gles and ^{31}P chemical shifts, with other factors playing a minor role, then these shifts may in turn be used to define solution structures. For example, Patel[12] has recently noted a substantial downfield shift (1.7 ppm) of the diester phosphate signal in a Watson-Crick type d-pGpC dimer upon complexation with the DNA inhibitor, Actinomycin D. Jain and Sobell[13] have proposed a model for this complex based upon related crystallographic data which has the aromatic ring of the actinomycin intercalated between the stacked, base pairs of the dimer. In their model this requires an expansion of the O-P-O diester bond to *ca.* 113°. Although our correlation would suggest an O-P-O bond angle of 109-110°, qualitatively, these results are in agreement. It may be possible now to utilize ^{31}P nmr spectroscopy to define structures of more complex phosphate esters, particularly the biochemically important nucleotides, including possibly small tRNA's[14] and DNA fragments.

Acknowledgment. Support of this research by the National Institutes of Health, the National Science Foundation, the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Dr. Jurgen Bode of Braunschweig, Germany, for helpful suggestions and ^{31}P spectra.

References and Notes

(1) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956); E. Dennis, Ph.D. Thesis, Harvard University 1967.
(2) G. M. Blackburn, J. S. Cohen, and Lord Todd, *Tetrahedron Lett.*, 2873 (1964); G. M. Blackburn, J. S. Cohen, and I. Weatherall, *Tetrahedron*, 27, 2903 (1971).
(3) J. H. Letcher and J. R. Van Wazer, *Top. Phosphorus Chem.*, 5 (1967).
(4) M. Cohn and T. R. Hughes, Jr., *J. Biol. Chem.*, **237**, 176 (1962).
(5) D. G. Gorenstein and A. M. Wyrwicz, *Biochem. Biophys. Res. Commun.*, **54**, 976 (1973).
(6) D. G. Gorenstein, A. M. Wyrwicz, and J. Bode, to be submitted.
(7) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954).
(8) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1955); J. R. Parks, *ibid.*, **79**, 757 (1957).
(9) D. Purdela, *J. Magn. Reson.*, 5, 23 (1971); D. Purdela, *Rev. Roum. Chim.*, **13**, 1415 (1968).
(10) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
(11) J. Gillespie and J. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957).
(12) Reference *w* in Table I.
(13) S. C. Jain and H. M. Sobell, *J. Mol. Biol.*, **68**, 1, 21 (1972).
(14) M. Gueron, *FEBS (Fed Eur. Biochem. Soc.) Lett.*, **19**, 264 (1971).
(15) Visiting Professor, Department of Chemistry, University of Wisconsin, Madison, Wis., 1975.

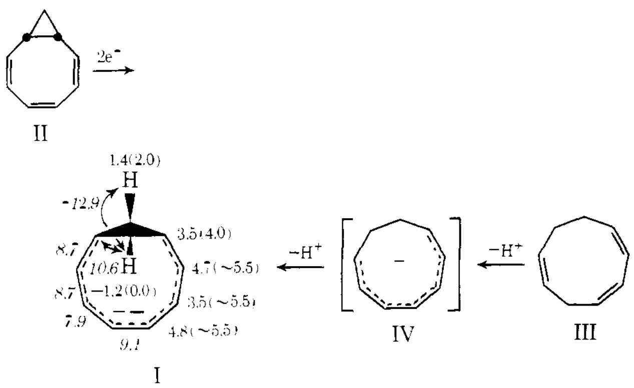
David G. Gorenstein[15]
Department of Chemistry, University of Illinois
Chicago, Illinois 60680
Received October 7, 1974

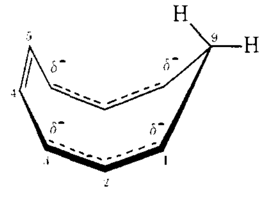
Homocyclooctatetraene Dianion: Preparation by Dimetalation; Geometry[1]

Sir:

The preparation of the title substance I by reduction of II with metallic potassium, and pmr shifts which supported the proposed structure, were reported in 1966.[2] We have found that I can readily be prepared as the dilithium salt by dimetalation of (*Z,Z,Z*)-1,3,6-cyclononatriene (III);[3] its proton-proton coupling constants help to reveal its geometry.

III is not metalated by *n*-butyllithium in THF, but in TMEDA III reacts to give a tan precipitate which is quite soluble in THF-d_8.[4] Quenching by addition to excess methanol at −78° gave back III in almost quantitative yield. Quenching with D_2O gave III containing by mass spectrometry 82.4% d_2, 12.8% d_1, and 4.8% d_0; pmr spectrometry showed this largely dideuterated material to be monodeuterated at C5 and also at either C8 or C9.[5] This is exactly the result expected from the quenching of I.





V

The ^1H nmr spectrum of this substance in THF-d_8 at 35° shows a ~1:1:1:1 quartet for 2 H at δ 4.8 (spacings 3.0, 2.5, and 3.0 Hz), a 1:2:1 triplet for 2 H at δ 4.7 (J = 8.7 Hz), a complex multiplet for 4 H at δ 3.5, and a doublet (J = 12.9 Hz) of triplets (J = 10.6 Hz) for 1 H at δ −1.2.[6] This is clearly not the ^1H nmr spectrum of the monoanion IV.[7] The shifts also differ considerably from those reported[2] for the dipotassium salt of the dianion I and given in δ units in parentheses on structure I. However, the dipotassium salt of I had very low solubility in THF and DME, and time averaging was used to obtain these shifts; no coupling constants were reported. Our pmr assignments for the much more soluble dilithium salt are shown on formula I (italicized numbers are coupling constants in hertz). They are supported by decoupling experiments: irradiation at δ 3.5 collapses the quartet at δ 4.8 and the triplet at δ 4.7 to singlets and the multiplet at δ −1.2 to a doublet; irradiation of a TMEDA-obscured proton at δ 1.4 reduces the multiplet at δ −1.2 to a triplet. The coupling constants J_{34} ($=J_{56}$) and J_{45} are not directly measurable from the spectrum, but were calculated by treating H3-H6 as an AA′XX′ system.[8] Using the position of a small line 10.4 Hz to the left of the center of the pattern for H4 and H5, the values shown for J_{45} and J_{34}($=J_{56}$) were calculated, and in addition, J_{36} = 0 and J_{35} = J_{46} = +0.6 Hz. The small line was calculated and observed to be about 11% as intense as the largest line in the pattern.

These coupling constants provide further evidence regarding the geometry of this dianion. The −12.9 Hz (sign assumed) coupling between the methylene protons is much too large for geminal protons in a three-membered ring[9] and rules out norcaradiene-like structures. The angle-strainless boat conformation V, analogous to the conformation of cycloheptatriene (homobenzene) favored in the vapor state,[10] is excluded since J_{34} = 7.9 Hz, far larger than the value of 0-1 Hz expected for V.[11] The similarity of vicinal coupling constants J_{12}, J_{23}, J_{34}, and J_{45} suggests a similar degree of twist about the corresponding carbon-carbon bonds around the ring. Since these values are all slightly below the value anticipated for a structure with C1-C8 coplanar,[12] it is likely that C1-C8 are not coplanar, but instead some twist is present about each of the bonds in the ring.

The proton-decoupled ^{13}C nmr spectrum of I shows peaks at δ 105.7, 97.9, 67.6, and 66.6, i.e., four of the five peaks expected with a symmetry plane perpendicular to the ring. The first two of these peaks are due to carbons 2, 4, 5, and 7, and the last (triplet in off-resonance spectrum and smaller than the other three) to carbon 9. The missing peak is probably obscured by the THF peak at δ 66.1.

Our failure to observe pmr peaks for the monoanion IV during the metalation of III to I contrasts with the metalation behavior of related acyclic alkenes[13] and is probably due partly to the instability of intermediate monoanion IV (angle strain in form with maximum π overlap) and partly to the stabilizing effect of developing homoaromaticity on the transition state between IV and I.

Since electron exchange between I and the anion-radical with one fewer electron is sufficiently rapid to cause broadening of the ESR lines of the latter species, it has been proposed that these species possess similar geometry.[14] To the extent that this is true, the evidence described herein for the shape of I applies to the anion-radical as well.

Acknowledgment. We thank the National Science Foundation for financial support (Grants GU-1534 and GP-21115).

References and Notes

(1) Presented in part at the First Fall Organic Conference, American Chemical Society, North Falmouth, Mass., Sept 30, 1973.

(2) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4731 (1966).

(3) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971).

(4) R. B. Bates, S. Brenner, and B. I. Mayall, *J. Am. Chem. Soc.*, **94**, 4765 (1972).

(5) We are indebted to W. H. Okamura for informing us of these deuteration results prior to publication.

(6) L. A. Paquette has kindly sent a preprint of a manuscript which describes the reductive preparation of the dipotassium salts of 9-methyl-I and 9,9-dimethyl-I in ND_3; these substances have very similar ^1H nmr parameters and thus presumably similar geometry. It was not possible to observe I itself in this way as it abstracted deuterium too rapidly from ammonia to give IV-*8-d*.

(7) S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 3437 (1973).

(8) Cf. G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963).

(9) A. A. Bothner-By, *Adv. Magn. Reson.*, **1**, 195 (1965).

(10) M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(11) The dihedral angle down the 3,4 bond was estimated from a Dreiding model of V to be 82°. The small positive value observed for the 4-bond coupling J_{35} also helps to rule out V (M. Barfield and B. Chakrabarti, *J. Am. Chem. Soc.*, **91**, 4346 (1969), and references therein).

(12) In the eight-membered ring of the planar benzocyclooctateraene dianion, the vicinal couplings average 11.2 Hz (A. Shyoukh, Ph.D. Dissertation, Universität zu Köln, 1972; we are grateful to a referee for calling this observation to our attention); slightly larger values might be expected in I with C1–C8 coplanar due to the larger ring size.

(13) R. B. Bates, W. A. Beavers, M. G. Greene, and J. H. Klein, *J. Am. Chem. Soc.*, **96**, 5640 (1974).

(14) F. J. Smentowski, R. M. Owens, and B. D. Faubion, *J. Am. Chem. Soc.*, **90**, 1537 (1968).

M. Barfield, R. B. Bates,* W. A. Beavers, I. R. Blacksberg
S. Brenner, B. I. Mayall, C. S. McCulloch
Department of Chemistry, University of Arizona
Tucson, Arizona 85721
Received March 14, 1974

Pyrolysis of 1-Phenyl-1,3-butadienes. A New Synthesis of 1,2-Dihydronaphthalenes

Sir:

The synthesis of specifically substituted dihydronapthalenes remains a challenge since there is no general simple procedure. Reduction of naphthalene by lithium or sodium in liquid ammonia yields a 1,4-dihydronaphthalene,[1-3] which can be isomerized by strong base to the thermodynamically more stable 1,2-dihydro isomer.[4,5] While this simple sequence is applicable to substituted naphthalenes, the choice of which ring undergoes reduction is determined by the position and type of substituent.[2] Substituents in the 1-position direct reduction to the adjacent ring if electron releasing and to the same ring if electron withdrawing. Thus 1-methylnaphthalene is reduced to the corresponding 1-methyl-5,8-dihydronaphthalene.[2] Clearly, other 1-methyldihydronaphthalene isomers are not accessible by this route. Several less direct but more specific synthetic routes exist. Addition of an appropriate Grignard or organolithium reagent to 1-tetralone followed by dehydration of the alcohol constitutes a general route to 1-substituted 3,4-dihydronaphthalenes,[6,7] while cyclization of 4-substituted 4-phenylbutyric acids by treatment with polyphosphoric acid yields 4-substituted 1-tetralones which can be reduced to the alcohol and dehydrated to 1-substituted 1,2-dihydronaphthalenes.[8-10] However, synthesis of 4-substituted 4-phenylbutyric acids needed for this procedure often involves several steps.

We should like to report a new synthetic route to substituted 1,2-dihydronaphthalenes based on gas phase pyrolysis under controlled conditions of the appropriate 1-phenyl-1,3-butadiene. Thus pyrolysis of *trans*-1-phenyl-1,3-butadiene[11] at 450° yields 1,2-dihydronaphthalene[12] in 81% yield. The other products isolated are *cis*-1-phenyl-1,3-butadiene (11%)[13,14] and naphthalene (6%). Yields reported are based on recovered starting material, 30%. The pyrolysis conditions are quite critical since pyrolysis of *trans*-1-phenyl-1,3-butadiene under more vigorous conditions (550°) yields naphthalene,[15,16] while pyrolysis of *trans,trans*-1,4-diphenyl-1,3-butadiene[17] under similar vigorous conditions yields 1-phenylnaphthalene as the major product.[18]

The formation of 1,2-dihydronaphthalene from *trans*-1-phenyl-1,3-butadiene can be rationalized by a three-step reaction sequence. The first step is an isomerization of *trans*-1-phenyl-1,3-butadiene to *cis*-1-phenyl-1,3-butadiene.[13,14] The second is an electrocyclic reaction converting a conjugated triene into a 1,3-cyclohexadiene in a thermally allowed disrotatory fashion.[19-22] The triene undergoing this reaction is composed of the two double bonds of the 1,3-butadiene and one double bond of the benzene ring. Clearly, this electrocyclic reaction involves disruption of the 6π electron system of the benzene ring. The high energy of activation required for the reaction probably reflects the loss of resonance energy in the transition state. A comparison between *trans,cis,trans*-octa-2,4,6-triene which is converted to *cis*-5,6-dimethylcyclohexa-1,3-diene at 130°[22] and *trans*-1-phenyl-1,3-butadiene which does not yield 1,2-dihydronapthalene till 400° may reflect this loss of aromatic stabilization. A related example of participation of a double bond of a benzene ring in an electrocyclic reaction is the pyrolysis of 1,2-dipropenyl benzene to yield 2,3-dimethyl-1,2-dihydronaphthalene.[23] The photochemical conversion of stilbenes to phenanthrenes under oxidizing conditions similarly involves participation of double bonds from two benzene rings in an electrocyclic reaction.[24-26] The final step in our reaction sequence would be a symmetry allowed 1,5-suprafacial sigmatropic hydrogen migration leading to restoration of the aromatic nucleus.[27]