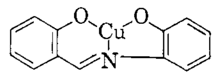
ogous compound was prepared by Pfeiffer.[13] Using *o*-aminophenol in place of methyl anthranilate he obtained VII



VII

As a final check, anthranilic acid, salicylaldehyde and Cu(II) acetate gave a product in every way identical with VI.

No mention was made by Pfeiffer[3] of the preparation of the tridentate chelate derived from the methyl ester of cystine. An attempt to prepare the cystine chelate by the method of Pfeiffer failed and extensive decomposition seemed to occur. It was not possible to prepare the Schiff base derived from salicylaldehyde and cystine methyl ester. Refluxing the forementioned compounds in ethanol for two hours yielded elemental sulfur and a small amount of an impure product which was not further identified.

Experimental

A. Preparation of Bis-(salicylaldimine]-Cu(II) Chelates. 1. Method of Pfeiffer.[3]—This method consists in refluxing in methanol solution 1:1:1 ratio by weight of bis-[salicylaldehyde]-Cu(II), sodium acetate and the aniline, amine or amino ester.

2. Method of Charles.[5]—To a methanolic solution of salicylaldehyde, a methanolic or aqueous solution of the amine or aniline is added to preform the Schiff Base ligand. Aqueous sodium acetate and copper acetate are then added and the mixture heated to reflux.

The aniline derived Schiff Bases are best made by the method of Charles. Only bis-[salicylaldehyde]-Cu(II) was recovered in attempting the method of Pfeiffer on *o*-nitroaniline, *o*-nitro-*p*-methoxyaniline and *o*-carbomethoxyaniline. The amino acid ester derived Schiff Bases are easily made by the method of Pfeiffer.

B. Amidation Reaction.—1.5 g. of ester was refluxed for 10 minutes in 30 ml. of *n*-butylamine. The excess amine was then removed by steam distillation. During removal of the amine, the black oil, which separated, gradually solidified becoming a grey-green, finally a light green powder. The product was filtered, washed, dried and purified by recrystallizing from a minimum quantity of hot dimethylformamide. The product precipitated out as a brown-green powder.

C. Amine Exchange Reaction.—1.5 g. of chelate (types II or III) was refluxed with 30 ml. of *n*-butylamine for 10 minutes. An equal volume of water was added to the hot reaction mixture followed by cooling in an ice-bath. The brown-green crystals that formed were filtered off and recrystallized from ethanol.

D. Transesterification Reaction.—The procedure of Pfeiffer[2] was followed.

E.—*p*-Chlorosalicylaldehyde was prepared by the method of Hodgson and Jenkinson.[14]

F.—**Infrared spectra** were run in Nujol mulls on a Baird Model 4–55 double beam recording spectrophotometer equipped with sodium chloride optics.

Acknowledgment.—A grateful acknowledgment must be given to Mr. Peter Andrellos whose advice and encouragement greatly aided this work.

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[13] P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Schill and H. Thielert, *J. prakt. Chem.*, **149**, 219 (1937).

[14] H. H. Hodgson and J. A. Jenkinson, *J. Chem. Soc.*, 1740 (1927).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Preparation of N-Trisubstituted Borazines by Reduction of B-Trichloroborazines[1]

BY LEO F. HOHNSTEDT[2] AND DANIEL T. HAWORTH

RECEIVED FEBRUARY 26, 1959

The reduction of B-trichloro-N-trisubstituted borazines with $NaBH_4$ in polyethyleneglycol–dimethyl ethers leads to good yields of the corresponding N-trisubstituted borazine, $B_3N_3R_3H_3$. The reaction of a primary amine and trichloroborane in chlorobenzene provides a convenient route for preparation of the B-trichloroborazines. The new compounds N-tri-*p*-tolylborazine, N-tri-*p*-anisylborazine and B-trichloro-N-tricyclohexylborazine are reported.

Over a period of years considerable effort has been devoted to the development of improved methods for the synthesis of borazine,[3] $B_3N_3H_6$, and various of its derivatives. As reported in an earlier communication,[4] borazine may be prepared in a reasonably satisfactory procedure based on the reduction of B-trichloroborazine, $B_3N_3H_3Cl_3$, with $LiBH_4$. As suggested at that time, it would be advantageous to use $NaBH_4$ as the reducing agent, since the diborane generated in the reduction can be allowed to interact with $NaBH(OCH_3)_3$ to regenerate $NaBH_4$ (eq. 1, 2). B-trichloroborazine and

$$3LiBH_4 + B_3N_3H_3Cl_3 \longrightarrow B_3N_3H_6 + 1.5B_2H_6 + 3LiCl \tag{1}$$

$$B_2H_6 + 2NaBH(OCH_3)_3 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3 \tag{2}$$

$NaBH_4$ failed to react in a variety of solvents in which B-trichloroborazine is soluble but in which $NaBH_4$ is insoluble. However, the desired reaction proceeds smoothly when the solvent is diethylene glycol–dimethyl ether, in which $NaBH_4$ and B-trichloroborazine are soluble. Borazine can be

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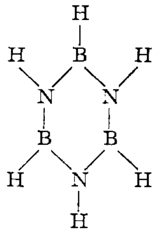
[1] Presented in part at the 132nd National Meeting of the American Chemical Society, New York, Sept., 1957.

[2] Department of Chemistry, St. Louis University, St. Louis. Missouri.

[3] Borazine has been recommended as the name for



which previously has been referred to as borazole. George W. Schaefer, Abstracts of Papers presented at the April Meeting of the American Chemical Society, p. 2L (1958).

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

TABLE I

B-TRICHLORO-N-TRISUBSTITUTED BORAZINES

Compound	M.p. (°C.)[a]	% yield	Analyses, %	B	N	Cl		Mol. wt.
$B_3N_3(CH_3)_3Cl_3$	162–164 (lit. 153–156)[11]	90.5	Found	14.46	18.59	47.07	Found	235, 238
				14.31	18.56	47.08	Calcd.	226
			Calcd.	14.37	18.60	47.08		
$B_3N_3(C_2H_5)_3Cl_3$	57–59 (lit. 55–57)[11]	52	Found	12.00	15.61	39.14	Found	263, 270, 276
				12.01	15.66	39.20	Calcd.	258
			Calcd.	12.11	15.68	39.69		
$B_3N_3(C_6H_{11})_3Cl_3$	217–219	75.6	Found	7.45	9.52	23.6	Found	408, 442
				7.62		24.7	Calcd.	430.3
			Calcd.	7.54	9.77	23.72		
$B_3N_3(C_6H_5)_3Cl_3$	273–275 (lit. 265–270)[10a]	52.8	Found	7.73	10.58	25.61	Found	410, 418
				7.81	10.74	25.68	Calcd.	412
			Calcd.	7.88	10.82	25.81		
$B_3N_3(p\text{-}C_6H_4CH_3)_3Cl_3$	307–309 (lit. 308–309)[10b]	67						
$B_3N_3(p\text{-}C_6H_4OCH_3)_3Cl_3$	233–238 (lit. 229–235)[10c]	74.9						

[a] M.p.'s taken in sealed nitrogen filled tubes.

$$B_3N_3H_3Cl_3 + 3NaBH_4 \longrightarrow B_3H_3H_6 + 1.5B_2H_6 + 3NaCl \quad (3)$$

recovered in better than 60% yields[5] according to equation 3. The reaction also can be carried out in triethylene glycol–dimethyl ether, from which yields in excess of 90% can be obtained.

In order to test the further applicability of this reduction technique a sample of B-trichloro-N-trimethylborazine, $B_3N_3(CH_3)_3Cl_3$, was synthesized[6,7] and reduced.[8] This led to the recovery of good yields of a material whose properties were that of the previously reported N-trimethylborazine.[9]

Therefore a variety of N-substituted chloroborazines were prepared by a modification of Brown and Laubengayer's technique for $B_3N_3H_3Cl_3$.[6] The reaction of BCl_3 and a primary amine[10] in hot chlorobenzene gives the corresponding borazine (eq. 4)

$$3BCl_3 + 3RNH_2 \longrightarrow B_3N_3R_3Cl_3 + 6HCl \quad (4)$$

Yields of purified product range as high as 90% and greater. The data for the chloroborazines are listed in Table I. The cyclohexyl compound has not been reported previously.

All the chloroborazines listed in Table I are reduced to the corresponding borazines by reaction with $NaBH_4$ according to eq. 5

$$B_3N_3R_3Cl_3 + 3NaBH_4 \longrightarrow B_3N_3R_3H_3 + 1.5B_2H_6 + 3NaCl \quad (5)$$

Triethylene glycol–dimethyl ether is a convenient solvent when the product is volatile at room temperature and can be distilled out of this solvent. The more volatile diethylene glycol–dimethyl ether is the indicated solvent when the product is of low volatility at room temperature, since the solvent then can be distilled away from the product at reduced pressure. Yields in the range of 60–90% were obtained as indicated in Table II, which includes data for the previously unreported *p*-tolyl, *p*-anisyl and cyclohexyl compounds. Table III lists analytical data for these three compounds. The diborane produced in the reduction reaction (eq. 5) can be disposed of by allowing it to react with $NaBH(OCH_3)_3$ (eq. 2).

Discussion

The reaction of primary amines with BCl_3 in hot chlorobenzene appears to provide a general scheme for the direct synthesis of B-trichloro-N-tri-substituted borazines.[12] There is no *a priori* reason to believe that this approach is limited to the specific compounds reported in this communication.[11] We have not had occasion as yet to prepare other chloroborazines in this fashion.

The $NaBH_4$ reduction of B-chloroborazine serves as a general method for the production of borazine and N-trisubstituted borazines and probably any B-haloborazine could be reduced in similar fashion. The diborane evolved during the reduction presents no problem when suitable experimental apparatus is used. Nevertheless, it would be convenient if the chloroborazines could be reduced with a reagent such that no diborane would be produced. Recent work, to be described in another communication, indicates that trialkoxyhydroborates, $NaBH(OR)_3$, may be used to reduce chloroborazines to borazines without the evolution of diborane.

Experimental

Apparatus.—In general standard vacuum line equipment was used, supplemented by complementary ground-glass equipment for use in bench-top procedures. Where necessary, materials were manipulated in a nitrogen-filled dry-box.

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(5) Leo F. Hohnstedt, Ph.D. Thesis, University of Chicago, 1955. The $NaBH_4$ reduction was developed as part of work performed on Contract N6 ori-20 under the direction of Dr. H. I. Schlesinger and is described in the Final Report on the contract for the period August 1, 1954 to July 31, 1955. The encouragement given us by Dr. Schlesinger to extend this work is appreciated sincerely.

(6) C. A. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).

(7) G. E. Ryschkewitz, J. J. Harris and H. H. Sisler, *ibid.*, **80**, 4575 (1958).

(8) The extension of the reaction described in equation 3 to the preparation of N-substituted borazines, as described herein, is taken in part from Daniel T. Haworth, Ph.D. Thesis, Saint Louis University, 1959.

(9) H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 1297 (1938).

(10) The synthesis of borazines based on the reaction of amines and BCl_3 has been reported in a series of papers: (a) R. G. Jones and C. R. Kinney, *ibid.*, **61**, 1378 (1939); (b) C. R. Kinney and M. T. Kolbezen, *ibid.*, **64**, 1584 (1942); (c) C. R. Kinney and C. L. Mahoney, *J. Org. Chem.*, **8**, 526 (1943); see also, S. J. Groszos and S. F., Stafiej, THIS JOURNAL, **80**, 1357 (1958).

(11) H. S. Turner and R. J. Warne, *Chemistry & Industry* (*London*), 526 (1958).

(12) L. F. Hohnstedt and D. T. Haworth, Abstracts of Papers presented at the September meeting of the American Chemical Society, p. 8-S(1957). Since then the N-ethyl compound has been synthesized, supporting our statement at that time concerning the probable general applicability of the method.

TABLE II

N-SUBSTITUTED BORAZINES PRODUCED BY REDUCTION OF CHLOROBORAZINES

R in $B_3N_3R_3H_3$	Reduction solvent	Yield, %	M.p. (°C.)[a]	Vapor pressure
H	[b]	92.6		85 mm. at 0°
CH_3	[b]	68.4	−7.8 (lit. −7.5)[9]	17 mm. at 27° (lit. 15 mm.)[9]
				28 mm. at 37° (lit. 27 mm.)[9]
C_2H_5	[b]	74	−49.1 (lit. −49.6)[13]	5.6 mm. at 32.5° (lit. 5.71)[13]
C_6H_{11}	[c]	87.9	98.9	Negligible at room temp.
C_6H_5	[c]	59.1	157–158 (lit. 154–5)[14]	Negligible at room temp.
p-$C_6H_4CH_3$	[c]	91.7	149–150	Negligible at room temp.
p-$C_6H_4OCH_3$	[c]	73.5	137–138	Negligible at room temp.

[a] The m.p.'s of non-volatile borazines were taken in sealed, nitrogen filled tubes. Other m.p.'s taken in a Stock apparatus. [b] Triethylene glycol–dimethyl ether. [c] Dimethylene glycol–dimethyl ether.

TABLE III

ANALYTICAL DATA FOR NON-VOLATILE N-SUBSTITUTED BORAZINES

R in $B_3N_3R_3H_3$	Boron, %		Nitrogen, %		Carbon, %		Total hydrogen %		Hydrolyzable hydrogen, %		Mol. wt.	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
C_6H_{11}	9.96	9.93	12.68	12.85	65.20	66.12	11.11	11.10	0.912	0.924	317	327
	10.10		12.90		65.38		11.18				320	
					65.65		11.19				333	
					65.71		11.21					
C_6H_5	10.70	10.51	13.31	13.61	68.95	70.00	5.81	5.88	.966	.979	304	308.8
			13.52		69.99		5.91				316	
							5.92					
p-$C_6H_4CH_3$	9.24	9.25	12.10	11.98	71.04	71.82	6.90	6.89	.859	.861	349	350.9
	9.30				71.23		6.95				353	
					71.35							
					71.51							
p-$C_6H_4OCH_3$	7.79	8.14	10.07	10.53	60.83	63.23	6.02	6.06	.765	.758	390	399
	8.11		10.20		61.76		6.15					
					62.53		6.16					

Materials.—(1) Trichloroborane (Matheson Co. Inc.) and sodium borohydride (Metal Hydrides, Inc.) were commercial grade and used without purification. (2) Diethylene glycol–dimethyl ether and triethylene glycol–dimethyl ether were Ansul Chemical Co.'s E-141 and E-161, respectively. These ethers were dried by refluxing over NaH, from which they were distilled. A middle cut of constant boiling point was collected for use. (3) Chlorobenzene, purified grade, was dried over anhydrous sodium sulfate and redistilled before use. (4) Benzene and hexane were dried over NaH and distilled off the NaH as needed. (5) Ammonium chloride was analytical reagent grade and was dried at 110° overnight before use.

Molecular Weights.—Molecular weights were determined cryoscopically in dilute benzene solutions, using a dry nitrogen atmosphere to minimize hydrolysis.

Preparation of B-Trichloroborazine.—B-Trichloroborazine was prepared in a manner similar to that previously described,[6] except that no ground glass was added to the reaction flask. In a typical run 135 g. (1.15 moles) of BCl_3 was added past a Dry Ice cold finger over a 3 hr. period to a slurry of 25 g. (0.47 mole) of NH_4Cl in about 300 ml. of chlorobenzene heated to gentle reflux. The mixture was heated for about 12 more hr. until no HCl or excess BCl_3 could be detected issuing from the reaction system. The solution was filtered hot (100°) and the solvent distillled from the filtrate at reduced pressure. The solids recovered from the filtrate were subjected to sublimation at 40° in a high vacuum and 12.5 g. (0.068 mole, 43.5% yield) of $B_3N_3H_3Cl_3$ was obtained. Returning the unsublimed solids to the reaction vessel increased the yields somewhat, but yields generally did not exceed 55%.

Preparation of B-Trichloro-N-trisubstituted Borazines.—B-Trichloro-N-trimethylborazine was prepared in similar fashion except that BCl_3 was added to the amine hydrochloride–solvent slurry for almost an hour at room temperature and addition continued as the mixture was heated to reflux. The addition of BCl_3 was stopped after about 20% excess had been introduced but the reaction mixture was kept at reflux temperature for 18 hr. The resulting solution was filtered warm (60°), the solvent removed by vacuum distillation, and the filtrate solids sublimed at 60° in high vacuum. This gave 25.5 g. (0.113 mole, 90.5% yield) of $B_3N_3(CH_3)_3Cl_3$ from 25 g. (0.37 mole) of $CH_3NH_2 \cdot HCl$. The crystals melted at 162–164°. It has been reported that use of a few per cent. excess of BCl_3 and extended reaction times can give practically quantitative yields of pure product.[7] Molecular weight determinations gave values of 238 and 235 (calcd. 225.96).

The synthesis of chloroborazines other than $B_3N_3H_3Cl_3$ and $B_3N_3(CH_3)_3Cl_3$ was effected by the use of the corresponding amine and excess BCl_3 in a procedure slightly modified from that described above. The amine was allowed to react with BCl_3 in chlorobenzene at room temperature or lower. Ethylamine and BCl_3 were introduced into the reaction flask simultaneously, with the amine inlet tube dipping into the solvent to prevent plugging. In the other cases the amine and solvent were mixed and BCl_3 then introduced past a −80° cold finger. The resulting mixture of solvent and amine–chloroborane adduct was heated to reflux, eliminating HCl, with the formation of the desired $B_3N_3R_3Cl_3$. The resulting solutions were cooled and filtered, and solvent was distilled off at reduced pressure, to give the crude yield of solid products. Cyclohexyl-, tolyl- and anisylborazine were obtained by extraction of the filtrate solids with an equal volume mixture of hexane and chloroform. The product was purified by recrystallization from hexane–chloroform. The ethyl derivative was obtained from the crude solid by high vacuum sublimation at room temperature; the phenyl derivative was purified by sublimation at 100°. Details of typical runs were as follows:

$B_3N_3(C_2H_5)_3Cl_3$.—Ethylamine (27 g., 0.33 mole) and BCl_3 (70 g., 0.60 mole) were introduced into 175 ml. of chlorobenzene at 0°, over a 6 hr. period with an additional hour of stirring. Then heating to reflux temperature was carried out for 21 hr.

$B_3N_3(C_6H_{11})_3Cl_3$.—Trichloroborane (19 g., 0.16 mole) was added over a 4 hr. period to cyclohexylamine (13 g.,

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(13) W. V. Hough, G. W. Schaeffer, M. Dzurus and A. C. Stewart, THIS JOURNAL, **77**, 864 (1955).

(14) H. F. Becker and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958).

0.13 mole) in 160 ml. of chlorobenzene at room temperature. After one hour additional stirring the mixture was heated to reflux for 15 hr.

$B_3N_3(C_6H_5)_3Cl_3$.—Trichloroborane (110 g., 0.94 mole) was added to 25 g. (0.27 mole) of aniline in 200 ml. of chlorobenzene at room temperature over a four hour period. Stirring at room temperature was continued 2 hr., followed by 14 hr. at gentle reflux.

$B_3N_3(C_6H_4CH_3)_3Cl_3$.—Trichloroborane (47 g., 0.40 mole) was added to 25 g. (0.23 mole) of *p*-toluidine in 175 ml. of chlorobenzene at room temperature over a 4 hr. period, stirred an additional 2 hr. at room temperature and at reflux temperature for 14 hr.

$B_3N_3(C_6H_4OCH_3)_3Cl_3$.—Trichloroborane (40 g., 0.34 mole) was added to *p*-anisidine (20.5 g., 0.17 mole) in 175 ml. of chlorobenzene at 0° over a 6 hr. period. After an additional 2 hr. at 0°, the mixture was heated to reflux temperature for 12 hr.

Preparation of Borazine, N-Trimethylborazine and N-Triethylborazine.—In a typical reduction of B-trichloroborazine, 4.9 g. (0.027 mole) of $B_3N_3H_3Cl_3$ was mixed with 4.2 g. (0.11 mole) of $NaBH_4$ in a dry-box. This mixture was placed in a 100-ml. flask equipped with a dropping funnel. The flask was attached to the vacuum line and evacuated. The flask was cooled with an ice-water bath (to prevent excessive frothing) and triethylene glycol-dimethyl ether admitted slowly through the dropping funnel while stirring was carried out using a Teflon coated magnet which had been placed in the flask. The reaction flask was open to a manifold of the vacuum system so that increase in pressure could be observed. About 20 ml. of solvent was required to facilitate stirring and the reaction proceeded smoothly at 0°. After the pressure in the system (reaction flask plus manifold) had built up to about $^1/_4$ atm. the system was opened briefly to pumping, with condensable gas being trapped at $-196°$ in the fractionation system of the vacuum line. The manifold then was shut off again from the rest of the vacuum line so that the pressure built up again as reaction proceeded. This procedure of periodically removing the gaseous products of the reaction was continued until the pressure fell to and remained at the slight value characteristic of the solvent. The combined volatile materials retained by $-196°$ were separated using a series of U-tubes cooled to $-23°$, $-112°$ and $-196°$. Any solvent present was retained by $-23°$; borazine was retained by $-112°$ and diborane by $-196°$. After fractionation using these temperatures, there was recovered 2.01 g. (0.0249 mole, 92.6% yield) of $B_3N_3H_6$, with vapor tension of 85 mm. at 0°.

N-Trimethylborazine was produced by a similar reduction of $B_3N_3(CH_3)_3Cl_3$. A $-80°$ bath was used in place of $-112°$ to retain the methylborazine in the fractionation procedure. From 8.5 g. (0.038 mole) of $B_3H_3(CH_3)_3Cl_3$ was produced 3.1 g. (0.025 mole) of $B_3N_3(CH_3)_3H_3$ for a 68% yield. The product melted at $-7.8°$ (lit.[9] $-7.5°$). It exhibited a vapor tension of 17 mm. at 27° and 28 mm. at 37° as compared to the previously reported values of 15 and 27 mm., respectively.[9]

N-Triethylborazine (0.4 g., 0.0024 mole) was prepared in 74% yield by reduction of 0.9 g. (0.0034 mole) of $B_3H_3(C_2H_5)_3Cl_3$. The product melted at $-49.1°$ (lit.[12] $-49.6°$). The vapor tension at 32.5° was 5.6 mm. as compared to the reported value of 5.71 mm.[12]

Preparation of N-Triphenyl, N-Tri-*p*-tolyl-, N-Tri-*p*-anisyl- and N-Tricyclohexylborazine.—These compounds were synthesized by reduction of their corresponding B-trichloroborazine in a manner similar to that described above for $B_3N_3H_6$, except that diethylene glycol-dimethyl ether was the solvent. The isolation of these non-volatile borazines is illustrated by the following typical run. An excess of $NaBH_4$ and 7.0 g. (0.017 mole) of $B_3N_3(C_6H_5)_3Cl_3$ were reacted in the solvent. After reaction was complete the last part of the diborane generated was pumped away and then the solvent was distilled out at reduced pressure and room temperature, leaving a white residue which contained $NaBH_4$ and NaCl in addition to the product. The reaction flask was filled with dry nitrogen and an equal volume mixture of hexane-chloroform was added through the dropping funnel. The solid residue was broken up by stirring, the flask warmed and the contents filtered hot through a sintered glass filter in a dry nitrogen atmosphere. The undissolved material was treated in similar fashion with four additional portions of hexane-chloroform. The filtrates were combined and the extraction solvent mixture was distilled off at reduced pressure at room temperature, leaving the crude solid $B_3N_3(C_6H_5)_3H_3$. This solid was subjected to repeated recrystallization from hexane-chloroform until the melting point of the recrystallized material remained unchanged by further recrystallization. The purified product weighed 3.1 g. (0.010 mole, 59.1% yield), melted at 157–158°, and its molecular weight was measured twice, giving values of 304 and 316 (calcd. 308.81). The other non-volatile borazines were prepared and isolated in the same manner. The percentage yields and melting points are given in Table II and complete analytical data in Table III.

B-Tribromo-N-triethylborazine.—Since ethylamine and trichloroborane are both gases at room temperature, their reaction was somewhat inconvenient to control. Therefore the reaction of the amine and BBr_3 in chlorobenzene and mixtures of chlorobenzene and bromobenzene was investigated. Under a variety of experimental conditions charring seemed to occur during the mixing of the reactants including cases in which the reaction flask was cooled to 0°. Small amounts of product were recovered in various runs after prolonged refluxing, by vacuum sublimation of the crude solids obtained from the reaction solvent after filtration. A 0.5960-g. sample of this volatile product was analyzed. Calcd. for $B_3N_3(C_2H_5)_3Br_3$: B, 8.09; N, 10.47; Br, 59.73. Found: B, 8.18, 8.12, 8.21; N, 10.50, 10.52; Br, 59.69, 59.83. The volatile material as generally collected softened and melted over the range 78–82°.

Hydrolysis.—B-Trichloro-N-trimethylborazine hydrolyzes vigorously in water, similar to $B_3N_3H_3Cl_3$. B-Trichloro-N-triethylborazine hydrolyzes readily but not quite so vigorously as the methyl compound. The other B-trichloro-N-trisubstituted borazines hydrolyze only slowly in water at room temperature. In these cases samples were hydrolyzed completely by digestion in a small amount of concd. H_2SO_4 at 100°. Several drops of 30% H_2O_2 were added as needed to give clear solutions. The solid reduced borazines, listed in Table III, were hydrolyzed in the same way to prepare a sample for analysis for boron and nitrogen.

Analysis.—(1) **Carbon and total hydrogen.** These were obtained by combustion analysis using Sargent combustion apparatus S-21580. Standard procedures were used without modification except for the method of heating the sample. The movable furnace was stopped about 3 cm. from the platinum boat used and time allowed for the sample to diffuse (at least partially) into the long burner. This minimized the formation of boron carbide and lessened the frequency of explosions. The boat was then heated in normal fashion. (2) **Hydrolyzable hydrogen.** This refers to the hydrogen bound to boron in the reduced compounds and which is liberated during hydrolysis to give one H_2 molecule per atom so bound. Samples were hydrolyzed by several hours heating at 100–150° in a sealed tube containing aqueous HCl. The tubes then were opened on the vacuum line and the evolved hydrogen measured volumetrically. (3) **Boron, nitrogen, chlorine.** Samples were hydrolyzed as described in the preceding section, the resulting solution made up to convenient volume, and aliquots taken for the various analyses. Nitrogen was present as ammonium salt and was determined by the Kjeldahl method. Chloride ion was determined gravimetrically or by Fajans' adsorption indicator method. Boron as boric acid was determined by titration of the mannitol complex after first removing ammonia from the aliquot by making it slightly basic with dilute NaOH and heating in a platinum dish.

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