Sulfur dioxide was Matheson anhydrous reagent and was distilled through a 24-in. column packed with phosphorus pentoxide and glass helices into a reservoir connected to the high vacuum system where it was stored until used.

7-Norbornadienyl chloride (1) was prepared as described previously[8] and purified by g.p.c. immediately before use. A 10 ft. × $^3/_8$ in., 10% didecyl phthalate on Chromosorb-W column was used at 130°.

Silver fluoroborate was obtained from Chemical Procurement Laboratories, Inc., and dried as described earlier.[8]

Preparation of 7-Norbornadienyl Fluoroborate (4).—Anhydrous silver fluoroborate 0.344 g. (1.77 mmoles), was placed, *via* a side arm, into a reaction vessel containing a stirring bar and sealed to a high vacuum system capable of attaining *ca.* 10^{-5} mm. After the side arm was sealed and the chamber was evacuated, the fluoroborate was heated for *ca.* 30 min. to 50–75° by means of an air heater to remove any trace of moisture. The salt was pumped-on for an additional 1.5 hr. A tube containing 0.2025 g. (1.60 mmoles) of 7-norbornadienyl chloride (1) was connected to the same system. This container was cooled, after flushing with argon, in liquid nitrogen and evacuated. After evacuation was complete the container was allowed to warm to room temperature.

The reaction vessel was then cooled by means of a Plexiglas jacket through which cold nitrogen was passed and the chloride 1 was distilled into a chamber directly above the main reaction chamber and separated from it by a break seal. Sulfur dioxide was distilled into this chamber after transfer of the chloride 1 was complete to give a total volume of *ca.* 1 ml.

Sulfur dioxide was also distilled into the reaction chamber to a volume of 6.5 ml. This mixture was stirred and cooled to −70°. The chloride 1 was introduced all at once by breaking the seal with a magnetic bar stored in a side arm. The upper part of the reaction vessel was flushed with additional sulfur dioxide and the total volume of solution was brought to 8 ml. Silver chloride precipitated immediately upon addition of 1. Stirring was continued for 30 min. while the temperature was maintained at −70°.

Approximately 4 ml. of this solution was removed by breaking a seal located below the surface of the solution and leading to a side arm which had been evacuated. The decanted solution was filtered by a fine porosity glass disk located in the side arm and situated so that the solution was filtered vertically through it. The filtration required *ca.* 30 min. To speed up this process, dry argon was introduced into the reaction chamber to create a greater pressure differential. The volume of filtered solution, which was colorless to this point, was reduced to slightly less than 1 ml. to give a solution approximately 0.8 to 1.0 *M* in fluoroborate 4. The concentrated solution, which had become slightly yellow, was passed by means of another break-seal connection through a medium porosity filter into an n.m.r. sample tube and sealed off for analysis.

Acknowledgments.—P. R. S. thanks Dr. Martin Saunders (Yale University) and several of his colleagues in the Chemistry Department, Bell Telephone Laboratories, for many helpful discussions and suggestions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGE WASHINGTON UNIVERSITY, WASHINGTON 6, D. C.]

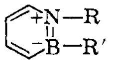
2-Phenyl-2,1-borazarene and Derivatives of 1,2-Azaboracycloalkanes

BY DAVID G. WHITE

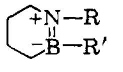
RECEIVED JULY 15, 1963

1-Methyl-2-phenyl-1,2-azaborolidine (IV), the first example of a 1,2-azaboracycloalkane, has been obtained by (a) the reaction of (allylmethylamino)phenylchloroborane (III) with lithium aluminum hydride and (b) by the slow addition of N-methylallylamine to a hot, dilute solution of trimethylaminephenylborane (V) in diglyme. The latter method also afforded 2-phenyl-1,2-azaboracyclohexane (IIa) from 3-butenylamine and V. When refluxed under nitrogen with 30% palladium-on-charcoal, IIa was slowly dehydrogenated to 2-phenyl-2,1-borazarene (Ib). The relative inertness of Ib toward oxidation and solvolysis indicates that the 2,1-borazarene ring is aromatically stabilized.

2,1-Borazaronaphthalene, 10,9-borazarophenanthrene, and numerous derivatives of these compounds have been studied extensively, chiefly by M. J. S. Dewar and co-workers. Their heteroaromatic character is demonstrated by their ultraviolet spectra, their readiness to undergo typical electrophylic substitution reactions, and the resistance of the boron–nitrogen link to solvolysis.[1] However, neither the benzene analog, 2,1-borazarene (Ia), nor any of its simple derivatives have been prepared. Dewar and Marr have reported the preparation of 2,3-diphenyl-6-(2-carbomethoxyethyl)-2,1-borazarene, but this was obtained by a method that does not appear to be of general utility.[2] It occurred to the present author that the dehydrogenation of a 1,2-azaboracyclohexane (II) might serve as a useful route to the 2,1-borazarene ring system, and this paper describes the synthesis of 2-phenyl-2,1-borazarene (Ib) by this procedure.

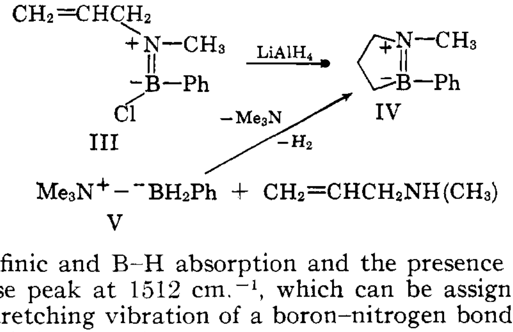


Ia, R = H, R′ = H
b, R = H, R′ = Ph



IIa, R = H, R′ = Ph

No 1,2-azaboracycloalkanes have been previously described. Therefore an initial study was undertaken to prepare a five-membered cyclic aminoborane of this type, namely 1-methyl-2-phenyl-1,2-azaborolidine (IV). This compound has been obtained in two ways. The first scheme involved the prior formation of (allylmethylamino)phenylchloroborane (III) by the straightforward reaction of phenyldichloroborane with N-methylallylamine, with the use of an equivalent amount of triethylamine to facilitate the elimination of hydrogen chloride. The procedure was that which has been employed to prepare a number of aminophenylchloroboranes derived from saturated secondary amines.[3] A 36% yield of IV was then obtained by adding III to a dilute ether solution of lithium aluminum hydride, followed by the introduction of trimethylammonium chloride and benzene, and heating to about 80°. The infrared spectrum of IV showed the absence of olefinic and B–H absorption and the presence of an intense peak at 1512 cm.$^{-1}$, which can be assigned to the stretching vibration of a boron–nitrogen bond with π-bond character.[4]



The reaction described above is thought to involve the intermediate formation (after the addition of

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(1) See P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962), for a review of these and other heterocyclic organic boron compounds and for the rules of nomenclature which are in use.

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

(3) K. Niedenzu and J. W. Dawson, *ibid.*, **82**, 4223 (1960).

(4) See, for example, G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).

trimethylammonium chloride) of an amine complex of phenylborane. Since tertiary amine complexes of borane[5] and *t*-butylborane[6] are known to undergo hydroboration reactions at moderate temperatures, we may expect that in this case the dissociation of the phenylborane complex would lead to hydroboration and (under dilute conditions) ring closure to yield a cyclic amineborane, *i.e.*, the 1,2-dihydro derivative of IV. Warming and the catalytic action of the trimethylammonium ion should then facilitate the loss of hydrogen to give IV. A competing reaction could be the formation of the B-hydridoaminoborane ($CH_2{=}CH{-}CH_2)(CH_3)N^+{=}{}^-BHPh$. However, presuming that this type of compound cannot undergo hydroboration, then its formation must be relatively slow compared to the rate of hydroboration. This seems probable in view of the fact that a diglyme solution of a secondary amine and the trimethylamine complex of an alkylborane, with dialkylammonium ion as catalyst, is reported to require a temperature of 100–150° to evolve trimethylamine plus hydrogen and form the corresponding aminoborane.[7]

In line with these ideas is the preparation of IV in 39% yield by the slow addition of N-methylallylamine to a hot, dilute solution of trimethylaminephenylborane (V) in diglyme.[8] The release of trimethylamine was obvious even at about 70°, suggesting the possibility of hydroboration at this temperature. However, if the cyclic amineborane intermediate had not been removed from the scene by elimination of hydrogen, then a subsequent step could have been the unwanted dihydroboration of phenylborane. Therefore the reaction was conducted at about 130–135°, at which temperature both hydrogen and trimethylamine were slowly evolved. On the other hand, a temperature higher than 135° was avoided during the addition, since this might have promoted the formation of the B-hydridoaminoborane.

A similar procedure afforded 2-phenyl-1,2-azaboracyclohexane (IIa) in higher yield (~50%) from equimolar amounts of 3-butenylamine and V. More dilute conditions and a slightly lower temperature (120–133°) were employed, and the rate of amine addition was slowed nearly to that at which an equivalent amount of hydrogen was evolved.

2-Phenyl-1,2-azaboracyclohexane (IIa) appeared quite stable when refluxed alone (*ca.* 230°) under an atmosphere of nitrogen. However, under the same conditions but with 30% palladium-on-charcoal[9] and with a very slow nitrogen sweep, IIa was slowly but cleanly dehydrogenated to a white, crystalline solid, 2-phenyl-2,1-borazarene (Ib). Its infrared spectrum (in carbon tetrachloride) indicated N–H absorption at 3419 cm.$^{-1}$, no C–H stretching vibrations below 3000 cm.$^{-1}$, and the appearance in the 6-μ region of a new peak at 1618 cm.$^{-1}$. In the ultraviolet this borazarene (in cyclohexane) showed maxima at 244 (ϵ 10,030) and 289 mμ (ϵ 10,860), and its spectrum resembles closely that of 2-phenylpyridine (in ethanol).[10] Pronounced similarities have previously been noted between the ultraviolet spectra of benzo derivatives of 2,1-borazarene and those of the isoconjugate nitrogen heterocycles, *e.g.*, 10,9-borazarophenanthrene and phenanthridine.[1] An examination of the n.m.r. spectrum of Ib (in $CDCl_3$) showed multiplets in the region τ = 2.2–3.7 but no signals at higher field.[11]

Preliminary observations of the chemical properties of Ib show that the solid is stable in air and unaffected (except for slight discoloring) in boiling ethanol solution. This resistance toward oxidation and solvolysis, which is not shared by the parent compound IIa, can be attributed to the aromatic stabilization of the 2,1-borazarene ring. This borazarene does appear to be readily attacked, however, in warm, strongly basic or acidic ethanol–water solutions.

Extensions of this method of synthesis to other 2,1-borazarenes are being explored; for example, it seems likely that the use of an N-alkyl (or N-aryl) 3-butenylamine should lead to the formation of N-substituted borazarenes. Also the availability of the tertiary amine complexes of borane and a variety of alkylboranes[12] suggests the possibility of synthesizing I where R′ is hydrogen or an alkyl group.

Experimental[13]

Reagents.—Phenyldichloroborane, $C_6H_5BCl_2$, b.p. 78.5–83° at 27.5 mm., was prepared from boron trichloride and tetraphenyltin employing a reported[3] procedure.

N-Methylallylamine was obtained by the method of Finholt, *et al.*[14]; fractionation through a 50-cm. column packed with glass helices gave a 72% yield of the amine, b.p. 62–65° (lit.[14] b.p. 64–68°).

3-Butenylamine was prepared by a described[15] route, b.p. 74–77° (lit.[15] b.p. 76–77°).

Trimethylaminephenylborane (V), m.p. 75.5–77°, was formed in 52% yield by a slight modification of the procedure of Hawthorne,[16] who reported a yield of 28% and a m.p. of 68–69°. A solution of 63.1 g. of diethyl phenylboronate[17] in 200 ml. of ether was added dropwise under nitrogen to a stirred solution of 12.0 g. of lithium aluminum hydride and 100 g. of trimethylamine in 1 l. of ether, held at −30 to −40°. After standing overnight, the mixture was cooled to 0° and 23 ml. of water was slowly introduced. The cold suspension was filtered, and the filtrate was dried over $MgSO_4$. Then the ether was partially evaporated, and cooling in a freezer gave 27.7 g. of the desired product. A second crop of crystals, m.p. 74.5–76.5°, weighed 5.1 g. and raised the total yield to 62%.

Diglyme was purified by distillation from lithium aluminum hydride at reduced pressure.

Compounds IIa, III, and IV showed no tendency to dimerize to solid materials on standing; however, like most monomeric aminoorganoboranes, they were susceptible to hydrolysis and oxidation when exposed to air. The preparations and reactions of these compounds were carried out under an atmosphere of prepurified nitrogen.

(Allylmethylamino)phenylchloroborane (III).—The reaction of phenyldichloroborane with N-methylallylamine was performed according to the general procedure of Niedenzu and Dawson.[3] Work-up gave a 70% yield of product, b.p. 84–86.5° at 1.9 mm. The liquid displayed a carbon–carbon double bond stretching frequency at 1645 cm.$^{-1}$ in the infrared.

Anal. Calcd. for $C_{10}H_{13}NBCl$: C, 62.07; H, 6.77; B, 5.59; Cl, 18.32. Found: C, 62.25; H, 7.02; B, 5.54; Cl, 18.15.

1-Methyl-2-phenyl-1,2-azaborolidine (IV) **from III and $LiAlH_4$.**—Compound III (9.6 g., 50 mmoles) was added slowly to a refluxing solution of 1.00 g. (26.4 mmoles) of lithium aluminum

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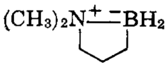
(5) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(6) M. F. Hawthorne, *ibid.*, **83**, 2541 (1961).

(7) M. F. Hawthorne, *ibid.*, **83**, 2671 (1961).

(8) R. M. Adams and F. D. Poholsky, *Inorg. Chem.*, **2**, 640 (1963), have recently described a related reaction; refluxing N,N-dimethylallylamine with trimethylamineborane in toluene gave the cyclic amineborane


$(CH_3)_2\overset{+}{N}{-}\overset{-}{B}H_2$ in 25% yield.

(9) Dehydrogenation with 10% palladium-on-charcoal and 1-hexene as a hydrogen acceptor has been found effective in the preparation of 12,11-borazarophenanthrene from its 1,2,3,4-tetrahydro derivative: M. J. S. Dewar, C. Kaneko, and M. K. Bhattacharjee, *J. Am. Chem. Soc.*, **84**, 4884 (1962).

(10) A. E. Gillam, D. H. Hey, and A. Lambert, *J. Chem. Soc.*, 364 (1941).

(11) The author is indebted to Dr. T. J. Batterham, Visiting Fellow at the National Institutes of Health, for obtaining the spectrum on a Varian Associates A-60 instrument.

(12) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 831 (1961).

(13) Carbon, hydrogen, nitrogen, and boron analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were recorded using a Perkin–Elmer Model 221 spectrophotometer with a NaCl prism-grating interchange. Melting points are uncorrected.

(14) A. E. Finholt, C. D. Anderson, and C. L. Agre, *J. Org. Chem.*, **18**, 1338 (1953).

(15) M. G. Ettlinger and J. E. Hodgkins, *J. Am. Chem. Soc.*, **77**, 1831 (1955).

(16) M. F. Hawthorne, *ibid.*, **80**, 4291 (1958).

(17) The phenylboronic acid used for the preparation of diethyl phenylboronate was kindly provided by the American Potash and Chemical Corp.

hydride in 500 ml. of ether. After refluxing overnight, the excess hydride was destroyed by adding 15.9 g. (166 mmoles) of dried trimethylammonium chloride. Then about 300 ml. of dry benzene was added. Distillation until the b.p. reached about 76°, filtration of the residue, and evaporation of the solvent under reduced pressure gave 2.8 g. (36%) of IV, b.p. 74–75° at 2.35 mm.

Anal. Calcd. for $C_{10}H_{14}NB$: C, 75.52; H, 8.87; N, 8.81; B, 6.80. Found: C, 74.72; H, 8.94; N, 9.46; B, 7.16.

1-Methyl-2-phenyl-1,2-azaborolidine (IV) from V and N-Methylallylamine.—A solution of 5.1 g. (34 mmoles) of V in 150 ml. of diglyme was stirred and gradually heated while 2.4 g. (34 mmoles) of N-methylallylamine in 50 ml. of diglyme was slowly added. The approximate temperature of the diglyme solution was measured by means of a thermocouple in contact with the outer wall of the flask. The gases emitted from the top of the reflux condenser were led through a mercury seal. Trimethylamine evolution was first observed at about 70°, but even at 130–135° the evolution of hydrogen and trimethylamine was slow. The diglyme solution was held at about this temperature as the remainder of the amine solution was added over a period of several hours. Then a small quantity of trimethylammonium chloride was introduced, and the diglyme solution was heated to reflux. Little, if any, additional hydrogen was evolved. Removal of the diglyme at reduced pressure left a liquid from which the crude product was stripped at 2.4 mm. About an equal volume of a solid remained as a residue. Redistillation of the volatile material gave 2.1 g. (39%) of IV, b.p. 78.5–81.5° at 2.55 mm., with an infrared spectrum identical with that of the product from the alternative synthesis.

2-Phenyl-1,2-azaboracyclohexane (IIa).—3-Butenylamine (3.65 g., 51.3 mmoles) in 250 ml. of diglyme was added over a period of about 5 hr. to a stirred solution of 7.65 g. (51.3 mmoles) of V in 350 ml. of diglyme at 120–133°. The gases which bubbled through the mercury seal were collected by displacement of hydrochloric acid, so that the approximate rate of hydrogen evolution could be observed. Hydrogen formation was evident only at about 120° and above. A work-up similar to the previous preparation, except that the trimethylammonium chloride was omitted, yielded 4.7 g. (58%) of crude product. Redistillation gave relatively pure IIa, b.p. 64–68° at 0.4 mm. The infrared spectrum of IIa included peaks at 3405 (N—H) and 1512 cm.$^{-1}$ (B=N).

Anal. Calcd. for $C_{10}H_{14}NB$: C, 75.52; H, 8.87; N, 8.81; B, 6.80. Found: C, 75.67; H, 8.95; N, 8.87; B, 7.17.

2-Phenyl-2,1-borazarene (Ib).—Compound IIa (0.55 g., 3.5 mmoles) was gently refluxed for 8 hr. with about an equal amount of 30% palladium-on-charcoal catalyst[18] in an apparatus similar to that described by Fieser.[19] A very slow stream of nitrogen served to sweep hydrogen from the system. Crystals began to deposit on the cold finger after about 5 hr. The resulting material was taken up in ether, filtered, and the filtrate was treated with wet ether to hydrolyze unreacted IIa. Evaporation of the ether and crystallization from petroleum ether (in which the hydrolyzed IIa was not appreciably soluble) gave 0.14 g. of crude product, m.p. 112–115°. Recrystallization from petroleum ether gave 0.085 g. (16%) of white crystals, m.p. 117–118°. A sample sublimed at 60° (0.5 mm.) and melted at 117–118.5°. The infrared spectrum of Ib (potassium bromide disk) showed maxima (above 1500 cm.$^{-1}$) at 1546, 1601, 1615, 3010–3075, and 3375 cm.$^{-1}$. The N–H stretching frequency was shifted to 3419 cm.$^{-1}$ in carbon tetrachloride solution.

Anal. Calcd. for $C_{10}H_{10}NB$: C, 77.49; H, 6.50; N, 9.04; B, 6.97; mol. wt., 155. Found: C, 77.35; H, 6.76; N, 8.84; B, 7.25; mol. wt. (Rast), 169

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[18] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 459.

[19] Reference 18, pp. 461–462.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY, MEDFORD 55, MASS.]

Conformational Studies. V.[1] Predominance of Intramolecularly Hydrogen Bonded Nonchair Conformations of *cis,cis,cis*-2,5-Di-*t*-alkyl-1,4-cyclohexanediols[2]

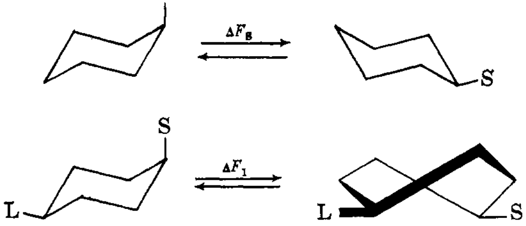
BY ROBERT D. STOLOW AND MARIA M. BONAVENTURA

RECEIVED AUGUST 7, 1963

cis,cis,cis-2,5-Di-*t*-butyl-1,4-cyclohexanediol (**1**), its monomethyl ether (**2**), and *cis,cis,cis*-2,5-di-*t*-pentyl-1,4-cyclohexanediol (**3**) have been prepared. Their infrared spectra, which show intense absorption attributable to transannular intramolecular hydrogen bonding in nonchair conformations, are interpreted in support of the assigned configurations and in terms of negligible populations of *chair* conformations for **1–3** in dilute solution in carbon tetrachloride at 25°.

By suitable choice of substituents, the usual position of equilibrium between chair and nonchair conformations of cyclohexane[3] may be reversed. We wish to report the first example of a monocyclic, saturated cyclohexane derivative for which it has been demonstrated unequivocally that the population of *chair* conformations is negligible.[4]

A *trans*-1,3- or *cis*-1,4-disubstituted cyclohexane in a chair conformation must have one axial substituent. However, in a nonchair conformation, both substituents simultaneously may occupy equatorial-like positions. Therefore, in general, since substituents encounter greater repulsive interactions when in axial positions than when in equatorial (or equatorial-like) positions, the population of nonchair conformations should be greater for a *trans*-1,3- or *cis*-1,4-disubstituted cyclohexane than the 0.1% nonchair population (at 25°) estimated for cyclohexane itself.[3,5] For example, it has been pointed out that the nonchair population of a *cis*-4-alkylcyclohexanecarboxylic acid in water solution at 25° should be *ca.* 20 times that of cyclohexane, or *ca.* 2%.[6] For many other *trans*-1,3- and *cis*-1,4-disubstituted cyclohexanes, an estimate of the nonchair population can be made by subtracting an experimental value,[5] $-\Delta F_S$, for the "smaller" substituent (S) from 4



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[1] (a) Paper I: R. D. Stolow, *J. Am. Chem. Soc.*, **81**, 5806 (1959); (b) Paper II: R. D. Stolow, *ibid.*, **83**, 2592 (1961); (c) Paper III: R. D. Stolow and C. B. Boyce, *ibid.*, **83**, 3722 (1961); (d) Paper IV: R. D. Stolow, *ibid.*, **84**, 686 (1962).

[2] The authors are grateful to the National Science Foundation for grants in support of this research. Presented at the XIXth International Congress of Pure and Applied Chemistry, London, July 15, 1963.

[3] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 8.

[4] Although considerable attention has been given the subject of nonchair conformations recently, few population studies have been reported for saturated, monocyclic cyclohexane derivatives. In this paper, attention is focused exclusively on such compounds. Nonchair conformations have been detected for numerous polycyclic and unsaturated cyclohexane derivatives, and for some heterocyclic six-membered ring compounds (substituted piperidines, tetrahydropyrans, etc.). Nonchair transition states have also been discussed for numerous reactions. See ref. 3, and references cited therein, and M. Tichý, J. Šipoš, and J. Sicher, *Collection Czech. Chem. Commun.*, **27**, 2907 (1962).

[5] Free energy differences between equatorial and axial substituents are tabulated in ref. 3, p. 236. Also see subsequent publications of Prof. E. L. Eliel.

[6] Reference 1a, and footnote 15 therein.