acid solution and hence the rate of flow would be greater.

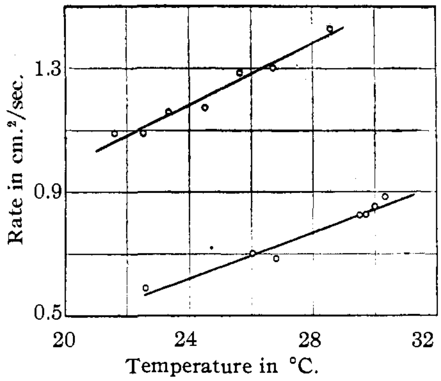


Fig. 3.

A study of film pressure–area relationships for stearic acid films under conditions identical with those for Tables I and II indicates that the transition from liquid to solid film takes place at about 27 dynes/cm. for both *p*H 7.0 and 3.8. The collapse of the film on the more acid solution occurred at a lower pressure, about 40 dynes/cm., than on the neutral solution, about 60 dynes/cm. The nearly vertical portions of the rate–pressure curves indicate that collapse of the film has taken place. In other words at the pressures at which the curve is nearly vertical the film crumples instead of flowing through the capillary. The results plotted in Fig. 2 indicate that the solid film flows through the opening more rapidly than the liquid film. This rather surprising observation may not seem so peculiar when one remembers that the film pressures on the solid film are greater than on the liquid film and that the rate of flow is determined not only by intermolecular friction between the like molecules in the film but also by friction between the film and the liquid on which it flows. While we would expect the friction between molecules of a solid film to be greater than that between molecules of a liquid film, the friction between the solid film and water should not be much different from that between the liquid film and water. Investigation of Fig. 2 and Table I indicates that the rate of flow of the solid film does not increase as rapidly, with increase in film pressure, as does the rate of flow of the liquid film. A consideration of the calculated values of viscosity shows that the solid film has a greater viscosity than the liquid film and that the viscosity of the solid film varies less with pressure than does the viscosity of the liquid film.

Our experiments indicate that for like pressures and hydrogen ion concentration films flow more rapidly at higher temperatures than at lower temperatures. Further the temperature coefficient seems to be greater at a low pressure than at a higher pressure.

Summary

The rate of flow of unimolecular surface films of stearic acid on water has been studied.

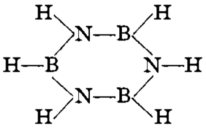
Observations have been made regarding the effect of film pressure, temperature, and hydrogen ion concentration of the substrate water, on the rate of flow.

LINCOLN, NEBRASKA RECEIVED FEBRUARY 17, 1938

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. IX. The Preparation of Some Methyl Triborine Triamines

BY H. I. SCHLESINGER, DAVID M. RITTER[1] AND ANTON B. BURG



Triborine triamine ($B_3N_3H_6$)[2] was first prepared by Stock and Pohland,[3] who assigned to it the ring structure shown, on the basis of the evidence available at the time. The electron diffraction work of Stock and Wierl[4] substantiated the ring structure. It was considered desirable, however, to test this structure further by a study of the methyl derivatives of the compound.

The preparation of derivatives in which methyl groups are attached to boron atoms of the ring, has been described by Schlesinger, Horvitz and Burg,[2] who found it possible to prepare three and only three such derivatives (by reactions of the methyl diboranes with ammonia), a result in agreement with the structure proposed by Stock and Pohland. The present work includes a parallel set of results: three and only three derivatives in which methyl groups are attached to the ni-

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(1) This paper is taken from a dissertation presented by David M. Ritter to the Faculty of the Division of Physical Sciences of the University of Chicago, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) This compound was not named at the time of its discovery. The name used here was suggested by Schlesinger, Horvitz and Burg. THIS JOURNAL, **58**, 409 (1936).

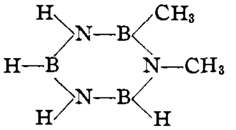
(3) Stock and Pohland, *Ber.*, **59B**, 2215 (1926).

(4) Stock and Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).

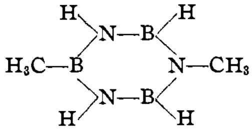
trogen atoms of the ring, resulted from the reaction of diborane with mixtures of ammonia and methylamine.

Although the work thus far described has led to the anticipated number of derivatives (for example, two and only two monomethyl triborine triamines, the B-methyl and the N-methyl), a final chemical proof of the ring structure must rest upon a study of the number of isomers resulting from replacement, by the same substituent, of hydrogen atoms attached to boron and hydrogen atoms attached to nitrogen. As a step in this direction, the action of boron trimethyl on mono-N-methyl triborine triamine has been studied. The reaction results in the formation of derivatives in which one, two, and three of the hydrogen atoms attached to boron are replaced by methyl groups, and, therefore, furnishes some of the desired derivatives, although in a roundabout, time-consuming fashion.

Of particular interest is the mono-N-methyl mono-B-methyl derivative. This should exist in two isomeric forms



and



The present method of preparation, by the action of boron trimethyl on mono-N-methyl triborine triamine, might be expected to yield a mixture of the two isomers. The material having this composition thus far, however, has given no indication of being a mixture; should it actually prove to be a pure substance, the fact would indicate a strong influence favoring substitution in the ortho rather than the para position, or *vice versa*. The indications arising from a study of the further substitution of the B-linked hydrogen atoms by methyl groups, are difficult to interpret; hence the question of such directive influences remains an interesting, though difficult, problem for further study.

In the course of this work, better conditions for the preparation of triborine triamine and its derivatives were found. These studies led also to the discovery of the new compound, B_2H_7N, whose preparation, properties, and structure, are to be described in another paper.

Experimental Methods

Apparatus and Technique.—The apparatus and technical methods employed in this investigation are like those of Stock[5] and of Schlesinger and Burg and their co-workers.[5]

Analytical Methods.—The analytical methods are substantially those employed in previous investigations of triborine triamine and its derivatives.[2,3] In those analyses in which nitrogen was determined as the free element, the procedure of Stock and Pohland[3] was modified in three details:

1. The combustion train was operated without the addition of oxygen gas.

2. A single combustion tube contained all of the substances required for the combustion and for the reduction of the oxides of nitrogen; it was packed with the materials required in the order: lead chromate, copper oxide, copper reduced from copper oxide, finely divided nickel.

3. The apparatus was arranged in the form of a circuit, including a small mercury vapor circulating pump by which any unburned vapors were fed back through the combustion tube, along with the nitrogen first produced. This system was checked before each determination, by the analysis of a sample of pure methylamine.

The N-methyl B-methyl triborine triamines were analyzed by the following procedure. The measured sample was condensed by means of liquid nitrogen in a tube containing an excess, measured quantity of standard hydrochloric acid. The tube was sealed off, heated in a steam-bath for several hours to ensure the complete hydrolysis of the sample, and again connected to the vacuum apparatus by means of the tube opener. The hydrogen resulting from hydrolysis was pumped through a trap and measured; the substances remaining in the tube and trap (at −196°) were warmed to room temperature and then washed into a flask. The excess of acid was titrated to the methyl red end-point, in order to determine the nitrogen as ammonia and methylamine (by difference); then mannite was added and the boric acid was titrated to the phenolphthalein end-point. In those analyses in which methylboric acid was produced by the hydrolysis, the determination of the total boron required that the solution be saturated with mannite.

Vapor Tensions.—The pressures of saturated vapor at different temperatures were determined in static systems. In cases of low volatility, the measurements were carried out at elevated temperatures by the aid of apparatus of the type designed for such purposes by Stock and Kusz.[6]

Gas Volumes.—All volumes, unless otherwise stated, are given in cubic centimeters of gas at 0° and 760 mm. pressure.

Molecular Weights.—The molecular weights of the various compounds were calculated from their vapor densities, determined at temperatures between 100 and 150°. The apparatus used for the measurements of volume was like that employed for vapor tensions at elevated temperatures, except that the small tube for containing the sample was replaced by a calibrated bulb large enough for the complete vaporization of the material. The agreement between the observed and calculated molecular weights was generally quite satisfactory, in view of the small sizes of the samples involved.

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[5] Stock, *Ber.*, **54A**, 142 (1921) and "Hydrides of Boron and Silicon," Cornell University Press, 1933, Chapter XXX; Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931); Burg, *ibid.*, **56**, 499 (1934).

[6] Stock and Kusz, *Ber.*, **47**, 3115 (1914).

The Preparation of Triborine Triamine and Its N-Methyl Derivatives

The Effect of Pressure upon the Yields of Triborine Triamine.—In a search for the best preparative conditions, the effect of the total pressure developed in the reaction, upon the yield of triborine triamine, was studied. The pressures were calculated from the total quantities of gaseous products and the volumes of the bomb-tubes employed for the reaction. The results are given in Table I.

TABLE I

RELATION OF PRESSURE TO YIELD OF TRIBORINE TRIAMINE

Press. at 200°, atm.	1.8	4.1	4.8	11
Yield, %	27	33	38	41.5

These results show that the yields of triborine triamine may be improved somewhat over those reported by Stock and Pohland,[3] by confining the reacting materials to a sufficiently small relative space. Incidentally, the observation of these authors, that a short period of heating (as brief as fifteen minutes) is sufficient for complete reaction, was confirmed.

Preparation of the N-Methyl Triborine Triamines.—The pyrolysis of samples obtained by mixing diborane, ammonia, and primary methylamine, yields triborine triamine and its N-methyl derivatives, in proportions depending upon the ratio of methylamine to ammonia. The general equation for the reactions involved is $3B_2H_6 + 2xCH_3NH_2 + 2(3 - x)NH_3 \longrightarrow 2B_3N_3H_{6-x}(CH_3)_x + 12H_2$. If ammonia is absent ($x = 3$), only the tri-N-methyl derivative is produced.[7] If the proportions of ammonia and methylamine correspond to $x = 1$, the principal product is the mono-N-methyl derivative, along with smaller quantities of the other compounds. When $x = 2$, however, there is obtained a mixture in which no one of the derivatives predominates; only triborine triamine itself appears in minor quantity.

For each of these experimental preparations, the reactants were measured as gases in the vacuum apparatus, and condensed one after the other into a bomb tube, which was next sealed off and immersed for fifteen to thirty minutes in an oil-bath at 200°.

The volatile reaction products were transferred from the bomb tube to the vacuum apparatus by means of the tube-opener, and the hydrogen was pumped off through a trap at −196°. The condensed products were separated by fractional condensation, through a series of U-tubes at −45, −65, −80, −90, and −196°, respectively. The first of these U-tubes held the tri-N-methyl triborine triamine; di-N-methyl triborine triamine was caught at −65°; the mono-N-methyl derivative condensed at −80°, along with a trace of triborine triamine itself; the U-tube at −90° held most of the triborine triamine, while any residual ammonia, methylamine, or diborane passed into the last trap. Each condensate was purified by further fractionation.

Large samples (*e. g.*, 50 cc. of gas) of the mono-N-methyl derivative were freed from triborine triamine by the aid of a very small fractionating column.[8] This column was operated under high vacuum (without pressure head), with the reflux temperature at −78.5°, and the effluent gases were condensed directly in a trap at −196°. Under these conditions, a small part of the mono-N-methyl derivative was carried past the reflux tube, but was easily recovered and purified by fractional condensation.

It was observed that the yields of the triborine triamine nucleus from mixtures containing methylamine, were higher than those obtained from pure $B_2H_6 \cdot 2NH_3$. Thus when ammonia was absent, the yields (of N-trimethyl triborine triamine) ran above 60%.

The analytical data on which the characterization of the three N-methyl derivatives is based, are given in Table II. All values here given are expressed in millimoles.

TABLE II

ANALYTICAL DATA FOR THE N-METHYL TRIBORINE TRIAMINES

Compound	Substance determined	Size of sample	Calcd. quantity	Quantity found
$N\text{-}CH_3B_3N_3H_5$	N_2	0.119	0.179	0.178
	CO_2	.151	.151	.153
	$B(OH)_3$	.151	.453	.462
	H_2	.139	.417	.415
$N\text{-}(CH_3)_2B_3N_3H_4$	N_2	.0745	.112	.115
	H_2	.223	.669	.684
$N\text{-}(CH_3)_3B_3N_3H_3$	N_2	.108	.162	.155
	CO_2	.120	.360	.368
	$B(OH)_3$	.120	.360	.366
	H_2	.162	.486	.469
	H_2	.140	.420	.422

The values for the molecular weights calculated from the experimentally determined vapor densities together with the values calculated from the formulas, are given in Table III.

TABLE III

MOLECULAR WEIGHTS OF THE N-METHYL DERIVATIVES

Compound	Temp., of detn., °C.	Molecular weight Obsd.	Calcd.
$N\text{-}CH_3B_3N_3H_5$	101	94.7	94.5
$N\text{-}(CH_3)_2B_3N_3H_4$	158	109	108.5
$N\text{-}(CH_3)_3B_3N_3H_3$	123	123	122.5

The temperatures at which the sample volumes were measured are significant, because of the tendency of these substances to associate in the vapor phase at lower temperatures. This effect seems most pronounced in the case of the mono-N-methyl derivative. At room temperature, two observations of the vapor density of this substance gave average molecular weights of 117 and 129, respectively, in contrast to the calculated 94.5. An attempt to measure the effect of pressure upon the degree of association of this de-

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(7) Incidental to such preparations was the preparation of the dimethylaminate of diborane, $B_2H_6 \cdot 2CH_3NH_2$. Quite in contrast to the diammoniate of diborane, this compound is a liquid at room temperature, although it cannot be volatilized without complete change of identity. Like the diammoniate of diborane, it appears to be entirely stable at room temperature.

(8) Burg, THIS JOURNAL, **56**, 499 (1934).

rivative was abandoned on account of the slowness with which the equilibrium was approached.

The vapor tensions of the three N-methyl derivatives of triborine triamine at different temperatures appear in Table IV, which gives also the corresponding temperatures, calculated from the equations of the type $\log p = B - A/T$. The constants for these equations, calculated by the method of least squares from the original data, appear in Table V, which gives also the calculated value of the boiling point, the molar heat of vaporization, and the Trouton constant, for each compound.

TABLE IV

VAPOR TENSIONS OF THE N-METHYL DERIVATIVES

$P_{\text{mm.}}$	$T_{\text{obsd.}}$	$T_{\text{calcd.}}$	$P_{\text{mm.}}$	$T_{\text{obsd.}}$	$T_{\text{calcd.}}$
$N\text{-}CH_3B_3N_3H_5$			$N\text{-}(CH_3)_2B_3N_3H_4$		
5.2	247.5	246.3	8.2	273.1	270.5
7.5	252.5	252.1	27.0	293.1	292.9
10.5	257.5	257.6	32.5	298.1	296.7
14.0	262.5	262.5	59.5	309.6	309.9
18.8	267.5	267.8	84.5	317.1	318.1
23.5	273.1	271.9	99.5	322.1	322.1
32.7	278.2	278.2	111.0	323.6	324.8
41.5	282.5	283.0	152.5	331.6	332.9
52.0	287.5	286.5	204	338.6	340.7
$N\text{-}(CH_3)_3B_3N_3H_3$			225	341.6	343.5
96	345.1	344.6	302	350.3	351.9
157	358.1	357.7	360	358.7	357.1
271	372.6	373.4	402	360.1	360.5
299	376.6	376.4	496	366.0	367.1
376	382.7	383.6	530	368.9	369.2
429	388.1	388.8	611	374.0	373.9
610	399.1	399.6	754	382.6	381.0
754	407.1	407.1			

TABLE V

PHYSICAL CONSTANTS FROM THE VAPOR TENSIONS

Compound	A	B	B. p., °C.	ΔH, cal./mole	Trouton constant
$N\text{-}CH_3B_3N_3H_5$	1713	7.669	84	7975	22.3
$N\text{-}(CH_3)_2B_3N_3H_4$	1832	7.685	108	8375	21.9
$N\text{-}(CH_3)_3B_3N_3H_3$	2009	7.812	134	9278	22.7

The B-Methyl Derivatives of N-Methyl Triborine Triamine

B-Methylation of Triborine Triamine.—The behavior of triborine triamine toward boron trimethyl and toward dimethylboric amide was studied as a test of the feasibility of the direct B-methylation of the N-methyl derivatives of triborine triamine. Both reagents gave B-methyl derivatives, along with non-volatile solid by-products, hydrogen, and occasionally methane. Boron trimethyl gave better yields of the desired products; the results of experiments with this reagent are given in Table VI.

TABLE VI

THE ACTION OF BORON TRIMETHYL UPON TRIBORINE TRIAMINE

Experiment		1	2	3
Reactants	$B_3N_3H_6$, cc.	8.7	7.9	14.8
	$B(CH_3)_3$	6.9	7.8	5.0
Temperature, °C.		200–225	100	100
Duration of heating, hrs.		1.75	24	6
Products	H_2, cc.	10.6	4.6	1.6
	CH_4, cc.	2.0	0.0	0.0
	$B\text{-}CH_3B_3N_3H_5$, cc.	0.6	0.4	0.14
	$B\text{-}(CH_3)_2B_3N_3H_4$, cc.	0.86		0.96
	$B\text{-}(CH_3)_3B_3N_3H_3$, cc.	1.5	4.6	1.5
	B_2H_6, $B(CH_3)_3$, and their reaction products, cc.	0.0	3.8	3.6
	Recovered $B_3N_3H_6$, cc.	0.0	0.0	9.1
Recovery of triborine triamine nucleus, %		34	63	79
Yield of substituted ring-compounds, %		34	63	46

B-Methylation of Mono-N-methyl Triborine Triamine.—The action of boron trimethyl on mono-N-methyl triborine triamine is similar to its action on triborine triamine itself. Three N-B-methyl derivatives were prepared by that method: mono-N-methyl mono-B-methyl triborine triamine, mono-N-methyl di-B-methyl triborine triamine, and mono-N-methyl tri-B-methyl triborine triamine. The data are listed in Table VII. This table does not give the yields of tri- and tetramethyl derivatives from each separate experiment, for the task of isolating these from each mixture was considered unprofitably cumbersome.

The method of purification of each of the two lighter N-B-methyl derivatives was the same as that used for the isomeric N-methyl derivative. Mono-N-methyl tri-B-methyl triborine triamine was purified by condensing it several times in a U-tube at −30°, while the more volatile substances passed through.

The analytical data upon which the characterization of the N-B-methyl derivatives is based, are listed in Table VIII. The quantities are given in millimoles.

The molecular weights found, together with the values calculated from the formulas, are given in Table IX.

The vapor tensions of the three B-methyl derivatives of N-methyl triborine triamine at dif-

TABLE VII

THE ACTION OF BORON TRIMETHYL UPON N-METHYL TRIBORINE TRIAMINE

Experiment	1	2	3	4	5	Totals
Reactants and Conditions:						
N-$CH_3B_3N_3H_5$, cc.	10.1	8.25	17.5	30.0	6.25	72.1
$B(CH_3)_3$, cc.	9.6	7.8	6.0	30.3	6.54	60.2
Pressure, atm.	1.1	1.0	1.3	3.3	0.15	——
Time, hours	6	48	30	12	12	——
Temperature, °C.	100	100	100	100	100	——
Products:						
H_2 (possibly with CH_4), cc.	Trace	1.94	6.0	1.2	0.06	9.3
N-B-$(CH_3)_2B_3N_3H_4$, cc.	1.8	1.1	3.1	Trace	——	6.5
N-B,B′-$(CH_3)_3B_3N_3H_3$, cc.	←——	present	————	————→	0.43	15.5
N-B,B′,B″-$(CH_3)_4B_3N_3H_2$, cc.	←——	present	————	————	————→	4.6

TABLE VIII

ANALYTICAL DATA FOR THE N-B-METHYL DERIVATIVES

Compound	Size of sample	H_2 Found	H_2 Calcd.	NH_3 and CH_3NH_2 Found	NH_3 and CH_3NH_2 Calcd.	Boric acids Found	Boric acids Calcd.
N-B-$(CH_3)_2B_3N_3H_4$	0.071	0.143	0.142	0.208	0.213	0.209	0.213
	.053	.107	.106	——	——	——	——
N-B,B′-$(CH_3)_3B_3N_3H_3$	.118	.116	.118	——	——	——	——
N-B,B′,B″-$(CH_3)_4B_3N_3H_2$	.199	.000	.000	0.591	0.596	0.592	0.596

TABLE IX

MOLECULAR WEIGHTS OF THE N-B-METHYL DERIVATIVES

Compound	Value found	Value calculated
N-B-$(CH_3)_2B_3N_3H_4$	109	108.4
N-B,B′-$(CH_3)_3B_3N_3H_3$	123.6	122.4
N-B,B′,B″-$(CH_3)_4B_3N_3H_2$	138	136.4

ferent temperatures appear in Table X, which gives also the corresponding temperature values calculated from the equations of the type $\log p = B - A/T$. The constants for these equations, calculated from the original data by the method of least squares, appear in Table XI, along with the calculated boiling points, molar heats of vaporization, and Trouton constants.

TABLE X

VAPOR TENSIONS OF THE B-METHYL DERIVATIVES OF N-$CH_3B_3N_3H_5$

N-B-$(CH_3)_2B_3N_3H_4$

$P_{mm.}$	$T_{obsd.}$	$T_{calcd.}$
4.2	261.9	261.5
5.7	266.9	266.9
7.4	271.9	271.6
9.5	276.9	276.3
12.7	281.9	282.0
16.9	286.9	287.8
22.0	291.9	293.4

N-B,B′,B″-$(CH_3)_4B_3N_3H_2$

$P_{mm.}$	$T_{obsd.}$	$T_{calcd.}$
27.8	339	339.2
84	365	365.1
112	373	372.5
153	380	380.6
268	397	397.1

N-B,B′-$(CH_3)_3B_3N_3H_3$

$P_{mm.}$	$T_{obsd.}$	$T_{calcd.}$
43.0	326.1	326.4
61.5	336.1	335.1
73.0	338.6	339.4
98.3	347.6	347.1
118.5	352.1	352.2
151.0	358.6	359.0
178.2	363.6	363.8
201.3	368.1	367.4
241.0	372.6	372.8

TABLE XI

PHYSICAL CONSTANTS FROM THE VAPOR TENSIONS

Compound	A	B	B. p., °C.	H, cal./mole	Trouton constant
N-B-$(CH_3)_2B_3N_3H_4$	1732	7.245	124	8013	20.2
N-B,B′-$(CH_3)_3$-$B_3N_3H_3$	1965	7.652	139	8916	21.6
N-B,B′,B″-$(CH_3)_4$-$B_3N_3H_2$	2294	8.207	158	10440	24.2

Acknowledgment.—We take pleasure in acknowledging the grant of the National Research Council for liquid nitrogen used in these investigations.

Summary

The mono-, di-, and tri-N-methyl derivatives of triborine triamine were prepared by brief heating of mixtures of diborane, ammonia, and methylamine. The mono-, di-, and tri-B-methyl derivatives of mono-N-methyl triborine triamine were prepared by heating the parent substance with boron trimethyl. The uniformity of each sample was confirmed by the agreement of the vapor tensions with the Clapeyron–Clausius equation. The production of these six derivatives, and no others, is a confirmation of the ring structure for triborine triamine.

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