SYNTHESIS AND AROMATIC CHARACTER OF 3-HYDROXY-3-CYCLOHEXENOBOREPIN AND 3-HYDROXY-3-BENZOBOREPIN

by

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TO MY WIFE KARIN
WHOSE PATIENCE WITH ME AND CHEMISTRY
APPEARED TO BE LIMITLESS

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor George Axelrad for suggesting the problem and for guidance past the numerous obstacles encountered.

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ABSTRACT

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PRINCIPAL ADVISOR: GEORGE AXELRAD

The preparation of 3-hydroxy-3-cyclohexenoborepin and 3-hydroxy-3-benzoborepin is accomplished by the treatment of the respective dialkylstannepin with boron trichloride followed by hydrolysis. The ir, uv, nmr, and mass spectra of the borepins are discussed. In addition, the initial investigation of their aromatic properties is described.

The aromatic character of 3-hydroxy-3-benzoborepin is assessed by comparing its uv spectrum to the uv spectrum of 4,5-benzotropone and to that of the 3-hydroxybenzotropylium ion. There is strong evidence that the 10-π-electrons of 3-hydroxy-3-benzoborepin are delocalized about the 11-p-orbitals, and that the 6-π-electrons of 3-hydroxy-3-cyclohexenoborepin are delocalized about 7-p-orbitals. The aromatic nature of the non-benzo-stabilized borepin ring is demonstrated by the correlation of the uv spectrum of 3-hydroxy-3-cyclohexenoborepin to the uv spectra of the hydroxytropylium ion and tropone.

The chemical shift of the nmr spectra of the seven-membered ring hydrogens of the borepins are in the region anticipated for aromatic compounds. This is demonstrated by the comparison of their nmr spectra to the nmr spectra of β-naphthol, phenol, and the nonaromatic 1-hydroxy-4,5-dihydroborepin.

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CHAPTER I

INTRODUCTION

The designation of compounds as "aromatic" was first applied to certain natural products on account of their characteristic flavors and odors. When it was determined by Kekulé that many of these compounds were derivatives of benzene, this olfactory classification took on structural significance and the term aromatic implied benzene and its derivatives.[1] Shortly thereafter, Erlenmeyer suggested that Kekulé's concept of aromaticity be extended to encompass substances of similar behavior rather than those with a common structural feature,[2] and "the possibility of these alternative interpretations has subsequently bedevilled organic chemistry".[3]

In 1925, Armit and Robinson formulated the concept of an aromatic sextet because the six π-electrons of benzene seemed to account for its unusual chemical stability. They realized that aromatic character was not a uniform property and that considerable variations might be evident between different aromatic compounds.[3]

Subsequently, this theory was shown to be compatible with the quantum physics of electrons. The Hückel rule states that fully conjugated, planar, monocarbocyclic poly-

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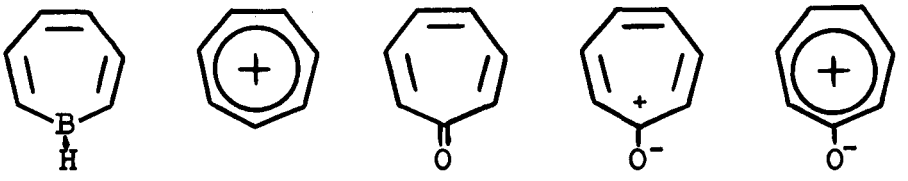
1. R. Robinson, Tetrahedron, 3, 323(1958).
2. E. Erlenmeyer, Justus Liebigs Ann. Chem., 137 327(1866).
3. D. Lloyd, "Carbocyclic Nonbenzenoid Aromatic Compounds", Elsevier, New York, N.Y., 1966, p 3-6.

olefins, possessing (4n+2) π-electrons, where n is an integer, will have special stability. Hückel calculated the π-electron resonance energies of the five-, six-, and seven-membered cyclic anions, radicals, and cations, providing a theoretical test of aromaticity. Tropylium chloride was isolated sixteen years later and constituted strong support for his theory.[4-8] This discovery also explained the apparent aromatic-like behavior of tropolone, which, up to this point had not been classified as an aromatic compound.

Further theoretical extensions of the (4n+2) rule included cross-conjugated systems (azulene) and, later, heterocycles that are iso-π-electronic to benzenoid aromatic compounds.[9] Borepin(I) is iso-π-electronic with benzene, with the tropylium ion(II), and with the polarized resonance forms (a and b) of tropone(III). The synthesis of the borepins would provide compounds to test the validity of the extensions of the Hückel rule.



I II III IIIa IIIb

4. H. J. Dauben Jr., and H. J. Ringgold, J. Amer. Chem. Soc., 73, 876(1951).

5. W. von E. Doering and F. L. Detert, ibid., 73, 876(1951).

6. W. von E. Doering and L. H. Knox, ibid., 76, 3203(1954).

7. W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. 1, Elsevier, New York, N. Y. 1955, p 673.

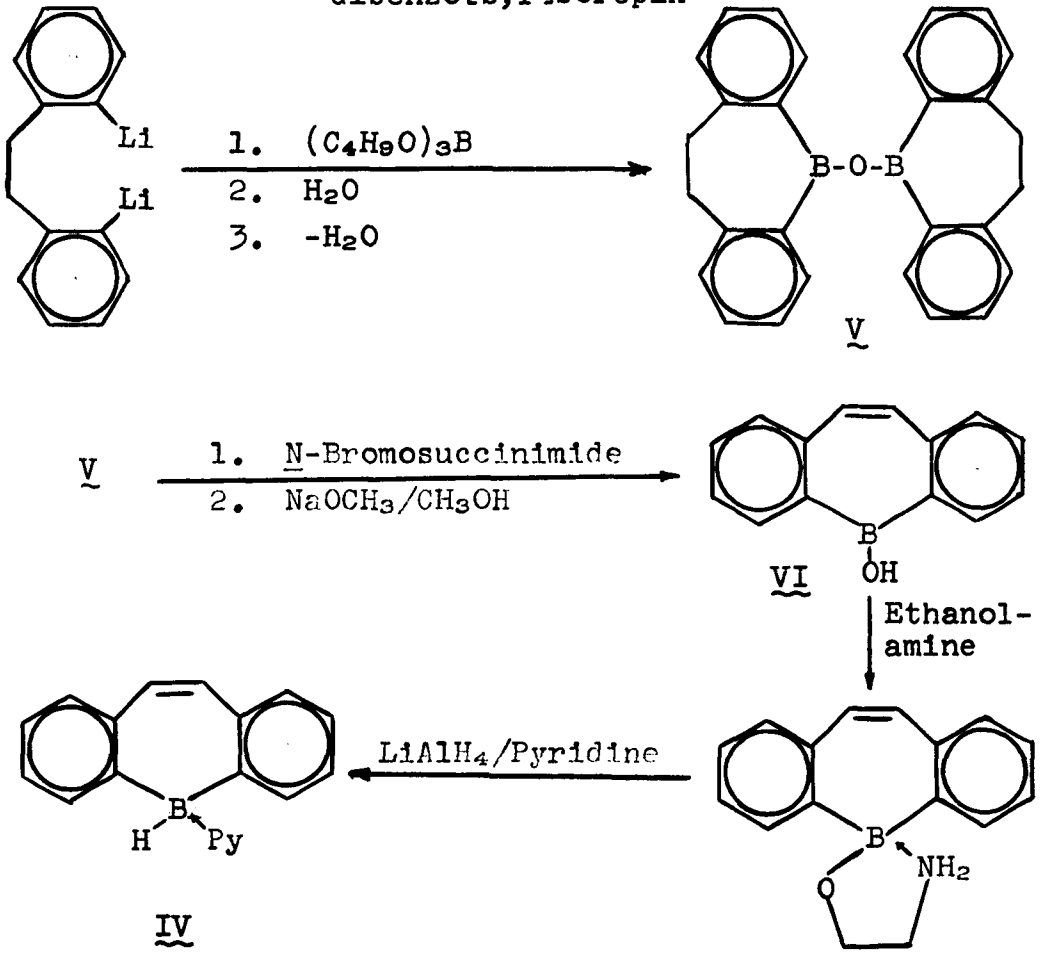
8. Ibid., p 588.

9. A. T. Balaban and Z. Simon, Tetrahedron, 18, 315(1962).

History of the borepins

Interest in the synthesis of the borepins increased as more non-benzenoid aromatic compounds were discovered. The pyridinium salt of dibenzo[b,f]borepin(IV) was the first to be prepared. Reaction of o,o'-dilithiobibenzyl with tri-n-butyl borate, followed by dehydration led to the anhydride of 5-hydroxy-10,11-dihydrodibenzo[b,f]borepin(V).[10]

Chart 1. Synthesis of the pyridinium salt of dibenzo[b,f]borepin



10. R. L. Letsinger and I. H. Skoog, J. Amer. Chem. Soc., 77, 5174(1955).

Bromination at the 10-position with N-bromosuccinimide and dehydrohalogenation resulted in 5-hydroxydibenzo-[b,f]borepin(VI). When the monoethanolamine ester of 5-hydroxydibenzo[b,f]borepin was treated with lithium aluminum hydride in pyridine, it gave the pyridinium salt of dibenzo[b,f]borepin;[11,12] however, the investigators made no clear statement concerning the aromatic character of dibenzo[b,f]borepin.[12]

Various attempts by Sheehan to synthesize the parent compound, borepin, from 1,1-di-n-butyl-4,5-dihydrostannepin (VII) resulted in several advances in the state of the art of organometallic synthesis, if not in success with the basic objective, as shown in chart 2.[13] It was known that the addition of organotin hydrides to terminal alkynes gave only the vinyltin adduct.[14] The condensation of 1,5-hexadiyne and di-n-butyltin dihydride, followed by depolymerization, resulted in 1,1-di-n-butyl-4,5-dihydrostannepin.[13,14] Using the established route for the disproportionation of organotin compounds, Sheehan combined 1,1-di-n-butyl-4,5-dihydrostannepin and phenylboron dibromide to obtain 1-phenyl-4,5-dihydroborepin(VIII) and di-n-butyltin dibromide. Similarly, boron trichloride and 1,1-di-n-butyl-4,5-dihydrostannepin gave 1-chloro-4,5-dihydroborepin(IX) and di-n-butyltin dichloride. All of Sheehan's attempts to dehydrogenate 1,1-di-n-butyl-4,5-dihydrostannepin were unsuccessful.[13]

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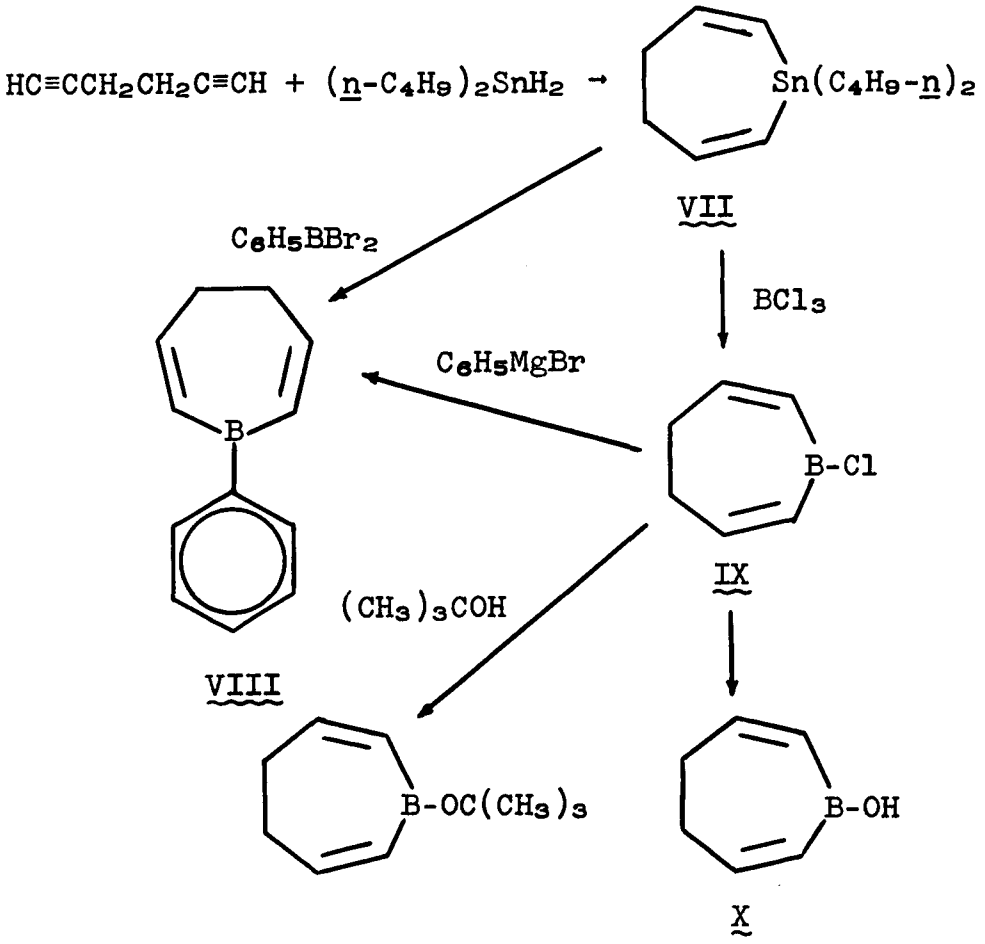
11. G. Brieger, Ph. D. Thesis, University of Wisconsin, Madison, Wisconsin, 1961

12. E. E. van Tamelen, G. Brieger, and H. G. Untch, Tetrahedron Lett., 1960, 14.

13. D. Sheehan, Ph. D. Thesis, Yale University, New Haven, Connecticut, 1965.

14. A. J. Leusink, J. G. Noltes, H. A. Budding, and J. G. M. van der Kerk, Rec. Trav. Chem. Pays-Bas, 83, 1036(1964).

Chart 2. Synthesis of the 4,5-dihydroborepins



A recent approach to the preparation of a 2,7-disubstituted borepin was attempted by the Raney nickel treatment of bis-(4-dithieno[3,2-b:2',3'-f]borepinyl) ether (XI). No report of the isolation of the monocyclic borepin (XII) by this route has appeared to date (Chart 3).[15]

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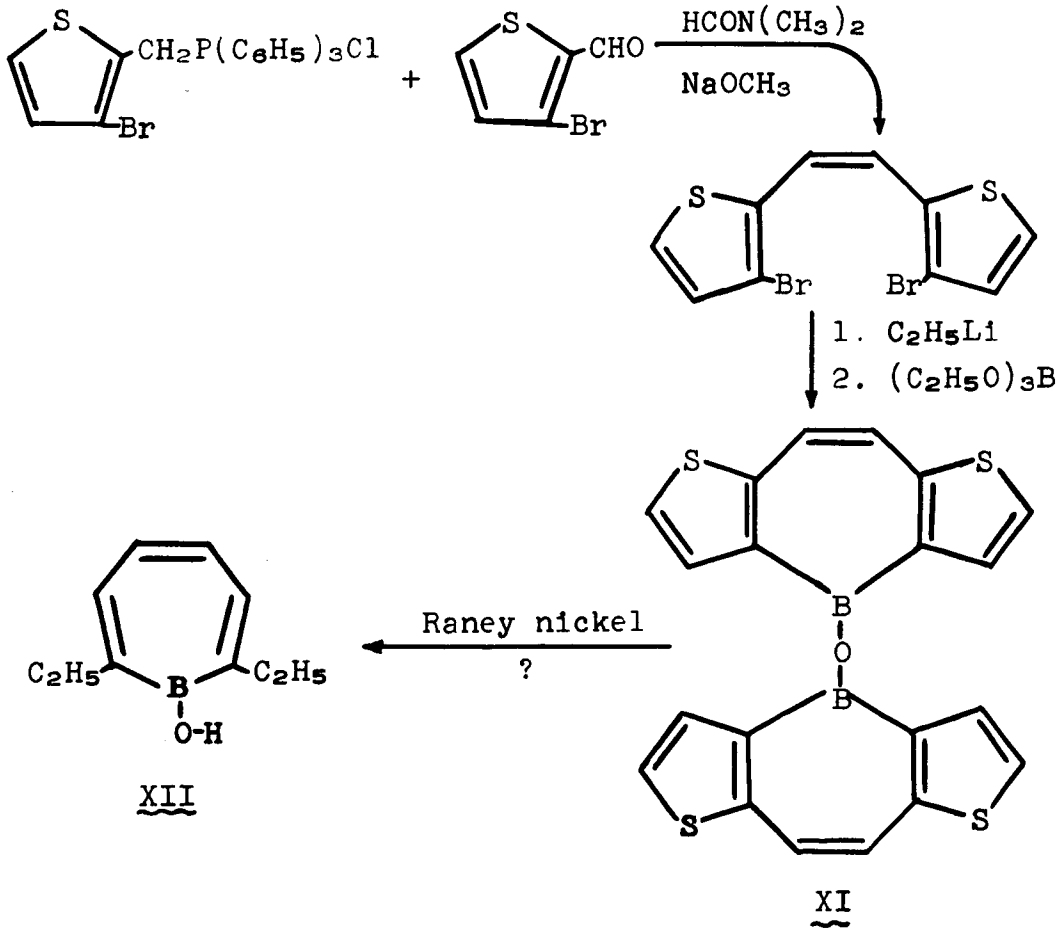
15. S. Gronowitz, P. Gassne, and B. Yom-Tov, Acta. Chem. Scand., 23, 2927(1969).

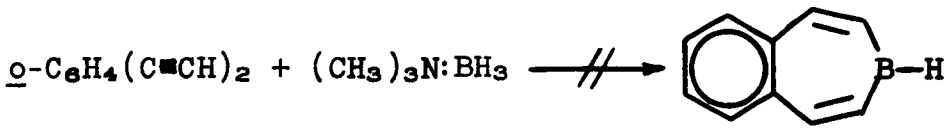
Chart 3. The 2,7-disubstituted borepin



XII

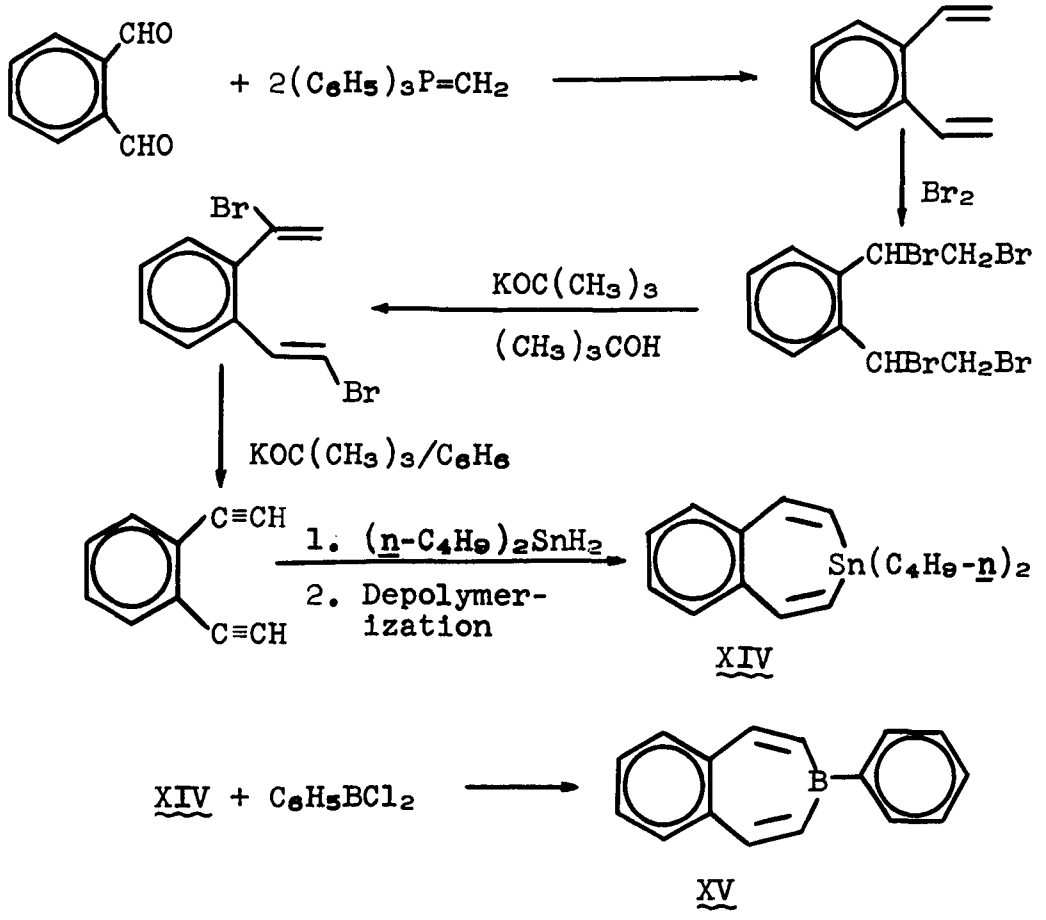
XI

In still another approach to the synthesis of a borepin, Brieger attempted to prepare 3-benzoborepin(XIII) directly from o-diethynylbenzene and the trimethylamine-borane complex, but without success.[11]



XIII

Chart 4. Synthesis of 3-phenyl-3-benzoborepin



In order to test the modifications of the Hückel rule by Balaban and Simon,[9] the synthesis of the benzoborepin series was undertaken. The initial part of this work was the substitution of o-diethynylbenzene for 1,5-hexadiyne in Sheehan's 1,5-hexadiyne-di-n-butyltin dihydride condensation,[13] thereby isolating 3,3-di-n-butyl-3-benzostannepin(XIV). Addition of phenylboron dichloride to 3,3-di-n-butyl-3-benzostannepin would be expected to give 3-phenyl-3-benzoborepin(XV). The shortest route to o-diethynylbenzene began with o-phthalaldehyde. It had been clearly established that the methylene ylide of triphenylmethylphosphonium bromide and o-phthalaldehyde gave

o-divinylbenzene,[16] which could then be brominated and dehydrohalogenated to give o-diethynylbenzene,[17] as shown in chart 4.

While preparing a sufficient quantity of o-divinylbenzene to complete the synthesis of o-diethynylbenzene, a brief communication by Leusink and coworkers appeared, reporting the synthesis of 3-phenyl-3-benzoborepin from 3,3-dimethyl-3-benzostannepin.[18] They compared the uv spectra of 3-phenyl-3-benzoborepin, the benzotropylium ion (XV), and the 3-methylbenzotropylium ion to conclude: "Thus, the uv spectral properties of 3-phenyl-3-benzoborepin are in accord with the view that the empty P_z-orbital participates in the π-electronic system of the ring, resulting in aromatic character."[18] Nmr spectral comparison of 1-phenyl-4,5-dihydroborepin, 3-phenyl-3-benzoborepin, and the dimethylamine adduct of the latter also led these authors to the same conclusion.[18]

It was felt that although the synthesis of 3-phenyl-3-benzoborepin was a major step in the study of the aromatic character of the borepins, conclusions concerning aromaticity based on spectral comparison of dissimilar compounds was somewhat equivocal. Furthermore, the fused benzo-ring and the phenyl substituent had very likely perturbed the spectrum of the borepin ring. In order to avoid the perturbation due to the phenyl substituent, the synthesis and spectral characterization of 3-hydroxy-3-benzobor-

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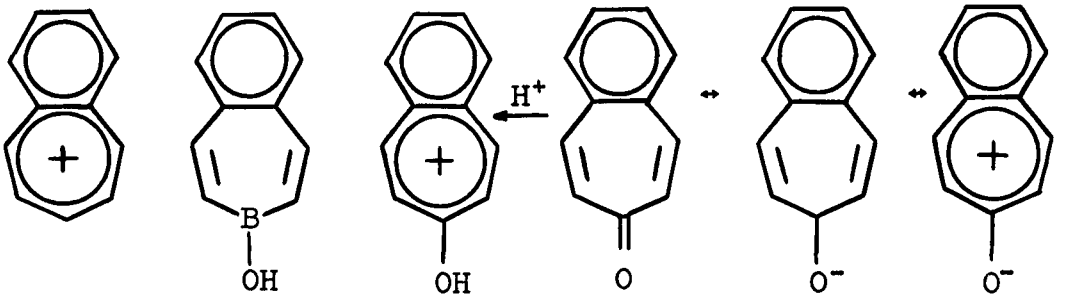
16. A Maercker, "Organic Reactions," Vol. 14, A. C. Cope, Ed., John Wiley and Sons, New York, N. Y., 1965, p 396.

17. O. Behr, G. Eglinton, A. Galbraith, and R. Raphael, J. Chem. Soc., 1960, 3620.

18. A. J. Leusink, W. Drenth, J. G. Noltes, and G. J. M. van der Kerk, Tetrahedron Lett., 14, 1263(1967).

epin(XVII) became the next objective of this investigation. Its uv and nmr spectra could properly be compared to the spectra of 4,5-benzotropone(XVIII) and the derived 3-hydroxybenzotropylium ion(XIX).



XV XVII XIX XVIII XVIIIa XVIIIb

CHAPTER II

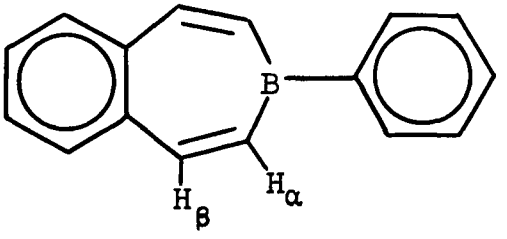
SYNTHESIS OF SUBSTITUTED BOREPINS

3-Phenyl-3-benzoborepin(XV)

The synthesis of 3-phenyl-3-benzoborepin was completed as outlined in Chart 4 and the analytical and spectral data were compared to the published report as shown in Table 1.[18]

TABLE 1

3-PHENYL-3-BENZOBOREPIN



XV

	This Study	Calculated Value	Leusink's Report[18]
	Microanalysis		
% C	89.19	88.93	89.2
% H	6.25	6.06	6.0
% B	4.80	5.01	...

TABLE 1. Continued

	This Study	Calculated Value	Leusink's Report[18]
Molecular Weight (Rast)			
	220	216.08	215
Melting Point			
Initial mp	162.0-163.1°		134-7°
Mp after exposure to air for 72 hr	155.5-157.0°		Reported stable to air
Ultraviolet Spectrum in nm (Log ε)			
	238(4.49) 285(4.71) 303(4.46) 322(3.98) 337(4.23)		232(4.50) 285(4.68) 301(4.45) 322(3.98) 336(4.22)
NMR Spectrum (τ units)			
H_α	obscured*		2.28
H_β	1.63		1.78

* Obscured by the complex multiplet from 1.76-2.56τ.

The difference in mps was puzzling in view of the similarity of the uv spectra. A possible explanation for the discrepency could be based on Leusink's statement

that "the compound is air stable."[18] In this study all manipulations of boron containing compounds were performed under nitrogen. Melting points were taken by degassing the capillary, adding the sample to the tube in an atmosphere of prepurified nitrogen, and flame sealing the capillary tube immediately on removal from a glove bag. The heptane used as a solvent for uv spectra was not degassed. Therefore, the uv spectrum may be the spectrum of a 3-phenyl-3-benzoborepin:oxygen complex. The mp of a sample of 3-phenyl-3-benzoborepin stored in this laboratory in a screw-cap container for six months dropped from 162.0-163.1° to 131.0-142.5° and its mass spectrum showed a prominent molecular ion + 16 peak ($M^+ + O^{16}$).

The elucidation of structure of 3-phenyl-3-benzoborepin was omitted in Leusink's brief communication.[18] Therefore, 3-phenyl-3-benzoborepin was treated with perdeuteroacetic acid and cis,cis'-o-divinylbenzene-d_2 was isolated.[18] Comparison of the nmr spectrum of the latter compound with the nmr spectrum of undeuterated o-divinylbenzene revealed the disappearance of H_b and the expected change from an ABX to an AX pattern as shown in Table 2.

Deboronation-deuteration was very successful as shown by the reduction of the area of the cis-peak to 9 percent of that in o-divinylbenzene. A 12 Hz doublet at 4.80 τ represented H_a. After deuteration, H_x is a multiplet, resulting from the doublet of doublets from the 9 percent H_b remaining undeuterated and further splitting from the ring protons.

To further confirm the structure assigned to 3-phenyl-3-benzoborepin, a mass spectrum was taken. The results are tabulated in Table 3.

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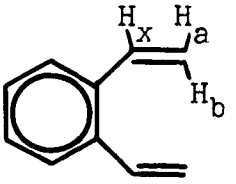
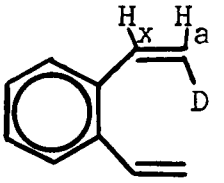
19. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds." 2nd ed. John Wiley & Sons, Inc. N.Y., N.Y. 1967, p 124.

TABLE 2

NMR SPECTRA OF DEUTERATED AND UNDEUTERATED o-DIVINYLBENZENE

				
	Chemical Shift(τ)	Integration	Chemical Shift(τ)	Integration
H_a	4.71(d-d)	2	4.58(d)	2
H_b	4.40(d-d)	2	...	...
H_x and ring	2.98(d-d)	6	2.80(m)	6

(d-d) = doublet of doublets

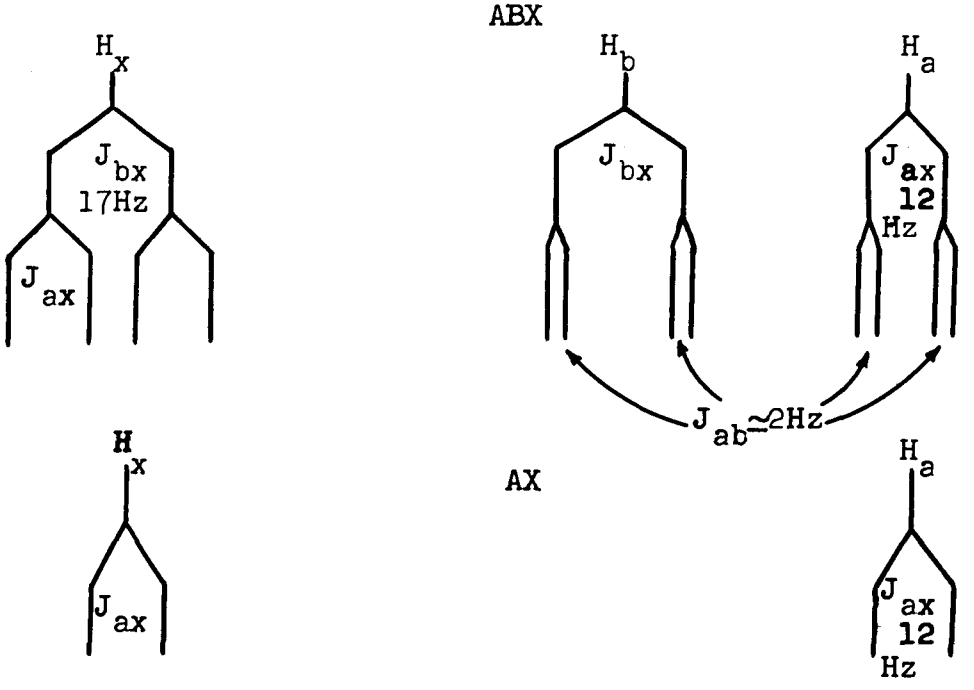


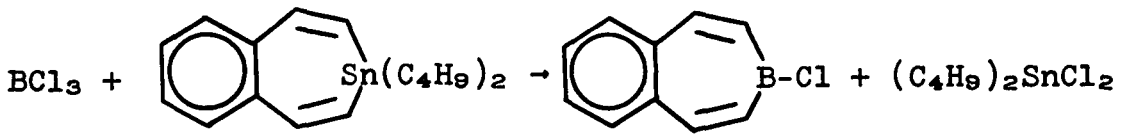
TABLE 3

MASS SPECTRUM OF 3-PHENYL-3-BENZOBOREPIN

m/e	% Abundance	Assignment
217	17	B^{11} molecular ion with 16% C^{13}
216	96	B^{11} molecular ion (M^+)
215	100	B^{11} (M-1) and B^{10} (M^+)
214	73	B^{11} (M-2) and B^{10} (M^+)
128	14	$C_{10}H_8^+$
108	4.5	$(M)^{+2}$
107.5	5.5	$(M-1)^{+2}$
107	13	$(M-2)^{+2}$
106.5	10	$(M-3)^{+2}$

3-Hydroxy-3-benzoborepin(XVII)

In view of Sheehan's successful preparation of 1-chloro-4,5-dihydroborepin from boron trichloride and 1,1-di-n-butyl-4,5-dihydrostannepin,[13] it was felt that a similar addition of boron trichloride to 3,3-di-n-butyl-3-benzostannepin(XIV) would result in 3-chloro-3-benzoborepin (XX). The latter was formed, but it codistilled with di-n-butyltin dichloride, as was indicated by the nmr spectrum of the distillate.



XIV XX

Due to its high reactivity, physical separation of 3-chloro-3-benzoborepin from di-n-butyltin dichloride by means other than distillation was not attempted. Chemical separation of 3-chloro-3-benzoborepin by hydrolysis with t-butanol, after removal of the excess t-butanol, resulted in a precipitate which was too soluble in organic solvents (30-60° petroleum ether, cyclohexane, etc.) to permit a clean removal of di-n-butyltin dichloride.

Advantage was taken of the extreme sensitivity of the B-Cl bond to moisture. The product of the reaction of 3,3-di-n-butyl-3-benzostannepin and boron trichloride was hydrolyzed to 3-hydroxy-3-benzoborepin by the addition of an equivalent of water. Purification of the product was accomplished by washing the precipitate from the hydrolysis reaction with heptane to remove entrained di-n-butyltin dichloride. It was dried under vacuum and recrystallized. The ir, uv, nmr, mass spectrum and elemental analysis were considered sufficient confirmation of structure, considering the elucidation of structure performed on 3-phenyl-3-benzoborepin.

3-Chloro-3-benzoborepin(XX)

The direct preparation of 3-chloro-3-benzoborepin from boron trichloride and 3,3-di-n-butyl-3-benzostannepin was not successful due to the problem of codistillation with di-n-butyltin dichloride. Since the most practical physical method failed, several chemical methods were attempted. The solution thought to be most promising was based on the concept that organotin compounds readily disproportionate. Disproportionation of tetravinyltin and tin tetrachloride was known.[20] The ease of displacement of the

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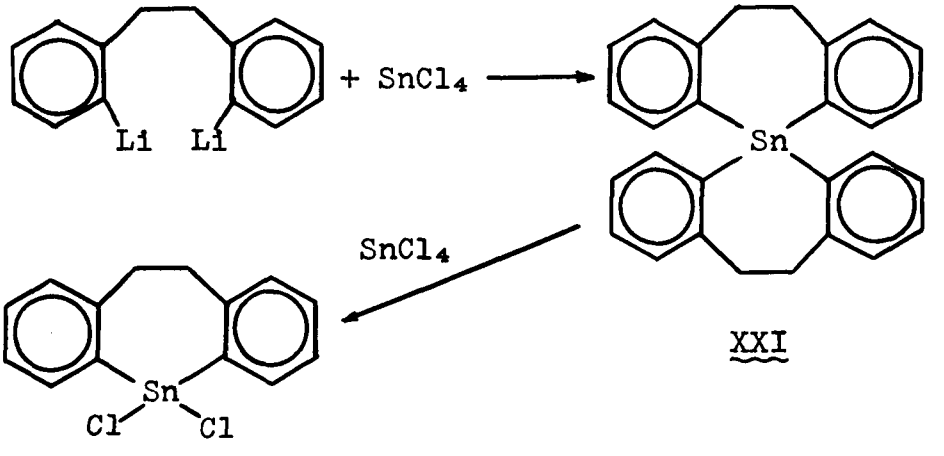
20. K. A. Kozschkow, Chem. Ber., 66, 1661(1933).

substituents of R_4Sn was well known and the phenyl group was most easily displaced: phenyl>vinyl>methyl>butyl.[21-23] Perhaps 3,3-di-n-butyl-3-benzostannepin would disproportionate with tin tetrachloride to give 3,3-dichloro-3-benzostannepin, which would not be expected to codistill with di-n-butyltin dichloride. Then di-n-butyltin dichloride would not be one of the products of the boronation reaction.

Kuivila had reported the disproportionation of the unisolated spiro intermediate(XXI) from the reaction of tin tetrachloride and o,o'-dilithiobibenzyl, leading to 5,5-dichloro-10,11-dihydro[b,f]stannepin(XXII) (Chart 5).[24]

Chart 5. 5,5-Dichloro-10,11-dihydro[b,f]stannepin



XXI

XXII

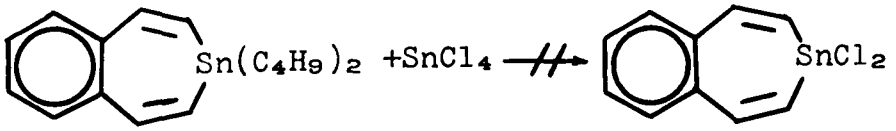
21. W. P. Neumann and G. Burkhardt, Justus Liebigs Ann. Chem., 663, 11(1963).

22. D. Seyferth and F. G. A. Stone, J. Amer. Chem. Soc., 79, 515(1957).

23. S. D. Rosenberg and A. J. Gibbons Jr., ibid., 79, 2138(1957).

24. H. G. Kuivila and O. F. Beumel Jr., ibid., 80, 3250(1958).

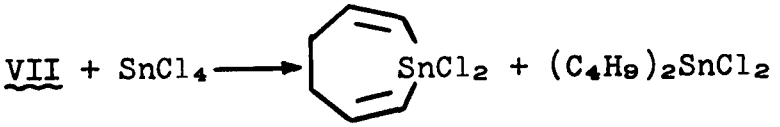
By analogy, if the following reaction were to take place, di-n-butyltin dichloride would be removed before 3-chloro-3-benzoborepin would be formed.



XIV XXIII

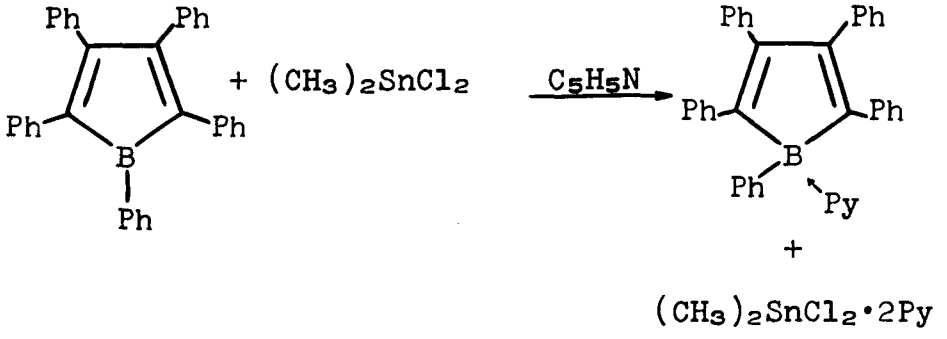
In that event, the reaction of 3,3-dichloro-3-benzostannepin(XXIII) and boron trichloride would result in 3-chloro-3-benzoborepin and tin tetrachloride, which certainly would not give codistillation problems.

Since 3,3-di-n-butyl-3-benzostannepin was prepared by a five step synthesis from o-phthalaldehyde, which is moderately expensive, it was decided that exploratory work on the chloro-dealkylation reaction should be performed on a model compound, 1,1-di-n-butyl-4,5-dihydrostannepin (VII). The reaction proceeded smoothly and 1,1-dichloro-4,5-dihydrostannepin(XXIV) was isolated and identified. The success with the model system, however, could not be similarly achieved in the reaction of 3,3-di-n-butyl-3-benzostannepin and tin tetrachloride. A low yield of a substance resulted, which, when treated with phenylboron dichloride, did not form 3-phenyl-3-benzoborepin.



XXIV

The isolation of a boron containing heterocycle from a mixture containing an organotin halide was accomplished in the case of pentaphenylborole by adding three equivalents of pyridine and removing the precipitated organotin complex.[25,26]



In a variety of solvents, addition of pyridine to the distillate containing 3-chloro-3-benzoborepin and di-n-butyltin dichloride resulted in no precipitate, or the precipitation of both compounds.

The synthesis of a reasonably pure sample of the highly reactive 3-chloro-3-benzoborepin was achieved when carbon tetrachloride solutions of 3-hydroxy-3-benzoborepin and phosphorus pentachloride were combined. After hydrogen chloride evolution ceased, the solution was refluxed and the carbon tetrachloride allowed to evaporate. The residual oil was transferred to a sublimation apparatus. The pressure was reduced to 0.19 mm to remove phosphorus oxychloride and excess phosphorus pentachloride. The temperature was raised to 135° and 3-chloro-3-benzoborepin was collected by sublimation.

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25. P. J. Grisdale and J. L. R. Williams, J. Organometal. Chem., 22, C19(1970).

26. J. J. Eisch, N. K. Hota, and S. Kozima, J. Amer. Chem. Soc., 91, 4575(1969).

The extreme reactivity of 3-chloro-3-benzoborepin, with traces of oxygen or moisture, made it necessary to use a freshly prepared sample in all studies. An analytically pure sample could not be obtained. The determination of structure of 3-chloro-3-benzoborepin was based on:

(a) Ir, uv, nmr, and mass spectral correlation with 3-hydroxy-3-benzoborepin.

(b) A small sample of 3-chloro-3-benzoborepin was hydrolyzed in water. The aqueous portion gave a positive test with silver nitrate. After drying, an ir of the insoluble organic portion was identical to the ir of 3-hydroxy-3-benzoborepin.

(c) Hydrolysis of 3-chloro-3-benzoborepin with absolute ethanol gave 3-ethoxy-3-benzoborepin.

3-Ethoxy-3-benzoborepin(XXV)

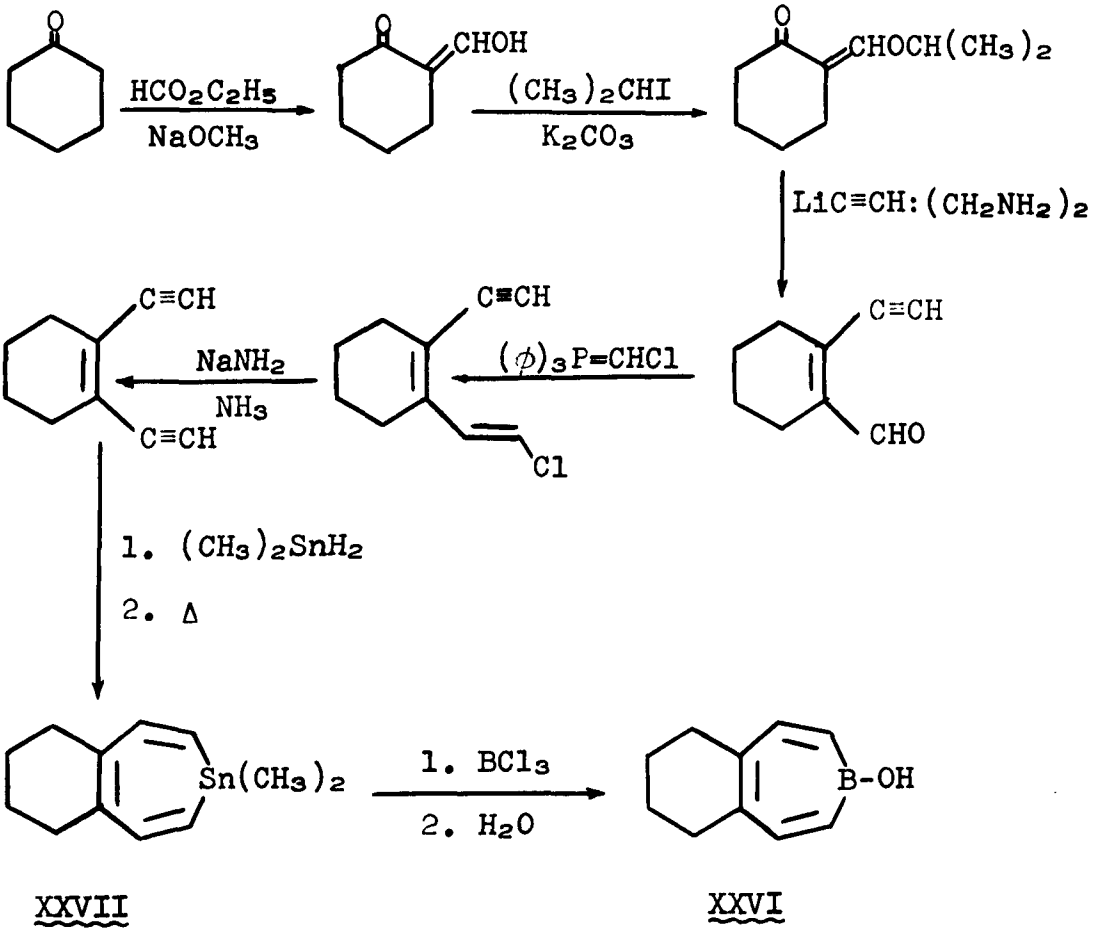
The addition of 3-chloro-3-benzoborepin to absolute ethanol, gave, on evaporation of the ethanol under nitrogen, a solid which melted at 39-45° after sublimation. The ir, uv, nmr, and mass spectra of the solid suggested that it was 3-ethoxy-3-benzoborepin.

3-Hydroxy-3-cyclohexenoborepin(XXVI)

In order to study the electronic spectrum of the borepin ring without any interference from the fused benzo-ring, the synthesis of 3-hydroxy-3-cyclohexenoborepin was planned. From previous work in this area, it was felt that organotin dihydride addition to 1,2-diethynylcyclohexene would result in the desired stannepin which could be converted to the borepin (see p 7). Initial attempts to prepare 1,2-diethynylcyclohexene from 1,2-diethynyl-1,2-dihydroxycyclohexane were unsuccessful. The method of Pilling and Sondheimer was used to successfully prepare

1,2-diethynylcyclohexene.[27-30] The synthesis of 3-hydroxy-3-cyclohexenoborepin(XXVI) via the stannepin(XXVII) was successfully completed as shown in chart 6.

Chart 6. 3-Hydroxy-3-cyclohexenoborepin



XXVII XXVI

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27. G. Pilling and F. Sondheimer, J. Amer. Chem. Soc., 90, 5610(1968).
28. W. S. Johnson and H. Posvic, ibid., 69, 1361(1947).
29. O. F. Beumel and R. F. Harris, J. Org. Chem., 28, 2775(1963), Ibid., 29, 1872(1964).
30. G. Köbrich, H. Trapp, K. Flory and W. Drischel, Chem. Ber., 99, 689(1966).

CHAPTER III

EVALUATION OF THE AROMATIC CHARACTER OF THE BOREPINS

The concept of aromaticity evolved from the ability of benzene and its derivatives to undergo substitution rather than addition reactions with electrophilic reagents. This view was formalized by Hückel's 4n+2 rule which was rapidly expanded by other workers to include heterocycles such as furan and pyrrole. This development forced a re-evaluation of one of the criteria of an aromatic substance: the unusual stability of the aromatic ring.

Pyrrole and furan undergo ring opening on treatment with acid and furan reacts almost explosively with halogens. Sodium pentadienide decomposes in protic solvents, tropylium chloride is unstable in basic media, and the dipotassium salt of cycloöctatetraene explodes when dry and exposed to air, but all are still considered aromatic because they are planar monocyclic compounds containing (4n+2) π-electrons with all ring protons being chemically and spectrally (nmr) equivalent. The uv spectra of non-benzenoid aromatic compounds exhibit the characteristic absorption patterns of benzenoid compounds in contrast to the spectra of conjugated polyolefins.

Electronic spectra

In 1949, Platt drew attention to the strong resemblance of the uv spectra of naphthalene and azulene.[31]

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31. C. W. Tector, G. W. Schaeffer, and J. R. Platt, J. Chem. Phys., 17, 464, 481(1949).

The vacuum uv spectrum of borazine, sometimes referred to as inorganic benzene by early workers, and benzene were also compared and show similar characteristics (Table 4).[31]

TABLE 4

UV SPECTRA OF BENZENE AND BORAZINE

Benzene[32]		Borazine[31]	
λ_{max}(nm)	Logε	λ_{max}(nm)	Logε
180-185	4.66	171	4.11
193-208	3.84	185	...
238-268	2.23	190-200	2.90

Dewar compared the uv spectra (Table 5) of 9,10-borazarophenanthrene,[33] 2,1-borazaronaphthalene,[34] and derivatives, to their benzenoid homologs to reach the conclusion that "the spectrum of 9,10-borazarophenanthrene itself is interesting. It resembles very closely that of phenanthrene in the position of the absorption bands, but the intensity of the α-band is much greater." The α- and β-bands arise from second and third order transitions which are degenerate for phenanthrene in simple molecular-orbital theory (The Clar notation is used; whereby the

32. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds." 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

33. M. J. S. Dewar, Ved P. Kubba, and R. Pettit, J. Chem. Soc., 1958, 3073.

34. M. J. S. Dewar and R. Dietz, ibid., 1959, 2729.

β-, para-, and α-bands correspond to E_1, E_2 and B bands respectively).[35]

TABLE 5

UV SPECTRA OF NAPHTHALENE AND
2,1-BORAZARONAPHTHALENE

Naphthalene[32]		2,1-Borazaronaphthalene[34]			
λ_{max}(nm)	Logε	λ_{max}(nm)	Logε	λ_{max}(nm)	Logε
221	4.98	210	4.7	217	4.6
286	3.62	263	4.1	270	4.1
312	2.40	307	3.9	320	3.9

As additional examples of heterocyclic compounds having the same ring geometry and unsaturation as their carbocyclic aromatic counterparts were discovered, investigators relied on spectroscopy to determine whether or not they were aromatic. Heteromolecules, whose π-electronic configurations can be represented by resonance contributing forms normally found in their carbocyclic analogs, appeared to have similar uv spectra.[31-39]

35. H. H. Jaffé and Milton Orchin, "Theory and Application of U.V. Spectroscopy," John Wiley and Sons, New York, N.Y., 1962, p 289.

36. S. Winstein, C. G. Kreiter, and J. I. Brauman, J. Amer. Chem. Soc., 88, 2047(1966).

37. M. Brookhart, M. Ogliaruso, and S. Winstein, Ibid., 89, 1965(1967).

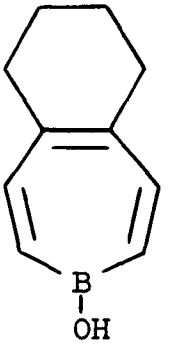
38. W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J. P. Weber, Helv. Chim. Acta, 51, 225(1968).

39. J. Feitelson, J. Chem. Phys., 43, 2511(1965).

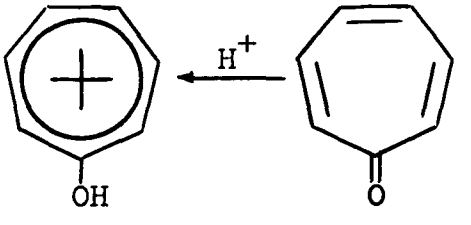
This technique has been used exhaustively to study bridged benzotropones and bridged benzotropylium ions.[38]

Interpretation of the uv spectrum of 3-hydroxy-3-cyclohexenoborepin(XXVI)

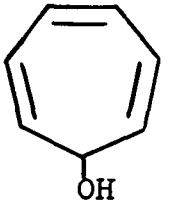
The uv spectra of 3-hydroxy-3-cyclohexenoborepin, the hydroxytropylium ion(XXVIII), and tropone(III), listed in Table 6, are almost identical, demonstrating the equivalence of their π-electron structures. The uv spectra of 1-hydroxy-2,4,6-cycloheptatriene(XXIX), cycloheptatriene (XXX), and thiapin-1,1-dioxide(XXXI) in no way correspond to the uv spectra in part A of Table 6. This is not surprising, since the compounds in part B are not expected to be aromatic.



XXVI



XXVIII III



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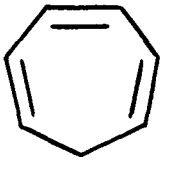

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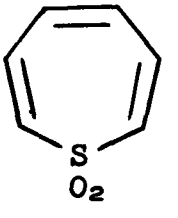

XXXI

TABLE 6

UV SPECTRA OF 3-HYDROXY-3-CYCLOHEXENOBOREPIN

[nm(Log ε)]

Part A

3-Hydroxy-3-cyclohexenoborepin*	225(4.33)		291(4.01)	301(3.96) 315(3.67)
Hydroxytropylium ion[5]	225(4.33)		297(3.74)	310(3.67)
Hydroxytropylium ion[37]	229(4.64)			306(4.04) 311(4.03)
Tropone[4]	225(4.33) 232(4.34)		304(3.90)	313(3.92)

Part B

Thiapin-1,1-dioxide[40]	215(4.11) 232(3.32)	262(3.66)		
Cycloheptatriene[6]		266(3.62)		
1-Hydroxy-2,4,6-cycloheptatriene[6]	222(3.37)	251(4.00)		

* Log ε is based on the nmr of the crude material, showing 81 per cent 1-hydroxy-4,5-cyclohexenoborepin and 19 per cent dimethyltin dichloride.

40. W. L. Mock, J. Amer. Chem. Soc., 89, 1281(1967).

Aromatic character of tropone(III)

Early investigators concluded that tropone was aromatic based on its ir, uv, nmr[3.1τ(60 MHz)] spectra and chemical properties.[4-6,27,41-44] With the goal of discounting the importance of contributing forms IIIa and IIIb, tropone was reinvestigated in 1969 using 100 MHz and 220 MHz instruments and computer matched spectra. The nmr spectra at both frequencies were very complex. Correlation of the empirically determined coupling constants, bond orders, and diamagnetic susceptibility, resulted in the conclusion that "tropolone appears to exhibit no greater degree of aromatic character than tropone." "Tropolone and cycloheptatriene have the same diamagnetic susceptibility discrepancies and neither has appreciable aromatic character."[45,46] The conclusion that tropone and tropolone have little aromatic character has not been greeted with universal acceptance.[27] Therefore, a brief review of the data concerning the aromatic character of tropone is presented.

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41. R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, J. Amer. Chem. Soc., 79, 4127(1957).

42. R. B. Turner, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publications, London, 1959, p 67 ff.

43. J. D. Bertelli, C. Golino, and D. L. Dreyer, J. Amer. Chem. Soc., 86, 3331(1964).

44. D. L. Pearson, Ph. D. Thesis, University of Washington, Seattle, Washington, 1955.

45. D. J. Bertelli and T. G. Andrews, J. Amer. Chem. Soc., 91, 5280(1969).

46. D. J. Bertelli, T. G. Andrews, and P. O. Crews, ibid, 91, 5286(1969).

"The differences in energy contents of conjugated and non-conjugated systems can be calculated from very precise measurements on the heat of hydrogenation."[8] The difference between the calculated heat of hydrogenation of a compound containing localized bonds, and the observed value, is the resonance energy.[47] The magnitude of the resonance energy was the first major criterion to be used for the evaluation of a compound's aromatic character.

The resonance energy of tropone, which was hydrogenated to cycloheptanone, was reported to be 2.9 Kcal/mole, based on the determined heat of hydrogenation of 1,3,5-cycloheptatriene.[41] Reevaluation of the resonance energy of tropone by the same investigators listed a new figure of 11.9 Kcal/mole (Table 7) when the calculated value of three times the heat of hydrogenation of cycloheptene is substituted for the experimentally determined value.[42] Although 11.9 Kcal/mole appears to be low when compared to benzene, the bond polarization energy for the conversion of the polar forms IIIa and IIIb to a carbonyl group is not considered in the calculated value.

It has recently been suggested by Dauben that the diamagnetic susceptability exaltation of a compound may be useful as an experimental criterion for aromatic character, since the difference between the calculated and observed values seems to increase with the degree of cyclic π-electron delocalization. Benzenoid and non-benzenoid aromatic compounds exhibit diamagnetic susceptibility exaltations greater than 12. Non-aromatic compounds, on the other hand, have diamagnetic susceptibility

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47. G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, chap. 3.

exaltations of less than 3, with two exceptions: cycloheptatriene and cyclopentadiene. Dauben suggests: "The existence of exaltation in cycloheptatriene and its derivatives is easily rationalized: these compounds possess aromatic character." The diamagnetic susceptibility exaltation for the tropylium ion is 19.5;[48] for the homotropylium ion it is 18.0;[48] and for tropone, 6.6.[46]

TABLE 7

HEAT OF HYDROGENATION OF CYCLIC OLEFINS

Substance	Heat of Hydrogenation (Kcal/mole)		Resonance Energy (Kcal/mole)
	Calculated[47]	Observed	
Cycloöctatetraene	92[a]	98.0[47]	...
Azulene	129.5[b]	99.0[47]	30.5
Cycloheptatriene	79.5[c]	70.5[47]	9.0
Tropone	70.5[d]	67.6[41]	2.9[e]
Tropone	79.5[c]	67.6[41]	11.9[42]
Tropylium Chloride	...	86.2[42]	...

a) Based on four times the heat of hydrogenation of cycloöctene.

b) Based on two times cyclopentene and three times cycloheptene.

c) Based on three times cycloheptene.

d) Based on cycloheptatriene.

e) Based on the reduction of tropone to cycloheptanone.

48. H. J. Dauben Jr., J. D. Wilson, J. L. Laity, J. Amer. Chem. Soc., 91, 1991(1969).

The properties of tropone cannot be considered to be those of a highly conjugated ketone. It is also not stabilized by resonance to the same degree as benzene. It will be left to later workers to assign a percent aromatic character or degree of aromaticity to tropone;[27,49] none the less, the exclusion of tropone in part A of Table 6 is not warranted.

Aromatic character of 3-hydroxy-3-benzoborepin

The iso-π-electronic resonance structures of 3-hydroxy-3-benzoborepin, 3-hydroxybenzotropylium ion, and 4,5-benzotropone form the basis of the discussion of the uv spectra (see page 8).

The uv spectra of 3-hydroxy-3-benzoborepin and 4,5-benzotropone are too rich in fine structure for correlation and are therefore found in the experimental portion of this thesis. Assignments and correlations are made less complicated by comparing the major bands with the three main bands of naphthalene in Table 8.

A survey of the compounds listed in part A of Table 8 show correlations that can be attributed only to conjugated delocalized 10-π-electron systems. All of the tropylium ions clearly show β-, <u>para</u>-, and α-band absorption in the anticipated regions. Comparison of the uv spectra of 3-hydroxy-3-benzoborepin and the 3-hydroxybenzotropylium ion show reasonable correlations of absorptions and intensities, whereas the compounds in part B of Table 8 can be viewed as <u>ortho</u> substituted benzene derivatives containing six π-electrons in the benzene ring with the remaining four π-electrons exo to the aromatic system.

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49. D. R. Burnham and M. J. Cook, <u>Tetrahedron Lett.</u> 1968, 3771.

These benzene derivatives do not have α-band absorptions in the 300 nm region; instead, they are in the region of the *para*-band absorptions of the conjugated 10-π-electron ring systems. The β-band absorptions are in the vacuum uv, similar to the β-band of benzene.

TABLE 8

UV SPECTRUM OF 3-HYDROXY-3-BENZOBOREPIN [nm(Logε)]

Compound	β-Band	*para*-Band	α-Band
Naphthalene[32]	221(4.98)	286(3.62)	312(2.40)
Part A			
3-Hydroxybenzotropylium ion	228(4.43)[a]	288(4.95)[a]	353(3.93)[a]
3-Hydroxy-3-benzoborepin	244(4.67)	275(5.02)	335(2.94)
4,5-Benzotropone	235(4.58)	264(4.56)	300(3.71)
4,9-Methano[11]-annulenone[50]	227(4.18)	285(4.58)	330(3.69)
Part B			
1,2-Benzo-1,3,5,7-cyclooctatetraene[51]	...	242(4.45)	275(3.35)[b]
3,4-Benzo-1,3,5-cyclooctatriene[51]	...	223(4.58)	250(3.88)[b]
3,4-Benzo-1,3,5-cycloheptatriene[51]	...	228(4.63)	255(3.70)[b]
o-Divinylbenzene[51]	...	232(4.30)	260(4.15)

a) 96 Percent sulfuric acid.

b) Shoulder.

Aromatic character of 4,5-benzotropone

The uv spectra of 4,5-benzotropone and 4,9-methano-[11]annulenone are similar and the assessment of their aromatic character would be of help in the evaluation of the aromatic character of 3-hydroxy-3-benzoborepin. Monocyclic annulenones are expected to be aromatic if they contain $(4n+3)$ π-electrons.[27] Tropone, 4,5-benzotropone, and 4,9-methano[11]annulenone are $(4n+3)$ annulenones. The arguments concerning the aromatic character of tropone would be expected to hold true for 4,5-benzotropone, since the resonance stabilization energy of the latter would be greater than the value for tropone. In addition X-ray data show that 4,5-benzotropone is planar with the exception of the carbon of the C-O bond being 0.1 Å and the oxygen atom being 0.2 Å from the mean plane. There is bond alternation in 4,5-benzotropone.[52]

The aromatic character of 4,9-methano-[11]annulenone from nmr spectra

An effect attributed to aromaticity, and observed in nmr spectroscopy, is the abnormal shielding due to ring current, of groups sterically fixed above an aromatic nucleus.[53,54] For example the 15,16-methyl groups fixed above 15,16-dihydro-15,16-dimethylpyrene absorb at 14.23 τ; a remarkable example of shielding affecting the chemical

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50. W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, J. Amer. Chem. Soc., 92, 6335(1970).
51. G. Wittig, H. Eggers, and P. Duffner, Justus Liebigs Ann. Chem., 619, 12(1958).
52. T. Hata, H. Shimanouchi, and Y. Sasada, Tetrahedron Lett., 1969, 753.
53. C. E. Keller and R. Pettit, J. Amer. Chem. Soc., 88, 606(1966).
54. E. Vogel, "Chemical Society Special Publication 21," 1967, p 113.

shift in a non-classical benzenoid compound.[55]

An interesting series of compounds, having classical aromatic counterparts, are the methano-bridged annulenes. The first to be prepared was bicyclo[4.4.1]undecapentaene(XXXII), whose chemical shift of the methano-bridged protons is 10.5 τ.[54] It is iso-π-electronic with naphthalene and considered to be aromatic. The methano-bridged analog of 4,5-benzotropone is 4,9-methano[11]annulenone(XXXIII). If the methano-bridged hydrogens of this annulenone are shielded, then the annulenone and its classical counterpart, 4,5-benzotropone can be considered aromatic.

The nmr of bicyclo[5.4.1]dodeca-2,4,6,8,10-pentaene(XXXIV) demonstrates the shielding of one of the methano-bridged protons. The spectra of compounds similar to the latter, 4,9-methano[11]annulenone(XXXIII) and their analogous tropylium ions,(XXXV) and (XXXVI), will be compared in order to determine which parts (A-ring or B-ring) of the molecule are responsible for the observed spectra.*

The pattern of the chemical shifts of the H_a and H_b protons of tricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene thru 1-keto-bicyclo[5.4.1]dodeca-4,6,8-triene in Table 9, are consistent. As the number of methylene groups is reduced from five to three, the chemical shift of H_b increases to 10.4 τ. This high value may be rationalized as the combined

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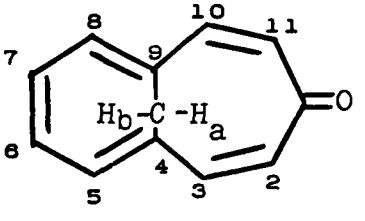
* The numbering system for the annulenones is not recommended by the IUPAC for all of the molecules. It was selected so that the protons so numbered, are structurally equivalent in all of the molecules.

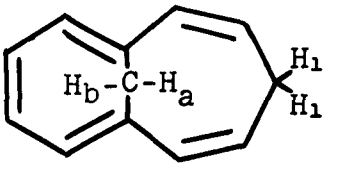
55. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds." Prentice Hall, Inc., Englewood Cliffs N.J., 1965, p 82.

effect of a cyclopropyl ring and/or a homoaromatic six-membered ring. The increase in H_a from 7.0 to 8.6 τ in going from XXXIX to XXXVII can only be attributed to a cyclopropane structure.[56] The non-conjugated carbonyl group in 1-ketobicyclo[5.4.1]dodeca-4,6,8-triene has no major effect on the chemical shift of H_a.

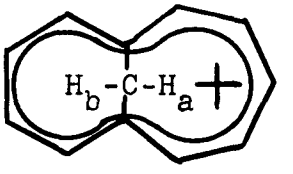
Chart 7. Methano-bridged annulenes



XXXIII

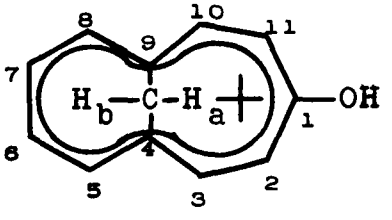


XXXIV

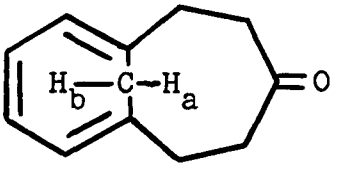


B-Ring A-Ring

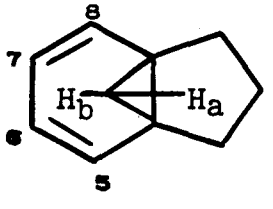
XXXV



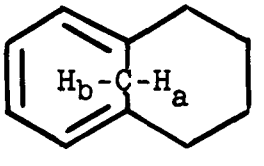
XXXVI



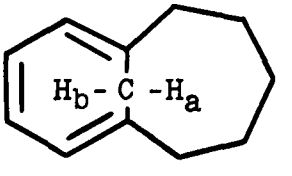
XL



XXXVII



XXXVIII



XXXIX

56. E. Vogel, Pure Appl. Chem., 20, 237(1969).

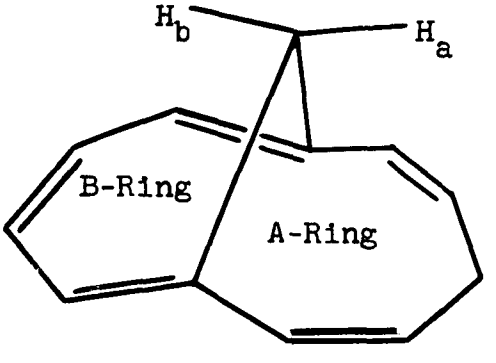
TABLE 9

NMR OF THE METHANO-BRIDGED PROTONS OF XXXVII-XL

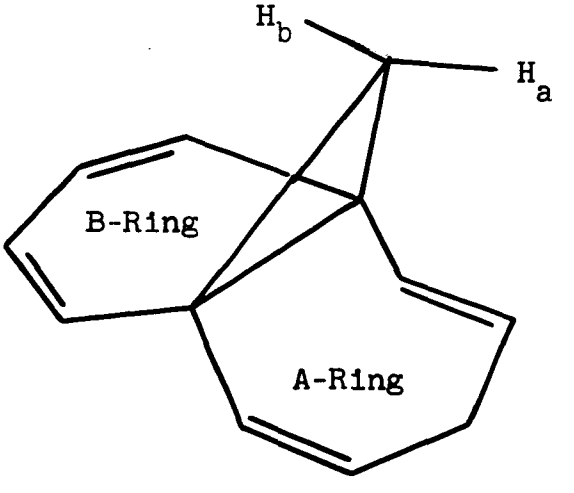
Compound	$H_a(\tau)$	J(Hz)	$H_b(\tau)$	J(Hz)
Tricyclo[4.3.1.$0^{1,6}$]-deca-2,4-diene(XXXVII)[56]	8.6	4.5	10.4	4.5
Bicyclo[4.4.1]undeca-1,3,5-triene(XXXVIII)[56]	7.0	10.0	9.2	10.0
Bicyclo[5.4.1]dodeca-7,9,11-triene(XXXIX)[56]	7.0	...	8.4	...
1-Ketobicyclo[5.4.1]dodeca-4,6,8-triene(XL)[50]	7.1-8.4*	...	8.4	12.4

* In a multiplet.

Comparison of the bridged protons of bicyclo-[5.4.1]dodeca-2,4,6,8,10-pentaene (H_a = 6.3 τ, H_b = 9.8 τ) and bicyclo[5.4.1]dodeca-7,9,11-triene shows H_a deshielded by 0.7 τ implying that the A-ring of bicyclo[5.4.1]-dodeca-2,4,6,8,10-pentaene has antiaromatic character.

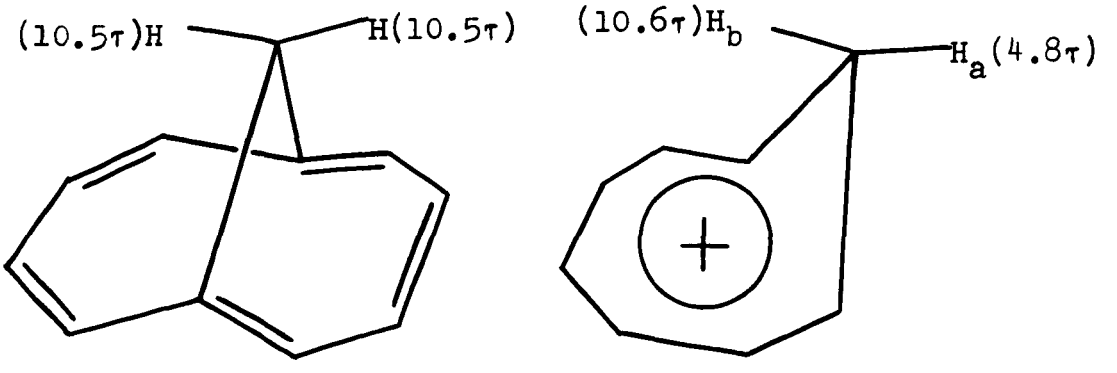


XXXIV



XXXIVa

Proton H_b is shielded by 1.4 τ, suggesting either the B-ring is homoaromatic or a cyclopropane ring is present.[57] The B-ring may be homoaromatic since the chemical shifts (H_8,H_7 = 3.2 τ; H_5,H_8 = 3.7 τ; H_2,H_{11} = 5.2 τ; H_3,H_{10} = 3.7 τ) of H_5-H_8 are about 1.0 τ upfield from bicyclo[4.4.1]undecapentaene(XXXII), where H_5-H_8 = 2.3-3.2 τ, and it is considered to be aromatic.[54] The equal chemical shifts of H_5,H_8 and H_3,H_{10} of bicyclo[5.4.1]-dodeca-2,4,6,8,10-pentaene are similar to the chemical shift of the X proton in o-divinylbenzene (see p 13). The only support for structure XXXIVa is the parallel shielding and deshielding in the homotropylium ion(XLI).[58]



XXXII XLI

Monocyclic annulenones are expected to be aromatic if they contain (4n+3) π-electrons.[27] The chemical shift of the multiplet (H_5-H_8) of bicyclo[5.4.1]dodeca-7,9,11-triene is at 3.9 τ. Proton H_b appears at 8.4 τ.[43] The B-ring protons of the 10-π-electron 4,9-methano[11]annule-

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57. W. Bleck, W. Grimme, H. Günther, and E. Vogel, Angew. Chem. Int. Ed., 9, 303(1970).
58. J. L. von Rosenberg, Jr., J. E. Mahler, and R. Petit, J. Amer. Chem. Soc., 84, 2842(1962).

none appear at 2.79 τ and 3.1 τ (average value = 2.95 τ).[50] This is a downfield shift of 1.0 τ from the B-ring protons of bicyclo[5.4.1]dodeca-7,9,11-triene and a 1.2 τ downfield shift from the homoaromatic protons of tricyclo[4.3.1.$0^{1,6}$]-deca-2,4-diene centered at 4.1 τ.[56] The nmr spectrum of 1-hydroxybicyclo[5.4.1]dodecapentaenylium ion (acidification of 4,9-methano[11]annulenone) shows a further downfield shift of 1.3 τ for the B-ring protons to 1.65 τ.[50] The A-ring protons are shifted in the direction of increasing aromaticity.

TABLE 10

CHEMICAL SHIFT OF THE B-RING PROTONS
OF XXXIII, XXXVI, XXXVII, XXXIX

Compound	B-Ring Protons
Tricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene(XXXVII)[56]	4.1 τ
Bicyclo[5.4.1]dodeca-7,9,11-triene(XXXIX)[56]	3.9 τ
4,9-Methano[11]annulenone(XXXIII)[50]	2.95 τ
1-Hydroxybicyclo[5.4.1]dodeca-pentaenylium ion(XXXVI)[50]	1.65 τ

The chemical shifts of the A-ring protons are listed in Table 11. The proposed argument that a downfield chemical shift in a series of compounds suggests increasing aromatic character holds true in this case too, with the qualification that one must consider that decreasing the electron density at a given carbon will also deshield the proton bonded at that site.

TABLE 11

CHEMICAL SHIFT OF THE A-RING PROTONS OF XXXIII-XXXVI

Compound	H_2, H_{11}	H_3, H_{10}
Bicyclo[5.4.1]dodecapentaene(XXXIV)[59]	5.3 τ	3.7 τ
4,9-Methano[11]annulenone(XXXIII)	3.98 τ	2.82 τ
1-Hydroxybicyclo[5.4.1]dodecapentaenylium ion(XXXVI)	1.98 τ	1.03 τ
Bicyclo[5.4.1]dodecapentaenylium ion(XXXV)	1.7 τ	0.40 τ

The methano-bridged protons on C_{12} of bicyclo[5.4.1]dodecapentaenylium ion, 4,9-methano[11]annulenone, and 1-hydroxybicyclo[5.4.1]dodecapentaenylium ion are now the key to any "observable" diamagnetic ring current in the nmr. The shielding effect on H_a going from a polyene system (XXXIV), a nonaromatic series (XXXVII-XXXIX), Sondheimer's (4n+3) compound (XXXIII), (4n+2) cationic molecules (XXXV) and (XXXVI), to a (4n+2) neutral molecule (XXXII), can only be viewed as a dramatic demonstration of shielding and the presence of the prerequesite ring current in 4,9-methano[11]annulenone. Since the annulenone is the analog of 4,5-benzotropone, one must assume that 4,5-benzotropone has the same magnitude of aromatic character in the same way that Vogel's aromatic methano-bridged compounds have classical benzenoid analogs.[50,54,56,57,59]

59. E. Vogel, R. Feldmann, and H. Düwell, Tetrahedron Lett., 1970(1941).

TABLE 12

NMR OF THE BRIDGEHEAD PROTONS
OF XXXII-XXXV, XXXVII-XXXIX

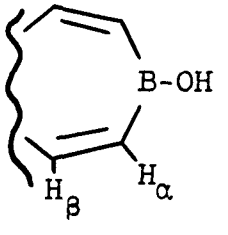
Compound	H_b	H_a
Tricyclo[5.4.1.$0^{1,6}$]deca-2,4-diene(XXXVII)	10.4 τ	8.6 τ
Bicyclo[4.4.1]undeca-1,3,5-triene(XXXVIII)	9.2 τ	7.0 τ
Bicyclo[5.4.1]dodeca-7,9,11-triene(XXXIX)	8.4 τ	7.0 τ
Bicyclo[5.4.1]dodeca-2,4,6,8,10-pentaene(XXXIV)	9.8 τ	6.3 τ
4,9-Methano[11]annulenone(XXXIII)	8.3 τ	9.9 τ
1-Hydroxybicyclo[5.4.1]dodeca-pentaenylium ion(XXXV)[60]	10.2 τ	10.6 τ
Bicyclo[5.4.1]undecapentaene(XXXII)	10.5 τ	10.5 τ

60. E. Vogel, W. Grimme, and H. Hoffman, Angew. Chem. Internat. Ed., 4, 354(1965).

NMR spectra of the borepins

The nmr chemical shift of an aromatic compound often appears to be a function of the delocalization of the π-electrons around the ring (ring current) and therefore a qualitative indicator of the aromatic character of a molecule.[61] It has also been suggested that the ring current resulting from a molecule's π-electron delocalization has little to do with its aromaticity.[62] A straightforward view of the chemical shifts of the borepin ring protons is complicated by the presence of a boron atom in the ring.

Comparison of the chemical shifts of the vinyl hydrogens of 3-hydroxy-3-cyclohexenoborepin to the chemical shifts of the vinyl hydrogens of the nonaromatic 1-hydroxy-4,5-dihydroborepin and 3,3-dimethyl-3-cyclohexenostannepin illustrates the deshielding due to the borepin ring (Table 13). The result is not dramatic, but the borepin ring protons are in the same general chemical shift region as phenol (2.68-3.35 τ) and tropone (3.31 τ).[43] The data appear even less dramatic for 3-hydroxy-3-benzoborepin, but its spectrum is in the generally accepted aromatic region as exemplified by β-naphthol, (2.14-2.99 τ).



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61. J. A. Elvidge and L. M. Jackman, J. Chem. Soc., 1961, 859.
62. J. I. Musher, J. Chem. Phys., 43, 4081(1965).

TABLE 13

NMR OF THE BOREPINS

Compound	Chemical Shift			
	α-Protons		β-Protons	
	(τ)	J(Hz)	(τ)	J(Hz)
3,3-Dimethyl-3-cyclohexenostannepin	4.02	13.0	3.31	13.0
1,1-Di-n-butyl-4,5-dihydrostannepin	3.96	13.5	3.18	m
1,1-Dichloro-4,5-dihydrostannepin	3.87	11.0	3.14	m
1-Hydroxy-4,5-dihydroborepin	4.18	...	2.90	...
3-Hydroxy-3-cyclohexenoborepin	3.47	13.5	2.63	13.5
3,3-Di-n-butyl-3-benzostannepin	3.58	14.0	2.39	14.0
4,5-Benzotropone	3.21	12.0	2.52	12.0
3-Hydroxy-3-benzoborepin	3.32	14.0	1.98	14.0
3-Hydroxybenzotropylium ion	2.53	12.0	1.48	12.0

m = Multiplet

Summary

When the uv spectra of the borepins are compared to their carbocyclic iso-π-electronic counterparts, there are clear spectral correlations. The uv spectra of 3-hydroxy-3-cyclohexenoborepin, the hydroxytropylium ion, and tropone are similar with respect to wavelengths and extinction coefficients. The correlation of the uv spectra of 3-hydroxy-3-benzoborepin, the 3-hydroxybenzotropylium ion, and 5-benzotropone show less correlation due to the benzo-ring. Considering earlier uv spectral correlations,[21,38-39] the uv spectra clearly show electron delocalization in the seven-membered ring.

The aromatic nature of tropone, and by implication 4,5-benzotropone, has been questioned.[45,46,49] Therefore, the shielding of the bridgehead hydrogens of 4,9-methano-[11]annulenone, a molecule whose π-electron delocalization is equivalent to 4,5-benzotropone's delocalization, has been compared to the shielding of other annulenes and their tropylium ions. The shielding of the methano-bridged hydrogens clearly shows the presence of a diamagnetic ring current in 4,9-methano[11]annulenone. The ring protons are deshielded when compared to a series of annulenes. Therefore, 4,5-benzotropone should be considered as an aromatic molecule.

Craig's statement: "...the kind of atom participating in the delocalized system is not important; the kind of orbital is."[63] appears to summarize why the borepins can be considered aromatic.

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63. D. P. Craig, "Theoretical Organic Chemistry" (Kekulé Symposium), Butterworths, London, 1958, p 20.

CHAPTER IV

REACTIONS OF THE BENZOBOREPINS

A preliminary investigation of the reactions of the benzoborepins was undertaken in order to determine the chemical properties of this novel ring system. This study was limited by the small amounts of the benzoborepins available and by the difficulties in handling these air sensitive materials. Optimum conditions for the reactions were not always determined. It was felt that a broad survey of possible reactions would have a greater chance for success than an exhaustive study of one or two reactions.

The low stability of 3-chloro-3-benzoborepin is emphasized by its liquefaction at room temperature in a sealed ampoule. It is rapidly hydrolyzed by water to 3-hydroxy-3-benzoborepin. In contrast to the conversion of chloroboranes to boron hydrides with lithium aluminum hydride, 3-chloro-3-benzoborepin is unreactive to this reagent. Although displacement reactions of boron halides and organotin compounds are well known,[13,20,23] no reaction occurrs between 3-chloro-3-benzoborepin and tetraphenyl tin.

The monoethanolamine and pyridine adducts of dibenzo[b,f]borepin were reported to be air stable,[11] the product of the reaction of 3-chloro-3-benzoborepin and monoethanolamine or pyridine did not result in substances that could be isolated and purified in air.

The anhydride of 3-benzoborepin was not formed when 3-chloro-3-benzoborepin and 3-hydroxy-3-benzoborepin were combined alone or with pyridine. This negative result parallels attempts to form the anhydride of 4,5-dihydroborepin.[13]

An ether solution of phenylmagnesium bromide and

3-chloro-3-benzoborepin resulted in a product whose spectrum suggested that 3-ethoxy-3-benzoborepin or an ether complex of 3-hydroxy-3-benzoborepin is formed instead of the phenyl derivative. Addition of absolute ethanol to 3-chloro-3-benzoborepin results in a substance whose ir, uv, nmr, and mass spectra suggest that 3-ethoxy-3-benzoborepin is formed.

Phenyllithium and 3-hydroxy-3-benzoborepin give the lithium salt which does not react with acetyl chloride. Potassium and 3-hydroxy-3-benzoborepin result in the potassium salt which does not react with either methyl iodide or acetyl chloride. Starting materials were recovered from the combination of acetyl chloride and 3-hydroxy-3-benzoborepin.

Phenylmagnesium bromide and 3-ethoxy-3-benzoborepin do not form 3-phenyl-3-benzoborepin, an unanticipated result in view of the facile reaction of Grignard reagents and borate esters. It appeared that 3-chloro-3-benzoborepin could cleave ethers (vide supra). It was therefore hoped that combination of 3-chloro-3-benzoborepin and the ethoxy-derivative would give the anhydride of 3-benzoborepin; only starting materials were recovered. Lithium aluminum hydride had been used to convert the monoethanolamine adduct of dibenzo[b,f]borepin to the unsubstituted parent compound,[11] but it had no effect on 3-ethoxy-3-benzoborepin.

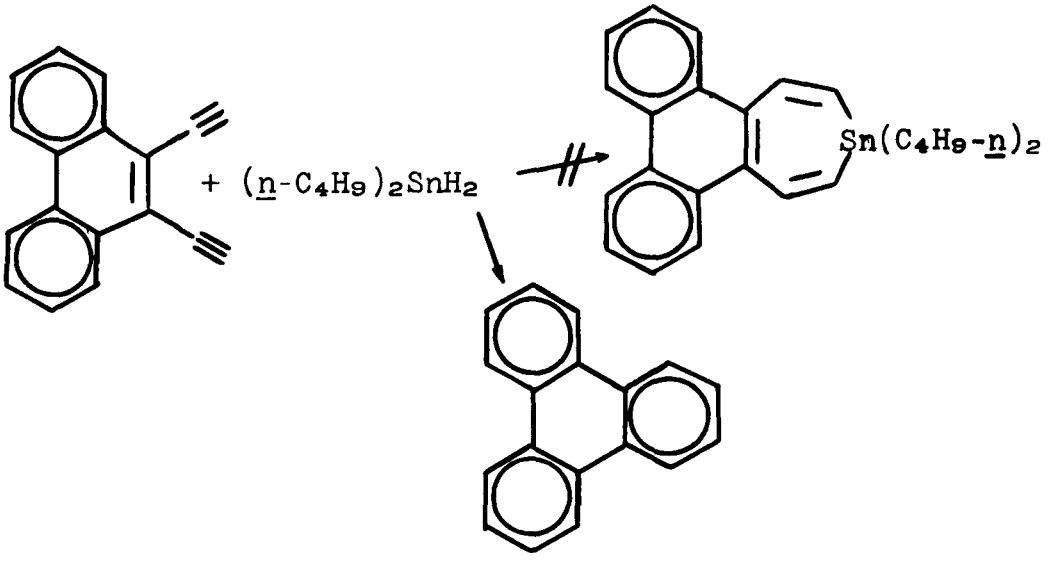
CHAPTER V

UNSUCCESSFUL ROUTES TO BOREPINS

Reaction of di-n-butyltin dihydride with 9,10-diethynylphenanthrene

The successful addition of di-n-butyltin dihydride to o-diethynylbenzene, its rearrangement to 3,3-di-n-butyl-3-benzostannepin, and conversion to the benzoborepin series suggested that the 3-phenanthroborepins could be prepared from 9,10-diethynylphenanthrene.[64-66]

Chart 8. Condensation of 9,10-diethynylphenanthrene and di-n-butyltin dihydride



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64. N. Rabjohn, Ed., "Organic Synthesis Collective Volume 4", John Wiley and Sons, Inc., New York, N. Y., 1963, p. 757.
65. W. Ried and H. Schmidt, Chem. Ber., 90, 2559 (1957).
66. Ibid., 91, 2477(1958).

None of the anticipated stannepin was isolated. Instead, a material whose nmr and uv spectra, and melting point were identical with those of triphenylene was isolated. A mixed mp with an authentic sample of triphenylene[67] confirmed the identification.

Attempts to prepare 1,2-diethynylcyclohexene

The concept of using an ene-diyne with the alkene fixed in the cis-position suggested the use of 1,2-diethynylcyclohexene to prepare a borepin whose unsaturation was not stabilized by an aromatic ring. One promising route to 1,2-diethynylcyclohexene was based on the conversion of cyclohexane-1,2-dione to 1,2-diethynyl-1,2-dihydroxycyclohexane.[68] Attempts to convert the diethynyldiol to 1,2-diethynylcyclohexene by the following methods were unsuccessful. Either no reaction, polymerization, or attack at the acetylene site of 1,2-diethynyl-1,2-dihydroxycyclohexane(XLII) resulted.

XLII + $CuCl_2$ + HCl + Cu/bronze	→ Polymerization or no reaction.
XLII + Lucas Reagent	→ XLII recovered unchanged.
XLII + $POCl_3$ + pyridine	→ Polymer.
XLII + CH_3SO_2Cl + quinoline	→ Polymer.
XLII + PCl_5	→ Complex mixture.
XLII + $(CH_3SO_2)_2O$	→ Unidentifiable products.
XLII + $(CH_3)_2SO_4$ + KOH	→ Monomethylation only.
XLII + $SOCl_2$ or XLII + $SOCl_2$ + pyridine	→ Dichlorosulfite which gave XLII with H_2O.

67. K and K Laboratories, Plainview, New York.

68. W. Ried and H. Schmidt, Chem. Ber., 90, 2499(1957).

The method of Pilling and Sondheimer was therefore used to prepare 1,2-diethynylcyclohexene.[27]

Attempts to prepare monocyclic borepins

1,1-Di-n-butyl-4-methoxy-4,5-dihydrostannepin was prepared by Sheehan who unsuccessfully tried to convert it to 1-phenyl-4-methoxy-4,5-dihydroborepin with phenylboron dichloride.[13] The explanation for his failure came from the work of Gerrard and Lappert who found that the addition of boron trichloride or phenylboron dichloride cleaved most ethers.[69]

$$C_6H_5BCl_2 + RCH_2OCH(R)_2 \rightarrow C_6H_5B(Cl)OCH_2R + R_2CHCl$$

Increasing the number of equivalents of phenylboron dichloride to eight did not result in either 1-phenyl-4-methoxy-4,5-dihydroborepin or 1-phenyl-4-chloro-4,5-dihydroborepin. Substitution of tin tetrachloride for phenylboron dichloride resulted in a substance whose nmr spectrum suggested 1,1-dichloro-4-methoxy-4,5-dihydrostannepin (see page 15). Regardless of the structure of the molecule, the methyl ether was present. Butyllithium and 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin gave an unidentifiable material that did not have the nmr spectrum anticipated for 1,1-di-n-butylstannepin.

Attempts to prepare 9-stanne- and the 9-borabicyclo[4.2.1]nonatriene

Sheehan unsuccessfully tried to prepare stannepins and borepins by the reaction of the cyclooctatetraene dianion and dimethyltin dichloride or aminoboron dichloride.[13] Recent publications describe the preparation of N-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene(XLIII) and its [6.1.0]

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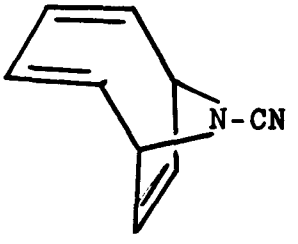
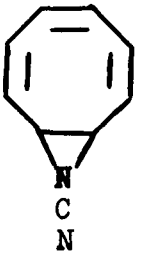
69. W. Gerrard and M. F. Lappert, J. Chem. Soc., 1957, 2893.

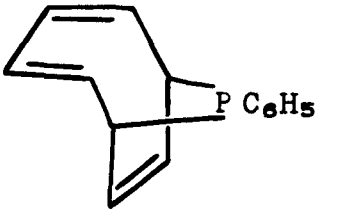
isomer(XLIV) from the cycloöctatetraene dianion and cyanonitrene,[70] and 9-phenyl-9-phosphorabicyclo[4.2.1]nonatriene(XLV) from the cycloöctatetraene dianion and phenylphosphorus dichloride.[71]



XLIII



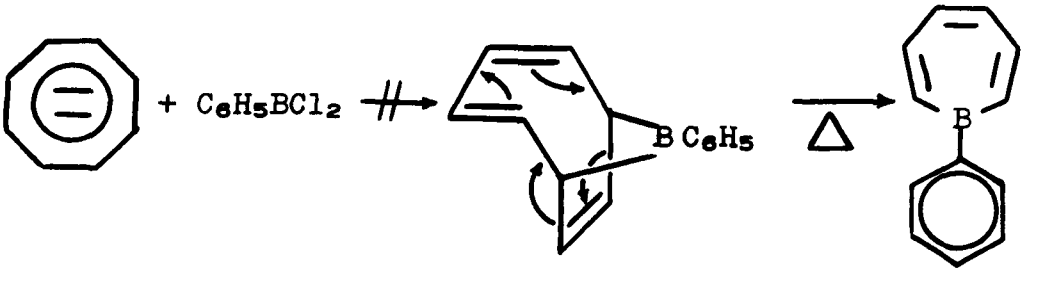
XLIV



XLV

By analogy, it was anticipated that 9-phenyl-9-borabicyclo[4.2.1]nona-2,4,7-triene could be prepared from the cycloöctatetraene dianion and phenylboron dichloride; a retro-Diels-Alder reaction would result in 1-phenylborepin (XLVII).

Chart 9. Cycloöctatetraene dianion and phenylboron dichloride.

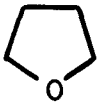


XLVI XLVII

70. A. Anastassiou, J. Amer. Chem. Soc., 90, 1527(1968).

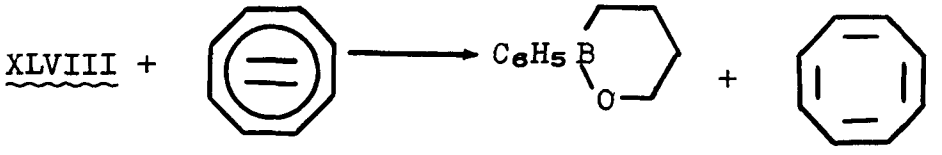
71. T. Katz, C. Nicholson, and C. Reilly, J. Amer. Chem. Soc., 88, 3832(1966).

Nmr and mass spectral data suggests that phenylboron dichloride reacted first with tetrahydrofuran, then with the cycloöctatetraene dianion to give 1-phenyl-2-oxa-1-borinane, instead of 9-phenyl-9-borabicyclo[4.2.1]nona-2,4,7-triene, by cleaving tetrahydrofuran.[69]



+ $C_6H_5BCl_2$ → $C_6H_5B(Cl)O(CH_2)_4Cl$

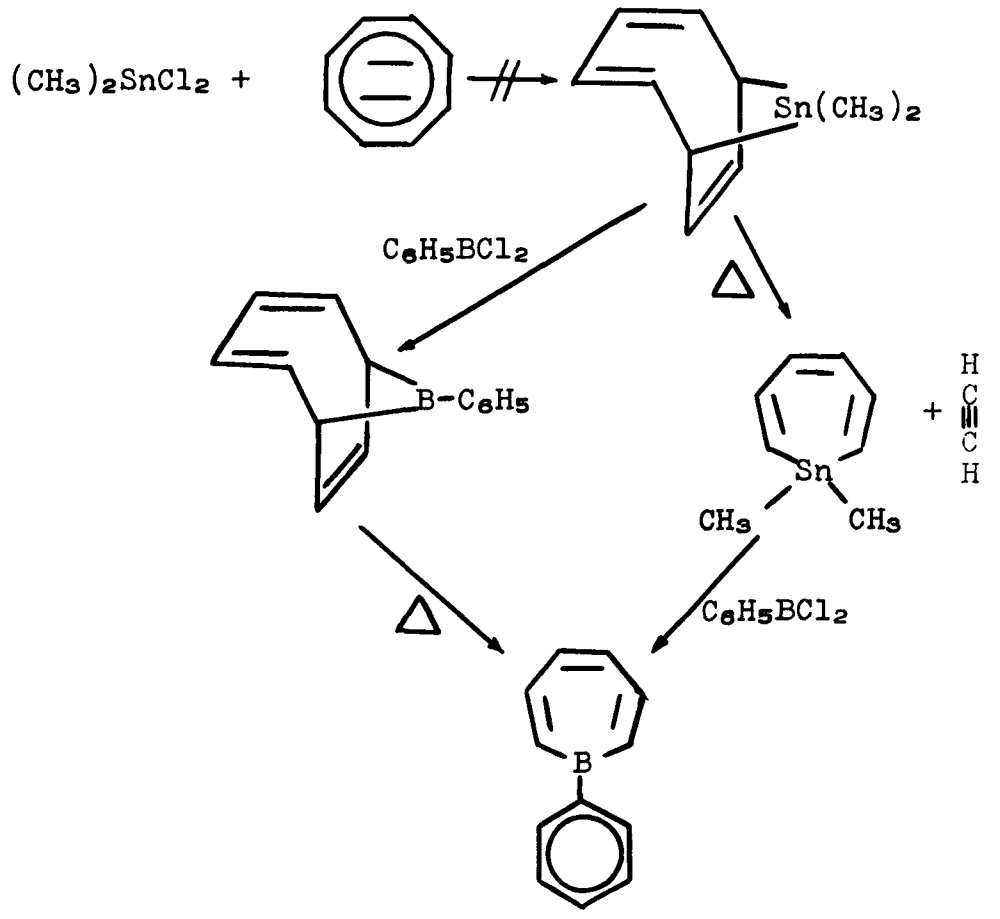
XLVIII



XLIX

The reaction of dimethyltin dichloride and the cycloöctatetraene dianion[13] was reinvestigated. The paper by Anastassiou provided spectral data for [4.2.1] systems,[70] and Sheehan had shown that haloboranes could displace the heteroatom of 1,1-di-n-butyl-4,5-dihydrostannepin with retention of the monomeric cyclic structure.[13] It was anticipated that substitution of dimethyltin dichloride for phenylboron dichloride in the cycloöctatetraene dianion reaction would avoid the solvent interaction and result in 1-phenylborepin as shown in Chart 10. After combining dimethyltin dichloride and the cycloöctatetraene dianion and vacuum stripping the tetrahydrofuran, the residue was observed to be gelatinous. Extracting the gel with benzene gave an amorphous substance whose nmr spectrum corresponded to a mixture of cycloöctatetraene and a substance showing a singlet at 9.55 τ.

Chart 10. Attempted synthesis of 1-phenylborepin



A series of polydimethyltin compounds were reported by Brown and Morgan with the following ir and nmr data:[72]

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72. T. Brown and G. Morgan, Inorg. Chem., 2, 1527(1968).

TABLE 14

NMR SPECTRA OF DIMETHYLTIN POLYMERS

	$(CH_3)_8Sn_3$ [72]	Linear $[(CH_3)_2Sn]_n$ [72]	Cyclic $[(CH_3)_2Sn]_6$ [72]	Unknown Substance
	Methyl bonded to a terminal tin			
τ	9.73	9.63		
J_{117} Sn-CH_3	45.8	46.0		
J_{119} Sn-CH_3	47.6	48.0		
J Sn-Sn-CH_3	15.6	15.7		
	Methyl bonded to an internal tin			
τ	9.6	9.35	9.45	9.55
J_{117} Sn-CH_3	42.8	40.4	41.2	41.0
J_{119} Sn-CH_3	44.3			43.0
J Sn-Sn-CH_3	20.2	20.6	20.6	19.0 21.2
J Sn-Sn-Sn-CH_3	...	...	1.3	...

When viewing the data concerning the unknown substance in the light of Brown and Morgan's data in Table 14, the chemical shift of 9.55 τ eliminates any terminal tin compound. The only compound having a terminal $C\underline{H}_3$- close to 9.55 τ, the linear polymer, would be expected to have an additional internal $-Sn(CH_3)_2-$ unit whose spectrum would appear at 9.35 τ. Consideration of the coupling constants for Sn^{117} and Sn^{119} isotopes in the previous table leads to the rejection of a linear polymeric structure for the unknown substance. It is therefore inferred to be a cyclic pentamer or hexamer. Although the possibility of having formed a unique cyclic stannane was interesting, it was not bringing the synthesis of a borepin any closer and work in this area was temporarily discontinued.

Attempted preparation of 1,1-di-n-butylstannepin

A report that triphenyltin hydride did not reduce methyl tosylate,[73] but added to the double bond in RCH=CHZ; Z = $-C\equiv N$, $-CO_2CH_3$, $-CO_2H$, $-CH(OC_2H_5)_2$,[74] suggested the possibility of synthesizing 1,1-di-n-butylstannepin from di-n-butyltin dihydride and 1,5-hexadiyne-3-tosylate.[13] The condensation was carried out like other diyne-tin hydride reactions and, after 2.5 hours, the very strong Sn-H peak at 1950-1900 cm^{-1} all but disappeared although an acetylene peak was still present at 3300 cm^{-1}. Since all of the di-n-butyltin dihydride had been consumed, the solvent was evaporated and the residue was distilled.

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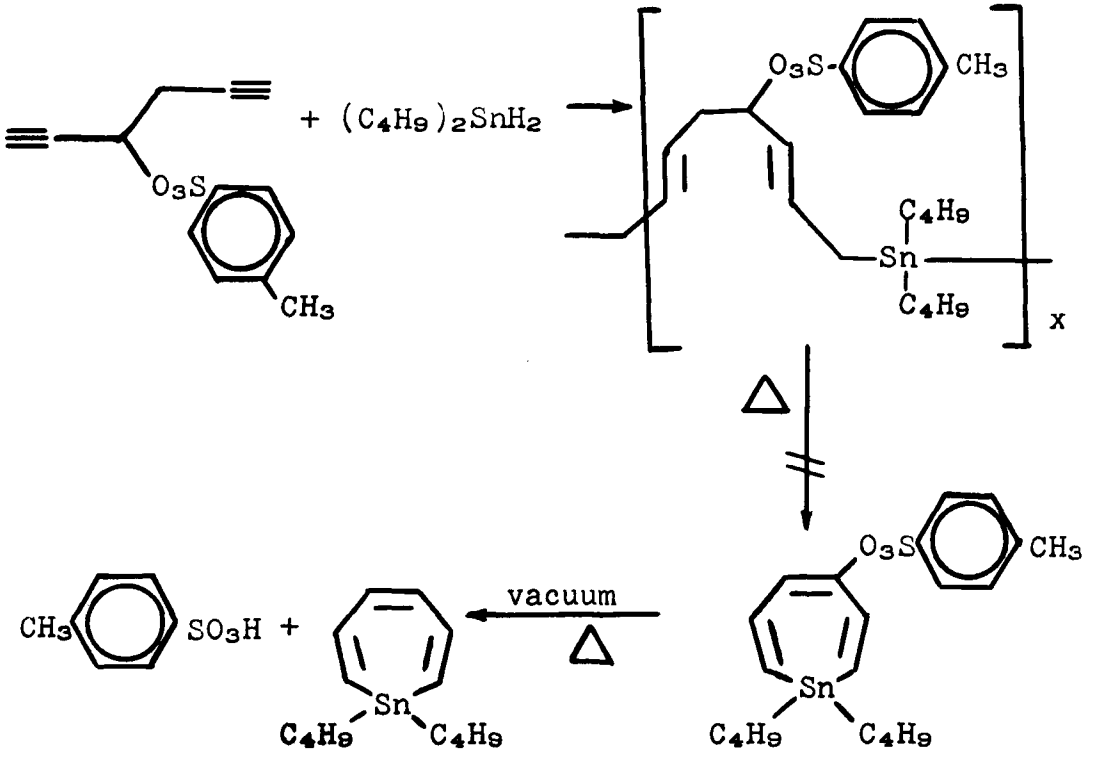
73. E. Becker, J. Org. Chem., 29, 1948(1964).
74. G. van der Kerk, J. Luitjen, and J. Noltes, Chem. Ind. (London), 1956, 352.

Chart 11. A projected route to
1,1-di-n-butylstannepin



Only n-butyltin polymers and a substance whose nmr spectrum suggested tri-n-butyltin tosylate were collected. The absence of a product containing an acetylenic linkage was puzzling until the material in the pump trap was examined. The ir spectrum showed a very strong terminal acetylene peak as well as a terminal allene peak. Peiffer had prepared 1,2-hexadiene-5-yne.[75] Salient ir peaks for the allene were 1970, 1700, and 840 cm^{-1}. All were present in the ir spectrum of the trap material.and were not due to chloroform, heptane(solvent), or 1,5-hexadiyne as determined by direct comparison of ir spectra. It was obvious that

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75. G. Peiffer, Bull. Soc. Chim. Fr., 1962, 776.

secondary tosylates were not immune to attack by di-n-butyltin dihydride and that, although a thorough study of the course of this reaction might have been rewarding, it was not directly related to our research interests at that time.

CHAPTER VI

EXPERIMENTAL

Melting points were determined in sealed soft glass capillary tubes using a Thomas Hoover apparatus. Both melting points and boiling points are uncorrected.

Microanalyses were performed by Galbraith Laboratory, Knoxville, Tennessee.

Infrared spectra were taken on a Perkin-Elmer Model 237B Spectrophotometer with the exception of spectra taken below 650 cm^{-1} for which a Beckman Model IR20 Spectrophotometer was used. Peak positions are indicated in wave numbers and parenthetically in microns; s = strong, m = medium, w = weak, b = broad, sh =shoulder.

Ultraviolet spectra were taken using a Cary Model 14 Spectrophotometer. Wavelengths for band maxima are indicated in nanometers.

Nuclear magnetic resonance spectra were determined on a Varian Model A-60A Spectrometer. Chemical shifts are specified in τ units with tetramethylsilane corresponding to 10 τ and the splitting constants are given in Hz. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Mass spectra were determined on a Varian Model CH-7 Spectrometer. Each sample was rerun with the addition of bromoform or perfluorokerosene as an internal standard. Only intense or structurally significant peaks will be listed.

All manipulations and reactions involving organometallic compounds, diacetylene compounds or ylides were performed under nitrogen. All compounds are assumed to be

air and/or moisture sensitive unless a statement to the contrary appears.

Compounds are listed in the order of appearance in the text.

1,1-Di-n-butyl-4,5-dihydrostannepin(VII)

1,5-Hexadiyne and di-n-butyltin dihydride were prepared and the initial condensation was carried out as outlined by Sheehan.[13] After the removal of heptane, the polymer was thermally rearranged and distilled in 48% yield; bp 71-3°(4×10^{-4} mm). The ir and nmr spectra were identical to those in the reference.[13]

3,3-Di-n-butyl-3-benzostannepin(XIV)

A solution of 8.91 g (38 mmol) of di-n-butyltin dihydride in 10 ml of heptane was added dropwise to a stirred solution of 4.77 g (38 mmol) of o-diethynylbenzene,[16,17] in 30 ml of heptane at 90°.

Caution: This reaction has an induction period. Rapid addition of di-n-butyltin dihydride can lead to an uncontrollable exothermic reaction.

The solution was maintained at 90° with stirring until its ir spectrum showed an absence of the terminal acetylene at ca 3300 cm^{-1} and tin hydride peak at ca 1800 cm^{-1}. Heptane was removed by increasing the nitrogen flow, and the viscous polymer was transferred to a short path distillation apparatus. The distillation flask contained a magnetic stirring bar and was not more than half filled. The receiver was fashioned from a standard taper joint, a 4 mm stopcock and a 10 ml bulb. Residual heptane was removed by a roughing pump. The high vacuum pump was engaged and when the vacuum reached 5×10^{-4} mm, the distilling flask was heated by an airbath. The distillate was collected until

an extremely viscous oil began to block the condenser. The yield of very crude product was 50-65%. Redistillation gave a 70% pure product (nmr); bp 113-114.5° (8×10^{-4} mm).

The spectral characteristics of XIV are as follows: ir ν (neat) 3058(3.77), 3021(3.31), 2959(3.38), 2924(3.42), 2882(3.47), 2857(3.51), 1460(6.85), 1374(7.28), 812(12.29); nmr τ ($CDCl_3$ and TMS) 9.3-8.95 (m, 18 H), 3.58 (d, 2 H, J = 14 Hz), 2.80 (m, 4 H, J < 1), 2.39 (d, 2 H, J = 14 Hz).

3-Phenyl-3-benzoborepin(XV)

In a glove bag, 3.60 g (10 mmol) of crude 3,3-di-n-butyl-3-benzostannepin was dissolved in 10 ml of carbon tetrachloride and 1.6 g (10.5 mmol) of phenylboron dichloride was added dropwise. The resulting precipitate was filtered, washed three times with spectrograde heptane, and dried under nitrogen, 1.17 g, 54%. The sample began to melt at 163.4°, stopped at 164.1°, and completely melted above 240°.

Anal. Calcd for $C_{16}H_{13}B$: C, 89.19; H, 6.25; B, 4.80. Found: C, 88.93; H, 6.06; B, 5.01.

Mol wt (Rast): Calcd for $C_{16}H_{13}B$: 216.08; Found 220.

The spectral characteristics of XV are as follows: ir ν (CCl_4) 3086(3.24) w, 3058(3.27) w, 2980(3.35) m, 2942(3.40) m, 1597(6.26) s, 1533(6.52) s, 1456(6.87) s, 1369(7.30) m, 1350(7.41) s, 922(10.85) m, 831(12.03) s, 702(14.25) m, 692(14.45) m. The uv and nmr spectra are on p 11. The mass spectrum is on p 14.

3-Hydroxy-3-benzoborepin(XVII)

In a 25-ml three-necked flask with a magnetic stirring bar and addition funnel containing 2.5 g (7 mmol based on 70% purity) of 3,3-di-n-butyl-3-benzostannepin in 5 ml of heptane, 0.82 g (7 mmol) of boron trichloride in 10 ml

of heptane was maintained at -15°. The solution of the benzostannepin was added dropwise with stirring at -15°, after which the solution was allowed to reach ambient temperature and stirred for an additional half hour. Excess boron trichloride was removed by increasing the nitrogen flow. The solution was filtered under nitrogen, then with vigorous stirring, 0.14 ml of water was added to the filtrate over ten minutes. The resulting precipitate was washed three times with heptane and dried *in vacuo*. The theoretical yield was 0.75 g; actual yield 0.58 g, 78 %. After recrystallization from chloroform, melting began at 110°, stopped at 113°, and was complete at 138°.

Anal. Calcd for $C_{10}H_9BO$: C, 77.00; H, 5,81; B, 6.96; O, 10.23. Found: C, 76.94; H, 5.88; B, 7.12; O, 10.06 (by difference).

The spectral characteristics of XVII are as follows: ir $\nu(CHCl_3)$ 3610(2.77), 3012(3.32), 2941(3.40), 1600(6.25), 1538(6.50), 1447(6.92), 1299(7.70), 1272(7.86), 1253(7.98), 1190(8.40), 991(10.09), 818(12.12); (CH_3CN) 746(13.4); uv $\lambda_{max}(\log\varepsilon)$ 233(4.59), 238sh(4.59), 244sh(4.67), 257(4.67), 268(4.10), 275(5.02), 286(3.49), 307(2.56), 319(2.61), 335(2.94); nmr τ ($CDCl_3$ and TMS) 3.58(s, 1 H), 3.68 (d, 2 H, J = 14 Hz), 2.11-2.51 (m, 4 H), 1.98 (d, 2 H, J = 14 Hz); mass spectrum 70 eV, m/e (relative intensity) 156 (93), 155 (72), 128 (100), 78 (11), 77.5 (9).

2,7-Dicarbomethoxy-4,5-benzotropone

The method of Cook and Forbes was used, substituting the dimethyl ester of acetonedicarboxylic acid.[76] A solution of 6.0 g (45 mmol) of o-phthalaldehyde, 8.26 g (63 mmol) of

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76. M. J. Cook and E. J. Forbes, Tetrahedron, 24, 450(1968).

the dimethyl ester of acetonedicarboxylic acid (Pfaltz and Bauer), and three drops of piperidine in 20 ml of benzene was refluxed for three hours and water was collected in a Dean-Stark trap. An additional 10 ml of benzene was removed by distillation.. The mixture was cooled and the precipitate separated by filtration. The crude precipitate was recrystallized (95% ethanol) in 40% yield, **20.1 g, mp 184.1-185.2°.**

The spectral characteristics of 2,7-dicarbomethoxy-4,5-benzotropone are as follows: ir ν ($CHCl_3$) 3003(3.33) m, 1718(5.82) s, 1645(6.08) b, 1618(6.18) b, 1550(6.45) m, 1431(6.99) s, 1269(7.88) s, 1233(8.11) m, 1193(8.38) m, 1081(9.25) s, 992(10.07) m; uv λ_{max}(log ε) 232(4.30), 306 (4.89), 360(3.86); nmr τ ($CDCl_3$ and TMS) 6.01 (s, 6 H), 2.12 (q, 4 H, J = 2 Hz), 1.69 (s, 2 H).

4,5-Benzotropone(XVIII)

A solution of 20 g (77 mmol) 2,7-dicarbomethoxy-4,5-benzotropone, in 100 ml of 95% ethanol containing 12.9 g (0.23 mol) of potassium hydroxide, was maintained at reflux for two hours. After two hours, the ethanol was removed by distillation while water was added periodically to maintain a volume of 75 ml. The aqueous solution was cooled and the pH was reduced to 8 (pH paper) with dilute hydrochloric acid. The aqueous solution was extracted once with ether. The aqueous solution was acidified to a pH of 3-4 with dilute hydrochloric acid and the precipitate was collected, washed once with water and dried at 0.1 mm. The yield of 4,5-benzotropone-2,7-dicarboxylic acid was 17.2 g, 96%. The previously prepared dicarboxylic acid, 7.72 g, was placed in a 25 ml flask with a magnetic stirring bar, short-path condenser, and fraction collector. The flask was slowly heated in an oil bath at an initial vacuum of

0.035 mm. As the bath temperature rose above 180°, distillation took place at an internal temperature of 160° at 1.5-1.7 mm. The crude yield was 70%. Recrystallization from 65-100° petroleum ether resulted in 2.78 g (57%) of 4,5-benzotropone, which melted at 68.1-69.5°; literature: 65-66°,[76] 66°.[77] The 4,5-benzotropones are air stable.

UV SPECTRUM OF 4,5-BENZOTROPONE

Experimental Data (Heptane)		Literature[78] (Cyclohexane)	
λ_{max}	Log ε	λ_{max}	Log ε
235	4.58	234	4.53
264	4.54	264	4.52
313	3.54	312	3.52
327	3.38	326	3.37
343	3.11	342	3.10

The spectral characteristics of XVIII are as follows: nmr τ ($CDCl_3$ and TMS) 3.21 (d, 2 H, J = 12 Hz), 2.52 (d, 2 H, J = 12 Hz), 2.38 (s, 4 H); mass spectrum 70 eV, m/e (relative intensity) 156 (73), 128 (100), 127 (34), 126 (19), 102 (27), 64 (39), 63.5 (8), 63 (30).

3-Hydroxybenzotropylium ion(XIX)

The 3-hydroxybenzotropylium ion was formed by adding 4,5-benzotropone to 96% sulfuric acid. It is air stable.

77. J. Thiele and E. Weitz, Justus Liebigs Ann. Chem., 377, 1(1910).

78. E. Kloster-Jensen, N. Tarkoy, A. Eschenmoser and E. Heilbronner, Helv. Chim. Acta, 95, 786(1956).

The spectral characteristics of XIX are as follows: uv λ_{max}(logϵ) 228(4.43), 288(4.95), 348(3.93), 358(3.93); nmr τ ($CDCl_3$ and TMS) 2.52 (d, 2 H, J = 11 Hz), 2.09 (d, 4 H, J = 2 Hz), 1.51 (d, 2 H, J = 11 Hz).

cis,cis'-o-Divinylbenzene-d_2

To 0.183 g (0.85 mmol) of 3-phenyl-3-benzoborepin in 4 ml of carbon tetrachloride, 0.11 g (1.69 mmol) of 99.5 % perdeuteroacetic acid (Stohler) was added and the mixture was agitated for one hour, then left for two days. The flask was placed on a vacuum line and degassed. Any substance whose vapor pressure at 27° was above 0.25 mm was discarded and a sample was collected below 0.25 mm. Comparison of the nmr spectra of the sample and of o-divinylbenzene showed that the sample collected below 0.25 mm showed the absence of the cis-vinyl hydrogens (Table 2).

3-Chloro-3-benzoborepin(XX)

In a nitrogen-filled glove bag, 0.7 g (4.5 mmol) of 3-hydroxy-3-benzoborepin and 4 ml of carbon tetrachloride were combined in a 25-ml flask containing a magnetic stirring bar. Phosphorus pentachloride, 1.4 g (6.7 mmol) was added cautiously with stirring and when the foaming ceased, the mixture was maintained at reflux for two hours. The reaction mixture was cooled and filtered. The precipitate (0.131 g) was 3-hydroxy-3-benzoborepin. Carbon tetrachloride was evaporated from the filtrate and the residue was placed in a sublimer. Phosphorus pentachloride and phosphorus oxychloride were removed from the sublimer by reducing the pressure (0.19 mm) and slowly warming the residue to 135°. An 86% yield (0.68 g) of 3-chloro-3-benzoborepin was obtained. An analytical sample could not be maintained. The structure was deduced from spectral data.

The spectral characteristics of XX are as follows: ir ν (CCl_4) 3049(3.28) m, 3003(3.33) m, 1585(6.31) s, 1517(6.59) b, 1475(6.78) s, 1431(6.99) s, 1339(7.47) s, 1300(7.69) s, 967(10.34) b, 935(10.70) b, 814(12.28) b; uv λ_{max}(logϵ*) 234(4.14), 237(4.14), 251(4.02), 255(4.03), 258 (4.05), 269(3.68), 277(3.60), 279(3.56), 288(3.36), 310(2.38), 322(2.38); nmr τ ($CDCl_3$ and TMS) 2.80 (d, 2 H, J = 14 Hz), 2.1-2.5 (m, 4 H) 1.85 (d, 2 H, J = 14 Hz); mass spectrum 70 eV, m/e (relative intensity)** 174 (100), 139, 128, 115, 102, 87.5, 87, 86.5.

Attempted preparation of 3,3-dichloro-3-benzostannepin(XXIII)

Under nitrogen, a solution of 2.24 g (6.2 mmol) of 3,3-di-n-butyl-3-benzostannepin in 5 ml of heptane was cooled to -5°. With stirring, 1.62 g (6.2 mmol) of freshly distilled tin tetrachloride was added dropwise over 15 minutes. The reaction was allowed to warm to ambient temperature and stirred for one hour. The reddish precipitate was removed by filtration. The filtrate was reduced to a solvent free residue and distilled. Di-n-butyltin dichloride was removed by heating to 72° at 0.05 mm ± 0.025 mm. When the residue in the distillation flask solidified, it was transferred to a sublimer and sublimed at 85° at 2×10^{-5} mm. An nmr of the sublimate showed only aliphatic protons. The residue and phenylboron dichloride did not form 3-phenyl-3-benzoborepin.

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* Logε is not quantitative due to the extreme reactivity of this compound.

** The mass spectrum of this compound is complicated by its high reactivity. The normal amounts of water and oxygen that are in the instrument were completely scavanged by XX.

1,1-Dichloro-4,5-dihydrostannepin(XXIV)

Under nitrogen, 9.38 g (30 mmol) of 1,1-di-n-butyl-4,5-dihydrostannepin[13] was dissolved in 10 ml of carbon tetrachloride and cooled to -5°. A solution of 7.79 g (30 mmol) of freshly distilled tin tetrachloride in 5 ml of carbon tetrachloride was added dropwise at -5° with stirring. After allowing the solution to slowly warm to room temperature over an hour, the solvent was removed and the residue distilled. The first fraction distilled from 68-72.8° at 0.08 mm. It was di-n-butyltin dichloride. After a noticable temperature drop, the second fraction distilled from 72-81° at 0.07 mm, 6.29 g (80% yield). It was triturated with carbon tetrachloride, dissolved in chloroform, and the solution cooled to 0°. About a ml of carbon tetrachloride was added and the resulting precipitate, 2.4 g of 1,1-dichloro-4,5-dihydrostannepin, was dried in vacuo and melted at 69.5-75.1°.

Anal. Calcd for $C_8H_8SnCl_2$: C, 26.72; H, 2.99; Sn, 44.00; Cl, 26.29. Found: C, 26.58; H, 2.99; Sn, 43.99 (by difference); Cl, 26.44.

The spectral characteristics of XXIV are as follows: ir ν ($CHCl_3$) 3008(3.32) w, 2930(3.41) w, 1613(6.20) s, 1430(7.00) w,b, 1332(7.51) w, 1305(7.66) w, 1250-1200(8.00-8.33) m,b; nmr τ ($CDCl_3$ and TMS) 7.49 (d-d, 2 H, J = 7 Hz, J = 2 Hz), 3.87 (d, 1 H, J = 11 Hz), 3.14 (m, 1 H, J = 7 Hz, J = 11 Hz); mass spectrum 70 eV, m/e (relative intensity)* 270 (<1), 235 (4), 200 (<1), 190 (2), 155 (16), 120 (11), 80 (90), 79 (100).

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* Ions containing tin are listed for the Sn^{120} isotope only. The isotopic clusters normally associated with organotin compounds were present.

3-Ethoxy-3-benzoborepin(XXV)

Under nitrogen, 0.23 g (1.3 mmol) of 3-chloro-3-benzoborepin in heptane, was treated with an excess of absolute ethanol. The solvents were removed in vacuo and the residue sublimed from 130-140°.at 0.2-0.5 mm. The yield of sublimate, 3-ethoxy-3-benzoborepin was 0.21 g (86%) and it melted at 39-45°.

The spectral characteristics of XXV are as follows: ir ν ($CHCl_3$) 2976(3.36) s, 1595(6.27) s, 1534(6.52) s, 1441(6.94) s, 1307-1260(7.65-7.94) b, 1193(8.38) s, 815 (12.27) b; uv λ_{max} (logε) 233(4.64), 238(4.66), 250(4.53), 258(4.56), 269(4.18), 276(4.11), 280(4.08), 287(3.87), 309(3.09), 322(2.93); nmr τ ($CDCl_3$ and TMS) 3.33 (d, 2 H, J = 14 Hz), 2.3-2.7 (m, 4 H) 2.10 (d, 2 H, J = 14 Hz); mass spectrum 70 eV, m/e (relative intensity)* 184 (>100), 169 (10), 155 (>100), 139 (45), 128 (>100), 115 (40),102 (45), 84.5 (16), 69.5 (23);

1-Ethynyl-2-β-chlorovinylcyclohexene

The synthesis of 1-ethynyl-2-β-chlorovinylcyclohexene was performed as outlined in references 27-30 with the exceptions of the preparation of chloromethyltriphenylphosphonium chloride[30] and the substitution of cyclohexanone for 2-methylcyclohexanone.[28] 1-Ethynyl-2-β-chlorovinylcyclohexene can be stored below 0° for long periods. It is moderately air stable.

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* Due to a malfunction in the galvanometer, the tops of all major peaks were cut off. For the peaks that appear to be mechanically shortened, the relative intensity is listed as (>100).

Chloromethyltriphenylphosphonium chloride

With vigorous stirring, 131 g (0.5 mol) of triphenylphosphine and 19 g (0.63 mol) of paraformaldehyde were dissolved in 250 ml of absolute ether containing 2 ml of thionyl chloride. Commercial hydrogen chloride, bubbled through concentrated sulfuric acid and passed through a calcium chloride tower, was bubbled into the vigorously stirred ether solution until the resulting precipitate appeared to dissolve or form an oil. The precipitate (hygroscopic) was collected, washed once with anhydrous ether and dissolved in 500 ml of methylene chloride. With stirring, 118 g (1 mol) of thionyl chloride was added cautiously. The stirred solution was heated to a boil and refluxed one hour. Methylene chloride and excess thionyl chloride were removed by an aspirator and the resulting hygroscopic precipitate was dissolved in 400 ml of boiling methylene chloride. After 5 g of decolorizing carbon was added and the solution filtered, the filtrate was cooled to 35° and anhydrous ether was added until a slight haze formed. The precipitate that formed on standing was collected and the resulting filtrate was reduced to half of its original volume. Ether was added in the same fashion to obtain a second crop. A third crop was also obtained. The three crops were combined and dried overnight in vacuo at 100°. The crude material, 110 g, was recrystallized in 1.5 l of boiling chloroform and dried in vacuo at 100°; mp 259-259.5°; literature 260-261° or decomposed at 267°.[30]

1,2-Diethynylcyclohexene

In a 250-ml three-necked flask equipped with a Hirshberg stirrer, one piece of potassium from 2.03 g (52 mmol) of potassium cut into small pieces, was added

to 70 ml of liquid ammonia. A few mg of ferric chloride was used to catalyze the reaction and the remainder of the potassium was added. When the blue color faded, 4.35 g (26 mmol) of 1-ethynyl-2-β-chlorovinylcyclohexene in 15 ml of anhydrous ether was added and stirred for one hour. Ammonium chloride was added and the ammonia boiled off. After the addition of 25 ml of water, the resulting solution was neutralized, extracted three times with ether, dried over sodium sulfate, and distilled in 45-50% yield; bp 52-56° (1.7 mm); literature 52-54° (18 mm).[27] The uv and nmr spectra essentially duplicated the literature values.[27]

3,3-Dimethyl-3-cyclohexenostannepin(XXVII)

A solution of 1.66 g (11 mmol) of dimethyltin dihydride in 10 ml of heptane was added dropwise to a stirred solution of 1.45 g (11 mmol) of 1,2-diethynylcyclohexene in 10 ml of heptane.

Caution: Several times in this laboratory, organotin hydrides have reacted violently with acetylenic compounds. Dimethyltin dihydride and/or its vapors are sometimes spontaneously flammable in air and/or shock sensitive.

After one hour the heptane solution was warmed to 80° and stirred overnight at 80°. A nitrogen stream evaporated the heptane and the viscous residue was distilled in 10% yield (0.3 g); bp 45-50° (5×10^{-4} mm). An nmr of the distillate showed that it was only 60% pure, the remainder being tin polymers.

The spectral characteristics of XXVII are as follows: nmr τ (CCl_4 and TMS) 9.88 (s), 8.42 (m), 8.04 (m), 3.88 (d, J = 13 Hz), 2.59 (d, J = 13 Hz); mass spectrum 70 eV, m/e (relative intensity) 281 (20), 267(11),

132 (100), 128 (28) 104 (100).*

3-Hydroxy-3-cyclohexenoborepin(XXVI)

A solution of 0.3 g (1.6 mmol) of crude 3,3-dimethyl-3-cyclohexenostannepin in 10 ml of hexane was added dropwise to a well stirred, cooled (-20°) solution of 0.2 g (1.7 mmol) of boron trichloride in hexane. Stirring continued for an hour while the solution warmed to room temperature. The solution was filtered and 30 µl of water was added to a vigorously stirred solution of the filtrate and 5 ml of hexane. The resulting precipitate (80 mg) was 81% pure (nmr).

The spectral characteristics of (XXVI) are as follows: ir ν ($CHCl_3$) 3623(2.76) s, 3003(3.33) w, 2976 (3.36) w, 2924(3.42) m, 2875(3.50) w, 1600(6.25) w, 1495 (6.69) s, 1449(6.91) s, 1282(7.80) m, 9.91(10.09) m,b, 800(12.50) m,b; uv λ_{max}(log ε) 225(4.33), 291(4.01), 301 (3.96), 315(3.67); nmr τ ($CDCl_3$ and TMS) 8.30 (m, 4 H), 7.33 (m, 4 H), 5.89 (s, 1 H) 3.44 (d, 2 H, J = 14 Hz), 2.63 (d, 2 H, J = 14 Hz); mass spectrum 70 eV, m/e (relative intensity) 160 (80), 132 (95), 118 (75), 104 (100).

Reaction of lithium aluminum hydride and 3-chloro-3-benzoborepin

Combination of 3.0 g (8.3 mmol) of 3,3-di-n-butyl-3-benzostannepin (70% pure) and 1.0 g (8.3 mmol) of boron trichloride in heptane resulted in a solution of 3-chloro-3-benzoborepin which was added dropwise to a vigorously stirred suspension of 0.48 g (12.4 mmol, 50 meq) of lithium aluminum hydride in 20 ml of anhydrous diethyl ether.

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* Clusters containing tin isotopes will be represented by the m/e for Sn^{120}.

After a vigorous exotherm subsided, the mixture was refluxed for a half hour and then cooled. The organic layer was decanted and the solvents were vacuum stripped. Distillation of the residue resulted in two fractions. The first fraction, bp 56-60° (1.2-5 mm), 0.6 g; showed only an ethyl and an aromatic pattern in the nmr spectrum. The ir spectrum confirmed that a B-H bond was not present.

Combination of 3-chloro-3-benzoborepin and tetraphenyltin

In a 10-ml flask containing a magnetic stirring bar, 0.12 g (0.69 mmol) of 3-chloro-3-benzoborepin and 0.29 g (0.69 mmol) of tetraphenyltin (M and T Chemical) were mixed and slowly heated to 175-180° until the reactants liquified. After 4 ml of heptane was added, the solution was left to reflux overnight. The resulting precipitate was collected (0.096 g); its ir spectrum was identical to that of tetraphenyltin's. The volume of the heptane solution was reduced and additional tetraphenyltin was collected by filtration. The anticipated product, 3-phenyl-3-benzoborepin, is insoluble in heptane and if any were present, it would have precipitated.

Reaction of 3-hydroxy-3-benzoborepin, 3-chloro-3-benzoborepin and pyridine

Addition of 0.055 g (0.7 mmol) of pyridine to a chloroform solution of 0.12 g (0.7 mmol) of 3-chloro-3-benzoborepin and 0.11 g (0.7 mmol) of 3-hydroxy-3-benzoborepin produced a vigorous reaction. After the solution was stirred overnight, chloroform was removed by vacuum and the gummy residue was triturated with carbon tetrachloride. Only 3-hydroxy-3-benzoborepin could be recovered.

Reaction of phenyllithium and 3-hydroxy-3-benzoborepin followed by acetyl chloride

The addition of 0.1 ml (2 mmol) of phenyllithium to a stirred solution of 0.18 g (1.1 mmol) of 3-hydroxy-3-benzoborepin in 20 ml of anhydrous diethyl ether resulted in a precipitate (extremely hygroscopic). Dropwise addition of 0.15 ml (2 mmol) of acetyl chloride, followed by the removal of solvent, gave a precipitate whose nmr spectrum contained only aromatic hydrogens; no hydroxyl or acetyl hydrogens were observed.

Reaction of potassium and 3-hydroxy-3-benzoborepin followed by the addition of methyl iodide

The addition of 0.04 g (1 mmol) of potassium to an ether solution of 0.156 g (1 mmol) of 3-hydroxy-3-benzoborepin resulted in a precipitate which, when collected, was extremely hygroscopic. The precipitate did not melt below 350°, and addition of a small amount of water resulted in a basic solution (pH paper). After excess methyl iodide and the precipitate had been stirred for an hour, the precipitate was recovered unchanged. The ir of the precipitate suggests that it was the potassium salt of 3-hydroxy-3-benzoborepin. The ir spectrum of the precipitate was: 3000, 1590, 1540, 1440, 1310-1260, 820 cm^{-1}.

Attempted reaction of phenylmagnesium bromide and 3-ethoxy-3-benzoborepin

The dropwise addition of 0.42 ml (1.3 mmol) of phenylmagnesium bromide to a diethyl ether solution of 0.21 g (1.14 mmol) of 3-ethoxy-3-benzoborepin was not exothermic. After refluxing the ether solution for an hour,

5 ml of aqueous saturated ammonium chloride solution was added and the ether layer was decanted, dried (Na_2SO_4), and the ether evaporated. The residue was not phenylboronic anhydride, 3-ethoxy-3-benzoborepin, or the desired 3-phenyl-3-benzoborepin.

Attempted preparation of 3-benzoborepin anhydride from 3-chloro-3-benzoborepin and 3-ethoxy-3-benzoborepin

A stream of nitrogen was maintained over a vigorously stirred heptane solution of 0.503 g (2.9 mmol) of 3-chloro-3-benzoborepin and 0.064 g (1.4 mmol) of absolute ethanol until there was no hydrogen chloride present in the nitrogen stream (bubbling the nitrogen through a silver nitrate solution). The solution was refluxed overnight. Evaporation of heptane gave a residue whose ir was a composite of 3-chloro-3-benzoborepin and 3-ethoxy-3-benzoborepin with the B-Cl and B-OC_2H_5 absorption bands present. Sublimation of the residue at 170° (2 mm), gave only 3-chloro-3-benzoborepin.

9,10-Diethynylphenanthrene and di-n-butyltin dihydride

A benzene solution of 0.67 g (3 mmol) of 9,10-diethynylphenanthrene[63-65] and 0.70 g (3 mmol) of di-n-butyltin dihydride was refluxed until an ir showed no C≡C-H or Sn-H absorption (six hours). After the removal of benzene, the residue was sublimed at 250° (1.2×10^{-3}-5×10^{-4} mm). The ir, uv, and nmr of the sublimate were identical with those of triphenylene. The sublimate melted at 191-195°. A mixed mp with triphenylene (K and K Laboratories) caused no depression.

Phenylboron dichloride and 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin

To a stirred solution of 6.35 g (40 mmol) of phenylboron dichloride in 35 ml of carbon tetrachloride, 1.71 g (5 mmol) of 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin was added over 10 minutes. After stirring for a day, carbon tetrachloride was removed. Hydrolysis of the distillate, collected from 7 mm to 0.1 mm at 30°, gave 3.70 g of phenylboronic anhydride (ir). High vacuum sublimation of the residue gave a series of fractions containing butyltin polymers alone or in combination with a polymer containing a phenyl group. There was no evidence of having formed 1-phenyl-4-methoxy-4,5-dihydroborepin, 1-phenyl-4-chloro-4,5-dihydroborepin, or 1-phenylborepin.

Tin tetrachloride and 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin

A stirred solution of 1.71 g (5 mmol) of 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin in 2 ml of carbon tetrachloride was maintained below 10° and 1.30 g (5 mmol) of tin tetrachloride in 1.5 ml of carbon tetrachloride was added dropwise. After a half hour of stirring at 0°, the solution was allowed to warm to room temperature. Distillation of the residue gave a crude product showing the presence of methoxy, vinyl, and allylic protons as well as a decrease in the proportion of butyl protons in the nmr spectrum.

Potassium and 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin

A well stirred mixture of 4 ml of heptane, 1.31 g (3.3 mmol) of 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin

and 0.13 g (3 mmol) of potassium was maintained overnight at 75°. After the heptane was removed, the residue was pyrolyzed to 240° ($3x10^{-4}$ mm). About 0.13 g of 1,1-di-n-butyl-4-methoxy-4,5-dihydrostannepin was recovered.

Reaction of phenylboron dichloride with cycloöctatetraene dianion

To 500 ml of freshly distilled tetrahydrofuran ($LiAlH_4$) cooled to -30° in a one-liter four-necked flask containing a nitrogen inlet and exit, a stirrer, and addition funnel, 10.4 g (0.1 mol) of cycloöctatetraene and 7.8 g (0.2 mol) of potassium were added and left stirring overnight. When no potassium remained, the solution was cooled to -80° and 1.71 g (0.11 mol) of phenylboron dichloride was added over five hours. The solution was stirred for a day and a half as it slowly warmed to 27°. Solvents were vacuum stripped. An aliquot was removed under nitrogen, dissolved in carbon tetrachloride, and transferred to a modified 50-ml distilling flask.

The flask was connected to a freeze-out-trap attached to a manifold leading to a vacuum pump and a high vacuum line. Dry-ice-acetone was placed in the trap and solvents were removed. Liquid nitrogen was placed in the trap and the high vacuum line engaged as the distilling flask was heated to 90-100° for 24 hours and the heating tape maintained at 86°. About 200 mg of 1-phenyl-2-oxa-1-borinane distilled.

The spectral characteristics of the product are as follows: ir ν (CCl_4) 3077(3.25), 3040(3.29), 2950(3.39), 1613(6.20), 1592(6.28), 1433(6.98), 1383(7.23), 1366(7.32), 1351(7.40), 1326(7.54), 1259(7.94), 1205(8.30), 998(10.02), 908(11.01), 857(11.67), 717(13.95), 693(14.43), 653(15.31); nmr τ (CCl_4 and TMS) [7.48 (t), 590 (t + m), 4.57 (t + m), 8 H], [2.79 (m), 2.33 (m), 5 H]; mass spectrum 70 eV, m/e

(relative intensity) 160 (6), 159 (1.5), 129 (3), 128 (3), 122 (4), 115 (3), 105 (23), 104 (19), 91 (16), 78 (29), 77 (16), 56 (100), 41 (46).

Reaction of dimethyltin dichloride with cycloöctatetraene dianion

To 625 ml of freshly distilled tetrahydrofuran ($LiAlH_4$) in a one-liter four-necked Morton flask containing nitrogen inlet and exit, alcohol thermometer, stirrer, and addition funnel, cooled to -37°, 10.4 g (0.1 mol) of cycloöctatetraene and 7.8 g (0.2 mol) of freshly cut potassium were added and stirred overnight. All of the potassium reacted and the reaction mixture cooled to -55°. A solution of 22.5 g (0.1 mol) of dimethyltin dichloride in 100 ml of dry tetrahydrofuran was added over 8.5 hours and stirred overnight. Solvents were removed by vacuum and an aliquot of the gelatinous residue was extracted three times with benzene under nitrogen. Benzene was evaporated in a nitrogen stream. The residue was a tin polymer.

The spectral characteristics of the residue are as follows: ir ν (CCl_4) 500(20.0), 492(20.3); nmr τ ($CDCl_3$ and TMS) 9.91, 9.75, 9.57, 9.40, 9.24, ratio 1:2:10:2:1.

Reaction of phenylboron dichloride with the cycloöctatetraene:dimethyltin adduct

A 5.13 g (1.26 mmol) aliquot of the gel, formed from the reaction of cycloöctatetraene dianion and dimethyltin dichloride, and assumed to be $C_8H_8{:}Sn(CH_3)_2{+}2KCl$, was dispersed in benzene and 2.0 g (1.26 mmol) phenylboron dichloride was added dropwise with stirring. A black solid precipitated, but neither the precipitate nor the filtrate yielded any identifiable product.

Reaction of 1,5-hexadiyne-3-tosylate with di-n-butyltin dihydride

The tosylate was prepared by the method outlined by Sheehan[13]. In an oven-dried 50-ml three-necked flask with nitrogen inlet and exit, magnetic stirrer, and reflux condenser, 5.92 g (24 mmol) of 1,5-hexadiyne-3-tosylate in 25 ml of spectrograde heptane and 5.61 g (24 mmol) of di-n-butyltin dihydride were combined and refluxed for 2.5 hours. An ir of the reaction solution showed an acetylene peak present, but all Sn-H absorption appeared to be absent in the 1950-1900 cm^{-1} region. Solvents were stripped and the residue distilled.

Fraction I: bp 80-100° (0.05 mm) showed only aliphatic protons in its nmr spectrum.

Fraction II: bp 190-200° (0.003) tri-n-butyltin tosylate.

Higher boiling fractions appeared to be n-butyltin polymers.

The residue in the pump trap was allowed to stand five days until the tin polymers precipitated as a gum. The trap residue was extracted with chloroform and distilled.

The presence of an allene, in addition to 1,5-hexadiyne, heptane, and chloroform, was observed in the distillate.

The nmr spectrum of the allene is as follows:
τ ($CDCl_3$ and TMS) 7.05, 6.62, 5.13, 4.08.

IR SPECTRUM OF 1,2-HEXADIENE-5-YNE

Observed (cm^{-1})	Literature[75] (cm^{-1})
1965	1970
1684	1700
851	840