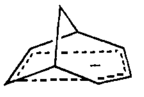
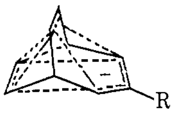
Reactions of the 3-Methylbicyclo[3.2.2]nonatrienyl Anion

Sir:

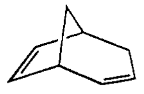
There has been much recent interest in the physical and chemical properties of mesomeric carbanions and, in particular, of carbanions which are stabilized by homoconjugation.[1-7] Several stable homoaromatic anions (including **1** and **2a**) have been directly observed by nmr spectroscopy[2-5] and evidence has been obtained by deuterium exchange experiments on **3** and **4** which demonstrates a large stabilizing effect in **1** due to homoconjugative interactions.[6] Molecular orbital symmetry arguments have been used which suggest that anion **2** should also have an enhanced stability (relative to an appropriate model);[7] the basis set of p orbitals of **2** is "Möbius"[8] or "anti-Hückel"[9] (*i.e.*, it has one inversion of phase) and therefore is aromatic when it contains $4n$ π electrons. We wish to report data which give an indication of the energetic effect of the delocalization in **2**.



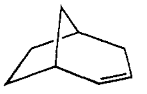
1



2a, R = H
b, R = CH_3

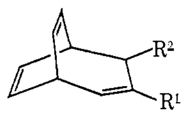


3

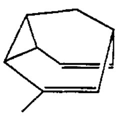


4

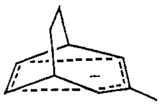
When 7-isopropenyl-1,3,5-cycloheptatriene[10] (7-*i*-PrCHT) ($\lambda_{\max}^{\text{hexane}}$ 257.5 mμ (ϵ 3140)) in N,N-dimethylacetamide (30%, w/w) was heated at reflux (*ca.* 167–168°) under nitrogen for 8.5 hr a 60–65% yield of a $C_{10}H_{12}$ fraction (bp 52–58° (5 mm)) was separated from a polymeric residue. This fraction was shown to consist of 1% unchanged 7-*i*-PrCHT, 52% 3-*i*-PrCHT ($\lambda_{\max}^{\text{hexane}}$ 225 mμ (ϵ 10,600) and 276.5 (9600)), 4% 2-*i*-PrCHT ($\lambda_{\max}^{\text{hexane}}$ 229 mμ (ϵ 19,000)), 16% 1-*i*-PrCHT ($\lambda_{\max}^{\text{hexane}}$ 222 mμ (ϵ 21,000), 227 (sh) (20,400), and 296 (7330)), and 26% 3-methylbicyclo[3.2.2]nona-2,6,8-triene (**5b**).[11,12] The latter isomer has a uv spectrum which shows only end absorption ($\epsilon_{220\,\text{m}\mu}^{\text{hexane}}$ 3400), and an nmr spectrum (CCl_4) which is similar to that reported[11b] for bicyclo[3.2.2]nona-2,6,8-triene (**5a**) with the main differences being that **5b** has an additional peak at τ 8.58 (singlet, 3 H, methyl) and no vinyl proton peak at 5.2, and that the C_4 methylene peak at 8.07 is a broad singlet (width at half-height = 7 Hz) instead of a quartet as in **5a**.



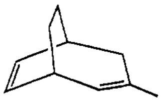
5a, $R^1 = R^2 = H$
b, $R^1 = CH_3$; $R^2 = H$
c, $R^1 = CH_3$; $R^2 = n\text{-}C_3H_7$



6



7



8

When various mixtures of **5b** in solutions of potassium or cesium amide in liquid ammonia were observed by nmr spectroscopy at 37°, the only spectrum obtained was that of the hydrocarbon. However, anion **2b** apparently is generated under these conditions since a 1:9 mixture of **5b** and 3-methyl-4-propylbicyclo[3.2.2]nona-2,6,8-triene (**5c**) was obtained when **5b** and 1-chloropropane were stirred for 15 min with potassium amide in liquid ammonia at *ca.* −33°. The major product was identified primarily on the basis of its molecular weight (molecular ion at *m/e* 174.133) and its nmr spectrum (CCl_4), which is similar to that for **5b** below τ 8.0 and, in addition, displays a multiplet at τ 8.0–8.4 (1 H, C_4 proton), a sharp multiplet centered at 8.58 (7 H, methylene and allylic methyl), and a distorted triplet at 9.04 (3 H, methyl).

Additional evidence for the formation of the anion of **5b** is provided by the fact that when a mixture of **5b** and potassium amide in liquid ammonia was warmed to 50° for 3 hr, a single isomer (molecular ion at *m/e* 132.093) was isolated as the only product.[13] This was identified as 3-methyltricyclo[3.3.1.0^{2,8}]nona-3,6-diene (methylbarbaralane) (**6**), primarily on the basis of its nmr spectrum (CCl_4), which is quite similar to that reported[14] for barbaralane with the exceptions that the downfield triplet (τ 5.52, vinyl) has a relative area of one and there is an additional peak (singlet, 3H, methyl) at 2.28. The observation of this rearrangement provides support for the suggestion that anion **2** undergoes deuterium scrambling *via* a barbaralyl intermediate.[4]

Evidence concerning the question of the stability of anion **2b** relative to an appropriate bishomoaromatic model[15] (*i.e.*, **7**) is provided by base-catalyzed deuterium-exchange experiments. Solutions of 0.1 *M* **5b** and **8**[16] were allowed to exchange in 1.00–1.03 *N* potassium *t*-butoxide in dimethyl-d_6 sulfoxide at 25° and the deuterium content was analyzed by low-voltage mass spectrometry. Appropriate corrections were made for the natural abundance of isotopes and for an M − 1

---

(1) S. Winstein, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5.

(2) (a) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4731 (1966); (b) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967).

(3) (a) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967); (b) J. M. Brown, *Chem. Commun.*, 638 (1967).

(4) J. B. Grutzner and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6562 (1968).

(5) W. A. Böll, *Tetrahedron Letters*, 5531 (1968).

(6) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); *J. Chem. Soc.*, *B*, 411 (1968).

(7) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967).

(8) H. E. Zimmerman, *ibid.*, **88**, 1564, 1566 (1966).

(9) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, Chapter 8.

(10) This was prepared by an extension of the method of A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(11) This thermal reorganization is analogous to several which have been reported: (a) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); (b) J. Daub and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, 7, 468 (1968).

(12) The nmr spectra provide the best evidence for the identification of the CHT isomers. All new compounds have been fully characterized by spectral methods.

(13) For a similar isomerization (in cesium cyclohexylamide–cyclohexylamine) see ref 1. Since anion **2** was generated in an aprotic medium (dimethoxyethane or diglyme)[4] it did not undergo protonation to form barbaralane. Interestingly, we did not observe this isomerization of **5b** in potassium *t*-butoxide–dimethyl sulfoxide (see footnote 19 and the discussion in ref 6).

(14) (a) U. Biethan, H. Klusacek, and H. Musso, *Angew. Chem. Intern. Ed. Engl.*, **6**, 176 (1967); (b) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(15) This comparison is concerned with the effect of the additional bridge which converts a bishomoaromatic ion into a bicycloaromatic ion.[4]

(16) H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc.*, *B*, 57 (1968).

peak in the mass spectrum of **5b**.[17] The empirical second-order rate constant for triene **5b** is $(1.05 \pm 0.2) \times 10^{-3}$ l. mole^{-1} sec^{-1} which is 7.5×10^{2} times greater than that determined for diene **8** $(1.40 \pm 0.1) \times 10^{-6}$ l. mol^{-1} sec^{-1}.[18] Samples of **5b** and **8** which had incorporated 2.8 and 0.6 atoms of deuterium, respectively, showed (by nmr spectroscopy) loss of hydrogen essentially only at C_2 and C_4.[19]

There are several factors which may contribute to the greatly enhanced rate of exchange of **5b** relative to **8**. These include the slight differences in the geometries of the two compounds and differences in the field and orbital electronegativity inductive effects for an ethano *vs.* an etheno bridge. Other work in these laboratories suggests that the first factor is probably quite small.[20] In addition, data in the literature suggest that a field effect is significant but probably not the major factor,[6,21] and that orbital electronegativity effects diminish rapidly with each intervening bond.[21b,c] We therefore believe that it is reasonable to attribute an important role to bicycloaromatic delocalization in explaining the present results.[22]

Acknowledgments. We are pleased to acknowledge the support of this work by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the National Science Foundation for a grant used for the purchase of a mass spectrometer.

---

[17] K. Biemann, "Mass Spectrometry. Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

[18] The second-order rate constants were calculated from the first-order constants by dividing by the base concentration. The latter constants were obtained from a least-squares fit of ln d_0 *vs.* *t*. The correlation coefficients were calculated to be 0.994 for triene **5b** and 0.999 for diene **8**.

[19] By this method of analysis not more than 0.05 of a deuterium atom per hydrogen atom could have been incorporated at other positions and not more than *ca.* 3% of diene **5b** could have been isomerized to methylbarbaralane.

[20] S. W. Staley and D. W. Reichard, to be published.

[21] (a) A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **87**, 5388 (1965); (b) A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *ibid.*, **90**, 1357 (1968); (c) relative rates for the solvent-base system used in ref 21a,b and for that used by us are generally, but not always, comparable; A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

[22] This is based upon the reasonable assumption that a linear free-energy relationship exists between the rates of exchange and thermodynamic acidities of **5b** and **8**.

Stuart W. Staley, Douglas W. Reichard
Department of Chemistry, University of Maryland
College Park, Maryland 20742

Received January 23, 1969

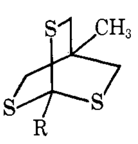
Intrinsically Anisochronous Nuclei in Propeller Molecules

Sir:

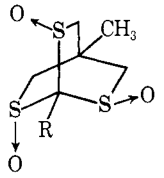
Geminal nuclei or groups of nuclei in molecules of the type RCG_2CXYZ are diastereotopic[1] and therefore anisochronous.[1] The time-averaged chemical shift difference is partly due to differences in conformer populations and partly due to an intrinsic effect.[2] The phenomenon is rather common and has been intensively investigated,[3] but very little is known about the relative importance of the two contributing terms. Unambiguous information exists only for the fluorine chemical shifts in the two molecules $BrCF_2CFBrCl$ and $BrCF_2CHBrCl$, for which the intrinsic terms could be calculated[4] from the chemical shifts of the individual frozen conformers at low temperature.[5] We wish to report the first direct measurements of time-averaged chemical shift differences that are exclusively due to intrinsic diastereotopism.

The basic idea was to construct model compounds of the general formula $RCG_2C(X^*)_3$, where X*'s are identical chiral substituents, all having the same configuration. In such "propeller" molecules the conformer populations are exactly equal by symmetry.[6]

When a solution of 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (**1a**)[7,8] in absolute tetrahydrofuran at −78° was treated with 1.1 moles of *n*-butyllithium and the lithium derivative **1b**[10] reacted with benzyl chloride, the substitution product **1c**[11] could be isolated in 84% yield. **1c** was independently synthesized by acid-catalyzed condensation of 1,1,1-trismercaptomethylethane with triethyl *o*-phenylacetate. Reaction of **1b** with acetone and hexafluoroacetone yielded **1d** and **1e**, respectively.



1



2

a, R = H
b, R = Li
c, R = $CH_2C_6H_5$
d, R = $C(CH_3)_2OH$
e, R = $C(CF_3)_2OH$

Treatment of slurries of **1a**, **c**, **d**, **e** in formic acid with 3 moles of hydrogen peroxide in formic acid at room temperature produced mixtures of at least three compounds in each case. They were separated by chromatography and fractional crystallizations.[12] Relevant nmr data of the components of interest in the present context (**2**)[13] are collected in Table I. The AA′A″-

---

[1] For notation see K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 1.

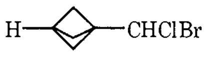
[2] H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

[3] For reviews, see M. L. Martin and G. J. Martin, *Bull. Soc. Chim. France*, 2117 (1966); M. van Gorkom and G. E. Hall, *Quart. Rev.* (London), **22**, 14 (1968).

[4] M. Raban, *Tetrahedron Letters*, 3105 (1966).

[5] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **39**, 3131 (1963); **43**, 602 (1965).

[6] As pointed out by Mislow and Raban in their review article,[1] the hypothetical molecule 3 would, in principle, also be suitable for a demonstration of intrinsic diastereotopism. Comparison of **2** and **3** reveals the necessary condition for this phenomenon. A molecule must contain two structural moieties of such a nature that, when joined together by a single bond, there exists the possibility of threefold degenerate rotation about this bond. One of the moieties must be chiral by itself and the other must contain two groups of sensor nuclei that are enantiotopic in the absence of the chiral moiety. We wish to thank Professor Mislow for an illuminating discussion on this point.



3

[7] W. von E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, **77**, 509 (1955).

[8] The literature procedure[7] proved to be unsatisfactory for the preparation of large quantities of **1a**. An alternative and superior method involves reaction of 1,1,1-tristosyloxymethylethane with sodium trithiocarbonate[9] in DMF-water followed by acid hydrolysis. Details of this procedure will be reported in the full paper.

[9] D. J. Martin and C. C. Greco, *J. Org. Chem.*, **33**, 1275 (1968).

[10] D. Seebach, *Angew. Chem.*, **79**, 468 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 442 (1967).

[11] Satisfactory elemental analyses and molecular weights were obtained for all new compounds.

[12] Details of these experiments and structure proofs for all new compounds will be published elsewhere.

[13] Compound **2a** has also been obtained by D. Jung (Institute of Technology, Darmstadt, Germany). We wish to thank Dr. Jung for informing us of his results prior to publication.