

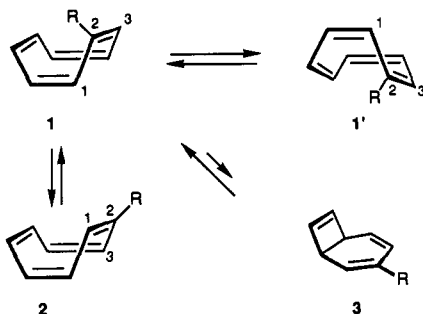
The Current View of Dynamic Change within Cyclooctatetraenes

LEO A. PAQUETTE

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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Not long after cyclooctatetraene (COT, 1, R = H) was convincingly shown to possess a D_{2d} ground-state conformation¹ was this polyolefin² recognized to be capable of *three* fundamental dynamic changes. Of these, ring inversion (RI, 1 \rightarrow 1') is clearly the least energy demanding since only carbon-carbon single bond rotations are necessary to interconvert 1 with 1'.³ When R is not a hydrogen atom, this equilibration generates a second tub conformer that is enantiomerically related to the first.⁴ A somewhat more deep-seated structural



modification is realized when the π -electrons "migrate" within the octagonal perimeter as in 1 \rightarrow 2.³⁻⁵ Bond shifting (BS) results in site exchange between the singly and doubly bonded carbon atoms. Valence isomerization with bicyclo[4.2.0]octa-2,4,7-trienes (3) is also possible. However, since ring closure in this fashion must overcome an energy barrier (ΔG^\ddagger) of 28.1 kcal/mol (when R = H),⁶ the equilibrium concentration of 3 is usually quite low (0.01% for COT at 100 °C).⁷ Such triene tautomers are often trapped in Diels-Alder reactions⁸ because COTs cannot offer dienophiles a 1,3-diene array sufficiently planar to be conducive to [4 + 2] cycloaddition.

The transition states associated with RI and BS have fascinated physical organic chemists for several decades.^{4,9} Little contested has been the original suggestion^{3a,5d} that ring inversion occurs by progressive flattening of the eight-membered ring until the so-called "planar alternate" arrangement 4 is reached. This maximum energy structure can presumably flex itself in either direction in order to return to the starting



conformer or move forward to the alternative tub form. Mechanistic interpretations of the bond-shifting process have proven far more controversial. The first proposal to be offered was the "planar delocalized" species 5 resulting from symmetrical C—C bond shortening and C=C bond lengthening.^{3a,5d} Should hypothetical transition states 4 and 5 both be involved, then an experimentally determined difference in free energies would constitute a direct measure of the resonance energy for a Hückel antiaromatic $4n$ system.¹⁰ Theoreticians have offered the greatest skepticism of this scenario. For example, Dewar has expressed the belief that the differences in ΔG^\ddagger between RI and BS (generally 2-4 kcal/mol) are much too low to be compatible with the energy gaps arrived at computationally.¹¹ The crown alternative advanced by him was later dismissed by Ermer,¹² who preferred a saddle-like

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

(2) Turner, R. B.; Meador, W. R.; Doering, W. von E.; Knox, L. H.; Mayer, J. R.; Wiley, D. W. *J. Am. Chem. Soc.* 1957, 79, 4127.

(3) (a) Anet, F. A. L. *J. Am. Chem. Soc.* 1962, 84, 671. (b) Oth, J. F. *M. Pure Appl. Chem.* 1971, 25, 573. (c) Luz, Z.; Meiboom, S. *J. Chem. Phys.* 1978, 59, 1077. (d) Naor, R.; Luz, Z. *J. Chem. Phys.* 1982, 76, 5662.

(4) Review: Paquette, L. A. *Tetrahedron* 1975, 31, 2855.

(5) (a) Gwynn, D. E.; Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* 1965, 87, 2862. (b) Oth, J. F. M.; Merenyi, R.; Martini, T. R.; Schröder, G. *Tetrahedron Lett.* 1966, 3087. (c) Buchanan, G. W. *Tetrahedron Lett.* 1972, 665. (d) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* 1964, 86, 3576. (e) Ganis, P.; Musco, A.; Temussi, P. A. *J. Phys. Chem.* 1969, 73, 3201.

(6) (a) Huisgen, R.; Meitzsch, F. *Angew. Chem.* 1964, 76, 36; *Angew. Chem., Int. Ed. Engl.* 1964, 3, 83. (b) Huisgen, R.; Meitzsch, F.; Boche, G.; Seidl, H. *Spec. Publ.—Chem. Soc.* 1965, 19, 3. (c) Vogel, E.; Keifer, H.; Roth, W. R. *Angew. Chem.* 1964, 76, 432; *Angew. Chem., Int. Ed. Engl.* 1964, 3, 442.

(7) Steric compression around the COT perimeter can cause the bicyclic triene tautomer to have the greater thermodynamic stability: (a) Criegee, R. *Angew. Chem.* 1962, 74, 703; *Angew. Chem., Int. Ed. Engl.* 1962, 1, 519. (b) Hanzawa, Y.; Paquette, L. A. *J. Am. Chem. Soc.* 1981, 103, 2269.

(8) See, for example: Paquette, L. A.; James, D. R.; Birnberg, G. H. *J. Am. Chem. Soc.* 1974, 96, 7454.

(9) (a) Schröder, G. *Cyclooctatetraene*; Verlag Chemie GmbH: Weinheim, 1965. (b) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: New York, 1978. (c) Paquette, L. A. In *Advances in Theoretically Interesting Molecules, Volume 2*; Thummel, R. P., Ed.; JAI Press Inc.: Greenwich, CT, 1992; pp 1-77.

(10) (a) Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* 1973, 29, 2519. (b) Wipff, G.; Wahlgren, U.; Kochanski, E.; Lehn, J. M. *Chem. Phys. Lett.* 1971, 11, 350. (c) Gardlik, J. M.; Paquette, L. A.; Gleiter, R. *J. Am. Chem. Soc.* 1979, 101, 1617.

(11) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* 1969, 91, 7521.

(12) Ermer, O.; Klärner, F.-G.; Wette, M. *J. Am. Chem. Soc.* 1986, 108, 4908.

Leo A. Paquette is a Distinguished University Professor at The Ohio State University, where he has been a faculty member since 1963. He received his Ph.D. in 1959 for research directed by Professor Norman A. Nelson at MIT, with added encouragement and scientific stimulation provided by George Büchi and Herb House. During 1959-1963, he served as a Research Associate at the Upjohn Company and had occasion to interact frequently with Professors Donald Cram, Melvin Newman, and Eugene van Tamelen, all of whom broadened his research interests. During the intervening years, his principal scientific activities have encompassed preparative and physical-organic chemistry, with a focus on the total synthesis of complex natural products and of molecules holding substantial theoretical significance.

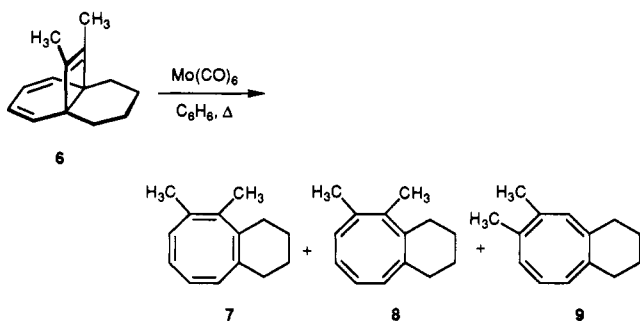
geometry because it best accommodated the associated potential energy surface. Very recently, Hrovat and Borden have insisted that only the D_{3h} geometry of **5** is compatible with sophisticated ab initio calculations.¹³

Thus, the transient existence of **5** has been the subject of ongoing controversy. Our interest in matters antiaromatic has led us to examine this particular phenomenon in considerable detail. In this Account, we address the correspondence between structural diversity and dynamic change in cyclooctatetraenes with a view to defining rather more precisely the mechanistic course of BS.

As in any problem of this type, transition-state structures are experimentally nonobservable because molecules spend the minimal amount of time in these arrangements. However, peripheral substituents appropriately selected to impact directly on ring dynamics were considered capable of providing kinetic profiles revealing of transition-state structure. Incremental alkyl/aryl substitution and bridging in the four possible ways across the COT nucleus with polymethylene chains of varying length were therefore investigated. Especially heavy reliance was placed on the acquisition and utilization of optically active substrates, although enantiomerically enriched COTs were virtually unknown at the outset of this study.¹⁴ Deuterium isotope labeling also proved to be an invaluable diagnostic tool.

The Consequences of Contiguous Peripheral Substitution

Positive encouragement came early during our examination of the $\text{Mo}(\text{CO})_6$ -promoted rearrangement of **6**.¹⁵ The pair of product hydrocarbons **7** and **8**, obtained



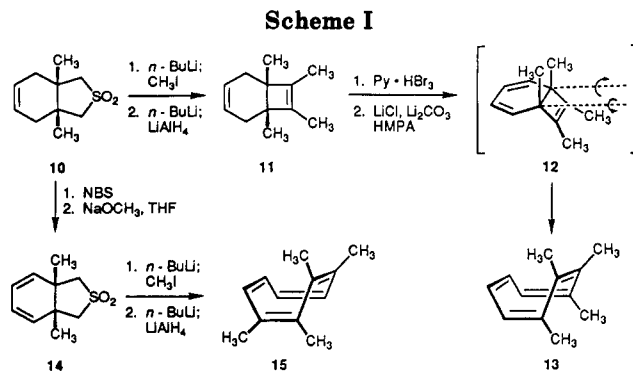
in equal amounts, were recognized to constitute the first shelf stable [8]annulene bond shift isomers. Their independent isolation and individually unique chemistry documented very convincingly that double-bond localization could be realistically achieved in COTs. Stated differently, steric and buttressing effects in combination can lead to the maintenance of individual tub conformations by increasing the barriers to RI and BS.

The synthetic pathways that were developed to gain access more broadly to key cyclooctatetraenes invariably

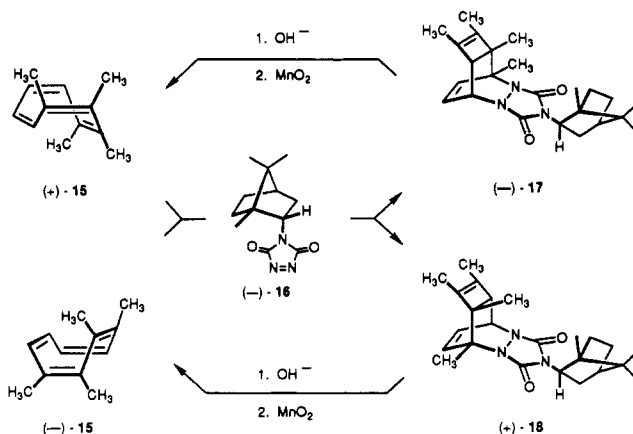
(13) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(14) Gust, D.; Senkler, G. H., Jr.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1345.

(15) (a) Paquette, L. A.; Photis, J. M.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3536. (b) Paquette, L. A.; Photis, J. M. *Tetrahedron Lett.* **1975**, 1145. (c) Paquette, L. A.; Photis, J. M.; Micheli, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 7899. (d) Paquette, L. A.; Micheli, R. P.; Photis, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 7911.



Scheme II



capitalized on the disrotatory electrocycloization¹⁶ of a suitably functionalized bicyclo[4.2.0]octatriene. To arrive at the 1,2,3,4-Me₄ and 1,2,3,8-Me₄ isomer pair, it was first necessary to develop an alkylative cyclic sulfone contraction that would lead from a five-membered cyclic sulfone such as is present in **10** to a 1,2-dimethylcyclobutene structural unit.¹⁷ Application of this new protocol to **10** gave **11**, bromination-dehydrobromination of which led via **12** to the desired **13** (Scheme I). If introduction of the conjugated diene subunit as in **14** were accomplished first, access could be gained quickly to the bond-altered isomer **15**.¹⁸

The resolution of **15** was accomplished directly through its Diels-Alder cycloaddition with optically pure (-)-endo-bornyltriazolinedione (**16**).¹⁹ As shown in Scheme II, the urazoles **17** and **18** that result are separated and reconverted to the individual [8]annulene enantiomers for the definitive designation of absolute configuration. The circular dichroism spectra of many optically active COTs have revealed that rotatory capacity can be related directly to the loci of the substituents.²⁰⁻²⁴ Hydrocarbon **13** is, of course, a meso compound not amenable to resolution.

(16) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie GmbH and Academic Press: New York, 1970.

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

(18) (a) Paquette, L. A.; Photis, J. M.; Ewing, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 3538. (b) Paquette, L. A.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4936.

(19) (a) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, *20*, 3597. (b) Paquette, L. A.; Doehner, R. F., Jr. *J. Org. Chem.* **1980**, *45*, 5105.

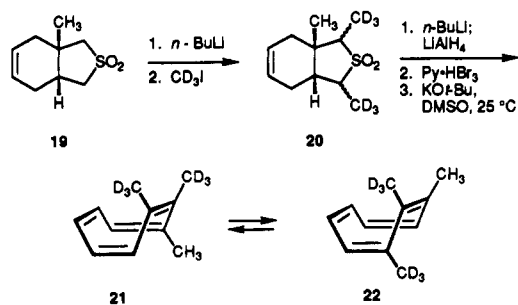
(20) Paquette, L. A.; Hanzawa, Y.; Hefferon, G. J.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 265.

(21) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Hanzawa, Y. *J. Am. Chem. Soc.* **1983**, *105*, 7644.

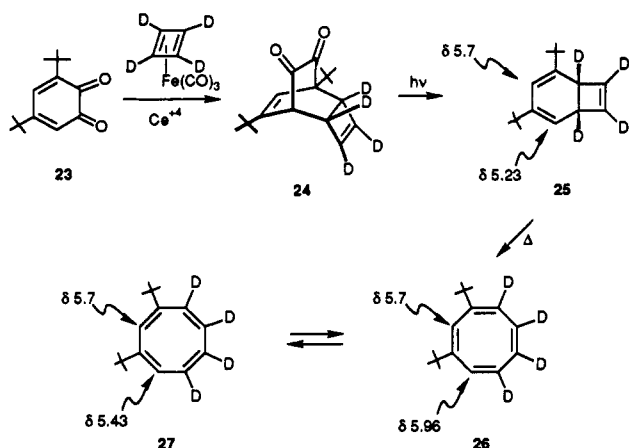
(22) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Samodral, R.; DeLuca, G.; Ouellette, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7649.

(23) Paquette, L. A.; Wang, T.-Z. *J. Am. Chem. Soc.* **1988**, *110*, 8192.

Scheme III



Scheme IV



Independent heating of 13 and *dl*-15 in diglyme at 160 °C has shown 13 to be the more stable isomer ($\Delta G^\circ = 0.7$ kcal/mol). This thermodynamic difference manifests itself also in the somewhat greater energy that must be expended by 13 relative to 15 while progressing to the common planar dianion under conditions of electrochemical reduction ($E_{1/2} = -2.54$ and -2.43 V vs SCE, respectively).

1,2,3-Me₃COT, which can be prepared economically in a parallel manner, differs from its tetramethyl homologues in the sense that its bond shifting is a degenerate process and therefore unrecognizable in the absence of a label.²⁵ In the wake of the preparation of 21 according to Scheme III, suitable kinetic data surrounding its interconversion with 22 could be obtained (the three methyl positions are characterized by unique chemical shifts).

Cyclobutadiene and its *d*₄ derivative have served well as progenitors of mechanistically relevant COTs. The 1,3-di-*tert*-butyl example, notably instructive because of its noncontiguous substitution plan, was obtained from *o*-quinone 23 (Scheme IV).²⁶ Although the *tert*-butyl singlets in 26 do overlap, the exchange with 27 could easily be monitored by the indicated differences in vinyl proton absorptions.

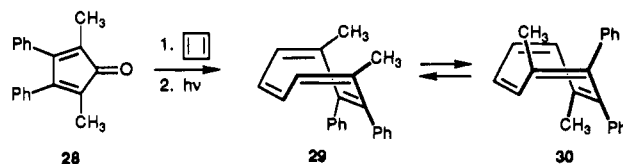
Interstitial phenyl substitution as in 29 could be achieved by the implementation of similar synthetic

(24) Paquette, L. A.; Trova, M. P.; Luo, J.; Clough, A. E.; Anderson, L. B. *J. Am. Chem. Soc.* 1990, 112, 228.

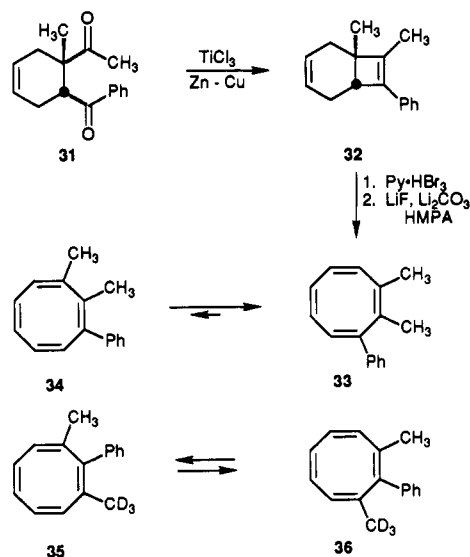
(25) (a) Paquette, L. A.; Gardlik, J. M.; Photis, J. M. *J. Am. Chem. Soc.* 1976, 98, 7096. (b) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* 1980, 102, 5016.

(26) (a) Wells, G.; Hanzawa, Y.; Paquette, L. A. *Angew. Chem.* 1979, 91, 578; *Angew. Chem., Int. Ed. Engl.* 1979, 18, 544. (b) Paquette, L. A.; Hanzawa, Y.; McCullough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* 1981, 103, 2262.

Scheme V



Scheme VI



tactics (Scheme V).^{20,27} The barrier to bond shifting within 30 is elevated by 4–5 kcal/mol relative to 15, thereby implicating the phenyl groups to be more space demanding than methyl at the BS transition state. A comparable rate retardation was noted for the conversion of 33 to 34 (Scheme VI).²² In contrast, 1,3-dimethyl-2-phenyl-COT (35) is more dynamically mobile than the 1,2,3-Me₃ derivative.²¹ The source of these dissimilar effects is believed to be the extent to which the pendant aryl group is rotated out of conjugation in the ground state. “Knife-edge” preorientation raises the ground-state energy, but introduces fewer non-bonded steric interactions than a methyl group as progress is made to a more crowded transition state. In the absence of this predisposition, phenyl is more bulky than methyl.

Racemization Rates

The reduction in level of optical activity (α) in chiral COTs is intricately related to operation of the two dynamical processes of interest. By defining the rates of RI and BS as k_1 and k_2 , respectively, it is possible to derive eq 1 for the overall rate of loss of α . Although

$$-\ln \alpha = 2(k_1 + 2k_2)t - \ln \alpha_0 \quad (1)$$

this rate law is applicable to all COTs, the identity is fortuitous since two quite different scenarios can apply. In the first instance exemplified by 1,2,3-Me₃COT, the multiplication factor of 2 materializes because both RI and BS result in production of the enantiomeric

(27) (a) Anderson, C. M.; McCay, I. W.; Warrenner, R. N. *Tetrahedron Lett.* 1970, 2735. (b) Warrenner, R. N.; Anderson, C. M.; McCay, I. W.; Paddon-Row, M. N. *Aust. J. Chem.* 1977, 30, 1481. (c) McCay, I. W.; Warrenner, R. N. *Tetrahedron Lett.* 1970, 4779, 4783. (d) Warrenner, R. N.; McCay, I. W.; Tan, R. Y. S.; Russell, R. A. *Tetrahedron Lett.* 1979, 3183.

Table I. Kinetic and Thermodynamic Parameters for BS and RI in Structurally Congested Cyclooctatetraenes

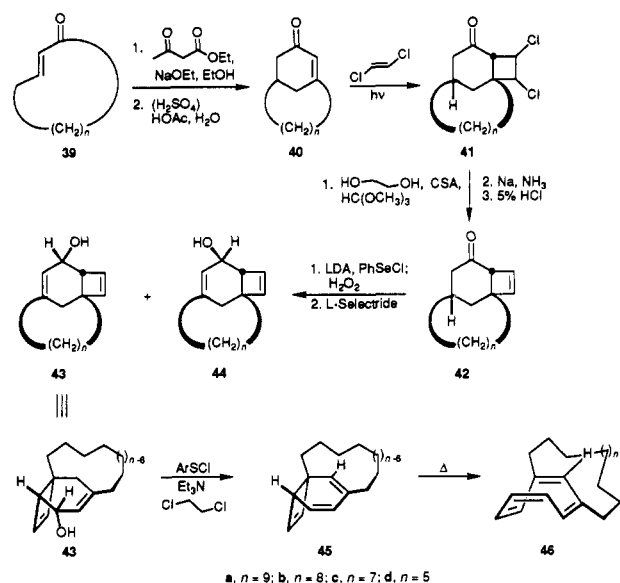
COT	Ea, kcal/mol	ln A	ΔH^\ddagger_{25} , kcal/mol	ΔS^\ddagger_{25} , eu	ΔG^\ddagger_{25} , kcal/mol	references
A. Bond Shifting						
	23.3	29.0	22.7	-2.9	23.6	26
	23.5	24.4	22.9	-12	26.5	25
	28.7	24.4	28.1	-13.3	32.0	18
	34.2	31.6	33.6	2.3	32.9	20
	33.6	30.9	33.0	+0.9	32.7	20
B. Ring Inversion						
	19.9	26.7	19.3	-7.5	21.6	26
	23.0	26.6	22.4	-7.7	24.4	25
	29.1	24.9	28.5	-11.0	31.8	18
	27.6	26.1	27.0	-8.8	29.7	20

structure, such that the magnitude of α is reduced twice as fast as the actual consumption of starting material. For a substrate such as 15, conversion to the enantiomer again leads to a 2-fold enhancement in the decrease of α . This is not the case when production of meso isomer 13 occurs, but this process takes place twice as rapidly, viz., $(k_1 + 2k_2)$, as does conversion to the enantiomer.

In the preceding kinetic treatment, k_2 has been defined so that every bond-switching event gives rise to a racemic product. Thus, a planar transition state of type 5 has been assumed for the purpose of normalization. An alternative mechanistic pathway via a structure of type 51 (presented later) would not, of course, be subject to the same limitation.

On this basis, the measurement of racemization rates provides for quantification of a composite rate expression that requires the independent assessment of either k_1 or k_2 . Since bond shifting lends itself ideally to NMR analysis and these measurements can often be made in the same temperature range used for the racemization studies, k_2 values were obtained experimentally and eq 1 was then solved for k_1 . Representative BS and RI data have been collected in Table I.

The ease of structural change within the COT nucleus is clearly impeded by proximal peripheral substitution.

Scheme VII

Unfortunately, the need to eclipse and buttress a contiguous array of alkyl (or aryl) groups levels the customarily distinguishable energy demands imposed intraannularly. The essential identity of the ΔG^\ddagger_{BS} and ΔG^\ddagger_{RI} values for 15 (32 kcal/mol) reflects this specific concern. As a consequence, a clear-cut definition of the manner in which COTs undergo bond shifting is masked by energy-demanding steric factors. Since simple mono- and difunctionalized derivatives provide no useful insight, we turned to annulation of the COT framework as a means of probing BS to a more sophisticated degree.

Dynamic Behavior of Annulated Cyclooctatetraenes

Limits were quickly established. 1,2-Belting as in 37 is accompanied by progressive flattening of the COT ring as n is reduced.^{28,29} Ring inversion heavily dominates the kinetic profiles under these circumstances.



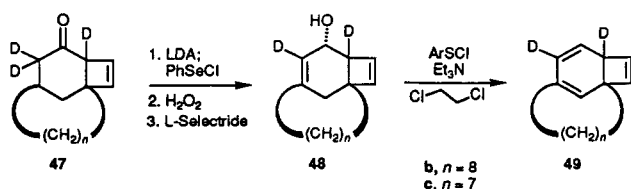
Equally important, bond shifting does not operate when n falls below 2. Therefore, members of this subclass were not further considered. (1,4)Cyclooctatetraenophanes such as 38, although intrinsically interesting compounds, possess structural characteristics that preclude their utility as mechanistic probes. Bond shifting cannot be tolerated in 38 even to the point when $n = 5$ because of impending Bredt rule like violations. With further contraction in the value of n , the COT ring is forced into its valence isomeric bicyclo[4.2.0]octatriene tautomeric form.³⁰ Racem-

(28) Paquette, L. A.; Wang, T.-Z.; Cottrell, C. E. *J. Am. Chem. Soc.* 1987, 109, 3730.

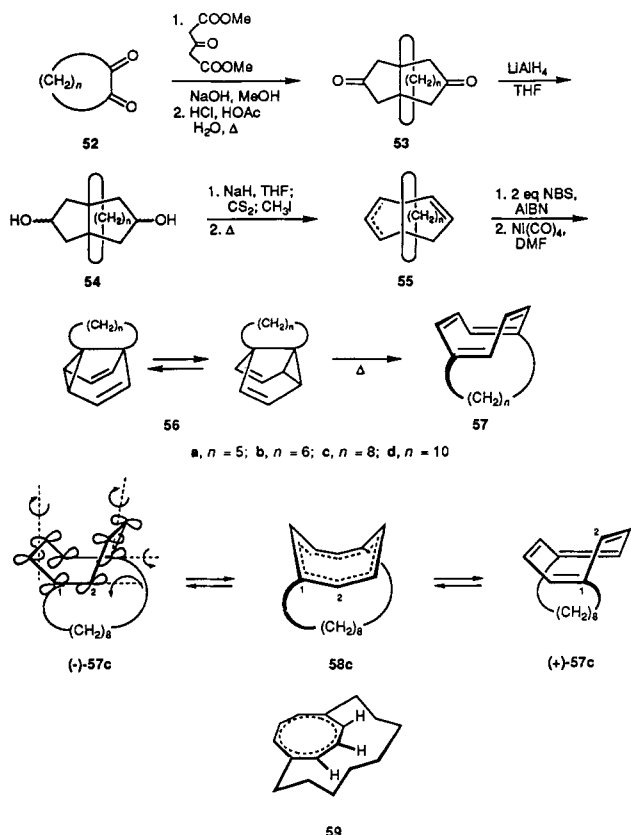
(29) Pirrung, M. C.; Krishnamurthy, N.; Nunn, D. S.; McPhail, A. T. *J. Am. Chem. Soc.* 1991, 113, 4910.

(30) (a) Paquette, L. A.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* 1972, 94, 4398. (b) Paquette, L. A.; Wingard, R. E., Jr.; Photis, J. M. *J. Am. Chem. Soc.* 1974, 96, 5801.

Scheme VIII



Scheme IX



ization by ring inversion is also nonfunctional at reasonable values of n , enantiomerization remaining inoperative to the point of thermal decomposition.³¹

The efficient 1,3-annulation pathway that was developed is outlined in Scheme VII. Once the 2-cyclohexenone part structure had been established as in 40, the two final carbons were introduced by [2 + 2] photocycloaddition. Hydride reduction of 42a affords principally 43a, but steric factors progressively reverse the stereoselectivity to the point where 42d gives 44d exclusively.³² Since dehydration was reliant upon [2,3] sigmatropy and 44d was unreactive to such treatment, only 46a–c were ultimately obtained. As a consequence of orbital symmetry control, the ring opening of 45 does not result in migration of the original cyclobutene double bond.

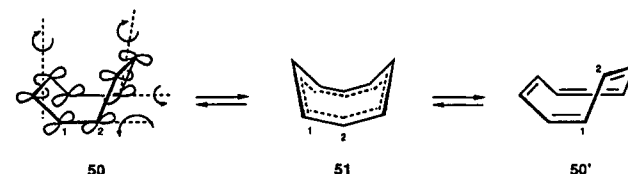
Notwithstanding our ability to transform 46 into diastereomerically pure adducts with (-)-16, careful hydrolysis–oxidation of these urazoles never yielded optically active (1,3)cyclooctatetraenophanes. In order to determine if BS or RI (or both) was unusually facile

(31) (a) Paquette, L. A.; Trova, M. P. *Tetrahedron Lett.* 1987, 2795; errata p 4354. (b) Paquette, L. A.; Trova, M. P. *J. Am. Chem. Soc.* 1988, 110, 8197.

(32) (a) Paquette, L. A.; Wang, T.-Z. *J. Am. Chem. Soc.* 1988, 110, 3663. (b) Paquette, L. A.; Wang, T.-Z.; Luo, J.; Cottrell, C. E.; Clough, A. E.; Anderson, L. B. *J. Am. Chem. Soc.* 1990, 112, 239.

in these systems, ketones 42 were subjected to base-catalyzed H–D exchange and subsequently processed to give 49 (Scheme VIII). As 49 underwent ring opening at room temperature, proton-decoupled ^2H NMR spectroscopy revealed the occurrence of rapid isotopic scrambling consistent with $k_1 \ll k_2$ (and its reversal k_{-2}). Dynamic NMR studies confirmed that bond shifting is indeed considerably accelerated in 46 (and 46-4,6- d_2) relative to unbridged congeners (Table II). Furthermore, while the enthalpies of activation for RI increased linearly as the polymethylene chain was shortened, BS was not affected in a comparable manner. This behavior is considered by us to be consistent with the need to pass a methine unit through the center of the loop during RI. In contrast, BS must occur via a pathway that skirts the need for experiencing comparable steric compression. In our view, pseudorotation mediated by a saddle-shaped geometry can lead to racemization without paying the relatively high price of intraannular compression.

The pseudorotation process as applied to COTs involves conrotation about transannularly positioned π -bonds (see 50). This motion induces twisting about each of the four olefinic linkages, ultimately dismantling the original double bonds and installing four new ones. This BS reaction channel, the transition state for which is saddle-shaped as in 51, has the important consequences of bypassing the need to widen internal bond angles and not requiring the COT ring to become planar at any time.



A comparable study of (1,5)cyclooctatetraenophanes, prepared according to Scheme IX,³³ substantially reinforced this mechanistic interpretation. Attachment of a loop in this manner could be achieved by making recourse to the flash vacuum pyrolysis of semibullavalenes such as 56.³⁴ To a greater extent than in 46, the ability of 57 to bypass a delocalized “planar alternate” transition state related to 5 for BS would have the effect of giving rise to values of ΔH^\ddagger and ΔG^\ddagger considerably lower than expected, especially as the chain length is decreased to eight or fewer CH_2 units. In actuality, the activation parameters for the interconversion of (-)-57c with (+)-57c (Table II) are well accommodated by adoption of that reaction pathway involving passage through the flattened saddle structure 58c produced by pseudorotation.³⁴ As in the 1,3-bridged systems, energy costs are not elevated because a twist of only 30° is required for incipient elaboration of the bond shift isomers. This level of deformation is not considered prohibitive since aromaticity can be maintained

(33) Paquette, L. A.; Trova, M. P.; Luo, J.; Clough, A. E.; Anderson, L. B. *J. Am. Chem. Soc.* 1990, 112, 228.

(34) (a) Zimmerman, H. E.; Iwamura, H. *J. Am. Chem. Soc.* 1970, 92, 2015. (b) Paquette, L. A.; Russell, R. K.; Wingard, R. E., Jr. *Tetrahedron Lett.* 1973, 1713. (c) Paquette, L. A.; Ley, S. V.; Meisinger, R. H.; Russell, R. K.; Oku, M. *J. Am. Chem. Soc.* 1974, 96, 5806. (d) Russell, R. K.; Wingard, R. E., Jr.; Paquette, L. A. *J. Am. Chem. Soc.* 1974, 96, 7483. (e) Martin, H.-D.; Urbaneck, T.; Walsh, R. *J. Am. Chem. Soc.* 1985, 107, 5532.

Table II. Kinetic and Thermodynamic Parameters for BS and RI in 1,3- and 1,5-Annulated Cyclooctatetraenes

COT	E_a , kcal/mol	$\ln A$	ΔH^{\ddagger}_{25} , kcal/mol	ΔS^{\ddagger}_{25} , eu	ΔG^{\ddagger}_{25} , kcal/mol	refs
A. Bond Shifting						
[7](1,3)-COT (46c)	22.7	34.4	22.0 (± 0.4)	7.7 (± 1.4)	19.76 (± 0.03)	32
[8](1,3)-COT (46b)	16.2	25.8	15.7 (± 0.9)	-9.4 (± 2.9)	18.40 (± 0.07)	32
[9](1,3)-COT (46a)	16.7	27.5	15.9 (± 0.8)	-6.7 (± 2.4)	17.87 (± 0.05)	32
[8](1,5)-COT (57c)	20.2	23.7	19.6	-13.4	23.6	33
B. Ring Inversion						
[7](1,3)-COT (46c)	19.3	31.4	18.7 (± 0.4)	1.9 (± 1.4)	18.09 (± 0.03)	32
[8](1,3)-COT (46b)	16.2	29.3	15.7 (± 0.5)	2.2 (± 1.7)	16.35 (± 0.05)	32
[9](1,3)-COT (46a)	12.5	23.2	12.0 (± 0.7)	-14.0 (± 2.5)	16.22 (± 0.11)	32

at $p\pi$ distortion levels beyond this limit³⁵ and *trans*-cycloalkenes can have their CC double bonds forced out of coplanarity to a comparable level.³⁶ The net result is, of course, that 58 is more easily accessed than 59. The level of strain in 59 can be approximated by conversion to the corresponding dianion: $E_{1/2} = -2.01$, -2.33 V (57d); -2.08 , -2.31 V (57c).

Concluding Remarks

Our studies of the dynamic behavior of substituted cyclooctatetraenes have demonstrated that bond shifting proceeds too rapidly in certain circumstances to involve sterically congested "planar alternate" transition

states. We have identified an alternative flattened saddle geometry as a more suitable energy minimum that can be attained by pseudorotation. This mechanistic proposal is advanced solely on the basis of kinetic data and cannot be construed as proof that the pseudorotation process actually operates. However, the model does conform nicely to the observed reactivity profiles and finds direct analogy in the dynamic behavior of heptalenes.³⁷

What are the implications regarding the parent hydrocarbon? The answer resides in part in the structural differences inherent to 1 ($R = H$) and the alkylated (arylated) analogues we have synthesized and investigated. Certainly, the presence of a polymethylene chain in 46 and 57 inhibits the ready attainment of planarity by these systems. Might it also predispose the [8]annulene core to pseudorotation? These and additional unanswered questions leave the door open for new probe experiments and theoretical treatments.

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(35) Blank, N. E.; Haenel, M. W.; Kruger, C.; Tsay, Y.-H.; Wientges, H. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1064.

(36) Shea, K. J. *Tetrahedron* 1980, 36, 1683.

(37) (a) Bernhard, W.; Brügger, P.; Daly, J. J.; Schönholzer, P.; Weber, R. H.; Hansen, H.-J. *Helv. Chim. Acta* 1985, 68, 415. (b) Bernhard, W.; Brügger, P.; Schönholzer, P.; Weber, R. H.; Hansen, H.-J. *Helv. Chim. Acta* 1965, 68, 429. (c) Bernhard, W.; Brügger, P.; Daly, J. J.; Englert, G.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* 1985, 68, 1010. (d) Weber, R. H.; Brügger, P.; Jenny, T. A.; Hansen, H.-J. *Helv. Chim. Acta* 1987, 70, 742. (e) Weber, R. H.; Brügger, P.; Schönholzer, P.; Arnold, W.; Hansen, H.-J. *Helv. Chim. Acta* 1987, 70, 1439. (f) Hafner, K.; Knaup, G. L.; Lindner, H. J.; Flötter, H.-C. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 212. (g) Hafner, K.; Knaup, G. L. *Tetrahedron Lett.* 1986, 27, 1665, 1673. (h) Hafner, K.; Hock, N.; Knaup, G. L.; Meinhardt, K.-P. *Tetrahedron Lett.* 1986, 27, 1669. (i) Hafner, K.; Knaup, G. L.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 633. (j) Hafner, K.; Knaup, G. L.; Lindner, H. J. *Bull. Chem. Soc. Jpn.* 1988, 61, 155.