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TETRAHEDRON REPORT

THE RENAISSANCE IN CYCLOOCTATETRAENE CHEMISTRY

LEO A. PAQUETTE
Evans Chemical Laboratories, The Ohio State University, Columbus, OH 43210, U.S.A.

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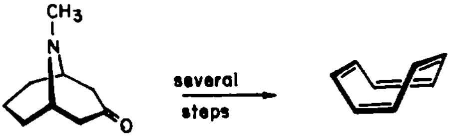
Historical background. With early recognition of the special statibility and reactivity of benzene and its derivatives arose a desire to prepare larger ring homologs of this hydrocarbon. Success was ultimately realized in 1911-13 when Willstätter and his coworkers achieved the conversion of pseudopelletierine (**1**) to cyclooctatetraene (COT, **2**).[1] Although elegant in concept, this synthetic entry did not represent a serviceable route to quantities of **2** despite later improvements.[2] However, Reppe's development of a process based upon the remarkable tetramerization of acetylene with nickel cyanide lent itself well to large scale commercial adaptation.[3] Nevertheless, with the possible exception of Cope's involvement with the cotetramerization of mixed acetylenes,[4] interest in cyclooctatetraene chemistry waned well into the 1950s as it became progressively evident that this 8π-electron system lacks significant resonance energy (2·4–4·8 kcal/mole[5]) and is a true polyolefin. Then a turning point was seemingly reached. Predictions having their basis in the Hückel rule prompted Katz in 1960 to examine the reduction of COT.[6] The stable delocalized cyclooctatetraene dianion (**3**) was thereby discovered. At approximately the same time, an awareness began to develop that the blatant nonaromaticity in **2** caused by its π-electronic instability and favored D_{2d} tub conformation,[7] coupled with obvious high levels of unsaturation, provided a molecule having unequaled facility for structural rearrangement. Ingenious routes to bullvalene (**4**),[8] the *syn*- and *anti*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dienes (**5**),[9] and cyclononatetraenide anion,[10] for example, were developed during this period. The evolution of such findings caused COT to become an increasingly attractive target of mechanistic investigation. The level of achievement attained by 1965 has been concisely reviewed by Schröder in his monograph on this subject.[11] Developments in the cyclooctatetraene area during the intervening 10 years have been rapid and varied. Our own contributions to this field were initiated in the belief that **2**, the smallest stable member of the nonaromatic annulenes, could provide an important backdrop to cyclic polyolefin chemistry, much in the same way that benzene has been indispensible to the development of aromatic theory.



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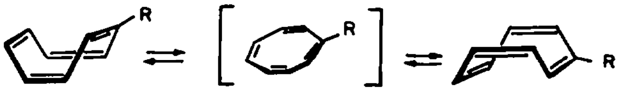
Accordingly, this review has been conceived as a synopsis of the renewed interest in COT chemistry during the period 1965–75. Its purpose is to provide a critical summary which, although not intended to be exhaustive, will hopefully prove provocative of new ideas.

Dynamic properties. With its nonplanar conformation and alternating single (1·48 Å) and double bond (1·34 Å) character, the COT ring system appears capable of three fundamental structural changes currently referred to as ring inversion, bond shifting, and valence isomerization. The first of these processes relates directly to the question of conformational mobility,[12–14] is thought to require a planar-alternate transition state (**6**),[15] and is demanding of the least energy ($\Delta G^{\neq} = 14\cdot7$ kcal/mole for **7**;[14] $\Delta G^{\neq} = 12\cdot7$ kcal/mole for **6**, $R = OCH(CH_3)_2$[15]). In the parent hydrocarbon (**6**, R = H), such flexing merely regenerates the starting molecule. In simple monosubstituted derivatives, however, this equilibration results effectively in racemization. Furthermore, if the sidechain possesses a chiral center, ring inversion now produces a diastereomer. Thus, a real potential for stereoisomerism exists,[16] but remains to be fully exploited in monocyclic cyclooctatetraenes.

Bond shifting seemingly also necessitates attainment of a planar form but with equal bond lengths (cf. **8**). As a consequence, this process has a latently higher energy barrier ($\Delta G^{\neq} = 17\cdot1$ kcal/mole for **7**[17]). In this connection, Anet's study of ester **9** is quite revealing.[18] Its ^1H NMR spectrum under ambient conditions expectedly displays four ring methyl signals. At the outset of ring inversion and in the absence of bond shifting, interconversion of diastereomeric pairs would operate exclusively. Sufficiently rapid exchange between structures **9a** ⇄ **9c** and **9b** ⇄ **9d** should result in coalescence of the methyl signals



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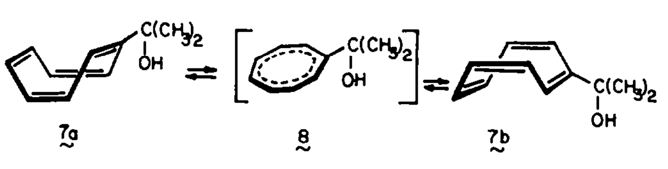
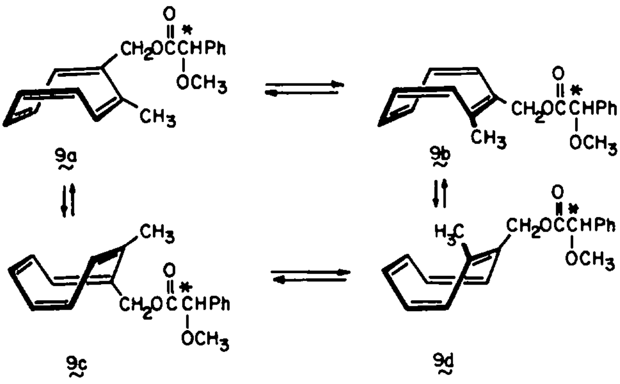
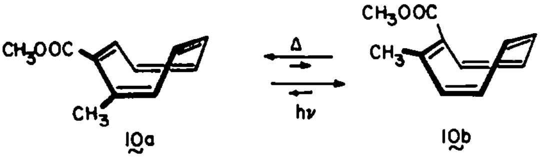


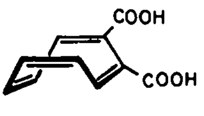
to two peaks. Since solutions of **9** heated to 70° do in fact generate precisely this spectrum, ring inversion must already be rapid when bond shifting is still slow on the NMR time scale.



The bond shift isomers of methyl 2-methylcyclooctatetraenecarboxylate (**10**) have been observed to be interconvertible under photochemical conditions.[18] The ^{1}H NMR spectrum of **10** at 27° shows both structures to be present with **10a** predominating to the extent of ~95%. Excitation with 3500 Å light at −30 to −50° produced a change in the relative intensities of the methyl signals until **10b** predominated by a small margin. Upon warming to −12°, equilibrium was rapidly established ($\Delta F^{\neq} = 18{\cdot}8$ kcal/mole).



Cyclooctatetraene-1,2-dicarboxylic acid is believed to exist exclusively in the bond shift isomeric form adopted by **11**.[19] Its spectra and reluctance to form anhydride **12** upon treatment with dicyclohexyl carbodiimide contrast with the properties of the π-locked benzo fused diacid **13** which forms a stable anhydride. Steric factors likely underlie the preference of **10a** and **11** for the 1,8 substitution plan.



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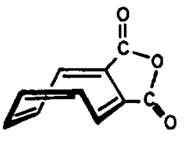

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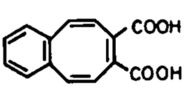

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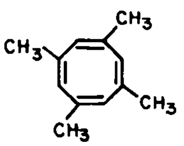
Bond shift isomers of 1,3,5,7-tetramethylcyclooctatetraene (**14**) are identical by virtue of symmetry. Intriguingly, however, the molecule has been found by Ganis[20] to have a barrier to bond shifting ($\Delta G^{\neq} = 22{\cdot}5$ kcal/mole at 120°) substantially larger than that reported for COT itself. This experimental finding and supportive theoretical calculations[15] leave little doubt that enhanced van der Waals interactions by substituents can impede the attainment of planarity by the [8]annulene ring.

When four substituents are placed upon contiguous ring carbons, the resulting buttressing effect contributes additionally to maintenance of the individual tub conformations such that shelf stable bond shift isomers exemplified by **15** and **16** have now become accessible.[21]



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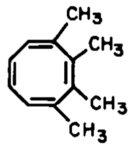

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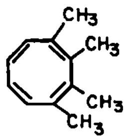

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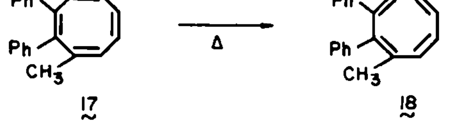
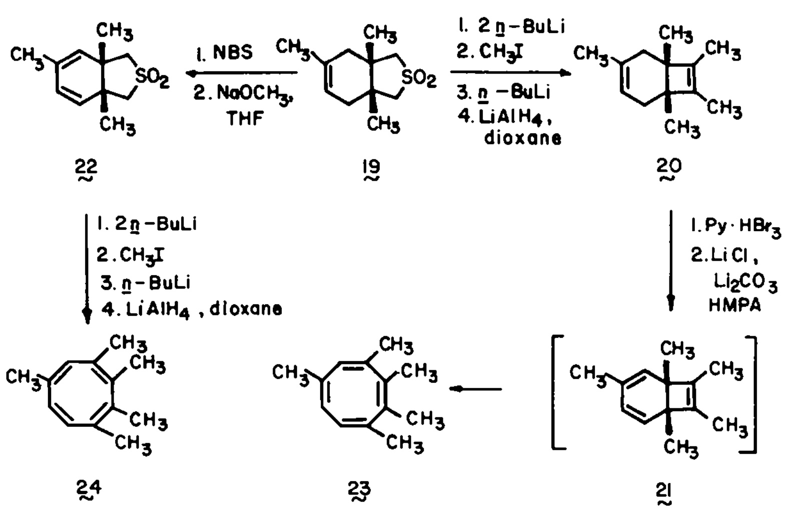
Although the activation energies for ring inversion and bond shifting in these tetramethyl derivatives are sizable, their interconversion can be achieved under certain conditions. Thus, thermal activation of either isomer in the gas phase (350–450°, contact time ~1 sec) or in solution (diglyme, 162°, 6 hr) provides a mixture containing 70% of **15** and 30% of **16**.[22] Similarly, direct irradiation results in a product mixture favoring **15** (~60%).[22]

McCay and Warrener have prepared **17** and report its unidirectional rearrangement to bond shift isomer **18** upon heating to 120° and above in $CDCl_3$.[23] Unfortunately, neither cyclooctatetraene was isolated in pure form by



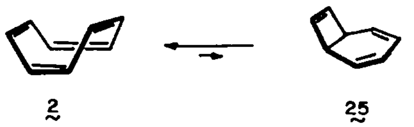


Scheme 1.

these workers, characterization resting upon ^{1}H NMR spectra of hydrocarbon mixtures and N-phenyltriazolinedione adducts.

The synthetic strategy employed in the preparation of **15**, **16** and related bond shift isomer pairs such as **23** and **24** is illustrated in Scheme 1. The attractive features of this chemistry are the modifications which allow for independent access to either polyolefin. Should the reductive ring contraction[24] of sulfone **19** be effected first, selective bromination of the trisubstituted double bond in **20** becomes possible for steric reasons (the cyclobutene double bond is quite inaccessible). Dehydrobromination provides a bicyclo[4.2.0]octatriene (**21**) which necessarily experiences disrotatory ring opening under orbital control by the cyclohexadiene moiety.[25] Bond shift isomer **23** is formed exclusively as a result.[22] If introduction of the 1,3-cyclohexadiene moiety is executed first and the diene sulfone (e.g. **22**) subsequently subjected to reductive desulfonylation, the double bond in the cyclobutene sector experiences perturbation and **24** is produced predominantly. This conversion may be the result of preferential non-vicinal ejection of the sulfur residue from hypothetical bicyclo[4.2.0]octadiene and/or cyclooctatriene intermediates.[21]

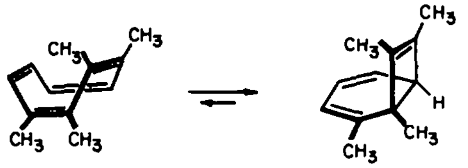
Isomerization with formation of valence tautomeric bicyclo[4.2.0]-octa-2,4,7-trienes comprises the third dynamic process available to cyclooctatetraenes. It is unrelated to the preceding two phenomena since ring flattening is not required. The ring closure is necessarily disrotatory and for most cases is the most energy demanding option ($\Delta G^{\neq} = 28{\cdot}1$ kcal/mole for **2**).[26,27] These data translate into an equilibrium concentration of **25** equivalent to 0·01% at 100°.[27] Notwithstanding, because the tub conformation of cyclooctatetraenes does not provide a framework with proper planar alignment of at least one conjugated diene unit, effective participation of such molecules as 4π components in the Diels-Alder reaction requires the prior formation of bicyclo[4.2.0]octatrienes such as **25** (*vide infra*).



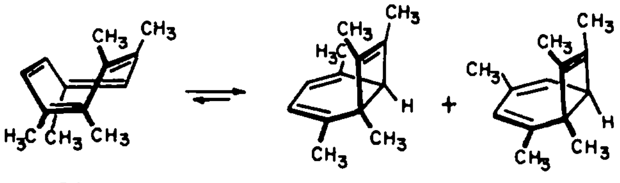
Suitable alkyl substitution of the COT ring is now recognized to provide increased thermodynamic stability to the bicyclic valence tautomer. For example, 1,2,3,4-tetramethyl derivative **16** at room temperature exists in equilibrium with 25% of **26**.[21] Pentamethyl congener **24** behaves comparably,[22] but **15** and **23** give no evidence of inhomogeneity within the limits of spectroscopic analysis. The fully methylated bicyclic hydrocarbon **30** has been described by Criegee as having greater stability than its monocyclic counterpart (**29**).[29]

Successful realization by Vogel of the synthesis of **25**[25] showed expectedly that this triene is unstable relative to **2** ($t_{1/2} = 14$ min at 0°). Activation parameters for the ring opening were experimentally determined to be $E_a = 18{\cdot}7$ kcal/mole and $A = 9{\cdot}1 \times 10^{11}$ sec^{-1}. The bicyclo[4.2.0]-octatriene moiety can be stabilized by bracketing, provided that the length of the methylene chain is sufficiently short (Table 1). An example of the generalized synthetic entry to such propellatrienes is outlined in Scheme 2.[29,30] The Ramberg-Bäcklund reaction[31] of tricyclic α-halo sulfones exemplified by **33** which serves to construct the cyclobutene ring in high yield is the pivotal step of the sequence. The remaining degree of unsaturation is subsequently introduced by bromination-dehydrobromination of the resulting propelladiene (e.g. **34**). If this order of events is reversed and dehydrogenation of the chloro sulfone is effected prior to treatment with strong base, a deep-seated structural change, termed a bishomoconjugative rearrangement, now operates preferentially (Scheme 3).[32] In addition to its mechanistic significance, this isomerization provides direct access to bridge sulfones such as **38** which may be converted readily to cyclooctatetraenes upon photochemical or thermal extrusion of sulfur dioxide. Thus, sulfide **32** and its congeners serve a dual role as convenient precursors to both 1,2- (e.g. **39**) and 1,4-annulated cyclooctatetraenes (e.g. **35**).

A glance at Table 1 reveals that the bicyclo[4.2.0]octatriene-cyclooctatetraene equilibrium is attainable when the "belt" is lengthened to incorporate five carbon atoms. This crossover point occurs expectedly at a larger bridge size than that witnessed for the structurally related norcaradiene-cycloheptatriene[33] and azanorcaradiene-azepine pairs[34] because of the greater "pinching effect" exerted by the two-carbon bridge. More



16 26



24 27 28

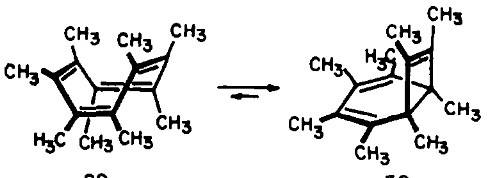


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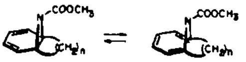
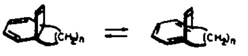
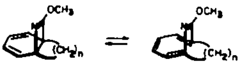
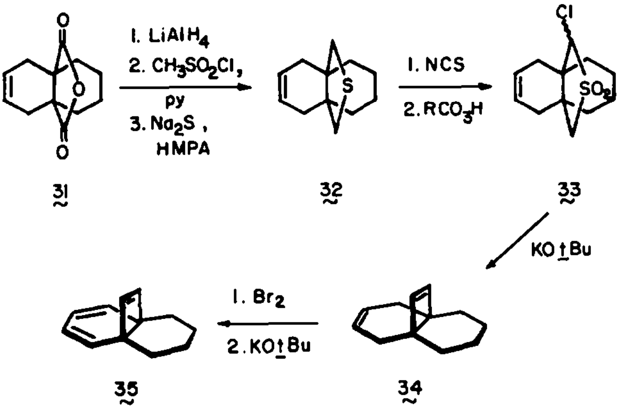
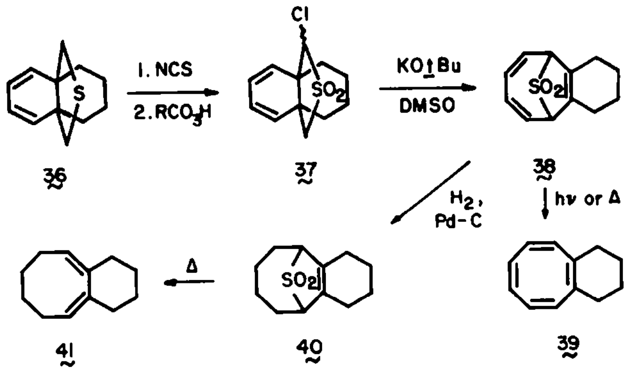
Table 1. Ground-state equilibrium effects in bridged propellanes

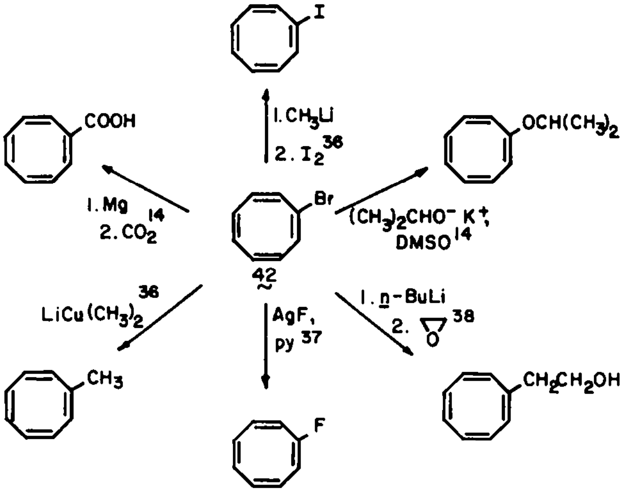
Ring system	Bridge size				Ref
	n = 3	n = 4	n = 5	n = 6	
	Tricyclic	Bicyclic			33
	Tricyclic	Bicyclic			34
	Tricyclic	Tricyclic	Bicyclic		30
	Tricyclic	Tricyclic	Tricyclic	Bicyclic	35



Scheme 2.



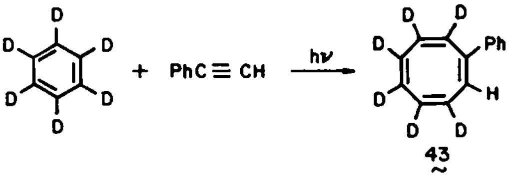
Scheme 3.



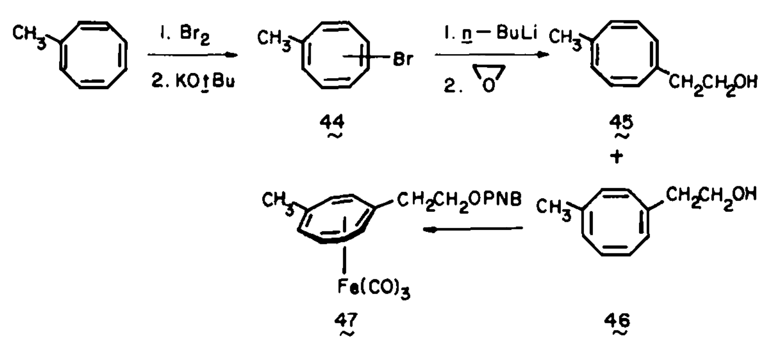
Scheme 4.

subtle electronic influences may be at work in the annulated azocine series such that bicyclic character does not develop until $n = 6$.[35]

Synthetic advances. Those improvements in the preparation of chloro- and bromocyclooctatetraene which have been made in Huisgen's laboratory[36] have led in turn to the availability of an extensive array of monosubstituted COT derivatives (Scheme 4). These "substitution" reactions take ready advantage of the facility with which **42** can be converted to organometallic compounds, undergo replacement of its vinyl halogen, and experience elimination-addition reactions (*vide infra*). These classes of transformations nicely complement the alternative preparative method currently in use, viz., the photoaddition of monosubstituted acetylenes to benzene.[17,39-41] A unique advantage enjoyed by the latter technique is its capacity for providing cyclooctatetraene-d_6 derivatives such as **43** in a high state of isotopic purity with a single manipulation.



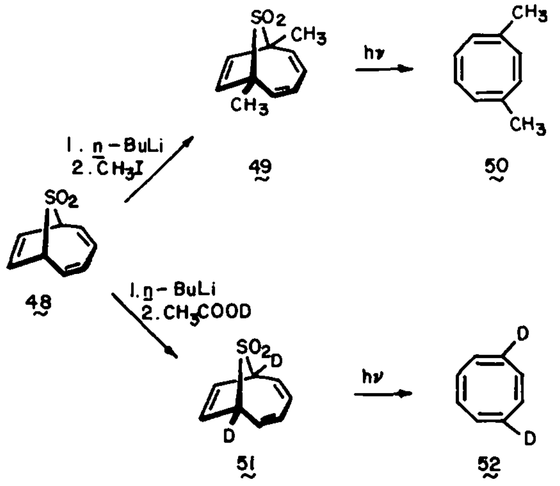
The synthesis of 1,2-disubstituted cyclooctatetraenes is similarly accomplished most readily by means of the benzene-acetylene photocycloaddition reaction.[40,42] In contrast to this quite satisfactory procedure, methodology for the directed synthesis of 1,3-, 1,4- and 1,5-disubstituted cyclooctatetraenes had been seriously lacking until recently. In the earliest recorded attempt to achieve multiple functionalization, Cope and Moore allowed phenyllithium to react with phenylcyclooctatetraene in anticipation of capitalizing on the disproportionation reactions of the initially formed monoanionic addition products.[43] The desired isomeric diphenyl derivatives were produced in very low yields and recourse to countercurrent distribution was necessary to effect their separation. In 1970, Huisgen and coworkers described the bromination-dehydrobromination of bromocyclooctatetraene and subsequent reaction of the resulting dibromide with lithium dimethylcuprate.[44] In contrast to the claim that the isomerically pure 1,4-dimethyl derivative is formed,[44] a considerable quantity of the 1,5-dimethyl isomer has subsequently been shown to be present as an undesirable, not easily separable, contaminant.[45] This is not to say that the method lacks utility, but only that it must be used with reservation in light of the existing evidence. In actuality, comparable bromination-dehydrobromination of methylcyclooctatetraene has provided a mixture of 4- and 5-bromo compounds (**44**) which when treated with *n*-butyllithium and ethylene oxide afforded **45** and **46** in a 1:3 ratio.[38] Structural elucidation



Scheme 5.

rests upon the X-ray crystal structure analysis of $Fe(CO)_3$ complex **47** (Scheme 5).[46] Clearly, there exists a preference for electrophilic addition to that double bond more remote from the bromo and methyl substituents which can be used to advantage.

A most promising approach to the synthesis of 1,4-disubstituted cyclooctatetraenes centers about the readily available bridged sulfone **48**[47,48] and the ease with which its intensely purple colored dianion[49] enters into subsequent reaction (Scheme 6). Photolysis of **49** and **51** provides the isomerically uncontaminated polyolefins **50** and **52** in high yields.[40,50] Ejection of sulfur dioxide is so rapid that possible photorearrangement of the COT products has not been encountered. The monoanion of **48** can also be prepared successfully,[51] thereby allowing for stepwise introduction of the two different bridgehead substituents if desired.



Scheme 6.

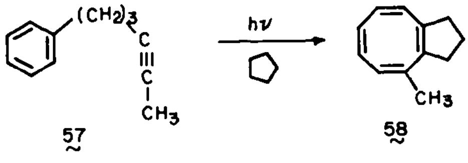
Thermal rearrangement of appropriately functionalized semibullvalens has been found to provide direct access to 1,3- and 1,5-disubstituted cyclooctatetraenes.[50,52,53] Because the reaction proceeds unidirectionally with highly specific two-bond cleavage (Scheme 7), excellent positional selectivity is attained. At the present time, this sequence qualifies as the preferred method for the directed synthesis of this pair of isomers. The requisite semibullvalenes are available in several steps if prepared by Askani's method.[54]

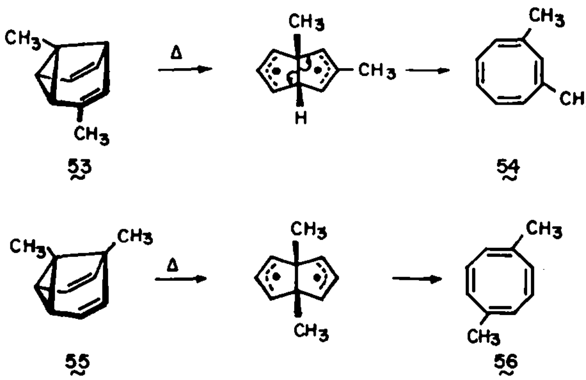
This expansion of the scope of COT syntheses holds considerable promise for rapid future developments in the area. Similarly, internal photocycloaddition reactions exemplified by the behavior of 6-phenyl-2-hexyne (**57**)[55] should allow for the control elaboration of yet more highly substituted congeners such as **58**.

By suitable chemical manipulation of certain 1,2-disubstituted cyclooctatetraenes, a number of interesting compounds have yielded to synthesis.

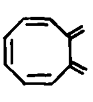
These include 1,2-dimethylenecyclooctatriene (**59**),[56,57] bicyclo[6.2.0]deca-1,3,5-triene (**60**),[57] [3,4-*c*]furooctalene (**61**),[58] benzo[*c*]octalene (**62**),[59] and 2-methylcycloocta[*b*]furan (**63**).[38]

As concerns novel hydrocarbon **65**, the rigidity of the biphenylene moiety and the size of the cyclobutadiene





Scheme 7.



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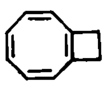

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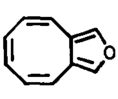

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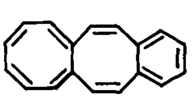

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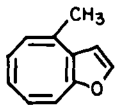

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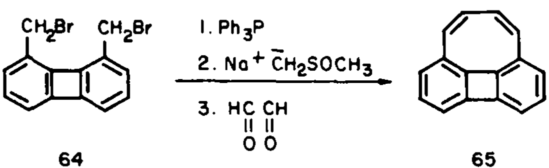
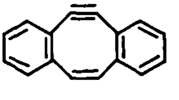
ring are expected to constrain the cyclooctatetraene subunit into a planar conformation. In addition, because **65** contains fused 4*n* rings having an algebraic structure count of 2, the molecule could in theory possess the potential for being simultaneously olefinic, aromatic, and antiaromatic. Wilcox's synthesis has provided **65** as a dark red substance with long wavelength absorption and ^{1}H NMR shifts showing a marked paramagnetic ring current.[60] The compound is also thermally stable and highly reactive toward electrophiles. Thus, **65** may possess the complete range of predicted properties, but we must await further study before accepting the reality of this unusual phenomenon.



64 65

The pivotal position of bromocyclooctatetraene in gaining access to COT derivatives is further demonstrated by its usefulness as a convenient precursor to 1,2-dehydrocyclooctatetraene (**66**). Best prepared by the reaction of **42** with potassium t-butoxide, this highly reactive intermediate is capable of entering into a wide variety of addition reactions (Scheme 8).[61-63] Although **66** has not been isolated, its dibenzo analog **73** has been obtained in crystalline form. However, **73** is very unstable, the solid decomposing upon standing at room temperature for a few minutes.[64] In contrast, diacetylene **74** enjoys far greater stability than **73**, a finding recently construed as an indication that the nonannulated parent ring system (**75**) may be capable of more than fugitive existence.[64]



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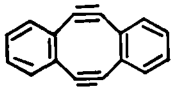

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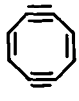
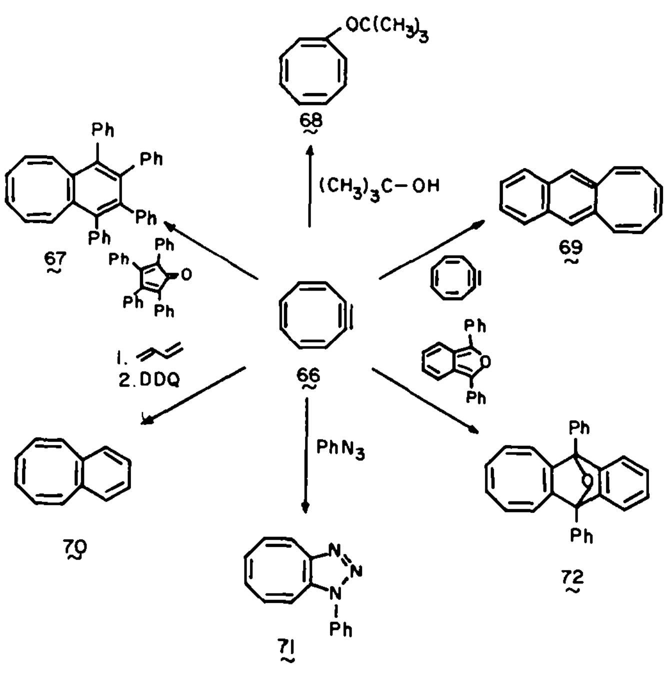
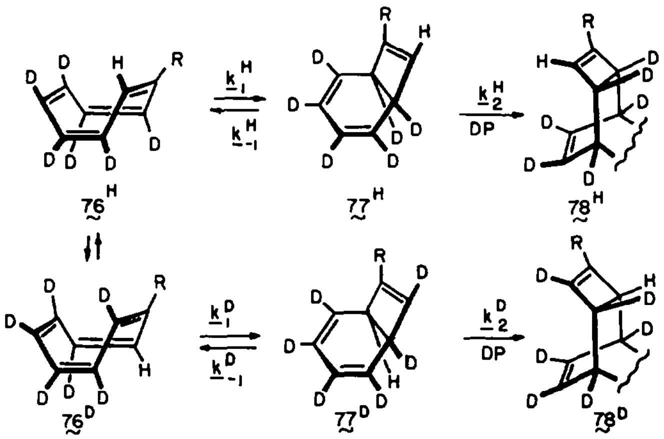


75

Cycloaddition reactions. Having identified the dynamic properties of the cyclooctatetraene nucleus, we can proceed to examine its involvement in various cycloaddition processes. Certainly the most widely studied of these is the Diels-Alder reaction in which the [8]annulene framework is required to play the role of 4π donor. As noted previously, however, the tub conformation of **2** deters attainment of requisite planarity by two neighboring double bonds, with the result that disrotatory ring closure to bicyclo[4.2.0]octatriene (**25**) generally precedes intermolecular bonding. The elegant work of Huisgen has shown not only that such preliminary valence isomerization is kinetically recognizable, but also that the rate-controlling step can vary as a function of the reactivity of the dienophile.[27] With sluggish dienophiles, the bimolecular addition is understandably rate-limiting. If the Diels-Alder reaction is very fast, then the ease of valence isomerism determines the rate. Intermediate stages are, of course, also possible. Although tedious dilatometric rate measurements were originally employed to elucidate the kinetic order, a simple experimental tool has recently appeared.[41] The test is dependent upon the correlatability of a predictable mechanistic trend (kinetic



Scheme 8.



a, R = CH_3 ; b, R = C_6H_5 ; c, R = $COOCH_3$; d, R = CN

Scheme 9.

order in this instance) with a somewhat unpredictable but mechanistically sensitive probe (secondary deuterium isotope effects).

For example, if valence tautomerism in hexadeuterio derivatives **76** occurs rapidly so that cycloaddition is rate-determining ($k_{-1} \gg k_2[\mathrm{DP}]$), the pertinent rate equation reduces to

$$\frac{\mathrm{d}\,\mathbf{78}^{\mathrm{H}}/\mathrm{d}t}{\mathrm{d}\,\mathbf{78}^{\mathrm{D}}/\mathrm{d}t}=\frac{[\mathbf{76}^{\mathrm{H}}]}{[\mathbf{76}^{\mathrm{D}}]}\frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{D}}}\frac{k_2{}^{\mathrm{D}}}{k_2{}^{\mathrm{D}}}\frac{k^{\mathrm{D}}_{-1}}{k^{\mathrm{H}}_{-1}}. \tag{1}$$

On the other hand, if the cycloaddition rate is very fast ($k_2[\mathrm{DP}] \gg k_{-1}$), then the ring closure is limiting and the rate equation is further simplified to

$$\frac{\mathrm{d}\,\mathbf{78}^{\mathrm{H}}/\mathrm{d}t}{\mathrm{d}\,\mathbf{78}^{\mathrm{D}}/\mathrm{d}t}=\frac{[\mathbf{76}^{\mathrm{H}}]k_1{}^{\mathrm{H}}}{[\mathbf{76}^{\mathrm{D}}]k_1{}^{\mathrm{D}}}. \tag{2}$$

Only when the two steps approach each other in rate does the kinetic expression (eqn 3) become rather unwieldy; nevertheless, the fractionation factors associated with adduct formation are so sensitive to the kinetic order that the observed gradation appears highly diagnostic.

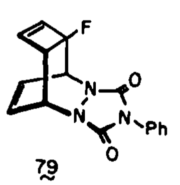
$$\frac{\mathrm{d}\,\mathbf{78}^{\mathrm{H}}/\mathrm{d}t}{\mathrm{d}\,\mathbf{78}^{\mathrm{D}}\mathrm{d}t}=\frac{[\mathbf{76}^{\mathrm{H}}]k_1{}^{\mathrm{H}}k_2{}^{\mathrm{H}}(k^{\mathrm{D}}_{-1}+k_2{}^{\mathrm{D}}[\mathrm{DP}])}{[\mathbf{76}^{\mathrm{D}}]k_1{}^{\mathrm{D}}k_2{}^{\mathrm{D}}(k^{\mathrm{H}}_{-1}+k_2{}^{\mathrm{H}}[\mathrm{DP}])}. \tag{3}$$

For the sliding scale of dienophilic [DP] reactivity ranging from maleic anhydride (MA, sluggish) to tetracyanoethylene (TCNE, moderately reactive) to dicyanomaleimide (DCMI, reactive), the four monosubstituted COT's **76** exhibit deuterium isotope effects ($\mathbf{78}^{\mathrm{H}}/\mathbf{78}^{\mathrm{D}}$) ranging from 1·08 to 1·55 (Table 2). The reactions of **76a** and **76b** with DCMI reach the limiting profile of eqn (2) and the isotope effect is uniquely k_1 dependent and small ($sp^2 \rightarrow sp^3$ hybridization in the transition state). The enormous k_H/k_D values resulting from the **76c** and **76d** cycloaddition reactions with maleic anhydride are viewed as the product of a multiplicative isotope effect ($k_1{}^{\mathrm{H}}k^{\mathrm{D}}_{-1}/k_1{}^{\mathrm{D}}k^{\mathrm{H}}_{-1}$) demanded of limiting behavior according to eqn (1). The remaining values are suggestive of a less imbalanced kinetic state of affairs (eqn 3). Thus, although all three dienophiles undergo cycloaddition to **76** with exclusive capture of the 7-substituted bicyclo[4.2.0]octatrienes (**77**), adduct formation is as sensitive to the nature of the ring substituent as to the dienophile.

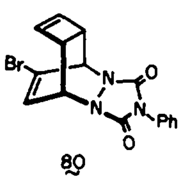
Table 2. Deuterium isotope effect data ($\mathbf{78}^{\mathrm{H}}/\mathbf{78}^{\mathrm{D}}$)[41]

	Dienophile		
Compd	MA	TCNE	DCMI
76a	1.26	1.08	1.08
76b	1.30	1.11	1.09
76c	1.55	1.39	1.20
76d	1.55	1.41	1.23

Further enhancement in the reactivity of the dienophile results in diminution of the regiospecificity of adduct formation. A recent detailed study of the trapping of isomeric monosubstituted bicyclo[4.2.0]octadienes with N-substituted triazolinediones has permitted assessment of electronic influences upon capture of the four possible quasi-planar diene systems.[65] The effects are wide-ranging and remain difficult to interpret completely. For example, the exclusive formation of **79** from fluoroCOT is not paralleled by other electron-withdrawing, but conjugatively interacting groups such as carbomethoxy and cyano which afford all four possible isomeric adducts.[65] When recourse is made to the indirect procedure of bromination → adduct formation → debromination,[65-67] the substituent can sometimes be directed to an alternative position in the adduct. BromoCOT (**42**) is an interesting case in point. Whereas **42** undergoes cycloaddition with PTAD to give chiefly the bromide analog of **79**,[68] the indirect method provides **80** exclusively.[65]

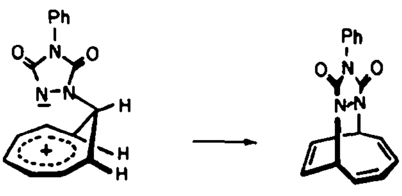


79



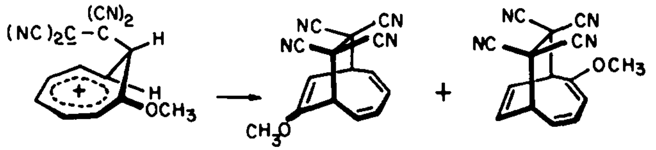
80

In contrast to most dienophiles, PTAD also exhibits a predilection for 1,4-cycloaddition to the monocyclic ring system.[65,69-71] Such behavior has been attributed to the ability of PTAD to enter into dipolar reactions and is the likely result of homotropylium zwitterion (**81**) intervention and subsequent intramolecular charge annihilation to



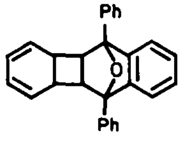
81 **82**

give **82**. Such 1,4 additions may be more accurately classified as electrophilic processes, a subject which is taken up later in the text. Suffice it to say that ring substituents are expected to play a significant role in directing cyclooctatetraene reactivity under these conditions, particularly as they influence the polarizability and electron density of the ring. This interplay of electronic effects is nicely illustrated by the behavior of methoxy-COT toward TCNE which proceeds exclusively via **83** to give adducts **84** and **85** rather than the more usual Diels-Alder products.[72]



83 **84** **85**

Sulfur monoxide adds to cyclooctatetraene in a 1,4-manner,[73] while 1,1-dichloro-2,2-difluoroethylene gives only the (2+2) adduct **86**.[74] Upon reaction with methyllithium, **86** is smoothly converted to the halogenated bicyclo[6.2.0]deca-2,4,6,9-tetraene derivative **87**, a colorless thermolabile liquid. As expected of a 1,3,5-cyclooctatriene derivative, **86** undergoes facile reaction with dienophiles. When dimethyl acetylenedicarboxylate is employed, the resulting adduct (**88**) can be thermolyzed to give bicyclo[2.2.0]hexene **89**, which when treated with methyllithium conveniently provides the Dewar benzene **90** (Scheme 10).[74]



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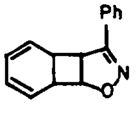
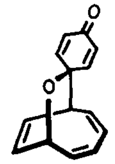


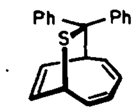
92

Cyclooctatetraene is also capable of dienophilic and dipolarophilic reactivity. In the presence of diphenylisobenzofuran for example, two isomeric adducts of structure **91** are obtained.[75] Tetrachlorocyclopentadienone ketals seemingly behave in analogous fashion, but further reaction gives isolable 2:1 adducts.[76] When COT is treated with nitrones,[77] nitrile oxides,[78] fulminic acid,[80] picrylazide,[81] or tetracyanoethylene oxide,[82] 1,3-dipolar addition occurs with ultimate formation of tricyclic structures such as **92** (from benzonitrile oxide). Subsequent chemical transformation of substances of this latter type has provided a useful synthetic entry to cyclobutane condensed heterocyclic systems.[77,78]

Interest in photochemical additions to cyclooctatetraene is on the upswing. The recent demonstration[83] that the 1:1 photoduct from benzoquinone is **93** rather than a 1,2 adduct[84] has been quickly followed by a report that irradiated thiobenzophenone likewise bonds to a conjugated diene segment with formation of **94**.[85] It seems that a more detailed examination of such excited state processes could prove highly informative.

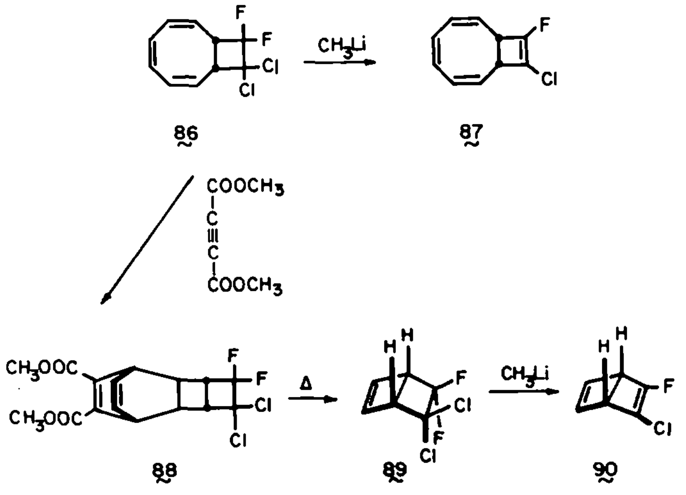


93



94

Electrophilic addition processes. By merely dissolving cyclooctatetraene in concentrated sulfuric acid, protonation occurs with formation of the monohomotropylium ion.[86] The ^{1}H NMR spectrum displays a series of signals in



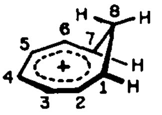
Scheme 10.

the ratio of 5:2:1:1, the chemical shifts of which are consistent with a delocalized structure enjoying considerable levels of 1,7 orbital interaction.[87-90] The attendant ring current in **95** appears chiefly responsible for the large difference in shielding observed for $H_{8_{endo}}$ and $H_{8_{exo}}$, a conclusion supported additionally by CMR studies[90,91] and theoretical calculations.[92,93] The process appears general for a wide range of substituted COT derivatives.[94-102]

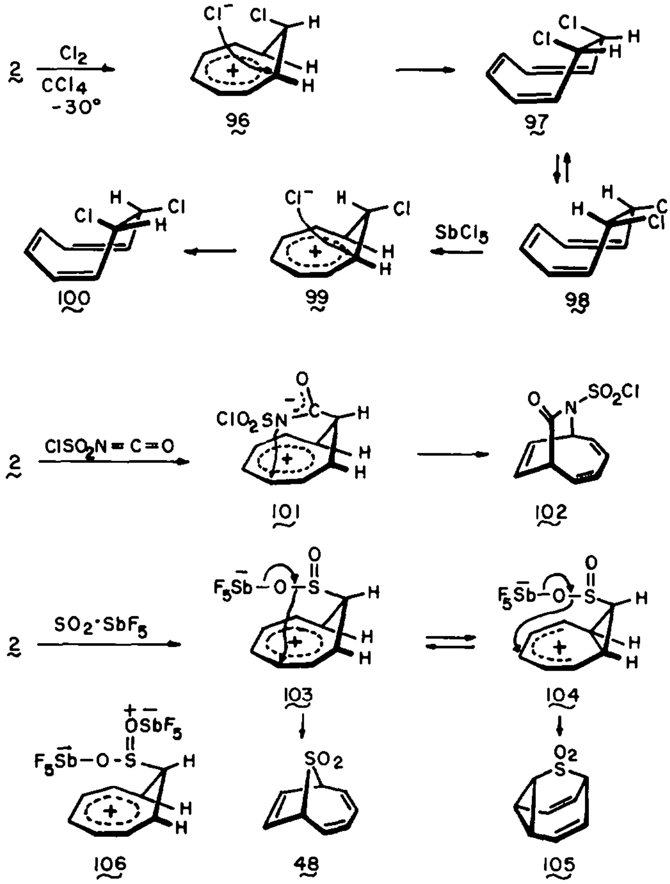
Treatment of **2** with D_2SO_4 at −15° results in positioning of the incoming deuterium at $H_{8_{endo}}$ to a level of approx. 80%.[103] On the basis of a number of more recent investigations, it now appears that electrophilic additions to COT proceed generally with high stereoselectivity from inside the tub conformation to produce *endo*-8-substituted homotropylium ions. In those cases where biparticulate electrophiles[104] such as chlorine[105] are involved, subsequent bonding of the counterion occurs at C_1 from that direction *syn* to the C_8 bridge. The result is formation of a *cis*-7,8-disubstituted cyclooctatriene. Treatment of **97** in dichloromethane with $SbCl_5$, SbF_5, $SnCl_4$ or $AgSbF_6$ produces the *exo*-8-chlorohomotropylium ion (**99**), presumably as the result of ionization from **98**.[106] Charge annihilation with covalent C–Cl bonding in **99** leads exclusively to **100** in accordance with the above generalization.

Although uniparticulate[104] electrophilic additions to COT likewise proceed with high stereoselectivity from the *endo* direction, intramolecular capture of the resulting zwitterions now generally utilizes a C_3 bonding scheme. The reactivity of **101**[107-109] and **103**[48,110] are exemplary. This reactivity difference may be a reflection of the energetic disadvantages to small ring formation experienced by these ions. The overall stereochemical consequences remain unchanged; however, 1,4-adducts now result. The SbF_5-promoted reaction of COT with liquid sulfur dioxide leads also to quantities of 9-thiabarbaralane 9,9-dioxide (**105**).[48] This one-step synthesis of a 9-heterobarbaralane is presumed to arise as the result of kinetically controlled cyclization of **104**. Although the formation of **105** represents an isolated example of 1,5-cycloaddition involving a classical bicyclo[5.1.0]octadienyl cation, it serves as an indication that the more stable homotropylium cations need not also necessarily be more reactive. Sulfones **48** and **105** both undergo rapid ring opening to **106** in the presence of 2–2·5 equivalents of SbF_5 in liquid sulfur dioxide at −50°.[110,111]

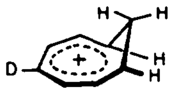
Upon storage at 32–37°, **95**-8-*endo*-*d* is converted with $\Delta G^{\neq} = 22{\cdot}3$ kcal/mole to its *exo* isomer in a reversible reaction.[103] Such *endo*-*exo* scrambling of the bridged methylene positions could result either by conformational inversion through a virtually planar classical cyclooctatrienyl cation or circumambulatory migration of C_8 around



95



the tropylium framework. Orbital symmetry restraints would presumably force the suprafacial [1,6] process to interchange the 8-*endo* and 8-*exo* substituents at each step.[112] In either scheme, homoaromaticity is temporarily sacrificed because of inadequate orbital overlap. The relative importance of the pair of mechanisms could not be judged *a priori*. However, investigations by Berson of ions **107** and **108**[113] and by Paquette of **109–111**[111] have shown these species to undergo *exo* equilibration without evidence of positional permutation. Conversion to the respective *exo* isomers must therefore necessarily occur with maintenance of the integrity of the seven tropylium positions. The non-least-motion circumambulatory rearrangement is therefore not implicated and ring inversion through the planar cyclooctatrienyl cation is seemingly the low energy pathway to C_8 epimerization.[92]



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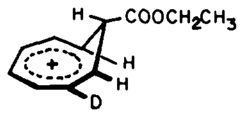

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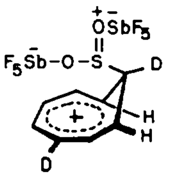

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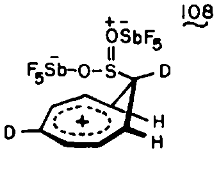

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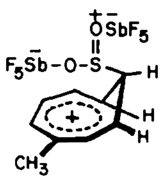
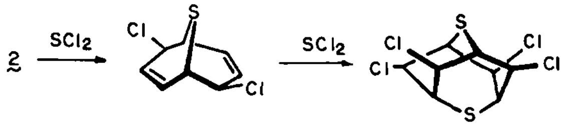


111

In methylene chloride solution at −10°, sulfur dichloride adds exothermically to **2** to give bridged adduct **112** in low yield.[114] A further transannular addition can be achieved upon introduction of a second mole of the reagent with formation of the 2,6-dithiaadamantane derivative **113**.



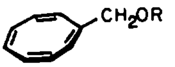
A synthetic application of SO_2 adduct **48** has been described earlier. Various other adducts have proven to be of considerable utility. Among these can be cited the dichlorides **97** and **98** which comprise the starting material for preparation of cyclobutadieneiron tricarbonyl[115,116] and N-chlorosulfonyl lactam **102** which is a precursor to various azabullvalenes.[117]

The marked susceptibility of cyclooctatetraene to electrophilic attack contrasts with the relative unreactivity of benzene under comparable conditions. This differing ease of protonation is comprehensible in terms of the conversion of polyolefinic **2** to resonance stabilized homotropylium cation (**95**) and the disruption of aromaticity which develops during formation of the benzenonium cation. Despite the energy disadvantage associated with the latter process, β-phenethyl derivatives frequently do solvolyze *via* σ-bridged phenonium ions.[118] Only recently has the latent potential of COT to function as a like neighboring group been examined.[38,119,120]

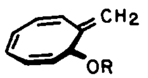
Cyclooctatetraenecarbinyl chloride (**114**) hydrolyses in buffered aqueous ethanol at a slower rate ($k_{40^\circ} = 4{\cdot}24 \times 10^{-5}$ sec^{-1}) than the structurally related homoallylic analog, Δ^1-cyclooctenylmethyl chloride ($k_{40^\circ} = 2{\cdot}16 \times 10^{-4}$ sec^{-1}).[38,119] This five-fold rate retardation does not necessarily signal the absence of anchimeric assistance, but probably is the consequence of sterically inhibited pπ interaction arising from the folded nature of the [8]annulene ring in carbocation intermediate **115**. Since the product mixture is comprised of **116a** (4%), **116b** (8%), **117a** (66%) and **117b** (22%), allylic rearrangement predominates.[121] Because hydrolysis of **114** proceeds with a $\Delta H^{\neq} = 20{\cdot}7$ kcal/mole, a mechanistic pathway dependent upon valence isomerization is excluded. The involvement of the 8-methylenehomotropylium ion is more difficult to dismiss and it remains a plausible kinetic intermediate. Isolation of **117a** and **117b** is seriously impeded by their rapid isomerization to *o*-tolylacetaldehyde (**118**),[119] particularly in the presence of trace quantities of acid. Extensive deuterium labeling studies have provided data showing that protonation of **117** does not result in return to the carbonium ion generated during the solvolytic procedure. Rather, proton transfer to the *exo* methylene carbon is believed to trigger formation of 8-hydroxyhomotropylium ion **119** which rearranges by way of the protonated 7-formylcycloheptatriene **120** to the aromatic product (Scheme 11).[119] It is seen that ring contraction of the 8-membered ring in **117a** takes place in two stages with concurrent stepwise construction of the sidechain. Entirely comparable mechanistic thinking serves nicely to rationalize the acid- and metal ion-catalyzed isomerizations of cyclooctatetraene epoxide and the aqueous mercuric acetate-promoted ring contraction of **2** to phenylacetaldehyde (two-carbon extrusions),[122–124] the conversion of **2** to cycloheptatriene 7-carboxaldehyde dimethylacetal with methanolic mercuric acetate (one-carbon extrusion),[124] and the rearrangement-ring contraction of 2-tropyl-2-phenethyl tosylate to 1,3-diphenylpropene under conditions of acetolysis.[125]

114

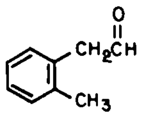
115



116a, R = H
b, R = C2H5

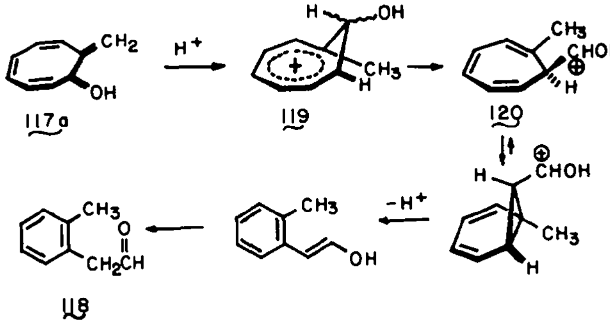


117a, R = H
b, R = C2H5

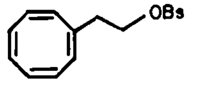


118

The solvolytic behavior of β-COTethyl brosylate (**121**)

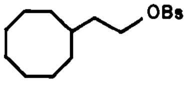


Scheme 11.



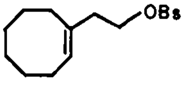
121

$k_{65°} = 6.58 \times 10^{-6}$ sec^{-1}



122

$k_{65°} = 1.43 \times 10^{-6}$ sec^{-1}



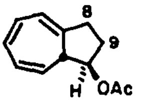
123

$k_{65°} = 3.74 \times 10^{-4}$ sec^{-1}

in buffered acetic acid is more akin to that of the fully saturated **122** than to that of **123**.[38] This comparison reveals that **121** is only moderately reactive; however, such comparisons can frequently be misleading.[126,127] Acetate **124** and the product of its further rearrangement, 1,2-dihydronaphthalene (**140**, R = H), are isolated in yields of 51–86% depending upon the buffer concentration. When the deuterated brosylates **125** and **126** are treated in an analogous manner, the isotopic label is seen to be distributed equally between carbons 8 and 9 of **124** in both cases.[38] That **124** arises from a symmetrical carbonium ion precursor is further substantiated by the behavior of **127**, the acetolysis of which gives a 1 : 1 mixture of **128** and **129**.[38] This intriguing rearrangement of **121**, **125**, **126** and **127** to tetrahydroazulenoid products imposes a number of limitations which are best satisfied by Scheme 12. Ionization of these brosylates is viewed as proceeding with participation by the double bond of the homoallylic systems with generation of intermediate spiro[7.2]nonatrienyl cations **130** which when R = H is a species of C_s symmetry. Whether **130** partakes of homoaromatic delocalization remains an open question. Subsequent conversion to cyclobutyl cations **131** and **132** initiates bond relocation[128–130] via **133** and **134** to the cycloheptatrienyl-norcaradienylcarbinyl cation pairs **135** ⇄ **137** and **138** ⇄ **141**. At high buffer concentrations, **135** and **138** capture acetate ion efficiently to give **136** and **139**. When the acetate levels are low, one such cation (**135**) can experience deprotonation with formation of dihydronaphthalene **130** via its valence isomer **137**. In contrast, the position of the R group in **141** precludes such aromatization.

When the sidechain is extended to three carbon atoms as in 3-cyclooctatetraenylpropyl *p*-nitrobenzenesulfonate, acetolysis gives at least 98% non-cyclized products.[120] In the case of 4-cyclooctatetraenylbutyl *p*-nitrobenzenesulfonate, cyclic products appear again (44%).[120]

Nonthermal structural reorganizations. The experiments now to be described corroborate the earlier claim that the polyolefinic nature of cyclooctatetraene lends itself to ready structural rearrangement. One must learn only how to make such bond reorganizations work to his advantage. A case in point is the "isomerization" of COT to semibullvalene (**145**) which would allow for the preparation of multigram quantities of this hydrocarbon and be of sufficient generality to be adaptable to derivatives of **145**. The generalized pathway which has been developed[131–135] is founded upon the smooth skeletal rearrangement which bishomocubanes undergo in the presence of silver(I) ion.[136,137] The direct route to **145** is summarized in Scheme 13 and is seen to involve sensitized photocyclization of Farnum's urazole diene (**142**),[138] transition metal-promoted isomerization of **143**, and alkaline hydrolysis-air oxidation of the diazasnoutane (**144**) so produced. In passing, it should be remarked that **144** represents a convenient, shelf-stable precursor to **145**. The overall transformation is seen to leave four of the original cyclooctatetraene



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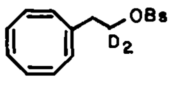

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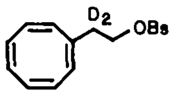

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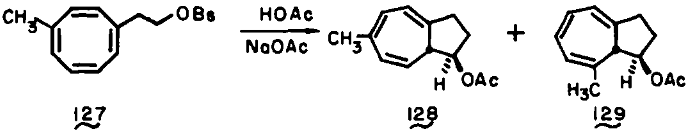
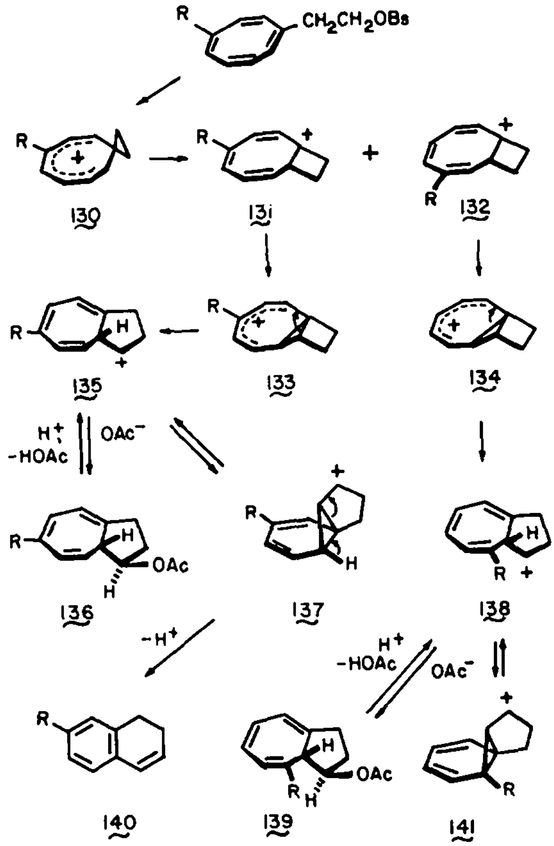


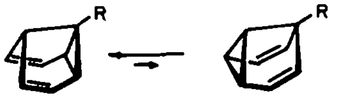
127 128 129



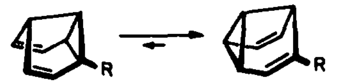
Scheme 12.

sp^2-hybridized carbons unaltered while transforming the remainder into cyclopropyl (3H) and aliphatic (1H) centers.

The two-step conversion of diazasnoutanes to semibullvalenes has proven entirely general, the method allowing for convenient access to 1(5)-, 2(4)- and 3-substituted derivatives.[135] In this connection, the question of electronic perturbation of the Cope equilibrium is immediately raised.[139,140] Analysis of the ^{1}H NMR spectra of derivatives of type **146** in the temperature range +40 to −120° has revealed the positional preference in all cases to be that with attachment of R to the cyclopropane ring as in **146a**. Equilibrium imbalance in this direction is maximized when R is cyano.[141] Comparable equilibrium data for **147** has shown isomer b to predominate.[135] Thus, there exists a bonding preference in the order olefinic > cyclopropyl > aliphatic irrespective of the electronic makeup of R. These energetic realities can be understood in some, but not all cases and sophisticated theoretical analysis of these questions is eagerly awaited.



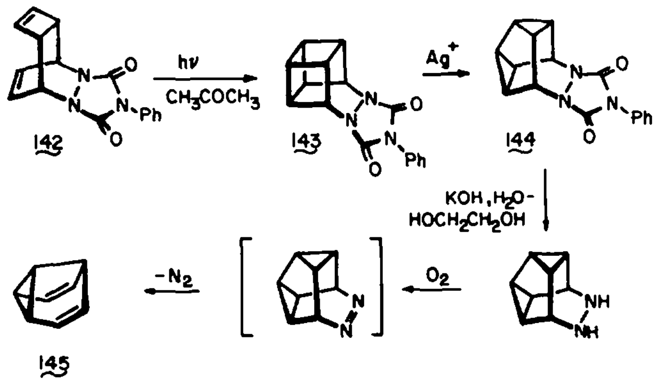
146a 146b



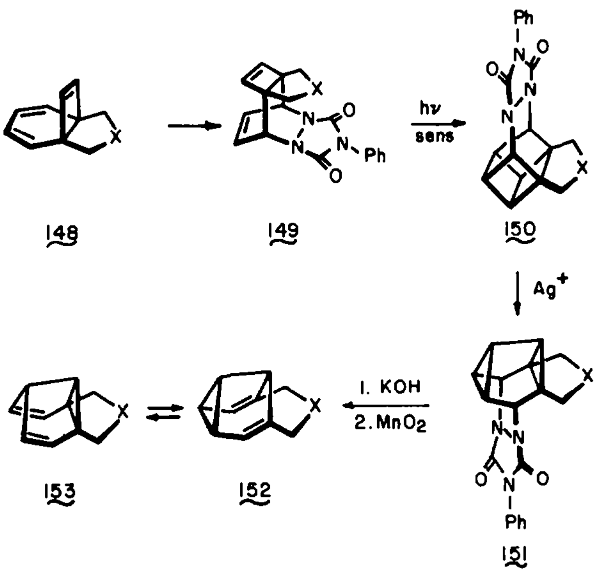
147a 147b

This marked sensitivity of semibullvalenes to substituent influences it also reflected in rather delicate responses to bracketing effects.[133,134] In contrast to the isomer pairs listed in Table 1, the **152** $\rightleftarrows$ **153** system does not possess a heavily weighted ground state preference for one of the constituent isomers since both forms are semibullvalenes. Wide variations in strain are no longer the necessarily dominant issue and consequently the various aliphatic chains might be expected to affect the position of equilibrium chiefly by inductive stabilization, provided that the "belt" is not excessively tight. Synthetic entry to such annulated semibullvalenes (Scheme 14) parallels that utilized above and is dependent upon the fact that propellatrienes of type **148** undergo Diels-Alder reaction with triazolinediones exclusively from the *endo* face to give adducts having proximal double bonds necessary for further elaboration of the cubyl framework.[133,134,142]

We see from the data in Table 3 that the assumedly lesser bracketing strain in **152a** $\rightleftarrows$ **153a** does not reveal itself by excessive weighting in the **152a** direction. Consequently, these systems are rather unlike those bracketed molecules studied earlier (Table 1) where it is recognized that lengthening of the bracket invariably leads to incrementally greater concentration levels of the monocyclic valence tautomer. The preferred directions of equilibrium for **152b** $\rightleftarrows$ **153b** and **152c** $\rightleftarrows$ **153c** are diametrically opposite, the tetramethylene derivative favoring valence isomeric form **152**. The equilibrium crossover which results from introduction of the double bond is believed to arise from the molecular constraints attending rehybridization from sp^3 to sp^2 at these sites. It is noteworthy that trimethylene bridged congener **d** does not attain compara-



Scheme 13.



Scheme 14.

Table 3. Computed equilibrium constants (K_{eq}) and Gibbs free energy values ($\Delta G°$) for the annulated semibullvalenes[133,134,142]

Compd	Bracket, X	Mole Fraction (40°) 152	153	K_{eq}, [152]/[153]	$\Delta G°$, cal/mole (40°)
a	$-CH_2CH_2CH_2-$	0.58	0.42	1.38	-200
b	$-CH_2CH_2-$	0.90	0.10	9.00	-1360
c	$-CH{=}CH-$	0.26	0.74	0.35	650
d	$-CH_2-$	0.43	0.57	0.75	175
e	-O-	0.003	0.997	3×10^{-3}	3600
f	-S-	0.105	0.895	0.12	1320
g	$>NCH_2C_6H_5$	0.071	0.929	7.6×10^{-3}	1600

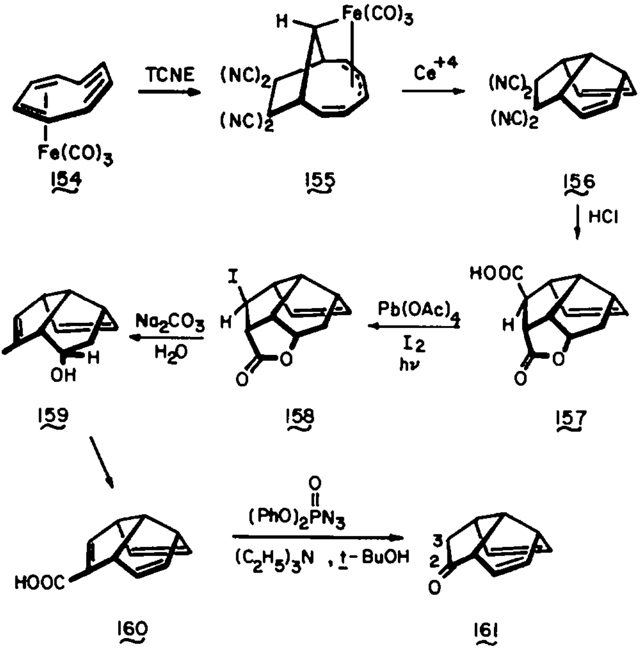
ble levels of the internal cyclopropane isomer (**153**) under the same conditions. However, replacement of the X=CH_2 group by a heteroatom results in a substantial shift in the direction of **153**. Although the level of equilibrium imbalance is seen to vary somewhat as a function of the heteroatom, a decided preference for that bonding arrangement where the cyclopropane ring occupies a central position is obvious. Consequently, those structural perturbations which involve an enhancement of electronegativity demands and enlargement of the bracket seemingly work together to favor **153**.

Because pentamethylene derivative **152a** ⇄ **153a** exists as a rather equitable distribution of valence isomers and possesses a K_{eq} having a reasonable temperature dependence, direct observations of two nondegenerate semibullvalene isomers has proven possible for the first time.[143] At the slow exchange limit (−120°), the ^1H NMR resonances clearly show 84% of **152a** and 16% of **153a** to be present, corresponding to a $\Delta G°$ of 505 cal/mole. As the temperature is allowed to increase, however, **153a** gradually gains the concentration advantage![134,143]

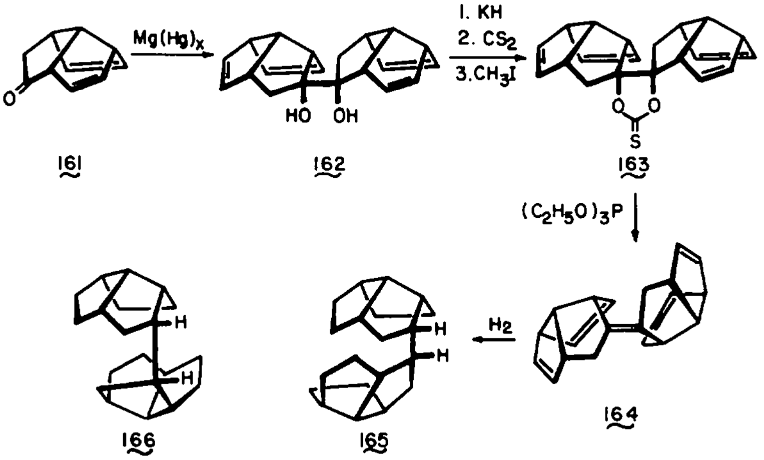
As will be discussed later, the chemical properties of cyclooctatetraene derivatives are substantially modified through coordination to a metal center. The course of the reaction of cyclooctatetraeneiron tricarbonyl (**154**) with tetracyanoethylene is of particular interest at this point, however, since 1,3 bonding to give **155** operates[144,145] to the exclusion of other pathways (erroneously formulated at an earlier date[146]). This unprecedented mode of cycloaddition, when coupled with the subsequent oxidative removal of iron from **155**, leads in high yield to the functionalized triquinacene derivative **156** (Scheme 15). This tetranitrile is readily converted to carboxylactone **157** by acid hydrolysis and this latter compound has been shown to be a most serviceable precursor to optically pure (+)-triquinacene-2-carboxylic acid (**160**)[147] and (+)-2,3-dihydrotriquinacen-2-one (**161**).[148] In an overall sense, therefore, atoms C_2 and C_3 in **161** arise from the trigonal carbons of TCNE, while the remaining eight carbons owe their origin to the COT ligand in **154**.

Our interest in chiral **161** derives from the possibility that suitable dimeric coupling of this ketone might lead to a potential precursor to dodecahedrane. Because the projected 1,4-disubstituted dodecahedrane is of C_2 symmetry, bonding between precursor halves of the same configuration becomes necessary.[147–149] With magnesium amalgam and trimethylchlorosilane in dry tetrahydrofuran, optically pure **161** undergoes pinacolic reduction exclusively with *exo,exo* carbon bond formation to give diol **162** (Scheme 16). Conversion of **162** to its thionocarbonate (**163**) and subsequent treatment with triethylphosphite provides olefin **164** stereospecifically. Catalytic hydrogenation gives rise cleanly to hydrocarbon **165** to which the trivial name *dl*-bivalvane has been appended.[149] It is important to distinguish **165** from *meso*-bivalvane (**166**) which has also been synthesized. The latter is constructed of two halves having opposite configuration; hypothetical transannular bonding of nearest carbon atoms cannot provide dodecahedrane but an isomer constructed of six- and four-membered rings. This is not so with **165**. Attempts to elaborate the dodecahedrane nucleus by chemical manipulation of **164**, **165**, and more highly functionalized derivatives are currently receiving attention.

Thermally promoted reactions. When heated neat in the temperature range 130–170°, cyclooctatetraene is dimerized to two highly caged hydrocarbons.[150–153] At temperatures in the vicinity of 100°, the simpler dimers **167** and **168** are formed instead.[154–156] Subsequent photo-fragmentation



Scheme 15.

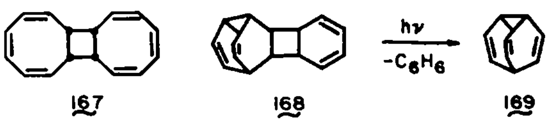


Scheme 16.

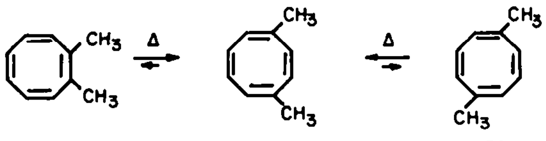
of **168** completes the quite remarkable two-step synthesis of bullvalene (**169**).[155,157]

The transition from liquid phase to gas phase has proven equally rewarding despite early indications to the contrary.[158] Under rather controlled conditions, for example, closure to dihydropentalene is realizable.[159] Also, the thermally induced isomerizations of the 1,3,5,7-tetramethyl[160] and octamethyl derivatives[161] to semibullvalenes have been achieved. This group of reactions seemingly occur via bicyclo[3.3.0]-octadienediyl intermediates produced upon transannular bonding.

Despite the extraordinary richness of this [8]annulene chemistry, discovery of the degenerate thermal behavior of COT and skeletal rearrangement of isomeric cyclooctatetraenes was not made until 1972.[162] In fact, variously derivatized COT's as well as the parent hydrocarbon itself are now recognized to indeed possess the fascinating capability for structural interconversion. That the constituent carbon atoms of the cyclooctatetraene ring find it possible to undergo deep-seated scrambling with reconstruction of the [8]annulene frame more rapidly than aromatization or other destructive irreversible reaction must be viewed as remarkable.



Clues to the mechanism of this rearrangement are available from several sources. Firstly, we see that both 1,2- and 1,5-dimethylcyclooctatetraenes (**170** and **172**) are first isomerized to the 1,4 isomer (**171**) at approximately 425° and 18 mm.[162] Secondly, the thermal activation of benzo fused derivative **173** requires much higher temperatures; although migration of deuterium first to C_4, C_7 (cf. **174**) and subsequently to C_5, C_6 is seen, the need for highly elevated temperatures leads also to competitive fragmentation. These excessive conditions have been interpreted



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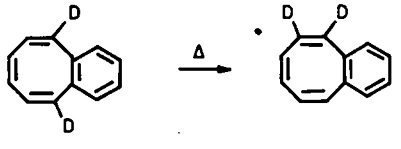


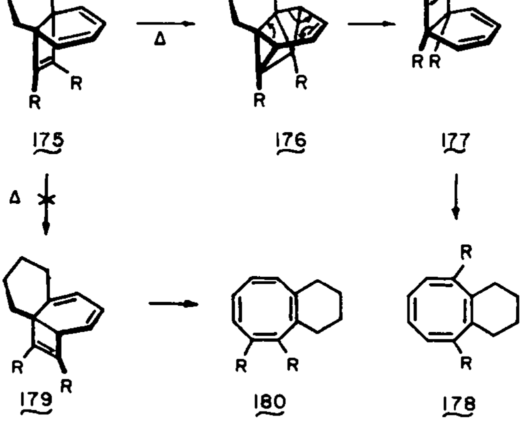
173 174

to be the result of short-circuiting by the benzo ring of the preferred rearrangement pathway.

Importantly, moderate heating of annulated bicyclo[4.2.0]octatrienes (**175**) results in like structural rearrangement with formation of 1,2-bridged cyclooctatetraenes (Scheme 17).[163] As a consequence of the behavior of the 11,12-dideuterio and 11,12-dimethyl derivatives, strong evidence has been gained for the intermediacy of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octenes (**176**). Thus, the intramolecular Diels-Alder pathway operates to the apparent exclusion of the [1,5]sigmatropic shift mechanism.

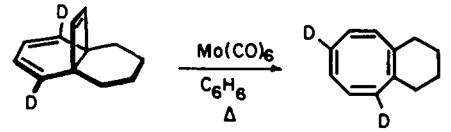
On this basis, it appears that cyclooctatetraenes rearrange thermally chiefly by analogous initial valence isomerization to one or more bicyclo[4.2.0]octatrienes, followed by intramolecular ($_{\pi}4_s+_{\pi}2_s$) cycloaddition to give tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene intermediates, and ultimate ($_{\sigma}2_s+_{\sigma}2_s+_{\pi}2_s$) bond shift in these *cis*^{2}-bishomobenzenes. The new bicyclo[4.2.0]octatrienes which arise in this manner must inescapably lead to a cyclooctatetraene carbon network different from that of the starting material. [1,5]Sigmatropic shift mechanisms do also gain importance in the monocyclic examples, but such pathways never appear to gain dominance.

The kinetically preferred Diels-Alder reaction of propellatrienes **175** can be efficiently blockaded and redirected in the presence of a transition metal catalyst such as Mo(CO)$_6$, the coordinative powders of which do not permit involvement of all six pπ electrons required for passage to **176**.[164] The parent hydrocarbon (**35**) is again converted to **178** (R = H) when heated at reflux with Mo(CO)$_6$ in benzene. The differing course or rearrangement is clearly revealed by the behavior of dideuterio-**175** (R = D) which under these conditions no longer affords **178** (R = D) but instead **180** (R = D).[164]



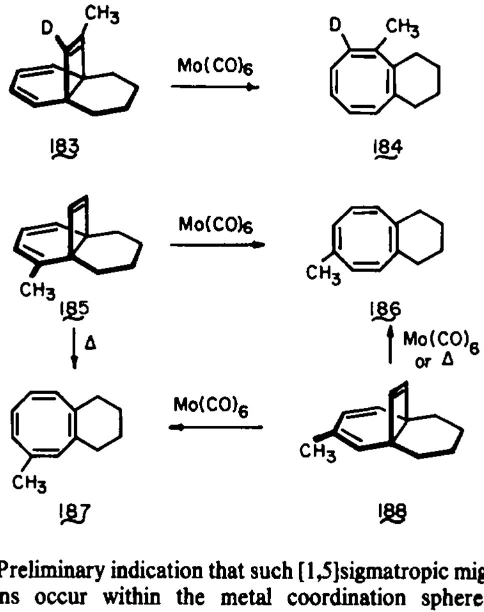
Scheme 17.

In this connection, the isomeric dideuterio propellatriene **181** is of special interest since its Mo(CO)$_6$-promoted isomerization exclusively to **182** connotes that [1,5]sigmatropic shifting of a trigonal cyclobutene carbon is formally operative.[165] When treated with Mo(CO)$_6$ in

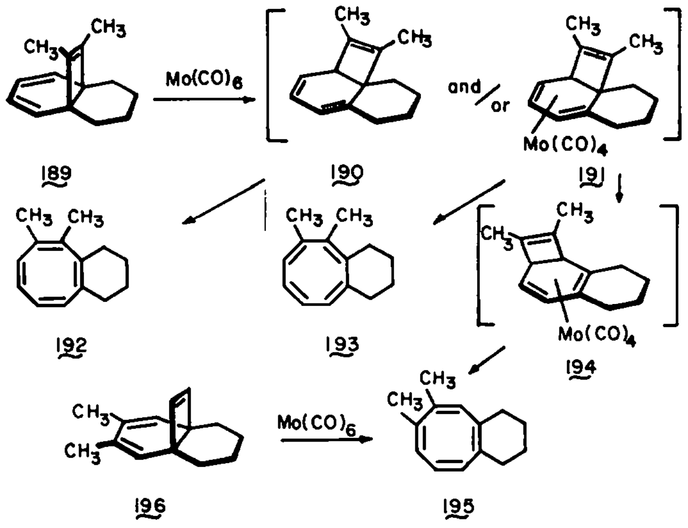


181 182

anhydrous fashion, **183** is converted cleanly to **184** while **185** is isomerized to **186**. As expected from our earlier discussion, thermal rearrangement of **185** leads instead to **187**. In the **183** and **185** examples, therefore, regiospecific 1,5 displacement of one cyclobutene carbon occurs while the other functions as a fulcrum. In **183** the less substituted carbon migrates preferentially, while **185** exhibits marked proclivity for migration toward the more highly substituted terminal butadiene carbon.[165] Since **188** provides both **186** and **187** during metal-promoted isomerization, the methyl substituent in this triene appears to be too distant to exert a directive effect.



Preliminary indication that such [1,5]sigmatropic migrations occur within the metal coordination sphere is available from the behavior of dimethyl propellatriene **189**.[166] Depending upon the level of pπ interaction to the Mo atom, hypothetical intermediates **190** and **191** would be expected to follow differing valence isomerization pathways. Insofar as the free ligand (**190**) is concerned, ring opening should operate under the control of the 1,3-cyclohexadiene moiety and lead by disrotatory central bond cleavage exclusively to **192** (Scheme 18). In metal complex **191**, disrotatory opening of the cyclobutene ring may result as the consequence of different prevailing orbital interactions;[167] with such constraints, bond shift isomer **193** can be expected. Since annulated cyclooctatetraenes **192** and **193** possess four vicinal substituents, the barrier to bond shifting is sufficiently enhanced that their isolation as discrete entities is possible (*vide supra*). The

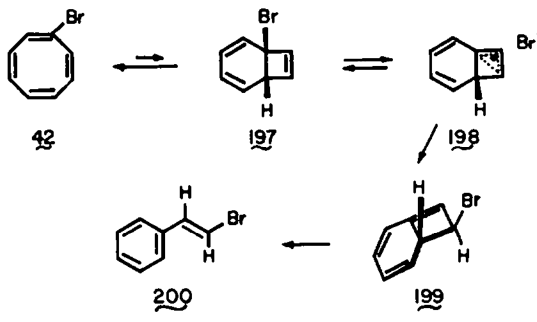


Scheme 18.

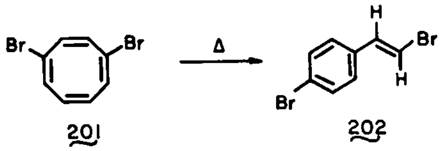
product mixture consists of *ca.* 36% **192**, 40% **193** and 24% **195**.[166] These data reveal not only that the two stable bond shift isomers are produced in comparable quantities, but also that two-fold cyclobutene circumambulation can occur along the periphery of the 1,3-cyclohexadiene unit. At this present level of insight, therefore, the propellatriene isomerization seemingly requires metal-ligand coordination of a rather specific type (**192** and **193** do not interconvert under the reaction conditions). Continuing studies are anticipated to shed light on more intimate mechanistic details.

Analogous rearrangements have not been encountered with simpler monocyclic cylooctatetraenes, very likely because the concentration levels of bicyclo[4.2.0]octatriene valence isomeric forms are low and the monocyclic structures otherwise provide a ready template for coordination[168] with attendant consumption of the active reagent.

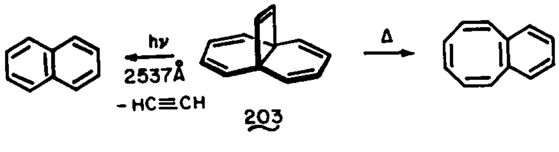
The presence of a halogen atom on the cyclooctatetraene ring promotes an entirely different reaction. Thus, bromocyclooctatetraene (**42**) at 100° is readily converted to *trans*-β-bromostyrene (**200**).[169] When **42** is rearranged in the presence of lithium iodide in acetone (80°), *trans*-β-iodostyrene is isolated in addition to **200**. Yet, **200** does not undergo halogen exchange under these conditions.[170] This and other exchange experiments indicate the presence of a reversible ionization step in the rearrangement scheme. Since the rate of reaction is solvent dependent, the ionization must be involved in the rate-determining step. These findings led Huisgen and his coworkers to propose that the reaction pathway proceeds by valence tautomerization to **197** which is subject to ionization with formation of the homocyclopropenium salt **198** (Scheme 19).[170,171] Ion recombination leads to cyclobutene derivative **199** which provides final product by conrotatory ring opening. This mechanism requires that the bromine in the starting material experience a 1,3 shift and no longer be attached to the original carbon atom. In accord with this analysis, dibromide **201** is converted in 92% yield to **202** when injected onto a VPC column heated to 180°.[171]



Scheme 19.



Photoisomerizations. There is ample evidence that light energy can effect the interconversion of cyclooctatetraene bond shift isomers.[18,22] At −60° in isopentane solution with acetone as sensitizer, cyclooctatetraene is converted to semibullvalene and benzene as the major volatile products.[160,172] In contrast, 1,3,5,7-tetramethylcyclooctatetraene is unreactive to these conditions. That the photo-induced aromatization process probably occurs through bicyclic valence isomer **25** is supported by its ready conversion to benzene when comparably irradiated. Propellatriene **35** and propellapentaene **203** behave analogously, loss of acetylene with formation of tetralin and naphthalene occurring rapidly upon exposure to 2537 Å light.[163] The contrasting thermal reactivity of **203** is noteworthy.



Electrochemical reducibility. The electrochemical reduction of cyclooctatetraene continues to be extensively examined despite two decades of active investigation. Early polarographic studies in aqueous ethanol[173] or 96% dioxane-water[174] revealed the reduction to be a two-electron process. When later examined under aprotic conditions (dry dimethylformamide solution), the actual process was seen to comprise two well-resolved one-electron steps.[175] Although the rate of the first electron transfer to COT is apparently quite slow, the second is rapid.[175,176] The retardation of the initial reduction step has been attributed to the energetically demanding activation barrier associated with conversion of the folded neutral molecule to a planar or nearly planar species at the transition state. A similar conformational distortion is not required for subsequent introduction of the second electron and it occurs with greater facility. More recent results in Anderson's laboratory obtained on anhydrous tetrahydrofuran solutions (Me_4N^+ salts as electrolyte) have been interpreted to mean that the electrochemistry of COT is limited in the accessible potential region to a one-electron reduction and that under commonly employed conditions the radical anion is protonated (e.g. by Hofmann elimination of the quaternary ammonium electrolyte, usually $(n\text{-Bu})_4N^+$ salts) with subsequent reduction of the radical occurring at a potential slightly more negative than the tetraene itself.[177] However, simultaneous electrochemical electron spin resonance studies by Allendoerfer rule out the possibility of such an *ece* mechanism.[178] Rather, the data conform uniquely to the earlier postulated *eec* sequence. This means that one or more alternative explanations must be sought for Anderson's phenomenon and these will presumably involve specific ion pairing[179,180] or electrolyte effects,[181,182] or a specific reaction between Me_4N^+ and $COT^{\cdot-}$ which is not seen with higher tetraalkylammonium ions.

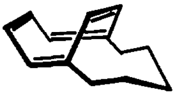
The electrochemical behavior of methoxy-,[183] benzo-,[184] dibenzo-[184,185] 1,3,5,7- and 1,2,4,7-tetraphenylcyclooctatetraenes[186] has also come under scrutiny by various groups. The widely variant inherent structural features of these derivatives and the differing experimental conditions employed in certain cases unfortunately do not make it possible to directly correlate halfwave potential with substituent permutation. In this context, the recent polarographic study of the four possible isomeric dimethylcyclooctatetraenes is rather informative.[50] The electrochemical behavior of this family of hydrocarbons in dry tetrahydrofuran ($Bu_4N^+ClO_4^-$ as electrolyte) is striking in that the $E_{1/2}$ values for the first wave appear to be a linear function of the distance separating the methyl groups (Table 4)! This effect may have its origin chiefly in steric parameters but this rationalization requires support from more varied examples. Significantly, the first waves are non-Nernstian, the irreversibility of the reductions being establised by cyclic voltammetry down to −78°.[50] Coulometric studies confirmed fractional electron uptake (n_{app} 1–2). Clearly, our understanding of the generation, structure,[187] and fate of COT radical anions leaves much to be desired. The corresponding dianions, formed independently by reaction with potassium in liquid ammonia, are stable, planar and diatropic (^{1}H NMR analysis).

Polarographic reduction of the tetramethyl bond shift isomers **15** and **16** in anhydrous hexamethylphosphoramide occurs virtually at the onset of discharge by solvent (−3·7 and −3·6 V vs s.c.e., respectively).[21] This technique provides therefore a quantitative measure of the difficulty experienced by these [8]annulenes in attaining a planar conformation. Expectedly then, the annulated polyolefin **204** is not reduced under such experimental conditions because of the structural inhibition to attainment of planarity by the cyclooctatetraene ring.[188]

Table 4. Summary of polarographic data[50]

Compd	$E_{\frac{1}{2}}$ (first wave)^a	$E_{\frac{1}{2}}$ (second wave)^a
1,2-Me_2COT	-2.33	-3.0
1,3-Me_2COT	-2.25	-3.07
1,4-Me_2COT	-2.22	-3.02
1,5-Me_2COT	-2.14	-2.95

^{a}Volts vs s.c.e.



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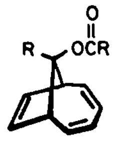
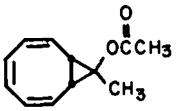
To all appearances, the COT radical anion is effectively planar.[174,189–192] There is no question about the planarity of the dianion species. A recent crystallographic structure analysis of K_2COT·diglyme has established that this state of affairs also persists in the solid state.[193] All eight atoms of the ring in this solvate lie within 0·01 ± 0·01 Å of the plane and the average C–C bond length is 1·40 ± 0·02 Å. The related molecule K_2-1,3,5,7-Me_4COT·diglyme is structurally comparable.[194]

Chemistry of cyclooctatetraenyl dianions. Upon reaction with proton sources, dilithio- and disodiocyclooctatetraenide yield mixtures of 1,3,5- and 1,3,6-cyclooctatrienes.[195] Alkylation reactions are equally indiscriminate as to site substitution.[196–198] With various acyl halides, in contrast, **3** behaves as a 1,2- and a 1,4-dicarbanionic reagent to provide structurally interesting and useful products. Thus upon treatment of **3** with acetyl and benzoyl chlorides, the bicyclics **205** and **206** are formed together with ring-opened products.[199] Presumably, the intermediate 7-acylcyclooctatrienyl anions which intervene can undergo either bicyclization and acylation to give **205** and/or **206**, or vicinal acylation with subsequent formation of 1,8-diacyl-1,3,5,7-octatetraenes. Dianion **3** also reacts with aldehydes and ketones to yield 5,8- and 7,8-bis(α-hydroxyalkyl)cyclooctatrienes.[200] Carboxylation yields chiefly 2,4,6,8-decatetraene-1,10-dioic acid, evidently by electrocyclic ring opening of the initially produced 1,3,5-cyclooctatriene-7,8-dicarboxylic acid.[201]



R = CH_3, C_6H_5

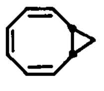
205



206

The reactions of **3** with doubly functionalized electrophilic reagents are perhaps the most interesting. As shown by Katz and Garratt,[10,202] dichloromethane and chloroform enter into condensation with formation of **207** and **208**. The latter chloride is a readily available precursor of the cyclononatetraenide anion (**209**) to which it is converted upon treatment with lithium or potassium metal.[10,102] Vicinal dialkylation continues to predominate when 1,2-dihaloethanes (→**210**)[203] and 1,3-dihalopropanes are employed.[204] In the latter situation, the tricyclic isomer (e.g. **212**) is the valence tautomer which ultimately predominates.

Dichlorophenylphosphine likewise reacts with



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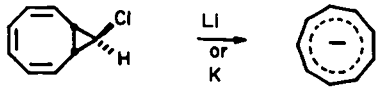
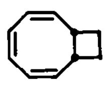


208 209



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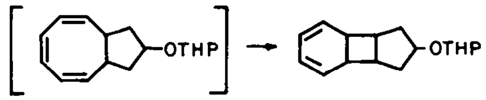
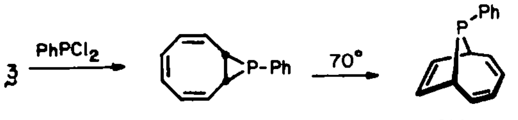


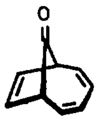
211 212

COT^{2-} exclusively by 1,2 addition, while sulfur dichloride simply causes oxidation to return COT in good yield.[205] When warmed to 70°, the phosphine initially formed (**213**) is isomerized to the bridged isomer **214**.



213 214

With dimethylcarbamoyl chloride[206] or phosgene,[207] **3** is converted directly by 1,4 adddition to bicylo[4.2.1]nona-2,4,7-trien-9-one (**215**), a theoretically important ketone.[208] The derived carbene, cation, radical, and carbanion are currently receiving attention in the context of their possible bicycloaromatic properties, as is exomethylene derivative **216**.[209,210] Photorearrangement of **215** leads directly to barbaralone (**217**),[32,206,211] this photorearrangement comprising a most convenient access route to this fluxional molecule. The ketoxime of **215** undergoes Beckmann fragmentation to give cyanocyclooctatetraene rather than lactam formation when treated with *p*-toluenesulfonyl chloride in pyridine.[206] Other types of ring expansion reactions are however realizable in high yield.[212-214]



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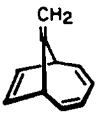

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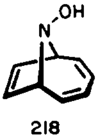
217

In parallel fashion, the reaction of COT^{2-} with isoamyl nitrite leads by formal 1,4 bridging to the bicyclic hydroxylamine **218** which upon zinc-acetic acid reduction is transformed to the parent 9-azabicyclo[4.2.1]nona-2,4,7-triene ring system.[215] Quaternization of **218** by benzyl bromide results in N-alkylation from the less congested etheno bridge direction to give **219**, treatment of which with potassium carbonate affords the corresponding amine oxide. Remarkably, titanium trichloride reduction of **218** provides pyrrocoline (**220**), perhaps with intervention of the nitrenium ion.[215]

The cyclooctatetraene radical cation. Our knowledge of the cyclooctatetraene radical cation is quite limited. Dewar's theoretical calculations of this molecule lead to the prediction of a nonplanar structure.[216] Recent experimental assessment of this question has been made by Dessau who prepared $COT^{\cdot+}$ in trifluoroacetic acid by cobaltic ion oxidation of **2** in a rapid mixing flow system.[217] Under these conditions, the ESR spectrum consisted of seven equally spaced lines (J = 1·5 G), the intensities of which were consistent with splittings caused by eight equivalent hydrogen atoms. For the planar radical anion, the reported proton splitting is 3·2 G;[189] the two ions cannot therefore be of identical geometry. The decreased magnitude of the interaction is best accounted for in terms of a nonplanar configuration for the radical cation, in agreement with theory.



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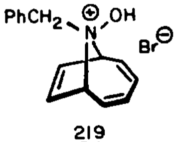

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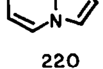
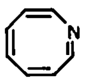


220

π-Equivalent nitrogen substitution

Azocine chemistry. A provocative challenge that the Hückel theory has posed to the organic chemist is its implication that π-equivalent heterocyclic congeners of "aromatic" molecules should possess comparable electronic properties. Although the nitrogen analog azocine **221** is expectedly unstable,[218] 2-methoxy derivatives (e.g. **222**) do not share this sensitivity and are readily synthesized (Scheme 20).[219] The method which is general in scope is based upon the monocycloaddition of chlorosulfonyl isocyanate to a 1,4-cyclohexadiene, followed by reduction and O-methylation of the N-(chlorosulfonyl) β-lactam (**223**), and ultimately bromination-dehydrobromination of the azetine so produced (**224**). The valence isomerization of these heterocycles has been examined. Although the tautomeric 7-azabicyclo[4.2.0]-octatriene forms such as **225** never gain a concentration gradient which permits them to be spectroscopically seen or identified, they can be trapped in Diels-Alder reactions. Adducts of type **227** are thereby produced. When recourse is made to bracketing effects, the situation is reversed and triene tautomers (**228**) predominate provided that the strain imposed on the azocine form remains sufficiently great ($n \leq 5$, Table 1).[35,219]



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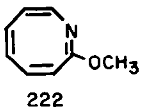
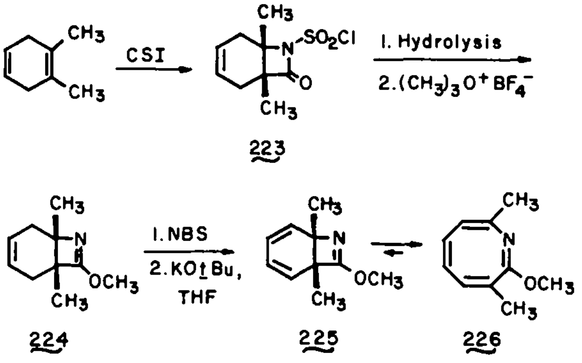
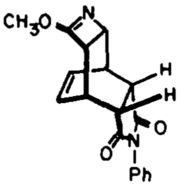


222

The azocines present an electrochemical profile strikingly different than their cyclooctatetraene counterparts.[220] In each of the examples studied, only a single polarographic reduction wave is seen, the diffusion current of which is clearly indicative of an overall two-electron transfer. These findings reveal that azocine radical anions are more easily reduced than the parent heterocycles, resulting in the immediate introduction of a second electron to form the stable dianion. In order to account for the immediate introduction of a second electron in this manner, an amount of stabilization equivalent to at least 0·4 V must be available to the azocinyl radical anions. The



Scheme 20.



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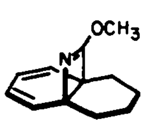


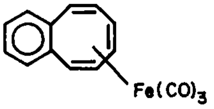
228

favorable energy gain upon formation of a ten π-electron aromatic anion is thought to be responsible,[221] and this conclusion is supported by the ^{1}H NMR spectral properties of the chemically generated (K, NH_3) azocinyl dianions.[221,222] The combined effects of extensive charge delocalization and appreciable ring current lead to substantial deshielding of the ring substituents. Such azocinyl dianions appear stable and do not undergo skeletal rearrangement. Protonation reactions occur initially at C_4, C_6 and C_8;[222] attack at the first two sites is predominant and this positional selectivity carries over to alkylation reactions.[223] When benzophenone is employed, the C_6 monoalkylation products (e.g. **228**) are stable, but the products of initial C–C bond formation at C_4 lead ultimately to 2,3-pyridocyclobutene derivatives (**229**) by valence isomerization, intramolecular [1,5] hydrogen shift, and aromatization with loss of methanol (Scheme 21).[223]

Electron delocalization in the azocinyl dianions is significantly affected by benzo fusion to the 8-membered ring,[224] but not to the extent that aromatic character is lost.[221] Such seemingly occurs when the ring size is homologated to the 1,6-methano[12]annulene level.[225]

Chemistry of metal complexes. The study of iron carbonyl complexes of cyclooctatetraene, first discovered more than 15 years ago,[226–228] has been actively pursued because of their especially intriguing fluxional character.[229–246] The early dilemma surrounding the true structure of the red 1:1 complex **154** arises from the fact that the iron atom must be η^4 bonded to the cyclooctatetraene ring which must therefore possess two uncoordinated double bonds. Yet, the IR spectrum shows no band attributable to such unsaturation and the ^{1}H NMR spectrum consists of a single line denoting the equivalency of all eight protons at room temperature. Additionally, the compound cannot be catalytically hydrogenated and is very reluctant to enter into cycloaddition reactions of the Diels–Alder variety. But Lipscomb's X-ray crystal structure analysis showed the iron tricarbonyl moiety to be bonded to two adjacent double bonds in the solid state as expected on theoretical grounds. Recourse was made to low temperature ^{1}H NMR spectroscopy, but interpretations still varied widely.[231,232–236] Finally, agreement has been reached that the stereochemical non-rigidity of **154** arises by a very rapid sequence of [1,2] shifts, a conclusion supported by ^{13}C NMR data.[246]

Comparison of the activation energies for this process in **154** (7·2 kcal/mole[233]) with those in benzocylooctatetraeneiron tricarbonyl (**230**, 18·6 kcal/mole) and its 2,3-naphtho analog (**231**, 31 kcal/mole)[240] probably reflects the



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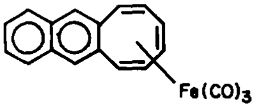

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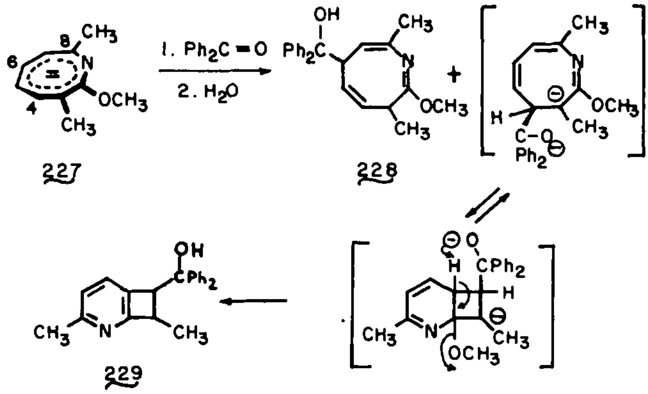
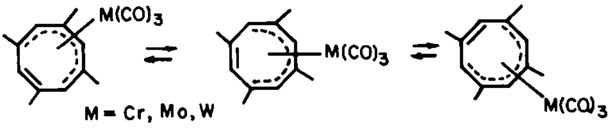


Scheme 21.

differing energy requirements for attaining ortho quinonoidal character in certain of the intermediates. At the experimental level, **230** and **231** provide well resolved low-temperature ^1H NMR spectra of a quality difficult to achieve with the parent iron complex. However, cyclooctatetraeneruthenium tricarbonyl has been reported to exhibit well defined limiting spectra.[247,248] Although only meager details are available for $C_8H_8Os(CO)_3$, it appears that the $Os(CO)_3$ group moves more slowly around the ring than either $Fe(CO)_3$ or $Ru(CO)_3$.[249]

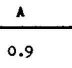
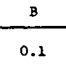
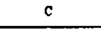
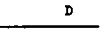
In the chromium family of cyclooctatetraene complexes, the ligand is required to supply 6π electrons to reach the next inert gas configuration, as contrasted to the iron family where 4 electrons are necessary. Thus, in the $Cr(CO)_3$, $Mo(CO)_3$ and $W(CO)_3$ series the metal will coordinate to three olefinic bonds. The variable temperature ^1H NMR spectra of these molecules[233,250] are exceedingly complicated and for this reason the reported activation energies are probably erroneous. By making recourse to the complexes of 1,3,5,7-tetramethylcyclooctatetraene, Cotton was able to reduce spin-spin coupling among the ring protons, lower the symmetry of the molecules, and consequently determine the rearrangement pathway.[251] X-ray crystallograpic studies have provided important detailed molecular dimensions.[252,253] In the temperature range −23 to +70°, the spectra implicate exchange of **232a** and **232b** only, i.e. only that 1,2 shift involving passage of $M(CO)_3$ over the face of a CH group has an appreciable rate on the NMR time scale. Above +70°, the spectra are consistent with the occurrence of both possible shifts.[251]



232a 232b 232c

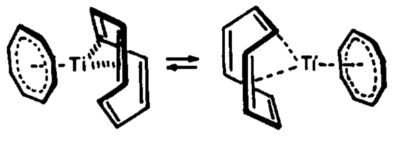
A comprehensive study of the ^1H NMR spectra of various monosubstituted cyclooctatetraeneiron tricarbonyl complexes by Bock[254] provides useful information on the prevailing tautomeric equilibria at room temperature (Table 5). Electron withdrawing groups are seen to force the iron residue to the side of the ring opposite the substituent, perhaps because the double bonds adjacent to the R group experience the greatest electron deficiency. Alkyl and heteroatomic groups give a more complex distribution. For the case where R = CH_3, the free energy of activation for valency tautomerism at −125° remains low (7·5 kcal/mole).[236]

Table 5. Tautomeric equilibria for various monosubstituted cyclooctatetraeneiron tricarbonyl complexes at room temperature

				
R	A	B	C	D
-COOR'	0.9	0.1		
-CN	0.9	0.1		
-COCH3	0.5	0.5		
-CHO	0.5	0.5		
-OCH3	~0.4	~0.4	?	?
-C6H5	0.5			0.5
-CH2OH	0.25	0.25		0.5
-CH3	0.2			0.8

Cyclooctatetraene shows a variety of other bonding modes to transition metals.[255] For example, the complexes formed upon reaction of COT^{2-} with anhydrous chloride salts of the actinides and lanthanides possess sandwich structures.[256,257] Uranocene (**233**), the most well studied of this class, possesses D_{8h} symmetry[258] and has planar 8-membered rings. The molecule shows good thermodynamic stability, but is quite sensitive to oxygen, bases, and strong acids. It reacts only slowly with water or acetic acid and is seemingly inert toward electrophilic substitution or metallation.[256]

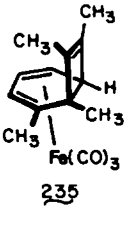
233



234a 234b

Crystal structure data[259,260] indicate non-equivalent metal-ring bonding in $(C_8H_8)_2Ti$ (**234**)[261] and in $(C_8H_8)_2Zr{\cdot}THF$.[262] In both complexes, the neutral C_8H_8 is bent while the $C_8H_8^{2-}$ ligand is planar. The titanium derivative exhibits a temperature dependent NMR spectrum attributable to a fascinating intramolecular redox reaction involving reciprocal flipping of the two rings with simultaneous formal transfer of two electrons [**243a** ⇄ **243b**].[263] The structure of $(COT)_3Ti_2$ is also known and two different types of COT bonding are again seen.[264] Each titanium atom is symmetrically coordinated to a planar 8-membered ring while the third COT ligand acts as a bridging group between the two metal atoms.

Only two reports describing the direct formation of bicyclo[4.2.0]-octatriene-metal complexes have appeared. Reaction of **16** with benzylideneacetoneiron tricarbonyl leads exclusively to **235** having η^4 bonding and assumed stereochemistry.[21] Direct treatment of 1,3,5,7-tetramethyl-COT with $Fe_2(CO)_9$ provides an analgous complex as one of several products.[251] It has proven possible to prepare parent system **236** by refluxing *syn*-tricyclo[4.3.0.0^{2,5}]octa-3,7-dieneiron tetracarbonyl in hexane.[265] Recent developments now point up the feasibility for efficient conversion of mono- and disubstituted cyclooctatetraeneiron tricarbonyl complexes to isomeric [4.2.0]bicyclic compounds by thermolysis.[266,267] This latter approach may prove to be of general applicability.



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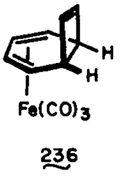
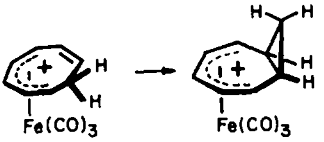
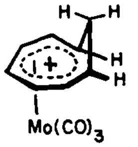


236

Low-temperature (−120°) protonation[268] of cyclooctatetraeneiron tricarbonyl in FSO_3H–SO_2ClF affords initially the monocyclic cation **237** which at −60° undergoes electrocyclic ring closure to **238**[269] with a $\Delta F^{\neq} = 15{\cdot}7$ kcal/mole. The monomethyl derivative under comparable conditions yields two monocyclic complexes.[268] The ^1H NMR spectrum of **238** displays the C_8 methylene protons at nearly the same chemical shift, thereby attesting to the classical nature of this complex in accord with the 4π preference of the iron atom.[87,270] The differing electronic demands within the $Mo(CO)_3$ complex is again revealed upon protonation. In **239**, the chemical shift difference between the inner and outer bridge protons is large (3·5 ppm) indicating that this cation adopts the homoaromatic homotropylium structure. Protonation of $C_8H_8{\cdot}W(CO)_3$ is entirely analogous.[270]



237 238

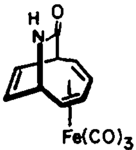


239

In the iron tricarbonyl complex, proton attack trans to the metal is kinetically preferred, such that the entering hydrogen ultimately occupies the *endo* H_8 position in **238**.[269] These results contrast with the *exo* stereochemistry attending protonation of $COT{\cdot}Mo(CO)_3$[87] and with the ultimate fate of the ruthenium and osmium analogs under similar conditions.[271]

A switch to tetracyanoethylene does not alter the direction of initial bonding to $C_8H_8{\cdot}Fe(CO)_3$, but ultimate cyclization proceeds by 1,3 bonding to give **155** quantitatively.[144,145] However, the site of initial attack is markedly influenced by electronic factors as witnessed by the behavior of methyl, phenyl, carbomethoxy, bromo and methoxy complexes.[272,273] The observed regioselectivity parallels to a remarkable degree the known tautomeric preferences of these complexes (Table 5).

Chlorosulfonyl isocyanate also adds stereospecifically from that direction *anti* to the metal. After dechlorosulfonylation, the lactam complex **240** is isolated.[145] This 1,4 addition represents an interesting divergence from the 1,3 bonding scheme followed by TCNE and is deserving of further study. A further mechanistic crossover is seen when $COT{\cdot}Fe(CO)_3$ is heated with certain acetylenes in refluxing mesitylene.[274] With tolan, for example, tetraene **241** is isolated directly in low yield together with a number of other products.



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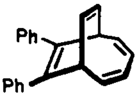
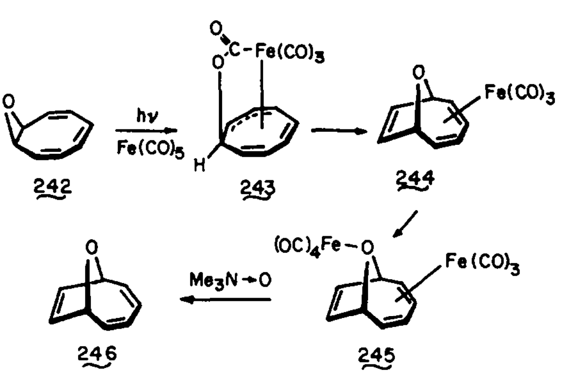


241

Further insight into the synthetic potential of COT derivatives has been gained by Aumann and Averbeck who discovered that epoxide **242** is converted via **243** and **244** to **245** (70% yield) when irradiated in the presence of iron pentacarbonyl.[275] Decomposition of this product with trimethylamine oxide serves as a unique method for the preparation of **246**.



242 243 244 246 245

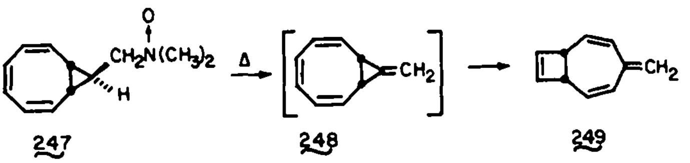
Monohomocyclooctatetraenes. The *cis*-bicyclo[6.1.0]nona-2,4,6-triene ring system, access to which may be gained chiefly by reaction of COT^{2-} with 1,1-dihalides[20,202–204,276,328] or by carbenic addition to COT itself,[277] has been the subject of widespread interest in recent years. A review of the early work in this field is available,[278] and consequently only very recent developments will be emphasized.

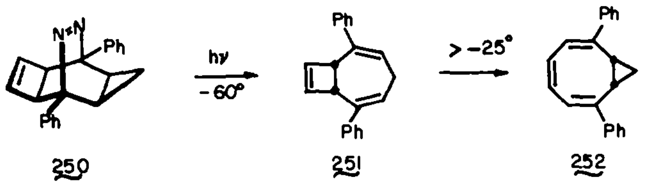
Other synthetic approaches to the title compounds do exist, those leading to **248** and **252** being of particular interest because of the differing properties of the resulting hydrocarbons. Heating of N-oxide **247** generates **248** (not interceptible) which rapidly suffers Cope rearrangement to its more stable [5.2.0]bicyclic counterpart **249**.[279] In contrast, **251** which is formed by photochemical extrusion of nitrogen from **250** at −60° isomerizes to [6.1.0]triene **252** at −25° and above.[280] Clearly, the degree and nature of the substitution in these two systems contribute substantially to the preferred direction of equilibrium.

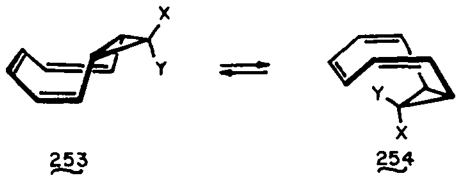
Much of the chemistry of simpler homocyclooctatetraenes is seemingly related to the conformational isomerization illustrated by **253** ⇄ **254**.

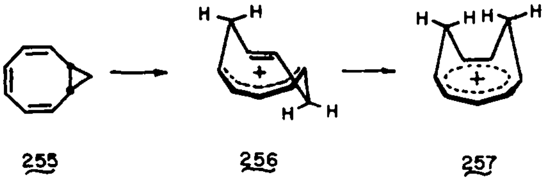
This conformational flexibility interchanges in a very fundamental way the spatial relationship of the cyclopropane ring to the nonplanar triene unit and is accompanied by distinctly different alignments of the $p\pi$ and internal cyclopropane orbitals. When steric consraints ($Y \neq H$) prevent attainment of the folded conformation (**254**), the molecule is restricted to the extended form (**255**) where orbital overlap is much less good. Under ordinary circumstances, the extended conformation appears to be thermodynamically preferred.[281] However, this conformer is also the less reactive.[282] Thus, protonation of *cis*-bicyclo[6.1.0]nonatriene (**255**) under long life conditions appears to involve initial attack on conformer **254** ($X = Y = H$) to give *trans* cation **256** which subsequently experiences conformational inversion of a methylene bridge with formation of the delocalized 1,3 bishomotropylium cation **257**.[90,283]

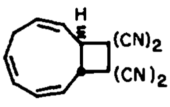
When treated with such reagents as tetracyanoethylene,[284–287] chlorosulfonyl isocyanate,[282,288,289] 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone,[290] α-pyrone,[291] and 1,3-diphenylisobenzofuran,[292] **255** reacts to form trans-fused 1:1 adducts such as **258**–**263**. Dimethyl acetylenedicarboxylate and maleic anhydride behave differently, undergoing $(\pi^4 + \pi^2)$ cycloaddition to the valence isomeric form and formation of a tetracyclic diester.[284,285,293] The TCNE and CSI adducts from ring methyl substituted derivatives of **255** are formed with remarkably high selectivity. Also, the 9-*anti* isomer behaves normally while the 9-*syn* isomer fails to react.[282,286,288] Kinetic studies of these cycloadditions[287,289]











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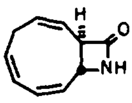

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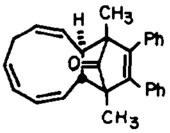

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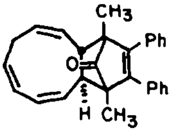

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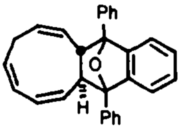

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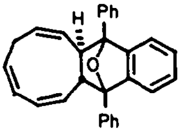

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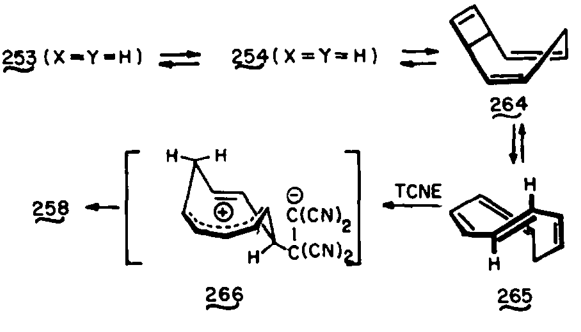
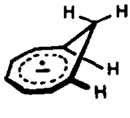
indicate a reaction course which proceeds by rate-determining valence isomerization of **255** to *cis,trans,cis,cis*-cyclonona-1,3,5,7-triene (**265**) which arises from folded conformation **254** (X = Y = H) in equilibrium with bicyclo[5.2.0]nona-2,5,8-triene (**264**, Scheme 22). Cation **266** represents a possible but not mandatory intermediate. As expected from this mechanism, a *syn*-9-methyl substituent precludes attainment of conformer **254** for steric reasons and further reaction is inhibited in this instance. The cycloaddition exhibits little solvent dependence, in agreement with formation of **265** in the rate-determining step. The observed stereoselectivity from methyl substituted analogs of **255** requires that the isomerization of **264** ⇄ **265** proceed via only one of two distinct conrotatory modes. Further work is required to confirm the essential features of this remarkable selectivity.

Irradiation of **255** under conditions of benzophenone sensitization at 0° leads exclusively to *cis*^{4}-cyclononatetraene.[294] Generation of this reactive polyolefin in this manner is unfortunately of limited synthetic value because of the rapid attainment of a photostationary state which heavily favors **255**. Low-temperature photolysis may be more useful; apparently, *cis*^{3},*trans*-cyclononatetraene is also formed under these conditions.[295] The photochemical behavior of the epimeric 9-chloro derivatives of **255** has also been examined.[296]



Scheme 22.

One-electron reduction of **255** proceeds with formation of the nine-electron homoaromatic radical anion **267**, the proton hyperfine coupling constants of which have been measured under a variety of conditions[297–299] and rationalized on theoretical grounds.[300] In contrast, comparable reduction of *trans*-bicyclo[6.1.0]nona-2,4,6-triene with potassium in tetrahydrofuran or dimethoxyethane solution at −90° leads to classical bicyclic radical anion **268**.[301] Here electrocyclic ring opening is apparently disallowed. Further reduction of **267** with potassium metal provides delocalized dianion **269**, structural assignment to which is founded chiefly on ^{1}H NMR shifts.[302] Attempts to generate this species in liquid ammonia at −60 to −78° leads to selective protonation and formation of **270**.[303,304] Methylated derivatives of **255** are reduced to their respective dianions which are seemingly less basic toward NH_3;[304] in these examples, the ^{1}H NMR spectra of the dianions could be recorded (in ND_3) prior to deuteration by solvent. Most recently, dianion **269** has been generated by dimetalation of **271** and its spectra analyzed in detail.[305] Electrochemical reduction studies of **255** and its trans-



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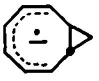

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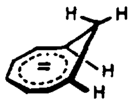
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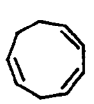
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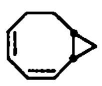
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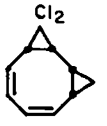

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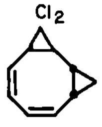

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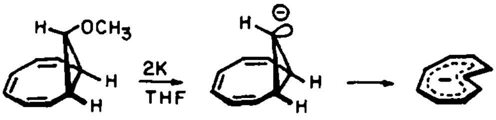
fused counterpart have failed to provide a polarographic criterion of homoaromaticity.[306] Rather, the first electron transfers occur much less readily than with COT and are observed in the region characteristic of medium-ring trienes.

Two reactions of dipotassio **269** generated by K-THF reduction have been documented. Protonation of this species with methanol at −80° gives bicyclic diene **272** as the major product in greater than 85% yield.[307] Treatment with carbon tetrachloride at −10° affords the related products **273** (60%) and **274** (30%).[308] Significantly different results have been realized from protonation of potassio and lithio **269** which have been generated in more polar media such as ammonia or HMPA-THF. Under these conditions, only the monocyclic cyclononatriene **271** is isolated.[303-305] When ring methylated derivatives of **269** are protonated, positional regioselectivity in the proton transfer steps is seen.[304] Alkylation reactions of **269** have also been examined.[309,310]

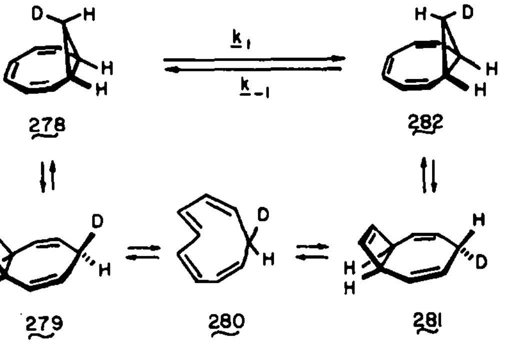
Reduction of the *anti*-9-methoxy derivative **275** with potassium in tetrahydrofuran proceeds presumably by way of cyclopropyl anion **276** and furnishes potassium *trans,cis*^{3}-cyclononatetraenide (**277**).[311] This anion is remarkably stable at −40°, but does proceed to the all-*cis* compound when allowed to stand at room temperature.



Since Vogel's initial observation[312] that **255** undergoes bond reorganization when heated at 90°, many C_9-substituted bicyclo[6.1.0]nonatrienes have been thermally isomerized.[313-324] The emphasis has been chiefly mechanistic and revolves about the fact that while the unsubstituted molecule and *anti*-9-monosubstituted derivatives rearrange mainly to *cis*-dihydroindenes, 9,9-dialkyl substitution results in formation of *trans*-dihydroindenes. When the 9 position carries dicyano,[325,326] spirofluorenyl, or spirocyclopentadienyl[277] functionality, bicyclo-[4.2.1]nonatrienes are produced. This latter reaction has commanded much less attention.

The stereochemically distinct isomerizations frequently proceed at differing rates and it has been suggested that the *cis*-dihydroindenes are formed from the folded arrangement **254** and the *trans* isomers from extended form **253** ($\Delta\Delta G^{\neq} \sim 4$ kcal/mole). This rationalization nicely explains why 9,9-disubstituted compounds fail to give *cis* product, but has been a long-standing problem in interpreting the behavior of *syn*-9-substituted derivatives. The latter should mimic their 9,9-disubstituted counterparts in thermal response, but do not. Rather, they provide quantities of *cis*-dihydroindenes as do their epimers.

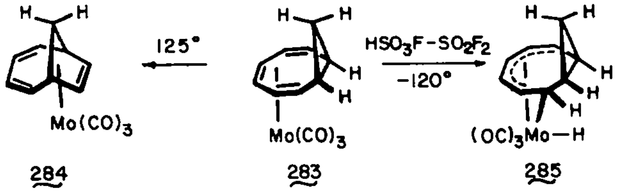
This seeming complication has now been resolved by the findings that *syn*-9-carbomethoxy,[327] -cyano,[321] -fluoro,[328] -methoxy,[328] dimethylamino[328] and -deuterio[329] substituted systems undergo facile epimerization at C_9, notwithstanding statements to the contrary in the case of the methyl and t-butyl derivatives.[317,321] The preferred epimerization pathway is seemingly that illustrated in Scheme 23 for the monodeuterated hydrocarbon,[329] rather than a process involving the intervention of tricyclic intermediates.[328] By treating the interconversion of **278** and **282** as a simple first-order process ($k_1 = k_{-1}$), k_1 was found to be $4{\cdot}5\times10^{-5}$ sec^{-1} (31·3°, CD_3CN) and $4{\cdot}7\times10^{-5}$ sec^{-1} (35°, $CDCl_3$) with $\Delta G^{\neq} \approx 24$ kcal/mole. If **280** is the intermediate responsible for epimerization, then its rate of formation should be double that of epimerization since independently generated **280** partitions itself equally between **278** and **282**. At the experimental level, this was found to be so. This mechanistic model can be used as well to explain adequately the differing product ratios from *syn*- and *anti*-9-substituted bicyclo[6.1.0]nonatrienes. However, since the rate-determining step involves the formation of **280**, *syn* epimers are transformed to their *anti* counterparts only after this rate-limiting ring opening.



Scheme 23.

Bicyclo[6.1.0]nonatrienemolybdenum tricarbonyl (**283**) is readily converted to complex **284** at 125° in an interesting rearrangement.[323] Such thermal isomerizations to [4.2.1]bicyclic frames do not occur in the free ligand except with certain substitution patterns (low yields). Consequently, this transformation could represent a true metal-promoted sigmatropic reaction. When protonated in HSO_3F-SO_2F_2 at −120°, proton addition occurs at the metal with π- to σ-electronic reorganization and formation of **285**.[330]

Homoazocines. Addition of dichloromethane to azocinyl dianion **227** affords the homoazocines **286** and **287**. Thermal activation of **287** provides in expected fashion the aza[4.3.0]bicyclic triene **288**.[310] Exposure of **287** to the action of 2 equivalents of potassium in liquid ammonia leads ultimately to monoanion **288**. Protonation of **289** occurs chiefly at the unsubstituted terminus of the azaheptatrienyl anion segment with formation of an unstable triene, closure of which is followed by aromatization with loss of methanol and production of pyridine derivative **290**. Methylation proceeds analogously to give **291**.[310]



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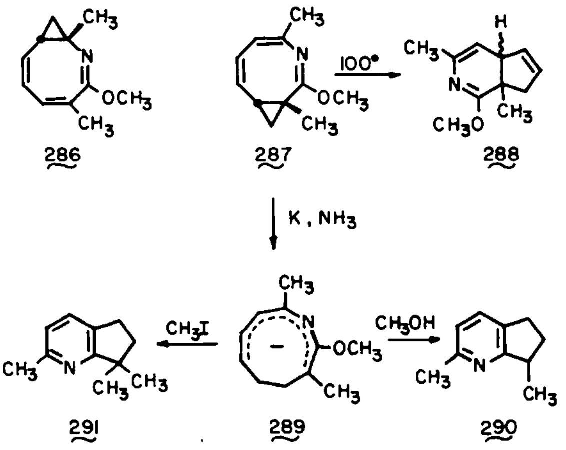

286 287 288 291 289 290

These early findings augur well for the richness of molecular rearrangements within this heterocyclic class.

Concluding remarks. Interest in cyclooctatetraene chemistry is clearly at an all-time peak. It is certain that rapid advances will continue to be made since the statements can confidently be made that relevant new synthetic methodology will continue to unfold, completely unexpected reactions will make their customarily periodic appearances, and theoretical advances will prompt yet more probing experimentation. All promise considerable excitement for the future. It is even possible, for example, that the syntheses of **75** and the cyclooctatetraenyl dication will have been completed before the appearance of this review. Notwithstanding, it is hoped that this survey sets the stage for an appreciation of these forthcoming developments. It remains only to close with a plea to the administrative directors of Badische Anilin und Soda Fabrik not to curtail production of this otherwise elusive hydrocarbon in the years to come.

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