

mechanism 1, and even given the integrated form 3 and tables of Bessel functions, it is easier to get [B] by setting up and running the Monte Carlo model than by evaluating and plotting (3). In usual applications, where to fit the experimental [B] curve (3) would have to be plotted for varying sets of rate constants, the saving would be still greater. The same Monte Carlo program would be used each time, and the rate constants varied by reading in one input card.

On the other hand, it would be difficult to get accuracy greater than 1% with a Monte Carlo model, and greater than 0.1% is probably impossible with present computers. This accuracy is sufficient for most rate studies, but where it is not a Monte Carlo model could give only a first approximation.

Numerical integration of rate equations has been used,⁵ but again each mechanism requires a rather different treatment. Accuracy varies from case to case, but would generally exceed that of a Monte Carlo model.

An analog computer method which simulates chemical reaction with models based on electrical circuits has had much application in chemical engineering.⁶ The purpose of this method, like that of the Monte Carlo model, is the construction of concentration-time curves without integration of rate equations. Accuracy of the two

(5) K. B. Wiberg and W. H. Richardson, *J. Am. Chem. Soc.*, **84**, 2800 (1962).

(6) T. J. Williams, *Ind. Eng. Chem.*, **50**, 1631 (1958).

is about the same. The usual much greater accuracy of digital over analog machine is lost in the Monte Carlo method because of its statistical nature. Choice between the two might often be governed by the type of machine available. One point strongly in favor of the analog method is its speed; only a few seconds of running time are required. On the other hand, a particular reaction either can or cannot be simulated on a given analog computer, but a Monte Carlo model of nearly any reaction can be run on nearly any digital machine by increasing computing time or by decreasing required accuracy.

With the analog machine, variation of rate constants must be done by trial-and-error manual adjustment of potentiometers.⁷ Because of the greater flexibility of the digital machine, it should be possible to construct a Monte Carlo model which would make an automatic least squares fit of the rate constants to give best agreement between model and experiment. We are at present considering this problem.

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(7) A combined digital-analog computer by Minneapolis-Honeywell which might overcome this difficulty was recently reported in *Chem. Eng.*, **70**, 42 (1963).

[CONTRIBUTION NO. 1154 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, IND.]

Studies of Boron-Nitrogen Compounds. VI.¹ Chemical Properties of the Isomers of 1,3,5-Trimethylcycloborazane

BY DONALD F. GAINES AND RILEY SCHAEFFER

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The unsymmetrical isomer II of 1,3,5-trimethylcycloborazane forms a 2-mono and 2,4-dichloro substitution product with hydrogen chloride at -78° and 0° , respectively. The symmetrical isomer I, however, forms a 2,4,6-trichloro substituted product at 0° . The acid-catalyzed methanolysis of II produces a 2-methoxy product at 0° , and rate studies indicate that the reaction is first order in both catalyst and II. The methanolysis of I under the same conditions, however, results in a mixture of mono-, di-, and trimethoxy substitution products. Dehydrohalogenation of the 2,4-dichloro substitution product of II with trimethylamine gives nearly quantitative yields of hydrogen and 1,3,5-trimethylborazine, presumably *via* the unstable analog of cyclohexadiene, $B_3H_4N_3H(CH_3)_3$. Dehydrogenation of I and II with sodium amide in liquid ammonia or trimethylamine yields 1,3,5-trimethylborazine.

Introduction

The addition to borazines of three equivalents of water, alcohols, and hydrogen halides was described some years ago² and was thought to result in cyclohexane-type products. However, little evidence was presented to support this assumption. The first example of an adequately characterized cycloborazane was 1,3,5-trimethylcycloborazane (prepared by Bissot and Parry in 1955).^{3,4} Subsequently, 1,3,5-hexamethylcycloborazane⁵ was prepared and n.m.r. studies⁶ indicated that it had a cyclohexane structure. Its chair-shaped conformation was established by single-crystal X-ray studies.⁷

1,3,5-Triethylcycloborazane⁸ and the parent cycloborazane^{9,10} have since been prepared by several methods, and two isomers of 1,3,5-trimethylcycloborazane¹ have been separated and characterized. Until recently, however, few chemical properties of the cycloborazanes have been reported.

Making use of the two isomers of 1,3,5-trimethylcycloborazane (both isomers probably are in the chair shape; in isomer I all three methyl groups are equatorial, whereas in isomer II two methyl groups are equatorial and the third axial), it has been possible to demonstrate that several of the reactions are definitely related to the structure of the isomers.

Experimental

I. A New Preparation of Cycloborazanes by Reduction of Hydrogen Chloride Adducts of 2,4,6-Trichloroborazines. A. 2,4,6-Trichloroborazine.—In a typical preparation, 2.49 mmoles

(1) For paper V in this series see D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

(2) E. Wiberg, *Naturwiss.*, **35**, 182, 212 (1948).

(3) T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955).

(4) For a description of the nomenclature of the cycloborazanes see ref. 1 and 10.

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TABLE I

REACTION OF HYDROGEN CHLORIDE WITH ISOMERS I AND II

Isomer	mmoles I or II	mmoles HCl	Time, hr.	Temp., °C.	mmoles hydrogen	H ₂ /I or II
I	0.353	Large exc.	22	Room temp.	1.082	3.07
I	.923	19.51	14	0	2.78	3.01
I	.751	22	14	-80	0.791	1.05
I	.283	11.18 ^a	12	0	.857	3.03
II	.619	17.2	5	-80	.604	0.98
II	3.19	20	17	0	6.32	2.00
II	.965	Large exc.	22	Room temp.	1.912	1.98

^a HBr instead of HCl.

of 2,4,6-trichloroborazine (generously contributed by U. S. Borax Research Corp.) were placed in a flask in a drybox. The flask was then attached to the vacuum line and about 5 ml. of dry ethylene glycol dimethyl ether and 14.96 mmoles of hydrogen chloride were condensed into it at -196°. After the flask had been warmed to -80° and stirred for 1 hr., the solvent and excess hydrogen chloride were evaporated. There were 8.81 mmoles of hydrogen chloride recovered; thus 2.47 mmoles of hydrogen chloride had been absorbed per mmole of 2,4,6-trichloroborazine. Fresh ethylene glycol dimethyl ether was condensed into the flask, which was then warmed to -78° under a nitrogen stream and 28 mmoles of sodium borohydride added. After warming the slurry to -45° and stirring for 1 hr. (during this time substantial amounts of hydrogen were formed), the volatile materials were fractionated and a 78% yield (5.85 mmoles) of diborane was found to have been produced based on the equation $B_3Cl_6N_3H_6 + 6NaBH_4 \rightarrow B_2H_6N_3H_6 + 6NaCl + 3B_2H_6$. Heating the residue to 100° under high vacuum resulted in sublimation of 17.3 mg. (0.20 mmole, 10% yield) of cycloborazine, identified by infrared analysis. Attempted reduction with lithium aluminum hydride produced hydrogen but no cycloborazine.

In other experiments (using as solvents carbon tetrachloride and a carbon tetrachloride-ethylene glycol dimethyl ether mixture), the number of moles of hydrogen chloride absorbed per mole of 2,4,6-trichloroborazine varied from 2.49 to 3.11.

B. 1,3,5-Trimethyl-2,4,6-trichloroborazine.—In a typical experiment, excess hydrogen chloride was bubbled into 100 ml. of a diethyl ether solution of 6.59 g. (29.2 mmoles) of 1,3,5-trimethyl-2,4,6-trichloroborazine (prepared by the method of Hohnstedt and Haworth¹¹). After stirring 4 hr. at room temperature the ether and excess hydrogen chloride were evaporated and 75 ml. of fresh ether added. A solution of 180 mmoles of lithium aluminum hydride in 70 ml. of ether was slowly added with vigorous stirring. The solvent was again evaporated, and the solid residue was slurried with 200 ml. of benzene overnight. The slurry was filtered and the benzene evaporated, yielding 1.1 g. of a mixture of the isomers of 1,3,5-trimethylcycloborazine (identified by infrared analysis), a yield of 29%. Reductions employing sodium borohydride in ethylene glycol dimethyl ether and tricaprylmethylammonium borohydride in toluene yielded large amounts of diborane and hydrogen, but no product was isolated.

C. ¹¹B N.m.r. Spectra of Hydrogen Chloride Adducts of 2,4,6-Trichloroborazines.—The ¹¹B n.m.r. spectra of ethylene glycol dimethyl ether solutions of 2,4,6-trichloroborazine and 1,3,5-trimethyl-2,4,6-trichloroborazine both contain only a single broad peak at $\delta = 30.6 \pm 0.5$ p.p.m. (lit.¹² 36.5; $BF_3 \cdot O(C_2H_5)_2 = 0.0$) and at $\delta = -32.0 \pm 0.5$ p.p.m. (lit.¹² -33.5), respectively. When hydrogen chloride was added to these solutions, much sharper peaks appeared at $\delta = 3.7 \pm 0.5$ p.p.m. and $\delta = -6.9 \pm 0.5$ p.p.m., respectively. When the ratio of hydrogen chloride to borazine was three or more, only the sharp upfield singlet was observed.

II. The Reaction of Isomers I and II with Hydrogen Chloride.—Compound I or II was weighed into a reaction flask, which was then attached to the vacuum line and evacuated. Dry diethyl ether and a measured amount of hydrogen chloride were condensed onto the solid at -196°. The flask was warmed to the desired temperature and maintained at this temperature until the pressure in the system reached equilibrium. The flask was then cooled to -196° and the hydrogen removed and measured with an automatic Toepler pump. The data, conditions, and results are summarized in Table I. Probably mixtures of isomers, the compounds presumed to be formed are very sensitive to moisture and were generally not isolated.

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III. Dehydrohalogenation of 1,3,5-Trimethyl-2,4-dichlorocycloborazine (III).—A sample of 2.41 mmoles of 1,3,5-trimethyl-2,4-dichlorocycloborazine (III), prepared from isomer II as described above, was treated with 14.64 mmoles of trimethylamine for 3.5 hr. at 0° *in vacuo*. When the reaction vessel was cooled to -196°, 2.28 mmoles of hydrogen was found to have been produced. The reaction flask was then warmed and the volatile materials passed through a trap at -78°. Trimethylamine, 10.00 mmoles, passed the trap; the loss by reaction was therefore 4.64 mmoles. The 0.239 g. of material retained by the -78° trap was shown by gas phase infrared analysis to be 1,3,5-trimethylborazine (2.39 mmoles). The quantities of reactants and products are in satisfactory agreement with the equation $B_3H_4Cl_2N_3H_3(CH_3)_3 + 2(CH_3)_3N \rightarrow B_3H_5N_3(CH_3)_3 + H_2 + 2(CH_3)_3NHCl$.

IV. Methoxy Derivatives of II. A. 1,3,5-Trimethyl-2-methoxycycloborazine (IV).—1,3,5-Trimethyl-2-methoxycycloborazine (IV), $B_3H_3(OCH_3)N_3H_3(CH_3)_3$, was first observed during the purification of I and II that had been prepared by the sodium borohydride reduction of 1,3,5-trimethyl-2,4,6-trichlorocycloborazine. The crude reduction product, which sublimed under high vacuum at about 100°, reacted with hot methanol, as shown by effervescence during an attempted recrystallization. The product crystallized as long needles that sublime at 70° under high vacuum and melt at 158.9°.

Anal. Calcd. for $B_3N_3H_9O_3$: C, 30.3; H, 12.7; B, 20.5; N, 26.5; O, 10.1. Found: C, 30.3; H, 12.3; B, 20.7; N, 26.1; O (diff.), 10.6.

It was found that the acid-catalyzed methanolysis of II yielded the same compound as above, as shown by its melting point and infrared spectrum. By using a large excess of methanol and measured catalytic amounts of hydrogen chloride, it was possible to follow the rate of methanolysis by measuring the hydrogen evolved (using a null-type manometer) as a function of time at 0° and to obtain pseudo-first-order rate constants, K'' , from the data. Using the relationships

$$K'' = K' [HCl]^m$$

or

$$\log K'' = \log K' + m \log [HCl]$$

where $K' = K[CH_3OH]^n$, a plot of $\log K''$ vs. $\log [HCl]$ gave a slope of 1.08, indicative of a first-order reaction with respect to hydrogen chloride.

B. 1,3,5-Trimethyl-2,4-dimethoxycycloborazine (V).—1,3,5-Trimethyl-2,4-dimethoxycycloborazine (V) was prepared by treating 1,3,5-trimethyl-2,4-dichlorocycloborazine with methanol and trimethylamine. The ¹¹B n.m.r. spectrum of the product in methanol solution consisted of a doublet partially overlapping with a higher field triplet (see Table II for chemical shifts and coupling constants). The doublet was approximately twice as intense as the triplet. The compound was difficult to purify, and though the infrared and ¹¹B n.m.r. spectra (Table II) are in agreement with the formula given, an elemental analysis was not obtained.

V. Methoxy Derivatives of I.—The acid-catalyzed methanolysis of I gave a mixture of products which were not easily separated and rate studies did not give readily interpretable data. Thin-layer chromatography (using a silica gel support, eluting with 10% ethanol in chloroform, and developing with a silver nitrate solution) indicated that at least three main components were present.

In a single experiment a catalytic amount of hydrochloric acid was added to a methanol solution of I and the solution boiled for a few minutes. After removal of solvent and recrystallization from hexane a small amount of an isomer of 1,3,5-trimethyl-2-methoxycycloborazine was obtained. It sublimed at 40-60° under high vacuum and melted at 138°. The ¹¹B n.m.r. spectrum was similar to that of 1,3,5-trimethyl-2-methoxycycloborazine (IV). At present no evidence is available to prove the stereochemistry of the isomer obtained.

Anal. Calcd. for $B_3N_3H_9O_2$: C, 30.3; H, 12.7. Found: C, 30.1; H, 12.3.

VI. Dehydrogenation of I and II with Sodium Amide.—Both I and II are readily dehydrogenated by sodium amide in ammonia or amine solutions. In a typical experiment, 2.48 mmoles of I and 1.08 mmoles of sodium amide (obtained through the courtesy of Professor Sheldon B. Shore of Ohio State University) were placed in a flask in a drybox. The flask was attached to the vacuum line and evacuated and about 3 ml. of dry trimethylamine was condensed into it at -196°. After warming to -78° overnight and to -23° for 5 hr., the flask and contents were cooled to -196° and 5.44 mmoles of hydrogen was found to have been produced. The volatile materials remaining were evaporated and passed through a trap at -78°. The 46.4

TABLE II
 THE ^{11}B N.M.R. SPECTRA OF SEVERAL CYCLOBORAZANES

Compound	B_x^x	B_x^H		B_H^H	
		δ^a	J	δ^a	J
$B_3H_5(OCH_3)N_3H_3(CH_3)_3$ (II) ^b		-4.6	112 ± 8	+4.4	101 ± 8
$B_3H_4(OCH_3)_2N_3H_3(CH_3)_3$ (II) ^b		-3.0	117 ± 3	+5.3	101 ± 3
$B_3H_3Cl_3N_3H_3(CH_3)_3$ ^c		-1.1	127 ± 5		
$B_3Cl_6N_3H_3(CH_3)_3$ ^d	-6.9				
$B_3Cl_6N_3H_6$ ^d	-3.7				
$B_3H_6N_3H_3(CH_3)_3$ ^b				5.8	101
$B_3H_6N_3H_6$ ^e				11.3	100

^a In p.p.m. from $BF_3 \cdot O(C_2H_5)_2$ as the zero reference; values are in general about ± 0.5 p.p.m. Solution in ^b methanol, ^c chloroform, ^d ethylene glycol dimethyl ether, ^e ammonia.

mg. of material retained by the trap was shown by gas phase infrared analysis to be 1,3,5-trimethylborazine (0.38 mmole).

Nuclear Magnetic Resonance Studies.—The ^{11}B n.m.r. spectra of a number of cycloborazanes have been obtained using a Varian Model 4300B spectrometer operating at 19.3 Mc./sec. Chemical shifts were determined relative to $BF_3 \cdot O(C_2H_5)_2$, using the side-band technique.

Discussion

Both I and II react with only one equivalent of hydrogen chloride at -78° . At 0° , however, II reacts with two equivalents of hydrogen chloride, whereas I reacts with three. Though no evidence as to the structure of these derivatives is available, it is interesting that structures predicted on the basis of analogies drawn from the cyclohexanes would lead to the reaction limits actually observed. Thus the most favorable position for a B-monosubstitution is in an equatorial position between two equatorial methyl groups. A second substitution on II would be expected to be axial, whereas on I it would probably be equatorial. Steric hindrance in II would probably reduce the possibility of a third substitution but would have little effect in the case of I.

The dehydrohalogenation of 1,3,5-trimethyl-2,4-dichlorocycloborazane (II), $B_3H_4Cl_2N_3H_3(CH_3)_3$, with trimethylamine at 0° did not yield the desired cyclohexadiene analog. The desired product was probably formed, but was unstable under the conditions of the reaction and dehydrogenated nearly quantitatively to 1,3,5-trimethylborazine and hydrogen.

The original isolation of 1,3,5-trimethyl-2-methoxycycloborazane (IV) probably resulted from the reaction of the partially reduced 1,3,5-trimethyl-2-chlorocycloborazane with methanol. Chlorination to the latter product has independently been shown to proceed readily in the presence of hydrogen chloride. Direct acid-catalyzed methanolysis of II also yields IV.

Rate studies of the acid-catalyzed methanolysis of II indicate that the reaction is first order with respect to both II and hydrogen chloride. The reaction can be conveniently envisioned as occurring *via* the formation

of the monochloro derivative which then reacts with methanol, forming the product and regenerating the hydrogen chloride.

The acid-catalyzed methanolysis of I results in a mixture of products that are not easily separated. Attempts to obtain meaningful rate data were not successful, presumably because of smaller barriers to formation of di- and trimethoxy derivatives in this more symmetrical molecule.

The structures of the methoxy derivatives of I and II would be predicted as for the chloro derivatives above. Steric hindrance, however, becomes a more important factor, especially in considering more than a monosubstitution on II.

The treatment of I or II with sodium amide in liquid ammonia or trimethylamine solutions at -45° or -23° , respectively, results in a rapid hydrogen evolution; when trimethylamine is the solvent, low yields of 1,3,5-trimethylborazine can be recovered. The reaction is necessarily of a complex nature, since the products react with ammonia and with sodium amide.^{13,14}

The Hydrogen Chloride Adducts of 2,4,6-Trichloroborazines.—The addition of hydrogen chloride to 2,4,6-trichloroborazines is apparently reversible. The only other reported example of such a reversible addition is that of hydrogen cyanide to borazine.¹⁴ One possible interpretation of the previous case is that reversible addition might result from formation of a quaternary salt at the nitrogen with the boron remaining tricoordinated. However, the chemical shift and sharpness of the ^{11}B n.m.r. spectra of the hexachloro derivatives suggest that the adducts contain tetracoordinated boron. Since both these factors are very sensitive to small changes in symmetry, the salt-type structure cannot be ruled out.

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