fact that cyclohexanol cannot inhibit the hydrolysis of 8-acetoxy-5-quinoline sulfonate with IV.

A scale molecular model of a complex of *p*-nitrophenyl acetate with IV can result in fixing the position of the ester group in close proximity to the secondary hydroxyl groups and imidazole group.

It should be pointed out that this newly prepared catalyst showed its rate acceleration around the same pH and possibly has the same mode of kinetics as chymotrypsin during the release of phenol (the acylation step) in the hydrolysis of ester. The present catalyst contains imidazole and hydroxyl groups in the same stereochemically correct manner as chymotrypsin does in its active site. This fact thus furnishes a better enzyme model for chymotrypsin catalysis.

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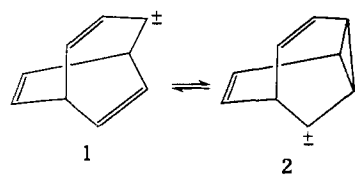
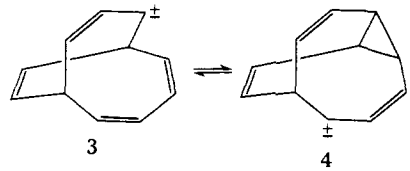
Degeneracy and Stability of the Homobullvalenyl Cation

Sir:

Winstein's concept of homoaromaticity[1] and the refining applications of MO theory by Goldstein and Hoffmann[2] to longicyclic systems of potential bicycloaromaticity[3] have led to considerable effort directed toward experimental tests of theory. In at least formal agreement with prediction the ion $\mathbf{1}^-$ has been found to be delocalized where $\mathbf{1}^+$ rearranges to $\mathbf{2}^+$.[4]

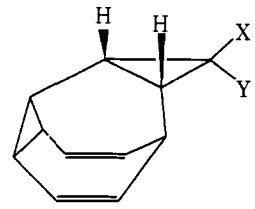


(1)



(2)

More recently approaches to precursors of **3** and **4** have appeared[5,6] since, in principle, electronic factors present in **1** should be reversed **3**. We report here the first experimental verification of this prediction and at the same time apply the first limits to the extent of homoaromatic or longicyclic stabilization in $\mathbf{3}^+$ and $\mathbf{4}^+$.



5, X = $OOCCF_3$; Y = Br
6, X = H; Y = OH
7, X = H; Y = OTf
7-*d*, X = D; Y = OTf

Our approach to **3** and **4** has been based upon functional group manipulation of the dibromocarbene adduct of bullvalene. The discovery that α-bromocyclopropyl trifluoroacetates can be reduced with sodium borohydride to cyclopropanols[7] has now afforded an entry to the parent $[CH]_{11}$ system. Thus, treatment of the α-bromotrifluoroacetate **5** with sodium borohydride in THF afforded[8] a 77% yield of the cyclopropanol **6**.[9] The NMR spectrum of **6** was similar to that of **5**[10] with an additional triplet (δ 3.17, J = 7.5 Hz) signaling the *cis*-cyclopropane vicinal coupling. Treatment of **7** with trifluoromethyl sulfonic anhydride in pyridine for 2 hr produced a 99% yield of the corresponding triflate **7**.

The solvolysis of **7** proceeded smoothly in 40% aqueous acetone (3 hr at 95°, 2,6-lutidine buffer) to give a mixture of two alcohols, **8** and **9**, which, upon Sarett oxidation,[11] afforded a 65% isolated yield of the known ketones **10**[6b] and **11**[5b] (relative amounts 17:83) (Scheme I). That the origin of **9** is due to a subsequent *thermal* process is confirmed by appropriate variations in the **8**/**9** ratio with time and temperature and the known parallel chemistry of **10**.[5b]

Formally, the conversion of **7** to **8** requries only the opening of two cyclopropane rings leading first to $\mathbf{4}^+$ and then to $\mathbf{3}^+$. Solvolysis of specifically labeled **7-*d***[12] has revealed far greater complexity. While the proton NMR spectra of **8**, **9**, and **10** are complex, that of **11** is nearly first order, and all

Scheme I

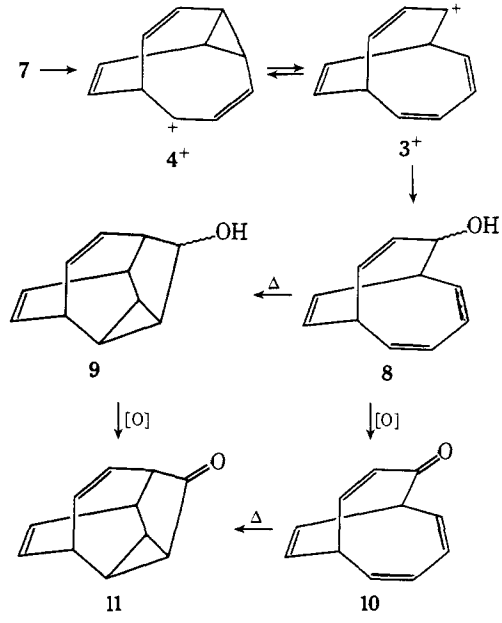


Table I. Relative ^{1}H NMR Deuterium Satellite Intensities (D)[a] for 11-*d*

Proton	a	b	c	d	e	f	g	h	i	j
D (obsd)	0.22	0.25	0.24	0.27	0.23	0.38			0.35	
D (statistical)	0.24	0.24	0.24	0.24	0.24	0.40	0.40	0.24	0.40	0.40
D (path a)	0.26	*0.41*	0.17	0.20	*0.41*	*0.20*	0.20	0.17	0.41	0.51
D (path b)	0	0	0.76	0	0.76	3.1	3.1	0.76	0.76	0
D (path c)	0.27	0.27	*0.12*	0.27	*0.12*	*0.27*	0.27	0.12	0.27	0.47

[a] The ratio of integrated ^{1}H NMR peak intensities for each methine proton with and without *adjacent* deuterium. Clear inflections in the integral could be discerned for each D (obsd) reported.

Table II. Acetolysis Rates for Cyclopropyl Triflates

Triflate	Rate at 100° (sec^{-1})	
endo-7-Norcaranyl	3.28×10^{-2}	*e*
	1.3×10^{-2}	*d*
exo-7-Norcaranyl	6.8×10^{-4}	16[a]
Cyclopropyl	4×10^{-4}	17
7[b]	2.44×10^{-4}	This work

[a] From the rate of tosylate solvolysis at 100°, cf. ref 17. [b] Good first-order kinetics were observed at six points over the range 70–95° in 40% aqueous acetone. $\Delta H^{\ddagger} = 29.6$ kcal/mol, $\Delta S^{\ddagger} = +9.7$ *G*. $k_1 = 7.9 \times 10^{-3}$ at 100°. [c] Determination by GLPC by observing the disappearance of **7** in acetic acid at 100°. [d] P. G. Gassman, private communication. [e] T. M. Su, Ph.D. Thesis, Princeton University, 1970.

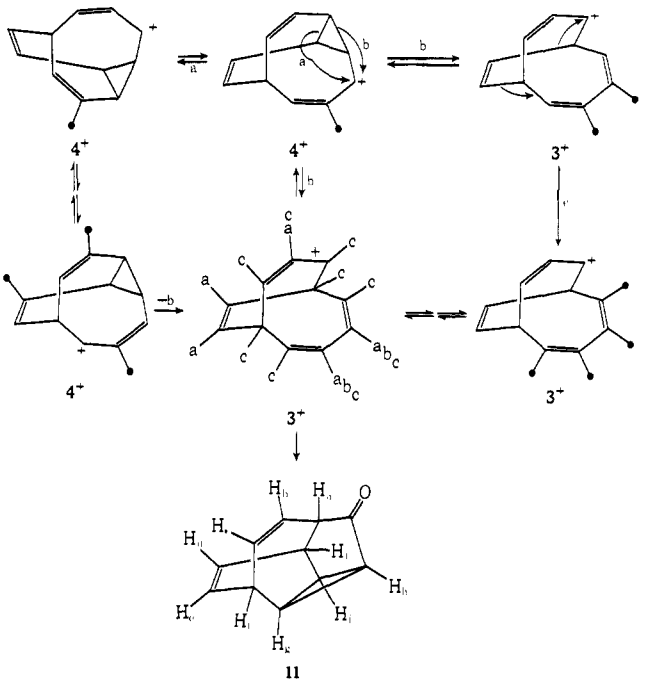
resonances have been unambiguously assigned.[5b] In addition, the thermal conversion of **10** to **11** by successive intramolecular Diels–Alder addition-Cope rearrangement, without unexpected positional scrambling,[13] has been established. Accordingly, the deuterium distribution in **11** can be related with confidence to the fate of 3^+ and 4^+. Integration of the ^{1}H NMR spectrum of **11-*d*** derived from **7-*d*** yielded normalized proton intensities of 0.90 ± 0.04 for every resonance and comparisons of mass spectra revealed that 0.11 deuterium atoms had been lost upon oxidation of **9-*d***. Most significantly, deuterium "satellites" in the ^{1}H NMR (Table I) and ^{13}C NMR spectra of **11-*d*** were consistent only with a statistical distribution of deuterium. Accordingly, the transformation **7** → **8** was accompanied by an *11-fold* degeneracy!

Based on precedent and prediction likely scrambling mechanisms for **4** are (a) threefold degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement, (b) cyclopropylcarbinyl–homoallyl rearrangement (**4** ⇄ **3**), and (c) similar perambulation of the ethylidene bridge in **3**[15] (Scheme II). No single process is consistent with either the proton intensities or the relative deuterium satellite intensities observed but statistical scrambling can be achieved by the simultaneous operation of (b) *and* either (a) or (c).

The rate of solvolysis of cyclopropyl derivatives has been shown to be a sensitive function of the degree to which substituent groups stabilize the incipient allyl cation.[16] Accordingly, energetically favorable charge delocalization in the transition state leading to 4^+ should be reflected in the solvolysis rate of **7**. In fact, **7** has been found to solvolyze at an inordinately slow rate (Table II).

The rate difference between **7** and *endo*-7-norcaranyl triflate, substitutionally and stereochemically similar to **7**, indicates that **7** encounters a 3.0–3.6 kcal/mol incremental barrier to ring opening. Models indicate that while the homotropilidene backbone of **7** can accommodate a two-carbon bridge with only a modest amount of distortion, nearly complete flattening of the ring is required to allow for a planar allylic cation as in 4^+.[18] A reasonably good estimate of the energetic cost of flattening the homotropilidene moiety can be made from the known inversion barrier

Scheme II



11

of tropilidene.[19] This value, 6.3 kcal/mol, would account substantially for the observed deceleration of **7**. Consequently, any *acceleration* due to favorable homoaromatic or bicycloaromatic effects must be small or nonexistent in the transition state leading to 4^+. Further, to the extent that the degeneracy observed is due to path b, 3^+ cannot be more than ca. 3 kcal lower in energy than 4^+.[20] In spite of this fact, however, the isolation of products derived from 3^+ to the exclusion of those from 4^+ confirms the prediction[2] that 3^+ should represent a relative energy minimum in this manifold[21] and in accord with prior suggestions the homobullvalenyl cation (4^+) is fully degenerate.[15]

Acknowledgments. Financial support by Research Corporation, the Merck Company Foundation for Faculty Development, and The University of Michigan are gratefully acknowledged.

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(6) (a) M. J. Goldstein, R. C. Krauss, and S.-H. Dai, *J. Am. Chem. Soc.*, **94**, 680 (1972); (b) M. J. Goldstein and S. A. Kline, *Tetrahedron Lett.*, 1089 (1973).
(7) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974).
(8) In a typical reaction 0.8 g of **5** and 0.27 g of $NaBH_4$ were stirred in 20 ml of freshly distilled THF for 30 min at 0°.
(9) Characterized as the mesylate, mp 120–121°, elemental analysis was within ±0.3% of expected values: *m/e* (relative intensity) 292 (9.9), 159 (100), 142 (89), 141 (81), 131 (81), 129 (89), 128 (73), 116 (64), 115 (84), 91 (93); ir (CCl_4) 3025, 2925, 1378, 1353, 1184, 992, 975, 936, 920, 891, 858, 708 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (2 H, m), 2.43 (2 H, m), 3.07 (3 H, s), 3.91 (t, J = 7 Hz) and 3.97 (m) total 5 H, 5.73 (2 H, apparent q, J = 9 Hz).
(10) Cf. ref 5b. Note that the entry δ 3.19 should read δ 3.9.
(11) CrO_3-pyr in CH_2Cl_2 at room temperature for 15 min.
(12) From the reaction of **5** with $NaBD_4$.
(13) M. J. Goldstein and S.-H. Dai, *Tetrahedron Lett.*, 535 (1974).
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(20) Neither can 3^+ be less than ca. 2.5 kcal/mol more stable than 4^+ to explain the exclusive formation of **8**.
(21) The observations reported here are in marked contrast to results obtained upon ionization of **8** in superacid which gives only rearrangement: M. J. Goldstein and S. A. Kline, *J. Am. Chem. Soc.*, **95**, 935 (1973).

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The Synthesis of Heptaphenylborepin via the Thermal Rearrangement of Heptaphenyl-7-borabicyclo[2.2.1]heptadiene[1]

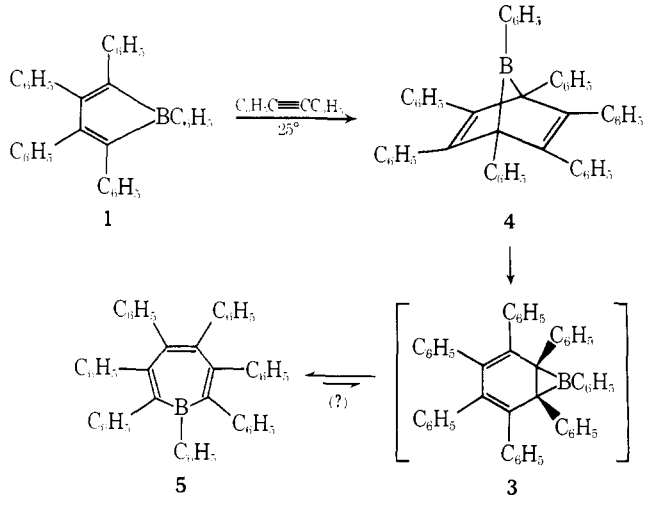
Sir:

From considerations of its covalent radius and electronegativity, an sp^2-hybridized boron atom would be expected to form cyclic conjugated systems with sets of sp^2-hybridized carbons.[2] Such boracyclopolyenes might display Hückel-aromatic or -antiaromatic character, depending upon the total number of π electrons. Thus, the recently prepared phenylborabenzene anion[3] and pentaphenylborole[4] represent nonfused, monocyclic examples of aromatic and antiaromatic boracarbocycles, respectively. Synthesis of other boracarbocycles has been limited to benzo-fused systems, such as the 3-benzoborepin,[5] dibenzoborepin,[6] and boraanthracene[7,8] systems, where the benzo annelation tends to obscure the unique electronic character of the boron ring.[9] Up to the present, the attempted syntheses of nonfused borepin and borirene rings have met with repeated failures, and only a circumstantial case can be made for the formation of the latter nucleus in solution.[2,10,11] Therefore, we are now pleased to report the synthesis of the first nonfused borepin, heptaphenylborepin (**5**), by a smooth [1,3] suprafacial sigmatropic rearrangement of heptaphenyl-7-borabicyclo[2.2.1]heptadiene (**4**), followed by a reversible, disrotatory ring-opening of intermediate **3** (Scheme I).

Thus, stirring a partial suspension of pentaphenylborole (**1**, 4.87 mmol[4]) and diphenylacetylene (**2**, 5.0 mmol) in 25 ml of toluene at 20–25° until the dark blue-green color of **1** had disappeared, followed by dilution with 75 ml of ethyl ether and filtration, gave a 60% yield of colorless **4**, mp 210° dec ($\lambda_{max}^{Et_2O}$ (ϵ): 318 (10,000)).[12] The structure of **4** follows from its spectral and analytical data, as well as from its acetolysis with hot glacial acetic acid to yield the previously identified *cis*-hexaphenyl-1,4-dihydrobenzene (**6**).[4] Now, heating **4** (2.23 mmol) in 30 ml of refluxing toluene for 24 hr, removing most of the toluene in vacuo, and diluting the residue with ethyl ether provided an 84% yield of fluorescent greenish yellow heptaphenylborepin (**5**).[13] Alternatively, the toluene solution obtained by allowing the borole **1** to react with the acetylene **2** could be heated directly to give **5** in an 82% yield. The solid borepin **5** was only slowly oxidized in air, but its solutions were rapidly attacked.

The structure assignment of the borepin **5** is based both upon its spectroscopic and chemical properties (Scheme II). Its electronic spectrum exhibited peaks at $\lambda_{max}^{Et_2O}$ (ϵ) 412 (6100), 342 (8080), 276 (22,700), and 245 (28,000), while the infrared spectrum had strong characteristic bands at 1590, 1240–1300, 770, 750, 740, 705, and 695 cm^{-1}. Pyridine forms an almost colorless complex with **5** that dissociates in warm toluene solution, but whose infrared spectrum lacks strong absorptions in the region of 1250–1350 cm^{-1}, present in uncomplexed **5** and generally considered characteristic of the conjugated heptaphenyltropenium ion ring.[14] Gaseous ammonia instantly discharges the green color of **4** and yields a complex with the following electronic spectrum: $\lambda_{max}^{Et_2O}$ (ϵ) 333 (8070), 265 (sh, 8700), and 243 (25,200). Chemical degradation of **5** by heating with acetic or propionic acid at reflux was slow and incomplete. On the other hand, **5** was smoothly mercurideboronated[15] by heating with an excess of mercuric chloride, lithium chloride, and potassium hydroxide in a THF–MeOH solvent mix-

Scheme I



Scheme II