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PROPELLANES. XLVI. STERIC AND ELECTRONIC EFFECTS AS OBSERVED IN REACTIONS
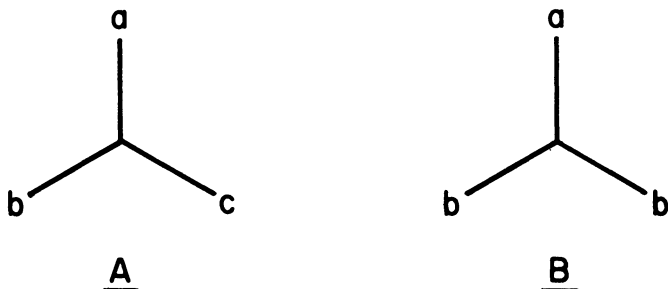OF PROPELLANES

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Abstract - The use of different propellane substrates indicates for a number of
chemical reactions that either repulsive steric interactions of the reactants or
attractive interactions of the secondary orbital type control the configuration of
the product.

The structure of propellanes is such that the three constituent rings divide space into three
distinct sectors. It is therefore possible to use suitably constructed propellanes in the
study of stereospecific and regiospecific reactions. Thus, if we have a propellane
comprising three different rings as indicated by the descriptors a, b, c in its Newman
projection A we may observe attack of ring a by a reagent operating within the sector defined
by rings a and b or within the sector defined by rings a and c, and analogously we may
observe attack of ring b or ring c in the alternatively possible sectors.

We have reported on the employment of propellanes as stereochemical models in simpler cases,
i.e. in compounds of type B having C_{2v} symmetry (1,2).

We have shown that in many propellanes having C_{2v} symmetry attack occurs exclusively, or
almost so, from the direction syn- to the hetero-ring as shown in 1, whilst in other cases of
such compounds attack occurs mainly from the direction anti- to the hetero-ring as shown in 2.

Diels-Alder Reaction
The oxidation state of the substrates attacked from the syn-direction doesn't appear to matter
when additional relatives are attacked in the same type of reaction. Thus, not only 1 but
also related compounds containing only one cyclohexadiene ring (e.g. 3,4,5) are attacked from
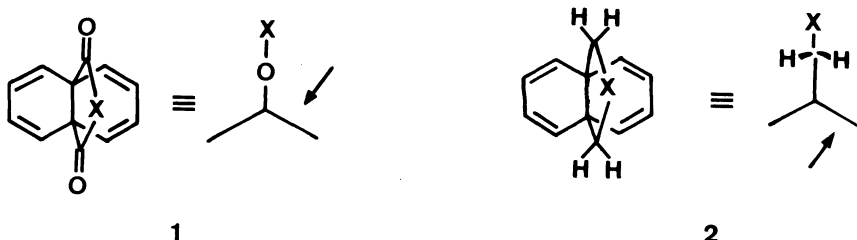

the syn-direction in the Diels-Alder reaction with the very reactive dienophiles of the cis-
azo type 6. Thus far mainly such adducts of azo-dienophiles have been studied because they
permit ready chemical proof of the configurations of the mono- and bis-Diels-Alder adducts

thus obtained.
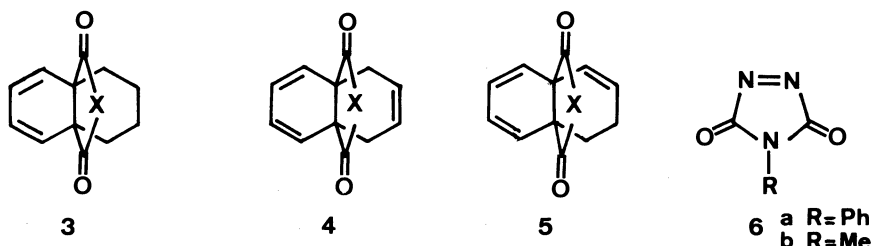
The strategy for such proof is shown in Scheme I (3). A tetraene of type 1 affords a mono-adduct 7 and a bis-adduct 8. Since 8 upon irradiation affords 9, a product of [2+2] photo-chemical cyclization, both moles of dienophile 6 must have attacked 1 from the syn-direction. It is mandatory by ironclad Talmudic logic that if both moles have attacked from the syn-direction then the first mole must also have attacked from the same direction. The configuration of the mono-adduct must be as shown in 7. Since 3, 4, and 5, other oxidation states of 1, give 10, 11, and 12, respectively, and since 10 by uptake of 1 mole of hydrogen, 11 and 12 by uptake of 2 moles of hydrogen and 7 by uptake of 3 moles of hydrogen afford one and the same product 13, it is proved with equal certainty that 3, 4 and 5 are also attacked by the dienophile 6 exclusively from the syn-direction. The correlations indicated in
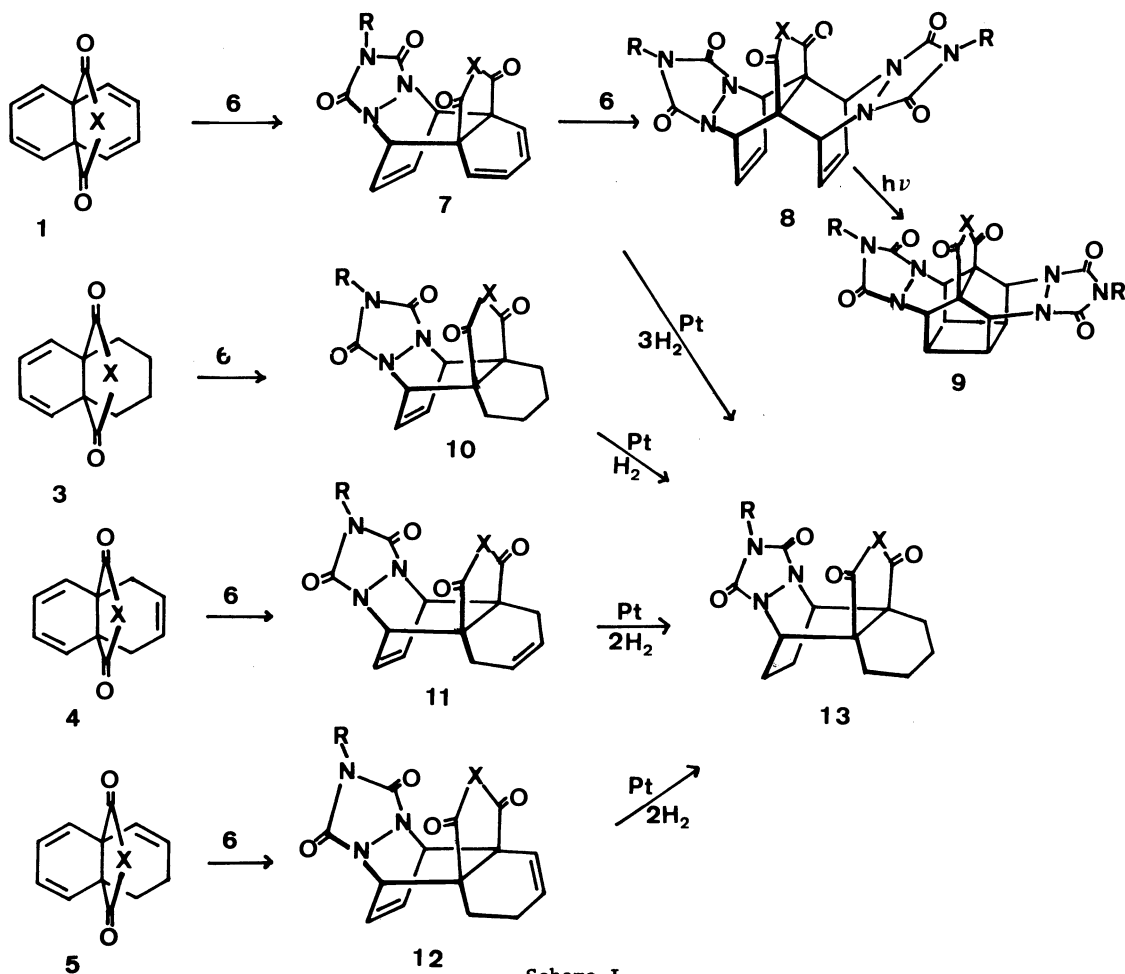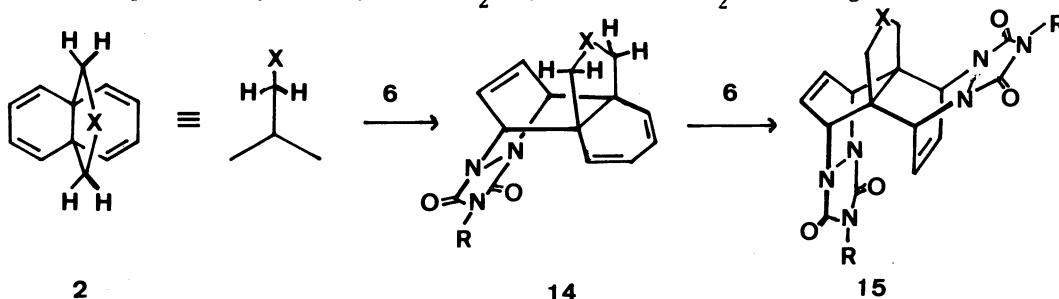

Scheme I

Scheme I require that 6 be reactive enough to give a bis-adduct. When a dienophile gives only a mono-adduct it is less simple to prove the full array of configurations. Chemical proof is more difficult than shown above, but if the X-ray crystallographer steps into the breach he can easily provide an unambiguous frame of reference (4). We are thus well aware that we must fill the lacunae and determine unequivocally through X-ray crystallography the extent to which the deductions made for adducts of 6 apply more generally to other dieno-

philes which, being less reactive, give only mono-Diels-Alder adducts for compounds of type 2.

We have shown for compounds of type 2 that the course of reaction is as shown in Scheme II. This has been proved unequivocally for X=CH$_2$, O, S but for X=NH$_2$ the configuration has been

2   14   15

Scheme II

inferred by analogy (1,6,7). For the cyclopentane analogs (X=CH$_2$) of different oxidation states as well as for that of the tetrahydrofuran analogs (X=O) the mono-adduct is also formed by attack of the dienophile from the direction anti- to the five-membered ring. (For behavior of the thioether analogs, see below).

The explanation invoked for the reaction course shown in Scheme II is a steric one. The hydrogen atoms in the five-membered ring in 2 (light type in 2) exert steric hindrance for syn-attack. The second mole of dienophile also exerts syn-attack upon the mono-adduct 14, to give 15 because this is the course of the lesser of two evils. The boat conformation (heavy lines in 14) exerts more steric hindrance towards attack of the adjacent cyclo- hexadiene from the anti-direction than is exerted by the hydrogen atoms which appear in heavy type in 2 and in 14.

It is clear that in all of the reactions discussed in schemes I and II we are dealing with kinetic products. We have shown that under the reaction conditions used and indeed at much higher temperatures there is no equilibration going on. The primary Diels-Alder adduct, whatever its configuration, does not undergo retro-Diels-Alder reaction and then forward reaction leading to the thermodynamically more stable isomer.

More recently we appear to have found that when such hydrogen atoms exerting steric hindrance upon syn-attack are more centrally located above the cyclohexadiene rings, not only does attack by the first mole of dienophile upon 16 occur from the anti-direction but the second mole of dienophile also attacks 17 from this direction to afford 18. Thus for the CH$_2$ hydrogens in 1,6-methano[10]annulene as well as the lone pairs on oxygen in the 1,6-oxa analog and by analogy, the 1,6-aza and 1,6-methylaza derivatives, the structural features of the bridging atom or group overpower the steric hindrance of the boat conformation shown in Scheme III (heavy type in 17) (8). Obviously in a three-membered ring these features are closer to where reaction takes place from corresponding features in a five-membered ring.

16   17   18
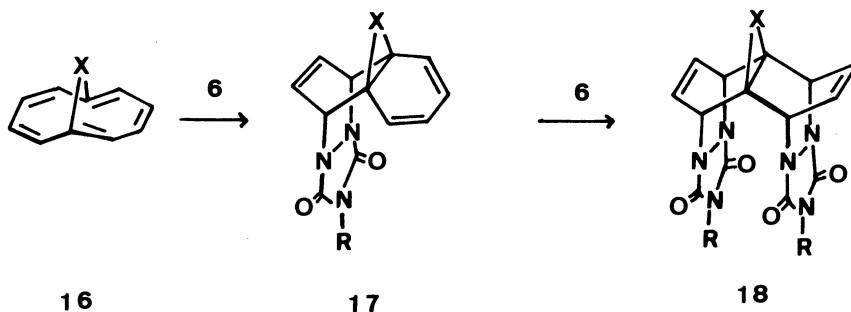
Scheme III

When compounds of type 2 and the bridged [10]annulenes undergo exclusive anti-attack by the first mole of dienophile one needs a satisfying explanation for the reverse behavior with respect to propellanes of type 1 and its relatives such as 3, 4, and 5. It is not sufficient to say that omission of the offending hydrogens should cause exclusive attack from the syn- direction; why not 50:50 attack, 60:40; 40:60; 70:30; 30:70; etc. etc.?! Why is there exclusive syn-attack for compounds of type 1? Their overall geometry is not all that differ- ent from that of compounds of type 2. Both types have Y-shaped geometry. The angles between

the projected rings need not be identical, but it does not appear reasonable that small
changes in such angles be responsible for the complete reversal in direction of attack.
The idea has therefore been advanced that the transition state for syn-attack of 1 (and its
relatives, e.g. 3, 4, 5) is stabilized by interactions between the dienophile and the diene
as shown in the representation of the transition state 19. We are thus invoking a secondary
orbital interaction to explain syn-attack in these cases.
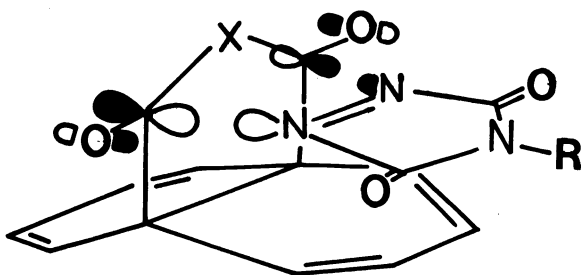
19

To pursue this idea further we have investigated (9) a part of the potential surface for the
reaction of 46 with 6, using the EH method. In Figure 1 we show an energy difference map
for the syn-approach of 6 to the butadiene plane (along the + z axis) and the anti-approach
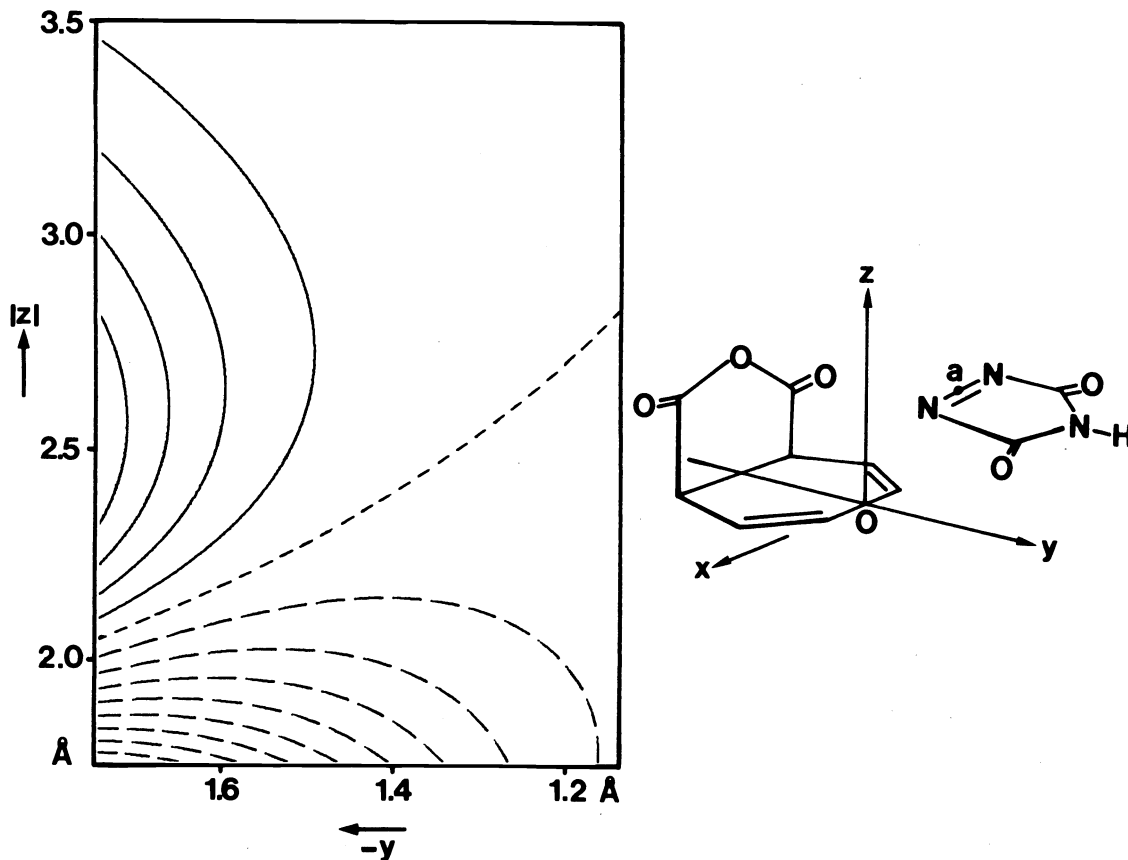(along the - z axis). The y-component of the 0-a vector is given along the abscissa.

Fig. 1. Contour diagram of the EH potential surface for the addition of 6 to
46. The contours are drawn every 0.2 eV and represent the difference in
energy between addition syn (+ z) and anti (- z) to the anhydride group. The
broken lines correspond to situations where syn-addition is energetically
favored;the full lines indicate anti-addition.

The full lines in Figure 1 indicate that <u>anti</u>-approach is more favored than <u>syn</u> (10). The broken lines indicate the reverse. The result of the calculation suggests attraction between y=-1.1 Å and z=+1.75 Å to +2.0 Å.

In principle, there are two effects which must be considered: a) The interaction of π_A(HOMO) of the butadiene moiety with π*(LUMO) of <u>6</u>. This interaction is responsible for the Diels-Alder reaction and has been treated by others extensively (11). b) A second interaction between the π-system of the anhydride and the lone pairs of the azo-group of 6.

The first mentioned effect is present whether approach is either <u>syn</u> or <u>anti</u>. The second interaction in propellanes of type <u>1</u>, <u>3</u>, <u>4</u> or <u>5</u> is only present for <u>syn</u>-approach (10). This is predicted to occur (Figure 1) at distances for which the HOMO-LUMO interaction leading to cycloaddition has not yet become significant. The model calculations permit us to rationalize the preferred approach on the basis of simple perturbation theory (12).
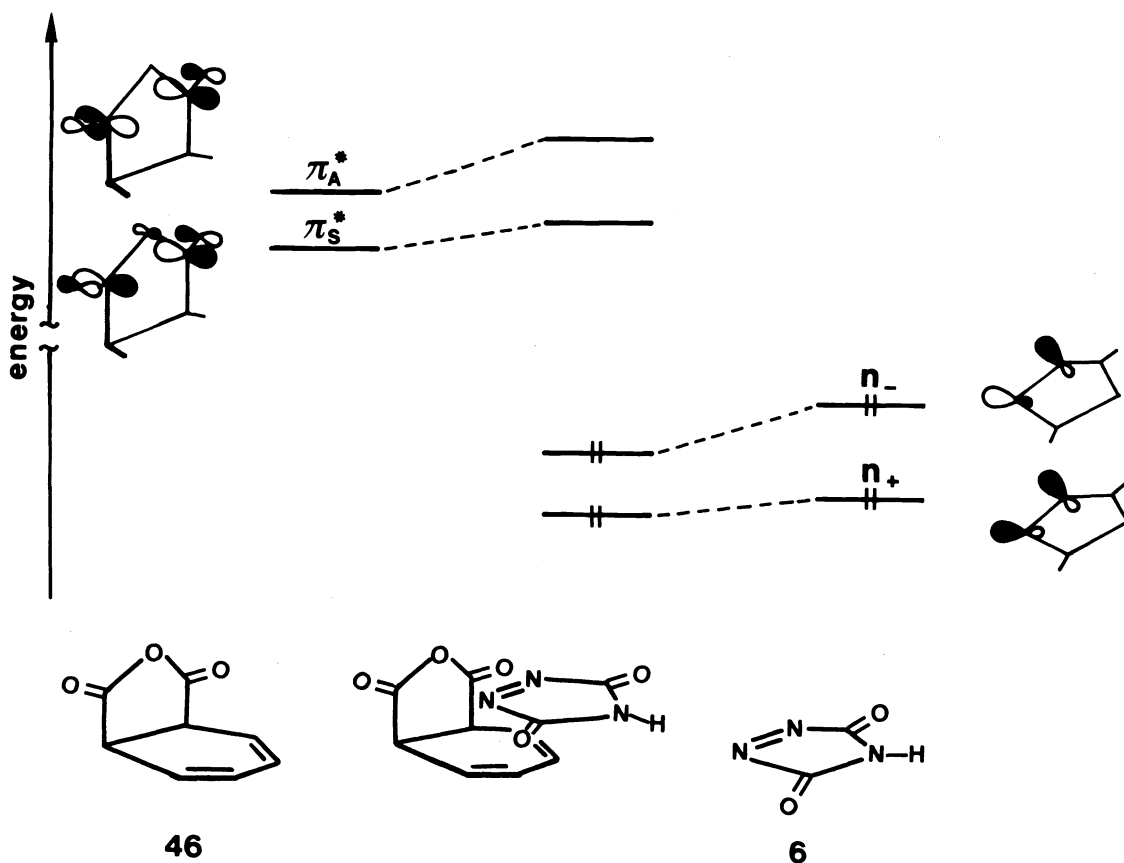

Fig. 2. Qualitative interaction diagram for the <u>syn</u>-approach of <u>6</u> to <u>46</u>. Only the interaction between the lone pairs on the nitrogen atoms of <u>6</u> and π* carbonyl orbitals is shown. The interaction between the π orbitals of the carbonyl group and the n orbitals of <u>6</u> is omitted.

In Figure 2 the interaction between the lone pairs of the azo group and the π*-orbitals of the dicarbonyl system is shown. A strong interaction is essential between n_- and π_A^*. This stabilizes the <u>syn</u>-approach transition state (+ z axis of Figure 1) which is favored over <u>anti</u>-approach (- z axis of Figure 1). Possibility of overlap between the n_+ or the n_- combination of <u>6</u> with the appropriate π*-combination of the diene moiety in <u>1</u>, <u>3</u>, <u>4</u> or <u>5</u>, may be neglected for energetic reasons.

An apparent exception

The course of the Diels-Alder reaction between <u>20</u> and <u>6a</u> has been proved unequivocally as shown in Scheme IV (13). The configuration of <u>21</u> is that shown because irradiation of <u>21</u> leads to <u>22</u>. It might, simplistically have been assumed that the transition state <u>23</u> (interaction between π* of the ethylene fragment with n_- of <u>6</u>) would be analogous to <u>19</u>.

20 **21** **R** **22** **23**
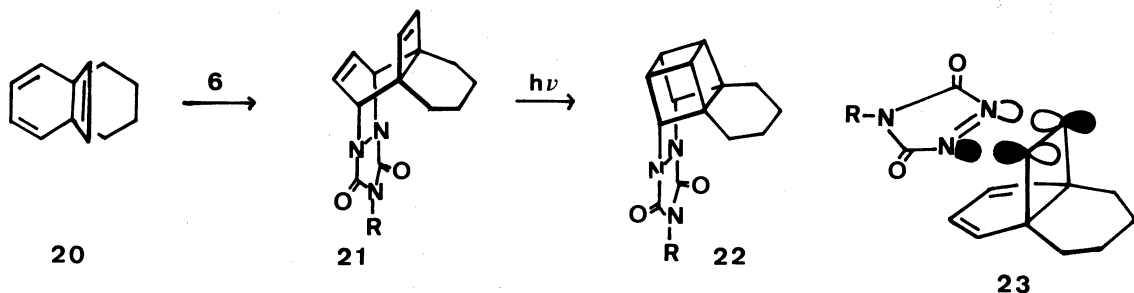
Scheme IV

However, semiempirical calculations of the EH type show that the interaction between the n_- and the ethylene π^*-orbital may be neglected as compared to that between the ethylene π-orbital and the n_+ linear combination of the lone pairs of the azo group. Since both of the latter MO's are occupied (see Figure 3), the net result is a destabilization of the transition state for syn-approach of 6 to 20. A plot of the difference in energy for syn- and anti-approach of 6, similar to that shown in Figure 1, yields a destabilization for the whole surface for syn-approach.

Similar arguments hold for substrates of type 2 (X=O,NR,S).

π^*

energy
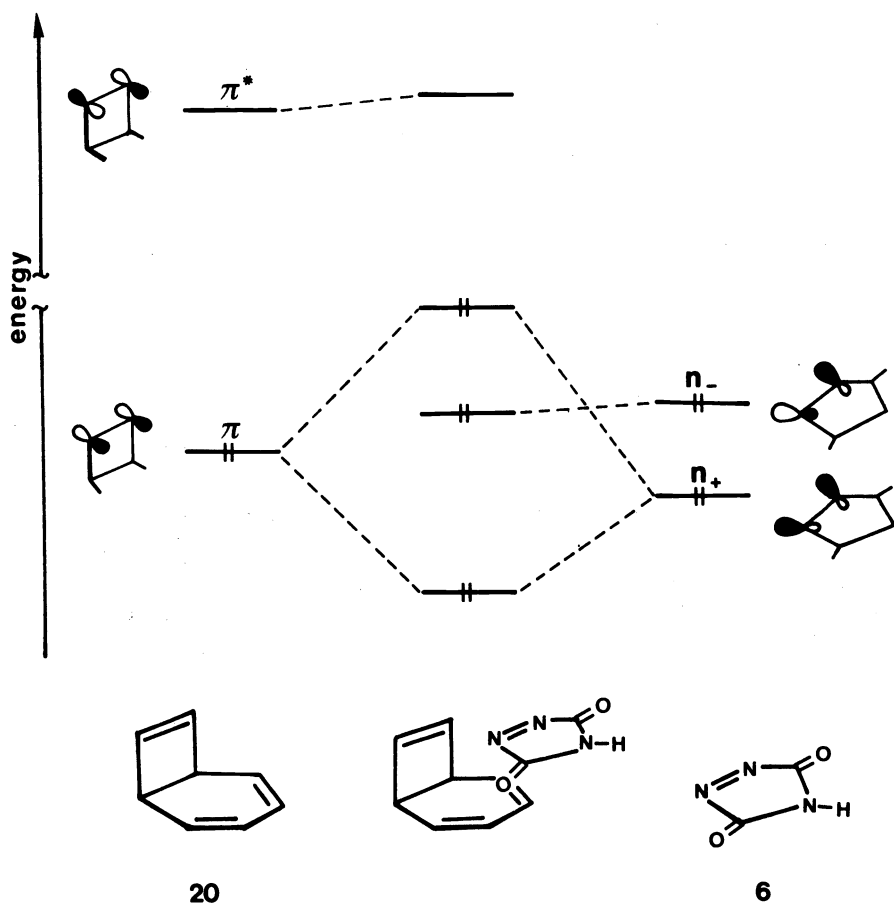
π

n_-

n_+

20 **6**

Fig. 3. Qualitative interaction diagram between the ethylene part of 20 and the lone pairs on the nitrogen atoms of 6.

It was indeed shown for other [4.4.2]propellanes and propellenes that attack of the first
(or only) cyclohexadiene ring occurs from the anti-direction. The explanation for the
behavior of 24 is analogous to that given above for 20 whilst for the cyclobutane analogs 25
and 26 clearly we have compounds of type 2 in which the steric hindrance exerted in the
syn-direction by the cyclobutane hydrogens is the cause for anti-attack by the first mole of

| 24 | 25 | 26 |
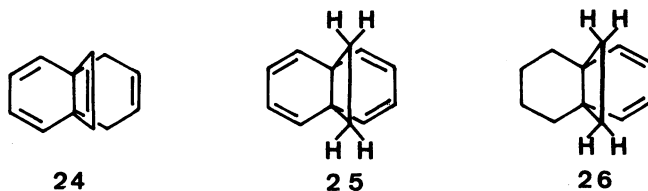
6a. For 25, the second mole of 6a attacks syn, in direct analogy to the behavior of the
compounds listed in Scheme II.

In summary, then, none of the [4.4.2]propellane derivatives constitutes an exception.

Real exceptions?
A family of sulfur-containing propellanes appeared to promise much potential interest in
buttressing or in destroying our thesis of secondary orbital overlap. We have already
mentioned 2 (X=S) as exhibiting the normal behavior of such substrates, i.e. anti-attack by
the first mole of dienophile (7). But the sulfoxide 27 and sulfone 28 are of even greater
interest.

| 27 | 28 |
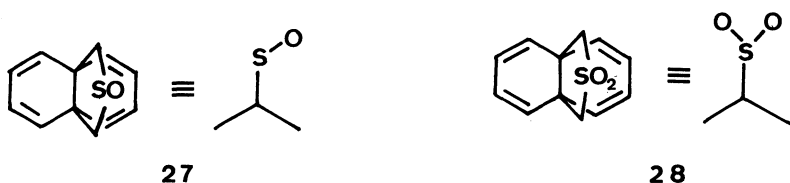
Both have hydrogen atoms adjacent to the functional group and are therefore, from this
vantage point, substrates of type 2. But in addition they include the polar groups SO and
SO_2 so that we superimpose an electronic effect upon the steric one even if not strictly
analogous to that of the π^* orbitals of substrates of type 1. Thus we did not expect as
clear a result for, say, 28 as for 1. Nevertheless 28 gave attack from above to the extent
of 95% rather than 100% and 2% of the isomeric mono adduct was isolated, in which attack
had occurred from below (7).

MO calculations suggest (9) a possible explanation which is due to the positive charge on
sulfur in alkyl sulfoxides and sulfones. The observed preferential addition to 6 from
above may be charge-controlled. In Figure 4 we have plotted the electrostatic potential
field (EPF) (13) of 2 (X = S) and 28, as well as the EPF of 6. Figure 4 clearly displays
a strongly negative field around the lone pairs of the azo group and a strongly positive
field around the sulfur of the sulfone group. One should note the strong positive potential
on top and on bottom of the triazoline plane which is prone to interact with the negative
potential around the oxygens. Translated into MO language this amounts to an interaction
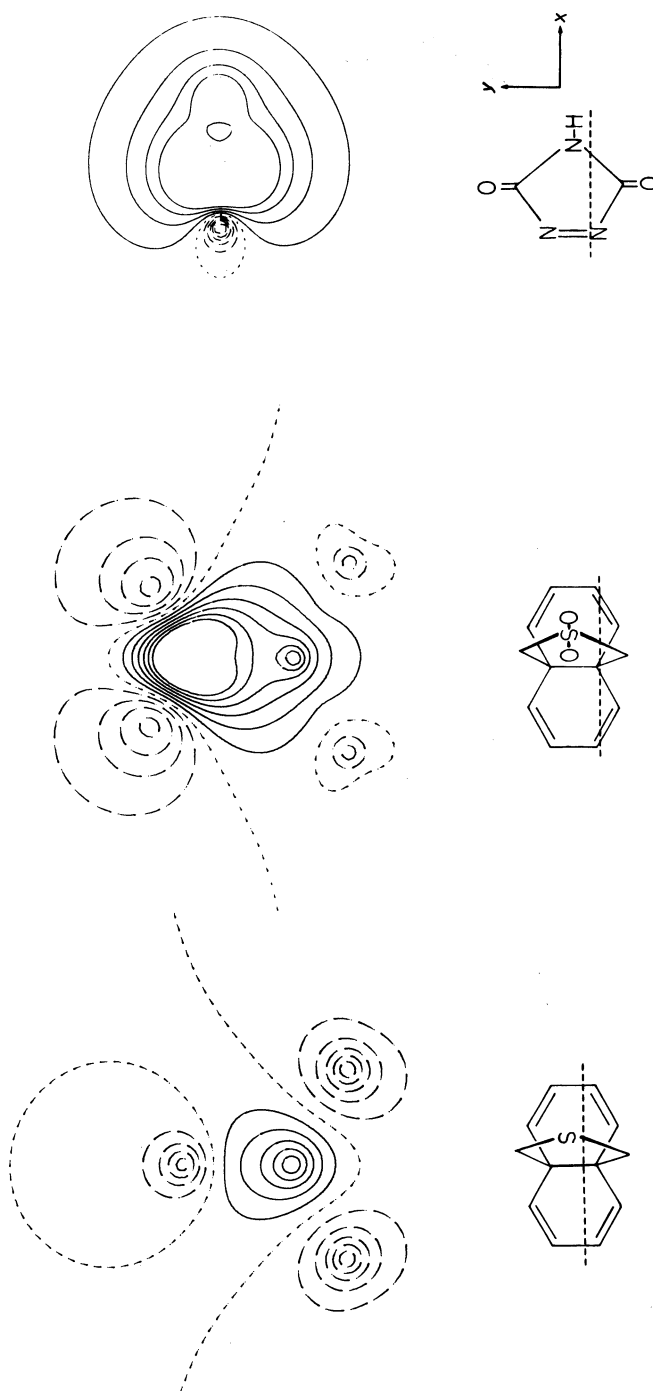between the lone pairs on the oxygen and the π^* orbital of 6.

Fig. 4. Contour diagrams of the calculated electrostatic potentials of 2
(X=S), 28 and 6. The maps are drawn in the plane parallel to the z,x-plane
indicated by the dashed line in the formulae. The interval between the
contours is 15 kcal/mol in the case of 2 (X=S) and 30 kcal/mol in the case
of 28 and 6. Positive potentials are indicated with full lines, negative
potentials with broken lines. Nodes are indicated by short dashes.

Substrate 28 affords more syn-attack than might have been expected and this may perhaps be
an exception. But worse still, the sulfone 29 and the thioether 30 are attacked from the
same direction as proved by the correlations listed in Scheme V (7).
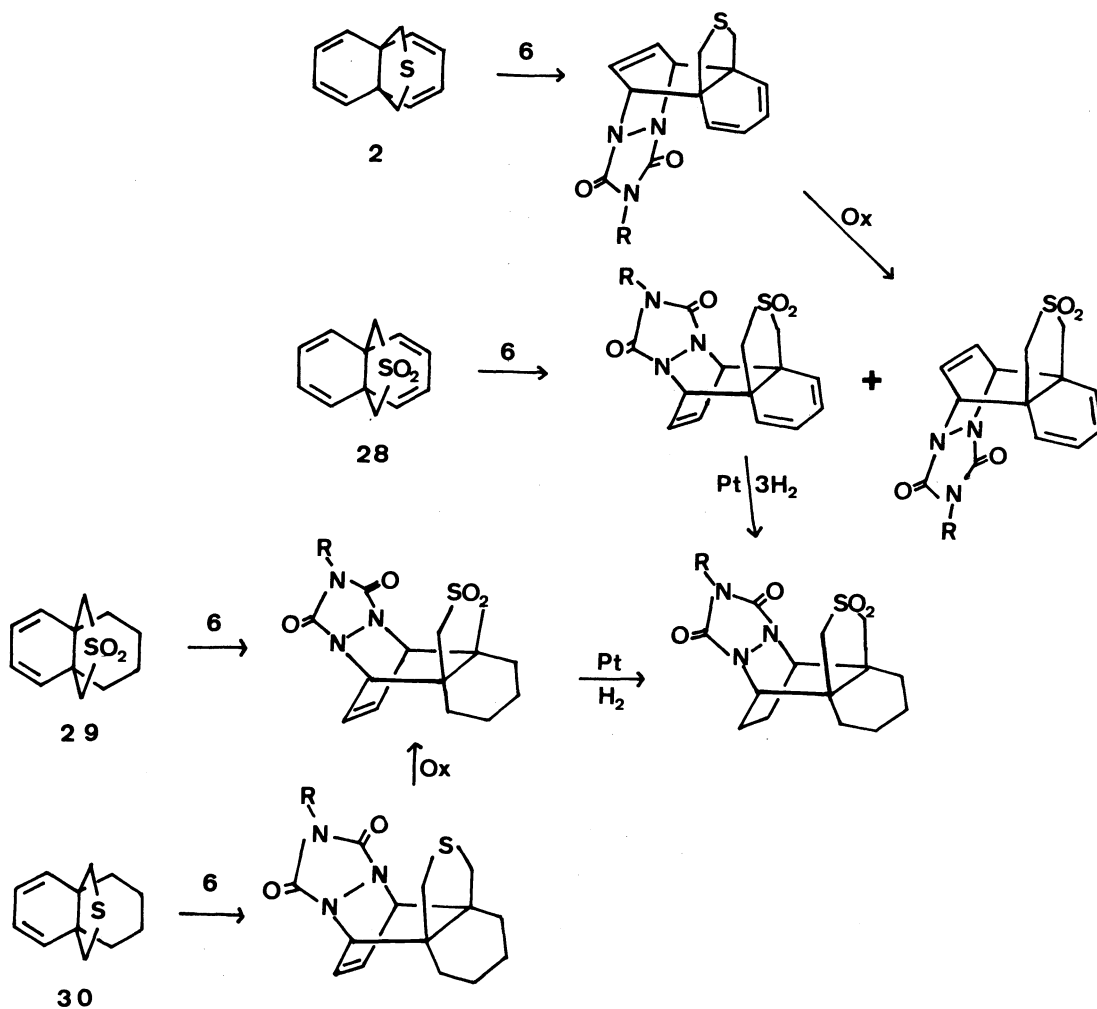
Scheme V

Equally bad, the thioether 31 and its corresponding sulfone 32 are attacked from the same side (14).


Thus we have here some internal contradictions between the pairs 2 (X=S) and 28, 29 and 30, and 31 and 32. Whether or not some of these constitute real exceptions to the thesis of secondary orbital overlap, invoked above, remains to be seen; we believe the further work will not necessarily bring about abandoning this thesis for compounds of type 1 in which such overlap may truly exist.

Using second order perturbation theory (12) it follows that 6 should add to 31 and 32 from the same side, namely anti- to the ether ring. The argument is an energetic one; the n_+-combination of the lone pairs of the azo group of 6 is closer in energy to the 2p lone pair of oxygen than for sulfur (9). Thus, for 31 the approach from the sulfur (thioether) side is a lesser disadvantage than from the oxygen (ether) side. For 32 the existence of the sulfone group causes the addition from the sulfone side to be even more attractive than

from the sulfur side of 31. X-ray crystallography has indeed shown that attack had occurred anti- to the ether ring (15).

The case of the sulfoxide 27 is expected to afford a more complex mixture of products merely for reasons of symmetry, or rather, lack thereof. Such are also the cases of the as yet unreported results for the substrates 33, 34a and 34b (16,17).

**33**   **34a**   **34b**
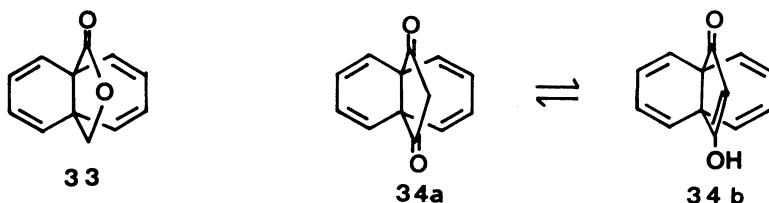
Also unreported as yet are the results concerning 35, 36 and 37 but the first two resemble 2 (X=CH₂) and 1,6-methano[10]annulene whilst the latter lacks the possibility of effective geometric interaction which exists in compounds of type 1 (18). All of these apparently give first anti-attack followed by syn-attack by the second mole of dienophile, as is found for the type 2 propellanes discussed above.

**3 5**   **3 6**   **37**
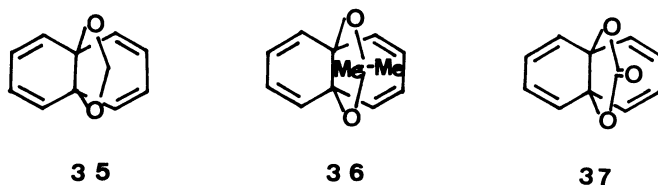
Interference with secondary orbital overlap

We longed for synthetic availability of compounds such as 38 because the large group L would effectively serve as an all-embracing umbrella for each syn-face of both cyclohexadiene rings and we might expect both moles of dienophile to attack from the anti-direction as actually obtained in the cases of the 1,6-bridged[10]annulenes. However, lack of synthetic success along with the known instability of the amine 2 (X=NH) which breaks up into naphthalene and into 39 caused us to be temporarily satisfied with analogs at the imide rather than amine oxidation state, i.e. 40, 41, and 42 which are formally compounds of type 1.

38 L large   **39**   **40**   **41**   **42**
group
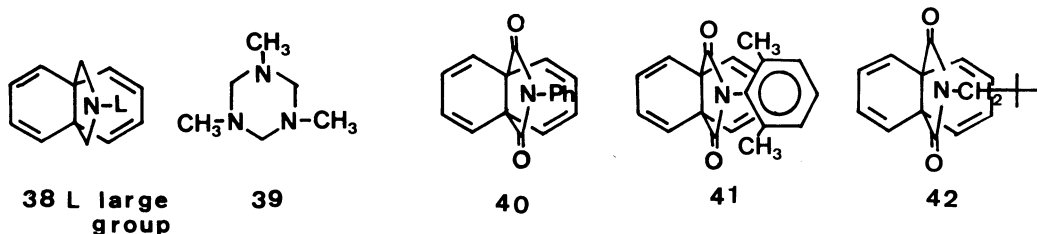
Since the heterocyclic rings in 40-42 are imide, not amine rings, one does not expect the same sort of equilibrium interconversion as in 38a ⇌ 38b.



38 a   **38 b**   **40a**   **40b**
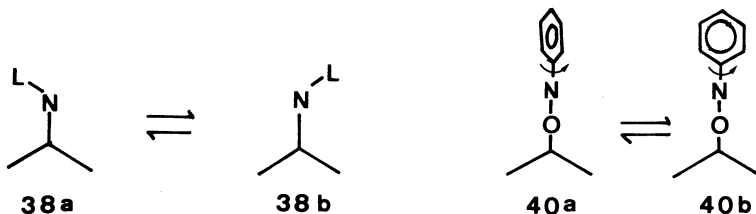
The Newman projections of 40 suggest the possibility of free rotation around the N-C bond as shown in 40a and 40b. If so, attack may be exclusively syn. In fact, by the usual strategy, the bis-adduct of 40 upon irradiation gave quantitatively a [2+2] photocycloaddition just as expected for an ordinary type 1 compound in which X=NPh (17).

In 41, however, free rotation is evidently not possible for it gave a 1:1 mixture of mono-adducts 43 and 44, i.e. in addition to the expected 43 the isomer 44 was also obtained. A

similar result was obtained for the neopentyl-imide 42 (17).

43   **44**
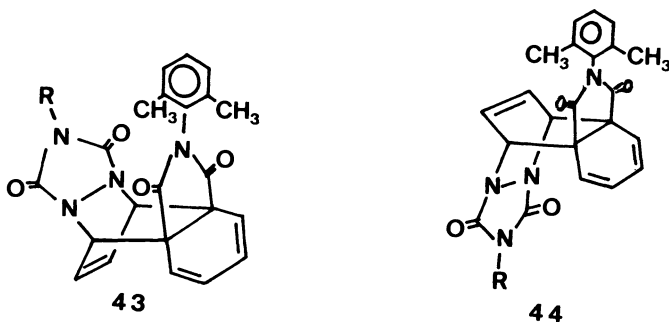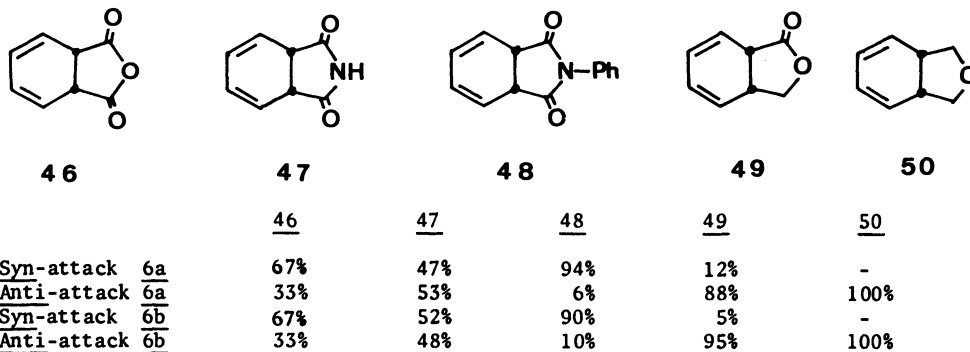
Similar results may be expected for chiral imide derivatives obtained by the reaction
sequence in Scheme VI (19). We turned to such compounds for a twofold reason. The first
is that by choosing readily available chiral α-amino-acids it is possible to obtain chiral
propellanes 45, in which both cyclohexadienes are covered by "umbrellas" of varying size.
We already know for the propellanes derived from leucine methyl ester that anti-attack
occurs as well as syn (1:1 and 2:3, respectively). More important, we may peer into these
molecules of type 1 even more intimately than heretofore by reacting them with dienophiles
of type 6 in which the substituent at position 4 is a chiral one, affording different
amounts of diastereomeric products.
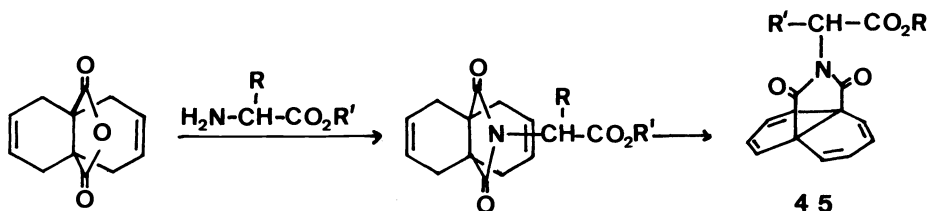
Scheme VI

Diels-Alder reactions have been carried out on the bicyclic compounds 46-50 (20). The
results obtained with 6a and 6b are tabulated in Scheme VII. The trend is similar to that
obtained in the propellane substrates albeit less clear cut.

| **46** | **47** | **48** | **49** | **50** |

		46	47	48	49	50
Syn-attack	6a	67%	47%	94%	12%	-
Anti-attack	6a	33%	53%	6%	88%	100%
Syn-attack	6b	67%	52%	90%	5%	-
Anti-attack	6b	33%	48%	10%	95%	100%

Scheme VII

Electrophilic reactions of Propellanes
a) Epoxidation
In the work done so far we find that whilst 51 affords upon epoxidation a 52:48 mixture, i.e.
1:1 of 52 and 53, the analog 54 affords 55 and 56 in a ratio of 7:1, respectively (21).
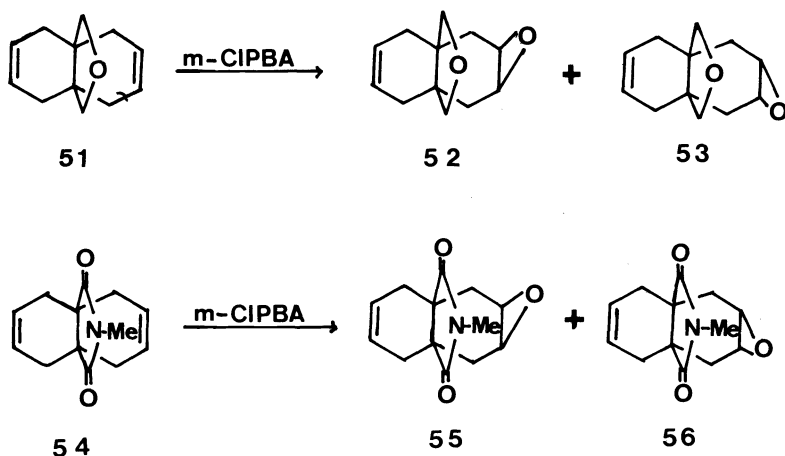
In peroxyacids (57) the HOMO is calculated (22) to be of π* type as shown in 58 while the second highest occupied MO of 57 resembles the HOMO of 6 as shown in 59 (23). Whether reaction occurs through the transition states 60 or 61, syn-attack from the top is always favored.
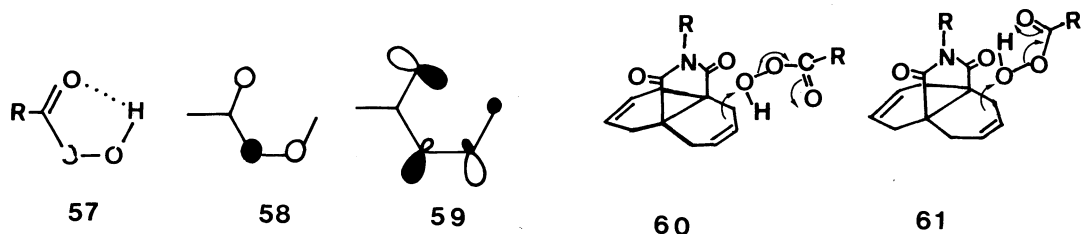

From these results it is reasonable to expect m-ClPBA to add to 54 from the syn-direction, since a secondary orbital interaction is possible, provided a more or less concerted mechanism for the epoxidation step is operating as indicated in 60 or 61. In case of 51 no such preference is possible and thus steric interactions should dominate.

b) Reaction with Ethyldiazoacetate
It is not clear whether the reagent which reacts with 54 in the presence of ethyl diazo-acetate and $CuSO_4$ in dichloroethane at 80° is carbethoxycarbene or a copper complex thereof. In any event the complex mixture obtained was separated into its components, these were correlated and a frame of reference determined by X-ray crystallography. The total anti-attack is greater than syn-attack by a ratio of ca 4:1 (25).

Although this is not strictly comparable, it has been found by calculation that carbene attack upon 62 should occur from the direction anti- to the anhydride ring (26).

62
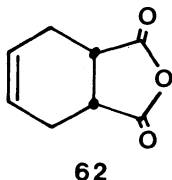
More secondary orbital effects
a) Reactions of propellanes with organometallic reagents
Since the ether 2 (X=0) reacts with $Fe(CO)_5$ to give 63 exclusively in high yield (27) it immediately seems reasonable to attribute this specificity to a secondary orbital interaction. This stereospecificity is all the more impressive in view of the complex mixture of products obtained from 2 with $Fe_2(CO)_9$, in which the non-discriminating species attacking the substrate in $Fe(CO)_4$. This will be discussed elsewhere within a more general discussion of organometallic compounds (28).

2 (X=O)   63
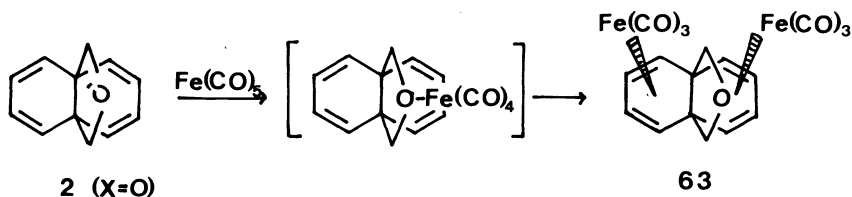
Similarly it has been shown that reduction of 2 (X=O) using deuterium in the presence of the homogeneous catalyst phenanthrene-chromiumtricarbonyl delivers the deuterium from the direction syn to each face, by 1,4-reduction, to yield 64 (29).

2 (X=O)   64
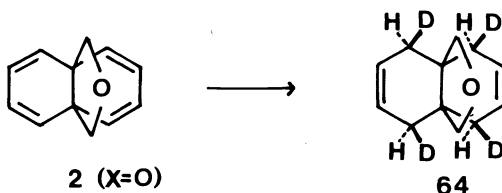
b) Reactions with singlet oxygen

Since in singlet oxygen the HOMO is of π* type (30) it was believed that singlet oxygen may also react from the syn-direction with compounds of type 1, we have begun investigating such reactions (31). Scheme 8 shows that the mono-peroxide 65 isolated from 1 (X=NMe) undergoes

1 (X=N-Me)   65

16 (X=CH₂)   66   68

                                                           67

3 (X=N-Me)   69   70
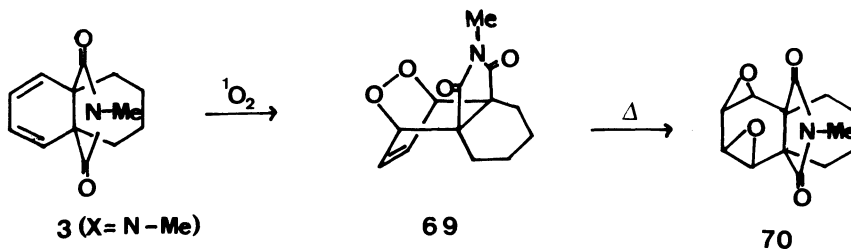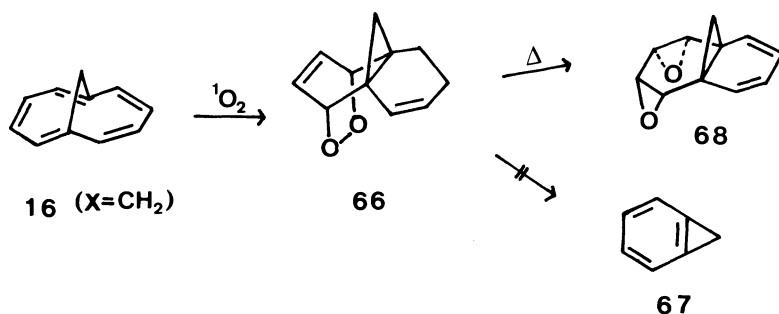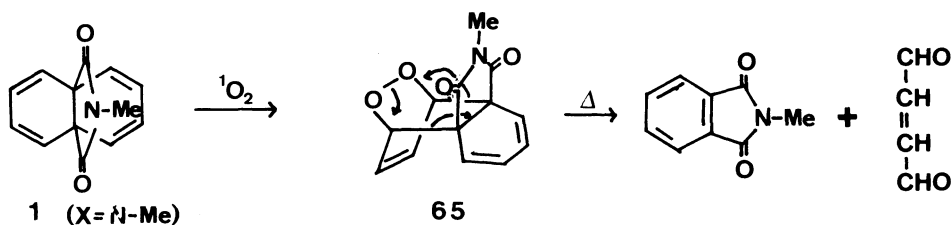
a thermal retro-reaction due to the driving force of aromatization. It is of interest to note that the formally analogous reaction of 66 formed from 16 (X=CH₂) does not occur because 67 is not sufficiently similar in stability to N-methylphthalimide; 67 may be obtained by a thermal retro reaction of another starting material, albeit at much higher temperature (32). Instead, 66 thermally affords the diepoxide 68 (33). When we subjected 3 (X=NMe) to reaction with ¹O₂, there being no driving force towards aromatization, the

product was the expected peroxide 69. At 120° this gave the diepoxide 70 whose configuration was proved by X-ray crystallography (15). Its crystal structure provided a bonus in that the ring containing the epoxides is twisted so as to bring one epoxide oxygen atom into close proximity with the carbon end of one of the carbonyls in the imide ring (34).

General comment

Finally we must make a general comment in criticism of our thesis regarding the efficacy of secondary orbital interactions in controlling the steric course of the various chemical reactions discussed above. As is usual in science we support our arguments by adding more and more constructions to buttress the battlements. We do not prove our thesis in the mathematical sense; we provide an interpretation which is apparently supported by more and more data but we must recognize that the interpretation is nevertheless not necessarily correct.

One other route to test such correctness is being pursued. We are slowly accumulating X-ray structural data regarding the structures of Diels-Alder mono-adducts resulting from type 1 and type 2 substrates. When enough of these are in hand we shall know whether all dienophiles cause syn-attack upon type 1 substrates and anti-attack upon those of type 2. If all dienophiles, including, say maleic anhydride or maleimide indeed take such a course then we cannot attribute the syn-attack to secondary orbital interactions for the carbon atoms of the dienophiles simply do not have lone pairs to undergo such interaction. One of the problems of science is, however, that even if all carbon dienophiles cause syn-attack upon type 1 propellanes, this does not prove that in the case of 6, factors other than secondary orbital effects are those in control.

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