TABLE I

A,[a] mμ	B,[b] mμ	C[c] mμ	C[c] log E_{max}
382	..	382	3.29
365	..	360	3.21
341	..	343	2.81
323[d]	..	318[d]	4.20
300	..	297	4.60
..	..	251	4.29
..	516	525	1.62
560	565	568	1.74
625	615	618	1.76
660	660	655[d]	
680	682	682	1.61
..	..	745	1.05
..	790	777	1.05

[a] A, pentane; I. R. Nunn and W. S. Rapson.[10] [b] B, pentane; E. A. Braude and W. F. Forbes.[11] [c] C, this study; ultraviolet—ethanol, visible—pentane, no reported peak. [d] Shoulder.

ring). The absence of absorbance between 2.90 and 6.80 indicates no vinyl hydrogen.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.15; H, 8.70.

1,2-Benzazulene.—The apparatus described by Anderson, Nelson and Tazuma[13] was used with the following modifications. A capillary micro dropping funnel with provision for positive nitrogen pressure was fitted in the top of the column. A flow rate of dry nitrogen at 0.5 ml./sec. was maintained. The 30-cm. vertical column was packed with 2.5% Pd-asbestos. The receiver was cooled (Dry Ice–acetone) and a vacuum of 60 mm. was applied to the column.

3,4,5,6,7,8-Hexahydro-1,2-benzazulene (0.69 g., 0.00038 mole), kept liquid by an infrared lamp, was added at the rate of one capillary drop every 10 minutes to the column heated to a stable temperature of 330° top, 310° bottom (addition time 8 hours). The product was dissolved in petroleum ether (30–60°) and chromatographed on alumina. Fraction 1, bluish crystals, was mostly recovered XII; fractions 2 and 3, dark green plates, melted at 175–177° dec. 1,2-Benzazulene is reported to melt at 176–177°.

The three fractions were dissolved in petroleum ether (b.p. 30–60°) and extracted three times with 85% phosphoric acid. The acid extract was added to ice (200 g.), and the resulting solution was extracted with ether. The ether extract was washed with 5% aqueous potassium carbonate, dried ($MgSO_4$) and concentrated affording green plates of 1,2-benzazulene (0.058 g., 8.7%, m.p. 180–181° dec.). The results of visible and ultraviolet spectra of 1,2-benzazulene are given in Table I. The general shape of the curves is quite similar to that reported by Nunn and Rapson.[10]

***o*-(1-Cyclopentenyl)-benzylamine Hydrochloride.**—The procedure employed was essentially identical with that described for the syntheses of VIIa. Since it was known that impurities and side products formed in these reactions were difficult to remove at steps prior to the formation of the basic amine, no rigorous purifications of intermediates were attempted.

From *o*-chlorobromobenzene (95.7 g., 0.5 mole), magnesium (12.2 g., 0.5 g. atom), cyclopentanone (42.1 g., 0.5 mole) and formic acid (88%, 110 ml.) there was obtained 51 g. (57% yield) of ***o*-(1-cyclopentenyl)-chlorobenzene**, b.p. 63–64° (0.15 mm.), $n^{25}D$ 1.5716. From crude Vc (14.9 g., 0.1 mole) and cuprous cyanide (11.7 g., 0.13 mole) after 36 hours at 250°, there was obtained 6.8 g. (46%) of crude ***o*-(1-cyclopentenyl)-benzonitrile**, b.p. 106–110° (0.7 mm.), $n^{25}D$ 1.5806. From *o*-(1-cyclopentenyl)-benzonitrile (14.4 g., 0.085 mole) and lithium aluminum hydride (3.5 g., 0.092 mole) there was obtained *o*-(1-cyclopentenyl)-benzylamine hydrochloride (white plates, m.p. 176–180° dec., 15.5 g., 87% yield). This material was recrystallized from absolute ethanol–ether and the pure amine hydrochloride was obtained as fine white crystals (m.p. 178° dec.).

Anal. Calcd. for $C_{12}H_{16}NCl$: C, 68.74; H, 7.64; N, 6.68. Found: C, 68.67; H, 7.57; N, 6.65.

Reaction of *o*-(1-Cyclopentenyl)-benzylamine Hydrochloride with Nitrous Acid.—*o*-(1-Cyclopentenyl)-benzylamine hydrochloride (5.0 g., 0.024 mole) was treated with sodium nitrite (2.1 g.) in water (60 ml.) as previously described for Ia and Ib. The product was fractionated through an 8″ spiral wire column and only one component appeared to be present in any significant amount; b.p. 78–82° (0.08 mm.), $n^{25}D$ 1.5746, 1.88 g., 46% yield calculated as *o*-(1-cyclopentenyl)-benzyl alcohol. The material was refractionated and samples showed essentially no variation in boiling point or refractive index.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.05. Found: C, 81.41, 80.79, 82.04; H, 8.09, 7.99, 8.66.

Attempts to cyclize the assumed *o*-(1-cyclopentenyl)-benzyl alcohol to **3,4,5,6-tetrahydro-1,2-benzpentalene**, by procedures essentially identical to those described for reactions involving VII and XII, were unsuccessful. The tarry products that resulted were extracted with petroleum ether and chromatographed on alumina as previously described. Only traces of oils resulted that could not be induced to crystallize. In one run (out of four) a small amount of solid (m.p. 58–62°) was obtained by recrystallization of the small amount of oil obtained from the chromatogram. This material was very sensitive to air and decomposed within minutes to an oil.

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(13) A. G. Anderson, J. A. Nelson and J. J. Tazuma, THIS JOURNAL, **75**, 4980 (1953).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL., AND THE DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, UNIVERSITY OF LONDON, LONDON E 1, ENG.]

New Heteroaromatic Compounds. Part X.[1] Grignard Reactions and Hydride Reductions of B-Oxides Derived from 10,9-Borazarophenanthrene and 2,1-Borazaronaphthalene[2]

BY MICHAEL J. S. DEWAR, ROY DIETZ, VED P. KUBBA AND ARTHUR R. LEPLEY

RECEIVED SEPTEMBER 28, 1960

Grignard reagents reacted with 2,1-borazaro-2-naphthyl ethers to give 2-methyl- and 2-phenyl-2,1-borazaronaphthalene while lithium aluminum hydride gave 2,1-borazaronaphthalene. Similar reactions with 10-hydroxy-10,9-borazarophenanthrene gave 10-methyl-10,9-borazarophenanthrene and 10,9-borazarophenanthrene. The yields in all these reactions were good. The preparation of the necessary ethers is described.

Previous papers,[3,4] in this series have described the preparation of derivatives of the novel aromatic compounds 10,9-borazarophenanthrene (I) and 2,1-borazaronaphthalene (II). The B-alkyl and aryl derivatives, and the parent compounds

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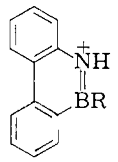
(1) Preceding paper, P. M. Maitlis, *J. Chem. Soc.*, in press.

(2) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; Abstracts of Papers, p. 54-P.

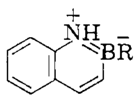
(3) M. J. S. Dewar, Ved P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(4) M. J. S. Dewar and R. Dietz, *ibid.*, 2728 (1959).

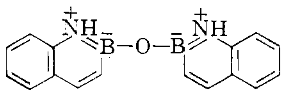
Ia, IIa, were prepared by treating the corresponding chloro compounds Ib, IIb, with organometallic reagents or lithium aluminum hydride. These reactions were never entirely satisfactory since the chlorides could not be purified easily; use of crude chlorides in the reactions gave impure products. The situation became even more difficult when pure 2-aminobiphenyl ceased to be commercially available[5]; the action of organometallic reagents on the crude chloride Ib prepared[4] from 2-aminobiphenyl of commercial grade contained impurities which were very difficult to remove.



Ia, R = H
b, R = Cl
c, R = OH
d, R = alkoxy
e, R = CH_3

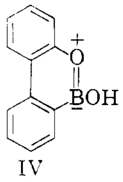


IIa, R = H
b, R = Cl
c, R = OH
d, R = alkoxy
e, R = CH_3
f, R = Ph
g, R = O^-

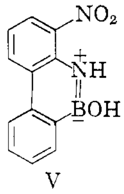


III

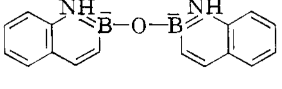
The hydrolysis products of the chlorides, Ic and bis-2,1-borazaro-2-naphthyl ether (III), are on the other hand easily purified, even when they have been prepared from impure starting materials. We therefore tried to find some way to replace the oxy- groups in them by alkyl, aryl or hydrogen. Attempts to convert them to the chlorides failed. We therefore turned to the reactions of the corresponding ethers Id, IId with organometallic reagents, following the procedure commonly used to prepare acyclic aryl- and alkylborons.[6] Previous work[7,8] had shown that 10-hydroxy-10,9-boroxarophenanthrene (IV) and 8-nitro-10-hydroxy-10,9-borazarophenanthrene (V) could be converted to their methyl or ethyl ethers simply by recrystallization from methanol or ethanol. We found that 10-hydroxy-10,9-borazarophenanthrene (Ic) and bis-(2,1-borazaro-2-naphthyl) ether (III) were converted to the corresponding ethers Id, IId by recrystallization from alcohol or by azeotropic distillation of a solution in alcohol–benzene.



IV



V



The structures of these ethers follow from the method of preparation, elementary analysis and molecular weight determination, the identification of bands in the infrared due to aliphatic C–H stretching, and the slow but quantitative hydrolysis of the alkoxyl group merely on standing in air. The behavior of III in alcoholic solution indicated that the B–O–B linkage is broken in hydroxylic solvents and that a solution of III in aqueous alcohol contains the corresponding hydroxy compound IIc which could not be isolated.[4] The low acidity of such solutions then further supports the aromatic formulation[4] of II. The acidity of boric acids must be due either to proton loss or to coördination with bases; both these processes should be inhibited by the transfer of negative charge to boron involved in an aromatic structure for II. The weak acidity of IIc itself must be due to deprotonation rather than to coördination with hydroxyl since the acidity was not increased by adding polyols. Alkaline solutions of IIe must contain the planar ion IIg.

Treatment of 2-methoxy-2,1-borazaronaphthalene (IId) with an excess of the corresponding Grignard reagent gave good yields of 2-methyl- (IIe) and 2-phenylborazaronaphthalene (IIf), identical with the compounds previously obtained from IIb. Their infrared spectra showed, respectively, bands at 3.41 μ (characteristic of alkyl) and at 14.25 μ (characteristic of phenyl). The same products were formed by the action of excess Grignard reagent on the bisborazaronaphthyl ether (III).

Treatment of 10-hydroxy-10,9-borazarophenanthrene (Ic) with excess methylmagnesium iodide gave the corresponding 10-methyl derivative Ie in good yield. This replacement of a hydroxyl group in a Grignard reaction is unusual if not unique; it provides an excellent route to 10-substituted 10,9-borazarophenanthrenes.

The parent 2,1-borazaronaphthalene (IIa) was formed in good yield by treating 2-methoxy-2,1-borazaronaphthalene (IId) with excess lithium aluminum hydride in ether, and in smaller yield by a similar reaction from the bisborazaronaphthyl ether (III). The excess metal hydride could be destroyed in the usual way by adding moist ether; no special precautions were taken during the isolation or purification of IIa.

The reduction of 10-hydroxy- (Ic) or 10-ethoxy-10,9-borazarophenanthrene (Id) to the parent borazarophenanthrene (Ia) was much more sensitive to the reaction conditions and work-up procedure since Ia is easily converted to the hydroxy compound Ic by both acids and bases. Addition of water at the end of the reaction to destroy any excess metal hydride consequently led to loss of Ia. A procedure eventually was devised whereby Ic could be converted to Ia in good yield under anhydrous conditions. A slight deficiency of lithium aluminum hydride was used, together with about one-third of a mole of aluminum chloride as a catalyst; insoluble material was removed by filtration and the borazarophenanthrene sublimed. This procedure failed when an excess of lithium aluminum hydride was used; apparently the excess

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(5) Most suppliers stopped making aminobiphenyls when the *para* isomer was found to be carcinogenic; 2-aminobiphenyl of commercial grade, apparently contaminated with the 4-isomer, can be obtained from Chemicals Procurement Co., 550 Fifth Ave., New York 36, N. Y.

(6) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

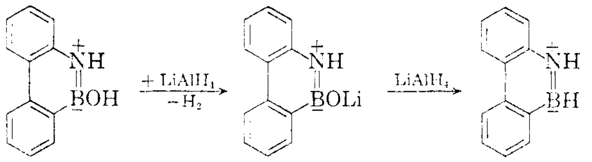
(7) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960).

(8) M. J. S. Dewar and Ved P. Kubba, *Tetrahedron*, **7**, 213 (1959).

hydride converted Ia into a stable non-volatile complex which could not be broken down without destroying the Ia. The amount of reducing agent was therefore critical and the best results were obtained by using standardized solutions of the metal hydride.

The borazaronaphthalene and borazarophenanthrene obtained in this way were identical with the products previously described.[3,4] Their infrared spectra showed bands at 2500 cm.$^{-1}$ characteristic of B–H stretching.[9]

These reductions can be formulated as nucleophilic replacements of groups OR from boron by H^-; this is supported by the fact that 0.25 molar equivalent was sufficient to reduce 10-ethoxy-10,9-borazarophenanthrene (Id). Apparently the imino group reacts more slowly than boron with the metal hydride under the conditions used so that reduction is complete before metallation of the imino group can occur. The reduction of the 10-hydroxy compound Ic must have involved a preliminary metallation of hydroxyl since in this case 0.5 molar equivalent of lithium aluminum hydride was required; *i.e.*



Experimental Part

Molecular weights were determined by the Rast method.

2-Methoxy-2,1-borazaronaphthalene.—Crystallization of bis-(2,1-borazaro-2-naphthyl) ether (III) from dry methanol gave the methyl ether IId as colorless plates, m.p. 57–58°. On standing in air, slow but quantitative hydrolysis to III took place.

Anal. Calcd. for $C_9H_{10}NBO$: C, 67.9; H, 6.4; N, 8.8; mol. wt., 157. Found: C, 67.7; H, 6.2; N, 8.8; mol. wt., 159.

10-Ethoxy-10,9-borazarophenanthrene.—Azeotropic removal of water from a solution of 10-hydroxy-10,9-borazarophenanthrene (Ic) in ethanol and benzene (20% alcohol) followed by vacuum drying gave the ether Id in quantitative yield, sufficiently pure for reduction. An analytical sample was prepared by vacuum distillation, b.p. 168–170° (0.5 mm.), m.p. 54–55°.

Anal. Calcd. for $C_{14}H_{14}NOB$: C, 75.4; H, 6.3; N, 6.3. Found: C, 76.2; H, 6.6; N, 6.8.

Grignard Reactions.—Bis-(2,1-borazaro-2-naphthyl) ether (III) (9.2 g., 0.034 mole) suspended in anhydrous ether (80 ml.) was added at room temperature to methylmagnesium iodide (from magnesium, 4.5 g., and methyl iodide, 24 g., 0.17 mole) in ether (130 ml.). After 1 hour at room temperature the mixture was boiled under reflux for 2 hours, cooled and hydrolyzed with sulfuric acid (2 *N*). The dried ($MgSO_4$) organic layer was evaporated and the oily residue (9.4 g.) chromatographed using petroleum ether (b.p. 40–60°) on a short alumina column (100–200 mesh, 6″ × 4″) giving 2-methyl-2,1-borazaronaphthalene (IIe) (9.1 g., 94%), m.p. and mixed m.p. 72.5–74°, raised by recrystallization from pentane to 73–74°.

Anal. Calcd. for $C_9H_{10}BN$: C, 75.6; H, 7.1; N, 9.8; B, 7.6; mol. wt., 143. Found: C, 75.7; H, 7.3; N, 9.8; B, 7.3; mol. wt., 137.

Essentially similar reactions produced 2-phenyl-2,1-borazaronaphthalene (IIf) (67%) from III, 2-methyl-(IIe) and 2-phenyl-2,1-borazaronaphthalene (IIf) from the 2-methoxy compound, and 10-methyl-10,9-borazarophenanthrene (Ie) from 10-hydroxy-10,9-borazarophenanthrene (Ic).

Preparation of 2,1-Borazaronaphthalene.—Lithium aluminum hydride (0.12 g., 0.003 mole) in dry ether (50 ml.) was added to a stirred ice-cold solution of 2-methoxy-2,1-borazaronaphthalene (from III, 0.93 g., 0.004 mole) in dry ether (30 ml.). After 30 minutes at room temperature the mixture was boiled under reflux for 1 hour, then cooled before addition of moist ether (30 ml.) followed by sulfuric acid (20 ml., 2 *N*). The dried ($MgSO_4$) organic layer was evaporated, leaving a white solid (0.82 g.) which sublimed at 90° (0.6 mm.) giving 2,1-borazaronaphthalene (IIa) (0.64 g., 77%), m.p. and mixed m.p. 98–99.5°. A similar reduction of III gave a much smaller yield (34%) of 2,1-borazaronaphthalene.

Preparation of 10,9-Borazarophenanthrene.—A solution of 10-hydroxy-10,9-borazarophenanthrene (Ic) in dry ether was added rapidly to a standardized solution of lithium aluminum hydride in dry ether. In some experiments a solution of aluminum chloride in ether was added at this stage. When the initial reaction had subsided the mixture was boiled under reflux and then filtered with suction into a sublimator. After removal of the ether by evacuation the residue was sublimed at 65–70° (0.5 mm.), giving pure 10,9-borazarophenanthrene (Ia), m.p. 69.5–70°. Hydrolysis of the residue in the sublimator regenerated Ic. The results of experiments carried out under various conditions are summarized in Table I.

TABLE I

Expt.	Ic[a]	$LiAlH_4$[a]	$AlCl_3$[a]	Reflux period, hr.	Yield,[b] %
1	49	25	0	3	35
2	44	26	0	3	0
3	45	26	0	24	0
4	65	26	0	3	9
5	65	26	1	2	22
6	55	26	52	3	[c]
7	56	26	4.5	3	75

[a] Amounts of all materials in millimoles. [b] Yields based on initial Ic. [c] The sublimate consisted of a mixture of Ia and aluminum chloride which hydrolyzed in air. Although it was not possible to separate Ia from the mixture, the hydrolyzed sublimate gave 77% recovery of Ic.

Acknowledgment.—R. D. thanks the University of London for the award of the William Lincoln Shelley Research Studentship.

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(9) L. J. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).