INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Electronic control of pi-facial stereoselectivity in the reactions of isodicyclopentadiene and related systems

Gugelchuk, Mary Melinda, Ph.D.

The Ohio State University, 1989
ELECTRONIC CONTROL OF PI-FACIAL STEREOSLECTIVITY IN THE REACTIONS OF
ISODICYCLOPENTADIENE AND RELATED SYSTEMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

by

Mary Melinda Gugelchuk, B.S.

The Ohio State University
1989

Dissertation Committee:
Prof. Leo A. Paquette
Prof. David J. Hart
Prof. Matthew S. Platz

Approved by
Leo A. Paquette
Adviser
Department of Chemistry
To my father
ACKNOWLEDGEMENTS

I would like to express my most sincere gratitude to Professor Leo A. Paquette for his guidance and encouragement during the course of my graduate career.

I also wish to thank my co-workers in the laboratory, past and present, for their insightful discussions and assistance. I am particularly grateful to Dr. Lilahdar Waykole, Dr. Hermann Künzer, Dr. Paul Pansegrau, Dr. Kevin Moriarty and Dr. Paul Galatsis for their guidance. Special thanks goes to Donna Rothe for all the typing and assistance she provided over the years. I am also indebted to Lubrizol for financial assistance in the form of a Graduate Fellowship.

Finally, I would like to thank my family for their love, encouragement and understanding throughout this time and to Professor David Hart for his guidance during my undergraduate training.
VITA

November 27, 1957. ................. Born - Ironton, Ohio

1981. .................................. B.S., cum laude,
                               The Ohio State University
                               Columbus, Ohio

1984-1985. ............................ Graduate Teaching Associate
                               Department of Chemistry
                               The Ohio State University
                               Columbus, Ohio

1985-1989. ............................ Graduate Research Associate
                               Department of Chemistry
                               The Ohio State University
                               Columbus, Ohio

Affiliations

Member, American Chemical Society
Honor Society of Phi Beta Kappa
Honor Society of Phi Kappa Phi

Publications

"Methods for Converting N-Alkyl Lactams to Vinylogous Urethanes and
Vinylogous Amides via (Methylthio)alkylidenumium Salts," Mary M.
Gugelchuk, David J. Hart and Yeun-Min Tsai, J. Org. Chem. 1981, 46,
3671.

"π-Facial and Tautomeric Selectivities during Diels-Alder Capture of
Isodicyclopentadienes by Highly Reactive Dienophiles," Leo A. Paquette,

"Bis(isodicyclopentadienyl) Complexes of the Group 4 Transition Metals.
Stereoselective Synthesis and Crystal Structures of the Titanocene and
Zirconocene Derivatives," Judith C. Gallucci, Bernard Gautheron, Melinda
Gugelchuk, Phillipe Meunier and Leo A. Paquette, Organometallics 1987,
6, 15.


Field of Study

Major Field: Organic Chemistry
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION. ................................................................. 11</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS. .......................................................... 111</td>
</tr>
<tr>
<td>VITA. ........................................................................ 1v</td>
</tr>
<tr>
<td>LIST OF TABLES. .............................................................. v1</td>
</tr>
<tr>
<td>LIST OF FIGURES ..........................................................</td>
</tr>
<tr>
<td>LIST OF SCHEMES ..........................................................</td>
</tr>
<tr>
<td>INTRODUCTION. ............................................................... 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. C Y C L O A D D I T I O N C H E M I S T R Y O F ISODICYCLOPENTADIENE WITH HIGHLY REACTIVE DIENOPHILES</td>
<td>51</td>
</tr>
<tr>
<td>Introduction ............................................................... 51</td>
<td></td>
</tr>
<tr>
<td>Results ........................................................................ 57</td>
<td></td>
</tr>
<tr>
<td>Discussion .................................................................... 65</td>
<td></td>
</tr>
<tr>
<td>II. C Y C L O A D D I T I O N C H E M I S T R Y O F (-)-PINENECYCLOPENTADIENE</td>
<td>69</td>
</tr>
<tr>
<td>Introduction ................................................................ 69</td>
<td></td>
</tr>
<tr>
<td>Results ..........................................................................</td>
<td></td>
</tr>
<tr>
<td>Stereochemical Course of [4 + 2] Cycloadditions to 62 .......... 75</td>
<td></td>
</tr>
<tr>
<td>Synthesis of Dimethylaminofulvene 63 ......................... 79</td>
<td></td>
</tr>
<tr>
<td>Conversion of 63 to Metallocene Derivatives .................. 80</td>
<td></td>
</tr>
<tr>
<td>Discussion .................................................................... 85</td>
<td></td>
</tr>
<tr>
<td>III. R E M O T E E L E C T R O N I C E F F E C T S I N C Y C L O A D D I T I O N R E A C T I O N S O F ( \rho )-X-PHENYLISODICYCLOPENTAFULVENES</td>
<td>88</td>
</tr>
<tr>
<td>Introduction .................................................................. 88</td>
<td></td>
</tr>
<tr>
<td>Part 1. Cycloaddition Chemistry of ( \rho )-X-Phenyl- isodicyclopentafulvenes ................................................. 93</td>
<td></td>
</tr>
<tr>
<td>Results ..........................................................................</td>
<td></td>
</tr>
<tr>
<td>Synthesis of ( \rho )-X-Phenylisodicyclopentafulvenes. ....... 93</td>
<td></td>
</tr>
</tbody>
</table>

v1
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (\pi)-Facial Selectivity Patterns in Cycloadditions with Isodicyclopentadiene (I)</td>
<td>30</td>
</tr>
<tr>
<td>2. (\pi)-Facial Selectivity Patterns in Cycloadditions with Modified Isodicyclopentadienes</td>
<td>35</td>
</tr>
<tr>
<td>3. (\pi)-Facial Selectivity Patterns in Singlet Oxygen Addition to Isodicyclopentadiene and Related Compounds</td>
<td>42</td>
</tr>
<tr>
<td>4. (\pi)-Facial Selectivity Patterns in Electrophilic Additions to Isodicyclopentadienedi Anions</td>
<td>44</td>
</tr>
<tr>
<td>5. (\pi)-Facial Selectivity Patterns in Metal Complexations to Isodicyclopentadienedi Anions and Derivatives</td>
<td>45</td>
</tr>
<tr>
<td>6. Comparison between Measured Vertical Ionization Potentials (I_{\nu,J}) and Calculated Orbital Energies</td>
<td>19</td>
</tr>
<tr>
<td>7. Four-Electron Destabilization Energies of Isodicyclopentadiene and Related Compounds</td>
<td>20</td>
</tr>
<tr>
<td>8. Compilation of Vertical Ionization Potentials (I_{\nu}) for Various Dienophiles and Isodicyclopentadiene</td>
<td>54</td>
</tr>
<tr>
<td>9. Comparative (^1\text{H}) NMR Spectral Data for Cycloadducts 64-72</td>
<td>79</td>
</tr>
<tr>
<td>10. Comparative (^1\text{H}) NMR Data for Metalloenes 75-78 and 80-83</td>
<td>83</td>
</tr>
<tr>
<td>11. Comparative (^1\text{H}) NMR Data for 91 and 92</td>
<td>98</td>
</tr>
<tr>
<td>13. Comparison of Experimentally Determined 91:92 Product Ratios with those Predicted on the Basis of Several Sigma Constants</td>
<td>100</td>
</tr>
<tr>
<td>14. Selected Proton Chemical Shifts of 85</td>
<td>101</td>
</tr>
</tbody>
</table>
15. DSP Analysis of Proton Shifts of 85 against \( \sigma^+ \) Values. . . 101
16. Tabulation of Orbital Energies for 84 . . . . . . . . . . . . . . . 108
17. Results of Linear Regression Analysis of Orbital Energies
   According to Hammett Sigma Values . . . . . . . . . . . . . . . . . . 108
18. Relative Reactivities in Cycloaddition of 84 with
   \((Z)-1,2\text{-bis(phenylsulfonyl)ethylene} . . . . . . . . . . . . . . . . . . . . 110
19. Cycloadduct Product Ratios and Yields from Diels-Alder
   Reaction of Fulvene-linked Aza-crown Ethers and
   \((Z)-1,2\text{-bis(phenylsulfonyl)ethylene} . . . . . . . . . . . . . . . . . . . . 115
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Contour plot of the $\pi$-electron density of the alkene bond in norbornene (32)</td>
<td>12</td>
</tr>
<tr>
<td>2. Origin and direction of nonequivalent HOMO extension of norbornene</td>
<td>13</td>
</tr>
<tr>
<td>3. Schematic representation of the $\pi_s$ orbital of 33 and 34 as obtained with various theoretical methods</td>
<td>17</td>
</tr>
<tr>
<td>4. Contour diagram of 34</td>
<td>17</td>
</tr>
<tr>
<td>5. Interaction between $\pi_s$ and dienophile HOMO for bottom and top attack</td>
<td>18</td>
</tr>
<tr>
<td>6. Lateral view of the STO-3G transition structures for the Diels-Alder reaction of butadiene with ethylene</td>
<td>24</td>
</tr>
<tr>
<td>7. MNDO forced-synchronous transition structures for top and bottom attack of ethylene on isodicyclopentadiene</td>
<td>25</td>
</tr>
<tr>
<td>8. Predicted torsional effects for top and bottom attack on isodicyclopentadiene</td>
<td>26</td>
</tr>
<tr>
<td>9. ORTEP drawings of 39 and 40</td>
<td>27</td>
</tr>
<tr>
<td>10. Newman projection showing the disrotation during endo bending</td>
<td>28</td>
</tr>
<tr>
<td>11. ORTEP drawings of 48. Non-hydrogen atoms are drawn with 50% probability ellipsoids, while hydrogen atoms are drawn with an artificial radius</td>
<td>60</td>
</tr>
<tr>
<td>12. Approach trajectories for anti-Alder cycloaddition to 62</td>
<td>85</td>
</tr>
<tr>
<td>13. Schematic representation of the predicted orbital tilting in the $\pi_s$ + Walsh of 24 and the $\pi_s$ MO of 25</td>
<td>90</td>
</tr>
<tr>
<td>14. Predicted deformation of the $\pi$-lobes of 20/21</td>
<td>91</td>
</tr>
</tbody>
</table>
15. Plot of the $\sigma_R^+$ values of X versus the experimental 91:92 product ratios. ........................................... 99
16. Change in favored FMO interaction with increasing sigma value .............................................................. 106
17. Correlation diagram for ionization energies of 84 .................................................................................. 107
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>SCHEME</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Synthesis of Isodicyclopentadiene (1)</td>
<td>1</td>
</tr>
<tr>
<td>II. Possible Stereochemical Courses in Diels-Alder Additions to Isodicyclopentadiene</td>
<td>2</td>
</tr>
<tr>
<td>III. Possible Angular Adducts from Diels-Alder Capture of Isodicyclopentadiene Tautomers</td>
<td>56</td>
</tr>
<tr>
<td>IV. Synthesis of (-)-Pinencyclopentadiene (62)</td>
<td>75</td>
</tr>
<tr>
<td>V. Preparation of Dimethylaminofulvene (63)</td>
<td>79</td>
</tr>
<tr>
<td>VI. Prototypical Transfer Reactions of 73 and 74</td>
<td>80</td>
</tr>
<tr>
<td>VII. Separation-Regeneration Scheme for Ferrocene Compounds (75-76)</td>
<td>82</td>
</tr>
<tr>
<td>VIII. Reaction Sequence for Separation of Ruthenocene Compounds (82-83)</td>
<td>84</td>
</tr>
<tr>
<td>IX. Preparation of Isodicyclopentafulvenes (84)</td>
<td>94</td>
</tr>
<tr>
<td>X. Preparation of Aldehydes (95a and 95b)</td>
<td>112</td>
</tr>
<tr>
<td>XI. Preparation of (-)-α-Fenchocamphorone (105)</td>
<td>123</td>
</tr>
<tr>
<td>XII. Proposed Mechanism for the Skattebøl Rearrangement</td>
<td>126</td>
</tr>
<tr>
<td>XIII. Proposed Synthetic Approach to 100 via Skattebøl Rearrangement</td>
<td>127</td>
</tr>
<tr>
<td>XIV. Proposed Synthetic Route to 100 via Wadsworth-Horner-Emmons Cyclization</td>
<td>128</td>
</tr>
<tr>
<td>XV. Proposed Route to 100 using Dimethyl 3-bromo-2-ethoxypropenylphosphonate</td>
<td>130</td>
</tr>
<tr>
<td>XVI. Proposed Route to 100 using Twofold Wittig Condensation</td>
<td>131</td>
</tr>
<tr>
<td>XVII. Synthesis of 5,5-Dimethylnorbornene</td>
<td>132</td>
</tr>
</tbody>
</table>
INTRODUCTION

REVIEW OF ISODICYCLOPENTADIENE CHEMISTRY

A great deal of experimental and theoretical investigation has been directed towards unraveling the origins of $\pi$-facial stereoselection in reactions of isodicyclopentadiene (1) since the initial report of its synthesis and Diels-Alder reactivity by Alder and coworkers in 1956. Their extremely direct route for preparing isodicyclopentadiene (1) is still the method of choice even though more exotic methodology exists today (Scheme I).

Scheme I. Synthesis of Isodicyclopentadiene (1).
The \( n \)-faces of isodicyclopentadiene are topographically distinct by virtue of the methano and ethano bridges. Therefore, two stereochemical courses are possible for the Diels-Alder addition of dienophiles. Above-plane attack on the methano side (also called exo addition) produces the anti-sesquinorbornene structure whereas below-plane attack (endo addition) yields products possessing the syn-sesquinorbornene architecture (Scheme II).

Scheme II. Possible Stereochemical Courses in Diels-Alder Additions to Isodicyclopentadiene.
The extraordinary degree of \( \pi \)-facial stereoselection in cycloadditions with isodicyclopentadiene and a wide variety of dienophiles has been solidly demonstrated. The results are summarized in Table 1. In most cases, there is an overwhelming preference for kinetically controlled below-plane capture of the dienophile. A few notable exceptions will be mentioned.

Maleic anhydride, historically the first dienophile reacted with isodicyclopentadiene, was reported by Alder\(^1\) to give a single cycloadduct. The product was tentatively assigned the anti/endo configuration 2. Several decades later, the stereochemistry of this reaction was reinvestigated by Paquette\(^2\). Exclusive formation of syn-sesquinoorbornene adducts 3 and 4 in a 2:1 ratio was observed. The stereochemical assignments were supported by chemical conversion of each isomer to a common structure. Shortly thereafter, Bartlett\(^3\) published their study of this reaction. In contrast, the Bartlett group found only the formation of syn/exo 3 and anti/endo 2 isomers. The stereochemistries were confirmed by X-ray crystallography. Moreover, the \( \pi \)-facial preference was modest and could be changed slightly by variations in solvent and reaction temperature (i.e., 55-35:45-65 respectively for 3:2).

![Diagram 2](image2.png)

![Diagram 3](image3.png)

![Diagram 4](image4.png)
While the examples are extremely rare, Bartlett\textsuperscript{14} demonstrated reversibility could be an important factor in some cases. The reaction of isodicyclopentadiene and tetracyanoethylene produced only the above-plane adduct (5) when the reaction and all subsequent manipulations are conducted below 0 °C. In solution at room temperature, 5 partially rearranged to the syn-isomer (6). The equilibrium ratio being 6.5:1 (5:6). Equilibration of cycloadduct with other isomeric cycloadducts has been demonstrated in only two other cases\textsuperscript{3b,17}. There are also two cases where equilibration of cycloadducts with the cycloaddends has been witnessed\textsuperscript{20,22a}.

![Diagram of 5 and 6]

An example where steric demand of the dienophile is thought to govern the \(\pi\)-facial selectivity is found with \textit{cis}- and \textit{trans}-1,2-bis(phenylsulfonyl)ethylene (7 and 8)\textsuperscript{10}. Cycloaddition of 8 with isodicyclopentadiene proceeds with exclusive top-face stereoselectivity to give adduct 9. The \textit{cis} isomer 7, on the other hand, affords a mixture of 10 and 11 in which there is a slight preponderance of the above-plane adduct (1.2:1 ratio).

![Diagram of 7 and 8]
It should be noted that the dehydro congener (12) of isodicyclopentadiene reacts with 8 to give a mixture of syn- and anti-adducts (13 and 14) in a ratio of 92:80:8-20 depending upon solvent and reaction temperature\textsuperscript{10}. This preference for top-face addition is consistent with that previously established by isodicyclopentadiene with this dienophile.
When 12 reacts with the cis isomer (7), only below-plane capture occurs. This result is in contrast to that with isodicyclopentadiene where stereoselectivity is substantially decreased (vide supra) and above-plane capture is slightly favored.

Perhaps the most enigmatic of the known exceptions are the triazolinediones. The stereochemical behavior of 1 and 12 with N-methyltriazolinedione was first reported by Paquette and coworkers\(^5\). A single stereoisomer was produced by both sources. The urazole products were assigned the syn-sesquino[2.2.1]bornene structure (15) on the basis of chemical interconversion and transformation to a known structure. In obvious contradiction, Bartlett published the observation of exclusive anti-adduct (16a) formation in the reaction of 1 with N-phenyltriazolinedione\(^14\). Structural proof was obtained by X-ray crystallography.

\[ \text{15} \quad \text{a saturated} \quad \text{b unsaturated} \]

The Paquette group later reexamined the stereochemical outcome of these reactions\(^6\) and found that isodicyclopentadiene reacted with the pair of triazolinediones to give only above-plane adducts (16a) whereas dehydroisodicyclopentadiene (12) provided only below-plane adducts.
(15b). An X-ray crystal structure confirmed the stereochemistry of the product \((16a, R = \text{Me})\). This complete crossover in \(\pi\)-facial stereoselection in going from the diene 1 to the triene 12 is unique to the triazolinediones. With most common dienophiles, 1 and 12 follow similar facial-bonding trends (see Tables 1 and 2).

Paquette suggested\(^6\) that the early timing of this transition state may cause the triazolinediones to add preferentially in Alder fashion whereby a unique sensitivity to steric effects becomes significant. Alternatively, these dienophiles possess an additional \(\pi\)-orbital orientated orthogonal to that involved in bonding that could strongly perturb the FMO's of the diene and triene resulting in alteration of bonding patterns.

In contrast to other dienophiles, singlet oxygen reactions with isodicyclopentadiene (1) and its dehydro derivative (12) proceed with only moderate facial stereoselectivity in favor of endo attack (Table 3). This reduction of selectivity was attributed to the difference in ionization potentials of singlet oxygen (16.12 eV) and normal dienophiles (10.5 - 11.5 eV)\(^5\)\(^0\)\(^a\).

In an attempt to discern the prominent factors responsible for stereoselectivity in this system, much experimental data have been gathered on structurally and electronically modified isodicyclopentadienes. Their \(\pi\)-facial selectivities in cycloaddition reactions are well documented. Table 2 summarizes the results. As can be seen from these studies, \(\pi\)-facial selectivities can be reversed or become virtually indiscriminate by very subtle structural changes.

For example, substitution at the methano bridge by isopropylidene
(17) or spirocyclopropyl (18) groups resulted in a loss of stereoselectivity in their reactions with N-phenylmaleimide and benzoquinone\(^{17,18}\).

The furan derivative 19, however, exhibited exclusive above-plane selectivity in contrast to its parent compound which gave solely below-plane cycloadducts\(^{8,18,22}\).

Conversion of the diene moiety to a fulvene system had little effect on the previously established facial preferences. Below-plane capture was still preferred by 20 and 21 with N-phenylmaleimide\(^{19a,20}\).
Fulvene 22 gave exclusive below-plane addition in contrast to 18 where dienophiles were facially indiscriminant\textsuperscript{19a}. In the case of 23, there was essentially no bonding preference in Diels-Alder addition with N-phenylmaleimide which is comparable to the parent system 17\textsuperscript{19a}.

![Diagrams of compounds 22 and 23]

An interesting crossover in facial selection was found with the spirocyclopropyl (24) and spirocyclopentyl (25) compounds. Spirocypropyl substitution was seen to still be conducive to exclusive below-plane addition\textsuperscript{21}. A complete change in facial preference was found for the spirocyclopentyl derivative. There was sole formation of above-plane cycloadducts. The only exception was with dimethyl acetylene-dicarboxylate where a 75:25 mixture of bottom to top addition occurred\textsuperscript{21}.

![Diagrams of compounds 24 and 25]

A change in the ring size of the bicyclic moiety as in 26, reduced the facial selectivity with the top-face adduct now being the major
product. In 27, the perturbation causes a reversal in bonding patterns. Only above-plane addition occurred except with dimethyl acetylenedicarboxylate which was indiscriminant.

Aside from cycloaddition chemistry, the observance of a remarkable degree of facial selectivity has also been found in the addition of electrophiles (Table 4) and in metal complexation to the isodicyclopentadiene anion (Table 5). Electrophiles predominantly add from the bottom face of 28. In contrast, the dehydro anion (29) gave 50:50 mixtures of below-plane to above-plane products.

The stereochemistry of metallocene formation with isodicyclopentadiene has been examined. In most cases there is an overwhelming preference for top-face bonding of the metal (see Table 4). However, in making mixed metallocenes, a temperature dependence on facial selectivity was observed. Keeping the reaction at dry ice-
acetone temperatures led to the exclusive formation of bottom-face complexes (e.g., 30), but if the reaction was run at room temperature or in refluxing tetrahydrofuran only top-face complexes (e.g., 31) were found.

Theoretical Analyses of Isodicyclopentadiene $\pi$-Facial Stereoselectivity

Dissection of the origins of $\pi$-facial stereoselection displayed by norbornyl-fused cyclopentadienes into its respective components has been a very fertile area. Over the years, a variety of theories have been put forth that attempt to rationalize the experimentally observed selectivity. However, the relative importance of these explanations remains to be unquestionably demonstrated.

Isodicyclopentadiene (1) contains a norbornane skeleton fused to the cyclopentadiene ring. This architecture provides an opportunity for examining the likelihood of electronic effects emanating from the bicyclo[2.2.1]heptyl frame since steric effects are lessened by moving the reaction site one atom out from the norbornyl fragment.
The possible existence of electronic factors controlling stereoselectivity was first examined by Fukui\textsuperscript{51} in his study of the preferential exo attack of electrophiles on norbornene (32). In this classic example of $\sigma/\pi$ interaction, Fukui determined by using second-order perturbation theory that the $\sigma$ electrons associated with the strained bridge of norbornene enter into $\sigma-\pi$ mixing with the olefinic orbital. As a result, the HOMO of norbornene extends non-equivalently in the exo and endo directions. A contour plot of the $\pi$-electron density is shown in Figure 1.

![Contour plot of the $\pi$-electron density of the alkene bond in norbornene (32).](image)

This non-equivalent frontier orbital extension causes the electron density to be greater on the exo face. The direction of the orbital extension was predicted on the basis of extended Hückel theory (EHT) and CNDO/2 calculations. Two significant modes of interactions were suggested. One is a stronger hyperconjugation with the methano bridge than with the ethano bridge. The other is a back-side interaction with the anti $\text{C-H}$ bond at the 7-carbon. Both interactions occur on the exo side of the $\pi$ orbital (see Figure 2).
Figure 2. Origin and direction of nonequivalent HOMO extension of norbornene.

Liotta has also advanced the principle of "orbital distortion"\textsuperscript{52} to account for the observed stereochemistry of allylic nucleophilic displacements\textsuperscript{53} and nucleophilic and electrophilic additions to enone and enol systems\textsuperscript{54}.

Wipff and Morokuma determined the fully optimized \textit{ab initio} (STO-3G) structures of norbornene and norbornadiene which revealed the nonplanarity of the $\pi$ systems\textsuperscript{55}. The C-H olefinic bonds are slightly bent endo. The out-of-plane deviation ($\theta$) is larger in norbornene ($4.9^\circ$) than in norbornadiene ($2.3^\circ$). The plot of the HOMO corroborated Fukui's orbital extension effect. This nonplanarity enhances the exo/endo differences as expected from perturbation results.

Independently, Houk and Geleter have also carried out these calculations and found similar deviations for norbornene ($3.4^\circ-4.2^\circ$)\textsuperscript{56a,56b} and norbornadiene ($1.7^\circ$)\textsuperscript{56a}. 
The concept of orbital tilting has been presented by Ito and Kakeh\textsuperscript{57} and was used to explain the non-equivalent orbital extension of norbornene in the exo direction. The tilt of (s,p)-hybrid $\sigma$-orbitals is involved and leads to a hybridization change on the basis of a hyperconjugative four-electron interaction between the methano-bridge methylene and the double bond. The orbital tilting is specified in such a way that the HOMO-HOMO minimum and HOMO-LUMO maximum overlap may be realized.

Gleiter also describes the $\sigma/\pi$ interaction in terms of a hyperconjugative mechanism\textsuperscript{58}. Hyperconjugation effects in norbornene are characterized by a marked repulsion between the $\pi$ orbital and occupied orbitals associated with the exo methylene bridge. Bending the double bond endo, the $\pi$ orbital is tilted away from the exo bridge; however, the $\pi\sigma$ orbital lobes are simultaneously rotated such that overlap with $\sigma$ orbitals of the bridge is efficiently reduced. As a result, repulsive interactions are reduced during endo bending.

The importance of these electronic influences on the preferred stereoselective course of addition to norbornene systems has yet to be universally accepted. Other explanations include steric effects\textsuperscript{59} where steric hindrance due to the endo C-5 and C-6 hydrogens blocks
endo attack, torsional effects\textsuperscript{60} in which a minimization of torsional effects involving the bridgehead C-H bond and the vinylic hydrogen occurs during exo attack, and anti-periplanar (or staggering) effects\textsuperscript{61} where the alkene pyramidalizes so as to produce a partially staggered conformation. By this mechanism, torsional strain is relieved in the ground state. Exo attack is promoted in the transition state due to the lower torsional strain present since nearly ideal staggering of the partially formed bonds can occur during exo attack. The tendency for staggering of vicinal bonds with respect to partially formed bonds was proposed to be greater than for fully formed bonds. This is essentially an application of the effect described by Felkin\textsuperscript{62a,b} and Ahn\textsuperscript{62c,d} for nucleophilic additions to carbonyl groups.

Fukui's non-equivalent orbital extension, Gleiter's hyperconjugative effects, and Houk's antiperiplanar effect have all been advanced as candidates for Huisgen's "x" factor\textsuperscript{63}. This "x" factor is responsible for providing the norbornene double bond with its extra reactivity and stereoselectivity.

Heilbronner and Schmelzer\textsuperscript{64} developed a method for analyzing interactions between various fragments of a molecule, such as $\sigma$-$\pi$ orbital mixing or $\pi$-$\pi$ orbital interactions. In this method, the set of occupied canonical molecular orbitals (CMO) is transformed into a set of localized molecular orbitals (LMO) or symmetry-adapted semilocalized molecular orbitals (SLMO) and precanonical molecular orbitals (PCMO).

Their analysis, carried out for cyclohexene and norbornadiene, shows that a strong interaction between $\sigma$ and $\pi$ wave functions in a molecule results in a disrotation of the $\pi$ lobes. The change in the
wave function is largely dependent upon the relative position of the basis orbital energies of the interacting wave functions and the size of the matrix element $F_{\mu\nu}$ (the interaction element with the $\mu$th localized orbital and the $\nu$th ribbon-type $\sigma$ orbital). With increasing $F_{\mu\nu}$, the level of the interaction is increased and the $\pi$ lobes experience progressively greater disrotation.

Paquette and Gleiter have applied this analysis to the simpler systems 33 and 34, as models to rationalize the stereoselective behavior exhibited by isodicyclopentadiene in its Diels-Alder reactions.

Semiempirical (MINDO/3, SPINDO, EHT, modified INDO) and ab initio (STO-3G) methods were used to calculate the orbital energies and the results compared to experimental photoelectron data. The INDO and SPINDO methods were judged most suitable for predicting the effect of $\sigma/\pi$ interaction. They found that the HOMO's of 33 and 34 do not significantly interact with the $\sigma$ frame. However, strong mixing occurs between the lowest occupied $\pi$ orbital ($\pi_s$) and the high-lying $\sigma$ orbitals of proper symmetry, causing disrotation of the terminal $\pi$ lobes of the butadiene fragment. As a result, the electron density is enhanced syn to the methano bridge. The central $\pi$ lobes rotate in the opposite way. The precise ordering (i.e., $\pi$ level above or below $\sigma$) is crucial.
MINDO/3 calculations predict opposite rotation in comparison to other methods. The MINDO/3 and EH procedures insert the $\sigma$ orbital between the $\pi$ orbitals whereas SPINDO, INDO, and STO-3G predict the $\pi$ orbitals above the $\sigma$ orbital. This is shown in Figure 3.

![Figure 3. Schematic representation of the $\pi_s$ orbital of 33 and 34 as obtained with various theoretical methods.](image)

The rotation of the terminal $\pi$ lobes for $\pi_s$ of 34 can be easily recognized in the contour diagram (Figure 4). The various theoretical methods predict levels of 20-40% $\sigma$ admixture at the diene carbon centers.

![Figure 4. Contour diagram of 34.](image)

The preferred addition of a dienophile anti to the methano bridge results from a smaller antibonding interaction between $\pi_s$ of the butadiene and the HOMO of the dienophile due to the different overlap
between the rotated π orbitals and the dienophile. This is shown qualitatively in Figure 5.

Figure 5. Interaction between π\(_S\) and dienophile HOMO for bottom and top attack.

According to this theory, the stereochemical preference is a result of an interaction between occupied molecular orbitals of the reacting partners.
The $\sigma/\pi$ interaction analysis was also extended to isodicyclopentadiene (1) and the dehydro compound (12). The photoelectron spectra were recorded and the data compared to that calculated by the various methods. The results are shown in Table 6. The photoelectron spectra were interpreted using Koopmans' theorem

\(-e_j = I_{v,j}\).

### Table 6. Comparison between Measured Vertical Ionization Potentials, $I_{v,j}$, and Calculated Orbital Energies (all values in eV).

<table>
<thead>
<tr>
<th>COMPD</th>
<th>$I_{v,j}$</th>
<th>assignment</th>
<th>INDO/3</th>
<th>SPINDO</th>
<th>EHT</th>
<th>INDO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.96</td>
<td>$\pi_A$</td>
<td>-8.60</td>
<td>-9.27</td>
<td>-12.13</td>
<td>-9.76</td>
<td></td>
</tr>
<tr>
<td>9.68</td>
<td>$\pi_S$</td>
<td>-9.80</td>
<td>-10.23</td>
<td>-12.85</td>
<td>-10.27</td>
<td></td>
</tr>
<tr>
<td>10.64</td>
<td>$\sigma$</td>
<td>-9.67</td>
<td>-11.03</td>
<td>-12.74</td>
<td>-10.79</td>
<td></td>
</tr>
<tr>
<td>8.06</td>
<td>$\pi_A$</td>
<td>-8.61</td>
<td>-9.16</td>
<td>-12.12</td>
<td>-9.78</td>
<td></td>
</tr>
<tr>
<td>8.90</td>
<td>$\pi_{\text{bridge}}$</td>
<td>-8.96</td>
<td>-9.87</td>
<td>-12.17</td>
<td>-9.84</td>
<td></td>
</tr>
<tr>
<td>9.85</td>
<td>$\pi_S$</td>
<td>-9.96</td>
<td>-10.18</td>
<td>-12.94</td>
<td>-10.60</td>
<td></td>
</tr>
<tr>
<td>10.50</td>
<td>$\sigma$</td>
<td>-9.73</td>
<td>-11.17</td>
<td>-12.81</td>
<td>-10.86</td>
<td></td>
</tr>
</tbody>
</table>

Again INDO and SPINDO methods gave the most suitable model molecular orbitals. The HOMO, $\pi_A^*$, shows negligible $\sigma/\pi$ interaction but $\pi_S$ interacts significantly with the $\sigma$ ribbon. The disrotation of the $\pi$ lobes leads to enhancement of the amplitudes syn to the methano bridge in $\pi_S$, similar to the case in simpler systems 33 and 34. Therefore, below-plane addition should be favored. Superimposed on this rotation is a second rotation which moves the $\pi\pi$ lobes parallel to the plane of symmetry. This causes a tilting of the terminal lobes away from the methano bridge and toward the ethano bridge. Approach of the dienophile syn to the ethano bridge is more favored since the repulsive interaction is felt at a smaller distance compared to anti approach.

The energy difference for exo and endo attack on 1 and 12 (Table 7)
has been estimated by calculation of the four-electron destabilization energies\textsuperscript{68} between the $\pi_s$ of the diene and the HOMO, $\pi_1$, of ethylene. These energies were calculated according to the following equation where $S_{ij}$ is the group overlap integral between $\pi_s$ and $\pi_1$; $\epsilon_{ij}$ is the average of their one-electron energies taken from PES data [(\(\epsilon_1 + \epsilon_j\))/2]; $H_{ij}$ is the interaction matrix element ($H_{ij} = kS_{ij}$\textsuperscript{69a}, $k = -39.7$ eV\textsuperscript{69b}): 

$$\Delta E_{ij} = 4(\epsilon_{ij}S_{ij} - H_{ij}S_{ij}) \over 1 - S_{ij}^2$$

The Diels-Alder transition state geometry was taken as having a 2.18 Å distance between the reacting centers.

### Table 7. Four-Electron Destabilization Energies of Isodicyclopentadiene and Related Compounds (in kcal/mol).

<table>
<thead>
<tr>
<th>COMPO</th>
<th>$\Delta E_{ij}^{\text{exo}}$</th>
<th>$\Delta E_{ij}^{\text{endo}}$</th>
<th>$\Delta \Delta E_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>![diene]</td>
<td>9.91</td>
<td>5.45</td>
<td>4.45</td>
</tr>
<tr>
<td>![diene]</td>
<td>7.02</td>
<td>3.98</td>
<td>3.04</td>
</tr>
<tr>
<td>![diene]</td>
<td>7.31</td>
<td>8.15</td>
<td>-0.84</td>
</tr>
</tbody>
</table>

The relatively large energy differences explain why below-plane attack is kinetically favored. In the case of the bicyclo[2.2.2]octane-fused system, the $\Delta \Delta E_{ij}$ is significantly reduced and now endo attack is slightly preferred. This is borne out experimentally. A 80:20 mixture of facial isomers (top:bottom) were consistently produced with several dienophiles\textsuperscript{2,5,25}.

A major concern of the $\sigma/\pi$ interaction model is that these
arguments are based on ground state electronic structures thereby assuming a time-independent interaction. Dienophiles that strongly perturb the diene's molecular orbitals in opposition to the ground state $\sigma/\pi$ interaction would not be expected to conform to these predictions.

In a different vein, Houk has proposed that $\pi$-bond pyramidalization of the exocyclic double bond, such as found in 2,3-dimethylenenorbornane, bends the terminal substituents in the exo direction and applied the analogy to isodicyclopentadiene to explain the preference for endo attack.

This theory was subsequently deemed unlikely by the observance of fully stereocontrolled below-plane capture of dienophiles by the fulvene systems shown below. X-ray analysis of 22, 23, and 35 confirmed the expected planar structure for the fulvene moiety.

Vogel has advanced the theory that the facial selection is governed by product stability in which the Bell-Evans-Polanyi principle is followed. In this case, the kinetic stereoselectivity
would parallel the thermodynamic selectivity. Vogel based his proposal on the observed facial selectivity of the oxa-isodicyclopentadiene (36). This furan added to maleic anhydride and dimethyl acetylenedicarboxylate over a range of temperatures (-60 to 120 °C) to give only below-plane adducts. At 21 °C, the cycloadducts could be equilibrated with the cycloaddends. The appearance of the above-plane isomer was never observed. Thus, the products seem to result from both thermodynamic and kinetic control.

\[
\text{36}
\]

The syn-adducts were found to be at least 2 kcal/mol more stable than the anti-adducts. Vogel attributes the relatively high stabilities to the "synergic" effect of the double bond \( \pi \)-anisotropy of the norbornene and 7-oxanorbornene subsystems joined at a common double bond. Later, Vogel observed cases involving substituted 7-oxa-2,3-dimethylenenorbornanes where the kinetic stereoselectivity was not explainable by the stability of the adducts\(^7\). Formation of charge-transfer complexes by the oxygen atom with the dienophile was cited as the cause for the reversal in facial selectivity. More recently, Vogel has prepared and investigated the stereochemical behavior of a variety of substituted exocyclic dienes grafted onto the 7-oxanorbornane skeleton\(^8\). The stereoselective outcome of these Diels-Alder reactions was found to vary with the nature of the dienophile. Coordination of
the dienophile to the oxa-bridge was not uniquely responsible for the observed facial preferences. The results were interpreted as arising from a competition between steric hindrance to the endo-face and a "steroelectronic factor" that is related to the nonplanarity of the norbornene bond and the higher stability of syn- versus anti-sesquino norbornenes.

Product stability arguments had earlier been dismissed by Paquette on the basis of results from their study with substituted 2,3-dimethylenenorbornanes (37 and 38). There is expected to be little thermodynamic difference between top and bottom addition since syn-sesquino norbornene structures are not produced. However, a high degree of below-plane bonding was observed.

![37](image1)

![38](image2)

Recently, Houk and Brown presented a different rationale for stereoselectivity in the reactions of isodicyclopentadienes. Their theory is based on torsional and steric effects in the transition state. From extensive ab initio calculations on the transition structure for the Diels-Alder addition of ethylene and butadiene, there was revealed several detailed geometric features of this transition state. The two reaction partners approach each other in a non-parallel plane fashion. The trajectories of bond formation are nearly tetrahedral on the alkene (109°) and somewhat smaller on the butadiene (101°). As a direct result
of the earliness of the transition state, a 14.9° out-of-plane bending of the hydrogens at C2 and C3 occurs (see Figure 6). There is substantial double bond character in the C1-C2 and C3-C4 bonds. C1 and C4 pyramidalize and rotate inward to achieve overlap of the p orbitals

![Diagram](image)

**Figure 6.** Lateral views of the STO-3G transition structures for the Diels-Alder reaction of Butadiene with Ethylene.

on these carbons with the ethylene termini. To maintain the π-bonding between C1-C2 and C3-C4, the p orbitals at C2 and C3 rotate inward on the side of the diene nearest the dienophile. This is necessarily accompanied by C2 and C3 hydrogen movement toward the attacking dienophile. When norbornene is fused at C2 and C3 of butadiene, the tendency of endo bending will be manifested in a preference for bottom attack in Diels-Alder reactions.

This pyramidalization suggests a direct relationship to the observed bottom-face stereoselection with isodicyclopentadiene (1). MNDO forced-synchronous transition structures were obtained for the reaction of 1 with ethylene. The transition structure for top attack is bent upward 4.2° whereas for bottom attack a 2.8° downward bending is seen. This is shown in Figure 7. The terminal carbons of the diene and
ethylene are significantly pyramidalized. The MNDO calculations, however, favor top attack by 0.3 kcal/mol.

![Diagram](image)

**Figure 7. MNDO forced-synchronous transition structures for top and bottom attack of Ethylene on Isodicyclopentadiene.**

Houk also developed a MM2 model for the reaction which reproduces the experimentally observed facial preferences for a wide variety of modified isodicyclopentadienes and dienophiles. The model was constructed by fixing the atoms of the cyclopentadiene and ethylene moieties at the MNDO geometries for top and bottom additions. The bridgehead atoms were fixed to maintain proper bending at the norbornene-cyclopentadiene fusion. All other atoms were fully optimized with MM2 parameters.

The MM2 calculations revealed an energy difference of 0.4 kcal/mol with bottom attack favored. The norbornene fragment was found to bend in an endo direction as was seen in norbornene itself. The endo bending relieves the torsional strain between bonds attached to atoms 2 and 3 and those attached to atoms 1 and 4 because a more staggered arrangement occurs. For top attack, these same torsional interactions are increased due to a more eclipsed arrangement in the exo bent structure. These
Interactions are illustrated in Figure 8. The Newman projections are viewed down the bond connecting the bridgehead carbon to the carbon at the intersection between the norbornene and cyclopentadiene moieties.

Figure 8. Predicted torsional effects for top and bottom attack on Isodicyclopentadiene.

The difference in torsional strain about the 2-3 bond was calculated to be 0.3 kcal/mol thus making isodicyclopentadiene favor bottom attack by 0.6 kcal/mol. These torsional effects will be more influential in late transition states than in early ones. With large dienophiles, steric effects can override the torsional preferences so that top-face attack becomes favored.

Hehre has meanwhile developed a model based on electrostatic interactions to predict facial selectivity in Diels-Alder cycloadditions. For this model, complementary energy surfaces are matched for the two cycloaddends. Reactions with electron-rich dienes and electron-poor dienophiles will favor addition to the diene face that is more reactive towards electrophiles. The converse will hold for inverse electron demand cycloadditions. Steric effects may overcome electrostatic control.
n-Bond Pyramidalization in Sesquino-bornene Structures

The structures of the syn- and anti-sesquino-bornene adducts have themselves generated a great deal of experimental and theoretical investigation. Bartlett\textsuperscript{3a} discovered from X-ray structures that in the syn-sesquino-bornene adduct (39) from maleic anhydride the C4a-C8a double bond was bent with a 16.4° deviation from planarity in the endo direction. This double bond in the anti-isomer (40) was essentially planar. The ORTEP drawings of these structures are shown below in Figure 9.

Figure 9. ORTEP drawings of 39 and 40.

Many other examples have surfaced\textsuperscript{5,6,8,10,17,18,21,23,77} since this discovery. The bending is a general phenomenon in derivatives of syn-sesquino-bornenenes. Anti-sesquino-bornenenes are generally planar but a few exceptions have been seen. To date, the largest deviations documented for this system are 22.1° found in benzyne adduct 41\textsuperscript{77f,g} and 22.68° found in 42\textsuperscript{47}. 
Bartlett has attributed the non-planarity of the \textit{syn}-sesquinorbornene system to repulsive interactions between the C4a-C8a $\pi$ cloud and the bonds involving C9 and C10. Partial rehybridization at the C4a and C8a centers results, which increases the electron density above the plane. These $\sigma$-$\pi$ repulsions are symmetrical in the anti compound therefore the double bond remains planar\textsuperscript{3a}.

Gleiter proposes the hinge-like bending is a result of $\sigma$-$\pi$ mixing on the basis of extended Huckel calculations\textsuperscript{55b}. The admixture of a contribution corresponding to the double bond causes a disrotatory motion of the $p$ lobes (see Figure 10). Bending endo increases $\phi$ and leads to rotation in the sense shown below. The rotation leads to less effective overlap with the $\sigma$ orbitals associated with the methano bridge.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure10.png}
\caption{Newman projection showing the disrotation during endo bending.}
\end{figure}
According to Houk, the pyramidalization of the double bond in the *syn*-sesquinorborne structure minimizes the torsional repulsions between the bridgehead C-H bond and the C-C bond from the alkene to the other bridgehead carbon. MM2 calculations predicted the *syn*-structure to be 2 kcal/mol more stable when bent. The MM2 structure of the anti-isomer was very sensitive to the input geometry due to the very low out-of-plane bending force constants of the alkene bonds. This is in line with other force-field calculations on these systems where non-planar energy minima were found for both isomers. On the other hand, MO methods gave planar optimized geometries for both these structures.

What is readily apparent from this review of the area is that a great deal of controversy still exists over the origins of facial stereoselectivity and π-bond pyramidalization in the isodicyclopentadiene and related sesquinorbornene systems. Additional experimental investigation is needed before the relative importance of the various aspects discussed can be ascertained. The research described herein was conducted with the hope that these results will shed additional light on the factors controlling the observed facial stereoselectivity in reactions of isodicyclopentadiene and eventually lead to a more comprehensive understanding of this system. The aspects examined include an assessment of the effect of transition state timing on the facial selectivity, modification of the bicyclic skeleton and the resultant bonding preferences in Diels-Alder and metal complexation reactions, the existence of long-range electronic effects in isodicyclopentafulvene systems and synthetic routes to geminal substitution on the ethano bridge of isodicyclopentadiene.
<table>
<thead>
<tr>
<th>DIENOPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO ((\text{bottom:top}))</th>
<th>REF</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{O} \\
\text{C} \\
\end{array}
\] \[
\begin{array}{c}
\text{O} \\
\text{C} \\
\end{array}
\] | warm ether | ambiguous | 1 |
| | benzene, RT | 100:0 | 2 |
| | Et\textsubscript{2}O, C\textsubscript{6}D\textsubscript{6}, CDCl\textsubscript{3} | 45-65:55-35 | 3 |
| | CH\textsubscript{3}CN, 6-80 °C | 45-65:55-35 | 3 |
| \[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\end{array}
\] | hexane, 50 °C | 100:0 | 4 |
| | CCl\textsubscript{4}, 42 °C | 100:0 | 2 |
| \[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\end{array}
\] | hexane, 40 °C | 100:0 | 4 |
| | CCl\textsubscript{4}, 42 °C | 100:0 | 2 |
| \[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{Me} \\
\end{array}
\] | EtOAc, -35 °C | 0:100 | 5,6 |
| | Et\textsubscript{2}O, -20 °C | 0:100 | 6 |
| \[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{Ph} \\
\end{array}
\] | Et\textsubscript{2}O, -20 °C | 0:100 | 6 |
| | Et\textsubscript{2}O, 0 °C | 0:100 | 14 |
| \[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{Ph} \\
\end{array}
\] | CHCl\textsubscript{3}, RT | 100:0 | 7 |
Table 1. (continued)

<table>
<thead>
<tr>
<th>DIENOPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (bottom:top)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>CHCl$_3$, 5 °C</strong></td>
<td>100:0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DME, reflux</td>
<td>100:0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DME, reflux</td>
<td>80:20</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td><strong>175 atm, 140 °C</strong></td>
<td>80:20</td>
<td>9</td>
</tr>
<tr>
<td>PhSO$_2$--SO$_2$Ph</td>
<td><strong>THF, 20 °C</strong></td>
<td>45:55</td>
<td>10</td>
</tr>
<tr>
<td>PhSO$_2$--SO$_2$Ph</td>
<td><strong>CHCl$_3$, 40-50 °C</strong></td>
<td>0:100</td>
<td>10</td>
</tr>
<tr>
<td>MeO$_2$C--CO$_2$Me</td>
<td><strong>CDCl$_3$, RT</strong></td>
<td>100:0</td>
<td>3b,11</td>
</tr>
<tr>
<td></td>
<td>t-BuC$_6$H$_5$, 169 °C</td>
<td>94:6</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 1. (continued)

<table>
<thead>
<tr>
<th>DIENOPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (bottom:top)</th>
<th>REF</th>
</tr>
</thead>
</table>
| \( \begin{array}{c}
\text{NC} \\
\text{CN} \\
\text{CN} \\
\text{NC}
\end{array} \) | Et₂O; CH₃CN; C₆H₆; toluene; <0 °C | 0:100 | 14 |
| \( \begin{array}{c}
\text{PhSO}_2
\text{SiMe}_3
\end{array} \) | toluene, 161 °C | angular* | 16 |
|  | \( \begin{array}{c}
\text{Br}
\text{Br}
\end{array} \) | \( \begin{array}{c}
\text{Ph}
\text{Br}
\text{Ph}
\end{array} \) | 17:83 | 15 |
|  | C₆H₆, RT | 10:90 | 15 |
|  | CH₃CN, RT, NaI, Cu | 22-50:78-50 | 15 |
|  | C₆H₆, 60 °C, Fe₂(CO)₉ glyme, heat, Zn-Cu | 9:91 | 15 |
|  | C₆H₆, 60 °C, Fe₂(CO)₉ | angular* | 16 |
Table 1. (continued)

<table>
<thead>
<tr>
<th>DIENOPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (bottom:top)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPh</td>
<td>toluene, 110 °C</td>
<td>75:25**</td>
<td>16</td>
</tr>
<tr>
<td>SOPh</td>
<td>benzene, 110 °C</td>
<td>92:8**</td>
<td>16</td>
</tr>
<tr>
<td>SO2Ph</td>
<td>CH2Cl2, reflux</td>
<td>100:0</td>
<td>2b,13</td>
</tr>
<tr>
<td></td>
<td>tBuC6H5, 169 °C</td>
<td>8:92**</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>angular*</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>α-dClC6H4, 180 °C</td>
<td>angular*</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>tBuC6H5, reflux</td>
<td>angular*</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 1. (continued)

<table>
<thead>
<tr>
<th>DIENOPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (bottom:top)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>benzene, 50 °C</td>
<td>100:0</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>pentane, -78 °C</td>
<td>90:10</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>CDC\textsubscript{3}, RT</td>
<td>100:0</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2}Cl\textsubscript{2}, 42 °C</td>
<td>94:6**</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>toluene, 120 °C</td>
<td>75:25**</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>acetone, RT, Me\textsubscript{3}NO</td>
<td>angular*</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>benzene, RT</td>
<td>100:0</td>
<td>a</td>
</tr>
</tbody>
</table>

(a) this work.

*Under these conditions, addition occurred to the bond-shift isomer only. **Ratio is for the relative amounts of below-plane adduct:angular adduct.
Table 2. π-Facial Selectivity Patterns in Cycloadditions with Modified Isodicyclopentadienes.

<table>
<thead>
<tr>
<th>COMPOD</th>
<th>R = Me</th>
<th>R = Ph</th>
<th>R = Ph</th>
<th>R = Ph</th>
<th>R = Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100:0</td>
<td>100:0</td>
<td>50:50</td>
<td>32:68</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>68:32</td>
<td>46:54</td>
<td>39:61</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>65:35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0:100</td>
<td>0:100</td>
<td>-</td>
<td>-</td>
<td>0:100</td>
</tr>
<tr>
<td></td>
<td>97:3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**RATIOS (BOTTOM:TOP)**
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>RATIOS (BOTTOM:TOP)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 1]</td>
<td>![Diagram 2] 56:40</td>
<td>19a</td>
</tr>
<tr>
<td>![Diagram 3]</td>
<td>100:0</td>
<td>19a,b</td>
</tr>
<tr>
<td>![Diagram 4]</td>
<td>100:0</td>
<td>19b,c</td>
</tr>
<tr>
<td>![Diagram 5]</td>
<td>100:0</td>
<td>20</td>
</tr>
<tr>
<td>![Diagram 6]</td>
<td>100:0</td>
<td>19b,20</td>
</tr>
<tr>
<td>![Diagram 7]</td>
<td>100:0 100:0* 100:0* 100:0*</td>
<td>21 36</td>
</tr>
</tbody>
</table>
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>[N\text{H}N\text{N-R} \quad \text{CO}_2\text{Me} \quad \text{CO}_2\text{Me} \quad \text{N-Ph} \quad \text{SO}_2\text{Ph} \quad \text{Ph} \quad \text{CO}_2\text{Me} \quad \text{Cyclooctane}</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100:0 100:0 100:0 100:0 100:0 100:0 100:0 100:0</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>100:0 100:0 100:0 100:0 100:0 100:0 100:0 100:0</td>
<td>8,22</td>
</tr>
<tr>
<td></td>
<td>75:25 100:0 75:25 100:0 100:0 100:0 100:0 100:0</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>70:30 78:22 78:22 70:30 70:30 70:30 70:30 70:30</td>
<td>21,46</td>
</tr>
<tr>
<td></td>
<td>70:30 70:30 70:30 70:30 70:30 70:30 70:30 70:30</td>
<td>16,23</td>
</tr>
<tr>
<td></td>
<td>0:100 0:100 0:100 0:100 0:100 0:100 0:100 0:100</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>0:100 0:100 0:100 0:100 0:100 0:100 0:100 0:100</td>
<td>37</td>
</tr>
</tbody>
</table>
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPO</th>
<th>RATIOS (BOTTOM:TOP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td><img src="image2.png" alt="Structure" /> <img src="image3.png" alt="Structure" /> <img src="image4.png" alt="Structure" /> <img src="image5.png" alt="Structure" /> <img src="image6.png" alt="Structure" /></td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure" /></td>
<td><img src="image8.png" alt="Structure" /> <img src="image9.png" alt="Structure" /> <img src="image10.png" alt="Structure" /> <img src="image11.png" alt="Structure" /> <img src="image12.png" alt="Structure" /></td>
</tr>
<tr>
<td><img src="image13.png" alt="Structure" /></td>
<td><img src="image14.png" alt="Structure" /> <img src="image15.png" alt="Structure" /> <img src="image16.png" alt="Structure" /> <img src="image17.png" alt="Structure" /> <img src="image18.png" alt="Structure" /></td>
</tr>
<tr>
<td><img src="image19.png" alt="Structure" /></td>
<td><img src="image20.png" alt="Structure" /> <img src="image21.png" alt="Structure" /> <img src="image22.png" alt="Structure" /> <img src="image23.png" alt="Structure" /> <img src="image24.png" alt="Structure" /></td>
</tr>
<tr>
<td><img src="image25.png" alt="Structure" /></td>
<td><img src="image26.png" alt="Structure" /> <img src="image27.png" alt="Structure" /> <img src="image28.png" alt="Structure" /> <img src="image29.png" alt="Structure" /> <img src="image30.png" alt="Structure" /></td>
</tr>
<tr>
<td>Compound</td>
<td>Ratios (Bottom:Top)</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------</td>
</tr>
<tr>
<td>0:100 R=Ph</td>
<td>50:50</td>
</tr>
<tr>
<td>85:15 R=Me</td>
<td>57:43</td>
</tr>
<tr>
<td>100:0 R=Me</td>
<td>16:84</td>
</tr>
<tr>
<td>100:0 R=Me</td>
<td>14:86</td>
</tr>
<tr>
<td>50:50 R=Me</td>
<td>50:50</td>
</tr>
<tr>
<td>-</td>
<td>50:50</td>
</tr>
</tbody>
</table>

Table 2. (continued)
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>N—CO</th>
<th>100:0</th>
<th>0:100</th>
<th>64:24</th>
<th>67:33</th>
<th>14:86</th>
<th>10:90</th>
<th>9:91</th>
<th>0:100*</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2 (continued)**

**RATIOS (BOTTOM:TOP)**

<table>
<thead>
<tr>
<th>REF</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>23</th>
<th>40</th>
</tr>
</thead>
</table>

*Note: The *符号 indicates a specific condition or note.*
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPO</th>
<th>R</th>
<th>R'</th>
<th>Ratios (Bottom:Top)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Compound 1" /></td>
<td>-</td>
<td>-</td>
<td>100:0* X=0</td>
</tr>
<tr>
<td><img src="image2" alt="Compound 2" /></td>
<td>44:56</td>
<td>R=Me</td>
<td>-</td>
</tr>
<tr>
<td><img src="image3" alt="Compound 3" /></td>
<td>100:0</td>
<td>100:0</td>
<td>100:0</td>
</tr>
<tr>
<td><img src="image4" alt="Compound 4" /></td>
<td>-</td>
<td>100:0</td>
<td>100:0</td>
</tr>
<tr>
<td><img src="image5" alt="Compound 5" /></td>
<td>-</td>
<td>100:0</td>
<td>100:0</td>
</tr>
</tbody>
</table>
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPOD</th>
<th>R</th>
<th>R'</th>
<th>CO_2Me</th>
<th>SO_2Ph</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Compound 1" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
<tr>
<td><img src="image6" alt="Compound 2" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
<tr>
<td><img src="image7" alt="Compound 3" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
<tr>
<td><img src="image8" alt="Compound 4" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
<tr>
<td><img src="image9" alt="Compound 5" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
<tr>
<td><img src="image10" alt="Compound 6" /></td>
<td><img src="image2" alt="R1" /></td>
<td><img src="image3" alt="R2" /></td>
<td><img src="image4" alt="CO2Me" /></td>
<td><img src="image5" alt="SO2Ph" /></td>
<td>a</td>
</tr>
</tbody>
</table>
Table 2. (continued)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>R</th>
<th>R'</th>
<th>O</th>
<th>O'</th>
<th>CO\text{Me}</th>
<th>CO\text{Me}</th>
<th>Ph\text{SO}_2</th>
<th>Ph\text{SO}_2</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
</tr>
</tbody>
</table>

(a) this work
(b) R = Tos; R' = H.
(c) R = Me_3Si; R' = NO_2.
(d) R, R' = CO_2Me

*A mixture of Alder/Anti-Alder adducts were formed.

**Product arises from a TMS-shift isomer.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (BOTTOM:TOP)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>73:27</td>
<td>50a</td>
</tr>
<tr>
<td></td>
<td>rose bengal, -78 °C, acetone-d₆, hv</td>
<td>63:37</td>
<td>50b</td>
</tr>
<tr>
<td></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>65:35</td>
<td>50a</td>
</tr>
<tr>
<td></td>
<td>methylene blue, CH₃CN</td>
<td>57:43</td>
<td>50a</td>
</tr>
<tr>
<td></td>
<td>tetraphenylporphyrin, benzene</td>
<td>67:33</td>
<td>50a</td>
</tr>
<tr>
<td></td>
<td>rose bengal, -78 °C, acetone-d₆, hv</td>
<td>55:45</td>
<td>50b</td>
</tr>
<tr>
<td></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>57:43</td>
<td>50d</td>
</tr>
<tr>
<td></td>
<td>rose bengal, MeOH, hv</td>
<td>82:28</td>
<td>50c</td>
</tr>
<tr>
<td></td>
<td>rose bengal, MeOH, hv</td>
<td>92:8</td>
<td>50c</td>
</tr>
<tr>
<td>COMPOUND</td>
<td>REACTION CONDITIONS</td>
<td>RATIO (BOTTOM:TOP)</td>
<td>REF</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
<td>--------------------</td>
<td>-----</td>
</tr>
<tr>
<td><img src="image1.png" alt="Molecule 1" /></td>
<td>rose bengal, MeOH, hv</td>
<td>14:86</td>
<td>50c</td>
</tr>
<tr>
<td><img src="image2.png" alt="Molecule 2" /></td>
<td>rose bengal, MeOH, hv</td>
<td>5:95</td>
<td>50c</td>
</tr>
<tr>
<td><img src="image3.png" alt="Molecule 3" /></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>0:100</td>
<td>50d</td>
</tr>
<tr>
<td><img src="image4.png" alt="Molecule 4" /></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>19:81</td>
<td>50d</td>
</tr>
<tr>
<td><img src="image5.png" alt="Molecule 5" /></td>
<td>methylene blue, RT, ClCH₂CH₂Cl, hv</td>
<td>0:100</td>
<td>50d</td>
</tr>
</tbody>
</table>
Table 4. π-Facial Selectivity Patterns in Electrophilic Additions to Isodicyclopentadienide Anions.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>ELECTROPHILE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (BOTTOM:TOP)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₂O</td>
<td>n-BuLi, THF, -78 °C</td>
<td>100:0</td>
<td>30,32</td>
<td></td>
</tr>
<tr>
<td>MeI</td>
<td>n-BuLi, THF, -78 °C</td>
<td>&gt;97:3</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>BrCH₂CD₂Cl</td>
<td>NaNH₂, NH₃</td>
<td>60:40</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CICH₂CD₂I</td>
<td>NaNH₂, NH₃</td>
<td>66:34</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CICH₂CD₂OTs</td>
<td>NaNH₂, NH₃</td>
<td>62:38</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>epichlorohydrin</td>
<td>NaNH₂, NH₃</td>
<td>72:28</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Cl(CH₂)₃CD₂I</td>
<td>NaNH₂, NH₃</td>
<td>100:0</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>BrCH₂CH₂C≡C(Me)₂</td>
<td>NaNH₂, NH₃</td>
<td>100:0</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CH₂Br</td>
<td>MeOD or tBuOD</td>
<td>n-BuLi, THF, -78 °C</td>
<td>82:18</td>
<td>33</td>
</tr>
<tr>
<td>AcOEt</td>
<td>n-BuLi, 0 °C</td>
<td>63:37</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Me₃SiCl</td>
<td>n-BuLi, THF, -78 °C</td>
<td>91:9</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>n-BuLi, THF, -78 °C</td>
<td>100:0</td>
<td>30,32</td>
<td></td>
</tr>
<tr>
<td>MeI</td>
<td>n-BuLi, THF, -78 °C</td>
<td>50:50</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Cl(CH₂)₃CD₂I</td>
<td>NaNH₂, NH₃</td>
<td>50:50</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>n-BuLi, THF, -78 °C</td>
<td>46:54</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>(CD₃)₃SiCl</td>
<td>n-BuLi, THF, -78 °C</td>
<td>50:50</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>COMPOUND</td>
<td>METAL SOURCE</td>
<td>REACTION CONDITIONS</td>
<td>RATIO (TOP:BOTTOM)</td>
<td>REF</td>
</tr>
<tr>
<td>------------</td>
<td>--------------</td>
<td>---------------------</td>
<td>--------------------</td>
<td>------</td>
</tr>
<tr>
<td>CpTiCl₃</td>
<td></td>
<td>-78 °C, THF</td>
<td>0:100</td>
<td>34,35</td>
</tr>
<tr>
<td>CpTiCl₃</td>
<td></td>
<td>RT, THF</td>
<td>100:0</td>
<td>34,35</td>
</tr>
<tr>
<td>Me-CpTiCl₃</td>
<td></td>
<td>-78 °C, THF</td>
<td>0:100</td>
<td>34,35</td>
</tr>
<tr>
<td>Me-CpTiCl₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>34,35</td>
<td></td>
</tr>
<tr>
<td>Me₅-CpTiCl₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>tBu-CpTiCl₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>tBu-CpTiCl₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Me₂-CpZrCl₃</td>
<td>reflux, toluene</td>
<td>100:0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Me₂-CpZrCl₃</td>
<td>reflux, toluene</td>
<td>100:0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Fe(II)(acac)₂(py)₂</td>
<td>reflux, toluene</td>
<td>100:0</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>TiCl₃</td>
<td>reflux, reflux, DME</td>
<td>100:0</td>
<td>36,37,40b</td>
<td></td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>reflux, reflux, DME</td>
<td>100:0</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>HfCl₄</td>
<td>reflux, reflux, DME</td>
<td>100:0</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>RuCl₃</td>
<td>reflux, DME</td>
<td>100:0</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>OsCl₄</td>
<td>reflux, DME</td>
<td>100:0</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>NiBr₂(glyme)</td>
<td>RT, THF</td>
<td>100:0</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>[Co(NH₃)₆]Cl₂</td>
<td>RT, THF</td>
<td>100:0</td>
<td>40a</td>
<td></td>
</tr>
<tr>
<td>CrCl₃</td>
<td>RT, THF</td>
<td>100:0</td>
<td>40a</td>
<td></td>
</tr>
<tr>
<td>VCl₃</td>
<td>0 °C-RT, THF</td>
<td>100:0</td>
<td>40a</td>
<td></td>
</tr>
<tr>
<td>[Ni(NH₃)₆]Cl₂</td>
<td>RT, THF</td>
<td>100:0</td>
<td>40a</td>
<td></td>
</tr>
<tr>
<td>ThSO₄</td>
<td>RT, NaOH-H₂O</td>
<td>78:22*</td>
<td>40c</td>
<td></td>
</tr>
<tr>
<td>FeCl₂</td>
<td>RT, THF</td>
<td>100:0</td>
<td>40c</td>
<td></td>
</tr>
</tbody>
</table>

Fe(II)(acac)₂(py)₂ | RT-65 °C, xylene | 100:0 | 36,37  |
<table>
<thead>
<tr>
<th>COMPO</th>
<th>METAL SOURCE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (TOP:BOTTOM)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)₆</td>
<td>reflux, THF</td>
<td>53:47</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Mo(CO)₆</td>
<td>reflux, THF</td>
<td>80:20</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>W(CO)₆</td>
<td>reflux, THF</td>
<td>89:11</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Cr(CO)₃(CH₃CN)₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Mo(CO)₃(CH₂CN)₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>W(CO)₃(CH₂CN)₃</td>
<td>reflux, THF</td>
<td>100:0</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Fe⁺(ξ-xylene)CpPF₆⁻</td>
<td>hv, CH₂Cl₂</td>
<td>65:35</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Ru⁺Cp(CH₃CN)₃PF₆⁻</td>
<td>reflux, CCl₂CH₂CH₂Cl</td>
<td>86:14</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>TiCl₄</td>
<td>Et₂O</td>
<td>0:100</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>TiCl₃</td>
<td>reflux, DME</td>
<td>10:90</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>CpTiCl₃</td>
<td>RT, THF</td>
<td>12:88</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>reflux, DME</td>
<td>7:93</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>CpZrCl₃</td>
<td>RT, THF</td>
<td>33:67</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Me₅-CpZrCl₃</td>
<td>reflux, toluene</td>
<td>42:58</td>
<td>43</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. (continued)

| COMPOUND | METAL SOURCE | REACTION CONDITIONS | RATIO (TOP:BOTTOM) | REF
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$_3$</td>
<td></td>
<td>reflux, DME</td>
<td>100:0</td>
<td>44</td>
</tr>
<tr>
<td>CpTiCl$_3$</td>
<td></td>
<td>-70 °C, THF</td>
<td>17:83</td>
<td>44</td>
</tr>
<tr>
<td>CpTiCl$_3$</td>
<td></td>
<td>RT-reflux, THF</td>
<td>75:25</td>
<td>44</td>
</tr>
<tr>
<td>ZrCl$_4$</td>
<td></td>
<td>reflux, DME</td>
<td>98:2</td>
<td>44</td>
</tr>
<tr>
<td>CpZrCl$_3$</td>
<td></td>
<td>-70 °C-reflux, toluene</td>
<td>0:100</td>
<td>44</td>
</tr>
<tr>
<td>CpZrCl$_3$</td>
<td></td>
<td>RT-reflux, toluene</td>
<td>78:22</td>
<td>44</td>
</tr>
<tr>
<td>Me$_5$-CpZrCl$_3$</td>
<td></td>
<td>-70 °C-reflux, toluene</td>
<td>67:33</td>
<td>44</td>
</tr>
<tr>
<td>Me$_5$-CpZrCl$_3$</td>
<td></td>
<td>RT-reflux, toluene</td>
<td>67:33</td>
<td>44</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td></td>
<td>norbornene, reflux</td>
<td>100:0</td>
<td>42</td>
</tr>
<tr>
<td>TiCl$_4$</td>
<td></td>
<td>0 °C-RT, Et$_2$O</td>
<td>100:0</td>
<td>42</td>
</tr>
</tbody>
</table>

| COMPOUND | METAL SOURCE | REACTION CONDITIONS | RATIO (TOP:BOTTOM) | REF
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$_3$</td>
<td></td>
<td>reflux, DME</td>
<td>0:100</td>
<td>45</td>
</tr>
<tr>
<td>CpTiCl$_3$</td>
<td></td>
<td>-70 °C or RT, THF</td>
<td>0:100</td>
<td>45</td>
</tr>
<tr>
<td>ZrCl$_4$</td>
<td></td>
<td>reflux, DME</td>
<td>0:100</td>
<td>45</td>
</tr>
<tr>
<td>Me$_5$-CpZrCl$_3$</td>
<td></td>
<td>reflux, toluene</td>
<td>0:100</td>
<td>45</td>
</tr>
<tr>
<td>CpZrCl$_3$</td>
<td></td>
<td>reflux, toluene</td>
<td>50:50</td>
<td>45</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_9$ **</td>
<td></td>
<td>reflux, hexane</td>
<td>100:0</td>
<td>49</td>
</tr>
<tr>
<td>BDAFe(CO)$_3$</td>
<td></td>
<td>reflux, benzene</td>
<td>100:0</td>
<td>49</td>
</tr>
</tbody>
</table>
Table 5. (continued)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>METAL SOURCE</th>
<th>REACTION CONDITIONS</th>
<th>RATIO (TOP:BOTTOM)</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(CO)₉</td>
<td>reflux, hexane</td>
<td>100:0</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>BDAFe(CO)₃</td>
<td>reflux, benzene</td>
<td>100:0</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺(p-xylene)C₆PF₆⁻</td>
<td>hv, CH₂Cl₂</td>
<td>73:27</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>Ru⁺⁺C₆(CH₃CN)₃PF₆⁻</td>
<td>reflux, CH₂CH₂Cl</td>
<td>93:7</td>
<td>a</td>
<td></td>
</tr>
</tbody>
</table>

(a) this work

*Minor isomer is the mixed top-face/bottom-face complex.
**BDAFe(CO)₃ = benzylideneacetone complex.
CHAPTER I

CYCLOADDITION CHEMISTRY OF ISODICYCLOPENTADIENE WITH HIGHLY REACTIVE DIENOPHILES

Introduction

The electronic control model\textsuperscript{2,65} proposed by Gleiter and Paquette serves as a complex example of secondary orbital interactions\textsuperscript{79} controlling the stereochemical outcome of reactions. The facial preference of dienophiles in their attack on isodicyclopentadiene is determined by the interaction of the tilted, lowest occupied $\pi$ molecular orbital, $\pi_5$, of the diene and the highest occupied $\pi$ orbital of the dienophile. This is a destabilizing interaction since four electrons are involved. The resultant stereoselection is due to the smaller antibonding interaction between these orbitals during bottom-face addition.

Normal Diels-Alder reactions have early transition states. As a result of such timing, the activated complex closely resembles a two-
plane orientation of the reactants. The success of perturbation theory, from which the Paquette-Gleiter theory is derived, will be greater the earlier the transition state. In this context, the electronic features of the diene should be most clearly manifested during reactions that occur rapidly at low temperatures.

The triazolinediones stand out as one of the more puzzling exceptions in the general trend of below-plane dienophilic attack on isodicyclopentadiene (I). Their extremely high dienophilic reactivity was considered ideal to study the electronic features of early transition states for [4 + 2] bonding. The observance of exclusive top-face addition by N-methyl and N-phenyltri azolinedione was not expected. Paquette attributed the complete crossover in facial preference to be an artifact of the very early transition state. The earliness of their transition state may cause the triazolinediones to add preferentially in Alder fashion. A unique sensitivity to steric effects would develop that is not particularly significant when less reactive reagents are involved. However, the question of Alder or anti-Alder type products is obscured by the facile pyramidalization at nitrogen.

The possibility that other highly reactive di enophiles may show a similar outcome in their Diels-Alder addition to isodicyclopentadiene led to the investigation discussed in this chapter.
To test this hypothesis, some measure of the relative reactivities of various dienophiles would be desirable. Frontier molecular orbital treatments can be used as a first approximation to a complete perturbation treatment of reactivity. In FMO terms, the HOMO-LUMO interactions dictate the reactivity of the addends in concerted [4 + 2] cycloaddition. For normal Diels-Alder reactions, the transition states have highly stabilizing HOMO(diene)-LUMO(dienophile) interactions. Correlations have been found between the ionization potential(diene)-electron affinity(dienophile) difference and the rate of the Diels-Alder reaction. Diminishing the FMO separation corresponds to a greater energy gain in the transition state and therefore a faster reaction.

Limited electron affinities are available in the literature to gauge the reactivity of other dienophiles with isodicyclopentadiene in comparison to the triazolinediones. The LUMO energy of tert-butyltriazolinedione has been estimated at -7.96 eV. Using Koopmans' theorem, the electron affinity can be set equal to the negative of the LUMO energy. Electron affinities of more common dienophiles, such as maleic anhydride, N-phenylmaleimide and benzoquinone range from 1.33-1.65, 1.36 and 1.34-1.98 eV, respectively. For more reactive dienophiles, such as benzyne and tetracyanoethylene, the electron affinities are 0.764-2.50 and 2.03-3.17 eV, respectively. The EA of cyclooctyne is 2.18 eV and the electron affinity of perfluoro-2-butyne has been estimated to be around 2.00 eV. Unfortunately, these values were determined by a variety of methods. The accuracy of some are questionable and so a direct comparison would be useless.

More readily available are ionization potentials which can be used
to estimate the HOMO energy level of the relevant dienophiles. Various ionization potentials have been gathered for comparison of HOMO energies (i.e., relative reactivities) and are listed in Table 8. A larger value corresponds to a lower energy.

Table 8. Compilation of Vertical Ionization Potentials, $I_v$, for Various Dienophiles and Isodicyclopentadiene.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$I_v$ (eV)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-benzyne</td>
<td>9.35-11.32</td>
<td>86b-c, 90</td>
</tr>
<tr>
<td>methyl acrylate</td>
<td>10.72 (10.8)</td>
<td>86c, 98</td>
</tr>
<tr>
<td>N-methyltriazolinedione</td>
<td>13.5-14.2*</td>
<td>91</td>
</tr>
<tr>
<td>N-phenyltriazolinedione</td>
<td>12.5-13.2*</td>
<td>91b</td>
</tr>
<tr>
<td>cyclobutadiene</td>
<td>8.2-8.5</td>
<td>92</td>
</tr>
<tr>
<td>cyclooctyne</td>
<td>9.18-9.20</td>
<td>93</td>
</tr>
<tr>
<td>ethylene</td>
<td>10.515 (10.5)</td>
<td>94, 96, 98</td>
</tr>
<tr>
<td>α-benzoquinone</td>
<td>10.29-10.93*</td>
<td>95</td>
</tr>
<tr>
<td>maleic anhydride</td>
<td>11.07</td>
<td>96</td>
</tr>
<tr>
<td>N-phenylmaleimide</td>
<td>10.69-11.01*</td>
<td>97</td>
</tr>
<tr>
<td>perfluoro-2-butyne</td>
<td>(12.70)</td>
<td>(98)</td>
</tr>
<tr>
<td>DMAD</td>
<td>(11.74)</td>
<td>(98)</td>
</tr>
<tr>
<td>tetracyanoethylene</td>
<td>(11.80)</td>
<td>(98)</td>
</tr>
<tr>
<td>C1CH=CHCl</td>
<td>9.81 (9.8)</td>
<td>96, 98</td>
</tr>
<tr>
<td>MeSO2CH=CHSO2Me</td>
<td>(12.75)</td>
<td>(98)</td>
</tr>
<tr>
<td>isodicyclopentadiene</td>
<td>9.68 ($\pi_s$)</td>
<td>2, 65</td>
</tr>
</tbody>
</table>

*Value corresponds to the highest occupied orbital of \(\pi\) character mainly localized on the reacting centers.
Values in parentheses were calculated using Jorgensen's CAMEO algorithm described in reference 98.
Turning back to the Paquette-Gleiter theory, if a large change in the reactivity of the dienophile produces a corresponding large change in the HOMO energy then the dienophile may be insensitive to the proposed stereoselective electronic interaction. PMO theory dictates that those orbitals will interact most which overlap the best and are closest in energy. From a qualitative standpoint, the triazolinediones would be expected to have a lower energy HOMO than any of the carbon-carbon containing $\pi$ bonds because the $p$ orbitals on nitrogen are much lower in energy than those on carbon. A very early transition state would imply that a greater degree of separation of the reactants exists than with lesser reactive dienophiles. With the triazolinediones, their highest occupied $\pi$ orbital energy may be disparate enough that its interaction with $\pi_s$ of isodicyclopentadiene is very weak. Other interactions may then become more dominant, which have opposite facial stereoselection.

Testing this idea with the available experimental data is difficult since most of the higher reactive dienophiles have only calculated $I_v$'s and thus only useful in a relative sense. The actual values could be very unreliable. However, as found in Table 8, the common dienophiles have HOMO energies in the range of 9-11 eV whereas the triazolinediones fall in the range 13-14 eV. This energy difference amounts to 69-92 kcal/mol.

To address the question of early transition state timing on the observed facial stereoselection, the facial preference of isodicyclopentadiene was examined when treated with highly reactive dienophiles such as hexafluoro-2-butyne, cyclooctyne, cyclobutadiene and
(methoxyvinylcarbene)tungsten pentacarbonyl. The widely different structural features of these dienophiles bear little resemblance to the triazolinedione system. Consequently, the manner in which they might react was not obvious. The possibility of uncovering new mechanistic information not provided with the earlier examples also exists. For these reasons, the following investigations were carried out.

An unanticipated factor arose during this work with respect to the capture of tautomeric forms of isodicyclopentadiene. Diels-Alder addition to the [1,5]-bond shift isomer of 1 had been reported only in the case of relatively sluggish dienophiles where elevated temperatures were required (c.f., Table 1). The thermodynamically favored tautomer 1 can be rapidly equilibrated with 43 by heating. Tautomer 43 has been estimated to be at least $10^4$ times more reactive than 1 in its Diels-Alder

Scheme III. Possible Angular Adducts from Diels-Alder Capture of Isodicyclopentadiene Tautomers.

Tautomer 44 is the least thermodynamically stable form. It is estimated to be at least 30 times slower than 1 in its Diels-Alder
Dienophiles have been added to this tautomer under conditions designed specifically for its formation. These Diels-Alder adducts, which are trans-fused to the norbornane unit are very strained and quite prone to cycloreversion or thermal isomerization.

Results

Reaction of 1 with excess hexafluoro-2-butyne in pentane solution under an inert atmosphere proceeded smoothly to completion within 4 h starting at -70°C then warming to 0°C. Gas chromatographic and \textsuperscript{1}H NMR analysis indicated that two cycloadducts had been produced quantitatively in a 9:1 ratio. The diminished efficiency with which major product 45 (45% isolated) could be obtained in a pure state following chromatographic separation from 46 (3% isolated) can be attributed to its volatility and to a marked propensity for air-oxidation, as witnessed by the isolation of epoxide 47 (6%) and diketone 48 (3%). Previous investigations have determined that epoxide and diketone products arise from reaction of syn-sesquinoisorbornadienes with triplet oxygen via a free radical process. In contrast, peracid oxidation of this system provides epoxides only.
Assignment of stereochemistry to the pair of dienes was initially arrived at on the basis of a $^1$H NMR chemical shift comparison. Especially diagnostic was the highly shielded nature of the endo ethano protons in 45 relative to those in 46 (see formulas). This phenomenon has been encountered previously$^{17,18,23}$. In the anti-sesquinorbornadiene (46), the bis(trifluoromethyl)-substituted double bond is no longer proximal to these hydrogens and a downfield shift of 0.47 ppm becomes evident (in CDCl$_3$ solution). In general, the isomers are distinguishable by spectroscopy. Characteristic of the syn isomer is the appearance of two shielded protons below 1 ppm ($0.7 \pm 0.2$ ppm). In the $^{13}$C NMR spectra, ethano carbons in syn compounds ($24.5 \pm 1.5$ ppm) are more shielded than in the anti ($26.1 \pm 1.0$ ppm). Likewise, the methano carbons in syn compounds ($47.5 \pm 2.0$ ppm) are more shielded than in anti ones ($53.2 \pm 2.0$ ppm)$^{14}$.

That 45 had been correctly formulated was indicated by an independent assessment of its susceptibility to oxidation. Exposure to air for 2 weeks resulted in complete conversion of a sample to a 57:43 mixture of 47 and 48 ($^1$H NMR integration of their respective bridgehead protons). As anticipated from precedent$^{20,21,23,97}$, 46 proved inert to the atmospheric environment. The syn architecture of 45 follows incontrovertibly from its $^{13}$C NMR spectrum where the consequences of oxirane magnetic anisotropy$^{102}$ have combined to shield both of its apical methylene carbons relative to those in 45 (see formulas). The configuration of the epoxide ring has been shown to have a large effect on the $^{13}$C NMR chemical shifts of the methano carbon bridge. In the norbornyl systems below an upfield shift of 24-26 ppm was observed$^{102}$. 
Shielding of both methano bridges is only possible in the syn-isomer.

Although diketone 48 proved to be of C_s symmetry, its three-dimensional features could not be ascertained with comparable confidence on the basis of NMR data alone. Consequently, recourse was made to X-ray crystallography. The ORTEP diagram of Figure 11 discloses that 48 is as anticipated, stereochemically related to 45. The conformation adopted by the diketone is of additional interest. Its two five-membered rings are almost parallel to each other, the dihedral angle separating them is only 5.1°. Of course, neither five-membered ring is fully planar, the dihedral angles between C(5)-C(6)-C(7) [plane I] and C(5)-C(1)-C(2)-C(7) [plane II] as well as between C(10)-C(11)-C(12) [plane III] and C(12)-C(13)-C(14)-C(10) [plane IV] being 23.8 and 28.4°, respectively. The angle between planes I and III is 32.7°, while that between planes II and IV is 19.6°.

Prior to this investigation, only three other diketone products had been isolated and characterized\textsuperscript{13,21}. They were prepared by bubbling oxygen through a solution containing the syn-sesquinorbomadiene. Bartlett has recently published crystal structures of two of these diketones\textsuperscript{93}. 
Figure 11. ORTEP drawing of 48. Non-hydrogen atoms are drawn with 50% probability ellipsoids, while hydrogen atoms are drawn with an artificial radius.

Cyclooctyne\textsuperscript{104}, a highly strained acetylene, is recognized to undergo \([4 + 2]\) cycloaddition with a variety of cyclic 1,3-dienes\textsuperscript{105}. Initial experiments suggested some competition from tautomers of 1 may be occurring. In order to best gauge its behavior toward the isodicyclopentadiene triad, condensation with 1 was effected at three different temperatures. In chloroform solution at 25 °C, cycloaddition proceeded very sluggishly. After 1 month, 70% conversion to cycloadduct 49 was noted by \(^1\)H NMR analysis. The unidirectionality of the process is to be noted and compared to the outcome of a like experiment performed in CD\(_2\)Cl\(_2\) at 42 °C. Under the latter conditions, 80% conversion to 49 and the isomeric adduct 50 occurred during 10 days. Hydrocarbon 50 now constituted 4% of the product mixture. When the same pair of reactants was heated to 120 °C in toluene for 12 h, 49 continued to be formed as the major cycloadduct (71%), but the relative amount of 50 (28%) was substantially larger. If the toluene solution of 1 was preequilibrated by heating at the reflux temperature for 30 min prior to
the addition of cyclooctyne and the reaction time was extended for only an additional 3 h, a closely comparable product distribution (75:25) was realized.

A solution was prepared at room temperature in bromobenzene-d$_5$ in order to establish whether 49 is subject to facile retrograde Diels-Alder fragmentation. Subsequent heating for relatively prolonged increments in the temperature range 42-120 °C (combined total of 63 h) gave rise to no observable NMR changes. Consequently, we consider the ratios determined for 49 and 50 to be the result of kinetic competition.

Whereas $^1$H NMR and $^{13}$C NMR analyses of the original reaction mixtures showed only 49 and 50 present, medium-pressure chromatographic purification (MPLC) on silica gel afforded not insignificant quantities of diketone 51 and tertiary alcohol 52 as well. It is possible that 52 arises as a consequence of the acidic nature of the silica gel causing formation of a cationic species (see formula). Ions of a closely related structural type are known to return unrearranged products with nucleophilic capture occurring on the exo surface$^{106}$.

The formation of an alcohol was substantiated by preparation of its $p$-nitrobenzoate 53 by conventional reaction with $p$-nitrobenzoyl chloride.
Autooxidation of 49 by overnight exposure of CDCl₃ solutions to air gave rise to a 27:73 mixture of 51 and epoxide 54. Although all attempts to purify these substances by chromatographic means resulted in the destruction of 54, $^1$H NMR assignments to this highly reactive substance could be made by suitable electronic subtraction of the signals due to 51.

The attempted epoxidation of 49 by bicarbonate-buffered MCPBA in dichloromethane only produced what appears to be a m-chlorobenzoate ester. This product has a $^1$H NMR spectrum that is very similar to that of alcohol 52. The shift of the bridgehead proton resonances to $\delta 3.18$,
3.11 and 2.91, which appear more downfield than they do in 49, is the same pattern found in 52. The $^{13}$C NMR spectrum suggests the alcohol-ester structure by the presence of two oxygen substituted carbons in the 25-line spectrum (97.81 and 90.49 ppm). The IR spectrum also indicates an alcohol. Exo addition is assumed on the basis of literature precedence.\textsuperscript{106}

The release of cyclobutadiene\textsuperscript{107} from its Fe(CO)$_3$ complex with ceric ammonium nitrate\textsuperscript{108} proved incompatible with 1. Numerous attempts under a variety of conditions to effect this decomplexation resulted in the rapid consumption of isodicyclopentadiene. The majority of the cyclobutadiene-iron complex could subsequently be recovered.

Success was achieved by making recourse instead to trimethylamine N-oxide\textsuperscript{109} as oxidant, although the process occurred slowly despite an 8-fold excess of the N-oxide. The cleanest reactions resulted when the reactants were stirred in acetone at 25 °C for 2 days. Neither an increase in the reaction time nor a higher temperature proved advantageous. Benzene proved to be a less desirable solvent than acetone in that only a 13% yield was observed.

Unexpectedly, the only cycloadduct formed from this reagent combination was 55 (42% isolated). The structural assignment to this polycyclic hydrocarbon was deduced primarily from its $^1$H NMR spectrum.
In common with all adducts of 43, 55 exhibits at δ 5.21 a vinyl proton (H\textsubscript{a}) coupled uniquely to a neighboring allylic bridgehead proton. This methine hydrogen, which is positioned at δ 2.75 and identified as H\textsubscript{b}, is the key to assignment of product stereochemistry. In view of its appearance as a well-resolved doublet whose multiplicity arises because of J\textsubscript{AB}, a lack of spin-spin coupling between H\textsubscript{b} and H\textsubscript{c} is clearly apparent. Accordingly, the cyclobutene ring must possess an exo orientation.

To confirm this stereochemical assignment an NOE study was carried out. NOE enhancement of a spin signal is observable when the proximity of the two nuclei are within 3.5 Å or less. In this case, the dipole-dipole coupling between the nuclei becomes the predominant mechanism for their spin-lattice relaxation (T\textsubscript{1}). The contribution to T\textsubscript{1} from the intramolecular dipole-dipole interaction between the proximate nuclei varies with r\textsuperscript{-6}, where r is the distance that separates them. The selective saturation of one nucleus (A) will result in redistribution of spin populations in the other (B), with a consequent change in the total intensity observed for nucleus B. The maximum enhancement factor for any intramolecular homonuclear NOE is 0.5\textsuperscript{110}.

The NOE study of 55 at 500 MHz showed the olefinic cyclobutene protons to be spatially proximal to H\textsubscript{d} (4% enhancement). Thus, the
capture of cyclobutadiene by 43 follows an anti-Alder course.

The highly dienophilic Fischer carbene complex\textsuperscript{111} 56 was found to react quickly and cleanly with 1 at room temperature to furnish cycloadduct 57 in 88\% isolated yield. Close monitoring of the progress of reaction by thin layer chromatography revealed that 1 was completely consumed within 15 min after its addition. Adduct 57 was oxidized to the corresponding methyl ester with dimethyl sulfoxide to establish that complete below-plane stereoselectivity had been realized in anti-Alder fashion. Exposure of structurally related carbene complexes to these mild reaction conditions has been shown not to alter stereochemical composition\textsuperscript{111}. Comparison of the spectral data for 58 with those of an authentic sample showed them to be identical\textsuperscript{2}.

\[ \begin{array}{c}
1 + \text{CH}_2=\text{CH}&\xrightarrow{\text{C}_6\text{H}_6, 20^\circ\text{C}}\xrightarrow{\text{DMSO}} \text{58} \\
\text{CH}_2=\text{CH}&\text{CH}_2\text{=CH}&\text{CH}_2=\text{CH}&\text{CH}_2\text{=CH} \\
\text{W(=O)}_2&\text{W(=O)}_2&\text{W(=O)}_2&\text{W(=O)}_2 \\
\text{56}&\text{57}&\text{58} \\
\end{array} \]

Discussion

The preceding experiments reveal that hexafluoro-2-butyne, cyclooctyne, and (methoxyvinylcarbene)tungsten pentacarbonyl exhibit a similar overwhelming preference for [4 + 2] bonding to 1 from its bottom surface. The reaction stereoselectivity adopted by the two acetylenic
reagents is therefore identical with that previously demonstrated for dimethyl acetylenedicarboxylate and conforms to theoretical expectation\textsuperscript{2,65}. From a qualitative viewpoint, hexafluoro-2-butyne reacts with 1 at a significantly slower rate than either of the \textit{N}-substituted triazolinediones examined previously. For this reason, the Diels-Alder transition-state options available to the hexafluorinated example can be thought of developing appreciably later in the reaction profile. One must inquire, however, if this issue bears directly on the stereoselection question.

Two facets of the behavior of cyclooctyne are noteworthy. The reduced dienophilicity of the somewhat distorted triple bond in this reagent is rather striking. After 1 month at room temperature, conversion to 49 proceeds only to the 70\% level. This kinetic retardation may reflect the inability of cyclooctyne to bond in Alder fashion to either face of the diene for the obvious steric reasons. This hypothesis cannot, of course, be put to experimental test since cycloadduct 49 lacks the capacity for stereochemical marking about the newly installed double bond.

The ability of cyclooctyne to add to \textit{[1,5]} hydrogen-shifted isodicyclopentadiene tautomer 43 at temperatures above 25 °C is unprecedented for triply unsaturated dienophiles when 1 serves as the precursor. Under conditions specifically designed to maximize the concentration of 43 available from 1, DMAD reacts exclusively with 1 to deliver the \textit{syn}-sesquinarbornadiene adduct\textsuperscript{11}. The inertness of DMAD toward 43 had originally been traced to steric crowding involving one ester group of the linear dienophile and the methano bridge\textsuperscript{11}. 
Apparently, the eight-membered ring in cyclooctyne pulls back the propargylic methylene groups to an extent adequate to deemphasize the steric feature (see below) and allow the greater inherent Diels-Alder reactivity of diene 43 to manifest itself. It remains important to recognize that DMAD does add smoothly to 43 which is free of 1 to give a single adduct in 82% yield\textsuperscript{3b}.

![Chemical Structure](image)

The heightened reactivities of carbene complexes such as 56 have been estimated to be greater than $10^4$ over that of methyl acrylate, their closest analogue and are believed comparable to that of AICl\textsubscript{3}-complexed methyl acrylate\textsuperscript{109}. The tungsten reagent does indeed cycloadd completely to 1 in highly stereoselective anti-Alder fashion at 25 °C within 15 min. The reaction stereochemistry happens to be identical with that observed for methyl acrylate alone where the reaction time is significantly longer. Therefore, a rate acceleration of this magnitude is not accompanied by a detectable level of stereochemical crossover, suggesting that stereoselection is not uniquely linked to transition-state timing and must be dictated by more complex factors.

The reaction course followed by cyclobutadiene has proven informative. As already noted, oxidation of its Fe(CO)\textsubscript{3} complex with ceric ammonium nitrate led to selective oxidation of 1. This untoward
process did not occur with trimethylamine N-oxide which instead acted slowly on the complex to liberate the cyclobutadiene reagent. Although kinetic data are not available, monitoring of the progress of reaction clearly demonstrated that decomplexation of the reactive dienophile was complete only after 2 days at room temperature. The gradual liberation of the cyclobutadiene in this fashion, coupled with its obvious reluctance to add to isodicyclopentadiene, proved particularly conducive to the capture of tautomer 43. The anti-Alder course of this cycloaddition is attributed to steric congestion present in the other possible alignment of reactants. Particularly relevant is the fact that 43 competes effectively to capture cyclobutadiene despite its very low concentration. The isolated yield of 55 (42% based on cyclobutadiene) indicates that possible dimerization to syn-tricyclooctadiene is significantly curtailed.

The stereoselectivity patterns documented here serve to reemphasize the uniqueness of triazolinediones. Their proclivity for capturing 1 from above-plane causes us to continue to regard them as "maverick" dienophiles.
INTRODUCTION

Considering the various theories that have been put forth to explain the stereoselective behavior of 1sodicyclopentadiene, only two remain as viable candidates, the $\sigma/\pi$ interaction concept of Paquette and Gleiter$^{2,65}$ and the torsional-steric control model of Houk and Brown$^{74}$. Additional experimentation is desirable for probing the validity of either hypothesis. Much of previous investigation has focused on substituent modification of the existing norbornyl and cyclopentadienyl systems. Very little examination has been directed towards the effect of an alteration of ring size in the bicyclic moiety. Other strained bicyclic systems with high lying $\sigma$ orbitals present the possibility of exhibiting $\sigma/\pi$ interactions.

It was previously known that enlargement of the bicyclic skeleton fused to the cyclopentadiene ring made a deleterious impact on the stereochemical outcome. In the bicyclo[2.2.2]octyl compound (26), a
reduction in stereoselection was seen in its Diels-Alder reactions. Preferential addition to the face opposite the etheno bridge was observed with acetylenic dienophiles in a consistent 80:20 ratio. In contrast, N-methyltriazolinedione, N-phenylmaleimide and maleic anhydride favored the face syn to the etheno bridge to a comparable degree. Top attack would appear contradictory to steric arguments since the etheno bridge is less sterically demanding. Both the Paquette-Gleiter and Brown-Houk theories have been extended to incorporate the results with this system.

MM2 calculations conducted by Houk, indicate the hydrogens on the etheno bridges bend toward the ethano bridge by 1.2° in the optimized geometry of bicyclo[2.2.2]octadiene. This bending is in the opposite direction to that found in norbornadiene. In norbornadiene, the olefinic hydrogens on one etheno bridge must bend toward the other etheno bridge to relieve eclipsing with bonds to the bridgehead. However, in bicyclo[2.2.2]octadiene, they must bend away from the other etheno bridge to relieve eclipsing. The attack of small dienophiles on 26 is predicted to occur from the side of the ethano bridge since bending about a double bond in bicyclo[2.2.2]octadiene is toward the ethano bridge. Bending at the cyclopentadiene-bicyclooctadiene fusion will occur in the direction favored in order to minimize torsional strain in the transition state. Only sterically demanding but highly reactive dienophiles are expected to attack from the less hindered etheno bridge side.

Brown and Houk have recently devised an MM2-based model for predicting stereochemistries in Diels-Alder reactions of unsymmetrically
substituted cyclopentadienes which are spiro fused at the 5-position to
norbornane or bicyclo[2.2.2]octane. The observed stereoselectivities
are attributed to steric effects. The predictions made by the MM2
models were nearly quantitative. They view the success of this model
as lending support to their theory on the origin of \( \pi \)-facial
selectivity in isodicyclopentadiene systems.

In terms of the orbital tilting concept, the lessened strain in a
bicyclo[2.2.2]octenyl system leads to a reduction in the energy of its
orbitals and a concurrent drop-off in the intensity of long-range
interaction. INDO and SPINDO calculations revealed some disrotatory
tilting of the terminal diene \( \pi \) orbitals toward the ethano bridge, but
to a much lesser degree than in isodicyclopentadiene. Above-plane
attack is predicted to be moderately favored. This also shows up in the
calculated four-electron destabilization energy difference between exo
and endo addition. Endo attack is favored by 0.84 kcal/mol.
Therefore, the release of ring strain by this magnitude lowers the
energies of the framework \( \sigma \) orbitals to levels which cause inefficient
mixing with the subajacent diene \( \pi \) orbital and thereby renders it
incapable of dramatically influencing \( \pi \)-face stereoselectivity.
Subsequent work in the Paquette laboratories showed that fusion of a cyclopropane ring to the ethano bridge of this system was ineffective in directing the stereochemical course of dienophile capture\textsuperscript{25}.

![Chemical Structures](image)

The stereochemical profile of 59 was similar to that observed for 26. On the other hand, 60 exhibited negligible selectivity in most cases.

Another interesting facet of isodicyclopentadiene chemistry deals with the stereoselective response of its corresponding anion to metal complexation (cf. Table 5). The isodicyclopentadienide anion has been given due consideration from the viewpoint of $\sigma/\pi$ interactions\textsuperscript{30}. From modified INDO\textsuperscript{66} calculations, the lowest occupied $\pi$ molecular orbitals of 28 and 29 contain significant contributions from the $\sigma$ frame. The strongest deformation along the $x$-axis direction is found at Cl. For both carbanions, INDO predicts a rotation toward the methylene bridge.
It was suggested that this unique orbital construct has several different product-determinative options which could operate during metal complexation. Should overlap control be dominant and orbital tilting restricted to the $\psi_1$ level, all metal ions might prefer approach from above-plane because their symmetry related $d_z^2$, s, and $p_z$ orbitals would be directed to the center of the more electron-rich cyclopentadienide core. Alternatively, it is possible that the $p\pi$ orbitals in $\psi_2$ are sufficiently tilted to override the effect of $\psi_1$, due to the generally greater importance of $d\pi-\psi_2$ interactions relative to those of the $d\sigma-\psi_1$ type. In this event, a metallic species with contracted $d\pi$ orbitals (i.e., a small metal or one in a high oxidation state) would likely favor top-face bonding, whereas one with diffuse $d\pi$ orbitals could enjoy better overlap on the bottom face.

Experimental findings run contrary to that predicted in the latter option. Isodicyclopentadienide anion 28 and dimethylaminofulvene system 61 preferentially coordinate to metals on the exo surface. There have been a few exceptional cases discovered in titanocene complexes where facial selectivity was dependent upon reaction temperature. In an effort to define more precisely the factors that contribute to the general relationship among structural and electronic
perturbations and stereoselection, the following investigation into the facial preferences of two chiral, nonracemic, bicyclo[3.1.1]heptyl-fused cyclopentadienes (62 and 63) was undertaken.

While it is clear that the two \( \pi \) faces in 62 and 63 are distinguished sterically by virtue of geminal dissubstitution on one of the bridges, its diene unit is not symmetrically disposed about the cyclobutane ring. The proximity to only one bridgehead C-H bond rather than to two (as in 1 and 12) was expected to generate torsional energy differences of unknown, though expectedly smaller magnitude\(^7\), to lessen substantially and perhaps curtail completely the \( \pi \)-orbital tilting believed to operate in 1 and 12\(^2,6\) and to eliminate essentially all polarizability factors\(^22,7\). In these terms, 62 and 63 can be seen to differ appreciably from the norbornenyl and norbornyl analogues. It was these perceived distinctions that led to the investigation of the \( \pi \)-facially selective course of Diels-Alder cycloadditions to 62 and of metal coordination to 63. The (-)-pinene cyclopentadiene 62 was synthesized by a route recently devised in the Paquette group\(^4\) (Scheme IV).
Scheme IV. Synthesis of (-)-Pinenecyclopentadiene (62).

\[
\begin{align*}
\text{OR} & \xrightarrow{\text{KO/Bu, DMSO, 75°C, 80%}} \text{CHBr}_3, 50\% \text{NaOH/KO/Bu, 80%} \\
\text{a, R=H} & \\
\text{b, R=Ts} \quad \xrightarrow{\text{CH}_3\text{Li, ether, 87%}} 62
\end{align*}
\]

Results

Stereochemical Course of [4 + 2] Cycloadditions to 62.

The Diels-Alder studies were carried out with several reagents recognized to possess varied dienophilic reactivity. In most of the reactions, the dimerization of 62 was seen to be modestly competitive with capture of the coreactant. Also, while one might reasonably expect concurrent addition to the several [1,5]-H shift isomers of 62, only traces of these adducts were seen and their characterization was not pursued.

Admixture of 62 with 1 equiv of N-phenylmaleimide in a benzene-hexane (10:1) solvent system at 25 °C led to the complete consumption of diene in 16 h. $^1$H NMR analysis of the product mixture immediately
following solvent evaporation revealed two adducts to be present in a 1:9 ratio. These isomers were readily separated by chromatography and identified as 64 and 65, respectively, on the basis of their spectra. Two groups of signals were particularly diagnostic of stereochemical detail. Whereas the methyl singlets of 65 are seen to be separated by 0.43 ppm, those associated with 64 are more widely spaced ($\Delta \delta_{\text{CH}_3} = 0.69$ ppm, see Table 9). This phenomenon is due entirely to upfield displacement of the inner methyl group in 64, which is attributed to its penetration into the shielding region of the internal $\pi$ bond. Norbornene double bonds are now well known to experience deformation in the endo direction, particularly in syn-sesquino-bornenes\textsuperscript{77,78}. Topological deformation in this sense can set the proper spatial proximity only in 64. Otherwise, the $>\text{CHCO}$ protons in both adducts appear as mutually coupled doublets with no evidence of spin-spin interaction with the neighboring bridgehead hydrogens\textsuperscript{110}, thereby indicating the maleimide ring to be configured exo in both instances.

\[ \text{64} \quad \text{65} \]

When 62 was allowed to stand with $p$-benzoquinone at room temperature for 24 h, a pair of adducts was produced in a 1:10 ratio. These were separated chromatographically and identified as 66 and 67, respectively. The exo orientation of the cyclohexenedione ring in both
compounds was apparent from the singlet nature of the pair of bridgehead protons. The absence of coupling to the \(\alpha\)-carbonyl hydrogens arises because of their endo disposition and approximately 90\(^\circ\) dihedral angle relationship\(^\text{110}\). Once again, the less dominant product exhibited the more widely spaced methyl singlets (Table 9). The notably shielded nature of the inner methyl absorption in 66 is, as before, consistent only with its positioning on the endo surface of the norbornene double bond.

![66](image)

![67](image)

The use of dimethyl acetylenedicarboxylate gave rise to a 1:6 mixture of adducts. The structural features of the resulting dienes were established in much the same manner, with \(\delta_{\text{CH}_3}\) for 68 (0.84 ppm) being double that for 69 (0.42 ppm).

![68](image)

![69](image)

The cycloaddition with (Z)-1,2-bis(phenylsulfonylethylene also led to a two-component product mixture (ratio 1:2.2). However, the
disulfones so produced exhibited \( \Delta \delta_{\text{CH}_3} \) values (0.47 and 0.56 ppm) that were not widely disparate and consequently did not conform to the precedent established in the three earlier examples. The underlying cause of this effect is that both 70 and 71 are the result of above-plane attack on 62. It proved an easy matter to subject each adduct to reductive desulfonylation. The identical hydrocarbon isolated from the two reactions exhibits a \( \Delta \delta_{\text{CH}_3} \) of 0.40 ppm in complete agreement with its formulation as 72. Assignment of exo stereochemistry to the phenylsulfonyl groups in major product 71 stems from the usual coupling constant measurements and the appearance of \( H_a \) (see formula) at \( \delta 0.50 \). Projection of the sulfone substituents into regions of space surrounding \( H_a \) as in 70 introduces a deshielding element that is clearly evident (\( \delta H_a = 1.32 \)).
Table 9. Comparative $^1$H NMR Spectral Data for Cycloadducts 64-72
(300 MHz, CDCl$_3$ Solution, $\delta$ Values)

<table>
<thead>
<tr>
<th>COMPD</th>
<th>endo CH$_3$</th>
<th>exo CH$_3$</th>
<th>$\Delta$H$_{CH_3}$, ppm</th>
<th>H$_a$ (syn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>0.61</td>
<td>1.30</td>
<td>0.69</td>
<td>1.24</td>
</tr>
<tr>
<td>65</td>
<td>0.87</td>
<td>1.30</td>
<td>0.43</td>
<td>0.68</td>
</tr>
<tr>
<td>66</td>
<td>0.54</td>
<td>1.28</td>
<td>0.74</td>
<td>1.22</td>
</tr>
<tr>
<td>67</td>
<td>0.86</td>
<td>1.30</td>
<td>0.44</td>
<td>0.62</td>
</tr>
<tr>
<td>68</td>
<td>0.41</td>
<td>1.25</td>
<td>0.84</td>
<td>1.28</td>
</tr>
<tr>
<td>69</td>
<td>0.86</td>
<td>1.25</td>
<td>0.39</td>
<td>0.67</td>
</tr>
<tr>
<td>70</td>
<td>0.82</td>
<td>1.38</td>
<td>0.56</td>
<td>1.30</td>
</tr>
<tr>
<td>71</td>
<td>0.73</td>
<td>1.20</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>72</td>
<td>0.89</td>
<td>1.29</td>
<td>0.40</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Synthesis of Dimethylaminofulvene (63).

The synthesis of pinenefulvene 63 was accomplished following a
procedure modeled after that described for cyclopentadiene$^{113}$ and
isodicyclopentadiene$^{41}$. Treatment of the lithium salt of 62 in cold
(-10 °C) tetrahydrofuran with the complex of dimethylformamide and
dimethyl sulfate afforded the 6-(dimethylamino)-substituted fulvene 63 as
a 1:1 mixture of $E/Z$ isomers in 25% yield (Scheme V).

Scheme V. Preparation of Dimethylaminofulvene (63).
Conversion of 63 to Metallocene Derivatives

The purpose of this phase of the investigation was to assess the stereochemical course of ligand substitution by 63 on metal transfer reagents under the conditions of light and heat. (η⁵-Cyclopentadienyl) (η⁶-2-xylene)iron(II) hexafluorophosphate (73) and (η⁵-cyclopentadienyl) tris(acetonitrile)ruthenium(II) hexafluorophosphate (74) have previously been utilized successfully for these purposes (Scheme VI) and were employed here.

Scheme VI. Prototypical Transfer Reactions of 73 and 74.

The photochemical reaction of 73 is speculated to result from LF excitation which predominately leads to products arising from metal-ligand bond scission. Dissociation of the arene gives FeCp⁺ species prior to attack by the incoming ligand. This ligand transfer reaction has also been induced thermally, but temperatures of 130-150 °C are necessary. In contrast, no observable reaction occurs upon photolysis of the ruthenium complex 74. The acetonitrile ligands can be
displaced, however, under thermal conditions\textsuperscript{114b}.

Irradiation of a solution of 63 and a slight excess of 73 in dichloromethane with a 250-W sunlamp for 24 h and subsequent alkaline hydrolysis gave rise to a 27:73 mixture of 75 and 76. It proved not feasible to separate these isomers chromatographically. Accordingly, the mixture was reduced with sodium borohydride to the corresponding alcohols 77 and 78, which were individually obtained in a pure state and reoxidized to 75 and 76, respectively, with manganese dioxide\textsuperscript{116} (Scheme VII). The alcohols were found to be relatively unstable to traces of acid and to light. This was especially true in the case of 78, which when dissolved in CDCl$_3$ deposited insoluble iron-containing decomposition products before a NMR spectrum could be successfully recorded. This complication could, however, be avoided by making recourse to C$_6$D$_6$ as solvent. When left exposed to laboratory light, once pure alcohols were rather quickly transformed into a multiplet mixture as determined by TLC. When protected from light, 77 and 78 were indefinitely stable.
Scheme VII. Separation-Regeneration Scheme for Ferrocene Compounds 75-76.

The major alcohol 77 was also transformed into dimeric ether 79 by reaction with 0.5 molar equiv of p-toluenesulfonyl chloride in the presence of triethylamine.

The stereochemical features of 75-78 were assigned on the basis of
their $^1$H NMR spectra (in C$_6$D$_6$ solution), particularly in relation to the chemical shifts of the pairs of hydrogen atoms and methyl groups on the one-carbon bridges. As in related molecules$^{41}$, the metal exerts a demonstrably strong deshielding influence on the syn, endo substituent. The appearance of the endo methyl singlet of 75 at $\delta$ 1.16 ($\Delta\delta_{CH_3} = 0.10$ ppm) is very telling, particularly in relation to its more normal location in the spectrum of 76 ($\delta$ 0.43, $\Delta\delta_{CH_3} = 0.75$). The situation is reversed for $H_a$, which appears at $\delta$ 0.61 in 75 and at $\delta$ 1.86 in 76. This long-range anisotropy has been observed as well in the dichlorotitanium complex$^{42}$ and is deemed to be entirely reliable as a diagnostic of stereochemistry. The assignments in the ruthenium series to follow are based as well on this deshielding phenomenon (Table 10).

<table>
<thead>
<tr>
<th>COMPD</th>
<th>endo CH$_3$</th>
<th>syn CH$_3$</th>
<th>$\Delta\delta_{CH_3}$ ppm</th>
<th>$H_a$ (syn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.16</td>
<td>1.26</td>
<td>0.10</td>
<td>0.61</td>
</tr>
<tr>
<td>76</td>
<td>0.43</td>
<td>1.18</td>
<td>0.75</td>
<td>1.86</td>
</tr>
<tr>
<td>77</td>
<td>1.54</td>
<td>1.24</td>
<td>0.30</td>
<td>0.73</td>
</tr>
<tr>
<td>78</td>
<td>0.53</td>
<td>1.24</td>
<td>0.71</td>
<td>2.30</td>
</tr>
<tr>
<td>80</td>
<td>1.05</td>
<td>1.14</td>
<td>0.09</td>
<td>0.89</td>
</tr>
<tr>
<td>81</td>
<td>0.62</td>
<td>1.20</td>
<td>0.58</td>
<td>1.52</td>
</tr>
<tr>
<td>82</td>
<td>1.19</td>
<td>1.25</td>
<td>0.06</td>
<td>0.99</td>
</tr>
<tr>
<td>83</td>
<td>0.70</td>
<td>1.25</td>
<td>0.55</td>
<td>1.81</td>
</tr>
</tbody>
</table>

When 63 was heated with ruthenium(II) salt 74 in 1,2-dichloroethane, ligand transfer smoothly took place to provide a 7:93 mixture of 80 and 81 after alkaline hydrolysis (Scheme VIII). As before, the aldehyde mixture was reduced to the corresponding alcohols (82 and 83) with
ethanolic sodium borohydride. At this point, it proved an easy matter to obtain the two isomers in isomerically pure form by chromatography.

Scheme VIII. Reaction Sequence for Separation of Ruthenocene Compounds.

![Scheme VIII](image)

A quick glance at Table 10 reveals that the diamagnetic shielding experienced by the endo methyl or syn apical hydrogen is significantly less for ruthenium than for iron. This phenomenon is likely linked to the distance of the metal from the centroid of the proximal cyclopentadienide ring, which is approximately 0.15 Å greater for Ru than for Fe."
Discussion

Where 62 is concerned, the collective Diels-Alder results show that [4 + 2] cycloaddition proceeds with a kinetic preference for bonding to that cyclopentadiene face which is syn to the less sterically congested methano bridge (see Figure 12). The remarkably comparable data for N-phenylmaleimide (10:1 or 91%) and p-benzoquinone (9:1 or 90%) reveal also that only anti-Alder alignment is involved in either approach trajectory. These features are illustrated below. The nonbonded steric repulsions generated during incipient bonding as shown on the right can be reasonably attributed to the cause of the 10-fold rate retardation.

![Figure 12. Approach Trajectories for Anti-Alder Cycloaddition to 62.](image)

Despite the rod-shaped nature of dimethyl acetylenedicarboxylate, the product ratio (6:1 = 86%) represents only a quite small difference from the cases just discussed. On the other hand, (Z)-1,2-bis(phenylsulfonyl)ethylene captures 62 only from the direction of its unsubstituted methano bridge. Another important distinction surfaces. This dienophile exhibits a greater demand for capture in the Alder mode
and actually delivers 70 as 30% of the product mixture. This feature may not have an electronic origin, but merely be the result of relatively longer C-S bonds such that the phenylsulfonyl groups are now projected further from the endo apical hydrogen.

Whereas reaction of 62 and the anion of 62, respectively, with Fe(CO)\textsubscript{5} and TiCl\textsubscript{4} likewise proceeds in stereochemically homogeneous fashion from the more open face\textsuperscript{42}, comparable levels of stereocontrol do not accompany the ligand transfer reactions involving 73 and 74, although the ruthenium example does sense a quite good kinetic driving force for complexation from the same direction. The stronger preference for Ru (7:93) relative to Fe (27:73) for bonding to the less hindered face of a 4-(dimethylamino)-substituted fulvene has been noted previously\textsuperscript{41} and remains to be satisfactorily rationalized.

It is not coincidental that 62 uniformly undergoes Diels-Alder capture and metal complexation from the less hindered above-plane direction (as drawn). Steric effects brought on by the endo-methyl substituent are controlling. This behavior is strikingly different from that earlier established for the norbornyl-\(\textsubscript{1}\) and norbornenyl-fused\(\textsubscript{12}\) cyclopentadienes, which generally experience [4 + 2] bonding predominantly from below-plane and metal complexation on their exo surface. This contrast draws one inevitably to the conclusion that the effects which emanate from the laterally fused bicyclo[2.2.1]heptane subunits in 1 and 12 have considerable impact on the \(\pi\)-face stereochemical outcome of the Diels-Alder reactions.

Subsequent to the completion of this work, a study was published\textsuperscript{24} concerning the stereochemical outcome from Diels-Alder reactions of
"homodehydroisodicyclopentadiene" (27). This structural perturbation was seen to completely reverse the observed facial selection in comparison to dehydroisodicyclopentadiene (12) except with dimethyl acetylenedicarboxylate where bonding occurred in equal proportions to both faces. The results could be satisfactorily rationalized on the basis of steric arguments.
CHAPTER III
REMOTE ELECTRONIC EFFECTS IN CYCLOADDITION REACTIONS OF \(\pi\)-X-PHENYLISODICYCLOPENTAFULVENES

Introduction

The basis for determining \(\sigma-\pi\) interactions and their effect on the tilt of the terminal \(\pi\) lobes of isodicyclopentadiene (1) relies on the relative orbital energies of the interacting wave functions and on the size of the interaction matrix element \(F_{\mu\nu}\). As \(F_{\mu\nu}\) increases, so does the level of interaction and a resulting greater disrotation of the lobes is experienced.

The potential for modulation of the extent and direction of \(\pi\) lobe disrotation has been demonstrated\(^{65}\). The relative position of the interacting high lying \(\sigma\) orbital and the affected \(\pi\) orbital (i.e. \(\pi\) either above or below the \(\sigma\) level) changes the predicted direction of disrotation. The rotation can be described roughly as the superimposition of the \(p_y\) component from the \(\sigma\) frame and the \(p_z\) component from the \(\pi\) network, as illustrated below.

\[\text{Diagram of rotation}\]

88
An approximate measure of the level of $\sigma/\pi$ interaction should be
the size of the $p_y$ coefficient in the wave function$^{18}$. Information
about the sense of rotation can be gleaned from the sign of the $p_y$
coefficient. If $p_y$ and $p_z$ show the same sign, the $p_z$ lobes are rotated
toward the methano bridge as in isodicyclopentadiene. Conversely, if the
signs of $p_y$ and $p_z$ are opposite, the lobes are tilted away from the
methano bridge. A reduction in the size of the $p_y$ coefficient is
expected to translate into a diminished stereoselectivity when steric
effects are negligible.

Alteration in the extent and direction of disrotation has been
realized by appropriate substitution at the methylene carbon of the
cyclopentadiene subunit and/or at the apical methano bridge
carbon$^{17,18,21}$. In the spiro-5 compound 25, molecular orbital
calculations predict the terminal $\pi$ lobes are rotated away from the
methano bridge. Superimposed on this rotation is a second tilting in
the $x/z$ plane wherein the terminal lobes are rotated outwardly from the
methano bridge, while the $2p_z$ lobes of the internal carbons are skewed
inwardly (see Figure 13). Above-plane approach of a dienophile is
favored. On the other hand, the spiro-3 compound 24, exhibits opposite
deformations and below-plane addition minimizes the four-electron
destabilization energy. These predictions have been substantiated
experimentally$^{21}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diagram.png}
\caption{Structures of compounds 24 and 25.}
\end{figure}
Figure 13. Schematic representation of the predicted orbital tilting in the $\pi_s +$ Walsh of 24 and the $\pi_s$ MO of 25.

In the case of apical-substituted derivatives 17 and 18, long-range through bond interactions reduce the size of the $p_y$ coefficients comparably and the stereoselectivity drops off to minimal levels$^{17,18}$. However, the structural modifications in 19, cause disrotation to occur away from the methano bridge and leads to preferential bonding to the top-face$^{18}$. 

17  
18  
19
The stereoselective response of several fulvene systems have been investigated. In all cases, an overwhelming predilection for below-plane capture of dienophiles was observed\textsuperscript{19,20}.

\[
\text{Interaction analyses of 20 and 21 were carried out using INDO and MINDO/3 calculations in conjunction with photoelectron spectroscopy}{^{20}}. \text{ Significant contributions from precanonical } \sigma\text{-ribbon orbitals were contained in the lowest occupied } n \text{ orbital. A pronounced rotation in the } n \text{ lobes occurs but is restricted to the longitudinal axis because the atomic orbital amplitudes of the } \sigma\text{-ribbon combination are large in this direction (see Figure 14). The } n \text{ lobes at the terminal carbon atoms of the diene fragment are rotated in the direction of the ethano bridge while the opposite deformation is predicted for C-1 and C-4/C-5.}
\]

\[
\text{Figure 14. Predicted deformation of the } n \text{ lobes of 20/21.}
\]
In the event of topside attack, an intense antibonding interaction develops between the occupied $\pi$ orbitals of the attacking dienophile and the lowest diene function because the $\pi$ lobes at C-2/C-3 are pointed toward the dienophile $2\pi$ component. This antibonding four-electron four-center interaction is substantially reduced during endo attack where the terminal $\pi$ lobes of the diene fragment are now rotated away from the dienophile.

The fact that these modest structural alterations can be satisfactorily explained by $\sigma-\pi$ interactions lends much support to the Paquette-Gleiter orbital tilting theory\textsuperscript{65}. Rationalization of these results by the Brown-Houk torsional control argument\textsuperscript{74} requires the modulation of stereoselectivity to be linked to changes in the dihedral angle relationship between the norbornyl bridgehead C-H bonds and those central to the cyclopentadiene ring. X-ray analyses of several fulvene derivatives reveal little or no dihedral angle modification amongst them; however, the stereoselectivity varied considerably\textsuperscript{19a}. These experimental observations appear inconsistent with Houk's torsional analyses.

No assessment has yet been made of the potential for modulating the $\pi$-facial selectivity of [4 + 2] cycloadditions in isodicyclopentafulvene systems by remote electronic perturbations. The examination of remote substituent effects on stereoselection in Diels-Alder cycloadditions to $\alpha$-substituted phenylisodicyclopentafulvenes (84) and possible theoretical implications are the subject of this chapter.
Part 1. Cycloaddition Chemistry of \( \varphi \)-X-Phenylisodicyclopentafulvenes.

It is reasonably assumed that torsional factors with respect to the norbornyl fragment should be invariant throughout the series. However, due to steric interactions, the phenyl ring will be twisted from coplanarity with the fulvene system presumably by a constant, yet undefined angle \( \phi^{117} \). If the twist angle is not greatly affected by the electronic character of X, then a nearly constant steric environment is presented to the approaching dienophile. Therefore, any alteration in facial bonding patterns will be solely due to extended electronic factors.

\[
\begin{align*}
\text{Results} \\
\text{Synthesis of Isodicyclopentafulvenes} \hspace{1cm} (84, X = H, Me, OMe, Cl, NMe_2)
\end{align*}
\]

Isodicyclopentafulvenes (84, \( X = H, Me, OMe, Cl, NMe_2 \)) were prepared by condensation of the appropriate 4-substituted benzaldehyde with isodicyclopentadiene at room temperature in the presence of alcoholic potassium hydroxide\(^{117a} \). The fulvenes were obtained as highly colored solids in moderate yields. These conditions were found incompatible for the preparation of fulvenes with strong electron
accepting substituents (i.e., \( X = F, \text{CF}_3, \text{NO}_2, \text{CN} \)). Satisfactory yields of these fulvenes were obtained by the use of sodium methoxide as base in methanol under reflux conditions (see Scheme IX).

**Scheme IX. Preparation of Isodicyclopentafulvenes (84).**

![Scheme IX](image)

**Cycloaddition Studies of Isodicyclopentafulvenes**

Since 84 is sluggish in its capacity as a 4\( \pi \) donor, elevated temperatures or high-pressure conditions were required to achieve reasonable rates. In fact, no reaction was observed in the case of \( N \)-methyltriazolinedione (\( \text{CH}_2\text{Cl}_2, -78^\circ \text{C to RT} \)), \( p \)-benzoquinone (\( \text{C}_6\text{H}_6, \text{RT to reflux} \)) or (methoxyvinylcarbene)tungsten pentacarbonyl (\( \text{C}_6\text{H}_6, \text{RT to reflux} \)).

The situation with \( N \)-phenylmaleimide (60-70 \( ^\circ \text{C, C}_6\text{H}_6 \)) involved exclusive formation of 85 by below-plane anti-Alder capture. The telltale stereochemical features of these adducts are (i) the high-field position (\( \delta \) 0.41-0.46) of their endo ethano protons\(^{14} \), (ii) the lack of coupling between the vicinal \( \alpha \)-carbonyl and bridgehead protons\(^{110} \), and (iii) the characteristic shielding of their apical methano and
methyldene carbons following epoxidation of the central double bond\textsuperscript{20,102}. Exemplary is the comparison between 85-OMe and 86-OMe. The methano and methyldene carbon of 86-OMe (37.51 and 137.69 ppm, respectively) are shifted upfield by 12.1 and 9.0 ppm relative to those in its precursor 85-OMe (49.56 and 146.65 ppm). The remote apical methyldene carbon of 86-OMe (119.82 ppm) exhibits a downfield shift of 5.8 ppm in comparison to its position in 85-OMe (114.04 ppm) which is consistent with that observed in similar systems\textsuperscript{20}.

Exposure of 84 to dimethyl acetylenedicarboxylate in warm benzene afforded the air-sensitive adducts 87 of related stereochemistry. The facility of autoxidation\textsuperscript{13}, the strong shielding of the endo ethano protons ($\delta$ 0.56-0.60), and the comparative $^{13}$C NMR data of 87 and 88 reflecting the strong shielding contributions of the oxirane ring proved particularly diagnostic in this series. An increased stability of 87-NMe$_2$ towards autoxidation was noted. Epoxide formation was never seen even after relatively long exposure to the atmosphere.
Benzyne, as generated from anthranilic acid and isoamyl nitrite\textsuperscript{118}, reacted with 84 in hot 1,2-dimethoxyethane to give 89. Purification of the cycloadducts 89 was hampered due to the extremely facile autoxidation process. Proton NMR spectra (300 MHz) were recorded for each adduct immediately after filtration of the reaction mixture through a small plug of silica gel (elution with 1-2% ethyl acetate in petroleum ether). Several \textsuperscript{13}C NMR spectra of cleaner mixtures were also obtained before transformation to the corresponding epoxides 90 by treatment with \textit{m}-chloroperbenzoic acid (MCPBA). Again, the dimethylamino cycloadduct was stable to both autoxidation and to epoxidation by MCPBA.

\begin{align*}
\text{89} & \\
\text{90} & 
\end{align*}

As before, product homogeneity was established by \textsuperscript{1}H/\textsuperscript{13}C NMR, and epoxidation was subsequently utilized to define stereochemistry. The most revealing aspect from analysis of the \textsuperscript{1}H NMR spectra of 89 is the extreme upfield shift of the endo ethano protons (\(\delta -0.02\) to \(-0.05\)). Long-range shielding of this magnitude could only arise from benzyne addition to the endo surface of 84. Representative \textsuperscript{13}C NMR spectral comparison of 90-Me showed the expected shielding of both the methano and methylidene carbons (34.44 and 154.89 ppm) and deshielding of the remote methylidene carbon (110.13 ppm) relative to those in 89-Me (47.20, 164.21 and 104.22 ppm, respectively).
The above results disclose that the response of 84 to highly reactive dienophiles is dictated overwhelmingly by the adjacent norbornane ring. This is, however, not the case with (Z)-1,2-bis(phenylsulfonyl)ethylene\(^{119}\). Following pressurization with 84 at 90,000 psi and 20 °C for 5-7 days, two adducts were isolated, chromatographically separated, and identified as 91 and 92. These sulfones exhibit highly characteristic \(^1H\) NMR spectra (see Table II). Their relative ratios were, as before, reproduced in duplicate and triplicate experiments and determined by HPLC analysis of the crude reaction mixtures.

The \(^1H\) NMR spectra of the major adducts 91 show endo ethano proton resonances at \(\delta 1.03-1.07\) whereas in 92 they are shifted upfield (\(\delta 0.73-0.74\)). The \(\alpha\)-sulfonyl protons in 91 are seen to couple to the vicinal bridgehead protons (J = 3 Hz) suggesting Alder-type products. On the other hand, these protons in 92 are not coupled and are shielded by 0.92 ppm relative to 91 which implies anti-Alder stereochemistry. Possibly the most revealing comparison is that the syn proton on the methano bridge in 91 is deshielded to an extent of 1.18 ppm with respect to its position in 92. Such a large difference is reasonable in view of the proposed stereochemical assignments. In 91, projection of the
phenylsulfonyl groups around this proton could be expected to have a deshielding effect\textsuperscript{42b}. In 92, this proton would project into the shielding cone of the apical double bond.

Table 11. Comparative \textsuperscript{1}H NMR Data for 91 and 92.

(300 MHz, CDCl\textsubscript{3} solution, \textDelta values)

<table>
<thead>
<tr>
<th>Compound</th>
<th>H\textsubscript{endo}</th>
<th>H\textsubscript{a-sulfonyl}</th>
<th>H\textsubscript{syn}</th>
</tr>
</thead>
<tbody>
<tr>
<td>91-H</td>
<td>1.06</td>
<td>4.25</td>
<td>2.25</td>
</tr>
<tr>
<td>92-H</td>
<td>0.74</td>
<td>3.33</td>
<td>1.07</td>
</tr>
<tr>
<td>91-Me</td>
<td>1.03</td>
<td>4.25</td>
<td>2.23</td>
</tr>
<tr>
<td>92-Me</td>
<td>0.74</td>
<td>3.32</td>
<td>1.07</td>
</tr>
<tr>
<td>91-OMe</td>
<td>1.05</td>
<td>4.23</td>
<td>2.24</td>
</tr>
<tr>
<td>92-OMe</td>
<td>0.74</td>
<td>3.37</td>
<td>1.06</td>
</tr>
<tr>
<td>91-NMe\textsubscript{2}</td>
<td>1.06</td>
<td>4.24</td>
<td>2.23</td>
</tr>
<tr>
<td>92-NMe\textsubscript{2}</td>
<td>0.73</td>
<td>3.34</td>
<td>1.07</td>
</tr>
<tr>
<td>91-Cl</td>
<td>1.07</td>
<td>4.24</td>
<td>2.24</td>
</tr>
<tr>
<td>92-Cl</td>
<td>0.65</td>
<td>3.25</td>
<td>1.03</td>
</tr>
<tr>
<td>91-NO\textsubscript{2}</td>
<td>1.04</td>
<td>4.17</td>
<td>2.26</td>
</tr>
<tr>
<td>92-NO\textsubscript{2}</td>
<td>0.73</td>
<td>3.33</td>
<td>1.09</td>
</tr>
<tr>
<td>91-F</td>
<td>1.05</td>
<td>4.23</td>
<td>2.24</td>
</tr>
<tr>
<td>92-F</td>
<td>0.74</td>
<td>3.30</td>
<td>1.07</td>
</tr>
<tr>
<td>91-CF\textsubscript{3}</td>
<td>1.05</td>
<td>4.24</td>
<td>2.25</td>
</tr>
<tr>
<td>92-CF\textsubscript{3}</td>
<td>0.73</td>
<td>3.32</td>
<td>1.08</td>
</tr>
<tr>
<td>91-CN</td>
<td>1.04</td>
<td>4.23</td>
<td>2.25</td>
</tr>
<tr>
<td>92-CN</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The preference for above-plane cycloaddition is attributed to steric factors arising from the relatively large steric bulk of the phenylsulfonyl groups\textsuperscript{10}. However, this contribution can reasonably be expected to be consistent throughout the series. Strikingly, the variation in the 91/92 ratio as a function of X (Table 12) adheres well to a linear free-energy relationship (Figure 15), the NO\textsubscript{2} and CN examples excepted. Maverick reactivity of p-NO\textsubscript{2} and p-CN substituted systems has been encountered frequently\textsuperscript{120, 121a}. Assuming the 91/92 ratio reflects kinetic differences, the mean value (3.3) provides an estimate of the difference in activation energy\textsuperscript{122} between top-face/endo and bottom-face/exo bonding of 0.69 kcal/mol.
Table 12. Statistical Analysis of Substituent Effects on the 91:92 Product Ratios by the DSP Method According to the Four Established Scale Parameters.

<table>
<thead>
<tr>
<th>scale parameter</th>
<th>data utilized</th>
<th>$\rho_I$</th>
<th>$\rho_R$</th>
<th>$\lambda$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_R^-$</td>
<td>all points</td>
<td>0.110</td>
<td>0.152</td>
<td>1.382</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>omit CN</td>
<td>0.375</td>
<td>0.591</td>
<td>1.576</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>omit NO$_2$, CN</td>
<td>1.471</td>
<td>2.264</td>
<td>1.539</td>
<td>0.604</td>
</tr>
<tr>
<td>$\sigma_R^0$</td>
<td>all points</td>
<td>-0.234</td>
<td>1.145</td>
<td>-4.893</td>
<td>0.167</td>
</tr>
<tr>
<td></td>
<td>omit CN</td>
<td>0.143</td>
<td>1.703</td>
<td>11.909</td>
<td>0.431</td>
</tr>
<tr>
<td></td>
<td>omit NO$_2$, CN</td>
<td>1.116</td>
<td>2.662</td>
<td>2.385</td>
<td>0.842</td>
</tr>
<tr>
<td>$\sigma_R(BA)$</td>
<td>all points</td>
<td>-0.349</td>
<td>1.074</td>
<td>-3.077</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>omit CN</td>
<td>0.061</td>
<td>1.413</td>
<td>23.164</td>
<td>0.570</td>
</tr>
<tr>
<td></td>
<td>omit NO$_2$, CN</td>
<td>0.961</td>
<td>1.897</td>
<td>1.974</td>
<td>0.923</td>
</tr>
<tr>
<td>$\sigma_R^+$</td>
<td>all points</td>
<td>-0.574</td>
<td>0.753</td>
<td>-1.312</td>
<td>0.430</td>
</tr>
<tr>
<td></td>
<td>omit CN</td>
<td>-0.161</td>
<td>0.887</td>
<td>-5.509</td>
<td>0.717</td>
</tr>
<tr>
<td></td>
<td>omit NO$_2$, CN</td>
<td>0.579</td>
<td>1.025</td>
<td>1.770</td>
<td>0.959</td>
</tr>
</tbody>
</table>

Figure 15. Plot of the $\sigma_R^+$ values of X versus the experimental 91:92 product ratios.
Statistical evaluation of the data was accomplished by means of the dual substituent parameter (DSP) method\textsuperscript{121}. The DSP analysis considers the electronic effect of a remote substituent to derive from two factors, its polar nature ($\sigma_I$) and its resonance contribution ($\sigma_R$). The range of $X$ was purposefully chosen to be broadly representative of $\sigma_I$ and $\sigma_R$. Multiple linear regression analyses provided fits expressed as $R^2$, the values of which can range from 0 to 1. The larger the value, the better the fit. The term ($\lambda = \sigma_R/\sigma_I$) is an indicator of the relative importance of resonance and inductive effects. The results, summarized in Table 13, indicate the model that best predicts the 91:92 ratios to depend on $\sigma_R^+$ values, particularly if NO$_2$ and CN are omitted from the regression analysis.

**Table 13. Comparison of Experimentally Determined 91:92 Product Ratios with those Predicted on the Basis of Several Sigma Constants.**

<table>
<thead>
<tr>
<th>$X$</th>
<th>obsd$^a$</th>
<th>pred-1$^b$</th>
<th>pred-2$^c$</th>
<th>pred-3$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe$_2$</td>
<td>1.8</td>
<td>2.1</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>OMe</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>F</td>
<td>3.3</td>
<td>3.1</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Cl</td>
<td>3.6</td>
<td>3.3</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>3.3</td>
<td>3.1</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>2.9</td>
<td>4.5</td>
<td>4.3</td>
<td>4.0</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>3.7</td>
<td>4.1</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td>CN</td>
<td>2.3</td>
<td>4.4</td>
<td>4.2</td>
<td>4.0</td>
</tr>
<tr>
<td>H</td>
<td>3.5</td>
<td>3.4</td>
<td>3.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

$^a$Average values derived from experiments performed at least in duplicate except for the chloro example (accuracy level = $\pm 0.2$). $^b$Calculated from correlation using $\sigma_R^0$ values, but omitting NO$_2$ and CN. $^c$As in using $\sigma_R(BA)$ values. $^d$As in using $\sigma_R^+$ values.

Para-substituent effects on the chemical shifts of H$_{cis}$ and H$_\alpha$ in 84, when analyzed by the DSP method, were also found to provide the best linear correlation when evaluated against $\sigma_R^+$ values. $H_{trans}$ gave a
poorer correlation (Tables 14 and 15).

Table 14. Selected Proton Chemical Shifts of 85.
(80 MHz, C6D6 solution, δ values)

<table>
<thead>
<tr>
<th>X</th>
<th>H_cis</th>
<th>H_trans</th>
<th>H_α</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe2</td>
<td>6.55</td>
<td>5.94</td>
<td>7.03</td>
</tr>
<tr>
<td>OMe</td>
<td>6.34</td>
<td>5.84</td>
<td>6.86</td>
</tr>
<tr>
<td>Me</td>
<td>6.33</td>
<td>5.82</td>
<td>6.88</td>
</tr>
<tr>
<td>H</td>
<td>6.24</td>
<td>5.78</td>
<td>6.84</td>
</tr>
<tr>
<td>F</td>
<td>6.10</td>
<td>5.75</td>
<td>6.67</td>
</tr>
<tr>
<td>Cl</td>
<td>6.06</td>
<td>5.73</td>
<td>6.61</td>
</tr>
<tr>
<td>CF3</td>
<td>6.01</td>
<td>5.70</td>
<td>6.60</td>
</tr>
<tr>
<td>CN</td>
<td>6.07</td>
<td>5.81</td>
<td>6.64</td>
</tr>
<tr>
<td>NO2</td>
<td>5.90</td>
<td>5.64</td>
<td>6.47</td>
</tr>
</tbody>
</table>

Table 15. DSP Analysis of Proton Shifts of 85 against σR+ values.

<table>
<thead>
<tr>
<th>proton</th>
<th>ρ_I</th>
<th>ρ_R</th>
<th>λ</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_cis</td>
<td>-0.467</td>
<td>-0.180</td>
<td>0.39</td>
<td>0.955</td>
</tr>
<tr>
<td>H_trans</td>
<td>-0.141</td>
<td>-0.082</td>
<td>0.58</td>
<td>0.742</td>
</tr>
<tr>
<td>H_α</td>
<td>-0.479</td>
<td>-0.125</td>
<td>0.26</td>
<td>0.950</td>
</tr>
</tbody>
</table>

One could question whether high pressure conditions would have any bearing on the stereoselective outcome. High pressure is known to strongly accelerate Diels-Alder reactions due to their large negative activation volumes (typically -31.5 to -42 cm³/mol)¹²³. The use of pressure also avoids retro Diels-Alder complications since activation volumes are positive.

It has been determined that for an increase in selectivity to occur by application of high pressure, the difference in activation volumes for the respective orientations needs to exceed ±1 cm³/mol¹²⁴. Typical ΔΔV⁺ values for endo/exo orientations of Diels-Alder addition to
cyclopentadiene are between 1.0 and -0.5 cm³/mol²⁴b. Therefore, stereoselectivity would not be expected to increase as a result of high pressure. In the case of hetero Diels-Alder reactions where the ΔW⁺ values are much larger (5.8 cm³/mol), diastereoselectivity has been enhanced by applying high pressure²⁴a.

Pressure effects on the facial selectivity of 84 can be dismissed since it would require that the difference in activation volumes is dependent upon the electronic nature of the substituent. It has been demonstrated that activation volumes for Diels-Alder reactions are independent of the substituent²⁵ within a given series of substrates.

The non-existence of pressure effects on facial selection was supported by subjecting a mixture of isodicyclopentadiene and (Z)-1,2-bis(phenylsulfonyl)ethylene to high pressure conditions. By ¹H NMR analysis of the crude reaction mixture, the same product ratio of top- to bottom-face adducts (1.2:1) was realized as was previously observed at atmospheric pressure¹⁰.

That the observed stereoselection is a result of kinetically-controlled dienophile capture was demonstrated by subjection of individual disulfone adducts admixed with isodicyclopentadiene to the high pressure reaction conditions. After 24 h, HPLC analysis of the mixtures showed no indication of retro Diels-Alder fragmentation of the initially formed cycloadduct.
Discussion

This work has shown that the stereochemical course of Diels-Alder cycloaddition to 84 is intrinsically related to the nature of para substituent X, provided the dienophile is only modestly reactive. Also disclosed is that a very good correlation exists between the top/bottom ratios and $\sigma_R^+$ values except for the NO$_2$ and CN substituents, which exhibit correspondingly unexalted effects. Multiple linear regression analyses demonstrated that subtle long-range electronic effects can control the extent to which one or the other $\pi$-surface of 84 is utilized during [4 + 2] bonding.

It is of interest to explore the mechanism(s) by which the substituent effect could be transmitted through the $\pi$ system. Several options are available for substituents attached to a conjugated system$^{126}$.

I. Through-space Transmission
   (a) direct electrostatic interactions
   (b) mesomeric field effect (a secondary electrostatic interaction in which changes are produced by polarization of a $\pi$ system)

II. Through-bond Transmission
   (a) resonance (charge transfer between substituent and the $\pi$ electron system)
   (b) $\pi$-inductive or $\pi$-polarization (redistribution of electron density due to the electronegativity of the substituent)
   (c) $\sigma$-inductive (redistribution of electron density via the $\sigma$ framework)

Numerous attempts have been made at separating the through-space effects from the electronic effects transmitted through-bond. As a result, a large variety of substituent constant scales have been developed. The substituent constants used for the DSP analyses were
chosen because they are well established measures of polar and resonance effects. Alternative scales such as the Swain-Lupton F/R values\textsuperscript{127} or Dewar's FMMF constants\textsuperscript{126a} were employed with similar results. Since none of these treatments take into consideration the ability and mode of transmitting the substituent effect, similar correlations would be expected.

The somewhat exceptional nature of NO\textsubscript{2} and CN can be understood in conformational and \(\pi\)-polarization terms. Under normal circumstances, the phenyl ring in 84 is forced out of coplanarity with the fulvene ring for steric reasons\textsuperscript{117}. Electron-releasing groups X increase the overlap of the phenyl and fulvene subsystems and significantly reduce the dihedral angle between the two rings. This expenditure of energy due to the unfavorable conformation is compensated by conjugation of the substituent with the fulvene system. When X is characterized instead by an elevated \(\sigma_R^+\) value, not only is the resonance effect strongly curtailed but \(\pi\)-electronic transmission is additionally attenuated because of the twist in existence about the bond interconnecting the two networks. The maximum deviation from coplanarity would be expected in the case of NO\textsubscript{2}\textsuperscript{128}.

On the basis of studies conducted on 4-substituted styrenes, resonance effects are expected to drop off by \(\cos^2\phi\) whereas \(\pi\)-polarization effects decrease by \(0.7\cos^2\phi\). This is due to a direct, independent polarization mechanism which exists at \(\phi = 90^\circ\) and accounts for 30\% of the \(\pi\)-polarization effect\textsuperscript{126b}. In coplanar systems, an "extended \(\pi\)-polarization" effect also operates.
An alternative explanation for the irregular behavior of NO₂ and CN lies in the fact that a linear correlation need not exist. Usually deviations from a linear free energy relationship are attributed to a change in the mechanism of the reaction. However, if one interprets substituent effects in view of PMO theory, it is possible to show the deviation in some cases to be a result of a crossover in the preferred frontier orbital interactions without a change of mechanism.¹²⁹

For the reaction of a series of dienes with the same dienophile, the greatest part of the interaction energy depends on the frontier orbital separation of the addends:

\[ \Delta E = AY^2[(H_0\text{dien} - LU_{\text{dienophile}})^{-1} + (H_0\text{dienophile} - LU_{\text{dien}})^{-1}] \]

The pattern of this function is represented by two branches of hyperbola. When both terms are important, superimposition of the two curves gives a U-shaped function. From this, three types of Diels-Alder reactions can be distinguished on the basis of relative frontier orbital separations. This is illustrated in the diagram below.

Substituent effects on all three reaction types have been
investigated\cite{130b,131} and excellent correlations between HOMO energies versus $\sigma^+$, log $k$ versus $\sigma^+$, and HOMO energies versus log $k$ exist for the normal and inverse types. Therefore the HOMO-LUMO energies of a diene must be a function of the substituents so that the Hammett substituent constants can be taken as a quantitative measure of the substituent effect on the HOMO-LUMO energies. As the sigma value increases, the HOMO-LUMO energies are lowered.

However, when both frontier molecular interactions are similar (i.e., neutral type reactions) a deviation from linearity in a Hammett plot could signal an inversion in preferred interactions (see Figure 16).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure16.png}
\caption{Change in Favored FMO Interaction with Increasing Sigma Value.}
\end{figure}

Photoelectron spectroscopic and theoretical studies on 84 have been conducted\cite{132}. The orbital assignments and correlation diagram is shown in Figure 17. The first two PE bands are due to ionization from the
fulvene-type $a_2$ and $b_1$ orbitals. Bands 3 and 4 arise from the two highest occupied $\pi$-MOs of the benzene ring. In contrast to the usual fulvene sequence ($a_2$ above $b_1$), MINDO/3 calculations predict a switch in this splitting pattern for 84.

\[ \text{Figure 17. Correlation Diagram for Ionization Energies of 84.} \]
Very good correlations are obtained using Hammett $\sigma_p$ values versus the experimental ionization potentials and calculated LUMO energies.

The results are summarized in Tables 16 and 17.

**Table 16. Tabulation of Orbital Energies for 84 (values in eV).**

<table>
<thead>
<tr>
<th>$X$</th>
<th>$I_{v,1}$</th>
<th>$I_{v,2}$</th>
<th>$I_{v,3}$</th>
<th>$I_{v,4}$</th>
<th>$-E_{\text{lumo}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe$_2$</td>
<td>6.90</td>
<td>7.60</td>
<td>8.30</td>
<td>8.70</td>
<td>0.61$^a$</td>
</tr>
<tr>
<td>OMe</td>
<td>7.65</td>
<td>7.71</td>
<td>9.12</td>
<td>9.22</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>7.60</td>
<td>7.90</td>
<td>8.90</td>
<td>9.30</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7.70</td>
<td>7.90</td>
<td>9.00</td>
<td>9.50</td>
<td>0.84</td>
</tr>
<tr>
<td>Cl</td>
<td>7.80</td>
<td>7.92</td>
<td>9.42</td>
<td>9.54</td>
<td>1.08</td>
</tr>
<tr>
<td>CN</td>
<td>8.00</td>
<td>8.30</td>
<td>9.70</td>
<td>9.78</td>
<td>1.30</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>8.00</td>
<td>8.30</td>
<td>9.50</td>
<td>10.00</td>
<td>1.41</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>8.10</td>
<td>8.40</td>
<td>9.70</td>
<td>10.02</td>
<td>1.71</td>
</tr>
</tbody>
</table>

$^a$Calculations carried out for NH$_2$.

**Table 17. Results of Linear Regression Analysis of Orbital Energies According to Hammett Sigma Values.**

<table>
<thead>
<tr>
<th>parameter</th>
<th>$\rho$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{v,1}$</td>
<td>1.35</td>
<td>0.943</td>
</tr>
<tr>
<td>$I_{v,2}$</td>
<td>1.74</td>
<td>0.952</td>
</tr>
<tr>
<td>$I_{v,3}$</td>
<td>1.08</td>
<td>0.949</td>
</tr>
<tr>
<td>$I_{v,4}$</td>
<td>1.20</td>
<td>0.970</td>
</tr>
<tr>
<td>$-E_{\text{lumo}}$</td>
<td>1.28</td>
<td>0.944</td>
</tr>
</tbody>
</table>

In the most basic sense, stereoselectivity in the Diels-Alder reaction of 84 with (Z)-1,2-bis(phenylsulfonyl)ethylene would be a result of kinetic differences between top-face and bottom-face addition. The observed linear relationship between the energy of the fulvene HOMO and the corresponding substituent constants demonstrates that the relative rates of reaction with a dienophile would be expected to follow the same trend.

If one assumes the substituent effect within this series influences the relative rates of top-face and bottom-face attack by comparable magnitudes (e.g., electron donation to the fulvene speeds up top-face
and bottom-face attack whereas electron withdrawal retards both rates to the same extent), then a linear relationship between product ratios and HOMO energies or substituent constants should be found. This explicitly assumes a normal Diels-Alder reaction.

If on the other hand, the energy difference between the HOMO of the fulvene and the LUMO of the dienophile is similar to the energy difference between the HOMO of the dienophile and the LUMO of the fulvene, a neutral Diels-Alder reaction would be expected. Perturbation theory (vide supra) predicts a parabolic relationship due to the importance of both frontier orbital interactions.

Knowledge of the HOMO-LUMO energies of this dienophile would be desirable to determine which category the reaction falls into. Since this information is lacking, an indication of which reaction type we are dealing with may be obtained indirectly. Linear plots were not obtained for the 91:92 product ratios verses either fulvene HOMOs or LUMOs. A least-squares regression analysis of the relationships gave correlation coefficients of -0.566 and -0.337, respectively. A linear relationship was found however with the 91:92 product ratios and the fulvene HOMO-LUMO energy differences (correlation coefficient = 0.862).

Competition studies were carried out with various combinations of two fulvenes. Dichloromethane solutions containing equimolar amounts of the two fulvenes and 0.5 equivalent of (Z)-1,2-bis(phenylsulfonyl)ethylene were pressurized at 6000 atm for periods ranging from 1-4 hours. HPLC analysis of the reaction mixtures was used to determine the relative proportions of the corresponding cycloadducts. From the results summarized in Table 18, it appears the relative rates do not
Table 18. Relative Reactivities in Cycloaddition of 84 with (Z)-1,2-bis(phenylsulfonyl)ethylene.

<table>
<thead>
<tr>
<th>$X_1/X_2$</th>
<th>Product Ratio$^a$</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$/H</td>
<td>1.3:1</td>
<td>H&gt;NO$_2$</td>
</tr>
<tr>
<td>NO$_2$/Cl</td>
<td>2.2:1</td>
<td>NO$_2$&gt;Cl</td>
</tr>
<tr>
<td>OMe/Me</td>
<td>1.1:1</td>
<td>OMe&gt;Me</td>
</tr>
<tr>
<td>NO$_2$/Me</td>
<td>1.9:1</td>
<td>Me&gt;NO$_2$</td>
</tr>
<tr>
<td>NMe$_2$/OMe</td>
<td>1.5:1</td>
<td>OMe&gt;NMe$_2$</td>
</tr>
<tr>
<td>Me/F</td>
<td>2.2:1</td>
<td>Me&gt;F</td>
</tr>
<tr>
<td>H/OMe</td>
<td>1.5:1</td>
<td>H&gt;OMe</td>
</tr>
<tr>
<td>F/NO$_2$</td>
<td>1.1:1</td>
<td>F&gt;NO$_2$</td>
</tr>
</tbody>
</table>

$^a$Product ratio determined for top-face adducts.

At this point, it becomes intriguing to inquire if the observed $\pi$-facial preferences have a rationale in terms of $\sigma-\pi$ interactions.

If one accepts the orbital tilting hypothesis and sets 84-H as the standard, the heightened production of 90 when $X$ is, for example, NMe$_2$ or OMe signals that electron-releasing groups provide an influence synergistic to the norbornane contribution, much as in isodicyclopentadienyl anion$^{30}$. Electron release into the fulvene ring may thus cause the $p\pi$ lobes at the reaction sites to experience disrotatory tilting toward the methano bridge$^{65}$ and/or deformation along the longitudinal axis in the direction of the ethano bridge$^{20}$. Tandem photoelectron spectroscopic/theoretical studies of 84 are expected to clarify which phenomenon is more dominant. Nonetheless, the correlation observed here provides striking confirmation that remote electronic influences can indeed directly affect Diels-Alder stereoselection.

With demonstration of the ability to modulate the \( \pi \)-facial selectivity of Diels-Alder reactions by means of remote electronic perturbation (\textit{vide supra}), we sought to examine the response of ionophoric molecules of type 93 to Diels-Alder reaction with \((Z)\)-1,2-bis(phenylsulfonyl)ethylene when free of metal coordination and when bound to either \( \text{Na}^+ \) or \( \text{K}^+ \) as appropriate. Electrostatic transmission through an arene ring has been earlier noted by Andrews, et al.\textsuperscript{134} in their probe of the electrochemical oxidizability of aza-15-crown-5-linked ferrocenes of type 94. Uncovered in the course of their studies was the fact that binding of \( \text{Li}^+ \) shifted the ferrocene oxidation wave to more positive potentials. However, no new ferrocene redox couples were seen when \( \text{Na}^+ \) or \( \text{K}^+ \) was brought into coordination, a phenomenon that has been attributed to the lower charge densities of these cations when compared to \( \text{Li}^+ \).
Results

Synthesis of Fulvene-linked Aza-crown Ethers

The aldehydes necessary for gaining access to 93a and 93b were prepared as shown in Scheme X according to published procedures\textsuperscript{135}. Several alkaline reagents were examined as promoters of the condensation of 95a and 95b with isodicyclopentadiene. Most gave disappointingly low yields of fulvene. Ultimately, we settled on sodium methoxide in refluxing benzene, this base-solvent system delivering 93a and 93b in 17 and 40% yields, respectively.

Scheme X. Preparation of Aldehydes 95a and 95b.
The metal complexes 96 and 97 were in turn readily prepared by dissolution of the fulvene in hot methanol with the appropriate salt. Expectedly, these complexes hold solvent quite tenaciously, a property also shared to a lesser extent by the parent ionophores themselves.

Cycloaddition Studies of Fulvene-linked Aza-crown Ethers

The cycloadditions of the fulvenes and their complexes were carried out with (Z)-bis(phenylsulfonyl)ethylene in a high pressure reactor. In general, the extent of adduct formation proved modest, even after relatively long reaction times. Variations in the amount of pressure and the duration of these conditions were examined in an effort to improve matters. In the vicinity of 90,000 psi, reactions conducted in dichloromethane solution were quite inefficient (3-5% isolated yields), even after one week. At 125,000 psi, the aza-crown ether complexes were seen to precipitate from solution. At the compromise pressure of 100,000 psi, the yields of adducts appeared to be optimized (31-53%). Purification of the products was somewhat complicated by their highly polar nature and instability (retro-Diels-Alder degradation). Many recrystallizations proved necessary to free the adducts of traces of the bright orange 93 and to obtain them as the white solids they are.
The ratios of exo-face to endo-face cycloadducts were determined by $^1$H NMR analysis of the unpurified reaction mixtures immediately following solvent removal in vacuo. Analytical HPLC methods were also explored, but these were found unsatisfactory in separating the isomers adequately. Where the metal complexed examples are concerned, product ratios were recorded both before and after decomplexation. No changes were seen within the limits of experimental error. The results are compiled in Table 19.

The stereochemical assignments to 98 and 99 are based on their $^1$H NMR spectra, alongside appropriate comparative reference to the spectral properties of 91 and 92 earlier recorded. With 93a and 93b, the above-plane cycloadducts 99 predominated, as was seen previously with 84 (X = NMe$_2$). However, the above-plane tendencies are evidently more intense in 93a (2.5) and 93b (3.1) than they are in the standard (1.8). When the aza-crown ethers are complexed, the $\pi$-facial selectivity drops to levels comparable to that seen with isodicyclopentadiene itself$^{10}$. These data go contrary to the usual trend observed for 84 (X now electron-
withdrawing) where a pronounced increase in the relative proportion of 91 invariantly materializes.

Table 19. Cycloadduct Product Ratios and Yields from Diels-Alder Reaction of Fulvene-linked Aza-Crown Ethers and (Z)-1,2-bis(phenylsulfonyl)ethylene\(^a\).

<table>
<thead>
<tr>
<th>Fulvene</th>
<th>Ratio 99/98</th>
<th>Yield, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93a</td>
<td>2.5</td>
<td>53</td>
</tr>
<tr>
<td>93b</td>
<td>3.1</td>
<td>31</td>
</tr>
<tr>
<td>96</td>
<td>1.4</td>
<td>49</td>
</tr>
<tr>
<td>97</td>
<td>1.2</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^a\)Average values derived from experiments performed at least in duplicate. Product ratios were determined by \(^1\)H NMR analysis of unpurified reaction mixtures.

Discussion

Inspection of the data in Table 19 reveals unusually high-product ratios for 93a and 93b, especially when viewed in light of the behavior of the simpler \(\varphi\)-dimethylamino substituted 84 (1.8). In actuality, the stereoselectivity patterns exhibited by the free ionophores compare more closely to those established earlier for the \(\varphi\)-methoxy- (2.4) and \(\varphi\)-methylphenylisodicyclopentafulvenes (3.3). The degree of electron release via resonance in 93a and 93b can be qualitatively gauged by the changes in chemical shift of the aryl protons ortho to the nitrogen substituent. For 93a and 93b, these hydrogens are seen at \(\delta 6.64\) and \(\delta 6.66\), respectively, in CDCl\(_3\). In 84 (\(X = \text{NMe}_2\)), the same hydrogens appear to lower field (\(\delta 6.69\)). Conjugative electron drift toward the fulvene ring will also affect the \(\pi\)-densities at the \(\alpha\)-fulvene carbon\(^{117}\), but the precise chemical shifts of these centers have proved difficult to unravel from the collection of signals present in the 140-160 ppm range. Nonetheless, the flanking aryl proton values implicate a
greater ability on the part of the \( p{-}N\text{Me}_2 \) group to engage in resonance relative to the aza-crown ether subunits. This dropoff in electronic delocalization may arise in part from the greater steric bulk of the heterocyclic rings which effectively precludes equally facile stereoaignment of the nitrogen electron pair and arene \( \pi \)-cloud.

To gain additional insight into the contrasting trends exhibited by the aza-crown ether compounds in comparison to the previous study on \( p \)-substituted phenylisodicyclopentafulvenes, the lithium complex of the aza-18-crown-6 fulvene (93b) and the methiodide of the dimethylamino fulvene (84) were prepared for spectral comparisons.

These compounds would hopefully give some indication of the extent of positive charge developing on the nitrogen atom upon complexation. In the methiodide, the nitrogen carries a full positive charge. This effect can be seen by examination of the aryl protons ortho to the nitrogen substituent. These protons are greatly shifted downfield (\( \delta 7.96 \)) in comparison to the dimethylamino derivative (\( \delta 6.69 \)). A shift of 1.27 ppm occurs with these protons. The rest of the protons of the \( \pi \)-system show little change except for the fulvene proton cis to the phenyl ring (\( \Delta \delta 0.26 \)) and the meta-protons (\( \Delta \delta 0.20 \)). The shielding effect on the cis fulvene proton has been attributed to an increased fulvene-phenyl dihedral angle resulting from reduced \( \pi \) delocalization with electron-withdrawing substituents\(^\text{117} \). The increased angle moves the cis fulvene proton into a more shielding region of the phenyl ring.

Using the methiodide as a standard for the maximum change in chemical shift, the crown ether complexes are seen to have much less than a full unit positive charge on the nitrogen atom. The change in
chemical shift of the ortho-hydrogens is only 0.19 ppm and 0.36 ppm for the aza-15-crown-5 and aza-18-crown-6 cases, respectively.

Additionally, there is very little change in the cis fulvene protons upon complexation. Only a 0.04-0.06 ppm shielding effect occurs. Thus, it can be concluded that coordination to the metal ion does not induce much of a positive charge on the nitrogen and therefore does not reduce the amount of electron donation into the π-system to the extent it does when the nitrogen carries a full charge.

The higher charge density of Li⁺ is thought to induce more of a positive charge on the nitrogen atom, as deduced from the electrochemical studies by Andrews. On this basis, the Li⁺ complex of the 18-crown-6 fulvene was prepared. It was expected that the greater interaction of Li⁺ with the nitrogen atom would be manifested by a larger change in
chemical shift of the ortho-protons upon complexation than was seen in
the Na⁺ and K⁺ cases.

The 15-crown-5 fulvene was examined first, but removal of the
solvent from the admixed fulvene and LiClO₄ led only to decomplexation.
More satisfactory results were obtained with the 18-crown-6 fulvene. ¹H
NMR analysis of the lithium iodide complex showed, however, the same
chemical shift as in the potassium complex.

The Diels-Alder cycloaddition with (Z)-1,2-bis(phenylsulfonyl)-
ethylene and the methiodide 84-²NMe₃ was briefly examined. The
reactants were dissolved in dichloromethane and subjected to 90,000 psi
pressure conditions for 4 days. ¹H NMR analysis of the crude reaction
mixture immediately after solvent removal showed the presence of two
cycloadducts in a 1.9:1 ratio (top:bottom). The stereochemistry of the
minor cycloadduct was confirmed by preparing the methiodide of the
previously known dimethylamino-substituted adduct. A small amount of
adduct arising from the trans-disulfone was also observed.

Although the 99/98 ratios for 93a and 93b are uncharacteristically
high, those of their complexes are exceptionally low but do compare
favorably with that obtained in the methiodide case. Coordination to
Na⁺ and K⁺ does have the consequence of deshielding the ortho aryl
protons (δ 6.66 for 96 and 7.02 for 97). A general downfield drift is
also clearly apparent at all the trigonal carbons when the ¹³C NMR
spectra of the free and coordinated ionophores are compared. Thus, it
is concluded that the major cause of the enhanced substituent-induced
above-plane π-facial stereoselectivity in the cycloaddition of (Z)-1,2-
bis(phenylsulfonyl) ethylene to 93a and 93b stems from a lessened π-
density redistribution relative to that operational in the p-
dimethylamino model. The electronegativity of the oxygen centers within
the crown rings almost certainly contributes as well to this overall
phenomenon.

Notwithstanding, these features do not adequately explain per se
the near equilization of \( \pi \)-facial stereoselectivity exhibited by the
complexes. Previously, the exceptionally low product distributions
resulting from 84-NO\(_2\) and 84-CN were understood in conformational and
\( \pi \)-polarization terms. Electron-releasing groups in 84 are recognized to
increase \( \pi \)-orbital overlap with resultant reduction in the dihedral
angle between the fulvene and phenyl rings. In contrast, when \( X \) is
powerfully electron-withdrawing, \( \pi \)-electronic transmission to the
fulvene ring is curtailed and the interconnective bond between the two
\( \pi \)-networks reassumes its sterically preferred twist. As concerns 96 and
97, the metal-coordinated nitrogen atom cannot be as electron-
withdrawing as nitro and cyano. Unlike the latter substituents, it does
not enter into \( \pi \)-electron withdrawal from the fulvene sector by "reverse
resonance". Only inductive schemes remain and correlation versus \( \sigma^+ \) is
not realistic. Since substituent constants for metal coordinated
nitrogen centers are not available, no analysis by dual substituent
parameter methods\(^{121}\) can be implemented.

It is of interest to examine the Hammett plot when these results
are added. The positions of the aza-crown ether linked-fulvenes were
estimated on the basis of their product ratios. Usually a deviation
from linearity such as this is attributed to a change in the rate
determining step. This is not applicable for a concerted Diels-Alder
reaction.

What is clear is that the metal-nitrogen coordination as in 96 and 97 is synergistic to the norbornane contribution (note that 84 with X = H generates an adduct ratio of 3.5). The latter strongly favors below-plane dienophile capture\textsuperscript{65} and is especially strong in structurally less encumbered isodicyclopentafulvenes\textsuperscript{19,20}. 
CHAPTER IV
ATTEMPTED SYNTHESSES OF OPTICALLY PURE AND RACEMIC 5,5-
DIMETHYLISODICYCLOPENTADIENE

Introduction

Optically active cyclopentadienes have recently commandeered a
great deal of synthetic interest due to their enormous potential for
controlling the stereochemical outcome of many reactions\textsuperscript{42-45, 136}. Their most obvious value as chiral building blocks lies in Diels-
Alder/retro Diels-Alder strategies\textsuperscript{137}. However, the use of chiral
cyclopentadienes as ligands to transition metals and the potential for
controlling stereoselectivity in reactions with them is a relatively new
and fertile area. Most notable is their use as catalyst precursors for
enantioselective hydrogenations\textsuperscript{138}.

It was envisioned that compound 100 could be obtained in optically
pure form from a suitable precursor from the chiral pool. This
isodicyclopentadiene, geminally substituted on the ethano bridge, also
provides the opportunity to examine whether the added steric bulk would
cause a crossover in the stereoselective response established by
isodicyclopentadiene.

Such substitution is expected to have little effect on the extent and direction of \( \pi \)-orbital tilting. Therefore, electronic factors should remain constant when compared to isodicyclopentadiene and the predicted stereochemical outcome should still be an overwhelming preference for below-plane addition of dienophiles. While the added bulk is rather remote from the reacting centers of the cyclopentadiene ring, it has been shown in the pinene-fused case 63 (discussed in Chapter II) that addition to the face opposite the geminally-substituted bridge was preferred. If steric factors become important in reactions of compound 100, then it should be manifested by a decreased penchant for below-plane facial selectivity.

At this point, only small progress has been made toward the preparation of 100. Both optically pure and racemic approaches have been examined. Suprisingly, much transformational resistance was discovered in preparing suitable precursors for the various cyclopentannulation strategies.
Results

Synthesis of (-)-β-Fenchocamphorone

Three separate synthetic approaches were examined in the preparation of optically pure 100. For each approach, a common precursor, (-)-β-fenchocamphorone, was needed. Since (-)-fenchone can be obtained in high optical purity (>97%, Aldrich) and its transformation into (-)-β-fenchocamphorone (see Scheme XI) was known\textsuperscript{139}, it seemed an ideal starting point.

Scheme XI. Preparation of (-)-β-Fenchocamphorone (105).

\[
\begin{align*}
(-)-\text{Fenchone} & \xrightarrow{\text{H}_2\text{NNNH}_2, \text{AcOH, EtOH}} \text{Fenchohydrazone} & \xrightarrow{\text{HgO (yellow), MeOH}} \text{101} & \xrightarrow{\text{KHSO}_4, \text{heat}} \\
\text{102} & \xrightarrow{\text{1. O}_3, 	ext{CH}_2\text{Cl}_2/\text{MeOH (3:1)}} \xrightarrow{\text{2. Me}_2\text{S}} \\
\end{align*}
\]

(-)-Fenchone was converted to its hydrazone in 96% yield by refluxing with 100% hydrazine and anhydrous acetic acid in absolute ethanol for 5 h. Oxidation of the hydrazone with yellow mercuric oxide in absolute methanol gave cyclofenchene (101) by the decomposition of the intermediate diazo compound to the carbene, which is followed by C-H
insertion into the neighboring endo proton bond. The yield of cyclofenchene varied widely depending upon the source of the mercuric oxide. Using commercially available yellow mercuric oxide, yields of cyclofenchene ranged from 47-71% with the formation of some α-fenchene (103) as by-product. Freshly prepared yellow mercuric oxide, from mercuric chloride and sodium hydroxide, provided cyclofenchene in 43-46% yield but without any by-product formation. Preparing yellow mercuric oxide from mercuric sulfate and sodium hydroxide gave much poorer yields of cyclofenchene (27%).

Acid-catalyzed rearrangement of cyclofenchene by refluxing with solid potassium bisulfate afforded a mixture of products via cleavage of the cyclopropane ring. This mixture contained seven components by capillary GC analysis. The four major compounds consisted of cyclofenchene, γ-fenchene (102), α-fenchene (103), and β-fenchene (104) in 39%, 9%, 16% and 36% yield, respectively. This mixture could be partially separated by spinning band distillation at atmospheric pressure. The lower boiling components could be reduced to give an enriched mixture of β- and α-fenchene (approximate 2:1 ratio).

Ozonolysis of the fenchene mixture (-78 °C, CH₂Cl₂/MeOH 3:1) provided the desired ketone mixture after dimethyl sulfide reduction of the ozonide. The ketones could be separated by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether) by collection of the first part and last part of the peak. The faster moving isomer, α-fenchocamphorone, could be obtained very pure (>99% by capillary GC). However, the desired β-isomer required several recycles through MPLC followed by preparative GC to reach a comparable state of purity. This
was clearly undesirable for the large scale operations needed to provide reasonable quantities of (−)-β-fenchocamphorone. Spinning band distillation of the ketone mixture was ineffective in separating the isomers.

In an attempt to improve matters, the fenchocamphorone mixture was converted into the corresponding semicarbazones. Recrystallization of the semicarbazone mixture five times from 65% ethanol in water provided the desired isomer (106) in 96% purity (by $^1$H NMR analysis).

A number of procedures for regeneration of the ketone were employed with varying degrees of success. Hydrolytic methods using reagents such as oxalic acid, acetone/pyridinium tosylate or sodium bisulfite had no effect on the semicarbazone. More satisfactory was the method described by Goldschmidt and Veer. Upon treatment of the semicarbazone with sodium nitrite in glacial acetic acid solution, complete disappearance of the semicarbazone occurred within 5-10 minutes. The yield and product purity was quite variable. Under identical conditions, the yields ranged from 36-74%. When the yields were high, the conversion was quite clean. However, due to the large material loss from recrystallization and the difficulty in regeneration of the ketone other purification methods were investigated.
The ketone mixture was then reduced with sodium borohydride to give a mixture of the corresponding endo alcohols, which could not be separated. At this point, it was clear that scaling-up was not feasible, but sufficient quantities of (-)-β-fenchocamphorone were available to explore several synthetic routes to optically pure 100.

Cyclopentannulation of (-)-β-Fenchocamphorone

Via Skattebøl rearrangement. The synthetic utility of the Skattebøl rearrangement\textsuperscript{44} for cyclopentadiene formation has been appreciated for some time\textsuperscript{44}. The proposed mechanism (Scheme XII) involves rearrangement of the initial vinlycyclopropylidene into a cyclopentylidene species, which inserts into the adjacent C-H bond to form the cyclopentadiene.

Scheme XII. Proposed Mechanism for the Skattebøl Rearrangement.

With the prior successes of the Skattebøl procedure in the preparation of (-)-pinene- and (+)-camphor-fused cyclopentadienes\textsuperscript{42}, dibromocyclopropane 109 became the targeted intermediate for the synthesis of 100 (see Scheme XIII). For this strategy to work, it is necessary for the dibromocarbene to react at the lesser substituted olefinic center. Although this reactivity pattern is contrary to that
usually followed by this reagent\textsuperscript{145}, exclusive cyclopropanation on the less substituted center has precedence\textsuperscript{42}.

Scheme XIII. Proposed Synthetic Approach to 100 via Skattebøl Rearrangement.

![Scheme XIII](image)

The Stille procedure\textsuperscript{146} for the palladium-catalyzed coupling of vinyl triflates and organostannanes worked quite well in this regard. The enol triflate of \((-\)-\(\beta\))-fenchocamphorone was readily obtained by condensation of its lithium enolate with N-phenyltriflimide\textsuperscript{147} in 63% yield, \([\alpha]_D^{20} -17.6^\circ\) (CHCl\(_3\)). Heating the triflate with trimethylvinyltin in the presence of a palladium(0) catalyst provided the diene product in excellent yield (98%). The optical rotation of this diene varied from \(-70.5^\circ\) to \(-216.3^\circ\) with different runs. The fluctuation was traced back to small amounts of hexamethylditin, which contaminated some of the material.

Dibromocyclopropanation\textsuperscript{18,42} of the diene either under phase-transfer conditions\textsuperscript{148} or with phenyl(tribromomethyl)mercury\textsuperscript{149} afforded a very unstable compound. Mass spectral data on this material indicated a
larger mass substance containing three bromine atoms. It seems likely that dibromocarbene addition occurred on the norbornene double bond. Products of this type are known to be unstable leading to rearranged compounds\textsuperscript{150a,b} (see below). 1,4-addition possibilities also exist\textsuperscript{150c,d}.

\[ \text{Via Intramolecular Wadsworth-Horner-Emmons Reaction.} \]

The next approach examined was modeled after that devised by Vollhardt\textsuperscript{136} for preparing (\(+\))-camphorcyclopentadiene. The key step would involve ring closure of the diketophosphonate 113 by a Wadsworth-Horner-Emmons condensation to give the enone (Scheme XIV). Reduction to to the allylic alcohol followed by dehydration would provide 100.

\textbf{Scheme XIV. Proposed Synthetic Route to 100 via Wadsworth-Horner-Emmons Cyclization.}
Alkylation of the lithium enolate of (-)-β-fenchocamphorone with methyl bromoacetate in the presence of 2.5 equivalents of HMPA provided the ketoester 110 in 75% yield. Protection of the ketone was required to ensure reaction at the less reactive ester carbonyl and was accomplished by standard methods\textsuperscript{151} to furnish ethylene ketal 111 (79% yield). Treatment of 111 with two equivalents of lithium dimethyl methylphosphonate\textsuperscript{152} in tetrahydrofuran gave no reaction at or below room temperature. Refluxing the reaction mixture for 24 h afforded 112 in poor yield (34% isolated). Deprotection of the carbonyl proved surprisingly difficult. Several general methods\textsuperscript{153} were investigated, but were unsuccessful. The only condition which provided any of the deprotected compound (113) was by refluxing with wet acetone in the presence of pyridinium p-toluenesulfonate (20% yield).

To avoid these difficulties, recourse was made to an alternate electrophile, dimethyl 3-bromo-2-ethoxypropenylphosphonate 114\textsuperscript{154}. This reagent would eliminate the need for protection/deprotection and thus directly provide the desired diketophosphonate upon hydrolysis of the enol ether (Scheme XV).
Alkylation of (-)-β-fenchocamphorone via its boron enolate was satisfactorily carried out with 114 in 82% isolated yield. Alkylation of the lithium enolate was found less efficient (44-52% yields). Hydrolysis of enol ether 115 provided the diketophosphonate 113. A variety of reagents and conditions were explored to effect cyclization of 113. Extensive polymerization was observed using standard sodium hydride methods. A very small amount of the enone was isolated (13%). Milder methods such as those employed by Aristoff (K$_2$CO$_3$, 18-crown-6, warm benzene) and Heathcock (tetrabutylammonium hydroxide, benzene-water, room temperature) did not lead to the desired product.

Normal chromatographic supports were incompatible for purification of the highly unstable enone (116). Florisil improved matters somewhat,
but distillation is probably the method of choice for larger scale syntheses.

Reduction of 116, using Dibal/\(\text{\textit{n}}\)-BuLi\(^{158}\) to ensure selective 1,2-reduction, yielded an unstable material. Purification of this compound was not attempted, rather the crude substance was dissolved in benzene and stirred in the presence of a catalytic amount of \(n\)-toluenesulfonic acid. Unfortunately, diene 100 could not be obtained by this method.

The apparent and unexpected instability of enone 116 to the Wadsworth-Horner-Emmons reaction conditions led to the abandonment of this route. However, further examination of cyclization conditions is warranted.

**Via the Bis-Wittig Manifold.** The bis-Wittig condensation\(^{159}\) has been successfully utilized in the preparation of several isodicyclopentadienes, which were otherwise inaccessible. The yields of these reactions are generally low partly due to the fact that intermolecular products are formed as well as cyclic ones.

Diketone 117 is a previously known compound\(^{160}\) obtainable by the selenium dioxide oxidation of (-)-\(\text{\textbeta}\)-fenchocamphorone. Condensation of this diketone with bisphosphonium salt 118\(^{161}\) would access the desired isodicyclopentadiene (Scheme XVI).

**Scheme XVI. Proposed Route to 100 using Twofold Wittig Condensation.**
Application of this extremely direct route was thwarted by the lack of reproducibility of the diketone synthesis. Instead of 117, there was consistently produced a dimeric compound, which has incorporated two selenium atoms (high resolution MS analysis). This dimer was inert to acid or base but was susceptible to treatment with 30% hydrogen peroxide to give unidentifiable material. Different solvents, different sources of selenium dioxide or sublimation of the dioxide had no effect on eliminating the formation of this untoward product. Only in one instance was the diketone produced albeit in a 3% yield.

Racemic routes were also studied, which would ultimately provide larger quantities of 100. The starting point of these strategies was 5,5-dimethylnorbornene 119. This compound was desirable not only because it can be produced in high yield (Scheme XVII) but also because methods exist for preparing it optically active once a successful synthetic route to 100 is developed.

Scheme XVII. Synthesis of 5,5-Dimethylnorbornene.

\[\text{Scheme XVII. Synthesis of 5,5-Dimethylnorbornene.}\]
Cyclopentannulation of 5,5-Dimethylnorbornene

Via Pauson-Khand Cycloaddition. The cobalt-catalyzed olefin acetylene cycloaddition, better known as the Pauson-Khand reaction, has been widely used for cyclopentenone construction. The mechanism shown in Scheme XVIII is initiated by complexation of the alkene to cobalt. This is followed by insertion of the alkene π-bond into one of the formal cobalt-carbon bonds of the alkyne complex. Subsequent CO insertion, reductive elimination of one cobalt and decomplexation of the other gives the cyclopentenone product.

Scheme XVIII. Proposed Mechanism of the Pauson-Khand Cycloaddition.

The synthetic approach towards the preparation of utilizing the Pauson-Khand reaction is outlined in Scheme XIX. Trimethylsilyl-acetylene was used instead of acetylene due to the reported higher yields and expected easy removal of the trimethylsilyl group at a later stage.
Scheme XIX. Proposed Route to 100 using the Pauson-Khand Cycloaddition.

Cycloaddition of trimethylsilylacetylene and 5,5-dimethylnorbornene proceeded smoothly to afford enone 120 as a mixture of regioisomers in 73% yield. The isomeric mixture was easily separable by MPLC on silica gel. Dibal reduction of the enone cleanly gave the corresponding allylic alcohols 121 in quantitative yield.

Numerous attempts to effect dehydration of alcohol 121 using a variety of reagents and conditions were unsuccessful as were protodesilylation methods on 120 or 121. In view of these setbacks, enone 120 was converted to its tosylhydrazone and subjected to Shapiro reaction conditions. The tosylhydrazone was consumed within 4 h; however, none of the expected diene was observed.

Concurrent with the above study, another approach based on Greene's method for cyclopentanone formation was under investigation (Scheme XX). Ultrasound-promoted cycloaddition of dichloroketene to 5,5-dimethylnorbornene rather conveniently provided dichlorocyclobutanone.
122 in good yield (74%). Ring expansion by treatment of 122 with ethereal diazomethane\textsuperscript{171} and subsequent monodechlorination\textsuperscript{172} in the presence of zinc/acetic acid led with clean conversion to chlorocyclopentanone 124 in 88% yield.

**Scheme XX. Proposed Synthetic Approach to 100 via Ring Expansion Chemistry.**

Attempts to dehydrohalogenate\textsuperscript{173} 124 all failed. The chlorocyclopentanone was then completely dechlorinated and the phenylselenide prepared by standard enolate chemistry\textsuperscript{174}. Subsequent treatment with 30% hydrogen peroxide under several conditions destroyed the selenide but gave no identifiable products.
Future Considerations

The experimental observations discussed above clearly indicate a reluctance of this system to installation of the second double bond into the cyclopentene moiety. While a wide variety of synthetic approaches were investigated, most seemed to fail at comparable stages. However, it is felt that several of the proposed routes are still promising candidates for the synthesis of 100.

Various reagents and reaction conditions were utilized but they encompass only the tip of the iceberg. In the Wadsworth-Horner-Emmons approach (Scheme XV), a more exhaustive examination of cyclization conditions may prove beneficial realizing the enone once formed may be very susceptible to side reactions under those conditions.

The bis-Wittig sequence (Scheme XVI) may still warrant further study if suitable conditions are found to prepare the diketone. Briefly examined was the conversion of the norbornanone to the α-hydroxyketone and subsequent oxidation to the diketone. These initial experiments indicated that great care would be necessary to avoid ring cleavage.

The ring expansion route (Scheme XX) could also be salvaged by reexamination of the selenoxide elimination sequence. The stereochemistry of the selenide may be unfavorable for the required syn elimination. Epimerization of the selenide may provide the necessary stereochemistry. Also, other methods for oxidation of the selenide should be explored such as NaIO₄ or m-chloroperbenzoic acid.
CONCLUSION

The results described herein represent only a small portion of the much larger continuing effort to define the origins of \( \pi \)-facial stereoselectivity observed with isodicyclopentadienes.

The experimental data clearly supports the premise that electronic factors arising from the norbornyl framework have a direct influence of the stereoselective behavior of isodicyclopentadiene and related systems and that suitable structural or electronic perturbations can moderate the extent of stereoselection.

Out of the study of cycloadditions with isodicyclopentadiene and very highly reactive dienophiles, it was concluded that the maverick behavior of the triazolinediones is not uniquely linked to transition state timing.

The contrasting facial preferences in Diels-Alder and metal complexation reactions that occur upon changing the bicycloheptyl framework from a [2.2.1] to a [3.1.1] system lends support to the importance of electronic influences emanating from the norbornyl skeleton in controlling facial selectivity.

The first example of remote electronic modulation of facial selectivity in isodicyclopentafulvene systems has also been uncovered. Further investigation from theoretical and experimental perspectives will be necessary to define the source of the observed substituent
effects and provide the basis for designing other compounds that could
control stereoselectivity as desired.

While theoretical controversy over the applicabilities of the
Paquette-Gleiter (electronic) and Brown-Houk (torsional) models still
rages, it is clear that additional experimental data, as reported here,
is needed before a universally accepted theory of \( \pi \)-facial
stereoselectivity in \( \pi \)-cyclopentadienes is developed.
EXPERIMENTAL

Melting points were taken on a Thomas Hoover (Uni-Melt) Capillary Melting Point Apparatus and are uncorrected. Infrared (IR) spectra were recorded in solution (CHCl₃) on a Perkin-Elmer 1320 Spectrophotometer and are reported in reciprocal centimeters (cm⁻¹). Proton nuclear magnetic resonance spectra (¹H NMR) were recorded at 300 MHz (Bruker WP 300 FT NMR Spectrometer) and the splitting patterns were designated as: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet; and br, broad. Carbon-13 nuclear magnetic resonance spectra (¹³C NMR) were recorded at 20 MHz (Bruker NR/80 FT NMR Spectrometer) or at 75 MHz (Bruker WP 300 FT NMR Spectrometer). The chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (δ0.00).

Elemental analyses were obtained from the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Exact mass determinations were obtained at the Ohio State University Chemical Instrument Center by use of a Kratos MS-30 mass spectrometer. Capillary GC analyses were carried out on a Carlo Erba Strumentazione Fractovap 4130 using a 30m x 0.25mm J and W Scientific, Inc. 0.25 m DB-5 Durabond column at a flow rate of 2mL/min calibrated at 100 °C and split ratio of 30:1 on injection.

Solvents were reagent grade and anhydrous solvents were dried prior to use.
CYCLOADDITION OF 1 WITH HEXAFLUORO-2-BUTYNE

A cold (-70 °C), magnetically stirred solution of 1 (1.0 g, 8.0 mmol) and hexafluoro-2-butyn (3.0 g, 19 mmol) in pentane (10 mL) was blanketed with nitrogen and allowed to warm slowly to room temperature during 4 h. Careful evaporation of the solvent left a dark orange residue from which a dark solid precipitated. The oil was decanted from the solid and subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether):

(1α, 4α, 5α, 8α)-1,2,3,4,5,6-Hexahydro-6,7-bis(trifluoromethyl)-1,4:5,8-dimethanonaphthalene (45).

1.02 g (45%) as a colorless solid, mp 34.5-35.5 °C; IR (CHCl₃, cm⁻¹) 2980, 2960, 1340, 1305, 1290, 1275, 1265, 1250, 1170, 1140, 1090, 995; ¹H NMR (300 MHz, CDCl₃) δ 3.75 (s, 2 H), 3.09 (s, 2 H), 2.51 (dt, J = 6.9, 1.9 Hz, 1 H), 2.17 (dd, J = 6.9 Hz, 1 H), 1.57-1.48 (m, 3 H), 1.20 (dt, J = 8.4, 1.5 Hz, 1 H), 0.53 (dd, J = 8.2, 2.4 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 158.40, 122.36 (q, J_CF = 270.9 Hz), 71.85, 50.99, 49.27, 42.62, 21.91; MS, m/z calcd (M⁺) 294.0843, obsd 294.0836.

Anal. Calcd for C₁₄H₁₂F₆: C, 57.15; H, 4.11.

Found: C, 57.26; H, 4.23.
(1α, 4α, 5β, 8β)-1,2,3,4,5,8-Hexahydro-6,7-bis(trifluoromethyl)-1,4:5,8-dimethanonaphthalene (46).

66 mg (3%) as a colorless oil that solidifies below room temperature; IR (CHCl₃, cm⁻¹) 2980, 2940, 2880, 1350, 1305, 1290, 1180, 1165, 1140; ¹H NMR (300 MHz, CDCl₃) δ3.75 (s, 2 H), 3.20 (s, 2 H), 2.60 (d, J = 6.4 Hz, 1 H), 2.10 (d, J = 6.0 Hz, 1 H), 1.76 (d, J = 7.3 Hz, 2 H), 1.38-1.35 (m, 1 H), 1.21 (d, J = 8.1 Hz, 1 H), 1.00 (dd, J = 7.4, 2.3 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 161.16, 122.15 (q, JCF = 270.6 Hz), 78.93, 51.59, 50.51, 43.37, 25.90; MS, m/z calcd (M⁺) 294.0843, obsd 294.0838.

(1α, 4α, 4αα, 5α, 8α, 8αα)-1,2,3,4,5,8-Hexahydro-6,7-bis(trifluoromethyl)-4α,8α-epoxy-1,4:5,8-dimethanonaphthalene (47).

141 mg (6%) as a colorless oil that solidifies below room temperature; IR (CHCl₃, cm⁻¹) 3000, 2970, 2940, 2890, 1650, 1475, 1450, 1350, 1290, 1270, 1250, 1180, 1170, 1140, 1000, 640; ¹H NMR (300 MHz, CDCl₃) δ3.36 (s, 2 H), 2.70 (s, 2 H), 2.25 (d, J = 8.4 Hz, 1 H), 2.00-1.95 (m, 1 H), 1.89 (dd, J = 8.2, 1.3 Hz, 1 H), 1.61-1.56 (m, 2 H), 1.08 (dd, J = 9.7, 3.0 Hz, 2 H), 0.95 (dd, J = 9.4, 1.0 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 121.43 (q, JCF = 271.0 Hz), 64.48, 57.87, 47.19, 39.66, 39.29, 24.26; MS, m/z calcd (M⁺) 310.0792, obsd 310.0788.
(1α, 3α, 6α, 8α)-4,5-Bis(trifluoromethyl)tricyclo[6.2.1.13,6]dodec-4-ene-2,7-dione (48).

70 mg (3%) of colorless crystals, mp 230-231 °C (from ethyl acetate); IR (CHCl₃, cm⁻¹) 2950, 1690, 1355, 1300, 1245, 1180, 1160, 1130, 940, 870; ¹H NMR (300 MHz, CDCl₃) δ 4.09 (d, J = 9.4 Hz, 2 H), 3.43 (t, J = 9.9 Hz, 2 H), 2.65-2.54 (m, 3 H), 2.32-2.23 (m, 3 H), 2.03-1.95 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 206.47, 120.29 (q, JCF = 274.6 Hz), 60.39, 54.28, 35.68, 31.98, 27.41.


Found: C, 51.63; H, 3.72.

AIR OXIDATION OF 45

A 100 mg sample of 45 was sealed into a 50 mL flask under air. After 2 weeks, ¹H NMR analysis of the material indicated that no 45 remained and that conversion to a mixture of 47 and 48 (ratio 57:43) had occurred completely. Separation of this mixture was effected by trituration with pentane in which 47 is soluble but 48 is not. Isolated were 55 mg (53%) of 47 and 45 mg (41%) of 48, the ¹H NMR spectra of which were identical with those isolated from the original reaction mixture.
DIELS ALDER REACTION OF 1 WITH CYCLOOCTYNE

A solution of 1 (2.12 g, 0.016 mol) and cyclooctyne (1.03 g, 0.010 mol) in dry dichloromethane (50 mL) was stirred at 42 °C for 1 week under a blanket of nitrogen. Removal of the solvent by distillation gave an oily residue that contained 49 and 50 in a ratio of 15:1 (¹H NMR analysis). MPLC purification on silica gel (elution with petroleum ether) afforded a mixture of 49 and 50 (215 mg, 9.4%) along with 205 mg of unreacted 1. Further elution with 28% ethyl acetate in petroleum ether led to the isolation of 51 and 52:

(1a, 4a, 6β, 12bβ)-2,3,4,6,7,8,9,10,11,12-Decahydro-1H-1,4:6,12b-dimethanocyclooct[a]naphthalene (50).

Preparative VPC (5% SE-30 on Chromosorb G, 180 °C) furnished 50 adequately free of 49 for spectral characterization; IR (CHCl₃, cm⁻¹) 3060, 2950, 2920, 2870, 2850, 1470, 1450, 910; ¹H NMR (300 MHz, CDCl₃) δ 5.88 (d, J = 2.7 Hz, 1 H), 3.16 (d, J = 2.6 Hz, 1 H), 2.82 (d, J = 4.2 Hz, 1 H), 2.47 (d, J = 3.9 Hz, 1 H), 2.42-2.21 (m, 4 H), 1.85-1.74 (m, 4 H), 1.69-1.26 (series of m, 12 H); ¹³C NMR (75 MHz, CDCl₃) ppm 169.04, 148.80, 143.17, 121.70, 72.72, 56.66, 44.19, 37.60, 37.07, 31.43, 30.93, 29.11, 28.97, 26.95, 26.83, 25.51, 24.39, 24.27; MS, m/z (M⁺) calcd 240.1878, obsd 240.1879.
(1a, 4a, 5a, 12a)-1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-1,4:5,12-
dimethanocycloocta[h]naphthalene (49).

Hydrocarbon 49 was not obtained sufficiently free from 50 for complete characterization. The \(^1\text{H} \, \text{NMR} \) and \(^{13}\text{C} \, \text{NMR} \) assignments that follow were arrived at by computer subtraction of the signals due to admixed 1; \(^1\text{H} \, \text{NMR} \) (300 MHz, \(\text{CDCl}_3\))

\[
\delta 2.98 \, (s, \, 2 \, \text{H}), \, 2.95 \, (s, \, 2 \, \text{H}), \, 2.17-2.12 \, (m, \, 4 \, \text{H}), \, 1.87 \, (d, \, J = 6.1 \, \text{Hz}, \\
1 \, \text{H}), \, 1.70-1.30 \, (\text{series of} \, m, \, 12 \, \text{H}), \, 1.04 \, (dt, \, J = 1.6, \, 8.2 \, \text{Hz}, \, 1 \, \text{H}), \\
0.42-0.37 \, (m, \, 2 \, \text{H}); \, ^{13}\text{C} \, \text{NMR} \, (75 \, \text{MHz}, \, \text{CDCl}_3) \, \text{ppm} \, 158.54, \, 142.67, \, 67.55, \\
54.33, \, 47.74, \, 43.08, \, 28.96, \, 27.18, \, 26.08, \, 22.49.
\]

(7a, 9a, 12a, 14a)-1,2,3,4,5,6,7,9,10,11,12,14-Dodecahydro-7,14:9,12-
dimethanocyclooctacyclodecene-8,13-dione (51).

77 mg (3%) as colorless needles, mp 146.5-147.5 °C (from ethyl acetate); IR 3000, 2930, 2850, 1675, 1460, 1260, 1160, 910, 875; \(^1\text{H} \, \text{NMR} \) (300 MHz, \(\text{CDCl}_3\)) \(\delta 3.61 \) (d, \(J = 9.6 \, \text{Hz}, \, 2 \, \text{H}), \, 3.25 \, (t, \, J = 9.8 \\
\text{Hz}, \, 2 \, \text{H}), \, 2.71 \, (dd, \, J = 3.8, \, 15.4 \, \text{Hz}, \, 2 \\
\text{H}), \, 2.71-1.89 \, (\text{series of} \, m, \, 8 \, \text{H}), \, 1.79-1.69 \, (m, \, 4 \, \text{H}), \, 1.59-1.35 \, (\text{series} \\
of \, m, \, 6 \, \text{H}); \, ^{13}\text{C} \, \text{NMR} \, (75 \, \text{MHz}, \, \text{CDCl}_3) \, \text{ppm} \, 212.90, \, 139.61, \, 63.20, \, 54.82, \\
33.26, \, 30.70, \, 29.59, \, 28.18, \, 26.21, \, 25.76; \, \text{MS, m/z} \, (M^+) \, \text{calcd} \, 272.1776, \\
\text{obsd} \, 272.1760.

\text{Anal. Calcd for C}_{18}H_{24}O_{2}: \, \text{C}, \, 79.37; \, \text{H}, \, 8.88.

\text{Found}: \, \text{C}, \, 78.96; \, \text{H}, \, 8.86.
(1a, 4a, 4aa, 5a, 12a, 12aa)-1,3,4,5,6,7,8,9,10,11,12,12a-Dodecahydro-1,4:5,12-dimethanocycloocta[b]naphthalen-4a(2H)-ol (52). 409 mg (17%) as colorless needles, mp 95-96 °C (from hexane); IR (CHCl₃, cm⁻¹)
3620, 3000, 2940, 2880, 2860, 1470, 1460, 1440, 1260, 1060, 980; ¹H NMR (300 MHz, CDCl₃) δ2.36-1.99 (series of m, 12 H), 1.69-1.44 (m, 9 H), 1.31 (dd, 1 = 1.2, 9.4 Hz, 1 H), 1.22-1.06 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃) ppm 140.39, 137.93, 89.67, 60.04, 57.59, 55.95, 47.71, 47.21, 45.13, 39.19, 28.99, 28.70, 28.65, 28.52, 26.31, 26.25, 23.61, 22.07; MS, m/z (M⁺) calcd 258.1984, obsd 258.1971.

Found: C, 83.67; H, 10.26.

(1a, 4a, 4aa, 5a, 12a, 12aa)-1,3,4,5,6,7,8,9,10,11,12,12a-Dodecahydro-1,4:5,12-dimethanocycloocta[b]naphthalen-4a(2H)-ol 4-nitrobenzoate (53). The 4-nitrobenzoate of 52, prepared by conventional reaction with 4-nitrobenzoyl chloride in pyridine solution, was obtained as pale yellow crystals, mp 210 °C (from ethanol-water); IR (CHCl₃, cm⁻¹) 3000, 2920, 2840, 1720, 1465, 1450, 1435, 1250, 1055, 975; ¹H NMR (300 MHz, CDCl₃) δ8.27, (d, 1 = 8.8 Hz, 2 H), 8.17 (d, 1 = 8.8 Hz, 2 H), 3.15 (s, 1 H), 2.92 (m, 1 H), 2.64 (m, 1 H), 2.46 (br s, 1 H), 2.33-2.31 (m, 4 H), 1.70-1.10 (series of m, 13 H).
Approximately 10 mg of 49 was dissolved in CDCl₃ in an NMR tube and exposed to the atmosphere overnight. ¹H NMR analysis after this lapse of time showed that complete conversion to a 27:73 mixture of 51 and 54 had occurred. Since all attempts to separate this mixture chromatographically selectively destroyed the epoxide, the ¹H NMR assignments to 54 were arrived at by subtraction of signals due to 51 which had been previously obtained pure: ¹H NMR (300 MHz, CDCl₃) δ2.71 (s, 2 H), 2.57 (s, 2 H), 2.39-2.14 (m, 5 H), 2.08 (d, J = 4.9 Hz, 2 H), 1.93 (d, J = 8.9 Hz, 2 H), 1.77-1.13 (series of m, 9 H), 0.78 (d, J = 8.7 Hz, 2 H).

To a solution of 1 (503 mg, 3.8 mmol) and (cyclobutadiene)iron tricarbonyl (405 mg, 2.1 mmol) in dry acetone (25 mL) was added trimethylamine N-oxide (1.21 g, 0.016 mol) in a single portion. The reaction mixture was stirred at room temperature under nitrogen for 2 days, diluted with ether (25 mL), and filtered through Celite to remove insoluble iron compounds. The filtrate was washed with water (3 x 50 mL) and the aqueous phases were extracted with ether (2 x 25 mL). The combined organic layers were
dried and concentrated to give a yellow oil, chromatography of which (MPLC) on silica gel (elution with petroleum ether) afforded 164 mg (42%) of 55 as a colorless liquid and 134 mg of recovered 1. An analytical sample of 55 was obtained by preparative VPC (5% SE-30 on Chromosorb G, 120 °C): IR (CHCl₃, cm⁻¹) 3020, 3000, 2960, 2925, 2880, 2860, 1450, 1300, 1285, 1175, 910; ¹H NMR (300 MHz, CDCl₃) 85.99 (d, J = 4.6 Hz, 1 H), 5.97 (d, J = 4.6 Hz, 1 H), 5.21 (d, J = 3.0 Hz, 1 H), 3.03 (t, J = 4.5 Hz, 1 H), 2.84 (d, J = 4.0 Hz, 1 H), 2.75 (d, J = 3.5 Hz, 1 H), 2.55-2.52 (m, 1 H), 2.24 (s, 1 H), 1.80 (dd, J = 1.7, 8.0 Hz, 1 H), 1.73-1.67 (m, 2 H), 1.55-1.45 (m, 3 H), 1.33 (d, J = 9.5 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 159.63, 140.88, 139.85, 111.61, 62.99, 54.07, 47.56, 47.09, 44.91, 42.27, 40.65, 38.54, 32.29, 24.86; MS, m/z (M⁺) calcd 184.1252, obsd 184.1253.

**Anal.** Calcd for C¹⁴H₁₆: C, 91.25; H, 8.75.

**Found:** C, 91.18; H, 8.73.

[OC-6-21-(1a, 2a, 4a, 5a, 8a)-Pentacarbonyl[methoxy(1,2,3,4,5,6,7,8-octahydro-1,4,5,8-dimethanonaphthalen-2-yl)methylene]tungsten (57).] Isodicyclopentadiene (73 mg, 0.55 mmol) was added to a magnetically stirred solution of 56 (290 mg, 0.74 mmol) dissolved in dry benzene (3 mL) under a nitrogen atmosphere. After 30 min, the solvent was evaporated to leave a dark red oil. Purification of this oil by MPLC on silica gel (elution with hexane) afforded 254 mg (88%) of the yellow-orange crystalline adduct.
57: mp 73 °C dec; IR (CHCl₃, cm⁻¹) 2960, 2930, 2880, 2860, 2070, 1975, 1935, 1460, 1380, 1260, 1100, 1065, 1015; ¹H NMR (300 MHz, CDCl₃) δ 4.60 (s, 3 H), 3.78 (m, 1 H), 3.05 (s, 3 H), 3.00 (s, 1 H), 1.72-0.82 (series of m, 10 H); ¹³C NMR (75 MHz, CDCl₃) ppm 338.99, 203.31, 197.52, 156.16, 151.81, 73.28, 70.65, 50.41, 48.76, 47.46, 43.10, 42.98, 42.73, 32.44, 25.81, 24.98; MS, m/z (M⁺) calcd 526.0613, obsd 526.0615.

Methyl (1a, 2a, 4a, 5α, 8α)-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene-2-carboxylate (58).

A solution of 57 (80 mg, 0.15 mmol) was dissolved in dimethyl sulfoxide (1 mL) and stirred under nitrogen at room temperature for 58 h. The reaction mixture was diluted with ether (25 mL) and washed with brine (5 x 25 mL) prior to drying and solvent evaporation. MPLC of the residue on silica gel (elution with 10% ethyl acetate in hexane) gave 27.8 mg (85%) of ester 58, whose spectra were identical with those recorded on an authentic sample: IR (CHCl₃, cm⁻¹) 2980, 2930, 2880, 1730, 1435, 1355, 1295, 1195, 1175, 1045; ¹H NMR (300 MHz, CDCl₃) δ 3.67 (s, 3 H), 3.14 (s, 1 H), 3.01 (s, 1 H), 2.06 (m, 1 H), 1.90 (dt, J = 4.0, 11.9 Hz, 1 H), 1.63-0.78 (series of m, 8 H).
CYCLOADDITION OF 62 WITH N-PHENYLMALEIMIDE

N-Phenylmaleimide (324 mg, 2.0 mmol) was added to a stirred solution of 62 (2.5 mL of 0.785 M in hexane, 2.0 mmol) in dry benzene (20 mL). Stirring was continued at room temperature under a blanket of nitrogen for 16 h. The solvent was removed to give a pale yellow residue consisting of 64 and 65 in a 1:9 ratio (\textsuperscript{1}H NMR analysis). The isomers were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether). A small amount of uncharacterized material was also obtained (<5%):

\[ \text{3aa, 4aa, 5aa, 7aa, 9aa-Octahydro-6,6-dimethyl-2-phenyl-4,9:5,7-dimethano-1H-benz[f][1]isoindole-1,3(2H)-dione (64).} \]

44 mg (7.1%) as a white, powdery solid, mp 167-169 °C (from hexanes); IR (CHCl\textsubscript{3}, cm\textsuperscript{-1}) 3025, 2985, 2935, 2875, 2825, 1765, 1698, 1595, 1498, 1465, 1455, 1375, 1265, 1215, 1180, 1130, 1080, 945, 870, 800, 689, 655, 615; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 7.50-7.25 (series of m, 5 H), 3.26 (s, 1 H), 3.24 (s, 1 H), 3.02 (d, J = 7.0 Hz, 1 H), 2.95 (d, J = 7.0 Hz, 1 H), 2.54-2.47 (m, 2 H), 2.38 (t, J = 5.3 Hz, 1 H), 2.25-2.15 (m, 2 H), 1.67 (d, J = 9.8 Hz, 1 H), 1.50 (d, J = 9.7 Hz, 1 H), 1.30 (s, 3 H), 1.24 (d, J = 8.8 Hz, 1 H), 0.61 (s, 3 H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) ppm 177.48, 177.32, 154.11, 137.64, 131.97, 129.14, 128.58, 126.40, 49.26, 48.67, 48.56, 47.83, 43.69, 42.53, 41.47, 40.01, 33.44, 29.15, 26.60, 21.56; [\textalpha]\textsubscript{D}\textsuperscript{23} = -8.5° (c 0.46, CHCl\textsubscript{3}); MS, m/z (M\textsuperscript{+}) calcd 333.1729, obsd 333.1740.
[3αR-(3α, 4β, 5α, 7α, 9β, 9α)]-3α, 4, 5, 6, 7, 8, 9, 9α-Octahydro-6, 6-
dimethyl-2-phenyl-4, 9: 5, 7-dimethano-1H-benz[f]isoindole-1, 3(2H)-dione (65).

259 mg (41.5%) as a white, powdery solid, mp 220-221 °C (from hexanes); IR (CHCl₃, cm⁻¹) 2980, 2930, 2875, 2820, 1765, 1700, 1595, 1500, 1465, 1455, 1420, 1375, 1285, 1280, 1270, 1260, 1215, 1180, 1130, 1080, 1060, 1030, 1020, 1005, 945, 920, 910, 890, 870, 690, 615; ¹H NMR (300 MHz, CDCl₃) δ 7.48-7.24 (series of m, 5 H), 3.26 (s, 1 H), 3.24 (s, 1 H), 2.96 (d, J = 7.1 Hz, 1 H), 2.83 (d, J = 7.1 Hz, 1 H), 2.51-2.43 (m, 2 H), 2.33 (t, J = 5.1 Hz, 1 H), 2.21-2.13 (m, 2 H), 1.65 (d, J = 9.7 Hz, 1 H), 1.48 (d, J = 9.7 Hz, 1 H), 1.30 (s, 3 H), 0.87 (s, 3 H), 0.68 (d, J = 8.8 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 177.18, 177.00, 152.36, 138.33, 131.91, 129.07, 128.50, 126.36, 49.49, 49.31, 48.26, 41.68, 41.51, 40.13, 33.48, 29.61, 26.50, 21.40; [α]²³D -76.5° (c 0.31, CHCl₃); MS, m/z (M⁺) calcd 333.1729, obsd 333.1742.


Found: C, 79.15; H, 7.06.
CYCLOADDITION OF 62 WITH \( \mu \)-BENZOQUINONE

To a stirred, deoxygenated solution of \( \mu \)-benzoquinone (198 mg, 1.8 mmol) in dry benzene (10 mL) was added 62 (2.5 mL of 0.785 M in hexane, 2.0 mmol) via syringe. The reaction flask was covered with foil and the reaction mixture was stirred at room temperature under nitrogen for 24 h. Removal of the solvent produced a bright yellow residue containing 66 and 67 in a ratio of 1:10 (\(^1\)H NMR analysis). The adducts were separated by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). A small amount of uncharacterized material was also isolated (>5%):

\[ \text{[1R-(1a, 3a, 8aa, 9a, 10a, 10aa)]-1,2,3,4,8a,9,10,10a-Octahydro-2,2-dimethyl-1,3:9,10-dimethanoanthracene-5,8-dione (66).} \]

13.6 mg (2.8%) as a pale yellow solid, mp 123.5-125 °C (from hexanes); IR (CHCl\(_3\), cm\(^{-1}\)) 3020, 2990, 2935, 2870, 2835, 1660, 1610, 1465, 1455, 1380, 1360, 1270, 1215, 1130, 1105, 1025, 885, 850; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 6.74 (s, 2 H), 3.12 (s, 1 H), 3.09 (s, 1 H), 2.67 (d, \( J = 8.0 \) Hz, 1 H), 2.61 (d, \( J = 8.2 \) Hz, 1 H), 2.51-2.40 (m, 3 H), 2.23 (dd, \( J = 2.3, 17.6 \) Hz, 1 H), 2.15-2.11 (m, 1 H), 1.44 (d, \( J = 9.0 \) Hz, 1 H), 1.35 (d, \( J = 9.0 \) Hz, 1 H), 1.28 (s, 3 H), 1.22 (d, \( J = 8.6 \) Hz, 1 H), 0.54 (s, 3 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) ppm 199.73, 199.51, 153.85, 141.73, 141.69, 137.20, 52.87, 51.44, 49.45, 49.08, 45.66, 42.56, 41.53, 40.09, 33.53, 29.04, 26.66, 21.41; [\( \alpha \)]\(_{D}^{23}\) +3.6° (c 0.22, CHCl\(_3\)); MS, m/z (M\(^+\)) calcd 268.1463, obsd 268.1453.
[IR-\{1\alpha, 3\alpha, 8\alpha, 9\beta, 10\beta, 10\alpha\}] - 1,2,3,4,8a,9,10,10a-Octahydro-2,2-dimethyl-1,3:9,10-dimethanoanthracene-5,8-dione (67).

193.2 mg (40%) as a pale yellow solid, mp 169-170 °C (from hexanes); IR (CHCl₃, cm⁻¹) 3020, 2980, 2930, 2870, 2820, 1660, 1605, 1465, 1460, 1380, 1365, 1270, 1215, 1140, 1130, 1105, 1025, 960, 895, 880; 855; ¹H NMR (300 MHz, CDCl₃) δ 6.74 (s, 2 H), 3.13 (s, 1 H), 3.10 (s, 1 H), 2.62 (d, J = 8.0 Hz, 1 H), 2.51-2.35 (series of m, 4 H), 2.21 (dd, J = 2.9, 17.6 Hz, 1 H), 2.16-2.11 (m, 1 H), 1.43 (d, J = 9.3 Hz, 1 H), 1.34-1.30 (overlapping d and s, 4 H), 0.86 (s, 3 H), 0.62 (d, J = 8.7 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 199.50, 199.26, 151.66, 141.79 (2 C's), 138.14, 52.98, 52.09, 50.30, 49.20, 43.31, 41.80, 41.58, 40.25, 33.38, 29.53, 26.58, 21.41; [α]²³D -70.5° (c 0.54, CHCl₃); MS, m/z (M⁺) calcd 268.1463, obsd 268.1453.


Found: C, 80.33; H, 7.53.

CYCLOADDITION OF 62 WITH DIMETHYL ACETYLENEDICARBOXYLATE

To a stirred, deoxygenated solution of 62 (2.5 mL of 0.785 M in hexane, 2.0 mmol) in dry benzene (10 mL) was added dimethyl acetylenedicarboxylate (0.25 mL, 2.0 mmol) via syringe. The solution was stirred under nitrogen at room temperature for 48 h. Evaporation of the solvent afforded a yellow oil shown to be a 1:6 mixture of 68 and 69 (¹H NMR analysis). The cycloadducts were separated by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether):
[IR-(1α, 3α, 5α, 8α)]-Dimethyl 1,2,3,4,5,8-hexahydro-2,2-dimethyl-1,3:5,8-dimethanonaphthalene-6,7-dicarboxylate (68).

0.129 g (21.4%) as a pale yellow oil; IR (CHCl₃, cm⁻¹) 3025, 2990, 2950, 2940, 2875, 2830, 1720, 1705, 1615, 1465, 1430, 1380, 1365, 1315, 1260, 1240, 1195, 1120, 1105, 1050, 1020; ¹H NMR (300 MHz, CDCl₃) δ3.80 (s, 3 H), 3.75 (s, 4 H), 3.65 (d, J = 1.7 Hz, 1 H), 2.59 (dd, J = 3.0, 17.6 Hz, 1 H), 2.52-2.34 (series of m, 3 H), 2.25 (dd, J = 2.4, 17.6 Hz, 1 H), 2.16-2.09 (m, 2 H), 1.28 (d, J = 8.2 Hz, 1 H), 1.25 (s, 3 H), 0.41 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) ppm 166.35, 165.61, 158.18, 153.60, 151.04, 142.97, 71.66, 56.20, 54.99, 51.95, 51.84, 43.29, 41.99, 40.86, 33.63, 31.18, 26.55, 21.38; [α]²³_D +37.7° (c 0.85, CHCl₃); MS, m/z (M⁺) calcd 302.1518, obsd 302.1515.

[IR-(1α, 3α, 5β, 8β)]-Dimethyl 1,2,3,4,5,8-hexahydro-2,2-dimethyl-1,3:5,8-dimethanonaphthalene-6,7-dicarboxylate (69).

0.407 g (67.3%) as a pale yellow oil; IR (CHCl₃, cm⁻¹) 3020, 2985, 2945, 2940, 2885, 2870, 2830, 1725, 1705, 1615, 1430, 1310, 1260, 1240, 1190, 1125, 1105, 1050, 1020, 910; ¹H NMR (300 MHz, CDCl₃) δ3.75 (s, 6 H), 3.71 (d, J = 1.4 Hz, 1 H), 3.64 (d, J = 1.2 Hz, 1 H), 2.57 (dd, J = 2.6, 17.6 Hz, 1 H), 2.43-2.16 (series of m, 5 H), 2.10-2.04 (m, 1 H), 1.25 (s, 3 H), 0.86 (s, 3 H), 0.67 (d, J = 8.7 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 165.96, 165.90, 157.75, 153.18, 152.26, 142.93, 69.88, 55.79, 55.15, 51.85, 51.82.
43.18, 41.42, 40.41, 33.04, 31.61, 26.42, 21.41; $[\alpha]_D^{23} = -51.4^\circ$ ($< 1.4$, CHCl$_3$); MS, m/z (M$^+$) calcd 302.1518, obsd 302.1507.

**CYCLOADDITION OF 62 WITH (Z)-1,2-BIS(PHENYLSULFONYL)ETHYLENE**

A solution of 62 (0.7 mL of 0.785 M in hexane, 0.5 mmol) and the disulfone (158 mg, 0.5 mmol) in dry benzene (10 mL) was heated at 45 °C under an atmosphere of nitrogen for 24 h. During this time a white precipitate formed. The reaction mixture was concentrated to leave a residue consisting of 70 and 71 in a ratio of 1:2.2 (1H NMR analysis). Recrystallization of this mixture from ethyl acetate-hexane provided pure 71. The mother liquor was concentrated and subjected to radial chromatography (silica gel, elution with 30% ethyl acetate in petroleum ether) to give 70 and additional 71:

**[IR-(1a, 3a, 5β, 6a, 7a, 8β)]-1,2,3,4,5,6,7,8-Octahydro-2,2-dimethyl-6,7-bis(phenylsulfonyl)-1,3:5,8-dimethanonaphthalene (70).**

25 mg (10.4%) as colorless crystals, mp 221 °C dec (from ethyl acetate-hexane);

IR (CHCl$_3$, cm$^{-1}$) 3050, 3020, 2980, 2930, 2870, 2830, 1445, 1340, 1330, 1260, 1150, 1085, 690, 650, 610; 1H NMR (300 MHz, CDCl$_3$) δ 8.05-7.51 (series of m, 10 H), 4.22 (dd, $\delta = 2.9$, 9.5 Hz, 1 H), 4.07 (dd, $\delta = 2.7$, 9.5 Hz, 1 H), 3.20 (s, 1 H), 3.01-2.95 (overlapping dd and s, 2 H), 2.59-2.54 (m, 1 H), 2.48 (t, $\delta = 5.4$ Hz, 1 H), 2.41 (dd, $\delta = 2.6$, 17.2 Hz, 1 H), 2.23-2.17 (m, 2 H), 1.77 (d, $\delta = 8.9$ Hz, 1 H), 1.38 (s, 3 H), 1.30 (d, $\delta = 8.6$ Hz,
[1R-(1α, 3α, 5β, 6β, 7β, 8β)]-1,2,3,4,5,6,7,8-Octahydro-2,2-dimethyl-6,7-bis(phenylsulfonyl)-1,3:5,8-dimethanonaphthalene (71).

118 mg (49.1%) as colorless solid, mp 204-205 °C (from ethyl acetate-hexane);
IR (CHCl₃, cm⁻¹) 3060, 3020, 2980, 2930, 2880, 2820, 1445, 1340, 1330, 1310, 1165, 1150, 1090, 1080, 690, 650; H NMR (300 MHz, CDCl₃) δ 8.02-7.67 (series of m, 10 H), 3.49 (dd, J = 2.0, 8.5 Hz, 1 H), 3.07 (s, 1 H), 3.04 (s, 1 H), 2.57 (dt, J = 1.7, 9.5 Hz, 1 H), 2.43-2.36 (m, 1 H), 2.26 (dd, J = 2.4, 17.9 Hz, 1 H), 2.06-2.10 (m, 1 H), 1.97 (t, J = 5.2 Hz, 1 H), 1.79 (dd, J = 2.9, 17.9 Hz, 1 H), 1.61 (d, J = 9.5 Hz, 1 H), 1.20 (s, 3 H), 0.73 (s, 3H), 0.50 (d, J = 9.0 Hz, 1 H); C NMR (75 MHz, CDCl₃) ppm 153.14, 141.09, 141.02, 139.31, 133.46, 128.95, 128.91, 128.87, 128.66, 69.30, 68.72, 50.38, 49.04, 44.05, 41.54, 41.26, 40.42, 33.75, 29.42, 26.34, 21.29; [α]_{D}^{23} = -40.40 (C 0.54, CHCl₃); MS, m/z (M⁺) calcd 468.1429, obsd 468.1458.

Anal. Calcd for C_{26}H_{28}O_{4}S_{2}: C, 66.64; H, 6.02.

Found: C, 66.66; H, 6.19.
Sodium amalgam (1.5% w/w, 1.45 g) was added in portions to a suspension of 71 (52.3 mg, 0.11 mmol) and sodium dihydrogen phosphate (300 mg) in anhydrous methanol (5 mL). The slurry was vigorously stirred under a nitrogen atmosphere for 3 h. The mercury was removed and water (25 mL) added. The mixture was transferred to a separatory funnel and extracted with dichloromethane (2 x 10 mL). The organic layer was dried, decanted, and carefully concentrated on a rotary evaporator. The resulting oil was passed through a small pipet column of silica gel (elution with pentane). Evaporation of the solvent gave 10.5 mg (50%) of hydrocarbon 72 as a colorless liquid: IR (neat, cm⁻¹) 3110, 3060, 2965, 2925, 2860, 2820, 1550, 1465, 1445, 1425, 1380, 1360, 1285, 1255, 1220, 1190, 1095, 1075, 1055, 1015, 890, 860, 805, 775, 720, 685, 670, 645; ¹H NMR (300 MHz, CDCl₃) δ6.81 (dd, J = 3.0, 5.0 Hz, 1 H), 6.71 (dd, J = 3.0, 5.0 Hz, 1 H), 3.32 (br s, 1 H), 3.26 (br s, 1 H), 2.55 (dd, J = 3.0, 17.8 Hz, 1 H), 2.33-2.29 (m, 2 H), 2.09-1.98 (m, 4 H), 1.29 (s, 3 H), 0.89 (s, 3 H), 0.68-0.63 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 156.97, 143.18, 142.46, 141.89, 72.10, 52.59, 51.67, 43.41, 41.62, 40.64, 32.92, 32.14, 26.68, 21.51; MS, m/z (M⁺) calcd 186.1409, obsd 186.1393.
REDUCTIVE DESULFONYLATION OF 70

The sodium amalgam mediated desulfonation of 70 (43.6 mg, 0.08 mmol) was performed as described above by using 1.21 g of 1.5% amalgam in phosphate-buffered methanol (5 mL) to give 6.2 mg (36%) of diene 26 identical with that obtained from 71 by $^1$H NMR analysis.

**N,N-Dimethyl-1-(4,5,6,7-tetrahydro-5,5-dimethyl-4,6-methano-2H-inden-2-ylidene)methanamine (63).**

Dimethyl sulfate (distilled from calcium oxide; 1.2 mL, 0.013 mol) was added dropwise to warm (50-60 °C), stirred dimethylformamide (distilled from calcium hydride; 1.0 mL, 0.013 mol) under a blanket of nitrogen. The solution was heated to 70-80 °C for 2.5 h and allowed to cool to room temperature.

In a separate flask, n-butyllithium (9.2 mL, 1.37 M in hexane, 0.013 mol) was added to a cold (-78 °C), magnetically stirred solution of 62 (16 mL of 0.785 M in hexane, 0.013 mol) in dry tetrahydrofuran (10 mL). After 40 min of stirring, the solution was warmed to -10 °C and the dimethylformamide-dimethyl sulfate complex was introduced via cannula. Once addition was complete, the reaction mixture was slowly warmed to room temperature and stirred overnight.

The dark orange mixture was filtered and the residue was washed with tetrahydrofuran until the washings were colorless. Evaporation of the filtrate gave a dark orange oil. The oil was dissolved in n-heptane (200 mL), decolorized with charcoal, and filtered. The filtrate was
concentrated to approximately 75 mL and set in a freezer. The precipitate was collected to provide 0.651 g (24%) of 63 as pale yellow plates, mp 119-120 °C (1:1 mixture of E/Z isomers): IR (CHCl₃, cm⁻¹) 2980, 2950, 2930, 2915, 2860, 2830, 2800, 1708, 1620, 1580, 1510, 1480, 1465, 1440, 1430, 1405, 1390, 1380, 1365, 1342, 1215, 1145, 1095, 1065, 1008, 945, 930, 808, 662, 625; ¹H NMR (300 MHz, CDCl₃) δ 86.82 (s, 2 H), 6.29 (s, 1 H), 6.12 (d, J = 1.9 Hz, 1 H), 6.02 (s, 1 H), 5.88 (d, J = 1.8 Hz, 1 H), 3.16 (s, 12 H), 2.88 (s, 2 H), 2.83 (s, 2 H), 2.74 (q, J = 5.2 Hz, 2 H), 2.69-2.62 (m, 2 H), 2.19-2.14 (m, 2 H), 1.37 (s, 3 H), 1.36 (s, 3 H), 1.33 (d, J = 4.5 Hz, 2 H), 0.76 (s, 3 H), 0.75 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) ppm 149.07, 143.79, 143.50, 142.69, 136.91, 130.46, 119.45, 117.60, 117.55, 115.33, 109.85, 106.04, 44.29, 43.60, 42.83, 42.77, 41.87, 41.79, 41.34, 41.28, 33.67, 33.48, 28.97, 28.31, 26.75, 21.91; [α]²³D -46.70 (c 0.39, CHCl₃); MS, m/z (M⁺) calcd 215.1674, obsd 215.1678.

Found: C, 83.41; H, 9.81.

REACTION OF 63 WITH (η⁵-CYCLOPENTADIENYL)(η⁶-XYLENE)IRON(II) HEXAFLUOROPHOSPHATE

A deoxygenated solution of 63 (99.7 mg, 0.46 mmol) and 73 (211.7 mg, 0.57 mmol) in dry dichloromethane (25 mL) was irradiated with a 250-W sunlamp for 24 h while being stirred under nitrogen. After the red solution cooled to room temperature, 2 N sodium hydroxide (10 mL) and ethanol (10 mL) were added. The mixture was stirred for 1.5 h, diluted with water (50 mL), and extracted into dichloromethane (2 x 50 mL). The
combined organic extracts were washed with brine (1 x 50 mL), dried, filtered, and concentrated to yield a red-orange oil. MPLC purification on silica gel (elution with 10% ethyl acetate in petroleum ether) afforded 123 mg (86%) of a 27:73 mixture of aldehydes 75 and 76. The key signals used for integration were the methyl signals (in CDCl3) due to 75 (δ 1.44, 1.36) and 76 (δ 1.35, 0.47).

\[(\eta^5-2,4\text{-Cyclopentadien-1-yl})\text{[(1,2,3,3a,7a-\eta)-4,5,6,7-tetrahydro-2-(hydroxymethyl)-5,5-dimethyl-4,6-methano-2H-1inden-1-yl]}\text{iron (77 and 78).}

A solution of the 75/76 mixture (173 mg, 0.6 mmol) in 95% ethanol (25 mL) was treated with sodium borohydride (35 mg, 0.9 mmol) and stirred at room temperature under nitrogen for 45 min. Water (50 mL) was added and the reaction mixture was extracted into ether (3 x 50 mL). The combined ether layers were dried, filtered, and concentrated to leave a yellow-orange solid. The alcohols were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether): 77: 50.7 mg (27%) as a dark orange solid, mp 84-86 °C; IR (CCl4, cm⁻¹) 3620, 3460, 3100, 2990, 2920, 2870, 1740, 1470, 1410, 1370, 1300, 1240, 1120, 1105, 1045, 1000, 940, 845, 705, 690, 670; ¹H NMR (300 MHz, CDCl₃) δ 4.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 5 H); ¹³C NMR (75 MHz, CDCl₃) ppm 98.50, 84.48, 81.40, 70.35, 54.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 5 H), 3.90 (s, 5 H); ¹⁳C NMR (75 MHz, CDCl₃) ppm 98.50, 84.48, 81.40, 70.35, 54.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 5 H), 3.90 (s, 5 H); ¹³C NMR (75 MHz, CDCl₃) ppm 98.50, 84.48, 81.40, 70.35, 54.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 5 H), 3.90 (s, 5 H); ¹³C NMR (75 MHz, CDCl₃) ppm 98.50, 84.48, 81.40, 70.35, 54.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 5 H), 3.90 (s, 5 H); ¹³C NMR (75 MHz, CDCl₃) ppm 98.50, 84.48, 81.40, 70.35,
69.80, 65.30, 61.80, 42.22, 41.44, 40.91, 36.28, 27.93, 27.23, 23.19;
$\left[\alpha\right]_{D}^{23} +280.5^\circ$ (c 0.69, CCl$_4$); MS, m/z (M$^+$) calcd 310.1020; obsd
310.1027.

78; 87.8 mg (48%); light yellow solid.
The analytical sample was obtained by sublimation [100 °C; 0.5 Torr]: mp 128.5 -129.5 °C; IR (CCl$_4$, cm$^{-1}$) 3620, 3570, 3090, 2985, 2920, 2880, 1460, 1445, 1410, 1380, 1365, 1250, 1105, 1020, 1000, 935;

$^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$4.21 (s, 1 H), 4.19 (s, 1 H), 3.93 (s, 6 H),
3.88 (s, 1 H), 2.59-2.57 (m, 2 H), 2.31-2.24 (m, 3 H), 2.00-1.95 (m, 1 H),
1.24 (s, 3 H), 1.06 (m, 1 H), 0.53 (s, 3 H); $^{13}$C NMR (75 MHz, C$_6$D$_6$) ppm
98.35, 85.30, 82.12, 69.79, 65.00, 63.98, 61.25, 42.18, 41.84,
41.34, 35.92, 27.75, 26.94, 21.52; $\left[\alpha\right]_{D}^{23} -338.7^\circ$ (c 0.39, CCl$_4$); MS,
m/z (M$^+$) calcd 310.1020; obsd 310.1022.

Anal. Calcd for C$_{18}$H$_{22}$FeO: C, 69.69; H, 7.15.
Found: C, 69.59; H, 7.15.
A deoxygenated suspension of 77 (26 mg, 0.085 mmol) and active manganese dioxide (30 mg, 0.339 mmol) in dry benzene (6 mL) was stirred at room temperature under a nitrogen atmosphere for 26 h. After filtration and concentration, the orange residue was purified by chromatography on neutral alumina (elution with 20% ethyl acetate in petroleum ether) to give 16 mg (62%) of pure 75 as a thick, orange oil: IR (CCl₄, cm⁻¹) 3100, 3000, 2930, 2750, 1730, 1680, 1475, 1460, 1415, 1388, 1370, 1115, 1010, 950, 845, 830, 720; ¹H NMR (300 MHz, C₆D₆) 8.97 (s, 1 H), 4.43 (s, 1 H), 4.28 (s, 1 H), 3.95 (s, 5 H), 2.47 (dd, 1 = 2, 16 Hz, 1 H), 2.30 (d, 1 = 9 Hz, 1 H), 2.23 (t, 1 = 5 Hz, 1 H), 2.14 (dd, 1 = 2, 16 Hz, 1 H), 1.86-1.82 (m, 1 H), 1.26 (s, 3 H), 1.16 (s, 3 H), 0.60 (d, 1 = 9 Hz, 1 H); [α]²⁵° +295.8° (c 0.22, CCl₄); MS, m/z (M⁺) calcd 308.0863, obsd 308.0861.

A deoxygenated mixture of 78 (14 mg, 0.045 mmol) in dry benzene (6 mL) containing active manganese dioxide (16 mg, 0.181 mmol) was stirred at room temperature under nitrogen for 23 h. The suspension was filtered through Celite and the filtrate was concentrated to leave a dark orange solid. MPLC on
silica gel (elution with 10% ethyl acetate in petroleum ether) provided 13 mg (94%) of pure 76 as an orange powder, mp 89-91 °C; IR (CCl₄, cm⁻¹) 3090, 3000, 2980, 2930, 2870, 1675, 1460, 1410, 1385, 1370, 1110, 1105, 1000, 840; ¹H NMR (300 MHz, C₆D₆) δ 9.92 (s, 1 H), 4.42 (s, 1 H), 4.39 (s, 1 H), 3.91 (s, 5 H), 2.51-2.45 (m, 2 H), 2.26-2.19 (m, 2 H), 1.88-1.85 (m, 1 H), 1.86 (d, J = 9 Hz, 1 H), 1.18 (s, 3 H), 0.43 (s, 3 H); ¹³C NMR (75 MHz, C₆D₆) ppm 193.19, 103.09, 87.07, 76.66, 70.63, 66.29, 65.49, 41.74, 41.66, 41.22, 35.43, 27.57, 26.70, 21.32; [α]²³_D -420.3° (c 0.25, CCl₄); MS, m/z (M⁺) calcd 308.0863, obsd 308.0865.

Bis(η⁵-2,4-cyclopentadien-1-yl)[μ-[1,2,3,3a,7a-η:1′,2′,3′,3′a,7′a-η-2,2′-[oxybis(methylene)]bis[4,5,6,7-tetrahydro-5,5-dimethyl-4,6-methano-1H-inden-1-yl]]d11ron (79).

A deoxygenated solution of 78 (20 mg, 0.065 mmol), p-toluenesulfonyl chloride (6.2 mg, 0.032 mmol), and triethylamine (4 drops) in dry benzene (20 mL) was stirred at room temperature under nitrogen for 44 h. Water was added and the product was extracted into ethyl acetate (3 x 30 mL). The combined organic extracts were dried, filtered, and concentrated. The yellow solid was purified by chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to afford 19 mg (46%) of 79 as a yellow-orange solid, mp 160.5-162 °C (from hexanes): IR (CCl₄, cm⁻¹) 3100, 2980, 2930, 2865, 1740, 1465, 1445, 1370, 1240, 1105, 1045, 1000, 938, 845; ¹H NMR (300 MHz, C₆D₆) δ 4.33 (s, 2 H), 4.32 (s, 2 H), 4.09 (s, 2 H), 4.06 (s, 2 H), 4.02 (s, 10 H), 2.66 (dd, J = 3, 16 Hz, 2 H), 2.62-
2.57 (m, 2 H), 2.34–2.28 (m, 4 H), 1.99–1.95 (m, 2 H); 1.24 (s, 6 H), 0.87 (t, J = 7 Hz, 2 H), 0.55 (s, 6 H); [α]$_D^{23}$ $-351.1^\circ$ (c 0.24, CCl$_4$); MS, m/z (M$^+$) calcd 602.1934, obsd 602.1895.

REACTION OF $\mathbf{63}$ WITH ($\eta^5$-Cyclopentadienyl)Tris(Acetonitrile)Ruthenium(II) Hexafluorophosphate.

A solution of $\mathbf{63}$ (102 mg, 0.472 mmol) and 74 (184 mg, 0.424 mmol) in 1,2-dichloroethane (40 mL) was heated to reflux under a blanket of nitrogen for 24 h. After being cooled to room temperature, 2 N sodium hydroxide (15 mL) and ethanol (15 mL) were added and the mixture was stirred for 90 min, diluted with water (100 mL), extracted into dichloromethane (2 x 100 mL), dried, filtered, and concentrated. Purification by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) provided a 7:93 mixture of 80 and 81 as a dark brown, viscous oil, 139 mg (93%). The key signals used for integration were the methyl signals (in C$_6$D$_6$) due to 80 (δ 1.14, 1.05) and 81 (δ 1.20, 0.62).

($\eta^5$-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η$^-$)-4,5,6,7-tetrahydro-2-(hydroxymethyl)-5,5-dimethyl-4,6-methano-2H-inden-1-yl]ruthenium (82 and 83).

A solution of the 80/81 mixture (85.4 mg, 0.242 mmol) in 95% ethanol (25 mL) was treated with sodium borohydride (15 mg, 0.386 mmol) and stirred at room temperature under nitrogen for 45 min. Water (50 mL) was added and the product was extracted into ether (3 x 50 mL). The combined ethereal extracts were dried, filtered, and concentrated to leave a pale yellow solid. The alcohols were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether).
82: 4.8 mg (6%) as a dark tan solid, mp 90–92 °C; IR (CCl₄, cm⁻¹) 3525, 3460, 3100, 2980, 2930, 2865, 2080, 1880, 1730, 1475, 1460, 1440, 1390, 1370, 1355, 1295, 1235, 1095, 1040, 995, 935, 915, 845, 630, 600; ¹H NMR (300 MHz, C₆D₆) δ 4.46 (s, 1 H), 4.38 (s, 5 H), 4.31 (s, 1 H), 4.02 (s, 2 H), 2.54 (dd, J = 2, 16 Hz, 1 H), 2.47–2.42 (m, 2 H), 2.36 (dd, J = 4, 16 Hz, 1 H), 2.30 (t, J = 5 Hz, 1 H), 1.93–1.91 (m, 1 H), 1.25 (s, 3 H), 1.19 (s, 3 H), 0.99 (d, J = 9 Hz, 1 H); [α]²³D +130.5° (c 0.19, CCl₄).

83: 62 mg (72%) as an off-white powder. The analytical sample was obtained by sublimation [95 °C, 0.5 Torr], mp 123–124 °C; IR (CCl₄, cm⁻¹) 3620, 3500, 3080, 2965, 2920, 2880, 1460, 1410, 1380, 1360, 1258, 1098, 1025, 995; ¹H NMR (300 MHz, C₆D₆) δ 4.54 (s, 1 H), 4.47 (s, 1 H), 4.38 (s, 5 H), 3.99 (d, J = 5 Hz, 2 H), 2.55 (dd, J = 3, 16 Hz, 1 H), 2.48 (d, J = 9 Hz, 1 H), 2.40 (dd, J = 3, 16 Hz, 1 H), 2.23 (t, J = 5 Hz, 1 H), 1.97–1.92 (m, 1 H), 1.81 (d, J = 9 Hz, 1 H), 1.25 (s, 3 H), 1.00 (t, J = 5 Hz, 1 H), 0.70 (s, 3 H); ¹³C NMR (75 MHz, C₆D₆) ppm 103.30, 93.17, 86.32, 71.71, 69.43, 67.67, 59.30, 42.53, 41.28, 37.61, 27.75, 27.12, 21.90; [α]²³D -186.6° (c 1.1, CCl₄); MS, m/z (M⁺) calcd 356.0708, obsd 356.0738.

A deoxygenated mixture of alcohol 83 (46 mg, 0.129 mmol) and active 
MnO₂ (45 mg, 0.517 mmol) in dry benzene (10 mL) was stirred under a
blanket of nitrogen at room temperature for 27 h. The suspension was
filtered through Celite and the filtrate concentrated to give a dark
brown oil. The oil was purified by chromatography on neutral alumina
(elution with 20% ethyl acetate in petroleum ether). There obtained was
aldehyde 81 along with a significant amount (40%) of a product
tentatively assigned as a dimer:

81: 9.9 mg (22%) as a dark brown oil; IR
(CCl₄, cm⁻¹) 3100, 2975, 2955, 2925,
2870, 2745, 1730, 1710, 1678, 1461, 1435,
1405, 1385, 1370, 1320, 1265, 1115, 1105,
1000, 940, 710, 700; ¹H NMR (300 MHz,
C₆D₆) δ 9.69 (s, 1 H), 4.91 (s, 1 H), 4.93
(s, 1 H), 4.30 (s, 5 H), 2.49-2.32 (m, 3 H), 2.18 (t, J = 5 Hz, 1 H),
1.91-1.85 (m, 1 H), 1.52 (d, J = 9 Hz, 1 H), 1.20 (s, 3 H), 0.62 (s, 3
H); ¹³C NMR (75 MHz, C₆D₆) ppm 189.11, 107.13, 90.08, 82.88, 73.20,
72.88, 69.41, 67.95, 42.15, 41.09, 37.43, 27.49, 26.91, 21.76; [α]²³_D
-108.4° (c 1.1, CCl₄); MS, m/z (M⁺) calcd 354.0552, obsd 354.0555.
4,5,6,7-Tetrahydro-2-[(4-nitrophenyl)methylene]-4,7-methano-2H-indene (84-NO₂).

To a stirred suspension of sodium methoxide (1.6 g, 0.03 mol) in anhydrous methanol (25 mL) was added isodicyclopentadiene (1.0 g, 8.0 mmol). After a few min, 4-nitrobenzaldehyde (1.12 g, 7.0 mmol) in methanol was added dropwise. The reaction mixture was heated to 60 °C and stirred for 4 h at this temperature. The mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 100 mL). The extracts were washed with brine, dried and concentrated to give a dark red oil. The oil was purified by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 0.749 g (38%) of the desired fulvene as dark red-orange flakes after recrystallization from ethanol, mp 123-124 °C; IR (CHCl₃, cm⁻¹) 3030, 2970, 2950, 2920, 2880, 1590, 1510, 1340, 1315, 1110, 1100, 950, 910, 890, 865, 840, 820, 695, 640; ¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, J = 8.8 Hz, 2 H), 7.63 (d, J = 8.8 Hz, 2 H), 6.91 (s, 1 H), 5.99 (s, 1 H), 5.68 (s, 1 H), 3.13 (s, 2 H), 1.90 (d, J = 7.9 Hz, 2 H), 1.77 (s, 2 H), 1.48 (d, J = 7.3 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 162.45, 157.24, 154.26, 146.81, 144.11, 130.36, 129.34, 123.66, 110.88, 104.28, 44.12, 38.91, 38.48, 28.74, 28.68; MS, m/z (M⁺) calcd 265,1103, obsd 265,1090.
2-[(4-Fluorophenyl)methylene]-4,5,6,7-tetrahydro-4,7-methano-2H-indene (84-F).

To a solution of 1sodicyclopentadiene (1.5 g, 0.011 mol) in anhydrous methanol (25 mL) was added sodium methoxide (2.5 g, 0.046 mol). After several min of stirring, 4-fluorobenzaldehyde (1.4 g, 0.011 mol) in anhydrous methanol (10 mL) was added dropwise. The mixture was stirred at reflux for 24 h, diluted with brine (250 mL) and extracted with dichloromethane (3 x 100 mL). The combined organic phases were dried over potassium carbonate, filtered and evaporated. The resulting oily residue was purified by chromatography on silica gel (elution with petroleum ether) to afford 0.355 g (13%) of the fulvene as an yellow-orange powder, mp 59-60 °C:

IR (CHCl₃, cm⁻¹) 3000, 2970, 2950, 2920, 2870, 1599, 1505, 1315, 1295, 1230, 1210, 1160, 1150, 1115, 1100, 945, 905, 885, 870, 830, 820, 635;

¹H NMR (300 MHz, CDCl₃) 87.51-7.46 (m, 2 H), 7.08-7.02 (m, 2 H), 6.88 (s, 1 H), 6.05 (s, 1 H), 5.68 (s, 1 H), 3.12 (s, 2 H), 1.91-1.45 (series of m, 6 H);

³C NMR (75 MHz, CDCl₃) ppm 162.55 (d, ¹JCF = 242 Hz), 160.94, 155.60, 150.76, 133.79 (d, ⁴JCF = 3 Hz), 131.68, 131.53 (d, ³JCF = 8 Hz), 115.44 (d, ²JCF = 21 Hz), 111.00, 104.47, 44.75, 38.96, 38.54, 28.88, 28.82; MS, m/z (M⁺) calcd 238.1158, obsd 238.1155.
4,5,6,7-Tetrahydro-2-[[4-(trifluoromethyl)phenyl]methylene]-4,7-methano-2H-indene (84-CF₃).

To a stirred suspension of sodium methoxide (1.6 g, 0.03 mol) in anhydrous methanol (20 mL) was added isodicyclopentadiene (1.00 g, 8.0 mmol) in methanol (5 mL). After a few min, 4-trifluoromethylbenzaldehyde (1.29 g, 7.0 mmol) in methanol (10 mL) was added dropwise. The reaction mixture was then heated to reflux for 4.5 h, cooled to room temperature, diluted with water (100 mL) and extracted with dichloromethane (3 x 100 mL). The combined extracts were washed with brine (100 mL), dried and concentrated to give a dark orange oil which was purified by chromatography on silica gel (elution with petroleum ether). The fulvene was isolated as an orange oil (822 mg, 38%): IR (CHCl₃, cm⁻¹) 3000, 2960, 2920, 2860, 1610, 1445, 1410, 1320, 1295, 1250, 1185, 1170, 1130, 1065, 1015, 950, 910, 885, 830, 820, 645; ¹H NMR (300 MHz, CDCl₃) δ7.59 (s, 4 H), 6.91 (s, 1 H), 6.01 (s, 1 H), 5.68 (s, 1 H), 3.11 (s, 2 H), 1.92-1.85 (m, 2 H), 1.76 (s, 2 H), 1.47 (d, J = 7 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 161.64, 156.60, 152.87, 141.08, 137.61 (q, δCF = 272 Hz), 130.60, 130.02, 125.26, 110.83, 104.50, 44.43, 38.93, 38.51, 28.75; MS, m/z (M⁺) calcd 288.1126, obsd 288.1130.
4-[(4,5,6,7-Tetrahydro-4,7-methano-2H-inden-2-ylidene)methyl]benzonitrile (84-CN).

To a stirred suspension of sodium methoxide (1.6 g, 0.03 mol) in anhydrous methanol (20 mL) was added isodicyclopentadiene (1.00 g, 8.0 mmol) in methanol (5 mL). After a few min, 4-cyanobenzaldehyde (0.97 g, 7.0 mmol) in methanol (10 mL) was added dropwise. The reaction mixture was then heated to reflux for 4.5 h, cooled to room temperature, diluted with water (100 mL) and extracted with dichloromethane (3 x 100 mL). The combined extracts were washed with brine (100 mL), dried and concentrated to give an orange oil which was purified by chromatography on silica gel (elution with petroleum ether followed by 5% ethyl acetate in petroleum ether). The fulvene was isolated as an orange solid (427 mg, 23%), mp 82-4 °C (from ethanol); IR (CHCl₃, cm⁻¹) 3000, 2980, 2940, 2860, 2220, 1600, 1495, 1410, 1315, 1250, 1190, 1100, 1080, 1060, 1020, 950, 910, 885, 830, 820; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, J = 8 Hz, 2 H), 7.57 (d, J = 8 Hz, 2 H), 6.86 (s, 1 H), 5.98 (s, 1 H), 5.66 (s, 1 H), 3.11 (br s, 2 H), 1.93-1.87 (m, 2 H), 1.76 (s, 2 H), 1.47 (d, J = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 162.18, 157.00, 153.70, 142.14, 132.10, 130.27, 129.89, 118.89, 110.84, 104.29, 44.23, 38.91, 38.49, 28.71; MS, m/z (M⁺) calcd 245.1204, obsd 245.1208.
Cycloaddition of \( \mu \)-X-Phenylisodicyclopentafulvenes (84) with \( N \)-Phenylmaleimide

A solution of 84 (0.20 g, 0.8 mmol) and \( N \)-phenylmaleimide (0.20 g, 1.1 mmol) in dry benzene (6-8 mL) was stirred for 24-30 h at 60-68 °C under a nitrogen atmosphere. The solvent was removed and the resulting solid residues purified by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give the cycloadducts 85 in yields ranging from 47-89%.

(3\(a\alpha\), 4\(a\), 5\(a\), 8\(a\), 9\(a\), 9a\(\alpha\))-3\(a\alpha\)4,5,6,7,8,9,9a-Octahydro-2-phenyl-10-(phenylmethylene)-4,9:5,8-dimethano-1H-benz[f]isoindole-1,3(2H)-dione (85-H).

65% yield as fine white needles, mp 187-188 °C (from ethyl acetate-petroleum ether); IR (CHCl\(_3\), cm\(^{-1}\)) 3020, 3000, 2965, 2920, 2880, 1770, 1700, 1595, 1495, 1440, 1380, 1270, 1240, 1180, 1110, 920, 860, 690, 620; \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 7.36-6.92 (series of m, 10 H), 5.79 (s, 1 H), 4.35 (s, 1 H), 3.60 (s, 1 H), 2.78 (s, 1 H), 2.70 (s, 1 H), 2.11 (br s, 2 H), 1.37-1.22 (m, 3 H), 0.80 (d, \( J = 8.1 \) Hz, 1 H), 0.43 (d, \( J = 6.9 \) Hz, 2 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) ppm 176.12, 176.07, 152.55, 152.52, 148.35, 135.81, 131.67, 129.05, 128.58, 128.53, 127.88, 127.03, 126.56, 113.85, 52.46, 49.54, 48.05, 47.88, 46.87, 43.23, 43.11, 25.40, 25.33; MS, \( m/z \) (M\(^+\)) calcd 393.1729, obsd 393.1721.

Anal. Calcd for C\(_{27}\)H\(_{25}\)N\(_2\)O\(_2\): C, 82.42; H, 5.89.

Found: C, 82.09; H, 5.98.
(3αα, 4α, 5α, 8α, 9α, 9αα)-3α,4α,5α,6α,7α,8α,9α-Octahydro-10-[(4-
 methoxyphenyl)methylene]-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isoindole-
1,3(2H)-dione (85-OMe).

89% yield as fine white needles, mp
183.5-184 °C (from ethyl acetate-
petroleum ether); IR (CHCl₃, cm⁻¹) 3020,
3000, 2990, 2920, 2880, 1870, 1705, 1500,
1380, 1185, 690, 615; ¹H NMR (300 MHz,
C₆D₆) δ 7.37-6.86 (series of m, 9 H), 5.81
(s, 1 H), 4.39 (s, 1 H), 3.62 (s, 1 H), 2.79 (s, 1 H), 2.71 (s, 1 H),
2.12 (s, 2 H), 2.00 (s, 3 H), 1.32-1.23 (m, 3 H), 0.79 (d, J = 8.1 Hz, 1
H), 0.44 (d, J = 6.3 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 176.22,
176.15, 152.65, 152.60, 147.57, 136.61, 132.97, 131.74, 129.26, 129.08,
128.60, 127.82, 126.63, 113.80, 52.53, 49.57, 48.13, 47.95, 46.90,
43.26, 43.15, 25.42, 25.35, 21.13; MS, m/z (M⁺) calcd 407.1885, obse
407.1885.

(3αα, 4α, 5α, 8α, 9α, 9αα)-3α,4α,5α,6α,7α,8α,9α-Octahydro-10-[(4-
 methoxyphenyl)methylene]-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isoindole-
1,3(2H)-dione (85-OMe).

72% yield as fine white needles, mp
184.5-185.5 °C (from ethyl acetate-
petroleum ether); IR (CHCl₃, cm⁻¹) 3020,
3000, 2965, 2880, 2840, 1765, 1700, 1605,
1510, 1380, 1295, 1250, 1180, 1030, 875,
860, 840, 830, 690, 610; ¹H NMR (300 MHz,
C₆D₆) δ 7.38-6.65 (series of m, 9 H), 5.78 (s, 1 H), 4.39 (s, 1 H), 3.63
(s, 1 H), 3.20 (s, 3 H), 2.80 (s, 1 H), 2.74 (s, 1 H), 2.14 (br s, 2 H),
1.33-1.25 (m, 3 H), 0.81 (d, J = 8.2 Hz, 1 H), 0.45 (d, J = 6.1 Hz, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 176.20, 158.68, 152.68, 152.63, 146.65, 131.75, 129.10, 129.05, 128.57, 128.42, 126.61, 114.04, 113.39, 55.20, 52.56, 49.56, 48.14, 47.96, 46.83, 43.26, 43.14, 25.40, 25.34; MS, m/z (M$^+$) calcd 423.1834, obsd 423.1861.

Anal. Calcd for C$_{28}$H$_{25}$N$_{2}$O$_{3}$: C, 79.41; H, 5.95.

Found: C, 79.30; H, 5.94.

(3αα, 4α, 5α, 8α, 9α, 9αα)-10-[[4-(Dimethylamino)phenyl]methylene]-3α,4,5,6,7,8,9,9α-octahydro-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isoindole-1,3(2H)-dione (85-NMe$_2$).

47% yield as fine white needles, mp 185-186 °C (from ethyl acetate-petroleum ether); IR (CHC$_3$, cm$^{-1}$) 3030, 3000, 2970, 2920, 2880, 2800, 1770, 1700, 1600, 1515, 1495, 1380, 1350, 1185, 1050, 820, 690, 615; $^1$H NMR (300 MHz, C$_6$D$_6$) δ 7.40-6.90 (series of m, 7 H), 6.47 (d, J = 8.6 Hz, 2 H), 5.87 (s, 1 H), 4.51 (s, 1 H), 3.66 (s, 1 H), 2.81 (s, 1 H), 2.75 (s, 1 H), 2.41 (s, 6 H), 2.17 (dd, J = 7.1, 11.3 Hz, 2 H), 1.34-1.26 (m, 3 H), 0.82 (d, J = 7.8 Hz, 1 H), 0.46 (d, J = 6.7 Hz, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 176.38, 176.35, 152.88, 152.67, 149.43, 144.97, 131.79, 129.04, 128.83, 128.50, 126.71, 113.68, 112.51, 52.62, 49.53, 48.32, 48.01, 46.90, 43.23, 43.11, 40.44, 25.38, 25.30; MS, m/z (M$^+$) calcd 436.2151, obsd 436.2148.
(3aa, 4a, 5a, 8a, 9a, 9aa)-10-[(4-Chlorophenyl)methylene]-3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isindole-1,3(2H)-dione (85-C1).

53% yield as a white powder, mp 172-173 °C (from ethyl acetate-petroleum ether); IR (CHCl₃, cm⁻¹) 3050, 2980, 2920, 2880, 1770, 1700, 1595, 1500, 1490, 1380, 1270, 1185, 1090, 1010, 880, 865, 820, 690, 615; ¹H NMR (300 MHz, CD₆D₆) δ 7.33-6.90 (series of m, 9 H), 5.58 (s, 1 H), 4.21 (s, 1 H), 3.56 (s, 1 H), 2.77 (s, 1 H), 2.71 (s, 1 H), 2.06 (s, 2 H), 1.32-1.22 (m, 3 H), 0.79 (d, J = 8.3 Hz, 1 H), 0.41 (d, J = 7.0 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 175.96, 152.55, 152.35, 149.03, 134.26, 132.85, 131.61, 129.12, 129.08, 128.73, 128.65, 126.43, 112.67, 52.49, 49.55, 47.90, 47.84, 46.79, 43.24, 43.13, 25.40, 25.34, 13.64; MS, m/z (M⁺) calcd 427.1339, obsd 427.1312.

Anal. Calcd for C₂₇H₂₂ClNO₂: C, 75.78; H, 5.18.

Found: C, 75.76; H, 5.22.

(3aa, 4a, 5a, 8a, 9a, 9aa)-3a,4,5,6,7,8,9,9a-Octahydro-10-[(4-nitrophenyl)methylene]-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isindole-1,3(2H)-dione (85-NO₂).

52% yield as pale yellow needles, mp 181-182 °C (from ethyl acetate-petroleum ether); IR (CHCl₃, cm⁻¹) 3020, 3000, 2970, 2920, 2880, 1770, 1705, 1595, 1515, 1495, 1380, 1345, 1185, 880, 860, 685, 615; ¹H NMR (300 MHz, CD₆D₆) δ 7.68 (d, J = 8.8 Hz, 2 H), 7.30-6.97 (series of m, 5 H), 6.83 (d, J = 8.7 Hz, 2 H),
5.47 (s, 1 H), 4.13 (s, 1 H), 3.54 (s, 1 H), 2.76 (s, 1 H), 2.74 (s, 1 H), 2.04 (s, 2 H), 1.32 (d, J = 7.1 Hz, 2 H), 1.23 (d, J = 8.4 Hz, 1 H), 0.79 (d, J = 8.3 Hz, 1 H), 0.41 (dd, J = 2.2, 7.6 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 175.74, 175.66, 152.44, 152.41, 152.02, 146.55, 142.48, 131.48, 129.12, 128.73, 128.47, 126.25, 123.92, 111.99, 52.61, 49.57, 47.76, 47.66, 46.88, 43.26, 43.16, 25.42, 25.37; MS, m/z (M⁺) calcd 438.1579, obsd 438.1597.

(3aa, 4a, 5a, 8a, 9a, 9aa)-10-[(4-Fluorophenyl)methylene]-3a,4,5,6,7,8,9,9a-octahydro-2-phenyl-4,9:5,8-dimethano-1H-benz[f]isoindole-1,3(2H)-dione (85-F).

58% yield as fine white needles, mp 174-175 °C (from ethyl acetate-petroleum ether); IR (CHCl₃, cm⁻¹) 3020, 2960, 2920, 2870, 1765, 1700, 1595, 1505, 1495, 1380, 1280, 1215, 1185, 1155, 1115, 1095, 1015, 950, 940, 905, 880, 860, 845, 835, 720, 690, 610; ¹H NMR (300 MHz, C₆D₆) δ 7.33-6.64 (series of m, 9 H), 5.65 (s, 1 H), 4.23 (s, 1 H), 3.58 (s, 1 H), 2.79 (s, 1 H), 2.73 (s, 1 H), 2.11 (s, 2 H), 1.32 (d, J = 7.4 Hz, 2 H), 1.25 (d, J = 8.2 Hz, 1 H), 0.80 (d, J = 8.2 Hz, 1 H), 0.48-0.43 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 176.06, 161.84 (d, ¹JCF = 245 Hz), 152.67, 152.45, 148.22, 131.88 (d, ¹JCF = 3 Hz), 131.68, 129.49 (d, ³JCF = 8 Hz), 129.10 (2C), 128.66, 126.50 (2C), 115.52 (d, ²JCF = 21 Hz), 112.74, 52.52, 49.58, 48.00, 47.90, 46.77, 43.27, 43.16, 25.43, 25.36; MS, m/z (M⁺) calcd 411.1634, obsd 411.1650.
(3a, 4a, 4a, 5a, 8a, 8a, 9a, 9a)-3a,4,5,6,7,8,9,9a-Octahydro-10-[(4-methoxyphenyl)methylene]-2-phenyl-4a,8a-epoxy-4,9:5,8-dimethano-1H-benz[f]isoindole-1,3(2H)-dione (85-OMe).

To a solution of 85-OMe (50 mg, 0.1 mmol) in dry dichloromethane (10 mL) at 0 °C was added MCPBA (0.039 g) in dry dichloromethane (10 mL). The reaction mixture was stirred at 0 °C for 4 h, washed with 5% sodium thiosulfate solution (3 x 25 mL), saturated sodium bicarbonate solution (4 x 25 mL) and water (25 mL). The organic layer was dried, filtered and concentrated to give a pale yellow residue. Purification by radial chromatography (silica gel, 1mm plate, 30% ethyl acetate in petroleum ether) gave 0.052 g (99%) of the the epoxide as a white powder, mp 245-246 °C; IR (CHCl₃, cm⁻¹) 3030, 3000, 2990, 2940, 1770, 1710, 1605, 1510, 1385, 1295, 1250, 1190, 1035, 885, 830, 690, 660; ¹H NMR (300 MHz, CDCl₃) δ7.38-7.32 (m, 3 H), 7.15 (d, J = 9 Hz, 2 H), 6.99-6.96 (m, 2 H), 6.81 (d, J = 9 Hz, 2 H), 6.10 (s, 1 H), 4.29 (s, 1 H), 3.78 (s, 3 H), 3.62 (s, 3 H), 2.94 (s, 2 H), 1.90 (d, J = 9 Hz, 1 H), 1.81-1.70 (m, 3 H), 0.84 (d, J = 9 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 176.34, 176.04, 158.76, 137.69, 131.55, 129.10, 129.05, 128.71, 128.17, 126.46, 119.82, 113.94, 57.59, 57.38, 55.20, 51.77, 46.66, 46.53, 46.15, 40.78, 40.68, 37.51, 26.58, 26.44; MS, m/z (M⁺) calcd 439.1783, obsd 439.1819.
To a cold (0 °C), stirred mixture of 85-Cl (28 mg, 0.07 mmol) and sodium bicarbonate in dichloromethane (5 mL) was added MCPBA (27 mg) in a single portion. After stirring 5 h at 0 °C, the reaction mixture was diluted with dichloromethane (25 mL) and washed with 5% sodium thiosulfate solution (4 x 25 mL), saturated sodium bicarbonate solution (3 x 25 mL). The organic layer was dried, filtered and evaporated to afford a white solid. Recrystallization from dichloromethane-ethanol gave pure epoxide (89% yield) as white needles, mp 230-231 °C; IR (CHCl₃, cm⁻¹) 3060, 3020, 3000, 2970, 2940, 2920, 2890, 2850, 1770, 1705, 1590, 1495, 1489, 1450, 1385, 1280, 1245, 1190, 1120, 1090, 1015, 960, 920, 900, 885, 845, 830, 690, 660, 640, 620; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.28 (m, 3 H), 7.24 (d, J = 8.6 Hz, 2 H), 7.12 (d, J = 8.5 Hz, 2 H), 6.99-6.96 (m, 2 H), 6.10 (s, 1 H), 4.24 (s, 1 H), 3.62 (br s, 3 H), 2.95 (br s, 2 H), 1.89 (d, J = 9.5 Hz, 1 H), 1.80-1.70 (m, 3 H), 0.87-0.83 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 176.07, 175.76, 140.41, 134.09, 133.12, 131.53, 129.16, 129.12, 128.80, 128.76, 126.33, 119.15, 57.55, 57.39, 51.84, 46.51, 46.49, 46.36, 40.81, 40.74, 37.46, 26.59, 26.49; MS, m/z (M⁺) calcd 443.1288, obsd 443.1299.
CYCLOADDITION OF 84 WITH DIMETHYL ACETYLENEDICARBOXYLATE

A solution of 84 (0.10 g, 0.4 mmol) and dimethyl acetylenedicarboxylate (74 µL, 0.6 mmol) in dry benzene (10 mL) was evacuated and flushed with nitrogen several times. The reaction mixture was warmed to 60-65 °C and stirred 1-3 days under nitrogen. Evaporation of the solvent provided oily residues which were purified by MPLC on silica gel (elution with 20-25% ethyl acetate in petroleum ether) to afford cycloadducts 87 along with the corresponding epoxides 88. Yields range from 52-69%.

Dimethyl (1α, 4α, 5α, 8α)-1,4,5,6,7,8-Hexahydro-10-(phenylmethylene)-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (87-H).

29% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3020, 2950, 2880, 2840, 1720, 1615, 1520, 1435, 1265, 1215, 1140, 1100, 1070, 1045, 930, 855, 810, 795, 735, 680, 630; 

1H NMR (300 MHz, CDCl₃) δ7.34-7.19 (m, 5 H), 5.56 (s, 1 H), 4.66 (s, 1 H), 4.18 (s, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.16 (s, 1 H), 3.13 (s, 1 H), 1.53-1.48 (m, 3 H), 1.33 (dt, J = 1.5, 8.6 Hz, 1 H), 0.60-0.56 (m, 2 H);

MS, m/z (M⁺) calcd 362.1518, obsd 362.1518.
Dimethyl (1α, 4α, 5α, 8α)-1,4,5,6,7,8-Hexahydro-10-[(4-methylphenyl)methylene]-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (87-Me).

49% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3020, 3010, 2970, 2950, 2880, 2840, 1715, 1610, 1510, 1435, 1305, 1280, 1260, 1220, 1180, 1100, 1050, 1020, 960, 910, 890, 865, 815; ¹H NMR (300 MHz, CDCl₃) δ 7.12 (s, 4 H), 5.53 (s, 1 H), 4.65 (s, 1 H), 4.17 (s, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.15 (s, 1 H), 3.12 (s, 1 H), 2.33 (s, 3 H), 1.55-1.50 (m, 3 H), 1.15 (d, J = 8.5 Hz, 1 H), 0.57 (d, J = 8.3 Hz, 2 H); MS, m/z (M⁺) calcd 376.1674, obsd 376.1714.

Dimethyl (1α, 4α, 5α, 8α)-1,4,5,6,7,8-Hexahydro-10-[(4-methoxyphenyl)methylene]-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (87-OMe).

42% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3020, 2960, 2930, 2870, 2840, 1720, 1510, 1475, 1425, 1330, 1220, 1210, 1090, 1035, 930, 850, 785, 735, 670, 630; ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.13 (m, 2 H), 6.88-6.83 (m, 2 H), 5.50 (s, 1 H), 4.63 (s, 1 H), 4.16 (s, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.15 (s, 1 H), 3.12 (s, 1 H), 1.55-1.51 (m, 3 H), 1.15 (dt, J = 1.4, 8.4 Hz, 1 H), 0.59-0.56 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 165.19, 163.34, 158.12, 157.33, 156.79, 149.62, 148.83, 129.10, 128.40, 113.75, 101.40, 56.38, 55.14, 52.13, 51.90, 47.79, 43.05, 43.00, 22.57; MS, m/z (M⁺) calcd 392.1624, obsd 392.1610.
Dimethyl (1α, 4α, 5α, 8α)-10-[[4-(Dimethylamino)phenyl)methylene]-1,4,5, 6,7,8-hexahydro-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (87-NMe2).  

56% yield as an orange oil; IR (CHCl3, cm⁻¹) 3030, 3000, 2970, 2950, 2920, 2870, 2800, 1720, 1710, 1610, 1515, 1435, 1355, 1310, 1290, 1250, 1165, 1100, 1050, 950, 910, 860, 775, 720, 670; ¹H NMR (300 MHz, CDCl3) δ7.13 (d, J = 8.7 Hz, 2 H), 6.69 (d, J = 8.8 Hz, 2 H), 5.47 (s, 1 H), 4.67 (s, 1 H), 4.15 (s, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.14 (s, 1 H), 3.11 (s, 1 H), 2.94 (s, 6 H), 1.54-1.48 (m, 3 H), 1.14 (d, J = 8.4 Hz, 1 H), 0.57 (d, J = 8.4 Hz, 2 H); ¹³C NMR (75 MHz, CDCl3) ppm 165.44, 165.39, 162.71, 157.54, 157.16, 149.96, 149.20, 128.96, 124.40, 112.57, 101.94, 56.67, 52.19, 52.15, 47.94, 43.18, 43.14, 40.60, 22.70; MS, m/z (M⁺) calcd 405.1940, obsd 405.1966.

Dimethyl (1α, 4α, 5α, 8α)-10-[[4-Chlorophenyl)methylene]-1,4,5,6,7,8-hexahydro-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (87-Cl).  

32% yield as a colorless oil; IR (CHCl3, cm⁻¹) 3020, 2960, 2880, 2840, 1725, 1490, 1435, 1270, 1220, 1099, 1045, 1015, 900, 820; ¹H NMR (300 MHz, CDCl3) δ7.28 (d, J = 9 Hz, 2 H), 7.15 (d, J = 9 Hz, 2 H), 5.50 (s, 1 H), 4.59 (s, 1 H), 4.17 (s, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.15 (s, 1 H), 3.12 (s, 1 H), 1.54-1.49 (m, 3 H), 1.18-1.14 (m, 1 H), 0.59-0.55 (m, 2 H); MS, m/z (M⁺) calcd 396.1128, obsd 396.1151.
Dimethyl (1α, 4α, 5α, 8α)-1,4,5,6,7,8-Hexahydro-10-[(4-nitrophenyl) methylene]-1,4,5,8-dimethanonaphthalene-2,3-dicarboxylate (87-No2).

49% yield as a yellow oil; IR (CHCl₃, cm⁻¹) 3020, 2980, 2960, 2875, 1725, 1710, 1620, 1595, 1520, 1435, 1345, 1310, 1280, 1255, 1180, 1110, 1100, 1050, 875, 860;
1H NMR (300 MHz, CDCl₃) 8.81 (d, J = 8.8 Hz, 2 H), 7.36 (d, J = 8.6 Hz, 2 H), 5.61 (s, 1 H), 4.63 (s, 1 H), 4.21 (s, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.17 (s, 1 H), 3.15 (s, 1 H), 1.56-1.51 (m, 3 H), 1.19 (d, J = 8.5 Hz, 1 H), 0.60-0.56 (m, 2 H); 13C NMR (75 MHz, CDCl₃) ppm 166.77, 164.88, 157.19, 156.29, 149.10, 148.23, 146.21, 143.13, 128.66, 123.78, 100.57, 56.50, 52.34, 51.93, 48.02, 43.21, 43.16, 22.75; MS, m/z (M⁺) calcd 407.1369, obsd 407.1343.

Dimethyl (1α, 4α, 5α, 8α)-10-[(4-Fluorophenyl)methylene]-1,4,5,6,7,8-hexahydro-1,4,5,8-dimethanonaphthalene-2,3-dicarboxylate (87-F).

62% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3040, 2970, 2955, 2880, 1710, 1615, 1600, 1505, 1435, 1310, 1280, 1255, 1235, 1195, 1180, 1160, 1100, 1050, 865, 830;
1H NMR (300 MHz, CDCl₃) 8.720-6.97 (series of m, 4 H), 5.51 (s, 1 H), 4.59 (s, 1 H), 4.17 (s, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.12 (s, 1 H), 1.54-1.49 (m, 3 H), 1.16 (d, J = 8.5 Hz, 1 H), 0.59-0.55 (m, 2 H); 13C NMR (75 MHz, CDCl₃) ppm 165.13, 164.25, 161.47 (d, 1J_{CF} = 245 Hz), 157.34, 156.65, 149.47, 148.70, 131.99, 131.97 (d, 1J_{CF} = 3
Hz), 129.57 (d, $^3\delta_{CF} = 8$ Hz), 115.22 (d, $^2\delta_{CF} = 22$ Hz), 100.89, 56.37, 52.19, 51.88, 47.89, 43.12, 43.07, 22.63 (2C); MS, m/z ($M^+$) calcd 380.1424, obsd 380.1438.

**Dimethyl (1α, 4α, 4α, 5α, 8α, 8α)-1,4,5,6,7,8-Hexahydro-10-(phenylmethylene)-4α,8α-epoxy-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (88-H).**

23% yield as a colorless oil; IR (CHCl$_3$, cm$^{-1}$) 3020, 2980, 2955, 2880, 2840, 1715, 1635, 1605, 1495, 1480, 1445, 1435, 1365, 1320, 1305, 1255, 1210, 1180, 1110, 1090, 1070, 1025, 955, 930, 905, 890, 850, 760, 700, 670, 630; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32-7.18 (series of m, 5 H), 5.73 (s, 1 H), 4.41 (s, 1 H), 3.91 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.76 (s, 1 H), 3.74 (s, 1 H), 1.89-1.86 (m, 1 H), 1.56-1.50 (m, 2 H), 1.29-1.22 (m, 2 H), 0.93 (d, $\delta = 9.4$ Hz, 1 H); MS, m/z ($M^+$) calcd 378.1467, obsd 378.1508.

**Dimethyl (1α, 4α, 4α, 5α, 8α, 8α)-1,4,5,6,7,8-Hexahydro-10-[(4-methylphenyl)methylene]-4α,8α-epoxy-1,4:5,8-dimethanonaphthalene-2,3-dicarboxylate (88-Me).**

17% yield as a colorless oil; IR (CHCl$_3$, cm$^{-1}$) 3020, 3010, 2970, 2960, 2880, 2840, 1715, 1635, 1605, 1510, 1480, 1450, 1435, 1360, 1325, 1305, 1260, 1220, 1180, 1110, 1070, 1020, 955, 905, 890, 865, 815; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.09 (s, 4 H), 6.19 (s, 1 H), 5.70 (s, 1 H), 4.40 (s, 1 H), 3.84 (s, 3 H), 3.82 (s, 3 H),
2.73 (s, 1 H), 2.70 (s, 1 H), 2.32 (s, 3 H), 1.88 (d, J = 8.7 Hz, 1 H),
1.55-1.51 (m, 2 H), 1.26-1.22 (m, 2 H), 0.93 (d, J = 9.3 Hz, 1 H); MS,
m/z (M⁺) calcd 392.1624, obsd 392.1577.

**Dimethyl (1α, 4α, 4aα, 5α, 8α, 8aα)-1,4,5,6,7,8-Hexahydro-10-
[(4-methoxyphenyl)methylene]-4a,8a-epoxy-1,4:5,8-dimethanonaphthalene-
2,3-dicarboxylate (88-OMe).**

10% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3020, 2960, 2930, 2870, 1720, 1630,
1610, 1565, 1510, 1475, 1460, 1435, 1390,
1375, 1325, 1285, 1250, 1225, 1210, 1150,
1140, 1070, 1040, 955, 930, 905, 890, 850,
760, 670, 630; ¹H NMR (300 MHz, CDCl₃) δ
7.12 (d, J = 8.7 Hz, 2 H), 6.83 (d, J = 8.7 Hz, 2 H), 5.67 (s, 1 H),
4.77 (s, 1 H), 4.38 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 2.73 (s, 1
H), 2.70 (s, 1 H), 1.87 (d, J = 9.0 Hz, 1 H), 1.53-1.51 (m, 2 H), 1.27-
1.19 (m, 2 H), 0.94-0.91 (m, 1 H); MS, m/z (M⁺) calcd 408.1573, obsd
407.1604.

**Dimethyl (1α, 4α, 4aα, 5α, 8α, 8aα)-10-[(4-Chlorophenyl)methylene]-1,4,5,6,7,8-Hexahydro-4a,8a-epoxy-1,4:5,8-dimethanonaphthalene-2,3-
dicarboxylate (88-Cl).**

29% yield as a white solid, mp 147-148 °C
(from n-heptane); IR 3010, 2960, 2940,
2880, 1725, 1710, 1605, 1490, 1475, 1450,
1435, 1375, 1360, 1325, 1310, 1255, 1225,
1175, 1090, 1070, 1045, 1010, 950, 905,
890, 865, 820; ¹H NMR (300 MHz, CDCl₃) δ
7.26 (d, J = 8.4 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 5.67 (s, 1 H),
4.34 (s, 1 H), 3.90 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 2.74 (s, 1
H), 2.71 (s, 1 H), 1.87 (d, J = 9.3 Hz, 1 H), 1.55-1.52 (m, 2 H), 1.27-
1.17 (m, 2 H), 0.93 (d, J = 9.4 Hz, 1 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) ppm
164.19, 164.11, 155.36, 148.79, 148.43, 134.48, 132.35, 129.31, 128.49,
108.46, 64.64, 64.56, 54.44, 52.55, 52.50, 50.21, 39.40, 38.19, 24.92,
24.85; MS, m/z (M\(^{+}\)) calcd 412.1077, obsd 412.1069.

**Anal.** Calcd for C\(_{23}\)H\(_{21}\)Cl\(_4\): C, 67.01; H, 5.13.

Found: C, 66.66; H, 5.12.

Dimethyl (1\(\alpha\), 4\(\alpha\), 4\(\alpha\)\(\alpha\), 5\(\alpha\), 8\(\alpha\), 8\(\alpha\)\(\alpha\))-1,4,5,6,7,8-Hexahydro-10-
[(4-nitrophenyl)methylene]-4\(\alpha\),8\(\alpha\)-epoxy-1,4:5,8-dimethanonaphthalene-2,3-
dicarboxylate (88-NO\(_2\)).

16% yield as a yellow oil; IR (CHCl\(_3\),

\(\text{cm}^{-1}\)) 3020, 2980, 2960, 2880, 1710, 1595,
1515, 1475, 1450, 1430, 1345, 1285, 1255,
1225, 1175, 1105, 1075, 905, 885, 875,
860; \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, J =
8.8 Hz, 2 H), 7.33 (d, J = 8.6 Hz, 2 H), 5.77 (s, 1 H), 4.39 (s, 1 H), 3.97 (s, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 2.76 (s, 1 H), 2.73 (s, 1 H), 1.86 (d, J = 9.5 Hz, 1 H), 1.56 (d, J = 9.4 Hz, 2 H), 1.28-1.22 (m, 2 H), 0.96 (d, J = 9.4 Hz, 1 H); \(^{13}\)C NMR
(75 MHz, CDCl\(_3\)) ppm 163.97, 163.88, 157.83, 148.55, 148.06, 146.39,
142.97, 128.62, 123.76, 107.96, 64.65, 64.51, 54.62, 52.66, 52.60,
50.39, 39.37, 38.07, 24.89, 24.81; MS, m/z (M\(^{+}\)) calcd 423.1318, obsd
423.1256.
Dimethyl (1α, 4α, 4αα, 5α, 8α, 8αα)-10-[(4-Fluorophenyl)methylene]-1,4, 5,6,7,8-hexahydro-4α,8α-epoxy-1,4:5,8-dimethanonaphthalene-2,3- dicarboxylate (88-F).

7 % yield as a white solid, mp 145.0-
145.5 °C (from n-heptane); IR (CHCl₃, cm⁻¹) 3020, 2960, 2930, 2880, 1710, 1600, 1505, 1480, 1435, 1320, 1285, 1205, 1100, 1070, 910, 780, 730, 670, 625; ¹H NMR (300 MHz, CDCl₃) δ 7.17-6.95 (series of m, 4 H), 5.68 (s, 1 H), 4.34 (s, 1 H), 3.90 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 2.74 (s, 1 H), 2.70 (s, 1 H), 1.87 (d, J = 9.4 Hz, 1 H), 1.59-1.50 (m, 2 H), 1.33-1.20 (m, 2 H), 0.93 (d, J = 9.4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 164.26, 164.16, 161.65 (d, JCF = 244 Hz), 154.80, 148.88, 148.48, 132.00 (d, JCF = 3 Hz), 129.57 (d, JCF = 8 Hz), 115.23 (d, JCF = 22 Hz), 108.48, 64.64, 64.56, 54.42, 52.52, 52.48, 50.15, 39.42, 38.23, 24.93, 24.86; MS, m/z (M⁺) calcd 296.1373, obsd 396.1361.

Anal. Calcd for C₂₃H₂₁FO₅: C, 69.69; H, 5.34.

Found: C, 69.56; H, 5.49.
CYCLOADDITION OF 84 WITH BENZYNE

A solution of 84 (0.10 g, 0.4 mmol) in dry dimethoxyethane (5 mL) was warmed to reflux under a nitrogen atmosphere. Solutions of anthranilic acid (66 mg, 0.5 mmol) in dimethoxyethane (5 mL) and isoamyl nitrite (90 µL, 0.7 mmol) in dimethoxyethane (5 mL) were added dropwise, simultaneously from separate addition funnels. After addition was complete, the reaction mixture was stirred at reflux for 1-3 h. Removal of the solvent followed by chromatography on silica gel (elution with 1-2% ethyl acetate in petroleum ether) gave cycloadducts 89 in yields of 27-78% overall.

\( (1\alpha, 4\alpha, 9\alpha, 10\alpha)-1,2,3,4,9,10\text{-hexahydro-11-(phenylmethylene)}-1,4:9,10\text{-dimethanoanthracene} \) (89-H).

This compound was too susceptible to air oxidation for complete characterization. 27% yield as a yellow oil: \(^1\)H NMR (300 MHz, CDCl₃) δ 7.36-6.89 (series of m, 9 H), 5.79 (s, 1 H), 4.74 (s, 1 H), 4.22 (s, 1 H), 3.17 (s, 1 H), 3.14 (s, 1 H), 1.45 (d, J = 8.3 Hz, 1 H), 1.27 (d, J = 7.6 Hz, 1 H), 1.06 (d, J = 8.3 Hz, 1 H), -0.04 (d, J = 7.5 Hz, 2 H).
(1α, 4α, 9α, 10α)-1,2,3,4,9,10-Hexahydro-11-[(4-methylphenyl)methylene]-1,4:9,10-dimethanoanthracene (89-Me).

78% yield as a yellow oil; IR (CHCl₃, cm⁻¹) 3050, 3000, 2970, 2920, 2870, 1675, 1510, 1450, 1445, 1300, 1270, 1250, 1180, 1155, 1125, 1110, 1010, 950, 880, 870, 855, 810, 650, 630; ¹H NMR (300 MHz, CDCl₃) δ7.16-7.02 (m, 6 H), 6.90-6.88 (m, 2 H), 5.72 (s, 1 H), 4.69 (s, 1 H), 4.18 (s, 1 H), 3.13 (s, 1 H), 3.09 (s, 1 H), 2.33 (s, 3 H), 1.41 d, 1 = 8 Hz, 1 H), 1.22 (d, 1 = 8 Hz, 1 H), 1.02 (d, 1 = 8 Hz, 1 H), -0.05 (d, 1 = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 164.21, 157.19, 156.97, 148.00, 147.58, 135.59, 134.09, 128.84, 127.95, 124.68, 124.48, 121.09, 120.91, 104.22, 54.63, 49.99, 47.20, 43.68, 43.62, 24.10, 21.10; MS, m/z (M⁺) calcd 310.1722, obsd 310.1716.

(1α, 4α, 9α, 10α)-1,2,3,4,9,10-Hexahydro-11-[(4-methoxyphenyl)methylene]-1,4:9,10-dimethanoanthracene (89-OMe).

63% yield as a yellow oil; ¹H NMR (300 MHz, CDCl₃) δ7.19 (d, 1 = 9 Hz, 2 H), 7.15-7.13 (m, 2 H), 6.90-6.88 (m, 2 H), 6.85 (d, 1 = 9 Hz, 2 H), 5.69 (s, 1 H), 4.67 (s, 1 H), 4.17 (s, 1 H), 3.80 (s, 3 H), 3.14 (s, 1 H), 3.10 (s, 1 H), 1.43 (d, 1 = 8 Hz, 1 H), 1.23 (d, 1 = 7 Hz, 2 H), 1.02 (d, 1 = 8 Hz, 1 H), -0.05 (d, 1 = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 163.74, 158.03, 157.36, 157.05, 148.17, 147.71, 129.66, 129.18, 124.71, 124.51, 121.11,
(1α, 4α, 9α, 10α)-4-[(1,2,3,4,9,10-Hexahydro-1,4:9,10-dimethanoanthracene-11-ylidenemethyl)-N,N-dimethylbenzamine (89-NMe2).

49% yield as an orange oil; IR (CHCl₃, cm⁻¹) 3060, 3030, 3000, 2960, 2920, 2870, 2810, 1680, 1590, 1560, 1505, 1490, 1440, 1345, 1320, 1255, 1190, 1160, 1130, 1100, 950, 910, 870, 820, 695, 655, 635; ¹H NMR (300 MHz, CDCl₃) δ7.45–6.87 (m, 8 H), 5.69 (s, 1 H), 4.71 (s, 1 H), 4.18 (s, 1 H), 3.36 (s, 6 H), 3.11 (br s, 2 H), 1.41 (m, 1 H), 1.22 (d, J = 7 Hz, 2 H), 1.02 (d, J = 9 Hz, 1 H), -0.05 (d, J = 8 Hz, 2 H); MS, m/z (M⁺) calcd 339.1987, obsd 339.2017.

(1α, 4α, 9α, 10α)-11-[(4-Chlorophenyl)methylene]-1,2,3,4,9,10-hexahydro-1,4:9,10-dimethanoanthracene (89-Cl).

This compound was too susceptible to air oxidation for complete characterization.

44% yield as a yellow-green oil; ¹H NMR (300 MHz, CDCl₃) δ7.55–6.88 (m, 6 H), 6.80 (d, J = 9 Hz, 2 H), 5.70 (s, 1 H), 4.65 (s, 1 H), 4.20 (s, 1 H), 3.15 (s, 1 H), 3.12 (s, 1 H), 1.42 (d, J = 8 Hz, 1 H), 1.24 (d, J = 9 Hz, 2 H), 1.04 (d, J = 9 Hz, 1 H), -0.04 (d, J = 8 Hz, 2 H).
(1α, 4α, 9α, 10α)-1,2,3,4,9,10-Hexahydro-11-[(4-nitrophenyl)methylene]-
1,4:9,10-dimethanoanthracene (89-NO₂).

63% yield as an orange oil; IR (CHCl₃,
cm⁻¹) 3070, 3020, 2970, 2920, 2870, 1670,
1590, 1510, 1490, 1450, 1445, 1345, 1270,
1160, 1015, 950, 885, 865, 825, 700, 635,
620; ¹H NMR (300 MHz, CDCl₃) δ 8.16 (d, J = 9 Hz, 2 H),
7.38 (d, J = 9 Hz, 2 H), 7.19-7.16 (m, 2 H), 6.96-6.93 (m, 2 H), 5.79 (s, 1 H), 4.69 (s, 1 H),
4.23 (s, 1 H), 3.16 (s, 1 H), 3.14 (s, 1 H), 1.42 (d, J = 9 Hz, 1 H),
1.25 (d, J = 7 Hz, 2 H), 1.05 (d, J = 8 Hz, 1 H), -0.03 (d, J = 7 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm
167.16, 157.08, 156.31, 146.97, 146.51,
145.76, 144.19, 128.47, 125.24, 125.00, 123.55, 121.28, 121.23, 102.94,
54.76, 49.95, 47.23, 43.67, 43.61, 24.09; MS, m/z (M⁺) calcd 341.1416,
obsd 341.1417.

(1α, 4α, 9α, 10α)-11-[(4-Fluorophenyl)methylene]-1,2,3,4,9,10-hexahydro-
1,4:9,10-dimethanoanthracene (89-F).

39% yield as a yellow oil; IR (CHCl₃,
cm⁻¹) 3060, 3000, 2960, 2940, 2920, 2865,
1600, 1505, 1445, 1370, 1295, 1270, 1250,
1230, 1190, 1155, 1060, 1010, 855, 780,
720, 670; ¹H NMR (300 MHz, CDCl₃) δ 7.23-
6.81 (series of m, 8 H), 5.70 (s, 1 H),
4.64 (s, 1 H), 4.19 (s, 1 H), 3.14 (s, 1 H), 3.11 (s, 1 H), 1.42 (d, J =
8 Hz, 1 H), 1.23 (d, J = 7 Hz, 2 H), 1.04 (d, J = 8 Hz, 1 H), -0.04 (d, J = 8 Hz, 2 H); MS, m/z (M⁺) calcd 314.1471, obsd 314.1440.
EPOXIDATION OF 89

To a cold (0 °C) bicarbonate-buffered solution of 89 (20-85 mg, 0.06-0.27 mmol) in dichloromethane (5-10 mL) was added 1.5 eq. of MCPBA in a single portion. The reaction mixture was stirred at this temperature for 4 h, washed with 5% sodium thiosulfate solution (4 x 25 mL), saturated sodium bicarbonate solution (3 x 25 mL), dried, filtered and concentrated to give nearly pure epoxides. Column chromatography on silica gel (elution with 2-5% ethyl acetate in petroleum ether) gave pure epoxides 90. Yields ranged from 41-76%.

(lα, 4α, 4aα, 9α, 9aα, 10α)-1,2,3,4,4a,9,9a,10-Octahydro-11-(phenylmethylene)-4a,9a-epoxy-1,4:9,10-dimethanoanthracene (90-H).

57% yield as a colorless oil; IR (CHCl₃, cm⁻¹) 3080, 3060, 3020, 3000, 2960, 2925, 2880, 2845, 1725, 1735, 1600, 1530, 1480, 1475, 1455, 1370, 1305, 1245, 1070, 1025, 960, 910, 890, 700, 635; ¹H NMR (300 MHz, CDCl₃) 87.28-6.94 (series of m, 9 H), 5.71 (s, 1 H), 4.49 (s, 1 H), 3.96 (s, 1 H), 2.67 (s, 1 H), 2.64 (s, 1 H), 1.81-1.75 (m, 1 H), 1.20-1.00 (m, 2 H), 0.64-0.55 (m, 3 H); MS, m/z (M⁺) calcd 312.1514, obsd 312.1539.
(1α, 4α, 4αα, 9α, 9αα, 10α)-1,2,3,4,4a,9,9a,10-Octahydro-11-[(4-methylphenyl)methylene]-4a,9a-epoxy-1,4;9,10-dimethanoanthracene (90-Me).

51% yield as white plates, mp 139.5-141°C (from dichloromethane-ethanol); IR (CHCl₃, cm⁻¹) 3060, 3040, 3000, 2960, 2920, 2880, 1685, 1475, 1455, 1365, 1305, 1180, 1160, 1115, 1020, 960, 905, 888, 870, 860, 820, 810, 690, 640, 620; ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.43 (m, 2 H), 7.29-7.23 (m, 6 H), 5.95 (s, 1 H), 4.74 (s, 1 H), 4.21 (s, 1 H), 2.94 (s, 1 H), 2.91 (s, 1 H), 2.50 (s, 3 H), 2.04 (d, J = 9 Hz, 1 H), 1.29-1.25 (m, 2 H), 0.91-0.85 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃) ppm 154.89, 148.36, 148.08, 135.75, 134.17, 128.83, 127.90, 126.04, 125.83, 122.57, 122.36, 110.13, 63.35, 63.20, 53.72, 49.21, 40.30, 37.44, 25.86, 21.12; MS, m/z (M⁺) calcd 326.1671, obsd 326.1680.

(1α, 4α, 4αα, 9α, 9αα, 10α)-1,2,3,4,4a,9,9a,10-Octahydro-11-[(4-methoxyphenyl)methylene]-4a,9a-epoxy-1,4;9,10-dimethanoanthracene (90-OMe).

49% yield as white plates, mp 164.5-166°C (from dichloromethane-methanol); IR (CHCl₃, cm⁻¹) 3060, 3000, 2960, 2930, 2880, 2835, 1605, 1505, 1455, 1295, 1245, 1175, 1035, 960, 885; ¹H NMR (300 MHz, CDCl₃) δ 7.27-7.25 (m, 2 H), 7.12-7.03 (m, 4 H), 6.83-6.79 (m, 2 H), 5.73 (s, 1 H), 4.53 (s, 1 H), 4.01 (s, 1 H), 3.78 (s, 3 H), 2.74 (s, 1 H), 2.72 (s, 1 H), 1.87-1.84 (m, 1 H), 1.09-
1.06 (m, 2 H), 0.72-0.65 (m, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 158.06, 154.31, 148.41, 148.08, 129.66, 129.07, 126.03, 125.81, 122.54, 122.34, 113.62, 109.71, 63.37, 63.22, 55.24, 53.67, 49.10, 40.29, 37.45, 25.86; MS, m/z (M$^+$) calcd 342.1620, obsd 342.1630.

Anal. Calcd for C$_{24}$H$_{22}$O$_2$: C, 84.18; H, 6.48. Found: C, 84.35; H, 6.61.

$(1\alpha, 4\alpha, 4a\alpha, 9\alpha, 9a\alpha, 10\alpha)-11-[(4-Chlorophenyl)methylene]-1,2,3,4,4a,9,9a,10-octahydro-4a,9a-epoxy-1,4:9,10-dimethanoanthracene (90-Cl)$.

76% yield as a colorless oil; IR (CHCl$_3$, cm$^{-1}$) 3060, 3000, 2940, 2920, 2870, 2840, 1485, 1455, 1445, 1395, 1375, 1325, 1290, 1265, 1200, 1090, 1010, 870, 860, 840, 710, 645; $^1$H NMR (300 MHz, CDCl$_3$) δ7.33-6.91 (m, 6 H), 6.77 (d, J = 8 Hz, 2 H), 5.23 (s, 1 H), 4.31 (s, 1 H), 3.76 (s, 1 H), 2.48 (s, 1 H), 2.46 (s, 1 H), 1.38-0.88 (series of m, 6 H); MS, m/z (M$^+$) calcd 346.1124, obsd 346.1174.

$(1\alpha, 4\alpha, 4a\alpha, 9\alpha, 9a\alpha, 10\alpha)-11-[(4-nitrophenyl)methylene]-4a,9a-epoxy-1,4:9,10-dimethanoanthracene (90-NO$_2$).

76% yield as a light yellow solid, mp 185-186 °C (from ethyl acetate-hexane); IR (CHCl$_3$, cm$^{-1}$) 3080, 3020, 3000, 2960, 2930, 2880, 1680, 1590, 1510, 1455, 1395, 1110, 960, 890, 875, 860; $^1$H NMR (300 MHz, CDCl$_3$) δ8.17 (d, J = 9 Hz, 2 H), 7.35-
7.30 (m, 4 H), 7.15-7.13 (m, 2 H), 5.86 (s, 1 H), 4.59 (s, 1 H), 4.13 (s, 1 H), 2.80 (br s, 2 H), 1.89 (d, J = 9 Hz, 1 H), 1.14 (d, J = 10 Hz, 2 H), 0.77 (d, J = 9 Hz, 1 H), 0.71 (d, J = 9 Hz, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 158.34, 147.44, 147.04, 146.02, 144.16, 128.43, 126.63, 126.38, 123.60, 122.69, 122.65, 108.74, 63.36, 63.20, 53.98, 49.47, 40.19, 37.23, 25.76; MS, m/z (M$^+$) calcd 357.1365, obsd 357.1332.

(1α, 4α, 4aα, 9α, 9aα, 10α)-1,2,3,4,4a,9,9a,10-Octahydro-11-
[(4-fluorophenyl)methylene]-4a,9a-epoxy-1,4:9,10-dimethanoanthracene
(90-F).

58% yield as a white solid, mp 154-155 °C
(from dichloromethane-ethanol); IR
(CHCl$_3$, cm$^{-1}$) 3060, 3040, 3000, 2960,
2930, 2880, 1600, 1505, 1475, 1455, 1365,
1310, 1295, 1255, 1230, 1195, 1160, 1120,
1090, 1025, 1015, 960, 905, 890, 860,
830, 690, 640, 620; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.28-6.92 (series of m, 8 H), 5.74 (s, 1 H), 4.50 (s, 1 H), 4.03 (s, 1 H), 2.75 (s, 1 H), 2.73 (s, 1 H), 1.86 (d, J = 9 Hz, 1 H), 1.09 (d, J = 8 Hz, 2 H), 0.72-0.66 (m, 3 H); MS, m/z (M$^+$) calcd 330.1420, obsd 330.1455.

Anal. Calcd for C$_{23}$H$_{19}$FO: C, 83.61; H, 5.80.

Found: C, 83.20; H, 5.90.
CYCLOADDITION OF 84 WITH (Z)-1,2-BIS(PHENYLSULFONYL)ETHENE

A solution of 84 (50 mg, 0.20 mmol) and the disulfone (300 mg, 1.0 mmol) in dry dichloromethane (2 mL) was pressurized to 90,000 psi for 3-7 days. Removal of the solvent followed by MPLC purification on silica gel (elution with 35-40% ethyl acetate in petroleum ether) gave adducts 91 and 92. Small amounts of adducts arising from the trans-disulfone isomer were detected but were not further characterized.

\[
(1\alpha, 4\alpha, 5\beta, 6\alpha, 7\alpha, 8\beta)-1,2,3,4,5,6,7,8-Octahydro-9-(phenylmethylene)-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (91-H).
\]

41% yield as a white solid, mp 157-157.5°C dec (from ethyl acetate); IR (CHCl3, cm\(^{-1}\)) 3060, 3020, 2980, 2940, 2910, 2860, 1445, 1330, 1310, 1150, 1085, 865, 690, 630, 610; \(^1\)H NMR (300 MHz, CDCl3) 8.09-8.03 (m, 4 H), 7.71-7.53 (m, 6 H), 7.24-7.12 (m, 3 H), 6.91 (d, J = 8 Hz, 2 H), 5.35 (s, 1 H), 4.28 (dd, J = 3, 9 Hz, 1 H), 4.21 (dd, J = 3, 9 Hz, 1 H), 4.11 (d, J = 3 Hz, 1 H), 3.38 (d, J = 3 Hz, 1 H), 3.29 (s, 1 H), 3.26 (s, 1 H), 2.25 (d, J = 8 Hz, 1 H), 1.80 (d, J = 8 Hz, 2 H), 1.43 (dd, J = 2, 7 Hz, 1 H), 1.06 (dd, J = 2, 7 Hz, 2 H); \(^{13}\)C NMR (75 MHz, CDCl3) ppm 151.27, 150.84, 150.11, 141.35, 140.58, 135.56, 134.50, 133.54, 133.46, 129.35, 129.03, 128.89, 128.84, 128.79, 128.46, 127.80, 126.79, 106.29, 70.92, 70.48, 51.48, 50.24, 46.33, 43.68, 43.45, 26.73, 26.04; MS (FAB) m/z (M\(^+\)) calcd 528.1, obsd 528.0.

**Anal. Calcd for C\(_{31}\)H\(_{28}\)O\(_4\)S\(_2\):** C, 70.43; H, 5.34.

**Found:** C, 70.02; H, 5.32.
(1α, 4α, 5β, 6α, 7α, 8β)-1,2,3,4,5,6,7,8-Octahydro-9-
[(4-methylphenyl)methylene]-6,7-bis(phenylsulfonyl)-1,4:5,8-di-
methanonaphthalene (91-OMe).

35% yield as a white solid, mp 148.5-150
°C dec (from ethyl acetate); IR (CHCl₃,
cm⁻¹) 3060, 3030, 3010, 2980, 2945, 2920,
2870, 1510, 1445, 1330, 1305, 1290, 1270,
1250, 1150, 1085, 905, 865, 830, 635,
605; ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J
= 7 Hz, 4 H), 7.66-7.53 (m, 6 H), 7.00 (d, J = 8 Hz, 2 H), 6.79 (d, J =
8 Hz, 2 H), 5.31 (s, 1 H), 4.27 (dd, J = 3, 9 Hz, 1 H), 4.20 (dd, J = 3,
9 Hz, 1 H), 4.09 (d, J = 3 Hz, 1 H), 3.37 (d, J = 3 Hz, 1 H), 3.27 (s, 1
H), 3.25 (s, 1 H), 2.28 (s, 3 H), 2.23 (d, J = 8 Hz, 1 H), 1.78 (d, J =
10 Hz, 2 H), 1.41 (d, J = 8 Hz, 1 H), 1.05 (d, J = 10 Hz, 2 H); MS,
(FAB) m/z (M⁺) calcd 542.16, obsd 542.19.

(1α, 4α, 5β, 6α, 7α, 8β)-1,2,3,4,5,6,7,8-Octahydro-9-
[(4-methoxyphenyl)methylene]-6,7-bis(phenylsulfonyl)-1,4:5,8-di-
methanonaphthalene (91-OMe).

23% as a colorless oil; IR (CHCl₃, cm⁻¹)
3060, 3020, 2980, 2960, 2860, 1725, 1605,
1510, 1445, 1330, 1250, 1155, 1090, 1035,
870, 840, 690, 635, 610; ¹H NMR (300 MHz,
CDCl₃) δ 8.07-8.02 (m, 4 H), 7.67-7.54 (m,
6 H), 6.84 (d, J = 9 Hz, 2 H), 6.75 (d, J
= 9 Hz, 2 H), 5.28 (s, 1 H), 4.27 (dd, J = 3, 9 Hz, 1 H), 4.19 (dd, J =
3, 9 Hz, 1 H), 4.09 (d, J = 3 Hz, 1 H), 3.76 (s, 3 H), 3.35 (d, J = 3
Hz, 1 H), 3.27 (s, 1 H), 3.25 (s, 1 H), 2.24 (d, J = 9 Hz, 1 H), 1.79
(d, J = 8 Hz, 2 H), 1.42 (d, J = 8 Hz, 1 H), 1.05 (dd, J = 2, 8 Hz, 2 H); MS, m/z [retro Diels-Alder]+ calcd 250.1346, obsd 250.1357.

(1α, 4α, 5β, 6α, 7α, 8β)-N,N-Dimethyl-4-[[1,2,3,4,5,6,7,8-octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalen-9-ylidene]methyl]-benzenamine (91-NMe2).

37% yield as an orange oil; IR (CHCl3, cm⁻¹) 3060, 3020, 3000, 2980, 2940, 2910, 2860, 2800, 1725, 1605, 1445, 1330, 1310, 1150, 1085, 950, 910, 870, 690, 635, 610; 1H NMR (300 MHz, CDCl3) δ 8.07-8.03 (m, 4 H), 7.71-7.54 (m, 6 H), 6.82 (d, J = 9 Hz, 2 H), 6.56 (d, J = 9 Hz, 2 H), 5.24 (s, 1 H), 4.29 (dd, J = 3, 9 Hz, 1 H), 4.19 (dd, J = 3, 9 Hz, 1 H), 4.15 (d, J = 3 Hz, 1 H), 3.33 (d, J = 3 Hz, 1 H), 3.27 (s, 1 H), 3.24 (s, 1 H), 2.91 (s, 6 H), 2.23 (d, J = 8 Hz, 1 H), 1.77 (d, J = 8 Hz, 2 H), 1.41 (d, J = 8 Hz, 1 H), 1.06 (d, J = 7 Hz, 2 H); MS, (FAB) m/z (M⁺) calcd 571.19, obsd 571.21.

(1α, 4α, 5β, 6α, 7α, 8β)-9-[(4-Chlorophenyl)methylene]-1,2,3,4,5,6,7,8-octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (91-Cl).

21% yield as a white solid, mp 140.5-149°C dec (from chloroform); IR (CHCl3, cm⁻¹) 3060, 3020, 3985, 2945, 2920, 2875, 1675, 1585, 1490, 1445, 1400, 1335, 1310, 1290, 1275, 1255, 1155, 1090, 1015, 1000, 910, 870, 835, 690, 650, 640, 610; 1H NMR (300 MHz, CDCl3) δ 8.06-8.02 (m, 4 H), 7.70-7.54 (m, 6 H), 7.17 (d, J = 9
Hz, 2 H), 6.82 (d, J = 9 Hz, 2 H), 5.30 (s, 1 H), 4.25 (dd, J = 3, 9 Hz, 1 H), 4.20 (dd, J = 3, 9 Hz, 1 H), 4.03 (d, J = 3 Hz, 1 H); 3.39 (d, J = 3 Hz, 1 H), 3.28 (s, 1 H), 3.27 (s, 1 H), 2.24 (d, J = 8 Hz, 1 H), 1.80 (dd, J = 3, 10 Hz, 2 H), 1.43 (d, J = 8 Hz, 1 H), 1.04 (d, J = 10 Hz, 2 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) ppm 151.71, 150.86, 150.00, 141.28, 134.02, 133.58, 132.61, 129.05, 128.99, 128.89, 128.79, 128.65, 105.14, 70.79, 70.35, 51.41, 50.22, 46.23, 43.65, 43.42, 26.74, 26.01; MS, m/z [retro Diels-Alder]+: calc 256.0832, obsd 256.0509.

\((10\text{a}, 4\text{a}, 5\beta, 6\alpha, 7\alpha, 8\beta)-1,2,3,4,5,6,7,8-\text{Octahydro}-9-(4\text{-nitrophenyl})-methylene]-6,7-\text{bis(phenylsulfonyl)}-1,4:5,8-\text{dimethanonaphthalene} (91-\text{NO}_2).\)

51% yield as a yellow solid, mp 176-177 \(^{0}\)C dec (from chloroform); IR (CHCl\(_3\), cm\(^{-1}\)) 3060, 3020, 3985, 2950, 2920, 2870, 1670, 1595, 1520, 1445, 1345, 1310, 1155, 1085, 910, 875, 865, 690, 645, 630, 610; \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) 8.09-8.03 (m, 6 H), 7.70-7.55 (m, 6 H), 7.03 (d, J = 9 Hz, 2 H), 5.41 (s, 1 H), 4.19 (dd, J = 3, 9 Hz, 1 H), 4.15 (dd, J = 3, 9 Hz, 1 H), 4.06 (d, J = 3 Hz, 1 H), 3.46 (d, J = 3 Hz, 1 H), 3.32 (s, 1 H), 3.30 (s, 1 H), 2.26 (d, J = 9 Hz, 1 H), 1.83 (d, J = 9 Hz, 2 H), 1.45 (d, J = 6 Hz, 1 H), 1.07-1.02 (m, 2 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) ppm 153.94, 150.80, 149.80, 146.35, 142.38, 141.20, 141.17, 133.70, 129.10, 128.96, 128.89, 128.81, 128.30, 123.85, 104.41, 70.60, 70.05, 51.60, 50.14, 46.35, 43.73, 43.51, 26.81, 26.01; MS, m/z [retro Diels-Alder]+: calc 265.1096, obsd
(1α, 4α, 5β, 6α, 7α, 8β)-9-[(4-Fluorophenyl)methylene]-1,2,3,4,5,6,7,8-octahydro-6,7-bis(phenylsulfonyl)-1,4,5,8-dimethanonaphthalene (91-F).

51% yield as fine, white needles, mp 157.5-158 °C dec (from ethyl acetate); IR (CHCl₃, cm⁻¹) 3060, 3020, 2980, 2940, 2910, 2860, 1725, 1600, 1505, 1445, 1335, 1310, 1215, 1155, 1090, 870, 840, 690, 635, 610; ¹H NMR (300 MHz, CDCl₃) δ 8.07-8.03 (m, 4 H), 7.70-7.54 (m, 6 H), 6.93-6.83 (m, 4 H), 5.31 (s, 1 H), 4.26 (dd, J = 3, 9 Hz, 1 H), 4.20 (dd, J = 3, 9 Hz, 1 H), 4.03 (d, J = 3 Hz, 1 H), 3.39 (d, J = 3 Hz, 1 H), 3.28 (s, 1 H), 3.26 (s, 1 H), 2.24 (d, J = 8 Hz, 1 H), 1.80 (d, J = 8 Hz, 2 H), 1.43 (d, J = 8 Hz, 1 H), 1.05 (d, J = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 161.51 (d, ¹JC₉ = 245 Hz), 151.09, 150.91, 149.96, 141.21, 133.58, 133.53, 131.51 (d, ¹JC₉ = 3 Hz), 129.28 (d, ³JC₉ = 8 Hz), 129.04, 128.85 (3 C), 128.75, 115.42 (d, ²JC₉ = 22 Hz), 105.19, 70.85, 70.33, 51.32, 50.27, 46.14, 43.63, 43.39, 26.77, 26.03; MS, m/z [retro Diels-Alder]⁺ calcd 238.1158, obsd 238.1156.
(1α, 4α, 5β, 6α, 7α, 8β)-1,2,3,4,5,6,7,8-Octahydro-6,7-bis(phenyl-sulfonyl)-9-[[4-(trifluoromethyl)phenyl]methylene]-1,4:5,8-dimethanono-naphthalene (91-CF3).

43% yield as a white powder, mp 177-178
°C dec (from dichloromethane-ethanol); IR
(CHCl3, cm⁻¹) 3060, 3020, 2980, 2940,
2910, 2860, 1670, 1610, 1440, 1410, 1320,
1250, 1190, 1165, 1150, 1130, 1085, 1065,
1015, 870, 685, 635, 605; ¹H NMR (300 MHz,
CDCl3) 8.07-8.03 (m, 4 H), 7.71-7.54 (m, 6 H), 7.45 (d, J = 8 Hz, 2 H),
6.99 (d, J = 8 Hz, 2 H), 5.38 (s, 1 H), 4.26 (dd, J = 3, 9 Hz, 1 H),
4.21 (dd, J = 3, 9 Hz, 1 H), 4.06 (d, J = 3 Hz, 1 H), 3.42 (d, J = 3 Hz,
1 H), 3.30 (s, 1 H), 3.28 (s, 1 H), 2.25 (d, J = 8 Hz, 1 H), 1.81 (d, J =
7 Hz, 2 H), 1.44 (d, J = 8 Hz, 1 H), 1.05 (d, J = 10 Hz, 2 H); ¹³C NMR
(75 MHz, CDCl3) ppm 152.82, 150.80, 149.91, 141.22, 139.20, 133.62,
129.07, 128.89, 128.78, 127.95, 127.58 (q, JCF = 271 Hz), 125.39,
104.98, 70.76, 70.19, 51.46, 50.18, 46.30, 43.70, 43.45, 26.76, 26.01;
MS, m/z [retro Diels-Alder]+ calcd 288.1126, obsd 288.1149.

Anal. Calcd for C₃₂H₂₇F₃O₄S₂: C, 64.41; H, 4.56.

Found: C, 64.04; H, 4.72.
(1α, 4α, 5β, 6α, 7α, 8β)-4-[[1,2,3,4,5,6,7,8-Octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalen-9-ylidene)methyl]benzonitrile (91-CN).

21% yield as a white solid, mp 180-181 °C dec (from ethyl acetate); IR (CHCl₃, cm⁻¹) 3020, 3000, 2960, 2910, 2880, 2860, 2220, 1600, 1445, 1330, 1310, 1290, 1250, 1200, 1150, 1120, 1080, 890, 875, 780, 720, 690, 665, 640, 605; ¹H NMR (300 MHz, CDCl₃) δ 8.06-8.02 (m, 4 H), 7.71-7.55 (m 6 H), 7.49 (d, J = 8 Hz, 2 H), 6.98 (d, J = 8 Hz, 2 H), 5.36 (s, 1 H), 4.25 (dd, J = 3, 9 Hz, 1 H), 4.20 (dd, J = 3, 9 Hz, 1 H), 4.05 (d, J = 3 Hz, 1 H), 3.44 (d, J = 3 Hz, 1 H), 3.31 (s, 1 H), 3.28 (s, 1 H), 2.25 (d, J = 8 Hz, 1 H), 1.82 (d, J = 8 Hz, 2 H), 1.45 (d, J = 8 Hz, 1 H), 1.04 (m, 2 H); MS, m/z [retro Diels-Alder]+ calcd 245.1204, obsd 245.1253.

(1α, 4α, 5α, 6α, 7α, 8α)-1,2,3,4,5,6,7,8-Octahydro-9-(phenylmethylene)-6,7-bis(phenylsulfonil)-1,4:5,8-dimethanonaphthalene (92-H).

12% yield as white needles, mp 174.5-175.5 °C dec (from ethyl acetate); IR (CHCl₃, cm⁻¹) 3060, 3020, 2960, 2880, 1445, 1345, 1335, 1310, 1290, 1150, 1085, 910, 690, 665; ¹H NMR (300 MHz, CDCl₃) δ 8.13-7.15 (series of m, 15 H), 5.90 (s, 1 H), 3.92 (s, 1 H), 3.88 (s, 1 H), 3.40 (d, J = 9 Hz, 1 H), 3.26 (d, J = 9 Hz, 1 H), 3.04 (s, 1 H), 2.97 (s, 1 H), 1.68 (d, J = 8 Hz, 2 H), 1.36 (d, J = 8 Hz, 1 H), 1.07 (d, J = 8 Hz, 1 H), 0.74 (d, J = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) ppm 153.77, 152.52, 148.87, 147.89, 140.58,
(1α, 4α, 5α, 6α, 7α, 8α)-1,2,3,4,5,6,7,8-Octahydro-9-[(4-methylphenyl)methylene]-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (92-Me).

11% yield as a white solid, mp 173.5-174°C dec (from chloroform); IR (CHCl₃, cm⁻¹) 3060, 3020, 2980, 2960, 2920, 2880, 1510, 1445, 1340, 1335, 1310, 1290, 1150, 1085, 1000, 910, 865, 845, 710, 680; ¹H NMR (300 MHz, CDCl₃) δ 8.11 (d, J = 7 Hz, 2 H), 7.71-7.34 (series of m, 8 H), 7.16 (d, J = 8 Hz, 2 H), 7.10 (d, J = 8 Hz, 2 H), 5.83 (s, 1 H), 3.96 (s, 1 H), 3.85 (s, 1 H), 3.38 (d, J = 9 Hz, 1 H), 3.27 (d, J = 9 Hz, 1 H), 3.03 (s, 1 H), 2.97 (s, 1 H), 2.40 (s, 3 H), 1.68 (d, J = 8 Hz, 2 H), 1.35 (d, J = 8 Hz, 1 H), 1.07 (d, J = 8 Hz, 1 H), 0.74 (d, J = 8 Hz, 2 H); MS, (FAB) m/z (M⁺) calcd 542.2, obsd 542.1.
(1α, 4α, 5α, 6α, 7α, 8α)-1,2,3,4,5,6,7,8-Octahydro-9-[(4-methoxyphenyl)-methylene]-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (92-OMe).

23% yield as a white solid, mp 169.5-170.5 °C dec (from chloroform); IR (CHCl₃, cm⁻¹) 3020, 2980, 2960, 2880, 1730, 1605, 1510, 1445, 1375, 1340, 1310, 1295, 1250, 1180, 1150, 1085, 1040, 865, 845, 690; ¹H NMR (300 MHz, CDCl₃) δ 8.12-8.09 (m, 2 H), 7.71-7.37 (series of m, 8 H), 7.15 (d, J = 9 Hz, 2 H), 6.89 (d, J = 9 Hz, 2 H), 5.82 (s, 1 H), 3.98 (s, 1 H), 3.85 (s, 3 H), 3.84 (s, 1 H), 3.37 (d, J = 9 Hz, 1 H), 3.28 (d, J = 9 Hz, 1 H), 3.02 (s, 1 H), 2.97 (s, 1 H), 1.67 (d, J = 8 Hz, 2 H), 1.35 (d, J = 8 Hz, 1 H), 1.06 (d, J = 8 Hz, 1 H), 0.73 (dd, J = 2, 8 Hz, 2 H); MS, (FAB) m/z (M⁺) calcd 558.2, obsd 558.2.

(1α, 4α, 5α, 6α, 7α, 8α)-N,N-Dimethyl-4-[[1,2,3,4,5,6,7,8-octahydro-9-(phenylmethylene)-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene-9-ylidene)methyl]benzenamine (92-NMe₂).

31% yield as a pale yellow solid, mp 165-166 °C dec (from dichloromethane-hexane); IR (CHCl₃, cm⁻¹) 3060, 3020, 3000, 2960, 2920, 2880, 2800, 1610, 1515, 1445, 1345, 1335, 1310, 1295, 1205, 1150, 1085, 910, 725, 690, 665; ¹H NMR (300 MHz, CDCl₃) δ 8.11 (d, J = 7 Hz, 2 H), 7.70-7.35 (series of m, 8 H), 7.10 (d, J = 9 Hz, 2 H), 6.72 (d, J = 8 Hz, 2 H), 5.72 (s, 1 H), 4.07 (s, 1 H), 3.79 (s, 1 H), 3.37 (d, J = 9 Hz, 1 H), 3.30 (d, J = 9 Hz, 1 H), 3.00 (br s,
8 H), 1.67 (d, J = 8 Hz, 2 H), 1.34 (d, J = 8 Hz, 1 H), 1.05 (d, J = 8 Hz, 2 H), 0.74 (d, J = 8 Hz, 2 H); MS, (FAB) m/z (M⁺) calcd 571.19, obsd 571.07.

(lα, 4α, 5α, 6α, 7α, 8α)-9-[(4-Chlorophenyl)methylene]-1,2,3,4,5,6,7,8-octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (92-Cl).

6% yield as a white solid, mp 170.5-171°C dec (from chloroform); IR (CHCl₃, cm⁻¹) 3060, 3020, 2960, 2920, 2850, 1490, 1445, 1395, 1385, 1360, 1345, 1150, 1090, 1020, 910, 870, 845, 710, 690, 670, 650;

₁H NMR (300 MHz, CDCl₃) δ 8.09 (d, J = 7 Hz, 2 H), 7.71-7.39 (series of m, 8 H), 7.33 (d, J = 8 Hz, 2 H), 7.17 (d, J = 8 Hz, 2 H), 5.90 (s, 1 H), 3.88 (s, 2 H), 3.37 (d, J = 9 Hz, 1 H), 3.26 (d, J = 9 Hz, 1 H), 3.03 (s, 1 H), 2.97 (s, 1 H), 1.69 (d, J = 8 Hz, 2 H), 1.36 (d, J = 9 Hz, 1 H), 1.07 (d, J = 8 Hz, 1 H), 0.73 (d, J = 8 Hz, 2 H); MS, m/z [retro Diels-Alder]⁺ calcd 254.0862, obsd 254.0929.

(lα, 4α, 5α, 6α, 7α, 8α)-9-[(4-nitrophenyl)methylene]-1,2,3,4,5,6,7,8-Octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (92-NO₂).

9% yield as pale yellow needles, mp 171.5-172°C dec (from chloroform); IR (CHCl₃, cm⁻¹) 3060, 3020, 2960, 2870, 1595, 1515, 1445, 1345, 1310, 1155, 1085, 865, 690, 670; ₁H NMR (300 MHz, CDCl₃) δ 8.23 (d, J = 9 Hz, 2 H), 8.07 (d, J = 9
7.70-7.59 (m, 6 H), 7.47-7.43 (m, 4 H), 6.08 (s, 1 H), 4.05 (s, 1 H), 3.92 (s, 1 H), 3.37 (d, J = 9 Hz, 1 H), 3.30 (d, J = 9 Hz, 1 H), 3.04 (s, 1 H), 3.01 (s, 1 H), 1.71 (d, J = 9 Hz, 2 H), 1.37 (d, J = 8 Hz, 1 H), 1.09 (d, J = 9 Hz, 1 H), 0.73 (d, J = 8 Hz, 2 H); 13C NMR (75 MHz, CDCl3) ppm 153.52, 152.17, 151.20, 146.58, 143.49, 140.58, 140.40, 133.81, 133.72, 129.26, 129.18, 129.04, 128.98, 128.20, 123.57, 113.55, 67.35, 66.79, 52.05, 49.92, 47.00, 43.09, 25.92, 25.75; MS, (FAB) m/z (M+) calcd 573.1, obsd 573.1.

(1α, 4α, 5α, 6α, 7α, 8α)-9-[(4-Fluorophenyl)methylene]-1,2,3,4,5,6,7,8-octahydro-6,7-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (92-F).

7% yield as fine, white needles, mp 173-174 °C (from ethyl acetate); IR (CHCl3, cm⁻¹) 3060, 3020, 2960, 2920, 2880, 1600, 1505, 1445, 1340, 1335, 1310, 1225, 1205, 1155, 1090, 845, 690, 665; 1H NMR (300 MHz, CDCl3) δ 8.10 (d, J = 9 Hz, 2 H), 7.71-7.39 (series of m, 8 H), 7.22-7.17 (m, 2 H), 7.08-7.02 (m, 2 H), 5.90 (s, 1 H), 3.91 (s, 1 H), 3.87 (s, 1 H), 3.37 (d, J = 9 Hz, 1 H), 3.27 (d, J = 9 Hz, 1 H), 3.03 (s, 1 H), 2.97 (s, 1 H), 1.69 (d, J = 8 Hz, 2 H), 1.35 (d, J = 9 Hz, 1 H), 1.07 (d, J = 9 Hz, 1 H), 0.73 (d, J = 8 Hz, 2 H); 13C NMR (75 MHz, CDCl3) ppm 161.88 (d, 1 JCF = 245 Hz), 153.80, 152.42, 147.87, 140.60, 140.36, 133.69, 133.49, 132.75 (d, 4 JCF = 3 Hz), 130.14 (d, 3 JCF = 8 Hz), 129.52, 128.91, 128.86, 128.40, 115.07 (d, 2 JCF = 21 Hz), 114.05, 67.70, 67.28, 51.79, 49.90, 47.06, 43.04, 25.86, 25.69; MS, m/z [retro Diels-Alder]+ calcd 238.1158, obsd 238.1180.
Anal. Calcd for $C_{31}H_{27}F_{4}S_{2}$: C, 68.11; H, 4.98.

Found: C, 67.73; H, 5.06.

(1α, 4α, 5α, 6α, 7α, 8α)-1,2,3,4,5,6,7,8-Octahydro-6,7-bis(phenyl-sulfonyl)-9-[[4-(trifluoromethyl)phenyl]methylene]-1,4:5,8-dimethanonaphthalene (92-CF$_3$).

9% yield as a white powder, mp 185 °C dec (from dichloromethane-methanol); IR (CHCl$_3$, cm$^{-1}$) 3060, 3020, 2960, 2920, 2870, 1610, 1445, 1325, 1290, 1250, 1190, 1165, 1150, 1130, 1085, 1065, 1020, 910, 865, 690, 665; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.11-8.08 (m, 2 H), 7.72-7.30 (series of m, 8 H), 6.01 (s, 1 H), 3.93 (s, 1 H), 3.85 (s, 1 H), 3.38 (d, $J$ = 9 Hz, 1 H), 3.26 (d, $J$ = 9 Hz, 1 H), 3.05 (s, 1 H), 2.98 (s, 1 H), 1.69 (d, $J$ = 9 Hz, 2 H), 1.37 (d, $J$ = 9 Hz, 1 H), 1.08 (d, $J$ = 9 Hz, 1 H), 0.73 (d, $J$ = 9 Hz, 2 H); MS, m/z [retro Diels-Alder]$^+$ calcd 288.1126, obsd 288.1153.

(1α, 4α, 5α, 6α, 7α, 8α)-4-[[1,2,3,4,5,6,7,8-Octahydro-6,7-bis(phenyl-sulfonyl)-1,4:5,8-dimethanonaphthalen-9-yldene]methyl]benzonitrile (92-CN).

12% yield as a white solid, mp 170 °C dec (from dichloromethane-ethanol); IR (CHCl$_3$, cm$^{-1}$) 3060, 3020, 2960, 2860, 2220, 1600, 1445, 1340, 1335, 1310, 1190, 1150, 1080, 690, 670; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08-8.02 (m, 4 H), 7.71-7.49 (m, 6 H), 7.47-7.37 (m, 4 H), 6.02 (s, 1 H), 3.99 (s, 1 H), 3.90 (s, 1 H),
3.35 (d, J = 8.9 Hz, 1 H), 3.28 (d, J = 8.9 Hz, 1 H), 3.03 (s, 1 H), 2.99 (s, 1 H), 1.69 (d, J = 8.6 Hz, 2 H), 1.36 (d, J = 8.5 Hz, 1 H), 1.08 (d, J = 8.5 Hz, 1 H), 0.72 (d, J = 8.2 Hz, 2H); MS, m/z [retro Diels-Alder]+ calcd 245.1204, obsd 245.1250.


To a stirred suspension of sodium methoxide (0.53 g, 9.8 mmol) in dry benzene (15 mL) were simultaneously added solutions of isodicyclopentadiene (0.53 g, 4.0 mmol) in benzene (10 mL) and 95a (1.03 g, 3.2 mmol) in benzene (10 mL) dropwise via a pair of addition funnels. The reaction mixture was heated to reflux under nitrogen. After 2 h, 4 Å molecular sieves were added and the heating was continued overnight. The solvent was removed from the cooled mixture and the residue taken up in dichloromethane. Passage through a small pad of silica gel removed the excess sodium methoxide. Evaporation of the solvent from the filtrate afforded an orange oil which was purified by chromatography on silica gel (elution with 50% ethyl acetate in petroleum ether followed by 80% ethyl acetate in petroleum ether). The desired fulvene was obtained as a thick orange oil (0.23 g, 17%) which solidified upon standing, mp 81-82 °C (from methanol); IR (CHCl₃, cm⁻¹) 3040, 2980, 2940, 2900, 2860, 2680, 2300, 1595, 1555, 1540, 1510, 1440, 1420, 1385, 1350, 1315, 1255, 1185, 1120, 1100, 980, 945, 910, 895, 815, 690, 665; ¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, J = 9 Hz, 2 H), 6.84 (s, 1 H), 6.64 (d, J = 9 Hz, 2 H), 6.19 (s, 1
H), 5.68 (s, 1 H), 3.68-3.60 (m, 20 H), 3.11 (br s, 2 H), 1.88 (d, J = 8 Hz, 2 H), 1.78 (d, J = 9 Hz, 1 H), 1.72 (d, J = 9 Hz, 1 H), 1.45 (dd, J = 2, 7 Hz, 2 H); 13C NMR (75 MHz, CDCl3) ppm 159.38, 153.43, 147.62, 146.53, 134.14, 131.74, 125.39, 111.35 (2C), 104.39, 71.27, 70.19, 70.09, 68.49, 52.52, 45.33, 39.06, 38.57, 29.01, 28.93; MS, m/z (M+) calcd 437.2566, obsd 437.2553.

Anal. Calcd for C27H35NO4: C, 74.11; H, 8.06. Found: C, 73.68; H, 8.14.

Aza-18-crown-6-fulvene (93b).

To a stirred suspension of sodium methoxide (2.05 g, 37.9 mmol) in anhydrous benzene (30 mL) was added isodicyclopentadiene (2.00 g, 15.1 mmol) in benzene (20 mL) via cannula. After a few minutes, aldehyde 95b (4.63 g, 12.6 mmol) was added and the mixture was refluxed under nitrogen for 24 h. The cooled reaction mixture was filtered through Celite and the Celite pad was washed with dichloromethane until the washings were colorless. Removal of the solvent gave an orange oil which was purified by chromatography on silica gel (elution with ethyl acetate) to give 93b as a viscous orange oil (2.42 g, 40%); IR (CHCl3, cm⁻¹) 2995, 2960, 2910, 2860, 1590, 1555, 1540, 1510, 1460, 1445, 1425, 1390, 1350, 1320, 1295, 1185, 1160, 1150, 945, 910, 890, 810; 1H NMR (300 MHz, CDCl3) δ 7.43 (d, J = 9 Hz, 2 H), 6.83 (s, 1 H), 6.66 (d, J = 9 Hz, 2 H), 6.19 (s, 1 H), 5.67 (s, 1 H), 3.71-3.65 (m, 24 H), 3.10 (br s, 2 H), 1.87 (d, J = 8 Hz,
Fulvene 93a was dissolved in methanol and a 1:1 stoichiometric amount of sodium perchlorate was added. The mixture was gently heated until all the salt had gone into solution. The solvent was removed and the dark orange residue was taken up in ethyl acetate. Pentane was added until the solution was cloudy. The complex precipitated as a yellow-orange hygroscopic solid, mp 110 °C dec; IR (CHCl\textsubscript{3}, cm\textsuperscript{-1}) 2940, 2910, 2865, 1595, 1555, 1510, 1465, 1445, 1385, 1350, 1320, 1290, 1270, 1185, 1170, 1145, 945, 910; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 7.47 (d, J = 9 Hz, 2 H), 6.86 (s, 1 H), 6.76 (d, J = 8 Hz, 2 H), 6.18 (s, 1 H), 5.69 (s, 1 H), 3.80-3.50 (m, 20 H), 3.12 (br s, 2 H), 1.89 (d, J = 8 Hz, 2 H), 1.79 (d, J = 9 Hz, 1 H), 1.73 (d, J = 9 Hz, 1 H), 1.47 (dd, J = 2, 7 Hz, 2 H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) ppm 159.77, 153.93, 147.65, 147.55, 133.57, 131.63, 127.75, 114.64, 111.28, 104.41, 70.64, 69.92, 69.77, 68.25, 53.37, 45.17, 39.02, 38.55, 28.96, 28.89; MS, (FAB) m/z (M\textsuperscript{+}) calcd 460.36, obsd 460.36.

Anal. Calcd for C\textsubscript{27}H\textsubscript{35}ClNNaO\textsubscript{8}: C, 53.60; H, 6.66.

Found: C, 53.77; H, 6.45.
Potassium Thiocyanate Complex 97.

Fulvene 93b was dissolved in methanol and a 1:2 stoichiometric amount of potassium thiocyanate was added. The mixture was heated until the salt had gone into solution. The solvent was removed and the residue taken up in ethyl acetate. Pentane was added until the solution became cloudy. The complex precipitated as a bright yellow hygroscopic solid, mp 114 °C dec; IR 2960, 2940, 2910, 2890, 2860, 2050, 1595, 1510, 1500, 1470, 1450, 1350, 1315, 1270, 1185, 1105, 950, 910, 885, 830, 815; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $\delta = 9$ Hz, 2 H), 7.02 (d, $\delta = 9$ Hz, 2 H), 6.88 (s, 1 H), 6.13 (s, 1 H), 5.68 (s, 1 H), 3.68 (br s, 12 H), 3.59-3.56 (m, 4 H), 3.49 (t, $\delta = 5$ Hz, 4 H), 3.34 (t, $\delta = 5$ Hz, 4 H), 3.12 (br s, 2 H), 1.89 (d, $\delta = 8$ Hz, 2 H), 1.78 (d, $\delta = 9$ Hz, 1 H), 1.74 (d, $\delta = 9$ Hz, 1 H), 1.46 (d, $\delta = 7$ Hz, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 160.38, 154.74, 149.22, 148.19, 132.66, 131.65, 131.33, 120.25, 111.15, 104.42, 70.19, 70.13, 70.03, 68.34, 54.75, 44.91, 38.96, 38.50, 28.88, 28.82; MS, (FAB) m/z (M$^+$) calcd 520.25, obsd 520.22.

Anal. Calcd for C$_{30}$H$_{39}$KN$_2$O$_5$S.1/3 H$_2$O: C, 61.61; H, 6.84.

Found: C, 61.73; H, 6.83.
CYCLOADDITIONS OF 93,96 AND 97 WITH (Z)-1,2-BIS(PHENYLSULFONYL)ETHYLENE

A solution of the fulvene (50-100 mg) and three equivalents of the dienophile in anhydrous dichloromethane (2 mL) was pressurized to 100,000 psi for 4-6 days. The solvent was evaporated and the crude reaction mixtures were directly analyzed by $^1$H NMR spectroscopy to obtain product ratios of the isomeric cycloadducts. In the case of the metal complexes, decomplexation was effected before purification by stirring in a 1:1 mixture of dichloromethane and water overnight. The layers were separated and the organic layer was washed with water, dried, filtered, and concentrated. Purification of the residue by column chromatography on silica gel (elution with ethyl acetate followed by 5-10% methanol in ethyl acetate) provided a mixture of cycloadducts. The isomers were separated by preparative TLC on silica gel (multiple elution with 5% acetone in dichloromethane). Yields ranged from 31-53%. Additional purification was achieved by recrystallization.

98a: mp 140-142 °C dec (from methanol-ether); IR (CHCl$_3$, cm$^{-1}$) 3020, 2980, 2940, 2900, 1620, 1525, 1455, 1395, 1355, 1345, 1320, 1305, 1200, 1155, 1100, 1000, 950, 850; $^1$H NMR (300 MHz, CDCl$_3$) δ8.11 (d, $\ J = 7.2$ Hz, 2 H), 7.70-7.55 (m, 6 H), 7.39 (m, 2 H), 7.06 (d, $\ J = 8.4$ Hz, 2 H), 6.64 (d, $\ J = 7.9$ Hz, 2 H), 5.70 (s, 1 H), 4.04 (s, 1 H), 3.81 (s, 1 H), 3.79 (m, 6 H), 3.70-3.65 (m, 14 H), 3.36 (d, $\ J = 8.9$ Hz, 1 H), 3.29 (d, $\ J = 8.7$ Hz, 1 H), 3.00 (s, 1 H), 2.97 (s, 1 H), 1.66 (d, $\ J = 7.9$ Hz, 2 H), 1.33 (d, $\ J = 8.0$ Hz,
1H), 1.05 (d, J = 8.4 Hz, 1 H), 0.74 (d, J = 6.1 Hz, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 153.87, 152.81, 146.52, 144.85, 140.48, 140.32, 133.59, 133.34, 129.67, 129.62, 128.79, 128.72, 124.25, 114.93, 111.15, 71.35, 70.22, 70.15, 68.65, 68.34, 67.66, 52.57, 51.99, 49.87, 47.29, 43.03, 25.82, 25.64; MS, (FAB) m/z (M$^+$) calcd 745.27, obsd 745.23.

99a: mp 126-128 °C dec (from methanol-ether); IR (CHCl$_3$, cm$^{-1}$) 2995, 2970, 2920, 2865, 2800, 1600, 1510, 1440, 1380, 1350, 1290, 1145, 1110, 1070, 980; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08-8.02 (m, 4 H), 7.66-7.54 (m, 6 H), 6.79 (d, J = 8.6 Hz, 2 H), 6.50 (d, J = 8.6 Hz, 2 H), 5.22 (s, 1 H), 4.28 (dd, J = 3.1, 9.2 Hz, 1 H), 4.18 (dd, J = 3.1, 9.2 Hz, 1 H), 4.15 (d, J = 2.9 Hz, 1 H), 3.79-3.53 (m, 20 H), 3.30 (d, J = 2.6 Hz, 1 H), 3.26 (s, 1 H), 3.23 (s, 1 H), 2.22 (d, J = 7.7 Hz, 1 H), 1.77 (d, J = 5.9 Hz, 2 H), 1.41 (d, J = 8.0 Hz, 1 H), 1.05 (d, J = 6.8 Hz, 2 H); MS, (FAB) m/z (M$^+$) calcd 745.27, obsd 745.49.

98b: mp 136-138 °C dec (from methanol-dichloromethane); IR (CHCl$_3$, cm$^{-1}$) 3060, 3020, 3000, 2950, 2920, 2870, 1605, 1510, 1470, 1440, 1385, 1370, 1345, 1310, 1290, 1270, 1210, 1140, 1115, 1085, 1045, 995, 945, 930, 865, 845; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.09 (d, J = 7.2 Hz, 2 H), 7.67-7.54 (m, 6 H), 7.39 (t, J = 7.8 Hz, 2 H), 7.07 (d, J = 8.7 Hz, 2 H), 6.66 (d, J = 8.7 Hz, 2 H), 5.69 (s, 1 H), 4.08 (s, 1 H), 3.77 (s, 1 H), 3.73-3.67 (m, 24 H), 3.35 (d, J =
8.9 Hz, 1 H), 3.29 (d, J = 8.8 Hz, 1 H), 2.99 (s, 1 H), 2.97 (s, 1 H), 0.74 (d, J = 7.7 Hz, 2 H); MS, (FAB) m/z (M+) calcd 789.30, obsd 789.35.

99b: mp 120-122 °C dec (from methanol-dichloromethane); IR (CHCl₃, cm⁻¹) 3000, 2950, 2915, 2860, 1605, 1515, 1445, 1350, 1330, 1150, 1120, 1085; ¹H NMR (300 MHz, CDCl₃) 8 8.04 (m, 4 H), 7.69-7.54 (m, 6 H), 6.79 (d, J = 8.6 Hz, 2 H), 6.52 (d, J = 8.6 Hz, 2 H), 5.21 (s, 1 H), 4.28 (dd, J = 2.9, 9.2 Hz, 1 H), 4.17 (dd, J = 3.0, 9.2 Hz, 1 H), 4.15 (br s, 1 H), 3.66-3.58 (m, 24 H), 3.30 (d, J = 2.6 Hz, 1 H), 3.26 (s, 1 H), 3.23 (s, 1 H), 2.22 (d, J = 7.6 Hz, 1 H), 1.77 (d, J = 5.9 Hz, 2 H), 1.41 (d, J = 8.0 Hz, 1 H), 1.05 (d, J = 6.3 Hz, 2 H); MS, (FAB) m/z (M⁺) calcd 789.30, obsd 789.17.

Methiodide Salt (84-⁺NMe₃).

To a suspension of the dimethylamino-fulvene 84-NMe₂ (89 mg, 0.34 mmol) in acetonitrile (2 mL) was added excess methyl iodide (2 mL, 2.28 mmol). A clear solution formed. The reaction mixture was stirred at room temperature for 5 days after which time the volatiles were removed in vacuo. A bright yellow solid remained that was pure methiodide (137 mg, 100%). The methiodide was recrystallized from 95% ethanol to obtain an analytically pure sample, mp 159.5-160 °C; IR (CHCl₃, cm⁻¹) 3000, 2940, 2860, 1505, 1495, 1480, 1460, 1440, 1410, 1310, 1215, 1110, 1095, 1010, 945, 930,
905, 880, 855; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.96 (d, $J = 9.1$ Hz, 2 H), 7.69 (d, $J = 8.9$ Hz, 2 H), 6.84 (s, 1 H), 5.95 (s, 1 H), 5.66 (s, 1 H), 4.05 (s, 9 H), 3.11 (s, 2 H), 1.90 (d, $J = 7.9$ Hz, 2 H), 1.76 (s, 2 H), 1.47 (d, $J = 7.7$ Hz, 2 H); MS, (FAB) m/z (M$^+$) calcd 278.19, obsd 278.24.

Anal. Calcd for C$_{20}$H$_{24}$NI: C, 59.27; H, 5.97.

(-)-5,5-Dimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (107).

A solution of lithium diisopropylamide was prepared by adding n-butyllithium (3.8 mL, 5.9 mmol) to a stirred, cooled (0 °C) solution of diisopropylamine (0.9 mL, 6.4 mmol) in dry tetrahydrofuran (100 mL). The reaction mixture was stirred 1 h at 0 °C then cooled to -78 °C. β-Fenchocamphorone (0.607 g, 4.4 mmol) in tetrahydrofuran (20 mL) was added via cannula. After 1 h, at -78 °C, N-phenyltriflimide in tetrahydrofuran (20 mL) was added dropwise. The reaction mixture was slowly warmed to room temperature with stirring for 18 h. The solvent was evaporated under reduced pressure and the orange residue purified by chromatography on silica gel (elution with petroleum ether) to give 0.753 g (63%) of enol triflate 107 as a colorless oil:

IR (neat, cm⁻¹) 2960, 2870, 1620, 1470, 1420, 1370, 1325, 1250, 1210, 1160, 1140, 1110, 1030, 940, 885, 840, 785, 765, 725; ¹H NMR (300 MHz, CDCl₃) δ 5.79 (d, J = 3.4 Hz, 1 H), 2.85 (br s, 1 H), 2.42 (dd, J = 1.7, 3.6 Hz, 1 H), 1.71 (d, J = 1.7 Hz, 1 H), 1.62 (dd, J = 3.6, 11.8 Hz, 1 H), 1.31 (dd, J = 0.8, 11.8 Hz, 1 H), 1.22 (s, 3 H), 0.95 (s, 3 H), 0.87 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 155.45, 120.29, 118.63 (q, JCF = 318.8 Hz), 52.39, 47.45, 45.49, 40.34, 39.43, 30.35, 27.72; MS, m/z (M⁺) calcd 270.0537, obsd 270.0524; [α]D²⁰ -17.6° (c 3.7, CHCl₃).
(-)-5,5-Dimethyl-2-ethenylbicyclo[2.2.1]hept-3-ene (108).

A nitrogen-blanketed mixture of lithium chloride (0.40 g, 9.0 mmol), Pd(PPh₃)₄ (0.03 g, 1.4 mol%), triflate 107 (0.48 g, 1.8 mmol) and vinyltrimethylstannane (0.386 g, 2.0 mmol) in anhydrous tetrahydrofuran (30 mL) was heated to reflux for 20 h, cooled to room temperature and diluted with pentane (250 mL) and water (200 mL). The aqueous phase was extracted with pentane (2 x 200 mL). The combined organic extracts were washed with saturated sodium bicarbonate solution (2 x 200 mL) then brine (2 x 200 mL) and dried. The solution was filtered through a small plug of silica gel and concentrated by distillation at atmospheric pressure to give a yellow oil. Chromatographic purification on neutral alumina (elution with petroleum ether) afforded 0.256 g (96%) of diene 108 as a colorless oil: IR (neat, cm⁻¹) 3080, 3040, 2950, 2860, 1620, 1560, 1465, 1445, 1380, 1360, 1290, 1275, 1260, 1190, 1130, 1080, 1025, 1000, 985, 895, 845, 820, 790, 765; ¹H NMR (300 MHz, CDCl₃) δ 6.38 (dd, J = 10.5, 17.4 Hz, 1 H), 6.00 (d, J = 2.9 Hz, 1 H), 5.15 (d, J = 17.2 Hz, 1 H), 4.99 (d, J = 10.4 Hz, 1 H), 3.00 (br s, 1 H), 2.32 (dd, J = 1.5, 3.1 Hz, 1 H), 1.69 (d, J = 8.2 Hz, 1 H), 1.51 (dd, J = 3.8, 11.3 Hz, 1 H), 1.18 (s, 3 H), 0.84 (s, 3 H), 0.91-0.82 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) ppm 148.03, 134.50, 132.04, 112.23, 53.97, 47.01, 42.76, 41.13, 40.83, 30.76, 28.26; MS, m/z (M⁺) calcd 148.1252, obsd 148.1223.
Methyl 6,6-Dimethyl-3-oxobicyclo[2.2.1]heptane-2-acetate (110).

To a stirred, cold (-78 °C) solution of lithium diisopropylamide (4.1 mmol) in tetrahydrofuran was added (-)-β-fenchocamphorone (0.495 g, 3.6 mmol) in tetrahydrofuran via cannula. The mixture was stirred 1 h at -78 °C then hexamethylphosphoramide (1.5 mL, 8.6 mmol) was added via syringe and the reaction mixture stirred for an additional 30 min. Methyl bromoacetate (0.5 mL, 5.3 mmol) in tetrahydrofuran (90 mL) was added dropwise. The mixture was allowed to warm to room temperature with stirring for 13 h. Evaporation of the solvent provided a dark yellow oil. The residue was taken up in pentane (1 L) and washed with water (3 x 500 mL) and brine (250 mL). The combined aqueous layers were back-extracted once with pentane (200 mL). The combined organics were dried, filtered and concentrated to give a yellow oil. Purification by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) provided 0.565 g (75%) of ketoester 110 as a colorless oil: IR (neat, cm⁻¹) 2950, 2860, 1735, 1470, 1435, 1415, 1390, 1365, 1320, 1245, 1220, 1170, 1125, 1100, 1040, 1010, 990, 970, 940, 920, 860, 820, 735, 695, 650; ¹H NMR (300 MHz, CDCl₃) δ 3.67 (s, 3 H), 2.72 (dt, J = 4.0, 10.9 Hz, 1 H), 2.58 (dd, J = 4.3, 16.2 Hz, 1 H), 2.48 (d, J = 5.1 Hz, 1 H), 2.22 (dd, J = 10.8, 16.2 Hz, 1 H), 2.10-1.94 (m, 2 H), 1.71 (d, J = 11.2 Hz, 1 H), 1.65 (dd, J = 5.0, 13.1 Hz, 1 H), 1.31 (dd, J = 2.1, 13.0 Hz, 1 H), 1.13 (s, 3 H), 1.10 (s, 3 H); MS, m/z (M⁺) calcd 210.1256, obsd 210.1220.
Methyl 6,6-Dimethyl-3-oxobicyclo[2.2.1]heptane-2-acetate ethylene ketal (112).

A solution of ketoester 110 (0.26 g, 1.2 mmol), ethylene glycol (0.3 mL, 5.4 mmol) and pyridinium tosylate (73.7 mg, 0.3 mmol) in benzene (20 mL) was refluxed with water separation under a Dean-Stark trap until the ketone was completely consumed (9 h). The solvent was evaporated under reduced pressure, the residue taken up in dichloromethane (500 mL) and washed with saturated sodium bicarbonate solution (2 x 500 mL) and brine (2 x 500 mL). The organic layer was dried, filtered and concentrated to give the ketal as a yellow oil. MPLC purification on silica gel (elution with 10% ethyl acetate in petroleum ether) afforded 0.243 g (79%) of ketal 111: IR (neat, cm$^{-1}$) 2950, 2865, 1730, 1470, 1430, 1360, 1315, 1270, 1260, 1185, 1095, 1035, 1010, 980, 970, 950, 920, 885, 735, 650; $^1$H NMR (300 MHz, CDCl$_3$) 8.91-3.75 (m, 4 H), 3.66 (s, 3 H), 2.62-2.47 (m, 2 H), 2.18 (dd, $J$ = 7.8, 15.7 Hz, 1 H), 1.97 (dd, $J$ = 1.4, 4.5 Hz, 1 H), 1.70-1.46 (m, 4H), 1.21 (dd, $J$ = 4.7, 12.5 Hz, 1 H), 1.12 (s, 3 H), 0.99 (s, 3 H); MS, m/z (M$^+$) calcd 254.1518, obsd 254.1564.
Dimethyl 3-[(Dimethyl-3-oxobicyclo[2.2.1]hept-2-yl ethylene ketal)-2-oxo-propyl]phosphonate (112).

\[\text{OMe} \quad \text{OMe} \]

D-Butyllithium (1.2 mL, 1.37 M in hexane, 1.6 mmol) was slowly added to a solution of dimethyl methylphosphonate (0.18 mL, 1.6 mmol) in anhydrous tetrahydrofuran (100 mL) blanketed in a nitrogen atmosphere. After the solution had stirred for 20 min, ketal ester III (0.20 g, 0.8 mmol) in tetrahydrofuran (45 mL) was added via cannula. The reaction mixture was stirred at 0 °C for 1 h, allowed to warm to room temperature for 1 h, then refluxed for 24 h. After this time, the mixture was poured into water (100 mL) and extracted with chloroform (3 x 100 mL). The organic extracts were washed with brine, dried and concentrated. The resulting oil was purified by chromatography on silica gel (elution with 5% methanol in ethyl acetate) to yield ketophosphonate 112 as a pale yellow oil (95.3 mg, 70% yield based on recovered starting material):

IR (neat, cm\(^{-1}\)) 2960, 2920, 2895, 2860, 1710, 1460, 1400, 1360, 1310, 1250, 1180, 1095, 1030, 980, 950, 870, 840, 820; \(^1\)H NMR (300 MHz, CDCl\(_3\))

\[\begin{align*}
&\delta 4.57-4.01 (m, 1 H), 3.90-3.85 (m, 1 H), 3.78 (d, J_{\text{HP}} = 11.1 \text{ Hz}, 6 H), \\
&3.75-3.70 (m, 2 H), 3.17-3.04 (m, 2 H), 2.81 (dd, J = 8,17 \text{ Hz}, 1 H), \\
&2.71-2.67 (m, 1 H), 2.41 (dd, J = 6,17 \text{ Hz}, 1 H), 1.95 (br s, 1 H), \\
&1.68-1.25 (series of m, 4 H), 1.19 (dd, J = 5,13 \text{ Hz}, 1 Hz), 1.13 (s, 3 H), 0.99 (s, 3 H).\end{align*}\]
Dimethyl 3-[[6,6-Dimethyl-3-oxobicyclo[2.2.1]hept-2-yl]-2-ethoxy-1-propenyl]phosphonate (115).

To a solution of (-)-β-fenchocamphorone (143 mg, 1.0 mmol) in anhydrous tetrahydrofuran (50 mL) under nitrogen and cooled to -78 °C was added potassium hexamethyldisilazide (2.0 mL, 0.5 M in toluene, 1.0 mmol). After stirring 30 min, triethylborane (1.5 mL, 1.0 M in THF, 1.5 mmol) was added and the mixture warmed to room temperature over 35-40 min and Pd(PPh3)4 (116 mg, 0.10 mmol) added. Bromide 114 in tetrahydrofuran (20 mL) was then added and the reaction mixture stirred overnight. Removal of the solvent gave a yellow residue which was taken up in ethyl acetate and passed through a short column of neutral alumina. The eluant was concentrated and purified by MPLC on silica gel (elution with ethyl acetate) to afford 0.280 g (82%) of 115 as a colorless oil: IR (neat, cm⁻¹) 3000, 2965, 2945, 2920, 2845, 1710, 1610, 1450, 1440, 1395, 1380, 1360, 1320, 1250, 1210, 1180, 1110, 1050, 1020, 970, 950, 870, 820, 790; ¹H NMR (300 MHz, CDCl₃) δ4.44 (d, J = 5.9 Hz, 1 H), 3.87-3.74 (m, 2 H), 3.69 (d, J = 11.1 Hz, 3 H), 3.67 (d, J = 11.3 Hz, 3 H), 2.90-2.81 (m, 1 H), 2.70-2.62 (m, 2 H), 2.49 (d, J = 4.6 Hz, 1 H), 2.01 (dd, J = 11.3, 20.2 Hz, 2 H), 1.89 (s, 1 H), 1.65 (dd, J = 5.0, 13.0 Hz, 2 H), 1.35-1.25 (m, 3 H), 1.13 (s, 3 H), 1.04 (s, 3 H); MS, m/z (M⁺) calcd 330.1596, obsd 330.1578.
Dimethyl 3-[(6,6-Dimethyl-3-oxobicyclo[2.2.1]hept-2-yl)-2-oxo-propyl]-phosphonate (113).

Aqueous 1N hydrochloric acid (0.5 mL) was added to a solution of enol ether 115 (90 mg, 0.3 mmol) in acetone (25 mL). The reaction mixture was stirred for 1.5 h. Solid potassium carbonate was added to neutralize the acid and the solvent was removed in vacuo. The residue was dissolved in dichloromethane (50 mL), washed with saturated sodium bicarbonate solution (2 x 50 mL) and dried. The solvent was evaporated to provide 0.257 g (84%) of pure diketophosphonate 113: IR (neat, cm\(^{-1}\)) 2950, 2900, 2860, 2700, 1735, 1710, 1470, 1450, 1400, 1370, 1255, 1180, 1050, 1030, 980, 910, 865, 820, 745; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.78 (d, \(J_{HP} = 11.3\) Hz, 6 H), 3.20-2.98 (m, 2 H), 2.84-2.71 (m, 2 H), 2.66 (d, \(J = 9.5\) Hz, 2 H), 2.48 (d, \(J = 4.3\) Hz, 1 H), 2.03-1.96 (m, 1 H), 1.72-1.62 (m, 2 H), 1.33 (dd, \(J = 2.1, 13.1\) Hz, 1 H), 1.15 (s, 3 H), 1.13 (s, 3 H); MS, \(m/z\) (M\(^+\)) calcd 302.1283, obsd 302.1293.
5,5-Dimethylbicyclo[2.2.1]heptane-2,3-dione (117).

(-)-α-Fenchocamphorone (0.40 g, 2.89 mmol) was dissolved in glacial acetic acid (5 mL), selenium dioxide (0.32 g, 2.89 mmol) added and the mixture refluxed for 4 h. The cooled reaction mixture was filtered, then neutralized with 30% aqueous potassium hydroxide. The aqueous suspension was extracted with dichloromethane (3 x 100 mL). The organic extracts were washed with water (100 mL), dried, filtered and concentrated. The yellow-orange oil was purified by MPLC on silica gel (elution with 7% ethyl acetate in petroleum ether) to give diketone 117 as a light yellow solid (14.1 mg, 3% yield): IR (CHCl₃, cm⁻¹) 3020, 2950, 2920, 2880, 1770, 1750, 1470, 1445, 1390, 1375, 1300, 1290, 1140, 1125, 1095, 1060, 980, 910; ¹H NMR (300 MHz, CDCl₃) δ2.60 (d, J = 2.6 Hz, 1 H), 2.55 (s, 1 H), 2.32-1.52 (complex m, 4 H), 1.12 (s, 3 H), 1.09 (s, 3 H); MS, m/z (M⁺) calcd 152.0837, obsd 152.0843.
5,5- and 6,6-Dimethyl-3a,4,5,6,7,7a-hexahydro-2-(trimethylsilyl)-4,7-methano-1H-inden-1-one (120a and 120b).

To trimethylsilylacetylene (2.87 g, 29.2 mmol) in petroleum ether (50 mL) under a nitrogen atmosphere was added dicolbaltoctacarbonyl (10.0 g, 29.2 mmol). Vigorous gas evolution was observed for 1 h. The reaction mixture was stirred an additional 2 h then filtered under nitrogen through a filter stick. The filtrate was concentrated and the dark red residue was dissolved in dry benzene (420 mL). 5,5-Dimethylnorbornene (3.57 g, 29.2 mmol) was added in benzene (20 mL) and the reaction mixture was warmed to 70 °C for 18 h. Removal of the solvent gave a dark brown oil. The oil was passed through a column of neutral alumina (elution with pentane followed by ether). The purple band containing the adduct was collected and concentrated. Further purification was achieved by chromatography on silica gel (elution with petroleum ether followed by 5% ethyl acetate) to give 5.32 g (73%) of 120. The regioisomers were separable by MPLC for characterization purposes.

120a: as a white solid, mp 102-103 °C (sublimed 95 °C/1.5 mmHg); IR (CHCl₃, cm⁻¹) 3000, 2950, 2900, 2860, 1680, 1570, 1465, 1450, 1380, 1365, 1310, 1295, 1275, 1265, 1245, 1180, 1165, 1030, 960, 850, 840, 820; ¹H NMR (300 MHz, CDCl₃) δ7.55 (d, J = 2.6 Hz, 1 H), 2.63-2.60 (m, 1 H), 2.51 (d, J = 5.1 Hz, 1 H), 2.09 (d, J = 4.1 Hz, 1 H), 1.94 (s, 1 H), 1.48 (dd, J = 4.5,12.2 Hz, 1 H), 1.35 (d, J = 10.9 Hz, 1 H), 1.07 (dd, J = 2.6,12.2 Hz, 1 H), 1.01 (s, 3 H), 1.00 (s, 3 H), 0.86 (d, J = 11.0 Hz, 1 H), 0.16 (s, 9 H);
13 C NMR (75 MHz, CDCl₃) ppm 215.93, 172.54, 150.51, 50.77, 49.81, 49.76, 45.69, 40.15, 36.48, 30.33, 30.27, 26.39, -1.80; MS, m/z (M⁺) calcd 248.1596, obsd 248.1619.

Found: C, 72.33; H, 9.82.

120b: as a white powder, mp 129.5-130.5°C (sublimed 95°C/1.5 mmHg); IR (CHCl₃, cm⁻¹) 3000, 2950, 2940, 2890, 2860, 1680, 1570, 1465, 1450, 1400, 1380, 1360, 1305, 1270, 1245, 1185, 1155, 1085, 1030, 970, 840, 810; ¹H NMR (300 MHz, COCl₃) 87.54 (d, J = 2.1 Hz, 1 H), 3.12 (br s, 1 H), 2.28 (d, J = 3.4 Hz, 1 H), 2.08 (d, J = 5.1 Hz, 1 H), 1.69 (s, 1 H), 1.41 (dd, J = 4.4, 12.2 Hz, 1 H), 1.34 (d, J = 10.8 Hz, 1 H), 1.04 (s, 3 H), 1.03 (s, 3 H), 1.01 (d, J = 12.2 Hz, 1 H), 0.90 (d, J = 10.8 Hz, 1 H), 0.15 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) ppm 214.78, 173.91, 150.43, 53.30, 48.56, 45.97, 44.89, 40.98, 37.42, 31.03, 30.53, 26.36, -1.79; MS, m/z (M⁺) calcd 248.1596, obsd 248.1607.

5,5- and 6,6-Dimethyl-3a,4,5,6,7,7a-hexahydro-2-(trimethylsilyl)-4,7-methano-1H-inden-1-ol (121a and 121b).

To a cold (0°C) solution of enone 120 (3.02 g, 12.2 mmol) in anhydrous ether (250 mL) under nitrogen was added Dibal (13.4 mL, 1.0 M in hexanes, 13.4 mmol) via syringe. The reaction mixture was warmed to room temperature and stirred 18 h, then poured into 10% aqueous HCl (200 mL). The layers were separated and the aqueous phase was extracted with
ether (3 x 250 mL). The combined organic extracts were washed with water (2 x 125 mL), dried and filtered. Removal of the solvent gave a pale yellow solid which was purified by MPLC on silica gel (elution with 1.5% ethyl acetate in petroleum ether) to give 2.61 g (71%) of the desired alcohol 121.

121a: as a white solid, mp 65-66 °C (sublimation 65 °C/0.05 mmHg); IR (CHCl$_3$, cm$^{-1}$) 3600, 3000, 2950, 2890, 2860, 1590, 1420, 1400, 1380, 1360, 1310, 1290, 1275, 1240, 1120, 1090, 1080, 1060, 1040, 1025, 1000, 985, 945, 920, 895, 870, 840; $^1$H NMR (300 MHz, CDCl$_3$) 85.85 (t, $\jmath = 1.7$ Hz, 1 H), 5.02 (t, $\jmath = 8.9$ Hz, 1 H), 2.63 (t, $\jmath = 8.0$ Hz, 1 H), 2.51 (d, $\jmath = 7.2$ Hz, 1 H), 1.88 (d, $\jmath = 4.2$ Hz, 1 H), 1.71 (s, 1 H), 1.45 (dt, $\jmath = 1.5,10.3$ Hz, 1 H), 1.34 (dd, $\jmath = 4.6,12.0$ Hz, 1 H), 1.24 (d, $\jmath = 9.2$ Hz, 1 H), 1.11 (d, $\jmath = 10.2$ Hz, 1 H), 0.87 (s, 6 H), 0.95 (dd, $\jmath = 2.4,12.0$ Hz, 1 H), 0.13 (s, 9 H); MS, m/z (M$^+$) calcd 250.1753, obsd 250.1785.

121b: as a white solid, mp 55-56 °C (sublimation 65 °C/0.5 mmHg); IR (CHCl$_3$, cm$^{-1}$) 3600, 3000, 2950, 2930, 2890, 2860, 1590, 1465, 1450, 1380, 1360, 1310, 1270, 1245, 1190, 1170, 1140, 1130, 1110, 1095, 1025, 1000, 980, 970, 955, 920, 895, 880, 865, 835; $^1$H NMR (300 MHz, CDCl$_3$) 85.82 (t, $\jmath = 1.7$ Hz, 1 H), 5.01 (t, $\jmath = 8.7$ Hz, 1 H), 3.03 (d, $\jmath = 7.1$ Hz, 1 H), 2.30 (d, $\jmath = 4.5$ Hz, 1 H),
2.15 (t, J = 7.8 Hz, 1 H), 1.53 (s, 1 H), 1.39 (dd, J = 1.4, 10.1 Hz, 1 H), 1.38 (dd, J = 4.8, 12.0 Hz, 1 H), 1.20 (d, J = 9.2 Hz, 1 H), 1.15 (dd, J = 1.1, 10.2 Hz, 1 H), 1.02 (s, 3 H), 0.99 (s, 3 H), 0.90 (dd, J = 2.6, 12.0 Hz, 1 H), 0.13 (s, 9 H); $^{13}$C NMR (75 MHz, CDCl$_3$) ppm 148.96, 145.24, 83.81, 51.93, 49.39, 47.85, 45.44, 37.45, 36.15, 32.74, 31.27, 26.30, -1.00; MS, m/z (M$^+$) calcd 250.1753, obsd 250.1760.

Anal. Calcd for C$_{15}$H$_{26}$O$_3$Si: C, 71.93; H, 10.46.

Found: C, 72.05; H, 10.44.
LIST OF REFERENCES


44. Paquette, L.A.; Moriarty, K.J.; Rogers, R.D., submitted for publication.


46. Shen, C.-C.; unpublished results.


101. Purchased from Peninsular Chemical Research, Gainsville, FL.


233


137. Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G.P. in "Natural
138. See reference 42a, 136 and references therein.

    (b) Kon, K. Ph.D. Dissertation, Osaka University, 1980.


143. (a) Skattebøl, L. *Tetrahedron* (1967), 3, 1107  
    (b) Holm, K.H.; Skattebøl, L. *Tetrahedron Lett.* (1977), 2347  

144. For examples see:  
    (a) Brinker, U.H.; Fleischhauer, I. *Tetrahedron* (1981), 37, 4495  
    (b) Butler, D.N.; Gupta, I. *Can. J. Chem.* (1978), 56, 80  
    (c) Reinartz, R.; Fonken, G. *Tetrahedron Lett.* (1973), 4591  
    (d) reference 42.


148. (a) Dehmlow, E.V.; Lissel, M. *Ann. Chem.* (1979), 181  
    (b) Dehmlow, E.M.; Lissel, M. *Chem. Ber.* (1978), 111, 3873  


150. (a) Jefford, C.W.; *Prod. Chem. Soc.* (1963), 64  


