Fig. 1.—Projection on (010) of the electron density distribution of D,L-cis-11,12-methyleneoctadecanoic acid, (i. e., racemate of lactobacillic acid).

Fig. 2.—Projection on (010) of the electron density distribution of lactobacillic acid, (D or L, cis-11,12-methylene-octadecanoic acid).

related left and right handed molecules in the racemate, an infinite sheet system of hydrogen bonds links the carboxylic acid groups in the lactobacillic acid. This is illustrated in Fig. 2.

While the atomic positions in projection are compatible with reasonable inter- and intra-molecular distances, no details of the stereo-chemistry or molecular packing can be obtained from this analysis. For this information a complete three-dimensional analysis would be necessary since the other projections do not give sufficient data for a reliable analysis owing to the large number of independent parameters. Despite many attempts at recrys-
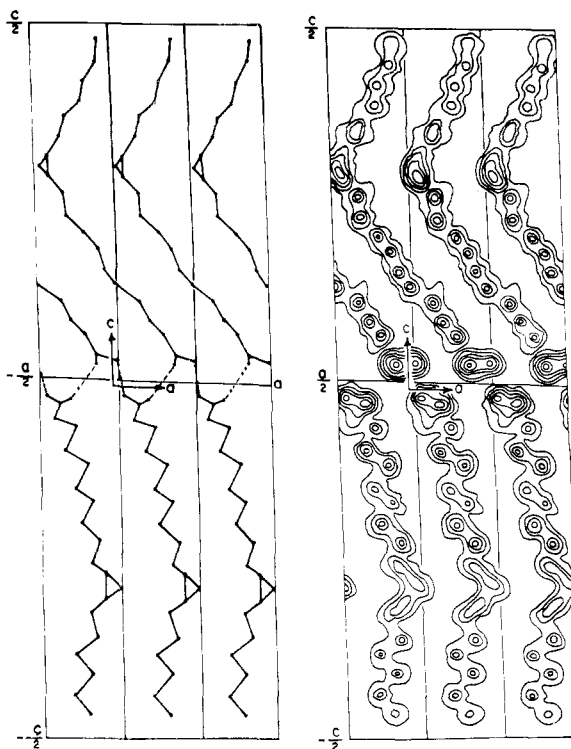
tallization of the comparatively small quantities of this compound which were available, no crystals of a quality which would justify an extensive three-dimensional analysis have hitherto been obtained.

Synthesis of B-Trisubstituted Borazines by Reaction of B-Trichloroborazine with Grignard Reagents[1]

By Daniel T. Haworth and Leo F. Hohnstedt

The reaction of $B_3Cl_3N_3H_3$ with Grignard reagents in diethyl ether serves as a convenient method for the preparation of B-trisubstituted borazines. B-Trimethylborazine can be isolated by fractionation of the volatile solvent-product mixture from the reaction of $B_3Cl_3N_3H_3$ with CH_3MgI. A similar procedure did not lead to isolation of B-triethylborazine, but this compound can be obtained in good yield by vacuum pyrolysis of the solids remaining after removal of solvent ether from the reaction mixture. B-Triphenylborazine and the BN-substituted compounds hexamethylborazine and hexaethylborazine have been prepared by this pyrolysis technique. Some data on the stability of borazine, B-trimethylborazine and B-triethylborazine are reported.

The reaction of B-trichloroborazine with Grignard reagents or other organometallic compounds presents an attractive method for the synthesis of B-trisubstituted borazines. R. Schaeffer[2] demon-

strated that B-trichloroborazine reacts with methyl magnesium iodide in ethyl ether at room temperature to give B-trimethylborazine

$$B_3Cl_3N_3H_3 + 3CH_3MgI \xrightarrow[\text{ether}]{\text{ethyl}}$$

$$B_3(CH_3)_3N_3H_3 + 3MgICl \quad (1)$$
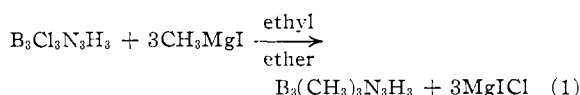
Satisfactory yields of B-trimethylborazine can be had by fractionation of the volatile solvent-product mixture resulting from this reaction.[3] Although B-triethylborazine could not be obtained using a similar fractionation technique, it has been found that $B_3(C_2H_5)_3N_3H_3$ can be obtained in a 70% yield by pyrolysis of the solid residue remaining after distillation of ether from the $B_3Cl_3N_3H_3$–C_2H_5MgI reaction mixture.[4] Similar pyrolysis procedure using phenylmagnesium iodide led to the recovery of B-triphenylborazine. To test the applicability of this technique to the preparation of borazines substituted on N as well as on B, hexamethylborazine and the new compound hexaethylborazine were prepared from the corresponding B-trichloroborazine and Grignard reagents

$$B_3Cl_3N_3R_3 + 3RMgI \longrightarrow B_3R_3N_3R_3 + 3MgICl \quad (2)$$
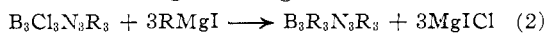
During the determination of the vapor pressure of B-triethylborazine it was observed that this compound starts to decompose at about 70°. This observation prompted an investigation of the stability of B-trimethylborazine and some further studies of borazine itself. The results indicate that the methyl compound is relatively stable[5] compared with borazine or B-triethylborazine.

Experimental

Apparatus and Technique.—Vacuum apparatus and techniques generally employed in the study of boron compounds were used. Samples for analysis were digested at 100° in concd. H_2SO_4 containing a few drops of 30% H_2O_2. Analytical details have been described.[6] Molecular weights were determined cryoscopically in benzene.

Intermediates.—$B_3Cl_3N_3H_3$, $B_2Cl_3N_3(CH_3)_3$ and $B_3Cl_3N_3(C_2H_5)_3$ were prepared by modifications of the Brown and Laubengayer method.[6,7]

$B_3(CH_3)_3N_3H_3$.—In a typical run 4.0 g. of $B_3Cl_3N_3H_3$ and 20 ml. of diethyl ether were placed in a dry 100 ml. flask, under a nitrogen atmosphere. The flask, which was attached to the vacuum line, was equipped with a dropping funnel containing methylmagnesium iodide (formed by reaction of 2 g. of Mg and 10 g. of CH_3I in ether). The Grignard reagent was added slowly while the contents of the flask were stirred. Grignard reagent in excess of that required for reaction according to eq. 1 was added and stirring continued for another hour. All volatile material then was transferred to the vacuum system and fractionated using a train of U-tubes at −45, −63 and −196°. Most of the product was retained at −45°. A little passed into the −63° tube but was recovered by further fractionation using a −63° bath which retains the borazine and allows the ether to pass.

The product was identified as B-trimethylborazine by its m.p. of 31.4° and vapor pressure of 16.3 mm. at 29.8°, 24.5 mm. at 37.4°. Lit. m.p. 31.5°; v.p. at 29.8°, 16.3 mm.; v.p. at 37.4°, 24.0 mm.[8] In various experiments in which less than 3 moles of Grignard reagent per mole of $B_3Cl_3N_3H_3$ was used, the products were mixtures from which no pure material could be isolated. However, one can obtain B-trimethylborazine even by adding CH_3I {to a mixture of Mg turnings and $B_3Cl_3N_3H_3$ in ether, provided Mg and CH_3I} are used in the amounts needed to completely methylate the $B_3Cl_3N_3H_3$ present.

$B_3(C_2H_5)_3N_3H_3$.—Ethyl magnesium iodide in ether (3.0 g. Mg and 17.5 g. C_2H_5I) was added dropwise to 5.0 g. of $B_3Cl_3N_3H_3$ in an ether slurry at room temperature in an atmosphere of dry nitrogen. After addition was completed, the reaction mixture was heated to reflux temperature for 12 hr., following which the ether was distilled away at room temperature under reduced pressure, leaving a white residue. The reaction flask was attached to the vacuum line and warmed to 100° under vacuum. A liquid distilled out of the flask and was fractionated using a U-tube at −45°. Ether, which is present in the volatile liquid, passes this temperature but the product is retained. The liquid retained at −45°, after repeated fractionation to remove traces of ether, melted sharply at −46.4°, exerted a vapor pressure that varied in nearly linear logarithmic fashion with $1/T$ and had an infrared spectrum similar to that of the other borazines. Molecular weight and analytical data support the identification of this product[9] as $B_3(C_2H_5)_3N_3H_3$.

Anal. Calcd. for $B_3(C_2H_5)_3N_3H_3$: B, 19.74; N, 25.53; mol. wt., 164.5. Found: B, 19.93; N, 25.72; mol. wt., 160.

The vapor pressure (Table I) in the range of 26.6 to 65.4° corresponds to the equation $\log P_{(mm.)} = 7.746 - 2167/T$, which indicates an extrapolated boiling point of 173° and a molar heat of vaporization of 9.88 kcal./mole and thus a Trouton constant of 22.1. A yield of 3.02 g. (69.8%) of this purified product was obtained.

TABLE I

VAPOR PRESSURE OF B-TRIETHYLBORAZINE

T, °C.	P (mm.)		ΔP (mm.)
	Obsd.	Calcd.	
26.6	3.35	3.36	−0.01
36.5	5.65	5.61	+ .04
42.5	7.60	7.62	− .02
49.4	10.55	10.52	+ .03
58.7	16.45	16.55	+ .10
65.4	22.50	22.20	+ .30
70.8	$(32.80)^a$	27.73	(+5.07)
79.5	$(50.95)^a$	39.72	(+11.23)

[a] Some decomposition of the sample had occurred.

$B_3(C_6H_5)_3N_3H_3$.—Using technique similar to that described for $B_3(C_2H_5)_3N_3H_3$, the compound $B_3(C_6H_5)_3N_3H_3$ was prepared from 1.54 g. of $B_3Cl_3N_3H_3$ and excess phenyl Grignard reagent. The product, 1.6 g. (59.9% yield), was obtained as white crystals depositing immediately above the heated zone by heating the dry solids of the reaction to 150° *in vacuo* after removal of solvent. The product had m.p. of 180–182° (lit. 184–185°, 181–182.5°, 175–181°).[10–12]

$B_3(CH_3)_3N_3(CH_3)_3$.—Hexamethylborazine was prepared from 1.09 g. of $B_3Cl_2N_3(CH_3)_3$ and excess methyl Grignard reagent. Pyrolysis of the residual solids after removal of the ether was done at 80° *in vacuo* and 0.7 g. (64% yield) of

(3) L. F. Hohnstedt, Ph.D. Thesis, University of Chicago, 1955. The synthesis of B-trimethylborazine was developed as part of work performed on Contract N6ori-20 under the direction of Dr. H. I. Schlesinger.

(4) The work reported herein, other than that involving the synthesis of B-trimethylborazine, was carried out in the Department of Chemistry, St. Louis University, and is taken in part from the Ph.D. Thesis of D. T. Haworth, St. Louis University, 1959.

(5) The stability considered here, *i.e.*, persistence of a species under given conditions, has been referred to as unreactivity by G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 368.

(6) L. F. Hohnstedt and D. T. Haworth, THIS JOURNAL, **82**, 89 (1960).

(7) C. A. Brown and A. W. Laubengayer, *ibid.*, **77**, 3699 (1955).

(8) A. B. Burg and H. I. Schlesinger, *ibid.*, **58**, 409 (1936).

(9) A. F. Zhigach, Ye. B. Kazakova and Ye. S. Krongauz, *Doklady Akad. Nauk, S.S.S.R.*, **111**, 1029 (1956); report on the preparation of $B_3(C_2H_5)_3N_3H_3$ by pyrolysis of ammonia–trimethylborane at 450°. A melting point of around −54° is given for the product isolated by distillation.

(10) W. L. Ruigh and F. C. Gunderloy, Abstracts of Papers presented at the April Meeting of the American Chemical Society, 1956, p. 40-N.

(11) B. M. Mikhailov and T. V. Kastroma, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1125 (1957).

(12) H. J. Becher and S. Frick, *Z. anorg. u. allgem. Chem.*, **295**, 83 (1958).

white, crystalline $B_3(CH_3)_3N_3(CH_3)_3$ was collected in a $-10°$ trap. This product melted at 97–98° (lit. 97.1°).[13]

$B_3(C_2H_5)_3N_3(C_2H_5)_3$.—Ethylmagnesium iodide (4 g. Mg plus 9 g. C_2H_5I reacted in ether) was added slowly from a dropping funnel to an ether slurry of 1.7 g. of $B_3Cl_3N_3(C_2H_5)_3$ which had been cooled to 0° in an atmosphere of nitrogen. Stirring was continued as the solution warmed to room temperature and for an additional 3 hr. After removal of the ether by distillation at room temperature, the reaction flask was kept under vacuum and heated at 100°. White needle crystals of product collected above the heated zone. This material melted at 89–90°.

Anal. Calcd. for $B_3(C_2H_5)_3N_3(C_2H_5)_3$: B, 13.04; N, 16.89; mol. wt., 248.8. Found: B, 12.96; N, 16.83; mol wt, 232, 241.

Stability of B-Substituted Borazine: 1. B-Triethylborazine.—As indicated in Table I, the pressure observed over a sample of $B_3(C_2H_5)_3N_3H_3$ begins to be higher than that expected for the vapor pressure of a pure material around 70°. Investigation showed that some slight decomposition occurs over the period of time ($\frac{1}{2}$ to 1 hr.) required to bring the sample to temperatures in this region and higher. If a sample is held at temperatures in this range for prolonged periods, more extensive decomposition occurs. For example, the value of 50.95 mm. recorded in Table I was the observed pressure after 1.5 hr. at 79.5°. After a further 95 hr. at this temperature the pressure was 69.15 mm. Another sample exhibited a pressure of 210.90 mm. after being held at 95.6° for 23 hr. (calcd. vapor pressure at 95.6°, 74.13 mm.). The decomposition products were more volatile than the $B_3(C_2H_5)_3N_3H_3$ and passed a U-tube at $-23°$, which was sufficient to retain the borazine. (Decomposition at 100° and normal pressure was reported in reference 9.)

2. B-Trimethylborazine.—In contrast to the behavior of the ethyl compound is that of the B-trimethylborazine. The vapor pressure of the methyl derivative at 100° is that expected by extrapolation from lower temperatures, and this pressure held constant over a 27 hr. period at 100° and was increased only slightly after 95 hr. at that temperature. The normal boiling point of the B-trimethylborazine used was determined by adjusting the temperature of a sample contained in a tensimeter until the pressure exerted in the tensimeter was 760.0 mm. The normal boiling point so determined was 129.1°. The pressure of the sample remained constant within experimental error over a 25 hr. period at 129.1°.

Borazine.—The literature already contained the information that borazine undergoes extensive decomposition when stored for prolonged periods at room temperature with a liquid phase present.[14] To get data under conditions comparable to those used in the study of the methyl and ethylborazines, borazine decomposition was studied at 50 and 100°. For both temperatures borazine samples were sealed in tubes small enough to insure a liquid phase. The tubes, removed from the constant temperature environment at various intervals, were opened and the undecomposed $B_3N_3H_6$ and non-condensable gas were measured volumetrically. (The gas, produced in the pyrolysis, which is non-condensable at $-196°$ is listed as H_2.) The data obtained are given in Table II, which also includes data for a sample heated at 300° for 1 hr. In all cases a non-volatile, white solid remained in the pyrolysis tube. In the pyrolyses at 50 and 100° over 50% of the borazine was recovered after 160 and 167 hr., respectively. However, no borazine could be recovered from a sample of 18.0 cc.[15] after heating at 300° for 1 hr. This 300° pyrolysis produced a small quantity (0.6 cc.) of condensable volatile material and 45.1 cc. of H_2, which represents a ratio of H_2 to $B_3N_3H_6$ of 2.51. The non-volatile, white residue reacted with water to give a basic solution and liberate approximately 8 cc. of H_2, bringing the ratio of liberated H_2 to $B_3N_3H_6$ up to 2.95. Thus the solid pyrolysis residue has an empirical formula intermediate between $(BN)_x$ and $(BNH)_x$.

(13) E. Wiberg and K. Hertwig, Z. anorg. Chem., **255**, 141 (1947).

(14) R. O. Schaeffer, M. Steindler, L. F. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3303 (1954).

(15) All volumes in this section refer to calculation of volume as a gas at STP.

TABLE II

PYROLYSIS OF LIQUID BORAZINE

Time elapsed (hr.)	$B_3N_3H_6$ recovered (cc.)	Total % decomp.	H_2 evolved (cc.)
1.	18.4 cc.[a] of $B_3N_3H_6$ heated at 50°		
5	18.0	2.2	0.03
42	15.0	18.5	0.7
160	10.5	43.0	5.7
2.	18.2 cc. of $B_3N_3H_6$ heated at 100°		
3	17.2	5.5	0.7
21	15.4	15.4	1.9
167	10.5	42.3	8.5
3.	18.0 cc. of $B_3N_3H_6$ heated at 300°		
1	0.0	100	45.1

[a] All volumes are calculated as gas volumes at STP.

Discussion

Simple distillation at room temperature does not remove all the ether from the material resulting from the interaction of $B_3Cl_3N_3H_3$ and C_2H_5-MgI in ether. Heating the residue in vacuum may serve to decompose a magnesium complex formed in ether and thereby liberate the observed B-triethylborazine-ether mixture. This mixture, as described in the experimental part, is liquid and readily fractionated after it has been removed from the reaction flask. It should be pointed out that efforts to free the ethylborazine by the alternate procedure of addition of various aqueous solutions to the reaction product did not lead to the recovery of any product and apparently caused hydrolysis of the borazine ring.[16]

Except for B-triethylborazine, no effort was made to recover the products by an extraction process since the technique reported herein gives fairly pure materials in good yields with a minimum of manipulation.[17]

It is evident that data must be obtained for more compounds before a relationship can be established between ring substitution and stability of substituted borazines. Convenient techniques for B-trisubstituted, N-trisubstituted[6] and B and N hexasubstituted borazines[16,18] now have been developed so that various studies of the effect of ring substitution on the properties of borazine may be carried out.

(16) S. J. Groszos and S. F. Stafiej, THIS JOURNAL, **80**, 1357 (1958), describe the application of such technique to liberation of N-triphenyl-B-trisubstituted borazines prepared by reaction of Grignard reagents and $B_3Cl_3N_3(C_6H_5)_3$.

(17) H. J. Becher and S. Frick, Z. anorg. u. allgem. Chem., **295**, 83 (1958), report the isolation of B-triphenylborazine by an extraction procedure, which also involved heating the crude solids *in vacuo.*

(18) G. E. Rysckkewltsch, J. J. Harris and H. H. Sisler, THIS JOURNAL, **80**, 4515 (1958).