetonitrile and dried under vacuum. Storage of bulk materials and transfer of reagents were carried out in nitrogen atmosphere within a drybox.

Monomethylformamide and Spectro grade dimethylformamide (Distillation Products Industries) were dried by passing through 30-in. columns of Linde Molecular Sieve 5A (activated at 350° with N_2). The DMF used for stoichiometric studies was dried further by distilling *in vacuo* onto molecular sieve which had been activated by heating at 350° under vacuum for 18 hr. After 2 hr. contact with the desiccant, the DMF was distilled into a storage bulb on the vacuum line. Standard vacuum line techniques were used in the stoichiometric studies. DMF was measured as a liquid in a small bulb with a calibrated capillary stem. Mixtures of DMF and amines were separated by fractionation through a series of traps at 0, −45, −78, and −196°; omission of either the −45 or −78° trap resulted in poor rectification of the mixtures. When mixtures of amines were obtained they were analyzed by vapor phase chromatography employing an *o*-toluidine on firebrick column.[15] Vapor phase chromatography using a silicone gum rubber column also was employed routinely for identification of DMF, MMF, aminoborazines, and the bis-borazyl oxides.

Molecular weights were determined by the freezing point method in benzene solutions. The cryoscopic cell described by Vofsi and Katchalsky[16] was employed, but the sample holder was omitted. Instead, transfer of solvent and solutions were carried out in a drybox. A Victory Engineering Corp. No. 32A1 thermistor was used as the temperature sensing element in conjunction with a bridge circuit and 10-mv. recorder. Molecular weights were reproducible within ±5%.

Preparation of B-Dimethylamino-B-dimethyl-N-triethylborazine and B-Bis-(dimethylamino)-B-methyl-N-triethylborazine.— A solution of 235 ml. of 2.75 M CH_3MgBr (0.587 mole) in diethyl ether was added dropwise to a stirred solution of 143 g. of Cl_3-$[BN]_3(C_2H_5)_3$ in 1500 ml. of *n*-heptane at 0°. The magnesium salts were filtered off and the filtrate, which contained a mixture of chloroborazines, was added dropwise to a solution of 100 g. of dimethylamine in 300 ml. of *n*-heptane. After stirring for 2 hr. at 25°, the mixture was filtered and the filtrate concentrated by distillation and finally dried at 25° and 1 mm. The residual liquid was then fractionally distilled through a Nester–Faust semimicro spinning-band column. B-Dimethylamino-B-dimethyl-N-triethylborazine was collected at 118° and 9 mm. and B-bis-(dimethylamino)-B-methyl-N-triethylborazine at 100° and 1.55 mm. *Anal.* Calcd. for $[(CH_3)_2N]_2CH_3[BN]_3(C_2H_5)_3$: B, 12.2; N, 26.5; C, 49.9; H, 11.4. Found: B, 12.2; N, 27.7; C, 48.6; H, 11.5.

Preparation of B-Bis-(dimethylamino)-B-n-butyl-N-trimethylborazine.—B-Dichloro-B-n-butyl-N-trimethylborazine[17] was treated with dimethylamine in the usual manner. Distillation of the crude product through a spinning-band column gave B-bis-(dimethylamino)-B-n-butyl-N-trimethylborazine at 112° and 0.6 mm. *Anal.* Calcd. for $[(CH_3)_2N]_2C_4H_9[BN]_3(CH_3)_3$: B, 12.2; N, 26.5; C, 49.9; H, 11.4. Found: B, 12.2; N, 26.7; C, 48.9; H, 11.3.

Reaction of a Chloroborazine with Dimethylamine and DMF.— A stirred slurry of 10 g. of $Cl_2CH_3[BN]_3(CH_3)_3$ in 30 ml. of DMF was treated with 5 g. of dimethylamine dropped in from a Dry

Ice condenser. As amine was added the solution warmed to *ca.* 70°, and near the end of the addition a white, gelatinous precipitate appeared. The mixture was stirred for 1 hr., and then excess amine was stripped off at 25 mm. Most of the DMF was distilled off at 60° and 25 mm., and the residue was dried at reduced pressure, finally heating to 90° at 0.5 mm. to ensure removal of solvent. The white residue was taken up in 50 ml. of petroleum ether and filtered through glass wool. The petroleum ether solution was evaporated to dryness, and the residue was extracted with benzene. This solution was filtered and the polymer recovered by evaporation. The polymer (5.3 g. or 72%) was a white powder which melted to an opaque fluid at 155–170° and was a stable and viscous melt at 300°. Cryoscopic measurements in benzene indicated an average molecular weight of 3200 corresponding to approximately 21 borazine rings per molecule. Another preparation gave a polymer which did not melt below 300° and had an average molecular weight of 8500.

In a similar manner, B-chloro-B-dimethyl-N-trimethylborazine gave a 58% yield of bis-(pentamethylborazyl) oxide and B-dichloro-B-*n*-butyl-N-trimethylborazine gave poly-(B-*n*-butyl-N-trimethylborazylene) oxide, m.p. 75–80°, in 100% yield. The average molecular weight of the polymer was 2630 corresponding to 14 borazine rings per molecule.

When trimethylamine was employed in place of dimethylamine, over 80% of the chloroborazine was recovered unchanged. Furthermore, when the reaction with dimethylamine was carried out in dimethylacetamide, no borazyl oxides were obtained, but only dimethylamine hydrochloride and the corresponding dimethylaminoborazine were recovered. When dibutylamine was added to a solution of the monochloroborazine in DMF, a 20% yield of bisborazyl oxide was obtained.

Stoichiometry of the Chloroborazine Reaction.—A mixture of 5.13 mmoles of B-dichloro-B-methyl-N-trimethylborazine, 2.41 ml. of DMF, and 24.0 mmoles of dimethylamine was stirred at 25° for 2 hr. The volatile products were stripped off and fractionated to yield 14.1 mmoles of dimethylamine, v.p. 45 mm. at −45° (lit.[18] 45 mm.), and 2.01 ml. of DMF, b.p. 3.5 mm. at 25° (lit.[9] 3.6 mm.). Hence, 9.87 mmoles of dimethylamine was consumed or 1.92 mmoles per mmole of borazine. Similarly, 0.40 ml. of DMF ($d_4{}^{20}$ 0.9445)[9] or 5.14 mmoles was consumed corresponding to 1.00 mmole per mmole of borazine. The nonvolatile residue was taken up in 5 ml. of benzene, the solution was filtered, and the insolubles were washed four times with the same solvent. Evaporation of the benzene extracts gave 0.70 g. (91% yield) of polymer, m.p. 160°.

Stoichiometry of the Aminoborazine Reaction.—Dimethylformamide, 2.61 ml., was condensed onto a mixture of B-dimethylamino-B-dimethyl-N-trimethylborazine, 5.28 mmoles, and dimethylamine hydrochloride, 2.80 mmoles, and the mixture warmed to 25°. After 18 hr., the volatiles were fractionated to give 5.49 mmoles of dimethylamine, v.p. 45 mm., and 2.41 ml. of DMF, v.p. 3.5 mm. These data define the ratios: aminoborazine/DMF = 2.02 and dimethylamine/aminoborazine = 1.04. The nonvolatile residue was extracted with benzene to give 0.83 g. (100% yield) of bis-(pentamethylborazyl) oxide, m.p. 132°, after sublimation at 80–100° and 0.1 mm. (identification was confirmed by infrared spectrum). The benzene insolubles were dissolved in 20 ml. of acetonitrile and precipitated by addition of 200 ml. of benzene. The salt was filtered off and dried to give white crystals, m.p. 145°. The infrared spectrum of the compound (in $CHCl_3$) suggested the amidine salt, $[(CH_3)_2NC(H)N(CH_3)_2]Cl$, with some contamination by dimethylamine hydrochloride. The data may be summarized by eq. 2.

Stoichiometric data were also obtained for various other combinations of aminoborazines and amine hydrochlorides in DMF. These reactions were carried out at 25° for periods of time ranging from 18 to 36 hr. Data for these experiments are recorded in Table II. For the reactions of B-methylamino-B-dimethyl-N-trimethylborazine with methylamine hydrochloride, high values for DMF consumption were observed due to MMF formation *via* the amino group exchange reaction. The greater part of the MMF so formed remained in the reactor after separation of the volatile materials. It was then recovered by heating the residue to 40–50° while pumping under high vacuum for 18 hr. Positive identification as MMF was made through the infrared spectrum and vapor phase chromatography.

Isolation and Identification of Tetramethylformamidinium Chloride: Control of Polymer Molecular Weight.—B-Bis-(dimethylamino)-B-methyl-N-trimethylborazine, 4.58 mmoles, and DMF, 2.42 ml., were stirred together for 18 hr. at 25°. The condenser connecting the reactor to the vacuum line was then cooled to 0°, and the volatiles were stripped off. Fractionation showed that DMF was the only volatile material present; since it was fully recovered no reaction had taken place. Dimethylamine hydrochloride, 3.53 mmoles, was then added and, after condensing the DMF back into the reactor, the mixture was stirred for 82 hr. at 25°. Recovery and fractionation of the volatiles yielded 7.15 mmoles of dimethylamine and 2.14 ml. of DMF.

(15) A. R. Amell, P. S. Lamprey, and R. C. Schiek, *Anal. Chem.*, **33**, 1805 (1961).

(16) D. Vofsi and A. Katchalsky, *J. Polymer Sci.*, **26**, 127 (1957).

(17) G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *J. Am. Chem. Soc.*, **80**, 4515 (1958).

(18) J. G. Aston, M. L. Eidinoff, and W. S. Forster. *ibid.*. **61**, 1539 (1939)

The benzene solubles were recovered in the usual manner to give 0.73 g. of polymer, m.p. 110–120°, mol. wt. 800. The benzene insolubles were taken up in acetonitrile and precipitated by addition of benzene to give a white solid, m.p. 140–145°. A second precipitation from acetonitrile raised the melting point to 152–154°. *Anal.* Calcd. for [(CH₃)₂NC(H)N(CH₃)₂]Cl: Cl, 26.0; N, 20.5. Found: Cl, 25.7; N, 20.7. The infrared spectrum of the salt in CHCl₃ was identical with that of a sample of tetramethylformamidinium chloride prepared according to a literature method.[19]

The experimental ratios are: DMF/(CH₃)₂NH₂Cl = 1.03 and (CH₃)₂NH/(CH₃)₂NH₂Cl = 2.02. Since two >BN(CH₃)₂ groups are consumed per DMF molecule, the fraction of >BNMe₂ groups consumed in the reaction, or the extent of reaction, p, = 7.30/9.19 = 0.797. The number average degree of polymerization, $\bar{P}_n$ = 1/1 − p,[20] is then 1/1 − 0.797 or 4.93. This $\bar{P}_n$ corresponds to an average molecular weight of about 750, the exact weight depending on the nature of the end groups.

Isolation and Identification of Trimethylformamidinium Chloride.—A mixture of 6.31 mmoles of B-dimethylamino-B-dimethyl-N-trimethylborazine, 3.06 mmoles of methylamine hydrochloride, and 2.71 ml. of DMF was stirred at 25° for 18 hr. After fractionation of the volatiles, 6.01 mmoles of dimethylamine, v.p. 44 mm. at −45.2°, 565 mm. at 0° (lit. 565 mm.), and 2.52 ml. of DMF were obtained. The nonvolatile residue was extracted with benzene to give 0.96 g. (96% yield) of bisborazyl oxide. The benzene insolubles were dried under vacuum to give trimethylformamidinium chloride, m.p. 129–131°. *Anal.* Calcd. for [(CH₃)₂NC(H)NHCH₃]Cl: Cl, 29.0; N, 22.9. Found: Cl, 29.3; N, 22.9. The infrared spectrum of the salt confirmed the amidine structure.

Reaction of B-Bis-(dimethylamino)-B-methyl-N-trimethylborazine with Aniline Hydrochloride and DMF.—The reaction of 4.72 mmoles of the borazine, 3.71 mmoles of aniline hydrochlo-

ride, and 2.62 ml. of DMF gave 6.95 mmoles of dimethylamine (v.p. = 44 mm. at −45.2°) and 2.30 ml. of excess DMF. The usual work-up gave 0.70 g. (98% yield) of poly-(tetramethylborazylene) oxide (identified through infrared spectrum) which melted over the range 110–120°. The benzene insolubles were reprecipitated from acetonitrile to give a white powder, m.p. 226–228°. *Anal.* Calcd. for [C₆H₅NHC(H)N(CH₃)₂]Cl: Cl, 19.2; N, 19.9. Found: Cl, 19.9; N, 16.4.

Infrared Spectra.—Spectra of the borazyl oxides were obtained on CCl₄ solutions. Since the amidine salts are insoluble in CCl₄, spectra of these compounds were obtained on chloroform solutions. The prominent absorption bands in cm.⁻¹ of the compounds examined are

O[(CH₃)₂[BN]₃(CH₃)₃]₂: 2960 m, 2930 m, 2850 w, 1450 s, 1410 s, 1383 vs, 1332 m, 1282 m, 1250 m, 1121 m, 1022 w, 946 w, 882 m, 697 w, 674 m, 663 w

[O(CH₃)[BN]₃(CH₃)₃]ₓ: 2970 m, 2930 m, 2860 w, 1454 s, 1402 vs, 1382 vs, 1350 s, 1272 m, 1253 w, 1209 m, 1191 w, 1110 m, 1053 m, 1021 w, 955 w, 883 w, 693 w

[O(C₄H₉)[BN]₃(CH₃)₃]ₓ: 2930 m, 2860 m, 1455 s, 1400 vs, 1380 vs, 1343 s, 1277 w, 1259 w, 1209 w, 1104 w, 1058 w, 1025 m, 952 w, 935 w, 699 w, 663 vw

O[(CH₃)₂[BN]₃(C₂H₅)₃]₂: 2980 m, 2930 m, 2870 w, 2780 vw, 1430 s, 1393 s, 1379 m, 1360 m, 1317 w, 1292 s, 1245 vw, 1212 vw, 1144 vw, 1119 m, 1091 m, 1048 n, 897 w, 884 m, 681 w

[O(CH₃)[BN]₃(C₂H₅)₃]ₓ: 2980 m, 2930 m, 2875 w, 1414 s, 1378 s, 1362 s, 1291 s, 1255 w, 1216 w, 1181 vw, 1118 w, 1091 w, 1048 m, 894 vw, 881 w, 698 w

[(CH₃)₂NC(H)N(CH₃)₂]Cl: 3310 m, 2880 s, 2700 w, 2430 m, 1703 s, 1490 m, 1449 s, 1401 s, 1271 m, 1230 m, 1160 m, 1108 w, 1087 w, 1052 w, 1007 vw, 880 vw, 865 m

[(CH₃)₂NC(H)NHCH₃]Cl: 3320 m, 3110 m, 2880 s, 2760 s, 2430 m, 2270 w, 1718 vs, 1621 vw, 1588 vw, 1488 w, 1446 s, 1368 s, 1265 w, 1140 s, 1084 w, 1063 m, 1005 m, 881 w, 858 m

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The Aporphine and Isoquinolinedienone Alkaloids of *Ocotea glaziovii*[1]

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From the leaves of *Ocotea glaziovii* have been isolated 3,5-dihydroxy-6-methoxyaporphine (I) and the isoquinolinedienone alkaloid glaziovine (III). The dienone–phenol rearrangement converts glaziovine to I, while by successive borohydride reduction and rearrangement, it is transformed to 5-demethylnuciferine (V).

The large and widely spread genus *Ocotea* of the family *Lauraceae* has already been the subject of considerable chemical study both as a source of alkaloids of the benzylisoquinoline group and of essential oils.[6] Although some 120 Brazilian species have been reported, chemical investigations seem to have been limited to a study of nonalkaloidal components.[6b] We therefore thought it of interest to study the alkaloids of *Ocotea glaziovii* Mez, collected in the Tijuca Forest of Rio de Janeiro.

Examination of the leaves provided two principal isomeric alkaloids of empirical formula $C_{18}H_{19}NO_3$. One of these, glaziovine, was isolable by chloroform

extraction from an acetic or tartaric acid solution of the total bases at pH 4–5, while the other base was only extracted by organic solvents after alkalinization of the aqueous solution. This latter base showed ultraviolet absorption typical of an aporphine oxygenated at positions 3, 5, and 6[7a,8] (see Experimental section) and was identified as (−)-3,5-dihydroxy-6-methoxyaporphine (I).[7a,b] Aporphine I was isolated as its hydrochloride and characterized as its methochloride monohydrate, prepared from the methiodide. Both the free base I and its methiodide suffer ready air oxidation. The n.m.r. spectrum was similar to that of tuduranine (3-hydroxy-5,6-dimethoxy-N-demethylaporphine, II)[9] as shown in Table I, the additional down-

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(6) See, for example, (a) M. J. Vernengo, *Experientia*, **19**, 294 (1963); (b) O. R. Gottlieb and M. T. Magalhães, *J. Org. Chem.*, **24**, 2070 (1959).

(7) (a) See T. Kitamura, *J. Pharm. Soc., Japan*, **80**, 1104 (1960), who obtained 3,5-dihydroxy-6-methoxyaporphine (I) in very low yield from the oil resulting from the reduction of domesticine with sodium in liquid ammonia, and characterized it as its hydrochloride, m.p. 277° dec. (b) The negative rotation of I points to the *R*-absolute configuration [C. Djerassi, K. Mislow, and M. Shamma, *Experientia*, **18**, 53 (1962); M. Shamma, *ibid.*, **18**, 64 (1962)] and this was confirmed by measurement of the rotatory dispersion of V.

(8) L. J. Haynes and K. L. Stuart [*J. Chem. Soc.*, 1789 (1963)] describe a number of aporphine derivatives oxygenated in these three positions (see ref. 16).