Preparation of 2-Methyladamantane (IIIf).—Methylene-adamantane (IIId) (1.42 g.) was hydrogenated in ether solution using PtO₂ catalyst, using a Parr apparatus. Evaporation of the solvent left a solid which was purified by sublimation to yield 1.1 g. of a white solid. Recrystallization from ethanol gave white crystals, m.p. 143.8–146.0°. The compound is quite different from 1-methyladamantane, m.p. 103°.[7]

Anal. Calcd. for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.67; H, 12.01.

Reaction of 2-Methyl-2-adamantanol with Formic Acid.—A solution of 1.0 g. of 2-methyl-2-adamantanol (IIIc) in 40 ml. of 98–100% formic acid was heated for 3 hours on the steam-bath. The reaction mixture was poured into water and extracted with ether. The ether extracts were dried over K₂CO₃ and Na₂SO₄. Evaporation gave 0.98 g. of an oil, which showed none of the bands characteristic of methyleneadamantane (IIId) in the infrared, but rather possessed a strong carbonyl peak at 5.78μ and a formate ester band[48] at 8.42μ.

The material, presumed to be the formate ester IIIe, was not characterized or purified further, but was saponified directly with 2.0 g. of KOH in alcohol solution. Work-up gave 0.85 g. of a yellow-white solid. One recrystalliza-tion from petroleum ether gave a white solid identical with the starting material, 2-methyl-2-adamantanol (IIIc).

Kinetic Procedures.—Standard titrimetric procedures were employed.[13–15,24–26,37,38,42,43] Aliquots of 0.03–0.04 molar solutions of the tosylate ester were sealed into ampoules. Carefully dried and fractionally distilled acetic acid was used as the solvent. At the appropriate times the aliquots were titrated with 0.05 molar sodium acetate in acetic acid to the brom thymol blue end-point. Experimentally determined infinity titers were used to calculate the rate constants. Two separate runs were made at each temperature; their agreement was good. The constant temperature baths were checked against an NBS calibrated thermometer.

Solvolysis Product of 2-Adamantyl Tosylate.—The combined acetic acid solutions from the kinetic runs were made "basic" by adding excess Na₂CO₃ and were refluxed overnight. The solution was poured into water, and extracted with ether. After washing and drying, the ether solution was evaporated to give an oil which had infrared peaks at 5.75 (ester carbonyl) and at 8.05μ (acetate).[48] The acetate was saponified in ethanol with 1 g. of KOH. The solid residue present after the work-up was sublimed to give a material whose infrared spectrum was identical with that of pure 2-adamantanol (IIIa).

[Contribution from the Department of Chemistry, Queen Mary College, University of London, London, Eng.]

New Heteroaromatic Compounds. Part VIII. The Reactions of Some Borazarophenanthrenes[1] with Methyl- and Phenyllithium

By M. J. S. Dewar[2] and P. M. Maitlis

Received June 27, 1960

Previous papers[3] in this series have described a number of derivatives of 10,9-borazarophenanthrene (I), all of which have an imino group in the 9-position. The original purpose of this investigation was to prepare 9-substituted-10,9-borazarophenanthrenes.


I, R = H
II, R = Me
III, R = Ph

IV
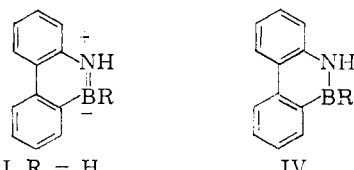
Since previous work[3] has indicated that these compounds are aromatic, the dipolar resonance structures I must make significant contributions to their ground states. (For this reason they are formulated[1,3] in terms of dipolar structures rather than uncharged structures (IV).) This suggests that the imino group should show acidity similar to that of the imino groups in five-membered heterocyclics such as pyrrole or indole where again dipolar resonance structures are important. We were therefore surprised to find that the 10-methyl derivative II failed to react with dimethyl sulfate in presence of alkali and that the potassio derivative could not be prepared by the usual methods.

It is true that the imino hydrogen exchanged rapidly in alkaline deuterium oxide, but this exchange could have involved an addition–elimination mechanism, *i.e.*
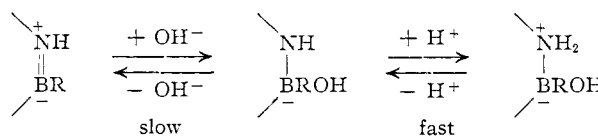
Attempts to methylate II with diazomethane also failed; a vigorous reaction took place leading to a polymer (presumably polymethylene), but II could be recovered quantitatively. Evidently II, like boron trifluoride, catalyzes the decomposition of diazomethane very efficiently; a likely mechanism seems to be

Here again the borazarophenanthrene acts as a Lewis acid rather than a proton donor.

We finally obtained the 9-lithio derivative (V) of II by reaction with one mole of methyllithium in ether, methane being evolved; and with freshly

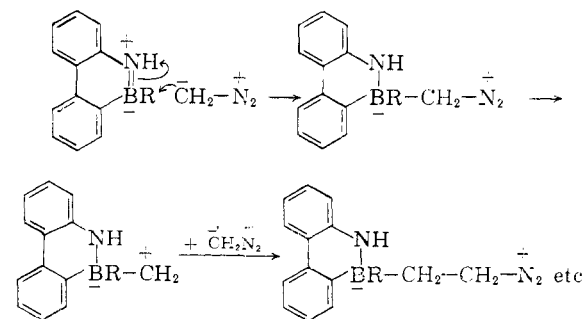(1) For nomenclature see M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

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(3) *Cf.* M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958). M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959)
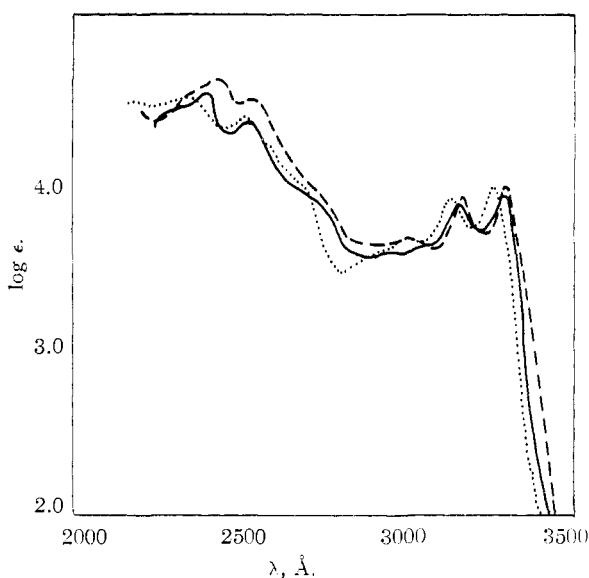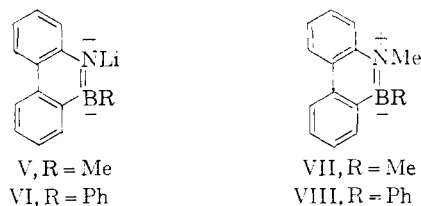
Fig. 1.—Ultraviolet spectra of: ————, 9,10-dimethyl-10,9-borazarophenanthrene (VII); ---------, 9-methyl-10-phenyl-10,9-borazarophenanthrene (VIII); ...., 10-methyl-10,9-borazarophenanthrene (II).

distilled dimethyl sulfate V gave 9,10-dimethyl-10,9-borazarophenanthrene (VII). The structure of VII was indicated by elemental analysis, by the similarity (Fig. 1) of its ultraviolet spectrum to that of II, by the disappearance of the NH band at 2.93 μ and the appearance of a new CH band at 3.46 μ (in addition to the band at 3.39 μ due to the B-methyl group) in the infrared spectrum, and by the fact that the n.m.r. spectrum showed the presence of two dissimilar methyl groups.

V, R = Me
VI, R = Ph

VII, R = Me
VIII, R = Ph

Similar treatment of III gave 9-lithio-(VI) and 9-methyl-(VIII) 10-phenyl-10,9-borazarophen-anthrene. The structure of VIII was indicated by the similarity of its ultraviolet spectrum (Fig. 1) to that of II or III, and by the appearance of a methyl band in the infrared spectrum at 3.46 μ.

When II was allowed to react with two moles of methyllithium, a brightly colored ethereal solution was obtained which apparently contained 9,9-dilithio-10,10-dimethyl-9,10-dihydro-10,9-boraza-rophenanthrene (IX), formed by addition of the second mole of methyllithium to the BN bond of V and stable only in the absence of oxygen and moisture. Addition of water to the solution led mainly to regeneration of the starting material; but treatment with carbon dioxide followed by dilute acid gave 10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XI), presumably via an unstable intermediate N-carboxylic acid. A similar reaction of III with two moles of phenyllithium, followed by carbonation and hydrolysis, gave

10,10 - diphenyl - 9,10 - dihydro - 10,9 - borazarophen-anthrene (XII).

IX, R = Me
X, R = Ph

XI, R = Me
XII, R = Ph

XIII, R = Me
XIV, R = Ph
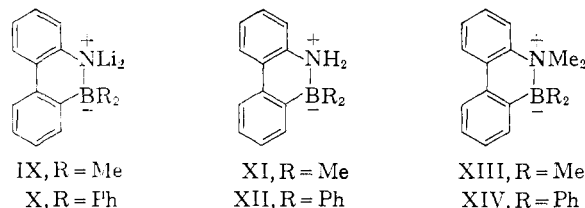
These are stable crystalline compound of novel type where the boron is internally chelated to nitrogen. That a strong chelation does occur is shown by the stability to aerial oxidation and heat of these compounds and to the lack of a tendency for XI, which is a derivative of dimethylphenyl-boron, to undergo disproportionation.

These structures have been assigned on the following evidence: (a) The ultraviolet spectra of the 10,10-dimethyl-(XI) and 10,10-diphenyl-(XII) 9,-10-dihydro-10,9-borazarophenanthrenes are nearly identical and bear a close resemblance to that of 9,10-dihydrophenanthrene (Fig. 2). The character-
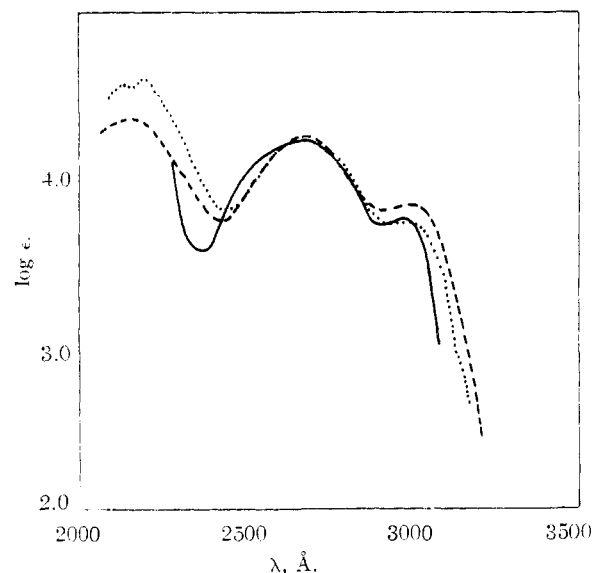

Fig. 2.—Ultraviolet spectra of: ......, 10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XII); ————, 10,10 - dimethyl - 9,10 - dihydro -10,9-borazarophenanthrene (XI); ————, 9,10-dihydrophenanthrene (from R. N. Jones, This Journal, 63, 1658 (1941)).

istic phenanthrene-type spectra of the starting materials has been completely lost. This implies that the conjugation across the hetero-ring has now been destroyed and that the only conjugation remaining is from the biphenyl rings. The similarity of the spectra of the B-dimethyl and B-diphenyl compounds again shows that the phenyl groups in the latter are quite isolated and not conjugated with the biphenyl rings, as would be expected with boron atoms in the sp³ state (due to three boron–carbon valences and the chelation from the nitrogen).

(b) Both compounds show two sharp peaks in the near infrared, at 3.04 and 3.16μ (for the B-
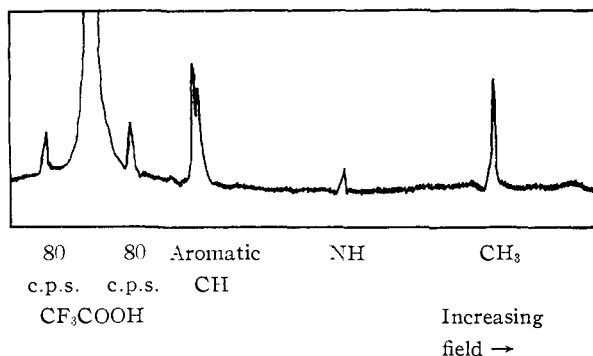
Fig. 3.—N.m.r. spectrum of 10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XI) in trifluoroacetic acid.

Fig. 4.—Ultraviolet spectra of: ————, 9,9,10,10-tetramethyl-9,10-dihydro-10,9-borazarophenanthrene   (XIII) ------,   9,9-dimethyl-10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XIV).

dimethyl) and 3.10 and 3.16 μ (for the B-diphenyl). These can only be due to an $-NH_2$ group.

(c) The proton magnetic resonance spectrum of 10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene in trifluoroacetic acid shows (Fig. 3) the presence of only one set of aliphatic hydrogens; furthermore the ratio of the areas of the methyl hydrogens in the spectrum to that of the amine hydrogens is roughly 3:1 which is the expected value.

(d) Degradation of XII with sulfuric acid gave 2-aminobiphenyl as the only detectable product.

(e) The ultraviolet spectra were unaltered by the addition of *small* amounts of acid, indicating that neither compound is appreciably basic. This must imply the presence of a strong BN bond; for rupture of this bond would give a basic derivative of 2-aminobiphenyl.

The dilithio derivatives IX, X are probably ionic in view of their strong color; their structure is discussed in more detail below. They gave on treatment with dimethyl sulfate in benzene 9,9,-10,10-tetramethyl-(XIII) and 9,9-dimethyl-10,10-diphenyl-(XIV) 9,10-dihydro-10,9-borazarophenanthrene, respectively. These like XI and XII were well-defined stable crystalline solids with moderate melting points.

The structures of XIII and XIV were assigned on the following evidence: (a) Unambiguous elementary analyses and molecular weights. (b) The similarity of the ultraviolet spectra to each other (Fig. 4), to those of the 10-disubstituted-9,10-dihydro-10,9-borazarophenanthrenes (V), and to 9,10-dihydrophenanthrene, showing that the same basic conjugated system must be present in all of these: (c) The absence in the infrared of any peaks due to N–H (or NH_2); the presence in the spectrum of the B-dimethyl-N-dimethyl compound XIII of a very strong band at about 3.43 μ (due to aliphatic C–H's) which must, by comparison with similar compounds, be due to the presence of a large number of methyl groups; and the presence of a band at *ca.* 3.4 μ in the spectrum of the B-diphenyl-N-dimethyl compound XIV due to aliphatic C–H's.[4] These bands are more diffuse and have suffered a slight shift by comparison with the 10-methyl- and 10-phenyl-9-methyl-10,9-bor-

(4) All the 10,9-borazarophenanthrenes and related compounds have the usual aromatic C–H bands at approx. 3.26 and 3.31 μ. These bands do not vary appreciably from these values.
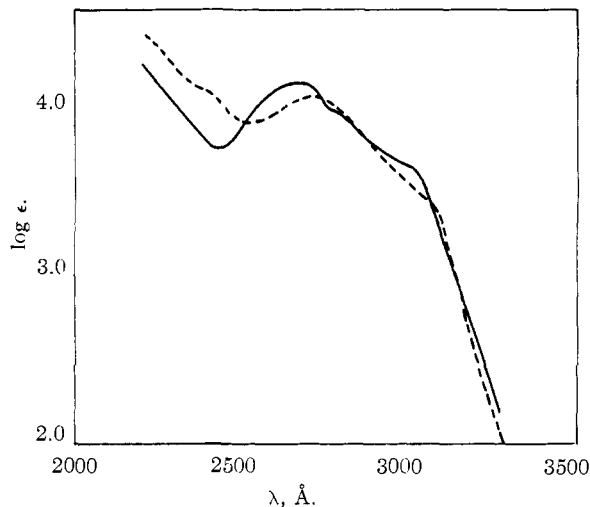
azarophenanthrenes (VII), (VIII), probably due to the increased steric hindrance which must be present in the former compounds.

The reactions of the dilithio compounds IX and X with water, leading to loss of methyl or phenyl and formation of II or III, are somewhat unusual. Evidently protons attack the methyl or phenyl groups more readily than they attack the nitrogen atoms. This could hardly be the case if both lithium atoms were present as ions; the dianion XV would surely react with water or acid to give a dihydroborazarophenanthrene. On the other hand, the intense color of the dilithio derivatives seems to exclude a purely covalent structure. This argument suggests that the dilithio compounds must have the structure XVI, one of the two lithium atoms being covalently bound to nitrogen, the other present as a cation. Water should convert XVI very rapidly to the covalent monolithio compound XVII, so the abnormal reaction probably involves hydrolytic rupture of this intermediate.
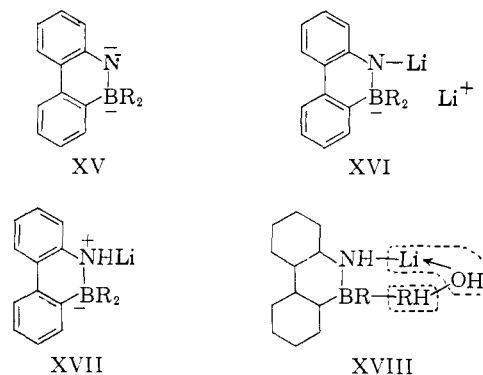
Now hydrolysis of the lithium in XVII could well be slow; the nitrogen atom in it is tetrahedral, and so approach of a proton to the nitrogen would be sterically hindered. On the other hand, water should coördinate readily with the lithium

TABLE I

REACTION OF 10-SUBSTITUTED-10,9-BORAZAROPHENANTHRENES WITH ONE MOLE OF ORGANOLITHIUM

No.	R = group in –NH·BR–	R' = group in R'Li	–NH·BR–, mM	R'–Li, mM	Reactant	Products (%)	
1	Me	Me	2.86	3.28	CO_2/dil. HCl	–NH·BMe–	2.6 (91)
2	Me	Ph	7.8	4.7	Dil. HCl	–NH·BMe–	6.2 (80)
3	Me	Me	8.3	10.0	Me_2SO_4 (21.0 mM)	–NMe·BMe–	8.0 (96)
4	Me	Ph	7.8	6.7	Me_2SO_4 (18.3 mM)	–NMe·BMe–	1.9 (25)
						–NH·BMe–	5.2 (67)

TABLE II

REACTION OF 10-SUBSTITUTED-10,9-BORAZAROPHENANTHRENES WITH TWO MOLES OF ORGANOLITHIUM

No.	R = group in –NH·BR– or RLi	–NH·Br–, mM	R–Li, mM	Reactant	Products (%)	
5	Me	9.9	21.4	Dil. HCl	–NH·BMe–	8.55 (87)
6	Me	3.6	25.0	Dil. HCl	–NH·BMe–	3.6 (100)
7	Me	9.9	21.4	(a) Dil. HCl	–NH·BMe–	5.7 (58)
					–NH$_2$··BMe$_2$–	0.14 (1.4)
				(b) CO_2/dil. HCl	–NH·BMe–	0.5 (5)
					–NH$_2$··BMe$_2$–	2.9 (29)
8	Ph	4.9	10.7	CO_2/dil. HCl	–NH·BPh–	0.4 (8)
					–NH$_2$··BPh$_2$	3.3 (67)
9	Ph	3.1	4.7	Me_2SO_4 (20 mM)	–NMe·BPh–	2.2 (71)
					–NMe$_2$··BPh$_2$–	0.8 (26)
10	Ph	3.1	7.2	Me_2SO_4 (2.14 mM)	–NMe$_2$··BPh$_2$–	1.9 (62)
11	Me	10.3	16.4	Me_2SO_4 (27 mM)	–NMe·BMe–	5.1 (49)
					–NMe$_2$··BMe$_2$–	3.2 (31)

TABLE III

EXCHANGE OF GROUPS ATTACHED TO BORON

No.	R = group in –NH·BR–	R' = group in R'Li	–NH·Br–, mM	R'–Li, mM	Reactant	Products (%)	
12	Me	Ph	6.5	10.4	Dil. HCl	–NH·BMe–	3.4 (52)
						–NH·BPh–	1.9 (27)
13	Me	Ph	4.9	10.7	Dil. HCl	–NH·BMe–	trace
						–NH·BPh–	4.1 (83)
14	Ph	Me	4.7	25.0	Dil. HCl	–NH·BPh–	3.5 (75)
15	Me	Et	5.1	10.7	Dil. HCl	–NH·BMe–	trace
						–NH·BEt–	2.9 (57)
16	Me	Ph	4.9	21.4	CO_2/dil. HCl	–NH·BMe–	trace
						–NH·BPh–	0.7 (14)
						–NH$_2$··BPh$_2$–	2.4 (49)
17	Ph	Me	4.9	14.4	CO_2/dil. HCl	Oil (1.25 g.), presumably –NH$_2$··BPhMe– which decomposes rapidly	

atom to give an adduct (XVIII) in which the indicated dismutation could lead directly to demethylation or dephenylation. The geometry of the adduct XVIII should be particularly favorable for such an intramolecular electrophilic proton attack on the methyl or phenyl group.

Exchange Reactions.—When 10-methyl-10,9-borazarophenanthrene (II) was treated with excess phenyllithium, the methyl group underwent replacement by phenyl. Two moles of phenyllithium gave, after hydrolysis, mostly 10-phenyl-10,9-borazarophenanthrene (III) together with some unchanged starting material (II). Addition of three moles of phenyllithium, followed by carbonation and acid hydrolysis, gave mainly 10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XII) together with a little III.

The formation of these products can be explained simply in terms of the addition reactions discussed above. The first mole of phenyllithium metallates the imino group of II, and the second adds to give the mixed dilithio compound XIX. This on

hydrolysis loses methyl rather than phenyl for two reasons; first, the B-methyl bond must be weaker than the B-phenyl bond since bonds formed by sp^2 carbon are stronger than those formed by sp^3 carbon[5]; secondly, there may possibly be a stabilizing resonance interaction between phenyl and the ring in III.
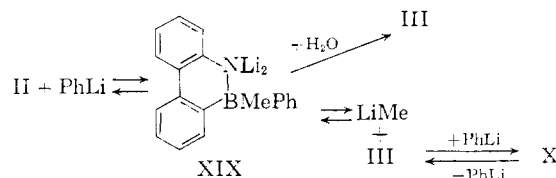
The formation of the diphenyldihydroborazarophenanthrene (XII) on treatment of II with three moles of phenyllithium must imply that addition to the BN bond of II is reversible; thus the adduct XIX can either revert to the starting materials

(5) See M. J. S. Dewar and H. N. Schmeising, *Tetrahedron,* **5,** 166 (1960).

<div align="center">TABLE IV</div>
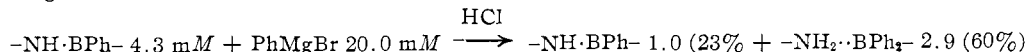
<div align="center">MISCELLANEOUS</div>

18 Reverse reaction

$$-NH_2 \cdot\cdot BMe_2-\ 1.44\ mM\ +\ MeLi\ 10.7\ mM\ \xrightarrow{\ HCl\ }\ -NH\cdot BMe-\ 1.0\ mM\ (71\%)\ +\ -NH_2\cdot\cdot BMe_2-\ (0.3\ mM\ (23\%)$$

19 Grignard reaction

$$-NH\cdot BMe-\ 7.85\ mM\ +\ MeMgI\ 12.9\ mM\ \xrightarrow{\ HCl\ }\ -NH\cdot BMe-\ 7.8\ mM\ (79\%)\ +\ -NH_2\cdot\cdot BMe_2-\ 1.2\ mM\ (12\%)$$

20 Grignard reaction

$$-NH\cdot BPh-\ 4.3\ mM\ +\ PhMgBr\ 20.0\ mM\ \xrightarrow{\ HCl\ }\ -NH\cdot BPh-\ 1.0\ (23\%\ +\ -NH_2\cdot\cdot BPh_2-\ 2.9\ (60\%)$$

II and phenyllithium, or dissociate to III and methyllithium. With an excess of phenyllithium, the III formed in this way can add a second mole of phenyllithium to form X, which on carbonation followed by hydrolysis gives XII.

This mechanism requires all the reactions in the formation of X to be reversible (as indicated in the scheme above); the fact that XII is obtained in good yield by using just three moles of phenyllithium must imply then that the equilibrium

$$II + PhLi \rightleftarrows III + MeLi \qquad (1)$$
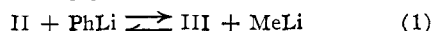
is far over to the right. This was confirmed by experiments in which III was treated with a large excess of methyllithium, and in which exchange of phenyl for methyl did not occur. Hydrolysis of the product gave only III, while carbonation followed by hydrolysis gave an intractable material which changed its nature during working up. Presumably XIX was formed, which on carbonation and hydrolysis gave 10-methyl-10-phenyl-9,10-dihydro-10,9-borazarophenanthrene; this in turn disproportionated to XI and XII, giving a mixture of at least three very similar products. A similar intractable product was obtained by carbonation and hydrolysis of XIX, formed by the action of two moles of phenyllithium on II. Evidently the replacement of methyl by phenyl is not easily reversed, confirming that the equilibrium of eq. 1 favors the phenyl compound III.

The fact that the equilibrium of eq. 1 lies far over to the right is interesting. It can be explained very simply in terms of the variation in bond energy of carbon bonds with hybridization[5]; bonds formed by sp² carbon are stronger than those formed by sp³ carbon. Now the C–Li bonds in organolithium compounds are much weaker than the C–B bonds in organoboron compounds; the difference in bond energy between bonds formed by sp² and sp³ carbon should therefore also be greater for bonds to boron than for bonds to lithium. Consequently the metathesis should be exothermic; and so the

$$C_{sp^2}-Li + C_{sp^3}-B \longrightarrow C_{sp^3}-Li + C_{sp^2}-B$$
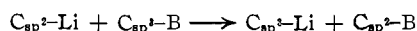
equilibrium of eq. 1 should favor methyllithium and phenylborazarophenanthrene—as is the case.

Methyl groups can also be replaced by ethyl; when II was treated with two moles of ethyllithium and the product hydrolyzed, a 57% yield of 10-ethyl-10,9-borazarophenanthrene was obtained The relatively low yield was undoubtedly due to the difficulty of separating the 10-ethyl compound from the starting material.

**Action of Grignard Reagents.**—The action of Grignard reagents on 10-substituted borazaro-

phenanthrenes has been briefly studied. The reactions seemed to follow the same general course as those with methyl- or phenyllithium, but hydrolysis of the adduct XX gave mainly a derivative of dihydroborazarophenanthrene, demethylation or dephenylation taking place to a much smaller extent than in the corresponding reactions of IX or X (that some anomalous hydrolysis took place even here was indicated by the recovery of 23% of III, even after reaction with five moles of phenylmagnesium bromide). This difference may be due
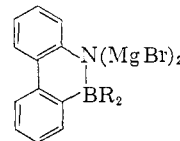

<div align="center">XX</div>

to the greater size of magnesium compared with lithium or to greater covalent character in the dimagnesium compounds XX compared with the dilithio compounds IX, X. The greater size may lead to increased strain in the cyclic transition state (cf. XVIII) involved in the internal rearrangement; while the groups attached to boron must be less negative in XX than in IX or X and so less susceptible to attack by protons.

Conclusions.—It is hard to find good analogies for the reactions described here; nucleophilic addition to BN bonds does not seem to have been observed, although similar additions of organometallic compounds across C=N bonds have long been familiar. Electrophilic addition of hydrogen halides to borazine (XXI) to form the trichloro or tribromo compounds XXII is well known, but the products are much less stable than the dihydroborazarophenanthrene derivatives described in this paper. No cases of exchange of methyl attached to boron for ethyl or phenyl seem to have been reported, while the fission undergone by our dilithio compounds IX, X on hydrolysis seems to be unique. This last reaction is particularly interesting since it suggests that the hydrolytic replacement of metals from metal–organic compounds may be a relatively slow process.
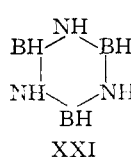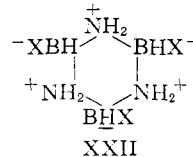
<div align="center">XXI   XXII</div>

<div align="center">Results</div>

For convenience the results together with the quantities of reactants and products, expressed

in millimoles, have been tabulated. It will be noted that the amounts of organolithium reagents used in the reactions were usually rather more than the calculated values. Unfortunately, only small quantities of the borazarophenanthrenes were available for this work, thus limiting the scale of the experiments. This necessitated the use of very small amounts of organolithium reagents and due to a number of causes such as residual wetness of solvents, inaccuracy in the determination of the concentration of organolithiums, etc., rather more than the stoichiometric amounts had to be used.

The following abbreviations are used: –NH·BMe– (10-methyl-10,9-borazarophenanthrene (II)); –NMe·BMe–(9,10 - dimethyl - 10,9 - borazarophenanthrene (VII)); –NH₂·BMe–₂(10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XI)); –NMe₂·BMe₂– (9,10-tetramethyl-9,10-dihydro-10,-9-borazarophenanthrene (XIII)); etc.

The total yields of products in these reactions were usually 80–95%; it is thought that these reactions in fact proceed quantitatively and that the loss of yield is due solely to difficulties of working up and of separating small amounts of the different compounds formed from each other.

Experimental

The starting materials, 10-methyl- and 10-phenyl-10,9-borazarophenanthrene were prepared as previously described[4]; for the deuterium exchange experiments the former was rigorously purified to m.p. 102.5–103° by crystallization from light petroleum. All crystallizations from light petroleum were carried out using the fraction b.p. 40–60°; chromatography was carried out on Peter Spence alumina type H, usually in petroleum ether, b.p. below 40°. Anhydrous magnesium sulfate was used for drying solutions. Ultraviolet spectra were determined in 95% ethanol on a Unicam S.P. 500 spectrophotometer. Infrared spectra were determined, either in carbon disulfide and carbon tetrachloride solutions or as mulls in Nujol and hexachlorobutadiene on a Grubb–Parsons double-beam spectrophotometer. Microanalyses were carried out by Alfred Bernhardt, Max-Planck-Institut für Kohlenforschung, Mülheim, Germany.

Hydrogen–Deuterium Exchange.—10-Methyl-10,9-borazarophenanthrene (0.45 g.) was dissolved in a solution of 0.45 g. of heavy water in 12 g. of dry, freshly distilled dioxane in which 0.02 g. of sodium had previously been dissolved. The contents were shaken for a minute to ensure complete solution and mixing; then the contents were transferred into a distilling flask and the solvent taken off in vacuo at room temperature until a dry residue was obtained. It was estimated that the solid could have been in contact with (at least traces of) solvent for up to 45 minutes, even under the most favorable conditions of rapid handling. The solid was then extracted with dry petroleum ether, the solution filtered and concentrated to give a quantitative yield of 9 - deuterio - 10 - methyl - 10,9 - borazarophenanthrene, m.p. 102.5–103°, no depression of m.p. on mixing with starting material. The infrared spectrum of this material showed that the strong N–H peak present in the undeuterated material at 2.93μ was almost completely absent and had been replaced by a new peak at 3.96μ due to N–D absorption.

Experiments carried out under the above conditions, but without sodium deuteroxide being present and which were left standing at room temperature, showed that after 24 hours there had been negligible exchange; only after 45 hours did exchange become appreciable.

Attempted Direct Methylations. (a) Using Alkaline Dimethyl Sulfate.—10-Phenyl-10,9-borazarophenanthrene (1.0 g.), dimethyl sulfate (1.5 ml.) and water (5 ml.) containing potassium hydroxide (1.5 g.) were refluxed together for 2 hours and then left for 60 hours. Hydrolysis and extraction with ether gave unchanged starting material, m.p. 109–110°, as the sole product in 70% yield.

(b) Using Diazomethane.—An ethereal solution of diazomethane[6] was added to solutions of 10-methyl- and 10-phenyl-10,9-borazarophenanthrene (0.2 g.) in ether (10 ml.). The diazomethane solution was instantaneously decolorized with evolution of nitrogen and deposition of a white fluffy insoluble precipitate, containing no B or N, and presumably consisting of polymethylene. There appeared to be no limit to the amount of diazomethane which these solutions would decolorize. A similar, though considerably slower, reaction was observed using solutions of 10,10-dimethyl- and 10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene. In all cases there was quantitative recovery of starting material.

Reactions of 10-Methyl- and 10-Phenyl-10,9-borazarophenanthrene with Methyl- and Phenyllithium.—Since the procedure followed was basically the same for all the experiments only a few typical ones will be described. All the essential data for the other experiments has been presented under Results.

Experiment 7.—A solution of methyllithium (21.4 mM) in ether (20 ml.) was added slowly to a solution of 10-methyl-10,9-borazarophenanthrene (1.9 g., 9.9 mM) in ether (15 ml.) at −10° with stirring under dry nitrogen. A vigorous evolution of gas was observed during the addition of half the methyllithium; thereafter the color of the solution, which had been very pale yellow, became very much deeper yellow. The solution was stirred for 5 minutes at this temperature, then part was poured into hydrochloric acid (50 ml., 2N) (fraction a) and the remainder poured onto solid carbon dioxide (fraction b).

Fraction a was extracted with ether and the ether evaporated leaving a reddish solid. This was chromatographed to give unchanged II (1.1 g., 58%) and 10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XI) (0.03 g., 1.4%).

When the carbon dioxide had evaporated, fraction b was acidified with dilute hydrochloric acid and worked up as described above. Chromatography of the product gave 10-methyl-10,9-borazarophenanthrene (0.1 g., 5%), m.p. 101–102°, and 10,10-dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XI), (0.6 g., 29%), m.p. 136°.

Anal. Calcd. for C₁₄H₁₆NB: C, 80.40; H, 7.65; N, 6.70; B, 3.30; mol. wt., 209. Found: C, 80.53; H, 7.37; N, 6.71; B, 3.20; mol. wt., 196.

Experiment 8.—Using a procedure identical with that used in Experiment 7b, III (1.25 g., 4.9 mM) was treated with ethereal phenyllithium to give a deep red solution; after carbonation and working up as described, unchanged III (0.1 g., 8%) and 10,10-diphenyl-9,19-dihydro-10,9-borazarophenanthrene (XII, 1.1 g., 67%), m.p. (in vacuo) 232°, were obtained.

Anal. Calcd. for C₂₄H₂₀NB: C, 86.50; H, 6.00; N, 4.20; B, 5.26. Found: C, 86.89; H, 5.87; N, 4.22; B, 5.47.

Experiment 17.—A solution of 10-phenyl-10,9-borazarophenanthrene (1.25 g., 4.9 mM) in ether (20 ml.) was treated with methyllithium (14.4 mM) in ether (20 ml.) and then carbonated. On working up and evaporating the solvent an oil (1.25 g.) was obtained which on treatment with ether and petroleum ether eventually solidified. Recrystallization of the solid (m.p. 140–160°) from ether–petroleum ether, from nitromethane, from benzene–petroleum ether (b.p. 100–120°) or ethanol–water only raised the m.p. to 180–190°; this, however, was raised to 205–210° on the addition of 10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene and it is presumed that this solid must contain some of the latter compound. As this material also chromatographed with the m.p. unchanged the impurity must be XI which chromatographs in the same way as XII. Thus the material obtained was a mixture of XI and XII; this could only have been formed if the initially formed B-methyl-B-phenyl-dihydroborazarophenanthrene disproportionated during the working up procedure.

Experiment 11.—A solution of methyllithium (16.4 mM) in ether (16 ml.) was added to one of 10-methyl-10,9-borazarophenanthrene (2 g., 10.3 mM) in benzene (20 ml.) at room temperature. After stirring for 5 minutes a solution of dimethyl sulfate (3.4 g., 27.0 mM; freshly distilled from potassium carbonate) in benzene (30 ml.) was added. The yellow color faded rapidly and after stirring for a few

(6) J. DeBoer, Rec. trav. chim., 73, 229 (1954).

minutes at room temperature the solution was refluxed for 1 hour, then treated with sodium hydroxide solution (50 ml., 2 N) and extracted with ether. Chromatography separated the residue (2.0 g.) from evaporation of the ether into three fractions. Each of these was again chromatographed into two fractions which were suitably combined to give VII (1.05 g., 49%), m.p. 117–118°, and XIII (0.75 g., 31%), m.p. 108–109°.

9,10-Dimethyl-10,9-borazarophenanthrene (VII).—Anal. Calcd. for $C_{14}H_{14}NB$: C, 81.16; H, 6.76; N, 6.76; B, 5.31; mol. wt., 207. Found: C, 81.13; H, 6.57; N, 6.59; B, 5.50; mol. wt., 189.

9,9,10,10-Tetramethyl-9,10-dihydro-10,9-borazarophenanthrene (XIII): Anal. Calcd. for $C_{16}H_{20}NB$: C, 81.01; H, 8.44; N, 5.90; B, 4.64; mol. wt., 237. Found: C, 80.84; H, 8.67; N, 5.66; B, 4.74; mol. wt., 206.

Experiment 9 was carried out exactly as described for experiment 11. Separation of the product by chromatography gave VIII, m.p. 122.5–123.5°, and XIV, m.p. 224–226°.

9-Methyl-10-phenyl-10,9-borazarophenanthrene (VIII): Anal. Calcd. for $C_{19}H_{16}NB$: C, 84.76; H, 5.95; N, 5.20; B, 4.09; mol. wt., 269. Found: C, 84.79; H, 5.85; N, 5.32; B, 4.40; mol. wt., 243.

9,9-Dimethyl-10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XIV): Anal. Calcd. for $C_{26}H_{24}NB$: C, 86.43; H, 6.65; N, 3.88; B, 3.05; mol. wt., 361. Found: C, 86.69; H, 6.81; N, 3.91; B, 3.23; mol. wt., 339.

The Conversion of 10,10-Dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XII) into 10-Methyl-10,9-borazarophenanthrene (II). Experiment 18.—A solution of methyllithium (10.7 mM) in ether (20 ml.) was added to one of XI (0.3 g., 1.4 mM) in ether (15 ml.). Gas was evolved and the solution turned yellow-green. After stirring for a few minutes the solution was poured into hydrochloric acid (30 ml., 2 N) and extracted with ether. Chromatography of the residue from evaporation of the ether gave II (0.2 g., 71%), m.p. 99–101°, mixed m.p. 101–102°. Elution of the column with ether gave starting material (0.07 g., 23%).

The reactions of B-methyl- and B-phenyl-borazarophenanthrenes with Grignard reagents were carried out in similar fashion to that described for experiment 7a.

Deboronation of 10,10-Diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XII).—The B-diphenyl compound (0.5 g.) was dissolved in cold concentrated sulfuric acid (15 ml.). After 7 hours at room temperature the solution was poured onto ice and neutralized with ammonia. Extraction with ether gave an oil which on chromatography yielded 2-aminobiphenyl (0.15 g., 58%), m.p. and mixed m.p. 50°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Synthesis of Pyranones and Benzofluorenones from Ketones and Carboxylic Acids[1]

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Two new reactions of methylene ketones with carboxylic acids in polyphosphoric acid are discussed. One leads to substituted pyran-4-ones (e.g., 1,3-diphenyl-2-propanone and acetic acid gave 2,6-dimethyl-3,5-diphenyl-4H-pyran-4-one) and the other to alkylated benzo[a] fluorenones (e.g., deoxybenzoin and acetic acid yielded 5-methyl-11H-benzo[a]fluoren-11-one). The reactions provide simple synthetic routes to these ring systems.

It was reported recently that ketone I condensed with acetic acid in hot polyphosphoric acid to give (76% yield) a substituted 4H-pyran-4-one (II).[3] This novel reaction appeared particularly interesting since, if general for methylene ketones, it would provide an unusually simple and convenient route to the pyranones. No study of the reactions of methylene ketones with carboxylic acids in polyphosphoric acid seems previously to have been made, although condensations of great variety have been effected by polyphosphoric

I   II
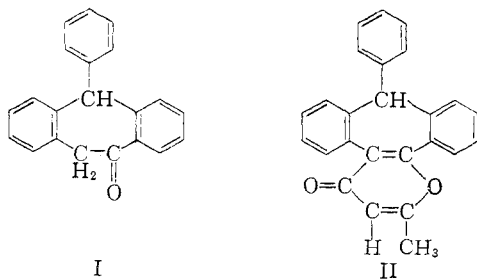
acid.[4] We therefore undertook an investigation of the scope of the reaction exemplified by the con-

version of I to II. The present paper is concerned with the transformations involving 1,3-diphenyl-2-propanone, phenyl-2-propanone, 3-pentanone and deoxybenzoin.

A crystalline product was isolated in 76% yield after the treatment of 1,3-diphenyl-2-propanone with acetic acid in hot polyphosphoric acid. The analysis was consistent with the formula $C_{19}H_{16}O_2$; in agreement with a pyranone formulation the substance was soluble in 4 M hydrochloric acid, yielded a thio derivative (V) when heated with phosphorus pentasulfide, and exhibited a triplet of bands in the infrared between 6.0 and 6.3 μ, characteristic of 4H-pyran-4-ones.[3] Two structures appeared feasible: one (III) would have been produced by a condensation analogous to that by which II was formed from I; the other (IV) would have resulted if the ketone had undergone diacylation to give 3,5-diphenyl-2,4,6-heptanetrione as an intermediate. That IV is the correct structure was established by the n.m.r. spectrum, which showed a single band in the region for aliphatic hydrogen absorption. A more complicated spectrum would be predicted for III.

Phenyl-2-propanone reacted with acetic acid in polyphosphoric acid similarly to the diphenylpropanone; the product, 2,6-dimethyl-3-phenyl-4H-pyran-4-one (VI), was obtained in 48% yield. In support of the assigned structure, VI was converted in high yield via typical reactions for

(1) Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 14, 1960.

(2) Standard Oil Co. of Indiana Fellow, 1958.

(3) R. L. Letsinger, J. D. Jamison and A. S. Hussey, J. Org. Chem., 48, in press (1960).

(4) F. D. Popp and E. McEwen, Chem. Revs., 58, 321 (1958).