546. *New Heteroaromatic Compounds. Part III.*[1] *2,1-Borazaronaphthalene (1,2-Dihydro-1-aza-2-boranaphthalene).*

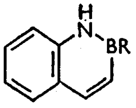
By M. J. S. Dewar and R. Dietz.

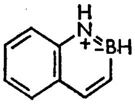
The synthesis of compound (II) and of some 2-substituted derivatives (I) is reported. The compounds show aromatic properties, and their spectra resemble those of corresponding naphthalene derivatives.

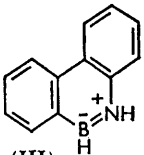
Nomenclature.—A nomenclature was desired which would take into account the fact that the group $-BH^{-}=NH^{+}-$ (equivalent to $-BH-NH-$) is isoconjugate with $-CH=CH-$ in an aromatic system. For instance, a name was desired which (*a*) would show that compound (I; R = H) (equivalent to II) is isoconjugate with naphthalene and (*b*) would not relate it to dihydronaphthalene as would strict systematic use of azabora-prefixes.* After consultation with the Editor, the prefix " aro " has been adopted, to be placed between the -a prefixes and the name of the cyclic hydrocarbon with which the compound is isoconjugate. Thus, compound (I; R = H) is named 2,1-borazaronaphthalene. For six- and five-membered rings the composite suffixes -arene and -arole, respectively, are proposed. The following are further examples: (III) 9,10-borazarophenanthrene; (IV) 1,2-borazarene; (V) 1,2-borazarole; (VI) 4,10-dibora-5,9-diazaropyrene.

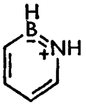
Previous papers in this series recorded boron compounds isoconjugate with indole, 2 : 3-benzofuran, thionaphthen,[1] and phenanthrene.[2] In this paper a new heteroaromatic system isoconjugate with naphthalene is described.

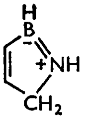
Reaction of 2-aminostyrene with boron trichloride in benzene in the absence of a catalyst gave hydrogen chloride and a white, sublimable solid, containing chlorine, which was hydrolysed with extreme ease. This chloro-compound with phenylmagnesium bromide gave a compound $C_{14}H_{12}NB$, identical with the product of the direct reaction between phenylboron dichloride and 2-aminostyrene. The stability of this compound towards hot dilute alkali and cold potassium permanganate, its methods of preparation, and its spectral similarity to 2-phenylnaphthalene (Fig. 1) show it to be the isoconjugate compound 2-phenyl-2,1-borazaronaphthalene (I; R = Ph). The chloro-compound is therefore the 2-chloro-compound (I; R = Cl).

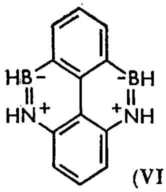

(I)


(II)


(III)


(IV)


(V)


(VI)

Hydrolysis of the chloro-compound gave bis-2,1-borazaronaphthyl ether and not the expected 2-hydroxy-compound (I; R = OH). The absence of a hydroxyl group was

---

* It is regretted that, owing to incorrect editorial advice, compounds such as (II) and (III) were incorrectly named in earlier Parts of this series.[1,2] For instance, compound (III) was there termed 9-aza-10-boraphenanthrene whereas, whether the Stelzner or the *Chemical Abstracts* system is used,[3] it should be regarded as an azabora-derivative of dihydrophenanthrene. Compounds (I) are similarly systematically named as derivatives of dihydronaphthalene. It is unnecessary to list the other errors from the earlier papers.

[1] Part II, Dewar, Kubba, and Pettit, *J.*, 1958, 3076.

[2] Part I, *Idem, J.*, 1958, 3073.

[3] " I.U.P.A.C. Nomenclature of Organic Chemistry, 1957," Butterworths, London, 1958, rule B-4.1, pp. 65—67.

confirmed by the infrared spectrum, and the fact that the compound was soluble in alkali only on prolonged boiling.

Reduction of the chloro-compound with lithium aluminium hydride gave the parent substance (I; R = H). With methylmagnesium iodide, the chloro-compound gave the methyl derivative.

The aromaticity of these compounds is evident in their spectral similarity to naphthalene derivatives and in their general stability, which is greater than the classical formula (I) would suggest. The insolubility of the ether in cold alkali is incompatible with its formulation as an anhydride of a boronous acid, and its stability to boiling alkali (Fig. 2) indicates that the compounds do not behave as cyclic boron amides. The unusual stability of the parent compound, a boron hydride, to hydrolysis is shown by the similarity of the spectra measured in cyclohexane and in 95% ethanol, even in the presence of acids (Fig. 3). The aromatic nature of the compounds is emphasised by the dipolar Kekulé structure (II). Structure (I; R = H) is, of course, more important than the corresponding excited structure of naphthalene.

FIG. 1.

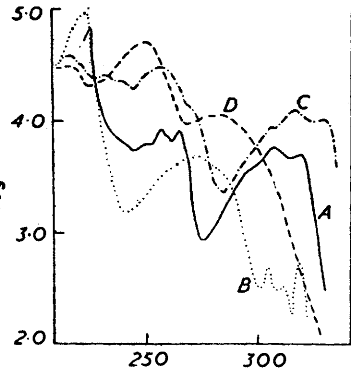


FIG. 2.

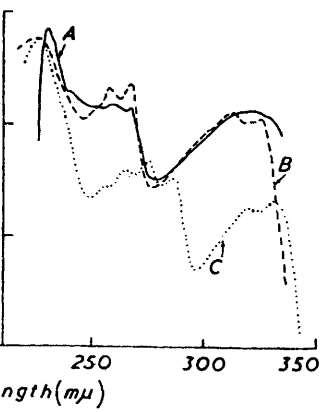


FIG. 3.

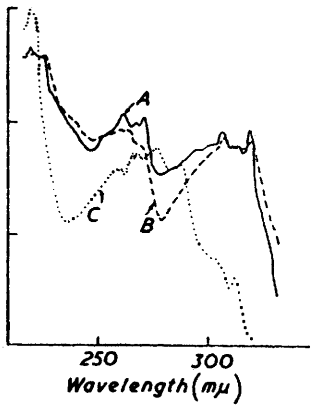


FIG. 1. *Ultraviolet spectra of* (*A*) 2-*methyl*-2,1-*borazaronaphthalene and* (*B*) 2-*methylnaphthalene in alcohol, and of* (*C*) 2-*phenyl*-2,1-*borazaronaphthalene and* (*D*) 2-*phenylnaphthalene in cyclohexane.*

FIG. 2. *Ultraviolet spectra of* (*A*) *bis*-2,1-*borazaro*-2-*naphthyl ether in* 10% *aqueous alkali after boiling and* (*B*) *in cyclohexane, and* (*C*) *of* 2-*naphthol in alcohol.*

FIG. 3. *Ultraviolet spectra of* 2,1-*borazaronaphthalene* (*A*) *in cyclohexane and* (*B*) *in alcohol with acid, and* (*C*) *of naphthalene in cyclohexane.*

The main absorption bands of 2,1-borazaronaphthalene correspond closely to those of naphthalene (Fig. 3), but the intensity of the α-bond (320 mμ region) is much greater. A similar phenomenon was observed in the case of 9,10-borazarophenanthrene and explained in terms of molecular-orbital theory.[2] That the spectrum of bis-2,1-borazaronaphthyl ether is little changed in aqueous alkali would be expected since conjugation between boron and oxygen is strong and is little affected by the electronic configuration of the oxygen atom.

The mild conditions under which these compounds are formed suggest that other suitably substituted ethylenes would condense with boron derivatives. An investigation of these reactions is in progress.

EXPERIMENTAL

Boron analyses were carried out by the volumetric method developed by Leigh, Fowler, and Kraus.[4] Molecular weights were determined by freezing-point depression in naphthalene. M. p.s are corrected.

---

[4] Leigh, Fowler, and Kraus, *J. Amer. Chem. Soc.*, 1940, **62**, 1143.

2-Aminostyrene was prepared from phenethyl alcohol.[5]

Bis-2,1-*borazaro*-2-*naphthyl Ether*.—A solution of 2-aminostyrene (1 g.) in dry benzene (40 ml.) was added slowly with stirring to a solution of boron trichloride (2 g.) in benzene (10 ml.) at room temperature. The mixture was boiled under reflux for 3 hr. The solvent was distilled off, and the residue crystallised from light petroleum to give the *ether* as colourless plates (0·51 g., 45%), m. p. 198—200° (Found: C, 70·1; H, 5·1; N, 10·3; B, 7·8. $C_{16}H_{14}ON_2B_2$ requires C, 70·6; H, 5·2; N, 10·3; B, 8·0%).

2-*Chloro*-2,1-*borazaronaphthalene*.—The previous experiment was repeated, and the solvent removed with exclusion of moisture. From the residue, 2-*chloro*-2,1-*borazaronaphthalene* sublimed at 60—65°/0·3 mm., in needles, m. p. 72—74°. Direct hydrolysis and titration with alkali gave Cl, 19·6% as a maximum value (C_8H_7NBCl requires Cl, 21·7%). Professional analyses of this compound gave very low chlorine values, and correspondingly high carbon, hydrogen, and nitrogen values. Hydrolysis is obviously rapid.

2,1-*Borazaronaphthalene*.—A solution of lithium aluminium hydride (0·5 g.) in dry ether was added in ½ hr. to a solution of crude 2-chloro-2,1-borazaronaphthalene (from 1 g. of 2-aminostyrene) in dry ether, between −5° and 0°. The mixture was stirred for 2 hr. at room temperature. Moist ether was added, and the solution filtered and evaporated to dryness. From the residue there sublimed at 80°/0·6 mm. a white solid, which, crystallised from light petroleum, gave 2,1-*borazaronaphthalene* (0·42 g., 40%), m. p. 100—101° (Found: C, 74·5; H, 6·2; N, 10·9; B, 7·9. C_8H_8NB requires C, 75·0; H, 6·3; N, 10·9; B, 8·4%).

2-*Phenyl*-2,1-*borazaronaphthalene*.—(a) *From phenylboron dichloride*. A solution of 2-aminostyrene (2 g.) in dry benzene (20 ml.) was added dropwise and with constant stirring to one of phenylboron dichloride (2·7 g.) in dry benzene (10 ml.) at room temperature in ½ hr. The mixture was then boiled under reflux for 2 hr. On cooling, a white solid was precipitated. Ether was added, and the solution washed with dilute aqueous sodium carbonate, dried, and evaporated. Crystallisation from light petroleum gave 2-*phenyl*-2,1-*borazaronaphthalene* in colourless plates (2·1 g., 69%), m. p. 137·5—139° (Found: C, 81·7; H, 6·1; N, 6·7; B, 5·1%; *M*, 205. $C_{14}H_{12}NB$ requires C, 81·9; H, 5·9; N, 6·8; B, 5·3%; *M*, 208).

(b) *By a Grignard reaction*. To a solution in dry ether of crude 2-chloro-2,1-borazaronaphthalene (from 1 g. of 2-aminostyrene) was added slowly one of phenylmagnesium bromide [from magnesium (1 g.) and bromobenzene (6·8 g.)], with ice-cooling in ¾ hr. The mixture was stirred for 2 hr. at room temperature and boiled under reflux 1 hr. Water was added and the organic layer separated, dried, and evaporated. Crystallisation from light petroleum gave 2-phenyl-2,1-borazaronaphthalene (0·65 g., 43%), m. p. and mixed m. p. 138—139°.

2-*Methyl*-2,1-*borazaronaphthalene*.—A similar Grignard reaction gave a 45% yield of 2-*methyl*-2,1-*borazaronaphthalene*, crystallising in plates (from light petroleum), m. p. 73—74° (Found: C, 74·3; H, 7·3; N, 9·8; B, 7·3%; *M*, 137. $C_9H_{10}NB$ requires C, 75·6; H, 7·1; N, 9·8; B, 7·6%; *M*, 143).

One of us (R. D.) thanks the British Petroleum Company for a Research Studentship; we are also grateful to the University of London for a grant for the purchase of apparatus.

CHEMISTRY DEPARTMENT, QUEEN MARY COLLEGE,
MILE END ROAD, LONDON, E.1.

[*Received, November* 18*th*, 1958.]

---

[5] Sabetay, Bleger, and de Lastrange, *Bull. Soc. chim. France*, 1931, **49**, 3.