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

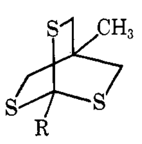
Intrinsically Anisochronous Nuclei in Propeller Molecules

Sir:

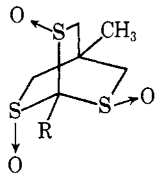
Geminal nuclei or groups of nuclei in molecules of the type RCG_2CXYZ are diastereotopic[1] and therefore anisochronous.[1] The time-averaged chemical shift difference is partly due to differences in conformer populations and partly due to an intrinsic effect.[2] The phenomenon is rather common and has 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.

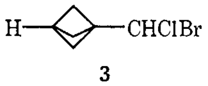
[2] H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

[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.

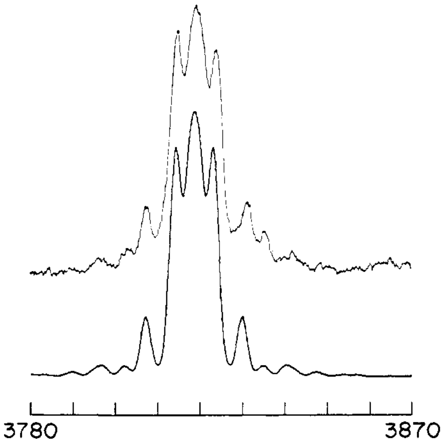


Figure 1. (a) Upper trace: fluorine nmr spectrum of **2e** at 56.4 MHz. (b) Lower trace: computed spectrum; the scale is in Hz upfield from internal $CFCl_3$.

BB′B′′ patterns of the ring-methylene protons in **2** unambiguously prove the desired propeller stereochemistry of the chiral sulfoxide groups.

Table I. Nmr Data for Compounds **2**

.Compd	$\delta_A{}^{a,b}$	$\delta_B{}^{a,b}$	J_{AB},[b] Hz	$J_{AB'}$,[b] Hz	Solvent
2a	3.77	2.81[c]	15.1	2.4	SO_2
2c	3.92	2.74	14.3	2.2	$CDCl_3$
2d	4.51	2.98	14.5	2.1	Pyridine
2e	4.44	3.24	14.1	1.7	CF_3COOH

[a] Ppm downfield from internal TMS. [b] AA′A′′BB′B′′ patterns; the computed spectra are independent of the relative signs of the coupling constants. [c] These protons show long-range coupling (J = 1.2 Hz) to the methine proton.

The detection of a small chemical shift difference of the intrinsically diastereotopic benzyl protons in **2c** was hampered by the low solubility of this compound in most solvents. No splitting of the signal at δ 4.40 ppm ($CDCl_3$) could be resolved in $CDCl_3$ or DMSO. The intrinsically diastereotopic methyl groups in **2d** show up as a doublet centered at 2.30 ppm (pyridine) with a solvent-dependent chemical shift difference; $\Delta\nu$ in Hz at 60 MHz: pyridine, 2.3;[14] DMSO, 1.2; D_2O, 0.4; $CDCl_3$, <0.2. At 56.4 MHz one observes a tightly coupled A_3B_3 pattern (Figure 1a) for **2e** in DMSO whose analysis (Figure 1b) yielded $\Delta\nu$ = 15.9 Hz and J_{AB} = 12.3 Hz.

The structure, solvent, and temperature dependence of the intrinsic anisochronism in an extended series of bicyclic and open-chain propeller molecules is presently being investigated.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The A-60A NMR instrument (and computer of average transients) used in this investigation were acquired under NSF Equipment Grant GP-6875.

---

[14] 3.56 Hz at 90 MHz. We are indebted to Professor J. B. Lambert and Mr. G. F. Jackson (Northwestern University) for the 90-MHz spectrum.

(15) Alfred P. Sloan Research Fellow.

(16) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-653.

Gerhard Binsch,[15] Gerald R. Franzen
Department of Chemistry and the Radiation Laboratory[16]
University of Notre Dame, Notre Dame, Indiana 46556
Received March 5, 1969

The Photoisomerization of 9-Thiabicyclo[3.3.1]non-6-en-2-one

Sir:

Past investigations of thioketones have shown that the ultraviolet characteristics of these compounds are substantially different from those of other saturated ketones.[1–5] This difference has been attributed to transannular interaction of a lone pair of electrons on sulfur with the carbonyl group, the coupling being strongly dependent on the orientation of the two groups.[6] Such interactions result both in the perturbation of the n–π^* carbonyl frequency and in the appearance of a charge-transfer absorption band in the 240–270-mμ region. Of the various effects which can be ascribed to the S–C_{CO} interaction, that which involves structural reorganization of the molecule in the excited state continues to attract widespread interest.[7] It was our intent to investigate systems in which these interactions lead to novel photochemical changes. In this communication we wish to report on a representative example involving the photochemistry of an unsaturated β-keto sulfide.

For reasons of synthetic accessibility and for its spectroscopic characteristics, 9-thiabicyclo[3.3.1]non-6-en-2-one (II) was chosen as the model substrate. 9-Thiabicyclo[3.3.1]-6-nonen-2-ol (I) was prepared by the transannular addition of sulfur dichloride to 1,5-cyclooctadiene[8,9] followed by thermal dehydrochlorination and aqueous solvolysis.[10] Sarett oxidation of I afforded 9-thiabicyclo[3.3.1]non-6-en-2-one (II) in good yield; mp 80–81°; λ_{max} (KBr) 5.82 μ; $\lambda\lambda_{max}$ (95% ethanol) 240 and 295 mμ (ϵ 290 and 275); nmr τ 7.54, 6.65, 3.86, ratio 6:2:2. *Anal.* Calcd for $C_8H_{10}SO$: C, 62.39; H, 6.54; S, 20.82. Found: C, 62.13; H, 6.50; S, 20.51.

The initial experiments were carried out in a nitrogen atmosphere using an internal water-cooled mercury

---

(1) N. J. Leonard, T. L. Brown, and T. W. Milligan, *J. Am. Chem. Soc.*, **81**, 504 (1959).

(2) N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).

(3) G. Bergson and A. L. Delin, *Arkiv Kemi*, **18**, 489 (1961).

(4) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).

(5) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(6) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(7) P. Y. Johnson and G. A. Berchtold, *ibid.*, **89**, 2761 (1967); W. C. Lumma and G. A. Berchtold; *ibid.*, **89**, 2761 (1967); K. K. Maheshwari and G. A. Berchtold, *Chem. Commun.*, 13 (1969); A. Schonberg, A. K. Fateen, and S. M. Omran, *J. Am. Chem. Soc.*, **78**, 1224 (1956); H. Hogeveen and P. J. Smit, *Rec. Trav. Chim.*, **85**, 489 (1966); R. B. LaCount and C. E. Griffin, *Tetrahedron Letters*, 1549 (1964); J. R. Collier and J. Hill, *Chem. Commun.*, 702 (1968).

(8) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).

(9) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).

(10) All new compounds were properly characterized and acceptable chemical analyses were obtained.