[Contribution from the Department of Chemistry, St. Louis University]

The Preparation, Identification and Characterization of N-Trialkylborazoles[1]

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An improved method for the preparation of N-trimethylborazole is described. Lithium borohydride and the appropriate monoalkylammonium halide react in diethyl ether, the ether is removed, and the residue so obtained is pyrolyzed to give the desired product. The method is extended to N-triethyl-, N-tri-*n*-propyl- and N-tri-isopropylborazoles. Physical properties of the new borazoles are given.

The preparation of trimethylamine–borine, N-dimethylaminoborine, and N-trimethylborazole accomplished by Schaeffer and Anderson[3] by the reaction of lithium borohydride with the appropriate methylammonium chloride, and the subsequent preparation of borazole[4] by the reaction of ammonium chloride with lithium borohydride presents a unique and general method for the establishment of a boron–nitrogen bond. The reaction of methylammonium chloride with lithium borohydride has been further investigated and the preparation of N-trimethylborazole has been improved and simplified. In addition, the reactions of several higher monoalkylammonium chlorides with lithium borohydride leading to the preparation of N-triethyl-, N-tri-*n*-propyl- and N-tri-isopropylborazole were investigated.

The reactions are most conveniently carried out in two steps, represented by the equations

$$LiBH_4 + RNH_3Cl = LiCl + BNH_5R + H_2 \quad (1)$$
$$BNH_5R = {}^1/_3B_3H_3N_3R_3 + 2H_2 \quad (2)$$

The first of these involves the addition of diethyl ether to a mixture of alkylammonium chloride and lithium borohydride, the latter taken in small excess. The addition of the ether solvent initiates the evolution of approximately one mole of hydrogen for each mole of alkylammonium chloride taken in accord with equation 1. The second step, represented by equation 2, is the pyrolysis of the white solid residue obtained by removal of the ether from the reaction mixture after completion of step one. Yields of 90% of the borazole derivative, based on the ammonium halide taken, are easily obtained.

Although the reaction is complete regardless of the reactant taken in excess, it is advantageous to use about 10% excess of lithium borohydride. Under these conditions the ammonium salt is completely consumed and contamination of the product by the amine, which would be produced during the pyrolysis if any unreacted ammonium salt remained, is avoided. Because volatile intermediates are produced during the pyrolysis, to assure maximum yield it is desirable that the products leave the reactor through a long heated zone, wherein intermediates are converted to the final product and that the volatile materials are slowly removed from the reactor, thus permitting sufficient time for reaction of the intermediates.

In the reaction of the borohydride with methyl- and isopropylammonium chlorides, it was possible to isolate from the intermediates homogeneous substances identified[5] as dimeric monoalkylaminoborines. The dimeric methylaminoborine, on pyrolysis under conditions used in the original preparation, gave the borazole but the dimeric monoisopropylaminoborine gave only non-volatile polymers. It does not seem possible that the latter could be a precursor of the borazole.

The new N-trialkylborazoles were identified, and a characterization of the new series was made by determination of some of the significant physical properties. In addition, the previously reported physical properties of N-trimethylborazole[6,7] were augmented by determination of liquid density, molar volume, refractive index and molar refraction.

Experimental

The sensitivity of lithium borohydride and the borazole derivatives to air and moisture necessitated the use of either a closed system which, when under dry nitrogen, would prevent the reactants and products from contact with the atmosphere, or the high vacuum techniques described by Stock[8] and Sanderson.[9]

(1) **Preparation of N-Trialkylborazoles.**—A system similar to that previously described for the preparation of borazole[4] was employed. However, the system was modified so that greater quantities might be conveniently handled. The traps adjoining the reactor were equipped with ground joints so that they could be removed, and a 100-ml. dropping funnel was provided above the reaction zone in order that solvent might be conveniently added to the reactor. A 250-ml. reactor was used, equipped with a neck 50 cm. in length. This reactor was provided with two heaters, a tube heater 40 cm. in length which surrounded the neck, and a furnace which surrounded the bulb in such a manner that none of the reactor would be exposed. The heaters were capable of heating the reactor to temperatures exceeding 400°.

In a nitrogen filled dry-box, the reactor is charged with approximately one-tenth mole of alkylammonium chloride and an excess (approximately 0.12 mole) of lithium borohydride. The reactants are mixed by shaking the reactor and the reactor is attached to the reaction system. Anhydrous diethyl ether, 35 to 45 ml., is added to the reactants whereupon evolution of hydrogen is immediately observed. After the evolution of gas subsides (a period of approximately 12 hours), the system is evacuated and the ether is removed from the reactor by vacuum condensation. A white, solid material remains in the bulb of the reactor.

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[2] Taken in part from theses submitted by Marcelline Dzurus and by William V. Hough to the Graduate School, St. Louis University, in partial fulfillment of the requirements for the degree of Master of Science.

[3] G. W. Schaeffer and E. R. Anderson, This Journal, **71**, 2143 (1949).

[4] G. W. Schaeffer, R. Schaeffer and H. I. Schlesinger, *ibid.*, **73**, 1612 (1951).

[5] The preparation of monoalkylaminoborines in this manner is being investigated and the results will be submitted for publication in the near future.

[6] H. I. Schlesinger, D. M. Ritter and A. B. Burg, This Journal, **60**, 1297 (1938).

[7] E. Wiberg, K. Hertwig and A. Bolz, *Z. anorg. Chem.*, **236**, 177 (1938).

[8] A. Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[9] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

The furnaces are arranged, as described above, for pyrolysis of the residue; and Dewar flasks containing liquid nitrogen are placed around the traps adjoining the reactor. The bulb of the reactor is heated to approximately 90° while the system is left open to the pump to ensure removal of the last traces of ether held by the excess borohydride. The tube heater surrounding the neck of the reactor is then preheated to the appropriate temperature and the reactor is slowly heated to the temperature (Initial H_2 evolution, Table I) at which hydrogen evolution is first observed. When these temperatures are reached the reactor is heated as rapidly as possible to the optimum temperature (final H_2 evolution, Table I) and both furnaces are maintained at the indicated temperatures until evolution of gas subsides (a period of approximately half an hour). The system is then opened to the pump and a sudden surge of colorless liquid, the desired N-trialkylborazole, into the trap adjoining the reactor is observed. (If the product is N-tri-*n*-propylborazole some of this remains in the bulb of the reactor. This is most successfully recovered by extraction of the pyrolysis residue with benzene followed by fractional distillation of the benzene solution.)

TABLE I

PYROLYSIS TEMPERATURES FOR PREPARATION OF N-TRIALKYLBORAZOLES, °C.

Product	Initial H_2 evolution Reactor	Initial H_2 evolution Neck	Final H_2 evolution Reactor	Final H_2 evolution Neck
$(CH_3)_3B_3N_3H_3$	100	275–290	250	275–290
$(C_2H_5)_3B_3N_3H_3$	95	250–275	230	250–275
$(n\text{-}C_3H_7)_3B_3N_3H_3$	85	225–250	200	225–250
$(\text{iso-}C_3H_7)_3B_3N_3H_3$	110	315–325	260	315–325

Table II shows some typical preparations with yields calculated on the basis of the ammonium chloride taken.

TABLE II

PREPARATION OF N-TRIALKYLBORAZOLES

R	RNH_3Cl, g.	$LiBH_4$, g.	Yield, %
Methyl	7.3	3.0	90
	8.3	3.3	87
Ethyl	12.2	3.6	94
	8.1	3.0	94
n-Propyl	8.3	2.4	92
	16.7	5.2	88
Isopropyl	5.3	1.9	66
	7.5	2.3	84

TABLE III

THE PHYSICAL PROPERTIES OF THE N-TRIALKYLBORAZOLES[a]

Compound	M.p., °C.	B.p., °C.	$\log P_{mm} = \frac{-A}{T} + B$ A	B	ΔH_{vap}, kcal./mole	Trouton constant	Liquid density $D = a - bt$ a	$b \times 10^4$	Molar vol.	Refractive index at 20°	Molar refraction
$B_3N_3H_6$	−58	55	1609	7.714	7.00	21.1	0.8613	9.70	93.5	1.3821	22.26
$(CH_3)_3B_3N_3H_3$	− 7.5	133	2009	7.812	9.20	22.9	.8699	9.00	141	1.4404	37.98
$(C_3H_7)_3B_3N_3H_3$	−49.6	184	2012.4	7.2836	9.21	20.2	.8604	8.56	192	1.4344	50.90
$(n\text{-}C_3H_7)_3B_3N_3H_3$	Glass	225	2190.4	7.2793	10.02	20.2	.8485	6.91	244	1.4484	66.39
$(\text{iso-}C_3H_7)_3B_3N_3H_3$	− 6.5	203	2249.0	7.6001	10.29	21.6	.8648	8.60	239	1.4434	64.66

[a] Data for $B_3N_3H_6$ and $(CH_3)_3B_3N_3H_3$ taken in part from references 3, 6 and 7.

(2) **Identification of N-Trialkylborazoles.** (a) **N-Trimethylborazole.**—N-Trimethylborazole was identified by its melting point,[3] −8 to −7.5°, compared to the reported[6,7] −9°, and its vapor tension, 28 mm. at 37° and 163 mm. at 85°, compared to the reported 27 and 158 mm.[6].

(b) **N-Triethylborazole.**—N-Triethylborazole was identified by combustion analyses and molecular weight determination. Calcd. for $(C_2H_7)_3N_3B_3H_3$: C, 43.5; N, 23.4; H, 11.6. Found: C, 43.5, 43.4; N, 23.8, 23.6; H, 11.5, 11.0. A molecular weight of 160 g./mole was obtained by depression of freezing point in benzene (calcd. 164.6).

(c) **N-Tri-*n*-propylborazole.**—N-Tri-*n*-propylborazole was identified by combustion and hydrolysis analyses and molecular weight determination. By combustion: Calcd. for $(C_3H_7)_3N_3B_3H_3$: C, 52.3; N, 20.3; H, 11.7. Found: C, 53.1, 53.6; N, 19.9, 19.7; H, 11.9, 12.1. By hydrolysis: Calcd. for $(C_3H_7)_3B_3N_3H_3$: B, 15.7; N, 20.3; H, hydrolyzable, 1.46; mol. wt., 206.7 g./mole. Found: B, 15.6; N, 19.8; H, hydrolyzable, 1.43; mol. wt., 212 g./mole.

(d) **N-Triisopropylborazole.**—N-Triisopropylborazole was identified by combustion and hydrolysis analyses and molecular weight determination. By combustion: Calcd. for $(C_3H_7)_3N_3B_3H_3$: C, 52.3; N, 20.3; H, 11.7. Found: C, 51.2, 51.3; N, 18.2, 18.1; H, 11.9, 11.9. By hydrolysis: Calcd. for $(C_3H_7)_3N_3B_3H_3$: B, 15.7; N, 20.3; H, hydrolyzable, 1.46; mol. wt., 206.7 g./mole. Found: B, 16.1, 15.5; N, 20.6, 20.6; H, hydrolyzable, 1.72, 1.50; mol. wt., 197 g./mole.

(3) **Physical Properties of the N-Trialkylborazoles.**—The N-trialkylborazoles are all clear, colorless liquids of rather low vapor pressure at room temperature. Their appearance is like that of the aromatic hydrocarbons and their odor resembles that of the amine from which they are derived, although not as repugnant. Physical constants are given in Table III. Melting points (°C.) were determined by visual observation or the drop-weight method of Stock,[8] boiling points (°C.), heats of vaporization (kcal./mole) and Trouton constants were calculated from the equation[10,11] $\log P_{mm} = A/T + B$. The densities of the liquid were determined for the range 0–60° and constants for the equation $D(\text{g./cc.}) = a - bt$ are given. Molar volumes at 0° and refractive indices and molar refractions at 20° were calculated. Observed and calculated values of the vapor pressure are compared in Table IV.

TABLE IV

VAPOR TENSIONS OF N-TRIALKYLBORAZOLES

N-Triethylborazole

t, °C.		5.8	31.5	40.6	59.3	78.2
P, mm.	Found	1.2	5.0	7.7	17.2	34.8
	Calcd.	1.2	4.8	7.8	17.1	34.9

N-Tri-*n*-propylborazole

t, °C.		56.6	75.2	88.0	114.7	130.1
P, mm.	Found	5.2	9.8	16.1	43.1	70.7
	Calcd.	5.2	9.8	16.4	42.9	70.4

N-Triisopropylborazole

t, °C.		71.3	89.1	106.3	119.4	126.5
P, mm.	Found	11.8	24.7	47.1	74.3	94.5
	Calcd.	11.8	24.7	47.2	74.4	94.1

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[10] Samples used for vapor tension measurements were purified by fractional distillation. Considerable care was necessary to eliminate traces of the ether used as the solvent during the preparation.

[11] H. C. Brown, M. D. Taylor and M. Gerstein, THIS JOURNAL, **66**, 431 (1944).