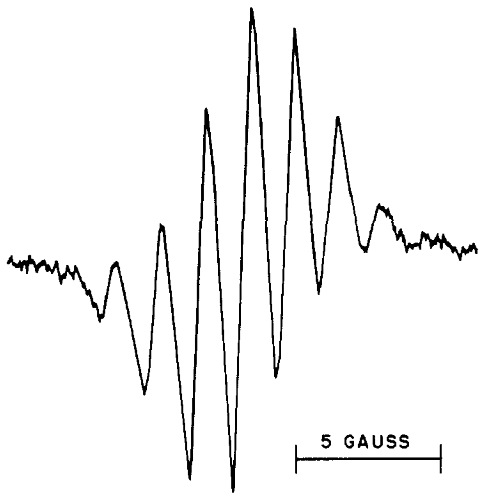
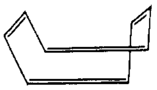
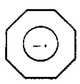


Figure 3. The esr spectrum of the cyclooctatetraene radical cation.

appear to be planar[13] (II). Recent theoretical calculations by Dewar, *et al.*,[14] predicted a nonplanar structure for the radical cation, and it was the purpose of this work to experimentally test this hypothesis.


I


II

The previously unreported cyclooctatetraene radical cation was prepared in pure trifluoroacetic acid (no BF_3 added) by cobaltic ion oxidation of cyclooctatetraene (10^{-3}–10^{-2} *M*) in a rapid mixing flow system. The esr spectrum (Figure 3) obtained under these conditions consisted of seven equally spaced lines separated by 1.5 G (with a peak-to-peak line width of 0.6 G). The observed line intensities were consistent with splittings caused by eight equivalent hydrogen atoms, the two outer lines being too small to be observed.

The reported[13d] proton splitting for the planar radical anion was 3.2 G. By analogy to aromatic ions,[16] the corresponding splitting for the radical cation would be expected to be somewhat greater than 3.2 G, if the geometry of the two ions were identical. The small splitting of 1.5 G found in the radical cation supports a nonplanar configuration for the cation. Spin polarization of the C–H bond by the spin on the α carbon will generate a *negative* spin density at the hydrogen atom. In a tub-shaped ion radical, the hydrogen can also interact in a hyperconjugative manner with a spin on a β carbon. This will generate a *positive* spin density at the hydrogen atom. The partial cancellation of these spin densities results in the lower splitting constant observed.

Further studies on other olefinic radical cations are currently in progress.

Acknowledgment. Helpful discussions with Drs. E. I. Heiba, P. L. Corio, and S. Shih as well as the skillful technical assistance of Mr. R. J. Cier are gratefully acknowledged.

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(16) G. Vincow, in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 151.

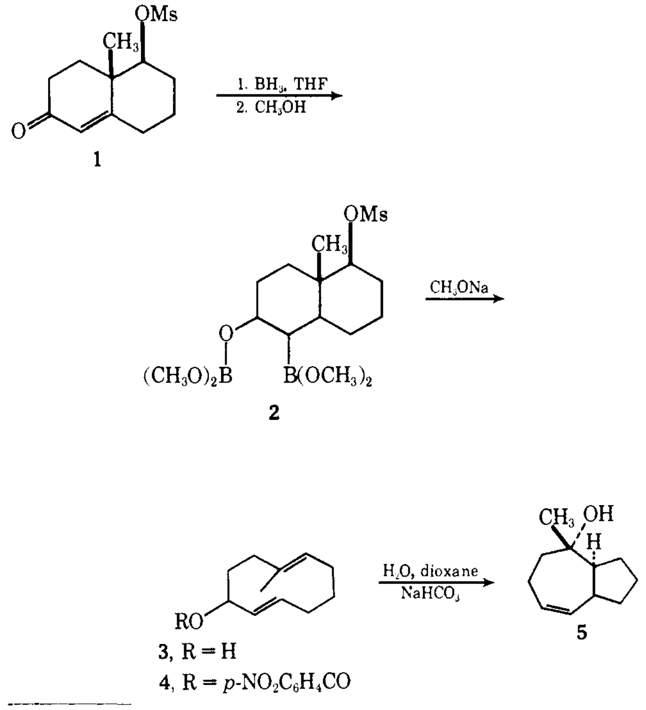
A New Synthetic Approach to Hydroazulenes

Sir:

A sizable group of natural products possess substituted hydroazulenic carbon skeletons, yet there are but a few general routes to such compounds.[1] During the past several years we have been seeking efficient stereoselective synthetic approaches to hydroazulenes which might solve the problems posed by this class of compounds. This report discloses preliminary findings on a novel approach based upon the positionally and stereochemically selective cyclization of cyclodecadienyl derivatives.[2]

Scheme I depicts the essential features of the synthetic pathway. The unsaturated keto mesylate **1**,[3] upon treatment with excess diborane in THF followed by methanolic sodium methoxide, afforded the cyclodecadienol **3**[4] [$\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.70 (vinyl CH_3), 3.89 (carbinyl H, multiplet), 4.74, and 5.20 ppm (vinylic H's, multiplets)]

Scheme I



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(1) *Cf.* J. A. Marshall and J. J. Partridge, *J. Amer. Chem. Soc.*, **90**, 1090 (1968); *Tetrahedron*, **25**, 2159 (1969), and references cited therein; J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970); C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968); M. Kato, H. Kosugi, and A. Yoshikoshi, *ibid.*, 185 (1960).

(2) An electrophile initiated *trans,trans*-1,5-cyclodecadiene cyclization process has been postulated in the biogenesis of hydroazulenes by J. B. Hendrickson [*Tetrahedron*, 7, 82 (1959)]. Recently both acid-catalyzed and thermal cyclizations of *trans,trans*-1,5-cyclodecadiene monoepoxides have been effected: E. D. Brown and J. K. Sutherland, *Chem. Commun.*, 1060 (1968); E. D. Brown, T. W. San, and J. K. Sutherland, *Tetrahedron Lett.*, 5025 (1969).

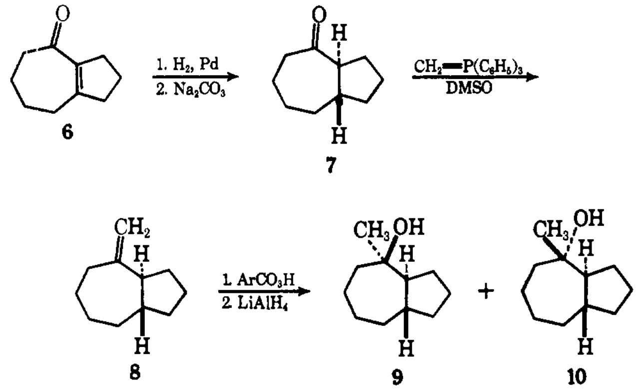
(3) *Cf.* C. B. C. Boyce and J. S. Whithurst, *J. Chem. Soc.*, 2680 (1960).

(4) Satisfactory combustion analysis data were secured for this substance.

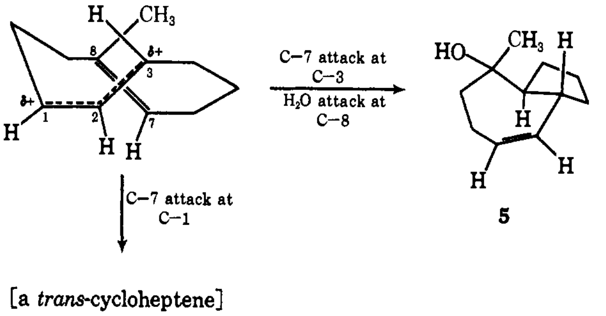
in 60% yield, presumably *via* the decalinboronate **2**.[5] Solvolysis of the *p*-nitrobenzoate derivative **4**[4] [mp 74-75°; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.55 (vinyl CH_3), 4.97 (carbinyl H, multiplet), 5.44, and 8.23 ppm (vinylic H's, multiplets)] in aqueous dioxane afforded the hydroazulenol **5**[4] [$\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.22 (vinyl CH_3) and 5.36 ppm (vinyl H, multiplet)] in 70% yield, along with 20% of unsaturated hydrocarbons according to gas chromatographic analysis. Several peaks possibly arising from isomers of **5** were also observed, but each of these accounted for less than 2% of the total product.

The structure of the major solvolysis product was ascertained through hydrogenation to the dihydro compound **10**[4] [$\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.05 ppm (CH_3); $\lambda_{\max}^{\mathrm{film}}$ 2.97 μ (OH)], which was independently synthesized as outlined in Scheme II. The known *trans*-hydroazulene **7**,[6] secured *via* hydrogenation of enone **6** followed by basic equilibration (85:15 cis:trans → 20:80 cis:trans) afforded the olefin **8**[4] [$\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.64 ppm (vinyl H multiplet); $\lambda_{\max}^{\mathrm{film}}$ 6.02 and 11.34 μ ($C{=}CH_2$)] upon treatment with methylenetriphenylphosphorane in DMSO.[7] Epoxidation with *m*-chloroperoxybenzoic acid (Na_2HPO_4 buffer) and reduction of the resulting 45:55 epoxide mixture with lithium aluminum hydride afforded a 45:55 mixture of the alcohols **9** and **10**. The former alcohol[4] [$\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.15 ppm (CH_3); $\lambda_{\max}^{\mathrm{film}}$ 2.91 μ (OH)] was also obtained (over 90% yield) through the addition of methyllithium to ketone **7**.

Scheme II



The above described transannular cyclization approach to hydroazulenes is predicated upon the specific electrophilic activation of one cyclodecadiene double bond through formation of an incipient allylic cation.[8] *A priori* a number of structural possibilities could be envisioned for the product(s) of such a cyclization process. The remarkable selectivity actually observed can be rationalized on the basis of the following scheme wherein the aforementioned ion is preferentially formed in the "sickle" as opposed to the "W" or "U" arrangement.[9] The crossed (*vs.* aligned) orientation of the transannular double bond systems presumably minimizes steric interactions in the transition state thereby favoring the trans fused product.[10] Attack of the isolated double bond at C-1 (*vs.* C-3) of the allylic cation would afford a hydroazulenic product containing a *trans*-cycloheptene double bond. The high degree of strain inherent in such an intermediate would expectedly prohibit this mode of cyclization.



Acknowledgments. We are grateful to the National Institutes of Health for a Research Grant (RO1 CA-11089) and a Fellowship (1 FO1 GM-41,066 to W. F. H.) in support of this work.

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(5) *Cf.* J. A. Marshall and G. L. Bundy, *J. Amer. Chem. Soc.*, **88**, 4291 (1966).

(6) W. Hückel and L. Schnitzspahn, *Justus Liebigs Ann. Chem.*, **505**, 274 (1933).

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(8) *Cf.* W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(9) For previous usage of these terms, see A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967); R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3031; 3033 (1963).

(10) An alternative pathway involving stereospecific SN2′ attack by the isolated double bond on the allylic *p*-nitrobenzoate could also account for the observed specificity of the cyclization reaction.

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Preparation of Difluoroaminodifluorophosphine

Sir:

Many workers have examined the physical and chemical properties of aminophosphines. Some of the results have been rationalized by suggesting that the N–P bond, which arises from hybridized atomic orbitals forming a σ molecular orbital, is supplemented by additional π molecular orbitals which arise from the delocalization of the lone pair of electrons on nitrogen into the empty d orbitals of phosphorus (a $(p \rightarrow d)\pi$ bond).[1] The most reliable support for the theory of a $(p \rightarrow d)\pi$ interaction in the P–N bond comes from stereochemical evidence. The results of two detailed structural studies are available. Morris and Nordman[2] have found through a single-crystal X-ray diffraction study of $(CH_3)_2NPF_2$ that nitrogen, when bonded to a PF_2 moiety, can achieve planarity. A detailed microwave spectral analysis of H_2NPF_2[3,4] indicates that nitrogen also is planar in this compound.

We wanted to prepare an aminophosphine which would be suitable for gas-phase structural investigations and which would have very electronegative groups

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(1) A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, **80**, 1107 (1958); G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 3984 (1962); R. R. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963); W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964); R. Schmutzler, *ibid.*, **3**, 415 (1964); A. H. Cowley and R. P. Pinnell, *J. Amer. Chem. Soc.*, **87**, 4454 (1965); A. H. Cowley and M. H. Hnoosh, *ibid.*, **88**, 2595 (1966); K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968); J. E. Clune and K. Cohn, *ibid.*, **7**, 2067 (1968); J. F. Nixon and M. D. Sexton, *J. Chem. Soc. A*, 1089 (1969); R. M. Kren and H. H. Sisler, *Inorg. Chem.*, **9**, 836 (1970).

(2) E. D. Morris and C. E. Nordman, *ibid.*, **8**, 1673 (1969).

(3) J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, in press.

(4) A. H. Brittain, J. E. Smith, and R. H. Schwendeman, unpublished results.