1985

Experimental and computational studies of theoretically significiant alkenes

Richard O. Angus Jr.
Iowa State University

Recommended Citation

Angus, Richard O. Jr., "Experimental and computational studies of theoretically significiant alkenes " (1985). *Retrospective Theses and Dissertations*. 12042.
https://lib.dr.iastate.edu/rtd/12042

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8524632

Angus, Richard O., Jr.

EXPERIMENTAL AND COMPUTATIONAL STUDIES OF THEORETICALLY SIGNIFICANT ALKENES

Iowa State University PH.D. 1985

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Experimental and computational studies of theoretically significant alkenes

by

Richard O. Angus, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Members of the Committee:

Signature was redacted for privacy.

Iowa State University
Ames, Iowa

1985

TABLE OF CONTENTS

LIST OF FIGURES

For Part II:

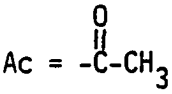
LIST OF TABLES

LIST OF SCHEMES

For Part II:

LIST OF ABBREVIATIONS

Organic Functional Groups


Ac = $-\overset{\overset{O}{\|}}{C}-CH_3$

E = ester moiety

Et = $-CH_2CH_3$

Me = $-CH_3$

ϕ, Ph = $-C_6H_5$

R = alkyl

Ts = $-SO_2$-p-$(C_6H_4)CH_3$

X, Y = electron withdrawing groups

Reagents and Solvents

DEAD = diethyl acetylenedicarboxylate
EtOAc = ethyl acetate
EVE = ethyl vinyl ether
HMPT = hexamethylphosphoramide
PyHOTs = pyridinium tosylate
THF = tetrahydrofuran
TMSCl = trimethylsilylchloride
TMSI = trimethylsilyliodide
TSA = tosylacetylene

DEDICATION

To Muz, Dad and Nanny.

"It is unworthy of excellent men to lose hours
like slaves in the labour of calculation"

Baron Gottfried Wilhelm von Leibnitz
(1646-1716)

ABSTRACT

The concept of a novel type of homoconjugation, henceforth referred to as columnar homoconjugation, is introduced. A new class of organic molecules which is expected to exhibit such interaction is devised; for this series, the name "columnene" is coined. Molecular Orbital calculations (Hückel, MNDO, and/or *ab initio*) for a series of columnenes as well as cyclic allenes, cyclicbutatrienes, and *trans* cyclic alkenes olefins are reported. These calculations lead to the prediction that alkene moieties easily withstand slight twisting and bending destabilization. Synthetic strategies towards columnenes are developed and are categorized by two approaches: butatriene and bis-allyl synthetic equivalent approaches. The utility of the butatriene synthetic equivalent approach for the synthesis of benzocyclobutenes is demonstrated. The first synthesis of 1,2,3-cyclononatriene, inspired by the results of MO calculations, is reported; the molecule is further characterized by complexation with Wilkinson's catalyst.

GENERAL INTRODUCTION

The synthesis and characterization of novel organic molecules long has provided a fascinating challenge and continues to be an active area of study. Over the decades, many extraordinary molecules have been synthesized. Sophisticated experimental and theoretical methods permit the study of highly reactive substances, which would have only fleeting existence under ordinary laboratory conditions.

Much can be learned by applying molecular orbital methods to real organic systems. The success of these methods instills confidence in their power to predict properties of systems before their synthesis. Importantly, accurate calculations may be performed on compounds which probably can never be isolated.

The present work developed as a combination of theory and experiment. Several fundamental questions of structural limitations were investigated. A novel and unknown class of olefins was studied by high level molecular orbital methods. These calculations led to the belief that the molecules could exist, and significant progress was made towards their synthesis. In another study, the structural limitations in cyclic cumulenes were explored. Theoretical analysis of cyclic butatrienes led to the prediction that 1,2,3-cyclononatriene should prove isolable. This molecule was subsequently synthesized for the first time. In closely related work, the electronic structure and chirality of highly strained cyclic allenes were investigated.

PART I. COLUMNAR HOMOCONJUGATION

Nonconjugated Interaction of π Orbitals

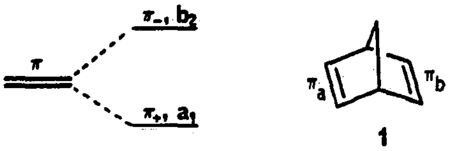
What is the effect of one double bond upon another nonconjugated double bond within the same molecule? The first qualitative answer to this question was offered by Hoffman *et al.*[1] in 1968. He attributed this orbital interaction phenomenon to the combined effects of orbital interaction through space (OITS) and orbital interaction through bonds (OITB). In the context of his analysis, two (or more) orbitals, ϕ_a and ϕ_b, of the same symmetry can interact if they are energetically similar and have a finite overlap integral ($S_{ab} = \left\langle \phi_a \phi_b \right\rangle > 0$). The resulting orbital interaction, to a first LCBO (linear combination of bond orbitals) approximation, requires representation of the resulting molecular orbitals (MO) as symmetric and antisymmetric combinations of the original bond orbitals; *i.e.*, ϕ_a and ϕ_b interact to give $\Psi_+ = \phi_a + \phi_b$ and $\Psi_- = \phi_a - \phi_b$. The magnitude of this interaction depends directly upon the magnitude of S_{ab}.

Experimental measurements of MO energy levels, especially for π and n MOs, are most readily accessible via photoelectron (PE) spectroscopy. PE spectroscopy yields the energy required to form each doublet radical-cation state ($^2\Psi_j$) from ionization of the closed shell molecule.[2,p9] By applying Koopmans' theorem[2,p11] (equation 1) and

$$E_j = I_{v,j}(\phi) \approx I_{max,j}(\phi) \qquad (1)$$

neglecting Jahn-Teller distortion[2,p238] and correlation energy differences, vertical ionization energies ($I_{v,j}$) may be equated to the energies of MOs from which the electron has been ejected. Nevertheless, PE spectroscopy cannot provide the symmetry of the ionized species. *Ab initio* MO calculations predict MO energy levels which can be compared with the PES data as well as predict the symmetry of each ionized state.

The classic example of such π bond interaction occurs in norbornadiene, **1**.[3] In this rigid molecule, the interaction of two formally isolated, isoenergetic, double bonds, π_a and π_b, is expected from the π orbital splitting of 0.85 eV observed in the PE spectrum and that predicted by extended Hückel calculations (0.43 eV).[3a] The explanation provided by Hoffmann was that through space π orbital interaction of π_a and π_b splits the formally degenerate energy levels. This purely through space interaction, termed homoconjugation, affords two new bonding combinations, $\pi_+ = \pi_a + \pi_b$, and $\pi_- = \pi_a - \pi_b$, of which π_+ (a_1 in C_{2v} symmetry) is of lower energy (Figure 1). The resulting order of MOs, π_+ below π_-, is referred to as the natural order of interacting π MOs.

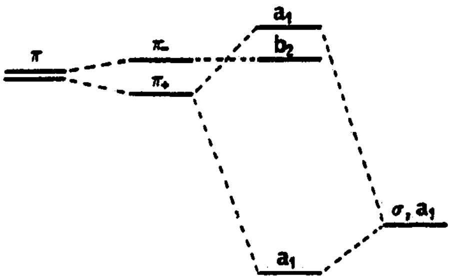


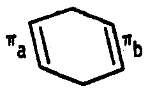
1

Figure 1[3a]. Simple MO representation of homoconjugative splitting of π orbitals

Comparison of **1** with 1,4-cyclohexadiene, **2**[3b,c] reveals important differences. The observed π-π gap for **2** is 1.0 eV, while a gap of 0.65 eV is predicted by extended Hückel MO calculations. Through space orbital interaction clearly cannot be greater for **2** than **1**, because in **2**, the geometrical constraint of the methano bridge is missing and the molecule is free to exist in an essentially planar conformation with minimal π overlap. Hoffman *et al.*[1] proposed that splitting in **2** is due to dominant through bond orbital interaction. High lying σ orbitals (predominantly from C-H bonds) interact with π_+ to such an extent that π_+ is raised 1.0 eV above π_-. This interaction, known as hyperconjugation, and the small contribution of homoconjugation in this system, are diagramed in Figure 2. The order of the resultant π MOs, π_- below π_+ is referred to as inverted order of interacting π MOs.

Systems in which both homo- and hyperconjugation can occur, provoke these questions: what is the ordering of these high lying MOs? and, which effect, through space or through bond, will dominate? These problems have been investigated through numerous





2

Figure 2[3]. Simple MO representation of hyperconjugative σ-π interaction theoretical and experimental studies and this topic has recently been extensively reviewed.[4] The importance of these interactions is evident from the dramatic difference in chemical reactivity between systems in which orbital interaction is important and those without such interaction. For example, norbonadiene undergoes Birch reduction ($Na/NH_{3(l)}$) much faster than norbornene[5] and cycloadds dicyanoacetylene[6] and other acetylenes[7] in a [2 + 4] manner. Orbital interaction also is evident from the long wavelength (230 nm) ultraviolet absorption of norbornadiene.[8] Some related examples of studies of 1,3- and 1,4-π-π orbital interactions will be discussed further.

Since PE spectroscopy cannot predict the ordering of π MOs, perturbation models which allow the inference of the symmetry of PES generated radical cations have been introduced. In such a model system, another π orbital of similar energy and of known symmetry is introduced to the original system. Since this perturbing orbital can interact only with orbitals of the same symmetry, the symmetry of any orbital with which it interacts can be inferred.

As a perturbation for norbornadiene, 1, a 7-methylene or 7-isopropylidene moiety, π_c, was introduced (Figure 3).[9] For 1 (C_{2v} symmetry), π_+ and π_- belong to the irreducible representations a_1 and b_2, respectively. The orbital providing the perturbation, π_c, belongs to b_2. The energy of $\pi_c(b_2)$ in 3 and 4 are similar to $\pi_+(a_1)$ and $\pi_-(b_2)$ and should mix with $\pi_-(b_2)$ while leaving $\pi_+(a_1)$ energetically unchanged.

From the PE spectra of 5, 1, 3, 7, 6, and 4, π MO energies for all π MOs were obtained via Koopmans' theorem. The data are diagramed in Figure 3.[9a] For each perturbed system, one π energy level remains essentially unchanged. This π MO must be the $\pi_+(a_1)$ of 1 which cannot interact with $\pi_c(b_2)$. In both perturbed systems the lower π level of 1 remained virtually unchanged. Thus, the $I_{v,2}$ of 1 was assigned to $\pi_+(a_1)$ and the original claim that 1 exhibits the natural order of π MOs is supported. The remaining π MOs $[\pi_-(b_2) \pm \pi_c(b_2)]$ lie ~ 0.5 eV above and below $\pi_-(b_2)$ and $\pi_c(b_2)$ due to their strong homoconjugation.

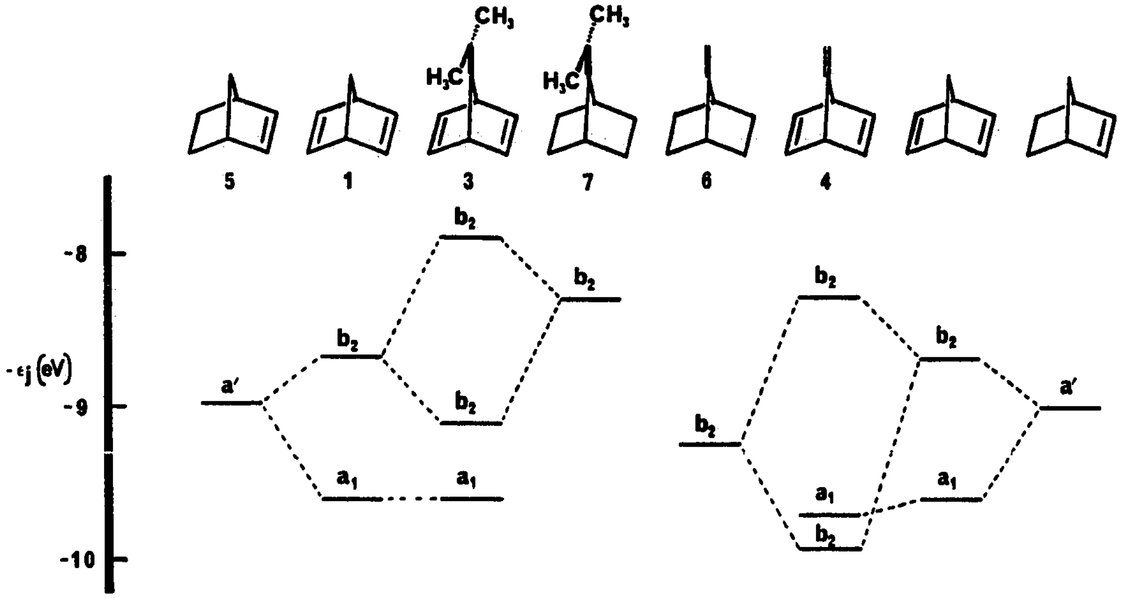
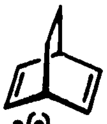


Figure 3[9a]. Inference of π MO level ordering in norbornadiene using a perturbation approach

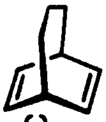
Since a similar orbital perturbation cannot be easily introduced into 2, Heilbronner has inferred the symmetry state ordering of the π MOs of 2 by a mathematical method based upon experimental and computational data.[10] From his results, he predicted an inverted order of the π MOs.

Heilbronner[10] and Goldstein *et al.*[11] further investigated the individual contributions of through space and through bond orbital

8(1)



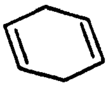
8(2)



8(3)

8(4)

8(n)



2

interaction in a series of norbornadienylogues **8(n)**, with n = 1-4. Diene **8(∞)**, the last of the series, was modeled by **2**. In this series orbital interaction was varied by varying the alkyl chain length (n) and thus the angle between the 2 π planes (ω). Calculated values of S_{ab} decrease smoothly with increasing ω (and n) as outlined in Figure 4. By increasing n in this series, through space orbital interaction and consequently the π MO gap should decrease monotonically if no through bond contribution is present. That the π MO gap in this series drops to a minimum for **8(3)**, followed by an increase to finally reach 1.0 eV for 2, indicates that while homoconjugation decreases, hyperconjugation increases. Goldstein *et al.*[11] explained that as ω and n increase, π_a-π_b interaction decreases and $\pi_+(a_1)$ mixes increasingly with a high lying $\sigma(a_1)$ orbital, thus raising the $\pi_+(a_1)$ level. The transition is smooth, as the π MO diagram in Figure 5 indicates. The crossover point (below which through space interaction dominates; above which through bond interaction dominates) was estimated to be at ω -130°. Using angular distribution PE spectroscopy, Kibel *et al.* have assigned the two highest π MOs of 2 to a_1 and b_2, respectively.[12]

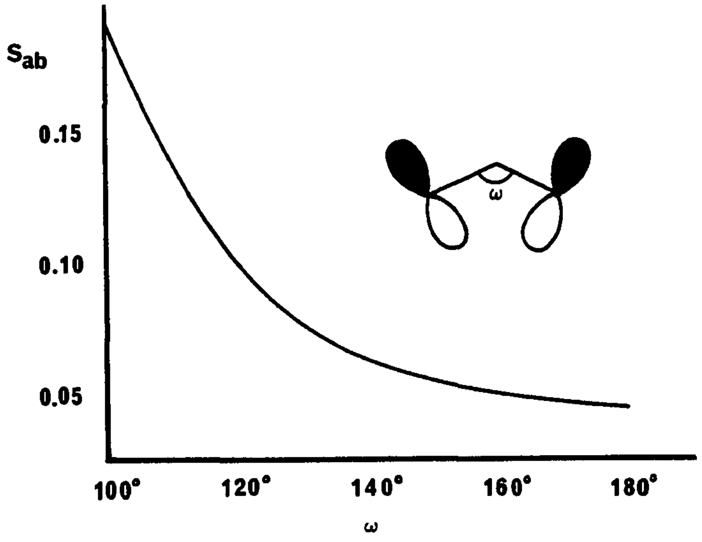


Figure 4[11]. Effect of dihedral angle, ω, upon S_{ab} for 1,4-cyclohexadienes

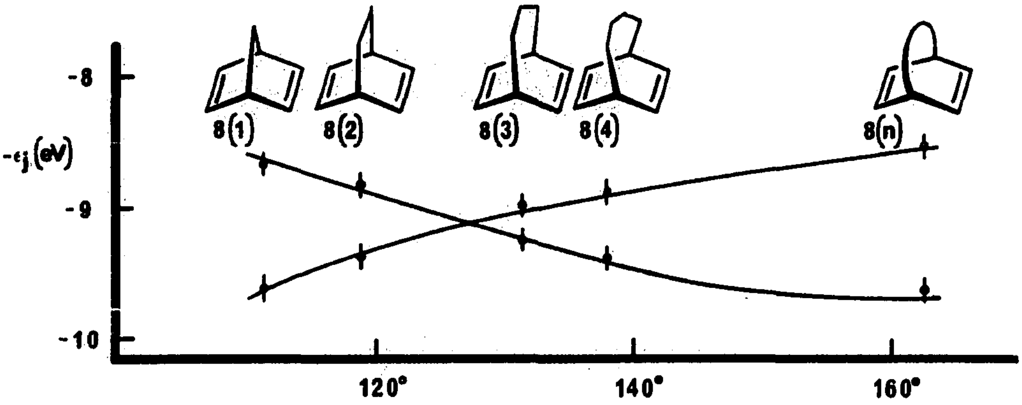
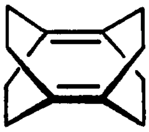


Figure 5[11] π MO energies of norbornadienylogue series as a function of dihedral angle ω

Among the many molecular systems expected to show similar π orbital interaction is the rigid 1,5-diene, **9**, recently prepared by Wiberg *et al.*[13] The two parallel π bonds in **9** are held rigid by four ethano



9

(CH_2CH_2) bridges. The separation of these π bonds was shown by X-ray crystallography to be 2.395Å.[14] This distance, about 1.0Å less than the π-π van der Waals contact distance of 3.4Å found in simple olefins,[15] indicates that strong interaction of the two π bonds may be expected. On this basis, this dominant through space orbital interaction should show a large π_+-π_- gap. The PE spectrum of **9**,[16] shows two well resolved bands at 8.6 and 9.3 eV, as well as a broad σ band beginning at 10.4 eV. Surprisingly, the 8.6 eV band was assigned to overlap of almost degenerate π_+ and π_- and the 9.3 eV band was assigned to a series of allyl C-C σ bonds. In an attempt to explain this assignment, MO energies were calculated (4-31G||STO-3G) as a function of π bond separation while maintaining the experimental values of all other bond lengths.[13] The MO energies thus obtained were plotted against π separation, as shown in Figure 6. These data show that at small separations (large π interactions), a large natural order π-π gap is predicted. But, this gap decreases and finally inverts with increasing π-π separation. Note also that the highest σ MO energy is predicted to be nearly invariant with π-π separation. This result indicates that the contribution of hyperconjugation can be large (with large π-π separation as in **2**) and is predicted to be very dependent upon slight geometric changes. For the equilibrium geometry of **9**, this calculation supports the experimentally observed near degeneracy of π levels.[16]

Similar π orbital interaction is expected in other noteworthy olefins, **10**, **11**, and **12**. A single broad PES ionization band at 9.1 eV was assigned to electron ejection from both π_+ and π_- of diene **10**,[17,18] which exists predominantly in the tub conformation (C_{2v}) depicted below. Effects of through space and through bond interactions apparently are nearly equal in this structure. In contrast, the more rigid **11** has two distinct ionizations at 9.1 and 9.45 eV and shows inverted π MO order.[17,18] This difference in the extent of orbital interaction may be attributed to variation of the π-bond separation (which unfortunately cannot be measured for 10) as well as differences in the σ framework.

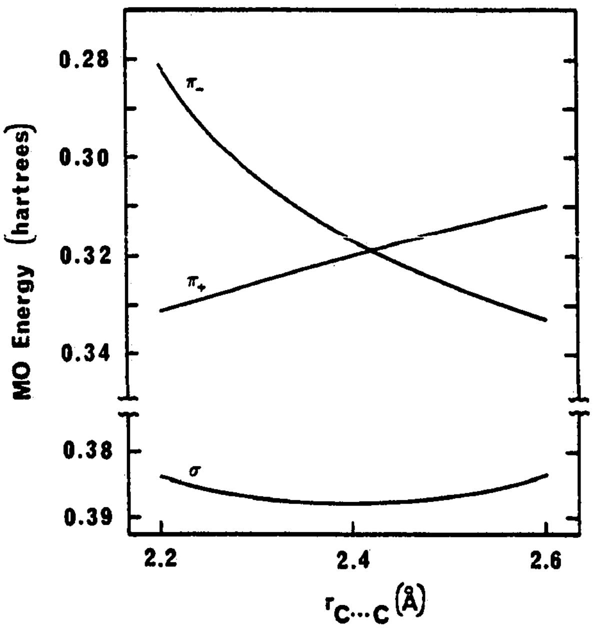
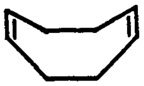
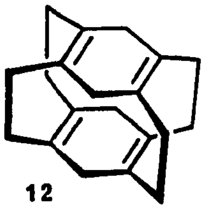


Figure 6[13] Change in energy of π, π and HO-σ-MO of **9** as a function of the distance between π bonds


10

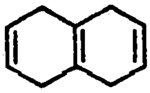

11

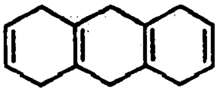

12

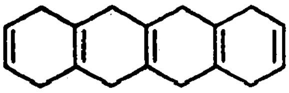
Tetraene 12, which results from Birch reduction of the corresponding cyclophane,[19] incorporates both the structure of 2 and 10 in its framework.[18] Separation of π planes (π_a and π_c) is ~ 3Å,[20] and, as a consequence, each 1,4-cyclohexadiene moiety is reportedly folded along a line joining the CH_2 groups, giving a dihedral angle, ω, of 140-150°. By analogy to the norbornadienylogues (Figure 5), it was expected that hyperconjugation may invert the π levels of this species. The PE spectrum[18] shows a broad π band beginning at -7.8 eV to which all four olefin ionizations were assigned. Korac *et al.*[18] claimed resonance integral (cross term, $\beta_{\pi\pi}$) values of $\beta_{\pi_a\pi_c} \sim 0$ and $\beta_{\pi_a\pi_b} = 0.3\text{-}0.4$ eV. Thus, they concluded that effects of through space and through bond orbital interaction between π_a and π_c nearly cancel, and the small predicted splitting of π_a and π_b, similar to that in 8(4), is obscured by other π ionizations.

In an attempt to understand these interactions better, Heilbronner *et al.* has investigated a series of higher homologues of 2.[21] In this series of molecules, 2 and 13 - 15, with n = 2 - 5 parallel double bonds, contributions from both through space and


2


13


14


15

through bond orbital interaction should be possible. By analogy to **2**, the through bond effect is expected to dominate.

From the reported He(I) PE spectra of **13** - **15**[21] the difference between the highest and lowest π energy for each molecule shows a variation of only 0.03 eV. Additionally, the mean π MO energy for each molecule (equation 2) decreases with increasing n. These trends,

$$\bar{\varepsilon}_{\pi} = \frac{\sum_{j}^{n} \varepsilon_{\pi j}}{n} \qquad (2)$$

Heilbronner *et al.* claim, suggest that through bond orbital interaction dominates. Heilbronner *et al.* next calculated resonance and Coulomb integrals from a simple model of this system. Coulomb integrals (self energies - α) and resonance integrals (cross terms - β) were estimated from π ionizations of ethylene, **2** and **13** - **15**, and previous experience. It was claimed that because the magnitude of $\beta_{\sigma\pi}$ is much larger than $\beta_{\pi\pi}$ that hyperconjugation will dominate throughout this series.

$$\alpha_{\pi} = \pi_{\alpha}|\mathcal{H}|\pi_{\alpha} = -10.3 \text{ eV}$$
$$\alpha_{\sigma} = \sigma_{s}|\mathcal{H}|\sigma_{s} = -14.7 \text{ eV}$$
$$\beta_{\pi\pi} = \pi_{a}|\mathcal{H}|\pi_{b} = -0.5 \text{ eV}$$
$$\beta_{\sigma\pi} = \pi_{a}|\mathcal{H}|\sigma_{s} = -1.7 \text{ eV}$$

In summary, theoretical and experimental studies have shown that formally nonconjugated π bonds may undergo substantial intramolecular interaction. This may occur through homoconjugation (through space) or hyperconjugation (through bond), depending primarily upon molecular geometry. Evaluation of the individual contributions of homoconjugation and hyperconjugation to the orbital interaction phenomenon is difficult; experimental techniques have not been able to satisfactorily solve this problem. MO calculations have been useful for predicting energies and symmetries of the MOs involved, but have been unable to evaluate individual contributions of homo- and hyperconjugation. It is possible that this interaction is so complex that the entire σ framework may be involved.[22]

Introduction to Columnenes

From the preceding historical discussion, it is apparent that much remains to be learned about homoconjugative orbital interactions. The present work arose from the desire to create specific molecular frameworks which engender significant homoconjugation. The type of orbital interaction chosen is depicted in Figure 7. Here three formally isolated π bonds are arranged parallel to and equidistant from a principal axis. Of course, this Hückel interaction may be extended to include any number of π bonds. Throughout this dissertation, this particular homoconjugative π-π interaction will be referred to as "Columnar" homoconjugation due to the analogy of π bond "columns" arranged along the periphery of a Greek arena. This orbital topology was inspired by a PES study of the Mobius array of π MOs of barrelene,[23] and related structures.

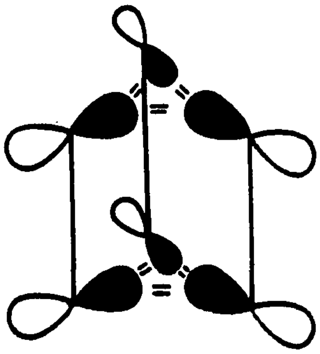
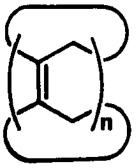
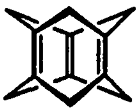


Figure 7. Orbital topology for columnar homoconjugation of three π bonds

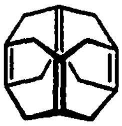
A search of the chemical literature showed no examples of molecules which exhibit columnar homoconjugation. The simplest means of connecting the columnar homoconjugated π bonds in a rigid framework, while concomitantly maintaining electronic isolation, may be connecting each end of adjacent π bonds with single methano (CH_2) bridges. The general class of molecules thus obtained **16**(n) is comprised of n 1,2-methano bridged parallel double bonds, held in a cyclic array with overall D_{nh} symmetry. This general structure and three of the smallest homologues (n = 3, 4, 5) of the series are depicted below. For these compounds, the trivial name "columnenes" is suggested. The above three homologues **17** - **19** will be referred to as tri-, tetra-, and pentacolumnene, respectively. This is a fundamental, yet unknown class of organic molecules.



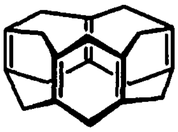
16(n)



17



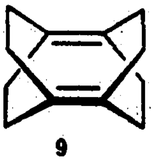
18



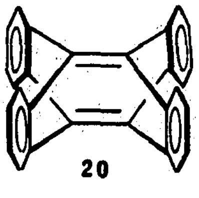
19

Can these molecules exist? From consideration of molecular models it is apparent that the small homologues will exhibit considerable strain. Large columnenes should be nearly free of strain. Some estimate of the potential isolability of columnenes may be derived from similar, known structures and from molecular orbital calculations.

The archetypal examples of similar strained compounds are rigid diene 9, which was recently prepared by Wiberg *et al.*,[13] and tetrabenzannulated derivative 20, prepared by Viavattene *et al.*[24] Parent



9

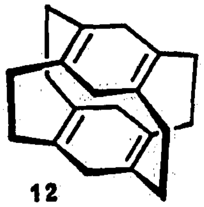


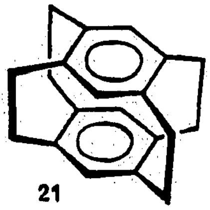
20

dimer 9, previously discussed in the historical section, is a stable, crystalline substance in which two parallel π bonds are held by ethano (CH_2CH_2) bridges in an orbital topology similar to those of columnenes. In fact, this molecule may be thought of as a homodicolumnene. To relieve the destabilization which accompanies the expected π-π interaction, and because of purely geometric strain, the π bonds of **9** are substantially pyramidalized (*i.e.*, rehybridized). The experimentally observed pyramidalization angle[1] in **9** is 27.3°. This rehybridization introduces s character to the p-π orbital, which counteracts the orbital energy level raising associated with pyramidalization. This effect also allows for increased π plane separation with π electron density concentrated in the exo-p-π orbital lobes. This is an important factor in the thermodynamic stability and reactivity of this and similar molecules.

Pyramidalization is expected to occur in columnenes because it should reduce the destabilization of through space orbital interaction, which is imposed by the rigid framework.

Orbital interactions which are similar to those expected in columnenes are found in [2.2.2.2](1,2,4,5)cyclophane (**21**) and its tetrahydro derivative, **12**, both reported by Gray and Boekelheide.[19]


12

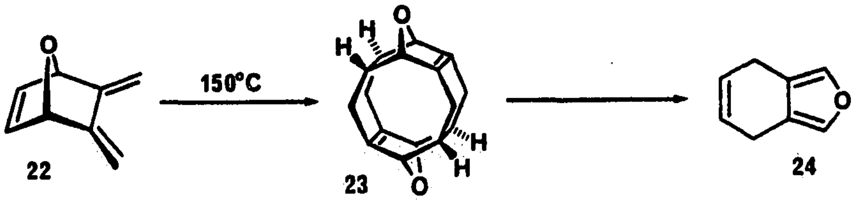

21

---

[1] This angle is defined as the angle between the vector coincident with the double bond and the plane defined by one olefinic C and its two singly-bonded substituents (*i.e.*, allylic C's for **9** and columnenes, **16(n)**).

Tetraene **12**, previously discussed in the historical section, can be thought of as a homotetracolumnene; *i.e.*, two opposing pairs of methano bridges of **18** are replaced with ethano bridges in **12**. The pyramidalization angle was not reported, but, from the geometry data given, this angle was estimated to be 8.5°. Thus, **12** is expected to be significantly less strained than **18**.

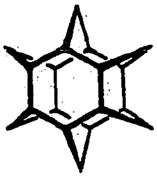
A molecule containing the tetracolumnene framework may have been generated as an intermediate. In the pyrolysis of exo-diene **22**, a columnene-like structure, **23**, was suggested as a transient structure which fragments to form furan **24**[25] (equation 3). However, no spectroscopic evidence for its existence was given. Note that columnenes cannot readily decompose via retro-Diels-Alder reaction.



(3)

Although columnenes are unknown, the fully saturated hydrocarbon skeletons for at least two columnenes have been the subjects of previous research. Iceane, **25**, formally hexahydrotricolumnene, has been prepared by several routes.[26] The proposed hexaasterane, **26**, which was investigated via force-field methods, incorporates the octahydrotetracolumnene skeleton within its structure.[27]

25



26

The initial goals of the present research were defined as the theoretical analysis of the effects of homoconjugation and the development of synthetic strategies for the preparation of columnenes. Of course, the ultimate goal is the synthesis of a series of columnenes, and a subsequent chemical and PE spectroscopic investigation of each columnene prepared. Correlation between the theoretical predictions and the PES data are desired. Ideally, this information may provide a better understanding of orbital interaction in terms of through space and through bond components. Beyond this, there exists a vast array of potential structural and chemical investigations of columnenes and related columnar structures.

Theoretical MO Analysis of Columnar Homoconjugation

Columnar homoconjugative interaction of n π bonds is expected to lead to n bonding and n antibonding π MOs.[28,p6] At the Hückel molecular orbital (HMO) level of approximation, π MO energies can be predicted by the simple Frost-Muslin circle mnemonic.[28,p24] This requires basis energies of $\pm 1\ \beta$ (π and π^*) and circles of radius $2\ \beta'$ where β' is the homoconjugative interaction parameter. Using this method, energy levels were calculated for n = 1 - 3 interacting π bonds. Resulting π MO energies are qualitatively diagramed in Figure 8. The bonding MOs are all occupied, thus the net delocalization energy is zero. The interaction is homoconjugative and not homoaromatic.[29] At this level of computation, no account of the overlap integral has been

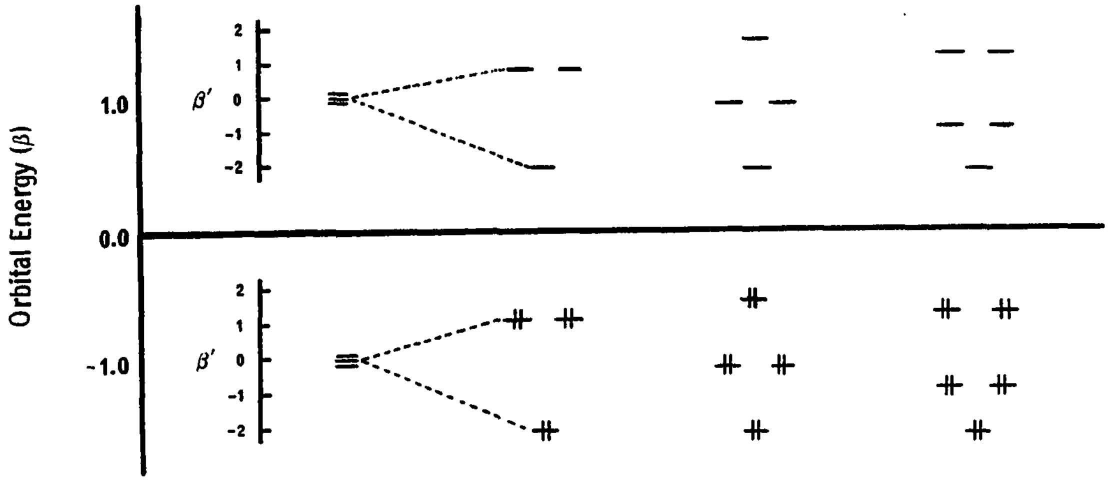


Figure 8. Hückel molecular orbital energy levels calculated for tri-, tetra-, and pentacolumnene

made and no net stabilization or destabilization is predicted; with inclusion of overlap the net effect will be destabilizing.

The first attempt at higher level calculations with the inclusion of overlap used the extended Hückel (EHMO) method.[30] This method generally is qualitatively reliable for homoconjugative systems and explicitly includes the overlap integrals. EHMO calculations were performed using molecular geometries for columnenes **17** - **19** which were estimated from molecular models. These geometries were created by assuming nearly planar π bonds with normal bond angles. The resulting π MO energies are diagramed in Figure 9. These results qualitatively paralleled the simple HMO predictions.

Although these extended Hückel calculations clearly indicate the effects of such homoconjugative interaction, it seemed desirable to proceed to higher level calculations in order to accurately predict geometries. Particularly interesting is the degree of

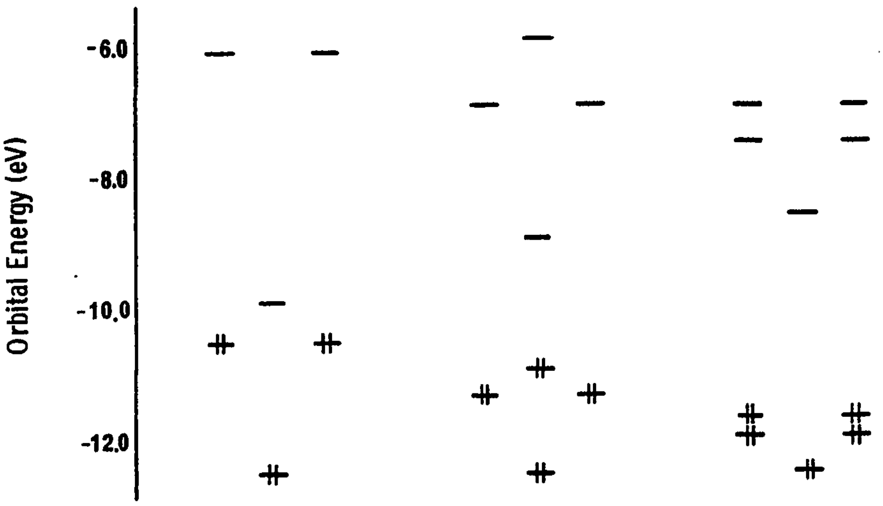


Figure 9. Extended Hückel molecular orbital energy levels calculated for tri-, tetra-, and pentacolumnene

pyramidalization of the double bonds, since this may best predict the isolability of columnenes.

Although they are exceptionally large molecules, it was decided to optimize molecular geometries[31] using *ab initio* gradient SCF methods.[2] Initial geometries similar to those used for the EHMO study were chosen as starting points. The minimal STO-2G basis set[32a] was chosen because of its computational economy and because past results show only small differences between the results of STO-2G and the more frequently used STO-3G basis. Calculations were enormously simplified due to the high molecular symmetry (D_{nh}) of columnenes. Each

---

[2] The program GAMESS, with an SCF gradient tolerance of 0.002 mdyn/Bohr, was used for all geometry optimizations.

has only four unique atoms: olefinic and allylic carbons and lateral[3] and radial[3] hydrogens. Such large *ab initio* calculations would have been impossible without the judicious use of symmetry generated atoms. Confidence in the resulting geometric predictions for this type of molecule is reinforced by the excellent agreement found between the experimentally determined and STO-3G predicted geometries for **9**.[13]

The coordinates of the resultant symmetry atoms are collected in Table 1. Salient MBS optimized geometric parameters are summarized in Table 2 and are discussed below. Figures 10 - 12 show top and side views of the equilibrium geometries. These optimized geometries undoubtedly are a vast improvement over the estimated geometries used in the EHMO calculation. Thus, trends within this series should be well represented.

As expected, the size of the cavity within the columnene framework increases with increasing n. This trend, shown in Table 2, is reported as the radial distance between the principal axis (C_n) and the olefinic carbon atoms. Olefinic and allylic bond lengths are slightly longer than those in unstrained systems and both decrease slightly with increasing n. This indicates the presence of distinct framework strain in **17** which decreases in each of the larger structures. As a measure of π-bond geometrical distortion, the pyramidalization angle is defined as the angle between the ${}_6C$-${}_5C$-${}_7C$

---

[3] Radial (lateral) hydrogen atoms are those with C-H bonds nearly parallel (perpendicular) to the principal axis.

Table 1. Cartesian Coordinates for Symmetry Atoms (Bohrs)[a]

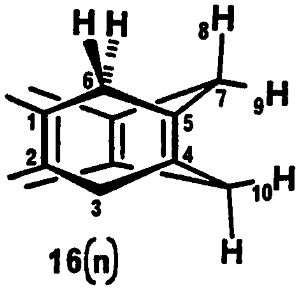
	Atom	x	y	z
17	C (sp^3)	2.799385	0.0	2.485700
	C (sp^2)	-2.562856	0.0	1.270009
(D_{3h})	H_{radial}	2.703176	0.0	4.553471
	$H_{lateral}$	4.792586	0.0	1.950599
18	C (sp^3)	2.532125	2.532135	2.551636
	C (sp^2)	3.256629	0.0	1.263231
(D_{4h})	H_{radial}	2.352433	2.352433	4.600346
	$H_{lateral}$	3.974500	3.974500	2.199582
19	C (sp^3)	4.348488	0.0	2.610534
	C (sp^2)	-3.962974	0.0	1.260373
(D_{5h})	H_{radial}	3.914073	0.0	4.635298
	$H_{lateral}$	6.418396	0.0	2.424158

[a] Principal axis is z.

plane and the $_{5}C$-$_{4}C$ vector (see the local numbering of the Figure in Table 2). Predicted pyramidalization is quite severe for **17** (43.7°) but decreases as one proceeds to higher columnenes (*e.g.*, 29.3° and 18.2° for **18** and **19**, respectively).

The origin of this pyramidalization may be attributed to two major contributors: a) purely geometric constraints imposed by the small, rigid molecular framework and b) electronic reorganization resulting in lowering of the total energy of the molecule. Geometric

Table 2. Optimized Geometric Parameters[a] for Columnenes



16(n)

Parameter	17 (D_{3h})	18 (D_{4h})	19 (D_{5h})
Distance (Å)			
double bond length	1.344	1.337	1.334
allylic bond ($_1C$-$_6C$)	1.562	1.552	1.548
$_1C$-C_n axis (radial)	1.356	1.724	2.098
π-bond separation ($_1C$-$_5C$)	2.349	2.437	2.465
distance $_9H$-$_{10}H$	2.631	2.328	2.566
Angle (degrees)			
pyramidalization	43.7	29.3	18.2
angle $_6C$-$_5C$-$_7C$	110.5	119.5	121.8
angle $_2C$-$_1C$-$_6C$	114.3	116.1	117.5
angle $_8H$-$_7C$-$_9H$	107.7	106.9	107.3

[a] Local numbering scheme is given in the Figure above.

distortion through pyramidalization is expected to be the important factor because it allows for increased π-bond separation. Concomitant orbital distortion will minimize endo π-lobe interaction and resultant homoconjugative destabilization. This combination of effects is known to be sensitive to slight geometric variation; *e.g.*, pyramidalization has been predicted by *ab initro* calculations to occur in molecules

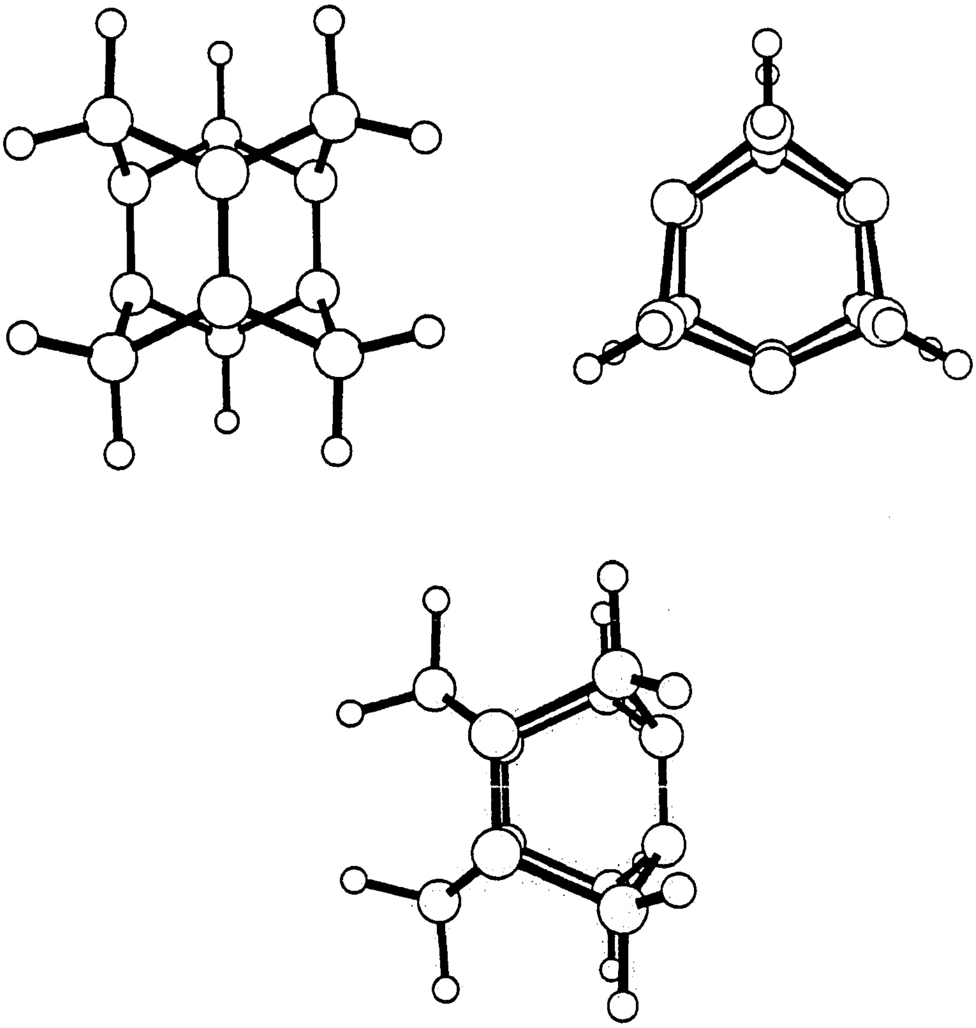


Figure 10. Optimized geometry for tricolumnene (17)

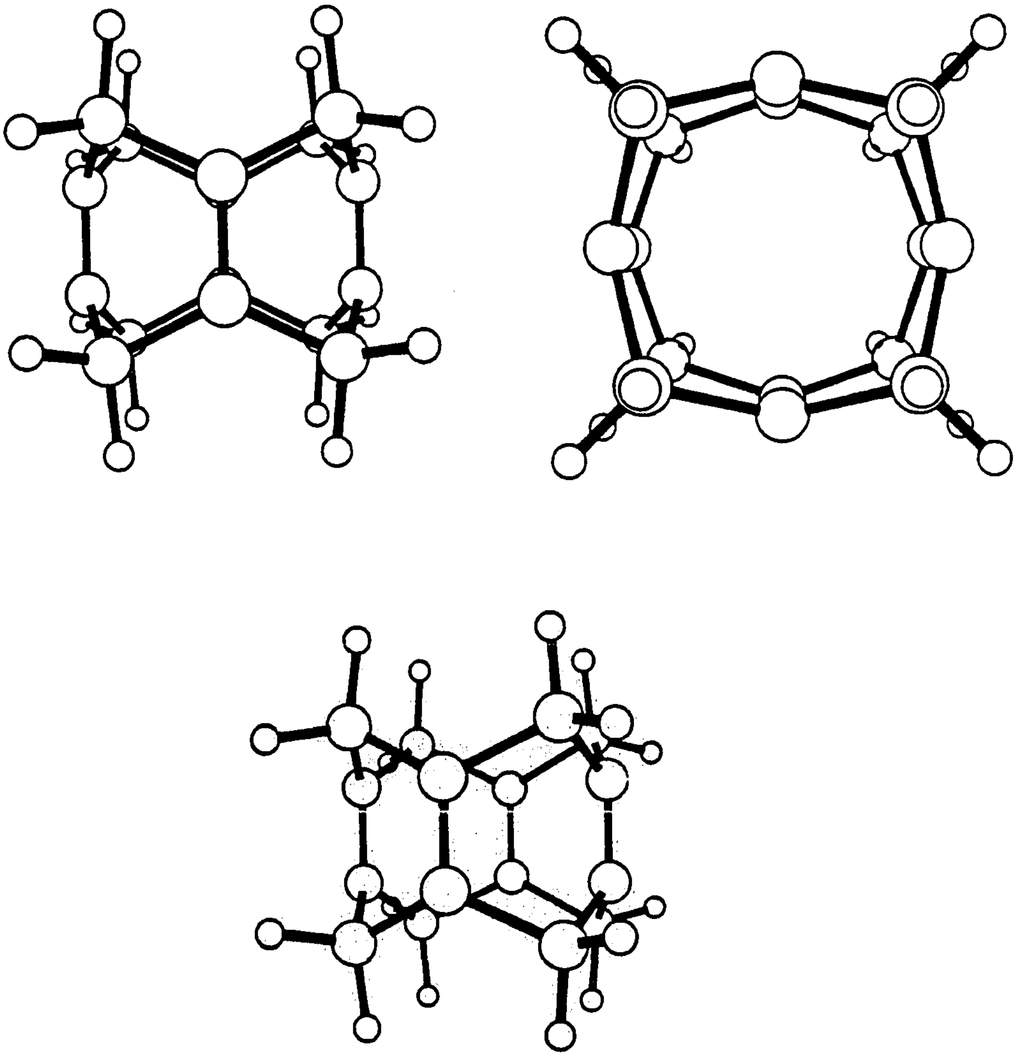


Figure 11. Optimized geometry for tetracolumnene (18)

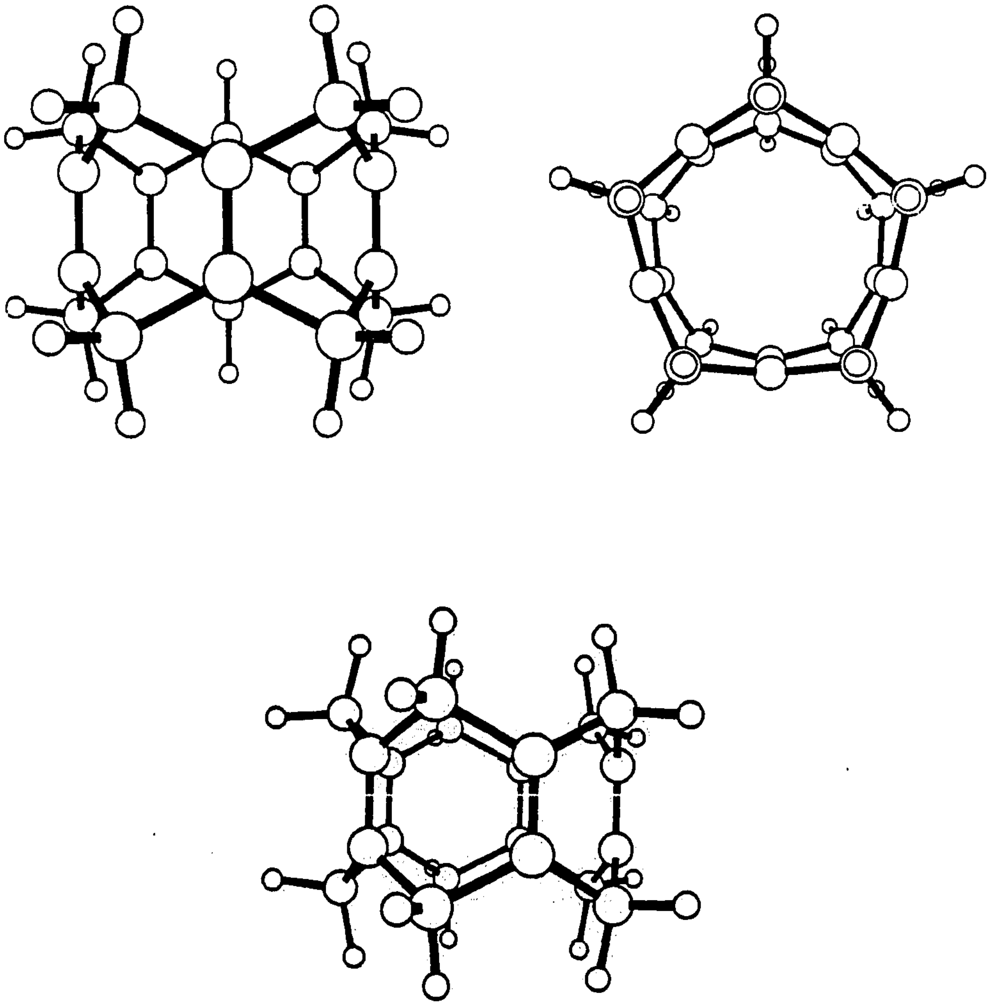


Figure 12. Optimized geometry for pentacolumnene (19)

27

such as 27 (*vide supra*) in which no bending constraints are imposed by the framework.[33] Thus, pyramidalization can be electronically favored.

One interesting trend to be noticed for this homologous series is that 1,3-π-bond separation (*i.e.*, distance $_1C-_5C$ in the figure of Table 2) increases only slightly. This constancy is due to the counterbalancing effects of decreasing olefin pyramidalization with increasing cavity size.

An additional small source of strain probably arises from the 1,4-lateral H-H interaction (distance $_9H-_{10}H$ in the figure of Table 2). This effect should be small since these distances (2.33 - 2.63 Å) are near the sum of two van der Waals radii (2.4 Å) for hydrogen. This trend with increasing *n*, however, is irregular; the smallest separation is predicted for **18**, while the larger values for **17** and **19** are nearly equal.

Good geometries are a prerequisite to the calculation of reliable energy levels. Due to the inability of MBS calculations to adequately reproduce vertical ionization potentials, a final calculation was performed at the split valence 3-21G level for each of the optimized geometries. The 3-21G basis set[32b] was chosen because it reproduces the first ionization potential for ethylene of 10.18 eV (lit. I_v[2,p105]

= 10.51 eV) and also because the memory requirements of calculations using this basis set would not exceed the storage capacity of the VAX system used. Nevertheless, 3-21G calculations for pentacolumnene ($C_{20}H_{20}$; 220 basis functions, 140 electrons) generates 7.8 million two-electron intergrals.

The 3-21G SCF energies for π and π* MOs of 17 - 19 are diagramed in Figure 13. Total energies, obtained from both STO-2G and 3-21G basis sets, are collected in Table 3. As expected, the ordering of π and π* MOs is consistent with the expected Hückel array. Assuming the validity of Koopmans' theorem[2,p11] and neglecting Jahn-Teller effects[2,p238] upon ionization from degenerate π MOs, the first ionization potentials are predicted to be 8.15, 3.54, and 7.68 eV for 17 - **19**, respectively. These values are expected to be reasonably accurate, although the calculated ionization potential for **18** is remarkably low.

Table 3. Total Energies for Columnar Structures (hartrees)

Structure	E_{TOT} (hartrees) STO-2G || STO-2G[a]	E_{TOT} (hartrees) 3-21G || STO-2G[a]	E_{TOT}/n (hartrees)
17 ($C_{12}H_{12}$)	-442.31335	-458.60633	-152.86878
18 ($C_{16}H_{16}$)	-589.95056	-611.30996	-152.82749
19 ($C_{20}H_{20}$)	-737.53746	-764.59463	-152.91893

[a] All calculations are at STO-2G optimized geometries.

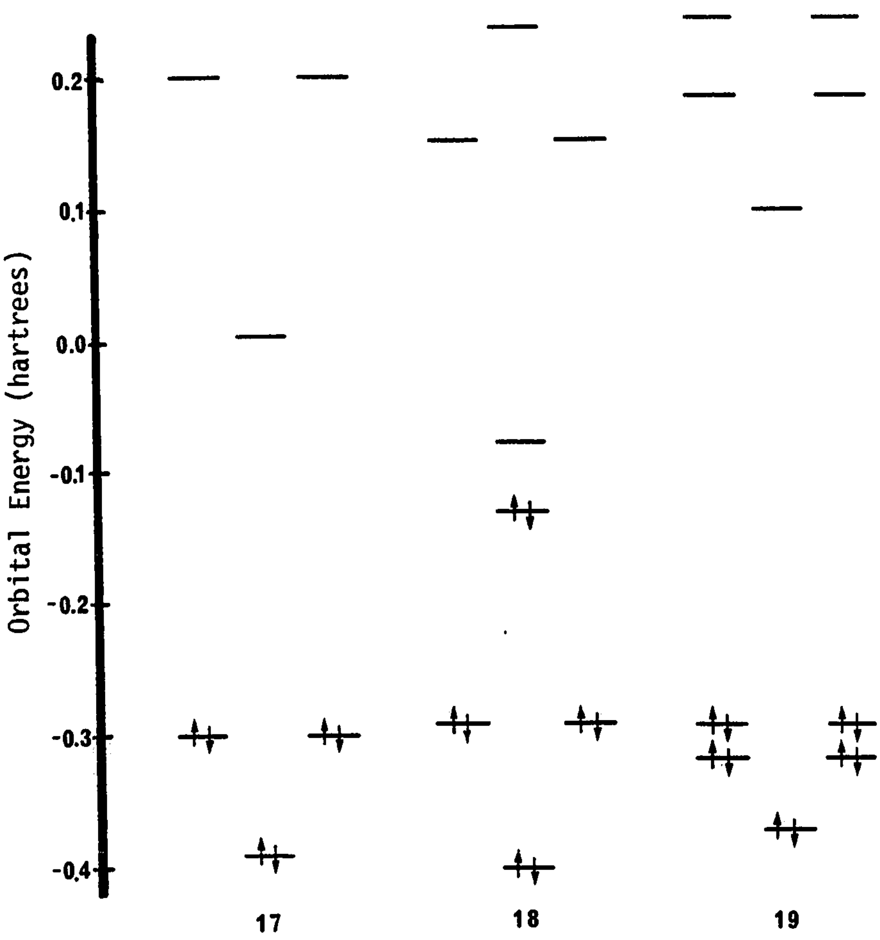


Figure 13. π Molecular orbital energies for 17-19

In principle, if one divides the value of the total electronic energy by n (n = 3, 4, 5) this should partition it into n $(CH)_4$ units, and afford some estimates of relative stability. These data are collected in Table 3. The STO-2G values are ignored in this discussion, because of their inherent unreliability with respect to relative energy prediction.

The $(CH)_4$ component energy at the 3-21G SCF level [-152.9189 hartrees/$(CH)_4$ subunit] of the least strained pentacolumnene was used to "predict" total energies for smaller homologues, relative to **19**. From this, tricolumnene (**3**) and tetracolumnene (**4**) are 94.5 and 230 kcal/mol *less* stable, respectively, than predicted. This is a crude estimate, but it leads to the interesting conclusion that the stability of columnenes will be in the order **5** > **3** > **4**. This relative destabilization of tetracolumnene is ascribed primarily to the extraordinarily high-lying HOMO; the energy of this predominantly antibonding MO is *ca.* 0.17 hartree (107 kcal/mol) above that of HOMOs for **3** and **5**.

Other noteworthy computational trends for the columnene series are collected in Table 4. In all of these, tetracolumnene is the least regular. The high lying HOMO leads to a predicted first ionization potential of only 3.54 eV for tetracolumnene.

Table 4. Columnene Trends Predicted from 3-21G||STO-2G Calculations

Parameter (eV)	Columnene (n) 17	 18	 19
$^{\varepsilon}$HO-σ-MO	-11.28	-11.24	-10.82
HO-LU gap	7.17	1.32	5.12
$^{\pi}$bonding range	2.49	7.30	2.14
first I_v	8.15	3.54	7.96
σ-π gap	0.64	0.39	0.72

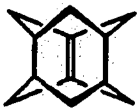
the highest and lowest bonding π MOs) which is nearly three times larger than either **17** or **19**. The Frost-Muslin circle mnemonic suggests that even n columnenes should have the highest energy π MO (destabilized by 2β') but the magnitude of this range (7.30 eV) is much larger than expected. As a result of this high-lying π MO, **18** is predicted to have a HOMO-LUMO gap of only 1.32 eV, considerably lower than for **17** or **19**. These results further support the contention that this molecule will be the least stable of the series; oxidation will be so facile that this molecule should be extremely reactive. For the series of polyhydroaromatics **2**, **13** - **15**, Heilbronner *et al.*[21] have observed very little variation of π-bonding range. For the columnene series, $\epsilon_{HO-\sigma-MO}$ increases with n. This may indicate an increasing availability of the σ MO for hyperconjugation, with increasing n. Goldstein *et al.*[11a] have observed the opposite trend in bicyclic systems, but this is not comparatively useful because the effect is probably very framework dependent.

The magnitude of the σ-π gap for **18** is about two-thirds the magnitude of the gap predicted for **17** or **19**. Thus, the σ and π MO interaction is favored in **18** on the basis of closeness of σ and π energies. Hyperconjugation may contribute more in **18** than **17** or **19**. The net effect of hyperconjugation should be destabilizing.

Conclusions

Members of the homologous series of columnenes should each show significant through space orbital interaction as a result of columnar homoconjugation. This net effect is destabilizing for neutral (2 n π electron) species. Columnenes minimize these destabilizing effects by pyramidalization and rehybridization of olefinic carbon atoms; however, pyramidalization also results from purely geometrical factors.

Will these molecules be isolable? From its high degree of π-bond pyramidalization (43.7°), it is believed that tricolumnene will be far too reactive for isolation. However, if it can be made, tetrahydro derivative **28** should be an interesting molecule from which to learn about geometrically constrained pyramidalization. Dihydro derivative **29** would be an excellent example for comparison of orbital interaction with norbornadiene, **1**. In principle, these might be prepared from the known iceane structure.[26]



28

29

Tetracolumnene is predicted to be the most destabilized and have the highest hyperconjugative contribution of the series. The first ionization potential predicted for **18** in only 3.54 eV and the 1.32 eV HOMO/LUMO gap is remarkably small. This small HOMO/LUMO gap is probably due to the fact that the HOMO is a totally through space antibonding combination of individual π MOs, while the LUMO is a through space bonding combination of individual π* MOs. Thus, this HOMO is a very destabilized bonding MO while the LUMO is stabilized by a bonding type homoconjugative overlap. This is depicted in Figure 14.

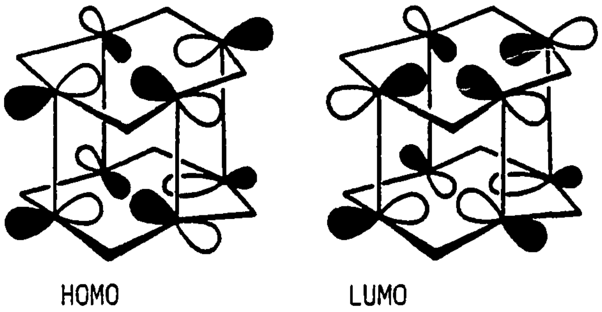


Figure 14. HOMO and LUMO orbital topology predicted for tetracolumnene

Tetracolumnene is expected to have a high degree of pyramidalization (29.3°) and a cavity size similar to the known crystalline diene **9**. Despite this analogy, it is believed that it may be unstable. Tetracolumnene has twice the number of π-bonds interacting in approximately the same space. Due to the high lying HOMO energy, **18** should be highly susceptible to oxidation. This may favor isolation of the mono- or dication instead of the neutral species.

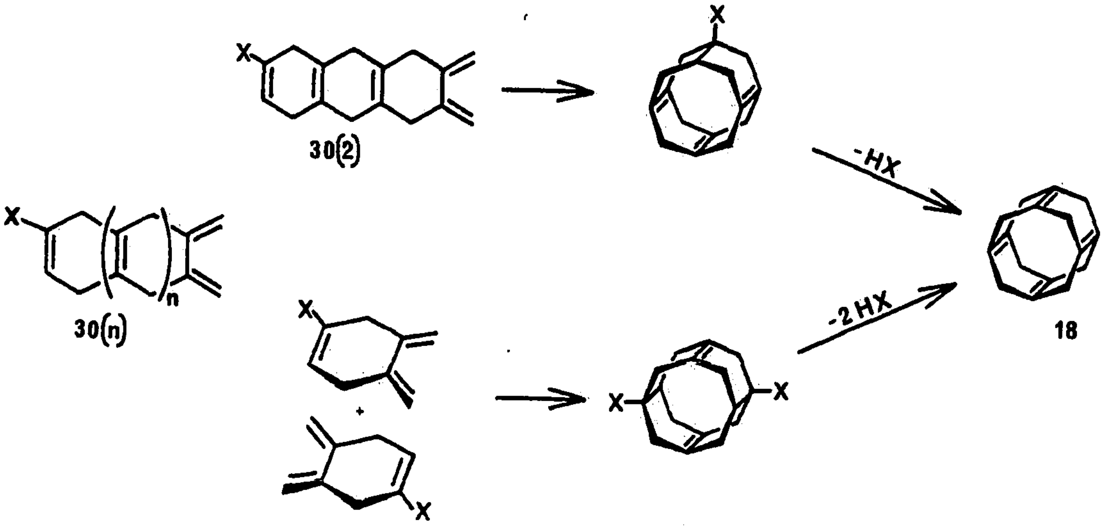
Pentacolumnene is the least distorted of the homologous series examined. Arrays of π and π* MOs are essentially as predicted and the lowest ionization potential, calculated to be 7.96 eV, is remarkably ordinary. The central cavity size (radius = 2.10 Å) engenders significantly less π orbital interaction than in smaller homologues. These data provide the argument that pentacolumnene should be the smallest isolable columnene. Higher homologues should also be isolable.

Synthetic Strategy toward Columnenes

Potential routes to columnenes must take into consideration their complex, but highly symmetrical (D_{nh}) polycyclic skeletons, the high degree of unsaturation of the $(CH)_4$ general structure, and their inherent molecular strain. Tricolumnene is expected to be the most strained of the series and its synthesis has not yet been attempted. Efforts to date have been directed towards the tetra-, penta-, and hexacolumnenes and related structures. All routes chosen rely strongly upon conservation of molecular symmetry and a variety of known synthetic transformations.

The conceptually simplest and most direct routes to columnenes are easily visualized through either an intramolecular Diels-Alder cycloaddition of an appropriate linear precursor (such as **30(n)**) or a dimerization route involving two sequential cycloadditions. This is outlined for Scheme 1. The function of the X group in **30(n)** is two

Scheme 1 Potential Diels-Alder routes to columnenes



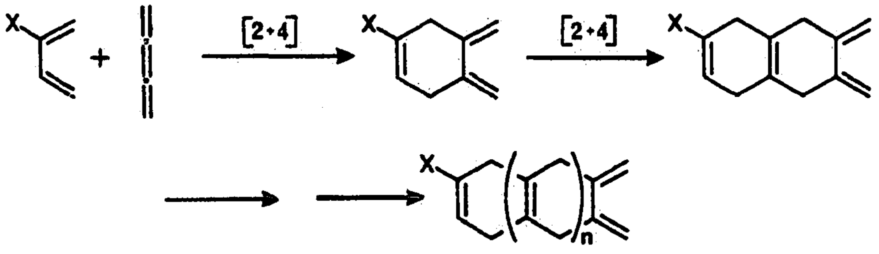
fold; first, X must be an electron withdrawing group to increase the dienophilicity of the olefin; second, X must be chosen such that it and the adjacent hydrogen should be easily eliminated to introduce the final double bond(s) in the columnene. The unique feature of these precursors is that they contain both a dienophile and a diene (enophile). For simplicity, such molecules will be referred to as ambiphiles throughout this dissertation.

This strategy presents two distinct and sequential challenges: construction of ambiphilic columnene precursors **30(n)** with various numbers of linearly connected 1,4-cyclohexadiene units, and effecting the inter- and intramolecular Diels-Alder cycloaddition, which is required for closure to the columnene ring skeleton. These challenges will be considered in turn below.

Butatriene synthetic equivalent

Conceptually, synthesis of the requisite columnene precursors may be effected by multiple, sequential, Diels-Alder cycloadditions of the central double bond of 1,2,3-butatriene to a 2-substituted 1,3-butadiene. This conceptual strategy is outlined in Scheme 2. Because of

Scheme 2 Conceptual preparation of columnene precursor **30(n)** via sequential Diels-Alder cycloaddition of butatriene

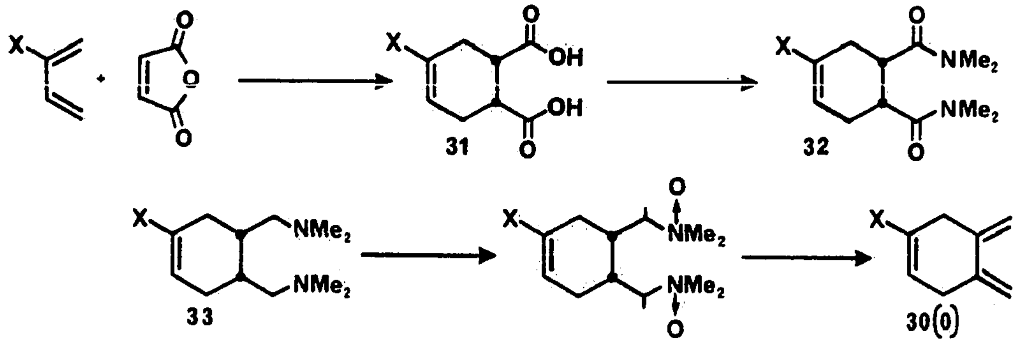


30(n)

its weakly dienophilic character[34] and tendency towards polymerization,[35] 1,2,3-butatriene is not appropriate for this homologation.

To avoid these limitations, a butatriene synthetic equivalent[4] was needed. In practice, the requisite reagent must be a four carbon dienophile with a central multiple bond. Its terminal functionality must be easily converted to exomethylene moieties after Diels-Alder cycloaddition with the appropriate diene. Traditional routes to this homologation have utilized maleic anhydride as the dienophile. Subsequent modification of the adduct involved pyrolysis of an amine oxide,[36] acetate,[37] or tetraalkylammonium salt.[38] An example of this strategy, employed by Middlemas and Quin,[36] is outlined in Scheme 3 (X = H). These procedures are of limited use for multiple homologation because of their poor yield and necessarily high pyrolysis temperatures, which

Scheme 3 Maleic anhydride as a butatriene synthetic equivalent



---

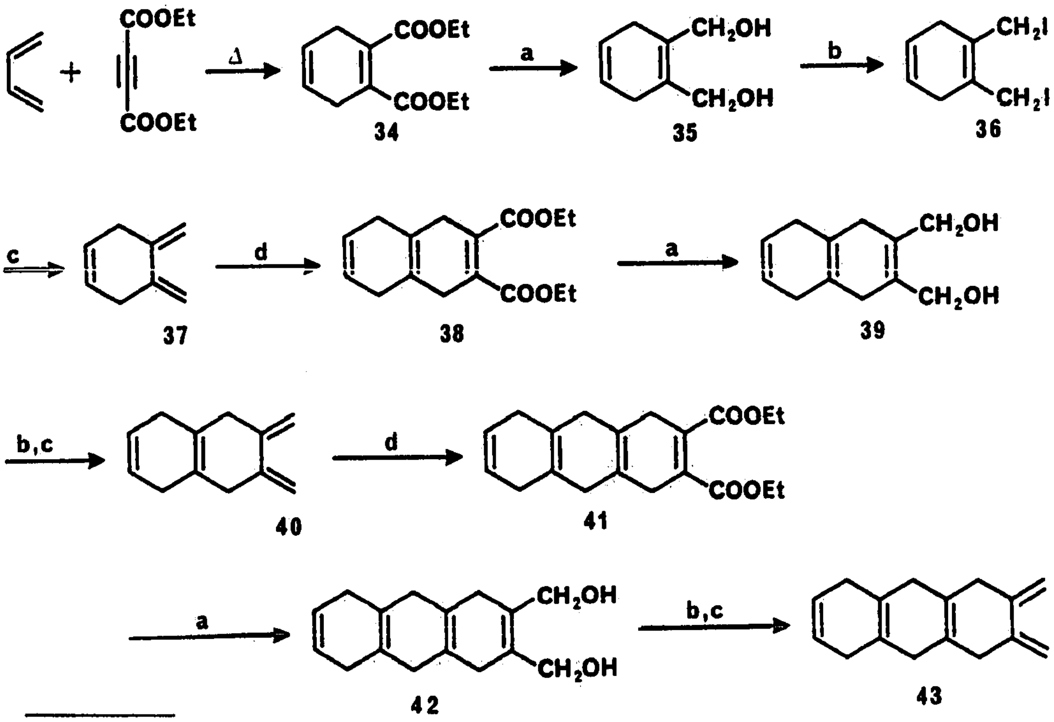
[4] By synthetic equivalent, what is meant is a reagent designed such that after its initial reaction with the substrate, it may be modified to give the same product as would have arisen from the conceptual reaction.

may be detrimental to polyhydroaromatics. An overall homologation yield of 30% was obtained by Middlemas and Quin.[36] When this route was repeated with X = Cl, the inefficiency (22%) of the amine oxide pyrolysis contributed to the poor (8%) yield for the homologation.

Diethyl acetylenedicarboxylate (DEAD) was introduced as a butatriene synthetic equivalent. DEAD is an excellent choice because it is easily prepared[39] and satisfies the requirements of a butatriene synthetic equivalent. This general procedure is outlined in Scheme 4.

Diels-Alder cycloaddition of DEAD with 1,3-dienes generally proceeds smoothly in benzene solution at or below reflux.

Scheme 4 Diethyl acetylenedicarboxylate as a butatriene synthetic equivalent



---

[a]LiAlH$_4$, ether. [b]NaI/TMSCl, ether. [c]Zn/Cu, ether. [d]DEAD, benzene.

1,3-Butadiene readily reacted with 1 equivalent of DEAD at 40-45°C to give diester **34** in nearly quantitative yield. Reduction with $LiAlH_4$ in anhydrous ether afforded 92% of the known diol **35**.[40] This was converted to the iodide **36** by treatment of an ethereal solution of **35** with iodotrimethylsilane (TMSI) or more commonly chlorotrimethylsilane and sodium iodide (TMSCl/NaI). This iodination is a modification of the general procedure of Olah *et al.*[41] In a typical preparative sequence, the diiodide **36** was not isolated, but instead was transferred via cannula to a stirring ethereal suspension of freshly prepared zinc-copper couple (Zn/Cu). The 1,4-elimination of iodine was facile and known diene **37**[36,42] was obtained, after aqueous workup, in 82% yield from diol **35**. The overall homologation yield was 74%. High temperature and acidic conditions are avoided by using this procedure.

The preparation of higher homologues **40** and **43** was accomplished in 43 and 13% yields, respectively, by straightforward repetition of this four-step sequence. The generality of this method was thus demonstrated but, unfortunately, the homologation yield dropped with each repetition. Efficiency of the third homologation was not optimized.

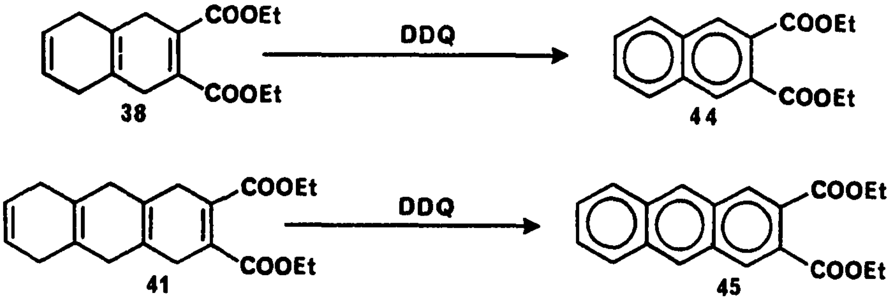
Shortly after this butatriene synthetic equivalent approach was published, the National Cancer Institute, Division of Cancer Treatment, Bethesda, MD 20205, requested samples of diols **35** and **39** for use in a preliminary biological activity screening tests. Both diols were found inactive at dose levels of 50-240 mg (diol)/kg(body weight).

Several difficulties in this repetitive sequence are worthy of comment. First, diols **39** and **42** were difficult to isolate because 10-30% of the reduction product remained entrained in the inorganic residue. Much of the entrained diol was recovered by continuous extraction of the residue with ether or ethyl acetate. Secondly, standard preparations of Zn/Cu[43] often failed to eliminate iodine in these systems. A new preparation of Zn/Cu, which invariably yielded a highly reactive couple in a few minutes, was developed. A mixture of Zn dust and $CuSO_4 \cdot 5H_2O$ (10:1) molar ratio was covered with a minimal amount of dimethylformamide (DMF), while under a nitrogen atmosphere. Within 1 minute, a rapid exothermic reaction yielded the black Zn/Cu ready for use. It is interesting to note that anhydrous $CuSO_4$ did not lead to Zn/Cu formation under these conditions. The water of hydration apparently played an important role in the reduction of $Cu^{(II)}$.

Another noteworthy point is the requirement of an ethereal solution for the compatability of the sequential iodination-elimination steps. Diethyl ether, THF, or a mixture have been satisfactorily used. THF is best suited to diols with low ether solubility.

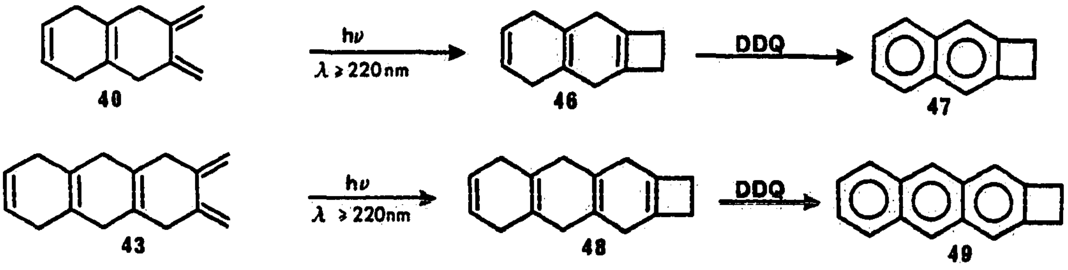
To establish further the structures of diesters **38** and **41**, each was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[44] to yield the known diethyl 2,3-naphthalene dicarboxylate, **44**,[45] and diethyl 2,3-anthracene dicarboxylate, **45**, respectively (Scheme 5). Structural assignment for each aromatic ester was consistent with all spectral data.

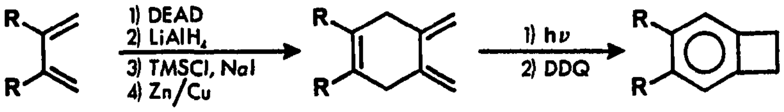
Scheme 5 Oxidation of diesters 38 and 41



This homologation procedure also provides a general and exceptionally simple route to benzocyclobutenes. Photocyclization of 37, followed by oxidation to benzocyclobutene was reported by Garrett and Fonken.[46] This two-step transformation was extended with the synthesis of naphtho[b]cyclobutene,[47] 47, and anthro[b]cyclobutene,[48] 49, as diagramed in Scheme 6. Dienes 40 and 43 were cyclized by irradiation as dilute solutions in pentanes, through a vycor cutoff filter ($\lambda \geq 220$ nm). The resulting cyclobutenes 46 and 48 were smoothly oxidized with DDQ to the known aromatics 47 and 49. Spectral data and melting points of these compounds agreed with literature values.

Scheme 6 Synthesis of naphtho[b]cyclobutene and anthro[b]cyclobutene





(4)

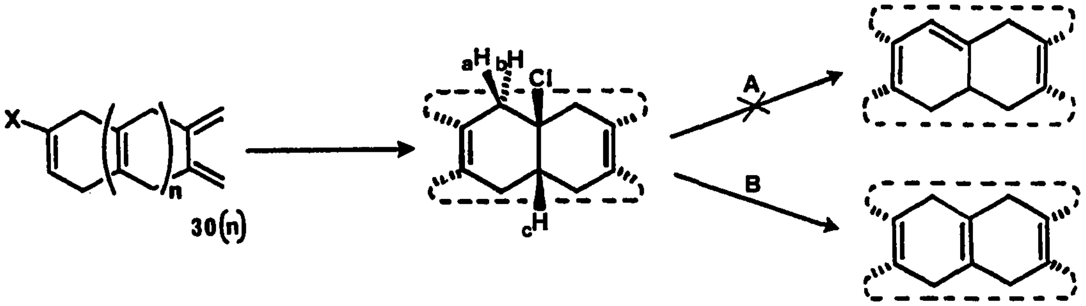
This overall sequence allows straightforward conversion of a diene moiety into a benzocyclobutene in six efficient steps (equation 4). A similar transformation using dimethyl cyclobutenedicarboxylate, **50**, suffered from an inefficient decarboxylation step.[49]

In summary, this technique provides a rapid, convenient, and efficient method of multiple linear homologation of diene moieties to build 1,4-cyclohexadienes. This butatriene synthetic equivalent approach should prove generally useful for the synthesis of columnene precursors, polycyclic aromatic compounds, and benzocyclobutenes. Additionally, a new Zn/Cu preparation was developed in the course of this work.[50]

Butatriene synthetic equivalent approach to columnenes

Synthesis of columnenes was first attempted via the butatriene synthetic equivalent approach to build precursors of the general structure **30(n)** (X = Cl). In principle, subsequent thermal intramolecular Diels-Alder cycloaddition of **30(n)** or suitable derivatives should occur in dilute solution, to give columnene skeletons with one double bond missing. The butatriene synthetic equivalent approach was applied to chloroprene, which was chosen because after cyclization of **30(n)** (Scheme 7), HCl should be most easily eliminated in the desired syn fashion. Elimination of $_aH$ or $_bH$ (path A) leads to a badly

Scheme 7 Expected elimination of HCl from **30(n)**



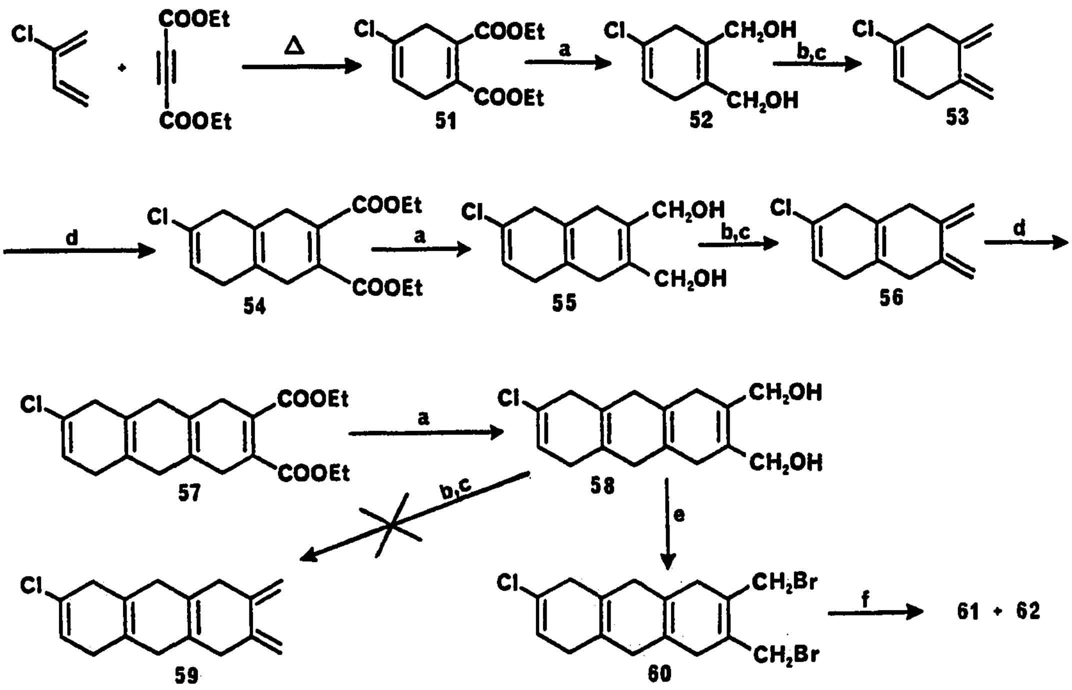
twisted π bond, thus elimination of $_cH$ (path B) should be preferred. Alternative (and more likely) strategies involved conversion of the vinyl chloride of **30(n)** to a cyclohexyne[51] as well as temporary modification of hybridization of sp^2 centers (*vide infra*).

Synthesis of tetracolumnene was first attempted by this route. Scheme 4 was thus repeated with chloroprene in place of 1,3-butadiene (Scheme 8). The first homologation proceeded to give diene **53** in 61% overall yield. Diene **53** was identical to a sample prepared in 8% overall yield by the general method of Middlemas and Quin[36] (*vide supra*).

The second ring homologation proceeded with an overall efficiency of 64%. Unfortunately the third failed because diol **58** failed to yield diene **59** via the standard iodination-elimination conditions. Possibly, this was due to the marginal solubility of **58** in THF.

In an alternate route to **59**, diol **58** was elaborated to dibromide **60** with $Ph_3P{\cdot}Br_2$ in CH_3CN,[52] but only in low yield. Bromination was chosen as a replacement to iodination because 1,4-dibromides such as **60** are known to eliminate bromine with Zn/Cu.[53] Indeed, this bromination was first introduced during the development of the butatriene

Scheme 8 Application of the butatriene synthetic equivalent approach to chloroprene



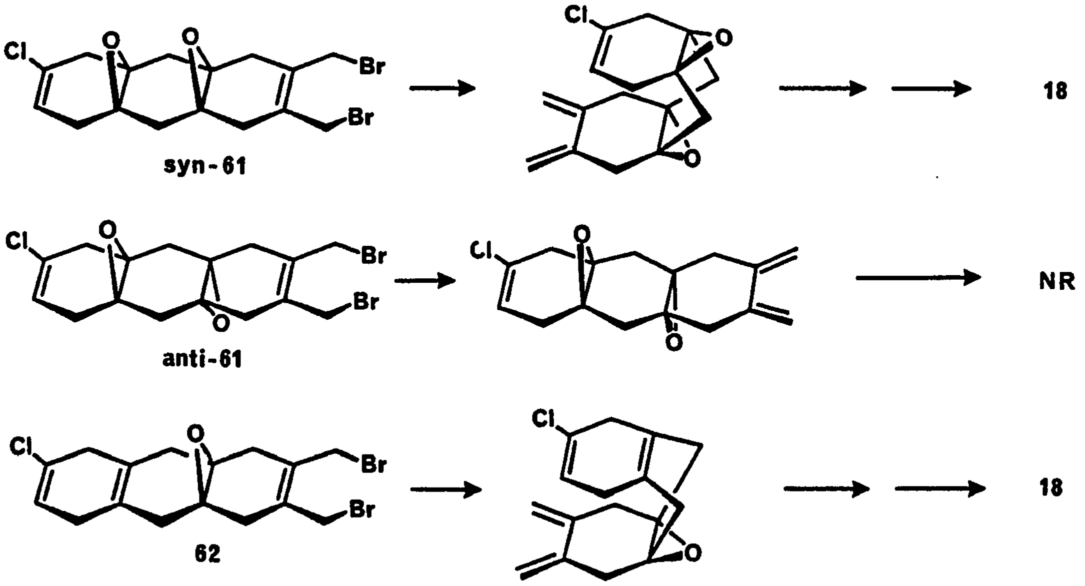
---

^{a}LiAlH$_4$, ether. ^{b}TMSCl/NaI, ether. ^{c}Zn/Cu, ether.
^{d}DEAD, PhH. ^{e}Ph$_3$P·Br$_2$, CH$_3$CN. ^{f}mCPBA, CDCl$_3$

synthetic equivalent approach and was later replaced with *in situ* iodination-elimination, in order to facilitate repetitive homologation. Due to the small quantities of dibromide 60 which were prepared, diene 59 was not prepared and a thorough cyclization study was not undertaken. Instead, a temporary modification of hybridization of internal double bonds was undertaken.

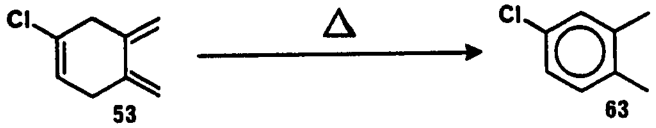
Dreiding molecular models show that, for ambiphile **59**, a conformation at which the diene and dieneophile of **59** are close enough for cycloaddition should be possible. Nevertheless, this extreme conformation is not expected to be favored because of the flat nature of olefins and the π orbital interaction which occurs in the center. However, rehybridization of one of the central double bonds from sp^2 to sp^3 would fold the molecule into a geometry which should be much more conducive to cyclization, as well as reduce π orbital interaction. Since the more activated internal double bonds in structures such as **60** are expected preferentially to undergo facile epoxidation with mCPBA, epoxidation of one or both double bonds (followed by de-epoxidation) offered a straightforward means of temporily modifying hybridization. *Bis*-epoxidation of **60**, it is believed, would occur synfacially since the first epoxidation should fold the molecule, making the anti (endo) face less accessible to reagent attack. The conformation of the resulting *syn-bis*-epoxide **61** should be even more conducive to cyclization than the monoepoxide **62**. This strategy is outlined in Scheme 9. Epoxides may be later eliminated to the corresponding olefins with low valent titanium[54] or other mild reagents known to effect this transformation.[55] Such reagents work on only the oxygen side of the molecule and were thus envisioned as ideal for the reintroduction of the double bond, after cyclization. Note, however, that *bis*-epoxidation with epoxide rings forming on opposite sides of the molecule would lead to an uncyclizable species.

Scheme 9 Temporary modification of internal double bonds in columnene precursor **30(n)**.



This approach has not yet been fully exploited. Preliminary results showed that at 0°C, one equivalent of mCPBA was rapidly consumed by a solution of **60** in $CDCl_3$. NMR analysis showed the formation of two products (~10:1), both of which appeared to be epoxy dibromides. Unfortunately, these were neither separable nor stable. Thus, given the minute quantities which could be prepared by this route, it was decided to pursue other strategies.

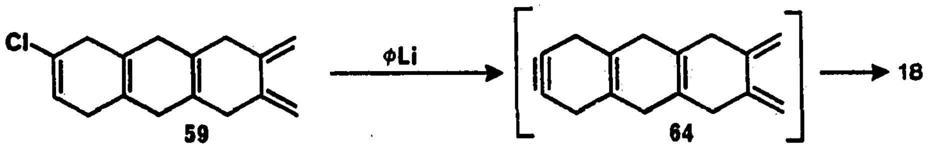
Dienes such as **30(n)** were soon shown to be sensitive to elevated temperature. One example of this thermal instability was observed during preparative gas chromatography of diene **53**. Attempted isolation with an injector temperature of 225°C yielded, along with **53**, *o*-xylene **63**. This result is most easily explained by surface catalized thermal isomerization of **53**, which is driven by aromaticity (equation 5). Thus, thermal cyclization of the vinyl chlorides **30(n)** (X = Cl) does not appear feasible. Additionally, the vinyl chlorides proved more sensitive towards polymerization than the parent hydrocarbons.



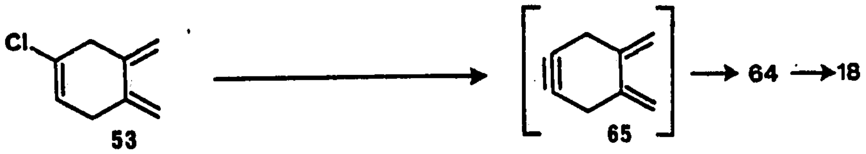
(5)

In an attempt to use the chloroolefin technology just developed, two new strategies were considered.

Cyclohexyne generation from **59** was investigated (equation 6). If generated, cyclohexyne **64** could, in principle, cyclize directly to tetracolumnene (equation 6). Actually, cyclohexyne **65** generated from **53** could lead to **64**, and hence to tetracolumnene (equation 7). As a model study, **53** was treated with PhLi in THF[51] in both the presence and absence of 9,10-diphenylisobenzofuran. All attempts lead only to the decomposition of **53**; no adduct, solvent insertion product or PhLi addition product were observed. It was concluded that the cyclohexyne never formed.



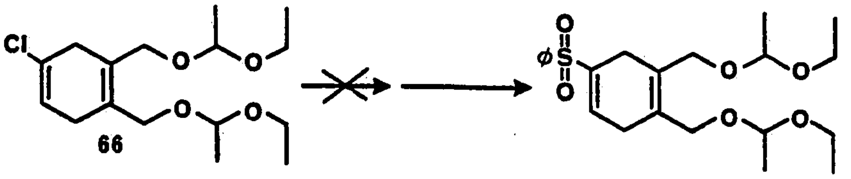
(6)



(7)

Brief consideration was given to the conversion of the vinyl chloride of **30(n)** (X = Cl) into an aryl sulfone because this functionality would make the olefin much more dieneophilic than the vinyl chloride. Elaboration of the sulfones to sulfoxides should provide an excellent route to olefins by synfacial extrusion of the sulfenic acid.[56] Thus this procedure seemed worthy of exploration.

Lithium-halogen exchange,[57] followed by a diphenyldisulfide quench (equation 8), was tried with model substrate **66**. This ethylvinylether (EVE) protected diol, **66**, was prepared by refluxing a solution of diol **52**, ethyl vinyl ether, and pyridinum tosylate in THF.[58] Treatment of **66** with lithium[57] in a variety of solvents, followed by PhSSPh quench, resulted only in the isolation of starting material. The absence of any hydrogen exchanged product, **37**, indicated that the vinyllithium never formed. As will be outlined in a subsequent section, an alternate route to the vinylsulfoxide was later developed.



66

(8)

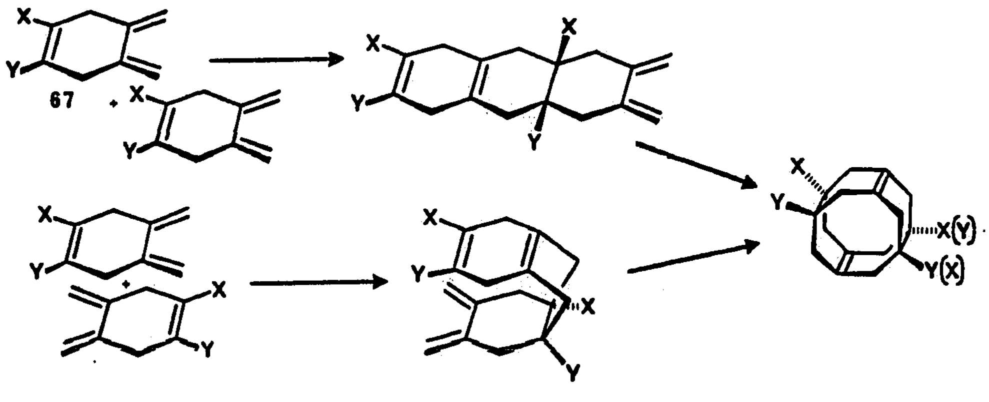
The butatriene synthetic equivalent approach showed its utility in the preparation of columnene precursors **30(n)**. However, the preparation **30(n)** (X = Cl, n≥ 1) is tedious and the likelihood of intramolecular Diels-Alder cyclization of the vinyl chlorides is expected to be small. Unfortunately, even cyclohexyne generation from **53** was unsuccessful. Other dienophiles (X functionality) were needed, and for this another strategy was developed.

Bis-allyl synthetic equivalent approach to columnenes

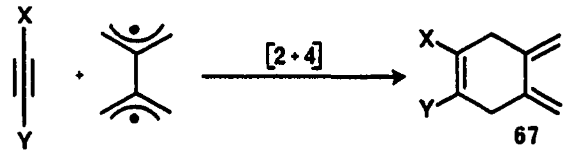
A second approach to columnar structures is through dimerization of small ambiphilic molecules. This convergent route has the advantage of being shorter than the butatriene synthetic equivalent approach. In principle, Diels-Alder dimerization followed by intramolecular Diels-Alder cyclization of ambiphiles like **67** could very quickly lead to the even-numbered columnenes. This route is outlined in Scheme 10. It should be noted that while secondary orbital overlap favors cycloaddition according to the first orientation (Scheme 10), reaction from the opposite orientation leads to the same product.

The requirements for the X and Y functionality in **67** are the same as for **30(n)**; *i.e.*, they should be electron withdrawing groups which can be eliminated after cycloaddition to produce an olefin. Synthesis of **67** from the requisite 2,3-disubstituted-1,3-diene via the butatriene

Scheme 10 Dimerization and cyclization of ambiphile **67**



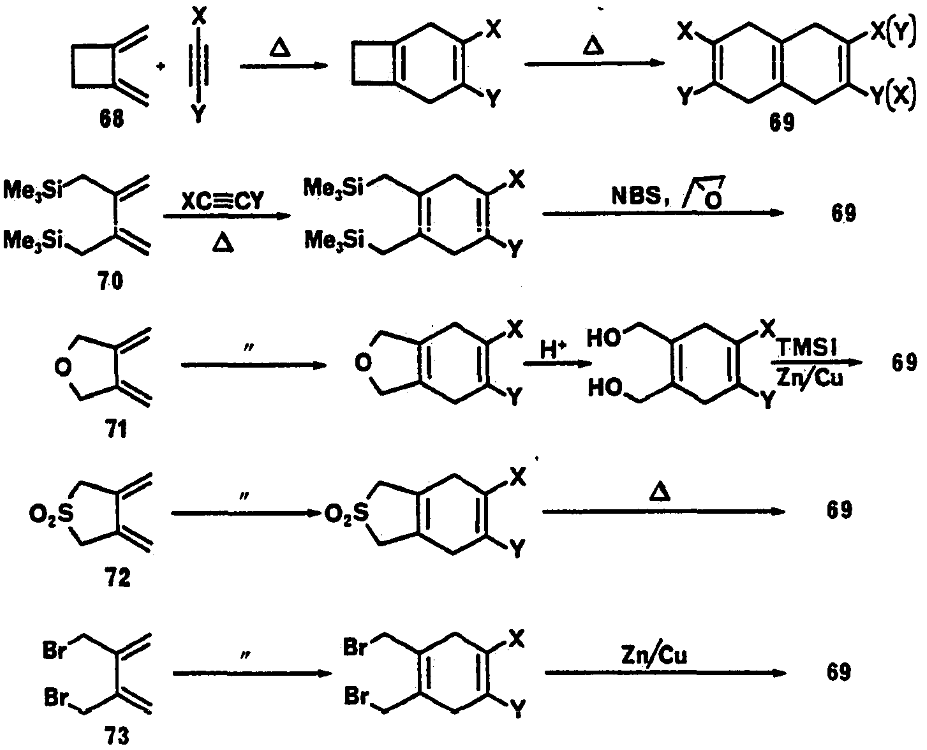
synthetic equivalent approach is not feasible for most electron withdrawing groups.[59] Thus, an alternate and general route to 67 was developed. Conceptually, the X and Y moieties may be introduced by the Diels-Alder cycloaddition of an appropriately substituted acetylene with a *bis*-allyl synthetic equivalent (equation 9). Such an equivalent



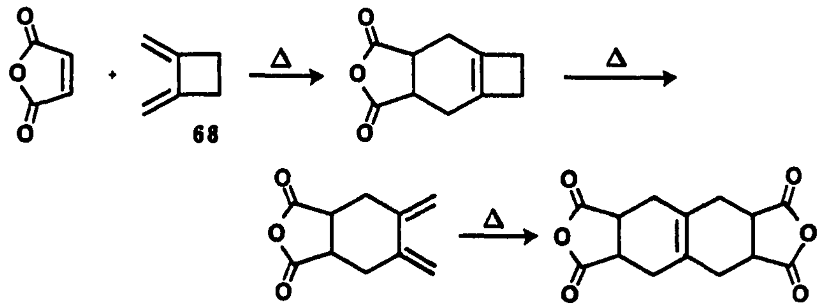
(9)

would be a six carbon 1,3-diene which, after its initial cycloaddition, could be easily modified to another 1,3-diene. Several such molecules exist; those considered (Scheme 11) will be discussed in turn.

Scheme 11 Various *bis*-allyl synthetic equivalents

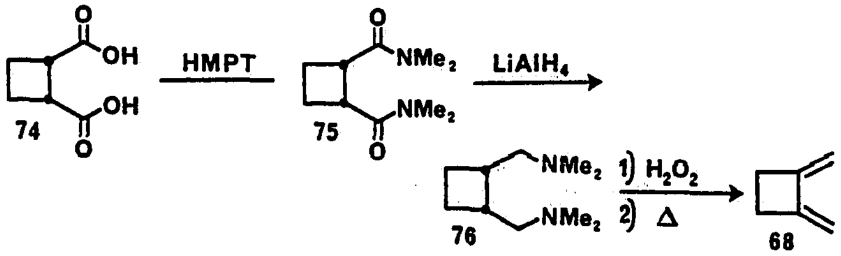


1,2-*Bis*(methylene)cyclobutane, **68**, has been shown by Bloomquist and Verdol[60] to function as a *bis*-allyl synthetic equivalent. They observed sequential cycloaddition of two equivalents of maleic anhydride to **68**. Cycloaddition at 78°C yielded a cyclobutene which, upon ring opening at 150°C, afforded the *bis*-adduct (equation 10).



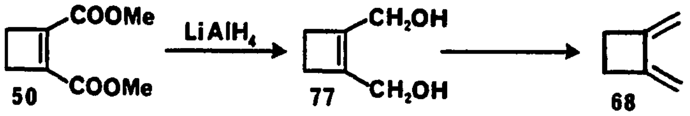
(10)

Drawbacks to the use of **68** are its facile polymerization and difficulty or expense of preparation. Diene **68** has been prepared on small scale from the dimerization of allene.[61] However, this method is not feasible for the present work. Other syntheses include dehydrohalogenation[62] and pyrolytic routes.[63] Unfortunately, when the pyrolytic sequence reported by Middlemas and Quin[36] (equation 11) was repeated, only polymeric material was obtained from the thermolysis.



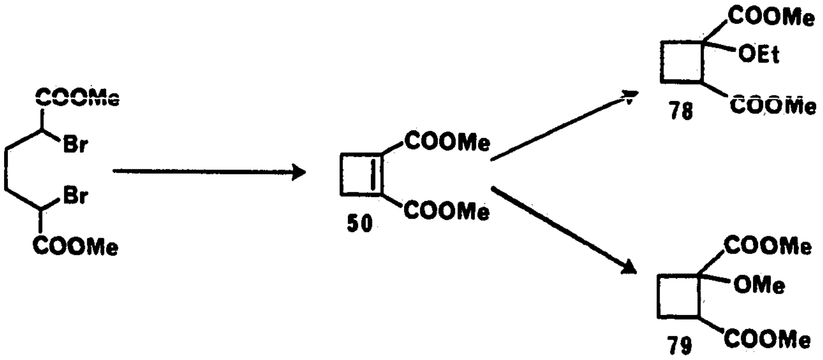
(11)

This failure appeared to be ring size dependent; an identical procedure easily afforded moderate yields of the larger, less strained diene **53** (*vide ante*). A potentially efficient route to diene **68** is application of butatriene synthetic equivalent technology to the well known diester **50**[64] (equation 12). Unfortunately, reaction of diester **50** with a variety of reducing agents failed to yield diol **77** and the use of **68** as a *bis*-allyl synthetic equivalent was not pursued further.



(12)

One noteworthy difficulty was encountered in the preparation of **50**. In the only synthetic route, reported by McDonald and Reitz,[64] 50 was prepared from α,α'-dibromoadipate by condensation followed by dehydrobromination (equation 13). Repetition of this procedure, precisely as described, unexpectedly lead to an erroneous product. The original paper failed to mention one salient experimental detail; workup must be done in alcohol free ether. It was postulated that under the basic reaction conditions, trace ethanol in commercial ether

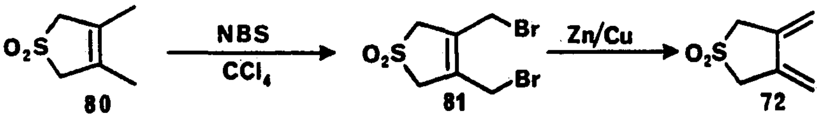


(13)

rapidly added across the double bond of **50** to give **78**. This was verified by quenching a reaction mixture of **50** and treatment of an authentic sample of **50** prepared with alcohol free ether, each with 1% MeOH/ether (equation 13). Both procedures afforded the same ether, **79**.

During the course of this work, Trost and Shimizo demonstrated the utility of the diene 70 as a *bis*-allyl synthetic equivalent.[65] The expense of this preparation and superiority of other routes (*vide supra*), however, have not encouraged its consideration for the present application.

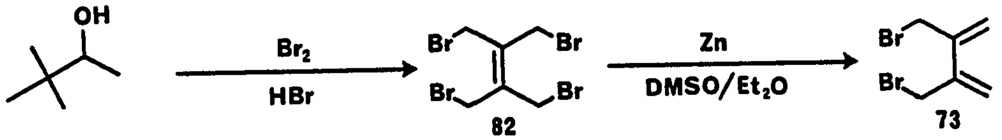
Dienes 71[66] and 72,[67] each *bis*-allyl equivalents, are available in a few steps from diene 73.[68] Since **73** itself is such an equivalent, synthesis of **71** and 72 from 73 was not tried. No useful alternative synthesis of **71** was devised. However, a potentially rapid synthesis of 72 was attempted (equation 14). Butler and Ottenbrite[69] reported the



(14)

preparation of **81** via the NBS bromination of the SO_2 adduct of 2,3-dimethyl-1,3-butadiene, **80**. Unfortunately, following their instructions and many other standard procedures, NBS bromination failed repeatedly in this laboratory. This failure is especially disappointing in view of the reported facile bromination of the SO_2 adduct of isoprene.[70]

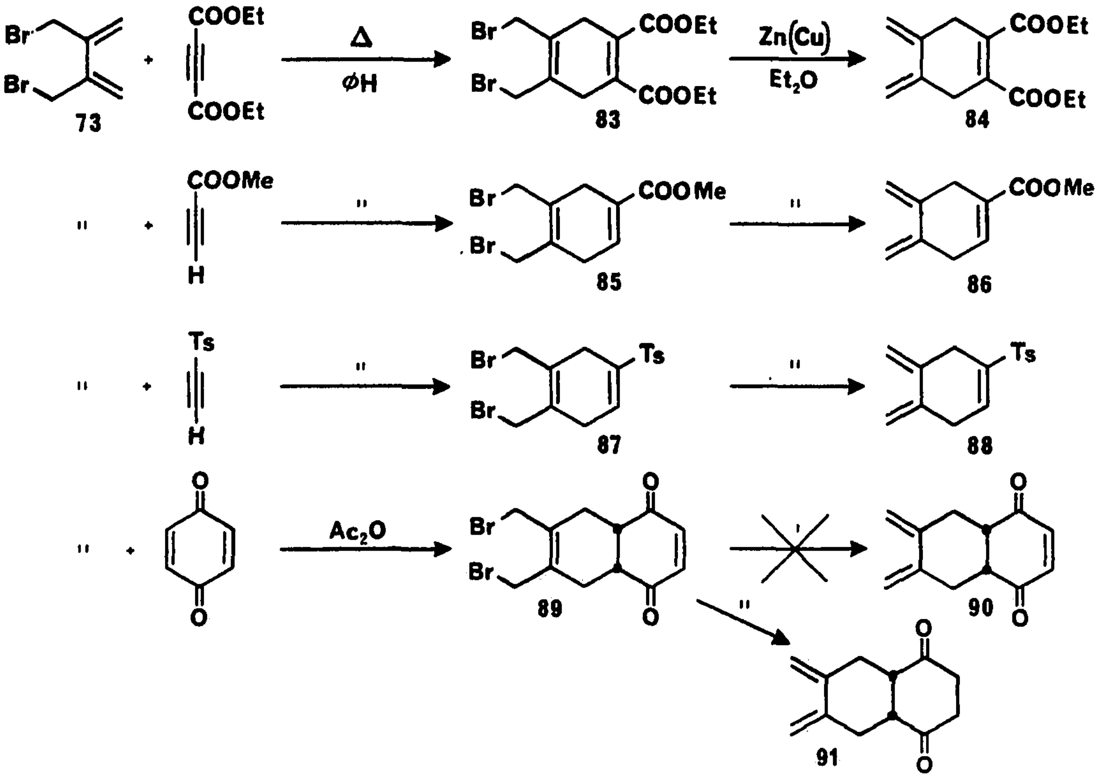
Dibromodiene 73 was not among the first selected *bis*-allyl synthetic equivalents due to its bulky bis(bromomethyl) substituents and moderate Diels-Alder reactivity. Despite this drawback, Gaoni has successfully used **73** for this purpose.[66-8] He reportedly prepared **73** in ~ 90% yield from tetrabromide 82[71] and Zn/Cu in a mixture of HMPA/ether.[66-8] Repetition of this procedure, in this laboratory, afforded only 60% of **73**. Since the use of HMPA was undesirable, a procedure in which HMPA was replaced by DMSO was developed (equation 15). This new method reproducibly afforded bulk production of 73 in 53% yield.



(15)

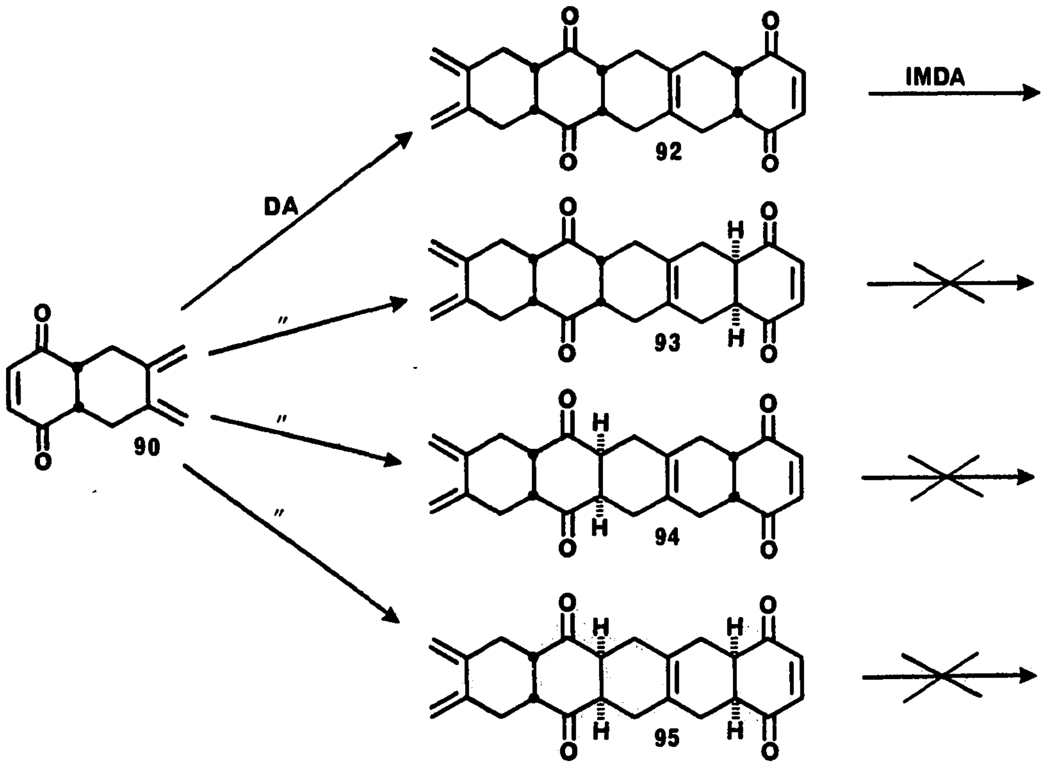
Given the availability of diene **73** on a multi-gram scale, this method was applied to four acetylene dienophiles as outlined in Scheme 12. These dienophiles were chosen to investigate the reactivity of a variety of functionality in ambiphiles. DEAD and (p-tolyl)(ethynyl) sulfone (TSA)[56] contain functionality which should, after Diels-Alder dimerization of ambiphiles **84** and **88**, and closure to the columnene skeleton, easily introduce the desired double bond as in Scheme 3 (*vide ante*) by decarboxylation[49] and thermal extrusion,[72] respectively. Both methods should, in principle, lead directly to columnenes. Methyl propiolate was chosen because the resulting ambiphile **86** will have a less substituted dienophile than **84**. The single ester substituent will polarize the double bond and make the dienophile a potential candidate for Lewis-acid catalysis[73] (*vide infra*). Thus, the dienophilicity of this ambiphile may be substantially greater than that of **84**. Although **86** will not lead

Scheme 12 2,3-*Bis*(bromomethyl)-1,3-butadiene as a bis-allyl synthetic equivalent



directly to a columnene, it was prepared in order to study the limitations of cycloadditions of these ambiphiles. p-Benzoquinone, the most unique of the dieneophiles, was chosen in order to build an ambiphile with a disubstituted dienophile. Ambiphile **90** was expected to be the most dienophilic of the series. Nevertheless, **90** suffers the drawback of having methine hydrogens α to the carbonyl which will partially fold the molecule and allow the possibility of antifacial dimerization; this could produce dimers (**92-95**) which are incapable of intramolecular Diels-Alder cycloaddition (Scheme 13).

Scheme 13 Expected dimerization of ambiphile 90



DEAD, methylpropiolate, and TSA were each refluxed with dibromide 73 in benzene for 2-3 days. The cycloadducts **83**, **85**, and **87** were obtained in ~50% yield. Cycloadduct **89** was obtained in up to 30% yield only when **73** and p-benzoquinone reacted as a concentrated solution in acetic anhydride at ambient temperature.[69] Bromine was eliminated with Zn/Cu in ether, producing dienes in greater than 80% yield for all adducts. Unfortunately, the double bond of endione **89** was reduced during the elimination reaction; the unexpected diene produced, **91**, was thus not ambiphilic.

In an attempt to dimerize them, each of the three new ambiphiles, **84**, **86**, and **88**, was thermalized in benzene. Thermolysis temperatures ranged from 50-80°C. Each trial gave only reclaimed starting material and/or decomposition products; no dimeric products were detected. This failure may be due to the low dienophilicity of the tri- and tetrasubstituted dienophiles. The best known examples of cycloaddition of highly substituted olefinic dienophiles are those which are aided by considerable bond strain.[49] The relatively strain-free ambiphiles of this study apparently have a substantial activation barrier to cycloaddition.

In an attempt to lower this activation energy, catalysis with Lewis acids was briefly investigated. Claims of enhanced cycloaddition reactivity of dienophiles complexed with Lewis acids abound in the literature[73] and a wide range of Lewis acids are available. According to the putative mechanism, the Lewis acid complexes with the polar functionality of the dienophile, thus polarizing the olefin. This method appears attractive for the cyclodimerization of ambiphiles.

A problem with the use of Lewis acids is that they can decompose diene moieties.[73a,b] Pretreatment of the dienophile with the Lewis acid before addition to the diene reduces this danger. However, with ambiphilic molecules, this is not possible. Addition of Lewis acids to the ambiphiles at low temperature is probably the best way to avoid excessive decomposition of the substrates.

A study of Lewis acid catalized Diels-Alder cyclodimerizations was undertaken for **84** and **86**. In a number of trials, chloroform or methylene chloride solutions of the ambiphile were treated with dilute solutions of various Lewis acids. The results are tabulated (Table 4) and discussed below.

The first Lewis acid chosen was $AlCl_3$. Its addition to solutions of ambiphiles caused rapid darkening of the solution and decomposition of the starting material even at 0°C. The less active Et_2AlCl showed slow reaction. After a few days at ambient temperature, the major components obtained from the mixtures were starting material and the corresponding *o*-xylene (as in equation 5). Warming of the solution to 50°C for a few hours lead to rapid decomposition of the ambiphile. Reaction with $BF_3{\cdot}OEt_2$ gave primarily the *o*-xylenes, a little starting material, as well as small quantities of many other products. The main products from all reactions were isolated by column chromatography. Of all isolated products which still contained the ester moieties, none appeared by ^1H NMR to have the symmetry necessary for the desired cyclodimers. Catalysis with $TiCl_4$ proceeded rapidly with **86** but slowly with **84**. Product mixtures from both reactions were similar to the results obtained with $BF_3{\cdot}OEt_2$. No condition investigated produced any isolable dimer.

These preliminary results indicate that the tri- and tetrasubstituted dienophiles prepared probably cannot cycloadd under these conditions. However, this method was not studied exhaustively and a

Table 5. Lewis Acid Catalized Diels-Alder Cyclodimerization Attempts

Substrate	Catalyst	Solvent	Temp(°C)	Time(h)	Results
75	0.1 eq $AlCl_3$	$CHCl_3$	0-23	5-15	1, 3
75	0.1 eq $BF_3 \cdot OEt_2$	CH_2Cl_2	23	48	3, 5, 6
75	0.1 eq $BF_3 \cdot OEt_2$	CH_2Cl_2	0-23	20	3, 5, 6
75	1.0 eq $BF_3 \cdot OEt_2$	$CDCl_3$	0-23	48	3, 5, 6
75	0.1-0.3 eq Et_2AlCl	$CHCl_3$	23-50	168	1, 2, 4
75	0.1 eq $TiCl_4$	CH_2Cl_2	0-23	120	4, 5, 6
77	0.1 eq $AlCl_3$	$CHCl_3$	0-23	24	1, 4
77	0.2 eq $BF_3 \cdot OEt_2$	CH_2Cl_2	0-23	55	3, 5, 6
77	0.2 eq Et_2AlCl	CH_2Cl_2	0-23	48	1, 4
77	0.2 eq $TiCl_4$	CH_2Cl_2	0-23	3	3, 5, 6

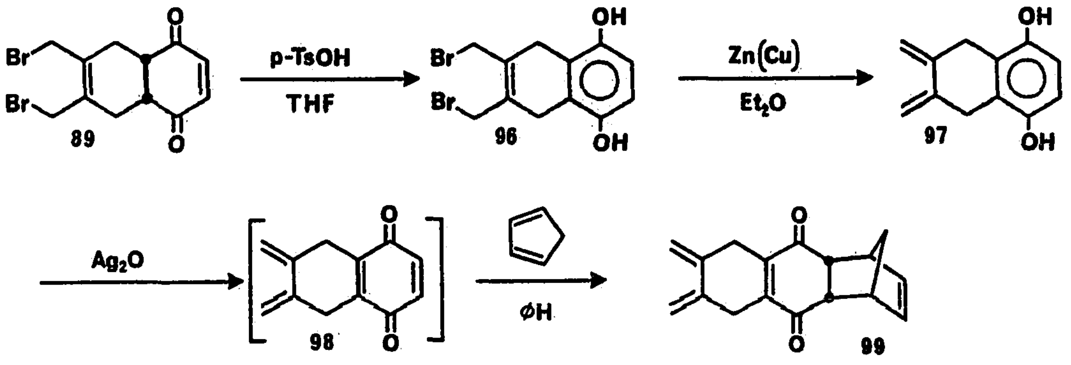
1. decomposition of starting material
2. low conversion
3. high conversion
4. slow reaction
5. many (>10) products observed by TLC analysis
6. gave corresponding *o*-xylene as product

persistent study may eventually show good results. In the present study, less substituted ambiphiles were pursued.

Quinone adduct **89** was reinvestigated. Since the original goal, synthesis of **90**, was precluded by undesirable reduction, **89** was used to synthesize another ambiphile. This synthetic route is outlined in Scheme 14.

Enedione **89** was isomerized to the hydroquinone **96** in 83% yield with 0.1 equivalent of p-toluene sulfonic acid in THF at ambient temperature. This was the most efficient method found after many attempts. The hydroquinone readily decomposed if stored at ambient temperature for longer than a day, but was stable at -20°C for about a week. Bromine was eliminated from **96** under standard conditions to yield 85% of **97**. This stable, white crystalline product was readily purified by recrystallization. Diene-hydroquinone **97** reacted rapidly with Ag_2O,[74] but the expected ambiphile **98** was too reactive to be isolated. However, the production of **98** was inferred by its successful trapping with 1,3-cyclopentadiene and a variety of spectral data. When **97** was oxidized in the presence of a greater than 20 fold excess of cyclopentadiene, adduct **99** was obtained in >53% yield.

Scheme 14 Generation and trapping of ambiphile **98**.



Clearly, ambiphile **98** was generated and its rapid cycloaddition at ambient temperature indicates that this molecule may cyclodimerize.

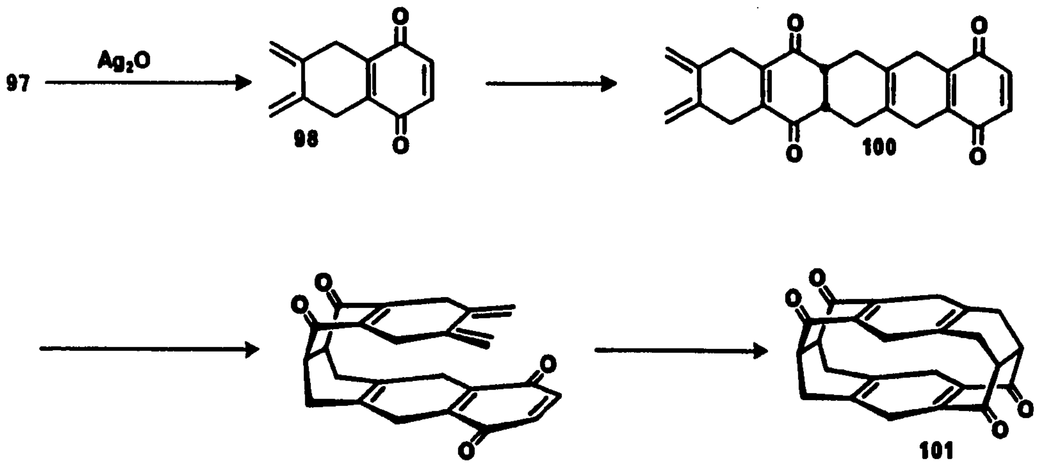
Hydroquinone **97** was successfully oxidized with Ag_2O in a wide variety of solvents, including $CHCl_3$, CH_2Cl_2, CCl_4, CH_3CN, dioxane, THF, and benzene. In the absence of a Diels-Alder trap, oxidation rapidly produced a bright yellow solution of quinone **98**, the intensity of which diminished with time. Dependent upon the initial concentration of **97**, this intense yellow color persisted for a few minutes to a few hours. Soon after the yellow color faded, a yellow-white precipitate fell from solution. At any time after the oxidation, removal of solvent at reduced pressure produced a yellow-white solid, identical to this precipitate. After a few hours, spectroscopic analysis revealed that almost nothing remained in solution. The precipitate, obtained in up to 90% yield, was a pale yellow-white amorphous solid which resisted melting at up to 375°C, and was nearly insoluble in most solvents. These results suggest a polymeric structure.

When the reaction was monitored by NMR ($CDCl_3$) soon after oxidation, nearly pure **98** was observed. The spectrum showed quinone hydrogens as a broad singlet at 6.73 ppm, a pair of broad singlets at 5.30 and 4.98 ppm for the diene hydrogens and a broad methylene singlet at 3.67 ppm. A carbonyl stretch, characteristic of quinones, was observed at 1656 cm^{-1} ($CHCl_3$) in the IR spectrum. The UV spectrum showed λ_{max} at 247, 338, and 412 nm, also consistent with a quinone moiety.

Samples of **97** in $CDCl_3$ and benzene-d_6 (≤0.001 M) were each oxidized with two equivalents of Ag_2O. NMR spectra, obtained after 10 minutes, showed only resonances consistent with **98**. Comparison of these resonance intensities with those of an internal standard, 1,2-dibromoethane, showed that the concentration of **98** decreased with time. After approximately 30 minutes, a small amount of a second component was observed. This component, displaying diene and quinone resonances that were different from those of ambiphile **98** in benzene, but not in $CDCl_3$, grew in at the expense of **98**. Within 4-8 hours, a third component with only aliphatic resonances appeared. This species grew in at the expense of the second component. Throughout the analysis, precipitate formed and the total concentration of soluble species decreased with time. Progress of the reaction of **98** was illustrated by representative ^1H NMR spectra recorded at various time intervals after oxidation. Spectra recorded using $CDCl_3$ and benzene-d_6 are reproduced in Figures 15 and 16, respectively. These data were taken as evidence that the second and third components observed were the dimers of **98** in the open (**100**) and closed (**101**) form (Scheme 15).

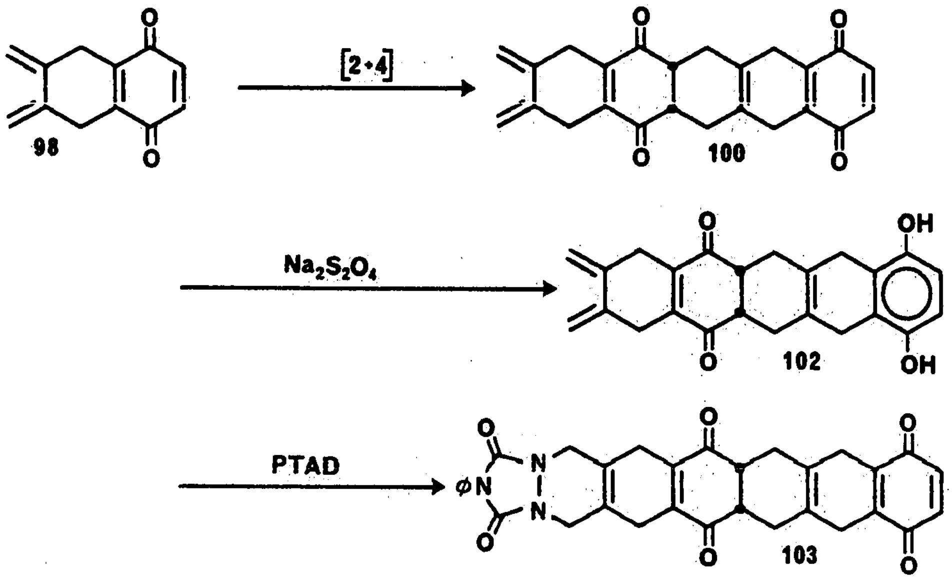
In order to obtain evidence for **100**, two trapping experiments were attempted. First, chloroform solutions of oxidation products were treated with aqueous $Na_2S_2O_4$[75] to reduce the benzoquinone moiety to a hydroquinone (Scheme 16). Under these conditions, greater than 85% of **97** was recovered when the reaction mixture was reduced soon after oxidation. In a variety of trials, equimolar solutions of oxidation products were treated at various time intervals with excess aqueous

Scheme 15 Dimerization of ambiphile 98



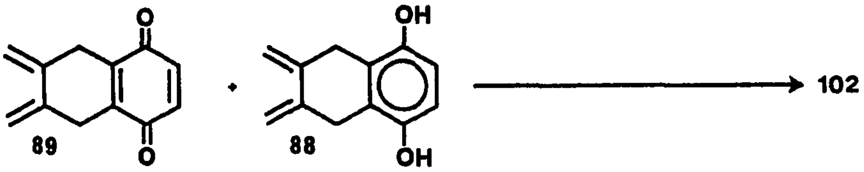
sodium dithionate. For trials with short time intervals, some 97 but no reduced dimer, 103, was isolated by column chromatography. At longer intervals, neither 97 nor 102 was isolated. ^{1}H NMR ($CDCl_3$) analysis of these mixtures immediately before each reduction clearly

Scheme 16 Attempted isolation of open-dimer 100



showed two quinone resonances, which were indicative of the presence of both **98** and **100**.

The independent synthesis of **102** was attempted via addition of 0.05 - 0.5 equivalents of Ag_2O to solutions of **97**. In this way, **98** was generated in the presence of a large excess of **97** which should favor Diels-Alder cycloaddition of **98** and **97** (equation 16). After slow portionwise Ag_2O additions were made, ^1H NMR ($CDCl_3$) analysis showed a new hydroquinone resonance at δ 6.51 ppm, as well as the 6.54 ppm resonance of **97**. This indicated that the cycloaddition probably had occurred, but the adduct, **102**, could not be isolated by column chromatography or crystallization.



(16)

In another attempt to derivatize **101**, excess N-phenyltriazolinedione (PTAD) was added to the reaction mixture of **98** and **100** to trap all 1,3-dienes (Scheme 16). As before, several solutions of **97** were oxidized and each sample was treated with excess PTAD at different time intervals. Before each addition of PTAD, the presumed dimer, 100, was observed by ^1H NMR. After each addition, ^1H NMR ($CDCl_3$) analysis showed that all diene moieties had disappeared and two distinct quinone resonances at δ 6.74 and 6.79 ppm remained. Unfortunately, column chromatographic isolation of these adducts failed.

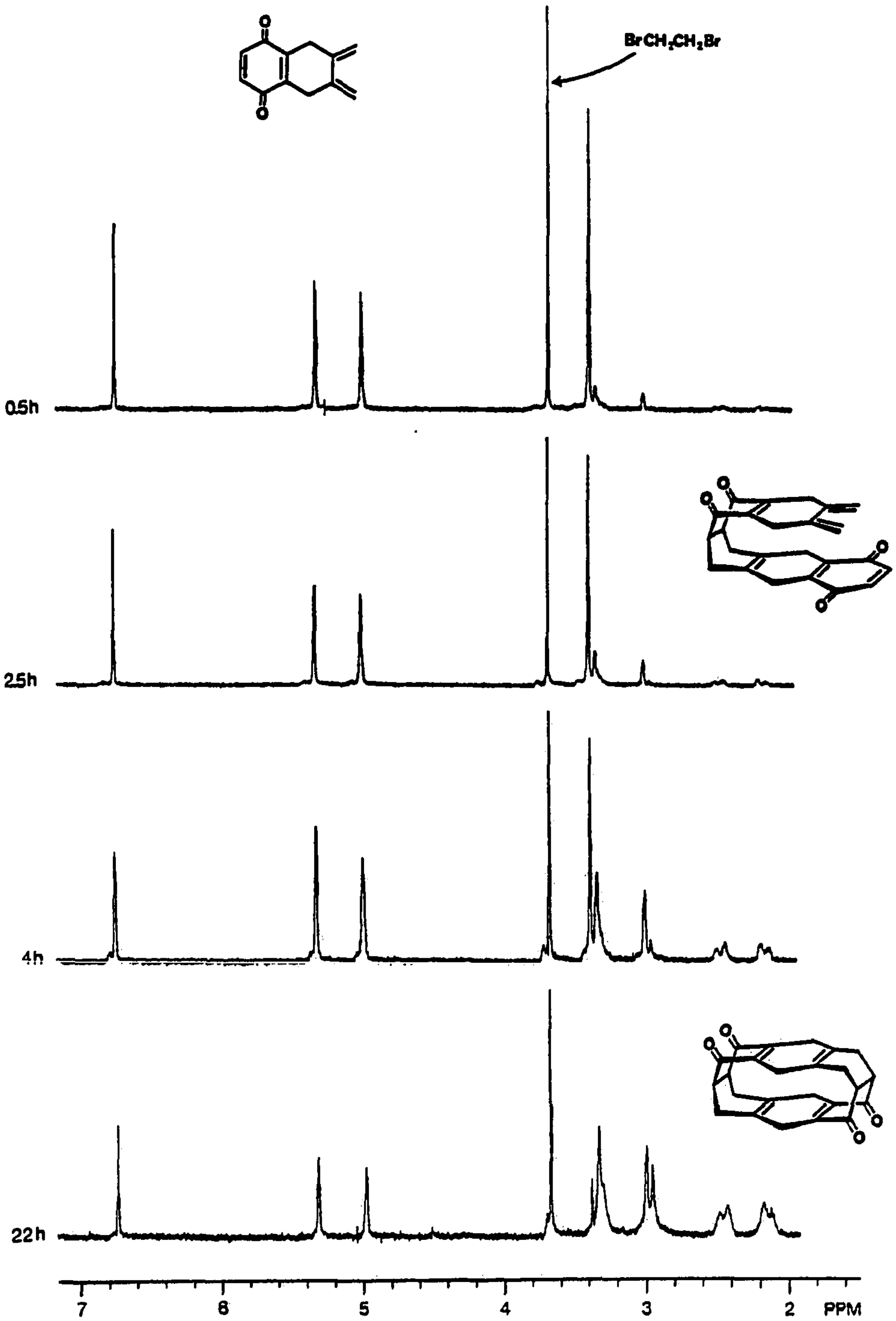


Figure 15. 300 MHz ^{1}H NMR (CDCl$_3$) analysis of the reaction of ambiphile **98** with time

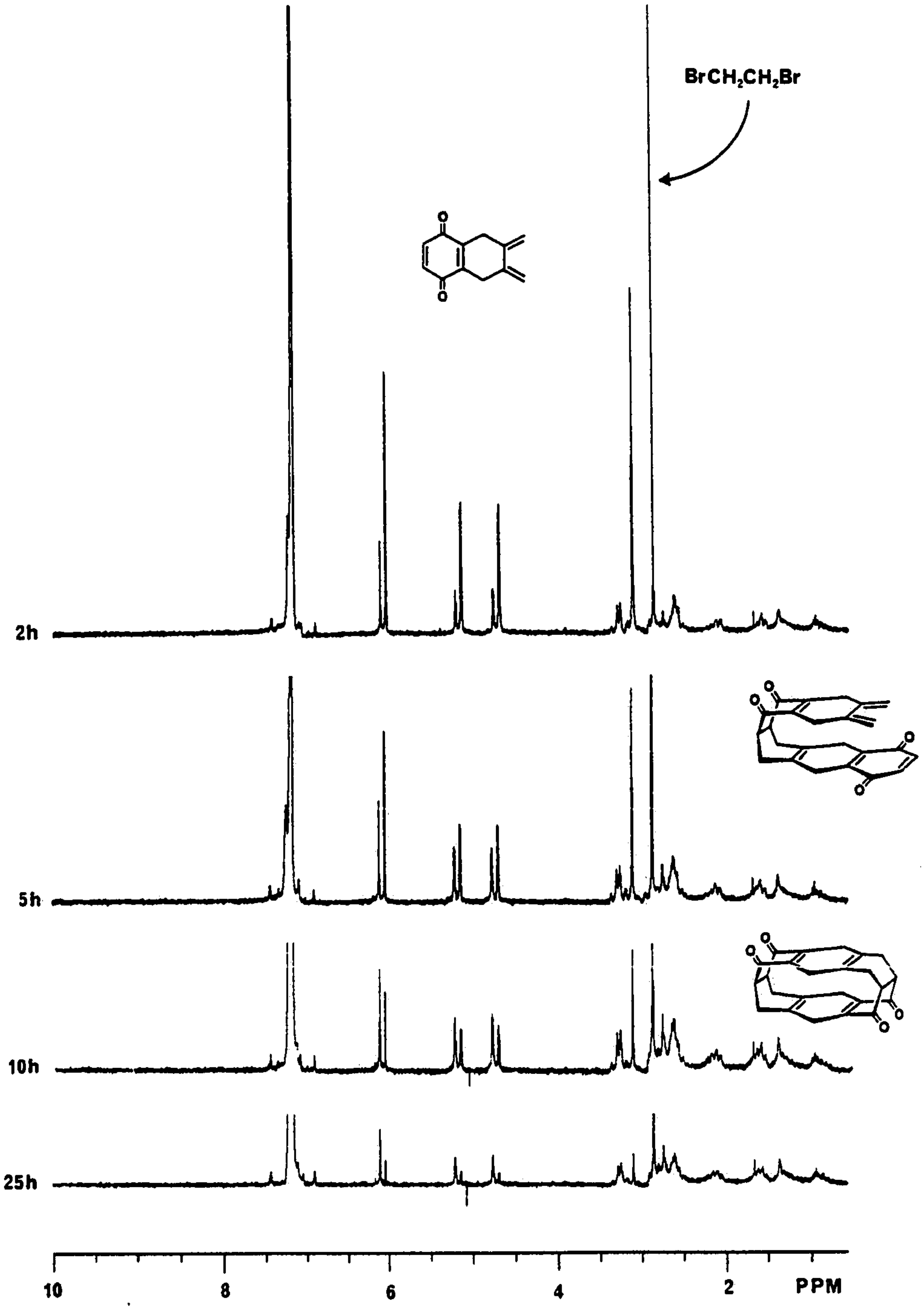
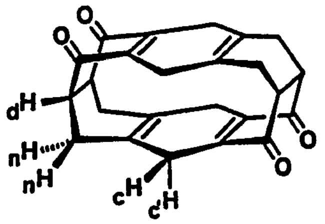


Figure 16. 300 MHz ^{1}H NMR (benzene-d_6) analysis of the reaction of ambiphile **98** with time

The desired derivatives were simply not isolable under the chromatographic conditions which were employed. The data collected were consistent with, but provided insufficient proof for, the existence of open dimer **100**. Nevertheless, this is a logical intermediate.

^{1}H NMR ($CDCl_3$) analysis of the third component, presumed to be the closed dimer **101**, revealed four broad multiplets at δ 3.29, 2.95, 2.43, and 2.12. These resonances were labeled $_d$H, $_c$H, $_{c'}$H, $_b$H and $_a$H, respectively. Resonance $_b$H and $_a$H each showed a coupling constant of about 16 Hz; this is a typical geminal coupling. Double irradiation experiments provided coupling information for each resonance; $_d$H was coupled to $_b$H and $_a$H, $_a$H and $_b$H were each coupled to $_d$H as well as to each other (J = 16 Hz), and no coupling of $_c$H or $_{c'}$H was detected. These spectral data are consistent with closed dimer **101**, if resonances are assigned as in Figure 17. This assignment assumes that $_c$H and $_{c'}$H have unresolved chemical shifts. Note also that $_a$H and $_b$H were not distinguishable from this data. The IR spectrum for this substance displayed a strong band at 1676 cm^{-1}. This was assigned to the stretching vibration of an unsaturated carbonyl. Mass spectral data was obtained by an unconventional procedure. Solvent was removed at reduced pressure from a solution of **101**, immediately after NMR analysis. The solid, thus obtained, was quickly inserted into the probe of a mass spectrometer. With mild heating, one fleeting volatile component passed into the ionization chamber. After heating above 200°C, no other volatile components were observed and a yellow-white solid remained in the probe. From this volative component, a



$_{n}$H = $_{a}$H or $_{b}$H

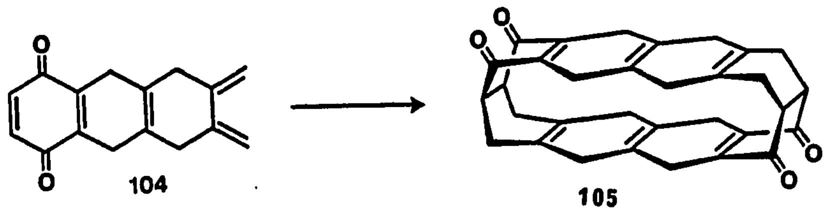
H	δ(ppm)	mult	J_{HH}
$_{d}$H	3.29	br s	
$_{c}$H	2.95	br s	
$_{b}$H	2.43	br d	~16 Hz
$_{a}$H	2.12	br d	~16 Hz

Figure 17. ^{1}H NMR spectral assignments for closed dimer **101**

peak at m/e 372 (1% of the intensity of the base peak, m/e 279) was observed. This peak corresponds to the expected parent ion of the dimer. The broad band proton decoupled ^{13}C NMR spectrum of a solution which showed predominantly **101** by ^{1}H NMR, was recorded. Prominant resonances were observed at δ 198.8, 142.0, 122.4, 46.5, 29.8, 28.5 ppm. These data are consistent with the highly symmetrical dimer **101**, although a trimer or larger homologue would have similar data.

It was concluded that ambiphile **98** is a highly reactive substance which successfully dimerized and cyclized to form the novel, closed dimer **101**. Unfortunately, the presumed closed dimer was not isolable, although, NMR, IR, UV and MS data support the proposed structure. During this reaction, much amorphous precipitate formed; this material is probably a reaction product of dimer **101**.

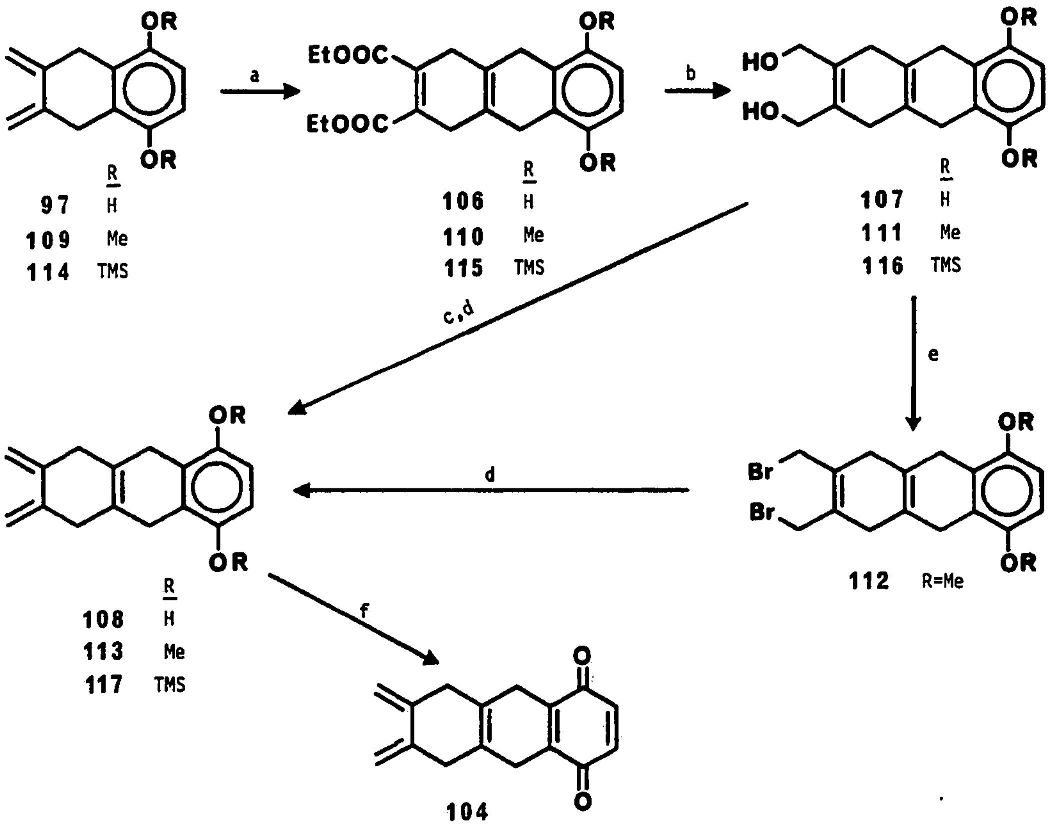
The inherent instability of **101** may well be avoided by designing a cyclic structure with a larger central cavity size. For example, homologue **105** should show less strain than **101**, and may be isolable. Dreiding molecular models of **105** show much more flexibility in its framework as well as a larger central cavity size than for **101**. This molecule should be readily available through the dimerization of 104 (equation 17).


104 **105** (17)

Preliminary studies have yielded key intermediates in the route to ambiphile **104**. The route chosen is outlined in Scheme 17; progress thus far is discussed below.

The butatriene synthetic equivalent approach was applied to diene **97**. The DEAD adduct of **97**, **106**, was prepared in 97% yield by cycloaddition in benzene. Since it seemed undesirable to work with the polar (hence, probably insoluble) tetraol **107**, the hydroquinone was protected as both methyl[77] and trimethyl silyl[78] ethers, **110** and **115**, respectively. Overall yields of the protected adducts were greater if the dienequinones were protected prior to cycloaddition. The reduction of diester **110** produced diol **111** in 86% yield, but subsequent iodination-elimination failed to produce diene **113**. Reduction of **115** via standard conditions afforded a mixture of products which contained only a small amount of diol **116**. Unfortunately, further progress has not been possible due to lack of time. A discussion of the remaining steps is found in a later section.

Scheme 17 Synthetic strategy towards ambiphile 104



---

[a]DEAD, benzene. [b]$LiAlH_4$, ether. [c]TMSCl, NaI. [d]Zn/Cu, ether. [e]$Ph_3P{\cdot}Br_2$, CH_3CN. [f][O].

Conclusions

The key step in the synthesis of columnene ring structures was envisioned as intramolecular Diels-Alder cycloaddition of appropriate precursors of the type 30(n). In order to build these molecules, the butatriene synthetic approach[50] was developed. This approach is general and efficient, although in the third homologation, only moderate yields were obtained. Potential columnene precursors were prepared by this method, but this approach was soon replaced by a more efficient convergent procedure. In addition to this application, the butatriene synthetic equivalent strategy is useful for the synthesis of benzocyclobutenes and other polycyclic compounds.

Next, columnene synthesis was attempted via dimerization of ambiphiles **84**, **86**, and **88**. Thermolysis of each in benzene solution lead only to decomposition of the starting material. Catalysis with Lewis acids gave myriad products, none of which were characterized as the desired dimer. Failure of the desired cycloaddition was probably due to the high substitution of each dienophile. With Lewis acids, the competitive ene reaction may have occurred.[79]

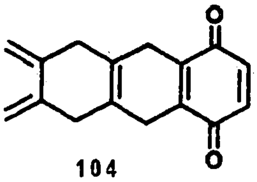
An ambiphile containing a quinone moiety (**98**) was generated and found to be very reactive. This unique structure dimerized rapidly and the resultant dimer cycloadded intramolecularly to form the desired novel cyclic structure, **101**. Unfortunately, neither 98 nor its dimer, **101**, was isolable. Although this molecule is not a columnene, it represents a fascinating and essentially unknown class of organic molecules.

In view of the resistance of **84**, **86**, and **88** to cycloaddition, this successful intramolecular Diels-Alder indicates that an active dienophile, such as the quinone moiety of **98**, is crucial to the success of cyclization. A cyclohexyne was expected to be an excellent choice for this strategy. Preliminary attempts to generate a diene substituted cyclohexyne failed. Effective conditions for this reaction were simply never found. However, given the success of **98**, ambiphiles in which the dienophile is a cyclohexyne moiety deserve further investigation.

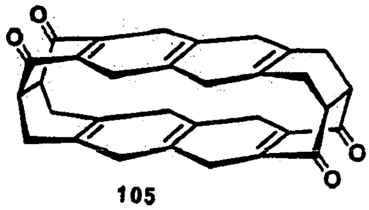
The size of **101** indicates that such cycloadditions should be useful for the synthesis of columnenes at least as large as hexacolumnene. Dimerization should provide an efficient route for the synthesis of the even-numbered columnenes and a variety of related columnar molecules.

Future Synthetic Work

The synthesis outlined in Scheme 17 (*vide ante*) should be completed. Conditions for the efficient reduction of diester **116** could probably be found. Subsequent iodination, elimination, then deprotection with fluoride,[80] should easily give diene **108**. Oxidation of **108** with Ag_2O is expected to produce the ambiphile **104**. If diol **111** cannot be iodinated via the butatriene synthetic equivalent approach, bromination with $Ph_3P{\cdot}Br_2$ to give **112** should be tried. Subsequent bromine elimination with Zn/Cu should generate diene **113**. Deprotection of the methyl ether[81] followed by oxidation with Ag_2O or direct oxidation of **113** with AgO[82] should provide alternate routes to **104**. Because it is larger than **101**, it is expected that the closed dimer of **104** resulting from Diels-Alder cyclization (**105**) should be isolable.



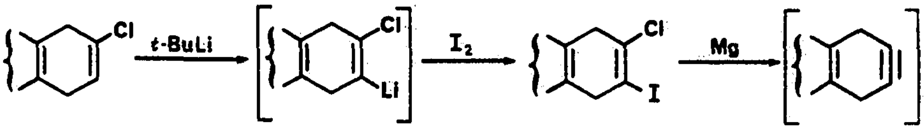
104



105

Further investigation of stable framework sizes should be available through the study of ambiphile **118**. A logical synthetic approach towards **118** is outlined in Scheme 18. Ambiphile **118** may best indicate the limitations of the minimum framework size possible via intramolecular Diels-Alder cyclization, by having the choice of dimerization to form **121** or trimerization to form **122**, as shown in Scheme 19. It was realized that a limitation of this study is that only the syn form of the open trimer **120** may cyclize. Partitioning of **118** between dimerization and trimerization should give a good indication of the limitations of the minimum size of a cyclized structure which can be successfully prepared by this route.

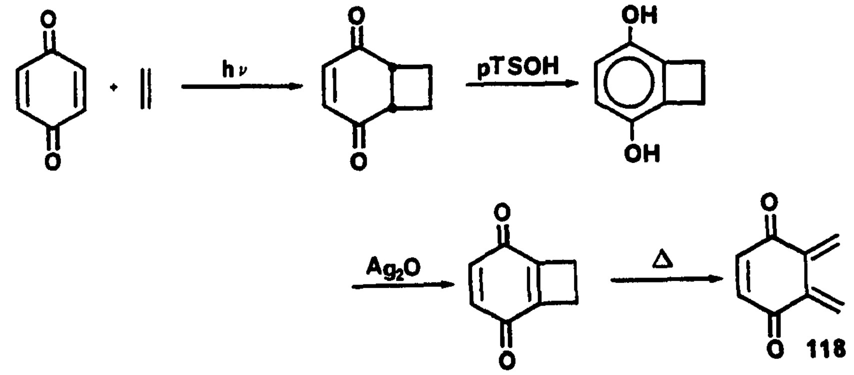
Since intramolecular Diels-Alder cyclization has occurred only with a good dienophile (*i.e.*, **98**), generation of a cyclohexyne, another excellent dienophile, should be reinvestigated. A well-known route to cyclohexynes from the treatment of 1,2-dihalocyclohexenes with magnesium[83] should be tried. The dihalo precursor might be prepared by lithiation of a vinyl chloride with t-BuLi[84] followed by quenching with I_2 (equation 18). Clearly an ambiphile containing such a strong



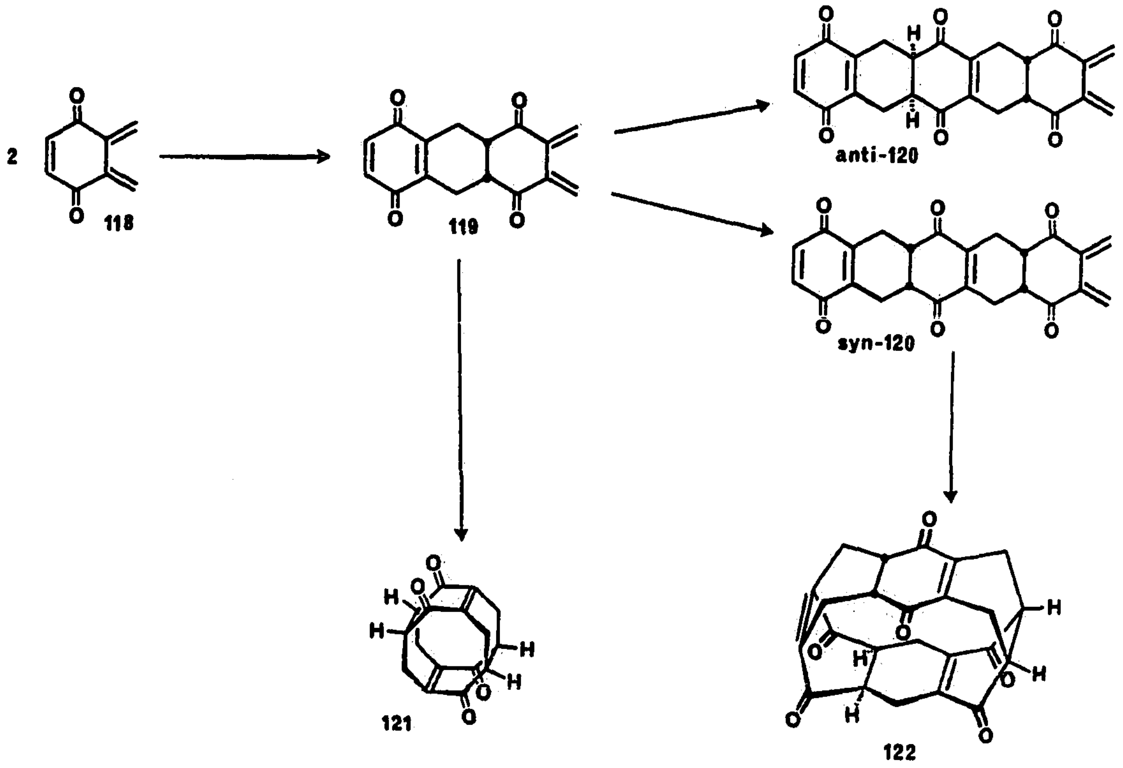
(18)

and unhindered dienophile should cyclize, and due to the large exothermicity expected for this reaction, formation of smaller columnenes may be possible via this method, than with quinone ambiphiles.

Scheme 18 Proposed synthesis of ambiphile **118**

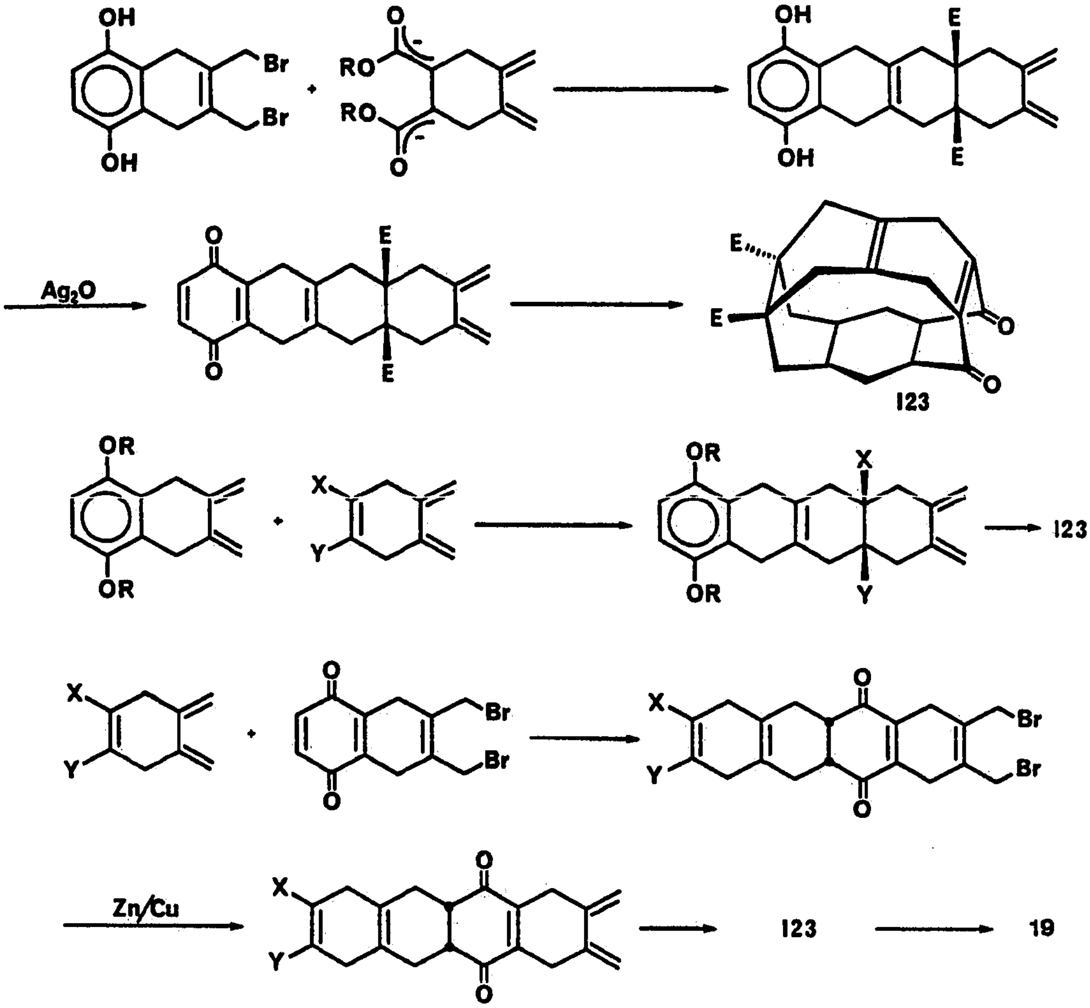


Scheme 19 Expected dimerization and trimerization of ambiphile **118**



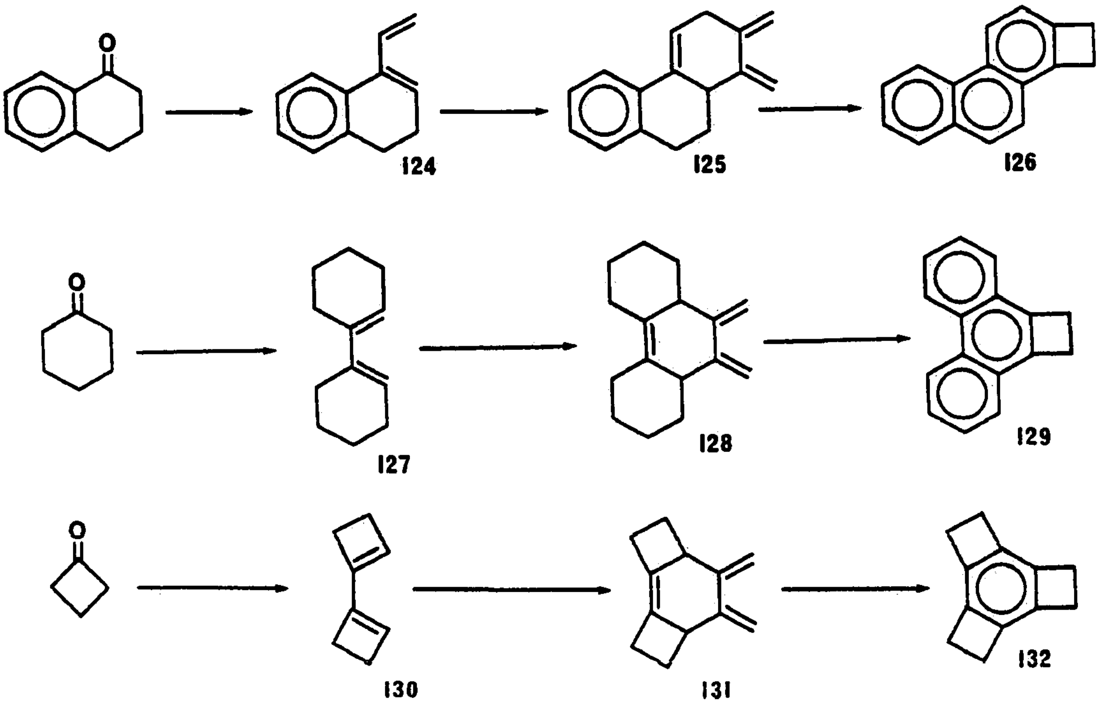
Thus far, only routes to the even n columnenes have been pursued. Since the synthesis of odd n columnenes is not possible via a dimerization route, convergent syntheses such as those outlined in Scheme 20 should be investigated.

Scheme 20 Potential synthetic routes to pentacolumnene



The butatriene synthetic equivalent approach, followed by ring closure and oxidation, is ideal for the preparation of polyaromatic cyclobutenes. The first examples of this route were the syntheses of naphtho[b]cyclobutene and anthro[b]cyclobutene (*vide supra*). Significant progress has been made towards synthesis of two phenanthrocyclobutenes (Scheme 21). Initial dienes **124**[85] and **127**[86] were each homologated once using the butatriene synthetic approach to afford **125** and **128** respectively. Photochemical ring closure was successful for **128**, but has not yet been tried for **125**. Oxidation of each to afford the aromatic hydrocarbons **126** and **129** will complete the sequences. It is hoped that these projects will one day be finished.

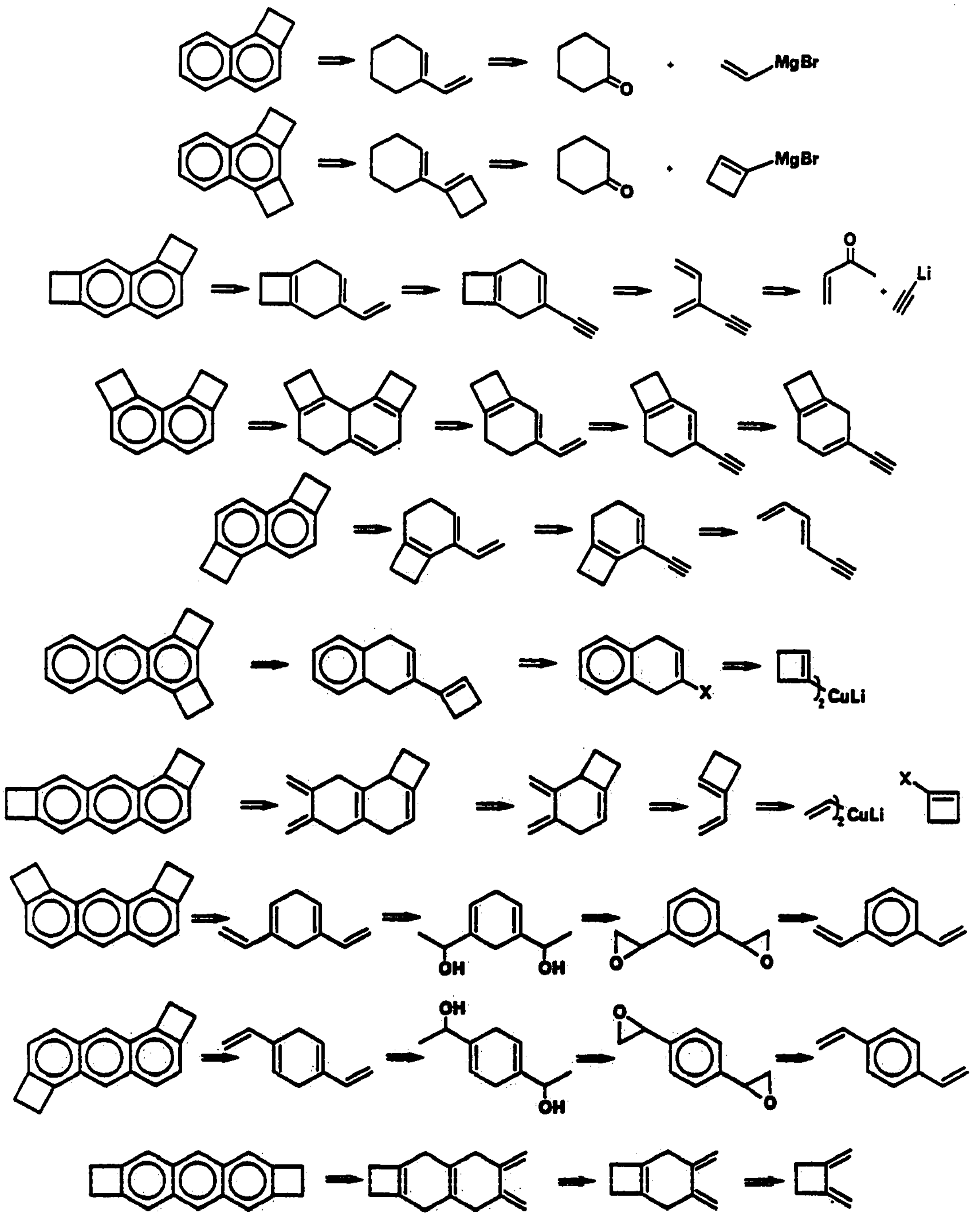
Scheme 21 Synthesis of cyclobutenes via the butatriene synthetic equivalent approach



Tricyclobutabenzene, **132**, is an interesting target for this strategy. This unique molecule was prepared first by Nutakul *et al.*[87] and very recently by Doecke *et al.*[88] From each synthesis, only minute quantities of **132** were isolated. It is expected that **132** should be available in large quantity from the application of the above route to bicyclobutenyl (Scheme 21).[89] The first three steps of the route of Doecke *et al.*,[88] in fact, essentially duplicate the butatriene synthetic equivalents strategy.

As well as the three cyclobutenes outlined, myriad others may be envisioned. A few such molecules, and their retrosynthetic strategies[90] are outlined in Scheme 22.

Scheme 22 Retrosynthetic strategies for selected cyclobutenes



Experimental Section

General Method

Instrumentation Melting points were determined on a Kofler hot stage and are corrected. Nuclear Magnetic Resonance (NMR) spectra were obtained on Hitachi R-20B, Varian EM-360, JEOLCO FX-90Q, Bruker WM-300, or Nicolet NT-300/NMC-1280 spectrometers with chemical shifts reported in ppm downfield from tetramethylsilane (δ). All ^{13}C NMR spectra were broad band proton decoupled. Infrared (IR) spectra were recorded on Beckman IR-4250 or Acculab 2 spectrophotometers and were calibrated with polystyrene film (1601 cm^{-1}). Fourier transform IR (FTIR) spectra were obtained using an IBM IR/98 instrument. Ultraviolet (UV) spectra were recorded on a Perkin Elmer 320 spectrophotometer. Mass spectra were obtained on an AEI-MS902 or Kratos MS-50TC high resolution mass spectrometer at 70 eV using perfluorokerosene (PFK) as an internal reference. Elemental combustion analyses were determined by Galbraith Laboratories, Inc.

Reagents and Procedures Before use, all solvents for reaction mixtures were purified and distilled from appropriate drying agents in accord with procedures outlined in the "Chemist's Companion".[91] Solvents used for extractions and chromatography were usually used without further purification. Many reagents were prepared and purified according to literature procedures. Unless stated otherwise, commercially available reagents were used without further purification.

All reactions were performed under an inert atmosphere of N_2 or Ar. Reactions run under Ar are so indicated. Unless stated otherwise, reactions were performed at ambient temperature and chromatographic separations were performed using silica gel. The term flash chromatography indicates that the method of Still *et al.*[92] was used.

Experimental Details

4-Chloro-cyclohex-4-ene-*cis*-1,2-dicarboxylic acid[93] (31). Chloroprene (5.00 g, 56.5 mmol) and maleic anhydride (5.03 g, 51.4 mmol) were heated to 50±5°C for 8 h, cooled to amb temp for 12 h, quenched with H_2O (50 mL), and refluxed for an additional 2 h. Crystallization from the aq soln at 5°C afforded 7.5 g (71%) of the hydrolyzed adduct: mp 161-3°C; 60 MHz ^1H NMR (acetone-d_6) δ 8.72 (br s, 2 H, COOH), 5.78 (br t, 1 H, =CH), 3.11 (cmplx mult, 2 H, CH), 2.74 (cmplx mult, 4 H, CH_2); mass spectrum, m/e 204 (M^+), 186, 160, 158, 123, 115, 113, 98, 79, 77, 72, 54 (base); high-resolution mass spectrum, obsd m/e 186.0077 (M^+-H_2O), $C_8H_7O_3Cl$ requires 186.0084.

cis-N,N,N',N'-tetramethyl-4-chloro-cyclohex-4-ene-1,2-dicarboxamide (32). Diacid 31 (1.58 g, 7.74 mmol) was suspended in benzene (5 mL). HMPT (1.40 mL, 1.26 g, 7.74 mmol) was added over 0.5 h with enough warming to maintain mild reflux. The reaction mixture was cooled to amb temp, dumped into satd, aq $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (5 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and concd to a pale yellow liquid. Recrystallization (ether) gave 1.52 g (76%) of the amide as a white solid: mp 105-6°C; 60 MHz

^{1}H NMR ($CDCl_3$) δ 5.83 (cmplx mult, 1 H, =CH), 3.07 (br s, 6 H, NCH_3), 3.00 (br s, 6 H, NCH_3), 3.25-2.35 (br cmplx mult, 6 H, CH CH_2); IR (neat) 2925s (br), 1649s, 1502m, 1423m, 1405m, 1262w, 1150m cm^{-1}; mass spectrum, m/e 258 (M^+), 216, 215, 214, 213, 72 (base); high-resolution mass spectrum, obsd m/e 258.1141. $C_{12}H_{19}N_2O_2Cl$ requires 258.1135.

cis-N,N,N',N'-tetramethyl-4-chlorocyclohex-4-ene-1,2-bis(dimethylamine) (33). To a suspension of $LiAlH_4$ (2.21 g, 58.3 mmol) in anhd ether (120 mL), a soln of diamide **32** (11.6 g, 44.8 mmol) was added during 0.5 h. The slurry was refluxed for 1 h after the addn, cooled to amb temp, and hydrolyzed with H_2O (5 mL), 10% aq NaOH (10 mL), and finally H_2O (5 mL). The white ppt which formed was filtered, rinsed with ether (4 x 50 mL) and discarded. The filtrate was dried ($MgSO_4$) and concd to afford 7.3 g of a yellow liquid. Distillation (134-6°C, 0.40 torr) gave 6.9 g (67%) of pale yellow liquid diamine. The spectral data were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.74 (cmplx mult, 1 H, =CH), 2.25 (br s, 12 H, NCH_3), 2.45-1.95 (cmplx mult, 6 H, CH CH_2); IR (neat) 2972s, 2942s, 2858m, 2820s, 2765s, 1456s, 1440m, 1260w, 1169w, 1144w,1040m, 1028m, 842w cm^{-1}; mass spectrum, m/e 230 (M^+), 185, 172, 170, 160, 101, 71 (base), 68; high-resolution mass spectrum, obsd m/e 230.1551, $C_{12}H_{23}N_2Cl$ requires 230.1550.

Diethyl 3,6-dihyrophthalate (34). Reaction of butadiene (20 g, 0.37 mol) and DEAD[39] (42.5 g, 0.250 mol) at 40±5°C in a pressure bottle for 5-6 days afforded 57.2 g (98%) of the adduct **34** as a colorless liquid: bp 90-95°C (0.8 torr); 60 MHz ^1H NMR ($CDCl_3$) δ 5.78 (s, 2 H, =CH), 4.27 (q, 4 H, J = 7 Hz, OCH_2), 3.01 (br s, 4 H, CH_2), 1.27 (t, 6 H, J = 7 Hz, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.4 (C=O), 132.0, 122.0, 60.5, 27.1, 13.6; IR (neat) 2980, 2900, 2880, 2830, 1720, 1680, 1645, 1255, 1055 cm^{-1}; mass spectrum, m/e 224 (M^+), 222, 178, 149 (base), 105; high-resolution mass spectrum, obsd m/e 224.1053, $C_{12}H_{16}O_4$ requires 224.1049.

1,2-Bis(hydroxymethyl)-3,6-dihydrobenzene (35).[40] Diethyl ester 34 was reduced with a twofold molar excess of $LiAlH_4$ in anhd ether at 0°C. Hydrolysis with 1 M aq K_2CO_3 and a standard workup afforded the diol (92%) as a crystalline solid: mp 46-47°C (lit.[40] mp 47-48°C); 22 MHz ^{13}C NMR (acetone-d_6) δ 131.8, 124.9, 61.6, 29.6.

Preparation of zinc/copper couple.[50] Dry DMF was added dropwise quickly under nitrogen to a magnetically stirred intimate mixture of finely powdered $CuSO_4 \cdot 5H_2O$ and Zn dust (1:10 molar ratio) until the surface was just covered. An exothermic reaction ensued, and the mixture immediately became black. Slight external cooling was used in the preparation of large quantities.

After cooling, the mixture was diluted with ether and used directly in elimination reactions. Attempted use of anhydrous $CuSO_4$ in this procedure did not lead to efficient couple formation.

4,5-Dimethylenecyclohexene (37).[42] A mixture of diol 35 (3.60 g, 25.7 mmol) and sodium iodide (11.6 g, 77.0 mmol) in anhd ether (450 mL) was treated[41] dropwise with Me_3SiCl (16.4 mL, 128.4 mmol). After 1 h, TLC analysis showed no remaining diol, and the mixture was transferred during 45 min via cannula to a stirred suspension of Zn/Cu couple (125 mmol) in anhd ether (50 mL). After 2 h more, the mixture was filtered, washed with satd, aq $NaHCO_3$ (4 x 100 mL), dried ($MgSO_4$), and concd to afford 2.4 g (82%) of essentially pure **37**: bp 65-71°C (60 torr) [lit.[42] bp 73-74°C (85 torr)].

Diethyl 1,4,5,8-tetrahydro-2,3-naphthalenedicarboxylate (38). A soln of diene **37** (2.44 g, 23.0 mmol), DEAD (3.52 mL, 3.74 g, 22.0 mmol) in benzene (100 mL) was heated to 45±5°C for 4 h. Concentration followed by recrystallization (hexanes) afforded 5.69 g (94%) of white solid adduct: mp 176-8°C; 60 MHz ^1H NMR ($CDCl_3$) δ 5.81 (m, 2 H, =CH), 4.27 (q, J = 7 Hz, 4 H, OCH_2), 2.89 (br s, 4 H, CH_2), 2.58 (br s, 4 H, CH_2), 1.31 (t, 6 H, J = 7 Hz, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.9 (C=O), 132.5, 124.0, 121.8, 61.0, 32.4, 30.2, 14.1; IR (KBr) 2980, 2880, 2840, 2815, 1725, 1660, 1255, 1065, 1035 cm^{-1}; mass spectrum, m/e 276 (M^+), 230 (base), 201, 129, 125, 98; high-resolution mass spectrum, obsd m/e 276.1361, $C_{16}H_{20}O_4$ requires 276.1362. Anal calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.295. Found: C, 69.34; H, 7.25.

2,3-Bis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene (39). A solution of diethyl ester **38** (6.09 g, 22.1 mmol) in ether (200 mL) was added dropwise to a stirred mixture of $LiAlH_4$ (1.68 g, 44.1 mmol) in anhd ether (450 mL) at 0°C. After 4 h more at amb temp, the mixture was hydrolyzed at 0°C with a large excess of 1 M, aq K_2CO_3. The copious white precipitate which fell from soln was carefully filtered. Concentration of the dried ($MgSO_4$) ether layer afforded 2.62 g of diol **39**. Continuous extraction (5 days) of the inorganic residue with ether gave an additional 0.962 g (total 85% yield) of diol: mp 147-149°C; 60 MHz ^1H NMR (acetone-d_6) δ 5.75 (br s, 2 H, =CH), 4.09 (br s, 2 H, CH_2O), 3.07 (br s, 4 H, OH), 2.66 (br s, 4 H, CH_2), 2.53 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR (acetone-d_6) δ 131.6, 125.0, 123.6, 60.9, 31.5, 30.8; IR (KBr) 3600-3050, 2864, 2835, 2803, 1665, 1442, 1052, 980 cm^{-1}; mass spectrum, m/e 192 (M^+), 174, 143 (base), 131, 91; high-resolution mass spectrum, obsd m/e 192.1150, $C_{12}H_{16}O_2$ requires 192.1150. Anal calcd for $C_{12}H_{16}O_2$: C, 74.69; H, 8.389. Found: C, 75.02; H, 8.48.

2,3-Dimethylene-1,4,5,8-tetrahydronaphthalene (**40**). Diol **39** (2.35 g, 12.2 mmol) and NaI (3.67 g, 24.4 mmol) in anhd ether (300 mL) and anhd THF (50 mL) was treated dropwise with Me_3SiCl (77.8 mL, 61.1 mmol). The mixture was added to freshly prepared Zn/Cu couple (60 mmol) in ether. A workup as above afforded the product as a colorless liquid, which was used immediately in the subsequent step. The spectral data were: 60 MHz ^1H NMR ($CDCl_3$) δ 5.68 (m, 2 H, =CH), 5.06 (br d, 2 H, =CH_2), 4.71 (br d, 2 H, =CH_2), 2.72 (br s, 4 H, CH_2), 2.48 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 145.4, 124.2, 124.1, 108.2, 37.9, 30.8; IR (neat) 2955, 2920, 2890, 2870, 2840, 2805, 1645, 1630, 1425, 880 cm^{-1}; mass spectrum, m/e 158 (M^+), 143, 128, 115, 91 (base); high-resolution mass spectrum, obsd m/e 158.1091, $C_{12}H_{14}$ requires 158.1096.

Diethyl 1,4,5,8,9,10-Hexahydroanthracene-2,3-dicarboxylate (41). Crude **40**, from above, was treated with DEAD (1.96 mL, 12.2 mmol) in benzene (50 mL) at 45±5°C during 4 h. Concentration and recrystallization (ether/hexane) yielded 2.21 g (55% overall from diol **39**) of **41** as colorless crystals: mp 99-103°C; 60 MHz ^1H NMR ($CDCl_3$) δ 5.63 (br s, 2 H, =CH), 4.20 (q, 4 H, J = 7 Hz, OCH_2), 2.85 (br s, 4 H, CH_2), 2.54 (br s, 4 H, CH_2), 2.41 (br s, 4 H, CH_2), 1.25 (t, 6 H, J = 7 Hz, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.9 (C=O), 132.6, 124.3, 123.1, 121.9, 61.1, 35.2, 32.1, 30.5, 14.1; IR (KBr) 2980, 2875, 2815, 1723, 1244, 1058, 1033 cm^{-1}; mass spectrum, m/e 328 (M^+), 282 (base), 252, 210; high-resolution mass spectrum, obsd m/e 328.1673, $C_{20}H_{24}O_4$ requires 328.1675.

2,3-Bis(hydroxymethyl)-1,4,5,8,9,10-hexahydroanthracene (42). Diethyl ester **41** (1.45 g, 4.40 mmol) was reduced as above with $LiAlH_4$ (344 mg, 8.80 mmol) in ether/THF (to improve solubility). The organic layer yielded 336 mg of product, and continuous extraction (5 days) of the inorganic residue yielded an additional 301 mg (total 60%): mp 210-213°C; 60 MHz ^1H NMR (DMSO-d_6) δ 5.66 (br s, 2 H, =CH), 4.06 (br s, 2 H, OH), 3.23 (br s, 4 H, CH_2O), 2.65 (br s, 4 H, CH_2), 2.51 (br s, 4 H, CH_2), 2.39 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR (DMSO-d_6) δ 130.3, 124.2, 122.9, 122.7, 59.8, 34.9, 33.1, 30.0; IR (KBr) 3600-3050, 2860, 2796, 1410, 1040, 988, 978, 958 cm^{-1}; mass spectrum, m/e 244 (M^+) 226, 210, 195 (base); high-resolution mass spectrum, obsd m/e 244.1466, $C_{16}H_{20}O_2$ requires 244.1463.

2,3-Dimethylene-1,2,3,4,5,8,9,10-octahydroanthracene (43). Diol **42** (182 mg, 0.745 mmol) was treated with NaI (223 mg, 1.49 mmol) and Me_3SiCl (474 µL, 3.73 mmol) in THF (40 mL). Elimination was effected by fresh Zn/Cu couple (3.7 mmol) in anhd ether (15 mL). Recrystallization of the product from pentanes afforded 61 mg (39%) of **42** as a colorless solid: mp 88.5-90°C; 60MHz ^1H NMR ($CDCl_3$) δ 5.68 (s, 2 H, =CH), 5.07 (d, J = 2 Hz, 2 H, $=CH_2$), 4.73 (d, J = 2 Hz, 2 H, $=CH_2$), 2.81 (br s, 4 H, CH_2), 2.51 (br s, 4 H, CH_2), 2.40 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 145.7, 124.4, 123.2, 108.5, 37.5, 36.0, 30.6; IR (CCl_4) 2960, 2868, 2840, 2808, 1655, 1645, 1631, 1427, 884 cm^{-1}; mass spectrum, m/e 210 (M^+ and base), 208, 194, 192, 140; high-resolution mass spectrum, obsd m/e 210.1403, $C_{16}H_{18}$ requires 210.1408.

Diethyl 2,3-naphthalenedicarboxylate (44).[45] Diester **38** (86 mg, 0.311 mmol) in benzene (2 mL) was added to DDQ[44] (141 mg, 0.622 mmol) in benzene (2 mL). After 15 min, the mixture was concentrated and chromatographed (20% EtOAc/hexane) to give 78 mg (92%) of **44**: mp 54-55°C (lit.[45] mp 55°C); 60 MHz ^1H NMR ($CDCl_3$) δ 8.15 (s, 2 H, ArH), 7.89-7.33 (m, 4 H, ArH), 4.33 (q, J = 7 Hz, 4 H, OCH_2), 1.33 (t, J = 7 Hz, 6 H, OCH_2CH_3); 22 MHz ^{13}C NMR δ 167.7 (C=O), 133.4 130.0, 128.9, 128.6, 128.4, 61.6, 14.2.

Diethyl 2,3-anthracenedicarboxylate (45). Diester **41** (195 mg, 0.594 mmol) was oxidized with DDQ (404 mg, 1.78 mmol) as above to afford 164 mg (84%) of **45**: mp 99-100°C; 60 MHz ^1H NMR ($CDCl_3$) δ 8.42 (s, 2 H, ArH), 8.37 (s, 2 H, ArH), 8.02-7.34 (m, 4 H, ArH), 4.38 (q, J

= 7 Hz, 4 H, OCH_2), 1.38 (t, J = 7 Hz, 6 H, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.7 (C=O), 133.0, 131.0, 130.4, 128.4, 128.0, 127.8, 126.7, 61.6, 14.2; IR (CCl_4) 2982, 1725, 1540, 1238, 998, 970 cm^{-1}; mass spectrum, m/e 322 (M^+ and base), 276, 248, 247; high-resolution mass spectrum, obsd m/e 322.1193, $C_{20}H_{18}O_4$ requires 322.1205.

1,4,5,8-Tetrahydronaphtho[b]cyclobutene (46). By use of a standard immersion-well apparatus, with a 450-W medium-pressure lamp, a solution of diene **40** (135 mg) in 200 mL of argon-degassed spectrograde pentane was irradiated for 25 min through a Vycor filter. Concentration and chromatography (hexane) yielded 130 mg (96%) of **46**: mp 78-81°C; 60 MHz ^1H NMR ($CDCl_3$) δ 5.53 (br s, 2 H, =CH_2), 2.49 (br s, 8 H, CH_2), 2.45 (sh, 4 H, CH_2), 2.34 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 139.0, 124.3, 31.8, 31.1, 30.9; IR (CCl_4) 2910, 2875, 2850, 2815, 1678, 1428, 1245 cm^{-1}; mass spectrum, m/e 158 (M^+ and base), 143, 129, 155; high-resolution mass spectrum, obsd m/e 158.1093, $C_{12}H_{12}$ requires 158.1096.

Naphtho[b]cyclobutene (47).[47] Hydrocarbon **46** (99 mg, 0.63 mmol) was oxidized with DDQ (284 mg, 1.25 mmol) in benzene (2 mL) during 0.5 h. Chromatography (hexanes) yielded 80 mg (81%) of **43**: mp 86-87°C (lit.[47] mp 84.5-86°C); 22 MHz ^{13}C NMR ($CDCl_3$) δ 144.7, 133.9, 128.0, 124.6, 120.3, 29.4 The ^1H NMR spectrum was as reported.[47]

1,4,5,8,9,10-Hexahydroanthro[b]cyclobutene (48). Diene **43** (40 mg) in argon-degassed spectrograde pentane was irradiated through

Vycor for 20 min. Concentration and chromatography (hexanes) yielded 36 mg (90%) of **48**: mp 143-145°C; 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.64 (s, 2 H, =CH), 2.52 (br s, 8 H, CH_2), 2.44 (br s, 8 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 139.2, 124.7, 123.3, 36.9, 30.8, 30.6, 30.5; IR (CCl_4) 2915, 2865, 2810, 1660, 1430 cm^{-1}; mass spectrum, m/e 210 (M^+ and base), 195, 193, 179, 178, 141, 128; high-resolution mass spectrum, obsd m/e 210.1410, $C_{14}H_{18}$ requires 210.1408.

Anthro[b]cyclobutene (**49**).[48] Cyclobutene **48** (23 mg, 0.11 mmol) in CCl_4 (2 mL) was oxidized with DDQ (75 mg, 0.33 mmol) as above. Chromatography (hexanes) yielded 18 mg (85%) of anthracene **49**: mp>240°C (lit.[48] mp 245-247°C); 22 MHz ^{13}C NMR ($CDCl_3$) δ 144.7, 130.9, 128.0, 126.0, 124.9, 119.8, 29.8. The ^{1}H NMR spectrum agreed with that previously reported.

Diethyl 4-chloro-3,6-dihydrophthalate (**51**). A soln of chloroprene (23.0 mL, 22.1 g, 250 mmol) and DEAD (36.0 g, 211 mmol) was refluxed for 3 days. Additional chloroprene (2 x 10 mL) was added at 1 day intervals. Distillation (133-4°C, 0.80 torr) of the crude reaction mixture afforded 45.9 g (84%) of pure liquid adduct. The spectral data were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.84 (cmplx mult, 1 H, =CH), 4.21 (q, J = 7 Hz, 4 H, OCH_2CH_3), 3.14 (br s, 4 H, CH_2), 1.28 (t, J = 7 Hz, 6 H, OCH_2CH_3); IR (neat) 2975, 2895, 1729 sh, 1720, 1678, 1650, 1255, 1050 cm^{-1}.

4-Chloro-1,2-bis(hydroxymethyl)-3,6-dihydrobenzene (52). Diol 52 was prepared in a manner analogous to the preparation of Diol 35. The product was isolated as a white solid: mp 80-83°C; 60 MHz ^{1}H NMR (acetone-d_6) δ 5.78 (cmplx mult, 1 H, =CH), 4.12 (br s, 2 H, CH_2O), 4.09 (br s, 2 H, CH_2O), 3.74-3.57 (br s, 2 H, OH), 2.96 (cmplx mult, 4 H, CH_2); mass spectrum, m/e 156 (M^+-H_2O), 140, 138, 127, 125, 105, 103, 91 (base), 79, 77, 51; high-resolution mass spectrum, obsd m/e 156.0348 (M^+-H_2O), C_8H_9OCl requires 156.0342.

1-Chloro-3,4-bis(methylene)cyclohex-1-ene (53), elimination route. To a soln of diol 52 (4.240 g, 24.30 mmol) and NaI (10.59 g, 97.19 mmol) in anhd ether (400 mL) was added, dropwise during 2 h, an ethereal soln of TMSCl (11.66 g, 9.99 mL, 77.75 mmol) in anhd ether (125 mL). The mixture was stirred vigorously for 2 h, during which the soln darkened to a deep red. Filtration through glass wool with concomitant cannula transfer to a slurry of freshly prepared Zn/Cu (122 mmol) during 0.5 h followed by stirring for 2 h effected the iodine elimination. The ethereal soln was washed with satd, aq $NaHCO_3$ (3 x 100 mL) until ZnI_2 ppt was no longer observed. The soln was dried ($MgSO_4$) and concentrated to afford 2.70 g ($\leq$ 79%) of diene as a nearly clear liquid. This product was used without further purification due to its facile polymerization. The spectral data were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.73 (cmplx mult, 1 H, =CH), 5.10 (br s, 2 H, $=CH_2$), 4.75 (br s, 2 H, $=CH_2$), 3.12-2.80 (cmplx mult, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 143.4, 142.6, 122.3 (coincidence), 110.6 (coincidence), 40.1, 33.5; IR (neat) 3100, 2995, 2930, 2885, 2830, 2780, 1672, 1642, 1428 cm^{-1}.

1-Chloro-3,4-bis(methylene)cyclohex-1-ene (53), pyrolysis route. A soln of diamine **33** (5.15 g, 22.4 mmol) in MeOH (7.5 mL), cooled to 0°C, was treated thrice with 30% aq H_2O_2 (7.6 mL, 67.0 mmol) portions at 3 h intervals. The mixture stirred for 40 h after which the excess H_2O_2 was quenched by slowly pouring the reaction mixture into a slurry of 10% Pt/Carbon (30 mg) in MeOH (3 mL) followed by stirring for 30 h. The catalyst was removed by filteration through Celite and the solvent was evacuated at reduced pressure. The amine oxide thus generated was thermalized (165±5°C, 22±5 torr) in a bulb to bulb distillation apparatus. The crude pyrolsate was collected at 0°C in less than 10 min, dissolved in pentanes (75 mL), and washed with H_2O (8 mL), 5% aq HCl (8 mL), satd, aq $NaHCO_3$ (2 x 8 mL) and satd, aq NaCl (2 x 8 mL). The pentanes soln was dried ($MgSO_4$) and solvent was removed at reduced pressure to afford 700 mg (22%) of nearly pure clear liquid diene. The spectral data are consistent with those known from the previous preparation.

Diethyl 6-chloro-1,4,5,8-tetrahydro-2,3-naphthalene dicarboxylate (54). Diester **54** was prepared in 89% yield, in a manner analogous to the preparation of **38**. The spectral date were: 60 MHz ^1H NMR ($CDCl_3$) δ 5.73 (cmplx mult, 1 H, =CH), 4.08 (q, J = 7 Hz, 4 H, OCH_2CH_3), 2.84 (br s, 4 H, CH_2), 2.72 (br s, 4 H, CH_2), 1.28 (t, J = 7 Hz, 6 H, OCH_2CH_3).

6-Chloro-2,3-bis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene (55). Diol **55** was prepared in a manner analogous to the preparation of **39**. The diol was obtained in 86% yield as a white solid: mp 159-60°C; 60 MHz ^{1}H NMR (acetone-d_6) δ 5.87 (cmplx mult, 1 H, =CH), 4.03 (br s 2 H, CH_2OH), 3.95 (br s, 2 H, CH_2OH), 3.09 (s, 2 H, OH), 2.69 (br s, 4 H, CH_2), 2.60 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR (acetone-d_6) δ 131.0, 130.8, 129.1, 123.2, 122.7 (coincidence), 60.6 (coincidence), 37.6, 33.8, 33.5, 32.7; IR (KBr) 3610-3020, 2855, 2794, 1658, 1414, 1252, 1000, 789 cm^{-1}; mass spectrum, m/e 226 (M^+), 208, 177, 143(base), 129, 115, 91, 77, high-resolution mass spectrum, obsd m/e 226.0762, $C_{12}H_{15}O_2Cl$ requires 226.0761.

6-Chloro-2,3-bis(methylene)-1,4,5,8-tetrahydronaphthalene (56). Diene **56** was prepared in a manner analogous to the preparation of **40**. The product was obtained in 83% yield as a clear easily polymerizable liquid. The spectral data were: 60 MHz ^{1}H NMR (CCl_4) δ 5.76 (cmplx mult, 1 H, =CH), 5.06 (cmplx mult, 2 H, =CH_2), 4.70 (cmplx mult, 2 H, =CH_2), 2.71 (cmplx mult, 8 H, CH_2); IR (neat) 3000, 2895, 2885, 2818, 1675, 1642, 1438, 990, 900, 805 cm^{-1}.

Diethyl 6-chloro-1,4,5,8,9,10-hexahydroanthracene-2,3-dicarboxylate (57). Diester **57** was prepared in a manner analogous to the preparation of **41**. The product was obtained in 78% yield as a white solid: mp 136-7°C; 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.74 (cmplx mult, 1 H, =CH), 4.20 (q, J = 7 Hz, 4 H, OCH_2CH_3), 2.88 (br s, 4 H, CH_2), 2.74 (br s, 4 H, CH_2), 2.45 (br s, 4 H, CH_2), 1.30 (t, J = 7 Hz, 6 H,

OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.8 (C=O), 132.5 (coincidence), 128.8, 122.8, 121.7, 121.5 (coincidence), 61.1, 37.5, 34.8, 34.5, 32.5, 32.0 (coincidence), 14.0; mass spectrum, m/e 362 (M^+), 316 (base), 287, 270, 243, 179, 129, 91, 77, 55; high-resolution mass spectrum, obsd m/e 362.1281, $C_{20}H_{23}O_4Cl$ requires 362.1285.

6-Chloro-2,3-bis(hydroxymethyl)-1,4,5,8,9,10-hexahydroanthracene (58). Diol 58 was prepared in a manner analogous to the preparation of 42. The product was isolated in 59% yield as a waxy white solid: mp 120-5°C; 60 MHz ^1H NMR (DMSO-d_6) δ 5.87 (cmplx mult, 1 H, =CH), 3.95 (br s, 2 H, CH_2OH), 3.88 (br s, 2 H, CH_2OH), 3.24 (s, 2 H, OH), 2.68 (br s, 4 H, CH_2), 2.52 (br s, 4 H, CH_2), 2.36 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR (DMSO-d_6) δ 128.1, 123.6, 123.4, 123.2, 123.0, 122.9, 122.5, 122.1, 63.3, 61.4, 37.5, 36.8, 35.3, 32.0, 31.2, 30.4; IR (nujol) 3630-3060, 2990, 2980, 2935, 2925, 1650, 1640, 1472, 1460, 1425, 1382, 1370, 1165, 1070, 1015, 982, 909 cm^{-1}.

6-Chloro-2,3-bis(bromomethyl)-1,4,5,8,9,10-hexahydroanthracene (60). A soln of Br_2 (478 μL, 1.491 g, 9.318 mmol) in CH_3CN (5 mL) was added drop-wise during 5 min to a 0°C suspension of Ph_3P (2.440 g, 9.318 mmol) in CH_3CN (20 mL). After the addition, no red-brown coloration remained. A soln of diol 58 (1.298 g, 4.659 mmol) in CH_3CN (120 mL) was added to the $Ph_3P \cdot Br_2$ slurry during 0.5 h. The mixture was warmed to amb temp and stirred for 4 h during which time all solid material dissolved. The mixture turned gray-green during the reaction. Evacuation of solvent at reduced pressure afforded a dark solid which was chromatographed (hexanes, florisil) to give 158 mg (9%) of the desired dibromide: mp 155-7°C. Impure **58** (~650 mg) was recovered from chromatography. The bromination yield was not optimized. The spectral data for **60** were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.76 (cmplx mult, 1 H, =CH), 3.50 (br s, 4 H, CH_2Br), 2.70 (br s, 4 H, CH_2), 2.41 (br s, 4 H, CH_2), 2.01 (br s, 4 H, CH_2); mass spectrum, m/e 407, 405, 403 (M^+), 369, 336, 323, 244, 91, 80 (base); high-resolution mass spectrum, obsd m/e 403.9371, $C_{16}H_{17}Br_2Cl$ requires 403.9365.

<u>4-Chloro-o-xylene</u> <u>(**63**)</u>. This compound was isolated from gas chromatography of **53** on 20% carbowax on chromosorb W at 150°C with an injector temp of 225°C. Under these conditions, both diene **53** (T_r = 8.5 min) and **63** (T_r = 12.3 min) were obtained in about equal amounts. The spectral data for **63** were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 7.10 (cmplx mult, 3 H, aryl H), 2.13 (s, 6 H, CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 138.3, 134.9, 131.2, 130.8, 129.4, 125.8, 19.6, 19.1; IR (neat) 3010, 2965, 2940, 2920, 1595, 1482, 1445, 1175, 1095, 875, 805; mass spectrum, m/e 140 (M^+), 125, 105, 77, 51; high-resolution mass spectrum, obsd m/e 140.0392, C_8H_9Cl requires 140.0393.

<u>4-Chloro-1,2-bis((α-ethoxy-ethoxy)methyl)-3,6-dihydrobenzene</u> <u>(**61**)</u>. A soln of diol **47** (2.72 g, 15.6 mmol), EVE (3.64 mL, 2.75 g, 31.2 mmol), and PyHOTs (783 mg, 3.12 mmol) in CH_2Cl_2 (80 mL) was stirred for 1.5 h, washed with satd, aq NaCl (3 x 30 mL), dried ($MgSO_4$) and concd to a pale yellow liquid. Chromatography (2% ether/hexanes) of the crude product mixture afforded 3.75 g (76%) of the protected

diol. The spectral data were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 5.63 (cmplx mult, 1 H, =CH), 4.53 (cmplx mult, 6 H, OCH, OCH_2), 3.97 (br s, 4 H, CH_2O), 2.87 (br s, 4 H, CH_2), 1.11 (cmplx mult, 12 H, CH_3).

Dimethyl 1-methoxy cyclobutane-1,2-dicarboxylate (**66**). To a soln of diester **50** (100 mg, 588 μmol) in MeOH (10 mL) under N_2, NaOMe (10 mg, 185 μmol) was added. The soln was stirred for 12 h, dumped into satd, aq NH_4Cl (10 mL) and extracted with ether (3 x 25 mL). The combined ether solns were dried ($MgSO_4$) and conc to a clear liquid. Distillation (bp 81-3°C, 0.1 torr) gave 104 mg (95%) of **66**. This product is identical to the anomalous product obtained from ether/methanol workup of **50**. The spectral data were: 60 MHz ^{1}H NMR ($CDCl_3$) δ 3.83, 3.77, 3.73, 3.67 (4 s, 6 H, COOMe isomers), 3.37, 3.24 (2 s, 3 H, OMe isomers), 2.60-2.04 (br mult, 5 H, CH, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 171.6 (C=O), 82.4, 52.9, 52.2, 51.9, (51.6), 47.1, (46.1), 28.5, (27.4), 16.19, minor isomer resonances are in parentheses; IR (neat) 2995, 2950, 2835, 1735 (broad), 1508, 1495, 1432, 1295 (broad), 1205 (broad), 1145, 1110, 1044, 1020 cm^{-1}.

Attempted reduction of diester **50**, method A,[94] with diisobutylaluminumhydride (DIBAH). A soln of DIBAH, 1.0 M (3.48 mL, 3.48 mmol) in toluene was added during 4 min to a soln of diester **50** (148 mg, 870 μmol) in benzene (10 mL) maintained at 55±5°C. After heating for 3 h, the mixture was cooled to amb temp and hydrolyzed with MeOH (3 mL). This hydrolysis step produced a gel. When EtOAc (25 mL) was added, the gel became a ppt and this was filtered. The filtrate was washed with satd, aq NaCl (3 X 1 mL), dried ($MgSO_4$) and conc at reduced pressure to afford 103 mg of a pale yellow liquid. TLC analysis showed many components in this mixture. ^1H NMR ($CDCl_3$) showed a small broad singlet resonance at δ 4.12 ppm, characteristic of the methylene of an allyl alcohol. The diol, if formed, did not survive chromatography.

Method B,[95] with sodium bis(2-methoxyethoxy)aluminumhydride (SMEAH). To a refluxing soln of diester **50** (150 mg, 882 mmol) in benzene (7 mL) was added, during 3 min, a soln of SMEAH, 3.40 M (0.519 mL, 1.76 mmol) in toluene. The mixture was refluxed for 1 h, cooled to amb temp, and hydrolyzed with 10% aq HCl (0.5 mL) overnight. The mixture was filtered through Celite and the filtrate was concd under reduced pressure to give 86 mg of yellow liquid. TLC analysis showed a mixture of many components. ^1H NMR analysis showed no resonance at δ 4.12 ppm as obtained in method A.

Method C, with lithium methoxyaluminumhydride[$LiAl(OMe)H_3$]. The reducing agent was prepared by adding MeOH (130 μL, 3.55 mmol) in anhd ether (1 mL) to a 0°C slurry of $LiAlH_4$ (135 mg, 3.55 mmol) in anhd ether (7 mL). A soln of diester **50** (151 mg, 887 μmol) in anhd ether (8 mL) was added to the hydride slurry and the mixture was stirred at 0°C for 0.5 h, then for 3 h at amb temp. Hydrolysis was effected with 1 M aq K_2CO_3 (1.8 mL) and the soln was dried (K_2CO_3) and concd under reduced pressure to a white liquid which was shown by TLC to contain many products. No diol was isolated from this mixture.

2,3-bis(Bromomethyl)-1,3-butadiene (73).[68] To a refluxing soln of tetrabromide 82 (1.60 mg, 4.00 mmol) in DMSO (4 mL) and anhd ether (28 mL), Zn (1.30 g, 20.0 mmol) was added in four 325 mg portions at 0.5 h intervals. The mixture was refluxed for 1 h and then filtered through Celite and concd to 8 mL. The mixture was quickly diluted with pentanes (35 mL) and washed with satd, aq NH_4Cl (10 mL), H_2O (3 x 10 mL), then dried ($MgSO_4$) and concd to a clear liquid which began to solidify. Rapid chromatography (florisil, pentanes at ~ 10°C) afforded 510 mg (53%) of a clear liquid which is best stored in soln (degassed ether, benzene) to avoid polymerization. Temperature of boiling and melting could not be determined due to facile polymerization. ^1H NMR, IR, & UV spectral data were as previously reported.[68] The ^{13}C NMR spectrum was: 75 MHz ^{13}C NMR ($CDCl_3$) δ 119.2, 96.2, 32.7.

Diethyl 4,5-bis(bromomethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (83). A freshly prepared sample of diene 73 (~12 g, ~50 mmol) and DEAD (11.2 mL, 11.9 g, 70.0 mmol) were dissolved in benzene (60 mL). The soln was refluxed for 3 days. Chromatography (florisil, 5% ether/hexanes) afforded 11.3 g (55%) of a white solid adduct. Recrystallization from hot ether or ethanol resulted in transformation to an unidentified adduct. The spectral data were: 60 MHz ^1H NMR ($CDCl_3$) δ 4.22 (q, J = 7.15 Hz, 4 H, OCH_2), 4.02 (br s, 4 H, CH_2Br), 3.16 (br s, 4 H, CH_2), 1.29 (t, J = 7.15 Hz, 6 H, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.0 (C=O), 131.4, 129.7, 61.4, 31.6, 29.3, 14.0; IR (KBr) 2990, 2945, 2880, 1725, 1664, 1292, 1260, 1046 cm^{-1}; mass spectrum, m/e 408 (M^+-2), 365, 329, 283 (base), 255, 204, 176, 148, 103, 91, 77; high-resolution mass spectrum, obsd m/e 364.9214 (M^+-OEt), $C_{12}H_{13}O_3Br_2$ requires 364.9211.

Diethyl 4,5-bis(methylene)-cyclohexene-1,2-dicarboxylate (**84**). A soln of dibromide, **83** (4.581 g, 11.17 mmol) in anhd ether (100 mL) was added dropwise over 25 min, while under N_2, to a slurry of freshly prepared Zn/Cu (55.84 mmol) in anhd ether (300 mL). The slurry was stirred for 4 h followed by filtration through a 0.5 cm pad of Celite. The water white filtrate was washed with satd, aq NH_4Cl (3 x 100 mL) until no further ZnBr ppt was obsd. The resulting ethereal soln was washed with H_2O (100 mL), dried ($MgSO_4$) and concd to a pale yellow liquid. Flash chromatography (2% EtOAc/hexanes) afforded 2.482 g, (89%) of desired diene. Attempted distillation aromatized the cmpd. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 5.23 (br d, J ≃ 1.2 Hz, 2 H, =CH_2), 4.89 (br d, J ≃ 1.2 Hz, 2 H, =CH_2), 4.23 (q, J = 7.1 Hz, 4 H, OCH_2), 3.25 (s, 4 H, CH_2), 1.30 (t, J = 7.1 Hz, 6 H, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 167.5 (C=O), 141.5, 133.6, 110.8, 61.3, 34.2, 14.1; IR ($CHCl_3$) 2943w, 2914w, 1715s, 1658m, 1368m, 1271-1190s, 1063m, 900s cm^{-1}; mass spectrum, m/e 250 (M^+), 205, 177 (base); high-resolution mass spectrum, obsd m/e 250.1209, $C_{14}H_{18}O_4$ requires 250.1205.

Methyl 4,5-bis(bromomethyl)cyclohexa-1,4-diene-1-carboxylate (85). Dibromodiene 73, prepared by the DMSO method starting with tetrabromide 82 (14.1 g, 35.3 mmol), and methyl propiolate (3.14 mL, 2.96 g, 35.3 mmol) was dissolved in benzene (40 mL). The mixture was sealed in glass and heated to 70±10°C for three days. Flash chromatography (5% EtOAc/hexanes) yielded 4.22 g (37% based upon 82) of adduct 85 which was recrystallized (ether/hexanes): mp 97-8°C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.93 (br t, J $\approx$ 2.0 Hz, 1 H, $=CH_2$), 4.04 (br d, J $\approx$ 2.0 Hz, 4 H, CH_2Br), 3.76 (s, 3 H, OCH_3), 3.08-3.04 (cmplx mult, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 166.4 (C=O), 134.7, 131.6, 129.7, 127.3, 51.7, 31.1, 30.0 (coincidence), 29.4; IR ($CHCl_3$) 2973m, 2954m, 2869m, 1709s, 1657m, 1435m, 1254-1189m, 1074m, 890s; mass spectrum, m/e 324 (M^+), 295, 293, 291, 245, 243, 164, 133, 131, 105 (base), 91, 77, 59; high-resolution mass spectrum, obsd m/e 323.9184, $C_{10}H_{12}O_2Br_2$ requires 323.9184, obsd m/e 292.8998, $C_9H_9OBr_2$ requires 292.9000.

Methyl 4,5-bis(methylene)cyclohexene-1-carboxylate (86). A soln of dibromide 85 (4.00 g, 12.3 mmol) in anhd ether (125 mL) and anhd THF (20 mL) was added dropwise over 0.3 h to a stirring suspension of freshly prepared Zn/Cu (62 mmol) in anhd ether (125 mL). Stirring was followed by filtration through Celite. The filtrate was washed with satd, aq NH_4Cl (6 x 60 mL) followed by H_2O (60 mL). The soln was dried ($MgSO_4$) and concd to a clear liquid which was flash-chromatographed (2% EtOAc/hexanes) to afford 1.23 g (61%) of the diene as a clear liquid. The boiling pt was not determined due to facile aromatization of the diene. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 6.94 (br s, 1 H, =CH), 5.16 (br s, 2 H, $=CH_2$), 4.85 (br d, J = 1.45 Hz, 1 H, $=CH_2$), 4.80 (br d, J = 1.45 Hz, 1 H, $=CH_2$), 3.72 (s, 3 H, $COOCH_3$), 3.16 (br s, 2 H, CH_2), 3.09 (br s, 2 H, CH_2); 75 MHz ^{13}C NMR ($CDCl_3$) δ 166.9 (C=O), 143.4, 142.9, 137.1, 128.9, 110.3, 110.0, 51.6, 33.6, 32.3; IR ($CHCl_3$) 2970m, 2948m, 2868m, 1709s, 1657s, 1637sh, 1436s, 1250-1180s, 1155m, 1074m, 894s cm^{-1}; mass spectrum, m/e 164 (M^+), 149, 133, 105 (base), 91; high-resolution mass spectrum, obsd m/e 164.0832, $C_{10}H_{12}O_2$ requires 164.0837.

1-(4,5-bis(bromomethyl))-cyclohexa-1,4-dienyl(p-methylphenyl)-sulfone (87). A soln of freshly prepared 73 (~3.9 g, ~16 mmol) and (ethynyl)(p-methylphenyl)sulfone (4.10 g, 23.0 mmol) in benzene (20 mL) was heated to 65±5°C for 1.5 days. The resulting black sample was flash chromatographed (10% EtOAc/hexanes) to afford 3.55 g (53%) of a clear liquid adduct. The spectral data were: 60 MHz ^1H NMR ($CDCl_3$) δ 7.73 (d, J = 8 Hz, 2 H, ArH), 7.30 (d, J = 8 Hz, 2 H, ArH), 6.90 (cmplx mult, 1 H, =CH), 3.92 (br s, 4 H, CH_2Br), 2.97 (br s, 4 H, CH_2), 2.41 (br s, 3 H, $ArCH_3$); 75 MHz ^{13}C NMR ($CDCl_3$) δ 144.8, 144.6, 137.1, 135.4, 133.2, 132.1, 129.9, 129.8, 30.89, 29.63, 29.40, 28.04, 27.60; IR (neat) 3070-3035w, 2980m, 2970m, 2932m, 2875m, 1734m, 1646w, 1597m, 1361s, 1317s, 1303s, 1291s, 1190s, 1176s, 1162s, 1143s, 1089s, 1043m, 993s cm^{-1}; mass spectrum, m/e 341, 339 (M^+-Br), 139 (base), 104, 91, 77, 65, 51, mass spectrum (Methane CI), m/e 449 ($M^+ + C_2H_5$), 423, 421, 419 (M^+ + H), 341, 339, 261 (base), 185, 157, 139, 121, 105, 83, 73; high-resolution mass spectrum (M^+ -Br), obsd m/e 339.0056, $C_{15}H_{16}O_2SBr$ requires 339.0054.

1-(4,5-bis(methylene)-cyclohexenyl)(p-methylphenyl)sulfone (**88**). To a Zn/Cu (16.7 mmol) slurry in anhd ether (50 mL) was added a soln of dibromide **87** (1.40 g, 3.33 mmol) in anhd ether (50 mL). The mixture was stirred for 1.5 h and filtered through Celite. The filtrate was washed with satd, aq NH_4Cl (3 x 100 mL) until no further $ZnBr_2$ ppt was obsd. The ethereal soln was dried ($MgSO_4$) and concd to a pale yellow liquid which was flash-chromatographed (5% EtOAc/hexanes) to afford 702 mg (81%) of the diene. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 7.77 (d, J = 7.7 Hz, 2 H, ArH), 7.33 (d, J = 7.7 Hz, 2 H, ArH), 7.01 (cmplx mult, 1 H, =CH), 5.18 (br d, J = 1.5 Hz, 2 H, $=CH_2$), 4.83 (d of d, J_a = 1.5 Hz, J_b = 6.5 Hz, 2 H, $=CH_2$), 3.17 (br s, 2 H, CH_2), 3.07 (br s, 2 H, CH_2), 2.44 (s, 3 H, $ArCH_3$); 22 MHz ^{13}C NMR ($CDCl_3$) δ 144.3, 141.5, 138.7, 136.2, 135.6, 129.8, 128.1, 111.8, 111.4, 104.3, 33.18, 30.80, 21.53; IR (neat) 3101w, 3080w, 3046w, 2966m, 2938m, 2880w, 1652m, 1640w, 1603s, 1498m, 1454m (broad), 1367s (broad), 1322s, 1306s, 1294sh, 1196-1171s, 1151s, 1093s, 1000s, 905s cm^{-1}; mass spectrum, m/e 260 (M^+), 186, 155, 139, 91 (base), 73; high-resolution mass spectrum, obsd m/e 260.0878, $C_{15}H_{16}O_2S$ requires 260.0871.

cis-6,7-Bis(bromomethyl)-5,8,9,10-tetrahydronaphtho-1,4-quinone (**89**).[69] Diene **73** was generated from tetrabromide **82** (21.38 g, 53.49 mmol) as previously discussed (*vide supra*). Solvent was removed at reduced pressure and the crude diene was dissolved in Ac_2O (21 mL). To this soln, freshly sublimed p-benzoquinone (5.780 g, 53.49 mmol) was added in two equal portions, separated by 7 h. The orange soln was stirred in the absence of light for 4 days by which time much white solid had precipitated. It should be noted that more dilute solns give little or no adduct. Crystallization at -20°C from the reaction mixture afforded 5.286 g (28% overall yield from 82) of white solid adduct: mp 133-4°C (lit mp[69] (dec) 154-6°C). In contradiction to a reported procedure, it was found that attempted recrystallization (hot benzene or EtOAc/hexanes) lead to decomposition of the adduct. The ^1H NMR was identical to that previously reported. Additional spectral data were: 22 MHz ^{13}C NMR ($CDCl_3$) δ 198.5 (C=O), 139.3, 131.5, 46.1, 30.2, 27.8; IR (nujol) 1693sh, 1673s, 1656sh, 1600m, 1435m, 1376w, 1365w, 1344w, 1270m, 1257w, 1218m, 1191m, 1145w, 1089m, 862w cm^{-1}; mass spectrum, m/e 350, 348 (M^+), 346, 269, 267, 188 (base), 173, 160, 145, 91, 81, 77; high-resolution mass spectrum, obsd m/e 347.9186, $C_{12}H_{12}O_2{}^{79}Br^{81}Br$ requires 347.9184.

<u>6,7-bis(methylene)-1,4-bis(oxo)-1,2,3,4,5,6,7,8,9,10-decahydronaphthalene (91)</u>. A soln of dibromide **89** (369 mg, 1.06 mmol) in anhd ether (10 mL) and anhd THF (20 mL) was added dropwise over 1 h to a vigorously stirring slurry of freshly prepared Zn/Cu (5.3 mmol) in anhd ether (25 mL). The soln was stirred for 24 h prior to filtration through Celite. The water-white filtrate was washed with satd, aq NH_4Cl (10 mL), H_2O (10 mL), then dried ($MgSO_4$). The crude, undesired,

reduced product **91** was obtained as a white solid upon conc of the ethereal soln. Recrystallization (hexanes) gave 167 mg (83%) of **91**: mp 92°C; 60 MHz ^1H NMR ($CDCl_3$) δ 5.03 (br d, J ~ 2 Hz, 2 H, $=CH_2$), 4.82 (br d, J ~ 2 Hz, 2 H, $=CH_2$), 3.27 (cmplx mult, 10 H, CH CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 208.4 (C=O), 115.0, 111.3, 47.9, 36.4, 33.5; IR (CCl_4) 2980w, 2960w, 2900w, 2850w, 1714s, 1425m, 1241m, 895m cm^{-1}; mass spectrum, m/e (rel intensity) 192 (1.17, M + 2), 191 (13.08, M + 1), 190 (base, M^+), 145 (11.2), 131 (36.7), 130 (85.2), 129 (23.0), 91 (19.6), 85 (16.3), M + 2, M + 1 isotope ratio for $C_{12}H_{14}O_2$ requires 1.21, 13.27.

<u>6,7-bis(bromomethyl)-5,8-dihydronaphtho-1,4-hydroquinone (**96**)</u>. Enedione, **89** (1.34 g, 3.86 mmol) was dissolved in anhd THF (150 mL). p-Toluenesulfonic acid (66.4 mg, 386 μmol) was added, and the golden soln was stirred overnight. The reaction mixture was dumped into satd, aq $NaHCO_3$ (150 mL) which was extracted with $CHCl_3$ (4 x 200 mL). The extracts were combined, dried (K_2CO_3), and concd to a brown solid. Flash chromatography (50% EtOAc/hexanes) yielded 1.11 g (83%) of a pale brown-white solid. Recrystallization from THF provided a pure white sample: mp 158°C (dec); 300 MHz ^1H NMR (acetone-d_6) δ 7.79 (s, 2 H, OH), 6.56 (s, 2 H, Ar-H), 4.39 (s, 4 H, CH_2Br), 3.47 (s, 4 H, CH_2); 75 MHz ^{13}C NMR (acetone-d_6 and DMSO-d_6) 147.7, 131.9, 121.3, 112.9, 32.57, 29.21; IR (nujol) 3470m (sharp), 3392m (broad), 1423w, 1297m, 1279m, 1258m, 1212w, 1183w, 1142w, 1033m, 972m, 958w, 814m, 738m cm^{-1}; mass spectrum, obsd m/e 350, 348 (M^+), 346, 331, 281, 265,

231, 188, 187 (base), 173, 145, 115, 82, 80, 69, 51; high-resolution mass spectrum, obsd m/e 345.9202, $C_{12}H_{12}O_2{}^{79}Br_2$ requires 345.9204.

6,7-bis(methylene)-5,8-dihydronaphtho-1,4-hydroquinone (97). To a suspension of Zn/Cu (115 mmol) in anhd THF (150 mL) was added, during 25 min, a soln of dibromohydroquinone **96** (8.010 g, 23.02 mmol) in anhd THF (100 mL). Stirring was maintained for 5 h and zinc residue was removed by filtration through Celite. The filtrate was dumped into EtOAc (400 mL) and washed with satd, aq NH_4Cl (2 x 100 mL) followed by H_2O (100 mL). The pale yellow EtOAc soln was dried ($MgSO_4$) and concd to a pale white solid. Flash chromatography (45% EtOAc/hexanes) afforded 3.691 g (85%) of diene as pure white needles: mp 173-4°C; 300 MHz ^1H NMR (acetone-d_6) δ 7.64 (s, 2 H, OH), 6.54 (s, 2 H, ArH), 5.30 (d, J = 1.4 Hz, 2 H, =CH), 4.93 (d, J = 1.4 Hz, 2 H, =CH), 3.52 (s, 4 H, CH_2); 75 MHz ^{13}C NMR (acetone-d_6) δ 147.6, 145.4, 124.9, 113.5, 108.6, 32.23; IR (nujol) 3199m (broad), 1490m, 1420m, 1395w, 1284m, 1247m, 1165w, 1013w, 885m, 803w, 742w cm^{-1}; mass spectrum, m/e 188 (M^+ and base), 173, 145, 115, 110, 91, 76, 71, 70; high-resolution mass spectrum, obsd m/e 188.0839, $C_{12}H_{12}O_2$ requires 188.0837.

6,7-bis(methylene)-5,7,8-tetrahydronaphtho-1,4-quinone (98). This preparation was successful in a variety of solvents. The general procedure follows: Under Ar, hydroquinone **97** (2.3 mg, 12 μmol) was added to Ar degassed $CDCl_3$ (1.5 mL). The mixture was cooled to 0°C and all did not dissolve. Silver(I)oxide (Ag_2O, 5.6 mg, 24 μmol) was added and the slurry was stirred vigorously in the dark for 10 min. Rapid filtration through Celite produced a yellow soln of the quinone which was immediately subjected to NMR analysis. Samples for IR and UV analyses were prepared in an analogous fashion. The spectral data were: 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.73 (s, 2 H, quinone H), 5.30 (s, 2 H, $=CH_2$), 4.98 (s, 2 H, $=CH_2$), 3.67 (s, 4 H, CH_2); 75 MHz ^{13}C NMR ($CDCl_3$) 186.5 (C=O), 141.0, 140.3, 136.3, 111.7, 30.4; IR ($CHCl_3$) 1676m, 1656s, 1632sh, 1603m, 1526m (br), 1476m, 1421s (br), 1212s (br), 1038m (br), 920s cm^{-1}; IR (CCL_4) 2954m, 2892w, 1681m, 1656s, 1638sh, 1601w, 1423w, 1246m, 902s, 856s; UV $\lambda_{max}^{CH_3CN}$ 247 (ε >19600), 338 (ε >1540), 412 (ε >8180).

Cycloadduct (99) To a soln of 1,3-cyclopentadiene (4 mL) and dienehydroquinone 97 (108 mg, 574 µmol) in benzene (15 mL), Ag_2O (226 mg, 1.15 mmol) was added. The mixture was stirred in the absence of light for 2 h. The silver residue was removed by filtration through sintered glass and the filtrate was flash-chromatographed (15% EtOAc/hexanes) to provide 77 mg of pure liquid cycloadduct (53%) and a slightly impure sample (9 mg). The spectral data were: 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.01 (s, 2 H, =CH), 5.27 (d, J = 1.2 Hz, 2 H, $=CH_2$), 4.93 (d, J = 1.2 Hz, 2 H, $=CH_2$), 3.54 (br s, 2 H, CH), 3.28 (br s, 2 H, CH), 3.24 (br s, 4 H, CH_2), 1.49 (cmplx mult, 2 H, CH_2, 1-bridge); 22 MHz ^{13}C NMR ($CDCl_3$) δ 197.6 (C=O), 146.6, 141.2, 135.2, 110.9, 48.8 (coincidence), 48.4, 31.0; IR (film) 3000m, 2935m, 2863m, 1656s (broad), 1630 (s), 1410m, 1371m, 1335w, 1301m, 1261s, 1237m, 1124w, 1080w, 1018w, 906sh, 887m, 697m cm^{-1}.

Attempted reduction of open dimer **100** with $Na_2S_2O_4$ Ambiphile **98** was generated in $CHCl_3$ (8 mL) from hydroquinone **97** (18 mg, 96 μmol). Twenty min after oxidation, a soln of $Na_2S_2O_4$ (133 mg, 765 μmol), and $NaHCO_3$ (48 mg, 573 μmol) in H_2O (4 mL) was added and the two-phase mixture was vigorously stirred. Within 0.5 h, the yellow quinone color had faded. The $CHCl_3$ layer was then decanted and the aq layer was extracted with $CHCl_3$ (4 x 20 mL). The $CHCl_3$ solns were combined, dried (K_2CO_3) and concd under reduced pressure to afford 15.5 mg (>85%) of pure hydroquinone **97** after flash-chromatography (25% EtOAc/hexanes). Next, another solution of **98** was treated with $Na_2S_2O_4$/$NaHCO_3$, 4.5 h after oxidation of **97**. Workup of the mixture, as above, followed by flash chromatography (50% EtOAc/hexanes or EtOAc) gave only 20% of hydroquinone **97** and no reduced dimer **102**. Further reduction attempts at 8, 12, and 24 h after oxidation of **97** failed to give either hydroquinone **97** or reduced dimer. Similar results were obtained when **97** was oxidized in benzene soln.

Attempted trapping of open dimer **100** with N-phenyltriazolinedione PTAD). Hydroquinone **97** (109 mg, 579 μmol) was oxidized in $CHCl_3$ (40 mL) as before. After 4 h, the mixture was titrated with a soln of PTAD (100 mg, 579 μmol) in $CHCl_3$ (0.5 mL) until the quinone soln retained the faint pink color of PTAD. ^{1}H NMR analysis of the product mixture revealed resonances at δ 6.79 and 6.74 in a 10:1 ratio (presumably quinone H), and no characteristic diene resonances, or resonances attributed to the closed dimer **101**. TLC analysis showed that all material remained at the origin even when eluted with 10% MeOH/EtOAc. All attempts at crystallizing any product from $CHCl_3$ or MeOH solns failed.

In a second trapping attempt, a sample of **97** (1.7 mg, 9.0 μmol) was oxidized as usual. After storage at -20°C for 1 week, ^1H NMR ($CDCl_3$) analysis revealed one quinone resonance at δ 6.79 ppm, diene resonances at δ 5.30 and 4.95 ppm as well as resonances attributed to the closed dimer **101**. The soln was titrated as before and after this ^1H NMR analysis showed only disappearance of the diene resonances and appearance of an aromatic multiplet. The quinone resonance persisted.

Presumed closed dimer of **98**, (**101**). A sample of **98** was prepared in $CDCl_3$ as before (*vide infra*). The sample remained at amb temp for 20 h after which ^1H NMR analysis showed that the closed form of the dimer predominated in soln. Evacuation of the solvent at reduced pressure gave a yellow-white solid, most of which would not dissolve upon immediate reintroduction of an identical amount of solvent. The solid showed no birefringence when obsd through crossed polarizers and resisted melting up to 375°C. This solid was not further investigated. Crude mass spectral data of the dimeric form of **98** were obtained by removing the solvent at reduced pressure from a sample of **101** and quickly introducing the solid mixture into the probe of the mass spectrometer. One volatile component passed into the ionization chamber and from that, a peak at m/e 372 (1% of base) was obsd. IR and UV analyses were performed on analogous samples prepared in $CHCl_3$ and dioxane respectively. Additional spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 3.29 (br d, 4 H, CH), 2.95 (br d, 8 H, CH_2), 2.43 (br d, 4 H, CH_2), 2.12 (br d, 4 H, CH_2); 75 MHz ^{13}C NMR ($CDCl_3$) δ 198.8 (C=O), 142.0, 122.4, 46.5, 29.8, 28.5; IR ($CDCl_3$) 1685sh, 1676s, 1630w.

Diethyl 5,8-dihydroxy-1,4,9,10-tetrahydroanthracene-2,3-dicarboxylate (**106**). A soln of diene **97** (997 mg, 5.30 mmol) and DEAD (860 μL, 901 mg, 5.30 mmol) in benzene (80 mL) and anhd THF (45 mL) was warmed to 65±5°C for 20 h. Evacuation of solvent at reduced pressure followed by flash chromatography (40% EtOAc/hexanes) gave 1.85 g (97%) of solid adduct: mp 170-1.5°C; 300 MHz ($CDCl_3$ and DMSO-d_6) δ 6.55 (s, 2 H, ArH), 4.25 (q, J = 7.13 Hz, 4 H, CH_2O), 3.19 (s, 4 H, CH_2), 3.02 (s 4 H, CH_2), 1.32 (t, J = 7.13 Hz, 6 H, OCH_3); 22 MHz ^{13}C NMR ($CDCl_3$ and DMSO-d_6) δ 167.8 (C=O), 146.8, 132.5, 121.9, 121.1, 112.2, 60.9, 32.3, 28.7, 13.9; IR (photoacoustic) 3505s, 3441s, 2986m, 2943w, 1732sh, 1709s, 1655m, 1477s, 1304s, 1234s, 1180s, 1096m, 1022m, 814m, 764m; mass spectrum, m/e 358 (M^+), 312, 279, 266, 253, 235, 211 (base), 165, 152, 127, 115, 55; high resolution mass spectrum, obsd m/e 358.1426, $C_{20}H_{22}O_6$ requires 358.1416.

1,4-Bis(methoxy)-6,7-bis(methylene)-5,6,7,8-tetrahydronaphthalene (**109**). To a soln of hydroquinone **98** (86 mg, 0.46 mmol) and MeI

(85 μL, 190 mg, 1.4 mmol) in acetone (5 mL), K_2CO_3 (129 mg, 932 μmol) was added. The slurry was refluxed for 2 days. Additional MeI (2 x 85 μL) was added at 20 and 30 h. Solvent was removed at reduced pressure and the resulting orange liquid was flash chromatographed (2% EtOAc/hexanes) to give 82 mg (83%) of clear liquid anisole **109**. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 6.64 (s, 2 H, ArH), 5.29 (d, J = 1.28 Hz, 2 H, =CH), 4.94 (d, J = 1.28 Hz, 2 H, =CH), 3.77 (s, 6 H, OCH_3), 3.55 (s, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 150.5, 143.9, 126.4, 108.8, 107.9, 55.9, 31.3; IR (CCl_4) 3090w, 3000w, 2953sh, 2940w, 2905w, 2835m, 1636w, 1603w, 1484s, 1464m, 1438m, 1292m, 1252s, 1160m, 1084s, 886m, 710m cm^{-1}; UV $\lambda_{max}^{pentane}$ 219sh (ε 32000), 242sh (ε 5300), 286 (ε 3500); mass spectrum, m/e 216 (M^+ and base), 201, 185, 170, 158, 141, 128, 115, 103, 91, 77; high-resolution mass spectrum, obsd m/e 216.1150, $C_{14}H_{16}O_2$ requires 216.1150, obsd m/e 217.1184, $^{13}C_1{}^{12}C_{13}H_{16}O_2$ requires 217.1184.

Diethyl 5,8-bis(methoxy)-1,4,9,10-tetrahydroanthracene-2,3-dicarboxylate (110). A soln of diene **109** (683 mg, 3.16 mmol), DEAD (506 μL, 537 mg, 3.16 mmol), and benzene (30 mL) was heated to 50±5°C and stirred for 20 h. Evacuation of solvents at reduced pressure followed by recrystallization (EtOAc/hexanes) gave 867 mg (71%) of white needles: mp 162.5-3°C; 300 MHz ^1H NMR ($CDCl_3$) δ 6.65 (s, 2 H, ArH), 4.25 (q, J = 7.1 Hz, 4 H, OCH_2CH_3), 3.79 (s, 6 H, OCH_3), 3.18 (br s, 4 H, CH_2), 3.02 (br s, 4 H, CH_2), 1.32 (t, J = 7.1 Hz, 6 H, OCH_2CH_3); 22 MHz ^{13}C NMR ($CDCl_3$) δ 168.0 (C=O), 150.9, 132.7, 124.1, 121.1, 107.0, 61.1, 55.7, 32.4, 28.7, 14.1; IR ($CHCl_3$) 3002m, 2993m, 2950w, 1739sh, 1735sh, 1725sh, 1713s, 1661m, 1483s, 1263s, 1123s, 1066s, 1030m, 947w, 865w, 707w cm^{-1}; UV $\lambda_{max}^{CH_3CN}$ 224 (ε 14000), 284 (ε 3500), 316 (ε 25); mass spectrum, m/e 386 (M^+ and base), 341, 310, 293, 283, 239, 188, 165, 152, 131, 115; high-resolution mass spectrum, obsd m/e 386.1732, $C_{22}H_{26}O_6$ requires 386.1730.

2,3-*Bis*(hydroxymethyl)-5,8-bis(methoxy)-1,4,9,10-tetrahydroanthracene (111). A soln of diester **110** (535 mg, 1.38 mmol) in anhd THF (30 mL) was added during 0.5 h to a 0°C slurry of $LiAlH_4$ (105 mg, 2.77 mmol) in anhd ether (35 mL). The mixture was warmed to amb temp and stirred for 8 h. The slurry was quenched at 0°C with 1N, aq K_2CO_3 (2.8 mL), stirred at amb temp for 3 h, and filtered to afford a water-white filtrate. Evacuation of solvent followed by recrystallization (EtOAc/pentanes) yielded 359 mg (86%) of white needles: mp 172-4°C; 300 MHz ^1H NMR (acetone-d_6) δ 6.70 (s, 2 H, ArH), 4.16 (br s, 4 H, CH_2O), 3.77 (s, 6 H, OCH_3), 3.11 (br s, 4 H, CH_2), 2.82 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR (acetone-d_6) δ 151.9, 132.1, 125.1, 123.1, 107.8, 61.6, 55.8, 34.8, 29.5,; IR (KBr) 3600-3100, 3004w, 2945m, 2875s, 2838s, 2812s, 1669w, 1603m, 1482s, 1434m, 1350m, 1253s, 1128m, 1080sh, 1064s, 988m (br), 944m, 784m, 712m, cm^{-1}; mass spectrum, m/e 302 (M^+ and base), 284, 282, 269, 255, 253, 241, 239, 223, 201, 188, 165, 152, 105, 91, 55; high-resolution mass spectrum, obsd m/e 302.1524, $C_{18}H_{22}O_4$ requires 302.1518.

1,4-bis(trimethylsiloxy)-6,7-bis(methylene)-5,6,7,8-tetrahydronaphthalene (114). A soln of hydroquinone 97 (605 mg, 3.21 mmol), TMSCl (1.23 mL, 1.05 g, 9.64 mmol), Et_3N (1.34 mL, 976 mg, 9.64 mmol), and THF (45 mL) was stirred for 8 h. The mixture was poured into 5% aq $NaHCO_3$ (50 mL) and the aq layer was extracted with ether (4 x 50 mL). The combined ether solns were dried ($MgSO_4$) and concd to a yellow liquid. Flash chromatography (5% EtOAc/hexanes) gave 965 mg (91%) of a water-white liquid. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 6.52 (s, 2 H, ArH), 5.32 (d, J = 1.4 Hz, 2 H, $=CH_2$), 4.93 (d, J = 1.4 Hz, 2 H, $=CH_2$), 3.46 (br s, 4 H, CH_2); 22 MHz ^{13}C NMR ($CDCl_3$) δ 146.1, 143.6, 128.6, 116.6, 108.3, 32.3, 0.46; IR (neat) 3095w, 2970s, 2907w, 2828w, 1639w, 1599w, 1474s, 1290s, 1259sh, 1251s, 1159m, 1023s, 938m, 875s, 840s, 750m cm^{-1}; UV $\lambda_{max}^{pentanes}$ 245 (ε >10000), 282 (ε 2500), 318sh (ε 70); mass spectrum, m/e 332 (M^+ and base), 317, 302, 243, 115, 73, 51; high-resolution mass spectrum, obsd m/e 332.1631 $C_{18}H_{28}Si_2O_2$ requires 332.1628.

Diethyl 5,8-bis(trimethylsiloxy)-1,4,9,10-tetrahydroanthracene-2,3-dicarboxylate (115). A soln of diene 114 (900 mg, 2.71 mmol) and DEAD (443μL, 460 mg, 2.71 mmol) in benzene (80 mL) was refluxed for 20 h. Removal of solvent at reduced pressure followed by recrystallization (hexanes) afforded 1.198 g (88%) of white needles: mp 147-7.5°C; 300 MHz ^1H NMR ($CDCl_3$) δ 6.52 (s, 2 H, ArH), 4.26 (q, J = 7.1 Hz, 4 H, OCH_2CH_3), 3.11 (br s, 4 H, CH_2), 3.03 (br s, 4 H, CH_2), 1.33 (t, J = 1.7 Hz, 6 H, OCH_2CH_3), 0.25 (s, 18 H, $OSiCH_3$); 22 MHz ^{13}C

NMR ($CDCl_3$) δ 168.0 (C=O), 146.8, 132.7, 126.4, 121.5, 115.6, 61.1, 32.6, 29.6, 14.1, 0.52; IR (CCl_4) 2990w, 2970w, 1739sh, 1726m, 1662w, 1474s, 1262s, 1252s, 1120m, 1065w, 1032w, 1002m, 877s, 843m cm^{-1}; mass spectrum, m/e 502(M^+), 457, 427, 335, 304, 282, 214, 73, 59; high-resolution mass spectrum, obsd m/e 502.2190 $C_{26}H_{38}O_6Si_2$ requires 502.2207.

References Cited

1. Hoffman, R.; Imamura, A.; Hehre, W. J. *J. Amer. Chem. Soc.* **1968**, *90*, 1499.

2. Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; John Wiley & Sons: New York, 1977.

3. a) Hoffman, R.; Heilbronner, E.; Gleiter, R. *J. Amer. Chem. Soc.* **1970**, *92*, 706. b) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 173. c) von Neissen, W.; Dierksen, G. H. F. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 351.

4. a) Martin, H. D.; Mayer, B. *Angew. Chem. Int. Ed. Eng.* **1983**, *22*, 283. b) Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1. c) Gleiter, R. *Angew. Chem. Int. Ed. Eng.* **1974**, *13*, 696.

5. a) Trayhnam, J. G. *J. Org. Chem.* **1963**, *28*, 1094. b) Ortiz de Montellano, B. R.; Loving, B. A.; Shields, T. C.; Gardner, P. D. *J. Amer. Chem. Soc.* **1967**, *89*, 3365.

6. Bloomquist, A. T.; Meinwald, Y. C. *J. Amer. Chem. Soc.* **1959**, *81*, 667.

7. Sasaki, T.; Eguchi, S.; Sugimoto, M.; Hibi, F. *J. Org. Chem.* **1972**, *37*, 2317.

8. Wilcox, C. F.; Winstein, S.; McMillan, W. G. *J. Amer. Chem. Soc.* **1960**, *82*, 5450.

9. a) Heilbronner, E.; Martin, H. D. *Helv. Chim. Acta* **1972**, *55*, 1490. b) Hoffman, R. W.; Schüttler, R.; Schäfer, W.; Schweig, A. *Angew. Chem. Int. Ed. Eng.* **1972**, *11*, 512.

10. Heilbronner, E. *Isr. J. Chem.* **1972**, *10*, 143.

11. Goldstein, M. J.; Natowsky, S.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1973**, *56*, 294.

12. Kibel, M. H.; Livett, M. K.; Nyberg, G. L. *J. Electron Spectrosc. Relat. Phenom.* **1978**, *14*, 155.

13. Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Amer. Chem. Soc.* **1984**, *106*, 2194.

14. Wiberg, K. B.; Adams, R. D.; Okarma, P. J.; Matturro, M. G.; Segmuller, B. *J. Amer. Chem. Soc.* **1984**, *106*, 2200.

15. Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, N.Y., 1960; p 262.

16. Honegger, E.; Heilbronner, E.; Wiberg, K. B. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *31*, 369.

17. Batich, C.; Bischof, P.; Heilbronner, E. *J. Electron Spectrosc. Relat. Phenom.* **1972/73**, *1*, 333.

18. Kovac, B.; Mohraz, M. Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Amer. Chem. Soc.* **1980**, *102*, 4314.

19. a) Gray, R.; Boekelheide, V. *J. Amer. Chem. Soc.* **1979**, *101*, 2128. b) Gray, R.; Boekelheide, V. *Angew. Chem. Int. Ed. Eng.* **1975**, *14*, 107.

20. Hanson, A. W. *Acta Crystallogr., Sect. B* **1977**, *33*, 2003.

21. Heilbronner, E.; Broglie, F.; Vogel, E. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 227.

22. Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 937.

23. Haselbach, E.; Neuhaus, L.; Johnson, R. P.; Houk, K.; Paddon-Row, M. N. *Helv. Chim. Acta* **1982**, *65*, 1743.

24. Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Amer. Chem. Soc.* **1974**, *96*, 4342.

25. Roth, W. R.; Humbert, H.; Wegener, G.; Erker, G.; Exner, H. D. *Chem. Ber.* **1975**, *108*, 1655.

26. a) Cupas, C. A.; Hodakowski, L. *J. Amer. Chem. Soc.* **1974**, *96*, 4668. b) Harman, D. P. G.; Taylor, G. F. *Tetrahedron Lett.* **1975**, 155. c) Tobler, H.; Klaus, R. O.; Ganter, C. *Helv. Chim. Acta* **1975**, *58*, 1455.

27. Engler, E. M.; Andose, J. D.; von R. Schleyer, P. *J. Amer. Chem. Soc.* **1973**, *95*, 8005.

28. Zimmerman, H. E.; "Quantum Mechanics for Organic Chemists"; Academic Press: New York, 1975.

29. Paquette, L. A. *Angew. Chem. Int. Ed. Eng.* **1978**, *17*, 106.

30. Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397.

31. Dupuis, M.; Spangler, D.; Wendoloski, J. J.; "NRCC Software catalog 1, Program No. QG01 (GAMESS), Lawrence Berkeley Laboratory, University of California: Berkeley, Calif., 1980.

32. a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Amer. Chem. Soc.* **1980**, *102*, 939.

33. Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; von R. Schleyer, P.; Pople, J. A.; Binkley, J. S. *J. Amer. Chem. Soc.* **1978**, *100*, 1210.

34. a) von Walter, R.; Neidhardt, R. *Liebigs Ann. Chem.* **1970**, *739*, 155. b) von Franz Wille, K. D.; Horst, K. *Liebigs Ann. Chem.* **1955**, *591*, 177.

35. Schubert, W. M.; Liddicoet, H.; Lanka, W. A. *J. Amer. Chem. Soc.* **1954**, *76*, 1929.

36. Middlemas, E. D.; Quin, L. D. *J. Org. Chem.* **1979**, *44*, 2587.

37. Bailey, W. J.; Rosenberg, J. *J. Amer. Chem. Soc.* **1955**, *77*, 73, 75, 1163.

38. Blomquist, A. T.; Verdol, J. A. *J. Amer. Chem. Soc.* **1955**, *77*, 1806.

39. a) Huntress, E. H.; Lesslie, T. E.; Bornstein, J. *Org. Synth. Coll. Vol. IV* **1963**, 329. b) Abbott, T. W.; Arnold, R. T.; Thompson, R. B. *Org. Synth. Coll. Vol. II* **1943**, 10. c) Rhinesmith, H. S. *Org. Synth. Coll. Vol. II* **1943**, 177.

40. Gaoni, Y.; Schoef, N. *Bull. Soc. Chim. Fr.* **1977**, 485.

41. Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. J. *J. Org. Chem.* **1979**, *44*, 1247.

42. Cope, A. C.; Ciganek, E. *Org. Synth.* **1959**, *39*, 40.

43. Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 82 and references within.

44. Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.

45. Buckle, D. R.; Morgan, N. J.; Ross, J. W.; Smith, H.; Spicer, B. A. *J. Med. Chem.* **1973**, *16*, 1334.

46. Garrett, J. M.; Fonken, G. J. *Tetrahedron Lett.* **1969**, 191.

47. Cava, M. P.; Shirley, R. L. *J. Amer. Chem. Soc.* **1960**, *82*, 654.

48. Thummel, R. P.; Cravery, W. E.; Nutakol, W. *J. Org. Chem.* 1978, *43*, 2473.

49. Vogel, E.; Roos, O.; Disch, K. H.; *Liebigs Ann. Chem.* 1962, *653*, 55.

50. Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* 1983, *48*, 273.

51. a) Caubere, P. *Acc. Chem. Res.* 1974, *7*, 301. b) Scardiglia, F.; Roberts, J. D. *Tetrahedron* 1957, *13*, 343. c) Montgomery, L. K.; Roberts, J. D. *J. Amer. Chem. Soc.* 1960, *82*, 4750. d) Montgomery, L. K.; Scardiglia, F.; Roberts, J. D. *J. Amer. Chem. Soc.* 1965, *87*, 1917.

52. Schaefer, J. P.; Higgins, J. G.; Shenov, P. K. *Org. Synth.* 1968, *48*, 51.

53. Talma, A. G.; Goorhuis, J. G. M.; Kellogg, R. M. *J. Org. Chem.* 1980, *45*, 2544.

54. McMurray, J. E.; Fleming, M. P. *J. Org. Chem.* 1975, *40*, 2555.

55. a) Calo, V.; Logez, L.; Mincozzi, A.; Pesce, G. *Synthesis* 1976, 200. b) Kochi, J. K; Singleton, D. M.; Andrews, L. J. *Tetrahedron* 1968, *24*, 3503. c) Denis, J. N.; Magnane, R.; van Ecnoo, M.; Krief, A. *Nouv. J. Chim.* 1979, *3*, 705.

56. DeLucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* 1984, *49*, 596.

57. Braude, E. A.; Timmons, C. J. *J. Chem. Soc.* 1950, 2000, 2007, 2014. Braude, E. A.; Timmons, C. J. *J. Chem. Soc.* 1951, 2078.

58. Chládek, S.; Smrt, J. *Chem. Ind.* 1964, 171.

59. Hamon, D. P. G.; Spurr, P. R. *Synthesis* 1981, 873.

60. Blomquist, A. T.; Verdol, J. A. *J. Amer. Chem. Soc.* 1956, *78*, 109.

61. Borden, W. T.; Reich, I. L.; Sharpe, L. A.; Weinberg, R. B.; Reich, H. J. *J. Org. Chem.* 1975, *40*, 2438.

62. Denis, J. M.; Niamayoua, R.; Vata, M; Lablache-Combier, A. *Tetrahedron Lett.* 1980, 515.

63. van Stratten, J. W.; van Norden, J. J.; van Schaik, T. A. M.; Franke, G. Th.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* 1978, *97*, 105.

64. McDonald, R. N.; Reitz, R. R. *J. Org. Chem.* **1972**, *37*, 2418.

65. Trost, B. M.; Shimizo, M. *J. Amer. Chem. Soc.* **1982**, *104*, 4299.

66. Gaoni, Y. *Tetrahedron Lett.* **1973**, 2361.

67. Sadeh, S.; Gaoni, Y. *Tetrahedron Lett.* **1973**, 2365.

68. a) Gaoni, Y. *Tetrahedron Lett.* **1973**, 2361. b) Gaoni, Y.; Sadeh, S. *J. Org. Chem.* **1980**, *45*, 870.

69. Butler, G. B.; Ottenbrite, R. M. *Tetrahedron Lett.* **1967**, 48/3.

70. a) Krug, R. C.; Yen, T. F. *J. Org. Chem.* **1956**, *21*, 1082. b) Frank, R. L.; Seven, R. P. *Org. Synth. Coll. Vol. III* **1955**, 499.

71. a) LeQuesne, P. W.; Reynolds, M. A.; Beda, S. E. *J. Org. Chem.* **1975**, *40*, 142. b)Cope, A. C.; Kagan, F. *J. Amer. Chem. Soc.* **1958**, *80*, 5499.

72. a) Steglich, W.; Wegmann, H. *Synthesis* **1980**, 481. b) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organometal. Chem. Syn.* **1971**, *1*, 145. c) Parham, W. E.; Stright, P. L. *J. Amer. Chem. Soc.* **1956**, *78*, 4783.

73. a) Inukai, T.; Kasai, M. *J. Org. Chem.* **1965**, *30*, 3567. b) Fray, G. I.; Robinson, R. *J. Amer. Chem. Soc.* **1961**, *83*, 249. c) Das, J.; Valenta, Z.; Liu, H.-J.; Ngooi, T. K. *Can. J. Chem.* **1984**, *62*, 481. d) Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1983**, 657. e) Fringvelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802. f) Fringvelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056. g) Fringvelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802. h) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801. i) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4267. j) Kakushima, M.; Allain, L.; Dickinson, R. A.; White, P. S.; Valenta, Z. *Can. J. Chem.* **1979**, *57*, 3354. k) Kishi, Y. *Tetrahedron Lett.* **1970**, 5127. l) Kojima, T.; Inukai, T. *J. Org. Chem.* **1970**, *35*, 1342. m) Houk, K. N. *J. Amer. Chem. Soc.* **1973**, *95*, 4092. n) Houk, K. N.; Strozier, R. W. *J. Amer. Chem. Soc.* **1973**, *95*, 4094.

74. Kraus, G. A.; Taschner, M. J. *J. Org. Chem.* **1980**, *45*, 1174.

75. a) Camps, F.; Coll, J.; Riba, M. *J. Chem. Soc., Chem. Commun.* **1979**, 1080. b) de Vries, J. G.; van Bergen, T. J.; Kellogg, R. M. *Synthesis* **1977**, 246.

76. Cookson, R. C.; Gupte, S. S. ; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.

77. Vyas, G. N.; Shah, N. M. *Org. Synth. Coll. Vol. IV* **1963**, 836.

78. Corey, E. J.; Snider, B. B. *J. Amer. Chem. Soc.* **1972**, *94*, 2549.

79. Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

80. Sweeley, C. C.; Bentley, R.; Makita, M.; Wells, W. W. *J. Amer. Chem. Soc.* **1963**, *85*, 2497.

81. Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.

82. Snyder, C. D.; Rapoport, H. *J. Amer. Chem. Soc.* **1972**, *94*, 227.

83. Wittig, G.; Krebs, A.; Pohlke, R. *Angew. Chem.* **1960**, *72*, 324.

84. Gassman, P. G.; Gennick, I. *J. Amer. Chem. Soc.* **1980**, *102*, 6864.

85. a) Suga, K.; Watanabe, S.; Kamma, K. *Can. J. Chem.* **1967**, *45*, 933. b) Robins, P. A.; Walker, J. *J. Chem. Soc.* **1952**, 642. c) Backer, H. J.; van der Bij, J. R. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 561. d) Kergomard, A.; Tardivat, J. C.; Vuillerme, J. P. *Bull. Soc. Chim. Fr.* **1975**, 297.

86. Mandelbaum, A.; Cais, M. *J. Org. Chem.* **1961**, *26*, 2633.

87. a) Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Amer. Chem. Soc.* **1979**, *101*, 770. b) Heilbronner, E.; Kovac, B.; Nutakul, W.; Taggart, A. D.; Thummel, R. P. *J. Org. Chem.* **1981**, *46*, 5279.

88. Doecke, C. W.; Garratt, P. J.; Shahriari-Zavaroh, H.; Zahler, R. *J. Org. Chem.* **1984**, *49*, 1412.

89. a) Heinrich, F. Ph.D. Dissertation, University of Gottingen, 1972. b) Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Amer. Chem. Soc.* **1979**, *101*, 1770.

90. Warren, S. "Designing Organic Syntheses"; John Wiley and Sons: New York, 1978.

91. Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; John Wiley and Sons: New York, 1972.

92. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

93. Carothers, W. H.; Williams, I.; Collins, A. M.; Kirby, J. E. *J. Amer. Chem. Soc.* **1931**, *53*, 4203.

94. Miller, A. E. G.; Biss, J. W.; Schwartzman, L. H. *J. Org. Chem.* **1959**, *24*, 627-30.

95. a) Ĉerný, M.; Màlek, J.; Capka, M.; Chvalovský, V. *Collect. Czeck. Chem. Commun.* **1969**, *34*, 1025. b) Bazant, V.; Ĉapka, M.; Ĉerný, M.; Chvalovsky, V.; Kochloefl, K.; Kraus, M.; Màlek, J. *Tetrahedron Lett.* **1968**, 3303.

PART II. STRUCTURAL LIMITATIONS OF STRAINED CYCLIC OLEFINS

Introduction to Cyclic Allenes

It is well known that incorporation of a single double bond in a hydrocarbon ring is possible for any ring size[1]; cyclopropenes, the smallest cycloalkenes, are generally stable at ambient temperature. Cyclic allenes smaller than nine carbons, though, usually are too reactive to be isolated.[1] Constraints of the small cyclic structure deform the normally linear, perpendicular allene moiety. Two types of deformations are imparted by a small cyclic structure. One is a bending about the central allenic carbon, which weakens the π-bond and introduces s character to the p orbital on the central carbon (Figure 1). Another deformation is a twisting of terminal carbons, which results in strong overlap of the formally orthogonal π systems (Figure 1). These effects, of course, are not separable in simple cyclic allenes and the resulting structure of small ring allenes will be both bent and twisted with respect to linear, perpendicular allene. Bent and twisted olefin moieties are well known in, *e.g.*, bridgehead olefins[1] and on this basis, cyclic allenes are expected to withstand some twisting and bending. Indeed, the smallest isolable cyclic allene, 1,2-cyclononadiene[2] 1 ($n = 9$), has been predicted to be bent by about 10°, and slightly twisted (2-3°).[3] Smaller, transient species should exist with more severe structural distortion.

For very small ring systems, the geometric distortion may become so severe as to force a planar, bent geometry; this is diagramed in

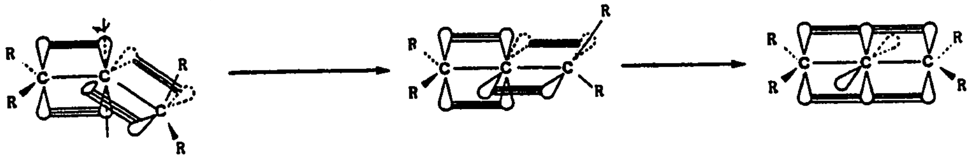
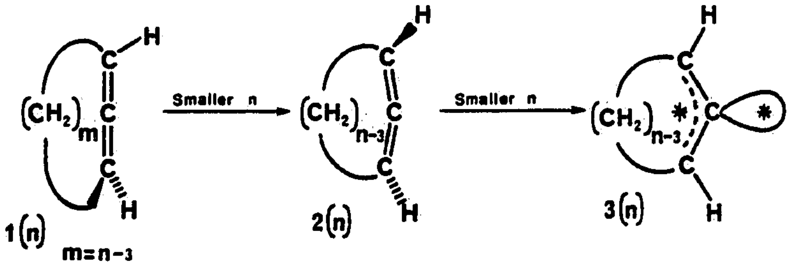


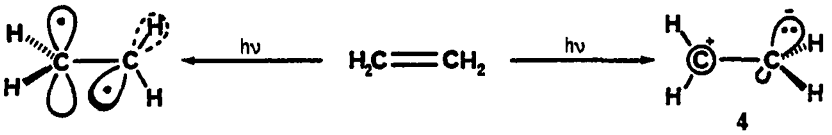
Figure 1. Independent bending and twisting of allenes

equation 1. One asks: what is the limiting size for the chiral, bent equilibrium structure, 2? and, what is the electronic nature of the ground state of the planar allene, 3? Neither of these questions is easily answered; considerable controversy over these structures has arisen, especially for 1,2-cyclohexadiene (*vide infra*).



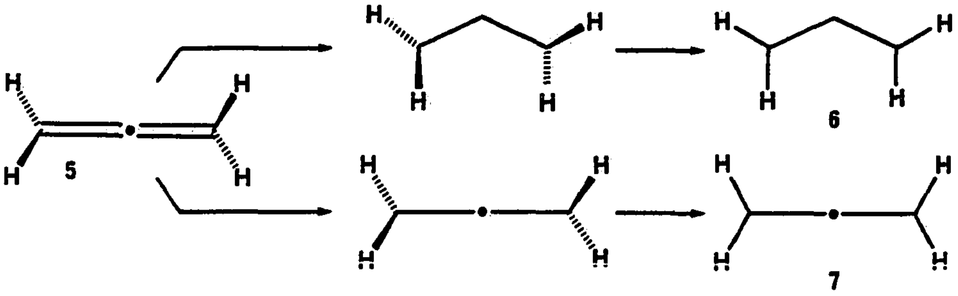
(1)

In order to investigate this phenomenon, it is imperative to understand the electronic nature of planar allene. This can be shown to be an extension of the olefin "sudden polarization" phenomenon, introduced by Salem,[4] to allenes. Salem proposed that twisted (nonvertical) singlet excited states of olefins which invariably correspond to excited state energy minima, should be zwitterionic rather than diradical. This is diagramed for ethylene in equation 2. The resulting zwitterionic excited state olefin, 4, thus has one end pyramidalized and is strongly polarized. Extension of this



(2)

concept to allene, 5, lead Lam and Johnson[5] to the conclusion that two polarized minima 6 and 7 should exist on excited state potential surfaces (equation 3). Roth *et al.*[6a] have suggested that in the ground state, racemization occurs through a planar transition state which is bent because the nonbonding ($2b_{2u}$) p orbital is expected to acquire s character, thus becoming a hybrid. Hence, if this orbital is occupied, the bent C-C-C geometry may be preferred. A bent racemization transition state is supported by *ab initio* calculations of Seeger *et al.*[6b]



(3)

In a small-ring system, the allene will necessarily be bent. Possible low lying electronic states of bent, planar allene (C_{2v}) are diagramed in Figure 2.[5] These arise from various electron populations of the nonbonding MOs, $6a_1$ (sp^2) and $1a_2$ (allyl-like, nonbonding MO). The first two states, denoted 8-Z_1 and 8-Z_2, are zwitterionic species, with opposite polarization. The second two states are singlet and triplet diradicals, denoted 8-^{1}D and 8-^{3}D. State symmetries are given in the figure.

One might initially expect the ground state of planar allene to be zwitterion 8-Z$_1$ and the open shell diradicals 8-^{1}D and 8-^{3}D to be excited states. However, the two nonbonding MOs 6a$_1$ and 1a$_2$ are nearly degenerate, and these energies are predicted to vary slightly with geometry.[5,6] At the one electron level of theory, states derived by various electronic populations of these orbitals would be nearly degenerate. *Ab initio* SCF and MCSCF calculations very clearly give the order 8-^{1}D ($^1A_2$) below 8-Z$_1$ (1^1A_1) with a gap of about 1 eV.[5,6] The simplest explanation for this result is that the closed shell state (Z$_1$) is of higher energy due to one additional intrapair electron repulsion.

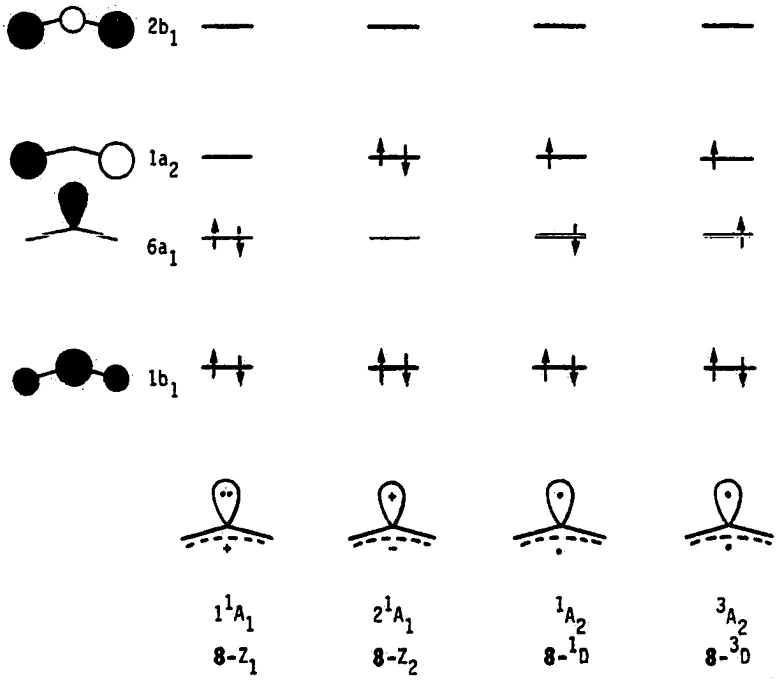


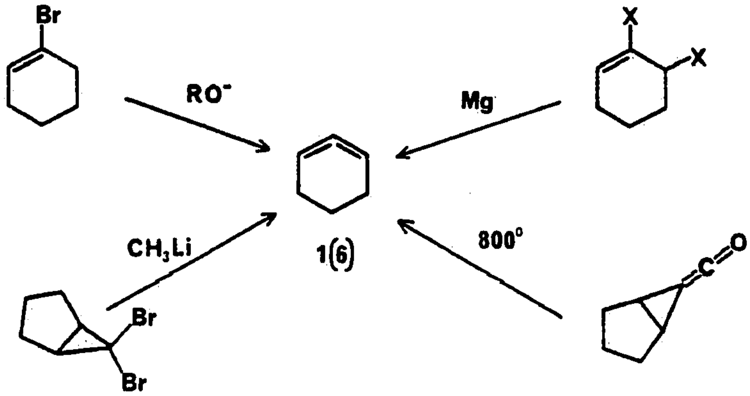
Figure 2.[5] Electronic configurations for bent planar allene

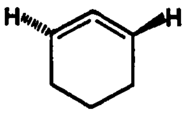
To complicate matters further, 8-^{1}D and 8-^{3}D are nearly degenerate. The explanation given by Seeger *et al.*[6b] is that this occurs because the exchange integral between the two odd electrons is very small, due to the orthogonality of the two singly occupied MOs. The resulting overall ordering of the four states shown in Figure 2 is thus predicted to be $^1D < {}^3D < Z_1 < Z_2$.[5,6]

1,2-Cyclohexadiene

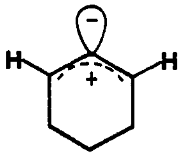
Much of the early work with cyclic allenes centered upon the synthesis of 1,2-cyclohexadiene **1(6)**. Its generation by various diverse routes is summarized in Scheme 1.[7] 1,2-cyclohexadiene, **1(6)**, is far too reactive to be isolated at ambient temperature, but has been trapped with a variety of reactions (*e.g.*, dimerization, protic solvent addition, etc.).[7] In the absence of any trapping agents, the formation of dimers,[8] trimers,[9], and two tetramers[9] has been reported. Strained allene **1(6)** has most frequently been described as one of the planar allene structures shown below. These correspond to

Scheme 1 Syntheses of 1,2-cyclohexadiene, **1(6)**

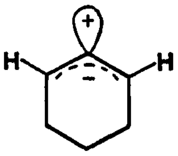




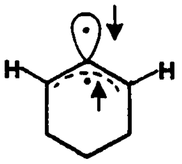
1(6)



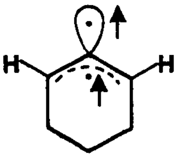
1(6)-Z$_1$



1(6)-Z$_2$



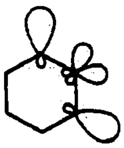
1(6)-^{1}D



1(6)-^{3}D

the electronic configurations for bent planar allene, as shown in Figure 2. The chiral 1,2-cyclohexadiene, **1(6)**, seems generally not to have been seriously considered. In the experimental work of Moore and Moser,[9] zwitterionic structure **1(6)**-Z$_1$ was proposed as the transient generated, but it was also noted that **1(6)**-^{3}D may be the ground state. INDO calculations of Dillon and Underwood[10] showed Z$_1$ allene to be an energy minimum and they concluded that **8**-Z$_1$ was the lowest singlet state of bent allene, although, **8**-^{3}D was considered to be of lower energy. This zwitterion, **8**-Z$_1$, is indeed an energy minimum, but on the excited state surface.[5] This state ordering is expected for cyclic systems as well.

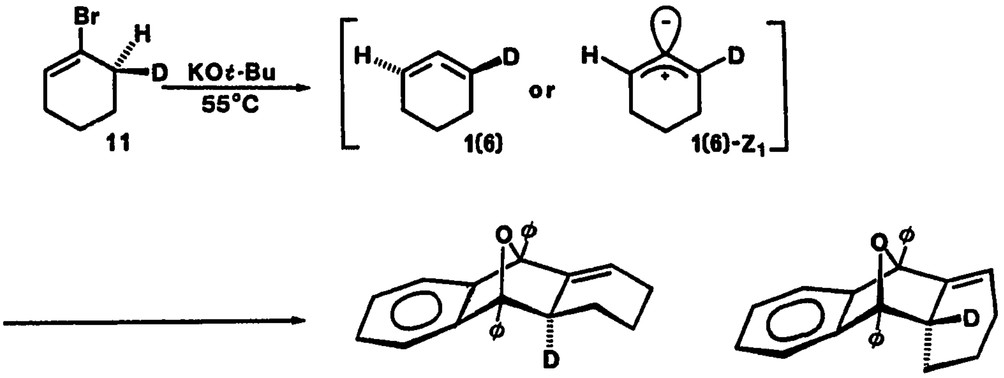
Bottini *et al.* have extensively studied 1,2-cyclohexadiene.[11] One of their conclusions was that a singlet diradical-like structure **1(6)**-^{1}D was involved in dimerization and trapping with dienes. Nucleophilic trapping at the central allenic carbon was suggested to occur through zwitterion **1(6)**-Z$_1$, or a badly twisted allene carbene which they represented as **9** or **10**. Balci and Jones[12] realized that of all the allenic species possible, only the nonplanar allene is chiral.



9

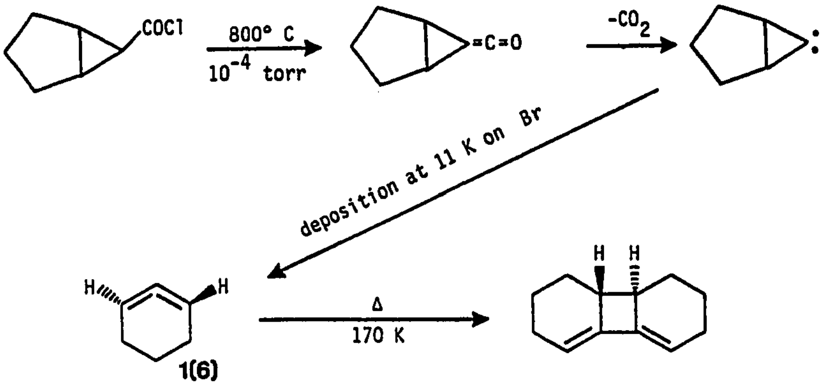
10

Scheme 2 Generation and trapping of optically active **1(6)**



Relying upon the primary deuterium isotope effect, base-induced dehydrobromination of the optically active deuterio-vinylbromide 11 with potassium tert-butoxide (Scheme 2) should generate an optically active allene only if the transient species was nonplanar. The allene thus generated was trapped with 9,10-diphenylisobenzofuran (DIBF) and the adduct mixture thus obtained proved to be optically active. This result demonstrated that 1,2-cyclohexadiene is chiral, and is best represented by **1(6)**. By increasing the reaction temperature, they inferred competitive racemization of the allene, from decreased optical activity of the cycloadduct mixture. Balci and Jones[12] thus concluded that 1,2-cyclohexadiene exists as a bent, chiral structure which is easily racemized. Further evidence for the nonplanar allene has been recently provided by Wentrup *et al.*[13] They trapped **1(6)** in a cryogenic matrix (11 K) and observed the IR spectrum, in which a strong band at 1886 cm^{-1} was attributed to the allene moiety (Scheme 3).

Scheme 3 Spectroscopic observation of twisted (C_2) allene 1(6)



Large ring cyclic allenes

In rings larger than six carbons, there seems to be little difficulty in accepting the possibility of a chiral allenic structure. Indeed, Balci and Jones[14] have generated optically active 1,2-cycloheptadiene **1(7)** by the same method which was employed for **1(6)**. The allene was trapped with DIBF and the cyclo-adduct mixture was found to be optically active. No evidence for competitive racemization was observed; thus, the rotational barrier in **1(7)** must be greater than in **1(6)**.

Visser and Ramakers have isolated stable platinum complexes of 1,2-cycloheptadiene, **1(7)**, and 1,2-cyclooctadiene **1(8)**.[15] When **1(7)** was liberated from the complex with CS_2 at -25°C, only its dimer was isolated. By contrast, 1,2-cyclooctadiene was sufficiently stable that its ^{1}H NMR spectrum and dimerization kinetics could be studied.[16] Manganiello *et al.* have recently isolated a fluxional Fp^+ complex [$Fp^+ = C_5H_5Fe(CO)_2$] of **1(7)**.[17] The barrier to interconversion of enantiomers (*i.e.*, the energy difference between the chiral allene and the planar transition state) was estimated to be >13.9 Kcal/mol.

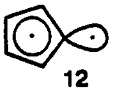
Two distinct vinyl protons of this complex, observed in the ^{1}H NMR spectrum at -40°C, coalesced at 29°C. 1,2-Cyclononadiene **1(9)** (*vide supra*), to date the smallest cyclic allene which is kinetically stable at ambient temperature, is readily prepared in large quantity and >99% purity by treatment of 9,9-dibromobicyclo[6.1.0]nonane with MeLi.[2]

Four- and five-membered cyclic allenes

What is the nature of the allene moiety in a four- or five-membered ring? At present, sufficient information to resolve this question is not available. Solution phase experiments designed to generate 1,2-cyclopentadiene **1(5)** instead gave evidence only for its isomer, cyclopentyne.[18] Attempts to isolate **1(5)** are as yet inconclusive.[19] Studies of the C_4H_4 potential surface are underway; 1,2-cyclobutadiene **1(4)** is among the species being investigated.[20]

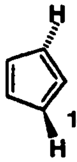
One novel possibility is that cyclopentadienylidene **13** could exist as allenic structure **14**. Chiral allene **14** has been ruled out as the ground state by ESR studies,[21] which show a triplet multiplicity. Nevertheless, many reactions of cyclopentadienylidene are attributed to a singlet.[22] Interestingly, MNDO calculations show an energy minimum for **14**, but this is predicted to be 21.2 Kcal/mol above triplet **12**.[23]

4,5-Benzannelation of cyclopentadienylidene may be expected to favor the allenic structure **16** over the unsaturated carbene **15**, due to the aromaticity of **16**. Tolbert and Siddiqui has reported the generation of a diphenyl derivative of **15**.[24] The allene **16** was briefly considered, but did not seem consistent with the electrophilicity of the intermediate.

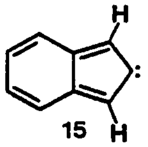


12

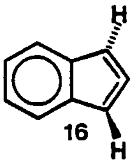
13



14



15



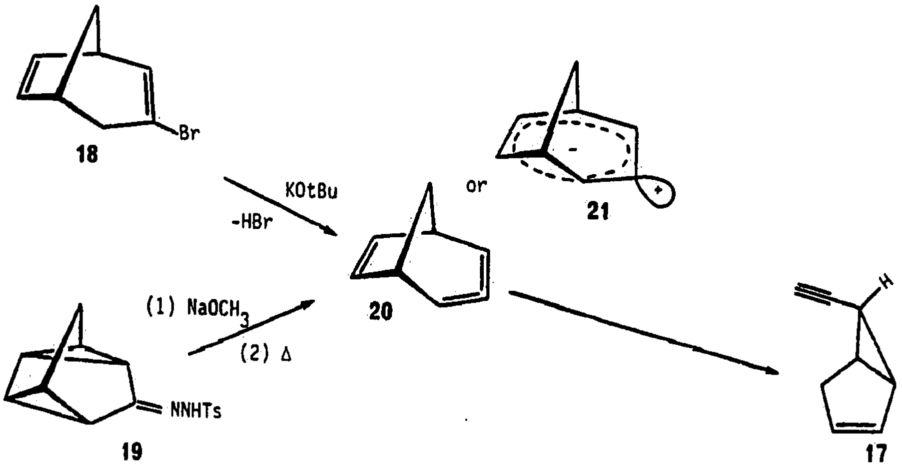
16

In conclusion, there are no reported experiments which presently demonstrate the intermediacy of a five-membered ring cyclic allene.

Bicyclo[3.2.1]octatrienes.

Bergman and Rajadhyaksha reported the formation of *endo*-6-ethynyl-bicyclo[3.1.0]hex-2-ene **17** as a result of both base treatment of vinyl bromide **18** and carbene generation from pyrolysis of tosylhydrazone **19**.[25] This is outlined in Scheme 4. They proposed the intermediacy of a "homoconjugated carbene" **21**, as opposed to the allene **20**, since the allenic structure seemed too strained. The zwitterionic structure **21**, with six electrons in a homoconjugated π system, was expected to show stability associated with homoaromaticity.

Scheme 4[25] Generation and rearrangement of bicyclic allene 20

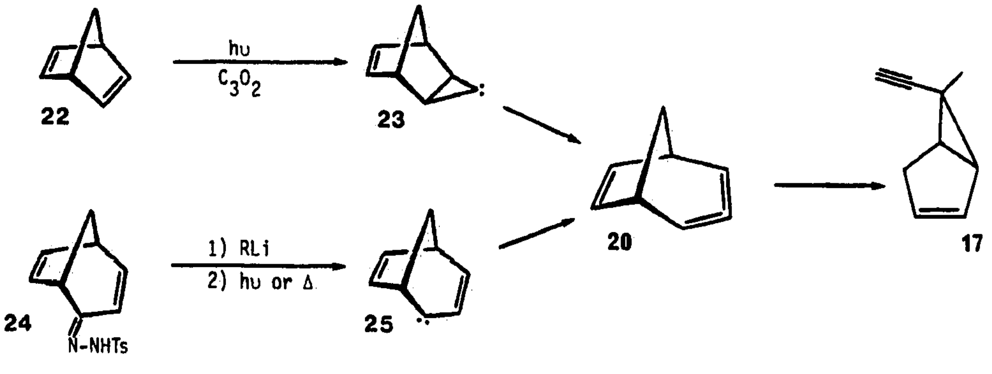


The same product, **17**, was isolated by Klump and van Dijk from the photolysis of carbonsuboxide in the presence of norbornadiene, **22** (Scheme 5).[26] More recently, Freeman and Swenson reported isolation of 3-17% of **17** from photolysis of tosylhydrazone **24** (Scheme 5).[27] Enyne **17** presumably arose from generation of carbenes **23** and **25** then ring opening and 1,2-H migration to form allene **20**, which subsequently rearranged to **17**.

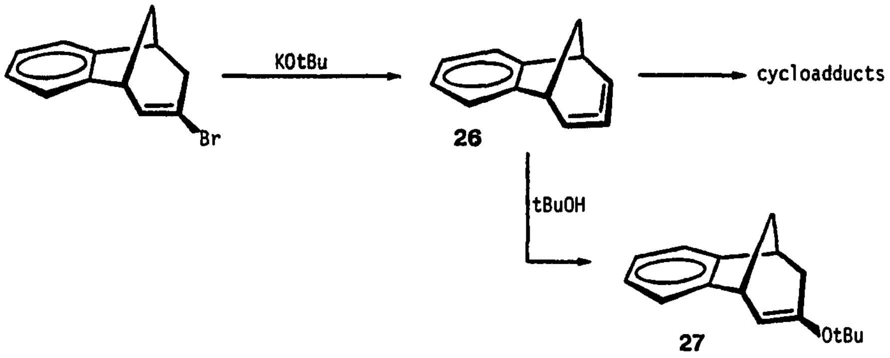
Balci and Harmandar reported generation of a benzannelated derivative, **26**, which was readily trapped with DIBF.[28] In the absence of diene traps, the *t*-BuOH addition product **27** was isolated (Scheme 6).[28]

Balci and Jones have once again used the inherent chirality of cyclic allenes to approach this problem.[29] Treatment of vinyl bromide **18** with potassium menthoxide in the presence of DIBF yielded an optically active cycloadduct mixture;[29] the activity of the adduct mixture decreased with increasing reaction temperature, which indicates competitive racemization. Additionally, enyne **17**, isolated in 2-3% yield in

Scheme 5 Generation and rearrangement of bicyclic allene **20**



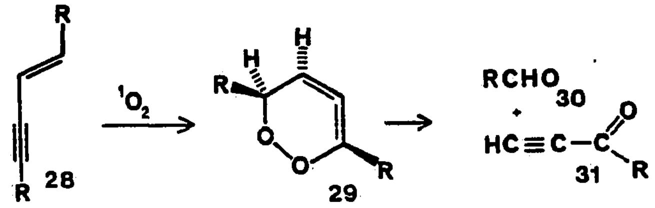
Scheme 6[28] Generation and trapping of allene **26**.



the absence of any trapping reagent, was optically active.[29] These data are consistent with the formation of the chiral allene **20**, which easily racemized.

Heterocyclic allenes

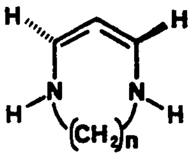
Several heterocyclic allene analogs have been reported. 1,2-Dioxacyclohexa-3,4-dienes, **29**, have been recently postulated as intermediates in the cycloaddition of singlet oxygen to but-1-ene-3-ynes, **28** (equation 4).[30] The cyclic allene, **29**, is expected to be unstable and apparently fragments to afford the observed aldehydes (**30**) and ketones (**31**). The authors briefly comment on results of *ab initio* geometry optimization for **29** (R=H), the results of which are



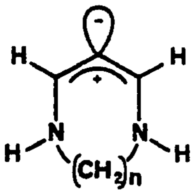
(4)

consistent with a chiral equilibrim geometry with an inversion barrier of 27.9 Kcal/mol. Unfortunately, no description of their computational methodology was reported.

Cuthbertson *et al.* have reported results of MNDO calculations of diazaallenes **32(n)**, n = 1 - 3 and higher homologues.[31] In all cases, a chiral allenic structure **32(n)** was preferred, despite the resonance stabilization expected for the zwitterionic species **33(n)**. These species reportedly react by protonation of the central allenic carbon.



32(n)



33(n)

Clearly, a thorough theoretical study of cyclic allenes is warranted to supplement this limited experimental data. Earlier theoretical work has been shown to be in error.[10] Due to the difficulties associated with the attempted generation of 1,2-cyclopentadiene **15**, theory (MO calculations) may best predict the stability and electronic nature of this ground state species. Since the racemization of cyclic allenes is expected to proceed through one of the planar states, this energy difference, which should be easily calculated, represents the barrier to inversion (racemization) and is thus a measure of the stability of cyclic allenes. As shown below, allene strain also may be estimated from this inversion barrier.

Theoretical Investigation of the Structural Limitations of Cyclic Allenes

The primary goal of the present research was to explore the electronic nature and structural limitations of cyclic allenes. This is best accomplished by calculating the structure and energetics of the chiral allene structure and the planar diradical (^1D). Since the chiral structure correlates with this diradical, the energy difference between the two represents the barrier to racemization. This is qualitatively diagramed for bent allene in Figure 3. Of course, the relative energies of planar and chiral structures will vary with the size of the ring. MCSCF calculations indicate that triplet planar allene 3 should be of higher energy than the singlet. This state correlation was derived from CI calculations on potential surfaces for twisting and bending in allene.[5]

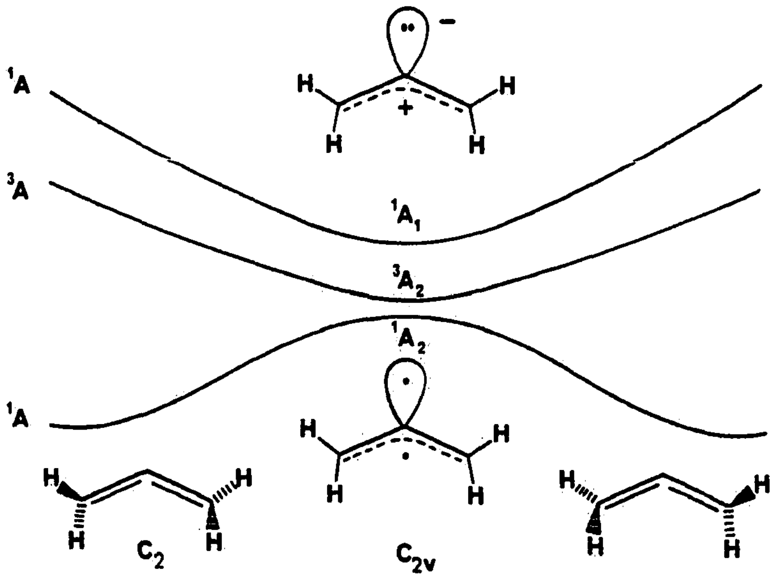
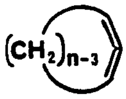
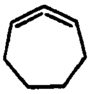


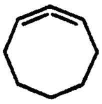
Figure 3. State correlation for racemization in C_2 allene

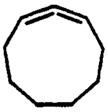
With this goal in mind, the series of cyclic allenes containing 4-9 carbons, **1(4-9)** was investigated. For this study, the semi-emperical MNDO method of Dewar and Thiel was chosen.[32] Full geometry optimization was carried out within appropriate symmetry constraints for all chiral allenes, and for diradicals **1(4-6)**. Chiral species were restricted to the C_2 point group, while all planar species were



1(n)







restricted to C_s. A final calculation in which all symmetry constraints were released was always performed for each equilibrium geometry in order to ensure that the resulting geometry was not an artifact of the symmetry constraint. The MNDO method was chosen for this task because it generally provides very good equilibrium geometries, and because of its computational efficiency.

Allene bending potential

The first study undertaken was a simple allene bending potential. The MNDO calculated equilibrium geometry of D_{2d} allene, **34** has been previously reported.[33] Further geometries **34**(α) were constrained in C_2 symmetry for various ${}_1C={}_2C={}_3C$ bending angles (α = 180-60°) while all other parameters were optimized; no twisting restrictions were maintained. These calculations predict that allene bending is accompanied by slight twisting of the dihedral $H-{}_1C={}_2C={}_3C$ angle (β) towards a C_s structure. Relative energies are shown in Figure 4. Side views of **34**(α) are diagramed in Figure 5.

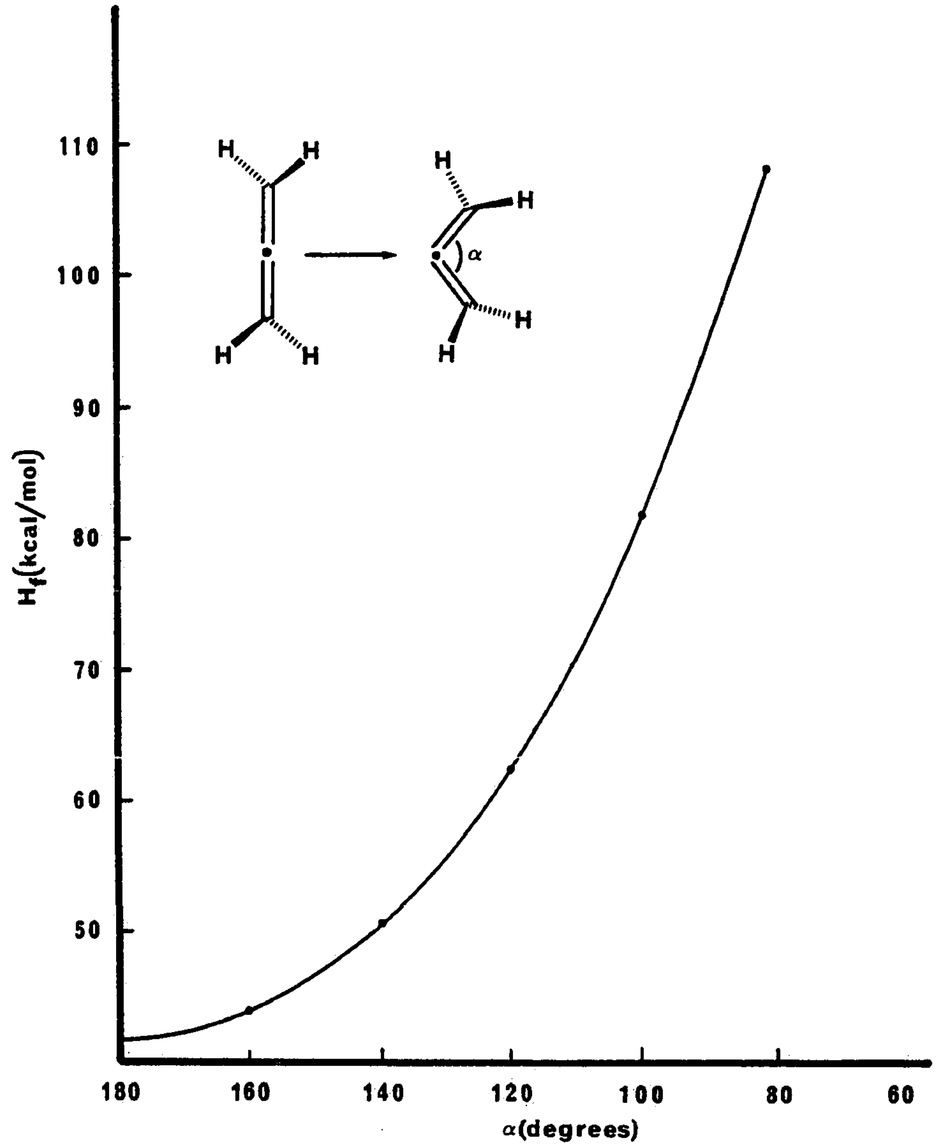


Figure 4. ΔH_f vs allene bending angle, α

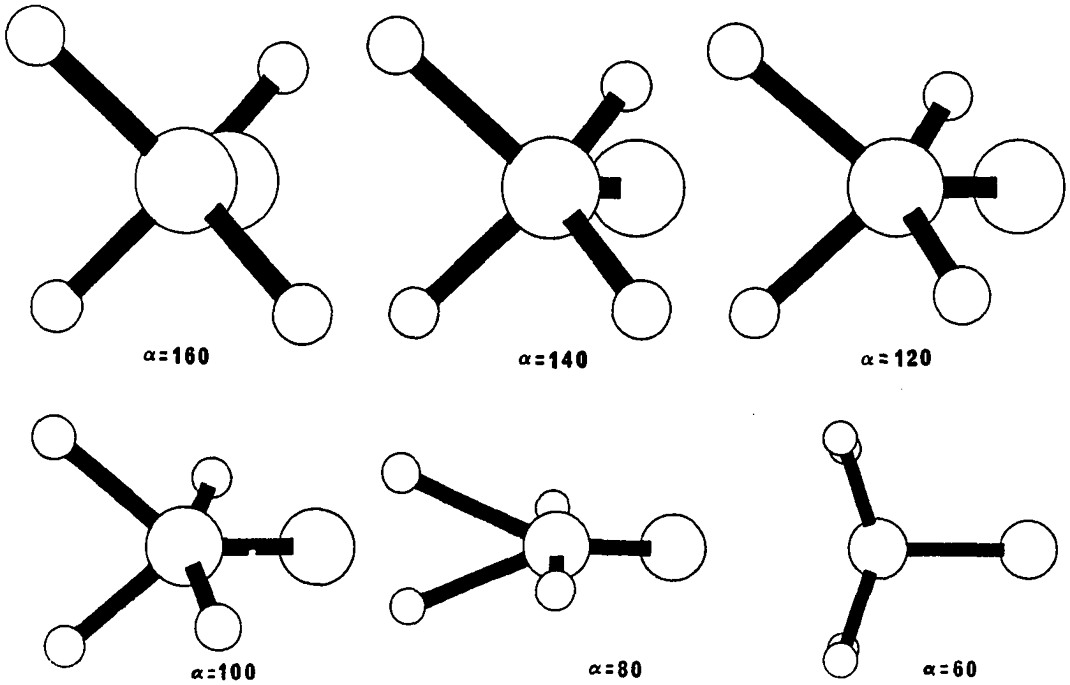
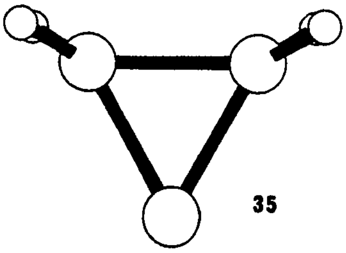


Figure 5. Bent allene, **34**(α), viewed along the C=C=C plane

The resulting ΔH_f values for C_2 bent allene **34**(α) relative to D_{2d} allene, **5**, ($\Delta\Delta H_f$) should thus approximate the strain that cyclic allenes must overcome to exist with such small allene bend angles, α. The value of $\Delta\Delta H_f$ increases smoothly with bending (decreasing α) to a point beyond α = 80°, where the energy of the bent species drops dramatically. This is due to "closure" to cyclopropylidene **35**, the equilibrium geometry of which is obtained if the constraint on α is removed from the geometry optimization of **34**(60°).

One significant result of this simplistic evaluation is that the initial bending potential is surprisingly soft. Bent allene **34**(α) is predicted to show only minor destabilization for small bends; 20°



35

bending destabilizes this model system by about only 5 kcal/mol. For large bends (α ~ 60°) however, cyclopropylidene **35** is the preferred structure. The allene-cyclopropylidene potential surface is currently under detailed investigation by another research group.[34] A second point of interest is that bending is accompanied by rotation towards planarity. Thus bending and π bond rotation are coupled motions in allene.

MNDO calculations for cyclic allenes

Equilibrium chiral (closed shell) structures for the allene series **1(n)**, n = 4-9, were next determined using MNDO (*vide supra*). ORTEP[35] diagrams of each equilibrium species are shown in Figure 6. Predicted heats of formation (ΔH_f) and salient geometric parameters for each are tabulated (Table 1).

The predicted geometries generally showed expected trends although it is remarkable that chiral structures can be calculated in the smaller rings. Bond lengths and angles for the series were predicted to be quite normal for cyclononadiene, **1(9)**; smaller rings showed evidence of more strain. This strain was manifested primarily in the high heat of formation and in the double bond length ($r_{C=C}$), which varies from a normal value of 1.31Å for **1(7-9)** to 1.40Å in **1(4)**. The longer double bond length is consistent with the decreased π overlap expected for the smaller allenes. Bend angles, α, and out of plane hydrogen bending angle, β, each decreased with decreasing ring size.

The heats of formation predicted for this series show the decreased stability which is expected for a series of diminishing ring size. Assuming α = 170° for **1(9)**, $\Delta\Delta H_f$ relative to **1(9)** versus α corresponds well to the allene bending potential shown in Figure 4. The MNDO results lead to the prediction that the $-CH_2-$ chain serves merely to impose the allene bend angle, α, on the system.

For the smaller and controversial members of this series **1(4-6)**, in which the electronic nature of the ground state is in question, planar, open-shell singlet (^1D) geometries were determined. Larger ring ^1D species were not calculated due to the expected large expenditure of CPU time required for open shell calculations, and the limited amount of information to be gained. For this series, ORTEP diagrams of MNDO optimized chiral cyclic allenes are shown in Figure 6 and energy and salient geometry data are listed in Table 1.

Relative energies for each species were improved by including limited configuration interaction (CI, 2x2 and 3x3 for closed and open shell structures, respectively). Triplet state energies were calculated at open-shell singlet optimized geometries. These data are also listed in Table 1.

The results predict the ^3D to be below ^1D by 0.7 - 2.0 kcal/mol for **1(4-6)**. This result is expected at the SCF level, but is reversed by the use of correlated wavefunctions. MNDO clearly predicts an

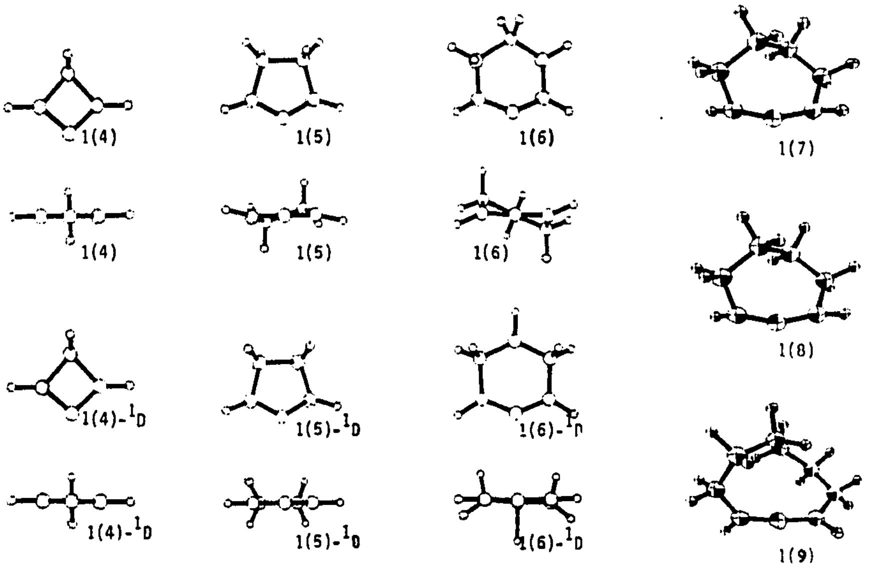


Figure 6. ORTEP representations of MNDO predicted geometries for cyclic allenes

equilibrium chiral structure for 1,2-cyclohexadiene **1(6)**. This is expected also for larger, hence less bent cyclic allenes. The ground states of **1(4-5)**, however, are predicted to be ^{3}D. These predictions are based only upon relative MNDO-SCF energies and should not be regarded as accurate. Calculations at this level thus support the findings of Balci and Jones[12] for 1,2-cyclohexadiene, although, the predicted (CI) energy barrier (5.7 kcal/mol) must be too small. Critical evaluation of the ground state energetics of 1,2-cyclopentadiene, however, will require further calculations at a higher level.

Chiral and planar states of another controversial allene, bicyclo[3.2.1]octa-2,3,6-triene, **20**, (*vide ante*) were also calculated by this method. The **21**-^{1}D geometry optimization did not converge

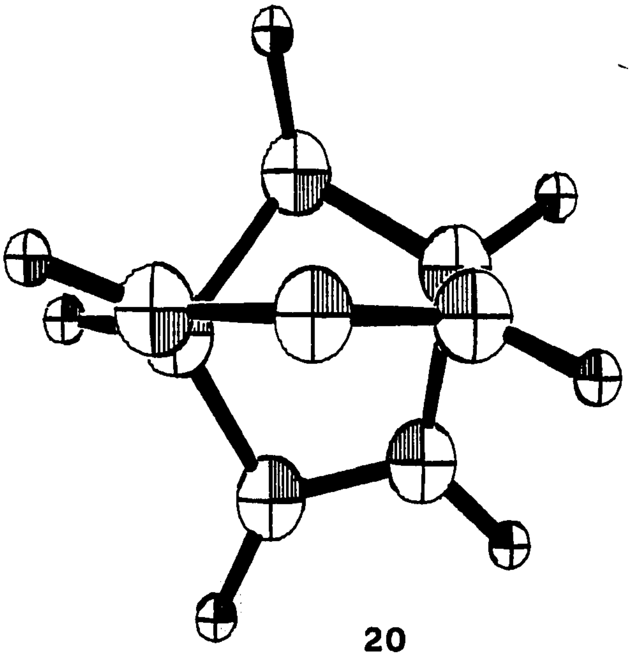
Table 1. MNDO results for cyclic allenes

	ΔH_f (kcal/mol)		α $_1C$-$_2C$-$_3C$	$r_{C=C}$	β^a H-$_1C$-$_2C$-$_3C$
Species	SCF	CI	(degrees)	(Å)	(degrees)
1(4)	156.9(0.0)[b]	166.2(0.0)	93.0	1.40	0.7
^1D	134.4(-22.5)	134.4(-31.8)	99.5	1.38	0.0
^3D	132.4(-24.5)		99.5		0.0
1(5)	104.3(0.0)	93.5(0.0)	121.0	1.34	13.0
^1D	90.2(-14.1)	90.2(-3.3)	119.9	1.37	0.0
^3D	89.0(-15.3)		119.9		0.0
1(6)	67.7(0.0)	63.5(0.0)	138.5	1.32	22.9
^1D	69.2(1.5)	69.2(5.7)	135.4	1.35	0.0
^3D	68.5(0.8)		135.4		0.0
1(7)	44.2		153.4	1.31	27.6
1(8)	32.7		161.5	1.31	31.0
1(9)	29.2		170.4	1.31	33.7
	122.9	117.4	111.7	1.33	
			180.0		45.0

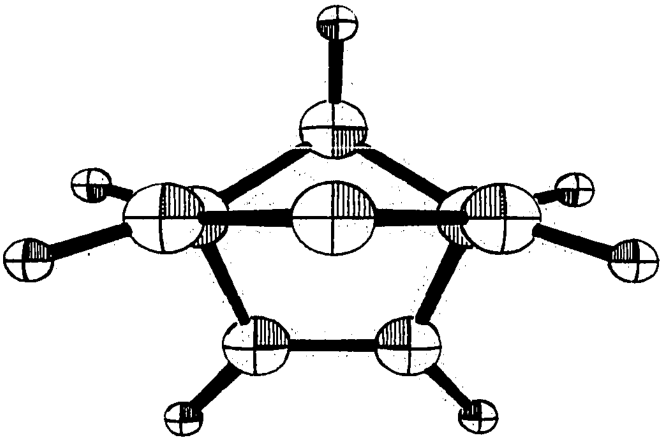
[a] Defined as the angle made by the C-H bond with the plane defined by C_1-C_2-C_3.

[b] Relative energies (kcal/mol) in parentheses.

satisfactorily after about 1 CPU hour, but by this time the energy of the ^1D structure was about 5.5 kcal/mol below that of chiral 20. ORTEP structures for 20 and 21-^1D are shown in Figure 7. This prediction would appear to contradict the experimental observation of chirality in 20.[20] Clearly, the MNDO method is not sufficient for a



20



21-^{1}D

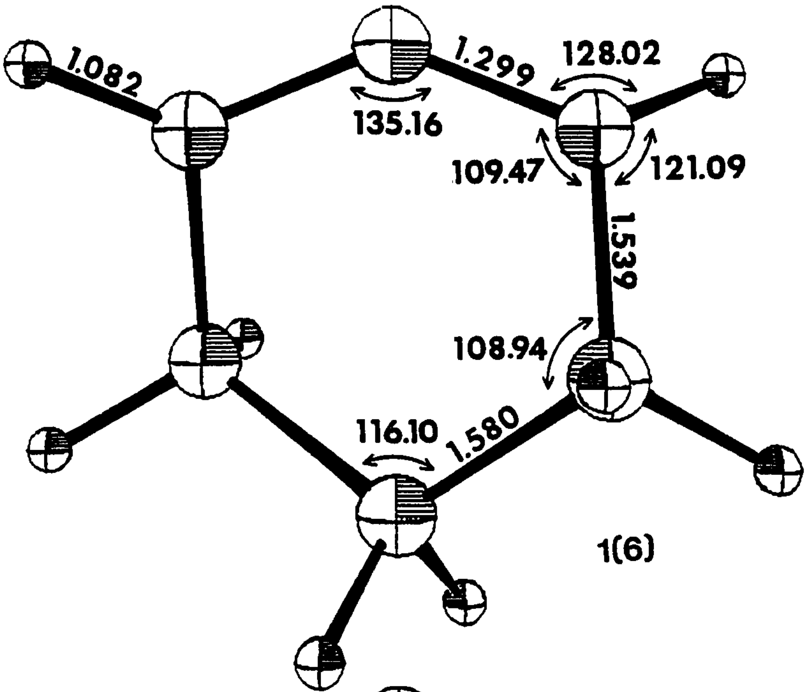
Figure 7. MNDO optimized geometry for bicyclo[3.2.1]octa-2,3,6-triene, 20 and its diradical 21-^{1}D

quantitatively accurate analysis of this problem. Model calculations on parent allene show a predicted MNDO rotational barrier of 31.4 kcal/mol whereas the experimental value is *ca.* 48-50 kcal/mol.[5]

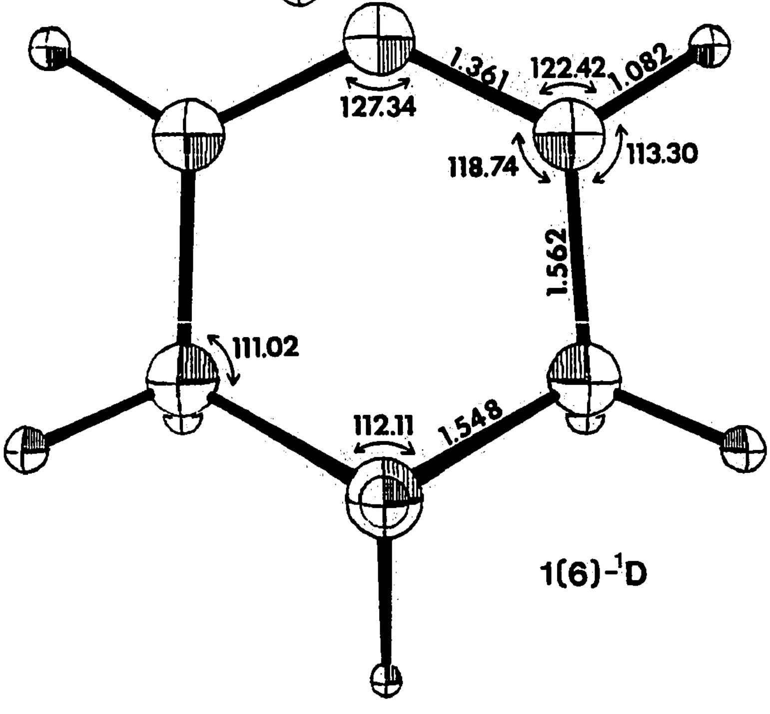
Ab initio calculations for 1,2-cyclopenta- and 1,2-cyclohexadiene[36,37]

This work has been extended to include *ab initio* calculations of both chiral and planar structures using STO-3G[38] and 3-21G[39] (+ polarization) basis sets. Geometries of **1(5)** and **1(6)**, optimized at the STO-3G level, were remarkably similar to those predicted by MNDO. ORTEP structures and salient geometric parameters for the STO-3G geometries are shown in Figures 8 and 9, respectively.

The relative energies of chiral and planar structures for 1,2-cyclohexadiene **1(6)**, are qualitatively in accord with the MNDO results.[36] More interesting results were obtained for 1,2-cyclopentadiene, **1(5)**.[37] The authors report "corrected" FORS-MCSCF calculations, which predict the chiral structure **1(5)** to be 4.9 kcal/mol more stable than the planar **1(5)**-^{1}D. Also noteworthy is that **1(5)**-^{1}D is predicted to be of lower energy than **1(5)**-^{3}D. This occurs because ^{1}D is lowered by correlation energy more than is ^{3}D. The lowest energy planar state therefore correlates with the chiral species; this chiral-planar gap is then best represented as a racemization barrier, as shown in Figure 3. The results for various levels of *ab initio* calculations of **1(5)** and **1(6)** are tabulated (Tables 2 and 3, respectively).



1(6)



1(6)-^{1}D

Figure 8.[36] STO-3G optimized geometries for chiral 1,2-cyclohexadiene 1(6) and the geometry 1(6)-^{1}D corresponding to its barrier to thermal racemization

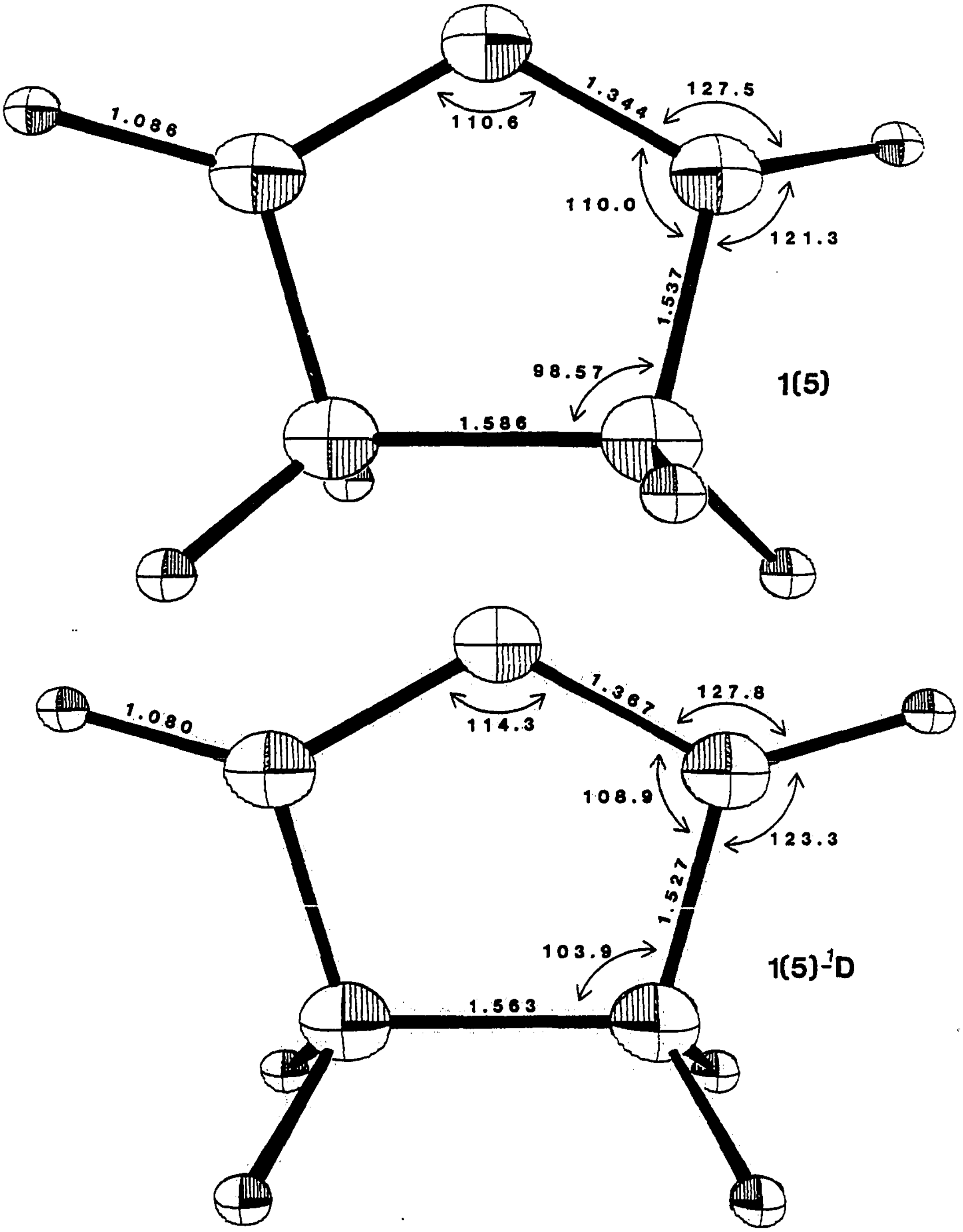
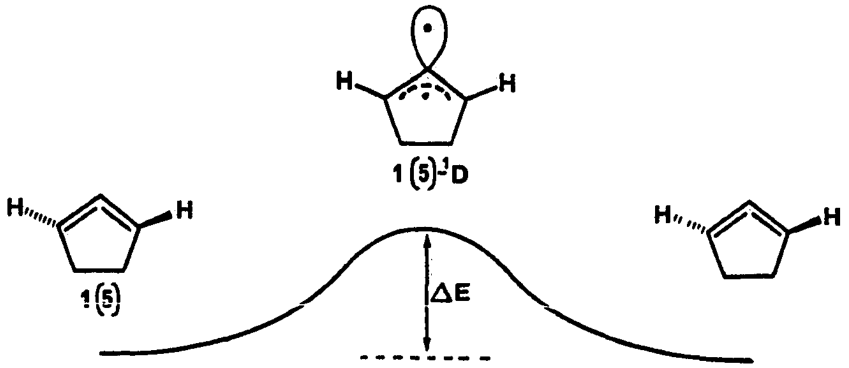


Figure 9.[37] STO-3G optimized geometries for chiral 1,2-cyclopentadiene 1(5) and the geometry 1(5)-^{1}D corresponding to its barrier to thermal racemization

Table 2. Racemization Barriers Predicted for 1,2-cyclopentadiene

Computational Method	ΔE (kcal/mol)
MNDO[a]	-14.2
MNDO/CI[a]	- 3.3
STO-3G||STO-3G[b]	-36.6
3-21G||STO-3G[b]	-24.0
3-21G*||STO-3G[b]	-18.1
MP2[b]	- 0.5
MP3[b]	- 4.3
3-21G FORS-MCSCF||STO-3G[b]	- 1.03
"corrected" FORS-MCSCF[b]	+ 4.9

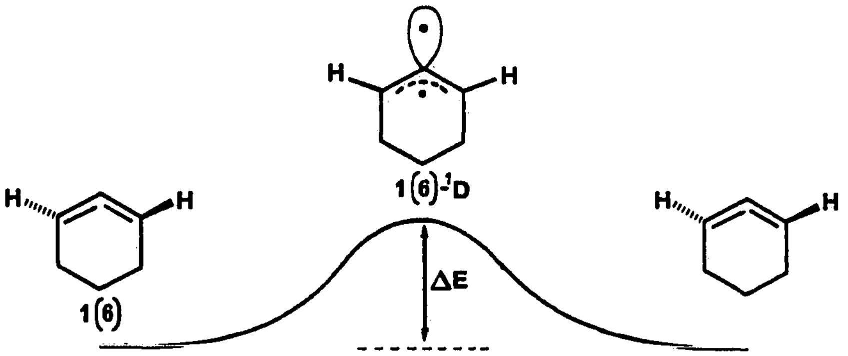


[a] This work.

[b] Reference 37. Correction is made for basis set improvements at the SCF level.

Table 3. Racemization Barriers Predicted for 1,2-cyclohexadiene

Computational Method	ΔE (kcal/mol)
MNDO[a]	1.5
MNDO/CI[a]	5.7
STO-3G||STO-3G[b]	- 4.4
3-21G||STO-3G[b]	3.5
3-21G|| FORS-MCSCF||STO-3G[b]	13.1
"corrected" FORS-MCSCF[b]	15.0
MP2[b]	21.8



[a] This work.

[b] Reference 36.

Conclusions

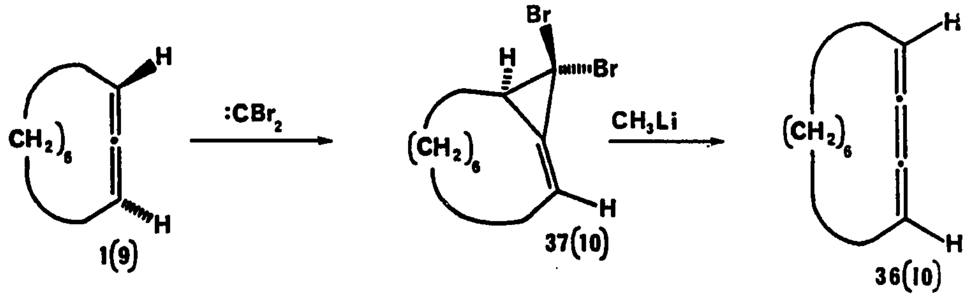
For cyclic allenes with six or more carbons, the predicted ground state structure is a chiral (C$_2$) allene. For 1,2-cyclohexadiene **1(6)**, this has been experimentally verified. Racemization of chiral **1(6)** has also been observed[12] and may be explained as occurring through the planar **1(6)**-^1D.[5,6] This is supported by *ab initio* MO calculations.[36,37] Planar **1(6)**-^3D is predicted to lie above **1(6)**-^1D due to correlation energy. The zwitterion 1(6)-Z_1, initially predicted to be the lowest singlet state by Dillon and Underwood,[10] has been shown to be an excited state.

The present calculations give a good estimate of the strain inherent in cyclic allenes. Due to the predicted preference for D_{2d} allene to racemize through a bent (C_{2v}) transition state, and the soft bending potential found for bent chiral allene, **34(α)**, the bend in cyclic allenes is not expected to contribute significant destabilization during racemization. Strain in the chiral structure reduces the racemization barrier by raising the energy of the chiral structure.

This work represents a convergence of experiment and theory for **1(6)** and larger cyclic allenes. For the smaller homologue, **1(5)**, calculations slightly favor a chiral ground state structure but the energy difference between the chiral and planar structures is within a reasonable estimate of computational error. Confirmation of this result awaits experimental observation of 1,2-cyclopentadiene.

Introduction to Cyclic Butatrienes

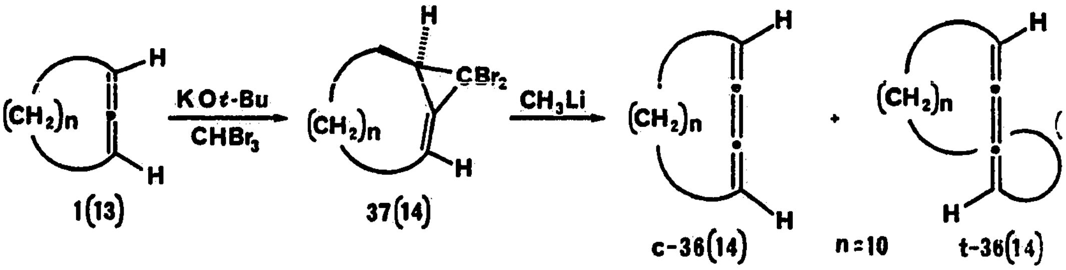
In contrast to the cyclic allenes, little is known about the structure and chemistry of cyclic butatrienes **36(n)**.[1a,b,d] The first stable cyclic butatriene to be reported was 1,2,3-cyclodecatriene, **36(10)**, prepared by Moore and Ozretich in 1965[40] (equation 5).



(5)

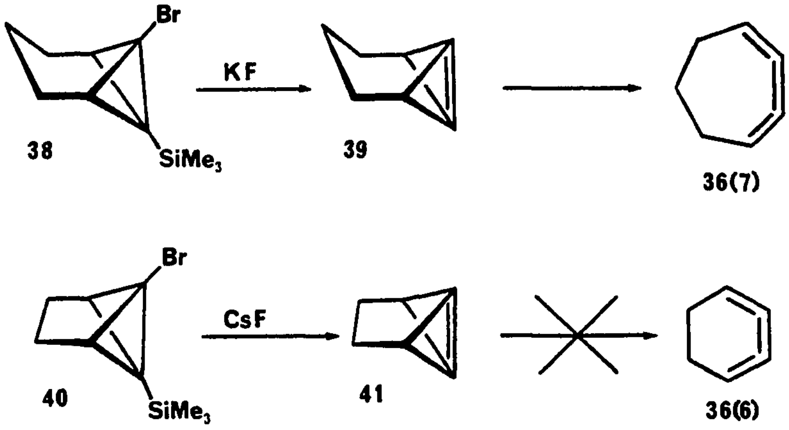
Butatriene 36(10), generally considered the smallest stable cyclic butatriene,[1a,b,d] was described as an air sensitive oil which, like many acyclic butatrienes, easily polymerizes when not in solution.

Bhagewat and Devaprabhakara have more recently prepared 1,2,3-tridecatriene, **36(13)**, via a more serendipitous route.[41] Although only one isomer of **36(13)** was reported, this large ring size should accommodate both *cis* and *trans* isomers. Preliminary investigation of 1,2,3-cyclotetradecatriene, **36(14)**, synthesized via the route outlined in equation 6,[42] has revealed what is believed to be a mixture of *cis* and *trans* isomers. Isolation of these two isomers is being pursued.[42]



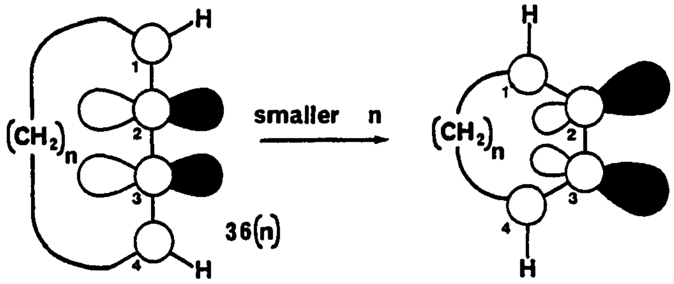
(6)

Zoch *et al.* have generated 1,2,3-cycloheptatriene, **36(7)**, which was observed as a transient product from the rearrangement of tricyclo-$[4.1.0.0^{2,7}]$hept-1(7)-ene, **39** (Scheme 7).[43] Treatment of TMS bromide **38** with fluoride ion gave bicyclobutene **39**, which rearranged to **36(7)**. In the presence of diphenylisobenzofuran (DIBF) or anthracene at 55°C, Scheme 7[43] Generation of transient cyclic butatriene **36(7)**.



Diels-Alder trapping of **39** was competitive with isomerization of **39** to **36(7)** and adducts of both **39** and **36(7)** were isolated. By raising the reaction temperature to 100°C, Diels-Alder adducts of **36(7)** were the exclusive products. Analogous attempts to generate 1,2,3-cyclohexatriene, **36(6)**, from tricyclic **40** yielded only the adduct of **41**, even at 80°C.[44] It was suggested that the failure of **41** to rearrange was due to the low exothermicity of this rearrangement, which results from the high strain of **36(6)**.

Incorporation of a butatriene into a small ring causes deformation of the normally linear geometry, with concomitant rehybridization at $_2$C and $_3$C. This bending should not substantially affect the out-of-plane 1,3-butadiene π system, but should introduce considerable strain in the in-plane ethylene system, due to weakening of the $_2$C-$_3$C in-plane double bond as hybridization changes from sp towards sp^2. For very small rings, the situation is similar to that of *ortho*-benzyne.



36(n)

The goal of this study was to investigate the effects of constraining 1,2,3-butatriene moieties in small cyclic systems. Since there is no question of the ground electronic state (as had been problematic with the cyclic allene study), a simple evaluation of strain engendered in small ring cyclobutatrienes was undertaken.

Theoretical Calculations

Butatriene bending potential

In order to estimate the energetic consequences of bending the butatriene moiety, a series of model calculations was performed on 1,2,3-butatriene, **42**. In this study, the MNDO equilibrium geometry for D_{2h} 1,2,3-butatriene, **42**, was calculated and then constrained in C_{2v} symmetry to various $_1C{=}_2C{=}_3C{=}$ bend angles (α = 180-130°). Similar calculations were described for cyclic allenes (*vide ante*). Single point *ab initio* calculations were then performed at each of these equilibrium geometries using STO-3G[38] and split valence 4-31G basis sets.[45] Energies relative to the D_{2h} butatriene were plotted against α. The resulting plot, summarized in Figure 10, shows remarkably good agreement among the three levels of calculation.

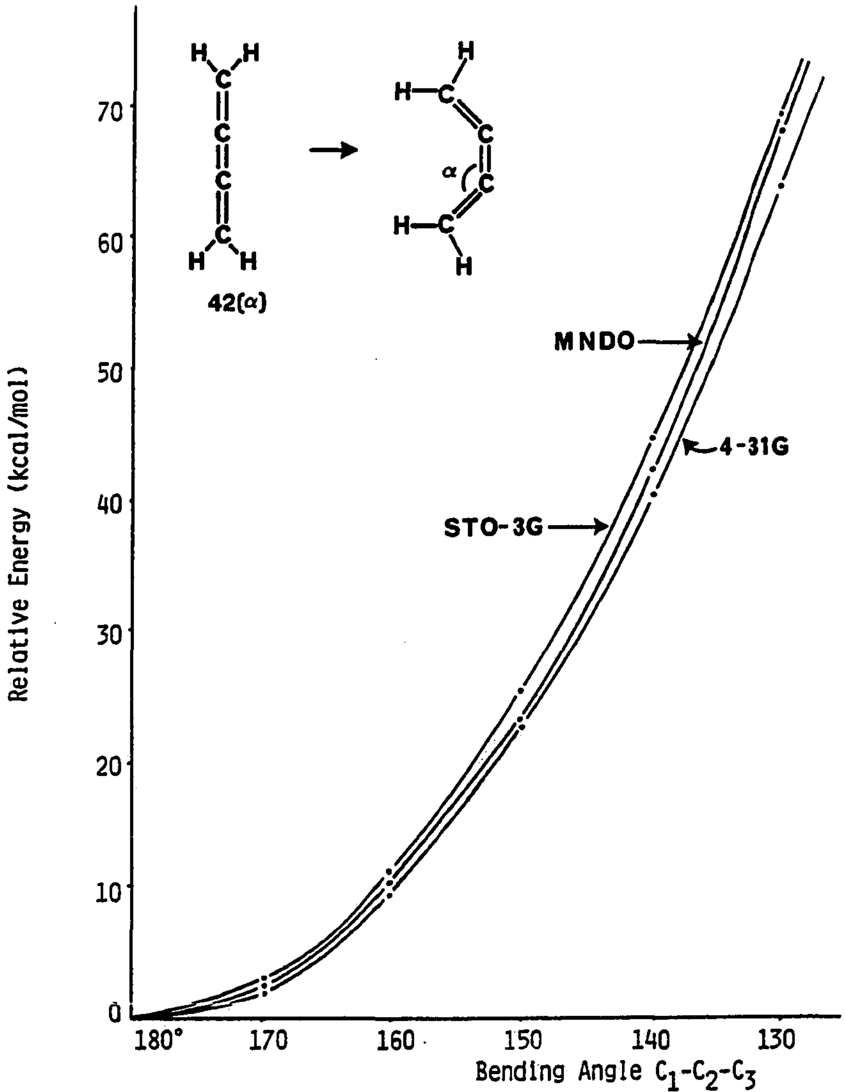
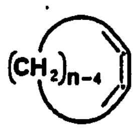


Figure 10. Butatriene bending potential

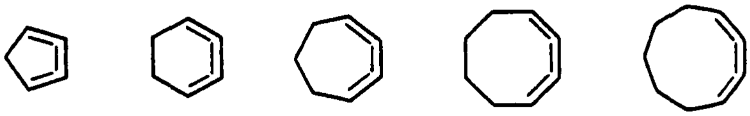
This study indicates that the initial bending potential is relatively soft. Especially noteworthy is the prediction that bending the butatriene by 20° introduces only about 10 kcal/mol of molecular strain.

Cyclic butatriene calculations

The series of cyclic butatrienes **36(n)**, n = 5-9, was next studied using the MNDO method.



36(n)



Geometries chosen for optimization were estimated from molecular models. For 5-8 membered rings, molecular models indicated only one feasible symmetrical conformation (C_2 or C_s) due to restricted rotation of the butatriene moiety. In 1,2,3-cyclononatriene, **36(9)**, conformations with C_2 and C_s symmetry seemed likely; thus, geometries for both were optimized. Other, less symmetrical conformations are possible, but probably will be of higher energy. The structure for the known 1,2,3-cyclodecatriene,[40] **36(10)**, was not optimized since molecular models showed sufficient flexibility to contain a linear butatriene. In all cases, geometric constraints were released in a final calculation, to ensure that a false (symmetry constrained) minimum had not been located.

ORTEP[35] representations of equilibrium geometries for the butatriene series are shown in Figure 10 and salient geometric parameters are tabulated (Table 4). Each structure shows the expected bent planar butatriene moiety. Even **36(6)**, which could have twisted to relieve methylene eclipsing torsional strain, remained planar. The ${}_1C\text{-}{}_2C$ bond distance changes only about 1.5% over the series, while the ${}_2C\text{-}{}_3C$ distance increases from 1.27 to 1.31Å. This is consistent with

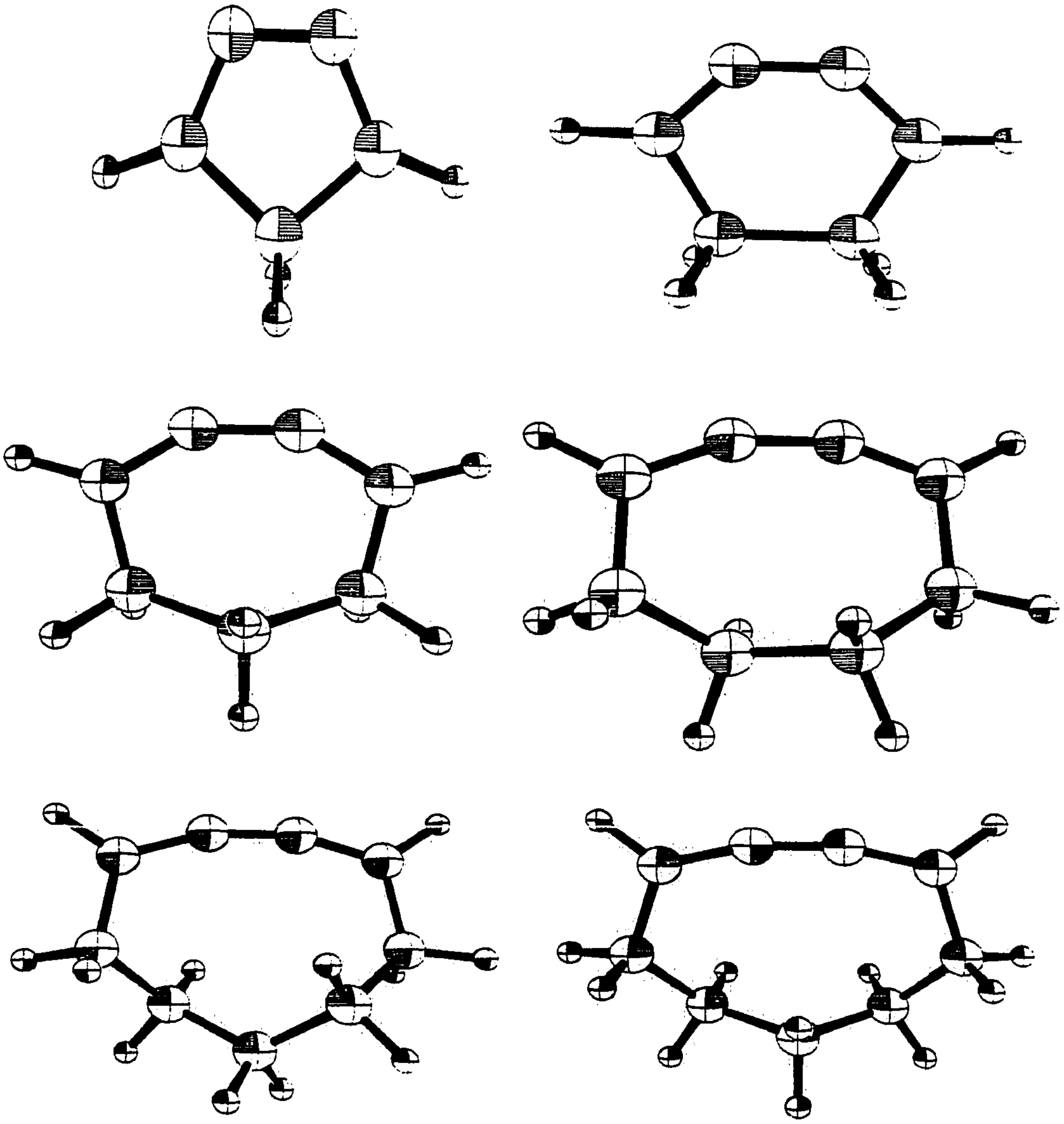


Figure 11. MNDO optimized geometries for cyclic butatrienes

decreased $_2C-_3C$ π bonding and the hybridization change from sp toward sp^2. The allylic bond in cyclopentatriene, **36(5)**, is quite long (1.58Å); this represents a compromise between single bond stretching and butatriene bending strains.

Using the MNDO equilibrium geometries, single point STO-3G SCF energies were calculated for each cyclic butatriene. MNDO heats of formation and STO-3G total energies are summarized in Table 5. For 1,2,3-cyclononatriene, MNDO and STO-3G predict a conformational preference of C_s over C_2 by 4.3 and 3.5 kcal/mol, respectively. This is primarily a consequence of greater butatriene bending in the C_2 structure. Correlation energy corrections (CI) were not included in these calculations, however, these should provide greater relative

Table 4. Selected MNDO Geometrical Parameters for Cyclic Butatrienes

	Bond Angles			Bond Lengths		
	$_1C-_2C-_3C$ (α)	$_5C-_4C-_3C$	$_2C-_1C-_6H$	$_2C-_3C$	$_1C-_2C$	$_4C-_5C$
36(5)	116.37	101.20	134.56	1.312	1.335	1.576
36(6)	132.23	109.06	131.11	1.292	1.317	1.547
36(7)	145.04	111.88	128.43	1.278	1.316	1.529
36(8)	156.29	115.98	126.08	1.271	1.315	1.519
36(9)(C_2)	161.94	118.28	124.38	1.269	1.315	1.517
(C_s)	165.14	120.05	123.35	1.268	1.315	1.513
42	180.0	122.75	122.75	1.270	1.310	

Table 5. Energies (ΔH_f) for Cyclic Butatrienes

Structure	Symmetry Restriction	ΔH_f (MNDO) (kcal/mol)	STO-3G Total Energy[a] (Hartrees)	Estimated Strain[b] (kcal/mol) $\Delta\Delta H_f$
36(5)	C_{2v}	186.28	-189.0279	~130
36(6)	C_2	129.46	-227.6845	60.5
36(7)	C_s	98.00	-266.3058	31.5
36(8)	C_2	74.94	-304.9137	14.0
36(9)	C_2	64.80	-343.4971	8.0
	C_s	60.54	-343.5026	5.5
	D_{2h}	70.95		

[a] At MNDO geometry.

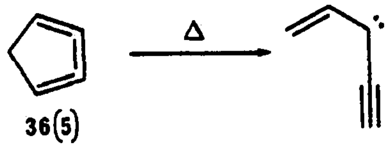
[b] From plotting optimized bending angle (Table 4) vs. Figure 9.

stabilization for the small homologs. Assuming that α = 165° for **36(9)**, values of ΔH_f and E_{total}, relative to **36(9)** ($\Delta\Delta H_f$) correspond well to the bending potential in Figure 9. Thus, destabilization in small cyclic butatrienes must be primarily due to weakening of the central double bond. These $\Delta\Delta H_f$ values, summarized in Table 5 under the heading Estimated Strain, indicate that *strain in the butatriene moiety approximately doubles with each decreasing carbon* in cyclic butatrienes.

These calculations suggest that in cyclic systems the 1,2,3-butatriene moiety is readily bent, and may remain intact in virtually any ring size. It is remarkable that even 1,2,3-cyclopentatriene, **36(5)**, is predicted to be an energy minimum. One must be suspicious of this result; higher level calculations for this strained (~130 kcal/mol) molecule may not predict a global minimum.

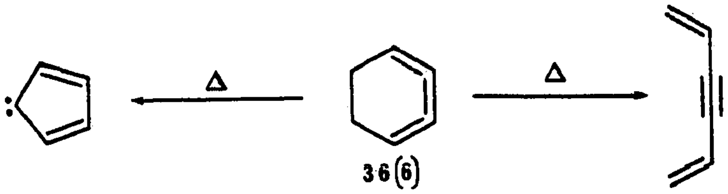
Cyclic butatrienes comprise a fascinating and fundamental collection of molecules, for which very little data presently are available. Based on these calculations, and comparison to the corresponding allenes, it seemed likely that 1,2,3-cyclononatriene, (estimated strain 5.5 - 8.0 kcal/mol), would be isolable. As already shown by the work of Zoch *et al.*[43], smaller members of this series will be highly reactive compounds whose chemistry is well worth exploring.

The strain in cyclopentatriene is sufficiently high that rearrangement to cyclopentadienylidene via 1,3-H shift, or ring opening to a vinylcarbene would seem facile (equation 7). 1,2,3-cyclohexatriene is also highly strained; this may undergo an allowed disrotatory ring opening to 1,5-hexadien-3-yne (equation 8).



36(5)

(7)



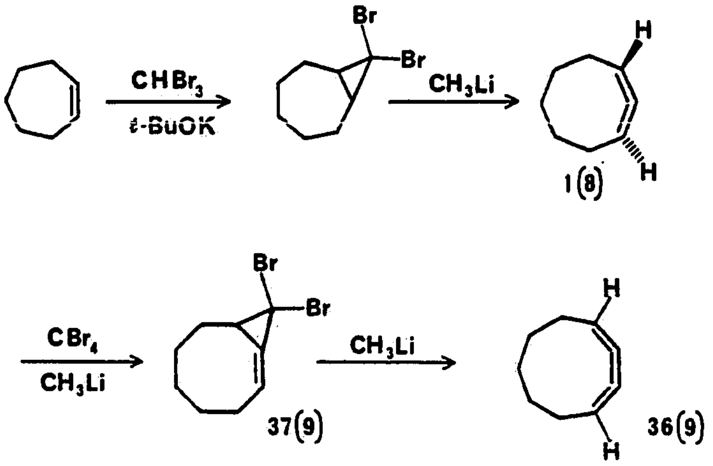
36(6)

(8)

Synthesis of 1,2,3-Cyclononatriene

With these predictions in hand, the synthesis of 1,2,3-cyclononatriene, **36(9)**, was undertaken. Using the strategy of Moore and Ozretich[40] (Scheme 8), the optimal precursor of **36(9)** should be methylenecyclopropane **37(9)**, the expected product of dibromocarbene addition to 1,2-cyclooctadiene, **1(8)**. Since strained allene **1(8)** readily dimerizes at ambient temperature,[16] it was prepared at < 0°C, then immediately reacted at -60°C with dibromocarbene, generated from CBr_4 and CH_3Li. The monoadduct **37(9)**, a rather sensitive compound, was obtained in 40-60% yield. Even after column chromatography and/or rapid distillation, samples were only about 90% pure, as estimated by ^1H NMR.

Scheme 8 Synthesis of 1,2,3-cyclononatriene, **36(9)**

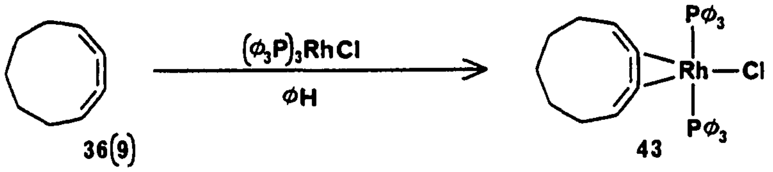


Treatment of an ethereal soln of **37(9)** at -78°C with CH_3Li, followed by aqueous washings at 0°C, afforded a clear liquid, which was shown by spectral data and chemical reactivity to be butatriene **36(9)** (*vide infra*). Samples of **36(9)** were moderately stable to silica gel chromatography and to storage in solution at low temperature, but polymerized rapidly upon evacuation of the solvent, or exposure to air. Such behavior is common for butatrienes. All attempts to crystallize **36(9)** from chromatographed samples failed. Thus rigorous purification of **36(9)** was not achieved.

The ^1H NMR spectrum of slightly impure **36(9)** showed a vinylic triplet ($J = 3.1$ Hz) at δ 5.58 ppm, essentially identical to that for an authentic sample of 1,2,3-cyclodecatriene, **36(10)**.[40] The UV spectrum was slightly red shifted from that of 1,2,3-cyclodecatriene. Olefinic resonances were observed in the ^{13}C NMR spectrum at δ 107.0 (sp^2) and 167.4 (sp) ppm. Hydrogenation over 10% Pd/C yielded cyclononane.

Due to the sensitivity of this strained species, it was decided to devise a chemical derivative which would be stable, isolable, and readily formed by an unambiguous route. The method chosen, η^2 π complexation with Wilkinsons catalyst, $(Ph_3P)_3RhCl$, has been successfully used to complex a series of eight linear butatrienes.[46,47] In all cases, complexation via the central double bond imparted a deformation of α 30°. Due to the enhanced $_2C$-$_3C$ double bond reactivity of cyclic butatrienes, complexation of **36(9)** was expected to be facile and the resulting complex should be much more stable than the parent hydrocarbon.

Reaction of a crude reaction mixture of **36(9)** with one equivalent of Wilkinsons catalyst afforded, after chromatography, a yellow, air-stable, crystalline solid complex, **43** (equation 9). The ^1H NMR spectrum of **43** is shown in Figure 11. Four distinct resonances were attributed to



(9)

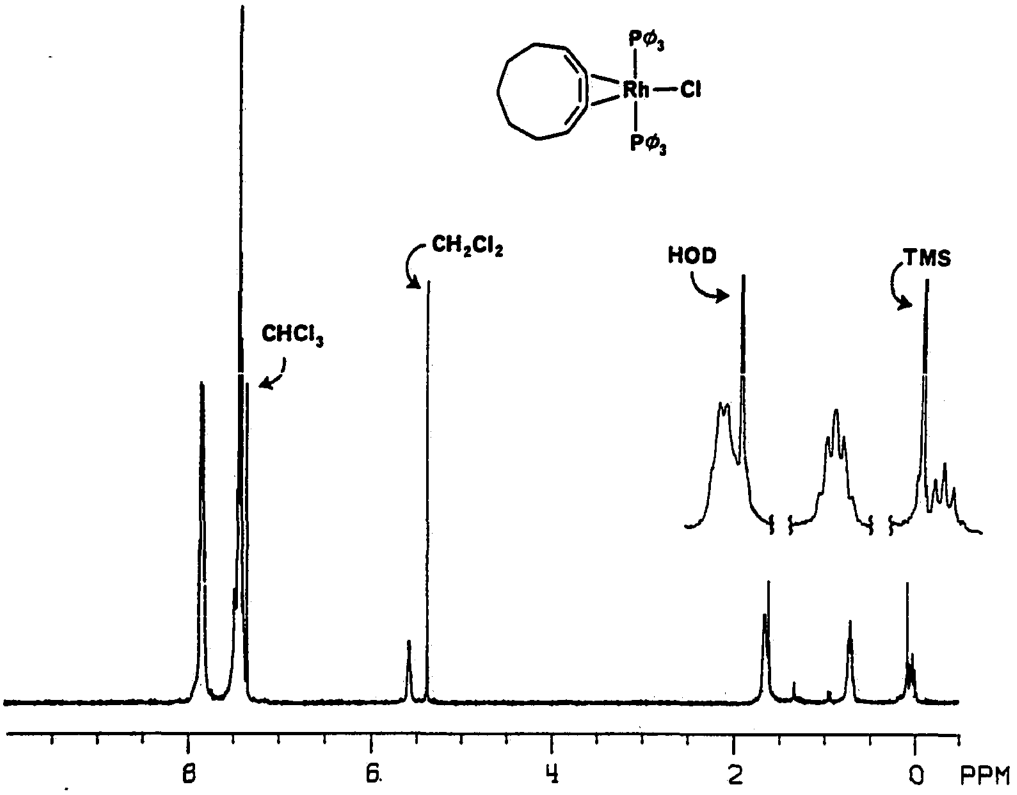


Figure 12. ^1H NMR spectrum of complexed 1,2,3-cyclononatriene

the butatriene ring. Each appears as a broadened complex multiplet. Recording the ^1H NMR spectrum at as low at 190K only reduced the resolution of these multiplets. The vinylic resonance occurs at δ 5.30 ppm. Methylene resonances occur at δ 1.5, 0.6, and -0.06 ppm with integration ratios (relative to the vinylic hydrogens) of 4 : 4 : 2, respectively. These shifts are assigned to the allylic methylene, homoallylic methylene and the $_7CH_2$, respectively. This high field shift of ring methylenes is most likely due to shielding by phenyl rings. The latter are observed as broad complex multiplets at δ 7.7 and 7.3 ppm in a 10 : 20 ratio. These data suggest that the phenyl rings and the chlorine ligand are staggered about the P-Rh bond, forcing localization of phenyl rings above and below the mean butatriene plane. The IR spectrum showed characteristic aromatic and aliphatic absorptions as well as a strong broad peak at 1992 cm^{-1}. The UV spectrum showed maxima at 266 and 365 mm. Fast atom bombardment (FAB) MS was successful in a matrix of *ortho*-nitrophenyloctylether. Although no parent ion was observed, weak peaks at m/e corresponding to parent ion less: a) Cl, b) C_9H_{12}, c) C_9H_{12} and Cl were observed. The intensities of these peaks were in accord with those of other butatriene complexes previously observed by Sharp *et al.*[48]

The structure of complex **43** was unequivocally proved by the solution of its crystal structure. A single crystal was grown from a concentrated solution of **43** in a mixture of *iso*-amyl acetate and pentanes. Crystal data were recorded using a Syntax diffractometer. An ORTEP diagram (hydrogens, except vinylic, are omitted for clarity)

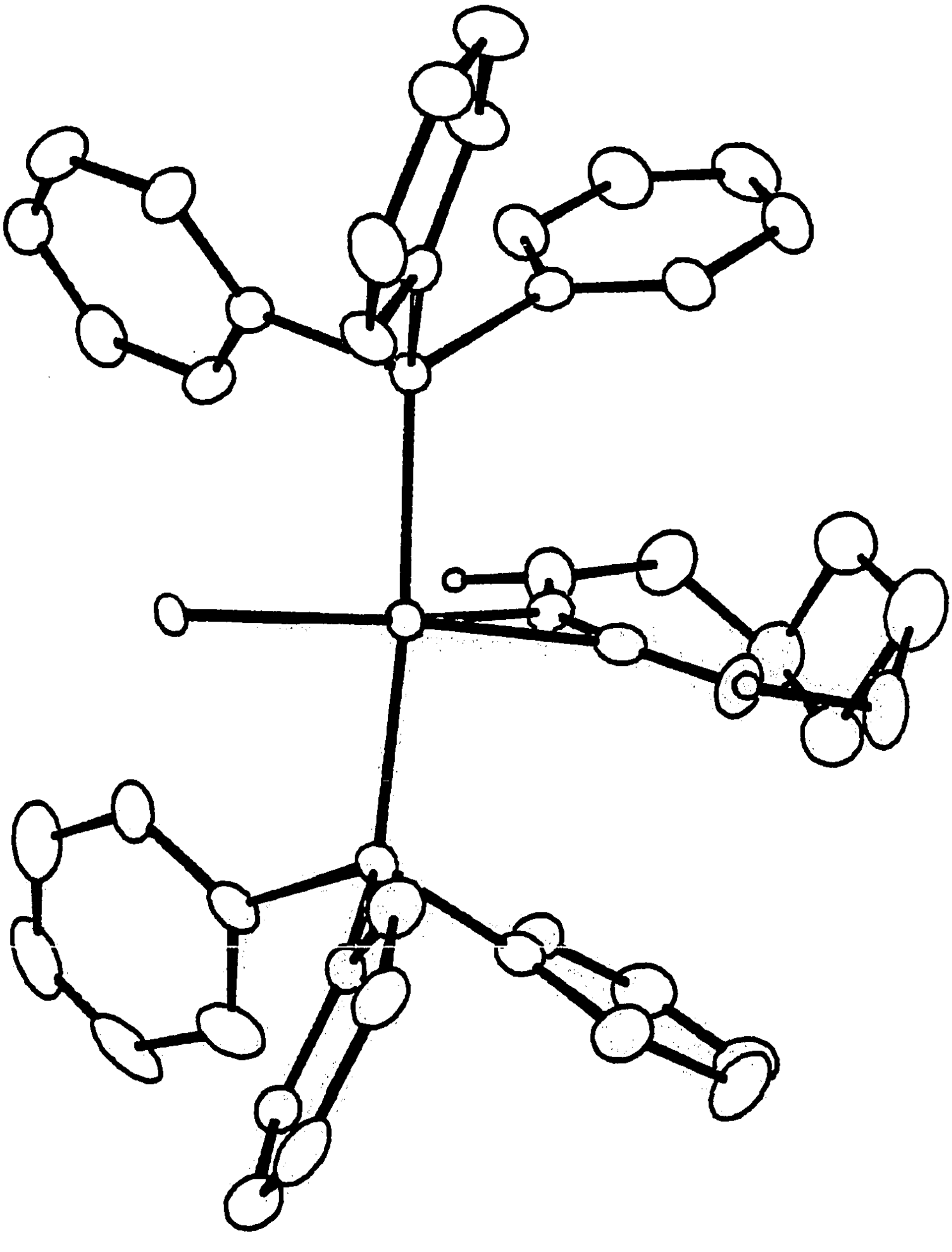


Figure 13. ORTEP representation of complex **43**

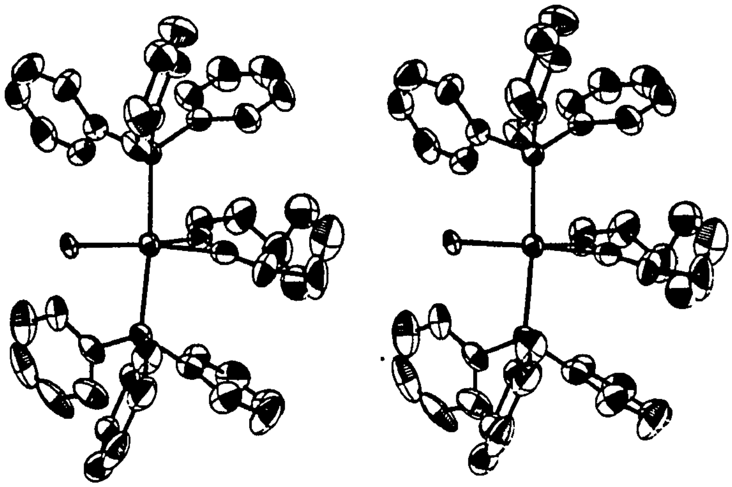


Figure 14. ORTEP stereoview of complex 43

of the structure is shown in Figure 12. A stereoview of **43** is shown in Figure 13. Remarkably, this structure shows two $_7C$ carbon atoms, each of which represents only 50% probability of location within the crystal. Additionally, the homoallylic carbon atoms show skewed elipsoids. This indicates that **43** is either conformationally fluxional in the crystal at ambient temperature or the crystal exists as an equal admixture of two conformers.

Conclusions

The MNDO bending potential for 1,2,3-butatriene suggests that a small amount of bending (10-20°) should destabilize the molecule by only about 3-10 kcal/mol. Calculations of the cyclic butatrienes **36(5-9)** show a similar amount of strain. In all cases, the butatriene moiety remained planar, indicating that the strain is localized in the central double bond. This strain approximately doubles with each decreasing carbon in the chain.[49]

Cyclononatriene, **36(9)**, bent only ca. 15°, was predicted to be isolable and may well be the smallest isolable cyclic butatriene. This compound was prepared,[49] isolated, and further characterized by complexation with Wilkinsons catalyst. 1,2,3-cyclooctatriene, **36(8)**, probably is too reactive to be isolated. The high reactivity of 1,2,3-cycloheptatriene, **36(7)**, has been shown by Zoch *et al.*[40] 1,2,3-Cyclohexatriene, **36(6)**, which proved too strained to be formed by the method of Schlüter *et al.*,[44] may react by an allowed electrocyclic process to give the ynediene as shown in equation 8 (*vide supra*). The very reactive 1,2,3-cyclopentatriene, if formed, may rearrange to give products attributed to a vinylcarbene (equation 7). These compounds pose difficult synthetic challenges.

Cyclic butatrienes are a fascinating and fundamental class of molecules which have not received much attention. It is hoped that this work will stimulate interest in related structures.

Experimental Section

Experimental details

9,9-Dibromobicyclo[6.1.0]non-1-ene [**37(9)**]. A soln of dibromide (9.71 g, 36.2 mmol) in dry ether (90 mL) was stirred for 15 min at -78°C during dropwise addition of CH_3Li (36.2 mmol). The mixture was warmed to 0°C for 20 min to allow formation of the allene **1(8)**. After cooling to -78°C, CBr_4 (4.81 g, 14.5 mmol) was added, followed by CH_3Li (14.5 mmol). After 0.5 h, the mixture was warmed to 0°, and quenched with ice (1 g). The etheral soln, maintained at 0°, was washed with satd, aq NaCl (3 x 50 mL), H_2O (50 mL), then dried ($MgSO_4$), and concentrated at reduced pressure to yield 7.03 g of yellow liquid. Chromatography (alumina, hexane elution at -25°C), followed by Kugelrohr distillation (85-90°C/0.15 torr), yielded 2 g (about 50% based on CBr_4) of colorless liquid. This was estimated to be 85-90% pure. Spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 6.58 (dd, J = 6.3, 3.1 Hz, 1 H), 2.53-0.96 (multiplet, 11 H); ^{13}C NMR δ 128.9, 126.6, 36.1, 31.4, 31.2, 28.9 (double intensity), 26.6, 23.8; IR (CCl_4) 1759 cm^{-1} (strong, C=C). The mass spectrum showed peaks at m/e 278, 280, and 282, with intensities consistent with a dibromide. Base peak: m/e 91.

<u>1,2,3-Cyclononatriene</u> [**36(9)**]. Freshly prepared dibromide **37(9)** (1.02 g, about 31 mmol) in ether (20 mL) was treated at -78°C with CH_3Li (36 mmol). The mixture was warmed to 0°C and stirred for 0.5 h. The reaction mixture then was quenched with ice (0.5 g), washed with 10% aq NaCl (3 x 15 mL), and H_2O (15 mL), and then dried ($MgSO_4$). Chromatography (Florisil, pentanes) of the partially concentrated soln yielded material estimated to be about 80% pure. Hydrogenation of an aliquot over Pd/C at 0° and 1 atmosphere H_2 yielded cyclononane [<u>ca</u>. 40% from **37(9)**], identical with an authentic sample. Concentration of solutions, or prolonged exposure to oxygen yielded insoluble material. The spectral data for **36(9)** were: 300

MHz ^1H NMR ($CDCl_3$) δ 5.58 (t, J = 3.1 Hz); 2.31 (complex mult, allylic H), 1.73 (complex pent, J ~ 6 Hz); ^{13}C NMR ($CDCl_3$) δ 167.4 (sp), 107.0 (sp^2), 30.8, 28.9, 25.0; IR (CCl_4) 3021 (sh) 2930, 2870, 2835, 1463, 1454, 1442, 1427, 1323, 1245, 854, 667 cm^{-1}; UV $\lambda_{max}^{pentane}$ at 232, 257 and 292 nm.

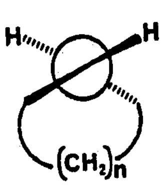
Bis(triphenylphosphine)chloro(2,3-η^2-1,2,3-cyclononatriene)-rhodium, (43). A crude etheral soln of cyclononatriene, 36(9), (610 μmol, estimated from hydrogenation of 2% of the soln) from the previous reaction was employed. The soln was diluted with benzene (10 mL), degassed with Ar, conc to 5 mL at amb temp, and rapidly dissolved in benzene (10 mL). To this, a soln of Wilkinsons' catalyst tris(triphenylphosphine)chloro rhodium (283 mg, 305 μmol) in benzene (20 mL) was added over 5 min. The deep red soln stirred at amb temp while under Ar for 5 h. The resulting pale orange soln was chromatographed (silica gel, 35% $CHCl_3/CCl_4$) to afford 137 mg (57%) of a yellow solid, mp 148-51°C. The spectral data were: 300 MHz ^1H NMR ($CDCl_3$) δ 7.74 (complex mult, 10 H, ArH), 1.57 (br d, J ≈ 4.5 Hz, 4 H, CH_2), 0.63 (br pent, J ≈ 6 Hz, 4 H, CH_2), 0.064 (br t, J ≈ 4-7 Hz, 2 H, CH_2). IR (CCl_4) 3088sh, 3072m, 2935m, 2864w, 1992br, m, 1492m, 1444s, 1097m, 751br, s; UV λ_{max}^{THF} 226 (ε 3.7 x 10^4), 365 (ε 2.2 x 10^3) nm. Fast atom bombardment mass spectrum (ONPOE), m/e 747 (M-Cl), 662 ($M-C_9H_{12}$), 627 ($M-C_9H_{12}-Cl$).

Introduction to *trans* Cyclic Olefins

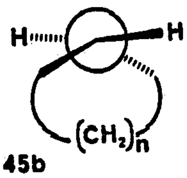
Small ring cyclic *trans* (E) olefins have been extensively studied.[1a,b,d] Many examples of E olefins are rigid bicyclic "bridgehead" olefins;[50] these will be excluded from the present discussion where only simple cyclic *trans* olefins **44(n)** will be considered.

Among this homologous series, the smallest isolable member is *trans*-cyclooctene **44(8)**. Larger members are generally isolable and *trans*-cyclododecene **44(10)** and *trans*-cycloundecene **44(11)** are actually more stable than their corresponding *cis* isomers. The smaller ring homologs, *trans*-cycloheptenes, **44(7)**, *trans*-cycloheptenones, and *trans*-cyclohexenes, **44(6)**, have been implicated in rearrangements and observed spectroscopically. For the next smaller homolog, *trans*-cyclopentene, **44(5)**, no experimental evidence exists.

To a first approximation, incorporation of a *trans* olefin in a cyclic system should impart a torsional (dihedral) deformation which would reduce p-p π overlap of the double bond. A Newman projection for this effect is represented by **45a**. Mock suggested that additional stabilization should be obtained if the p-π orbitals rehybridized by incorporating some s character.[51] The result would be pyramidalization of the π bond carbon atoms as represented by **45b**.

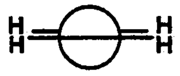


45a

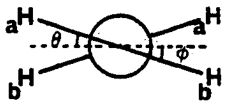


45b

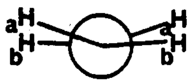
A MO study at the STO-3G level by Radom *et al.* supported this suggestion.[52] Torsional restrictions in ethylene, **46a**, chosen as a model study, were investigated. To examine purely torsional strain, the geometry of ethylene was optimized with the CH_2s of the π system restricted to a 20° dihedral angle ($\theta = \phi = 10°$) as in **46b**. To approximate the situation in a *trans* cyclic olefin, only two *trans* hydrogens, $_aH$, were restricted ($\theta = 10°$) and all other geometric parameters were optimized. The resulting equilibrium geometry, **46c**, was strongly pyramidalized. Relative to **46a**, the STO-3G results suggest that the purely torsional distortion diagramed in **46b** destabilizes the structure by 7.1 kcal/mol while pyramidalization occuring in **46c** reduces this destabilization to 3.0 kcal/mol. Thus pyramidalization affords a means of reducing the strain of the torsional *trans* distortion. Such pyramidalization is evident in the crystal structure of the 3',5'-dinitrobenzoate of *trans*-cyclooctene-3-ol, 47.[53]



46a



46b

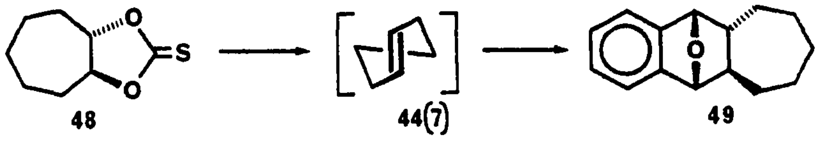


46c

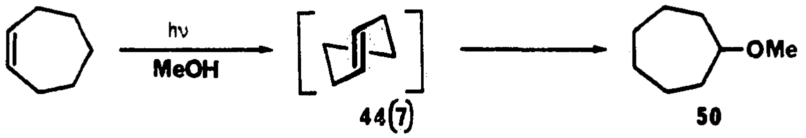
trans-Cyclooctene, **44(8)**, first reported by Cope *et al.* in 1953[54] is, to date, the smallest isolable *trans* cyclic alkene. The chirality inherent in its structure[55,56] was confirmed[57] through its resolution. Optically active **44(8)** retains its enantiomeric purity even after seven days at 61°C.[56] It was suggested that this high barrier to racemization, 36 kcal/mol,[58] results from the destabilization of the transition state in which the vinylic hydrogen passes through the interior of the $-CH_2-$ ring. (Thus, π bond rotation need not occur.) *trans*-Cyclononene, **44(9)**,[58] racemizes much more readily $\Delta G^{\ddagger}_{rac}$ = 20 kcal/mol[58]) as the increased ring size makes it flexible enough for the vinylic hydrogen to pass through the center of the ring. Due to the ease of this conformational racemization, *trans*-cyclodecene, **44(10)**, ($\Delta G^{\ddagger}_{rac}$ = 10 kcal/mol[58]) was too conformationally mobile to be resolved. However, the bulk of dimethyl substitution in *trans*-1,2-dimethylcyclodecene and *trans*-1,2-dimethylcycloundecene allowed the isolation of optically active samples of each to be prepared.[59] In rings smaller than eight carbons, this conformational racemization is impossible.

Trans-cyclooctene, **44(8)**, has been the subject of numerous physical investigations. The strain in **44(8)** was estimated by Traetteberg to be 22 kcal/mol as compared to only 10.4 kcal/mol for the *cis* isomer.[60] From relative heats of hydrogenation, Rogers *et al.* found a 11.4 kcal/mol energy difference between the *cis* and *trans* isomers.[61] A gas phase electron diffraction study indicated that **44(8)** existed in a distorted chair conformation[62] while the X-ray crystal structure of *trans*-cyclooctene-3-ol-3',5'-dinitrobenzoate 47 revealed a C_2 twist conformation.[53] Molecular mechanics calculations also predicted the C_2 twist conformation.[63,64] The dihedral torsion angle of 136°[60] agrees well with the molecular mechanics prediction of 138°.[63]

Smaller *trans*-cyclic olefins have been generated as transient species, which have been trapped and/or observed spectroscopically. The first example of *trans*-cycloheptene, **44(7)**, was reported by Corey *et al.*[65] In their route, transient **44(7)** was generated from the *trans*-thionocarbonate **48** and trapped with DIBF to give adduct **49** (equation 10). Through photochemical generation and a subsequent dark reaction with acidic MeOH, transient **44(7)** was inferred from the product, methoxy cycloheptane **50** (equation 11).[66]



(10)



(11)

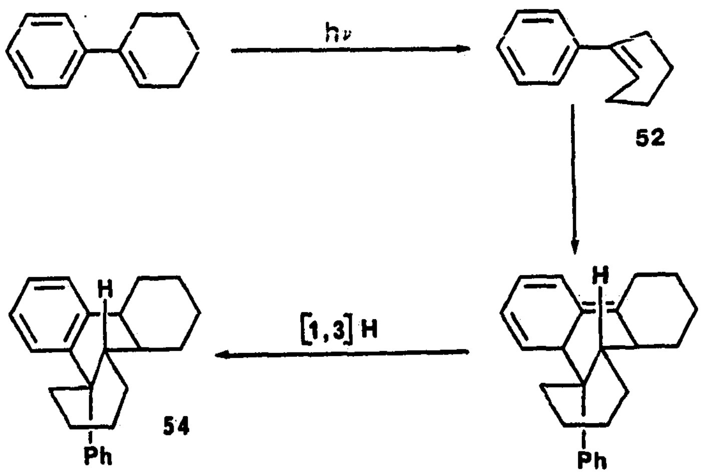
Subsequent kinetic studies on photochemically generated **44(7)** resulted in a calculated ambient temperature lifetime (τ) of 47 sec and an activation energy for *cis-trans* isomerization of 18.7 kcal/mol.[66]

Bonneau *et al.* have also generated *trans*-cyclic olefins by flash photolysis and found that each *trans* olefin was substantially red shifted with respect to its *cis* isomer.[67] Inoue *et al.* have generated **44(7)** and measured a lifetime of 23 min (-10±2°C) for this structure.[68] No examples of free *trans*-cyclohexenes or pentenes have been reported.

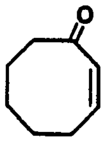
1-Phenyl substitution has been introduced in an attempt to spectroscopically observe small ring *trans*-cyclic olefins. Bonneau *et al.*[69,70] have generated *trans*-1-phenylcycloheptene **51** and hexene **52** from direct irradiation of the corresponding *cis* isomer in both a low temperature glass and in solution. The UV spectrum of **51** and **52** showed absorption maxima at 300 and 380 nm, respectively.[69] *Trans*-1-phenyl cyclohexene **52** has been generated at -75°C by Dauben *et al.* via the above solution method.[71] In methanol, 1-methoxy-1-phenyl cyclohexane, **53**, was isolated. In nonpolar media, however, *trans*-1-phenyl cyclohexene **52** was inferred as in intermediate from the structure of the observed dimer **54** (Scheme 9).[71]

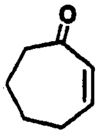
Trans-cyclic olefins have been detected also in conjugated enone systems. *Trans*-cycloocten-2-one **55(8)** and *trans*-cyclohepten-2-one **55(7)** have been prepared by triplet sensitized irradiation of the

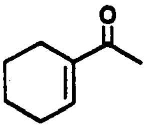
Scheme 9 Generation and trapping of *trans*-1-phenylcyclohexene

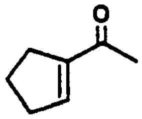


corresponding *cis* isomers.[72,73] For these substrates, *cis-trans* isomerization is the most facile process. Of the two *trans* species, only **55(8)** is stable;[72] the existence of **55(7)** has been inferred by trapping in a dark reaction with electron rich olefins.[73] This concept has been applied to the six and five carbon homologs but no evidence for *cis-trans* isomerization was found; instead, fragmentation was observed.[74] In a series of 1-acetyl cycloalkenes, **56(n)**, photochemical *cis-trans* isomerization was inferred for 1-acetylcyclohexene **56(6)** and larger ring structures;[74] 1-acetylcyclopentene, **56(5)**, however did not isomerize.[74]


55(8)

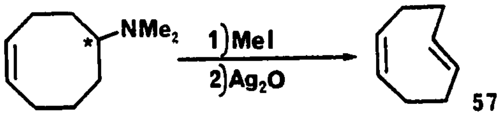

55(7)


56(6)

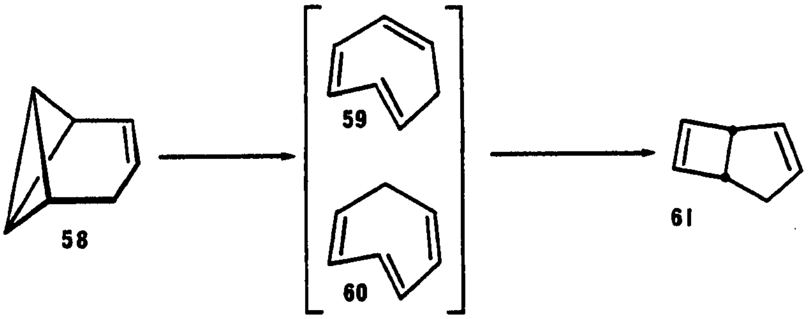

56(5)

A number of cyclic dienes and trienes containing *trans* double bonds have been generated or postulated as reaction intermediates. Cope *et al.* have prepared optically active samples of *cis-trans*-1,5-cyclooctadiene[57a,75] **57** by Hofmann elimination (equation 12). In a novel thermal rearrangement of tricyclic **58** (equation 13), Christl and Brüntrup have implied the existence of *cis,cis,trans*-trienes **59** and/or **60** in the formation of the observed product, **61**.[76] More recently, Coates and Last suggested a *cis,trans*-cycloheptadiene **63** in the rearrangement of **62** (equation 14).[77]

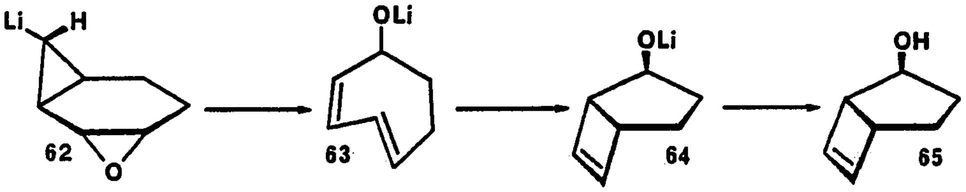
Some examples of *trans*-cyclic olefins complexed to transition metals are known. Platinum complexes have been used in the resolution



(12)



(13)



(14)

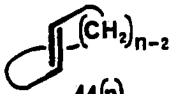
of racemic *trans*-olefin mixtures (*vide supra*). Copper (I) triflate complexes of *cis* cyclic olefins have been shown to isomerize efficiently to the *trans* complex as a result of irradiation.[78] In a study of *trans*-cycloheptene copper(I) complexes, force field calculations of free *trans*-cycloheptene have been performed and the results were compared to MNDO calculations.[79]

Small *trans* cyclic olefins are strained and kinetically reactive molecules. Transient species as small as six carbons have been detected. Kinetic and thermodynamic studies have provided some estimation of the destabilizing effect of the distorted *trans* double bond in known systems. Nevertheless, the limitations of these *trans* alkenes are not thoroughly understood.

trans-Cyclic olefins are a class of molecules which have received little theoretical attention. Only a few structures have been studied, primarily by molecular mechanics and no systematic study of the destabilization and/or limit of existence of these structures has been reported. Such a study would be desirable due to the insight that it may provide, especially into the potential existence of *trans*-cyclopentene.

MNDO Study of *trans*-Cyclic Olefins

The series of *trans*-cyclic olefins containing 5 to 8 carbons, **44(5-8)**, was chosen for this initial study. This selection represents the range from the smallest isolable member, *trans*-cyclooctene **44(8)** to the smallest of which one can easily make a (strained) molecular model, *trans*-cyclopentene, **44(5)**.



44(n)

The geometry of each of these structures was optimized with the MNDO method (*vide supra*) for closed shell configurations. Remarkably, a global minimum was found even for **44(5)**, *trans*-cyclopentene. Such calculations have been previously performed only for **44(7)**;[79] the present geometries for **44(7)** differ significantly only in the value of the $H-{}_1C-{}_2C-H$ dihedral angle.

The geometric parameter which varies most dramatically in this series is, as expected, the H-C=C-H dihedral angle, henceforth referred to as α. For **44(8)**, (α = 165.6°) the rather minimal strain of this stable molecule gives a slightly twisted double bond. At the opposite extreme, **44(5)** shows a badly twisted (α = 142°) double bond. Predicted double bond lengths vary only 0.06Å, from 1.35Å in **44(8)** to 1.41Å in **44(5)**. This is consistent with the expected reduced p-p π overlap. Such stretching frequently is found in small strained ring systems.[49] Vinylic H-C=C bond angles are almost invariant with n, as are the allylic carbon-carbon and carbon-hydrogen bond lengths. For comparison, the equilibrium geometry of *cis*-cyclopentene was also calculated. These data are tabulated (Table 6) and diagramed (Figure 15).

In this series, **44(n)**, n = 5-8, the single configuration SCF heat of formation increases smoothly with decreasing ring size (n). In the previous calculation for **44(7)**, the slightly different geometry gave a small energy difference. With the inclusion of limited (2 x 2) CI, dramatic lowering of all ΔH_f values was observed. These data are tabulated (Table 7). This suggests that a significantly improved representation of the wavefunction would be biconfigurational (*i.e.*, S_2 contributes significantly). Preliminary TCSCF *ab initio* calculations for **44(5)** show about 40% contribution of S_2 to the wavefunction.[80]

For the smallest two structures **44(5)** and **44(6)**, open shell singlet (S_1) and triplet (T_1) configurations were investigated.

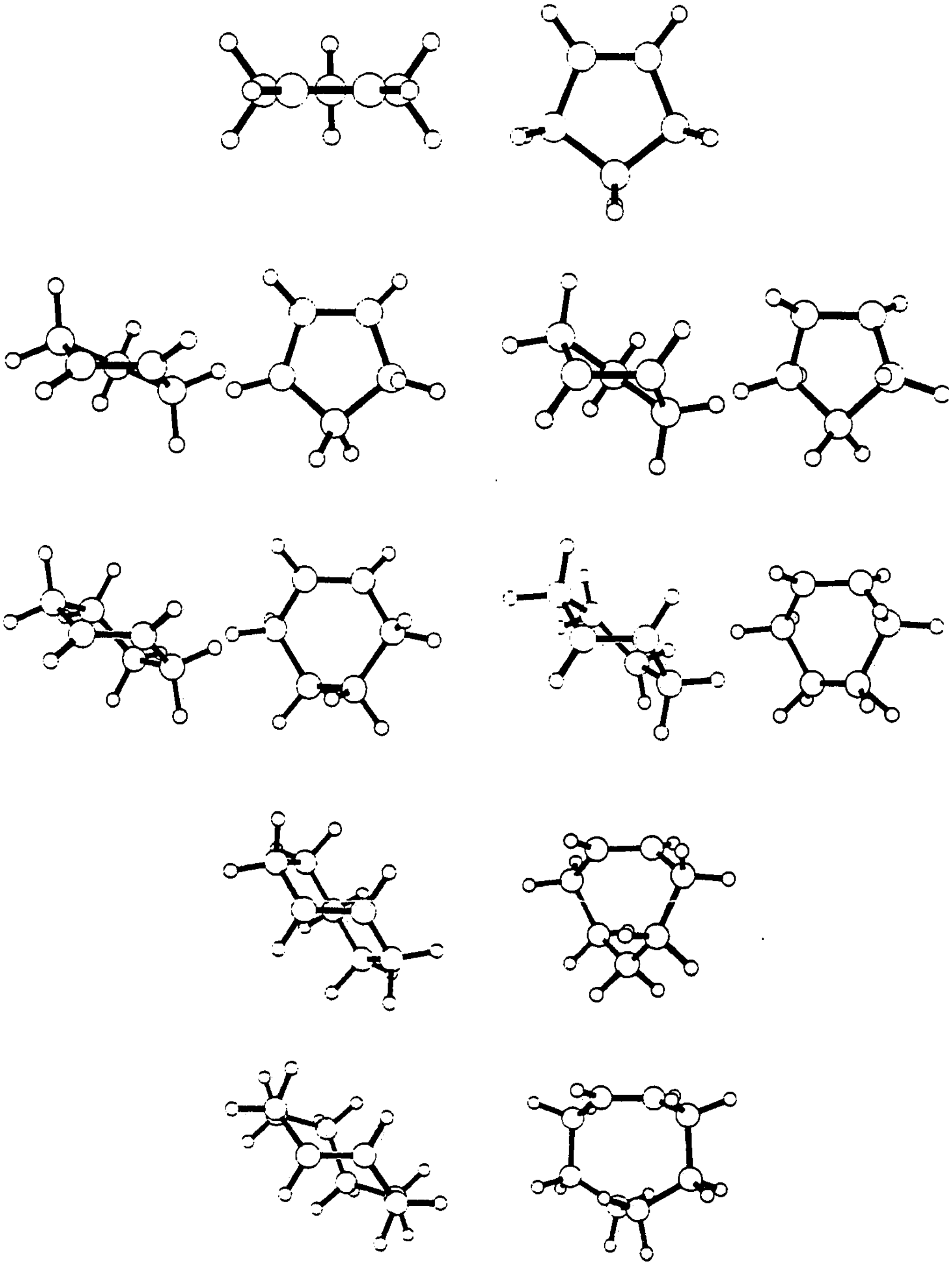


Figure 15. ORTEP representations of *trans* cyclic olefins

Table 6. Selected geometric parameters of *trans* cyclic olefins

			Bond Angle (deg)		Bond Length (Å)		
Structure	State	Formula	$H\text{-}{}_1C{=}{}_2C\text{-}H$	$H\text{-}{}_1C{=}{}_2C$	${}_1C{=}{}_2C$	${}_2C\text{-}{}_3C$	${}_1C\text{-}H$
44(8)	S_0	$t\text{-}C_8H_{14}$	165.6	121.3	1.35	1.50	1.094
44(7)	S_0	$t\text{-}C_7H_{12}$	159.9	122.2	1.36	1.50	1.093
			113.3[a]		1.36[a]	1.50[a]	
44(6)	S_0	$t\text{-}C_6H_{10}$	153.5	122.7	1.38	1.50	1.091
	S_1		81.6	124.8	1.36	1.50	1.097
44(5)	S_0	$t\text{-}C_5H_8$	142.0	124.0	1.41	1.51	1.087
	S_1		72.7	128.6	1.38	1.50	1.087
	S_0	$c\text{-}C_5H_8$	0.08	126.9	1.35	1.51	1.084
	S_1		0.64	125.2	1.44	1.48	1.080

[a] Values previously reported, reference 79.

Geometries for each were optimized as before. *Trans*-singlet geometries were easily obtained; salient geometry and energy data are tabulated (Tables 6 and 7, respectively). Attempted optimization of the geometries of the *trans*-triplet structures afforded only the *cis* equilibrium geometry.

The predicted geometries of the two S_1 structures differ from the corresponding S_0 structures most significantly in the value of the dihedral angle, α, which in S_1 is approximately half of that found in S_0. Surprisingly, the double bond length in S_1 is predicted to be slightly shorter than in S_0. The remaining geometric parameters are about the same, regardless of electron configuration.

Table 7. MNDO heats of formation of *trans*-cyclic olefins

		ΔH_f (kcal/mol)		
Structure	Formula	S_0[a]	S_0/CI[b]	S_1[c]
44(8)	t-C_8H_{14}	4.48	-2.70	
44(7)	t-C_7H_{12}	28.80 23.3[d]	20.17	
44(6)	t-C_6H_{10}	50.61	37.64	89.26
44(5)	t-C_5H_8	93.50	60.46	129.93
	c-C_5H_8	-0.38	-7.09	116.99

[a] SCF calculation of closed shell state.

[b] CI calculation at SCF geometry.

[c] SCF calculation of open-shell singlet state.

[d] MNDO result from reference 79.

The results collected thus far lead to the prediction that open shell (S_1) states of both **44(5)** and **44(6)** are of significantly higher energy (15.0 and 38.6 kcal/mol, respectively) than the S_0 states. With the inclusion of limited CI, S_0 is lowered significantly, S_1 remains unchanged, and the S_0-S_1 energy gap widens to 48.1 and 41.6 kcal/mol, respectively.

This apparent prediction is not based upon a true representation of S_0. Since a significant amount of S_2 contributes to the closed shell state and the geometry was determined via a single configuration SCF procedure, the calculations of this state are clearly in error. In addition, the open shell MNDO results are probably not accurate in this study because the MNDO method overestimates diradical character.

Conclusions

The principal conclusion which can be made from these data is that higher level multiconfiguration calculations will be necessary to properly investigate this system. The MNDO predicted geometries, however, are an excellent starting point for such studies.

If one temporarily ignores the above mentioned flaw, some tentative conclusions about this series of *trans*-cyclic olefins may be drawn. The energy apparently increases smoothly with decreasing ring size and the transition from **44(6)** to **44(5)** represents a substantial increase in destabilization. Dihedral twisting (α) also becomes severe; the geometry of **44(5)** is closer to *cis* than *trans*. These preliminary data seem to indicate that the most substantial energy and geometry differences of this series will occur between **44(5)** and **44(6)**. This is consistent with the experimental observation of substituted *trans*-cyclohexenes and the absence of experimental evidence for **44(5)**. One particularly fascinating possibility is that *trans*-cyclopentene may actually exist as a shallow minimum. This clearly bears further theoretical investigation.

References Cited

1. a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. b) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. c) Wiberg, K. B.; Bonneville, G; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. d) Johnson, R. P. In "Molecular Structures and Energetics"; Liebman, J. F., Greenberg, A., Eds.; Verlag-Chemie International: New York, (publication anticipated in late 1985); Vol. 3.

2. Skattebol, L.; Solomon, S. *Org. Synth.* **1969**, *49*, 35.

3. a) Anet, F. A. L.; Yavari, I. *J. Amer. Chem. Soc.* **1977**, *99*, 7640. b) Traetteberg, M.; Bakken, P.; Almennengen, A. *J. Mol. Struct.* **1981**, *70*, 287.

4. Salem, L. *Acc. Chem. Res.* **1979**, *12*, 87.

5. Lam, B.; Johnson, R. P. *J. Amer. Chem. Soc.* **1983**, *105*, 7479.

6. a) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48. b) Seeger, R.; Krishnan, P.; Pople, J. A.; von R. Schleyer, P. *J. Amer. Chem. Soc.* **1977**, *99*, 7103. c) Dykstra, C. E. *J. Amer. Chem. Soc.* **1977**, *99*, 2060. d) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89. e) Krogh-Jespersen, K. *J. Comput. Chem.* **1982**, *3*, 571, and references therein.

7. Hopf, H. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; John Wiley and Sons: New York, 1980; Part 2, Chapter 20, p. 779.

8. Wittig, G.; Fritze, P. *Angew. Chem. Int. Ed. Eng.* **1966**, *5*, 846.

9. Moore, W. R.; Moser, W. R. *J. Amer. Chem. Soc.* **1970**, *92*, 5469.

10. Dillon, R. W.; Underwood, G. R. *J. Amer. Chem. Soc.* **1974**, *92*, 779.

11. a) Bottini, A. T.; Cabral, L. J.; Dev, V. *Tetrahedron Lett.* **1977**, 615. b) Bottini, A. T.; Carson, F. P.; Fitzgerald, R.; Frost, K. A. *Tetrahedron* **1972**, *28*, 4883. c) Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* **1975**, *31*, 1997. d) Bottini, A. T.; Corson, F. B.; Fitzgerald, R.; Frost, K. A. *Tetrahedron Lett.* **1970**, 4753.

12. Balci, M.; Jones, W. M. *J. Amer. Chem. Soc.* **1980**, *102*, 7607.

13. Wentrup, C.; Gross, G.; Maquestian, A.; Flammary, R. *Angew. Chem. Int. Ed. Eng.* **1983**, *27*, 542.

14. Balci, M.; Jones, W. M. *J. Amer. Chem. Soc.* **1980**, *102*, 7608.

15. Wisser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

16. a) Marquis, E. T.; Gardner, P. *Tetrahedron Lett.* **1966**, 2793. b) Wittig, G.; Dorsch, H. L.; Menske-Schüler, J. *Liebigs Ann. Chem.* **1968**, *711*, 55. c) Reese, C. B.; Shaw, A. *J. Chem. Soc., Chem. Commun.* **1972**, 787.

17. Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *J. Organomet. Chem.*, submitted for publication.

18. a) Montgomery, L. K.; Scardiglia, F.; Roberts, J. D. *J. Amer. Chem. Soc.* **1965**, *87*, 1917. b) Montgomery, L. K.; Applegate, L. E. *J. Amer. Chem. Soc.* **1967**, *89*, 2952. c) Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1972**, *756*, 1.

19. Chapman, O., University of California, Los Angeles, Calif., personal communication, 1984.

20. Berson, J., Yale University, personal communication, 1984.

21. Wasserman, E.; Barash, L.; Trozzolo, A. M.; Murray, R. W.; Yager, W. A. *J. Amer. Chem. Soc.* **1964**, *86*, 2304.

22. a) Moss, R. A. *J. Org. Chem.* **1966**, *31*, 3296. b) Moss, R. A.; Przybla, J. R. *J. Org. Chem.* **1968**, *33*, 3816. c) Durr, H.; Werndorff, F. *Angew. Chem. Int. Ed. Eng.* **1974**, *13*, 483.

23. Johnson, R. P., Iowa State University, Ames, Ia., personal communication, 1984.

24. Tolbert, L. M.; Siddiqui, S. *J. Amer. Chem. Soc.* **1984**, *106*, 5538.

25. Bergman, R. G.; Rajadhyaksha, V. J. *J. Amer. Chem. Soc.* **1970**, *92*, 2163.

26. Klumpp, G. W.; van Dijk, P. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 381.

27. Freeman, P. K.; Swenson, K. E. *J. Org. Chem.* **1982**, *47*, 2033.

28. Balci, M.; Harmandar, M. *Tetrahedron Lett.* **1984**, *25*, 237.

29. Balci, M.; Jones, W. M. *J. Amer. Chem. Soc.* **1981**, *103*, 2874.

30. Lee-Ruff, E.; Maleki, M.; Duperrouzel, P.; Lien, M. H.; Hopkinson, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 346.

31. a) Cuthbertson, A.F.; Glidewell, C.; Hoyd, D. *J. Chem. Res.* **1982**, 80. b) *J. Chem. Res.* **1983**, 48. c) Lloyd, D.; Mackie, R. K.; Richardson, G.; Marshall, D. R. *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 190 and references within.

32. Dewar, M. J. S.; Thiel, W. J. *J. Amer. Chem. Soc.* **1977**, *99*, 4899.

33. Dewar, M. J. S.; Thiel, W. J. *J. Amer. Chem. Soc.* **1977**, *99*, 4907.

34. Valtazanos, P., Iowa State University, Ames, Ia., personal communication, 1985.

35. Johnson, C. K. "FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration". *ORN-3794* (Rev.); Oak Ridge National Laboratory, Oak Ridge, Tenn.

36. Schmidt, M. W.; Angus, Jr., R. O.; Johnson, R. P. *J. Amer. Chem. Soc.* **1982**, *104*, 6838.

37. Angus, Jr., R. O.; Schmidt, M. W.; Johnson, R. P. *J. Amer. Chem. Soc.* **1985**, *107*, 532.

38. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

39. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Amer. Chem. Soc.* **1980**, *102*, 939.

40. Zoch, H. G.; Szeimies, G.; Römer, R.; Schmitt, R. *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 877.

41. Bhagewat, M. M.; Devaprabhakara, D. *Indian J. Chem.* **1975**, *13*, 506.

42. Price, J. P., Iowa State University, Ames, Ia., personal communication, 1985.

43. Moore, W. R.; Ozretich, T. M. *Tetrahedron Lett.* **1967**, 3205.

44. Schlüter, A.-D.; Belzner, J.; Heywang, V.; Szeimies, G. *Tetrahedron Lett.* **1983**, 891.

45. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

46. a) Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720. b) White, M. R.; Stang, P. J. *Organometallics* **1983**, *2*, 1382.

47. Hagelee, L.; West, R.; Culabrese, J.; Norman, J. *J. Amer. Chem. Soc.* **1979**, *101*, 4888.

48. Sharp, T. R.; White, M. R.; Davis, J. F.; Stang, P. J. *Organic Mass Spectrometry* **1984**, *19*, 107.

49. Angus, Jr., R. O.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880.

50. a) Szeimies, G. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, Chapter 5, p. 299. b) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. c) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. d) Wiseman, J. R.; Pletcher, W. A. *J. Amer. Chem. Soc.* **1970**, *92*, 956.

51. Mock, W. L. *Tetrahedron Lett.* **1972**, 475.

52. Radom, L.; Pople, J. A.; Mock, W. L. *Tetrahedron Lett.* **1972**, 479.

53. Ermer, O. *Angew. Chem. Int. Ed. Eng.* **1974**, *13*, 604.

54. Cope, A. C.; Pike, R. A.; Spenser, C. F. *J. Amer. Chem. Soc.* **1953**, *75*, 3212.

55. Nakazaki, M.; Yamamoto, K.; Naemura, K. *Top. Curr. Chem.* **1984**, *125*, 1.

56. Bloomquist, A. T.; Liu, L. H.; Bohrer, J. C. *J. Amer. Chem. Soc.* **1952**, *74*, 3643.

57. a) Cope, A. C.; Ganellin, C. R.; Johnson, H. W.; von Auken, T. V.; Winkler, H. J. S. *J. Amer. Chem. Soc.* **1963**, *85*, 3276. b) Cope, A. C.; Ganellin, C. R.; Johnson, H. W. *J. Amer. Chem. Soc.* **1962**, *84*, 3191.

58. Cope, A. C.; Pawson, B. A. *J. Amer. Chem. Soc.* **1965**, *87*, 3649.

59. Marshal, J. A.; Konicek, T. R.; Flynn, K. E. *J. Amer. Chem. Soc.* **1980**, *102*, 3287.

60. Traetteberg, M. *Acta Chem. Scand., Ser. B.* **1975**, *29*, 29.

61. Rogers, D. W.; Voitkenberg, H.; Allinger, N. L. *J. Org. Chem.* **1978**, *43*, 360.

62. Galvin, Jr., R. M.; Wang, Z. F. *J. Amer. Chem. Soc.* **1973**, *95*, 1425.

63. Ermer, O. *Struct. Bonding* **1976**, *27*, 196.

64. Allinger, N. L.; Sprague, J. T. *J. Amer. Chem. Soc.* **1972**, *94*, 5734.

65. Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Amer. Chem. Soc.* **1965**, *87*, 934.

66. Inoue, Y.; Veoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1031.

67. Bonneau, R.; Joussot-Dubien, J.; Yarwood, J.; Pereyre, J. *Nouveau. J. Chim.* **1977**, *1*, 31.

68. Inoue, Y.; Takamura, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635.

69. Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. Y. *J. Amer. Chem. Soc.* **1976**, *98*, 4329.

70. Bonneau, R.; Joussot-Dubien, J.; Yarwood, A. Y.; Pereyre, J. *Tetrehedron Lett.* **1977**, 235.

71. Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Amer. Chem. Soc.* **1979**, *101*, 6383.

72. Eaton, P. E.; Lin, K. *J. Amer. Chem. Soc.* **1964**, *86*, 2087.

73. Corey, E. J.; Tada, M.; LeMahieu, R.; Libit, L. *J. Amer. Chem. Soc.* **1965**, *87*, 2051.

74. Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50.

75. Cope, A. C.; Howell, C. F.; Knowles, A. *J. Amer. Chem. Soc.* **1962**, *84*, 3190.

76. Christl, M.; Brüntrup, G. *Angew. Chem. Int. Ed. Eng.* **1974**, *13*, 208.

77. Coates, R. M.; Last, L. A. *J. Amer. Chem. Soc.* **1983**, *105*, 7322.

78. Evers, J. Th. M.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1979**, *78*, 423.

79. Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Amer. Chem. Soc.* **1983**, *105*, 4550.

80. Johnson, R. P., Iowa State University, Ames, Ia., personal communication, 1985.

GENERAL CONCLUSION

In this work, a novel class of olefins was introduced and investigated; significant progress was made toward synthesis of its members. During the investigation of this synthetic strategy, a useful approach to a synthetic equivalent of 1,2,3-butatriene was developed. Theoretical investigation of small ring cyclic butatrienes lead to the first synthesis of 1,2,3-cyclononatriene. In depth theoretical studies of the racemization barrier of small ring cyclic allenes supported the experimental observation of twisted (C_2) 1,2-cyclohexadiene and lead to the remarkable prediction that C_2 1,2-cyclopentadiene may exist as a shallow energy minimum. Overall, this work demonstrates how molecular orbital methods can be an important tool of the physical organic chemist, and makes a fundamental contribution to our understanding of structural limitations in organic compounds.

ACKNOWLEDGMENTS

For my success during this project, I owe gratitude to many. To Dr. Johnson, I owe thanks for the conception of this project, his guidance throughout my graduate experience, and his persistence during times of slow progress. During this work, I had the pleasure of guiding both Cathie Hawtrie and David Weissing through their own benzocyclobutene syntheses and, for their participation, I am grateful. Funding was kindly provided by the Petroleum Research Foundation.

Such a diverse project required collaboration in fields in which I am not proficient. I thank Michael W. Schmidt for his interest and participation in the cyclic allene *ab initio* investigation. For their assistance with the Ames Laboratory VAX system and unending willingness to explain MO theory I am indebted to Petros Valtazanos and Steve Elbert. Thanks go to John McClelland for providing photoacoustic IR spectroscopy and to M. Janakaraman for the many hours spent solving the crystal structure of *bis*(triphenylphosphine)chloro-(2,3-N^2-1,2,3-cyclononatriene)rhodium.

I would like to extend thanks to all the friends whom I have met while living in Ames: housemates Jon Nagy and Joseph Kaczvinsky, with whom I lived for over three years; Rick Grote, for a half year of cycling, rock climbing, and sundry outdoor activities; the Iowa chapter of the Sierra Club for helping me maintain sanity; and the last, Bette the gerbil, for laboratory companionship.

Of course, such an accomplishment could not have been possible without the support and blessing of my parents and for that they deserve more than I have been able to give. I would also like to express my appreciation to Mr. and Mrs. Burke who were like parents to me during my stay in Ames.