

proximately parallel position is 0.88  $D$ , and in the approximately antiparallel position 2.28  $D$ . If the  $C_{ar}Cl$  moment is located, following Meyer,<sup>44</sup> at a point seven-eighths of the distance from carbon to chlorine, and the  $C_{ar}SiMeH_2$  moment at the silicon atom, the difference between the energies of the approximately parallel and anti-parallel positions as given by the formula of Jeans<sup>45</sup>  $V = \mu_1\mu_2(\cos \chi - 3\cos\alpha_1\cos\alpha_2)/R^3$ , where  $\chi$  is the angle between the dipoles and  $\alpha_1$  and  $\alpha_2$  are the angles between the dipole axis and the line along which  $R$  is measured, amounts to 0.5 kcal. per mole, or  $0.8kT$  at 25°. Although the energy difference is small, the difference between the moments is pronounced, and a rough calculation using a weighted average of their horizontal components showed it to be sufficient to account for the deviation of the observed moment from the calculated value.

The value for the  $C_{ar}SiH$  moment, 0.41  $D$ , reported here is obtained from two much larger values, the chlorophenyl moment and the over-all dipole moment of *m*-chlorophenylsilane. For this reason the calculated value for the  $C_{ar}SiH$  moment is relatively insensitive to changes in the over-all moment. Furthermore a direct inductive effect from the *meta* position and an opposing indirect effect resulting from resonance of the chlorine with the adjacent *ortho* and *para* positions may affect the measured moment. By the use of a strongly

(44) L. Meyer, *Z. physik. Chem.*, **8B**, 27 (1930).

(45) J. H. Jeans, "Electricity and Magnetism," The University Press, Cambridge, 1920, p. 354; quoted by J. W. Smith, work cited in footnote 32, p. 284.

electron-withdrawing substituent on the phenyl group the direction of the  $C_{ar}SiH$  moment has been clearly established, but at the price of some uncertainty in its magnitude. In this connection it may be noted, however, that the value for the  $Me-SiC_{ar}$  moment calculated from *m*-chlorophenyltrimethylsilane is in agreement with the dipole moment of trimethylphenylsilane.<sup>34,35,41</sup>

The value found for the  $C_{ar}SiH$  group moment comprises two bond moments,  $SiC_{ar}$  and  $SiH$ , the sum of which is directed away from the ring. This result definitely implies that the negative end of the  $SiH$  dipole is toward the hydrogen; the reverse supposition, requiring silicon to be so strongly electronegative that it would withdraw electrons from the ring to an extent sufficient to outweigh an  $HSi$  moment directed toward silicon, is most unlikely.

The direction, but not the magnitude, of the  $SiH$  bond moment has been established. To determine its magnitude a knowledge of that of the  $SiC_{ar}$  moment would be required. Petro and Smyth<sup>43</sup> have reported a value of 0.84  $D$  for this moment, though with reservations. It was based on one of 0.2  $D$  for the  $MeSi$  moment,<sup>13</sup> based in turn on one of 1.0  $D$  for the  $SiH$  moment.<sup>13</sup> If the  $C_{ar}SiH$  moment is 0.41  $D$ , directed away from the ring, and the  $SiC_{ar}$  moment is 0.84  $D$ , directed toward the ring, then  $Si-H$  must be 1.25  $D$ . Considering all the assumptions involved, the agreement is surprisingly good.

**Acknowledgment.**—The authors are indebted to Dr. O. K. Johansson for many helpful discussions

[CONTRIBUTION FROM THE OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT]

## Synthesis of Diborane by the Hydrogenolysis of Trialkylborons<sup>1a</sup>

BY RALPH KLEIN,<sup>1b</sup> ARTHUR BLISS, LOUIS SCHOEN<sup>1b</sup> AND HERBERT G. NADEAU

RECEIVED JANUARY 16, 1961

A new synthesis of diborane is obtained by the hydrogenolysis of trialkylborons. Reaction temperatures from 150° and hydrogen pressures of 1500 to 2000 p.s.i. give good diborane yields starting with trimethyl or trialkylborons. Catalysts are effective in shortening the reaction time and lowering the temperature required, although the maximum yield does not appear to be affected. The success of the synthesis is due to the inhibiting effect of hydrogen on the diborane pyrolysis. A reversible reaction between initial decomposition product and hydrogen accounts for this inhibition and leads to a maximum in the diborane yield.

The chemistry of the boranes has become increasingly important in recent years. In particular, contributions to various areas of technology have been made by selective utilization of the higher boron hydrides and their derivatives.<sup>2</sup> In order to prepare these compounds, a primary synthesis of diborane generally is required. Furthermore, for those applications which demand an appreciable quantity of end product, the production of diborane by an efficient, inherently simple and economical process is essential. The background and details of a new method for the preparation of diborane, suited to these requirements, will be described.

(1) (a) This work was completed in 1956 and security restrictions removed in 1960. (b) National Bureau of Standards, Washington, D. C.

(2) Dallas T. Hurd, "An Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952.

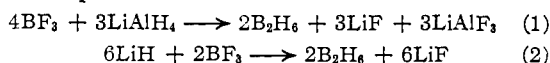
### Introduction

The boron hydrides were first prepared by the acid hydrolysis of powdered metal borides.<sup>3</sup> This is a low yield process giving poorly characterized products. Subsequently, it was found that circulation of a mixture of a boron halide and hydrogen through a high-voltage discharge at pressures between 5 and 10 mm. resulted in the formation of chlorodiborane which disproportionated into diborane and the original halide during fractionation at 0°.<sup>4</sup> Conversions of 30% per pass and yields averaging 55% were obtained. The process was suitable only for the production of relatively small quantities of product. The preparation of diborane

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, and B. D. Steele and J. E. Mills, *J. Chem. Soc.*, 74 (1930).

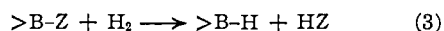
(4) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).

in quantity was made possible by the discovery that a metallic hydride and a boron halide will react in anhydrous diethyl ether solution according to the equations<sup>5</sup>



For large-scale production, however, these reactions have certain disadvantages, among which are the costly recycle process involving recovery of the alkali metal and the handling of large quantities of diethyl ether.

We have found that diborane can be synthesized in good yields by the reaction of hydrogen with the trialkylborons. The method was suggested in part by simple thermodynamic considerations. The hydrogenolysis of a boron compound is represented by



A criterion of feasibility is that  $D(\text{H-Z}) - D(\text{B-Z})$  be greater than, equal to or not much less than  $D(\text{H-H}) - D(\text{B-H})$ ,  $D$  being the bond energy and  $Z$  an appropriate element. This of course neglects the important entropy and kinetic considerations, but it serves as a useful guide in indicating which compounds merit further study. Some bond energies pertinent to the discussion are listed in Table I. The data indicate that B-C bonds are likely to undergo successful hydrogenolysis, as is the case for B-B bonds.

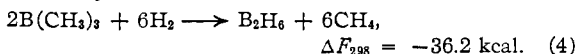
TABLE I<sup>a</sup>

BOND ENERGIES (KCAL.) FOR ASSESSING THE HYDROGENOLYSIS OF B-Z COMPOUNDS

Z	$D(\text{H-H}) - D(\text{B-H}) = 12 \text{ kcal.}$		
	$D(\text{B-Z})$	$D(\text{H-Z})$	$[D(\text{H-Z}) - D(\text{B-Z})]$
C	89	99.5	10.5
N	90	80	-10
S	115	81	-34
O	185	117	-68
F	153	134	-19
Cl	106	102	-4
Br	89	89	0.3
I	71	73	2.7
B	69	93	24

<sup>a</sup> Data from Cottrell, "The Strength of Chemical Bonds," and W. H. Evans, D. D. Wagman and E. J. Prosen, N.B.S. Report No. 6252, 1958.

Trimethylboron is one of the simplest compounds containing B-C bonds, and its thermodynamic properties have been evaluated.<sup>6</sup> The reaction with trimethylboron is



This is highly favorable thermodynamically, but the kinetic parameters are lacking. Diborane, however, is unstable with respect to decomposition to its elements, with  $\Delta F_{298} = -19.6 \text{ kcal.}$  Reaction 4 must be effected under conditions such that extensive diborane decomposition is avoided. The kinetics of the pyrolysis of diborane have been

(5) H. I. Schlesinger and H. C. Brown, U. S. Patents 2,543,511 and 2,544,472.

(6) W. H. Evans, D. D. Wagman and E. J. Prosen, N.B.S. Report 4943, "Thermodynamic Properties of Some Boron Compounds," Aug. 31, 1956.

studied<sup>7,8</sup> and found to occur at conveniently measurable rates above 80° with an activation energy of the rate-controlling step of 25 kcal./mole. The observation of Clarke and Pease<sup>7</sup> that hydrogenolysis considerably decreases the rate of diborane pyrolysis suggests that the hydrogenolysis reaction be carried out at high hydrogen pressures. A slightly favorable mass action effect with respect to diborane production is associated with reaction 4.

### Experimental

The initial experiments were the circulation of mixtures of trimethylboron and hydrogen at atmospheric pressure over various catalysts with an all glass pump. Over a temperature range up to 300°, all attempts to prepare diborane were unsuccessful. Methane was recovered with a few catalysts indicating that some reaction had occurred. It must be assumed that the diborane had decomposed completely under the reaction conditions employed. An attempted liquid phase hydrogenolysis using palladium black with tributylboron at temperatures up to 200° was also ineffective.

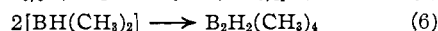
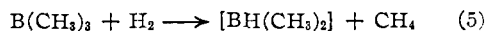
The high pressure reactions, on the other hand, give high yields and provide a new synthesis of diborane. A 105 ml. thermostatted stainless steel autoclave was used for the experiments. It was flushed with nitrogen prior to the introduction of the alkyl borane. Hydrogen was added to an appropriate pressure. The mixture was heated and maintained at the reaction temperature for several hours. It was established that the trialkylboron heated to 200° for 1 hr. in the presence of effective catalysts, but without hydrogen, could be recovered quantitatively. Therefore, for closer control of reaction time, the initial charge, less hydrogen, could be heated and then the hydrogen added. The reaction products were collected by venting through liquid nitrogen cooled traps. The condensables were measured after warm-up and determined by infrared analysis. In some experiments the reaction was quenched by sharing the reaction volume with a previously evacuated vessel, the contents of the latter then being recovered and analyzed.

Trimethyl- and triethylboron were prepared by reaction of the appropriate alkylmagnesium halide with boron trifluoride in butyl ether.<sup>9</sup> Tri-*n*-butylboron was prepared in ethyl ether solution from *n*-butylmagnesium bromide and boron trifluoride.<sup>10</sup> Trimethylboron was purified by fractionation. Triethylboron b.p. (758 mm.) 95.2-95.5°, reported<sup>8</sup> b.p. (20 mm.) 94-97° and tri-*n*-butylboron b.p. (14 mm.) 100-101°, reported<sup>9</sup> b.p. (9 mm.) 90-91°, (20 mm.) 108-110° were purified by distillation in an inert atmosphere using a three-foot spinning band column.

Several commercial catalysts were tested for efficacy. Also tested were Raney nickel W-2, prepared by the method of Mozingo,<sup>11</sup> and palladium black prepared by the formaldehyde reduction of palladium chloride by a technique similar, except for the omission of the carrier, to that of Mozingo<sup>12</sup> for the preparation of barium sulfate-supported palladium. Data, some of which are given in Tables II through VI, were obtained. The results for the three trialkylborons are shown in Table II. Table III illustrates the effect of temperature. The reaction time was varied from 0.5 to 12 hr. with the results shown in Table IV. The effect of the initial hydrogen pressure and trialkylboron concentration on the yield is shown in Table V.

### Discussion

It is probable that reaction 4 occurs stepwise by way of methylsubstituted diboranes. These undergo disproportionation and further hydrogenolysis.



(7) R. P. Clarke and R. N. Pease, *J. Am. Chem. Soc.*, **73**, 2132 (1951).

(8) J. K. Bragg, L. V. McCarty and F. J. Norton, *ibid.*, **73**, 2134 (1951).

(9) H. C. Brown, *ibid.*, **67**, 374 (1945).

(10) J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **60**, 115 (1938).

(11) R. Mozingo, "Organic Syntheses," Coll. Vol. III, p. 181.

TABLE II  
VARIATION OF ALKYL GROUP AND DIBORANE YIELD  
 $2R_3B + 6H_2 \longrightarrow B_2H_6 + 6RH$

R	Weight, g.	Pd black catalyst, mg.	H <sub>2</sub> , p.s.i.g.	Temp., °C.	Time, hr.	RH %	Yield, B <sub>2</sub> H <sub>6</sub> %	Remarks
CH <sub>3</sub>	2.5	40	2200	180	12	0	0	(CH <sub>3</sub> ) <sub>3</sub> B 100%
CH <sub>3</sub>	2.5	40	2200	210	12	90	60	White solid
C <sub>2</sub> H <sub>5</sub>	2.6	50	2100	150	12	93	75	
C <sub>4</sub> H <sub>9</sub>	3.0	40	2150	150	12	0	0	(CH <sub>3</sub> ) <sub>3</sub> B 100%
C <sub>4</sub> H <sub>9</sub>	3.7	40	2100	200	12	70	30	Glassy solid

TABLE III  
TRIETHYLBORON HYDROGENOLYSIS—EFFECT OF TEMPERATURE, Pd BLACK CATALYST

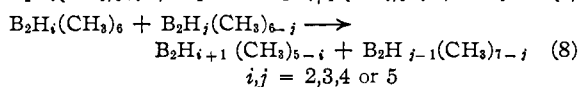
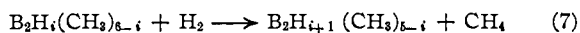
Et <sub>3</sub> B, g.	Pd black, mg.	H <sub>2</sub> , p.s.i.g.	Temp., °C.	Time, hr.	Yield, % EtH	Yield, % B <sub>2</sub> H <sub>6</sub>	Other
1.4	38	1700	190	5	90.3	47.8	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	40	1700	195	5	87.8	42.1	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	39	1700	206	5	86.4	17.8	Yellow solid

TABLE IV  
REACTION TIME AND ITS EFFECT ON DIBORANE YIELD

Et <sub>3</sub> B, g.	Pd black, mg.	H <sub>2</sub> , p.s.i.g.	Temp., °C.	Time, hr.	Yield, % EtH	Yield, % B <sub>2</sub> H <sub>6</sub>	Other
1.4	34	2000	200	0.5	69.8	22.0	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	40	1980	200	1	95.6	70.2	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	40	1950	200	4	95.3	50.9	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	50	2150	200	12	90	58	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z

TABLE V  
PRESSURE VARIATION AND ITS EFFECT ON DIBORANE YIELD

Et <sub>3</sub> B, g.	Cat., mg.	H <sub>2</sub> , p.s.i.g.	Temp., °C.	Time, hr.	Yield, % RH	Yield, % B <sub>2</sub> H <sub>6</sub>	Other
A—Hydrogen							
1.4	50	500	200	12	85	15	Yellow solid
1.4	50	1600	200	12	91	60	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
1.4	50	2150	200	12	90	58	Et <sub>2</sub> B <sub>2</sub> H <sub>6</sub> -z
B—Triethylboron							
3.4	51	1700	200	5	90.7	26.4	Yellow solid
4.7	53	1700	200	5	87.3	8.9	Yellow solid



Reaction 6 is a consequence of the stability of the B-H-B bridge structure. Reactions 7 in conjunction with (8) lead finally to diborane. It may be suggested that the hydrogenolysis occurs by (5), followed by a series of disproportionations found to occur for the methyl diboranes by Schlesinger, *et al.*<sup>14,15</sup> The system of reversible reactions leads to the establishment of an equilibrium involving diborane and all its methyl derivatives.<sup>16,17</sup> The

(12) Ref. 12, p. 685.

(13) H. G. Nadeau and D. M. Oaks, *Anal. Chem.*, **32**, 1480 (1960).

(14) H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 621 (1935).

(15) H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

(16) W. J. Lehman, C. O. Wilson and I. Shapiro, *J. Chem. Phys.*, **32**, 1088 (1960), also note that disproportionation of monomethyl diborane occurred at such a rate that within fifteen minutes at room temperature the infrared spectrum showed traces of diborane and 1,2-dimethyl diborane.

(17) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

rates of the set 7 with respect to the set 8 have not been determined.

The success of the synthesis of diborane described here can be attributed in part to the inhibiting effect of hydrogen on the diborane pyrolysis. According to the data of Bragg, *et al.*,<sup>8</sup> the decomposition of diborane at 150° would be fairly rapid with  $k = 45$  l./mole hr. for hydrogen formation. Since in some of the experiments described previously a 12 hr. reaction time at 150° did not adversely affect the diborane yield, the observation of Clarke and Pease<sup>7</sup> on the inhibition of the diborane pyrolysis by hydrogen is confirmed and extended.

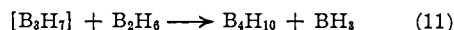
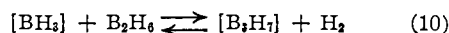
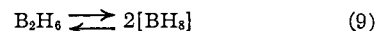
Low diborane yields invariably were accompanied by white or yellow solids, the latter indicative of even lower yields than the former. The degradation of B<sub>2</sub>H<sub>6</sub> results in such solids and their further decomposition proceeds finally to boron and hydrogen. These solids are mixtures of the higher diboranes including polymers with a relatively high boron-to-hydrogen ratio. A detailed knowledge of the complex diborane pyrolysis is lacking.

Some further generalizations on the hydrogen plus trialkylboron reaction may be made. It is clear that high temperatures and long reaction times have in general an adverse effect. The best catalyst among those tried is palladium black. The hydrogenolysis can be carried out at 200° and high hydrogen to trialkylboron ratios without a catalyst to give only a slightly less yield than at 150° with a catalyst. This is shown in Table VI.

Triethylboron, according to Table II, undergoes hydrogenolysis more easily than trimethylboron. This may reflect the greater ease of breaking a secondary, compared with a primary, carbon bond. The butyl compound is complicated because of the probable presence of the reactant as a liquid.

Extensive data were not obtained on the detailed effect of reaction time, but Table IV shows that at 200° the reaction is complete in one hour, at least with respect to ethane formation. The diborane yield passes through a maximum at 1 hr. according to Table IV, and then decreases to a constant value.

The formation of diborane by the hydrogenolysis of the trialkylboron is followed by an equilibrium between diborane, its pyrolytic products, and hydrogen. The initial reactions proposed for the diborane pyrolysis<sup>7</sup> are



A more complete understanding of the thermal degradation of diborane is required in order to characterize the hydrogenation reactions. It is

TABLE VI  
 EFFECT OF CATALYST

Et <sub>3</sub> B, g.	Catalyst	H <sub>2</sub> , p.s.i.g.	Temp., °C.	Time, hr.	EtH, %	B <sub>2</sub> H <sub>6</sub> , %	Remarks
1.4	None	1620	150	10	7.6	0	Et <sub>3</sub> B, Et <sub>2</sub> B <sub>2</sub> H <sub>2</sub> also present in products
1.4	None	1580	200	10	90.7	63.8	Glass liner in vessel
1.4	None	1600	200	10	89.6	67.8	No liner
2.6	Pd black, 50 mg.	2100	150	12	93	75	

recognized that the diborane decomposition is complicated by heterogeneous reactions. A suitable catalyst must be effective for the trialkylboron hydrogenation but ineffective for the decomposition of diborane. Some catalysts such as palladium black

are quite satisfactory. As noted, a catalyst is not required for the diborane synthesis, and it is probable that even higher temperatures and hydrogen pressures will result in good yields in reasonably short times.

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIFORNIA]

### Thermal Stability of Substituted Borazoles<sup>1</sup>

BY H. C. NEWSOM, W. D. ENGLISH, A. L. McCLOSKEY AND W. G. WOODS

RECEIVED FEBRUARY 14, 1961

The thermal degradation of a series of substituted borazoles has been carried out at 370–525°, in order to determine the effect of substituents on the stability of substituted borazoles and the mode of their pyrolytic decompositions. The following order of increasing thermal stability was observed at 450°: B-triphenyl-N-trimethylborazole < hexaphenylborazole < B-trimethyl-N-triphenylborazole < B-triphenylborazole < hexamethylborazole. Product analyses indicate that boron-carbon homolysis is the primary step in most cases, but hexaphenylborazole decomposition may proceed through initial boron-nitrogen cleavage.

#### Introduction

A few reports have been published on the thermal stabilities of substituted borazoles, but no systematic investigation of their decomposition products or relative stabilities has been presented. Borazole has been reported<sup>2</sup> to undergo slow decomposition in the liquid phase at room temperature to produce hydrogen, diborane and a non-volatile solid. The authors pointed out the apparent difference in rate of decomposition in the liquid and the vapor phase, the former being more rapid. At 300°, borazole was completely decomposed<sup>3</sup> in 1 hr. At higher temperatures (340–475°) B-bis-(amino)-borazole and the borazole analogs of biphenyl and naphthalene were identified<sup>4</sup> among the solid products from borazole pyrolysis. The B-triethylborazole decomposed below 100°, whereas B-trimethylborazole was reported<sup>3</sup> to be stable at that temperature for extended periods. Hexamethylborazole was reported<sup>5</sup> to survive treatment at 480°. The thermal decomposition of a series of alkyl- and aryl-substituted borazoles has been studied in an attempt to gain an insight into the effect of structure on the stability of substituted borazoles and to determine their decomposition mechanisms.

(1) This research was sponsored by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contracts AF 33(616)-5931 and AF 33(616)-7303. It was presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) R. O. Schaeffer, M. Steindler, L. F. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 3303 (1954).

(3) D. T. Haworth and L. F. Hohnstedt, *ibid.*, **82**, 3860 (1960).

(4) A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *ibid.*, **83**, 1337 (1961).

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

#### Results and Discussion

The method followed involved treatment of the various borazoles in evacuated sealed ampoules at high temperatures, followed by analysis of products and recovery of unreacted starting material. The results are listed in Table I.

TABLE I  
 PYROLYSIS PRODUCTS OF SUBSTITUTED BORAZOLES,  
 (RBNR')<sub>3</sub>

R	R'	Conditions	Products (mole/mole reactant)
C <sub>6</sub> H <sub>5</sub> -	CH <sub>3</sub> -	420–450°, 4 hr.	H <sub>2</sub> (1.5) + CH <sub>4</sub> + C <sub>6</sub> H <sub>6</sub> (0.36) + C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (0.02)
C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -	440–490°, 15 hr.	C <sub>6</sub> H <sub>6</sub> (1.5) + H <sub>2</sub> (0.2–0.4) + N <sub>2</sub> (0.2–0.4) + C <sub>6</sub> H <sub>5</sub> NHNHC <sub>6</sub> H <sub>5</sub> (0.08) + C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub> (0.02)
CH <sub>3</sub> -	C <sub>6</sub> H <sub>5</sub> -	435–440°, 3 hr.	Gas (1.46) + 37% recovery <sup>a</sup>
		430–490°, 3 hr.	CH <sub>4</sub> (1.1) + H <sub>2</sub> (0.66)
C <sub>6</sub> H <sub>5</sub> -	H-	425–475°, 15 hr.	C <sub>6</sub> H <sub>6</sub> (2.2)
CH <sub>3</sub> -	CH <sub>3</sub> -	435–475°, 3 hr.	100% recovery <sup>a</sup>
		520–525°, 3 hr.	50% recovery <sup>a</sup>

<sup>a</sup> Unchanged starting material.

No volatile boron-containing decomposition products were identified, so the nonvolatile residues must have contained most of the original boron. The color of these residues in most cases precluded the presence of appreciable quantities of boron carbide or carbon. It seems likely that linked and fused ring compounds may have remained unidentified in the nonvolatile products (*cf.* ref. 4).

Part of the solid residue from B-triphenyl-N-trimethylborazole pyrolysis gave an elemental analysis and a molecular weight corresponding to starting material but exhibited quite different physical properties. A thermal reaction involving elimination of hydrogen and formation of a five-membered ring was postulated to explain these data.