Bond Fixation in Annulenes. 3. The Structural Consequences of Tetra- and Pentamethyl Substitution of the Cyclooctatetraene Ring[1]

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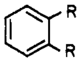
Abstract: The 1,2,3,4- and 1,2,3,8-tetramethylcyclooctatetraenes as well as the higher homologous 1,2,3,4,6- and 1,2,3,5,8-pentamethyl derivatives have been prepared conveniently in isomerically pure form by procedures which hold promise of considerable generality. One scheme consists in elaboration of a suitably substituted 8-thiabicyclo[4.3.0]non-3-ene dioxide, its alkylative desulfonylation with ring contraction to introduce a 1,2-dimethylcyclobutene part structure into a bicyclo[4.2.0]-octa-3,6-diene framework, and ultimate selective bromination–dehydrobromination to generate the corresponding triene which undergoes disrotatory electrocyclic ring opening under strict control of the cyclohexadiene moiety. The second synthetic approach involves a different ordering of the above reactions. Evidence is presented that these hydrocarbons are resistant to attainment of a planar conformation, a phenomenon which contributes to maintenance of the individually distinctive tub conformations except at elevated temperatures or when irradiated. Conversion to planar diatropic dianions is possible by alkali metal reduction in liquid ammonia at low temperatures, presumably as the consequence of the gain in electronic delocalization in such 10π Hückeloid systems. Oxidation with iodine in pentane returns mixtures of the two isomers. When subjected to polarographic reduction in anhydrous HMPA, the [8]annulenes were found to exhibit greatly reduced electron affinities because of the inhibition to planarity at the transition state for radical anion formation. For the pair of tetramethylcyclooctatetraenes, a free-energy difference ($\Delta G°$) of 730 cal/mol (at 162 °C) has been determined and shown to favor the 1,2,3,8 isomer. This is attributed to a decrease in the level of nonbonded methyl-methyl interactions which is best achieved by orienting the alkyl groups on as many double bonds as possible. When this cannot be achieved because of structural constraints, the substituted cyclooctatetraene exists in equilibrium with substantial concentration levels of its bicyclic valence isomer. Finally, placement of four alkyl groups at the 1,2,5,6 and 1,4,5,8 positions was seen to deter bond shifting somewhat, but not at the level which would permit the isomers to have an extensive shelf life. In the two sets of molecules prepared, differences in the preferred direction of equilibrium were noted, and the factors which likely underlie these thermodynamic imbalances are discussed.

Kekulé's initial suggestion in 1865 of a cyclohexatriene formulation for benzene met with almost immediate objection, chiefly on the grounds that four disubstituted derivatives (one para, one meta, and two ortho isomers) should be isolable but were not. Such negative evidence prompted Claus (in 1867), Dewar (in 1867), and Ladenburg (in 1869) to propose alternative, but ultimately erroneous formulations for this ring system.[2] The absence of such double bond fixation as would permit independent existence of the ortho isomer pair **1** and **2**, an active but vain pursuit of chemists of the Kekulé era, is now understood to be the result of effective π-bond delocalization which renders all benzenoid bonds essentially equivalent.



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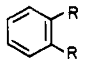

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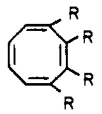
Much later, Hückel (in 1938) proposed that this partiality for π-electronic delocalization should be a common feature of planar or nearly planar $(4n + 2)\pi$ conjugated cyclic molecules, both neutral and charged. Experimental findings supportive of this theory continue to appear.[3] In $4n\pi$ systems, this stabilizing influence does not operate, and a planar geometry is frequently not maintained for energetic reasons. A case in point is cyclooctatetraene (COT) which adopts a D_{2d} tub conformation having alternating single (1.48 Å) and double bonds (1.34 Å).[4] Earlier studies of bond shifting in several mono- and disubstituted cyclooctatetraenes by NMR spectroscopy have shown the process to have an appreciable energy barrier (12–19 kcal/mol).[5] In the 1,3,5,7-tetramethyl example, the relevant $\Delta G^{\ddagger}$ is raised to 22.5 kcal/mol (at 120 °C).[6] These experimental findings and supportive theoretical calculations[7] left little doubt that attainment of the planar transition state necessary to bond shifting could be impeded by the proper disposition of substituents. Accordingly, we have sought to achieve bond fixation in isomers of type **3** and **4** having alkyl groups attached to four contiguous carbon atoms, in order that buttressing effects might contribute additionally to maintenance of the individual tub conformations. This goal has been successfully realized, and we herein detail the preparation of such valence isomers which, in actuality, comprise stable higher vinylogs of **1** and **2**.



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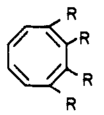

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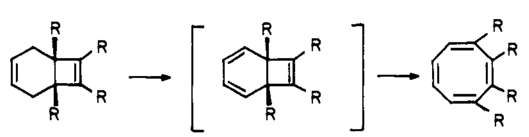
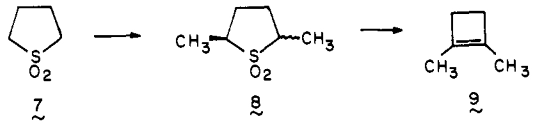
Strategy and Development of the Requisite 1,2-Dimethylcyclobutene Synthesis. Conceptually, the most direct approach to bond shift isomer **3** consists of suitable elaboration of bicyclo[4.2.0]octatriene **6**, central bond cleavage in which should operate disrotatorily under the control of the 1,3-cyclohexadiene moiety.[8] Given such constraints, the formation of that isomer having its two "internal" R groups bonded to a single double bond was expected. Since **6** should be accessible by controlled bromination–dehydrobromination of **5**, we were led to a search for a convenient and versatile synthesis of 1,2-dialkylcyclobutenes. The approach takes advantage of Dodson's past findings that *cis*- and *trans*-2,4-diphenylthiethane 1,1-dioxides are capable of ring contraction to *trans*-1,2-diphenylcyclopropanesulfinic acid when treated with ethylmagnesium bromide.[9] Under comparable conditions, 2,5-diphenyltetrahydrothiophene dioxide is converted to 1,2-diphenylcyclobutene.[10] To achieve ultimate elimination of the

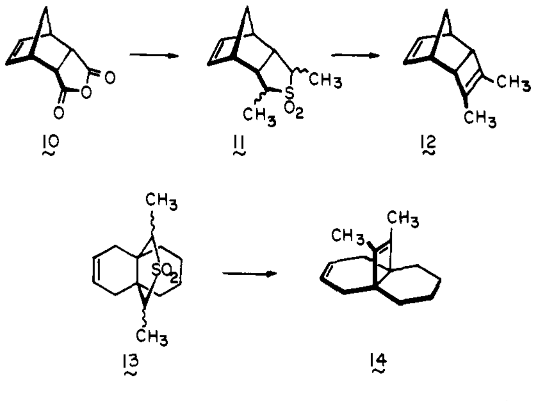


5 **6** **3**

sulfur residue in an unactivated system, it appeared that the reductive properties of lithium aluminum hydride would be serviceable since this reagent could also function simultaneously as a base and a Lewis acid. In an initial test of this concept, sulfolane (**7**) was dimethylated by sequential treatment with 2 equiv of *n*-butyllithium in tetrahydrofuran at −80 °C and excess methyl iodide. Without purification, the crude product, which consisted chiefly of **8** (^{1}H NMR analysis), was dissolved in anhydrous dioxane, treated at 0 °C with 1 equiv of *n*-butyllithium, and introduced via syringe into a refluxing slurry of LiAlH$_4$ in dioxane. The product, which was collected in a dry ice trap as it was liberated, could be isolated by careful processing and identified as **9** (20%).[11]

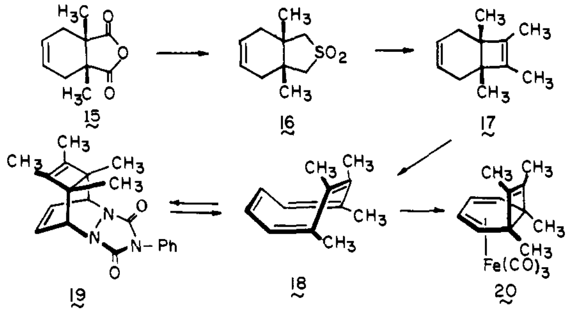


To ascertain that this synthetic procedure could accommodate conversion of succinic anhydrides to 1,2-dimethylcyclobutene derivatives, the commercially available anhydride **10** was transformed by standard methodology to the 2,5-dialkyltetrahydrothiophene dioxide **11**. Treatment of this sulfone as before afforded **12** in 22% yield. When the level of steric hindrance about the sulfonyl group was increased as in **13**, the efficiency of the ring contraction was enhanced (67% of **14**), probably because competing hydride reduction to sulfide was still more sterically impeded. In short, a number of such ring contractions have now been examined and 1,2-dimethylcyclobutenes are obtained in fair to good yield. There is every indication that the reaction is fully applicable to a broad spectrum of structural types.[12]



1,2,3,8-Tetramethyl Derivatives. Sulfone **16** was prepared from anhydride **15**[13] according to the predescribed method.[14] α,α'-Dimethylation of **16** and lithium aluminum hydride reduction of the derived α-sulfonyl carbanion gave diene **17** in 34% yield. Subsequent bromination-dehydrobromination[15] of this diene led to a transient bicyclo[4.2.0]octatriene, ring opening of which under the conditions of the experiment furnished exclusively **18** (99%; Scheme I). The ultraviolet spectrum of this pale yellow liquid consists only of a shoulder at 220 nm, as is typical of cyclooctatetraenes.[16] The C_s symmetry of this [8]annulene is suggested by its ^{1}H and ^{13}C NMR spectra. The former shows (in CDCl$_3$) two somewhat broadened olefinic singlets at δ 5.35 (2 H) and 5.70 (2 H) and two methyl singlets at 1.80 (6 H) and 1.67 (6 H).[17] The greater $W_{1/2}$ of the 1.80 peak identifies it as belonging to the "outer" methyls, the broadening arising because of allylic coupling to the neighboring vinyl protons. The six carbon signals appear at 144.86, 132.46, 130.51, 122.96, 22.12, and 17.16 ppm downfield from Me$_4$Si.

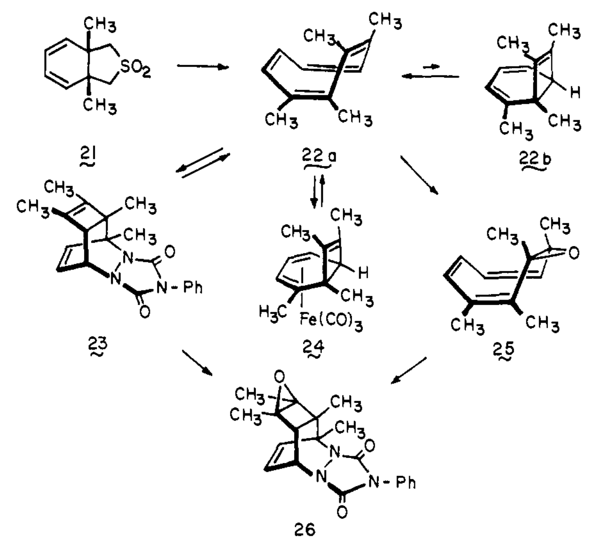
Scheme I



Further evidence that the double bond between the inner methyl groups had not been perturbed during conversion to **18** was indicated by high yield conversion to adduct **19** upon treatment with *N*-phenyltriazolinedione and by ligand exchange with benzylideneacetoneiron tricarbonyl[18] to give **20.** The protons of this complex give rise to a clean first-order spectrum (in CCl$_4$): δ 5.30 and 2.85 (dd, J = 5.0 and 2.6 Hz, 4 H, olefinic), 1.34 and 1.06 (s, 12 H, methyls). On the strength of these findings, there was obvious reason to believe that a dramatic decrease in the flexibility of the medium ring had been engineered.

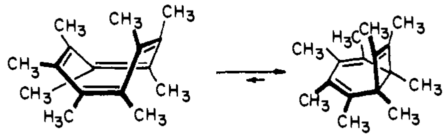
1,2,3,4-Tetramethylcyclooctatetraene. Access to valence isomer **22a** was gained by initial conversion of **16** to its diene counterpart **21.**[14] Analogous alkylative desulfonylation of **21** led to a mixture of **22** (70–80%) and **18** (Scheme II). Separation of the pair of isomers was easily achieved by treatment with *N*-phenyltriazolinedione and fractional crystallization of the adducts (**23** and **19**, respectively) so produced. In contrast to the symmetrical nature of **19** which generates only four sets of ^{1}H NMR signals in addition to the aryl multiplet, the features of the spectrum of **23** reflect the positioning of one methyl group at a bridgehead site, the presence of an allylic cyclobutene proton, and the magnetic nonequivalence of its four methyl substituents (see Experimental Section). The conversion of **21** chiefly to **22** may be the result of disrotatory opening in the bicyclo[4.2.0]octa-2,4-diene intermediate produced upon sulfolane ring contraction and ensuing preferential ejection of the sulfur residue by 1,8 rather than 1,2 elimination. Whatever the precise mechanistic details, the two central methyl groups in **22a** are now not attached to the same π bond.

Scheme II



Hydrolysis-oxidation[19,20] of adducts **19** and **23** returned the individual colorless tetramethylcyclooctatetraenes **18** and **22.** However, in contrast to **18,** which is homogeneous within the limits of spectroscopic analysis, the 1,2,3,4-tetrasubstituted isomer is seen to contain ca. 25% of bicyclooctatriene **22b** as determined by appropriate ^{1}H NMR integration.[17] To gain convincing proof of the true position of the **22a** $\rightleftarrows$ **22b** equilibrium, the cyclooctatetraene was converted to η^4 complex **24.** When oxidized with ceric ammonium nitrate in acetone at −30 °C, **24** returned a mixture of **22a** and **22b** having an identical composition within the limits of measurement. Consequently, alkyl substitution of the COT ring as in **22** appreciably enhances the thermodynamic stability of the bicyclic valence tautomer. In this connection, the fully methylated bicyclic hydrocarbon **28** has been described by Criegee as having greater stability than its monocyclic counterpart **27.**[21] This behavior differs dramatically from that of the parent hydrocarbon where only 0.01% of the bicyclo[4.2.0]octatriene is present in the equilibrium at 100 °C.[22,23]

The inherent twofold symmetric nature of **22a** is borne out by its ^{13}C spectrum which exhibits only six signals (137.20, 127.28, 122.12, 116.97, 18.45, and 17.75 ppm). However, an alternative formulation can be envisioned for this hydrocarbon which could account equally well for the inherent C_2 symmetry of the species and the observed equilibrium with **22b.** Thus, it became mandatory to exclude the possibility that reversible conrotatory cyclobutene ring opening was operating in **22b** to give the *cis*^{3}, *trans*-cyclooctatetraene **29.**[24] In 1964, Vogel demonstrated convincingly the exclusive disrotatory characteristics of the isomerization of **30** to COT.[25] In higher homologue **31,** conrotatory opening apparently occurs readily,[26] but both component rings of this bicyclic hydrocarbon are exerting comparable electrocyclic influences,[27] quite unlike the situation prevailing in **30.** Relevantly, kinetic data for a variety of thermal reactions support the generalization that disrotatory 1,3-cyclohexadiene → 1,3,5-hexatriene conversions proceed with greater facility than conrotatory cyclobutene → 1,3-butadiene transformations.[28-30] Although the thermodynamic impact of the four methyl groups in our molecule was not expected to reverse this trend (note **6** $\rightleftarrows$ **3** and **27** $\rightleftarrows$ **28**), it remained to make the distinction between **22** and **29.** Since the trans double bond in **29** should be particularly reactive toward electrophilic reagents,[31,32] the COT was epoxidized with ethereal monoperphthalic acid and the unpurified product treated directly with *N*-phenyltriazolinedione. The isolated adduct proved to be identical with the substance obtained from comparable oxidation of **23** and must therefore be **26.** Since the oxirane ring in **26** is of cis stereochemistry, it could have arisen from disrotatory closure of epoxide **25.**[33] However, the relative positioning of the oxygen atom need not disqualify **29** from consideration, since the possibility that **22b** is more reactive than either monocyclic structure cannot be unequivocally dismissed (Curtin–Hammett principle). On the other hand, the demonstrated *reversible* conversion of the COT to a cis^4 dianion (see below) cannot easily be reconciled in terms of the trans isomer.



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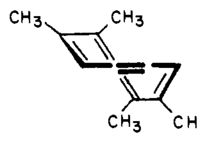

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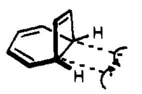

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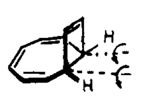

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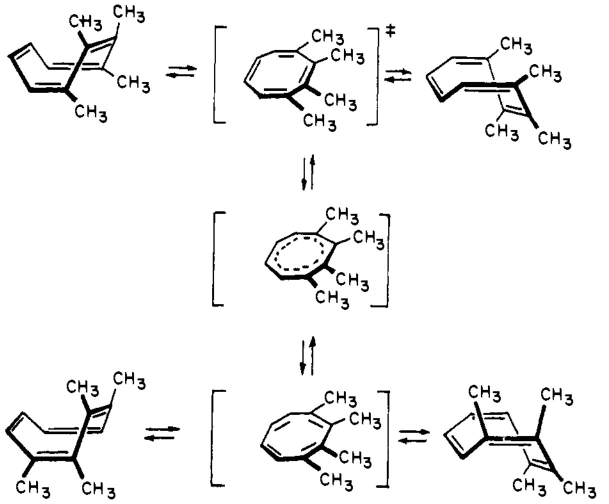
Chemical Behavior of the Tetramethyl Bond Shift Isomers. The successful synthesis of the shelf stable pair **18** and **22** made possible a study of their interconversion. In preliminary experiments, gas phase pyrolyses of **18** were conducted up to 430 °C (contact time 1-3 s),[34] but no evidence was gained for conversion to **22.** In contrast, thermal activation of **22** at 350 °C resulted in low level conversion to **18,** and increased heat input (405-475 °C) led with regular progression to increased proportions of this latter valence isomer. However, because of low yields and the formation of by-products, it was not feasible to derive reliable quantitative information from these data. Somewhat more meaningful results were realized by heating each isomer in refluxing diglyme (bp 162 °C) for 6 h. An equilibrium mixture consisting of approximately 70% of **18** and 30% of **22** was obtained from either isomer in 60-70% yield after preparative VPC isolation.[35] On the basis of these results, the free-energy difference $\Delta G°$ is calculated to be 730 cal/mol at 162 °C. Computer assessment of the relative energies of **18** and **22a** by the molecular mechanics (SCF-Westheimer) method[7] indicates the meso isomer to be 1.0 kcal more stable than that which has the twofold axis of symmetry.[36] Since the entropy difference between the two valence isomers is 0, this value is an enthalpy term. Accordingly, computational assessment of the question provides the answer that C_s form **18** should dominate by approximately 85% at room temperature or 78% at 100 °C, in very good agreement with our experimental findings.

Although this close correspondence with theory is gratifying, knowledge of the energy difference between **18** and **22a** represents only a single parameter in the overall mechanistic profile which is illustrated in Scheme III. To gain complete knowledge of this system, it is important to determine as well the individual barriers to ring inversion and bond shifting. The former requires the preparation of optically active **22** (**18** cannot support chirality) and is demanding (for enantiomerically pure material) of the development of a new synthesis which by-passes the utilization of symmetrical intermediates of the type **15, 16,** and **21.** Such work is in progress.

Scheme III



Irradiation of either cyclooctatetraene through quartz with 2537 Å light also resulted in the formation of bond shift isomer mixtures slightly favoring **18.** However, these reactions were complicated by the formation of *o*-xylene,[37] with the greater amount of aromatic arising from **22.** This was expected, since the [2+2] cycloreversion involves the bicyclo[4.2.0]octatriene tautomer and produces 2-butyne as a by-product.[20]

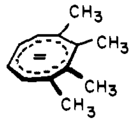
Table I. Summary of Polarographic Data (Anhydrous HMPA Solution)[38]

Compound	$E_{1/2}$[a]	Ref
18	−2.43[b]	This work
22	−2.54[b]	This work
1,2,3-Me$_3$COT	−2.20	*c*
1,5-Me$_2$COT	−1.87	*d*
1,2-Me$_2$COT	−1.95	*d*
MeCOT	−1.73	*d*
COT	−1.61	*d*

[a] The $E_{1/2}$ values were obtained vs. AgClO$_4$/Ag and are corrected to SCE by adding 0.36 V. [b] The earlier reported values[1b] of −3.7 and −3.6 V. are erroneous values arising from typographical error. [c] Unpublished results of S. Traynor. [d] D. Taggart, private communication.

Polarographic reduction of **18** and **22** provided a quantitative measure of the difficulty experienced by these annulenes in attaining a planar conformation. The measurements were conducted in anhydrous hexamethylphosphoramide solution using a vacuum line cell designed for total exclusion of oxygen and moisture;[38] a comparison of $E_{1/2}$ values with those of lesser alkylated derivatives is given in Table I. The rate of the first electron transfer to COT is quite slow relative to the second,[39] a finding which is attributed to that conformational readjustment involving conversion of the buckled neutral molecule to a planar or nearly planar radical anion species at the transition state. A similar structural distortion is not required for subsequent introduction of the second electron and it occurs with greater facility. Consequently, the potential at which the first electron is added should be directly relatable to the ease of ring flattening, and the data of Table I nicely reflect this state of affairs.

Despite the high level of strain which prevails, **18** and **22** have been successfully reduced to the identical dianion (**32**)



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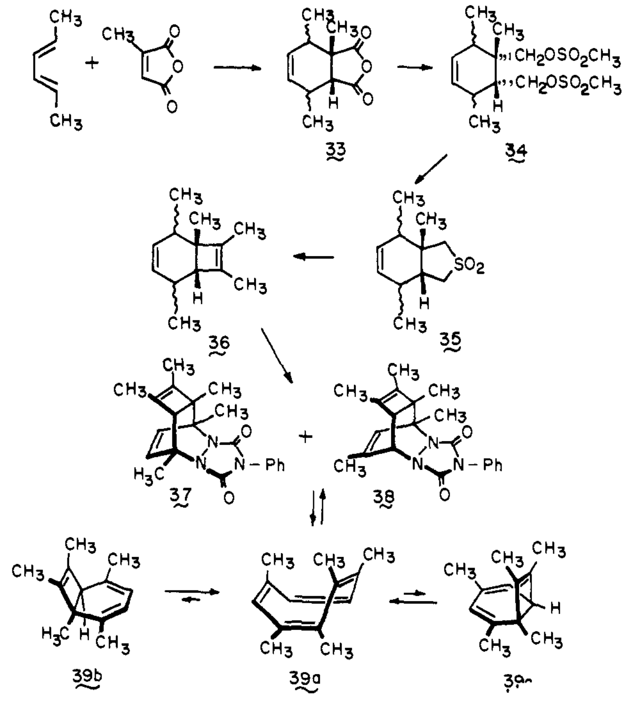
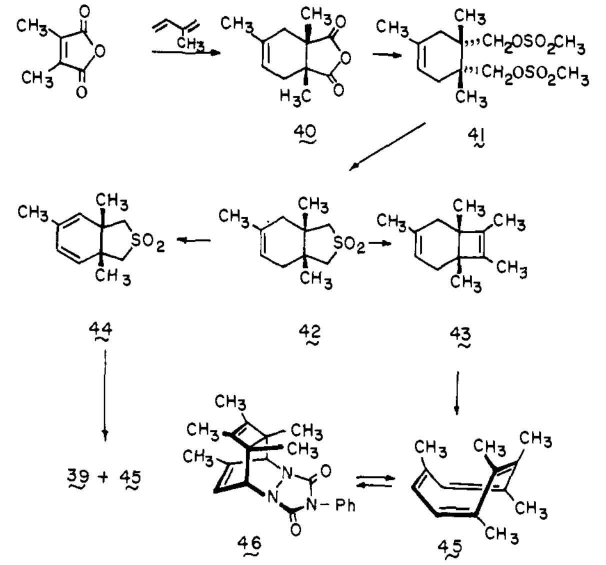
with potassium in ND$_3$.[40] The ^{1}H NMR spectrum of this species consists of an olefinic proton multiplet at δ 5.20–5.59 (4 H) and two methyl singlets (6 H each) at 2.79 and 2.62.[22] These features accord fully with those of various dimethylated derivatives[41] and serve as the basis for assignment of the planar (or effectively planar), symmetrical delocalized structure. When this species is oxidized with iodine in pentane[42] at −55 °C, a 1:1 mixture of **18** and **22** is returned.

1,2,3,5,8- and 1,2,3,4,6-Pentamethylcyclooctatetraenes. In order to extend the scope of the syntheses developed in Schemes I and II and to provide additional examples of shelf-stable COT bond-shift isomers, attention was turned to the pentamethyl derivatives **39** and **45**. The first approach (Scheme IV) takes advantage of the relative ease with which citraconic anhydride and 2,4-hexadiene enter into Diels–Alder reaction. Adduct **33** was transformed without difficulty into sulfone **35** which underwent conversion to pentamethyldiene **36** in 48% yield. Subsequent bromination–dehydrobromination of **36** proceeded poorly (5.4%) but gave uniquely **39** as determined spectroscopically and by the isolation of adducts **37** and **38**. This pair of compounds was not amenable to ready separation; however, this was unimportant since the hydrolysis–oxidation of either isomer liberates only **39**.

Scheme IV



Scheme V



The 1,2,3,5,8-pentamethyl derivative **45** was accessible from dimethylmaleic anhydride and isoprene by an analogous series of reactions (Scheme V). Again, bromination–dehydrobromination of the dimethylcyclobutene intermediate (**43** in this instance) afforded a unique annulene by disrotatory electrocyclic opening. Identification of the product as **45** rests upon its spectra, reaction with *N*-phenyltriazolinedione to give **46** (a reversible chemical change), and its formation along with **39** in the reductive desulfonylation of diene sulfone **44**.

The ^{1}H NMR spectrum of **45** (Figure 1) bears a striking similarity to that of **18** and likewise indicates the essentially homogeneous monocyclic features of this isomer at this temperature. Pentamethylcyclooctatetraene **39a** is seen in contrast to contain an appreciable concentration of the bicyclic valence isomers **39b** and **39c**, a property which it shares with **22a**. Its spectrum (Figure 1) shows a high field methyl singlet at δ 1.2, relevant olefinic resonances, and a weak broadened signal at ca. 2.7 assignable to the angular proton in these bicyclooctatrienes. If the relative rates of *N*-phenyltriazolinedione addition to **39** serve as useful analogy (not necessarily so), then **39b** enjoys a significant concentration advantage over **39c** (**37**:**38** = 95:5). This question is difficult to resolve spectroscopically, but the dominance of **39b** agrees in principle with the antici-

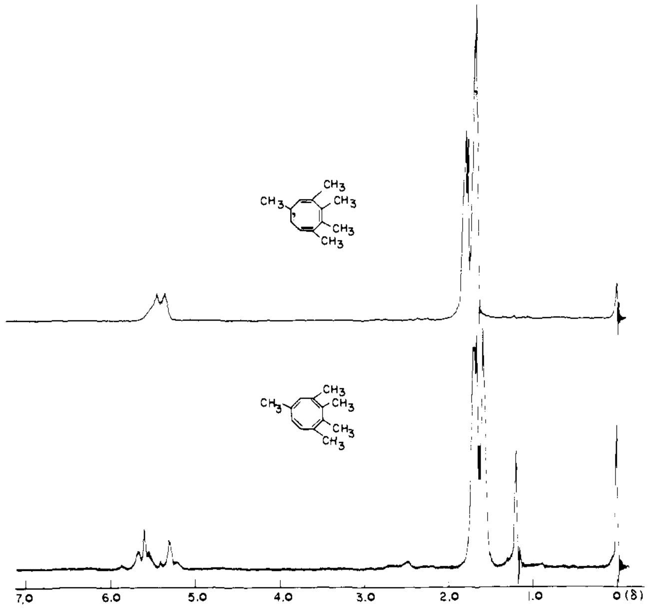
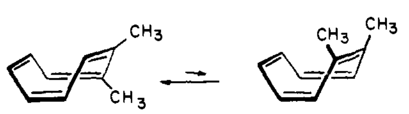


Figure 1. ^{1}H NMR spectra (60 MHz, $CDCl_3$ solution) of: (top) 1,2,3,5,8-pentamethylcyclooctatetraene (**45**) and (bottom) the 1,2,3,4,6-pentamethyl bond shift isomer **39**.

pated thermodynamic advantage of 1,4- over 1,3-dialkyl substitution in a conjugated diene (the substitution pattern about the cyclobutene ring is otherwise identical in these structures).

Clearly, there exist in the permethylated cyclooctatetraenes **22a**, **27**, and **39a** interaction energies which are unimportant in cyclooctatetraene, **18**, and **45**. If, as is customarily assumed,[43] the free energies of conformational isomers are additive functions of those energy terms associated with nonbonded interactions, then the untoward energetics of two methyl groups on the same double bond might well determine the position of COT-bicyclooctatriene equilibria in certain examples. An indication that this assumption is valid comes from our earlier variable temperature ^{1}H NMR examination of 1,2-dimethylcyclooctatetraene.[41] At 40 °C, this hydrocarbon (in $CDCl_3$) displays two sharp singlets at δ 1.68 and 1.82 of unequal weighting (the downfield signal is the more intense). At 94 °C, appreciable broadening of the two peaks is evident and at 122 °C coalescence occurs with appearance of a sharp singlet at δ 1.75. This entirely reversible behavior is attributed to a thermodynamic preference for **47** where methyl-methyl interactions are lessened because of their placement on neighboring double bonds. The C_2 symmetry of **47** leads to identity of its methyl groups and the appearance of the sharp singlet at 1.82. Bond shift isomer **48** is already accessible at



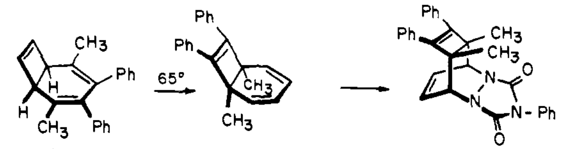
47 **48**

ambient temperature as indicated by the singlet at 1.68, but its concentration lags behind that of **47** until temperatures in excess of 100 °C are reached. Since **48** is of C_s symmetry, there is no entropy of mixing and the equilibrium is enthalpy controlled.

Because **22a**, **27**, and **39a** are sterically inhibited from entering into bond shifting and probably ring inversion as well, valence isomerization is made recourse to instead. In the case of COT itself, electrocyclic closure is the least favorable of the fundamental structural changes available (ring inversion > bond shifting > valence isomerization),[44] the extremes of these processes differing energetically by approximately 16 kcal/mol. We see therefore that this ordering can be inverted by appropriate ring methylation, particularly if by so doing the molecule is sterically precluded from adopting a planar conformation. Electrocyclization in **22a** and **39a** takes a very specific course, namely that which places one methyl group in that environment where it is bonded to an sp^3-hybridized carbon at the fold of the bicyclooctatriene frame. The dihedral angle made by this C-CH_3 bond with those external to the two adjacent carbons results in steric decompression of appreciable magnitude.

Since both **18** and **45** contain only one disubstituted double bond and give no evidence of valence isomerization, it would appear that this phenomenon is detectable only when two such functionalities are present. Significantly, the remaining methyl substituents in these two COT's do not engender additional nonbonded interactions of meaningful proportions.

McCay and Warrener's observation that bicyclo[4.2.0]-octatriene **49** undergoes irreversible isomerization to **50** at 65



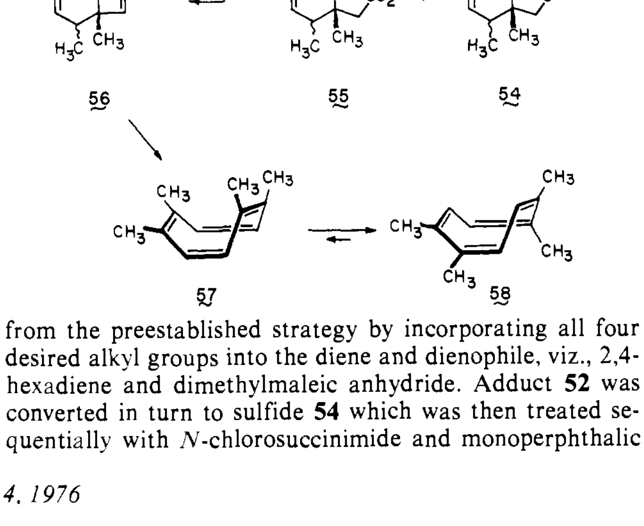
49 **50** **51**

°C (via the cyclooctatetraene) may be considered a further example of structural rearrangement to accommodate steric strain release.[45] However, this bond reorganization may be somewhat complicated by the effect of developing stilbene conjugation which should also facilitate the conversion to **50**.

As with the tetramethyl examples, **39** and **45** exhibit the characteristic of stability to mutual interconversion under ambient conditions in the absence of light.

Noncontiguous Tetraalkyl Substitution. It remained an open question whether bond fixation could be realized in tetraalkylcyclooctatetraenes where substitution was not restricted to four contiguous carbon atoms. This problem was addressed initially by synthesis of the 1,2,5,6-/1,4,5,8-tetramethyl isomer pair as summarized in Scheme VI. In this instance, we deviated

Scheme VI

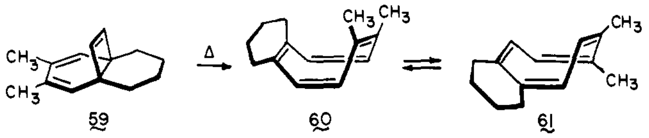


from the preestablished strategy by incorporating all four desired alkyl groups into the diene and dienophile, viz., 2,4-hexadiene and dimethylmaleic anhydride. Adduct **52** was converted in turn to sulfide **54** which was then treated sequentially with *N*-chlorosuccinimide and monoperphthalic acid. Ramberg-Bäcklund rearrangement[46] of the resulting α-chloro sulfone (**55**) led to diene **56**, bromination-dehydrobromination of which proceeded in 91% yield with formation of **57** and **58**. The ^{1}H NMR spectrum of the hydrocarbon product (in CCl_4) displays two olefinic singlets at δ 5.52 and 5.41 having relative areas of 1:10, respectively, and a pair of methyl singlets (1.74, 1.63) having the reverse relative intensity ratio. Identification of the individual isomers was made possible by the work of Anet, Bourn, and Lin[5a] who established in COT-dimethylcarbinol-*2,3,4,5,6,7-d_6* that the higher field olefinic proton signal arises from attachment to that olefinic linkage which also carries the alkyl group. On this basis, the dominant isomer is **58** (~90%) in agreement with prior observations.

Gas phase pyrolysis of this mixture between 350-405 °C served to decrease the ratio to 3:1. More effective at enriching the level of **57** was irradiation through quartz at 2537 Å which led to a 1:1 distribution of the two isomers. Both of these product mixtures reverted to the original composition after standing at room temperature for several hours or upon attempted VPC purification.

These data reveal that the 1,2,5,6(1,4,5,8)-tetramethyl substitution plan does not provide a barrier adequate to prevent bond shifting at room temperature. However, **57** and **58** do give evidence of being individually more stable than the bond shift isomers of 1,2-dimethyl-[41] and 1-carbomethoxy-2-methylcyclooctatetraene (rapid interconversion at −12 °C).[5b]

Although the 1,4,5,8-tetramethyl structure (**58**) predominates by a substantial margin because it enjoys lesser steric encumbrance, this preference can be eliminated if two vicinal methyl groups are incorporated into a six-membered ring as in **60** $\rightleftarrows$ **61**. Prepared by thermal rearrangement[20] of [4.4.2]propellatriene **59**, this pair of bond shift isomers was found to exhibit, in addition to the multiplet at δ 2.35–1.30 arising from the methylene groups, equal intensity pairs of olefinic (δ 5.50, 5.41) and methyl singlets (1.74, 1.63). Thus the ratio of **60** to **61** is unity, signifying that these isomeric COT's are isoenergetic at ambient temperature and that the cyclohexene part structure in **60** imparts somewhat more thermodynamic stability than its 1,2-dimethylenecyclohexane counterpart in **61**. This may be a manifestation of the conformational preference of a tetramethylene loop on the tub-shaped COT ring or a matter of the destabilizing effect of double bonds which are exocyclic to a six-membered ring.



59 60 61

In conclusion, the present findings have demonstrated that pairs of [8]annulene bond shift isomers having sufficient stability to be capable of independent existence and storage in separate vials are now readily accessible.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A and HA-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

1,2-Dimethylcyclobutene from Sulfolane. A solution of sulfolane (18.0 g, 0.15 mol) in 300 ml of anhydrous tetrahydrofuran was treated with 150 ml of 2.2 M *n*-butyllithium (0.33 mol) under nitrogen at −78 °C. After 15 min, 70 g (0.2 mol) of methyl iodide was introduced by syringe at this temperature. The white precipitate which formed was removed by filtration, and the filtrate was evaporated and distilled. There was obtained 7.4 g (33%) of colorless liquid, bp 81 °C (0.3 mm), the ^{1}H NMR spectrum of which indicated it to be chiefly the 2,5-dimethyl sulfone (lit.[47] bp 107–108 °C at 2.0 mm): $\delta_{Me_4Si}(CDCl_3)$ 3.0 (m, 2), 1.35 (d, J = 2 Hz, 3), 1.32 (s, 4), and 1.25 (d, J = 2 Hz, 3).

A stirred solution of this sulfone (20.0 g, 0.135 mol) in 150 ml of dry dioxane was chilled in an ice bath and treated under nitrogen with 61.5 ml of 2.2 M *n*-butyllithium in hexane (0.135 mol). After 15 min, this solution was removed via syringe in 50-ml aliquots and added slowly to a refluxing mixture of lithium aluminum hydride (12.9 g, 0.34 mol) in 700 ml of dioxane. A slow stream of nitrogen was passed into the reaction mixture, and the gas stream was led from the top of the condenser to a trap cooled in dry ice-acetone. Refluxing with magnetic stirring was continued for 9 h with intermittent changing of the trap. The contents of the traps were combined and distilled through a Vigreux column. A fraction of bp 68–69 °C was obtained, but product was collected until a temperature of 100 °C was realized. Five fractions were obtained. These were combined, washed with saturated sodium sulfate solution, extracted into pentane, and dried. Redistillation gave 2.2 g (20%) of dimethylcyclobutene: $\delta_{Me_4Si}(CDCl_3)$ 2.21 (s, 4) and 1.54 (s, 6).[48]

***endo*-3,4-Dimethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (12).** A solution of *endo*-2-thia-1,2-dihydrodicyclopentadiene[49] (12.4 g, 0.081 mol) in ether (200 ml) cooled to 0 °C was treated dropwise with 256 ml of 0.645 N monoperphthalic acid (0.165 mol) in ether. After 4 h, the mixture was extracted with saturated sodium bicarbonate solution to which sodium chloride had been added to reduce the solubility of the sulfone in water. There was obtained 12.4 g of colorless crystalline sulfone; calcd *m/e* 184.0558, obsd 184.0562.

This material was dissolved in 150 ml of dry tetrahydrofuran and treated at −78 °C with 61.5 ml of 2.2 M *n*-butyllithium in hexane under nitrogen. Excess methyl iodide was introduced and 15 min later the predescribed workup procedure was utilized. The resulting dimethyl sulfone (**11**, 10.0 g, 0.0471 mol) in 80 ml of dry dioxane was converted to its monoanion at 5 °C with 21.4 ml of 2.2 M *n*-butyllithium in hexane (0.0471 mol). After stirring for a few min, this solution was added via syringe to a refluxing mixture of 4.5 g (0.118 mol) of lithium aluminum hydride in 800 ml of dioxane under nitrogen. After 15 h at the reflux temperature, workup as before and distillation gave 1.60 g (22%) of **12**. An analytical sample was obtained by VPC purification on a 10 ft × 0.25 in. 5% Carbowax column (Chromosorb G) at 100 °C: $\delta_{Me_4Si}(CCl_4)$ 5.73 (m, 2), 2.36–2.72 (br m, 4), 1.84 (m, 1), 1.28–1.58 (m, 1), and 1.40 (s, 6).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.22; H, 9.78.

11,12-Dimethyl[4.4.2]propella-3,11-diene (14). To a chilled (−78 °C) solution of 22.4 g (0.10 mol) of 12-thia[4.4.3]propell-3-ene 12,12-dioxide[50] in 250 ml of dry tetrahydrofuran under a dry nitrogen atmosphere was introduced 91.0 ml (0.200 mol) of a 2.2 M solution of *n*-butyllithium in hexane via syringe. After a few minutes 42.6 g (0.30 mol) of methyl iodide was introduced (again via syringe), and the reaction mixture was allowed to warm to room temperature. Water and ether were added. The organic layer was separated, washed twice with water, dried, and concentrated to give 25.4 g (100%) of an oily mixture of dimethyl sulfones predominating in **13** (^{1}H NMR analysis).

Dry dioxane (ca. 150 ml) was added to dissolve this oil, and the solution was stirred magnetically under nitrogen in a cold water bath. This solution was treated with 45.5 ml (0.100 mol) of a 2.2 M *n*-butyllithium solution in hexane. The resulting mixture was transferred to a 500-ml dropping funnel under a stream of nitrogen and introduced dropwise to a refluxing, mechanically stirred slurry of 19.0 g (0.500 mol) of lithium aluminum hydride in 2 l. of anhydrous dioxane under nitrogen. Refluxing was maintained for 20–24 h. A freshly prepared, saturated aqueous sodium sulfate solution was then cautiously added dropwise until all the hydride salts had been destroyed and the precipitate was white in color. The solids were removed by suction filtration and amply washed with petroleum ether (bp 30–60 °C). The combined filtrates were diluted with additional petroleum ether, and the dioxane was removed by repeated (four–five times) extraction with water. The organic layer was dried and concentrated to give an oil which was subjected to sublimation (90 °C, 0.10 mm). There was obtained 12.6 g (67%) of **14** as a white semi-solid. Preparative VPC (6 ft × 0.25 in. 5% XF-1150 on Chromosorb G, 120 °C) gave material of mp 56–58 °C: $\delta_{Me_4Si}(CCl_4)$ 5.56 (m, 2 H, olefinic), 2.00–1.70 (m, 4 H, allylic), 1.44 (s, 8 H, methylenes), and 1.38 (s, 6 H, methyls).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.19; H, 10.66.

1,6,7,8-Tetramethylbicyclo[4.2.0]octa-3,7-diene (17). Using the procedure developed above, 20.0 g (0.100 mol) of 1,6-dimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (**16**)[19] was treated in turn with 80 ml of a 2.5 M (0.200 mol) *n*-butyllithium solution in hexane, 50 g (0.35 mol) of methyl iodide, an additional 40 ml (0.100 mol) of the *n*-butyllithium solution, and 18.0 g (0.500 mol) of lithium aluminum hydride in 1.2 l. of anhydrous dioxane. Workup and distillation (0.10 mm, oil bath 90 °C) afforded 5.5 g (34%) of **17**: $\delta_{Me_4Si}(CCl_4)$ 5.57 (m, 2 H, olefinic), 1.92–1.70 (m, 4 H, allylic), 1.35 and 0.99 (s, 6 H each, methyl).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.82; H, 11.23.

1,2,3,8-Tetramethylcyclooctatetraene (18). A magnetically stirred solution of 4.7 g (0.029 mol) of **17** in 130 ml each of carbon tetrachloride and glacial acetic acid was treated with 10.2 g (0.0319 mol) of pyridinium hydrobromide perbromide. After 1 h, workup gave a colorless, oily dibromide which was dehydrobrominated in 260 ml of dry hexamethylphosphoramide with 12.2 g (0.29 mol) of anhydrous lithium chloride and 21.5 g (0.29 mol) of anhydrous lithium carbonate at 90–95 °C for 18 h. Workup[20] afforded a crude product which was passed through Florisil (pentane elution). There was obtained 4.6 g (99.4%) of **18** as a pale yellow liquid: bp 25–26 °C (0.10 mm); λ_{max} (EtOH) 220 nm (sh); ν_{max} (neat) 3010, 2940, 1640, 1440, 880, and 735 cm^{-1}; $\delta_{Me_4Si}(CCl_4)$ 5.35 and 5.70 (br s, 4 H, olefinic), 1.80 and 1.67 (s, 12 H, methyl).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.79; H, 10.37.

1,6,7,8-Tetramethylbicyclo[4.2.0]octa-2,4,7-trieneiron Tricarbonyl (20). A magnetically stirred solution of 340 mg (2.12 mmol) of **18** and 3.0 g (10.5 mmol) of benzylideneacetoneiron tricarbonyl[23] in 10 ml of benzene was heated at 60 °C for 48 h under a dry nitrogen atmosphere. Chromatography of the resulting solution on silica gel (pentane elution) gave 450 mg of a 1:1 mixture of starting material and complex. Slow rechromatography on silica gel provided a pure sample of complex **20** as a pale yellow oil: $\delta_{Me_4Si}(CCl_4)$ 5.30 and 2.85 (dd, J = 5.0 and 2.6 Hz, 4 H, olefinic), 1.34 and 1.06 (s, 6 H, methyl).

Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37. Found: C, 60.01; H, 5.59.

1,2,3,4-Tetramethylcyclooctatetraene (22). Reaction of 19.8 g (0.100 mol) of **21**[19] with 91.0 ml of a 2.2 M (0.200 mol) *n*-butyllithium solution in hexane followed by 50.0 g (0.350 mol) of methyl iodide and subsequent reaction with 10.0 g (0.27 mol) of lithium aluminum hydride in 1 l. of refluxing dioxane afforded 6.0 g of a pale yellow liquid after distillation [bp 23 °C (0.30 mm)]. Analysis by gas chromatography (6 ft × 0.25 in. 5% Carbowax 20M on Chromosorb G, 110 °C) indicated the substance to contain approximately 30% dioxane. A sample of the hydrocarbon fraction obtained by preparative scale VPC was determined by ^{1}H NMR spectroscopy to be an ca. 25:75 mixture of **18** and **22** (integration of the methyl region).

To a magnetically stirred solution of this oil in 100 ml of ethyl acetate was added dropwise a solution of 6.55 g (0.0375 mol) of *N*-phenyltriazolinedione in 100 ml of ethyl acetate. After the addition was complete, heating at reflux was maintained for 30 min. Removal of the solvent and chromatography on Florisil with ether elution gave 4.3 g (12.8% from **21**) of a mixture of **19** and **23** (from ether–hexane). Fractional recrystallization gave **23** in the first fractions: mp 180–181 °C; $\delta_{Me_4Si}(CDCl_3)$ 7.57–7.20 (m, 5 H, aromatic), 6.08 (d, J = 3.5 Hz, 2 H, olefinic), 4.98 (q, J = 3.5 Hz, 1 H, >N–C–H), 2.60 (br d, J = 4.0 Hz, 1 H, cyclobutenyl), 1.80 and 1.33 (s, 6 H, methyl), and 1.49 (s, 6 H, methyl).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.71; H, 6.07; N, 12.18.

Pure **19** was obtained from the later fractions: mp 175–176 °C; $\delta_{Me_4Si}(CDCl_3)$ 7.58, 7.25 (m, 5 H, aromatic), 6.21 (t, J = 3.5 Hz, 2 H, olefinic), 4.58 (t, J = 3.5 Hz, 2 H, >N–C–H), 1.42 and 1.27 (s, 12 H, methyl).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.39; H, 6.04; N, 11.65.

Hydrolysis–Oxidation of Adduct 19. A magnetically stirred mixture of 2.4 g (7.17 mmol) of **19**, 2.87 g (71.7 mmol) of sodium hydroxide, and 100 ml of 2-propanol was refluxed under nitrogen for 3 h, chilled, acidified with 3 N hydrochloric acid and made alkaline with 3 N aqueous ammonia. Pentane (~100 ml), followed by 6.2 g (71.7 mmol) of manganese dioxide, was added. After 3 h of additional stirring at room temperature, the pentane layer was separated, washed twice with dilute hydrochloric acid and twice with water, dried, and concentrated at reduced pressure below 20 °C. There was obtained 1.10 g (96%) of pure **18**.

Hydrolysis–Oxidation of Adduct 23. Treatment of 0.85 g (2.54 mmol) of **23** with sodium hydroxide (1.02 g, 25.4 mmol) in refluxing 2-propanol (50 ml) for 3 h, followed by sequential addition of 3 N hydrochloric acid, 3 N aqueous ammonia, and manganese dioxide (2.2 g, 25.4 mmol) in accordance with the procedure given above gave 406 mg (100%) of **22**; λ_{max} (EtOH) (ϵ) 275 nm (6700) and end absorption; ν_{max} (neat) 3000, 3920, 2860, 1650, 1620, 1440, 775, and 715 cm^{-1}; $\delta_{Me_4Si}(CCl_4)$ (for **22a**) 6.00–5.40 (pseudo q, J = 11.0 Hz, 4 H, olefinic), 1.67 (m, 6 H, methyl), and 1.58 (s, 6 H, methyl); also (for **22b**) 5.60–5.25 (weak m, olefinic), 2.70 (weak br s, angular H), and 1.20 (s, angular methyl).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.64; H, 10.08.

Epoxidation of 22. A magnetically stirred solution of **22** (140 mg, 0.875 mmol) in 4 ml of ether cooled to 0 °C was treated dropwise with 1.6 ml of 0.60 N monoperphthalic acid in ether (0.960 mmol). After 1 h at 0 °C, the mixture was stirred at room temperature for 8 h, diluted with ether, extracted with 0.2 N sodium hydroxide solution (2 × 50 ml), and washed with water (2 × 50 ml) before drying. Careful evaporation left an oil (70 mg) which after dissolution in pentane (2 ml) was treated with 50 mg (0.182 mmol) of *N*-phenyltriazolinedione in ethyl acetate. After 30 min, the product was isolated by chromatography on Florisil (ether elution) and crystallization from ether–pentane: mp 187–189 °C; $\delta_{Me_4Si}(CDCl_3)$ 7.37 (s, 5 H, aromatic), 6.37 (m, 2 H, olefinic), 4.95 (m, 1 H, >N–CH<), 2.29 (d, J = 5.0 Hz, 1 H, cyclobutenyl), 1.90 (s, 3 H, methyl), 1.17–1.45 (three overlapping s, 9 H, methyls).

Anal. Calcd for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.21; H, 5.86; N, 11.92.

Independent Synthesis of 26. A 50-mg (0.149 mmol) sample of **23** dissolved in 10 ml of ether was treated as above with 0.5 ml of ethereal monoperphthalic acid (0.30 mmol). After 20 h, the solvent was evaporated, and the residual solid was triturated with warm ether: dichloromethane (1:1). Cooling of the filtrate yielded 45 mg (86%) of **26**, mp 187–189 °C, which proved identical with the sample isolated above.

1,2,7,8-Tetramethylbicyclo[4.2.0]octa-2,4,7-trieneiron Tricarbonyl (20). A magnetically stirred solution of 250 mg (1.56 mmol) of **18** and 490 mg (1.71 mmol) of benzylideneacetoneiron tricarbonyl in 13 ml of benzene was heated at 60 °C for 48 h under dry nitrogen. Chromatography of the resulting solution on silica gel (pentane elution) afforded 360 mg (76.8%) of **20** as a bright orange colored oil. The analytical sample was obtained by bulb-to-bulb vacuum distillation; $\delta_{Me_4Si}(CCl_4)$ 5.37–5.10 (m, 2 H, olefinics), 3.23–2.91 (m, 1 H, olefinic), 2.30 (br d, J = 4.0 Hz, 1 H, methine), 1.52, 1.42, and 1.25 (s, 12 H, methyls).

Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37. Found C, 60.25; H, 5.48.

3,4,6-Trimethyl-*cis*-4,5-bis(methanesulfonyloxymethyl)cyclohexene (34). An autoclave containing 100 g (0.894 mol) of citraconic anhydride, 150 ml of crude 2,4-hexadiene,[51] and 500 ml of dioxane was heated at 170 °C for 24 h. Direct distillation afforded 118.0 g (68.1%) of anhydride **33** as a pale yellow colored oil. Reduction of **33** with 35.0 g (0.92 mol) of lithium aluminum hydride in tetrahydrofuran for 7 h followed by reaction with 240 ml (355 g, 3.1 mol) of methanesulfonyl chloride in pyridine gave 64.0 g (30.9%) of crystalline dimesylate **34**: mp 104–106 °C (from methanol); $\delta_{Me_4Si}(CDCl_3)$ 5.50 (m, 2 H, olefinics), 4.54–3.98 (m, 4 H, $-CH_2O-$), 3.05 (s, 6 H, $-SO_2CH_3$), 2.80–1.80 (br m, 3 H, allylics and methine), and 1.25–0.90 (m, 9 H, methyls).

Anal. Calcd for $C_{13}H_{24}O_6S_2$: C, 45.86; H, 7.11; S, 18.84. Found: C, 45.72; H, 7.14; S, 18.55.

1,2,5-Trimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (35). Dimesylate **34** (62.0 g, 0.182 mol) was transformed to the sulfide with an anhydrous slurry of sodium sulfide nonahydrate (130 g, 0.542 mol) in 900 ml of HMPA which was heated at 120 °C for 18 h with stirring. Workup in the predescribed manner[19] led to the isolation of 30.0 g (90.5%) of product after bulb-to-bulb vacuum distillation. Conversion to the corresponding sulfone was accomplished by treatment in ether at 0 °C with an ethereal solution of monoperphthalic acid (500 ml of a 0.70 N solution, 0.350 mol). There was obtained 16.0 g (45.4%) of white crystalline **35:** mp 67–69 °C (from ether–petroleum ether); $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 568 (br s, 2 H, olefinics), 3.48–2.20 (m, 5 H, $-\mathrm{CH_2}-\mathrm{SO_2}-$ and methine), 2.20–1.60 (br m, 2 H, allylics), 1.35 (s, 3 H, angular methyl), and 1.30–0.90 (m, 6 H, methyls).

Anal. Calcd for $\mathrm{C_{11}H_{18}O_2S}$: C, 61.64; H, 8.47; N, 14.96. Found: C, 61.56; H, 8.38; N, 14.78.

1,2,5,7,8-Pentamethylbicyclo[4.2.0]octa-3,7-diene (36). Methylation of 14.0 g (0.0655 mol) of sulfone **35** with 52.5 ml of a 2.5 M (0.131 mol) *n*-butyllithium solution and 30 g (0.211 mol) of methyl iodide, followed by ring contraction by sequential treatment with 40.0 ml (0.100 mol) of the *n*-butyllithium solution and 6.5 g (0.171 mol) of lithium aluminum hydride in 800 ml of refluxing dioxane for 22 h, afforded 5.6 g (48%) of **36:** $\delta_{\mathrm{Me_4Si}}(\mathrm{CCl_4})$ 5.33 (s, 2 H, olefinics), 2.45–1.65 (br m, 3 H, allylics and methine), 1.55 (m, 6 H, cyclobutene methyl), and 1.30–0.90 (m, 9 H, methyls).

Anal. Calcd for $\mathrm{C_{13}H_{20}}$: C, 88.56; H, 11.44. Found: C, 88.67; H, 11.39.

Bromination–Dehydrobromination of 36. Bromination of 5.3 g (0.030 mol) of **36** with 10.6 g (0.033 mol) of pyridinium hydrobromide perbromide in 100 ml each of carbon tetrachloride and acetic acid for 90 min was followed by dehydrobromination with a mixture of dry lithium carbonate and dry lithium chloride (22.2 g and 12.6 g, respectively, 0.30 mol each) in 300 ml of hexamethylphosphoramide for 20 h at 90–95 °C. Subsequent treatment with *N*-phenyltriazolinedione in ethyl acetate solution yielded 550 mg (5.4%) of a mixture of adducts **37** and **38** (~95:5). This solid could not readily be separated into the components by recrystallization: mp 164–165 °C; $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 7.60–7.20 (m, 5 H, aromatics), 5.95 (pseudo q, J = 8.0 Hz, 2 H, olefinics), 2.36 (br s, 1 H, cyclobutenyl), 1.89, 1.79, 1.48, and 1.30 (s, 15 H, methyls); also 5.65, 4.76, and 2.55 (weak br m, due to the olefinic, bridgehead, and cyclobutenyl protons of **38**).

Anal. Calcd for $\mathrm{C_{21}H_{23}N_3O_2}$: C, 72.18; H, 6.63; N, 12.03. Found: C, 72.03; H, 6.58; N, 11.99.

Hydrolysis–Oxidation of Adducts 37 and 38. Treatment of 300 mg (0.86 mmol) of the (95:5) mixture of adducts **37** and **38** sequentially with 344 mg (8.6 mmol) of sodium hydroxide in 30 ml of 2-propanol, 3 N hydrochloric acid, 3 N aqueous ammonia, and 746 mg (8.6 mol) of manganese dioxide according to the procedure employed earlier gave 141 mg (94.5%) of **39:** ν_{max} (neat) 2920, 1720, 1660, 1440, 1380, 840, and 760 cm^{-1}; $\delta_{\mathrm{Me_4Si}}(\mathrm{CCl_4})$ 5.64 (pseudo q, J = 11.5 Hz, 2 H, olefinics), 5.28 (s, 1 H, olefinic), and 1.82–1.50 (m, 15 H, methyls); also 5.55, 5.40, and 5.20 (weak br m, olefinics), 2.75–2.40 (weak br m, methine), and 1.19 (s, angular methyl).

Anal. Calcd for $\mathrm{C_{13}H_{18}}$: C, 89.59; H, 10.41. Found: C, 89.78; H, 10.44.

1,4,5-Trimethyl-*cis*-4,5-bis(methanesulfonyloxymethyl)cyclohexene (41). A mixture of 47.0 g (0.373 mol) of dimethylmaleic anhydride, 100 ml (68.1 g, 1.00 mol) of isoprene, and 50 ml of dioxane was heated in a rocking autoclave for 24 h. Workup as above gave 42.0 g (58.5%) of anhydride **40** which solidified on standing. The anhydride (42.0 g, 0.216 mol) was reduced with 10.0 g (0.263 mol) of lithium aluminum hydride in 1 l. of tetrahydrofuran at the reflux temperature for 18 h. The resulting oily diol was converted to its dimesylate with 50 ml (74.0 g, 0.645 mol) of methanesulfonyl chloride in 1 l. of pyridine during 2 h at −5 to 0 °C. There was obtained 58.0 g of **41** (79% from **40**): mp 64–66 °C (from methanol); $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 5.40 (br s, 1 H, olefinic), 4.19 (s, 4 H, $-\mathrm{CH_2O}-$), 3.04 (s, 6 H, $-\mathrm{SO_2CH_3}$), 1.97 (br s, 4 H, allylics), 1.70 (d, J = 1.2 Hz, 3 H, methyl), and 1.05 (s, 6 H, angular methyls).

Anal. Calcd for $\mathrm{C_{13}H_{24}O_6S_2}$: C, 45.86; H, 7.11; S, 18.84. Found: C, 46.05; H, 7.18; S, 18.55.

1,3,6-Trimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (42). From 120.0 g (0.50 mol) of sodium sulfide nonahydrate, 1 l. of hexamethylphosphoramide, and 57.0 g (0.168 mol) of dimesylate **41**, there was obtained 30.3 g (100%) of sulfide. Treatment of an ethereal solution of this sulfide as before with 470 ml of a 0.70 N (0.33 mol) solution of monoperphthalic acid in ether afforded 24.4 g (68.1%) of **42:** mp 122–124 °C (from ether–methylene chloride); $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 5.39 (br m, 1 H, olefinic), 3.10 (s, 4 H, $-\mathrm{CH_2SO_2}-$), 2.40–1.97 (m, 4 H, allylics), 1.70 (br s, 3 H, methyl), and 1.21 (s, 6 H, angular methyls).

Anal. Calcd for $\mathrm{C_{11}H_{18}O_2S}$: C, 61.64; H, 8.47; S, 14.96. Found: C, 61.55; H, 8.40; S, 14.85.

1,3,6,7,8-Pentamethylbicyclo[4.2.0]octa-3,7-diene (43). A 9.0-g (0.042 mol) sample of sulfone **42** was treated in turn with 31.0 ml of a 2.7 M (0.084 mol) hexane solution of *n*-butyllithium, 20 ml of methyl iodide, 15.0 ml (0.0405 mol) of the *n*-butyllithium solution, and 8.0 g (0.210 mol) of lithium aluminum hydride in 500 ml of dioxane for 20 h with close adherence to the procedural details given earlier. Workup and chromatography on Florisil (pentane elution) afforded 3.0 g (40.5%) of oily **43:** $\delta_{\mathrm{Me_4Si}}(\mathrm{CCl_4})$ 5.22 (br s, 1 H, olefinic), 1.85–1.55 (m, 7 H, allylics and methyl), 1.33 and 0.95 (s, 6 H, methyls).

Anal. Calcd for $\mathrm{C_{13}H_{20}}$: C, 88.56; H, 11.44. Found: C, 88.47; H, 11.39.

1,3,6-Trimethyl-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-Dioxide (44). Reaction of sulfone **42** (8.3 g, 0.0387 mol) with *N*-bromosuccinimide (7.7 g, 0.0433 mol) and a catalytic amount of benzoyl peroxide in 300 ml of refluxing carbon tetrachloride for 5 h, followed by treatment with 20.0 g (0.370 mol) of sodium methoxide in 600 ml of tetrahydrofuran according to the predescribed procedure,[19] gave a yellow oil. The oil was vacuum distilled in bulb-to-bulb fashion to give 3.5 g (42.6%) of impure **44** as a white solid, mp 71–85 °C. Sublimation did not improve the purity: calcd *m/e* 212, obsd 212; $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 5.75 (br q, J = 9.5 Hz, 2 H, olefinics), 5.26 (br s, 1 H, olefinic), 3.50–2.80 (m, 4 H, $-\mathrm{CH_2SO_2}-$), 1.80 (d, J = 1.5 Hz, 3 H, methyl), and 1.20 (s, 6 H, angular methyls).

Bromination–Dehydrobromination of 43. Bromination of dimethylcyclobutene **43** (3.0 g, 0.0170 mol) with pyridinium hydrobromide perbromide (6.0 g, 0.0187 mol) in carbon tetrachloride–acetic acid (75 ml each) and dehydrobromination with a mixture of 7.15 g (0.170 mol) of dry lithium chloride and 12.6 g (0.170 mol) of dry lithium carbonate in 150 ml of hexamethylphosphoramide led to the isolation of 1.1 g of a colorless oil after bulb-to-bulb vacuum distillation at 0.10 mm. Treatment of the oil with excess *N*-phenyltriazolinedione in ethyl acetate afforded 22 mg of colorless crystalline **46:** mp 193–194 °C (from petroleum ether–ethyl acetate); $\delta_{\mathrm{Me_4Si}}(\mathrm{CDCl_3})$ 7.62–7.20 (m, 5 H, aromatics), 5.77 (m, 1 H, olefinic), 4.30–4.60 (m, 2 H, >NCH<), 1.85 (d, J = 2.0 Hz, 3 H, methyl), 1.50 and 1.29 (s, 12 H, methyls).

Anal. Calcd for $\mathrm{C_{21}H_{23}N_3O_2}$: C, 72.18; H, 6.63; N, 12.03. Found: C, 71.89; H, 6.59; N, 12.06.

1,2,3,5,8-Pentamethylcyclooctatetraene (45). Hydrolysis–Oxidation of *N*-Phenyltriazolinedione Adduct 46. A magnetically stirred solution of 349 mg (1.0 mmol) of adduct **46** and 400 mg (10.0 mmol) of sodium hydroxide in 20 ml of 2-propanol was refluxed for 3 h, chilled, and treated subsequently in the predescribed manner. Manganese dioxide (870 mg, 10.0 mmol) and pentane were added; after 2.5 h, workup afforded 150 mg (86.3%) of **45:** ν_{max} (neat) 2950, 1650, 1440, 1380, and 825 cm^{-1}; $\delta_{\mathrm{Me_4Si}}(\mathrm{CCl_4})$ 5.60–5.26 (br m, 3 H, olefinics), 1.78 (d, J = 1.8 Hz, 6 H, methyls), and 1.67 (s, 9 H, methyls).

Anal. Calcd for $\mathrm{C_{13}H_{18}}$: C, 89.59; H, 10.51. Found: C, 89.78; H, 10.40.

Reductive Desulfonylation of Diene Sulfone 44. Successive treatment of 5.5 g (0.026 mol) of somewhat impure **44** with 21.0 ml of a 2.5 M (0.052 mol) *n*-butyllithium solution in hexane, 10 ml of methyl iodide, 10.5 ml (0.026 mol) of the *n*-butyllithium solution, and 3.2 g (0.084 mol) of lithium aluminum hydride in 400 ml of dioxane afforded 3.3 g of a colorless oily mixture of hydrocarbons after passage through Florisil (pentane elution). Treatment with excess *N*-phenyltriazolinedione in ethyl acetate and chromatography on Florisil with ether gave an oil which was fractionally crystallized from petroleum ether–(30–60 °C) ethyl acetate to give 400 mg (4.4%) of **46** in the first fraction, mp 193–194 °C. From the second fraction there was obtained 130 mg (1.4%) of a mixture of adducts **37** and **38** (ca. 95:5 ratio), mp 164–165 °C.

3,4,5,6-Tetramethyl-*cis*-4,5-bis(methanesulfonyloxymethyl)cyclohexene (53). A rocking autoclave was charged with 150 ml of crude 2,4-hexadiene [prepared according to the procedure of Adams and Geissman[51] from 305 g (2.80 mol) of ethyl bromide, 64.0 g (2.66 g-atoms) of magnesium turnings, and 160 g (2.29 mol) of crotonaldehyde, followed by slow distillation from 10 ml of aqueous hydrobromic acid], 150 g (1.19 mol) of dimethylmaleic anhydride, and 500 ml of dioxane and heated at 150 °C for 30 h. The solvent was removed on a rotary evaporator and the residual black oil was subjected to bulb-to-bulb vacuum distillation. The yellow colored distillate was dissolved in ether and repeatedly extracted with 10% aqueous potassium carbonate solution until the evolution of gases ceased. Evaporation of the ether phase gave 50.0 g of an oily yellow product (**52**) which could not be induced to crystallize.

A solution of this oil in 200 ml of tetrahydrofuran was treated with a slurry of 12.0 g (0.316 mol) of lithium aluminum hydride in 2 l. of the same solvent for 5 h as previously described. Subsequent reaction of the diol with 62.0 ml (91.6 g, 0.80 mol) of methanesulfonyl chloride in 1 l. of pyridine at −5 to 0 °C for 2 h gave 19.0 g (4.5% yield from dimethylmaleic anhydride) of crystalline dimesylate **53:** mp 94–96 °C (from methanol); δ_{Me_4Si}($CDCl_3$) 5.45 (s, 2 H, olefinics), 4.28 (s, 4 H, $-CH_2O-$), 3.00 (s, 6 H, $-SO_2CH_3$), 2.48–1.95 (m, 2 H, allylics), and 0.90–1.20 (m, 12 H, methyls).

Anal. Calcd for $C_{14}H_{26}O_6S_2$: C, 47.44; H, 7.39; S, 18.09. Found: C, 47.35; H, 7.41; S, 17.93.

1,2,5,6-Tetramethylbicyclo[4.2.0]octa-3,7-diene (56). An 18.0-g sample (0.0509 mol) of dimesylate **53** was heated with 36.0 g (0.150 mol) of sodium sulfide nonahydrate in 300 ml of anhydrous hexamethylphosphoramide for 18 h at 120 °C. The predescribed workup yielded 8.8 g (86.2%) of sulfide **54** as a colorless oil after bulb-to-bulb vacuum distillation: δ_{Me_4Si}(CCl_4) 5.32 (m, 2 H, olefinics), 2.60 (ABq, 4 H, $-CH_2S-$), 2.28–1.80 (m, 2 H, allylics), and 1.20–1.05 (m, 12 H, methyls). Chlorination of the sulfide (8.8 g, 0.0449 mol) with *N*-chlorosuccinimide (6.0 g, 0.0449 mol) in 170 ml of carbon tetrachloride, followed by oxidation with 140 ml of a 0.70 N (0.098 mol) solution of monoperphthalic acid in ether and subsequent treatment of the α-chloro sulfone (**55**) with 28.0 g (0.250 mol) of potassium *tert*-butoxide in tetrahydrofuran for 3 h led to the isolation of 3.6 g (49.6% from sulfide) of cyclobutene **56** as a colorless oil: δ_{Me_4Si}(CCl_4) 5.83 (s, 2 H, cyclobutenes), 5.28 (s, 2 H, olefinics), 2.15–1.70 (m, 2 H, allylics), 1.11 (s, 6 H, angular methyls), and 0.95 (d, J = 7.0 Hz, 6 H, methyls).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.49.

1,2,5,6- and 1,4,5,8-Tetramethylcyclooctatetraenes (57 and 58). A 2.0-g (0.123 mol) sample of **56** was treated in turn with 4.4 g (0.0137 mol) of pyridinium hydrobromide perbromide in 60 ml each of carbon tetrachloride and glacial acetic acid (1:1) for 2 h at ambient temperature, followed by a mixture of 5.2 g of lithium chloride and 9.15 g (0.124 mol each) of lithium carbonate in 100 ml of HMPA at 90–95 °C for 20 h. Workup and distillation afforded 1.8 g (91.6%) of an ca. 1:10 equilibrium mixture of **57** and **58:** δ_{Me_4Si}(CCl_4) 5.52 and 5.41 (s of unequal intensity, total 4 H, olefinics), 1.74 and 1.63 (s of unequal intensity, total 12 H, methyls).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.84; H, 10.09.

1,2-Dimethyl-5,6-tetramethylene- and 2,2-Dimethyl-6,7-tetramethylenecyclooctatetraenes (60 and 61). A 100-mg (0.538 mmol) sample of **59**[1a] was slowly vaporized into a flow system of nitrogen into a quartz reactor packed with quartz chips[52] heated to 470 °C (15 mm). The pyrolysate (74 mg, 74%) consisted of a mixture of **60** and **61** in an approximate ratio of 1:1: δ_{Me_4Si}(CCl_4) 5.50 and 5.41 (s, 2 H, each, olefinics), 2.35–1.30 (m, 8 H, methylenes), 1.74 and 1.63 (s, 3 H each, methyls).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.35; H, 9.83.

Acknowledgment. The authors thank the National Science Foundation, National Cancer Institute, and Eli Lilly Co. for their generous financial support of this research. The specialized efforts of L. B. Anderson, G. D. Ewing, and D. Taggart were similarly appreciated.

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Stereochemical Analysis of 1,1,2,2-Tetraarylethanes. 1. Static Stereochemistry

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Abstract: Empirical force field calculations on 1,1,2,2-tetraphenylethane (TPE) and 1,1,2,2-tetrakis(2,6-xylyl)ethane (TXE) show that these molecules adopt a $\mathbf{C}_2$ ground-state conformation in which the methine hydrogens are in anti positions. The dihedral angles of all four rings are equally signed; these systems can therefore be viewed as four-bladed molecular propellers. Comparison of the geometric parameters for TPE and TXE reveals that TXE is a highly strained molecule, as demonstrated by the unusual elongation of the central C–C bond and the unusual enlargement of the central C–C–C angles. The ^{1}H NMR spectra of tetramesitylethane (TME) and 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**2**) at the slow exchange limit are also consistent with a $\mathbf{C}_2$ conformation in solution. The racemic and meso forms of **2** have been separated and configurations have been assigned to the two stereoisomers on the basis of their NMR spectra. Treatment of the static stereochemistry of 1,1,2,2-tetraarylethanes in terms of a group theoretical approach leads to a description of the full permutation-inversion group, to the calculation of the number of isomers for any given substitution pattern in such systems, and to the recognition of systems which are stereochemically correspondent to 1,1,2,2-tetraarylethanes.

In continuation of our recent investigations dealing with the static and dynamic stereochemistry of molecules possessing two or more aryl groups attached to a central atom,[2] we extended our field of inquiry to the more complex 1,1,2,2-tetraarylethane system, in which *two* central atoms each bear a complement of aryl groups. Such systems have been investigated in the past, notably in conjunction with the radical dissociation process,[3] the pinacol-pinacolone rearrangement,[4] ethane rotation barriers,[5] and conformer determination with regard to the central ethane bond.[5,6] However, the ground-state geometry and conformational dynamics of 1,1,2,2-tetraarylethanes have so far received little attention, and the present work was initiated in order to provide a deeper insight into these problems.

Ground-State Conformation of Tetraarylethanes

The Anti Conformation. In 1,1,2,2-tetraarylethanes (hereafter simply referred to as tetraarylethanes), the ethane torsional angle represents an additional variable parameter which is not present in systems containing aryl rings attached to only one central atom. Previous reports dealing with dipole moment measurements on tetraarylethanes[6] and 1,2-dichloro-1,1,2,2-tetraphenylethane[5] have concluded that the most stable rotamer is the one in which the methine hydrogens or chlorines are in anti (trans) positions.

In order to obtain more detailed information, we turned to empirical force field calculations (molecular mechanics).[2h,7] Our calculations, which will be fully described in a later section, reveal that in 1,1,2,2-tetraphenylethane (TPE), the energy content of the least strained gauche rotamer is ca. 5 kcal/mol above that of the anti form, whence it follows that the equilibrium population of the gauche rotamers is vanishingly small as compared to that of the anti form. This energy difference can be expected to be even greater for bulkier aryl groups, and consequently we can generalize our conclusion that only those staggered rotamers are significantly populated in the ground state in which the methine hydrogens occupy the anti positions.

Orientation Capabilities of the Aryl Rings. The most symmetric structure for a tetraarylethane in the anti conformation is one possessing $\mathbf{C}_{2h}$ symmetry. This symmetry imposes constraints on the relative values of the four dihedral angles (ϕ) which describe the orientations of the four aryl rings, and which are defined by the four atoms joined by the three bonds leading from a methine hydrogen to an ortho benzene carbon atom ($H–C_{ethane}–C_{aryl}–C_{ortho}$). For example, in 1,1,2,2-tetrakis(2,6-xylyl)ethane (TXE, Figure 1) these angles are H1–C1–C2–C3, H1–C1–C8–C9, H1′–C1′–C2′–C3′, and H1′–C1′–C8′–C9′. The sign of the dihedral angle is defined as positive if, looking down the $C_{ethane}–C_{aryl}$ bond axis (e.g., C1–C2) from the ethane carbon atom (C1 or C1′), a counterclockwise rotation of the aryl group is required to eclipse the nearest $C_{aryl}–C_{ortho}$ (e.g., C2–C3) and $H–C_{ethane}$ (e.g., H1–C1) bonds ($\phi = 0°$). Thus, dihedral angles ranging from -90 to $+90°$ suffice to describe all of the possible orientations for an aryl ring possessing a local C_2 axis. In the ground state of TXE, all four dihedral angles are of the same sign (negative for the enantiomer depicted in Figure 1). On the other hand, if a ring lacks a local C_2 axis, values ranging from -180 to $+180°$ are required to describe all possible orientations.

Desymmetrization of the $\mathbf{C}_{2h}$ structure results in forms with $\mathbf{C}_s$, $\mathbf{C}_i$, $\mathbf{C}_2$, and $\mathbf{C}_1$ symmetry (the subgroups of $\mathbf{C}_{2h}$) and is accomplished by removing at least two of the three nontrivial symmetry elements (C_2, σ, i) in the $\mathbf{C}_{2h}$ form. In Figure 2 are depicted representative structures which belong to these various point groups; note that there are no constraints on the value of each individual ϕ within each point group, and that an infinite number of conformations are therefore possible within each class.

In principle, tetraarylethanes can exist in conformations belonging to any one of the symmetries described above.

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