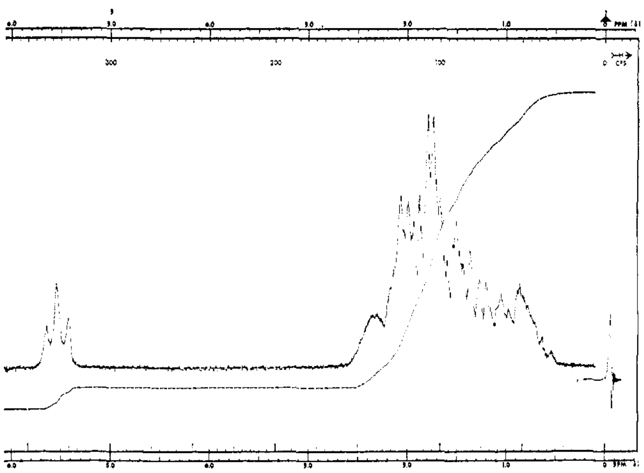
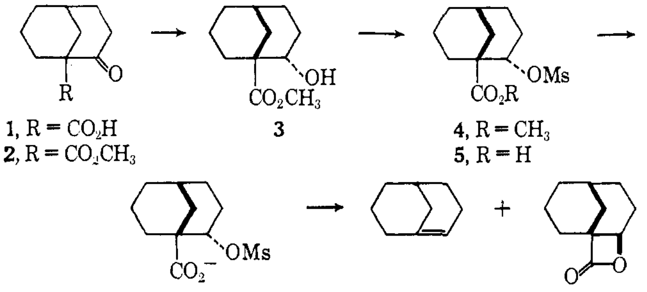


Figure 1. The 60-MHz nmr spectrum of bicyclo[3.3.1]non-1-ene (neat sample relative to external tetramethylsilane).

pounds, thus placing the practical limit for Bredt's rule at $S = 7$ instead of $S = 9$.[3] We have indeed found this to be the case and now report a synthesis of the most flagrant violator of Bredt's rule known to date, bicyclo[3.3.1]non-1-ene (**7**).

Keto ester **2** [mp 70–70.5°, λ_{max}^{KBr} 5.75 (ester CO), 5.87 (ketone CO), 8.02, 8.34, and 9.28 μ] upon hydrogenation over platinum afforded the hydroxy ester **3** [mp 39–39.5°; λ_{max}^{film} 2.90 (OH), 5.78 (ester CO), 8.00, 9.00, 9.27, 9.48, 10.27, 11.40, 12.80, and 14.5 μ; $\delta_{TMS}^{CCl_4}$ 3.95 (H-2, X of ABX, $J_{AX} + J_{BX} = 16$ Hz), 3.65 (CH_3O), 3.17 ppm (OH)]. The same hydroxy ester was obtained *via* reduction of keto ester **2** with sodium borohydride. The *endo* orientation of the hydroxyl grouping is assigned from the nmr spectrum and by analogy with the reduction of bicyclo[3.3.1]nonan-2-one (**1**, R = H) to the *endo* alcohol.[7] The mesylate derivative **4** [λ_{max}^{film} 5.78 (ester CO), 8.49, 9.29, 9.45, 10.29, 10.82, 11.33, 11.56, and 11.95 μ; $\delta_{TMS}^{CCl_4}$ 5.1 (H-2, X of ABX, $J_{AX} + J_{BX} = 17$ Hz), 3.66 (CH_3O), and 2.88 ppm (CH_3SO_3)] of hydroxy ester **3** afforded the acid **5** [mp 115°; λ_{max}^{KBr} 3.0–3.8 (OH), 5.90 (CO), 8.13, 8.49, 10.6–10.8, 11.29, 11.53, 11.98, 12.70, 13.00, 13.38, 13.58, and 14.70 μ; $\delta_{TMS}^{CDCl_3}$ 12.0 (OH), 5.42 (H-2, X of ABX, $J_{AX} + J_{BX} = 18$ Hz), and 3.12 ppm (CH_3SO_3)] upon saponification with alcoholic potassium hydroxide followed by acidification. The acid **5** was treated with a 0.07 *M* solution of dimethylsulfinylsodium in dimethyl sulfoxide[8] containing slightly less than 1 molar equiv of the base. The mixture was stirred at 60° for 30 hr whereupon the evolution of carbon dioxide essentially ceased and, after an additional 8 hr, the neutral material was isolated by extraction with pentane–ether and chromatography on silica gel. The material eluted with pentane was distilled affording bicyclo[3.3.1]non-1-ene [15% yield, bp 60° (bath temperature) at 5 mm, λ_{max}^{film} 3.33 (vinyl C–H), 6.15 (C=C), 8.09, 8.21, 9.06, 9.72, 9.83, 10.03, 10.30, 10.42, 11.57, 12.01, 12.32 (vinyl C–H bend), 12.60, and 14.00 μ]. The structure of this olefin is supported by its mass spectrum ($P = 122$), its nmr spectrum (Figure 1), and its rapid and nearly quantitative hydrogenation over platinum to bicyclo[3.3.1]nonane, identified by comparison with an authentic specimen.[9] Continued elution of the aforementioned chromatographic column and sublimation of the ether–pentane fractions afforded the β-lactone **8** [30% yield; mp 109–111°; λ_{max}^{KBr} 5.50 (CO), 8.38, 8.79, 9.45, 10.83, 11.36, and 11.89 μ; $\delta_{max}^{CCl_4}$ 4.22 ppm (H-2, X of ABX, $J_{AX} + J_{BX} = 16$ Hz)].



1, $R = CO_2H$

2, $R = CO_2CH_3$

3

4, $R = CH_3$

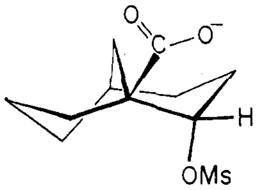
5, R = H

6

7

8

Models reveal that the chair–chair form of the carboxylate mesylate precursor **6** of olefin **7** and β-lactone **8** cannot attain the preferred orientation for concerted β fragmentation[10] (leading to olefin **7**) or internal displacement (leading to β-lactone **8**). However, with both rings in twist-boat conformations, these groupings can adopt a nearly *anti*-periplanar orientation as illustrated in **6a**. This conformation appears to best meet the stereoelectronic requirements of the reactions leading to the observed products. We plan to examine the chemistry of these products in the near future.



6a

Acknowledgment. We thank the Hoffmann-LaRoche Foundation for an unrestricted research grant and the National Science Foundation for a research grant (GP-4174) in support of this work. Support from the Public Health Service (to H. F.) is also gratefully acknowledged. We are indebted to Dr. J. A. Roth for the mass spectral data.

---

[7] *Cf.* J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, 32, 1372 (1967).

[8] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

[9] We are grateful to Professor R. L. Burwell, Jr., and Dr. J. A. Roth for providing this sample.

[10] C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, 6, 1 (1967).

[11] (a) Fellow of the Alfred P. Sloan Foundation. (b) Public Health Service Fellow of the National Institute of General Medical Sciences.

James A. Marshall,[11a] Hermann Faubl[11b]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received September 14, 1967

Bredt's Rule. Bicyclo[3.3.1]non-1-ene

Sir:

In the early part of this century Bredt formulated his familiar rule in a series of papers published over a period of more than 20 years.[1,2] Bredt's rule may be

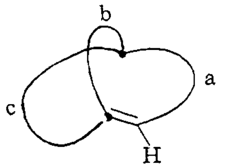
---

[1] J. Bredt, H. Thouet, and J. Schmitz, *Ann.*, 437, 1 (1924), and references therein.

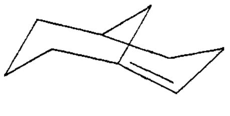
[2] For reviews and discussions see (a) F. S. Fawcett, *Chem. Rev.*, 47, 219 (1950); (b) V. Prelog, *J. Chem. Soc.*, 420 (1950); (c) R. C. Fort, Jr., and P. von R. Schleyer in "Advances in Alicyclic Chemistry," Vol. I,

stated in qualitative terms: a double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without excessive strain. The strain results from torsional forces on the double bond which tend to twist the p_z orbitals of the doubly bonded carbon atoms away from the parallel condition required for maximum overlap. Many examples of β-keto acids which do not decarboxylate, alcohols which do not dehydrate, and ketones which do not exchange their α-hydrogen atoms substantiate the rule, and it is frequently invoked in structural and mechanistic discussions of bridged ring systems.

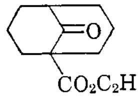
The most serious attempt at definition of the limits of Bredt's rule has been made by Fawcett,[2a] who proposed that the sum of the number of atoms in the bridges of a bicyclic system (S number) determines whether that system can accommodate a bridgehead double bond. Fawcett made the tentative generalization that compounds with bridgehead double bonds should be isolable for $S \geqq 9$, and that transient intermediates with bridgehead double bonds should be possible for $S \geqq 7$. We propose the use of a more fundamental criterion which will allow one to discern easily whether a double bond can be placed at the bridgehead of a bicyclic system, as well as which branches of the system can contain such a double bond.



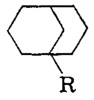
1



2



3



4, R = $CO_2C_2H_5$
5, R = CO_2H
6, R = NH_2
7, R = $N(CH_3)_2$
8, R = $N^+(CH_3)_3I^-$
9, R = $N^+(CH_3)_3OH^-$

Structure **1** represents a generalized bicyclic system with a double bond in branch a terminating at the bridgehead. The three branches of the ring system comprise three rings (ab, ac, and bc). The double bond is exocyclic to ring bc, but it is endocyclic in rings ac and ab. Since the double bond is at the branching point of the two rings, it must be substituted *cis* in one of the rings and *trans* in the other. In structure **1** the double bond is *trans* in ring ac. We believe the strain of bridgehead double bonds is closely related to the strain of *trans*-cycloalkenes. *trans*-Cyclooctene has been known for many years as an unstable but isolable compound,[3] and *trans*-cycloheptene has been prepared only as a transient reactive species.[4] A similar relationship exists for *trans*-2-cyclooctenone[5] and *trans*-2-cycloheptenone.[6] By analogy, a bicyclic bridgehead alkene should be isolable when the larger of the two rings containing the double bond contains at least eight atoms, and certain bicyclic bridgehead alkenes possibly may be preparable with double bonds contained in seven-membered rings. Similarly, transient intermediates with bridgehead double bonds should be possible when the larger ring containing the double bond is seven membered. Decarboxylation studies of bicyclic β-keto acids provide qualitative support for this argument.[2,7–9]

A β-keto acid which has its carboxylate function at the bridgehead of a bicyclic system is believed to decarboxylate through a bridgehead enol.[10] The size of the larger of the two rings containing the enol determines the ease of decarboxylation of the keto acid. Acids which lead to enols contained in rings larger than eight atoms lose carbon dioxide readily.[2a,b] When the larger ring containing the enol is eight membered, temperatures in the neighborhood of 150° are required.[7] β-Keto acids which lead to enols contained in seven-membered rings decarboxylate at temperatures between 200 and 320°,[8,9] and keto acids which require enols contained in rings no larger than six atoms generally fail to decarboxylate, or decarboxylate with rearrangement.[2a,11–13]

Since there are no known bridgehead alkenes in which both rings containing the double bond are smaller than nine atoms,[14] we decided to test the above postulate concerning isolable compounds by attempting the synthesis of bicyclo[3.3.1]non-1-ene (**2**). The synthesis was accomplished with standard synthetic reactions starting with 1-ethoxycarbonylbicyclo[3.3.1]nonan-9-one (**3**).[16] The keto function of **3** was reduced by conversion to the ethylene dithioketal followed by reduction with Raney nickel. The ester **4**, obtained in 96% yield, was quantitatively hydrolyzed to the corresponding acid **5**, mp 98–99°, which was transformed by the Curtius procedure to the bridgehead amine **6**, mp 119–120°, in 74% yield. The primary amine **6** was methylated by the Clark–Eschweiler technique to give the tertiary amine **7** in 95%, yield, and treatment of the tertiary amine **7** with methyl iodide produced the quaternary salt **8**, mp 259–262°, in 98% yield. The quaternary iodide **8** was converted to the hydroxide **9** by treatment with silver oxide.

Pyrolysis of the quaternary ammonium hydroxide **9** at 140° produced the bridgehead alkene **2** in good yield (40% after purification by glpc). Also produced in the reaction was the tertiary amine **7** (*ca.* 5%), but no

---

H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, pp 364–370; (d) H. H. Wasserman in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 351–354; (e) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 298–302.

(3) K. Ziegler and H. Wilms, *Naturwissenschaften*, **34**, 157 (1948); *Ann.*, **567**, 1 (1950).

(4) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965).

(5) P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

(6) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2041 (1965); P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

(7) J. P. Ferris and N. C. Miller, *ibid.*, **85**, 1325 (1963).

(8) J. P. Ferris and N. C. Miller, *ibid.*, **88**, 3522 (1966).

(9) R. D. Sands, *J. Org. Chem.*, 29, 2488 (1964).

(10) F. H. Westheimer and W. A. Jones, *J. Am. Chem. Soc.*, **63**, 3283 (1941).

(11) S. Beckmann and O. S. Ling, *Ber.*, **94**, 1899 (1961).

(12) C. F. H. Allen, G. A. Reynolds, S. K. Webster, and J. L. R. Williams, *J. Org. Chem.*, 27, 1447 (1962).

(13) However, see P. C. Guha, *Ber.*, 72, 1359 (1939).

(14) Bicyclo[4.3.1]dec-1-ene[15] has its double bond in a nine-membered ring.

(15) Professor William G. Dauben, personal communication; F. T. Bond, Ph.D. Thesis, University of California, Berkeley, Calif., 1962.

(16) E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965).

other compounds with retention times comparable to the alkene were detected.

The structure of the alkene **2** rests on its spectra and chemical reactivity. The nmr spectrum shows a triplet at δ 5.68 (area 0.97) and a complex absorption at δ 0.8–2.8 (area 13.0), the infrared spectrum (CCl_4) shows significant peaks at 3050 and 1620 cm^{-1}, and the mass spectrum shows the molecular ion at m/e 122. The intensities of the isotopic peaks at m/e 123 and 124 (10.1 and 0.7%, respectively) correspond to those calculated for the formula C_9H_{14}. On standing in air **2** reacts with oxygen and polymerizes. Treatment of a solution of **2** in 80% aqueous acetone (6 ml) with one drop of 70% perchloric acid at room temperature produces a high yield of bicyclo[3.3.1]nonan-1-ol, identical with an authentic sample.[17] No other volatile products of this reaction could be detected by glpc. We are currently investigating the chemistry of this and other highly strained alkenes in our efforts to delineate the limits of Bredt's rule.[18,19]

---

(17) Kindly supplied by Professor William G. Dauben.

(18) This work was generously supported by grants from the Petroleum Research Fund and from the Faculty Research Fund of the Horace H. Rackham School of Graduate Studies of the University of Michigan.

(19) NOTE ADDED IN PROOF. Since submission of this paper Professor James A. Marshall has informed us that his research group has independently prepared bicyclo[3.3.1]non-1-ene (2) using a completely different synthetic approach. We thank Professor Marshall for his cooperation in communicating his results to us prior to publication.

John R. Wiseman
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104
Received August 31, 1967

Electron Transfer between Anion and Molecule of Hexahelicene

Sir:

Earlier measurements of electron-transfer rates between anions and neutral molecules of an optically active substance have revealed only a small difference in the transfer rates between like optical configurations and between enantiomers.[1] The optical activity in the case first reported, 1-(α-naphthyl)-1-phenylethane, originates in an asymmetric center at which the density of the transferring electron is small.

We now report measurements with hexahelicene, a molecule in which a large asymmetry exists in the π-electron system.[2,3] The measurements have been carried out in the fast exchange limit[4] for the potassium salt in tetrahydrofuran. At 23° the results are $k_{DD} = [(6.9 \pm 0.2) \times 10^8]\nabla\ M^{-1}\ sec^{-6}$ and $k_{DL} = [(1.7 \pm 0.2) \times 10^8]\nabla\ M^{-1}\ sec^{-1}$, where ∇ is the second moment. The ratio of rates obtained from the above data does not require measurement of the second moment. The measured second moment is 17.6 $gauss^2$. The absolute rates are then $k_{DD} = (1.2 \pm 0.3) \times 10^{10}\ M^{-1}\ sec^{-1}$ and $k_{DL} = (3.0 \pm 0.3) \times 10^9\ M^{-1}\ sec^{-1}$, where the errors include the uncertainties in the second moment.

It is possible that the difference is directly related to the asymmetry in the π-electron distribution. If the wave function for the transferring electron in the enantiomers is represented by

$$\psi^{\pm} = a\psi_S \pm b\psi_A$$

where ψ_S and ψ_A are the symmetric and antisymmetric parts with respect to inversion, the interactions between like and unlike enantiomers are given by

$$V_{++} = V_{--} = a^2V_{SS} + b^2V_{AA}$$
$$V_{+-} = V_{-+} = a^2V_{SS} - b^2V_{AA}$$

$V_{++} = V_{--}$ is the interaction energy between a radical ion and neutral molecule of the same optical configuration; V_{+-} is the corresponding quantity for an enantiomeric pair. V_{SS} is the interaction term between the symmetric parts of the functions in the two reacting molecules, and V_{AA} is the interaction between their antisymmetric parts.

The next step in our work is a search for the connection between the electronic behavior as revealed by optical rotations of the anions and the rate measurements.

Acknowledgment. We wish to thank Professor M. S. Newman, who generously supplied both the racemic and the optically active hexahelicene used in the experiments. The preparation of the hexahelicene was supported by the Petroleum Research Fund of the American Chemical Society. This work has been supported by the National Institutes of Health under Grant GM 13205 and by the National Science Foundation.

Raymond Chang, S. I. Weissman
Department of Chemistry, Washington University
St. Louis, Missouri 63130
Received August 28, 1967

---

(1) W. Bruning and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 373 (1966).

(2) (a) M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956); (b) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(3) The anions exhibit large rotations and Cotton effects in the visible region. The observation will be reported in another communication.

(4) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **46**, 2314 (1967).

Mechanisms of Photochemical Reactions in Solution. XLVII.[1] Cyclization of Compounds Containing Phenyl and Conjugated Dienyl Chromophores

Sir:

Molecules containing two unconjugated chromophoric units have been of considerable interest to spectroscopists.[2,3] Coupling between the groups leads to perturbation of both the energies and intensities of spectroscopic transitions compared to those of model systems in which the chromophores are isolated. Such coupling should also have significant implications for photochemistry. For example, cases are known in which the lowest lying excited singlet state is mainly localized in one part of a molecule and the lowest triplet in another, with weak coupling between the units providing an efficient path for energy transfer between the chromophores.[4] Internal energy transfer as a precursor to occurrence of photoreactions characteristic

---

(1) Part XLVI: H. Gotthardt, R. Steinmetz, and G. S. Hammond, *Chem. Commun.*, 480 (1967).

(2) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 437–449.

(3) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 7.

(4) P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963).