were extracted with methylene chloride. The extracts were dried, filtered, and stripped. The residues were stirred with methanol and the mixtures were filtered. Further purification was effected by recrystallization from heptane. Properties of the products are listed in Table IV.

Transition Metal Phenyltris(1-pyrazolyl)borates. To 100 g (1.46 moles) of pyrazole stirred in 240 ml of toluene was added over 2 hr a solution of 20 g (0.12 mole) of phenyldichloroborane in 35 ml of toluene. The reaction was exothermic, the temperature of the solution rising to 45–55°. The solution was cooled to room temperature and was stirred with 170 ml of a 0.5 *M* solution of the appropriate cation. The resulting mixture was filtered and the product was recrystallized from *o*-dichlorobenzene. The original toluene solution was stripped to dryness and the residue was triturated with ether to yield a second crop of the same material. Properties of the products are summarized in Table IV.

Transition Metal Difluorobis(3,5-dimethyl-1-pyrazolylborates). To sodium 3,5-dimethylpyrazolide (prepared from 16 g (0.167 mole) of 3,5-dimethylpyrazole and sodium hydride) in 300 ml of dry tetrahydrofuran was added 0.083 mole of boron trifluoride etherate and the reaction mixture was refluxed overnight. It was then evaporated to dryness, taken up in water, and extracted once with benzene. The benzene extracts were discarded. The aqueous layer was divided into two halves which were treated, respectively, with 40-ml portions of 0.5 *M* $Ni(OAc)_2$ and $Co(OAc)_2$ solutions. The precipitated solids were filtered, washed with water, and air dried.

The orange nickel chelate, obtained in 1.8 g (10%) yield, was purified by sublimation, mp 349–350°.

Anal. Calcd for $C_{20}H_{28}B_2F_4NiN_8$: C, 44.7; H, 5.22; N, 20.9; F, 14.2. Found: C, 44.6; H, 5.25; N, 20.9; F, 14.9.

The deep violet cobalt chelate, obtained in 1.8 g (10%) yield, was purified by chromatography on alumina, eluting with methylene chloride. The pure compound melts at 279–280°.

Anal. Calcd for $C_{20}H_{28}B_2CoF_4N_8$: C, 44.7; H, 5.22; N, 20.9. Found: C, 44.6; H, 5.09; N, 20.6.

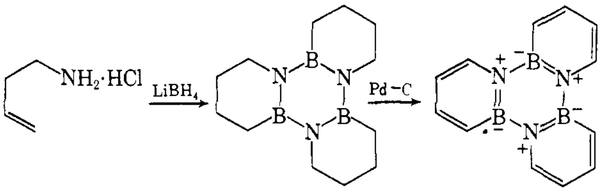
New Heteroaromatic Compounds. XXVI.[1] Synthesis of Borazarenes[2]

Keith M. Davies,[3] Michael J. S. Dewar,[4] and Peter Rona

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received July 24, 1967*

Abstract: Hydrolysis of 14,16,18-tribora-13,15,17-triazarotriphenylene (II) gave bis(2-borazaryl) ether which reacted with phenylmagnesium bromide to give 2-phenylborazarene and with lithium aluminum hydride to give, apparently, borazarene. Other derivatives of borazarene were obtained by reactions of I with lithium alkyls.

An earlier paper of this series[5] described the synthesis of 14,16,18-tribora-13,15,17-triazarotriphenylene (II) by the route given in eq 1. Treatment of II with alkali led to its rapid destruction, as indicated by the disappearance of the characteristic triphenylene-like absorption in the ultraviolet spectrum, and it was thought at that time that the reaction had in fact led to a fission of the central borazine ring of II to give three molecules of 2-hydroxyborazarene (IIIa). This seemed a very interesting observation, for previous studies of the "borazaro" series of heteroaromatics had shown these to be compounds of remarkable stability to hydrolysis and oxidation[6] and it seemed very likely that the same would prove true of borazarene itself. Since in compounds of this kind hydroxyl attached to boron can be replaced[6] by alkyl, aryl, or hydrogen by treatment with appropriate organometallic reagents or metal hydrides, a synthesis of IIIa would be expected to provide a very general route to other borazarene derivatives. Previously only two derivatives of borazarene had been reported, methyl β-(2,3-diphenyl-5-borazaryl)propionate (IV)[7] and 2-phenylborazarene (IIIb),[8] both of which were obtained by routes that could not easily be generalized. We have therefore reexamined the reaction of II with alkali, establishing that it does indeed lead to IIIa, and we have studied the preparation and properties of various borazarene derivatives derived in this or analogous ways from II.



I II (1)

The first problem was the synthesis of II itself. Not only were the yields in the original synthesis very low at each of the two key steps (<20%), but they were also very erratic; more often than not, the reactions failed completely. We have therefore reexamined the hydroboration of aminobutene and the dehydrogenation of I to II in detail, using a very wide variety of conditions, hydroborating agents, and dehydrogenation catalysts. The conditions reported here still give poor yields, but these are at least reproducible. It should be added that attempts to dehydrogenate I by chemical means (sulfur, selenium, manganese dioxide, etc.) were uniformly unsatisfactory.

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[1] Part XXV: M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc.*, **89**, 2408 (1967).

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

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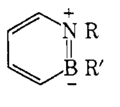
[5] G. C. Culling, M. J. S. Dewar, and P. A. Marr, *J. Am. Chem. Soc.*, **86**, 1125 (1964).

[6] See M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964); M. J. S. Dewar in Advances in Chemistry Series, No. 42, K. Niedenzu, Ed., American Chemical Society, Washington, D. C., 1964, p 227.

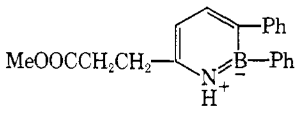
[7] M. J. S. Dewar and P. A. Marr, *J. Am. Chem. Soc.*, **84**, 3782 (1962).

[8] D. G. White, *ibid.*, **85**, 3634 (1963).

Alkaline hydrolysis of II gave a colorless crystalline material which appeared to be the anhydride or ether (IIIc) of IIIa; the mass spectrum showed a strong parent peak corresponding to IIIc, together with a peak corresponding to 2-hydroxyborazarene (IIIa). The initial product was therefore probably IIIa, which underwent dehydration during purification by sublimation; this kind of behavior is well known among borazaro compounds containing a hydroxyl attached to boron.[6] Unfortunately the compound resinified so rapidly on standing, even in an inert atmosphere, that we could not obtain elemental analyses. The structure was confirmed by its conversion with phenyllithium to IIIb, apparently identical with the material described by White.[8]



IIIa, R = H; R′ = OH
b, R = H; R′ = Ph
c, R = H; R′ = ½O
d, R = R′ = H
e, R = H; R′ = Me
f, R = H; R′ = *n*-Bu
g, R = CH$_2$Ph; R′ = Ph



IV

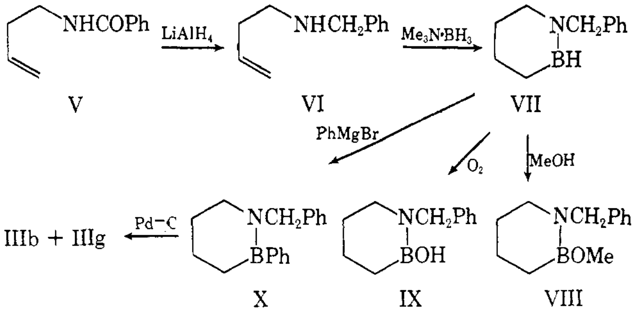
Polycyclic analogs of IIIa or IIIc can be reduced to the parent BH compounds with lithium aluminum hydride;[6] similar treatment of IIIa in ether gave a solution whose mass spectrum showed only weak peaks for IIIa or IIIc, but a strong new peak at mass number 79, corresponding to borazarene (IIId). Unfortunately all attempts to isolate this failed, since it also resinified rapidly, even in an inert atmosphere.

Since the hydrolysis of II to III involves a nucleophilic attack by alkali, we next studied the reactions of II with organolithium compounds in the hope of obtaining 2-substituted borazarenes directly. Indeed, treatment of II with phenyllithium gave IIIb and treatment with methyl- or *n*-butyllithium gave oils that appeared from mass spectrometric analysis to be mixtures of IIIa or IIIc with the corresponding 2-alkylborazarenes, IIIe and IIIf. Here again we were unable to isolate the compounds in pure condition since they resinified so readily.

Attempts to prepare IIId directly, from II and metal hydrides, also failed. The only conditions under which reaction took place was with sodium hydride in tetrahydrofuran. Since lack of II forced us to work on a very small scale and since IIId is apparently unstable to glc, we could not separate the product from the solvent. However an immediate reaction took place on adding benzyl bromide to the solution containing II and sodium hydride and on further addition of phenylmagnesium bromide (which in analogous cases is known to replace by phenyl a hydrogen atom attached to boron) a compound was obtained which appeared to be 1-benzyl-2-phenylborazarene (IIIg). The mass spectrum showed peaks of *m/e* 154 (phenylborazarene (IIIb) − H) and 91 (benzyl), corresponding to rupture of IIIg at the benzyl–nitrogen bond, as would be expected, and the proton nmr spectrum showed aromatic absorption (δ 7.2–7.7) together with a sharp singlet at δ 2.95, the ratio of integrated absorptions being approximately that expected for IIIg. We were unfortunately unable to obtain elemental analyses for IIIg since it resinified rapidly, even in an inert atmosphere; this is in remarkable contrast to the corresponding compound with hydrogen in place of benzyl, *i.e.*, 2-phenylborazarene (IIIb). Another curious feature of IIIg was the ease with which it sublimed; it could be sublimed under vacuum at temperatures as low as 30°. This behavior seems unreasonable for a material with so high a molecular weight (calculated for IIIg, 245); yet a Rast determination gave a value (291) of the expected order. The structure of IIIg was in any case established by an independent synthesis (see below).

The difficulty experienced in preparing II led us to try numerous other routes, all of which were uniformly unsuccessful. One of these involved dehydrogenation of 1-benzyltetrahydroborazarene (VII) which we hoped would lead directly to II, by loss of benzyl. We were able to obtain VII in excellent yield by hydroboration of 4-benzylamino-1-butene (VI), which in turn was readily prepared by reduction of the corresponding benzamide (V) with lithium aluminum hydride; however, all attempts to dehydrogenate VII, using a variety of conditions and catalysts, failed. It was interesting to find that VII underwent immediate oxidation in air to form the corresponding borinic acid IX and that it reacted with methanol exothermically to give the corresponding methoxy derivative VIII; this is in remarkable contrast to the corresponding aromatic compounds where hydrogen attached to boron is rather inert (Scheme I).

Scheme I



We were, however, able to use VII to synthesize IIIg by an unambiguous route. Phenylmagnesium bromide reacted with VII to give 1-benzyl-2-phenyltetrahydroborazarene; dehydrogenation of this over palladized charcoal gave a mixture of IIIg, identical with that prepared from II, together with some of the debenzylated analog IIIb.

Borazarene therefore seems to be a very reactive and chemically unstable system, prone to polymerization and other reactions; this is in marked contrast to its polycyclic analogs,[6] most of which are stable indefinitely in air and resist attack by boiling concentrated hydrochloric acid or strong alkali. The stability of borazarene can apparently be somewhat enhanced by phenyl groups attached to nitrogen or boron, for IIIb is certainly much less reactive than borazarene or its alkyl or hydroxyl derivatives, and the same is true of the only other derivative of borazarene that has previously been reported, *i.e.*, IV. This extra stabilization is presumably due to conjugation between the benzene and borazarene rings; in IIIg, where the "*ortho*" benzyl groups will force the rings out of coplanarity, the stability is again low.

This is a very disappointing conclusion, for derivatives of borazarene could be of biological interest if they were stable. The novel boron-containing aromatics described in this series of papers are derived from "normal" aromatics by replacing pairs of adjacent carbon atoms by boron–nitrogen or boron–oxygen and the physical properties of the boron-containing analogs are similar to those of the "normal" aromatics to which they are related. Analogs of biologically active benzene derivatives might therefore show biologically interesting properties. The stable boron-containing heterocycles described in previous papers[1,5] of this series were nearly all related to normal aromatic systems that do not as a rule occur in living matter and so are of much less interest from the biological standpoint.

Experimental Section

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-14,16,18-tribora-13,15,17-triazarotriphenylene (I). (*Note:* this preparation must be carried out with carefully dried, freshly distilled solvents in baked-out apparatus, with exclusion of all traces of air and moisture.) The apparatus consisted of two three-necked flasks, (A) 0.5 l. and (B) 2 l., each equipped with a sintered-glass inlet tube and a magnetic stirrer, the outlet from A being connected to the inlet of B. In addition, A had a pressure-equalized dropping funnel and B a condenser with mercury trap. A solution of sodium borohydride (14.7 g) in diglyme (300 ml) was placed in the dropping funnel, one of boron trifluoride ethereate (80 g) in diglyme (40 ml) in A, and one of 4-amino-1-butene (21.2 g) in toluene (1 l.) in B. The apparatus was thoroughly flushed out with argon and a slow stream of argon passed through A and B; the stirrers were started and B was cooled in an ice–salt bath. The borohydride solution was then added dropwise to it over 2 hr, the ice–salt bath removed, and the reaction continued at room temperature for 18 hr. The solution in B was then boiled under reflux for 24 hr, the ether from the boron trifluoride ethereate and other low-boiling products being allowed to escape. The solvent was then distilled and the residue crystallized from acetone–benzene, giving I (6.52 g, 27%), mp 183–184° (lit.[5] mp 184–186°). The mass spectrum showed a parent peak at *m*/*e* 243. The nmr spectrum ($CDCl_3$) showed peaks at δ 0.8–1.15 (broad multiplet), 1.2 (singlet), 1.33 (singlet), 1.4–1.75 (broad multiplet), and 3.07–3.33 (broad multiplet).

14,16,18-Tribora-13,15,17-triazarotriphenylene (II). A mixture of I (3.0 g), palladized charcoal (0.6 g of 10%), and 1-hexene (15 ml) was heated in a stainless-steel autoclave under argon for 22 hr at 315–325°. The product was isolated with chloroform and chromatographed with hexane–methylene chloride on alumina (Baker, 60 g). The product (1.3 g, mp 110–130°) was rechromatographed from pentane on neutral alumina and then crystallized from hexene, giving pure II (0.24 g), mp 196.5° (lit.[5] mp 193–195°). The nmr spectrum ($CDCl_3$) showed a triplet at δ 6.45 (J = 6.5 Hz), a doublet at 6.99 and 7.17, a quartet at 7.68, 7.78, 7.86, 7.96, and a doublet at 8.07 and 8.19. The ultraviolet spectrum (ethanol) showed peaks at 277 nm (log ϵ 4.69), 287 (4.71), 304 (4.03), and 316 (3.80). The compound was homogeneous to glpc (SE-30 column at 230°).

Bis(2-borazaryl) Ether (IIIc). Hydrolysis of II (0.5 g) with alcholic potash (10 ml of 10%) for 20 min, followed by dilution with water and extraction with ether, gave a yellow oil which showed strong peaks on the mass spectrum at *m*/*e* 172 (IIIc), 95 (IIIa), and 94 (IIIa − H). Sublimation at 100° (1 mm) left a crystalline residue which after sublimation at 120° (0.1 mm) formed white crystals, mp 53–59°, showing a strong peak in the mass spectrum of *m*/*e* 172 and weak ones at 95 and 94. The crystals were probably composed of IIIc, contaminated by a little IIIa.

2-Phenylborazarene (IIIb). A. From IIIc. The crude product from II (0.5 g) and alkali was treated in dry ether (50 ml) with phenylmagnesium bromide (25 ml of 3 *M*) and the mixture stirred 30 min at room temperature. Addition of water and evaporation of the ethereal layer left a brown solid which on sublimation and crystallization from petroleum ether (bp 60–68°) gave shining white plates (100 mg), mp 112–114°, which appeared from glpc to be a mixture of IIIb and biphenyl in the ratio 4:1. Chromatography from petroleum ether on alumina gave pure IIIb (25 mg), mp 117–118° (lit.[8] 117–118.5°).

B. From II. A slight excess of ethereal phenyllithium was added to a stirred solution of II (0.5 g) in dry ether at room temperature and a few drops of water were then added. The ether layer was dried and evaporated and the residue then chromatographed from petroleum ether (bp 60–86°) on neutral alumina, giving a trace of biphenyl and some unreacted II. The column was then eluted with benzene, giving IIIb (80 mg), which after sublimation at 100° (1 mm) had mp 113–115°, not depressed by an authentic sample.

Attempted Preparation of Borazarene. A solution of crude IIIa (0.44 g) in ether (30 ml) was added to a suspension of lithium aluminum hydride (0.20 g) in ether (10 ml) and the mixture refluxed 1 hr. Moist ether (20 ml) was then added and the ether evaporated in dry nitrogen to give a pale yellow oil. The mass spectrum showed two strong peaks, one corresponding to IIIa, the other to borazarene (IIId). The latter peak was not present at all in the mass spectrum of IIIa (or IIIb). On glpc, the crude product gave only a single peak, corresponding to IIIa; all attempts to isolate the borazarene on a variety of columns failed.

Reaction of II with Methyllithium. Ethereal methyllithium (5.9 ml of 5.21%) was added to a stirred solution of II (0.65 g) in dry ether (20 ml) at room temperature. After 20 min, a few drops of water were added to coagulate the inorganic salts and the ethereal layer was dried and evaporated, leaving an evil-smelling red oil. Distillation at 70° (30 mm) gave a yellow oil which rapidly darkened in air. The mass spectrum showed strong peaks at *m*/*e* 93 (IIIe), 78 (IIId − H), 52 (C_4H_4 and 39 C_3H_8), together with a peak at 172 (IIIc). The ultraviolet spectrum in ethanol had a strong maximum at 273 nm and a shoulder at 215 nm. The infrared spectrum had bands at 293 (m, N–H), 322–339 (m, C–H), and 6.19 K (C═C).

Reaction of II with *n*-Butyllithium. Analogous treatment of II with *n*-butyllithium gave a yellow oil, n^{28}D 1.5180, whose mass spectrum showed major peaks at *m*/*e* 172 (IIIc), 135 (IIIf), 95 (IIIa), 79 (IIId), and 78 (IIId − H). The ultraviolet spectrum resembled closely that of the methyl analog (peak at 275 nm, shoulder at 216 nm).

4-Benzamido-1-butene (V). Benzoyl chloride (66.5 g) was added to a stirred suspension of 4-amino-1-butene (30.7 g) in 10% aqueous sodium hydroxide (250 ml) at 0° and the mixture stirred overnight at room temperature. Benzoyl chloride (25 g) and 10% aqueous sodium hydroxide (125 ml) were then added and stirring was continued for 24 hr. The benzoyl derivative V was isolated with benzene and distilled at 110° (0.03 mm) as a colorless oil (61.6 g), n^{25}D 1.5460, homogeneous to glpc.

Anal. Calcd for $C_{11}H_{12}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.26; H, 7.42; N, 8.01.

The infrared spectrum showed carbonyl absorption at 1650 K. The nmr spectrum ($CDCl_3$) showed quartets at δ 2.35 and 3.52 (two protons each), complex multiplets at δ 5.1, 5.25, and 5.65 (one proton each), a broad structureless line at 6.55 (NH), and aromatic absorption at 7.3–7.9 (five protons).

4-Benzylamino-1-butene (VI). A solution of V (8.2 g) in dry ether (20 ml) was added to a suspension of lithium aluminun hydride (1.8 g) in dry ether (150 ml) under argon at such a rate as to keep the solution refluxing. After refluxing for 48 hr, the solution was cooled to 0° and water (1.8 ml) added dropwise, followed by 10% aqueous sodium hydroxide (2.7 ml) and then water (14 ml). The ethereal layer was decanted, the residue was washed with ether, the combined ether extracts were evaporated, and the residue was distilled, giving VI (6.17 g) as an oil: bp 74° (1 mm) n^{27}D 1.5130.

Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 81.54; H, 9.49.

1-Benzyltetrahydroborazarene (VII). A solution of VI (6.11 g) in dry xylene (100 ml) was added slowly (0.5 hr) to a boiling solution of trimethylamine–borane (2.77 g) in dry xylene (900 ml) under argon. After refluxing for a further 3 hr, the solvent was distilled under reduced pressure at 80° and the residue fractionated, giving VII (3.2 g); bp 52° (0.02 mm); n^{27}D 1.5229.

Anal. Calcd for $C_{11}H_{16}BN$: C, 76.38; H, 9.26; B, 6.26; N, 8.10; mol wt, 173. Found: C, 76.38; H, 9.53; B, 6.49; N, 8.52; mol wt (mass spectrum), 173.

The infrared spectrum showed strong absorption at 2515 K (BH). On standing in air, the material rapidly underwent oxidation.

1-Benzyl-2-phenyltetrahydroborazarene (X). Ethereal phenylmagnesium bromide (2.9 ml of 3 *M*) was added to a stirred solution of VII (1.05 g) in dry ether (60 ml) under argon. After 3 hr at room temperature, the mixture was boiled under reflux for 0.5 hr and extracted with water, and the ethereal layer was distilled, giving X (1.12 g) as a colorless oil; bp 136° (0.4 mm); n^{25}D 1.5745.

Anal. Calcd for $C_{17}H_{20}BN$: C, 81.95; H, 8.09; B, 4.34; N, 5.62; mol wt, 249. Found: C, 81.86; H, 7.95; B, 4.12; N, 5.80; mol wt (mass spectrum), 249.

The infrared spectrum showed bands at 3060, 3040, 2980, 2855 (CH), 1600 (C–C), and 1500 K (B–N). The ultraviolet spectrum showed end absorption below 275 nm. The nmr spectrum ($CDCl_3$) showed a broad aromatic multiplet at δ 7.3, a sharp singlet at 4.3 ($PhCH_2$), and broad multiplets at 3.6, 2.9, and 1.7 (aliphatic protons in the tetrahydroborazarene ring).

1-Benzyl-2-phenylborazarene (IIIg). A. From II. Sodium hydride (0.18 g, 55% emulsion in heavy oil) was added to a stirred solution of II (0.15 g) in dry tetrahydrofuran under argon. After 1 hr at room temperature, the mixture was heated to 65° for 0.5 hr, benzyl bromide (0.3 ml) was then added, and the mixture was allowed to cool to room temperature. Ethereal phenylmagnesium bromide (1 ml of 3 *M*) was then added, mixture heated to 60° for 0.5 hr, cooled, and treated with water, and the organic layer dried and evaporated. Chromatography of the residue from pentane on neutral alumina gave a crystalline solid (200 mg) which after repeated sublimation at 28° (0.4 mm) had mp 58–60°, but resinified on standing. The nmr spectrum showed aromatic peaks at δ 7.2–7.7 and a sharp singlet at 2.95. The mass spectrum showed strong peaks at *m/e* 154 (IIIb − H) and 91 ($PhCH_2$). The infrared spectrum (KBr disks) showed peaks at 1435, 1480, 1600, 1625, 1645, 2930, and 3030–3060 K. The ultraviolet spectrum in hexane showed a peak at 244 nm (log ϵ 4.39). The molecular weight (Rast) was 291.

B. From X. An intimate mixture of X (0.5 g) and 10% palladized charcoal (0.5 g) was heated in a stream of argon in a sublimator to 210–220° for 6 hr. Extraction with methylene chloride and chromatography from pentane on alumina gave IIIg which after sublimation at room temperature had mp 58–61.5°, mmp 58–60.5°; the ultraviolet, infrared, and nmr spectra were identical with those of the material described above. The alumina column was then eluted with hexane–methylene chloride (3:1), giving IIIb which, after sublimation at 80° (0.5 mm), had mp 115–115.5° (lit.[8] mp 117–118.5°). The infrared spectrum was identical with that reported by White.[8] The nmr spectrum ($CDCl_3$) contains a triplet at δ 6.3 (J = 6 Hz), signals at 7.06, 7.15, and 7.19, three unresolved peaks at 7.32–7.38, and a broad structureless line at 8.1 (NH).

1-Benzyl-2-methoxytetrahydroborazarene (VIII). Addition of VII (1.45 g) to dry methanol (5 ml) led to an exothermic reaction with evolution of hydrogen. Distillation gave VIII (1.42 g) as an oil: bp 99° (0.5 mm); n^{25}D 1.5188.

Anal. Calcd for $C_{12}H_{18}BNO$: C, 70.97; H, 8.93; N, 5.32; mol wt, 203. Found: C, 70.92; H, 8.90; B, 5.16; mol wt (mass spectrum), 203.

1-Benzyl-2-hydroxytetrahydroborazarene (IX). Aerial oxidation of VII gave IX as a colorless crystalline solid which after recrystallization from hexene had mp 107.5–109°.

Anal. Calcd for $C_{11}H_{16}BNO$: B, 5.72; N, 7.41; mol wt, 189. Found: B, 6.02; N, 7.85; mol wt (mass spectrum), 189, (Rast) 185.

Difluorodiazirine. VII. N-Cyanophosphorus Imides and Difluorophosphoranes

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Abstract: Difluorodiazirine reacts with trivalent organophosphorus derivatives to form N-cyanophosphorus imides and difluorophosphoranes. The generality of the reaction has been demonstrated with phosphines, phosphites, thiophosphites, and aminophosphines. The mechanism of the reaction is discussed in terms of primary nucleophilic attack of the phosphorus on a nitrogen atom in CF_2N_2. The N-cyanophosphorus imides undergo reaction with HN_3 to form N-(5-tetrazoyl)phosphorus imides. The stereochemistry of the difluorophosphoranes is examined by F^{19} nmr spectroscopy.

A limited number of recent publications have described the unique ability of trivalent phosphorus derivatives to effect low-temperature defluorination of fluorine bonded to carbon. In the systems in which this rather unusual defluorination has been observed, removal of fluorine from carbon occurs at the position α to a carbonyl[1] or a di- or polysulfide[2] moiety with formation of a phosphorus–fluorine bond. In large part, the chemistry of difluorodiazirine, CF_2N_2, which has appeared in the literature has been that of difluorocarbene generated by photolysis or pyrolysis of this fluorocarbon heterocycle.[3] As a part of our continuing exploratory investigation into the reactions of fluorodiazirines, we would like to report an unprecedented diazirine ring-opening defluorination reaction which is effected by trivalent organophosphorus derivatives. It is appropriate to note that bis(trifluoromethyl)diazirine does not react with triphenylphosphine even under forcing conditions.[4]

Results and Discussion

Difluorodiazirine reacts, in many cases at temperatures below −78°, with trivalent organophosphorus compounds to give N-cyanophosphorus imides, $R_3P{=}NC{\equiv}N$, and difluorophosphoranes, R_3PF_2. In this reaction the phosphorus compound is apparently reacting primarily as a reducing agent yielding the difluorophosphorane as the major by-product. Thus,

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(4) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 3617 (1966).