[CONTRIBUTION FROM THE LEWIS RESEARCH CENTER, NATIONAL AERONAUTICS AND SPACE ADMINISTRATION]

Preparation and Properties of Some Trialkylboranes[1]

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Triethyl-, tri-*n*-propyl-, and tri-*n*-butylborane were prepared and fractionated under an inert atmosphere to prevent oxidation. Triethylborane and tri-*n*-propylborane were obtained in purities of 99.8 and 99.7 mole percent, respectively, while tri-*n*-butvlborane underwent thermal decomposition during distillation. The following physical and thermodynamic properties of triethylborane and tri-*n*-propylborane were determined: freezing point, boiling point, refractive index, density, dielectric constant, and heat of combustion.

As part of an evaluation program of boron compounds as potential high-energy fuels, a survey was made of the properties of the trialkylboranes. It was noted that the literature offered values for only some of the properties of current interest[2-7] and that among these values there were occasional discrepancies. Since the trialkylboranes are extremely susceptible to air oxidation, it was felt that the discrepancies in the property values might well be due to the presence of small amounts of oxidation products in the material. With this in mind the preparation, purification, and measurement of several properties of triethyl-, tri-*n*-propyl-, and tri-*n*-butylborane were undertaken in an inert environment.

Triethyl- and tri-*n*-propylborane were prepared in purities of 99.8 and 99.7 mole percent, respectively. Tri-*n*-butylborane was not obtained in a pure form, since it readily decomposed during distillation.[8]

RESULTS AND DISCUSSION

Physical properties. Table I presents freezing points, boiling points, refractive indices, densities, and dielectric constants for triethyl- and tri-*n*-propylborane. The molar refractions were calculated by means of the Lorentz-Lorenz equation from the values for refractive index and density.

An examination of the values listed in Table I, when compared with the previous literature values (footnotes *a* to *h*), in several instances, shows discrepancies that cannot be explained in terms of experimental error. The probable cause of these discrepancies presents itself when the trends in the values are noted. The refractive index reported for tri-*n*-propylborane[7] is lower and the densities for triethylborane and tri-*n*-propylborane[3,7] are higher than the values obtained in this present investigation. When a trialkylborane is oxidized, the product is an alkyldialkoxyborane.[9] Although no refractive index and density data are available for these compounds where R = ethyl or propyl, there are data for the closely related trialkoxyboranes.[10] The trialkylboranes, when compared with the corresponding trialkoxyboranes, are found to have higher refractive indices (approx. 0.02 higher) and lower densities (approx. 0.15 g./ml. lower). The alkyldialkoxyboranes would be expected to have refractive index and density values between those of the trialkylboranes and the trialkoxyboranes. This contention holds for the case where R = butyl.[10] Therefore, it would be expected that contamination of the trialkylboranes with their oxidation products would tend to lower the refractive index and elevate the density values beyond those of the pure compound.

The above explanation was further substantiated by a crude experiment run on a sample of tri-*n*-propylborane. The sample was placed in a refractometer and then exposed to air. The refractive index was observed to decrease rapidly, over period of several seconds, as the sample oxidized.

Experimental values for the refractive index of triethylborane and the dielectric constant of triethyl- and tri-*n*-propylborane are reported here for the first time.

Thermodynamic properties. Heat of combustion. The values for the heats of combustion of triethyl- and tri-*n*-propylborane are listed in Table II. The uncertainty associated with the over-all raw heat-of-combustion determination was about 0.3%, and that associated with the estimation of unburned material and the corrections thereof was about 0.2%. The over-all uncertainty was therefore estimated to be 0.5%.

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[1] The material presented in this paper is a revision and an extension of work discussed in NACA RM E55E06, Nov. 1, 1955.

[2] E. Frankland and B. F. Duppa, *Ann. Chem. und Pharm.*, **115**, 319 (1860).

[3] A. Stock and F. Zeidler, *Ber. deut. chem. Ges.*, **A54**, 531 (1921).

[4] E. Krause and R. Nitsche, *Ber. deut. chem. Ges.*, **B54**, 2784 (1921).

[5] A. W. Laubengayer, R. P. Ferguson, and A. E. Newkirk, *J. Am. Chem. Soc.*, **63**, 559 (1941).

[6] C. H. Bamford, D. L. Levi, and D. M. Newitt, *J. Chem. Soc.*, 468 (1946).

[7] P. L. Pickard and M. K. Patterson, Jr., Callery Chemical Co. Rept. No. CCC-1024 TR-45, Univ. Oklahoma, September 29, 1954.

[8] L. Rosenblum, *J. Am. Chem. Soc.*, **77**, 5016 (1955).

[9] J. R. Johnson and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 121 (1938).

[10] M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

TABLE I

PHYSICAL PROPERTIES OF TRIETHYLBORANE AND TRI-*n*-PROPYLBORANE

	F.P.	B.P.	Temp., t	Refractive index			Molar Refraction R_D	Density, d_4^t	Dielectric constant
				n_D^t	n_{Hgg}^t	$n_{Hgb.v.}^t$			
$B(C_2H_5)_3$	−92.93[a]	95.0[b]	20	1.3971	1.3988	1.4060	34.46	0.6850[c]	1.974
			30	1.3920	1.3939	1.4013		0.6761[c]	1.962
$B(n\text{-}C_3H_7)_3$	−64.92[d]	159.6[e]	20	1.4143[f]	1.4164	1.4241	48.43[g]	0.7232[h]	2.026
			30	1.4099[f]	1.4119	1.4195		0.7158[h]	2.013

[a] Reported[3] m.p. −92.9°. [b] Reported[3] b.p. 95°. [c] Reported[3,5] d_4^{23} 0.6931 and d_4^{30} 0.6774, respectively. [d] Reported[6] m.p. −65.5°. [e] Reported[4,6] b.p. 156° and 164.5°, respectively. [f] Reported[4,7] $n_D^{22.5}$ 1.4135 and n_D^{20} 1.4090, respectively. [g] Reported[7] R_D 45.33. [h] Reported[4,7] $d_D^{24.7}$ 0.7204 and d_4^{20} 0.7639, respectively.

TABLE II

THERMODYNAMIC PROPERTIES, TRI-*n*-ALKYLBORANES

Compound, BR_3, R =	Heat of combustion, ΔH_c, kcal./mole	Heat of formation at 25°, kcal./mole		Average bond energy, $\bar{D}(B—R)$, kcal./mole
		Liquid $\Delta H_{f(l)}$	Gas $\Delta H_{f(g)}$	
Methyl	− 658.0[a]	−34.8	−30.1	88.1
Ethyl	−1096.9[b]	−51.4[b]	−42.6	86.0
n-Propyl	−1529.4	−74.4	−63.4	89.5
n-Butyl	−1965[c,d]	−94[d]	−80	92

[a] Footnote 11. [b] Calculated ΔH_c, −1101.5 from reported[15] value $\Delta H_{f(l)}$, −46.8. [c] Footnote 12. [d] Calculated ΔH_c, −1975.4 from reported[15] value $\Delta H_{f(l)}$, −83.9.

For purposes of comparison, the values of the heat of combustion, ΔH_c, for trimethylborane[11] and tri-*n*-butylborane[12] are also included. The average incremental contribution to the ΔH_c made by each CH_2 group is approximately 145.3 kcal./mole. As would be expected, this is about the same as the average CH_2 contribution (145.7 kcal./mole) in the normal paraffin series.[13]

Heat of formation and bond energy. The values listed in Table II for $\Delta H_f(l)$ were calculated for the reaction:

$$BR_3(l) + O_2(g) \longrightarrow B_2O_3\text{ (amorph)} + CO_2(g) + H_2O(g)$$

The values for $CO_2(g)$ and $H_2O(g)$ were taken from NBS Circular 500[14] and for B_2O_3(amorph) from a report by Wagman *et al.*[15]

The values of $\Delta H_f(g)$ were calculated using the heats of vaporization of triethylborane[16] and tri-n-propylborane.[6]

The values for B—R average bond energy, $\bar{D}(B—R)$, were calculated for the reaction:

$$BR_3(g) \longrightarrow B(g) + 3R(g)$$

The heat of formation of B(g) was from Searcy and Myers[17] and of R(g) was calculated from Stevenson's data.[18]

For comparison the $\Delta H_f(g)$, $\Delta H_f(l)$, and $\bar{D}(B—R)$ for trimethylborane and tri-*n*-butylborane were calculated as above using the ΔH_c data of Long and Norrish[11] and Tannenbaum,[12] respectively. These values are listed in Table II.

EXPERIMENTAL

Materials. Ethyl, *n*-propyl, and *n*-butyl bromide were washed with water, dried over anhydrous sodium sulfate and distilled. The refractive indices of the purified bromides were n_D^{20} 1.4242, 1.4341, and 1.4399, respectively. Matheson boron trifluoride, 97% pure, was used directly from the cylinder. The ethyl ether was dried over calcium hydride. The butyl ether was percolated through a column packed with activated aluminum oxide and dried over calcium hydride.

Preparation. Tri-n-butyl and tri-n-propylborane. A modification of the procedure of Johnson, Snyder, and Van Campen[19] was used. The preparation of tri-*n*-butylborane is described to illustrate the procedure.

n-Butylmagnesium bromide was prepared in a 5-gal. stainless steel reactor by the addition of 20 moles of *n*-butyl bromide in 3 l. of ethyl ether to 20 moles of magnesium turnings in 2 l. of ethyl ether. The Grignard solution was stored in a 5-gal. tank under nitrogen until needed. An ether solution of boron trifluoride etherate was prepared by the slow addition, with stirring, of 6 moles of boron trifluoride to 2 l. of ethyl ether at 10°.

The apparatus for the preparation of tri-*n*-butylborane consisted of a 12-l. three-neck flask equipped with a stirrer, a large capacity stainless steel condenser, and a graduated

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(11) L. H. Long and R. G. W. Norrish, *Phil. Trans. Roy. Soc. London*, **A241**, 587 (1949).

(12) S. Tannenbaum and P. F. Schaeffer, *J. Am. Chem. Soc.*, **77**, 1385 (1956).

(13) F. D. Rossini, *et al. Selected Values of Properties of Hydrocarbons*, Natl. Bur. Standards Circ., C461, November 1947.

(14) F. D. Rossini, *et al. Selected Values of Chemical Thermodynamic Properties*, Circ. 500, Natl. Bur. Standards, February 1, 1952.

(15) D. D. Wagman, T. L. Munson, W. H. Evans, and E. J. Prosen, *Thermodynamic Properties of Boron Compounds*, Rept. 3456, Natl. Bur. Standards, August 30, 1954.

(16) G. T. Furukawa, *Heat Capacity, Heats of Fusion and Vaporization and Vapor Pressure of Triethylborane*, Natl. Bur. Standards, Rept. 3712, February, 1, 1955.

(17) A. W. Searcy and C. E. Myers, *J. Phys. Chem.*, **61**, 957 (1957).

(18) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(19) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., *J. Am. Chem. Soc.* **60**, 115 (1938).

dropping funnel. The entire apparatus was enclosed in a dry box under a nitrogen atmosphere.

Three liters of Grigard solution were siphoned into the 12-l. flask from the storage tank. Then boron trifluoride etherate solution was added with stirring at such a rate (about 250 ml./hr.) as to promote vigorous refluxing. After approximately 650 ml. of the boron trifluoride etherate solution had been added, the reaction mixture separated quite suddenly into two layers, the bottom layer apparently consisted of Grignard solution and magnesium salts. This layer, which was black with white saltlike solid suspended throughout it, reacted vigorously with water, evolving gas. The clear pale yellow top layer showed no reaction with water and was apparently an ether solution of tri-*n*-butylborane. This top layer was siphoned into a large separatory funnel through a tube having a sintered-glass disk fused on one end to act as a filter. When the entire top layer had been removed, another 3-l. portion of Grignard reagent was added to the reaction flask, and the entire procedure was repeated. A total of 8300 ml. of Grignard solution and 5.9 moles of boron trifluoride etherate was used. There was a slight excess of Grignard reagent remaining after the last of the boron trifluoride had reacted.

The top layers obtained from the above reaction were washed in the separatory funnel with a saturated aqueous solution of ammonium chloride and then with water. Finally the ether solution was transferred to a distillation flask, and the ether was removed by vacuum distillation. The liquid residue, which contained a small amount of salt, was filtered. The total weight of crude produce was 989 g.; the yield was 91% based on boron trifluoride.

Triethylborane. Ten moles of this compound were prepared in a 5-gal. reactor by the method of Krause and Nitsche.[4] Throughout the entire operation a positive pressure of helium was maintained in the reactor to exclude oxygen.

Purification. The crude reaction products were distilled through a 22-mm. by 6-ft. Podbielniak column. The entire distillation setup was enclosed in a dry box inerted with helium.

Triethylborane was distilled at atmospheric pressure, while tri-*n*-propylborane and tri-*n*-butylborane were distilled at pressures of 20 and 10 mm., respectively. Triethylborane and tri-*n*-propylborane were successfully distilled, but tri-*n*-butylborane decomposed during distillation. The decomposition products of tri-*n*-butylborane adulterated the distillate besides causing the column to flood continuously. Lowering the pot temperature about 20° by lowering the distillation pressure did not noticeably decrease the decomposition or the flooding. By rapidly distilling the tri-*n*-butylborane through an 18-in. glass-helix packed column, the amount of decomposition was reduced. However, the distillate was not considered to be sufficiently pure to warrant the measurement of its properties.

Physical properties. Samples of triethylborane and tri-*n*-propylborane of 99.8 and 99.7 mole % purity, respectively, were used to obtain values for the following physical properties.

Freezing point. The freezing points were determined by means of a solenoid-stirred freezing point apparatus charged with 10-ml. samples. The apparatus was loaded and sealed in a dry box inerted with helium; subsequent operations were conducted outside the box. The thermometric system consisted of a 25-ohm platinum resistance thermometer, a resistance bridge (Mueller type), and a highly sensitive galvanometer. The freezing point and the freezing point at zero impurity were obtained by analysis of the freezing curves.[20,21] These data, together with the values of the heat of fusion, were used to calculate the purity of the samples.[21] Duplicate determinations of the freezing point on a given sample differed by not more than 0.002°.

Boiling point. The boiling points were determined in an ebulliometer[22] equipped with a platinum resistance thermometer. The measurements were made in a helium atmosphere with an estimated accuracy of ±0.1°.

Refractive index. The refractive indices were measured with a Bausch and Lomb precision Abbé refractometer enclosed in a dry box with a helium atmosphere. Measurements were made at 20.0 ± 0.1° and 30.0 ± 0.1° and three wave lengths of light at each temperature. The spectral lines used were the sodium D (5893A), the mercury Hg_g (5460.7A), and the mercury $\text{Hg}_{\text{b.v.}}$ (4358.3A). The estimated accuracy of the measurements was ±0.0001.

Density. The densities were measured with a modified Lipkin pycnometer. The modification consisted of fusing a standard taper male joint onto the ends of the pycnometer. These ends could then be capped with a female joint equipped with a small stopcock. Once the pycnometer was filled, it could be closed off without disturbing the level of the sample in the arms. The pycnometer was loaded and sealed in a dry box inerted with helium. The densities were measured outside the box at 20.00° ± 0.05° and 30.00° ± 0.05° with an estimated accuracy of ±0.0002 g. per ml.

Dielectric constant. The dielectric constants were measured in a cell of 25-ml. capacity. After being filled in the dry box, the cell was sealed off and removed from the box for the capacity measurements. Measurements of the dielectric constant were made at 20.0° ± 0.1° and 30.0° ± 0.1° with a probable accuracy of ±0.2%. The dielectric constant apparatus has been previously described.[23]

Thermodynamic properties. Heat of combustion. Heats of combustion were determined for triethylborane and tri-*n*-propylborane in a Parr adiabatic calorimeter with an Illium constant-volume bomb.[24] Temperatures were measured with a mercury thermometer (calibrated by the Natl. Bur. of Standards) which could be read to ±0.005°F. The bomb was calibrated using standard benzoic acid supplied by the Parr Instrument Co. Because of their volatility and susceptibility to oxidation, the samples of trialkylboranes were introduced into the bomb in small thin-walled glass bulbs. In the first few runs the glass bulbs were suspended on an iron ignition wire, and the bomb was charged with 30 atm. of oxygen. Combustion was initiated by passing current through the iron wire. The heat generated ruptured the bulb and ignited the sample. Complete combustion was not realized with this method. Apparently the trialkylborane would flow out of a crack in the bulb and burn. The oxides formed would then impede sample flow and combustion would not be completed.

Better combustion was obtained by sealing the iron ignition wire through the wall of the glass bulb so that it passed through the interior of the bulb. The section of ignition wire inside the bulb was filed thin in one spot to ensure a hot spot at this point. Even with this method combustion often was poor. In over fifty runs only three were considered good.

Completeness of combustion was determined by visual inspection of the interior of the bomb and by analyses of the combustion gases for carbon dioxide and of the residue for boron oxide and boric acid. In the good runs the combustion of boron was 99 to 100% complete, and carbon was from 90 to 100% complete. Hydrogen combustion was assumed to be 100% in all cases. Corrections were made for unburned material on the assumption that it was exclusively

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[20] W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).

[21] A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[22] L. C. Gibbons, *et al.*, *J. Am. Chem. Soc.*, **68**, 1130 (1946).

[23] A. P. Altshuller and L. Rosenblum, *J. Am. Chem. Soc.*, **77**, 282 (1955).

[24] *Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods*, Parr Manual No. 120, Parr Instrument Company, Moline, Ill.

elemental amorphous carbon and boron. Additional corrections were made to fit the bomb combustion to the over-all process at 25°:

$$BCH_{(liq.)} + O_{2(gas,\ 1\ atm)} \longrightarrow CO_{2(gas,\ 1\ atm)} + H_2O_{(gas,\ 1\ atm)} + B_2O_{3(amorph)}$$

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[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

Compounds Related to 2,3,4-Triphenylbutyric Acid[1]

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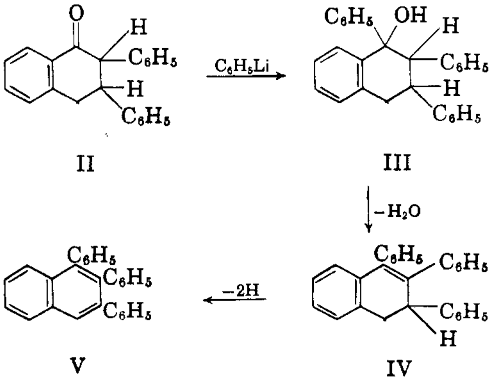
The structure of a by-product in the preparation of 2,3-diphenyltetralone from 2,3,4-triphenylbutyric acid, has been shown to be I. Various compounds related to the ester are described.

Several years ago, in the preparation of 2,3-diphenyltetralone[2,3] for use in other studies, traces of a compound I melting at 211–212° were obtained in several reactions. In one reaction in which the tetralone was prepared by treating 2,3,4-triphenylbutyryl chloride with anhydrous aluminum chloride, the yield of I was 18 g., 12% based on the weight of acid used. Analyses for carbon and hydrogen agreed with the values calculated for the tetralone but the molecular weight was much too high. Only one form of the tetralone, that melting at 147–148°, has been reported although many people have reported making it and diastereoisomers should be possible.

A series of reactions was planned which would test the hypothesis that I was an isomeric tetralone. The 147° tetralone II was treated with phenyllithium to give a new tertiary alcohol III. This alcohol was dehydrated to give the known 1,2,3-triphenyl-3,4-dihydronaphthalene[4] IV which was then dehydrogenated to give the known 1,2,3-triphenylnaphthalene[4] V. Earlier[3] the tetralone had been reduced to a secondary alcohol by aluminum isopropoxide and this alcohol had been dehydrated and dehydrogenated to give 2,3-diphenylnaphthalene.



These two series of reactions, applied to I, should have led to the same final products if I had been an isomeric tetralone. Aluminum isopropoxide was without effect on I. Phenyllithium reacted with I to give two products, neither of which could be dehydrated by heating with Lucas' reagent or with potassium hydrogen sulfate. Since I was not an isomeric tetralone, the problem was temporarily dropped.

Interest in I was aroused again when it was shown[5] that 2,3,4-triphenylbutyric acid could be cyclized by hydrogen fluoride to give a small amount of 2-phenyl-3-benzylindanone as well as the more common tetralone.

From the infrared spectrum of I, Dr. Gilbert Stork of Columbia University suggested to us that the carbonyl group might be presented as an ester. This proved to be the case. The ester resulted from the reaction of unconverted acid chloride with the enol form of the tetralone. The following chart shows the relationships of the compounds involved.

Hydrolysis of I led to the known acid VI and a neutral oil which could not be crystallized but whose infrared spectrum indicated that it was the known tetralone II. Reaction of I with phenyllithium gave the known ketone VIII[6] and a compound VII whose properties indicate that it may be isomeric with the ketone VIII. Ketone VIII was synthesized by the reaction of phenylmagnesium bromide on either the 87° or the 130° nitrile IX.[2,3] Mixed melting points showed no depression and the infrared spectra were the same. Under forcing conditions phenylmagnesium bromide also reacted with I to give VIII. The

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[1] Presented at the fall meeting of the American Chemical Society in Atlantic City in September 1959.

[2] H. M. Crawford, J. C. Davidson, and M. A. Plunkett, *J. Am. Chem. Soc.*, **66**, 2010 (1944).

[3] H. M. Crawford and H. B. Nelson, *J. Am. Chem. Soc.*, **68**, 134 (1946).

[4] F. Bergmann, D. Schapiro, and H. E. Eschinazi, *J. Am. Chem. Soc.*, **64**, 559 (1942).

[5] D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, **80**, 3409 (1959).

[6] E. Bergmann, D. Winter, and W. Schreiber, *Ann.*, **500**, 122 (1933).