of thionyl chloride was allowed to stand overnight and was then heated under reflux 1.5 hr before removal of the excess thionyl chloride under reduced pressure. To the residue was added 2.00 g of phenol in 25 ml of benzene, and the resulting mixture was boiled under reflux for 1 hr. Filtration and cooling of the solution after clarification with charcoal yielded 5.73 g (89%) of the phenyl ester, mp 147.5-149°. A crystallization from acetone-water gave needles, mp 150-150.5°.

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.66; H, 4.79.

Phenyl 2-Phenyl-1-phenanthrenecarboxylate (8).—A suspension of 1.00 g of phenyl 2-methoxy-1-phenanthrenecarboxylate in 20 ml of benzene was added to the Grignard reagent prepared from 0.24 g of magnesium and 1.88 g of bromobenzene in 15 ml of ether. The reaction mixture was heated under reflux for 2.5 hr and hydrolyzed with ice and ammonium chloride. The organic layer and three benzene extracts of the aqueous portion were combined. Steam distillation removed the organic solvents and a small amount of biphenyl. The residue from the distillation was separated by filtration and dried in air. Crystallization from acetone afforded 0.91 g (80%) of white crystals, mp 185-186°. Sublimation in high vacuum gave an analytically pure sample mp 185.5-186°.

Anal. Calcd for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.28; H, 4.75.

11H-Indeno[2,1-*a*]phenanthren-11-one (9). From Pure 8.—A solution of 100 mg of the ester **8** in 5 ml of concentrated sulfuric acid was allowed to stand at room temperature for 1.5 hr. The permanganate-colored mixture was poured into ice water, and the resulting yellow precipitate was collected by filtration, washed with 5% aqueous sodium carbonate and water, and dried in air to give 53 mg (71%) of material, mp 207-212°. Crystallization from ethyl acetate gave golden yellow needles of the ketone **9**, mp 213.5-214°; crystallization from acetic acid produced a darker product melting over a wider range at a lower temperature. The sample crystallized from acetic acid had properties more in keeping with those described in the literature[7] (reddish orange needles, mp 207-208°).

11H-Indeno[2,1-*a*]phenanthren-11-one (9). From 3 without Isolation of Pure 8.—A solution of 657 mg of phenyl 2-methoxy-1-phenanthrenecarboxylate (**3**) in 40 ml of benzene was added to the Grignard reagent prepared from 0.24 g of magnesium and 1.88 ml of bromobenzene in 15 ml of ether. The reaction mixture was heated under reflux for 2.5 hr and hydrolyzed with ice and ammonium chloride. The organic layer and three benzene extracts of the aqueous portion were combined and steam distilled. The solid in the cooled residue was separated by filtration and dried in air. The solid was next stirred into 15 ml of concentrated sulfuric acid and allowed to stand at room temperature for 1.5 hr. The permanganate-colored mixture was poured onto ice; the resulting precipitate was collected by filtration and washed with 5% aqueous sodium carbonate solution and water. Crystallization of the dried material from ethyl acetate furnished 341 mg (61%) of **9** as golden yellow needles, mp 214-214.5°.

11H-Indeno[2,1-*a*]phenanthrene (1).—The ketone **9** was reduced by the Wolff-Kishner reaction as modified by Weisburger and Grantham.[17] A suspension of 36 mg of ketone **9** in 20 ml of distilled diethylene glycol and 2 ml of 85% hydrazine hydrate was warmed at 100° for 5 min; 1 ml of 10% potassium hydroxide in the same solvent was added; and the solution was kept at 100° for 10 min longer. Water was driven off until the temperature rose to 200°; further heating for 2 hr was continued under reflux. The reaction mixture was cooled and poured into 100 ml of cold water and filtered. The solids were washed with water and dried in air to give 27.4 mg (80%) of the crude hydrocarbon, mp 330-331° (uncor). Crystallization from benzene gave blades, mp 331-332° (uncor) and 335-336° (uncor, in a sealed, evacuated capillary) (lit.[11] mp 335-336°).

7-Methyl-11H-indeno[2,1-*a*]phenanthren-11-one (10).—A solution of 200 mg of **3** in 6 ml of benzene was added to the Grignard reagent prepared from 82 mg of magnesium and 0.48 ml of *o*-bromotoluene in 8 ml of ether. Treatment of the reaction mixture was similar to that described for the direct preparation of **9** from **3**. Crystallization of the crude, dry ketone from ethyl acetate gave 89 mg (49%) of **10** as yellow needles, mp 211-212°. After sublimation and recrystallization from ethyl acetate, the ketone melted at 213-214° (lit.[8] mp 209-210°).

7-Methyl-11H-indeno[2,1-*a*]phenanthrene (2).—Reduction of 20 mg of the ketone **10** by the procedure described for the preparation of **1** gave 16 mg (84%) of the crude, colorless hydrocarbon, mp 272.5-274°. Sublimation followed by crystallization from ethyl acetate gave colorless crystals, mp 274-275° (lit.[8] mp 275-276°).

Registry No.—**1,** 220-97-3; **2,** 16793-26-3; **3,** 16793-27-4; **8,** 16793-28-5; **9,** 4599-92-2; **10,** 16793-30-9.

10-Hydroxy-10,9-boroxarophenanthrene. A Lewis Acid[1]

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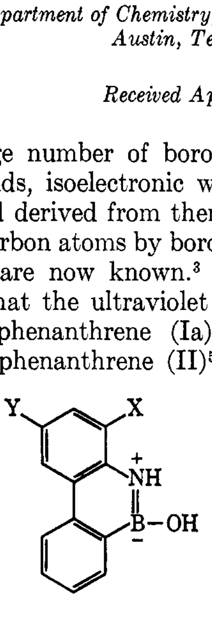
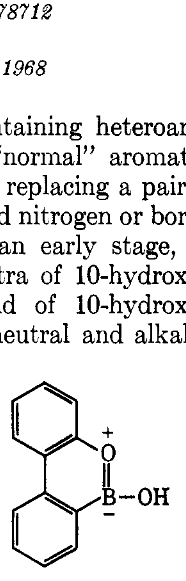
Received April 9, 1968

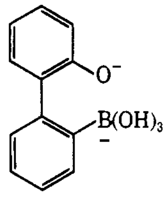
A large number of boron-containing heteroaromatic compounds, isoelectronic with "normal" aromatic systems and derived from them by replacing a pair of adjacent carbon atoms by boron and nitrogen or boron and oxygen, are now known.[3] At an early stage, it was shown that the ultraviolet spectra of 10-hydroxy-10,9-borazarophenanthrene (Ia),[4] and of 10-hydroxy-10,9-boroxarophenanthrene (II)[5] in neutral and alkaline solution suggested that these compounds behaved as protic acids, unlike normal boronic or borinic acids that seem to form salts by addition to boron. This difference was attributed to aromatic stabilization of the boron-containing rings, and indeed was cited as evidence that such compounds are aromatic. Since that time it has usually been assumed that other analogous hydroxyborazaro and hydroxyboroxaro compounds show similar behavior to base by acting as protic acids, rather than Lewis acids.



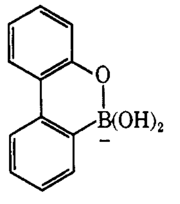
Ia, X = Y = H
b, X = H; Y = NO_2
c, X = NO_2; Y = H



II



III



IV

Recently[6] it was shown that ^{11}B nmr spectroscopy provides a simple and unambiguous criterion of the mode of

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[1] This work was supported by a grant from The Robert A. Welch Foundation.

[2] Robert A. Welch Postdoctoral Fellow, 1966-1968.

[3] See M. J. S. Dewar, *Prog. Boron Chem.*, **1**, 235 (1964); R. F. Gould, "Boron-Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.

[4] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

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

[6] M. J. S. Dewar and R. Jones, *J. Amer. Chem. Soc.*, **89**, 2408 (1967).

reaction of boron acids with base. Salt formation by addition of base to boron leads to a very large upfield shift (~25 ppm) with narrowing of the ^{11}B resonance, while salt formation by loss of a proton leads to a downfield shift of *ca.* 5 ppm with extreme broadening, the half-width of the ^{11}B absorption increasing to 1–3 kHz. Application of this technique to several β-hydroxyborazaro compounds, including Ia, showed that they do indeed behave as protic acids, confirming the earlier conclusions based on uv spectroscopy. No measurements were made at that time on the oxygen analog II, since no sample was available and since the uv spectrum seemed to provide equally definitive evidence that it too functions as a protic acid.

We have now measured the ^{11}B nmr spectrum of II in alcohol and in alcoholic potash and have found, much to our surprise in view of the uv evidence, that it does in fact act as a Lewis acid, rather than as a protic acid. As the results in Table I show, salt formation leads to a large upfield shift and a narrowing of the ^{11}B resonance, in analogy to phenylboronic acid and in marked contrast to the protic acid (Ia) where salt formation leads to a large downfield shift with extreme broadening of the ^{11}B nmr line.

TABLE I

^{11}B NMR SPECTRA OF BORON ACIDS IN NEUTRAL AND ALKALINE SOLUTIONS

Compd	Solvent	Chemical shift[a]	Line width[b]
Ia	EtOH	−29.3[c]	221
	EtOH–5% KOH	−43.9[c]	2500
Ib	DMSO	−36.9[c]	1250
	DMSO–5% KOH	−12.5[c]	780
Ic	THF	−41.0[c]	380
	THF–5% KOH	−21.5[c]	310
II	EtOH	−28.8	233
	EtOH–5% KOH	−5.5	162
PhB(OH)$_2$	EtOH	−28.4	272
	EtOH–5% KOH	−3.2	80

[a] In parts per million relative to boron trifluoride-etherate. [b] At half-height, in hertz (Hz). [c] Reference 9.

Since the original spectroscopic evidence seemed to provide convincing evidence that II behaves as a protic acid, we reexamined the uv spectrum (Figure 1). Addition of alkali to a solution of II in ethanol did indeed lead to a bathochromic shift of *ca.* 20 mμ, and the long wave absorption maxima of the salt was at much longer wavelength than that of 2-hydroxybiphenyl (286 mμ); however, the long wave band of II in alkali (Figure 1) consisted of a single maximum only, whereas the long wave bands of I or II in ethanol, or of Ia in alcoholic potash, showed double maxima, and the bathochromic shift of II on addition of alkali was much greater than that observed in the case of I.

The spectrum of II in alkali was in fact almost identical with that of the 2-hydroxybiphenate ion (Figure 1), suggesting that base converts II into the dianion III, with opening of the central ring. However, two lines of evidence show that this cannot be the case. First, the ^{11}B nmr spectrum of II in alkali differed very markedly from that of phenylboronic acid, both in chemical shift and line width, although in ethanol both compounds show very similar spectra (Table I). Secondly, the proton nmr spectrum of II in ethanol was almost unchanged by addition of base, retaining a two-proton signal 48 Hz downfield from the remaining aromatic protons; this behavior is characteristic of the hindered 4 and 5 protons in phenanthrene and compounds of related structure and is not observed in derivatives of biphenyl.[7] The anion formed from II by base must therefore have the structure IV.

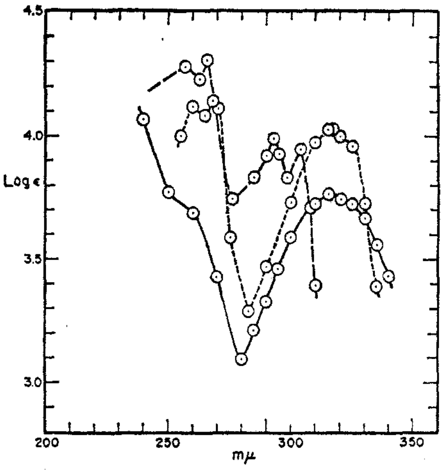

Figure 1.—Ultraviolet spectra of II in ethanol (— —) and 5% ethanolic potassium hydroxide (- - - -) and of 2-hydroxybiphenyl in 5% ethanolic potassium hydroxide (——).

A referee has suggested that hydrogen bonding in III might lead to a sufficient degree of coplanarity for the 4 and 5 protons to remain hindered; this, however, seems very unlikely, for two reasons.

First, the effect depends very critically on the degree of coplanarity of the rings, separation of the 4- and 5-proton signal from the main aromatic multiplet being much less (27 Hz) for 9,10-dihydrophenanthrene than for phenanthrene (55 Hz) or for II in ethanol (48 Hz). Even dibenzothiophene shows a reduced separation (39 Hz), due presumably to bending of the bond joining the phenyl groups with a consequent small increase in the distance between the 4 and 5 protons. As examination of models shows that the dihedral angle in III must be at least as great as that in 9,10-dihydrophenanthrene, the fact that the separation of the 4- and 5-proton signal of II is unchanged by alkali seems to show unambiguously that the resulting anion is not III.

Secondly, the sulfur analog of II *does* undergo ring opening on treatment with alkali; in the resulting solution, containing the sulfur analog of III, the nmr signal for the aromatic protons appear as a single multiplet.[8]

It is not of course surprising that II should, unlike I, behave as a Lewis acid; for II should be, and is, less aromatic that I. It is, however, very surprising that the spectrum of II in alkali should be so nearly identical with that of 2-hydroxybiphenyl for it implies that combination of the ion ArO$^-$ (Ar = 2-biphenyl) with trivalent boron to form an ion of the type ArOBR$_3^-$ leads to no change in the absorption spectrum, whereas combination of ArO$^-$ with a proton to form ArOH leads to a large hypsochromic shift. From the accepted theory of the spectra of phenols and phenolate ions, one would conclude that oxygen has the same effective electronegativity in ArOBR$_3^-$ as in ArO$^-$, clearly a very unexpected and theoretically interesting result.

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(7) C. Reid, *J. Mol. Spectrosc.*, **1**, 18 (1957).

(8) F. A. Davis and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **90**, 3511 (1968).

In conclusion, it should be added that, in the course of another investigation in these laboratories, it has been found that the 6-nitro II (Ib) and 8-nitro II (Ic) derivatives of I also function as Lewis acids and that their salt formation is also accompanied by large bathochromic shifts.[9] Here, however, one cannot make an analogous comparison of the groups $ArNH^-$ and $ArNHBR_3^-$ since the ion $ArNH^-$ cannot of course exist in ethanol.

Experimental Section

^{11}B nmr spectra were measured with a Varian DP-60 spectrometer using procedures described[6] previously. Ultraviolet spectra were measured using a Beckman DK-2 spectrometer. The nmr spectra were measured on a Varian A-60 instrument.

10-Hydroxy-10,9-boroxaropheanthrene[5] (II).—The proton nmr spectrum of II in chloroform-*d* consists of multiplets at δ 8.2 and 7.4 (ratio of integrated intensities 1:3). There was no change in the multiplets position on using ethanol or 5 or 10% potassium hydroxide in ethanol as the solvent.

Registry No.—Ia, 17012-25-8; Ib, 15813-11-3; Ic, 15889-55-1; II, 14205-96-0; $PhB(OH)_2$, 98-80-6.

[9] M. J. S. Dewar, R. Jones, and R. Logan, Jr., *J. Org. Chem.*, **33**, 1359 (1968).

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cis- and *trans-*Bicyclo[6.1.0]nonan-2-one

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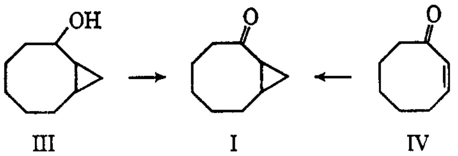
Received February 5, 1968

In connection with our continuing interest in cyclopropane chemistry, we have had occasion to synthesize both *cis-* and *trans-*bicyclo[6.1.0]nonan-2-one (I and II, respectively). We wish to report this synthesis and to describe the behavior of the strained *trans* isomer II.

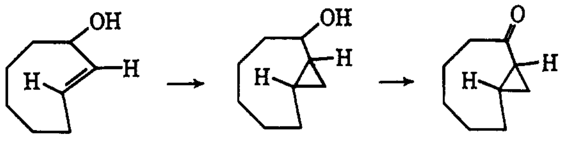
Strained bicyclic compounds are ordinarily quite stable. However, in the case of II, a ready pathway is available for isomerization to the *cis* isomer I, *viz.*, enolization. We were interested in knowing how facile this epimerization process was. Furthermore, studies with molecular models indicated that there just might be little difference between the free energies of I and II. We therefore were interested in determining if substantial amounts of II existed when equilibrium was established between the two isomers.

The *cis* ketone I was synthesized by the Jones oxidation[1] of *cis*-bicyclo[6.1.0]nonan-2-ol[2] (III) and also by the Corey procedure[3] by allowing *cis*-cycloocten-3-one[4] (IV) to react with dimethyloxosulfonium methylide. The material obtained by either route was identical in all respects.



III I IV

The *trans* ketone II was synthesized by the Jones oxidation[1] of *trans*-bicyclo[6.1.0]nonan-2-ol (VI), which was prepared by the Simmons–Smith reaction[5] of *trans*-cycloocten-3-ol[6] (V).



V VI II

Samples of I and II were shown to be different by comparison of their nmr and infrared spectra and vpc retention times and by comparison of the melting points of their 2,4-dinitrophenylhydrazone derivatives. The structure of the *trans* ketone was conclusively established when it was found that the ketone could be isomerized to the *cis* ketone I by treatment with base (*vide infra*).

It was first established that the *cis* ketone I was inert to the usual acid or base treatments. When treated with sodium methoxide in methyl alcohol, potassium *t*-butoxide in *t*-butyl alcohol, or 2 *N* sulfuric acid in ether, I was recovered unchanged.

Next, the *trans* ketone II was subjected to a variety of basic and acidic reaction conditions. After being treated with 2 *N* sulfuric acid in ether for 15 hr at room temperature, or after being eluted through grade I neutral Woelm alumina, II was recovered unchanged. However, after being treated with 1.5 *M* sodium methoxide in methyl alcohol for 87 hr at room temperature, II was completely converted into the *cis* ketone I (>99%); the half-life for this conversion was found to be about 8 hr. When treated with 1.5 *M* sodium hydroxide in methyl alcohol, the rate of isomerization was about the same. The *trans* ketone II could also be isomerized with sodium carbonate in 50:50 water–methyl alcohol, but the reaction was slower; after 16 hr at room temperature, about 2% conversion into I had occurred, whereas after 15 hr at reflux (73°), complete conversion into I had occurred.

These isomerization studies thus establish that I and II are epimers and that the structure of II is that formulated above. These studies further prove that the *cis* ketone I is much more thermodynamically stable than the *trans* ketone II. Finally, it has been shown that II is stable under mild acidic treatment but is readily isomerized by base.

There is one reference in the literature to the *cis* ketone I. Gutsche[7] has claimed that I is one of the products obtained when N,N′-dicarbethoxy-N,N′-dinitroso-1,3-propane is treated with cyclohexanone in the presence of base. However, the infrared and nmr data of his ketone and the melting point (113–114°) and color (blood red) of its 2,4-dinitrophenylhydrazone derivative are clearly incompatible with those of the ketone and its 2,4-dinitrophenylhydrazone derivative studied by us. In view of the two unambiguous syntheses of I described in this communication, we feel that

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[1] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

[2] A. C. Cope, *et al.*, *ibid.*, **79**, 3900 (1957).

[3] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

[4] A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).

[5] W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

[6] G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967). We are indebted to Dr. Whitham for supplying us with the detailed procedure for synthesizing V.

[7] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).