

TABLE VI
 EFFECT OF CATALYST

Et ₃ B, g.	Catalyst	H ₂ , p.s.i.g.	Temp., °C.	Time, hr.	EtH, %	B ₂ H ₆ , %	Remarks
1.4	None	1620	150	10	7.6	0	Et ₃ B, Et ₂ B ₂ H ₂ 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.

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Thermal Stability of Substituted Borazoles¹

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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 reported² 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 decomposed³ in 1 hr. At higher temperatures (340–475°) B-bis-(amino)-borazole and the borazole analogs of biphenyl and naphthalene were identified⁴ among the solid products from borazole pyrolysis. The B-triethylborazole decomposed below 100°, whereas B-trimethylborazole was reported³ to be stable at that temperature for extended periods. Hexamethylborazole was reported⁵ 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.

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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.

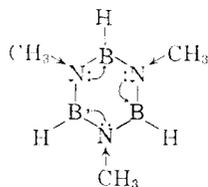
TABLE I
 PYROLYSIS PRODUCTS OF SUBSTITUTED BORAZOLES,
 (RBNR')₃

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

^a 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.



phenylborazole. In the case of B-triphenyl-N-trimethylborazole and B-trimethyl-N-triphenylborazole, which have *ortho* methyl groups, this interaction is eliminated by the inability of the phenyl rings to achieve coplanarity with the borazole nucleus.

It is instructive to consider the thermal stability of substituted borazoles in the light of these data on their electron distribution and steric requirements. In order to assess relative stabilities, conditions were chosen that would provide a convenient spread in amount of decomposition. When the various borazoles were heated in sealed ampoules at 450° for 3 hr., the order of thermal stability shown in Table III was observed.

TABLE III

RELATIVE THERMAL STABILITY OF SUBSTITUTED BORAZOLES, (RBNR')₃

Compound	R	R'	% Decomposed
I	C ₆ H ₅ -	CH ₃ -	100
II	C ₆ H ₅ -	C ₆ H ₅ -	77.5
III	CH ₃ -	C ₆ H ₅ -	73.5
IV	C ₆ H ₅ -	H-	15
V	CH ₃ -	CH ₃ -	0
VI	H-	CH ₃ -	0
VII	CH ₃ -	H-	0

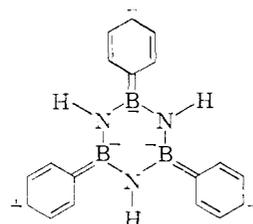
As was mentioned earlier, the formation of benzene from all B-phenylborazoles made it appear that the boron-carbon bond is vulnerable. In the case of compound I, B-triphenyl-N-trimethylborazole, the pi cloud of the phenyl group is not aligned with the *p*-orbital of boron, due to the *ortho* effect of the N-methyl groups. Strengthening of this bond by tautomeric donation from phenyl to boron would therefore be eliminated and boron-phenyl homolysis could occur with relative ease.

Compound II, hexaphenylborazole, has phenyl substituents on nitrogen and would be expected to achieve very little aromatic character in the borazole ring because of the electron withdrawing effect of the (non-conjugated) phenyl group. The fact that this compound produced nitrogen and hydrazobenzene on pyrolysis indicates that the decomposition may have proceeded through initial cleavage of the boron-nitrogen single bonds of the borazole ring (*vide supra*). This type of cleavage also would be facilitated by the fact that each fragment from the first homolysis would be stabilized by the same type of resonance as has been demonstrated¹² to be important for benzyl free radicals. Thus it is not surprising that hexaphenylborazole is one of the least stable of the compounds investigated. Borazole aromaticity is lost also in B-trimethyl-N-triphenylborazole (III) because of the inductive effect of the phenyl group, but it appears that the borazole ring does not rupture

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as readily in this case as in compound II (no nitrogen, benzene or hydrazobenzene produced), perhaps because of poorer stabilization of the resultant radicals. In addition, the steric situation is probably somewhat better in compound III than in hexaphenylborazole.

A much more stable situation was encountered in the case of B-triphenylborazole (IV). Here, borazole aromaticity is probably maintained to some extent by the inductive effect of the phenyl group. The tautomeric electron release of phenyl would serve to strengthen the boron-carbon bonds, but the boron-nitrogen skeleton would thereby be weakened due to reduction of double bond character in the borazole ring. The stability of the



compound is considered to result from a favorable balance between the requirements of the borazole ring and those of the boron-carbon bonds.

The most stable compound investigated was hexamethylborazole (V). The ability of the N-methyl groups to function as electron sources decreases the tendency of the nitrogen atoms to maintain localization of their unshared electrons, so that considerable aromatic character is maintained in the borazole nucleus. At the same time, the boron-carbon bond is relatively electron-rich (compared with compound I).

Compounds V, VI and VII were observed to be completely vaporized during the 450° pyrolysis suggesting that their apparent stabilities may have resulted from being entirely in the gas phase (as has been pointed out in the case of unsubstituted borazole).² The true stability of hexamethylborazole was verified by recovering it unchanged after treatment in the liquid phase at 385-405° for 24 hr.—conditions which led to complete decomposition of B-triphenyl-N-trimethylborazole. The high volatilities of compounds VI and VII precluded similar liquid phase treatment, so that their true position in regard to liquid phase stability is still uncertain.

Experimental

Materials.—All of the borazoles investigated were prepared by known methods and purified by distillation, sublimation or crystallization. Their identities were established by comparison of melting points with published values and by their infrared spectra. The thermal decompositions were carried out in Pyrex ampoules which had been flamed *in vacuo*, charged with sample in a dry box, evacuated and flushed with oxygen-free dry nitrogen several times, then evacuated again and sealed. The samples were heated at 385-525°, then cooled and opened into an evacuated system of known volume which contained a cold trap and manometer. From a consideration of the possible gaseous products of the pyrolysis, hydrogen, nitrogen and methane were concluded to be the only products which would be non-condensable at -196°. In the absence of methane, which could be identified by infrared analysis, the relative amounts of the other two species were calculated from a determination

of the average molecular weight of the gas. The work up of the less volatile materials involved sublimation and recrystallization techniques. The procedure was varied for duplicate runs on the same borazole so that resolution was attempted on each mixture by a variety of methods. Some solid materials remained unidentified in most cases. These were non-volatile glasses and wide-melting powders and probably consisted of complex mixtures of various structures analogous to those described by Laubengayer.⁴ In the following sections, only the operations which led to identifiable compounds are described; the other resolution attempts have been omitted in the interest of brevity.

Pyrolysis of Hexaphenylborazole.—Hexaphenylborazole, 1.484 g. (2.93 mmoles), m.p. 406–412°, lit.^{13,14} m.p. 421–423°, 413–415°, was treated at 450–470° for 15 hr. The ampoule was cooled to room temperature and opened into an evacuated system containing a –78° trap. Unidentified gas, noncondensable at –78°, was evolved and a colorless solid was collected in the –78° trap. This solid, which was liquid at room temperature, was identified as benzene by infrared and gas chromatographic analysis. A colorless solid, 8.7 mg., m.p. 71–72°, was recovered from the reaction mixture by sublimation at 210° (0.2 mm.). The infrared spectrum of this solid was identical with an authentic sample of biphenyl. The sublimation residue was triturated with tetrahydrofuran, the soluble material isolated and extracted with ether and the ether-soluble fraction recrystallized from benzene-petroleum ether to yield 24 mg. of colorless solid, m.p. 126–131° (lit.¹⁵ m.p. for hydrazobenzene: 126–129°). The infrared spectrum of the material matched that of hydrazobenzene.

In another trial, 895.3 mg. (1.665 mmoles) of hexaphenylborazole was pyrolyzed at 440–480° for 15 hr. The tube was cooled and opened into an evacuated system and 0.479 mmole of gas, non-condensable at –196°, was collected. Since the gas had no absorption in the infrared, it was concluded that no methane was present and the gas consisted of hydrogen and nitrogen. An average molecular weight of 12.6 was obtained, indicating an approximately equimolar mixture of the two gases. Recrystallization of the non-gaseous reaction products from benzene and petroleum ether did not yield pure compounds.

A 1.515-g. sample of hexaphenylborazole (2.82 mmoles) was treated at 450–490° for 15 hr. The cooled tube was opened into an evacuated system and 2.12 mmoles of gas, non-condensable at –196°, was evolved. On the basis of the previous experiment, this gas was assumed to be hydrogen and nitrogen. Benzene (4.21 mmoles) was collected in the –78° trap. A small amount of colorless solid was also obtained, m.p. 69–71° (presumably biphenyl). No sharply melting components could be isolated by recrystallization of the solid residue.

Pyrolysis of B-Triphenyl-N-trimethylborazole.—B-Triphenyl-N-trimethylborazole, 606 mg. (1.73 mmoles) m.p. 261–267°, lit.¹⁶ m.p. 270°, was heated at 420–450° for 4 hr. The tube was opened into an evacuated system containing a trap at –196°, and 2.59 mmoles of noncondensable gas was collected. The infrared spectrum of this gas indicated the presence of a trace of methane, and the average molecular weight observed was 5.04. This fact precluded the presence of an appreciable quantity of nitrogen, and it was therefore concluded that approximately 2.5 mmoles of hydrogen had been observed. The condensable gases were not investigated at this point, but the reaction tube was heated to 100° under vacuum, and 53 mg. of a volatile liquid was obtained. Gas chromatographic analysis indicated that the liquid was a mixture of 93% benzene and 7% toluene. The residue was a yellow powder, m.p. 110–115° with gas evolution. Sublimation at 250° (1 mm.) gave a glassy residue and a wide-melting sublimate which could not be resolved by recrystallization.

A sample of 411.9 mg. (1.175 mmoles) of B-triphenyl-N-trimethylborazole was sealed in an evacuated tube as usual and heated with the ampoule of hexamethylborazole described below, under "Liquid Phase Pyrolysis of Hexamethylborazole" (385–405° for 24 hr.). Unidentified non-condensable gas, 0.205 mmole, and methane (identified

by its infrared spectrum), 0.155 mmole, were evolved when the ampoule was opened. Several wide-melting fractions were obtained by sublimation and recrystallization of the reaction solids, but no starting material was recovered.

Analysis of Product from B-Triphenyl-N-trimethylborazole Pyrolysis.—The glassy residue produced by treatment of B-triphenyl-N-trimethylborazole at 405–420° for 48 hr. was heated at reduced pressure and a sample collected at 175–240° (0.25 mm.). The distillate was a green glass and had the following properties: m.p. 60–72° (m.p. (C₆H₅BNCH₃)₃: 265–267°); mol. wt. (cryoscopic in benzene), 345 (mol. wt. (C₆H₅BNCH₃)₃: 350).

Anal. Calcd. for C₂₁H₂₄B₃N₃: C, 71.88; H, 6.89; B, 9.25; N, 11.98. Calcd. for C₂₁H₂₂B₃N₃: C, 72.29; H, 6.36; B, 9.30; N, 12.05. Found: C, 71.08; H, 6.33; B, 9.11; N, 12.1.

A 303.5-mg. sample (0.88 mmole) of this distillate was added to a solution of 154.8 mg. of silver nitrate in 3.0 ml. of water plus sufficient 10% ammonium hydroxide to dissolve the precipitate. An immediate exothermic reaction occurred, causing the solution to boil, and the reaction mixture became black. Sodium hydroxide (0.7 g.) was added and a black insoluble material was separated by filtration. The filtrate was extracted with ether and the ether evaporated to yield a yellow oil. Distillation of the oil produced benzylamine, identified by infrared and gas chromatographic analysis.

Pyrolysis of B-Trimethyl-N-triphenylborazole.—B-Trimethyl-N-triphenylborazole, 543.5 mg. (1.548 mmoles), m.p. 263.6–269°, lit.¹⁴ m.p. 267–269°, was pyrolyzed in the usual manner at 435–440° for 3 hr. When the ampoule was cooled and opened, 103.5 mm. of unidentified gas was obtained in an 82-ml. system, corresponding to 1.46 moles of gas per mole of borazole. The reaction solids were sublimed at 200° (1 mm.) to give 350 mg. of sublimate and 60 mg. of residue. The volatile fraction, on recrystallization from toluene, yielded 200 mg. of needles, m.p. 257–264°. The infrared spectrum agreed with that of B-triphenyl-N-trimethylborazole, indicating a recovery of 37% unreacted material.

In another run, 319.8 mg. (0.912 mmole) of B-trimethyl-N-triphenylborazole was heated at 430–490° for 3 hr. The reaction tube was opened into an evacuated system and the gases passed through a liquid nitrogen trap. A pressure of 259 mm. resulted in the 82 ml. system, and a mass spectral analysis made on the gas gave these values in mole per cent.: H₂, 52.9; CH₄, 45.4; C₂H₆, 0.8; C₂H₂, 0.5; n-C₄H₁₀, 0.3; C₆H₆, 0.1. When the liquid nitrogen bath was removed, the pressure immediately increased to 345 mm. The infrared spectrum of the total gaseous material matched that of methane, so it was concluded that the gas which was freed by removal of the liquid nitrogen bath was methane. The gaseous products, therefore, consisted of 1.01 mmoles of methane and 0.61 mmole of hydrogen.

Pyrolysis of B-Triphenylborazole.—A 287-mg. sample (0.93 mmole) of B-triphenylborazole, m.p. 180–182°, lit.¹⁷ m.p. 181–182.5°, was heated at 425–475° for 15 hr. When the reaction tube was opened into an evacuated system, 161 mg. (2.06 mmoles) of benzene was obtained in a liquid nitrogen trap (identified by infrared and gas chromatographic analysis). No noncondensable gas was observed. The residue in the reaction tube, 100 mg., was a shiny black brittle material.

Pyrolysis of Hexamethylborazole.—Hexamethylborazole, 429.3 mg. (2.61 mmoles), m.p. 97.6–99°, lit.⁵ m.p. 97°, was treated at 435–475° for 3 hr. The sample, which was entirely gaseous during the pyrolysis, solidified on cooling, and no gases were evolved when the reaction tube was opened at room temperature. The solid which was collected weighed 430 mg., m.p. 91–97°, and had an infrared spectrum identical with that of starting material.

Hexamethylborazole, 312.2 mg. (0.633 mmole), was pyrolyzed at 520–525° for 3 hr. The reaction tube contained a yellow gas which condensed to a light yellow solid on cooling. When the cooled tube was opened, 0.211 mmole of an unidentified gas was evolved. The solid was recrystallized from diethyl ether and 20–40° petroleum ether to yield 160 mg. of material, m.p. 80–95°. Its infrared spectrum indicated it to be slightly impure starting material.

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

Liquid Phase Pyrolysis of Hexamethylborazole.—An ampoule was charged with 318.5 mg. (19.4 mmoles) of hexamethylborazole and sealed as usual. The tube was then heated to 400°, and a major portion of the material was observed to be in the liquid phase; heating was continued at 385–405° for 24 hr. When the tube was cooled and opened, no gases were evolved. Sublimation of the solid at 100° (0.8 mm.) produced 296.8 mg. of hexamethylborazole, m.p. 96–100°.

Relative Thermal Stabilities of Borazoles.—The ampoules were charged and sealed as described earlier, then heated for 3 hr. in a fused salt bath maintained at 450 ± 2°. The cooled tubes were opened into an evacuated system containing a -196° trap, manometer and molecular weight bulb. The temperature of the trap was raised to -78°, and the pressure increase due to liberated methane (infrared identification) in the 131-ml. system was recorded.

I. B-Triphenyl-N-trimethylborazole.—A sample of 478.8 mg. (1.365 mmoles) of B-triphenyl-N-trimethylborazole produced 0.212 mmole of noncondensable gas after pyrolysis. Increasing the trap temperature to -78° liberated 0.25 mmole of methane. Sublimation of the reaction solids at 200° (0.1 mm.) produced a non-volatile clear yellow glass, 86 mg., and a white volatile solid. Recrystallization procedures on the latter fraction produced only wide-melting materials, and no unreacted starting material was isolated. A clear liquid, 15.5 mg., was collected in a trap maintained at -78° during the sublimation. On the basis of its odor and the results of a previous experiment (see above), this liquid was assumed to be benzene (0.199 mmole).

II. Hexaphenylborazole.—On opening a sample of 178 mg. (0.332 mmole) of hexaphenylborazole after pyrolysis, 0.028 mmole of gas was obtained. The -78° trap in the vacuum line contained 7.0 mg. of liquid (0.09 mmole, assuming benzene as before). The solid, 120 mg., was recrystallized from tetrahydrofuran-petroleum ether to give 40 mg. of powder, m.p. 385–397°. The infrared spectrum matched that of hexaphenylborazole.

III. B-Trimethyl-N-triphenylborazole.—Pyrolysis of B-trimethyl-N-triphenylborazole, 301.9 mg. (0.861 mmole) produced a total of 0.106 mmole of gas. Sublimation of the solid at 185–195° (0.1 mm.) left 9.0 mg. of a clear yellow glassy residue. The sublimate, m.p. 230–255°, was recrystallized from benzene to give 80 mg. of B-trimethyl-N-triphenylborazole, m.p. 260–265°.

IV. B-Triphenylborazole.—No gases were evolved from the ampoule after reaction of 340.8 mg. (1.104 mmoles) of B-triphenylborazole under the conditions described above. The solid was sublimed at 200° (0.1 mm.) giving 290 mg. of sublimate, m.p. 177–180° (85.4% recovery). In a second trial, 235.6 mg. (0.746 mmole) of B-triphenylborazole produced a total of 0.11 mmole of gas. Sublimation of the solid at 180° (0.1 mm.) gave 20½ mg. of sublimate, m.p. 175–180° (87% recovery). A small amount of clear yellow resin remained as a residue.

V. Hexamethylborazole.—A sample of hexamethylborazole, 162.5 mg. (2.96 mmoles) produced 0.018 mmole of gas and 171.4 mg. of solid, m.p. 95.8–98.6° (105% recovery).

VI. N-Trimethylborazole.—Pyrolysis of a 209.5-mg. sample (1.71 mmoles), b.p. 128–130°, lit.¹⁸ b.p. 134°, produced a total of 0.0776 mmole of gas.

VII. B-Trimethylborazole.—A 224.2-mg. sample (1.835 mmoles) of this borazole, b.p. 128–129°, m.p. 31.4–32.2°, lit.¹⁹ b.p. (extrap.) 129°, m.p. 31.5°, produced no gaseous material, and 218 mg. of solid, m.p. 32–33° (97.3% recovery), was obtained.

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Molecular Addition Compounds of Boron. V. Proton Chemical Shifts and the Stability of Adducts^{1,2}

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The proton chemical shifts in some boron-containing addition compounds of Lewis bases in which the donor atom has an ethyl substituent have been measured in an attempt to correlate the separation of the absorptions due to the methylene and methyl protons of the ethyl groups with the stability of the addition compounds. The n.m.r. spectra of a number of other molecular addition compounds of boron were also examined in order to try to correlate the chemical shifts of methyl protons in adducts of methyl substituted bases, and the chemical shifts of B-methyl protons of adducts of trimethylboron, with the strengths of the donor-acceptor bonds in the various complexes. The results show that the chemical shift criterion is not uniformly successful in predicting the stabilities of addition compounds.

The simple qualitative description of the formation of molecular addition compounds by electron donor-acceptor interactions implies that the electron-attracting power of the donor and acceptor atoms in an adduct will be somewhat different from that in the free Lewis base and acid, and will depend in part upon the strength of the coordinate bond. On these grounds, the empirical relationship⁴ between the electronegativity of substituents and the internal chemical shifts⁵ in ethyl deriva-

tives was applied recently to an investigation of the triethyl derivatives of aluminum and gallium and their diethyl etherates.⁶ The results of that study indicated that the apparent electronegativity of the Group III acceptor atom is diminished by complex formation and that the electronegativity of the donor atom is increased with increasingly strong coordination.

These results, if generally applicable, suggest that the internal chemical shift might provide a welcome new technique for establishing the relative stabilities of molecular addition compounds, applicable to those cases in which the acid or base, or both, are ethyl-substituted. Furthermore, the relation between electronegativity and chemical group and is taken as positive when the methyl absorption is at higher applied field.

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(2) The work described in this paper was made possible by the award of a grant (G14610) from the National Science Foundation.

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(5) The term internal chemical shift refers to the separation of the absorptions due to the methylene and methyl protons of an ethyl