Acknowledgment. This work was supported by the National Science Foundation. Spectra were obtained in the NMR Facility for Biomedical Research (National Institutes of Health Grant No. FR-00292).

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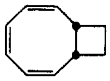
trans,cis,cis,trans-1,3,5,7-Cyclodecatetraene–*trans*-Bicyclo[6.2.0]deca-2,4,6-triene, a Rapidly Interconverting Möbius Tautomeric System

Sir:

Insights derived from "orbital symmetry" considerations[1] have brought about widespread acceptance of the idea that most low-energy thermal reactions occur *via* "aromatic" activated complexes.[2] One of the more intriguing aspects of the general problem of aromaticity is concerned with the consequences of delocalization through a "Möbius" array of orbitals.[1b,3,4] We now report the observation of a rapidly interconverting "Möbius"[1b] tautomeric pair of hydrocarbons.

When *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)[5] (0.2% (v/v) in pentane) was irradiated in quartz with a low-pressure mercury lamp, a single component (**a**) was formed as the primary product. The uv spectrum of **a** showed $\lambda_{\max}^{\text{hexane}}$ 291 nm (ϵ 3480) and elemental analysis indicated a $C_{10}H_{12}$ composition.

Of particular interest is the nmr spectrum (60 MHz), which consists of two complex multiplets at τ 3.7–5.2 and 6.7–8.6 at −76°. As the temperature is raised both multiplets are broadened and portions of each move toward the center of the spectrum. The coalescence temperature (T_c) is 48 ± 2° in carbon disulfide and 50 ± 2° in carbon tetrachloride. At 76° the spectrum consists of three multiplets at τ 3.9–4.7, 5.8–6.5, and 7.5–8.4 in the ratio 6:2:4. It is important to note that only two protons undergo site exchange in this process.



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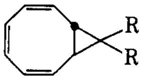
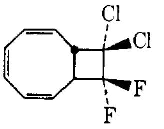
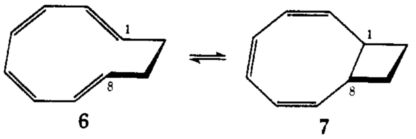


3a, R = H
b, R = CH_3

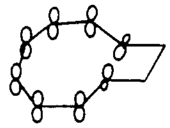


5

In view of the fact that *cis*-bicyclo[6.1.0]nona-2,4,6-triene[6] (**2a**) and its 9,9-dimethyl analog[7] **2b** and *cis*-9,9-dichloro-10,10-difluorobicyclo[6.2.0]deca-2,4-6-triene[8] (**4**) are initially converted to the corresponding trans isomers (**3a**, **3b**, and **5**) upon photolysis, we interpret the nmr temperature dependence of component **a** on the basis of a rapid and reversible valence tautomerism between the title compounds **6** and **7**. The coalesced two-proton peak at τ 6.18 in the 76° spectrum represents a weighted average of the signals for H-1 and H-8 in **6** (vinyl) and **7** (bridgehead).[9] Since the orbitals of the reacting bonds consitute a Möbius array and contain eight electrons, the activated complex **8** can be considered to be "aromatic."



6 7



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Strong support for the above interpretation is provided by the 220-MHz nmr spectrum[10] of **a** (in carbon disulfide) at *ca.* −25° which displays a "deceptively simple" triplet at τ 3.97 (H-4 and H-5 of **6**, line separation = 9 Hz), a complex multiplet at 4.2–4.5 (H(2)–H(7) of **7** and H-3 and H-6 of **6**), a doublet of doublets at 4.60 (H-2 and H-7 of **6**, J_{21} = 16.5 Hz, J_{23} = 8 Hz), a broadened doublet at 4.83 (H-1 and H-8 of **6**, J_{12} = 16.5 Hz), and multiplets at 7.16 (H-1 and H-8 of **7**), 7.46 (H-9 and H-10 of **6**), 7.93 (H-9 and H-10 of **6** and H-9 and H-10 of **7**), and 8.23 (H-9 and H-10 of **7**). The integrated area of each signal is consistent with the ratio of combined vinyl to combined nonvinyl protons (*vide infra*). In double resonance experiments we have shown that irradiation of the multiplet at τ 7.46 alters the signal at 4.83 and that irradiation of the latter causes collapse of the former into a broadened doublet (line separation = 7 Hz).

Chemical evidence for the above equilibrium is provided by the observation that component **a** was catalytically hydrogenated (in ethanol) to produce a mixture which contained 36% cyclodecane, 29% *cis*-cyclodecene, and 7% *trans*-bicyclo[6.2.0]decane. Each of these products was identified by comparison of its infrared spectrum with that of an authentic sample.[11] That cyclodecene and cyclodecane did not arise prin-

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[1] Reviews: (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970; (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapter 8.

[2] For an initial application of this idea to the Diels–Alder and related reactions see M. G. Evans, *Trans. Faraday Soc.*, **35**, 824 (1939).

[3] (a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); (b) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

[4] (a) J. B. Grutzner and S. Winstein, *ibid.*, **90**, 6562 (1968); (b) S. W. Staley and D. W. Reichard, *ibid.*, **91**, 3998 (1969).

[5] This was prepared in 52% yield and >99.5% purity by the dropwise addition of 0.1 mol of 1,2-dibromoethane in 20 ml of ether to the tan suspension generated by addition of 0.1 mol of freshly distilled cyclooctatetraene to 0.2 g-atom of lithium in 250 ml of liquid ammonia, followed by 4-hr stirring at *ca.* −33°, work-up, and distillation: bp 55° (4.6 mm); uv $\lambda_{\max}^{\text{hexane}}$ 250 nm (ϵ 2090); nmr (CCl_4) slightly broadened singlet at τ 4.25 (6 H, vinyl) and complex multiplets at 6.7–7.1 (2 H, bridgehead) and 7.5–8.4 (4 H, cyclobutyl).

[6] (a) E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Lett.*, 391 (1965); (b) G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 2179 (1968); (c) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

[7] S. W. Staley and T. J. Henry, unpublished results.

[8] T. Martini, Ph.D. Thesis, University of Karlsruhe, 1968 (in collaboration with G. Schröder).

[9] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter VII.

[10] We are most grateful to Dr. Lloyd Kaplan, Mr. A. Geigley, Dr. J. E. Hennessey, and Mrs. Valerie Robinson for assistance in obtaining 100- and 220-MHz nmr spectra.

[11] (a) *cis*-Cyclodecene and cyclodecane: A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952). (b) Authentic *trans*-bicyclo[6.2.0]decane was prepared from *cis*-9,10-dicarbomethoxy-*trans*-bicyclo[6.2.0]decane by saponification, electrolytic decarboxylation, and catalytic hydrogenation. We thank Dr. Jordan Bloomfield for a sample of the starting material.

cipally by hydrogenolysis of the strained C(1)–C(8) bond in **7** is shown by the fact that the even more strained **3a** was hydrogenated to yield *ca.* 90% *trans*-bicyclo[6.1.0]-nonane[12] under identical conditions.

From the area ratio (1.31 ± 0.03) of the vinyl and nonvinyl multiplets at −76 and 2.5°, an equilibrium constant (K_{eq}) of 1.48 ± 0.2 can be calculated for $\mathbf{6} \rightleftharpoons \mathbf{7}$. In addition, it can be calculated from the chemical shift of the coalesced peak (τ 6.18), and of those for H-1 and H-8 in **6** (4.83) and **7** (7.16), that $K_{eq} = 1.38 \pm 0.2$ at 76°.[9] It can be seen from the near constancy (*ca.* −0.2 kcal/mol) of the corresponding values of the Gibbs energy of isomerization (ΔG_{isom}) that ΔS_{isom} for this process is essentially zero, thereby indicating that tetraene **6** has a rigidity comparable to that of its bicyclic isomer (**7**). The nonequivalency of the two protons at C-9 (or C-10) in **6** (see nmr data) lends support to this conclusion.

One can also calculate (from T_c and the chemical shifts of H-1 and H-8 in **6** and **7** at −76°) that $\Delta G^{\ddagger}$ for either the forward or reverse reaction is *ca.* 15 kcal/mol at 48°.[9,13] This value agrees closely with $\Delta H^{\ddagger}$ for the cyclization of *trans,cis,cis,trans*-2,4,6,8-decatetraene to *trans*-7,8-dimethyl-1,3,5-cyclooctatriene, for which $\Delta S^{\ddagger} = -19$ eu,[14] and suggests that $\Delta S^{\ddagger}_{6\rightarrow7} \approx 0$; *i.e.*, the restriction of internal rotation in the ground and transition states is comparable. This is consistent with the conclusion that ΔS_{isom} is also *ca.* 0.

Although the ambient temperature nmr spectrum of $\mathbf{6} \rightleftharpoons \mathbf{7}$ can be reproduced after heating the sample to 76°, these isomers are transformed into *trans*-1,2-divinyl-1,3-cyclohexadiene (**9**)[15] on heating at 98° (0.15% (v/v) in refluxing heptane). This conversion, which has an approximate half-life of 1 hr, can be formulated as an "allowed" [3,3] sigmatropic (Cope) rearrangement of **6**.[16] Additional products, which apparently arise from **9**, are formed at higher temperatures or over longer periods of time.

Finally, it is of interest to note that a related compound, **5**, exists essentially completely in the bicyclic form.[7] Thus the effect of substituents appears to parallel that found for the 1,3,5-cyclooctatriene-bicyclo-[4.2.0]octa-2,4-diene equilibrium;[17] the same effects are presumably responsible for the similar behavior of these two systems.[18]

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[12] E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968).

[13] Strictly, this calculation requires that $K_{eq} = 1$; however, the deviation from 1 is small in the present case.

[14] R. Huisgen, A. Dahmen, and H. Huber, *Tetrahedron Lett.*, 1461 (1969).

[15] This structure assignment, which is consistent with ir and nmr spectral data and an elemental analysis, was confirmed by catalytic hydrogenation (4 mol equiv) to *trans*-1,2-diethylcyclohexane.[16a] We thank Professor C. A. Grob for a copy of the ir spectrum of the latter compound.

[16] For related rearrangements of *trans,trans*-1,5-cyclodecadiene and derivatives see (a) C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963); (b) T. G. Halsall and D. W. Theobald, *Quart. Rev., Chem. Soc.*, **16**, 101 (1962); (c) P. S. Wharton and R. A. Kretchmer, *J. Org. Chem.*, **33**, 4258 (1968); (d) E. N. Marvell and W. Whalley, *Tetrahedron Lett.*, 509 (1970); (e) A. J. Weinheimer, W. W. Youngblood, P. H. Washecheck, T. K. B. Karns, and L. S. Ciereszko, *ibid.*, 497 (1970), and references cited; (f) T. C. Jain, C. M. Banks, and J. E. McCloskey, *ibid.*, 841 (1970); (g) K. Takeda, I. Horibe, and H. Minato, *J. Chem. Soc. C*, 1142 (1970), and references cited.

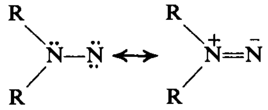
[17] R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *ibid.*, 5215 (1968).

[18] The complexity of this problem is illustrated by a recent study in which five different effects were used to rationalize the positions of seven related tautomeric equilibria: L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpass, *ibid.*, 1455 (1969).

O to N Migration in Reactions of O-Substituted Hydroxylamines[1]

Sir:

Nitrene intermediates stabilized by electron donation from adjacent atoms have been studied in detail only for the case of adjacent nitrogen.[2] These *N*-nitrenes (**1**, diazenes, azanitrenes) have been generated by a number of techniques including oxidation of 1,1-disubstituted hydrazines (eq 1) and base-catalyzed α elimination from *p*-toluenesulfonyl hydrazines (eq 2).



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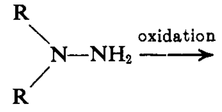
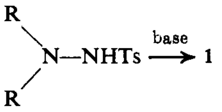


(1)



(2)

We have applied these methods to the generation of *O*-nitrenes (**2**, oxyazenes, oxynitrenes) and have observed several instances in which migration of the substituent from oxygen to nitrogen occurs.

$$\mathrm{R{-}O{-}\ddot{N}} \longleftrightarrow \mathrm{R{-}\overset{+}{O}{=}\overset{-}{N}}$$

2

O-Diphenylmethylhydroxylamine (**3**)[3] was converted to the corresponding *N*-*p*-toluenesulfonyl derivative **4**,[4] mp 182°, then to the lithium salt of **4** with 1.1 equiv of butyllithium and heated at 165° in triglyme for 18 hr to afford, after work-up, quantitative yields of benzophenone oxime (**5**) and *p*-toluenesulfinic acid.

$$\underset{\mathbf{4}}{\mathrm{Ph_2CHONHTs}} \xrightarrow{\mathrm{BuLi}} \mathrm{Ph_2CHO\overset{-}{N}Ts} \xrightarrow{165^\circ} \underset{\mathbf{5}}{\mathrm{Ph_2C{=}NOH}} + \mathrm{Ts^-}$$

Similarly, the sodium salt of **4** was prepared with sodium hydride in tetrahydrofuran, isolated, and pyrolyzed in triglyme to again yield **5** (57%). Com-

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[1] Research supported by a grant from the National Science Foundation (No. GP-9550).

[2] (a) C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969), and references cited therein; (b) D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964); (c) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

[3] E. L. Schumann, R. V. Heinzelman, M. E. Greig, and W. Veldkamp, *J. Med. Chem.*, **7**, 329 (1964).

[4] Satisfactory analyses (C, H, N, and S) and consonant ir and nmr spectra were obtained for all new compounds.