FACIAL SELECTIVITY IN THE DIELS-ALDER REACTION OF PLANE-NONSYMMETRIC CYCLOPENTADIENE DERIVATIVES

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Facial Selectivity in the Diels-Alder Reaction of Plane-Nonsymmetric Cyclopentadiene Derivatives

by

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A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science

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Abstract

\(\pi\)-Facial selectivity in the Diels-Alder reaction of 1,3-cyclopentadienes substituted at C-5 with various halogens (Cl, Br, I) and alkyl groups (Me, Et, \(n\)-Bu, CH\(_2\)OCH\(_3\)) is detailed. It was found that \(N\)-phenylmaleimide, 4-phenyl-1,2,4-triazoline-3,5-dione and tetra-cyanoethylene gave markedly different diastereofacial outcomes with a given diene thus proving that the nature of the dienophile as well as the C-5 substituent on the diene imparts a significant influence on the reaction.

The results obtained were investigated by collaborators using high level 6-31G* theoretical calculations. The mechanism of facial selectivity is explained on the basis of a steric interaction between the diene and the dienophile that induces bending mainly in the diene. This bending translates into torsional strain in the diene in its syn transition state and the amount of distortion that occurs determines the diastereofacial outcome of the reaction. It was also found that the dienophiles studied imparted different steric effects on the substituted dienes thereby each affording different facial outcomes with a given diene. These results also disprove many popular theories that have recently been proposed involving the mechanism of \(\pi\)-facial selectivity in Diels-Alder reactions.
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I would like to extend my sincere appreciation to my supervisor, Dr. D. Jean Burnell, for his instruction and guidance throughout my research project.

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<td>dimethyl acetylenedicarboxylate</td>
</tr>
<tr>
<td>FMO</td>
<td>frontier molecular orbital theory</td>
</tr>
<tr>
<td>FT</td>
<td>Fourrier transform</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>ir</td>
<td>infrared (spectroscopy)</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MA</td>
<td>maleic anhydride</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>ms</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance (spectroscopy)</td>
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<td>NOE</td>
<td>nuclear Overhauser effect</td>
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<td>NPM</td>
<td>N-phenylmaleimide</td>
</tr>
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<td>PTAD</td>
<td>4-phenyl-1,2,4-triazoline-3,5-dione</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>TCNE</td>
<td>tetracyanoethylene</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
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<td>UV</td>
<td>ultraviolet</td>
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Introduction

It has been nearly 70 years since German researchers Otto Diels and Kurt Alder reported the reaction between \( p \)-benzoquinone and \( 1,3 \)-cyclopentadiene and proposed the correct structure of the product as the bridged tricyclic compound 1 (Scheme 1).

![Scheme 1](image)

Scheme 1. The seminal discovery of Diels and Alder

They went on to demonstrate that reactions between \( 1,3 \)-dienes and alkenes substituted with an \( \alpha \)-electron-withdrawing group were of wide applicability, and for this discovery they were awarded the Nobel Prize in chemistry in 1950. Reactions of this sort have been named Diels-Alder reactions, and these reactions have become an indispensable part of the organic chemist's repertoire of synthetic methodology. The reason for the popularity of the Diels-Alder reaction becomes clear when one considers that, in a single predictable synthetic operation, two new \( \sigma \)-bonds are formed and up to four new contiguous stereogenic centers develop.

The mechanism by which the Diels-Alder reaction takes place has been the source of much debate. Although stepwise mechanisms have been postulated, including the
consideration of diradical and zwitterionic intermediates, it is now generally accepted that the reaction takes place by a concerted, thermally allowed $4\pi_e + 2\pi_e$ mechanism with the formation of the two new $\sigma$-bonds taking place simultaneously (Scheme 2).²

\[ \text{ Scheme 2. Concerted mechanism for the Diels-Alder reaction } \]

There are a number of features of the Diels-Alder reaction that determine the outcome: the conformation of the diene, the substitution patterns of the diene and the dienophile, and the manner in which the diene and dienophile approach each other. The diene in the Diels-Alder reaction can react when it is in an $s$-cis geometry but not in an $s$-trans geometry.⁶ Therefore, of the simple examples below, only 2 and 3 are reactive as Diels-Alder dienes, whereas 4 and 5 are not. The $s$-cis geometry is essential for the concerted overlap of the $p$-orbital components of both termini of the diene and dienophile.

The dienophile may contain a double or triple bond. Its reactivity is enhanced

\[ \text{ 2 } \quad \text{ 3 } \quad \text{ 4 } \quad \text{ 5 } \]
significantly by an electron-withdrawing substituent. Furthermore, it has been shown that the placement of more than one withdrawing group in the allylic position further increases the reactivity of the dienophile dramatically.  

When the diene and the dienophile are unsymmetrically substituted, different regioisomers can be formed in the Diels-Alder reaction. Frontier molecular orbital (FMO) theory has been used to predict successfully the regiochemistry of many Diels-Alder reactions. One theory developed by Houk states that the Diels-Alder transition state will be stabilized by favourable interaction of components of the diene HOMO (highest occupied molecular orbital) and dienophile LUMO (lowest occupied molecular orbital). The orbital coefficients of the p-orbitals of the diene HOMO, when the diene is substituted by an electron-donating group at either the 1 or 2 position, are as in structures 6 and 7 (Scheme

Scheme 3. FMO rationalization of regiochemistry in the Diels-Alder reaction
3). For the dienophile, an electron-withdrawing group in the allylic position leads to the LUMO depicted in structure 8. There is a marked difference in the size of the coefficient of the wavefunction for each case. (A shaded circle indicates a positive component and an open circle represents a negative component; the relative size of the circle indicates the relative size of the coefficient.) Based on Houk's theory, the diene and the dienophile prefer to orient themselves in the manner that the terminal coefficients that are closer in energy will become bonded preferentially. Thus, an electron-donating group on the end of a diene gives mainly an "ortho-disubstituted" product, whereas a diene substituted by an electron-donating group in the 2-position yields the "para-disubstituted" product predominantly.

Different stereochemical outcomes are possible in the Diels-Alder reaction. Endo-addition occurs when the reference substituent on the dienophile is oriented towards the \( \pi \)-orbitals of the diene. Oppositely, exo-addition has the substituents on the diene and the dienophile pointing away from each other as the reacting partners come together. Endo-addition products predominate in most Diels-Alder reactions, and this also has been rationalized on the basis of FMO theory. For instance, with 1,3-cyclopentadiene and 1,4-naphthoquinone (Figure 1), the exo orientation can only exhibit primary interactions between the HOMO and LUMO at the centres of the new bond formation. However, the transition state for endo-addition is further stabilized by secondary orbital interactions between the double bonds of the diene and carbonyl components of the dienophile. The presence of this secondary effect serves to lower the activation energy for endo-addition. In fact, this reaction gives a mixture of 9, the endo-addition product, and 10, the exo-addition product, in a ratio of greater than 99 : 1, respectively (Scheme 4).
Scheme 4. The Diels-Alder reaction between 1,3-cyclopentadiene and 1,4-naphthoquinone

Figure 1. Simple FMO diagram for endo and exo transition states

Another stereoechemical aspect of the Diels-Alder reaction becomes important when the two faces of the diene are not equivalent, i.e., the diene is plane-nonsymmetric. To illustrate this, consider a Diels-Alder addition involving 1,3-cyclopentadiene that has been substituted by a group (R) in the 5-position. Syn addition is defined in this thesis as the approach of the dienophile to the same side as this substituent group, and this gives generalized structure 11 as the product. Anti addition arises from the attack of the dienophile to the face opposite the substituent, giving generalized structure 12 (Figure 2).
It will be the primary focus of this thesis to address the factors governing \( \pi \)-facial diastereoselectivity. The ability to understand the factors controlling this phenomenon is of great interest to theoreticians and those concerned with synthesis because the presence of a stereogenic center can exert a significant influence on facial approach.\(^9\)\(^10\) Facial selectivity can also be influenced by blocking one face of the diene or the dienophile with a chiral auxiliary.\(^11\) However, the demands of modern synthesis cannot always accommodate such features. It has been shown that the presence of a plane-nonsymmetric substituent in the allylic position of the diene can exert a surprisingly strong influence over facial selectivity. This effect has surfaced in Corey's prostaglandin synthesis,\(^12\) wherein the

![Diagram of syn and anti addition of a dienophile to a plane-nonsymmetric diene](image.png)

Figure 2. Syn and anti addition of a dienophile to a plane-nonsymmetric diene
use of 5-methoxymethyl-1,3-cyclopentadiene 13 led to a reaction with complete
diastereofacial control, affording only the anti adduct 14 (Scheme 5).

```
   MeO
  / \  
 H   +    CH2—COCl   Cu(BF4)x.H2O
   \  /  \                     0°C, 18 h, 94%
  H        

13       14
```

Scheme 5. \( \pi \)-Facial selectivity in Corey's prostaglandin synthesis\(^{12} \)

In other instances, such as in Paquette's dodecahedrane synthesis,\(^{13} \) the placement of
a relatively large cyclopentadiene group in the 5-position of 1,3-cyclopentadiene 15 showed
a surprisingly small influence on facial selectivity. This reaction proceeded to give a mixture
of 16 (syn) and 17 (anti) adducts in a ratio of 58 : 42, respectively (Scheme 6).

\( \pi \)-Facial selectivity has been rationalized in many ways, and the remainder of this
introduction is an overview of the experimental data supporting each theory. Particular
attention will be applied to cyclic dienes in which problems with conformation are much less
contentious than with acyclic dienes. The three remaining factors that may be important in
determining facial selectivity for cyclic dienes are steric, torsional and stereo-electronic
effects. More than one of these factors may be operating, and there can be debate over
which is playing the most prominent role in controlling the diastereofacial outcome of a
reaction.
Scheme 6. \(\pi\)-Facial selectivity in Paquette's dodecahedrane synthesis

**Steric Effects**

Recent investigations in our laboratory by Burry et al.\textsuperscript{13} showed that facial selectivity with 1,2,3,4,5-pentachloro-5-methoxy-1,3-cyclopentadiene 18 is controlled mainly by steric and / or torsional effects. Dienophiles of various types were reacted with this diene (Scheme 7). Some reactions were expected to proceed via the inverse-electron-demand mode (entry 1), whereas others were of the normal electronic configuration (entry 2). However, the facial selectivity in every case was the same, i.e., 100% syn to the methoxy group, despite the electronic nature of the dienophile used. This ruled out any possibility that a stereoelectronic factor was controlling facial selectivity in this type of system.

Another investigation by Valenta and Burnell\textsuperscript{15,16} also pointed towards a predominant steric effect in the determination of facial selectivity for the bridged-ring-substituted 1,3-cyclopentadienes 19 and 20. The results shown in entries 3 and 4 of Scheme 7 indicate
that the methine hydrogen is more sterically demanding than the methylene hydrogens. The methine hydrogen is pointed directly towards the incoming dienophile, whereas the methylene hydrogens are oriented in such a manner that they are angled slightly away from the incoming dienophile (Figure 3). The facial selectivity was modelled successfully using steric factors as the basis of facial difference.\textsuperscript{16}

Another case of sterically controlled facial selectivity involves the reaction of benzene oxide 21 with \( N \)-phenylmaleimide which results in addition anti to the oxygen.\textsuperscript{17} This anti addition is in marked contrast to many examples of an allylic oxygen atom directing addition syn to itself. While it has been argued that electronic factors predominantly govern facial selectivity in allylic oxygen bearing dienes, it was suggested that a steric interaction between the allylic oxygen and the dienophile might be causing this anti result.\textsuperscript{17} Indeed, it was shown that the geometry of 21 is such that the oxygen is almost perpendicular to the plane of the diene moiety, whereas the allylic hydrogens lie roughly coplanar with the diene. This would cause a significant steric interaction between an incoming dienophile on the syn-face, leaving the anti face open for dienophile approach.

Electronic Effects

The first example of a C-5 heteroatom-substituted 1,3-cyclopentadiene was reported by Woodward \textit{et al.}\textsuperscript{18} who reacted 5-acetoxy-1,3-cyclopentadiene 22 with ethylene (Scheme 8, entry 1). This was accomplished through the thermolysis of diacetoxydicyclopentadiene in the presence of ethylene. They reported a single adduct, arising from the attack of the dienophile onto the face of the diene syn to the acetox y group. Clearly, this is a contrasteric
Scheme 7. Major adducts for sterically controlled Diels-Alder reactions
(NPM = N-phenylmaleimide, MA = maleic anhydride)
Scheme 7. Continued
NPM = \textit{N}-phenylmaleimide

Figure 3. Facially distinct addition with a bridged-ring-substituted diene 20
result, although with the conditions employed some argument can be made as to whether or not the observed product was derived through a kinetic process. Nevertheless, other investigations into the Diels-Alder reactions of 5-hydroxy-23 and 5-acetoxy-1,3-cyclopenta-diene 24 derivatives also afforded exclusively the product of addition syn to oxygen. The stereochemistry of the adducts was not the consequence of hydrogen bonding between an allylic oxygen substituent and the dienophile since reaction of styrene with 24 also led to addition syn to hydroxyl (Scheme 8, entry 4). More recently, the fluorinated diene 25 was synthesised, and it displayed addition exclusively syn to the fluorine, also. The pentachloro diene 26 displayed a preference for syn addition. Furthermore, the proportion of this syn adduct was shown to increase with the addition of a Lewis acid.

These results, which should be disfavoured on steric grounds, were explained on the basis of an attractive interaction between the allylic substituent on the diene and the dienophile through dipole-dipole, dipole-induced-dipole or London dispersion forces. These interactions would be enhanced by complexing the dienophile with a Lewis acid and thereby increasing the preference for addition syn to chlorine. This was consistent with experimental results.

5-Chloro-1,3-cyclopentadiene 27 has also been synthesised and it reacted in a Diels-Alder fashion with dimethyl acetylenedicarboxylate (DMAD) to give a mixture of syn and anti adducts, showing a slight preference for the latter. Interestingly, the reaction of 5-thiophenyl-1,3-cyclopentadiene 28 with maleic anhydride (MA) yielded the same facial diastereoselectivity as 27. However, 5-bromo-1,3-cyclopentadiene 29 afforded only the anti adduct on reaction with DMAD. This result was echoed by the reaction of
Scheme 8. Major Diels-Alder adducts with various 1,3-cyclopentadiene derivatives
Scheme 8, Continued

DMAD = dimethyl acetylenedicarboxylate, MA = malic anhydride
Scheme 8. Continued
MA = maleic anhydride, DMAD = dimethyl acetylenedicarboxylate
PTAD = 4-phenyl-1,2,4-triazole-3,5-dione
5-iodo-1,3-cyclopentadiene 30, which furnished exclusively the anti Diels-Alder adduct on reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Furthermore, it was shown that the phenylselenyl derivative 31 also reacted with complete diastereofacial selectivity in which addition of the dienophile was anti to the heteroatom.

In Scheme 8 we see a syn (contrasteric) approach to the C-5 substituent when it is O or F, and a mixture of diastereomers when the substituent is Cl or S. Larger atoms like Br, I and Se direct addition towards the anti-face of the diene. While it may be argued that steric repulsion may dominate with the latter group of atoms, it has been suggested by Anh that a beneficial interaction between the C-5 substituent and the incoming dienophile may play an important role in facial selectivity. The syn selectivity for atoms like oxygen was explained on the basis of an interaction between the C-S substituent's lone pairs and the LUMO of the syn-adding dienophile. This "attraction" allows for better interaction between the symmetrical π-orbital of the diene and the vacant π* orbital of the dienophile, and thus provides a net stabilization towards syn approach to the heteroatom (Figure 4). When the energy of this molecular orbital becomes significantly different from that of the dienophile's LUMO, this stabilizing interaction is diminished and steric hindrance controls the stereochemistry of the reaction. Although this theory can be successfully applied to a large number of experimental results, it cannot be extended in a straightforward manner to explain syn selectivity with substituents like F and Cl, whose symmetrical π-orbital is significantly different in energy to the π* orbital of the dienophile and should therefore not be able to stabilize the syn approach by this mechanism.
The apparent contrasteric addition of 5-heterosubstituted cyclopentadienes has also been explained by an hypothesis offered by Fukui and coworkers.\textsuperscript{27,28,29} They suggested that orbital mixing between the lone pair electrons of the allylic heteroatom and the diene HOMO causes this HOMO to be biased towards the syn surface, thereby inducing kinetically controlled dienophile attack to this face. However, this theory cannot explain the preference for anti addition with atoms like chlorine and sulphur for which the $n_{\pi}$ orbital energy for the heteroatom is close to the $\pi$-orbital energy of the diene. Significant $n$-$\pi$ mixing should occur in the diene HOMO thereby promoting high facial selectivity. However, there is no agreement between the computational data and the experimental results for this case. Furthermore, this hypothesis has been discounted recently by Werstiuk and coworkers\textsuperscript{30} who claimed that $n$-$\pi$ orbital mixing cannot be the source of $\pi$-facial diastereoselectivity. They based this argument on ab initio / AM1 calculations and photoelectron spectroscopy, which showed no significant mixing of the lone pair orbitals of
the allylic substituent and the π-system. Furthermore, Poirier and Burnell\textsuperscript{11} showed that there is an insignificant difference in the hybridization of the 5-substituent in the syn or anti transition states and that the bond orders between the allylic heteroatom and C-1 or C-4 of the diene are negligible at the transition states.

Another hypothesis has been offered to explain the range of facial selectivities encountered for heteroatom substituents by Ishida, Aoyama and Kato.\textsuperscript{22} They proposed that the syn attack towards many heteroatoms may be stabilized by favourable interactions of the π-electrons in the developing norbornene bond with the back lobe of the polarized carbon-heteroatom bond (Figure 5). Since the electronegativities of the heteroatoms decrease in the order of F > O > S > Se, the tendency to add syn to these atoms will tend to decrease in that order.

![Figure 5. Depiction of Ishida's mechanism for stabilization in the syn transition state](image-url)
Up to this point, we have only considered factors governing facial selectivity for the simplest of diene systems. In each case, facial selectivity was considered for an allylic substituent relative to a hydrogen. More complicated systems exist wherein the $\pi$-facial diastereoselectivity is relative to a substituent other than hydrogen. The most comprehensive databases of diastereofacial selectivities for this type of system have been acquired through investigations on 5-substituted-1,2,3,4,5-pentamethyl-1,3-cyclopentadienes and substituted cyclohexadiene systems (Scheme 9). As with many of the simple 5-substituted 1,3-cyclopentadiene systems, a facial preference for addition syn to oxygen in competition with a methyl group was observed. 5-Hydroxy-1,2,3,4,5-pentamethylcyclopentadiene 32 and the cyclohexadiene derivative 33 both gave addition syn to oxygen exclusively. Furthermore, this high level of selectivity can be extended towards nitrogen derivatives, as the amine 34 also afforded exclusively the syn diastereomer. However, in marked contrast to the simple 1,3-cyclopentadiene derivative 27, the chloro derivative of 1,2,3,4,5-pentamethylcyclopentadiene 35 provided exclusively the syn adduct whereas the thiophenyl derivative 36 exhibited almost exclusive diastereofacial selectivity for the anti adduct.

The results for these cycloadditions established the strong preference for syn additions towards N, O, Cl and anti towards S. Previous explanations of facial selectivity have tended to focus on some ground state property of the allylic substituent that invoked the $\pi$-facial diastereoselectivity. Cieplak pioneered what would later be developed into an alternative analysis by investigating the mode of facial attack towards carbonyls. He observed that both thermal and photochemical additions occurred at the face anti to the $\alpha$
Scheme 9. Major Diels-Alder adducts for various pentamethyl-1,3-cyclopentadiene derivatives and a cyclohexadiene derivative
MA = maleic anhydride, DMAD = dimethyl acetylenedicarboxylate
NPM = N-phenylmaleimide
Scheme 9: Continued

MA = maleic anhydride

substituent that was the better sigma donor. This would be favoured by mixing of the $\sigma^*$ of the forming bond with the filled $\sigma$-orbital of the $\alpha$ C-X bond. For example, additions to the carbonyl of cyclohexanone favour axial attack because the $\alpha$ C-H bond is a better $\sigma$ donor than the $\alpha$ C-C bond (Figure 6). This observation was extended by Fallis86 to account for facial selectivity in Diels-Alder reactions. He proposed that, based on Cieplak's hypothesis, one should expect cycloaddition involving plane-nonsymmetric dienes to display a preference for addition anti to the antiperiplanar bond that is the better $\sigma$ donor. A list in

```
Figure 6. Cieplak's hypothesis for the axial attack on cyclohexanone
```
increasing order of σ-donating ability for common atoms is C-O < C-N < C-Cl < C-H < C-S. Therefore, when a diene is substituted with a C-S bond and a C-C bond, addition should occur anti to the C-S bond since it is the better σ donor (Figure 7).

![Image of SH and CH₃ with σ and σ* orbitals](image)

*Figure 7. Depiction of σ donation from the anti substituent into the σ* orbital of the forming bond.*

π - Facial selectivity with bridged-ring cyclopentadienes has also received considerable attention. Diels-Alder reactions with isodicyclopentadiene 37 (Scheme 10) proceeded exclusively anti to the methano bridge. Dienes 38 and 39 behaved similarly, affording exclusively the products of addition anti to the methano moiety. The cause of this behaviour cannot be steric since additions occurred syn to the larger, ethano bridge. Paquette rationalized this facial selectivity by proposing that orbital mixing of the non-reactive portion of isodicyclopentadiene with the π_diene orbital is important. This interaction causes an inward tilt of the diene orbitals resulting in a minimization of the antibonding interaction on the below-plane face of the diene, which in turn results in preferred addition to this side (Figure 8).
Figure 8. Depiction of rotation of the terminal $p_\pi$ lobes for $\pi_5$ in 37

This was supported by calculations on the simpler system 40, which indicated that there is significant mixing between the lowest occupied $\pi$-orbital and high lying $\sigma$-orbitals. Significant differences in the frontier electron distribution on the above-plane and below-plane diene surfaces resulted in the rotation of the $p_\pi$ orbital for the $\pi_5$. It is this orbital tilting that was proposed to be responsible for the addition anti to the methano bridge. The different overlap between the dienophile and the rotated $\pi$ orbital of the terminal carbon atoms of the diene causes the antibonding interactions between the $\pi_5$ of the diene fragment and the HOMO of the dienophile to be diminished for below-plane attack relative to above-plane attack (Figure 9). However, cycloadditions with 41 occurred predominantly from the above-plane face. On the basis of the photoelectron spectra of 41 and extensive INDO (incomplete neglected differential overlap) calculations, it was suggested that the terminal $\pi$ lobes of these dienes are rotated away from the methano bridge, in a manner
Entry | % Adduct
--- | ---
1 | 100% ref. 38
2 | 100% ref. 38
3 | 100% ref. 38
4 | 54% ref. 40

Scheme 10. Syn : anti ratios for various isodicyclopentadiene derivatives
NPM = N-phenylmaleimide
Figure 9. Qualitative diagram of the interaction between the $\pi_s$ of the butadiene unit in 40 with ethylene. On the left, below-plane approach is depicted and, on the right, above-plane approach.
opposite to 37, 38, and 39 and thus addition occurs from the above-face.

Diels-Alder reactions with heterocyclic propellanes have received considerable attention. For example, the reaction between propellane 42 and PTAD afforded the syn adduct (Scheme 11). However, replacement of the carbonyls by methylenes as in 43, provided anti adducts exclusively. It was proposed that this crossover in facial selectivity was due to stabilization from secondary orbital overlap between the π components of the carbonyl carbons and the lone pair orbitals on the nitrogens of the dienophile (Figure 10). Clearly, no such overlap would be possible for additions of PTAD to 43, and hence the anti product predominates. Furthermore, addition of a carbon-based dienophile to 42 should provide the anti adduct because no secondary overlap would be possible. Therefore, it can be concluded that for propelladienes, secondary orbital overlap favours syn addition when possible, otherwise steric effects dominate and the anti adduct is observed.

Halperman and co-workers attempted to establish conclusively the importance of electronic interactions in determining the diastereoselective outcome in the Diels-Alder reaction. This was approached by the investigation of facial selectivity for 1,3-cyclopentadienes with sterically unbiased, yet electronically different substituents in the allylic position (Scheme 12). The Diels-Alder reaction of diene 44 with DMAD showed a preference for addition syn to the substituted phenyl group. However, diene 45 afforded more of the adduct from anti addition. It seemed apparent that addition occurred anti to the more electron-rich phenyl ring. These findings are consistent with Fallis' suggestion that dienophile additions should occur to the diene face opposite the better σ donor.

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Scheme 11. Major Diels-Alder adducts for selected propelladienes
PTAD = 4-phenyl-1,2,4-triazoline-3,5-dione, NPM = N-phenylmaleimide

Figure 10. Secondary orbital overlap for the approach of a heteroatom-based dienophile to an anhydride-bridged propelladiene
Halterman's study supported the idea that in the absence of steric factors, diastereoselective control in the Diels-Alder reaction can be significantly altered by internal electronic parameters.

Inagaki has proposed that selectivity for Diels-Alder reactions is controlled by the reactivity of the dienophile. He supported this theory on the basis of the diastereoselective

<table>
<thead>
<tr>
<th>Entry</th>
<th>% Adduct</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>68%</td>
</tr>
</tbody>
</table>

Scheme 12. Major Diels-Alder adducts for additions to sterically unbiased, yet electronically different dienes
outcome of the reactions of 5-thiophenyl-1,3-cyclopentadiene 28 with dienophiles of different reactivities (Table 1). The selectivity changed from a slight preference for anti attack with a less reactive dienophile to exclusive anti attack with a highly reactive dienophile. On the basis of these data, he concluded that selectivity should increase with the reactivity of the dienophile. This also suggested that if the reactivity of the dienophile is enhanced by a Lewis acid the selectivity should also increase. Currently there is very little

<table>
<thead>
<tr>
<th>Dienophile</th>
<th>Reactivity  (L/mol·sec)</th>
<th>Syn / Anti</th>
<th>$\Delta \Delta G^\ddagger$ (Syn / Anti) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 600</td>
<td>40 : 60</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>70 500</td>
<td>30 : 70</td>
<td>0.46</td>
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<tr>
<td></td>
<td>16 000 000</td>
<td>14 : 86</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>430 000 000</td>
<td>100% anti</td>
<td>3.8</td>
</tr>
</tbody>
</table>
experimental evidence supporting this argument.\textsuperscript{15,16} Furthermore, there seems to be little correlation between the $\Delta G^2$ for the modes of facial approach (syn:anti ratio) and the reactivity of the dienophile.

This introduction has reviewed many antithetical theories regarding $\pi$-facial selectivity in the Diels-Alder reaction. A serious problem with the development of any unified theory explaining facial selectivity in Diels-Alder reactions is that carefully and systematically prepared data for the simplest of dienes are unavailable. Therefore, we sought to develop an efficient route towards the synthesis of 5-substituted-1,3-cyclopentadienes, which are among the most rudimentary class of cyclic plane-nonsymmetric dienes, and to react these with various dienophiles. The inherent simplicity of this type of diene should minimize secondary steric, torsional and electronic interactions between the diene and the dienophile. Furthermore, cyclic dienes obviate the conformational ambiguities that are inherent to acyclic systems, allowing the effects of the allylic substituent on $\pi$-facial selectivity to be studied unobtrusively. Reactions involving dienes of this size can also be studied computationally by using ab initio methods at a high level of theory. These synthetic studies and some aspects of the results of the theoretical studies are described in the remainder of this thesis.
Results

5-Alkyl-substituted cyclopentadienes

In the 1960's there were attempts, largely unsuccessful, at synthesizing 5-alkyl-substituted-1,3-cyclopentadienes. Nevertheless, McLean and Haynes\textsuperscript{46} published the synthesis of 5-methyl-1,3-cyclopentadiene 46 by the reaction of sodium with cyclopentadiene, to give the cyclopentadienide anion, which was subsequently treated with dimethyl sulfate to provide 46 in extremely poor yield. This was due, in part, to the inherent lability of this compound, which can readily undergo a 1,5-hydrogen shift to give the regioisomers 47 and 48 (Scheme 13). Indeed, it was shown that the rearrangement of 5-methyl-1,3-cyclopentadiene (46) to give 47 and 48 follows first order kinetics with the $t_{1/2}$ for 46 being less than 30 minutes at 20°C.\textsuperscript{47,48} Furthermore, polymethylation products arising

Scheme 13. Synthesis and rearrangement of 5-methyl-1,3-cyclopentadiene
from the reaction of excess base with the methylated diene 47 and subsequent re-methylation accounted for a significant portion of side product. To avoid the problem associated with the rearrangement of 46, the diene was trapped as a Diels-Alder adduct by reacting it with NPM, which gave a mixture of syn and anti diastereomers in equal amounts\(^\text{46}\) (Scheme 14). However, at approximately the same time, Mironov and co-workers\(^\text{49}\) reported a Diels-Alder addition of MA with 46, which they claimed showed a strong preference for addition anti to the methyl group. These contradictory results involving the reactions of 46 with very similar dienophiles had yet to be resolved.

Furthermore, assignment of the stereochemistry relied on different long range NMR

![Scheme 14. Diels-Alder adducts for the reaction of 5-methyl-1,3-cyclopentadiene with NPM and MA. NPM = N-phenylmaleimide, MA = maleic anhydride.](image-url)

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coupling patterns\textsuperscript{10} of the protons on the newly generated double bond of the norbornene skeleton with the substituent at the apex of the methylene bridge. Today, assignments based on such data would be deemed unreliable in the absence of supporting NOE (nuclear Overhauser effect) or X-ray data.

It was in our interest to devise an efficient, general synthetic strategy to produce 5-alkyl-1,3-cyclopentadienes and to examine subsequently the effect of the alkyl substituents on \(\pi\)-facial selectivity in Diels-Alder reactions. From McLean's results we immediately realised that we would be required to take precautions to avoid the isomerization of the substituted dienes and the generation of polyalkylated side products.

Freshly cracked 1,3-cyclopentadiene (pKa 16)\textsuperscript{11} was treated with a slight excess of \(n\)-butyllithium in tetrahydrofuran (THF) to give a solution of the cyclopentadienide anion. The use of a base such as \(n\)-butyllithium ensured that nearly a stoichiometric amount of base was added and therefore minimized the generation of polyalkylated side products by the presence of an excess of base. Addition of this solution to an excess of an appropriate alkyl halide at -20°C afforded the desired 5-alkyl-1,3-cyclopentadienes 46, 49, and 50 (Scheme 15).

We found that rearrangement could be curtailed by performing the reaction at a low temperature (-20 °C) without adversely affecting the alkylation process. Since we were interested solely in the Diels-Alder adducts, isolation of the dienes was not attempted. The original idea was to react the dienes \textit{in situ} with a suitable dienophile in order to generate the Diels-Alder adducts. However, direct addition of the dienophile to the reaction mixture resulted in the immediate generation of a thick black liquid, which after washing and
Scheme 15. General synthetic strategy towards 5-alkyl-1,3-cyclopentadienes

removal of the solvent, furnished a black tarry material that we were unable to identify by
NMR. Since most dienophiles bear a double bond α to a carbonyl, it was suspected that
some unreacted cyclopentadienide anion was attacking the dienophile by a 1,2- or
1,4-process to give undesired products. The diene was therefore quickly washed with a cold
brine solution to quench any remaining organolithium species. Subsequent addition of
dienophile afforded Diels-Alder adducts 51 - 65 in reasonable yields (Scheme 16). The
product ratios are presented in Table 3 at the end of this section.

Separation and purification of the diastereomeric adducts was performed by flash
chromatography and/or recrystallization, which provided each diastereomer in
homogeneous form. Boiling solutions of each of the isolated diastereomers in benzene for
extended periods showed no equilibration, which indicated that the adduct ratios were
kinetically derived. The stereochemistry of each diastereomer was determined by NOE
difference experiments in its $^1$H NMR spectrum. For example, one adduct from the
cycloaddition between 5-methyl-1,3-cyclopentadiene and NPM is shown in Figure 11. The
structure of the syn adduct, 51, was assigned based on the NOE enhancement of the signal
Scheme 16. Diels-Alder products generated from the alkyl-substituted dienes
NPM = N-phenylmaleimide, PTAD = 4-phenyl-1,2,4-triazoline-3,5-dione,
TCNE = tetracyanoethylene
Figure 11. NOE difference spectra of 51

simple spectrum without irradiation.

C-8Me
C-8H
C-4H
C-7H
C-7aH
C-3aH
C-5H
C-6H
Figure 12. NOE difference spectra of 52
for the hydrogen on C-8 upon saturation of the signals for C-5H and C-6H. This result was confirmed by an NOE enhancement for C-5H and C-6H signal upon saturation of the C-8H signal. It can be noted that the NOE enhancements are uncharacteristically small in these cases due to the relatively large distance that separates the protons at C-5 and C-6 from the one at C-8. However, saturation of C-3aH and C-7aH provided a relatively large NOE enhancement of the C-8Me signal and vice versa. Based on these data, we could unambiguously assign 51 as the product of syn-addition. The stereochemistry of the anti-addition product 52 was also assigned by a similar argument based on NOE experiments (Figure 12). Thus, saturation of the C-3aH and C-7aH signals resulted in a significant NOE enhancement of the signal for C-8H. This stereochemistry was confirmed by the fact that saturation of C-8H led to an NOE enhancement of the C-3aH and C-7aH signals.

We found that the major impurities in the reactions of 5-substituted 1,3-cyclopentadienes were 66, 67, or 68, which were obviously derived from unsubstituted 1,3-cyclopentadiene. We therefore looked into optimizing the alkylation step. The alkylation step was most effective when an alkyl iodide was used as the electrophile. While alkyl bromides would work, the yield of the substitution reaction was poor, and alkyl chlorides did not alkylate under the conditions employed. Table 2 reports the results of varying the reaction time for alkylation and the number of equivalents of alkylation agent. The alkylation products and unreacted 1,3-cyclopentadienes were trapped as Diels-Alder adducts with N-phenylmaleimide. From this study, the proportion of substituted adduct was increased to 93%, as measured from the NMR spectra of the crude adduct mixtures.
Table 2. Variation in the conditions of the alkylation step shown in Scheme 15

<table>
<thead>
<tr>
<th>conditions</th>
<th>substituted : unsubstituted</th>
<th>total yield of adducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min @ 1.5 eq. EtI</td>
<td>1.1 : 1</td>
<td>88%</td>
</tr>
<tr>
<td>60 min @ 1.5 eq. EtI</td>
<td>2.2 : 1</td>
<td>85%</td>
</tr>
<tr>
<td>120 min @ 2.3 eq. EtI</td>
<td>6.2 : 1</td>
<td>90%</td>
</tr>
<tr>
<td>180 min @ 1.5 eq. EtI</td>
<td>6.9 : 1</td>
<td>92%</td>
</tr>
<tr>
<td>30 min @ 7.5 eq. EtI</td>
<td>22 : 1</td>
<td>93%</td>
</tr>
<tr>
<td>60 min @ 5.0 eq. EtI</td>
<td>24 : 1</td>
<td>93%</td>
</tr>
</tbody>
</table>

5-Halogen-substituted cyclopentadienes and methoxymethyl-substituted cyclopentadienes

We also wanted to investigate the effect of an allylic heteroatom substituent on π-facial selectivity. It had been demonstrated that 5-halo-1,3-cyclopentadienes bearing an allylic heteroatom substituent, or a methoxymethyl substituent, could be efficiently synthesized through the reaction of cyclopentadienyllithium 69 with an N-halosuccinimide, or bromomethyloxymethyl ether. The inherent lability of these halogenated dienes is considerably lower than that of their alkyl-substituted counterparts. Breslow reported that with a chlorine substituent (70), the time required for the "diene to equilibrate" with its regioisomers was two hours at 75°C. However, when the substituent was bromine (71) the time required for equilibration was found to be two hours at 100°C, whereas with iodine (72), six hours at 100°C were required to reach equilibrium. No equilibration studies have been reported for the methoxymethyl compound. We suspect that the increased stability associated with larger heteroatoms is in part due to the eclipsing interaction that the molecule would have to endure if the heteroatom were forced into either the 1 or 2 position.
We used 69 to generate the 5-halo-1,3-cyclopentadienes or
5-methoxymethyl-1,3-cyclopentadienes 70 - 73 (Scheme 17). These were subsequently
allowed to react in situ with a variety of dienophiles to give the Diels-Alder adducts 74 - 91
(Scheme 18).

![Scheme 17. Synthesis of 5-halo-1,3-cyclopentadienes and 5-methoxymethyl
1,3-cyclopentadiene](image)

Each adduct was again proven to be the kinetic product. Syn to anti ratios, isolation
and characterisation of these adducts were performed by the same methods as described
earlier. In some cases, NOE experiments were inconclusive and X-ray crystallography was
used to assign unequivocally the stereochemistry of the product. For example, the
Diels-Alder reaction of 5-iodo-1,3-cyclopentadiene and tetracyanoethylene (TCNE)
afforded exclusively the anti diastereomer 90, which could not be assigned by NOE. The
X-ray crystal structure is shown in Figure 13.

We also attempted to synthesize various other 1,3-cyclopentadiene derivatives.
These are summarized in Scheme 19. Generating a methyl ketone functionality in the
5-position of 1,3-cyclopentadiene (92) was unsuccessful by the reaction of lithium
Scheme 18. Diels-Alder products generated from halo and methoxymethyl substituted dienes
NPM = N-phenylmaleimide, PTAD = 4-phenyl-1,2,4-triazoline-3,5-dione, TCNE = tetracyanoethylene
Figure 13. X-Ray structure of 90
cyclopentadienide with acetyl bromide. Cyanogen bromide did not exhibit any desired reactivity towards the cyclopentadienide anion in attempts to generate 5-cyano-1,3-cyclopentadiene 93, instead an adduct of diene 71 was obtained. Reaction of dimethyl disulphide with the anion of cyclopentadiene also failed to generate any of the desired thiomethyl compound 94. Attempts to place an acetylene group in the allylic position of 1,3-cyclopentadiene also were unsuccessful. This was attempted by displacement of the iodine in 95 with lithium acetylide ethylene diamine complex.

Adduct Ratios

Many dienophiles proved to be too unreactive towards the 5-substituted dienes under the cold conditions that were necessary to prevent isomerization of the diene. The dienophiles that were not useful were: dimethyl acetylenedicarboxylate, methyl acrylate, dimethyl fumarate, dimethyl maleate, \( p \)-benzoquinone and 1,4-naphthoquinone. Fortunately, three structurally different dienophiles did have reasonable reactivity under the cold conditions. These were the ethylene-based dienophile \( N \)-phenylmaleimide, the heteroatom-based dienophile 4-phenyl-1,2,4-triazoline-3,5-dione and the highly reactive, but more sterically demanding dienophile, tetracyanoethylene. The ratio of the syn to anti diastereomers was determined by careful integration of the NMR spectrum of the crude adduct mixture. The reactions of the synthesized dienes 46, 49, 50 and 70 - 73 with the previously mentioned dienophiles allowed us to generate the facial selectivities presented in Table 3.
Williamson\textsuperscript{21,22} suggested, on the premise of his hypothesis regarding facial selectivity, that selectivity in the Diels-Alder reaction would be enhanced in the presence of a Lewis acid. We chose to investigate the effect of a Lewis acid catalyst on facial selectivity with dienes 46, 70 and 71. This was undertaken simply by the addition of a catalytic amount

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=0.3\textwidth]{example.png}};
\end{tikzpicture}
\end{center}

Scheme 19. Unsuccessful attempts at generating 5-substituted-1,3-cyclopentadienes
(0.3 molar equivalents) of SnCl₄ to the dienophile before introducing the solution of the diene. The results of this investigation are also shown in Table 3. It was concluded that the catalyst had a negligible effect on the diastereofacial outcome of the reaction.
Table 3. Syn : anti facial selectivity for 5-substituted-1,3-cyclopentadienes with 
N-phenylmaleimide, 4-phenyl-1,2,4-triazoline-3,5-dione and tetracyanoethylene
Bracketed ratios indicate reactions in the presence of SnCl₄

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<thead>
<tr>
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<th>N=O-Ph</th>
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<td>Cl</td>
<td>3.7 : 1</td>
<td>1 : 1.4</td>
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<td>100%</td>
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<td>Me</td>
<td>1 : 1.5</td>
<td>3.8 : 1</td>
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</tr>
<tr>
<td>Et</td>
<td>1 : 2.2</td>
<td>2.3 : 1</td>
<td>100%</td>
</tr>
<tr>
<td>n-Bu</td>
<td>1 : 2.8</td>
<td>1.9 : 1</td>
<td>100%</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>5.2 : 1</td>
<td>5.1 : 1</td>
<td>100%</td>
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</table>

46
Discussion

A major problem with the facial selectivities reported in the literature on substituted 1,3-cyclopentadienes is centered around the fact that these results have been derived from isolated studies on single dienes using different dienophiles. Furthermore, there has only been a very limited number of substituted dienes studied. Thus, it has been very difficult to rely on these data as a basis of formulating any hypothesis for the mechanism of facial selectivity in the Diels-Alder reaction.

Table 3 is the most complete series of facial selectivities with substituted 1,3-cyclopentadienes in existence. We have demonstrated the effect, using different dienophiles, of increasing the size of an alkyl or halo group. The results clearly show that both the dienophile and the allylic substituent on the diene have pronounced effects on the diastereofacial outcome of the reaction.

Inagaki recently proposed that the reactivity of the dienophile is directly proportional to the selectivity of the Diels-Alder cycloaddition (Table 1). Our results demonstrate that such a simplistic model cannot be a significant factor in determining facial selectivity: addition of 5-chloro-1,3-cyclopentadiene to NPM, PTAD, and TCNE resulted in syn:anti ratios of 3.7:1, 1:1.4, and 1:2.2, respectively. This clearly shows a decrease and a reversal of the facial selectivity with an increase in the reactivity of the dienophile. Other contradictions to this hypothesis are also prevalent in our investigations on additions with the alkyl-substituted 1,3-cyclopentadienes.
Other groups have linked facial selectivity to stereoelectronic effects in the diene. Such phenomena have been used to explain the preference for syn attack towards O, F and N, however they cannot be extended in a straightforward manner to explain facial selectivity towards larger groups. We postulate that this syn-driving phenomenon for atoms like O, F and N can be extended to include many other atoms, but for steric reasons many of the larger substituents give the anti product. Referring to Table 3, a slight preference for syn-addition to chlorine is observed with NPM. However, bromine, due to its increased size, affords more of the anti product, and iodine gives exclusively the anti diastereomer. This suggests that electronic factors may not play as large a role in influencing facial selectivity as has been previously claimed. Indeed, Halterman's studies showed that a fairly large difference in the electronic nature of the allylic substituent resulted in only a very modest degree of facial selectivity in the Diels-Alder reaction (Scheme 12).

To investigate the presence of any correlation between facial selectivity and the electronic or steric properties of the allylic substituent, the difference in the Gibbs free energy for the syn : anti ratios in Table 3 was plotted against various electronic and physical properties of the substituent on the diene. Molar refractivities, u-values and A-values are included since they have been widely used for the estimation of the spatial requirements of various substituents. A list of van der Waals' radii for the substituents under consideration also provides data of the effective "size" of the group, whereas the electronegativity estimates an electronic property. Table 4 compares these values for cycloadditions with NPM. The molar refractivities of ethyl, n-butyl and methoxymethyl groups do not reflect conformational effects that would likely render the methyl and ethyl rather similar in
Table 4. Plotted data for additions to NPM

<table>
<thead>
<tr>
<th>Atom or group</th>
<th>Ratio with NPM (syn : anti)</th>
<th>ΔΔG⁺ (kcal/mol)</th>
<th>MR* (cm²/mol)</th>
<th>Pauling's Electronegativity (kcal/mol)</th>
<th>n-value</th>
<th>A-value (kcal/mol)</th>
<th>van der Waals' radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>79 : 21</td>
<td>-0.73</td>
<td>5.8</td>
<td>3.03</td>
<td>8.1</td>
<td>0.43</td>
<td>1.75</td>
</tr>
<tr>
<td>Br</td>
<td>15 : 85</td>
<td>0.96</td>
<td>8.7</td>
<td>2.8</td>
<td>9.2</td>
<td>0.38</td>
<td>1.85</td>
</tr>
<tr>
<td>I</td>
<td>100% anti</td>
<td>3.8**</td>
<td>14</td>
<td>2.28</td>
<td>9.9</td>
<td>0.43</td>
<td>1.98</td>
</tr>
<tr>
<td>Me</td>
<td>40 : 60</td>
<td>0.22</td>
<td>5.7</td>
<td>2.3</td>
<td>8.5</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Et</td>
<td>31 : 69</td>
<td>0.44</td>
<td>10.3</td>
<td>2.3</td>
<td>----</td>
<td>1.75</td>
<td>----</td>
</tr>
<tr>
<td>n-Bu</td>
<td>26 : 74</td>
<td>0.58</td>
<td>19.6</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>84 : 16</td>
<td>-0.91</td>
<td>12.1</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

* MR = molar refractivity; **based on a 0.1 : 99.9 ratio

Effective size. This conformational effect is seen in the practical identity of the methyl and ethyl A-values, but the A-values show no difference in "size" for the halogens due to the A-value being effected by the C-X bond length. Thus we have not plotted the data for ethyl, n-butyl and methoxymethyl substituents in Figures 14-17.

A plot of molar refractivity as well as the electronegativity as a function of the difference in the Gibbs free energy for the syn : anti ratios revealed a fairly linear relationship for the halogen substituents and the methyl group (Figures 14 and 16). However, a linear correlation was not observed when the electronegativity and van der Waals' radii were plotted versus the difference in Gibbs free energy for the reaction (Figures 15 and 17). (The A-values showed no correlation with the Gibbs free energy.)

These results readily suggest an hypothesis that, with a simple carbon based dienophile, a steric effect appears to be more important than an electronic one on governing
Figure 14. Plot of molar refractivities as a function of $\Delta \Delta G^\ddagger$ for syn:anti ratios with NPM.

Figure 15. Plot of Pauling's electronegativities as a function of $\Delta \Delta G^\ddagger$ for syn:anti ratios with NPM.
Figure 16. Plot of $n$-values as a function of $\Delta \Delta G^\dagger$ for syn:anti ratios with NPM

Figure 17. Plot of van der Waals' radii as a function of $\Delta \Delta G^\dagger$ for syn:anti ratios with NPM
facial selectivity. Nevertheless, the steric factor is not a straightforward analogy to the axial - equatorial relationships in cyclohexanes (A-values) or on simple "size", because of the lack of correlation with van der Waals' radii. The importance of steric interactions is in agreement with the observation of Breslow that 70, 71, and 72 react with N-phenylmaleimide more slowly than does 1,3-cyclopentadiene itself.

The results obtained with PTAD and TCNE (Tables 5 and 6) showed no correlation between the properties of the allylic substituent and the difference in the Gibbs free energy for the syn : anti ratios of the resulting cycloadditions. This may be due to an added complexity with these dienes. PTAD bears lone pairs on the reacting moiety of the dienophile which might complicate the mechanism by an added electrostatic parameter, and TCNE imposes an overwhelming steric interaction as it comes in contact with a diene due to the larger size of the cyano groups compared to hydrogens.

A detailed investigation into the mechanistic pathway of the Diels-Alder reaction is underway through a comprehensive ab initio computational study being performed in our group by James Xidos in collaboration with Cory Pye and Dr. Ray Poirier. Many of the dienes in both the ground state and their syn and anti transition states (with ethylene as the dienophile) have been fully optimized with the 6-31G* basis set using gradient optimization methods. In spite of the rather simple model for the dienophile, the calculated facial selectivities are similar to the experimental data in Table 3, particularly for the carbon-based dienophile N-phenylmaleimide. In order to identify the factors responsible for facial selectivity, the amount of energy required to deform the diene and the dienophile from the ground state to their syn and anti transition state geometries was calculated. The total
### Table 5. Plotted data for additions to PTAD

<table>
<thead>
<tr>
<th>Atom or group</th>
<th>Ratio with PTAD (syn:anti)</th>
<th>$\Delta \Delta G^2$ (kcal/mol)</th>
<th>MR* (cm$^3$/mol)</th>
<th>Pauling's Electronegativity (kcal/mol)</th>
<th>n-value (kcal/mol)</th>
<th>A-value (kcal/mol)</th>
<th>van der Waal's radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>42:58</td>
<td>0.18</td>
<td>5.8</td>
<td>3.03</td>
<td>8.1</td>
<td>0.43</td>
<td>1.75</td>
</tr>
<tr>
<td>Br</td>
<td>100% anti</td>
<td>3.8**</td>
<td>8.7</td>
<td>2.8</td>
<td>9.2</td>
<td>0.38</td>
<td>1.85</td>
</tr>
<tr>
<td>I</td>
<td>100% anti</td>
<td>3.8**</td>
<td>14</td>
<td>2.28</td>
<td>9.9</td>
<td>0.43</td>
<td>1.98</td>
</tr>
<tr>
<td>Me</td>
<td>79:21</td>
<td>-0.73</td>
<td>5.7</td>
<td>2.3</td>
<td>8.5</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Et</td>
<td>70:30</td>
<td>-0.47</td>
<td>10.3</td>
<td>2.3</td>
<td>---</td>
<td>1.75</td>
<td>---</td>
</tr>
<tr>
<td>n-Bu</td>
<td>66:34</td>
<td>-0.37</td>
<td>19.6</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH$_2$OMe</td>
<td>84:16</td>
<td>-0.91</td>
<td>12.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

*MR = molar refractivity, ** based on a 0.1:99.9 ratio

### Table 6. Plotted data for additions to TCNE

<table>
<thead>
<tr>
<th>Atom or group</th>
<th>Ratio with TCNE (syn:anti)</th>
<th>$\Delta \Delta G^2$ (kcal/mol)</th>
<th>MR* (cm$^3$/mol)</th>
<th>Pauling's Electronegativity (kcal/mol)</th>
<th>n-value (kcal/mol)</th>
<th>A-value (kcal/mol)</th>
<th>van der Waal's radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>31:69</td>
<td>-0.73</td>
<td>5.8</td>
<td>3.03</td>
<td>8.1</td>
<td>0.43</td>
<td>1.75</td>
</tr>
<tr>
<td>Br</td>
<td>100% anti</td>
<td>3.8</td>
<td>8.7</td>
<td>2.8</td>
<td>9.2</td>
<td>0.38</td>
<td>1.85</td>
</tr>
<tr>
<td>I</td>
<td>100% anti</td>
<td>3.8</td>
<td>14</td>
<td>2.28</td>
<td>9.9</td>
<td>0.43</td>
<td>1.98</td>
</tr>
<tr>
<td>Me</td>
<td>100% anti</td>
<td>3.8</td>
<td>5.7</td>
<td>2.3</td>
<td>8.5</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Et</td>
<td>100% anti</td>
<td>3.8</td>
<td>10.3</td>
<td>2.3</td>
<td>---</td>
<td>1.75</td>
<td>---</td>
</tr>
<tr>
<td>n-Bu</td>
<td>100% anti</td>
<td>3.8</td>
<td>19.6</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH$_2$OMe</td>
<td>100% anti</td>
<td>3.8</td>
<td>12.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* MR = molar refractivity, ** based on a 0.1:99.9 ratio
activation energy for each reaction was then compared with the deformation energies of the diene and the dienophile. The dienophile underwent very little deformation at the transition state and consequently displayed only a small range of activation energies. However, the calculated deformation energies for the diene were in a range of 8.9 kJ/mol for the anti transition states. These values were in fact clustered around the activation energy for cyclopentadiene itself (Figure 18). Thus, addition towards the anti-face of an allylically-substituted cyclopentadiene is not that much different energetically than an addition to 1,3-cyclopentadiene (Scheme 20).

Scheme 20. Transition states for 1,3-cyclopentadiene and the anti transition state for a 5-substituted 1,3-cyclopentadiene.

The dienophile and the diene experience essentially the same environment in each case, and the anti substituent that is pointing away on the opposite side of the diene exerts little influence on the reaction. The range of activation energies for the syn transition state was significantly larger, exhibiting a range of 57.9 kJ/mol calculated for various allylic substituents (Figure 19). Furthermore, the diene deformation energies correlated very well with the computed activation energies. This reveals that it must largely be the deformation of the diene that accounts for the range of activation energies observed for the diene bearing
Figure 19: Diene deformation energies as a function of activation energy for syn transition states

\( \text{sym} \cdot \sigma \text{-cyclopentadiene} \) (1 cal = 4.184 J)
Figure 18. Diene deformation energies as a function of activation energy for anti transition states
* anti, ◊ cyclopentadiene (1 cal = 4.184 J)
different substituents. Thus, it appears that direct interactions such as steric effects between the addends have already translated largely into deformation of the diene at the transition state.

A closer look at the diene in its calculated syn transition state reveals that the diene adopts a geometry in which the syn substituent lies close to the plane of the diene moiety and the bond of the C-5 substituent that is anti is almost perpendicular to that plane. The anti bond is lengthened and the syn bond is shortened. The fact that diene deformation energies for syn additions to F, NH₂ and OH are significantly lower than that for 1,3-cyclopentadiene itself indicates that these dienes, deformed into their transition state geometries, are stabilized by these substituents. The mechanism of this stabilization is not clear. While it may be tempting to propose that stabilization could arise from interaction with the coplanar syn substituent, in every case that was studied there was an insignificant difference in hybridization of the allylic group in the syn and anti transition state.

Furthermore, bond orders between the allylic substituent and C-1 or C-4 of the diene were found to be negligible. It has been speculated that syn stabilization may be effected by the fact it should be generally easier to compress the syn C-X bond over the anti C-H bond. However, any such stabilization is offset as the substituent atom becomes larger. More energy is associated with the syn transition state due to the large amount of deformation which the diene must endure to adopt the required transition state geometry. For example, when the substituent is SiH₃, there is a very large (30.9°) angular change about the C-2 - C-1 - C-5 bond angles for the syn transition state and hence syn-addition would be disfavoured.
For the favoured anti transition state the C-2 - C-1 - C-5 bond angles are only distorted by 4.5°.

We compared the computational results with the experimental data from Table 3. The experimental results of cycloadditions with NPM show a slight preference for syn-addition to chlorine whereas additions towards bromine and iodine afford the anti adduct. A slight preference for anti-addition is observed towards methyl which becomes more pronounced as the length of the alkyl chain is increased.

From our studies, we now offer the following hypothesis for the mechanism of facial selectivity in the Diels-Alder reaction: A syn-driving phenomenon, so far unknown in nature, predisposes the diene towards syn-addition, but then steric interactions between the diene and the dienophile induce bending in the diene, which translates into torsional energy mainly in the diene (Scheme 21). With smaller substituents such as chlorine there is not a large amount of steric repulsion between the diene and the dienophile and hence less deformation of the diene results. The syn product is therefore observed. However, if the diene is substituted with a larger group, greater steric interactions between the diene and the dienophile result. This translates into more deformation of the diene and addition anti to larger groups is therefore favoured.

The results for cycloadditions with NPM agree quite well with the computational predictions for facial selectivity calculated using ethylene as the dienophile. This may be because these two dienophiles closely resemble each other with respect to their reacting moieties. Since the simple dienophile that was used computationally is dissimilar to the structures of PTAD and TCNE, the computational predictions cannot be directly used to
Scheme 21. Syn and anti transition states for 1,3-cyclopentadienes substituted with a small and a large allylic substituent
explain the facial selectivities obtained using these dienophiles.

The Diels-Alder additions with PTAD resulted in preferred addition anti to chlorine which increased to exclusively anti-addition with bromo- and iodo-substituted 1,3-cyclopentadienes. Furthermore, in marked contrast to the earlier results with NPM, a propensity for syn-addition was observed towards all alkyl groups which decreased in magnitude as the size of the alkyl chain increased.

The preferred addition anti to heteroatoms can be rationalized on the basis of closed-shell lone-pair lone-pair electrostatic repulsions between the nitrogens on the dienophile and the allylic heteroatom substituent (Scheme 22). This repulsion may result in a significant amount of deformation on the part of the diene in the syn transition state and as a result anti-addition could be expected. However, since the diene bears no substituent on the double bond it should exhibit a smaller steric interaction upon initial contact with an alkyl-substituted diene. This in turn will impart a significantly smaller amount of deformation in the syn transition state than did NPM, and therefore a preference for syn-addition occurs.

Anti-addition is almost exclusively favoured with TCNE. Cycloadditions with this dienophile should experience a significant amount of steric repulsions upon initial contact between the two addends. This is because in contrast to NPM and PTAD, TCNE bears larger cyano groups. As the reacting partners come together, larger steric repulsions between TCNE and the C-5 substituent of the diene force such a large amount of deformation in the diene that the anti pathway is always more favourable.

The addition syn to the methoxymethyl group with NPM has not yet been discussed. It is expected that the conformation of the substituent may be playing a prominent role in
Scheme 22. Disfavored syn transition state for additions of PTAD to 5-hetero-substituted 1,3-cyclopentadienes
determining facial selectivity for this diene. Burnell and Valenta\textsuperscript{15,16} illustrated the importance of this effect in studies on Diels-Alder additions towards bridged-ring cyclopentadienes wherein it was observed that a hydrogen pointing directly at the dienophile imparted a larger steric influence than two hydrogens staggered away from the incoming dienophile (Scheme 7, entries 3 and 4). On the basis of this we expect that the conformer of the allylic alkyl group may be significant. Therefore, for additions of 5-ethyl-1,3-cyclopentadiene to NPM (syn : anti 1 : 2.8) we expect the likely reacting conformers are 49a, 49b, or 49c but not 49d (Scheme 23). Extending this to the methoxymethyl group, we suggest that, in contrast to the likely reacting conformers for 49, the preferred reacting conformer for the methoxymethyl analogue must be 73a. Detailed computational investigations examining the effect of the conformation of the allylic substituent on facial selectivity are in progress. Preliminary results indicate that this phenomenon may influence facial selectivity significantly. The results described in this thesis demonstrate that there is
Scheme 23. Likely reacting conformers for 5-ethyl-1,3-cyclopentadiene and 5-methoxymethyl-1,3-cyclopentadiene.

Also a need for the computational study to be expanded to include structurally different dienophiles. Work in this area is now being undertaken.

Many groups have postulated different mechanisms to account for facial selectivity in Diels-Alder reactions. Phenomena that have been implicated and covered in the introduction of this thesis are: a favourable admixture of the C-5 substituents' lone pair with the LUMO of the syn-adding dienophile, energetically different interactions of a dienophile with a π-system that is facially biased in terms of either electron density or nucleophilicity by a C-5 substituent, dienophile interactions with tilted p-components of the π-orbitals of a plane-nonsymmetric diene, and facially different dipole-dipole or electrostatic interactions.
Such phenomena should be evident at the transition state if they play a significant role in determining facial selectivity. However, no evidence of such interactions has been found at the transition state. Furthermore, Fallis' proposal that facial selectivity is controlled by $\sigma$-donation from the anti-face can be discounted since this mechanism would predict a large range of activation energies for anti-addition.

In summary, $\pi$-facial selectivity for simple plane-nonsymmetric 1,3-cyclopentadiene derivatives is almost entirely the result of the difference in the energetics of distorting the addends, principally the diene. Computational studies into the effect of structurally different dienophiles and the conformation of the allylic substituent on the diene are ongoing.
Experimental

General:

Reactions requiring nonaqueous conditions were performed in high temperature-dried glassware under a positive pressure of nitrogen. All solvents were purified by distillation. Tetrahydrofuran was distilled from sodium metal/benzophenone. Cyclopentadiene was fractionally distilled from dicyclopentadiene and dried over MgSO₄ just prior to use. Cyclopentadienylthallium was purified by sublimation of commercial material. All other reagents were used without purification. Reactions were monitored by thin-layer chromatography using Baker-Flex silica gel plates which were visualized by UV fluorescence, or by spraying with a solution of phosphomolybdic acid, ceric sulphate and sulphuric acid followed by heating. Flash chromatography was performed on Merck type 60 silica gel, 230-400 mesh. Melting points were performed on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Mattson Polaris FT instrument. Nuclear magnetic resonance spectra were obtained on a 300 MHz General Electric 300-NB instrument. The $^1$H NMR shifts were measured relative to tetramethylsilane internal standard. The $^{13}$C NMR shifts were calibrated to the solvent resonance signal. The relative stereochemistry of products was determined from NOE data obtained from a set of interleaved $^1$H experiments (16K) of 8 transients cycled 16 to 32 times through the list of irradiated frequencies. The decoupler was gated on continuous-wave mode for 6 seconds with sufficient attenuation to give a 70-90% reduction in intensity of the irradiated signal. Frequency changes were preceded by a 60 second delay. Four scans were used to equilibrate spins before data acquisition but a relaxation was not applied between scans of
the same frequency. The NOE difference spectra were obtained by zero-filled 32K data
tables to which a 1-2 Hz exponential line broadening was applied. The NOE results are
reported in the following format: δ saturated signal: enhanced signal (% enhancement).
Mass spectral data were obtained from a V.G. Micromass 7070 HS instrument. Gas
chromatography - mass spectra data were acquired on a Hewlett-Packard system (model
5890 gas chromatograph equipped with a 12.5 m or 25 m fused silica capillary column with
cross-linked dimethylsilicone coupled to a Hewlett-Packard model 5980 mass selective
detector). X-ray crystallographic data was collected by using a Rigaku AFC6S
diffractometer by Dr. J. N. Bridson. Elemental analyses was performed by Canadian
Microanalytical Service Ltd., Vancouver, B.C.

Regarding Diels-Alder Reactions:

No diene was isolated because of the well-known tendency of 5-substituted
1,3-cyclopentadienes to undergo 1,5-sigmatropic rearrangement. To the cold solution of a
crude, freshly prepared diene was added a solution of the dienophile. After 12-14 hours
the reaction mixture was washed, dried and concentrated under vacuo. The mass of the
residue was always very similar to the sum of the expected mass of the diene and the
dienophile. The adduct ratios were determined by careful integration of the NMR spectrum
of the crude adduct mixture. In some instances, the adducts were the major component in
the crude mixture, whereas in others there appeared to be considerable amounts of products
of decomposition of the diene along with unreacted dienophile. Not all reactions were
repeated, but in the instances that were carried out many times, e.g. the reactions of 49 and
with N-phenylmaleimide, the adduct ratios proved to be very similar. In many instances the assignment of the relative stereochemistry was carried out on adducts isolated by careful chromatography and crystallization. The emphasis was on obtaining homogeneous materials, so the isolated "yields" quoted below reflect not only the extent of adduct formation but also the ease of purification.
A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with n-butyllithium (2.20 mL, 5.47 mmol) at 0°C and stirred for 10 min. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodomethane (1.54 mL, 24.9 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 1 h, transferred to a separatory funnel and quickly washed with cold brine (2 x 10 mL). N-Phenylmaleimide (0.861 g, 4.97 mmol) was added to the organic layer and the resulting solution was stirred at -20°C for 3 h, washed with water (2 x 10 mL) and dried over anhydrous MgSO₄. Rotary evaporation of the solvent furnished a pale yellow solid. ¹H NMR analysis indicated a 1.5 : 1 ratio for 52 to 51.

Flash chromatography afforded adducts 52 (0.288 g, 23%) and 51 (0.143 g, 11%) as
colorless solids, which were recrystallized from 5% dichloromethane / pentane to give materials homogeneous by NMR.

For 52: mp 133 - 134.5 °C; ir νmax: 2993, 2952, 1713, 1499, 1375, 1182 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.47-7.34 (3H, m, C-3'H, C-4'H, C-5'H), 7.15 (2H, br d, J = 7.0 Hz, C-2'H, C-6'H), 6.30 (2H, apparent t, J = 2.0 Hz, C-5'H, C-6'H), 3.48 (2H, dd, J = 1.6, 2.9 Hz, C-3aH, C-7aH), 3.18 (2H, m, C-4H, C-7H), 2.22 (1H, q, J = 6.8 Hz, C-8H), 0.94 (3H, d, J = 6.8 Hz, C-8Me); NOE results δ: 6.30: 3.18 (4%), 2.22 (1.2%), 3.48: 3.18 (6%), 0.94 (3%), 3.18: 6.30 (5%), 3.48 (4%), 2.22 (8%), 0.94 (0.8%), 2.22: 6.30 (0.7%), 3.18 (2%), 2.22 (5%); ¹³C NMR (CDCl₃) δ: 177.4 (C-1, C-3), 136.3 (C-5, C-6), 131.9 (C-1'), 129.1 (C-3', C-5'), 128.5 (C-4'), 126.6 (C-2', C-6'), 59.1 (C-8), 49.3 (C-4, C-7), 44.0 (C-3a, C-7a), 13.7 (CH₃); ms m/z (%): 253 (M⁺, 21), 239, (1), 173 (31), 145 (2), 129 (6), 106 (8), 91 (2), 80 (100), 65 (6), 51 (5). Exact mass calc. for C₁₆H₁₆NO₂: 253.1102, found: 253.1108.

For 51: mp 129 - 130 °C; ir νmax: 2991, 2907, 1713, 1497, 1380, 1176 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.45-7.33 (3H, m, C-3'H, C-4'H, C-5'H), 7.14 (2H, br d, J = 7.0 Hz, C-2'H, C-6'H), 6.13 (2H, apparent t, J = 1.9 Hz, C-5'H, C-6'H), 3.42 (2H, dd, J = 1.4, 2.9 Hz, C-3aH, C-7aH), 3.23 (2H, m, C-4H, C-7H), 2.22 (1H, q, J = 6.3 Hz, C-8H), 0.91 (3H, d, J = 6.3 Hz, C-8Me); NOE results: 6.13: 3.23 (2%), 0.91 (0.3%), 3.42: 3.23 (3%), 2.22 (7%), 3.23: 6.13 (3%), 3.42 (2%), 2.22 (4%), 0.91 (1.1%), 2.22: 3.42 (4%), 3.23 (2%), 0.91 (1.2%), 0.91: 6.13 (1.1%), 3.23 (3%), 2.22 (5%); ¹³C NMR (CDCl₃) δ: 176.6 (C-1, C-3), 134.7 (C-1'), 131.7 (C-5, C-6), 128.9 (C-3', C-5'), 128.4 (C-4'), 126.5 (C-2', C-6'), 58.5 (C-8), 50.5 (C-4, C-7), 46.0 (C-3a, C-7a), 11.6 (CH₃); ms m/z (%): 253 (M⁺, 20), 239 (1), 217 (10),...
173 (27), 145 (2), 129 (6), 106 (8), 91 (18), 80 (100), 65 (6), 51 (5). Exact mass calc. for C_{16}H_{12}NO₂: 253.1102, found: 253.1110.

(3α, 4α, 7α, 7αα, 8s)-8-Ethyl-3α, 4, 7, 7α-tetrahydro-2-phenyl-4, 7-methano-1H-
isoindole-1, 3-(2H)-dione (53)

and

(3α, 4α, 7α, 7αα, 8t)-8-Ethyl-3α, 4, 7, 7α-tetrahydro-2-phenyl-4, 7-methano-1H-
isoindole-1, 3-(2H)-dione (54)

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with n-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodoethane (0.60 mL, 7.46 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 10 min, transferred to a separatory funnel and quickly washed with cold brine (2 x 10 mL). N-Phenylmaleimide (0.861 g, 4.97 mmol) was added to the organic layer and the resulting solution was stirred at -20°C for 2 h, washed with water (2 x 10 mL) and dried over anhydrous MgSO₄. Rotary evaporation of the solvent afforded a yellow oil. ¹H NMR analysis indicated a 1.8 : 1 ratio for 54 to 53. Flash chromatography afforded adducts 54 (0.298 g, 22%) and 53 (0.136 g, 10%) as colorless solids.
For 54: mp 144 - 145 °C; ir ν_{max}: 2962, 1715, 1536, 1372, 1180 cm⁻¹; ¹H NMR

(CDCl₃) δ: 7.46 - 7.35 (3H, m, C-3'H, C-4'H, C-5'H), 7.13 (2H, br d, J = 7.0 Hz, C-2'H, C-6'H), 6.13 (2H, apparent t, J = 1.7 Hz, C-5'H, C-6'H), 3.42 (2H, dd, J = 1.6, 3.0 Hz, C-3aH, C-7aH), 3.34 (2H, m, C-4H, C-7H), 2.00 (1H, t, J = 7.2 Hz, C-8H), 1.34 (2H, apparent quintet, J = 7.4 Hz, C-8 Et), 0.83 (3H, t, J = 7.5 Hz, C-8 Et); NOE results δ: 6.13: 3.34 (2%), 1.34 (0.5%), 3.42: 6.13 (0.4%), 2.00 (7%), 3.34: 6.13 (3%), 2.00 (4%), 1.34 (1.0%), 0.83 (0.7%), 2.00: 3.42 (4%), 3.34 (2%), 1.34 (1.0%), 0.83 (0.9%), 1.34: 6.13 (1.0%), 3.34 (2%), 2.00 (2%), 0.83 (2%), 0.83: 6.13 (0.2%), 3.34 (2%), 2.00 (2%), 1.34 (2%); ¹³C NMR (CDCl₃): 8:176.7 (C-1, C-3), 134.1 (C-1'), 131.8 (C-5, C-6), 129.0 (C-3', C-5'), 128.5 (C-4'), 126.5 (C-2', C-6'), 66.4 (C-8), 48.6 (C-4, C-7), 45.9 (C-3aH, C-7aH), 19.1 (CH₃CH₂), 12.9 (CH₃CH₂); ms m/z (%): 267 (M⁺, 41), 252 (1), 173 (30), 119 (11), 94 (100), 79 (54), 65 (8), 51 (5). Exact mass calcd. for C₁₇H₁₇NO₂: 267.1258, found: 267.1253.

For 53: mp 124.5 - 125 °C; ir ν_{max}: 2963, 1715, 1563, 1373, 1182 cm⁻¹; ¹H NMR

(CDCl₃) δ: 7.46 - 7.36 (3H, m, C-3'H, C-4'H, C-5'H), 7.15 (2H, br d, J = 7.0 Hz, C-2'H, C-6'H), 6.31 (2H, apparent t, J = 1.9 Hz, C-5'H, C-6'H), 3.42 (2H, dd, J = 1.6, 2.7 Hz, C-3aH, C-7aH), 3.28 (2H, m, C-4H, C-7H), 2.02 (1H, t, J = 7.6 Hz, C-8H), 1.26 (2H, apparent quintet, J = 7.4 Hz, C-8 Et), 0.91 (3H, t, J = 7.5 Hz, C-8 Et); NOE results δ: 6.31: 3.28 (3%), 2.02 (1.4%), 3.42: 3.28 (3%), 1.26 (5%), 3.28: 6.31 (4%), 3.42 (3%), 2.02 (6%), 1.26 (1.0%), 2.02: 6.31 (0.7%), 3.28 (3%), 2.02 (0.9%), 1.26: 3.42 (5%), 3.28 (1.2%), 2.02 (2%), 0.91 (1.2%), 0.91: 3.28 (2%), 2.02 (2%), 1.26 (1.4%); ¹³C NMR

(CDCl₃) δ: 177.3 (C-1, C-3), 136.1 (C-6, C-5), 131.9 (C-1'), 129.0 (C-3', C-5'), 128.5
(C-4'), 126.6 (C-2', C-6'), 66.9 (C-8), 47.4 (C-4, C-7), 44.1 (C-3aH, C-7aH), 21.2
(CH₂CH₃), 11.9 (CH₂CH₃); ms m/z (%): 267 (M⁺, 73), 252 (5), 213 (3), 173 (42), 119 (27),
94 (100), 79 (62), 65 (11), 51 (7). Exact mass calc. for C₁₇H₁₂NO₂: 267.1258, found:
267.1256.

(3α,4α,7α,7αa,8γ)-8-n-Butyl-3α,4,7,7α-tetrahydro-2-phenyl-4,7-methano-1H-
isoindole-1,3-(2H)-dione (55)

(3α,4α,7α,7αa,8γ)-8-n-Butyl-3α,4,7,7α-tetrahydro-2-phenyl-4,7-methano-1H-
isoindole-1,3-(2H)-dione (56)

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (10 mL) under a
nitrogen atmosphere was treated with n-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The
resulting cloudy solution was added dropwise over 15 min to a -20°C solution of
1-iodobutane (2.00 mL, 17.6 mmol) in THF (10 mL) under nitrogen. The reaction mixture
was stirred for a additional 2 h, transferred to a separatory funnel and quickly washed with
cold brine (2 x 10 mL). N-Phenylmaleimide (0.861 g, 4.97 mmol) was added to the organic
layer and the resulting solution was stirred at -20°C overnight, then gradually warmed to rt.
The resulting solution was washed with water (2 x 10 mL) and dried over anhydrous
MgSO₄. Rotary evaporation of the solvent afforded the product. ¹H NMR analysis indicated a 2.8 : 1 ratio for 56 to 55. Flash chromatography afforded adducts 56 (0.356 g, 24%) and 55 (0.111 g, 8%) as colorless solids.

For 56: mp 145 - 146 °C; ir ν_max.: 2983, 2922, 2852, 1713, 1534, 1377, 1169 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.45-7.35 (3H, m, C-3'H, C-4'H, C-5'H), 7.13 (2H, br d, J = 8.6 Hz, C-2'H, C-6'H), 6.13 (2H, apparent t, J = 1.7 Hz, C-5H, C-6H), 3.42 (2H, dd, J = 1.6, 2.9 Hz, C-3aH, C-7aH), 3.33 (2H, m, C-4H, C-7H), 2.07 (1H, t, J = 7.0 Hz, C-8H), 1.28 (6H, m, C-8 CH₂CH₂CH₃), 0.87 (3H, t, J = 7.1 Hz, C-8 CH₂CH₂CH₃); NOE results δ: 6.13: 3.33 (3%), 3.42: 2.07 (9%), 3.33: 6.13 (3%), 2.07 (4%), 1.28 (14%), 0.87 (2%), 2.07: 3.42 (5%), 3.33 (3%), 1.28 (1.2%), 0.87 (1.5%), 1.18: 6.13 (0.8%), 3.33 (2%), 2.07 (3%), 0.87 (2%); ¹³C NMR (CDCl₃) δ: 176.8 (C-1, C-3), 131.9 (C-5, C-6), 129.0 (C-3', C-5'), 128.5 (C-4'), 126.6 (C-2', C-6'), 64.7 (C-8), 48.9 (C-4, C-7), 45.9 (C-3a, C-7a), 30.0 (butyl), 25.8 (butyl), 22.7 (butyl), 14.0 (butyl); ms m/z (%): 295 (M⁺, 13), 239 (1), 173 (14), 122 (14), 119 (12), 91 (21), 80 (100), 65 (5). Exact mass calcd. for C₁₉H₂₁NO₂: 295.1571, found: 295.1565.

For 55: mp 82 - 84 °C; ir ν_max.: 2927, 2885, 1707, 1511, 1389, 1187 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.45-7.36 (3H, m, C-3'H, C-4'H, C-5'H), 7.14 (2H, br d, J = 7.1 Hz, C-2'H, C-6'H), 6.31 (2H, apparent t, J = 2.0 Hz, C-5H, C-6H), 3.43 (2H, dd, J = 1.6, 2.8 Hz, C-3aH, C-7aH), 3.25 (2H, m, C-4H, C-7H), 2.07 (1H, t, J = 6.8 Hz, C-8H), 1.26 (6H, m, C-8 CH₂CH₂CH₂CH₃), 0.91 (3H, t, J = 6.9 Hz, C-8 CH₂CH₂CH₂CH₃); NOE results δ: 6.31: 3.25 (3%), 2.07 (1.0%), 3.43: 3.25 (4%), 1.26 (2%), 3.25: 6.31 (4%), 3.43 (2%), 2.07 (6%), 1.26 (1.0%), 2.07: 6.31 (1.1%), 3.25 (3%), 1.26 (0.9%), 1.26: 3.43 (3%), 3.25
A solution of 1,3-cyclopentadiene (0.20 mL, 2.5 mmol) in THF (10 mL) under a nitrogen atmosphere was treated with n-butyllithium (1.10 mL, 2.73 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodomethane (0.73 mL, 12 mmol) in THF (7.0 mL) under nitrogen. The reaction mixture was stirred for an additional 2 h, transferred to a separatory funnel and quickly washed with cold brine (2 x 10 mL). 4-Phenyl-1,2,4-triazoline-3,5-dione (0.434 g, 2.48 mmol) was added to the organic layer, and the solution was stirred at -20°C overnight, then gradually
warmed to rt. The resulting solution was washed with water (2 x 10 mL) and dried over
anhydrous MgSO₄. Rotary evaporation of the solvent afforded a beige solid. ¹H NMR
analysis indicated a 3.8 : 1 ratio for 57 to 58. Flash chromatography afforded adducts 57
(0.127 g, 20%) and 58 (0.057 g, 9%) as colorless solids.

For 57: mp 140 - 141 °C; ir ν max: 3073, 1724, 1503, 1395, 1248, 1133 cm⁻¹; ¹H NMR
(CDCl₃) δ: 7.47-7.33 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.47 (2H, apparent t, J
= 1.9 Hz, C-6H, C-7H), 4.77 (2H, dd, J = 1.5, 3.1 Hz, C-5H, C-8H), 2.36 (1H, q, J = 6.5
Hz, C-10H), 1.21 (3H, d, J = 6.5 Hz, C-10 CH₃); NOE results δ: 6.47: 4.77 (5%), 2.36
(2%), 4.77: 6.47 (5%), 2.36 (10%), 1.21 (1.4%), 2.36: 6.47 (2%), 4.77 (6%), 1.21 (0.9%),
1.21: 4.77 (2%), 2.36 (4%); ¹³C NMR (CDCl₃) δ: 159.1 (C-1, C-3), 132.9 (C-6, C-7),
131.4 (C-1'), 129.1 (C-3', C-5'), 128.3 (C-4'), 125.5 (C-2', C-6'), 68.3 (C-5, C-8), 55.9
(C-10), 12.8 (C-10 CH₃); ms m/z (%): 255 (M⁺, 21), 240 (1), 214 (2), 177 (5), 121 (15),
119 (55), 91 (24), 80 (100), 77 (21), 64 (15), 51 (13). Exact mass calcd. for C₁₉H₁₄N₂O₂:
255.1007, found: 255.1012.

For 58: mp 126 -127.5 °C; ir ν max: 2989, 1725, 1491, 1397, 1235, 1129 cm⁻¹; ¹H NMR
(CDCl₃) δ: 7.48-7.32 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.37 (2H, apparent t, J
= 1.8 Hz, C-6H, C-7H), 4.86 (2H, dd, J = 1.7, 3.2 Hz, C-5H, C-8H), 2.86 (1H, q, J = 6.5
Hz, C-10H), 0.96 (3H, d, J = 6.5 Hz, C-10 CH₃); NOE results δ: 6.37: 4.86 (4%), 0.96
(0.7%), 4.86: 6.37 (3%), 2.86 (7%), 0.96 (1.3%), 2.86: 4.86 (4%), 0.96 (2%), 0.96: 6.37
(2%), 4.86 (5%), 2.86 (11%); ¹³C NMR (CDCl₃) δ: 158.6 (C-1, C-3), 135.4 (C-6, C-7),
131.2 (C-1'), 129.1 (C-3', C-5'), 128.3 (C-4'), 125.5 (C-2', C-6'), 68.9 (C-5, C-8), 54.6
(C-10), 10.9 (C-10CH₃); ms m/z (%): 255 (M⁺, 8), 240 (1), 214 (1), 177 (9), 121 (18), 119
(52), 91 (24), 79 (100), 77 (26), 64 (16), 51 (14). Exact mass calcd. for C_{14}H_{13}N_{3}O_{2}:
255.1007, found: 255.0998.

A solution of 1,3-cyclopentadiene (0.34 mL, 4.3 mmol) in THF (10 mL) under a nitrogen atmosphere was treated with n-butyllithium (1.89 mL, 4.71 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodoethane (1.71 mL, 21.4 mmol) in THF (7.0 mL) under nitrogen. The reaction mixture was stirred for an additional 40 min, transferred to a separatory funnel and quickly washed with cold brine (2 x 10 mL). 4-Phenyl-1,2,4-triazoline-3,5-dione (0.750 g, 4.28 mmol) was added to the organic layer, and the solution was stirred at -20°C overnight, then gradually warmed to rt. The resulting solution was washed with water (2 x 10 mL) and dried over anhydrous MgSO_{4}. Rotary evaporation of the solvent afforded a yellow oil. \(^1\)H NMR analysis indicated
a 2.3 : 1 ratio for 55 . Flash chromatography afforded adducts 59 (0.161 g, 14%) and 
60 (0.053 g, 5%).

For 59: mp 108.5 - 109 °C; ir ν max: 2971, 1724, 1502, 1400, 1252, 1135 cm⁻¹; 
¹H NMR (CDCl₃) δ: 7.44-7.32 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.44 (2H, 
apparent t, J = 1.9 Hz, C-6H, C-7H), 4.82 (2H, dd, J = 1.5, 3.1 Hz, C-5H, C-8H), 2.11 
(1H, t, J = 7.2 Hz, C-10H), 1.57 (2H, m, C-10 CH₂CH₃), 0.95 (3H, t, J = 7.3 Hz, C-10 
CH₂CH₃); NOE results δ: 6.44 : 4.82 (6%), 2.11 (3%), 4.82 : 6.44 (7%), 2.11 (13%), 1.57 
(2%), 0.95 (1.4%), 2.11 : 6.44 (1.4%), 4.82 (6%), 1.57 (2%), 1.57 : 4.82 (3%), 2.11 (5%), 
0.95 (2%), 0.95 : 4.82 (3%), 2.11 (4%), 1.57 (3%); ¹³C NMR (CDCl₃) δ: 158.7 (C-1, C-3), 
132.4 (C-6, C-7), 131.1 (C-1'), 128.8 (C-3', C-5'), 128.0 (C-4'), 125.2 (C-2', C-6'), 66.3 
(C-5, C-8), 63.0 (C-10), 20.0 (C-10 CH₂CH₃), 11.5 (C-10 CH₂CH₃); ms m/z (%): 269 (M⁺, 
11), 240 (2), 214 (1), 177 (2), 120 (13), 119 (48), 94 (42), 79 (100), 77 (36), 65 (16), 51 
(13). Exact mass calcd. for C₁₅H₁₅N₃O₂: 269.1163, found: 269.1156.

For 60: mp 105 - 106 °C; ir ν max: 2963, 1725, 1501, 1395, 1232, 1130 cm⁻¹; 
¹H NMR (CDCl₃) δ: 7.46-7.32 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.35 (2H, apparent t, J 
= 1.6 Hz, C-6H, C-7H), 4.92 (2H, dd, J = 1.6, 3.2 Hz, C-5H, C-8H), 2.68 (1H, t, J = 7.6 
Hz, C-10H), 1.30 (2H, m, C-10 CH₂CH₃), 0.89 (3H, t, J = 7.4 Hz, C-10 CH₂CH₃); NOE 
results δ: 6.35 : 4.92 (6%), 1.30 (0.8%), 4.92 : 6.35 (6%), 2.68 (9%), 1.30 (2%), 0.89 (2%), 
2.68 : 4.92 (5%), 1.30 (2%), 0.89 (1.2%), 1.30 : 6.35 (2%), 4.92 (3%), 2.68 (5%), 0.89 
(1.3%), 0.89 : 6.35 (0.8%), 4.92 (4%), 2.68 (5%), 1.30 (2%); ¹³C NMR (CDCl₃) δ: 158.5 
(C-1, C-3), 131.1 (C-1'), 129.2 (C-6, C-7), 129.0 (C-3', C-5'), 128.2 (C-4'), 125.4 (C-2', 
C-6'), 67.4 (C-5, C-8), 61.3 (C-10), 18.7 (C-10 CH₂CH₃), 12.2 (C-10 CH₂CH₃); ms m/z
Exact mass calc. for C_{11}H_{11}N_{2}O_{2}: 269.1163, found: 269.1168.

\[(\text{10r})-10-n\text{-Butyl}-5,8\text{-dihydro-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]-pyridizine-1,3-} (2H)\text{-dione (61)}\]

and

\[(\text{10s})-10-n\text{-Butyl}-5,8\text{-dihydro-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]-pyridizine-1,3-} (2H)\text{-dione (62)}\]

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with \(n\)-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of 1-iodobutane (2.00 mL, 17.6 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 2 h, transferred to a separatory funnel and quickly washed with cold brine (2 x 10 mL). 4-Phenyl-1,2,4-triazoline-3,5-dione (0.871 g, 4.97 mmol) was added to the organic layer, and the solution was stirred at -20°C overnight, then gradually warmed to rt. The resulting solution was washed with water (2 x 10 mL) and dried over anhydrous MgSO_{4}. Rotary evaporation of the solvent afforded a yellow oil. \(^1\)H NMR analysis indicated a 2.0 : 1 ratio for 61 to 62. Flash chromatography afforded adducts 61
(0.461 g, 31%) and 62 (0.265 g, 18%), which were recrystallized from 20% dichloromethane/hexane to yield colorless crystals.

For 61: mp 85.5 - 86 °C; ir νmax: 2961, 2929, 1779, 1726, 1502, 1394, 1251, 1018 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.46-7.35 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.48 (2H, apparent t, J = 1.9 Hz, C-6'H, C-7'H), 4.85 (2H, dd, J = 1.8, 3.3 Hz, C-5'H, C-8'H), 2.21 (1H, t, J = 7.1 Hz, C-10H), 1.59 (2H, m, C-10 CH₂CH₂CH₂CH₃), 1.35 (4H, m, C-10 CH₂CH₂CH₂CH₃), 0.93 (3H, t, J = 6.8 Hz, C-10CH₂CH₂CH₂CH₃); NOE results δ: 6.48: 4.85 (3%), 2.21 (0.3%), 4.85: 6.48 (5%), 2.21 (5%), 1.59 (0.7%), 1.35 (0.8%), 2.21: 6.48 (1.0%), 4.85 (4%), 1.59 (0.9%), 1.35 (0.5%), 1.59: 4.85 (2%), 2.21 (3%), 1.35 (0.6%), 1.35: 4.85 (2%), 2.21 (3%), 1.59 (1.2%), 0.93 (2%), 0.93: 1.35 (1.1%); ¹³C NMR (CDCl₃) δ: 159.0 (C-1, C-3), 132.6 (C-6, C-7), 131.3 (C-1'), 129.0 (C-3', C-5'), 128.3 (C-4'), 125.5 (C-2', C-6'), 66.8 (C-10), 61.7 (C-5, C-8), 29.5 (butyl), 26.8 (butyl), 22.5 (butyl), 13.9 (butyl); ms m/z (%): 297 (M⁺, 8), 254 (3), 241 (2), 178 (2), 135 (4), 119 (47), 91 (33), 80 (100), 66 (19), 51 (11), 41 (11). Exact mass calcd. for C₁₁₇₁₇₁₇₁₇₁₇:o: 297.1476, found: 297.1473.

For 62: mp 74 - 75 °C; ir νmax: 2959, 2931, 1775, 1725, 1502, 1234, 1017 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.46-7.34 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.35 (2H, m, C-6H, C-7'H), 4.92 (2H, dd, J = 1.8, 3.5 Hz, C-5'H, C-8'H), 2.75 (1H, m, C-10H), 1.27 (6H, m, C-10 CH₂CH₂CH₂CH₃), 0.89 (3H, t, J = 7.0 Hz, C-10CH₂CH₂CH₂CH₃); NOE results δ: 6.35: 4.92 (3%), 1.27 (0.1%), 4.92: 6.31 (4%), 2.75 (5%), 1.27 (0.9%), 2.75: 4.92 (4%), 1.27 (1.0%), 1.27: 6.31 (3%), 4.92 (4%), 1.27 (1.0%), 1.27: 6.31 (3%), 4.92 (8%), 2.75 (11%), 0.89 (3%), 0.89: 1.27 (1.0%); ¹³C NMR (CDCl₃) δ: 158.6 (C-1, C-3), 131.2 (C-1'), 78
129.2 (C-6, C-7), 129.1 (C-3', C-5'), 128.3 (C-4'), 125.4 (C-2', C-6'), 67.8 (C-10), 59.8 (C-5, C-8), 30.1 (butyl), 25.3 (butyl), 22.5 (butyl), 13.8 (butyl); ms m/z (%): 297 (M⁺, 2), 254 (1), 240 (1), 135 (2), 119 (41), 93 (11), 79 (100), 66 (19), 51 (12), 41 (10). Exact mass calcd. for C₁₇H₁₉N₃O₂: 297.1476, found: 297.1489.

(7s)-7-Methyl-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (63)

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with n-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodomethane (1.54 mL, 24.9 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 40 min, transferred to a separatory funnel and quickly washed with cold brine (2 x 15 mL). Tetracyanoethylene (0.637 g, 4.97 mmol) was added to the organic layer, and the solution was stirred at -20°C overnight, then gradually warmed to rt. The resulting solution was washed with water (2 x 15 mL) and dried over anhydrous MgSO₄. Rotary evaporation of the solvent afforded a yellow, oily semi-solid. ¹H NMR analysis indicated 100% anti addition to give 63. Flash chromatography afforded adduct 63 (0.766 g, 74%) as a light grey solid, which was recrystallized from 40% dichloromethane/ethyl acetate to give 63 as a colorless solid, homogeneous by NMR: mp 193 - 194 °C; ir
\[ \nu_{\text{max}}: 2933, 2968, 2252, 1581, 1452, 1336, 1259 \text{ cm}^{-1}; \quad ^1H \text{ NMR (CD}_2\text{COCD}_2) \delta: 6.67 (2H, apparent t, }J = 1.9 \text{ Hz, C-}5\text{H, C-}6\text{H), 4.16 (2H, dd, }J = 1.6, 3.3 \text{ Hz, C-}1\text{H, C-}4\text{H), 2.80 (1H, m, C-}7\text{H), 1.12 (3H, d, }J = 6.3 \text{ Hz, C-}7\text{CH}_3); \text{ NOE results } \delta: 6.67: 4.16 (5\%), 2.80 (0.5\%), 1.12 (0.5\%), 4.16: 6.67 (5\%), 2.80 (6\%), 1.12 (1.1\%), 2.80: 4.16 (3\%), 1.12 (2\%), 1.12: 6.67 (1.4\%), 4.16 (4\%), 2.80 (8\%); ^{13}C \text{ NMR (CD}_2\text{COCD}_2) \delta: 136.8 (C-5, C-6), 114.3 (C-2\text{CN, C-}3\text{CN}), 113.3 (C-2\text{CN, C-}3\text{CN}), 61.5 (C-1, C-4), 54.8 (C-7), 11.9 (C-}7\text{CH}_3); \text{ ms m/z } (\%): \text{ no } M^+, 180 (5), 155 (2), 143 (3), 128 (41), 102 (5), 80 (100), 79 (70), 77 (22), 76 (46), 65 (8), 51 (12), 50 (11). \text{ Anal. calcd for C}_{12}\text{H}_{12}\text{N}_4: C 69.22, H 3.87, N 26.91; \text{ found: C 69.22, H 3.85, N 27.18.}

(7s)-7-Ethyl-2,2,3,3,-tetracyanobicyclo[2.2.1]hepta-5-ene (64)

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with \( \mu \)-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of iodoethane (1.98 mL, 24.9 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 40 min, transferred to a separatory funnel and quickly washed with cold brine (2 x 15 mL). Tetracyanoethylene (0.637 g, 4.97 mmol) was added to the organic layer and the solution was stirred at -20°C overnight, then gradually warmed to rt. The resulting
solution was washed with water (2 x 15 mL) and dried over anhydrous MgSO₄. Rotary evaporation of the solvent afforded an oily semi-solid. ¹H NMR analysis indicated 100% anti addition to give 64. The crude product was dissolved in hot methanol, filtered through a small portion of charcoal and recrystallized upon cooling to yield 64 (0.744 g, 67%) as colorless crystals upon cooling: mp 175.5 - 176 °C; ir ν max: 3097, 2976, 2251, 1579, 1450, 1381, 1343, 1256, 1142 cm⁻¹; ¹H NMR (CD₂COCD₃) δ: 6.68 (2H, apparent t, J = 1.9 Hz, C-5H, C-6H), 4.25 (2H, apparent s, C-1H, C-4H), 2.55 (1H, t, J = 6.9 Hz, C-7H), 2.05 (2H apparent quintet, J = 7.3 Hz, C-7CH₂CH₃), 0.96 (3H, t, J = 7.5 Hz, C-7CH₂CH₃); NOE results δ: 6.68: 4.25 (4%), 2.05 (0.4%), 4.25: 6.68 (5%), 2.55 (7%), 2.05 (1.3%), 0.96 (1.2%), 2.55: 4.25 (3%), 2.05 (2%), 0.96 (0.8%), 2.05: 6.68 (0.8%), 4.25 (2%), 2.55 (6%), 0.96: 4.25 (0.9%), 2.55 (3%); ¹³C NMR (CD₂COCD₃) δ: 136.8 (C-5, C-6), 114.2 (C-2CN, C-3CN), 113.3 (C-2CN, C-3CN), 62.0 (C-7), 60.0 (C-1, C-4), 20.2 (C-7CH₂CH₃), 13.3 (C-7CH₂CH₃); ms m/z (%): no M⁺, 194 (2), 180 (2), 167 (2), 140 (2), 128 (61), 102 (7), 94 (63), 93 (11), 91 (12), 79 (100), 77 (42), 76 (68), 65 (11), 51 (11), 50 (10). Anal. calcd. for C₁₅H₁₀N₄: C 70.26, H 4.54, N 25.21; found: C 70.02, H 4.48, N 25.12.
(7s)-7-n-Butyl-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (65)

A solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in THF (15 mL) under a nitrogen atmosphere was treated with n-butyllithium (2.20 mL, 5.47 mmol) at 0°C. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of 1-iodobutane (1.98 mL, 24.9 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred for an additional 40 min, transferred to a separatory funnel and quickly washed with cold brine (2 x 15 mL). Tetracyanoethylene (0.637 g, 4.97 mmol) was added to the organic layer, and the solution was stirred at -20°C overnight, then gradually warmed to rt. The resulting solution was washed with water (2 x 15 mL) and dried over anhydrous MgSO₄. Rotary evaporation of the solvent afforded a brown oily solid. ¹H NMR analysis indicated 100% anti addition to give 65. The crude product was dissolved in hot dichloromethane / pentane, filtered through a small portion of charcoal and recrystallized upon cooling to yield 65 (0.742 g, 59%) as colorless crystals: mp 131 - 132.5 °C; ir ν_max:

2964, 2923, 2861, 2250, 1451, 1340 cm⁻¹; ¹H NMR (CD₂COCD₃) δ: 6.68 (2H, m, C-5H, C-6H), 4.24 (2H, dd, J = 1.5, 3.2 Hz, C-1H, C-4H), 2.61 (1H, apparent t, J = 6.9 Hz, C-7H), 1.50 (2H, m, C-7CH₂CH₂CH₂CH₃), 1.32 (4H, m, C-7CH₂CH₂CH₂CH₃), 0.89 (3H, t, C-7CH₂CH₂CH₂CH₃); NOE results δ: 6.68: 4.24 (3%), 1.50 (0.5%), 4.24: 6.68 (3%), 2.61 (4%), 1.50 (1.2%), 1.32 (0.8%), 2.61: 4.24 (3%), 1.50 (2%), 1.32 (0.7%), 1.50: 6.68 (1.3%), 4.24 (4%), 2.61 (7%), 1.32: 6.68 (0.5%), 4.24 (4%), 2.61 (7%), 0.89 (2%), 0.89: 1.32 (1.3%); ¹³C NMR (CD₂COCD₃) δ: 136.4 (C-5, C-6), 113.8 (C-2CN, C-3CN), 112.8 (C-2CN, C-3CN), 59.8 (C-7), 59.7 (C-1, C-4), 47.9 (C-2, C-3), 31.0 (C-7 butyl), 26.0 (C-7 butyl), 23.1 (C-7 butyl), 14.2 (C-7 butyl); ms m/z (%): no M⁺, 129 (9), 128 (100), 102 (9),
Anal. calcd. for \( \text{C}_{15}\text{H}_{14}\text{N}_{2} \): C 71.98, H 5.64, N 22.38; found: C 71.69, H 5.44, N 22.38.

\[(3\alpha, 4\alpha, 7\alpha, 7\alpha\alpha, 8s)-8\text{-Chloro-3}\alpha, 4, 7, 7\alpha\text{-tetrahydro-2-phenyl-4,7-methano-1}\text{H}-\text{isoindole-1,3-}(2\text{H})\text{-dione (74)}\]

\[(3\alpha\alpha, 4\alpha, 7\alpha, 7\alpha\alpha, 8\alpha)-8\text{-Chloro-3}\alpha, 4, 7, 7\alpha\text{-tetrahydro-2-phenyl-4,7-methano-1}\text{H}-\text{isoindole-1,3-}(2\text{H})\text{-dione (75)}\]

A solution of cyclopentadienylthallium (0.576 g, 2.14 mmol) and \( N \)-chlorosuccinimide (0.293 g, 2.14 mmol) in diethyl ether (20 mL) under nitrogen was immersed in an ice bath and stirred for 1 hour. The resulting suspension was filtered through a glass wool plug on sintered glass into a solution of \( N \)-phenylmaleimide (0.370 g, 2.14 mmol) in benzene (10 mL). The reaction mixture was returned to the ice bath and stirred overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a cream-colored solid. \(^{1}\text{H NMR analysis indicated a 3.7} : 1\text{ ratio for 74 to 75. Flash chromatography afforded adducts 74 (0.216 g, 37\%)}\) and 75 (0.074 g, 13\%) as colorless solids. The sample of adduct 74
contained a small amount of N-phenylmaleimide so it was recrystallized from 40% ethyl acetate / hexane to give an analytical sample that was homogenous by NMR.

For 74: mp 166 - 167.5 °C; IR \( \nu_{max} \): 3015, 3063, 1711, 1495, 1380, 1186 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \): 7.44 - 7.37 (3H, m, C-3'H, C-4'H, C-5'H), 7.14 (2H, br d, J = 8.2 Hz, C-2'H, C-6'H), 6.32 (2H, apparent t, J = 2.1 Hz, C-5H, C-6H), 4.07 (1H, m, C-8H), 3.81 (2H, dd, J = 1.6, 3.0 Hz, C-3aH, C-7aH), 3.48 (2H, m, C-4H, C-7H); NOE results \( \delta \): 6.32: 4.07 (1.3%), 3.48 (3%), 4.07: 6.31 (0.7%), 3.48 (3%), 3.81: 3.48 (4%), 3.48: 6.32 (3%), 4.07 (7%), 3.81 (4%); \(^13\)C NMR (CDCl\(_3\)) \( \delta \): 176.1 (C-1, C-3), 134.7 (C-5, C-6), 131.7 (C-1), 129.1 (C-3', C-5'), 128.7 (C-4'), 126.5 (C-2', C-6'), 70.7 (C-8), 50.3 (C-4, C-7), 43.7 (C-4a, C-7a); ms \( m/z \) (%): 273 (M\(^+\), 85), 238 (6), 210 (5), 173 (89), 145 (16), 129 (55), 119 (100), 103 (22), 91 (82), 65 (67), 54 (45), 50 (26). Exact mass calcd. for \( C_{13}H_{12}^{\text{13}}\text{CINO}_2 \): 273.0556, found: 273.0547.

For 75: mp 169.5 - 171 °C; IR \( \nu_{max} \): 3071, 3003, 1719, 1562, 1498, 1375, 1266, 1179 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \): 7.47 - 7.38 (3H, m, C-3'H, C-4'H, C-5'H), 7.14 (2H, br d, J = 6.9 Hz, C-2'H, C-6'H), 6.26 (2H, m, C-5H, C-6H), 4.06 (1H, m, C-8H), 3.64 (2H, m, C-4H, C-7H), 3.49 (2H, dd, J = 1.6, 3.0 Hz, C-3aH, C-7aH); NOE results \( \delta \): 6.26: 3.64 (3%), 4.06: 3.64 (3%), 3.64 (4%), 3.64: 6.13 (3%), 4.06 (4%), 3.49 (1.3%), 3.49: 4.06 (10%), 3.64 (4%); \(^13\)C NMR (CDCl\(_3\)) \( \delta \): 174.9 (C-1, C-3), 131.6 (C-5, C-6), 129.2 (C-3', C-5'), 128.8 (C-4'), 126.5 (C-2', C-6'), 72.5 (C-8), 51.5 (C-4, C-7), 42.8 (C-4a, C-7a); ms \( m/z \) (%): 273 (M\(^+\), 74), 238 (4), 210 (3), 173 (100), 145 (6), 129 (23), 119 (33), 100 (15), 77 (11), 65 (24), 54 (13). Exact mass calcd. for \( C_{13}H_{12}^{\text{13}}\text{CINO}_2 \): 273.0556, found: 273.0549.
(3α,4α,7α,7α,8α)-8-Bromo-3α,4,7α-tetrahydro-2-phenyl-4,7-methano-1H-isooindole-1,3-(2H)-dione (76) and
(3α,4α,7α,7α,8α)-8-Bromo-3α,4,7α-tetrahydro-2-phenyl-4,7-methano-1H-isooindole-1,3-(2H)-dione (77)

A solution of cyclopentadienylthallium (0.930 g, 3.45 mmol) and N-bromosuccinimide (0.614 g, 3.45 mmol) in diethyl ether (35 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of N-phenylmaleimide (0.597 g, 3.45 mmol) in benzene (15 mL). The combined solutions were returned to the ice bath and to stirred overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a pale yellow solid. \(^1\)H NMR analysis indicated a 5.2 : 1 ratio for 77 to 76. Flash chromatography afforded adducts 77 (0.581 g, 53%) and 76 (0.024 g, 2%) as colorless solids, which were recrystallized from 17% dichloromethane / hexane to afford samples that were homogeneous by NMR.

For 76: mp 194.5 - 196 °C; \(\nu_{\text{max}}\) : 3063, 1714, 1594, 1497, 1377, 1185 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 7.47 - 7.37 (3H, m, C-3'H, C-4'H, C-5' H), 7.14 (2H, br d, \(J = 7.0\) Hz, C-2'H, C-6'H), 6.32 (2H, apparent t, \(J = 2.2\) Hz, C-5'H, C-6'H), 4.15 (1H, s, C-8'H), 3.88
(2H, dd, J = 0.8, 2.5 Hz, C-3aH, C-7aH), 3.53 (2H, m, C-4H, C-7H); NOE results δ: 6.32: 4.15 (1.5%), 3.53 (3%), 4.15: 6.32 (0.6%), 3.53 (3%), 3.88: 3.53 (4%), 3.53: 6.32 (3%), 4.15 (6%), 3.88 (4%); 13C NMR (CDCl3) δ: 176.2 (C-1, C-3), 135.2 (C-5, C-6), 131.6 (C-1'), 129.1 (C-3', C-5'), 128.8 (C-4'), 126.5 (C-2', C-6'), 61.4 (C-8), 50.7 (C-4, C-7), 44.0 (C-3a, C-7a); ms m/z (%): 319 (23) and 317 (24) both M⁺, 174 (23), 173 (100), 144 (7), 129 (16), 119 (11), 91 (33), 65 (32), 54 (10). Exact mass calcd. for C11H12BrNO2 (M⁺ - Br): 238.0867, found: 238.0862.

For 77: mp 188 - 189 °C; ir νmax: 3063, 1716, 1594, 1497, 1377, 1185 cm⁻¹; 1H NMR (CDCl3) δ: 7.47 - 7.37 (3H, m, C-3'H, C-4'H, C-5'H), 7.13 (2H, br d, J = 7.0 Hz, C-2'H, C-6'H), 6.26 (2H, apparent t, J = 1.8 Hz, C-5'H, C-6'H), 4.06 (1H, s, C-8H), 3.66 (2H, m, C-4H, C-7H), 3.47 (2H, dd, J = 1.4, 2.9 Hz, C-3aH, C-7aH); NOE results δ: 6.26: 3.66 (3%), 4.06: 3.66 (3%), 3.47 (5%), 3.66: 6.26 (4%), 4.06 (5%), 3.47 (3%), 3.47: 4.06 (9%), 3.66 (4%); 13C NMR (CDCl3) δ: 174.8 (C-1, C-3), 132.5 (C-5, C-6), 131.5 (C-1'), 129.2 (C-3', C-5'), 128.9 (C-4'), 126.4 (C-2', C-6'), 63.2 (C-8), 51.9 (C-4, C-7), 42.8 (C-3a, C-7a); ms m/z (%): 319 (63) and 317 (66) both M⁺, 239 (19), 173 (100), 146 (5), 129 (11), 91 (12), 65 (33), 54 (36), 51 (17). Exact mass calcd. for C11H12BrNO2 (M⁺ - Br): 238.0867, found: 238.0863.
A solution of cyclopentadienyllithium (0.200 g, 0.742 mmol) and N-iodosuccinimide (0.167 g, 2.04 mmol) in diethyl ether (15 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of N-phenylmaleimide (0.129 g, 0.742 mmol) in benzene (10 mL). The combined solutions were returned to the ice bath and stirred overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a pale yellow solid. \(^1\)H NMR analysis indicated 100% anti addition. (The structure was confirmed by X-ray analysis as 78.) Flash chromatography afforded adduct 78 (0.120 g, 41%) as a beige solid. Adduct 78 was recrystallized from 25% hexane/dichloromethane to give a colorless crystals: mp 211 - 212.5 °C; \(\nu_{\text{max}}\): 1707, 1377, 1177 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 7.47 - 7.38 (3H, m, C-3'H, C-4'H, C-5'H), 7.11 (2H, br d, \(J = 6.9\) Hz, C-2'H, C-6'H), 6.29 (2H, apparent t, \(J = 1.8\) Hz, C-5'H, C-6'H), 4.03 (1H, br s, C-8'H), 3.69 (2H, m, C-4'H, C-7'H), 3.57 (2H, dd, \(J = 1.5, 2.9\) Hz, C-3a'H, C-7a'H); NOE results \(\delta\): 6.29: 3.69
(4%), 4.04: 3.69 (3%), 3.57 (6%), 3.69: 6.29 (4%), 4.03 (5%), 3.69: 3.69 (2%), 3.57: 4.03 (11%), 3.69 (5%); $^{13}$C NMR (CDCl$_3$) $\delta$: 174.6 (C-1, C-3), 134.3 (C-5, C-6), 131.4 (C-1'), 129.1 (C-3', C-5'), 128.8 (C-4'), 126.4 (C-2', C-6'), 53.1 (C-4, C-7), 42.6 (C-3a, C-7a), 41.0 (C-8); ms m/z (%): 365 (M$^+$, 33), 238 (39), 210 (17), 192 (41), 173 (48), 145 (3), 129 (16), 119 (16), 95 (11), 91 (65), 77 (16), 69 (39), 65 (100), 57 (43). Exact mass calc. for C$_{11}$H$_{12}$INO$_2$ (M$^+$ - 1): 238.0868, found: 238.0859.

(3α,4α,7α,7α,8s)-3α,4,7,7a-Tetrahydro-8-methoxymethyl-2-phenyl-4,7-methano-1H-isooindole-1,3-(2H)-dione (79) and
(3α,4α,7α,7α,8r)-3α,4,7,7a-Tetrahydro-8-methoxymethyl-2-phenyl-4,7-methano-1H-isooindole-1,3-(2H)-dione (80)

A suspension of cyclopentadienylthallium (0.750 g, 2.78 mmol) in THF (1.5 mL) at -20°C under nitrogen was treated with chloromethoxymethane (0.42 mL 5.56 mmol) and stirred for 5 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of N-phenylmaleimide (0.481 g, 2.78 mmol) in ethyl ether (5 mL). The combined solutions were stirred at -20°C overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a yellow solid. $^1$H NMR analysis indicated a 5.0 : 1 ratio for
79 to 80. Flash chromatography afforded adducts 79 (0.197 g, 25%) and 80 (0.065 g, 9%) as colorless solids.

For 79: mp 113.5 - 114 °C; ir νmax: 3014, 2893, 1714, 1496, 1376, 1183 cm⁻¹; ¹H NMR (C₆D₆) δ: 7.37 - 7.14 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 5.94 (2H, apparent t, J = 1.9 Hz, C-5'H, C-6'H), 3.01 (2H, m, C-4'H, C-7'H), 2.98 (3H, s, C-8 CH₂OCH₃), 2.66 (2H, dd, J = 1.3, 2.8 Hz, C-3aH, C-7aH), 2.59 (2H, d, J = 7.4 Hz, C-8 CH₂OCH₃), 2.04 (1H, t, J = 7.4 Hz, C-8H); NOE results δ: 5.94: 3.01 (5%), 2.04 (2%), 2.66: 3.01 (5%), 2.98 (2%), 2.04: 5.94 (1.3%), 3.01 (5%); ¹³C NMR (C₆D₆) δ: 176.2 (C-1, C-3), 136.3 (C-5, C-6), 133.6 (phenyl), 129.2 (phenyl), 128.7 (phenyl), 70.9 (C-4, C-7), 63.9 (C-3a, C-7a), 59.1 (C-8), 46.8 (C-8 CH₂OCH₃), 44.6 (C-8 CH₂OCH₃); ms m/z (%): 283 (M⁺, 17), 251 (3), 210 (1), 186 (4), 173 (28), 129 (10), 119 (11), 110 (22), 103 (10), 91 (29), 78 (21), 65 (16), 45 (100). Exact mass calcd. for C₁₇H₁₇NO₃: 283.1207, found: 283.1208.

For 80: mp 118.5 - 119 °C; ir νmax: 2922, 1703, 1495, 1380, 1167 cm⁻¹; ¹H NMR (C₆D₆) δ: 7.33 - 7.13 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 5.78 (2H, apparent t, J = 1.7 Hz, C-5'H, C-6'H), 3.07 (2H, m, C-4'H, C-7'H), 2.96 (3H, s, C-8 CH₂OCH₃), 2.85 (2H, d, J = 7.0 Hz, C-8 CH₂OCH₃), 2.65 (2H, dd, J = 1.2, 2.8 Hz C-3a, C-7a), 1.80 (1H, t, J = 7.0 Hz, C-8H); NOE results δ: 5.78: 3.07 (8%), 2.85 (0.9%), 3.07: 5.78 (10%), 2.85 (2%), 2.65 (7%), 1.80 (7%), 2.96: 5.78 (0.8%), 2.65: 3.07 (10%), 1.80 (18%), 1.80: 3.07 (4%), 2.85 (2%), 2.65 (9%); ¹³C NMR (C₆D₆) δ: 175.8 (C-1, C-3), 132.4 (C-5, C-6), 129.2 (phenyl), 128.7 (phenyl), 128.4 (phenyl), 127.2 (phenyl), 69.9 (C-4, C-7), 64.0 (C-3a, C-7a), 58.9 (C-8), 47.7 (C-8 CH₂OCH₃), 46.1 (C-8 CH₂OCH₃); ms m/z (%): 283 (M⁺, 14),

89
Exact mass calc. for C_{17}H_{17}NO_{3}: 283.1207, found: 283.1213.

(10s)-10-Chloro-5,8-dihydro-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]-pyridazine-1,3-(2H)-dione (81)
and
(10r)-10-Chloro-5,8-dihydro-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]-pyridazine-1,3-(2H)-dione (82)

A solution of cyclopentadienyllithium (0.439 g, 1.63 mmol) and N-chlorosuccinimid (0.220 g, 1.63 mmol) in diethyl ether (20 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0.291 g, 1.63 mmol) in benzene (15 mL). The combined solutions were returned to the ice bath and stirred for 4 h. Rotary evaporation of the solvent furnished a pale orange product. $^1$H NMR analysis of the crude product indicated a ratio of 1.4 : 1 for 82 to 81. Flash chromatography afforded adducts 82 (0.177 g, 39%) and 81 (0.120 g, 27%) as colorless solids. Adduct 82 was recrystallized from 20% ethyl acetate / hexane to give colorless crystals.
For 81: mp 175.5 - 176 °C; ir ν_max: 2978, 1725, 1491 cm⁻¹; ¹H NMR (CDCl₃) δ:
7.47-7.38 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.56 (2H, apparent t, J = 2.1 Hz, C-6H, C-7H), 5.05 (2H, dd, J = 2.0, 3.5 Hz, C-5H, C-8H), 4.23 (1H, t, J = 1.3 Hz, C-10H); NOE results δ: 6.56: 5.05 (3%), 4.23 (1.4%), 4.23: 6.56 (0.5%), 5.05 (3%); ¹³C NMR (CDCl₃) δ: 158.0 (C-1, C-3), 132.8 (C-6, C-7), 129.2 (C-1', C-3', C-5'), 128.6 (C-4'), 125.6 (C-2', C-6'), 67.8 (C-5, C-8), 65.6 (C-10); ms m/z (%): 275 (M⁺, 36), 240 (100), 214 (2), 156 (4), 119 (63), 100 (56), 91 (23), 78 (28), 65 (41), 51 (9). Exact mass calcd. for C₁₁H₁₀ClN₂O₂: 275.0461, found 275.0453. Anal. calcd. for C₁₁H₁₀ClN₂O₂: C 56.72, H 3.63, N 15.27; found: C 56.66, H 3.69, N 15.36.

For 82: mp 166.5 - 167.5 °C; ir ν_max: 1719, 1408 cm⁻¹; ¹H NMR (CDCl₃) δ:
7.47-7.34 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.47 (2H, apparent t, J = 1.9 Hz, C-6H, C-7H), 5.11 (2H, dd, J = 1.8, 3.6 Hz, C-5H, C-8H), 4.56 (1H, t, J = 1.1 Hz, C-10H); ¹³C NMR (CDCl₃) δ: 157.9 (C-1, C-3), 129.2 (C-6, C-7), 129.0 (C-1', C-3', C-5'), 128.7 (C-4'), 125.5 (C-2', C-6'), 78.5 (C-5, C-8), 66.4 (C-10); ms m/z (%): 275 (M⁺, 41), 240 (43), 214 (24), 156 (24), 119 (3), 100 (100), 91 (27), 78 (22), 65 (58), 51 (11). Exact mass calcd. for C₁₁H₁₀ClN₂O₂: 275.0461, found 275.0453. Anal. calcd. for C₁₁H₁₀ClN₂O₂: C 56.72, H 3.63, N 15.27; found: C 56.66, H 3.69, N 15.36.

91
A solution of cyclopentadienylthallium (0.850 g, 3.15 mmol) and N-bromosuccinimide (0.561 g, 3.15 mmol) in diethyl ether (40 mL) under nitrogen was immersed in an ice bath and stirred for 1h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0.552 g, 3.15 mmol) in benzene (25 mL). The combined solutions were returned to the ice bath and stirred at -20°C for 22 h while gradually warmed to rt. Rotary evaporation of the solvent furnished a pale red product. ¹H NMR analysis of the crude product indicated 100% anti addition. (The structure of 83 was confirmed by X-ray analysis.) Flash chromatography afforded adduct 83 (0.552 g, 55%) as a colorless solid. Adduct 83 was recrystallized from 20% dichloromethane/hexane to give a colorless crystalline material: mp 170 - 170.5 °C; ir νₘₐₓ: 2928, 1719, 1494, 1399, 1234, 1136 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.45-7.34 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.47 (2H, apparent t, J = 1.8 Hz, C-6H, C-7H), 5.15 (2H, dd, J = 1.9, 4.1 Hz, C-5'H, C-8'H), 4.51 (1H, t, J = 1.8 Hz, C-10H); ¹³C NMR (CDCl₃) δ: 158.7 (C-1, C-3), 130.9 (C-1'), 129.6 (C-6, C-7), 128.7 (C-4'), 125.4 (C-2', C-6'), 68.9 (C-5,
C-8), 55.2 (C-10); ms m/z (%): 321 (11), 319 (12) both M+, 240(28), 200 (6), 146 (62), 144 (64), 121 (20), 119 (50), 91 (19), 65 (100), 51 (8). Exact mass calc'd. for: C_{13}H_{10}N_{3}O_{2}
(M^+-Br): 240.0772, found 240.0757.

(10r)-5,8-Dihydro-10-iodo-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H)-dione (84)

A solution of cyclopentadienylthallium (0.550 g, 2.04 mmol) and N-iodosuccinimide (0.460 g, 2.04 mmol) in diethyl ether (25 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0.359 g, 2.04 mmol) in benzene (10 mL). The combined solutions were returned to the ice bath and stirred overnight in the absence of light while gradually warmed to rt. Rotary evaporation of the solvent gave a red solid. $^1$H NMR analysis indicated 100% anti addition. (The structure of was determined by X-ray analysis as 84.) Flash chromatography afforded adduct 84 (0.260 g, 35%) as a beige solid, and crystallization from 30% ethyl acetate / hexane to gave 84 as colorless crystals: mp 133.0 - 134.0°C; ir ν_{max}: 1712, 1493, 1400 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ: 7.44-7.34 (5H, m,
C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.47 (2H, apparent t,  J = 1.8 Hz, C-6H, C-7H), 5.19 
(2H, dd,  J = 1.7, 3.4 Hz, C-5H, C-8H), 4.42 (1H, m, C-10H); 13C NMR (CDCl₃)  δ: 157.6 
(C-1, C-3), 130.7 (C-6, C-7), 129.1 (C-1', C-3', C-5'), 128.6 (C-4'), 125.4 (C-2', C-6'), 70.2 
(C-5, C-8), 30.0 (C-10); ms m/z (%): 367 (M⁺, 12), 240 (20), 192 (69), 177 (17), 
151 (5), 119 (62), 91 (14), 65 (100). Exact mass calcd. for: C₁₁H₁₄N₃O₂: 366.9818, found 
366.9799.

(10s)-5,8-Dihydro-10 methoxymethyl-2-phenyl-5,8-methano-1H-[1,2,4]-
triazolo[1,2-a]pyridazine-1,3-(2H)-dione (85) 
and 
(10r)-5,8-Dihydro-10 methoxymethyl-2-phenyl-5,8-methano-1H-[1,2,4]-
triazolo[1,2-a]pyridazine-1,3-(2H)-dione (86)

A solution of cyclopentadienylthallium (1.00 g, 3.71 mmol) and bromomethoxy-
methane (1.21 mL, 14.8 mmol) in diethyl ether (10 mL) under nitrogen was stirred for 5 h 
at -20°C. The resulting mixture was filtered through a glass wool plug on sintered glass into 
a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0.520 g, 2.04 mmol) in ethyl ether (10 
ml). The combined solutions were stirred overnight at -20°C. Rotary evaporation of the 
solvent gave a pale yellow solid. ¹H NMR analysis indicated a ratio of 3.8 : 1 for 85 to 86 (
86 was not isolated). Flash chromatography afforded adduct 85 (0.511 g, 48%) as a white solid which contained a small amount of 86, the minor anti diastereomer.

For 85: mp 150 - 151.5 °C; ir $v_{max}$: 3085, 2929, 1713, 1493, 1396, 1244 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$: 7.47-7.36 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.49 (2H, apparent t, $J = 1.9$ Hz, C-6H, C-7H), 4.98 (2H, dd, $J = 1.5$, 3.3 Hz, C-5H, C-8H), 3.52 (2H, d, $J = 6.7$ Hz, C-10 CH$_2$OCH$_3$), 3.38 (3H, s, C-10 CH$_2$OCH$_3$), 2.51 (1H, t, $J = 6.6$ Hz, C-10H); NOE results $\delta$: 6.49: 4.98 (3%), 2.51 (2%), 4.98: 6.49 (3%), 3.52 (1.3%), 2.51 (6%), 3.52: 4.98 (2%), 2.51 (4%), 3.38: 4.98 (0.7%), 3.52 (1.0%), 2.51: 6.49 (0.8%), 4.98 (3%), 3.52 (1.3%); $^{13}$C NMR (CDCl$_3$) $\delta$: 158.7 (C-1, C-3), 132.3 (C-6, C-7), 131.2 (C-1'), 129.1 (C-3', C-5'), 128.4 (C-4'), 125.5 (C-2', C-6'), 69.2 (C-10 CH$_2$OCH$_3$), 65.6 (C-5, C-8), 60.4 (C-10 CH$_2$OCH$_3$), 59.2 (C-10); ms m/z (%): 285 (M$^+$, 11), 255 (5), 253 (3), 177 (3), 119 (15), 91 (8), 78 (11), 45 (100). Exact mass calcd. for C$_{17}$H$_{15}$N$_3$O$_3$: 285.1112, found: 285.1102.

For 86: (from mixture): $^1$H NMR (CDCl$_3$) $\delta$: 7.47 - 7.36 (5H, m, C-2'H, C-3'H, C-4'H, C-5'H, C-6'H), 6.38 (apparent t, $J = 1.8$ Hz, C-6H, C-7H), 5.01 (2H, dd, $J = 1.8$, 3.6 Hz, C-5H, C-8H), 3.30 (3H, s, C-10 CH$_2$OCH$_3$), 3.25 (2H, d, $J = 7.0$ Hz, C-10 CH$_2$OCH$_3$), 2.50 (1H, t, $J = 6.9$ Hz).
(7r)-7-Chloro-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (87)
and
(7s)-7-Chloro-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (88)

A solution of cyclopentadienylthallium (0.550 g, 2.05 mmol) and
N-chlorosuccinimide (0.280 g, 2.04 mmol) in diethyl ether (20 mL) under nitrogen was
immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a
glass wool plug on sintered glass into a solution of tetracyanoethylene (0.260 g, 2.04 mmol)
in ethyl acetate (5.0 mL). The combined solutions were returned to the ice bath and stirred
overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a brown
solid. 'H NMR analysis indicated a 2.3 : 1 ratio for 88 to 87. Flash chromatography afforded
adduct 88 (0.169 g, 36%) and 87 (0.80 g, 17%) as white solids. Adduct 88 was crystallized
from 20% hexane / dichloromethane to give a colorless crystals: mp 206 - 207.5 °C; ir νmax:
3029, 2982, 2255, 1338, 1271 cm⁻¹; 'H NMR (CDCl₃) δ: 6.69 (2H, m, C-5H, C-6H), 4.44
(1H, apparent t, J = 0.9 Hz, C-7H), 4.09 (2H, dd, J = 2.0, 3.6 Hz, C-1H, C-4H); ¹³C NMR
(CD₂COCD₃) δ: 136.2 (C-5, C-6), 112.7 (C-2CN, C-3CN), 111.9 (C-2CN, C-3CN), 68.1
(C-7), 60.8 (C-1, C-4), 46.0 (C-2, C-3); ms m/z (%): no M⁺, 193 (7), 166 (13), 102 (54),
101 (13), 100 (100), 76 (15), 65 (46), 64 (13), 63 (16), 51 (13), 50 (14). Exact mass calcd. for C_{11}H_{8}ClN_{4} (M^+ - Cl): 193.0514, found 193.0514.

For 88: mp 200 - 201 °C; ir ν max: 3010, 2254, 1332, 1272 cm⁻¹; ¹H NMR (CDCl₃) δ: 6.79 (2H, apparent t, J = 2.2 Hz, C-5H, C-6H), 4.35 (1H, apparent t, J = 1.5 Hz, C-7H), 4.04 (2H, dd, J = 1.9, 3.9 Hz, C-1H, C-4H); ¹³C NMR (CD₃COCD₃) δ: 140.0 (C-5, C-6), 113.0 (C-2CN, C-3CN), 111.8 (C-2CN, C-3CN), 66.2 (C-7), 59.6 (C-1, C-4), 46.3 (C-2, C-3); ms m/z (%): no M⁺, 193 (5), 166 (10), 139 (4), 128 (4), 102 (39), 101 (9), 100 (100), 76 (11), 65 (11), 63 (10), 50 (7). Exact mass calcd. for C_{11}H_{8}N_{4} (M^+ - Cl): 193.0514, found 193.0506.

(7s)-7-Bromo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (89)

A solution of cyclopentadienylthallium (0.555 g, 2.06 mmol) and N-bromosuccinimide (0.367 g, 2.06 mmol) in diethyl ether (20 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of tetracyanoethylene (0.263 g, 2.06 mmol) in ethyl acetate (10 mL). The combined solutions were returned to the ice bath and stirred overnight, then gradually warmed to rt. Rotary evaporation of the solvent gave a black solid. ¹H NMR
analysis indicated 100% anti addition. (The structure was confirmed by X-ray analysis as 89.) Flash chromatography afforded adduct 89 (0.269 g, 48%) a white solid, which was crystallized from 15% hexane/dichloromethane to give colorless crystals: mp 215.5 - 217 °C; ir ν max: 3104, 3025, 2984, 2254, 1336, 1268 cm⁻¹; ¹H NMR (CD₂COCD₂) δ: 6.80 (2H, apparent t, J = 2.0 Hz, C-5H, C-6H), 4.48 (1H, s, C-7H), 4.13 (2H, dd, J = 1.8, 3.5 Hz, C-1H, C-4H); ¹³C NMR (CD₂COCD₂) δ: 137.3 (C-5, C-6), 113.0 (C-2CN, C-3CN), 112.1 (C-2CN, C-3CN), 61.4 (C-1, C-4), 56.7 (C-7), 45.9 (C-2, C-3); ms m/z (%): no M⁺, 193 (5), 166 (12), 146 (73), 144 (75), 128 (10), 102 (64), 76 (17), 75 (11), 65 (100), 50 (11).

Exact mass calcd. for C₁₁H₁₅N₇ (M⁺ - Br): 193.0514, found 193.0515.

(7s)-2,2,3,3-tetracyano-7-iodo-bicyclo[2.2.1]hept-5-ene (90)

A solution of cyclopentadienylthallium (0.570 g, 1.93 mmol) and N-iodosuccinimide (0.434 g, 1.93 mmol) in diethyl ether (20 mL) under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of tetracyanoethylene (0.220 g, 1.71 mmol) in ethyl ether (10 mL). The combined solutions were returned to the ice bath and stirred overnight in the absence of light, then gradually warmed to rt. Rotary evaporation of the solvent gave a black solid. ¹H NMR analysis indicated 100% anti addition. Flash chromatography through a column
containing charcoal and SiO₂ afforded adduct 90 (0.260 g, 42%) as a white solid, which was crystallized from 15% hexane/dichloromethane to give colorless crystals: mp 186.0 - 188.5 °C; ir ν<sub>max</sub>: 3092, 3018, 2252, 1333, 1254, 1205 cm⁻¹; <sup>1</sup>H NMR (CDCl₃) δ: 6.71 (2H, m, C-5H, C-6H), 4.44 (1H, apparent δ, J = 0.8 Hz, C-7H), 4.11 (2H, dd, δ = 1.5, 3.2 Hz, C-1H, C-4H); <sup>1</sup>C NMR (CDCl₃) δ: 139.1 (C-5, C-6), 113.4 (C-2CN, C-3CN), 112.2 (C-2CN, C-3CN), 13.2 (C-1, C-4), 44.9 (C-2, C-3), 30.3 (C-7); m/z (%): no M⁺, 320 (8), 193 (39), 192 (47), 166 (4), 128 (13), 102 (3), 76 (13), 65 (100). Exact mass calcd. for C₁₁H₁₄N₄ (M⁺ - I): 193.0514, found 193.0515. Anal. calcd. for C₁₁H₁₄N₄: C 41.28, H 1.57, N 17.50; found: C 41.27, H 1.58, N 17.68.

(7s)-2,2,3,3-tetraeyano-7-methoxymethyl-bicyclo[2.2.1]hept-5-ene (91)

A solution of cyclpentadienylthallium (0.450 g, 1.67 mmol) and bromomethoxy-methane (0.54 mL, 6.68 mmol) in THF (10 mL) under nitrogen was stirred for 3.5 h at -20°C. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of tetracyanoethylene (0.214 g, 1.67 mmol) in ethyl ether (10 mL). The combined solutions were stirred for 1 h at -20°C. Rotary evaporation of the solvent afforded a pale red solid. <sup>1</sup>H NMR analysis indicated 100% anti addition as to give 91. The crude material was
recrystallized from dichloromethane using charcoal to afford 91 (0.211 g, 53%) as colorless crystals: mp 143 - 144 °C; ir ν<sub>max</sub>: 2924, 2267, 1547, 1331, 1107 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 6.61 (2H, m, C-5H, C-6H), 3.92 (2H, dd, J = 1.7, 3.4 Hz, C-1H, C-4H), 3.34 (2H, d, J = 7.0 Hz, C-7CH<sub>2</sub>OCH<sub>3</sub>), 3.30 (3H, s, C-7CH<sub>2</sub>OCH<sub>3</sub>), 2.92 (1H, t, J = 6.9 Hz, C-7H); NOE results δ: 6.61: 3.92 (3%), 3.34 (0.6%), 3.92: 6.61 (3%), 3.34 (1%), 2.92 (4%), 3.34: 6.61 (0.8%), 3.92 (2%), 2.92 (6%), 3.30: 6.61 (0.4%), 3.92 (0.9%), 2.92 (3%), 2.92: 3.92 (2%), 3.34 (0.8%); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: 136.6 (C-5, C-6), 113.9 (C-2CN, C-3CN), 112.9 (C-2CN, C-3CN), 68.9 (C-7CH<sub>2</sub>OCH<sub>3</sub>), 59.4 (C-1, C-4), 59.3 (C-7), 58.5 (C-7CH<sub>2</sub>OCH<sub>3</sub>), 48.2 (C-2, C-3); ms m/z (%): no M<sup>+</sup>, 179 (15), 173 (39), 141 (20), 128 (42), 110 (100), 109 (73), 95 (32), 79 (56), 76 (51), 58 (23). Anal. calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O: C 65.54, H 4.23, N 23.52; found: C 65.22, H 4.19, N 23.55.

Attempts to prepare adducts of 92, 93 and 94

A solution of 1,3-cyclopentadiene in THF under a nitrogen atmosphere was treated with n-butyllithium (1.1 molar equivalents) at 0°C and stirred for 10 min. The resulting cloudy solution was added dropwise over 20 min to a -20°C solution of acetyl bromide, cyanogen bromide or dimethyldisulfide (2-5 molar equivalents) in THF under nitrogen. The reaction mixture was stirred for up 30 h at -20°C, transferred to a separatory funnel and quickly washed with cold brine. N-Phenylmaleimide, tetracyanoethylene or 4-phenyl-1,2,4-triazoline-3,5-dione was added to the organic layer and the resulting solution was stirred at -20°C for up to 48 h, washed with water and dried over anhydrous MgSO<sub>4</sub>. Rotary
Attempts to prepare adduct(s) of 95

A solution of cyclopentadienylthallium and N-iodosuccinimide (1 molar equivalent) in diethyl ether under nitrogen was immersed in an ice bath and stirred for 1 h. The resulting mixture was filtered through a glass wool plug on sintered glass into a solution of lithium acetylide, ethylenediamine complex (1-5 molar equivalents) in THF, and the reaction mixture was stirred at -20°C for up to 30 h. N-Phenylmaleimide, tetracyanoethylene or 4-phenyl-1,2,4-triazoline-3,5-dione (1 molar equivalent) was added to the reaction mixture and the resulting solution stirred for up to 48 h. Rotary evaporation of the solvent furnished only starting materials and other materials unidentifiable by NMR.
References


Appendix

Selected $^1$H NMR spectra of adducts are arranged in the order in which they appear in the text. For the instrument and conditions employed see Experimental - General.