**57**

The Current View of Dynamic Change within Cyclooctatetraenes

Leo A. Paquette

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

Not long after cyclooctatetraene (COT, **1**, R = H) was convincingly shown to possess a D_{2d} ground-state conformation[1] was this polyolefin[2] recognized to be capable of *three* fundamental dynamic changes. Of these, ring inversion (RI, **1** → **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

1   **1′**

2   **3**
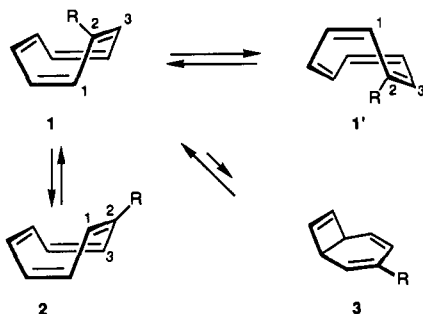
modification is realized when the π-electrons "migrate" within the octagonal perimeter as in **1** → **2**.[3-5] Bond shifting (BS) results in site exchange between the singly and doubly bonded carbon atoms. Valence isomerization with bicyclo[4.2.0]octa-2,4,7-trienes (**3**) is also possible. However, since ring closure in this fashion must overcome an energy barrier ($\Delta G^{\ddagger}$) 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 reactions[8] 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

4   **5**

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 $\Delta G^{\ddagger}$ 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.

58 *Acc. Chem. Res., Vol. 26, No. 2, 1993*

Paquette

geometry because it best accommodated the associated potential energy surface. Very recently, Hrovat and Borden have insisted that only the D_{8h} 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 anti-aromatic 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 Mo(CO)$_6$-promoted rearrangement of **6**.[15] The pair of product hydrocarbons **7** and **8**, obtained
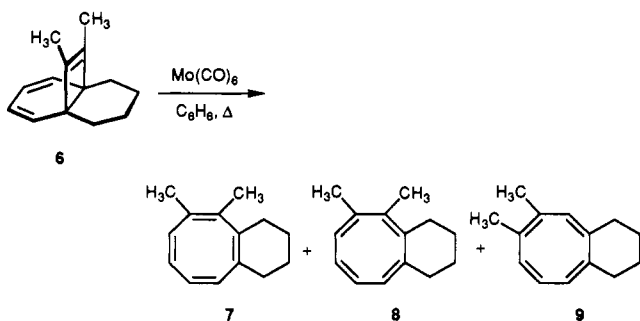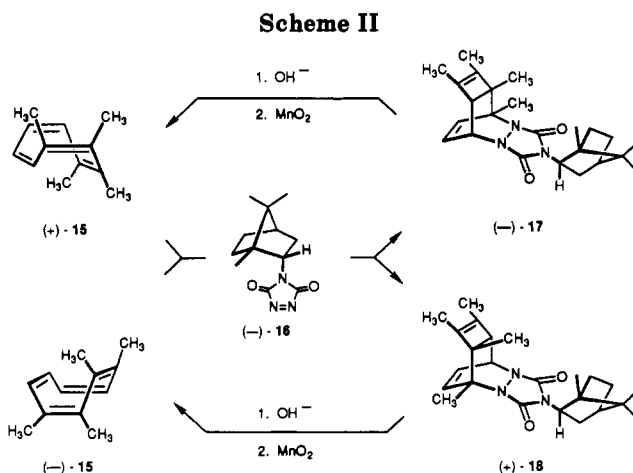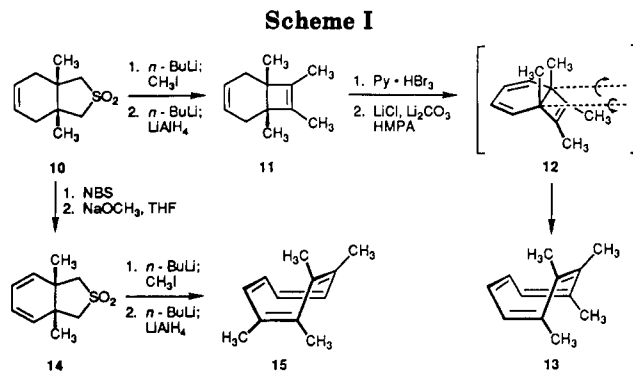

in equal amounts, were recognized to constitute *the first shelf stable [8]annulene bond shift isomers*. Their independent isolation and individually unique chemistry documented very convincingly that double-bond localization could be realistically achieved in COTs. Stated differently, steric and buttressing 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

---

Scheme I

Scheme II

capitalized on the disrotatory electrocyclization[16] of a suitably functionalized bicyclo[4.2.0]octatriene. To arrive at the 1,2,3,4-Me$_4$ and 1,2,3,8-Me$_4$ isomer pair, it was first necessary to develop an alkylative ring 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.

(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.

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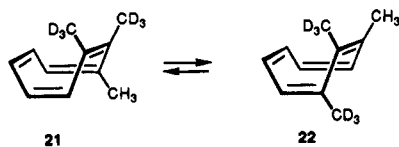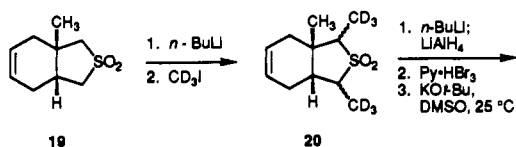
(20) Paquette, L. A.; Hanzawa, Y.; Hefferon, G. J.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 265.

(21) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Hanzawa, Y. *J. Am. Chem. Soc.* **1983**, *105*, 7644.
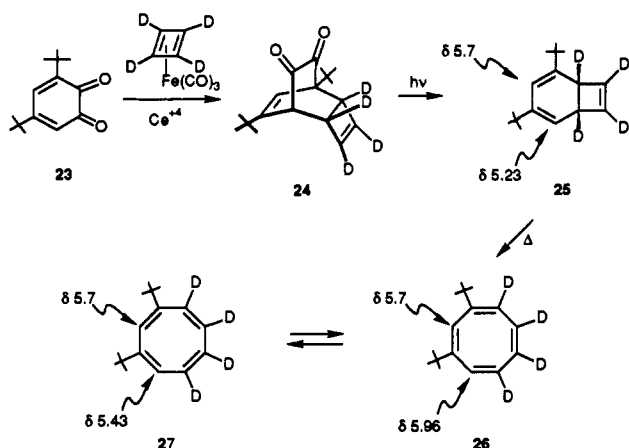
(22) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Samodral, R.; DeLucca, G.; Ouellette, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7649.

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

Scheme III

Scheme IV

Scheme V

Scheme VI

Independent heating of **13** and *dl*-**15** in diglyme at 160 °C has shown **13** to be the more stable isomer ($\Delta G°$ = 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-Me$_3$COT, 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.
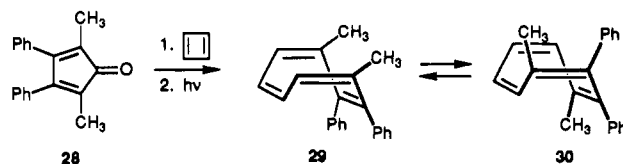
Interstitial phenyl substitution as in **29** could be achieved by the implementation of similar synthetic

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-Me$_3$ 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 nonbonded 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
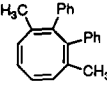
The reduction in level of optical activity (α) in chiral COTs is intricately related to operation of the two dynamical processes of interest. By defining the rates of RI and BS as k_1 and k_2, respectively, it is possible to derive eq 1 for the overall rate of loss of α. Although

$$-\ln \alpha = 2(k_1 + 2k_2)t - \ln \alpha_0 \tag{1}$$

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-Me$_3$COT, the multiplication factor of 2 materializes because both RI and BS result in production of the enantiomeric

(24) Paquette, L. A.; Trova, M. P.; Luo, J.; Clough, A. E.; Anderson, L. B. *J. Am. Chem. Soc.* **1990**, *112*, 228.
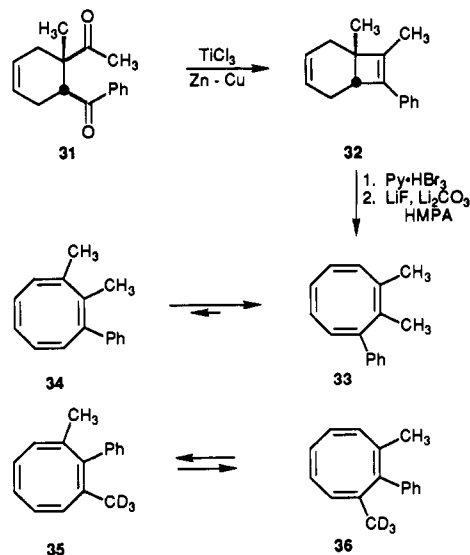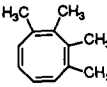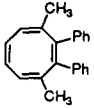
(25) (a) Paquette, L. A.; Gardlik, J. M.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 7096. (b) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5016.
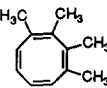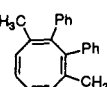
(26) (a) Wells, G.; Hanzawa, Y.; Paquette, L. A. *Angew. Chem.* **1979**, *91*, 578; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 544. (b) Paquette, L. A.; Hanzawa, Y.; McCullough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1981**, *103*, 2262.

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

60 *Acc. Chem. Res., Vol. 26, No. 2, 1993*

Paquette

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

COT	E_a, kcal/mol	ln A	$\Delta H^{\ddagger}_{25}$, kcal/mol	$\Delta S^{\ddagger}_{25}$, eu	$\Delta G^{\ddagger}_{25}$, 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

Scheme VII

a, $n = 9$; b, $n = 8$; c, $n = 7$; d, $n = 5$

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.
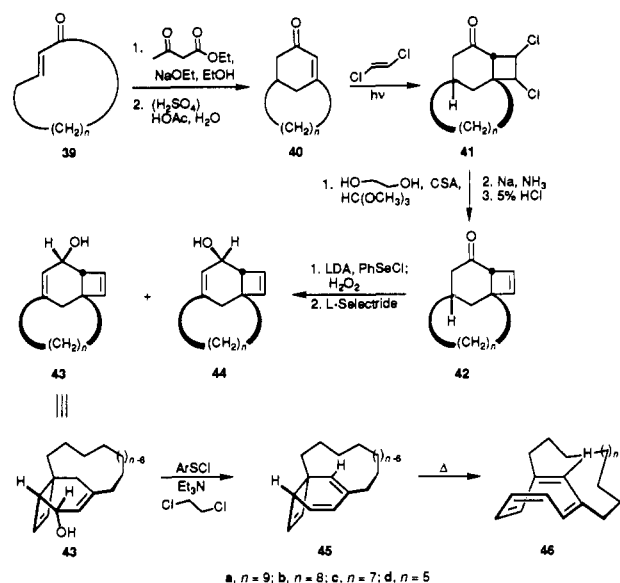
Unfortunately, the need to eclipse and buttress a contiguous array of alkyl (or aryl) groups levels the customarily distinguishable energy demands imposed intraannularly. The essential identity of the $\Delta G^{\ddagger}_{BS}$ and $\Delta G^{\ddagger}_{RI}$ values for **15** (32 kcal/mol) reflects this 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.
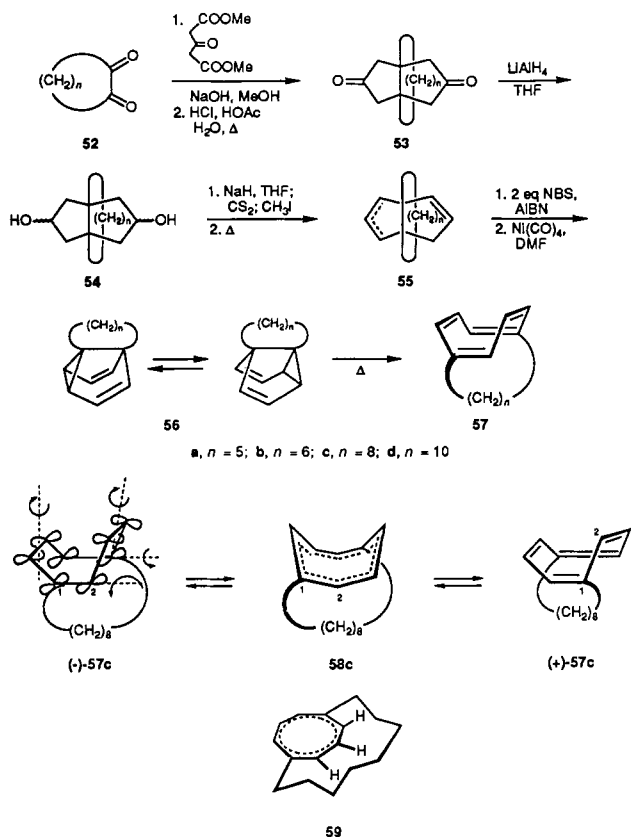
(29) Pirrung, M. C.; Krishnamurthy, N.; Nunn, D. S.; McPhail, A. T. *J. Am. Chem. Soc.* **1991**, *113*, 4910.

(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
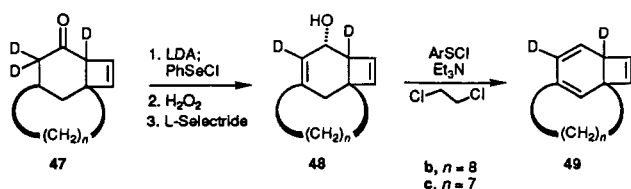
Scheme IX

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

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.
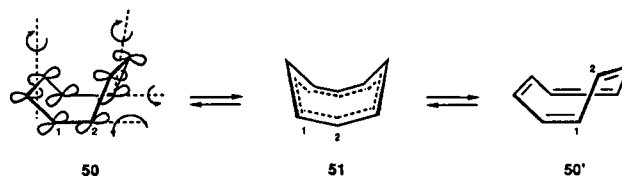
A comparable study of (1,5)cyclooctatetraenophanes, prepared according to Scheme IX,[33] substantially reinforced this mechanistic interpretation. Attachment of a loop in this manner could be achieved by making recourse to the flash vacuum pyrolysis of semibullvalenes such as **56**.[34] To a greater 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 $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ 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

(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.

(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.; Urbanek, T.; Walsh, R. *J. Am. Chem. Soc.* **1985**, *107*, 5532.

62 *Acc. Chem. Res., Vol. 26, No. 2, 1993*

Paquette

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	$\Delta H^{\ddagger}_{25}$, kcal/mol	$\Delta S^{\ddagger}_{25}$, eu	$\Delta G^{\ddagger}_{25}$, 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 limit[35] 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.

(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* **1985**, *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.; Brüger, 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.