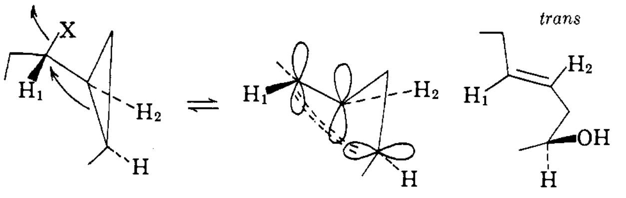
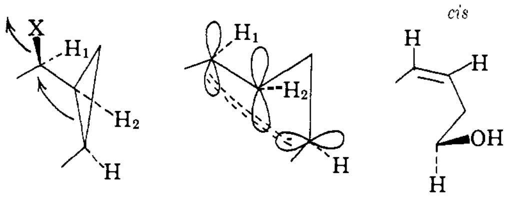
from the *syn* starting material, a *trans* from the *anti*. These stereochemical features are just those to be expected from reactions proceeding by way of homoallylic ions[2d] formed by the anchimerically assisted ionization of the cyclopropylcarbinyl derivative which involves mainly participation by the C_β–C_γ secondary–secondary cyclopropane bonding electrons. This is shown in the sequence XVI → XVII → XVIII for an *anti* derivative and XIX → XX → XXI for a *syn* epimer.[13] For the C_β–C_γ bond of the cyclopropane ring of *anti*-XVI to participate in the ionization, rotation about the C_α–C_β bond must occur so as to place H_1 and H_2 in a *trans* relationship in the ion XVII and in the expanded product XVIII. Conversely, a *cis* relationship of H_1 and H_2 is expected in ionization of *syn*-XIX. One additional stereochemical feature is predicted on the basis of the usual stereoelectronic considerations, namely, inversion of configuration at C_γ. While the cyclopropylcarbinyl compounds described above were insufficiently labeled to test this point, this stereochemical question is dealt with in the following communication.[14]



XVI XVII XVIII



XIX XX XXI

The present stereochemical results differ considerably from those observed with smaller ring systems. Thus, with I–III where $n = 5, 6,$ or 7, recollection of configuration at C_α of the cyclopropyl carbinol II tends to be largely or completely lost and only a *cis* olefinic group seems to be formed in the ring-expanded III.[2a-c] Until more ring systems are investigated it is not clear which ones can be expected to yield the stereospecific results described.

[13] Homoallylic ions XVII and XX are employed for simplicity, but "symmetrical homoallyl" or "bisected" type ions[2d] could account for the facts if delocalization of the C_β–C_γ cyclopropane electrons is much more important than C_β–C_δ in the transition states.

[14] D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6384 (1967).

M. Gašić, D. Whalen, Brian Johnson, S. Winstein
Contribution No. 2171, Department of Chemistry
University of California, Los Angeles, California 90024

Received October 12, 1967

Single and Double Homoallylic Ring Expansions[1]

Sir:

In the preceding communication[2] we reported solvolyses and homoallylic ring expansions of several cyclopropylcarbinyl derivatives which proceeded with retention of configuration at C_α and stereospecific formation of either a *cis* or a *trans* olefinic group depending on the epimer employed for the homoallylic ring expansion. We now report so-called single and double homoallylic ring expansions of the trismethylene adducts of *cis,cis,cis*-2,4,7-cyclononatrienol which show the same stereochemical features but, in addition, demonstrate the inversion of configuration at C_γ expected from a homoallylic intermediate.

Addition of excess zinc–methylene iodide reagent to 2,4,7-cyclononatrienol (I) yielded two bis adducts,[3] bis-A (II), mp 72–73°, and bis-B (III), mp 92–93°, and two tris adducts, tris-A (IV), mp 117–119°, and tris-B (V). Relative to the hydroxyl group, the *anti* disposition of cyclopropane ring 1 in II–V is clear from the previous work. The *syn* disposition of cyclopropane ring 3 in II and IV and the *anti* disposition in III and V is clear from the fact that the bis-A and tris-A adducts are also produced by the Simmons–Smith reaction on alcohol VI,[4] mp 45–46°, λ_{max} 218 mμ (ϵ 17,800, 95% EtOH), with a *syn* relationship of the cyclopropane ring and OH group. The *trans* relationship of cyclopropane rings 1 and 2 in the tris adducts is clear from the chemical behavior of IV and V (see below).

Solvolysis of IV-OPNB, mp 131–132°, in 80% aqueous acetone or treatment of IV with 0.04 *N* $HClO_4$ in 80% aqueous dioxane (Table I) gave rise cleanly to monoexpanded VII, mp 65.5–67.5°, ν_{max} 963 cm^{-1} (CS_2), with a *trans* olefinic group.[5] Less than 1% of the epimer of VII could be detected. The liquid epimeric alcohol was prepared by oxidation of VII to the ketone followed by $LiAlH_4$ reduction (>99% stereospecific). Extended treatment of VII with 0.04 *N* $HClO_4$ in 80% dioxane yielded a mixture containing *ca.* 70% of bis-expanded alcohol VIII, mp 61–62°, with two *trans*

Table I. Sovolysis and Isomerization Rate Constants

System	ROPNB, 80% acetone[a] Temp, °C	 10^5k, sec^{-1}	ROH, 80% dioxane, 0.025 *N* $HClO_4$, 75.0° 10^4k, sec^{-1}
IV[b]	75.0	2.54 ± 0.05	*Ca.* 85[c]
VII	75.0	0.264 ± 0.007	
IX[d]	75.0	0.717 ± 0.005	1.59 ± 0.1
X	75.0	0.845 ± 0.014	*Ca.* 9
XI	75.0	0.120 ± 0.002	2.69 ± 0.33
XV	100.0	2.53 ± 0.05	*Ca.* 1
XVI	100.0	2.15 ± 0.06	*Ca.* 1.1

[a] Some ion-pair return usually detected. [b] 8% VII-OPNB isolated. [c] 0.041 *N* $HClO_4$. [d] 13% XI-OPNB isolated.

---

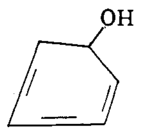
[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) research supported in part by the National Science Foundation.

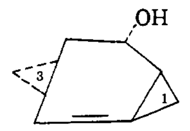
[2] M. Gašić, D. Whalen, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6382 (1967).

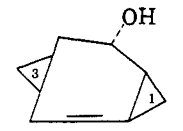
[3] All new compounds gave satisfactory elemental analyses and displayed appropriate nmr and infrared spectra.

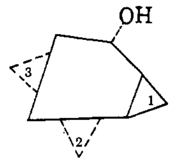
[4] Alcohol VI was obtained by KOBu-*t*–DMSO treatment of the monoepoxide prepared from the crownlike monomethylene adduct of 1,4,7-cyclononatriene.

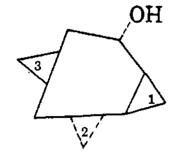
[5] With olefinic systems containing cyclopropane rings, we usually observed additional medium absorptions in the 960–990-cm^{-1} region, obscuring somewhat the diagnosis for a *trans* olefinic group based on a strong 965-cm^{-1} band.[2] In some of these cases the corresponding ketones showed only weak absorption in the 960–990-cm^{-1} region. Additional help in assigning olefinic configurations was obtained from vinyl coupling constants and the various chemical interrelationships.

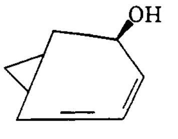

I

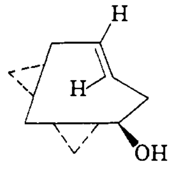

II

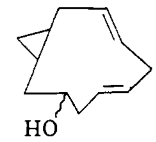

III

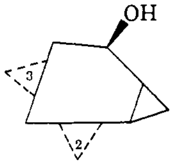

IV

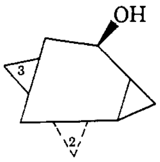

V

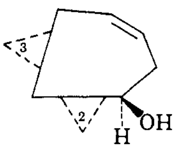

VI

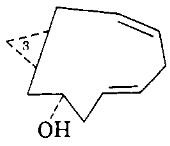

VII

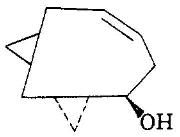

VIII

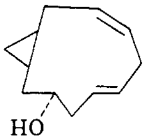

IX

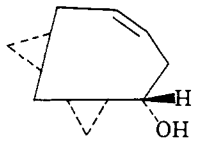

X

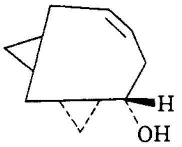

XI

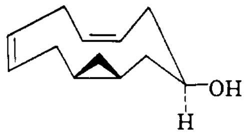

XII

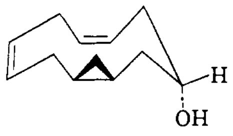

XIII


XIV


XV


XVI


XVII


XVIII

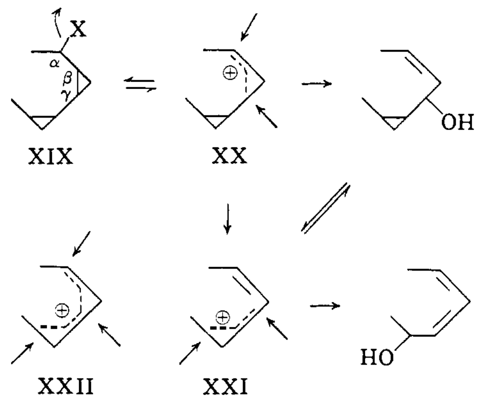
olefinic groups (strong 965-cm^{-1} absorption, 700-cm^{-1} absorption absent[6]).

Oxidation of IV and V to the ketones, mp 44–45° and 49–51°, respectively, with CrO_3 in moist ether, followed by $LiAlH_4$ reduction, led to the epimers of IV and V, namely IX and X, mp 60–62°, mp of IX-OPNB 150–152°, mp of X-OPNB 139–140°.

Solvolysis of IX-OPNB in buffered 80% aqueous acetone gave rise to a 75:25 mixture of mono-expanded XI,[7] mp 58–60°, with a *cis* olefinic group, and bis-expanded XII, mp 56–58°, with one *cis* and one *trans* olefinic group. Acid treatment of IX gave rise cleanly to bis-expanded XII. Analogously, solvolysis of X-OPNB gave rise to a 75:25 mixture of mono-expanded XIII[7] and bis-expanded XIV, mp 82–84°, respectively, while acid treatment of X led quite cleanly to bis-expanded XIV. Each mono-expanded product was free of its epimer (<2%), and this was also true of the bis-expanded products (<1% epimer). Solvolysis of XI-OPNB, mp 120–122°, gave rise to a 50:50 mixture of XI and XII, each one free of its epimer.

The epimers of XI and XIII, XV,[7] mp 77–78°, and XVI,[7] respectively, were prepared by oxidation to XI-ketone, mp 39–42°, and XIII-ketone, mp 75–76°, followed by $LiAlH_4$ reduction (*ca.* 96% stereospecific). Acid-catalyzed expansion of XVI proceeded smoothly to yield a single alcohol, XVIII,[8] free from its epimer (<5%) and possessing both olefinic groups *cis* (ν_{max} 700 cm^{-1}, CS_2). Solvolysis of XVI-OPNB, mp 125°, led to a 75:25 mixture of XVIII and XVI, each one free of its epimer. While acid-catalyzed expansion of XV yielded a mixture containing not only XVII[8] but also a rearranged trienol and an unidentified component, the desired expanded XVII was free of epimer XVIII.

The various transformations described above illustrate the three kinds of stereospecificity which could conceivably arise in reactions of cyclopropylcarbinyl derivatives, namely, retention of configuration of C_α and stereospecific formation of a *cis* or a *trans* olefinic group with inversion of configuration at C_γ in the production of the homoallylic ring-expanded product.[2] These results are all explicable on the basis of nonclassical homoallylic ions such as XX. Indeed, the stereoelectronic principles involved were extremely helpful in guiding us in the development of this most convenient synthetic route to such unusual molecules as *cis,cis,cis*-3,6,9-cycloundecatrienol described in the previous communication[2] and its monomethylene adducts XVII and XVIII described above. Such molecules, with prescribed stereochemistry and spacing of hydroxyl, olefinic, and cyclopropane groups, would be extremely difficult to synthesize by more conventional methods.



XIX XX XXII XXI

It is worth commenting on the formation of bis-expanded products XII and XIV from solvolysis of IX-OPNB and X-OPNB or acid-catalyzed isomerization of IX and X. While some of the bis-expanded products arise from successive reaction of mono-expanded alcohols XI and XIII or XI-OPNB and XIII-OPNB from ion-pair return, the indications are that at least some of the formation of bis-expanded products is more direct. While this situation is being studied further, it seems as though some leakage from an initial homo-

---

[6] *trans* vinyl coupling constants of 16.0 and 16.5 cps, respectively, were obtained in decoupling experiments.

[7] The hydroxyl group stereochemistry was assigned *anti* to the adjacent cyclopropane group in XI and XIII and *syn* in XV and XVI on the basis of infrared and nmr data, as well as the stereochemistry of reduction of the corresponding ketones.

[8] XVII and XVIII were oxidized to the same ketone.

allylic ion, *e.g.*, XX, to a second such ion involving the second cyclopropane ring, *e.g.*, XXI, occurs competitively with solvent attack on the first homoallylic ion. Perhaps a bishomopentadienyl[9] ion such as XXII needs to be considered.

Acknowledgment. We are indebted to Dr. Arthur Diaz for assistance in connection with some of the solvolysis kinetics. We are grateful to Drs. G. Hummel and F. Ebel of the Badische Anilin and Soda Fabrikwerke in Ludwigshafen, Germany, for generous supplies of the necessary cyclooctatetraene starting material.

(9) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, 2, 423 (1963).

Dale Whalen, M. Gašić, Brian Johnson, H. Jones, S. Winstein
Contribution No. 2172, Department of Chemistry
University of California, Los Angeles, California 90024

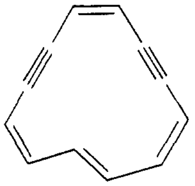
Received October 12, 1967

5-Bromo-1,9-bisdehydro[12]annulene. A Verification of an Induced Paramagnetic Ring Current in a $4n$ π-Electron System

Sir:

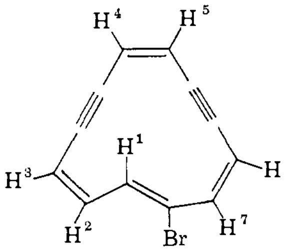
Recently we presented a theory[1,2] and some evidence that conjugated cyclic $4n$ π-electron systems display an induced paramagnetic ring current in a magnetic field, *i.e.*, a ring current opposite in sign from the familiar induced diamagnetic ring current associated with aromatic or $4n + 2$ π-electron systems. Since our report, more evidence has been uncovered which lends additional support to this generalized description. The nmr spectra of [16]-,[3] 1,9-bisdehydro[16]-,[4] 1,11-bisdehydro[20]-,[4] and [24]annulenes[5] have now been studied at lower temperatures (where valence and/or conformational interconversions have been slowed or stopped) and found to be qualitatively as expected from the generalized explanation, *i.e.*, inner hydrogens shifted upfield, outer hydrogens downfield for $4n + 2$ π-electron systems; inner hydrogens downfield, and outer hydrogens upfield for $4n$ π-electron systems.

A compound synthesized by Wolovsky and Sondheimer,[6] 1,5-bisdehydro[12]annulene (I), is a particularly interesting $4n$ π-electron system in regard to induced paramagnetic ring currents because of the unusually low value of the chemical shift (τ scale) observed for the two hydrogens of the *trans* double bond. We have suggested[1] that the nmr signal of these two hydrogens at τ -0.9 is the result of an averaging process caused by interconversion between two equivalent *planar* conformers. The nmr spectrum of I has been found to be temperature dependent and the absorption of the *trans* double bond hydrogens is broadened and shifted downfield by *ca.* 0.4 ppm at $-80°$.[4] Unfortunately, spectra taken at still lower temperatures, wherein the noninterconverting conformer might be observed, are not yet available.

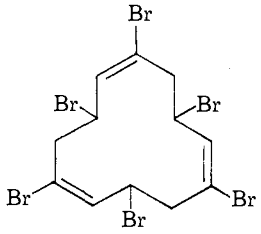


I

We wish to report here the synthesis of a molecule, 5-bromo-1,9-bisdehydro[12]annulene (II), that strikingly verifies the expectations for chemical shifts of hydrogens of $4n$ π-electron systems based on the idea of an induced paramagnetic ring current. The oily isomeric mixture of 1,3,5,7,9,11-hexabromo-*cis,cis,cis*-1,5,9-cyclododecatriene (III) resulting from the bromination (NBS) of 1,5,9-tribromo-*cis,cis,cis*-1,5,9-cyclododecatriene (IV), after chromatography (SiO_2, hexane–CCl_4), was separated; the crystalline isomer V, mp 185°, was obtained in *ca.* 15% yield; the oily isomer in *ca.* 60%.[7] The oily hexabromocyclododecatriene with 4 equiv of sodium ethoxide in ethanol (18 hr, room temperature) gave II (17% yield after silicic acid column chromatography) as a reddish brown oil. Mass measurement of the *two* isotopic parent molecular ions dictates the molecular formula for II; calcd for $C_{12}H_7Br$: 229.9732, 231.9712; found: 229.9743, 231.9732. The infrared spectrum of II (liquid film) exhibited absorptions at 3.28 (m), olefinic CH; 4.62 (w), triple bond; 6.24 (m), conjugated double bond; 7.72 (s), *cis* olefinic CH; 12.06 (s), trisubstituted olefinic CH; and 13.37 (vs) μ, disubstituted *cis* double bond.[8] Twelve absorptions correspond very closely to those reported[6b] in the infrared spectrum of I. The ultraviolet spectrum of II is very similar to that of I.[6b] It has absorptions at 244 mμ (sh) (ϵ 33,000), 251 (35,000), 290 (sh) (1150), and 466 (200).[9] The nmr spectrum (Figure 1) provides the added data necessary for the structural assignment of II and reveals the unique absorption of the inner hydrogen of this cyclic $4n$ π-electron system. The spectrum is partially interpretable by first-order analysis. The low-field absorption due to H^1 (area 1) is a doublet ($J_{12} \simeq 9.4$ cps) with additional splittings; H^2 (area 1) is an apparent triplet; H^3 (area 1) is seen as a doublet ($J_{23} \simeq 10.2$ cps, typical for *cis* olefinic hydrogens) with additional splittings; H^4, H^5 (area 2) and



II



III

---

(1) J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 88, 4811 (1966).

(2) Essentially the same theoretical conclusions have been independently reached by H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109, and by F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(3) G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

(4) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75 (privately communicated by F. Sondheimer).

(5) I. C. Calder and F. Sondheimer, *Chem. Commun.*, 904 (1966).

(6) (a) F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); (b) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965).

(7) K. G. Untch and D. C. Wysocki, *ibid.*, **88**, 2608 (1966).

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(9) The ϵ values may be low since the sample used was not a crystalline compound.