[1,5] carbon shifts can be described as processes involving specific coordination of the unsaturated propellane to molybdenum with suprafacial migration operating strictly under the control of the metal. Whether intermediates such as **2** undergo decomplexation to give **3** at rates competitive with ring opening remains an open question.

Lastly, we note that the conversion of **1** to **7** represents to this time a unique example of a metal catalyzed twofold circumambulatory rearrangement.[13]

Supplementary Material Available. The crystallographic data for **8** (fractional coordinates (Table I), bond distances (Table II), and bond angles (Table III)) and **9** (fractional coordinates (Table IV), bond distances (Table V), and bond angles (Table VI)) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3536.

References and Notes

(1) L. A. Paquette and J. M. Photis, *Tetrahedron Lett.*, 1145 (1975).

(2) L. A. Paquette, J. M. Photis, J. Fayos, and J. Clardy, *J. Am. Chem. Soc.*, **96**, 1217 (1974).

(3) J. M. Photis and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 4715 (1974); L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *ibid.*, **96**, 5801 (1974).

(4) L. A. Paquette, J. M. Photis, and G. D. Ewing, following paper in this issue.

(5) As before, the η^4 designation is utilized to simplify structural depiction. We do not rule out the possibility of alternative coordination levels involving also, for example, the cyclobutene double bond. This would, however, require the molybdenum carbonyl moiety to reside on the upper face of the tricyclic structure (as presently drawn). Nor do we have information on the question of relative metal–olefin stereochemistry at this stage of our investigation (see ref 2).

(6) (a) For kindred experimental findings, see W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); C. J. Attridge and S. J. Maddock, *J. Organomet. Chem.*, **26**, C65 (1971); H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 831 (1967); H. C. Volger and M. M. P. Gaasbeck, *ibid.*, **87**, 1291 (1968); (b) for a theoretical analysis, see F. D. Mango, *Fortschr. Chem. Forsch.*, **45**, 39 (1974), and references contained therein.

(7) This composition was ascertained by integration of several ^{1}H NMR spectra. Because of peak overlap, the level of accuracy must be regarded as ±10%.

(8) Partial decomposition of **7** is seen during this treatment.

(9) P. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **24**, 274 (1970).

(10) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL", USAEC Report IS-2625, Iowa State University–Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(11) D. R. James, G. H. Birnberg, and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 7465 (1974); R. E. Wingard, Jr., R. K. Russell, and L. A. Paquette, *ibid.*, **96**, 7474 (1974).

(12) Full spectral details will be given in a subsequent full paper.

(13) We thank the National Cancer Institute (Grant CA-12115), Chevron Research Co., and Atomic Energy Commission for financial support.

(14) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1972–1977; Alfred P. Sloan Foundation Fellow, 1973–1975.

Leo A. Paquette,* James M. Photis
Evans Chemistry Laboratories, The Ohio State University
Columbus, Ohio 43210

Kirsten B. Gifkins, Jon Clardy*[14]
Ames Laboratory-USAEC and Department of Chemistry
Iowa State University
Ames, Iowa 50010

Received January 10, 1975

1,2,3,4-Tetramethylcyclooctatetraene and 1,2,3,8-Tetramethylcyclooctatetraene. Stable [8]Annulene Bond Shift Isomers

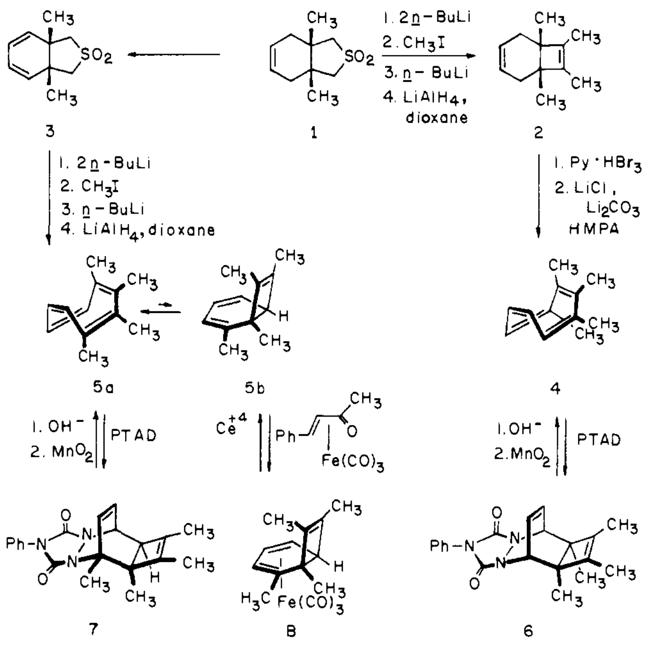
Sir:

The cyclooctatetraene (COT) ring system, recognized to possess alternate single and double bonds and a tub (D_{2d}) conformation,[1] can undergo three fundamental structural changes: ring inversion, bond shifting, and valence isomerization. The first of these requires a planar-alternate transition state and is least energy demanding ($\Delta G^\ddagger = 14.7$ kcal/mol for cyclooctatetraenedimethylcarbinol).[2] Bond shifting necessitates attainment of a planar form with equal bond lengths and has a somewhat higher energy barrier ($\Delta G^\ddagger = 17.1$ kcal/mol for cyclooctatetraenedimethylcarbinol).[2] Isomerization with formation of bicyclo[4.2.0]octa-2,4,7-triene has the most elevated transition state ($\Delta G^\ddagger = 28.1$ kcal/mol).[3] The first two processes are clearly related by virtue of requisite ring flattening.

The recent experimental findings by Ganis, et al.[4] of a significant increase in the free energy of activation for bond shifting in 1,3,5,7-tetramethylcyclooctatetraene ($\Delta G^\ddagger = 22.5$ kcal/mol at 120°) and supportive theoretical calculations by Allinger and his coworkers[5] leave little doubt that enhanced van der Waals interactions by substituents can seriously impede the attainment of planarity by the [8]annulene ring.[6] On this basis, we have entertained the possibility of preparing shelf stable bond shift isomers of COT, and have directed attention initially to the 1,2,3,4- and 1,2,3,8-tetramethyl derivatives where buttressing effects were expected to contribute additionally to maintenance of the individual tub conformations. Since these isomers should be recalcitrant to interconversion, it appeared equally desirable to develop independent synthetic approaches to the two polyolefins. We here report successful realization of these goals.

The reaction of sulfone **1**[7] with 2 equiv of *n*-butyllithium and excess methyl iodide, followed by lithium aluminum hydride reduction of the dimethylated α-sulfonyl carbanion gave **2** (34%)[8] (Scheme I). Subsequent bromination–dehydrobromination[9] transformed this diene into the corresponding bicyclo[4.2.0]octatriene, the ring opening of which to furnish exclusively **4** (98%) proceeds disrotatorily

Scheme I



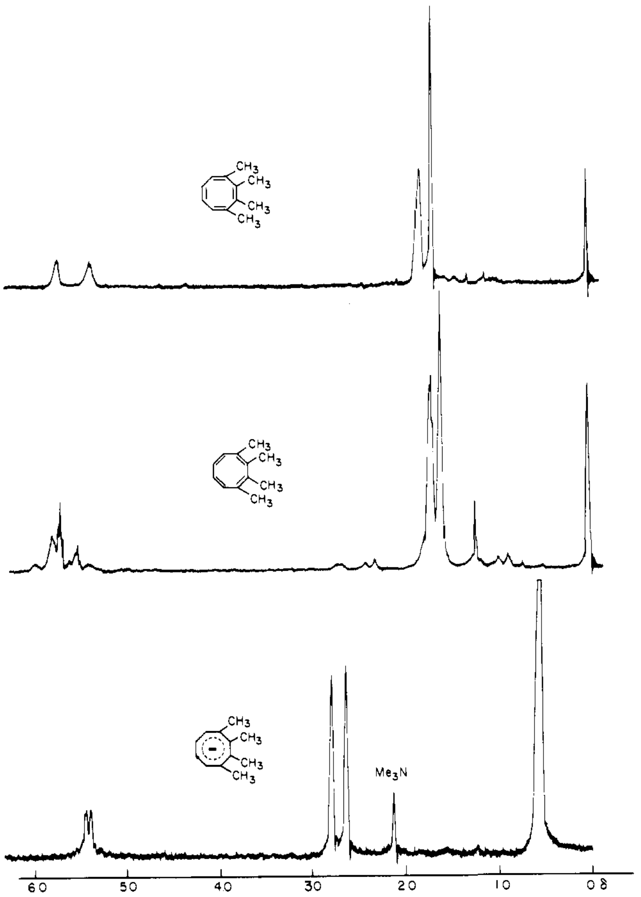


Figure 1. ^1H NMR spectra (60 MHz) of: (top) 1,2,3,8-tetramethylcyclooctatetraene (**4**) in $CDCl_3$; (middle) 1,2,3,4-tetramethylcyclooctatetraene (**5a** ⇄ **5b**) in $CDCl_3$; (bottom) dipotassio-1,2,3,4-tetramethylcyclooctatetraenide (**9**) in ND_3 at −55° (Me_3N present as internal standard, δ_{TMS} 2.135). The upfield peak in this spectrum is due to protiocontaminated solvent.

under control of the cyclohexadiene ring. The positioning of the double bond between the two central methyl groups is thereby not perturbed. In contrast, prior dehydrogenation of **1** to **3**[7] and analogous reductive desulfonylation[8] of this sulfone led to a mixture of **5** (70-80%) and **4**. Separation of the two COT isomers was conveniently effected by conversion to their *N*-phenyltriazolinedione (PTAD) adducts **6** (mp 175-176°) and **7** (mp 180-181°) which proved to be easily separable by fractional crystallization from ether-hexane. The symmetrical nature of **6** is revealed by the presence of only four sets of ^1H NMR signals (δ 6.17 (t, J = 3.5 Hz, 2), 4.54 (t, J = 3.5 Hz, 2), 1.38 (s, 6), and 1.22 (s, 6) in $CDCl_3$) in addition to the aryl multiplet. The features of the spectrum of **7** (in $CDCl_3$) reflect replacement of one bridgehead hydrogen by methyl and the presence of an allylic cyclobutene proton (δ 7.2-7.55 (m, 5), 6.08 (d, J = 3.5 Hz, 2), 4.98 (dd, J = 3.5 and 4 Hz, 1), 2.61 (br d, J = 4 Hz, 1), 1.80 (s, 3), 1.48 (s, 6), and 1.34 (s, 3)). The conversion of **3** principally to **5** may proceed by valence isomerism in that bicyclo[4.2.0]octa-2,4-diene intermediate, which is produced upon C-C bond formation and ensuing preferential ejection of the sulfur residue by 1,8- rather than 1,2-elimination. Whatever the precise mechanistic details, the two central methyl groups are now not attached to the same π bond.

Hydrolysis-oxidation[10] of adducts **6** and **7** returned the individual colorless tetramethylcyclooctatetraenes **4** and **5**, respectively. The C_s symmetry of **4** follows convincingly from its ^1H NMR (Figure 1) and ^{13}C NMR spectra (17.16, 22.12, 122.96, 130.51, 132.46, 144.86 ppm from TMS). Not only are the pairs of olefinic protons differentially shifted but the 3- and 8-methyl groups appear expectedly as a broadened singlet due to allylic coupling with the neighboring ring hydrogens. In contrast to **4** which is homogeneous within the limits of spectroscopic analysis, its bond shift isomer is seen to consist of a mixture of valence tautomers in which **5a** predominates over **5b** by ca. threefold. Although the identical composition was seen in three independent preparations of **5**,[11] convincing proof of the true position of equilibrium was still lacking. This ambiguity was removed upon reaction of **5** with 1.1 mol equiv of benzylideneacetoneiron tricarbonyl[12] in benzene at 60° for 2 days.[13] These conditions led in 79% yield to η^4 complex **8** (assumed stereochemistry; ^1H NMR ($CDCl_3$) δ 5.1-5.4 (m, 2), 2.9-3.2 (m, 1), 2.15-2.4 (br d, 1) 1.52 (s, 3), 1.42 (s, 6), and 1.26 (s, 3)), which when oxidized with ceric ammonium nitrate in acetone (−30°) returned the identical mixture. The presence in **5a** of a twofold symmetry axis is borne out by its ^{13}C NMR spectral features (17.75, 18.45, 116.97, 122.12, 127.28, and 137.20 ppm).[14]

Polarographic reduction of **4** and **5** provided a quantitative measure of the difficulty experienced by these [8]annulenes in attaining a planar conformation. In anhydrous hexamethylphosphoramide, the respective $E_{1/2}$ values are seen at −3.7 and −3.6 V vs. SCE, virtually at the onset of discharge by solvent.[15] The slightly better reducibility of **5** may arise from enthalpy differences which favor **4** by an estimated 1.0 kcal.[16] Despite the high level of strain, **4** and **5** have been successfully reduced to the identical dianion (**9**) with potassium in ND_3. The ^1H NMR spectrum of this species (Figure 1) accords fully with those of the various dimethylated derivatives[17] and serves as the basis for assignment of the planar (or effectively planar), symmetrical delocalized structure. Oxidation of this species with iodine in pentane[18] returned a mixture of **4** and **5**.

In attempts to effect bond shift isomerization in **4**, gas phase experiments were conducted up to 430° (contact time 1-3 sec).[19] No evidence was gained for the formation of **5**. By way of contrast, thermal activation of **5** at 350° resulted in low level conversion to **4**. In the temperature range of 405-475°, the proportion of **4** increased regularly with added heat input. Interconversion can also be achieved photochemically[6b] in quartz with 2537 Å light; *o*-xylene is produced concomitantly.[20]

We conclude that the activation energies for ring inversion and bond shifting in **4** and **5**, although sizable, are nevertheless attainable under certain conditions. [8]Annulenes substituted in this manner should consequently be resolvable into stable enantiomers and may perhaps be convertible into stable (heretofore elusive[21]) trans isomers. Such research is being continued.[22]

References and Notes

(1) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952); W. B. Person, G. C. Pimentel, and K. S. Pitzer, *J. Am. Chem. Soc.*, **74**, 3437 (1952); M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966); G. Avitabile, P. Ganis, and V. Petraccone, *J. Phys. Chem.*, **73**, 2378 (1969); J. Bordner, R. G. Parker, and R. H. Stanford, Jr., *Acta Crystallogr., Sect. B*, **28**, 1069 (1972).

(2) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964).

(3) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, **19**, 3 (1965).

(4) P. Ganis, A. Musco, and P. A. Temussi, *J. Phys. Chem.*, **73**, 3201 (1969).

(5) N. L. Allinger, J. T. Sprague, and C. J. Finder, *Tetrahedron*, **29**, 2519 (1973).

(6) (a) F. A. L. Anet and B. Gregorovich, *Tetrahedron Lett.*, 5961 (1966); (b) F. A. L. Anet and L. A. Bock, *J. Am. Chem. Soc.*, **90**, 7130 (1968).

(7) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **95**, 2230 (1973).

(8) J. M. Photis and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 4715 (1974).

(9) L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *J. Am. Chem. Soc.*, **96**, 5801 (1974).

(10) D. R. James, G. H. Birnberg, and L. A. Paquette, *J. Am. Chem. Soc.*, **96**,

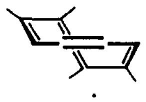
7465 (1974); R. E. Wingard, Jr., R. K. Russell, and L. A. Paquette, *ibid.*, **96**, 7474 (1974).

(11) J. M. Photis, unpublished results.

(12) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 330 (1972); G. Scholes, C. R. Graham, and M. Brookhart, *J. Am. Chem. Soc.*, **96**, 5665 (1974).

(13) Isomer **4** is much less reactive toward this reagent. Heating with 5 mol equiv of the ligand transfer reagent is required for formation of the 1,6,7,8-tetramethylbicyclo[4.2.0]octatriene·$Fe(CO)_3$ complex.

(14) Trans isomer i has the same C_2 symmetry as **5a** and might also be in equilibrium with bicyclic isomer **5b** as the result of a thermally allowed conrotatory butadiene–cyclobutene isomerization. The ^1H and ^{13}C NMR spectra, together with formation of adduct **7** and complex **8**, could therefore be construed as evidence for this species. While these data are most assuredly compatible with either **5a** or i, it is more difficult to reconcile reversible conversion to dianion **9** on the basis of the trans isomer. Also, the trans double bond in i should be highly reactive toward peracids. Yet, we find that treatment of the polyolefin with monoperphthalic acid affords exclusively the C_7,C_8 epoxide of **5b**, the likely (but not necessary) result of disrotatory closure of epoxy-**5a**. No evidence was found for oxygenation between the central methyl groups as expected for i.



i

(15) L. B. Anderson and D. Taggart, private communication.

(16) N. L. Allinger, private communication. The entropy difference between the two isomers is 0.

(17) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96**, 5806 (1974).

(18) S. W. Staley, G. M. Camer, and A. W. Orvedal, *J. Am. Chem. Soc.*, **96**, 7433 (1974). We thank Professor Staley for experimental directions in advance of publication.

(19) Compare L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **94**, 9224 (1972); L. A. Paquette and M. Oku, *ibid.*, **96**, 1219 (1972); L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *ibid.*, **96**, 5815 (1974).

(20) Compare the behavior of bicyclo[4.2.0]octatrienes: ref 9.

(21) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Am. Chem. Soc.*, **91**, 523 (1969).

(22) The financial support of the National Science Foundation, National Cancer Institute, and Eli Lilly Company is gratefully acknowledged.

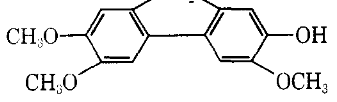
Leo A. Paquette,* James M. Photis, Gary D. Ewing
Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

Received January 10, 1975

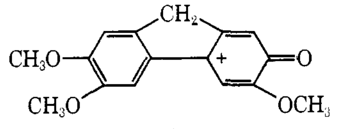
Effect of Forced Coplanarity of Biphenyl Rings on the Ease of Formation and Stability of Phenolic Cations

Sir:

The methylene bridge in the phenolic biphenyl (**1**) forces the two rings to be coplanar which has a profound effect upon the ease of oxidation and the stability of the resulting cations. Here we report the direct observation of the cation radical of **1** and the corresponding phenoxonium ion (**2**). The phenoxonium ion shows limited stability in acetonitrile while the cation radical is indefinitely stable in media containing trifluoroacetic acid (TFA).

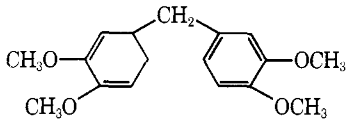


1

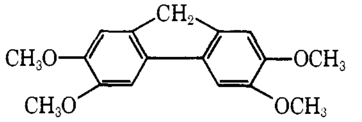


2

Anodic oxidation of the tetramethoxydiphenylmethane (**3**) in dichlormethane–TFA (3:1) containing the nucleophile scavenger, trifluoroacetic acid anhydride[1] (TFAn), proceeds in the normal manner[2] giving the bridged biphenyl (**4**) in high yield. However, in the presence of 1% H_2O, oxidation was accompanied by first cyclization to **4** and then anodic cleavage of the ether group[3] giving **1** in high yield. Neither the corresponding ethane nor the propane underwent demethylation under the latter conditions.[4] When **4** was subjected to the same electrolysis conditions, the yield of **1** was nearly quantitative.

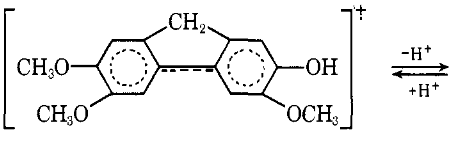


3

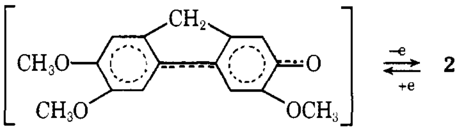


4

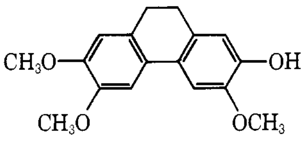
The cyclic voltammogram of **1** in acetonitrile consisted of a quasi-reversible 2e oxidation peak at +0.70 V[5] and the corresponding reduction peak at +0.66 V (voltage sweep rate 40 mV/sec). The peak separation increased with increasing voltage sweep rate indicating that the electron transfers are coupled with a chemical step, i.e., deprotonation of the initial cation radical (**5**) to **6** which is further oxidized to **2**. Voltammograms of **7** and **8** under identical conditions showed oxidation peaks at +0.85 and +1.01 V, respectively. The phenoxonium ion (**9a**) from the dimethylene bridge compound could be observed by cyclic voltammetry at slow sweep rates while **9b** was much less stable. The lifetime of **2** in acetonitrile was estimated to be an order of magnitude greater than **9a** under comparable conditions. In fact, two-electron oxidation of **1** in acetonitrile at room temperature gave a solution of **2** (~25% yield) which had a half-life of about 5 min.



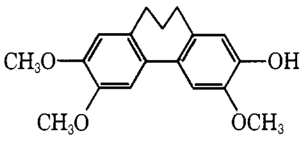
5



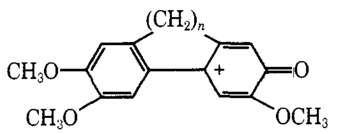
6



7



8



9a, $n = 2$
b, $n = 3$

The cyclic voltammogram of **1** in dichloromethane–TFA (3:1) is illustrated in Figure 1a. The voltammogram consists of two consecutive one-electron redox couples, the first