DEWAR FURANS
(CYCLOBUTADIENE OXIDES)

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The work described in this thesis is my own, except where specific reference is made to the contributions of other workers.

(I.G. Pitt)
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PUBLICATIONS

Some of the work described in this thesis has been published in the following papers.


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ABSTRACT

The propellane (163) is synthesised from cyclobutadieneirontricarbonyl (140) by the sequence outlined below, in which the key intermediate is the transient Dewar benzene oxide (160), which incorporates the previously unknown 3-azabicyclo[3.2.0]hept-1(5)-en-2,4-dione moiety.

![Chemical structures](image)

1,2-Photoaromatisation of (163) generates Dewar furan (10) which undergoes quantitative isomerisation to cyclopropene-3-carboxaldehyde (164), even at -80°C. These two isomers are trapped as isobenzofuran adducts (166) to (169), the structures of which are confirmed by independent synthesis.

The same approach is used to synthesise tetramethyl Dewar furan (231). This derivative also undergoes quantitative isomerisation below -80°C, in this case affording the stable cyclopropene (238). Isotopic labelling of the transient Dewar isomer is used to confirm that this ring contraction proceeds via initial
C-O cleavage, and the homoaromatic betaine (240) is postulated as a replacement for the vinyl carbene intermediate originally proposed for Dewar furan ring contraction.

Trimethyl Dewar furan (256) is similarly synthesised, and the isolation of a single ring contracted isomer (259) is rationalised in terms of cyclobutenyl cation intermediate (261). A bicyclobutyl cation intermediate is invoked to explain the formation of the novel bicyclic isomer (248) of tetramethyl Dewar furan, isolated following pyrolysis of the epoxide (285). The three related intermediates described above are combined in a general mechanism for Dewar furan ring contraction.
A further representative of the Dewar furan ring system, the highly strained (360), is generated from its dibromide and trapped as Diels-Alder adducts with furan.

The first authentic example (370) of the norbornadien-7-one ring system is synthesised, and characterised by low temperature NMR spectroscopy.
CHAPTER ONE

ORIGINS OF THE DEWAR FURAN QUESTION

In 1867, Dewar reported "a mechanical arrangement adapted to illustrate structure in the non-saturated hydrocarbons" and demonstrated its application with the construction of the theoretical isomers (1) to (7) of benzene. Although the Kekulé structure (2) was soon accepted as representing benzene, the bicyclic isomer (6) became the subject of considerable research interest and, perhaps unfairly to Dewar, became associated with him through name.

Dewar benzene was first synthesised in 1963, by van Tamelan and Pappas. Since then, interest has extended to the isoelectronic, five membered heterocyclic analogues, (8) to (10), which have also taken on Dewar's name.
2.

Heicklen reported the first such structure, \( \textit{tetraakis(trifluoromethyl)} \)Dewar thiophene (12) in 1970.\(^5\) The Dewar isomer was synthesised by vapour phase photolysis of the corresponding thiophene (11) and, after some equivocation,\(^6\) the Dewar structure was confirmed by the symmetry of the \( ^{19} \)F NMR spectrum.\(^7\) Kobayashi and his coworkers have subsequently improved the synthesis and studied the reactions of this remarkable molecule (Scheme 1).\(^8\) When (12) is dissolved in dimethylformamide, dimethylsulphoxide or triethylamine the dimer (14) crystallises immediately; otherwise, the Dewar structure is stable, undergoing aromatisation to (11) only at elevated temperatures (\( t_b = 5.1 \) hrs at 160°C). The \( \pi \)-bond of (12) exhibits high dienophilicity and an adduct forms even with the normally unreactive pyrrole;\(^9\) the crystal structure of the tetramethylfuran adduct (13) confirms the Dewar structure of (12).\(^8\) Automerisation of (12) via sulphur walk has been observed by \( ^{19} \)F NMR above 100°, and it was originally proposed that the sulphur \( d \)-orbitals participated in a 6-electron, pseudopericyclic mechanism,\(^{10a}\). However, an analogous walk rearrangement was subsequently observed in carbocyclic systems, and the low activation energy was attributed to the high ground state enthalpy of bicyclopentenes;\(^{10b}\) in addition, the 6-electron pseudopericyclic mechanism could not be distinguished theoretically from a 4-electron pericyclic mechanism.\(^{10c}\)
In 1979, Barltrop and his coworkers reported the trapping in high yield of a Dewar thiophene during photolysis of 3-cyanothiophene. The same Dewar isomer was trapped, albeit in lower yield, during photolysis of 2-cyanothiophene, a result of sulphur walk in the Dewar intermediate. The isolation of the methylated analogue (17) was announced in the same year (Scheme 2) and a single adduct (19) resulted from its reaction with 1,3-diphenylisobenzofuran. The isomeric Dewar thiophene (18) could not be detected spectroscopically, but its existence in equilibrium with (17) was exposed when furan adducts of each, (20) and (21), were isolated. Direct observation by $^{1}H$ NMR of the less stable Dewar isomer (18) was achieved following low temperature photolysis of the thiophene (16), but isomerisation to (17) and (16) took place rapidly ($t_{1/2} = 2$ mins at $-35^\circ$). In contrast, aromatisation of the more stable Dewar isomer (17) to thiophene (15) was only observed above $90^\circ C$.
The sulphur walk has also been documented for other trifluoromethyl substituted Dewar thiophenes. Thus vapour phase photolysis of 2,3-bis(trifluoromethyl)thiophene (22) afforded a mixture (8:1) of Dewar isomers (23) and (24). Their dynamic equilibrium was confirmed when a single adduct (25) formed with 2,5-dimethylfuran (Scheme 3). Similar results have been reported for the two isomers of tris(trifluoromethyl)Dewar thiophene.

Very recently, Strausz and his coworkers demonstrated that thiophene itself photoisomerises to its Dewar isomer.
(8) by isolating two stereoisomeric adducts (26) and (27), following photolysis of furan solutions of thiophene.\textsuperscript{15} The Dewar isomer was not observed directly but could be prepared in a glassy matrix at \(-170^\circ\text{C}\) and subsequently trapped in the same way. This evidence, together with the low primary yield (2.5-3\%) of adducts, indicates that the parent Dewar heterocycle is markedly less stable than its isolable derivatives, all of which carry electronegative substituents on the \(\pi\)-bond.

\begin{center}
\begin{tabular}{c}
\includegraphics[width=0.2\textwidth]{26.png} \\
(26) \\
\includegraphics[width=0.2\textwidth]{27.png} \\
(27)
\end{tabular}
\end{center}

Hiraoka provided the first evidence for photoisomerisation of a pyrrole to its Dewar isomer in 1971, when he reported that photolysis of methanol solutions of 2-cyano-\(N\)-methylpyrrole (28) gave rise to the addition compound (31) of the intermediate Dewar pyrrole (29).\textsuperscript{16} The structure of this adduct was corrected to (32) by Barltrop and his coworkers in 1978, on the basis of the multiplicities in the \(^{13}\text{C}\) NMR spectrum.\textsuperscript{17} The formation of two isomeric furan adducts (33a) and (33b) was also reported, but neither tautomer of the Dewar pyrrole was observed directly.
Kobayashi and his coworkers have reported the isolation of several tetrakis(trifluoromethyl)Dewar pyrroles, bearing different substituents on nitrogen. These were synthesised from the stable tetrakis-(trifluoromethyl)Dewar thiophene (Scheme 5) and are themselves thermally stable, although they undergo rapid photoaromatisation. One representative, (36e), prepared by pyrolysis of (39), is fairly stable at 200°C.4,19 Automerisation via a nitrogen walk could not be detected by NMR, over a wide range of temperatures. The N-phenyl derivative (36a) isomerised spontaneously via a (3,3) sigmatropic rearrangement to the indole derivative (38), which was also isolated following photolysis of the pyrrole (37a). Thus the Dewar structure is strongly implicated in pyrrole photoisomerisation, although to date no representatives have been isolated using this direct approach.
It is still not known whether Dewar furan (10) is capable of existence, although it was proposed as a discrete intermediate in photolysis of furan in 1973, by Tsuge and his coworkers. When iodine was employed to "assist the valence isomerisation" of furan, the products from photolysis of furan solutions of 2,5-diphenyl-1,3,4-oxadiazole (40) were 3-benzoylfuran (43) and its benzoylhydrazone (42). It was proposed that these products were obtained via the photoadduct (41) of Dewar furan with the oxadiazole (Scheme 6) since the normal photoadduct (44), obtained in the absence of iodine, was resistant to further photolysis in the presence of iodine. However, the authors' statement that the degraded products (42) and (43) were not accompanied by the normal photoadduct (44) suggests that this last compound is in fact photolabile, and a plausible precursor to (42) and (43).
It is now well accepted that the immediate result of photolysis of furans is C-O bond cleavage, and that the plethora of products observed (Table 1) are formed by further rearrangements of the resultant diradical. Van Tamelan\textsuperscript{22} proposed a general mechanism for the photorearrangements of five membered heterocycles (Scheme 7) in which the diradical (46) evolves into the acyl cyclopropene (47) which is in equilibrium with the bicyclic Dewar isomer (49), but warned that formation of a strong bond, such as a carbonyl group, would lead the reaction entirely by way of the intermediate containing that bond. This prediction has been borne out by experiment, in that Dewar isomers of thiophenes and pyrroles have been produced by photolysis, as already described, but Dewar isomers of furans have not. All the products obtained from photolysis of furans (Table 1) can be explained in terms of the ring contracted intermediate (47) without recourse to Dewar isomers, although a vinyl carbene
intermediate (46c) has been invoked to account for the interesting photoisomer (66) of 2,5-dimethylfuran.\textsuperscript{27}

Thus, acyl cyclopropenes have been isolated following photolysis of various substituted furans by Srinivasan,\textsuperscript{27} van Tamelen\textsuperscript{22,28} and Fielding,\textsuperscript{32} with their coworkers, while Hiraoka has trapped such an intermediate, containing a conjugated double bond, through Michael addition of methanol.\textsuperscript{16,31} Lablache-Combier and his coworkers have also trapped intermediates during furan photolysis, in this case with propylamine.\textsuperscript{29,30} It was proposed that the pyrroles isolated were formed via both acyl cyclopropenes and bicyclic isomers, following a comparison of the products from photolysis in propylamine of a series of substituted furans and their thiophene analogues.\textsuperscript{30} However, no convincing evidence has yet been presented to support the intermediacy of the Dewar isomer (10) in furan photolysis.
Table 1. Photochemistry of Furans

<table>
<thead>
<tr>
<th>FURAN DERIVATIVE</th>
<th>PHASE</th>
<th>PHOTOLYSIS PRODUCTS</th>
<th>REF.</th>
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<tr>
<td></td>
<td>vapour &lt; 0.2 atm</td>
<td>CO (53) H (54)</td>
<td>(55) (56)</td>
</tr>
<tr>
<td>(52)</td>
<td>vapour &gt; 0.2 atm</td>
<td></td>
<td>(57) (58) (59)</td>
</tr>
<tr>
<td>cyclo-pentane solution</td>
<td>polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(60)</td>
<td>vapour</td>
<td>CO (53) H (61)</td>
<td>(62) (63)</td>
</tr>
<tr>
<td>(63)</td>
<td>vapour</td>
<td>CO (53) H (64)</td>
<td></td>
</tr>
<tr>
<td>(65)</td>
<td>vapour</td>
<td></td>
<td>(66) (67) (68)</td>
</tr>
<tr>
<td>(75) tBu</td>
<td>pentane</td>
<td></td>
<td>(69) (70) (71) (72) (73) (74) (53)</td>
</tr>
<tr>
<td>(77) tBu</td>
<td>pentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relative energies of furan and Dewar furan have been evaluated using semi-empirical (CNDO/2) and ab initio (STO-3G) calculations; the former method provides an energy difference of approximately 200 kJ/mol. Identical calculations for benzene indicate that its Dewar isomer is higher in energy by more than 300 kJ/mol, yet Dewar benzene exhibits sufficient resistance to aromatisation to allow isolation (tₙₕ = 50 hrs at 20°C). The generally accepted
reason for this stability, that the opening of a cyclobutene ring to a 1,3-diene has high activation energy because symmetry forbidden, should also operate to stabilise Dewar furan with respect to aromatisation and allow its isolation, unless alternative pathways to lower energy species are open to this hitherto elusive molecule.

Before the commencement of this thesis, a single example of the Dewar furan ring system had been reported, by Wirth and Lemal in 1982. As might be expected, this sole representative is completely substituted with trifluoromethyl groups. Its synthesis proceeds in several steps from the stable Dewar thiophene (12) to the precursor and formal Diels-Alder adduct (101), which fragments to pyrrole and the Dewar furan (102) on pyrolysis (Scheme 8). High dienophilicity is reported for (102), which reacts instantaneously with pyrrole to return (101), and with furan three orders of magnitude faster than the corresponding Dewar thiophene.

Scheme 8
The isolation of (102) provides yet another example of the efficacy of the perfluoroalkyl effect\textsuperscript{38} in stabilising strained carbon frameworks. The protection afforded by perfluoroalkyl substituents has been ascribed to their ability to deter electrophilic attack\textsuperscript{38} and minimise transfer of vibrational energy to the fragile carbon skeleton following collisions.\textsuperscript{39} In this case, the perfluoroalkyl effect furnishes a molecule which is stable at room temperature but which isomerises on warming to the acyl cyclopropene (90) ($t_{1/2} = 20$ mins at $95\degree C$) rather than the furan (88). The vinyl carbene intermediate (103) was proposed for this isomerisation (Scheme 9) and in support of this proposal the authors calculated (MNDO) that the formation of the lowest singlet state of vinyl methylene (104) from fully optimised Dewar furan is endothermic by only 17 kcal/mol. Thus the synthesis of Dewar furan, a declared objective of these authors, promises to be challenging.

\begin{center}
\textit{Scheme 9}
\end{center}

\begin{center}
\begin{tikzpicture}
\node (102) at (0,0) {\textbf{(102)}};
\node (103) at (1.5,0) {\textbf{(103) $R = CF_3$}};
\node (104) at (1.5,-1) {\textbf{(104) $R = H$}};
\node (90) at (3,0) {\textbf{(90)}};
\draw [->] (102) -- (103);
\draw [->] (103) -- (90);
\end{tikzpicture}
\end{center}

The proposal that the acylcyclopropene (90) forms from a vinyl carbene intermediate is acceptable insofar as
14.

Closure of vinyl carbenes in this fashion is regarded as their most characteristic reaction. However, these reactive intermediates frequently undergo alternative intramolecular rearrangements, sometimes to the exclusion of cyclopropene formation. Thus the vinyl carbene (106), generated by photolysis of the acylcyclopropene (105), formed the products (107) and (108) by insertion into both aromatic and aliphatic C-H bonds. Another option taken by this acyl vinyl carbene was electrocyclisation to the furan (109) (Scheme 10). In contrast, the sulphur substituted carbene (111), generated by gentle thermolysis of the cyclopropene (110), isomerised to the 1,3-diene (112), via a hydrogen migration.

Scheme 10

![Scheme 10](image)

Certain intermolecular reactions are also characteristic of carbenes and have been used to infer their existence. Vinyl carbenes are commonly trapped with alcohols, as exemplified by the formation of allyl ethers (114) from thermolysis of (110) in methanol (Scheme 11). Reactions of vinyl carbenes with alkenes,
15. forming allylcyclopropanes, have also been reported; alkenes employed in this trapping role include 2,3-dimethylbut-2-ene,\textsuperscript{43,44} allyl ethers,\textsuperscript{45} furan,\textsuperscript{45,46} and even benzene.\textsuperscript{46}

*Scheme 11*

![Diagram showing the reaction process](image)

In view of the diverse chemistry of vinyl carbenes, it is perhaps surprising that the acylcyclopropene (90) was the sole product from thermolysis of the Dewar furan (102). The formation of the putative vinyl carbene intermediate (103) is equally surprising as it represents an unprecedented thermal fragmentation of an oxirane to a carbene. This fragmentation is generally regarded as involving two steps, the first being thermal or photochemical ring opening of the oxirane to a dipolar species (119) known as a carbonyl ylid.\textsuperscript{47} This cleavage is favoured by substituents capable of stabilising negative charge, as well as by ring strain; a significant example of this is the thermal equilibrium between the cyclobutene
oxide (115) and the coloured carbonyl ylid (116), which has been trapped with dipolarophiles (Scheme 12). 48

Scheme 12

\[
\begin{align*}
\text{Scheme 12} & \quad \text{Ph} \quad \text{Ph} \\
\text{(115)} & \quad \rightarrow & \quad \text{Ph} \\
\text{(116)} & \quad \rightarrow & \quad \text{Ph} \\
\text{(117)}
\end{align*}
\]

In contrast to the initial ring opening of oxiranes, the subsequent fragmentation of carbonyl ylids to carbenes has only been observed photochemically, 49 and this process has been confirmed as thermally forbidden by orbital correlation diagrams. 50 The alternative mode of cleavage of oxiranes, between carbon and oxygen, leads generally to carbonyl compounds via group migration (Scheme 13) and carbenes have not been observed.

Scheme 13

\[
\begin{align*}
\text{Scheme 13} & \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_4 \\
\text{(118)} & \quad \rightarrow \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_4 \\
\text{C-C cleavage} & \quad \rightarrow \quad \text{C-O cleavage} \\
\text{(119)} & \quad \rightarrow & \quad \text{R}_1 \quad \text{R}_2 \\
\text{(120)} & \quad \rightarrow & \quad \text{R}_1 \quad \text{R}_2 \\
\text{(121)} & \quad \rightarrow & \quad \text{R}_1 \quad \text{R}_2 \\
\text{(122)}
\end{align*}
\]
Lemal and Wirth have cited the high dienophilicity of the Dewar furan (102) as evidence for antihomoaromaticity, or cyclobutadienoid character. Accordingly, one might anticipate Dewar furan to mimic some of the chemistry of cyclobutadiene.

Cyclobutadiene and its derivatives are destabilised by cyclic conjugation, in contrast to benzene, and are said to possess antiaromatic character. This confers extreme reactivity, including a readiness to undergo Diels-Alder reactions, both as diene and dienophile, and susceptibility to autoxidation. Simple cyclobutadienes are only isolable in low temperature matrices, or as transition metal complexes. The ring system is stabilised by high substitution, and the sterically hindered derivatives (123), (124), and (125) are isolable at normal temperatures, although even the highly substituted derivative (125) dimerises to (126) at ambient temperature.

Recently, the isolable cyclobutadiene (127) has been studied by Regitz and his coworkers and found to suffer electrophilic attack from certain 1,3-dipoles and dienophiles, in addition to the more usual cycloaddition.
reactions. These findings are summarised in Scheme 14. The ring contraction of (127) to (129) bears an uncanny resemblance to that of Dewar furan (102).

Scheme 14

The key to the mechanism of Dewar furan ring contraction was alluded to by van Tamelan when he cited the isomerisation of photo-α-pyrone (133) to the Corey lactone (137) as support for his proposed equilibrium between (49) and the ring contracted (47). Corey and Pirkle investigated the mechanism of this extraordinarily facile isomerisation using an isotopic label (Scheme 15) and found the intermediate to be a dipolar species analogous to
the betaines proposed by Regitz.†

Accordingly, if Dewar furans follow the same path to ring contracted isomers, one would anticipate production of cyclopropene and bicyclobutane derivatives. In contrast, isomerisation to a vinyl carbene intermediate, as proposed by Wirth and Lemal, should lead to a much greater variety of rearranged products in addition to cyclopropene derivatives. The reader should bear this in mind during the description of Dewar furan and its derivatives that follows.

† The question of whether the two resonating forms of (135) should be considered a single structure with cyclic charge delocalisation, as represented by Regitz, will be returned to in Chapter three of this thesis.
In selecting a synthetic route to Dewar furan, it was decided to take advantage of the successful synthesis of cyclobutadiene devised by Masamune (Scheme 16). The final step in this sequence, a 1,2-photoaromatization reaction, has been used successfully to introduce a π-bond into other 4-membered rings. The reader will note that Masamune's synthetic scheme passes through a Dewar furan precursor in (144), but the photolysis of this compound has not been investigated.

The ether bridge in Masamune's cyclobutadiene precursor (145) prevents opening of the bicyclo[4.2.0]-octadiene moiety, an undesired reaction which can dominate the photochemistry of these systems. However, while the final photoaromatization of (145) proceeds quantitatively, the preceding synthesis is laborious and inefficient,
discouraging repetition of this work. In pursuit of a rapid and high yielding synthesis of the Dewar furan precursor (144), or a substituted analogue, we chose to begin construction with the cyclic acetylene synthon (148) and proceed via the novel Dewar benzene derivative (150). This proposed synthetic intermediate contains the hitherto unknown 3-azabicyclo[3.2.0]hept-1(5)-en-2,4-dione moiety (155), which is reportedly "too strained for normal existence."65

\[
\text{Scheme 17}
\]

\[
\begin{align*}
&\text{(148)} & \text{+} & \text{Fe(co)}_3 & \rightarrow & \text{(140)} \\
&\text{(149)} & \rightarrow & \text{(150)} & \rightarrow & \text{(151)} \\
&\text{(152)} & \rightarrow & \text{(155)} & \rightarrow & \text{(153)} & \text{+} & \text{(154)} \\
\end{align*}
\]

In practice, cyclobutadiene, liberated from its iron-tricarbonyl complex (140), underwent cycloaddition with the maleimide (148) to form a single adduct, presumed to have the endo stereochemistry (149) common to cyclobutadiene adducts, in high yield. This adduct underwent debromination in boiling tetrahydrofuran when treated with zinc-silver couple; the resultant Dewar benzene could not be isolated, in keeping with prediction,
but was trapped in moderate yield with 2,5-dimethyl-3,4-diphenylcyclopentadienone (152), generated in situ from its dimer. Two competing factors contributed to the disappointing yield of the adduct (153): slow debromination resulted in formation of bis adducts (154), while rapid debromination produced N-methylphthalimide (151) as the major product, because of the slow production of the trapping agent (152) from its dimer.

The poor yield of (153) discouraged its development to a derivative of the target molecule (144); however, since imides are known to be photoactive,66 the photochemistry of (153) was studied to determine whether the succinimide ring would participate in undesired side reactions. The formation of the phthalimide (157), via photodecarbonylation followed by photoaromatisation, and the syn dimer (158) of cyclobutadiene as major products provided sufficient encouragement to retain the succinimide ring in our synthetic objectives.

Scheme 18

![Scheme 18](image-url)
23.

Because of the synthetic complications arising from the dienophilicity of the cyclobutenes (149) and/or (153), it was decided to epoxidise (149) prior to debromination. This was achieved using \textit{m}-chloroperbenzoic acid (\textit{m}CPBA) in chloroform at reflux; the \textit{exo} stereochemistry of the epoxide ring in the single product (159) is the consequence of attack at the less hindered face of the cyclobutene. As before, the intermediate (160) resulting from debromination could not be isolated, but in this case trapping afforded the adduct (161) in good yield (Scheme 19). Synthetic elaboration of this adduct allowed the assignment of its stereochemistry as shown: reduction with sodium borohydride in methanol produced a single alcohol (162) from hydride attack at the more accessible face of the ketone, while pyrolysis in boiling diglyme afforded the Dewar furan precursor (163) in high yield. The upfield shift of the bridge protons in (161) (δ2.85 ppm) is a result of the proximity of the anisotropic carbonyl group; the corresponding proton resonance in systems lacking this structural feature, such as (159) (δ3.43 ppm), (162) (δ3.33 ppm) and (163) (δ3.22 ppm), appears at lower field.

The 1,2-photoaromatisation of (163) proceeded smoothly to afford the phthalimide (157) as a single product in quantitative yield. No other fragments were detected by \textsuperscript{1}H NMR at ambient temperature, but analysis of the low temperature photolysate at -80°C by \textsuperscript{1}H NMR allowed detection of traces of furan, because of the fortuitous crystallisation of the major component (157).
In subsequent, larger scale photolyses, the yield of furan was increased to a level where it could be detected by routine low field $^1$H NMR, although never beyond a limit of 15%. Furan was, however, found to decompose under the conditions of photolysis, presumably because of polymerisation, as previously observed.\(^{25}\)

Scheme 19

![Scheme 19](image)

Strausz and his coworkers were able to entice Dewar thiophene into cycloaddition with furan.\(^{15}\) However, attempts to trap Dewar furan, the presumed intermediate from photoaromatisation of (163), by carrying out the photolysis in furan-2,5-$d_2$, were fruitless. This suggested that Dewar furan, if formed, was too short lived to allow time for reaction with the trapping agent. Use of a more reactive trapping agent, freshly prepared isobenzofuran (165),\(^{67}\) produced the fruitful result. Thus a small amount of this trapping agent was found to suppress furan formation...
from the photoaromatisation in NMR experiments, while the adducts of isobenzofuran with Dewar furan and cyclopropene-3-carboxaldehyde were isolated, in essentially quantitative yield, from preparative experiments (Scheme 20), together with isobenzofuran dimers.68

The temperature dependence of the product ratios indicated that the cyclopropene (164) was produced by thermal isomerisation of the first formed Dewar furan, with primary adducts (166) and (167) (ratio ca. 3:2) predominating at lower temperatures, and the secondary adducts (168) and (169) (ratio ca. 3:1) at higher. The formation of furan in the absence of trapping agent may proceed via photochemical ring expansion of the
26.

acylcyclopropene, which has ample precedent,\textsuperscript{23,24} or directly from Dewar furan by photochemically allowed ring opening of the cyclobutene, as exemplified by the photoaromatisation of Dewar pyrroles.\textsuperscript{18}

The structures of the primary adducts (166) and (167) were confirmed by independent synthesis. Isobenzofuran, prepared by the $s$-tetrazine route of Warrener,\textsuperscript{67} underwent cycloaddition with the cyclobutene (172) in boiling tetrahydrofuran to produce three adducts (Scheme 21), the stereochemistries of which can be deduced from their $^1$H NMR spectra (Figure 1). Thus only one of the adducts exhibits the bridgehead coupling characteristic of endo stereochemistry, and the relatively high field of the $\alpha$-chloro protons in this isomer supports structure (174), in which these protons are shielded by the aromatic ring. A distinction between the two exo adducts can be made on the basis of the distinctive coupling pattern of the all cis cyclobutyl protons in (173), which is identical to that observed for the corresponding cyclopentadiene adduct of known stereochemistry.\textsuperscript{69}

Dechlorination of these adducts with zinc in ethanol afforded the two cyclobutenes, in which the exo stereochemistry of (177) was immediately apparent from its unpleasant aroma, similar to that of (170) and apparently an olfactory consequence of the spatially proximate ether and olefin functionalities. Each cyclobutene underwent ready epoxidation, presumably from the less hindered face, to afford single products (166) and (167) (Scheme 21).
Figure 1. $^1$H NMR spectra of isobenzofuran adducts (173)-(175), with selected high resolution expansions.
These are the same products obtained from cycloaddition of isobenzofuran at the less hindered face of Dewar furan (Scheme 20), and the pair of isomers prepared by each route proved identical.

**Scheme 21**

The stereochemistries of the isobenzofuran adducts are well supported by their lanthanide induced shift (l.i.s.) profiles (Figure 2). In every case, the favoured site of complexation with the shift reagent Eu(fod)$_3$ is the oxygen in the five membered ring, since the bridgehead protons are always the most deshielded. However, it appears that secondary complexation to the epoxide oxygens contributes to deshielding, since the two pairs of cyclobutyl protons in the epoxide (167) have almost identical l.i.s. profiles, whereas the α-chloro protons in
29.

the corresponding dichloride (174), which can not benefit from secondary complexation, exhibit a much more shallow l.i.s. profile than the neighbouring cyclobutyl pair. The behaviour of the adduct (173), in which the spatially proximate chlorine atoms render the ether almost totally inactive towards Eu(fod)$_3$, provides dramatic evidence for its structure and supports the proposal for secondary complexation to the epoxide but not to the dichloride. However, effects other than secondary complexation also contribute to the pronounced deshielding of the epoxide protons in (166) and (167): in the \textit{exo} adduct these protons are deshielded because of spatial proximity to shift reagent complexed at the five membered cyclic ether, and in the \textit{endo} because of their situation near the magnetic axis of such complexes.\footnote{The magnitude of the induced chemical shift is provided by the McConnell-Robertson equation: \( \Delta \delta = K(\cos^2 \theta - 1)/R^3 \), where the angle, \( \theta \), and distance, \( R \), are defined by the metal atom, the nucleus affected, and the principal magnetic axis of the complex.}

Although the success of the trapping experiments (Scheme 20) lent much needed credibility to a reaction that until then had afforded an undesirable product, furan, in meagre yield, questions remained to be answered. In particular, our inability to isolate the cyclopropene aldehyde (164) that was so readily trapped was disturbing, especially since Igeta and his coworkers reported the isolation, in 1973, of this compound, following photolysis of pyridazine \( N \)-oxide.\footnote{Accordingly, we subjected a pure sample of cyclopropene aldehyde to our photolysis conditions,}
Figure 2: Lanthanide induced shift profiles of five isobenzofuran adducts.

Mole ratio: shift reagent/substrate
and observed polymerisation, but no formation of furan. This accounts for our failure to observe (164), and suggests that furan is formed by photoaromatisation of its Dewar isomer, or from some intermediate species between this and the cyclopropene aldehyde (164) to which it isomerises.

The sample of (164) required for the above experiment was synthesised by an alternative method to that published, in which the intermediacy of Dewar furan is implicated, although not proven. Thus flash vacuum pyrolysis (FVP) of the epoxide (179) caused aromatisation to dimethylphthalate (182), together with the production of mixtures of cyclopropene aldehyde (164) and furan, the latter predominating at higher temperature. Separate experiments confirmed that furan was produced by thermal ring expansion of cyclopropene aldehyde (164) (Scheme 22), a reaction that reportedly proceeds at room temperature for 1-methyl-3-acetylcyclopropene.27

\[
\text{Scheme 22}
\]

\[
\begin{align*}
(178) & \rightarrow (179) + (180) \rightarrow (181) \\
\downarrow & \\
(182) + (10) & \rightarrow \text{CHO} \rightarrow (52)
\end{align*}
\]
32.

The synthesis of (179), by stereospecific and regiospecific epoxidation of the cyclobutene (178), was reported surprisingly recently by a Russian research group. This regiospecificity was not fully observed when this work was repeated, using m-chloroperbenzoic acid in place of p-carbomethoxyperbenzoic acid, and the by product (180) proved difficult to separate from (179). Recrystallisation provided (179) in >90% purity, but pure samples of the two isomers could only be obtained after repeated chromatography. The low melting point reported for (179) suggests that the by product (180) was produced but overlooked in the reported synthesis.

The isolation of bis-epoxide (181), in addition to the two mono epoxides, allows confirmation of the regiospecificity and stereospecificity of the epoxidation, through comparison of the $^1$H NMR spectra (Figure 3). Thus epoxidation at the cyclobutene produces an upfield shift of the formerly allylic protons (to $\delta$2.4) in (179) and (181), with the higher field of the epoxide protons ($\delta$3.6) in (179), relative to (181), reflecting shielding by the adjacent double bond. The higher field of the epoxide protons ($\delta$3.3) in (180), relative to (181), similarly supports the stereochemistry depicted.

The structures of the cyclopropene aldehyde adducts (168) and (169) from the trapping experiment (Scheme 20) were confirmed by direct synthesis from isobenzofuran and cyclopropene aldehyde (164) isolated by the above route, which provided the same two isomers in identical ratio.
Figure 3: $^1$H NMR spectra of epoxides (179)-(181), with selected high resolution expansions.
Each isomer exhibits the large formyl proton coupling constant characteristic of cyclopropane aldehydes. The stereochemistry of the endo adduct (169) follows from the high field of its α-formyl proton (δ1.0) compared to that of the exo adduct (168) (δ2.8), a consequence of shielding by the aromatic ring. No such evidence is available to determine the stereochemistry of the exo adduct, but structure (168), resulting from cycloaddition at the less hindered face of (164), is the more plausible.

In summary, Dewar furan, prepared here for the first time, is a molecule with finite existence in solution, even at -5°C, but with very low thermal stability. Isomerisation to cyclopropene aldehyde (164) takes place even at low temperature, proving competitive with trapping at -65°C, and chances of direct observation of the bicyclic isomer in solution appear remote. Only traces of furan were observed when this was attempted, using 1H NMR at -80°C, and it appears that Dewar furan undergoes photoaromatisation, since efficient trapping suppressed furan formation and furan could not be produced from cyclopropene aldehyde (164) by photolysis. The efficiency with which Dewar furan isomerises to cyclopropene aldehyde (164) again raises the question of whether a vinyl carbene intermediate is plausible for this novel isomerisation, but this must await further investigation.

Finally, the successful trapping of Dewar furan allowed confirmation of van Tamelan's prediction that
photolysis of furan would not give rise to its Dewar isomer. Thus irradiation of a solution of isobenzofuran (20%) and furan (20%) in anhydrous tetrahydrofuran gave rise only to isobenzofuran dimers,\(^6\) with no trace of the adducts (166) to (169) arising via Dewar furan formation. This is consistent with the observation by Srinivasan\(^{25}\) that solution photolysis of furan produces only polymeric material.

Added in proof: The photolysis of liquid furan (\(\lambda = 214\)nm or 229nm) has very recently been studied by Strausz and his coworkers (W.A. Rendall, M. Torres and O.P. Strausz, *J. Org. Chem.*, 1985, 50, 3034-3038). Lengthy irradiation in a flow system at 25°C provided small amounts of the four adducts (386) to (389) in addition to polymer. No evidence for the Dewar isomer (10) was obtained and the four adducts appear to arise via initial C-O cleavage of the furan (*vide supra*). The stereochemistries of the cyclopropanecarboxaldehydes (386) and (387) were assigned on the basis of the relatively small coupling constant (ca. 2.5Hz) of the trans protons in the cyclopropane ring; similar analysis confirms the stereochemistries assigned to the corresponding isobenzofuran adducts (168) and (169).
In 1971, van Bekkum and his coworkers reported that 2-butyne underwent reaction with aluminium chloride to form a stable organometallic complex, formulated as (184) on the basis of NMR evidence, from which tetramethylcyclobutadiene was apparently liberated on treatment with dimethylsulphoxide, being trapped in situ as the Diels-Alder adduct (186).\textsuperscript{74}

\textit{Scheme 23}

\begin{center}
\includegraphics[width=\textwidth]{figure23.png}
\end{center}

The crystal structure of this stable organometallic intermediate, published in 1974,\textsuperscript{75} sheds further light on its bonding. Thus although the hybridisation states of the ring carbons, estimated from bond angles, and the bond lengths between them are consistent with structure (184), the closeness of the termini of the allylic system suggests a transannular interaction, and in its folded structure the complex resembles a bicyclobutyl cation (189) rather than a planar cyclobutenyl carbon (187)/(188) as represented by (184). Accordingly, the structure of the complex is better represented by (190), in which
three resonating structures (187) to (189) contribute to the overall bonding.

\[
\begin{align*}
C_1-C_2 &= 1.51\text{Å} \\
C_2-C_3 &= 1.39\text{Å} \\
C_2-C_4 &= 1.78\text{Å} \\
\theta &= 148.5^\circ
\end{align*}
\]

The proposal that the complex (190) has bicyclobutyl character finds support in the recent announcement, by Hogeveen and his coworkers, that it enters into reaction at -70°C with N-tert-butylsulphinylamine to form two equilibrating aluminium chloride complexes, (192) and (193), and the close relationship between bicyclobutyl and cyclobutenyl cations is further established by the acid catalysed isomerisation of the uncomplexed bicyclobutane (195) to the corresponding cyclobutene (194).\(^{76}\)

Olah and his coworkers\(^{77}\) united the bicyclobutyl and cyclobutenyl cations as the homocyclopropenium ion (196) following a study by NMR of it and its methylated derivatives in super acid media. A transannular interaction, resulting in transfer of positive charge to the central carbon, was deduced from a comparison of the
$^1$H and $^{13}$C chemical shifts for the homocyclopropenium ion and larger cyclic allyl cations (Figure 4). At room temperature, rapid interconversion of the two isomers of (196) resulted in magnetic equivalence of its methylene protons, but these were resolved at -115°C. Complete line shape analysis of the temperature dependent $^1$H NMR spectra was used to determine the activation energy for this interconversion. Since (196) represents the simplest potentially homoaromatic two $\pi$-electron system the value obtained, 8.4 kcal/mol, has been termed the homoaromatisation energy.78

Theoreticians continue to differ on the somewhat qualitative question of whether (196) is homoaromatic, and Haddon has recently summarised the various molecular orbital calculations reported for this species and the planar cyclobutenyl cation which is the presumed transition state
for ring inversion. The experimentally determined structure and homoaromatisation energy are successfully reproduced by semi empirical treatments (MINDO/2, MINDO/3) while *ab initio* calculations (STO-2G, STO-3G) tend towards a planar cyclobutenyl structure with very little barrier to ring inversion. However, the most recent *ab initio* calculations, carried out with the inclusion of electron correlation, produce results consistent with experiment. Haddon argues that this is further evidence for homoaromaticity, but Cremer and his coworkers take an opposing view, claiming that the calculated charge distributions give no indication of the incipient formation of a transannular bond, and that other weak interactions in the cyclobutenyl cation may be responsible for its unusual molecular properties.

*Figure 4:* $^{13}$C($^1$H)NMR chemical shifts for cyclic allyl cations.

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Shift 1</th>
<th>δ (ppm)</th>
<th>Shift 2</th>
<th>δ (ppm)</th>
<th>Shift 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>6188 (9.72)</td>
<td>(196)</td>
<td>6146 (8.65)</td>
<td>(197)</td>
<td>6137 (8.32)</td>
<td>(198)</td>
</tr>
<tr>
<td>6130 (7.95)</td>
<td>6235 (11.26)</td>
<td>6218 (10.25)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Leaving aside the possible homoaromatic properties of the aluminium chloride complex (190), synthetic advantages accrued from its ability to deliver tetramethylcyclobutadiene upon decomplexation. A potentially general protocol for synthesising
Dewar furan from cyclobutadiene was developed in the previous chapter, and rapid entry to its tetramethyl derivative can thus be envisaged.

In practice, the adduct (199) was isolated in high yield using the procedure of van Bekkum and his coworkers; the *endo* stereochemistry follows from the work of Criegee and Zanker on the corresponding anhydride. Debromination proceeded as before, using zinc/silver couple, to afford the intermediate Dewar benzene (200) which could be trapped in high yield with furan or the cyclone (152), and in moderate yield with pyrrole. In each case a single adduct formed, and it seems probable that they share the same stereochemistry, resulting from stereospecific attack at the *exo* face of the maleimide π-bond. The situation with 2,5-dimethyl-furan was less clear cut: the two adducts isolated could represent two stereoisomers resulting from attack at the one face, or one stereoisomer from each. Cycloadditions from the *endo* face of Dewar benzene derivatives have not previously been reported, but model experiments confirmed this possibility in the present case. Thus debromination of (199) in the presence of the diene (207) gave rise to two aromatic products (209) and (210), resulting from decarbonylation of the first formed norbornadienone isomers (208). This second step simplifies the stereochemical outcome of cycloaddition with (200) to a single isomer from each face.
Assignment of stereochemistry to the isomeric adducts (209) and (210) was made possible using the nuclear Overhauser effect. Irradiation of the highest field methyl resonance in the major adduct caused an 8% enhancement of the doublet at δ3.2 belonging to one pair of methylene protons in the cyclohexene ring. No such effect was observed for the minor isomer. Accordingly, this must have structure (210), indicating that the exo face of the Dewar benzene (200) is the more susceptible to attack.
Hexamethyl Dewar benzene \((t_\text{b} = 105 \text{ hours at } 120^\circ\text{C})\) is markedly more stable than the parent system \((t_\text{b} = 3 \text{ mins at } 90^\circ\text{C})\), and so the reactive derivative (200) was considered a suitable target for isolation, despite previous predictions to the contrary. Till now, slow debromination had been essential to allow maintenance of an equilibrium concentration of the trapping agent (152), and a granular reagent had been employed. In order to expedite the formation of (200) a powdered zinc/silver couple was prepared, and it was found that use of a large excess of this reagent in tetrahydrofuran at reflux led to complete debromination of (200) within five minutes. Under these conditions, roughly equimolar amounts of the phthalimide (201) and its Dewar isomer (200) were isolated, and relatively pure samples of the unstable (200) could be obtained by rapid chromatography over silica. The high degree of strain in this reactive Dewar benzene was reflected in its ready aromatisation, even at room temperature \((t_\text{a} = 44 \text{ mins at } 30^\circ\text{C})\), and its instantaneous reaction with furan, forming (202).

The photochemistry of the cyclone adduct (204) was investigated, and products arising via photodecarbonylation and subsequent photoaromatisation were again observed (Scheme 26) as described in the previous chapter. However, in this case the tetramethylcyclobutadiene liberated upon aromatisation could be visibly observed, in a glassy matrix at \(-196^\circ\text{C}\), as a red charge transfer complex (213) with the phthalimide. The excellent donor properties of
tetramethylcyclobutadiene have previously been noted in this fashion.\textsuperscript{87}

\textit{Scheme 26}

Thermolysis of the cyclone adduct (204) in boiling diglyme followed the same pathway of decarbonylation followed by aromatisation, and the tetramethylcyclobutadiene liberated was trapped in high yield with 1,3-diphenylisobenzofuran (\textit{Scheme 27}).

\textit{Scheme 27}

Epoxidation of the cyclone adduct (204) with \textit{mCPBA} at ambient temperature proceeded selectively at the cyclobutene double bond to give (219), the penultimate
precursor to tetramethyl Dewar furan. This compound was also synthesised unambiguously by the epoxidation of (199) under slightly more forcing conditions, followed by debromination and trapping (Scheme 28).

Scheme 28

The intermediate Dewar benzene oxide (218) could be isolated, as before, by rapid debromination and chromatography, and exhibited slightly greater stability ($t_{1/2} = 77$ mins at 30$^\circ$C) than the Dewar benzene (200). Its reaction with furan proceeded instantaneously, forming a single adduct (220), but in the absence of trapping agent, solutions of (218) turned orange with the formation of a single product, the benzene oxide/oxepin tautomers (221) and (222). However, further isomers of this compound were observed in the by products from preparation of (219), and a mixture of isomers resulted from the retro Diels-Alder cleavage of furan from the adduct (220) by FVP; the structural elucidation of these new compounds, described in the following pages, proved quite diverting.
After much chromatography, the mixture of isomers arising from thermolysis of the Dewar benzene oxide (218) was resolved into three components. The oxepin structure of the two most mobile of these was evident from the relatively low field of their $^1$H NMR methyl resonances, and the homoallylic coupling between them. These isomers were found to exist in thermal equilibrium at $100^\circ$C and assigned the structures (221)/(222) and (223)/(224), related through their benzene oxide tautomers via the well documented oxygen walk. In addition, both decomposed to the third, least mobile component, the $^1$H NMR spectrum of which contained two separate vinyl methyl resonances, and a higher field singlet representing geminal methyl groups, a consequence of methyl group migration forming the cyclohexadienone (226).

The position of the benzene oxide/oxepin equilibrium has been found experimentally and theoretically to depend on the substitution pattern, with $\alpha$-substituents favouring
the oxepin tautomer and β-substituents the benzene oxide form. This phenomenon has been rationalized by treating the substituent as a π-electron donor or acceptor, and comparing the possibilities for interaction with the π-system of each tautomer. However, the dominant factor governing the equilibrium positions of the two fully substituted derivatives described here appears to be the strain inherent in a maleimide π-bond. In the case of the unsymmetrical isomer, the oxide form (223) containing this substructure is only present in low concentration at equilibrium, and the quaternary $^{13}$C NMR resonances are well resolved (Figure 5) with chemical shifts characteristic of the fully unsaturated, open tautomer (224). In contrast, roughly equal proportions of the oxepin (222) and benzene oxide (221) tautomers of the symmetrical isomer are present at equilibrium. The $^{13}$C NMR resonances for the 7-membered ring are broadened as a result of the rapid, dynamic equilibrium, and the chemical shift of the α-carbons (δ106.3) lies roughly midway between those for benzene oxide (δ56.6) and oxepin (δ141.8).

Figure 5: $^{13}$C NMR spectrum of a 1:5 mixture of oxepins (222) and (224).
The chemical behaviour of the symmetrical and unsymmetrical isomers is fully supportive of the above explanation. Thus each isomer is hydrolysed, via the oxide tautomer (221) or (223), by aqueous acidic tetrahydrofuran. Pure samples of the unsymmetrical isomer were readily recovered following hydrolysis of mixtures with the symmetrical isomer, confirming the low concentration of the oxide form (223) at equilibrium. In addition, hydrolysis of the pure isomers gave rise to the same, symmetrical 1,2-diol in each case; accordingly, the maleimide containing carbonium ion (228), resulting from protonation and cleavage of the oxide (223), must isomerise to (227) prior to hydration. The structure of the resultant diol (229), which is evident from its symmetry, supports the structure (226) assigned to the cyclohexadienone obtained by thermolysis, or acid catalysis under anhydrous conditions, of either oxepin.

Scheme 30
Before returning to the tetramethyl Dewar furan precursor (219), the synthesis of which gave rise to the by products described above, another brief aside may be in order. The reader will recall that furan was the only isolable photoproduct from the parent precursor (163), in the absence of trapping agents, and this provided the impetus for studying the low temperature solution photochemistry of tetramethylfuran.

In the event, photolysis of acetone-$d_6$ solutions of tetramethylfuran at \(-70^\circ C\) gave rise to two new products, in somewhat inconstant ratio, which reverted slowly to the furan at ambient temperature. Each of these products was characterised by a pair of methyl singlets, and the appealing notion that these belonged to the Dewar (231) and valene (232) isomers generated a temporary euphoria. However, closer inspection of the $^1H$ NMR spectra revealed that one of these pairs of singlets was associated with a pair of quartets at lower field, representing a pair of homoallylically coupled methyl groups. Accordingly, a better interpretation of this photochemical behaviour is production of the mono and $bis$ oxetans (233) and (235), and this was confirmed following isolation of the undeuterated species (234) and (236) from photolysis of (230) in acetone.

\[ (230) \quad \text{Scheme 31} \]

(231) + (232) $\rightarrow$ (230) $\rightleftharpoons$ (233) $R = CD_3$

(234) $R = CH_3$

(235) $R = CD_3$

(236) $R = CH_3
With this information in mind, attention was turned to generation of tetramethyl Dewar furan via the photoaromatisation approach. This could be achieved directly from adduct (219) which underwent rapid photodecarbonylation; however, the 1,3-diene so generated, also prepared by thermal means (boiling diglyme), was generally used as the precursor for (231). As in the parent case, tetramethyl Dewar furan escaped detection completely, even using $^1$H NMR at $-80^\circ$, and the sole product observed, in yields of 90% or more, was the ring contracted isomer (238), which in this case proved photostable. The structure of this product is readily apparent from the symmetry of the $^1$H and $^{13}$C NMR spectra and the carbonyl resonance of the latter. In addition, the acylcyclopropene structure became manifest during subsequent thermal transformations of (238).

Thus it would appear that tetramethyl Dewar furan behaves in the same way as both the parent molecule and Lemal's stable trifluoromethylated derivative 37 in undergoing facile ring contraction. However, an important difference from the parent system is the total absence of the corresponding furan, or any products derived therefrom, following photochemical generation of (231). Indeed, $^1$H NMR integration indicates that formation of the ring contracted isomer (238) is essentially quantitative. This
appears counterintuitive, given that methyl substitution should stabilise the Dewar furan ring system, by analogy with the Dewar benzene case, and furan is thought to be formed by photoaromatisation of its Dewar isomer during the latter's brief existence. Accordingly, attention must be given to the possibility that tetramethyl Dewar furan is less stable than the unsubstituted system, in the absence of any evidence to the contrary. A consideration of the possible intermediates involved in the thermal isomerisation reveals why this might be so.

Two mechanisms can be envisaged for the ring contraction of Dewar furans. The first, proposed by Lemal,\textsuperscript{37} involves a vinyl carbene intermediate in which both C-C and C-O bonds of the epoxide have broken. In contrast, simple heterolytic C-O cleavage leads to a zwitterionic species which, on the basis of the evidence presented to date, may be formulated as (240). The stabilising effect of methyl substitution on such a system is evident from the remarkable stability of the aluminium chloride salt (190), and may be sufficient to promote extremely rapid decomposition of the strained Dewar isomer.

In an effort to distinguish between these mechanistic alternatives, photoaromatisation of (237) was carried out in methanol solution, and a new product was isolated in which one equivalent of methanol had been incorporated. The presence of two olefinic carbon atoms, and the absence of a carbonyl group, confirmed the cyclobutene structure (242) and it was initially thought that this confirmed the
second mechanism (Scheme 33). However, control experiments revealed that the cyclopropene (238) also underwent methanol addition to give the same product, and with more care it was possible to isolate (238) from methanol photolyses.

Scheme 33

Breslow and his coworkers, in their kinetic study of the solvolyses of certain cyclopropenylcarbinyltosylates, demonstrated that the double bond plays no part in the ring expansion and that delocalisation of a ring single bond, generating a cyclobutenyl cation intermediate, is involved. Methanolysis of (238) presumably follows the same pathway, generating either (244) or its protonated form as an intermediate. In this instance, the intermediate behaves as a classical cyclobutenyl cation in giving rise only to a cyclobutenyl product.
A similar ring expansion of (238), presumably acid catalysed, was sometimes observed in deuteriochloroform solution at ambient temperature. This reaction was more consistently reproduced by FVP (Scheme 34) and the product (245) is logically derived from the dipolar species (244). Once again, the structure of the product was readily apparent from the $^{13}$C NMR spectrum, in particular the high field methylene resonance which indicates polarisation of the exocyclic double bond, as in (246); further evidence was provided by the ready dehydration of (245) at higher temperatures to the known cyclobutene (247). The bicyclobutyl isomer (248) was not observed, suggesting that the intermediate in ring expansion of (238) is a classical cyclobutenyl cation (244) rather than a delocalised homocyclopropenium cation (240).

Scheme 34
The above findings suggest that, should the first step in Dewar furan ring contraction involve C-O cleavage, then structure (244) may be a better representation of the intermediate than (240). Further support for this contention was obtained from a study of trimethyl Dewar furan (256), in which the disruption of symmetry in the molecule gives rise to two possible ring contracted products. Before addressing this question, the synthesis of (256) will be briefly outlined.

The essential starting point for this synthesis was the AlBr$_3$-cyclobutadiene α-complex (250), the preparation of which, by treatment of a 1:1 mixture of propyne and but-2-yne with the Lewis acid at -85°, was reported by Hogeveen and Kok in 1980. When subjected to the decomplexation conditions of van Bekkum and his coworkers, albeit at -78°, complex (250) proved an excellent source of trimethylcyclobutadiene, which was readily converted to the Dewar furan precursor (255) in four steps, with an overall yield of better than 50%.

The epoxide (255) underwent efficient photoaromatisation, as anticipated from the behaviour of the two other representatives of this system described in the preceding pages. As before, the trimethyl Dewar furan liberated could not be detected by $^1$H NMR at -80°, and a single ring contracted product, the cyclopropene (259), was observed, albeit in only 40% yield.
It is difficult to see why fragmentation of (256) to a vinyl carbene intermediate would favour structure (257) over (258) and thus account for this apparent specificity. In contrast, if C-O bond cleavage occurs to produce a fundamentally allylic cyclobutenyl cation, then isomer (261) is clearly preferred because of the stabilising effects of the methyl substituents at the main sites of positive charge. Cyclobutenyl cations are known to exhibit partial 1,3-bonding and so the final formation of cyclopropenes can readily be rationalised; in this case, only cyclopropene (259) would result, as observed. A third possibility, involving direct formation of the transannular bond through participation of the π-bond in C-O bond cleavage, can be eliminated using similar arguments. Thus cleavage of the weaker, disubstituted side bond in the more stable bicyclobutyl cation (262) would lead to cyclopropene (260), which is not observed.
Definitive evidence ruling out the vinyl carbene mechanism was provided by isotopic labelling experiments on tetramethyl Dewar furan. The label was introduced by catalytic deuteration of the exocyclic 1,3-diene in (263), itself readily available from the previously described cyclobutene (204) (*vide infra*). In the event, complete scrambling of the label in the vinylic methyls of (264) was observed, although mass spectral analysis confirmed that the theoretical level of deuterium had been introduced. The effect of this on the $^1$H NMR spectrum was as expected: for example, in the spectrum for (265) a singlet at $\delta 1.35$ ppm attested to unlabelled methyl groups,
while a slightly higher field triplet ($\Delta \delta = 0.016 \text{ ppm}^*$) was clear indication for a CH$_2$D contribution. Part of a higher field pentet, representing CHD$_2$ groups, could also be distinguished in the high resolution spectrum.

Scheme 37

The scrambling of the label during heterogeneous catalytic hydrogenation of (263) is consistent with the accepted mechanism for this process, originally proposed in 1934 by Horiuchi and Polanyi.$^{100}$ In this mechanism, chemisorption of hydrogen and olefinic substrate on the catalyst surface (represented by asterisks in Scheme 38) causes cleavage of the single bond in the former, and the double bond in the latter. Transfer of a hydrogen atom then occurs, leading to a "half-hydrogenated state" (i.e. a radical bound to the catalyst surface) and a period follows, during which exchange between this radical and other bound hydrogen atoms occurs, before transfer of the second hydrogen atom completes the hydrogenation.

* This value corresponds with those for toluene-$\alpha$-$d$ ($\Delta \delta = 0.015 \text{ ppm}^*$)$^{97}$ and the residual proton in acetone-$d_5$ ($\Delta \delta = 0.034 \text{ ppm}^*$).$^{98}$
Very similar scrambling patterns were reported by Meyer and Burwell, following deuteration of 1,3-butadiene in a flow system, using palladium on alumina, and the degree of scrambling was notably higher for the 1,3-diene than for its isomers 1,2-butadiene and 1-butyne. These workers invoked an adsorbed 1-methyl-π-allylic species as their "half-hydrogenated state" in order to explain the results, and such an intermediate presumably forms during hydrogenation of (263).

The introduction of the symmetrically distributed label to the transient tetramethyl Dewar furan (271) proved sufficient to confirm that the intermediate involved in its ring contraction has the symmetry of the cyclobutenyl cation (274), thus ruling out the vinyl carbene (272). The $^1$H NMR resonance for the acetyl group in the ring contracted product, which is fully labelled regardless of mechanism (Scheme 39), took the form of a singlet with a slightly upfield triplet ($J = 2.1$ Hz), as described for the labelled photo-substrate (265). A similar upfield triplet was observed as part of the aliphatic methyl resonance, but its
intensity was approximately half that of the acetyl triplet (Figure 6) as required for a mechanism proceeding via the cyclobutenyl cation (274) or some intermediate of equivalent symmetry.

Figure 6. $^1$H NMR resonances for aliphatic (61.17) and acetyl (61.80) protons in the mixture of cyclopropenes (273) and (275) obtained following generation of the labelled Dewar furan (271)
The proton ratios of the vinylic and aliphatic protons to the constant acetyl protons were calculated, assuming two residual protons in each labelled methyl group and an equal distribution of products (273) and (275), and compared with the ratios obtained experimentally using $^1$H NMR integration (Table 2). The results support the mechanistic distinction made above, and rule out the vinyl carbene intermediate (272).

**Table 2: Ratios of vinylic and aliphatic protons to acetyl protons for cyclopropenes (273)/(275)**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Product</th>
<th>Vinylic Protons</th>
<th>Aliphatic Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl carbene</td>
<td>(273)</td>
<td>$5/2 = 2.5$</td>
<td>$3/2 = 1.5$</td>
</tr>
<tr>
<td>C-O cleavage</td>
<td>(273)/(275)</td>
<td>$\frac{5}{2} (5/2+6/2)=2.75$</td>
<td>$\frac{3}{2} (3/2+2/2)=1.25$</td>
</tr>
<tr>
<td>Experimental results:</td>
<td></td>
<td>$2.9 \pm 0.3$</td>
<td>$1.25 \pm 0.15$</td>
</tr>
</tbody>
</table>

The results discussed to date in this chapter support a cyclobutenyl cation intermediate for the ring contraction, in solution, of tetramethyl Dewar furan. Thermolysis (FVP) of the ring contracted isomer (238) regenerates this intermediate which, under these different conditions, isomerises to a methylenecyclobutene (*Scheme 34*). Bicyclobutyl products are not observed and this, together with the product distribution from trimethyl Dewar furan (256), appears to exclude direct participation of the $\pi$-bond in C-O cleavage. However, the results to be
presented in the remainder of this chapter suggest that this point of view is not universally applicable.

The previous chapter contained a thermal route to Dewar furan in the pyrolysis of epoxide (199). The necessary ring skeleton for an analogous tetramethyl Dewar furan precursor was constructed in 1961, by Cookson and his coworkers, who heated a solution of the tetramethylcyclobutadiene dimer (212) with the acetylene diester (278) in n-butyl acetate to produce the adduct (280). It was proposed that the adduct formed by ring opening of the cyclobutene (212) to produce the bicyclic form (276) of octamethylcyclooctatetraene (277), which was trapped by (278). However, the following year Criegee reported that the isolable bicyclic structure (276) was inert to acetylene diesters, and doubts remained about the structure of the adduct until 1976, when Askani demonstrated that Criegee had mistakenly assigned structure (276) to the semibullvalene (281), and reported the isolation of (276) for the first time, via low temperature generation of the diazo compound (279). The bicyclic structure (276) proved to be in equilibrium with the isomeric cyclooctatetraene (277), isomerising to the monocyclic form below room temperature. The structure of Cookson's diester (280) was confirmed when the same compound was isolated following reaction of the dienophile (278) with the cyclooctatetraene (277) in boiling toluene.
In practice it was found more convenient to synthesise Cookson's diester by the original method, since the starting material (212) was readily available from the AlCl₃-tetramethylcyclobutadiene σ-complex. Part of Cookson's original evidence for the structure of his adduct was its aromatisation, in the melt at 330-350°, to the phthalate (282). However, the yield was low (12%) and the tetramethylcyclobutadiene presumably liberated was not detected. These poor results proved quite reproducible, but adoption of more modern pyrolysis techniques clarified the issue. Thus when (280) was subjected to FVP at 470°, a mixture of (280) and its isomer (284) (ratio 1:2) was obtained, together with a little phthalate (282). The unsymmetrical diester derives from the symmetrical via successive Cope rearrangements, as documented for the unsubstituted system, and the two isomers were shown to be in equilibrium when FVP of pure (284) produced an identical
62.
mixture. Static thermolysis of the parent ring system (178) also leads to naphthalene derivatives, and this behaviour presumably complicates the static thermolysis of Cookson's diester.

Scheme 41

Epoxidation of (280) and (284), as well as being essential to produce a tetramethyl Dewar furan precursor, also helped establish the stereochemistries of the two isomers. Thus Cookson's diester produced two epoxides, (285) and (286) (ratio ca.1:2), neither of which underwent subsequent epoxidation. In contrast, the unsymmetrical isomer produced two mono epoxides, (287) and (288) (ratio ca.7:2), and a bis epoxide (289), in which formation of the second epoxide ring is no longer faced with insurmountable steric restraints. Site specificity of epoxidation was easily confirmed by FVP, isomers (285) and (287) undergoing clean aromatisation to the phthalate (282), now that the complicating possibilities of Cope rearrangements no longer apply.
While the heavier fragments from pyrolysis of (285) were immediately identified, the volatile fragments, isolated in a cold trap and presumably derived from tetramethyl Dewar furan, presented a more difficult structural challenge. Two were recognised as the cyclopropene (238) and the methylenecyclobutene (245), the latter present in only small amounts and possibly derived by secondary pyrolysis of (238) \(\text{vide supra}\). The third and major component was new and had a simple \(^1\text{H} \text{NMR} \) spectrum, with broad singlets at 61.7, 2.0 and 4.1 ppm (ratio 6:3:2). This component slowly decomposed at room temperature, but was destroyed immediately on addition of tetracyanoethylene, or even by the normally harmless operation of filtration through cotton wool. The symmetry of the spectrum, and the low stability of this product suggest that it has structure (248); the high field of the methylene resonance suggests a significant contribution from the dipolar species (249),
which contains a homocyclopropenium cation. The same effect has recently been invoked to explain the high field ($\delta$3.5) of the exocyclic methylene protons in methylenecyclopropene.\textsuperscript{105}

\begin{center}
\textit{Scheme 43}
\end{center}

The $^{13}$C NMR spectrum of this unusual product confirmed the presence of the terminal methylene group ($\delta$89.7, $J$157.2 Hz), but at first sight appeared to conflict with structure (248) in that no high field quaternary resonances were visible, even when different solvents were employed to rule out possible shift equivalence with methyl resonances. The bridgehead carbons in methyl substituted bicyclobutanes typically resonate between 37-47 ppm, and the non-bridgehead between 19-32 ppm.\textsuperscript{106} The chemical shifts for the new product ($\delta$109.2, 138.7, 145.7) made structure (248) difficult to accept, but the lack of any alternative structure, containing an exocyclic methylene group and having the same symmetry, made it equally difficult to reject. The solution to this dilemma was to accept structure (248) without its bridging bond or, more correctly, to regard the dipolar resonance structure (249) as the major contributor to bonding. In this way, the observed
spectrum became consistent with those for the organo-metallic complex (190) and the remarkably stable homocyclopropenium cation (290) reported very recently by Maier and his coworkers.

Figure 7: $^{13}$C Chemical Shifts of Some Homocyclopropenium Cations

The formation of this unusual bicyclic isomer of tetramethyl Dewar furan once again raises the question of how this unstable species undergoes ring contraction. Earlier in this chapter, the conclusion was reached that the initial step was C-O cleavage, in which the $\pi$-bond plays a passive role but stabilises the developing carbonium ion. It now appears that the $\pi$-bond plays an active role, since the predominance of the bicyclic product (248), particularly compared to the methylene cyclobutene (245), is best explained by the intermediacy of a discrete bicyclobutyl cation. Of course, these opposing conclusions regarding the role of the $\pi$-bond were made following experiments in solution and in the vapour phase (or possibly, in the case of FVP, on a surface) and the relative energies of solvated and unsolvated species will
be different. Accordingly, a general mechanism for Dewar furan ring contraction must recognise these dual possibilities, and that sketched below (Scheme 44) attempts to do this.

Thus the first step in isomerisation of Dewar furans is C-O cleavage, with or without participation by the π-bond, to form a bicyclobutyl cation (293) or a cyclobutenyl cation (292), each of which may lead directly to products. Alternatively, each may isomerise to the homocyclopropenyl cation (294) which then proceeds to products. This mechanism is consistent with all that is known about the Dewar furan ring system, while the original vinyl carbene alternative of Lemaï 37 can no longer be supported. In addition, this mechanism accounts for the high stability of the only isolable Dewar furan (102), and suggests that substitution of the ring system by electronegative groups, particularly on the π-bond, may provide further isolable derivatives in the future.
The synthesis of the Dewar furan photo-precursor (163) was facilitated by its high thermal stability, which results from the clamping effect of the succinimide ring on the otherwise labile bicyclo[4.2.0]octadiene moiety. This principle has been used to confer stability to other labile systems, notably benzene oxide and its carbocyclic analogue, norcaradiene. The epoxides (295) and (297), clamped by bridges of three and four carbon atoms, are stable, but the five membered bridge does not prevent ring opening to the oxepin (300). Norcaradiene appears to require more rigid clamping, since bridges of more than three carbons are too large to prevent ring opening to cycloheptatrienes (304) and (306).

The clamping effect of a 1,4-bridge has been studied for an analogous series of Dewar benzenes. As
before, the smallest bridge confers the greatest stability, with the Dewar benzene (307) proving stable even at 300°C.\textsuperscript{110}

The four carbon bridge of (309) provides a Dewar benzene with lesser thermal stability ($t_1 \approx 30$ mins at 140°C) which fragments to ethylene and p-xyylene rather than aromatising to (310).\textsuperscript{111} Aromatisation of the Dewar isomer (311) to the rather unstable [5]paracyclophane (312) has only recently been achieved, by photolysis at -60°C.\textsuperscript{112}

Before the vinyl carbene mechanism for Dewar furan ring contraction, with its implicit C-C cleavage, became untenable, it was hoped that bridging of the epoxide carbons might provide an isolable derivative of the elusive Dewar furan ring system. Initial attempts to introduce this bridge concentrated on the tetramethylcyclobutadiene adduct (199), which underwent radical bromination to produce a mixture of tetrabromides, from which the symmetrically substituted (313) was isolated in moderate yield. Selective debromination to the 1,3-diene (315) was achieved using unactivated zinc powder in boiling ether, and subsequent cycloaddition
with the triazolinedione (316) completed the construction of the required bridge.

A significant side reaction during debromination of (313) was production of the dimer (319) of the intermediate Dewar o-xylylene (318). In an attempt to prevent this dimerisation, debromination of (313) was carried out in boiling tetrahydrofuran in the presence of the cyclone (152) as trapping agent. However, no trace of the expected adduct (263) of the intermediate Dewar o-xylylene (318) was detected, and the dimer (319) was only a minor product, being exceeded threefold by its stereoisomer (321).

The reversal of facial selectivity in the two reactions can be rationalised by invoking the o-xylylene (320) as a transient intermediate in the higher boiling solvent, tetrahydrofuran. This proposal is supported by
the kinetic studies of Bauld and his coworkers on Dewar 
_\text{o-xylylene itself}:^{113} \text{ at 60-80°, this Dewar isomer}
undergoes reaction with moderately reactive dienophiles
with first order kinetics, indicating that ring opening
to _\text{o-xylylene precedes cycloaddition}. The reasons for
the preferential attack of the _o-xylylene \text{(320) at the}
_\beta\text{-face of its Dewar isomer (318) are not immediately}
clear, but it is interesting to note that the orbital
symmetry of the two reactants is such that a favourable
secondary orbital overlap, between the terminal methylene
groups of (318) and the methyl bearing carbons of the
tetraene (320), appears possible in this attack mode.

\text{Scheme 47}

The stereochemistries of the dimers (319) and (321)
were established by _n.O.e. difference spectroscopy, in
which irradiation of the high field methyl singlet caused
an 8\% _n.O.e. of one of the aliphatic methylene resonances
in dimer (319), but not in its stereoisomer (321). The same irradiation also produced a 5% n.O.e. of the higher field olefinic resonance in each dimer, indicating that these signals represent the outer protons of the 1,3-diene moieties, in agreement with the general assignment of Butler and Snow for such systems.

The resistance of the triazolinedione adduct (317) towards epoxidation prevented its further elaboration to a Dewar furan photo-precursor, and was ascribed to the heteroatoms β to the double bond. This problem could not be overcome by using conventional carbon dienophiles in place of the triazolinedione (316) since the diene (315) proved inert to such reagents, a consequence of the large distance between the termini of the diene system. The solution to this problem was contained in the dimerisation of (318), which suggested that suitably activated maleimides might undergo cycloaddition with (315). In practice, the 7-oxanorbornadiene (322) (vide infra) was found to embody the necessary properties of reasonable stability and high dienophilicity, reacting rapidly with (315) to produce a single adduct (323) which slowly extruded dimethylfuran, leaving (324) as the final product.
Since dibromides such as (324) are generally more resistant to epoxidation than the adducts derived therefrom, the debromination and trapping of (324) was carried out. The desired cyclone adduct (327) was isolated in only 5% yield, the major product being the somewhat intractable phthalimide (326), which precipitated during the reaction.

Scheme 40

Since the instability of the Dewar benzene intermediate (325) reduced its synthetic utility, attention turned to producing the desired adduct (327) by synthetic elaboration of the cyclone adduct (204). In initial experiments this compound proved unaccountably inert towards radical bromination, but after an induction period of several hours bromination of (204) proceeded rapidly, affording the readily isolable dibromide (328) and tribromide (329). Each of these was debrominated to the same 1,3-diene (263), the latter via the bromodiene
(330), but the dibromide (328) proved the more reliable precursor for (263).

The desired adduct (327) was isolated in good yield following reaction of the diene (263) with the dienophile (322) or, more conveniently, following debromination of their dibromides (328) and (357) in the same reaction vessel; the former method allowed NMR observation of the single, isomeric intermediate (331). The cyclobutene (327) was readily oxidised to the bridged epoxide (332), which was used in preference to the 1,3-diene (333), obtained from thermal decarbonylation, for solution photolyses, because of its greater solubility.

Given that Dewar furan undergoes ring contraction via C-O rather than C-C cleavage, it came as no surprise when the bridged derivative (334) was not detected
following photodecarbonylation and 1,2-photoaromatisation of the bridged epoxide (332), even using NMR at -80°C. The sole product observed was characterised by two high field methyl singlets, which can most plausibly be assigned to structure (336), since the two methyl groups in the Dewar isomer (334) and the spirocyclic cyclopropene (337) are equivalent. However, since this product could not be isolated its structure must remain speculative.
If Dewar furans were not to be isolated, then secondary evidence for their existence had to be gathered, and with this in mind attention turned to the synthesis of derivatives carrying electron withdrawing substituents on the \( \pi \)-bond, in order to facilitate Diels-Alder trapping. The use of cyclobutadienes bearing such substituents as starting materials for such a synthesis was precluded by problems of regioselectivity and possible dimerisation, and it was necessary to employ a cyclobutadiene transfer reagent. The tricyclic diester (339) fulfilled this role, undergoing photoaddition to the maleimide (148) to form a single product (340), which ejected the furan (341) upon FVP. Unfortunately, the desired cyclobutene (342) so liberated proved too unstable for isolation, and underwent ring opening followed by loss of bromine to afford the phthalimide (344) as the only isolable product.
Debromination of the photoadduct (340) produced the same phthalimide (344), notwithstanding the use of the cyclone (152) as trapping agent. Even when a large excess of furan was employed in this trapping role the yield of adduct (346) was low, reflecting the low stability of the intermediate cyclobutene diester (345).

Scheme 54

At this stage, a more direct entry to a Dewar furan derivative of exceptional dienophilicity was developed. Epoxidation of the photoadduct (348) of 2-butyne and the maleimide (148) provided the two stereoisomeric epoxides
(349) and (350), each of which, while resistant to zinc/silver couple, was debrominated by a reagent prepared from zinc powder and a catalytic amount of titanium tetrachloride in anhydrous tetrahydrofuran. The Dewar furan (351) so produced could not be isolated, but was trapped as two stereoisomeric adducts (352a,b) when furan was used as cosolvent. A third adduct was assigned the chlorohydrin structure (353) on the basis of elemental analysis and spectral characteristics, and was also isolated when the epoxide adducts (352a,b) were subjected to the same debromination conditions. Formation of chlorohydrins by treatment of epoxides with titanium tetrachloride has ample precedent.

Scheme 55

The powerful zinc/titanium tetrachloride reagent also proved capable of debrominating the cyclobutene (348), although in this case the cyclobutene (354) was a major
by-product. The structure of this latter cyclobutene was confirmed by photochemical synthesis from 2-butyne and \( N \)-methylmaleimide. The highly strained cyclobutadiene (355) was trapped in modest yield as a single adduct (356) with furan; the somewhat higher yield of Dewar furan adducts (352a,b) obtained under the same conditions suggests that the cyclobutadiene (355) is rather less stable than its epoxide (351).

Scheme 56

Flash vacuum pyrolysis of the Dewar furan adducts (352) at 500°C resulted in the isolation of the bicyclic furan (360). While it is tempting to interpret this result in terms of retro Diels-Alder cleavage of furan from the adducts (352) followed by ring opening of the Dewar furan (351) so produced, radical mechanisms for fragmentation of the adducts (352), which need not proceed via the Dewar isomer (351), can not be ruled out.

The structure of the bicyclic furan (360) was confirmed by independent synthesis. Hydrogenation of the adduct (357) of dimethylfuran (65) with the maleimide (148), followed by debromination, afforded the stable
maleimide (359). This compound extruded ethylene on FVP (550°C) to produce the furan (360) in high yield.

While debromination of (358) was readily effected using unactivated zinc powder in boiling ether, formation of the 7-oxanorbornadiene (322) from dibromide (357) relied on the more powerful zinc/silver powder in boiling tetrahydrofuran, and was complicated by the by-products (361) and (362). The stereochemistry of the bis-adduct (361) is readily apparent from the non-equivalence of its two pairs of methyl groups, and this product arises through retro Diels-Alder cleavage of the furan (65) from adduct (357) followed by reaction with the activated maleimide (322). Deoxygenation of 7-oxanorbornadienes by metals, in this case producing the phthalimide (362), is an established synthetic method.¹¹⁸
Reasonably pure samples of the 7-oxanorbornadiene (322) could be isolated by recrystallisation, but yellowed rapidly on exposure to the air, in contrast to the stable 7-oxanorbornene (359). This difference in stability parallels that observed between the stable norbornene (363) and the norbornadiene (364), which can only be stored at -60°C under nitrogen. Similar large differences in Diels-Alder reactivity between (359) and the highly dienophilic (322) were observed (see Experimental Section).

In addition to the synthesis of highly dienophilic Dewar furan derivatives, the development of highly reactive dienes received early consideration during this research project. One such candidate was o-xylylene, which because of its high reactivity would require generation in situ. A potential o-xylylene precursor, 5,6-bis(methylene)-norborn-2-en-7-one (365), previously prepared only in
unsubstituted form,121 was subjected to retrosynthetic analysis, and its synthesis was reduced to two steps: cycloaddition of cyclopentadienone with a butatriene equivalent, followed by formation of the exocyclic double bonds. This methodology was successfully applied to the substituted system (207), as outlined in Scheme 59. The initial cycloaddition proceeded in poor yield, because of the formation of intractable by-products, but dehydrobromination of adduct (367), using fluoride ion as the base,122 provided the desired (207) in excellent yield.

Decarbonylation of (207) was accomplished by FVP, which afforded the benzocyclobutene (369), presumably via the o-xylylene (368) as is well documented.123 Unfortunately, the ketone (207) proved photostable, ruling out its use as a trapping agent for photochemically generated Dewar furans.
Although not applicable to the Dewar furan problem, the ketone (207) found use in the preparation of another highly labile ring system, the long sought norbornadiene-7-one (375). Decarbonylation of such species occurs readily because concerted loss of carbon monoxide is permitted by orbital symmetry\textsuperscript{124} and leads directly to aromatic products. Prior to this work, the only isolable derivatives of (375) had both double bonds incorporated in aromatic rings,\textsuperscript{125} or coordinated in an irontricarbonyl complex.\textsuperscript{126} Early claims to have isolated simpler derivatives were convincingly refuted by Yankelevich and Fuchs\textsuperscript{127} and the only subsequent report of this nature,\textsuperscript{128} in which the norbornadienone was allegedly synthesised by dehydrogenation of the corresponding norbornenone using bromine in boiling bromobenzene, is clearly incorrect: despite the severity of their conditions, these workers appear to have recovered their norbornenone unchanged.

The first authenticated example of the elusive norbornadiene-7-one ring system was achieved by reaction of the 1,3-diene (207) with the triazolinedione (316) at -40°C. The resultant adduct (370) decarbonylated rapidly to form the aromatic compound (371) below ambient temperature, but was sufficiently stable for characterisation by \textsuperscript{13}C NMR at -40°C (Figure 8).
Scheme 01

Figure 8. $^{13}$C NMR spectra of the norbornadienone (370) and the aromatic compound (371)

Norbornadien-7-one itself (375) has subsequently been synthesised, by photolysis of the α-diketone (372) or the azo compounds (373) and (374). The parent
system is significantly less stable ($t_{1/2} = 25$ mins at $-60^\circ C$) than the heavily substituted derivative (370) reported here, and the $^{13}$C carbonyl resonance of (375) appears at characteristically high field ($\delta$ 194.9).\textsuperscript{129}

**Scheme 62**

The unusually high field $^{13}$C carbonyl resonances of the norbornadienones (370) and (375) appears to result from delocalisation of the positive charge on the carbonyl carbon through cross conjugation with the proximate $\pi$-bonds, as in structure (377). This phenomenon has been documented for an extensive series of norbornanones and norbornenones,\textsuperscript{131} from which the three representatives (378) to (380) illustrate the upfield trend that accompanies such charge delocalisation.
The direct observation of the norbornadienone (370) demonstrates the utility of low temperature solution NMR for characterisation of labile ring systems. Unfortunately, the extreme instability of simple Dewar furans places them beyond the limits of this technique, and future efforts to observe such species directly will have to rely on cross polarisation-magic angle spinning of matrix isolated Dewar furans, a recently developed technique for which a single and particularly simple application has been reported.\textsuperscript{132}
General Procedures

Melting points were recorded on a Reichert hot-stage microscope, and are uncorrected, except those reported in sealed tubes, which were recorded on an Electrothermal melting point apparatus. Microanalyses were performed by the Australian National University Microanalytical Service. Routine $^1$H NMR spectra were recorded on a Varian CFT-20 80 MHz spectrometer, and lower temperature $^1$H NMR spectra on a Brücker HFX-270 270 MHz instrument. $^{13}$C NMR spectra were recorded on this latter instrument, operated at 67.89 MHz, or on a Brücker CXP-200 spectrometer, operated at 50.3 MHz. Nuclear Overhauser difference spectra were also recorded on this last instrument. All spectra were recorded in deuteriochloroform solution, unless otherwise stated, using tetramethylsilane as internal standard. Low resolution mass spectra were recorded on a Varian MAT CH7 mass spectrometer.

Column chromatography was carried out over Merck 60 silica gel or Spence type H activated alumina. Layer chromatography utilised Merck 60 PF254 silica coated to glass plates, either conventionally (preparative layer chromatography) or, following the acquisition of a Chromatotron Model 7924 T, entirely with the aid of this instrument (centrifugal layer chromatography). HPLC utilised a Waters Associate Series 6000 system, incorporating Whatman Partisil prepacked silica columns.
All solvents for HPLC were distilled prior to use; ether and tetrahydrofuran were dried over sodium wire and distilled from lithium aluminium hydride immediately before use. Solvent extracts were dried over magnesium sulphate.

Photolyses were carried out in quartz vessels, using an American Hanovia medium pressure mercury arc lamp (450w) in a Vycor filter (λ > 225nm) or a spiral low pressure mercury arc lamp (λ = 254nm). Low temperature photolyses utilised the apparatus described by Tan.133

Flash vacuum pyrolyses (FVP) were carried out through an evacuated quartz tube (5 x 200mm) packed with quartz chips, which was heated by a furnace comprising a larger quartz tube wrapped with heating tape and asbestos tape. The temperature was measured using a single thermocouple at the centre of the furnace.

The following compounds were prepared according to published procedures: cis-3,4-dichlorocyclobutene (172),134 cyclobutadieneirontricarbonyl (140),135 dibromo-N-methyl maleimide (148),136 the dimer (381) of 2,5-dimethyl-3,4-diphenylcyclopentadienone (152),137 1,4-dihydro-1,4-endoxynaphthalene (170),138 dimethyltricyclo[4.2.2.0^2,5]-deca-3,7,9-triene-7,8-dicarboxylate (178),139 furan-2,5-\(\bar{d}\)2,140 N-p-tolyltriazolinedione (316),141 1,3-diphenylisobenzofuran (214),142 tetramethylfuran,143 decamethyltricyclo[4.2.2.0^2,5]deca-3,7,9-triene-7,8-dicarboxylate (280)101 and 2,3-bis(trifluoromethyl)-7-oxanorbornadiene (338).144

\[ \text{cis-3,4-dichlorocyclobutene (172)} \]

\[ \text{cyclobutadieneirontricarbonyl (140)} \]

\[ \text{dibromo-N-methyl maleimide (148)} \]

\[ \text{the dimer (381) of 2,5-dimethyl-3,4-diphenylcyclopentadienone (152)} \]

\[ \text{1,4-dihydro-1,4-endoxynaphthalene (170)} \]

\[ \text{dimethyltricyclo[4.2.2.0^2,5]-deca-3,7,9-triene-7,8-dicarboxylate (178)} \]

\[ \text{furan-2,5-\(\bar{d}\)2} \]

\[ \text{N-p-tolyltriazolinedione (316)} \]

\[ \text{1,3-diphenylisobenzofuran (214)} \]

\[ \text{tetramethylfuran} \]

\[ \text{decamethyltricyclo[4.2.2.0^2,5]deca-3,7,9-triene-7,8-dicarboxylate (280)} \]

\[ \text{2,3-bis(trifluoromethyl)-7-oxanorbornadiene (338)} \]
Granulated zinc/silver couple was prepared according to the method of Conia et al., with the omission of the acetic acid wash, and stored under anhydrous ether prior to use.

Activated zinc for dechlorination was prepared by the published method, involving stirring zinc powder with ammonium chloride solution, and stored under absolute ethanol prior to use.

\[(\text{1a,2a,5a,6a})-1,6\text{-Dibromo-8-methyl-8-azatriacyclo[4.3.0.0^2,5]non-3-ene-7,9-dione (149)}\]

A solution of cyclobutadieneirontricarbonyl (140) (1.60g; 8.3mmol) and dibromo-N-methylmaleimide (148) (2.20g; 8.2mmol) in 96% ethanol (130cm^3) was cooled to 0°C and stirred vigorously while being treated with small portions of ceric ammonium nitrate (35g) during thirty minutes. After stirring for a further ten minutes, the mixture was poured into water (300 cm^3) and extracted with dichloromethane (3 x 50cm^3). The combined extracts were washed with water, dried, and evaporated to afford a yellow solid, which crystallised from methanol as pale yellow plates (1.84g) of the product. Centrifugal layer chromatography (5% ethyl acetate in hexane) of the residues from the mother liquors returned 0.16g of unreacted maleimide (149) followed by further product, raising the yield to 2.20g (90%).

M.p. 158-9°. Found: C, 34.00; H, 2.26; N, 4.28.
Calc. for C₉H₇Br₂NO₂: C, 33.68; H, 2.20; N, 4.36.

¹H NMR δ 3.08, s, 3H, CH₃; 3.95, t, J 1.4Hz, 2H, H2, H5; 6.32, t, J 1.4Hz, 2H, H3, H4. Mass spectrum m/z 276 (4%).
A solution of the dibromide (149) (200mg; 0.62 mmol) and the cyclone dimer (381) (160mg; 0.31mmol) in anhydrous tetrahydrofuran (4cm³) was heated to reflux, stirred for five minutes, treated with granulated zinc/silver couple (ca.1g) and stirred under reflux for one hour. The reaction mixture was poured into 2M hydrochloric acid, and extracted with dichloromethane. The dichloromethane extracts were washed sequentially with water, saturated sodium bicarbonate solution and water, dried, and evaporated to afford a colourless oil, the components of which were separated by preparative layer chromatography (dichloromethane). The less mobile constituent, N-methylphthalimide (151) (45mg; 45%), crystallised from methanol as white needles, m.p. 133-4° (lit. 147-132°). The slightly more mobile adduct (153) (115mg; 44%) crystallised from methanol as white crystals.

M.p. 177° (decomposition). Found: C, 79.79; H, 5.55; N, 3.37. Calc. for C₂₈H₂₃N₂O₃: C, 79.79; H, 5.50; N, 3.32. ¹H NMR δ 1.47, s, 6H, 2 x CH₃; 3.00, s, 3H, NCH₃; 3.34, t, J 1.3Hz, 2H, H8, H9; 6.32, t, J 1.3Hz, 2H, H10, H11; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 421(3%), 393(22), 377(34), 193(16), 105(11), 52(100).

Photolysis of (153)

A solution of the cyclobutene (153) (12mg) in
acetone-\textsubscript{d\textsubscript{6}} (0.3cm\textsuperscript{3}) was freeze-thaw degassed, sealed in \textit{vacuo} in a quartz \textsuperscript{1}H NMR tube, cooled to -80\textdegree C and irradiated (\(\lambda = 254\text{nm}\)) for 90 minutes. The \textsuperscript{1}H NMR spectrum of the photolysate indicated that little starting material remained, and that the major photoproduct was the phthalimide (157). A single resonance occupied the olefinic region of the spectrum, at the unusually high field of 65.96. This was assigned to the \textit{syn} dimer (158) of cyclobutadiene (lit.\textsuperscript{148} 65.95). A number of smaller resonances between 1 ppm and 4 ppm were not identified.

\begin{equation}
\text{la,2a,3S,5S,6a,7a)-1,7-Dibromo-9-methyl-4-oxa-9-azatetracyclo[5.3.0'\textsubscript{2,6}.0\textsubscript{2,5}]-deca-6,8-dione (159)}
\end{equation}

A solution of the cyclobutene (149) (2.30g; 7.2mmol) in ethanol free chloroform (30cm\textsuperscript{3}) was heated to reflux and treated with \textit{m}-chloroperbenzoic acid (85%, 4 x 1.0g; 19.7mmol) at 12 hour intervals. After stirring under reflux for a total of 48 hours, the reaction mixture was poured into 2M NaOH (150cm\textsuperscript{3}) and extracted into dichloromethane (3 x 40cm\textsuperscript{3}). The combined dichloromethane extracts were washed successively with 2M NaOH (50cm\textsuperscript{3}) and water (100cm\textsuperscript{3}), dried, and evaporated to afford a pale yellow solid, which crystallised from methanol as white needles (1.52g) of the product. The mother liquors were eluted through an alumina column with dichloromethane, and again recrystallised, raising the yield to 1.80g (75%).

M.p. 177-8°. Found: C, 31.78; H, 2.22; N, 4.00.
Calc. for C\textsubscript{9}H\textsubscript{7}Br\textsubscript{2}N\textsubscript{0}\textsubscript{3}: C, 32.08; H, 2.09; N, 4.16.

\textsuperscript{1}H NMR \(\delta \ 3.16, \text{ s, } 3\text{H}, \text{CH}_3; 3.43, \text{ d, } J \text{ 3.8Hz, } 2\text{H, H2, H6;}
\)
3.99, d, 3.8 Hz, 2H, H3, H5. Mass spectrum m/z 258 (42%), 256(40), 172(21), 170(20), 145(22), 143(26), 92(31), 68(100), 63(54).

\[(\text{la}^{12S},3a^{8},5a,6B,7a,8B,11B)-8,11,13-
\text{Trimethyl-9,10-diphenyl-4-oxa-13-azahexacyclo[8.4.3.1^{18},11.0^{1},7.0^{2},6.0^{3},5]}-pentadec-9-ene-12,14,15-trione (161)\]

A solution of the dibromide (159) (0.80g; 2.4 mmol) and the cyclone dimer (381) (0.62g; 1.2 mmol) in anhydrous tetrahydrofuran (15cm³) was heated to reflux, stirred for five minutes, treated with granulated zinc/silver couple (ca.2g), stirred under reflux for one hour, and worked up in the manner described for the adduct (153). The product was isolated by crystallisation from methanol/dichloromethane as white needles (0.58g). Further product was isolated from the mother liquors by preparative layer chromatography (dichloromethane), raising the yield to 0.74g (71%).

M.p. 220-1° (decarbonylation). Found: C, 76.45; H, 5.34; N, 3.33. Calc. for C\textsubscript{28}H\textsubscript{23}N\textsubscript{O}\textsubscript{4}: C, 76.87, H, 5.30; N, 3.20.

\[^{1}\text{H} NMR \delta 1.46, s, 6H, 2 \times \text{CH}_3; 2.86, d, J 4.0 Hz, 2H, H2, H6; 3.05, s, 3H, NCH\textsubscript{3}; 3.98, d, J 4.0 Hz, 2H, H3, H5; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 437 (48), 410(23), 409(74), 340(81), 339(100).

\[(\text{la}^{12B},3a^{8},5a,6B,7a,8B,11B,15B)-15-
\text{Hydroxy-8,11,13-trimethyl-9,10-diphenyl-4-oxa-13-azahexacyclo[5.4.3.1^{18},11.0^{1},7.0^{2},6.0^{3},5]}pentadec-9-ene-12,14-dione (162)\]
A solution of the ketone (161) (26mg) in methanol (3cm³) was stirred under reflux with sodium borohydride (ca. 100mg) for two hours, poured into water, and extracted into chloroform. The chloroform extract was washed with water, dried, and evaporated to afford a white solid, which crystallised from hexane as white needles (21mg; 80%).

M. p. 230° (decomposition). Found: C, 76.31; H, 5.94; N, 3.14. Calc. for C₂₈H₂₅N₂O₄: C, 76.52; H, 5.73; N, 3.19.¹H NMR δ 1.47, s, 6H, 2 × CH₃; 2.92, s, 3H, NCH₃; 3.33, d, J 3.7Hz, 2H, H₂, H₆; 3.71, s, 1H, H₁₅; 3.86, d, J 3.7Hz, 2H, H₃, H₅; 6.8–7.2, m, 10H, aromatic. Mass spectrum m/z 439 (84%), 342(27), 341(100), 252(34).

(1α,2α,3α,5α,6β,7α)-8,11,13-Trimethyl-8,10-diphenyl-4-oxa-13-azapentacyclo[5.4.3.0₁,7.0₂,6.0₃,5]tetradeca-8,10-diene-12,14-dione (163)

A solution of the ketone (161) (400 mg; 0.92mmol) in diglyme (6cm³) was stirred under reflux for one hour. Solvent was removed under high vacuum and the product was isolated from the crystalline residue by centrifugal layer chromatography (5-10% ethyl acetate in hexane) as a white crystalline solid (328mg; 88%) which was recrystallised from methanol.

s, 6H, 2 x CH₃; 3.16, s, 3H, NCH₃; 3.22, d, J 3.6Hz, 2H, H2, H6; 3.94, d, J 3.6Hz, 2H, H3, H5; 6.7-7.1, m, 10H, aromatic. Mass spectrum m/z 410 (15%), 409(50), 340(68), 339(100), 310(47).

Low temperature solution photolyses of (163)

(i) Acetone solution: ¹H NMR analysis at 30°C

A solution of the Dewar furan precursor (163) (4.2mg) in acetone- d₆ (0.3cm³) was freeze-thaw degassed, sealed under argon, cooled to -70°C, and irradiated (λ = 254nm) for 70 minutes. The ¹H NMR spectrum of the photolysate, recorded at 30°C, indicated that ca. 90% of the photosubstrate (163) had undergone conversion to the phthalimide (157). Furan was present, at the limits of spectroscopic detection (ca. 5% yield).

A solution of (163) (3.9mg) and furan (ca. 10mg) in acetone- d₆ (0.3cm³) was prepared in the same way, and photolysed simultaneously. In this case, photoaromatisation was >95% complete after 70 minutes, and only ca. 30% of the furan originally present remained. No other products could be detected.

(ii) Acetone solution: ¹H NMR analysis at -80°C

A solution of the Dewar furan precursor (163) (ca. 5mg) in acetone-d₆ (0.3cm³) was freeze-thaw degassed, sealed in vacuo in a quartz ¹H NMR tube, cooled to -85°C, and irradiated (λ = 254nm) for one hour. The photolysate was cooled to -110°C, and allowed to warm to -80°C in a precooled ¹H NMR probe. The ¹H NMR spectrum revealed the presence of three products, in a molar ratio of ca. 5:1:1; these were the phthalimide (157), furan, and unreacted...
(163). When the $^1$H NMR spectrum was recorded at 30°C, the ratio of the same three products was ca. 20:1:1.

An identical experiment was performed, and solvent and volatile products were transferred under high vacuum to a clean $^1$H NMR tube, cooled in liquid nitrogen, prior to analysis at -80°C. No products other than furan were detected.

(iii) Tetrahydrofuran solution: $^1$H NMR analysis at 30°C

A solution of the Dewar furan precursor (163) (20 mg) in tetrahydrofuran-$d_8$ (0.3cm$^3$) was cooled to -85°C and irradiated ($\lambda = 254$nm) for one hour. The $^1$H NMR spectrum of the photolysate indicated that ca. 35% of the precursor had undergone photoaromatisation. The presence of furan (ca. 15% yield) was confirmed by the addition of authentic material. No new products were detected.

An identical solution was prepared, and treated with freshly prepared isobenzofuran$^{67}$ (ca. 0.8 eq) prior to photolysis ($\lambda = 254$ nm) at -60°C for one hour. The extent of photoaromatisation was again ca. 35% but furan could not be detected. Approximately half of the isobenzofuran remained, while the formation of adducts was apparent from signals in the region of 5 ppm. The presence of the isobenzofuran photodimer (170), and the exo adducts (166) and (168) (ratio ca. 4:1) was confirmed, following change of solvent to chloroform-$d$, by comparison with authentic material.

(iv) Furan solution: $^1$H NMR analysis at 30°C

A solution of the adduct (161) (ca. 15 mg) in
furan-2,5-\textsubscript{d}\textsuperscript{140} (0.3 cm\textsuperscript{3}) was irradiated (\(\lambda = 254\) nm) at 30°C for 40 minutes. Solvent was recovered by distillation (17 torr) and the residue was dissolved in chloroform-\(d\) and analysed by \(^1\text{H}\) NMR. The initial adduct (161), the Dewar furan precursor (163), and the phthalimide (157) were present, in a molar ratio of ca. 1:1:5. Small traces of other compounds were evident, but none corresponded to an adduct of Dewar furan with furan.

(v) Tetrahydrofuran/isobenzofuran solution: isolation of adducts

Isobenzofuran was prepared by the method of Warrener.\textsuperscript{67} A solution of the endoxynaphthalene (170) (0.50g; 3.5 mmol) in anhydrous dimethylsulphoxide (5cm\textsuperscript{3}) was treated with dipyridyl-s-tetrazine (171) (0.84g; 3.6mmol) and the resultant suspension was stirred occasionally during 20 minutes at ambient temperature (external cooling required). The yellow dihydropyridazine adduct (ca. 0.7g; 60%) was isolated by filtration, washed with anhydrous ether and dried in vacuo prior to pyrolysis (120°/0.01 torr). A plug of cotton wool prevented physical transfer of pyridazine during the vigorous sublimation that ensued, a problem cited by other workers,\textsuperscript{149} and pure isobenzofuran (ca. 0.2g) collected as a white crystalline solid in a flask cooled to -78°C.

Isobenzofuran, so prepared, was dissolved in cold (<0°C) anhydrous tetrahydrofuran (1.0cm\textsuperscript{3}), and transferred to a quartz \(^1\text{H}\) NMR tube containing the Dewar furan precursor (163) (100mg; 0.24mmol). The solution that resulted from
vigorous shaking below 0°C was then irradiated (λ = 254nm) for one hour.

Products were separated by centrifugal layer chromatography (5-25% ethyl acetate in hexane) and identified by $^1$H NMR, in order of elution, as isobenzofuran, the phthalimide (157), unreacted precursor (163), a mixture of isobenzofuran adducts, dimer (170) and traces of phthalaldehyde (382), and endo aldehyde adduct (169). The exo/endo ratios of the primary and secondary pairs of adducts remained constant, but the ratio of one pair to the other varied with temperature, as tabulated below. The previously unreported phthalimide (157) was recrystallised from methanol.

<table>
<thead>
<tr>
<th>Photolysis temp., °C</th>
<th>Yield, mg, from initial separation</th>
<th>Total adducts, mg, (%)</th>
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<tbody>
<tr>
<td></td>
<td>(157) (163) (170) (166) (167) (168) (169)</td>
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<tr>
<td>-5</td>
<td>47 44 10 3 2 16 5</td>
<td>26(100)</td>
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<tr>
<td>-25</td>
<td>53 38 11 6 4 15 4</td>
<td>29(100)</td>
</tr>
<tr>
<td>-45</td>
<td>40 52 19 8 5 7 2</td>
<td>22(100)</td>
</tr>
<tr>
<td>-65</td>
<td>44 47 13 10 7 5 2</td>
<td>24(100)</td>
</tr>
</tbody>
</table>

The unresolved mixture of adducts was separated by HPLC (Whatman Partisil M9 10/25) using 10% ethyl acetate in hexane at 4cm$^3$/min. Retention times were: (170)13.3; (382)16.0; (168)17.7; (167)18.7; (166)22.3 mins. Epoxides (166) and (167) crystallised as white needles from hexane.

(1αα,1ββ,2α,7α,7αβ,7βα)-1α,1β,2,7,7α,7β-Hexahydro-2,7-epoxynaphtho[2',3':3,4]cyclobuta[1,2-b]oxirene (166)
Hexahydro-2,7-epoxynaphtho[2',3':3,4]cyclo-
buta[1,2-b]oxirene (167)

Reaction of isobenzofuran with cis-3,4-dichlorocyclobutene

A solution of dipyridyl-s-tetrazine (171) (1.70 g; 7.2 mmol) and 3,4-dichlorocyclobutene (172) (0.70 g; 5.7 mmol) in anhydrous tetrahydrofuran (10 cm³) was stirred under reflux while being treated with a solution of the endoxynaphthalene (170) (1.00 g; 6.9 mmol) in anhydrous
tetrahydrofuran (5cm$^3$) during 30 minutes. After a further 10 minutes at reflux, the reaction mixture was worked up, in the manner described for the adduct (153), to afford a mixture of three adducts. These were separated by centrifugal layer chromatography (3-5% ethyl acetate in hexane) and identified, in order of elution, as (175) (0.21g; 15%), (174) (0.22g; 16%) and (173) (0.36g; 26%). Each adduct crystallised from dichloromethane/hexane.

(1a,2a,2aa,3B,8B,8aa)-1,2-Dichloro-1,2-2a,3,8,8a-hexahydro-3,8-epoxy cyclobuta[b]-naphthalene (175)

M.p. 126-7°. Found: C, 59.84; H, 4.20. Calc. for C$_{12}$H$_{10}$Cl$_2$O: C, 59.78; H, 4.18. $^1$H NMR δ 2.72, m, 2H, H2a, H8a; 4.39, m, 2H, H1, H2; 5.31, s, 2H, H3, H8; 7.21, m, 4H, aromatic. Mass spectrum m/z 242(12%), 240(17), 207(35), 205(100), 169(43), 141(41), 118(80), 115(50).

(1a,2a,2aa,3a,8a,8aa)-1,2-Dichloro-1,2,2a,3,8,8a-hexahydro-3,8-epoxy cyclobuta[b]napthalene (174)

M.p. 165-6°. Found: C, 59.27; H, 4.03. Calc. for C$_{12}$H$_{10}$Cl$_2$O: C, 59.78; H, 4.18. $^1$H NMR δ 3.24, d, J 1.1Hz, 2H, H1, H2; 3.35, m, 2H, H2a, H8a; 5.47, m, 2H, H3, H8; 7.33, m, 4H, aromatic. Mass spectrum m/z 242(6%), 240(8), 207(37), 205(100), 169(45), 141(40), 118(92), 115(60).

(1a,2a,2ab,3a,8a,8ab)-1,2-Dichloro-1,2,2a,3,8,8a-hexahydro-3,8-epoxy cyclobuta[b]napthalene (173)

C\textsubscript{12}H\textsubscript{10}Cl\textsubscript{2}O: C, 59.84; H, 4.18. \textsuperscript{1}H NMR \delta 2.78, m, 2H, H2a, H8a; 4.84, m, 2H, H1, H2; 5.51, s, 2H, H3, H8; 7.21, m, 4H, aromatic. Mass spectrum m/z 242(7%), 240(9), 207(19), 205(51), 169(28), 141(25), 118(100), 115(33).

(2aa,3β,6β,8αa)-2a,3,8,8αa-Tetrahydro-3,8-epoxycyclobuta[b]naphthalene (177)

A solution of the dichloride (175) (100mg; 0.41mmol) in absolute ethanol was stirred under reflux with activated zinc (ca. 1g) for fifteen hours. The reaction mixture was filtered through celite, and the residue was washed thoroughly with dichloromethane. The filtrate was then worked up, in the manner described for the adduct (153), to afford the cyclobutene (177) as an ill-smelling white solid (64mg; 91%) which crystallised from petroleum ether.

M.p. 73-4\textdegree. Found: C, 84.45; H, 6.04. Calc. for C\textsubscript{12}H\textsubscript{10}O: C, 84.68; H, 5.92. \textsuperscript{1}H NMR \delta 2.75, s, 2H, H2a, H8a; 4.92, s, 2H, H3, H8; 6.24, s, 2H, H1, H2; 7.19, m, 4H, aromatic. Mass spectrum m/z 170(44%), 169(27), 142(68), 141(100), 115(63).

Epoxidation of (177)

The reaction between the cyclobutene (177) (32mg; 0.19mmol) and m-chloroperbenzoic acid (ca. 1.5 eq) in chloroform-\textit{d} (0.5cm\textsuperscript{3}) was monitored by \textsuperscript{1}H NMR and found to proceed to a single product, the epoxide (166), and to be >95% complete after two hours at ambient temperature. After a total of 4 hours reaction the product was isolated by standard work up (cf. epoxide (159)) as a white solid (34mg;
97%) which crystallised from hexane as white needles, m.p. 123-4°.

\((2\text{aa}, 3\text{a}, 8\text{a}, 8\text{aa})-2\text{a}, 3, 8, 8\text{a}-\text{Tetrahydro-3,8-epoxycyclobuta}[b]\text{naphthalene} (176)\)

The dichloride (174) was dechlorinated in the same way as its isomer (175) to afford a mixture of unreacted dichloride and the cyclobutene (176). Centrifugal layer chromatography (4% ethyl acetate in hexane) returned the dichloride (17mg) followed closely by the cyclobutene (176) (49mg; 84%), an odourless white solid which crystallised from petroleum ether as white needles.

M.p. 54-5°. Found: C, 84.69; H, 6.02. Calc. for C\(_{12}\text{H}_{10}\text{O}\): C, 84.68; H, 5.92. \(^1\text{H} \text{NMR} δ 3.47, m, 2\text{H}, H_2\text{a}, H_8\text{a}; 5.21, m, 2\text{H}, H_3, H_8; 5.76, s, 2\text{H}, H_1, H_2; 7.15, s, 4\text{H}, \text{aromatic}. \text{Mass spectrum} m/z 170(35%), 169(27), 142(74), 141(100), 115(62).

**Epoxidation of (176)**

The reaction between the cyclobutene (176) (29mg; 0.17mmol) and \(\text{m-chloroperbenzoic acid} (\text{ca. 1.5 eq})\) in chloroform-\(d\) (0.5cm\(^3\)) was monitored by \(^1\text{H} \text{NMR} \) and found to proceed to a single product, the epoxide (167), and to be >90% complete after two hours at ambient temperature. After a total of six hours reaction the product was isolated as before as a white solid (31mg; 98%) which crystallised from hexane as white needles, m.p. 130-1°.

**Lanthanide induced shift studies**

A solution of the adduct (166) (4.6mg; 24.7 \(\mu\text{mol}\) in chloroform-\(d\) (1.0cm\(^3\)) was added in portions to
Eu(fod-\textit{d}$_9$)$_3$ (15.7mg; 14.8 \textmu mol) in a $^1$H NMR tube, and the $^1$H NMR spectra of the solutions obtained after each addition were recorded. Results for this and identical experiments, involving (167) (4.5, 15.7mg), (173) (5.3, 15.2mg), (174) (6.0, 15.6mg) and (175) (5.4, 15.2mg), are tabulated below.

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<th>Volume, ( \mu l )</th>
<th>( \Delta \delta )</th>
<th>( \text{H3} )</th>
<th>( \text{H2a} )</th>
<th>( \text{H2} )</th>
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<th>( \Delta \delta )</th>
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| (175)          |                |       |       |       | (174)          |                |       |       |       |
| 250            | 9.8            | 5.6   | 4.0   |       | 250            | 9.6            | 5.2   | 3.1   |       |
| 300            | 9.2            | 5.3   | 3.8   |       | 310            | 9.1            | 4.9   | 2.9   |       |
| 360            | 8.6            | 4.9   | 3.6   |       | 380            | 8.4            | 4.5   | 2.7   |       |
| 430            | 8.0            | 4.6   | 3.3   |       | 460            | 7.8            | 4.2   | 2.5   |       |
| 510            | 7.5            | 4.3   | 3.1   |       | 550            | 7.3            | 3.9   | 2.3   |       |
| 600            | 6.9            | 4.0   | 2.9   |       | 650            | 6.7            | 3.6   | 2.1   |       |
| 700            | 6.4            | 3.7   | 2.6   |       | 750            | 6.1            | 3.3   | 1.9   |       |
| 800            | 5.9            | 3.4   | 2.4   |       | 870            | 5.5            | 3.0   | 1.8   |       |
| 900            | 5.4            | 3.1   | 2.2   |       | 1000           | 5.0            | 2.7   | 1.6   |       |
| 1000           | 5.0            | 2.9   | 2.1   |       |                |                |       |       |       |

| (173)          |                |       |       |       | (173)          |                |       |       |       |
| 250            | 1.0            | 0.6   | 0.6   |       | 500            | 0.7            | 0.4   | 0.4   |       |
| 320            | 0.9            | 0.5   | 0.5   |       | 640            | 0.6            | 0.4   | 0.4   |       |
| 400            | 0.8            | 0.5   | 0.5   |       | 800            | 0.6            | 0.4   | 0.3   |       |
| 1000           | 0.5            | 0.3   | 0.3   |       |                |                |       |       |       |
Epoxidation of dimethyltricyclo[4.2.2.0²,6]deca-8,7,9-triene-7,8-dicarboxylate (178)

A solution of the diester (178) (5.8g; 23.6mmol) and m-chloroperbenzoic acid (ca. 60%; 8.0g; 27.7mmol) in dichloromethane (60cm³) was set aside at ambient temperature for fifteen hours and worked up in the manner described for the epoxide (159) to afford a clear, viscous oil. This was chromatographed on a column of silica gel (35-70 mesh; 110g), using ethyl acetate (10-80%) in hexane as eluent, and separated into three fractions. The most mobile (ca. 50mg) was unreacted (178); this was followed by a monoepoxide fraction (5.0g; 81%) and a bis epoxide (1.2g; 18%). The monoepoxide fraction contained (179) and (180) (ratio 3:1) and was recrystallised from methanol as a white crystalline mass, m.p. 89-94°, containing <10% (180). Analytical samples of the two monoepoxides were obtained by repetitive centrifugal layer chromatography (5-15% ethyl acetate in hexane), (179) eluting first, followed by recrystallisation from methanol. The bis epoxide fraction was homogeneous, and crystallised from methanol as white plates.

(1a,2b,3a,5a,6b,7a)-Dimethyl-4-oxatetracyclo[5.2.2.0²,6]undeca-8,10-diene-8,9-dicarboxylic acid (179)

M.p. 101-2° (lit. 72° 96°). ¹H NMR as reported. ³

(1a,2a,5a,6a,7b,8b)-Dimethyl-8-oxatetracyclo-[4.3.2.0²,5.0³,6]undeca-3,10-diene-10,11-dicarboxylic acid (180)

M.p. 63-4°. Found: C, 64.37; H, 5.54. Calc. for C₁₄H₁₄O₅: C, 64.12; H, 5.38. ¹H NMR 62.84, br.d,
$J\ 3.2\text{Hz},\ 2\text{H},\ H_{2},\ H_{5};\ 3.31,\ \text{dd},\ J1.6,\ 3.2\text{Hz},\ 2\text{H},\ H_{7},\ H_{9}$; 3.48, m, 2H, H1, H6; 3.77, s, 6H, 2 x CH$_3$; 6.31, s, 2H, H3, H4. Mass spectrum m/z 262(2%), 231(26), 203(22), 202(18), 201(40), 197(29), 171(31), 163(11), 144(17), 143(35), 131(12), 129(12), 116(28), 115(100), 91(13), 89(12), 77(15), 68(21).

(1α,2α,3β,6β,7α,8β,10β)-Dimethyl-4,9-dioxapentacyclo[5.3.2.0$^2$6.0$^3$6.0$^8$10]-dodeca-11-ene-11,12-dicarboxylic acid (181)

Calc. for C$_{14}$H$_{14}$O$_6$: C, 60.43; H, 5.07. $^1$H NMR δ 2.36, m, 2H, H2, H6; 3.48, dd, $J1.6$, 3.2Hz, 2H, H8, H10; 3.64, m, 2H, H1, H7; 3.76, s, 6H, 2 x CH$_3$; 3.94, d, $J2.5\text{Hz},\ 2\text{H},\ H_{3},\ H_{5}$. Mass spectrum m/z 247(12%), 210(42), 77(50), 68(100).

Flash vacuum pyrolysis of (179)

Samples of the epoxide (179) (40mg) were subjected to FVP at a pressure of 0.01 torr, over a range of temperatures. Unchanged epoxide and/or dimethylphthalate condensed near the exit from the pyrolysis tube. Mixtures of furan and cyclopropene aldehyde (164) were collected in a cold trap containing chloroform-$d$ (0.4 cm$^3$) at -196°C. The two fractions were analysed by $^1$H NMR to produce the results tabulated below. Yields of volatile products were measured by $^1$H NMR integration, using methylene bromide as internal standard, and were nearly quantitative at lower temperatures.
<table>
<thead>
<tr>
<th>Pyrolysis temperature °C</th>
<th>Aromatisation, %</th>
<th>Cyclopropene, %</th>
<th>Furan, %</th>
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<tr>
<td>420</td>
<td>10</td>
<td>100</td>
<td>0</td>
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<tr>
<td>450</td>
<td>30</td>
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<tr>
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<td>100</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>540</td>
<td>100</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

Reaction of (164) with isobenzofuran

The epoxide (179) (ca. 90%, 330mg; 1.1mmol) was subjected to FVP (490°C; 0.01 torr) and the volatile materials from the cold trap were dissolved in anhydrous tetrahydrofuran (2cm³) at -78°C and treated with a cold solution of freshly prepared isobenzofuran (ca. 200mg) in anhydrous tetrahydrofuran (2cm³). Solvent was removed at room temperature and the adducts were isolated by centrifugal layer chromatography (10-30% ethyl acetate in hexane), the exo isomer (168) (68mg) eluting before the endo (169) (24mg), as clear, colourless oils.

¹H NMR analysis of the less volatile products from pyrolysis indicated that aromatisation had been 80% effective. The combined adduct yield of 92mg represents 34mg of cyclopropene aldehyde, or 55% of the mixture of C₄H₄O isomers from fragmentation.

The two adducts each crystallised from hexane as white plates.
(1α,1αa,2β,2β,7βα)-1α,2,7,7α-Tetrahydro-2,2-epoxy-1H-cyclopropa[b]naphthalene-1-carboxaldehyde (168)

M.p. 80–2°. Found: C, 77.27; H, 5.45. Calc. for C12H10O2: C, 77.40; H, 5.41. 1H NMR δ 1.94, d, J 2.7 Hz, 2H, H1α, H7α; 2.84, dt, J 2.7, 4.4 Hz, 1H, H1; 5.18, s, 2H, H2, H7; 7.20, m, 4H, aromatic; 9.33, d, J 4.4 Hz, 1H, CHO. Mass spectrum m/z 186 (7%), 158 (9), 157 (11), 130 (14), 129 (100), 128 (49), 127 (22), 118 (8).

(1α,1αa,2α,7α,7αα)-1α,2,7,7α-Tetrahydro-2,2-epoxy-1H-cyclopropa[b]naphthalene-1-carboxaldehyde (169)

M.p. 103–4°. Found: C, 77.34; H, 5.20. Calc. for C12H10O2: C, 77.40; H, 5.41. 1H NMR δ 0.99, dt, J 2.5, 3.5 Hz, 1H, H1; 2.82, dd, J 1.8, 2.5 Hz, 2H, H1α, H7α; 5.43, dd, J 0.5, 1.8 Hz, 2H, H2, H7; 7.18, s, 4H, aromatic; 9.13, d, J 3.5 Hz, 1H, CHO. Mass spectrum m/z 186 (16%), 158 (10), 157 (31), 130 (14), 129 (100), 128 (65), 127 (30), 118 (27).

Cyclopropene-3-carboxaldehyde (164)

1H NMR δ 2.32, dt, J 1.3, 7.1 Hz, 1H, H3; 7.12, d, J 1.3 Hz, 2H, H1, H2; 8.85, d, J 7.1 Hz, 1H, CHO. This data was previously misreported.71

Pyrolysis of (164)

A solution of the cyclopropene (164) (ca. 6mg), contaminated with furan (ca. 10%), in chloroform-d (0.4 cm³) containing methylene bromide (5μl) as internal standard, was frozen in liquid nitrogen and allowed to thaw under vacuum. The resultant vapours were condensed
at -196°C following FVP (530°C), allowed to thaw, and analysed by $^1$H NMR. A mixture of cyclopropene (164) and furan (ratio $\text{ca. } 2:3$) was recovered, in $\text{ca. } 70\%$ yield.

**Photolysis of (164)**

The epoxide (179) ($\text{ca. } 90\%; 0.25g; 0.86\text{mmol}$) was subjected to FVP (490°C; 0.01 torr), and the volatile fragments that collected in a liquid nitrogen cooled trap were dissolved in dichloromethane ($2\text{cm}^3$). Careful evaporation of this solution at $\text{ca. } 17$ torr returned an oil which was distilled under high vacuum (0.01 torr) to afford pure cyclopropene-3-carboxaldehyde ($26\text{mg}; 45\%$), an acrid smelling, clear, colourless oil.

The sample of (164) so prepared was dissolved in acetone-$d_6$ ($0.4\text{cm}^3$) and the solution was cooled to $-60^\circ\text{C}$ before irradiation ($\lambda = 254\text{nm}$) for one hour. Approximately 70% of the cyclopropene (164) was destroyed, but no new products were detected. Broad, featureless resonances in the $^1$H NMR spectrum ($\delta 1-3$ and 9-10ppm) attested to polymer formation.

$$\text{(1a,2a,5a,6a)-1,6-Dibromo-2,3,4,5,8-}
\text{pentamethyl-8-azatricyclo[4.3.0.0^{1,6,0^{2,5}}]-non-3-ene-7,9-dione (199)}$$

A solution of 2-butyne (10.0g; 1.19mol) in dichloromethane ($30\text{cm}^3$) was added dropwise during five minutes to a briskly stirred, ice-cooled suspension of anhydrous aluminium chloride (12.4g; 0.093mol) in dichloromethane ($35\text{cm}^3$). The mixture was stirred for a further twenty minutes at $0^\circ\text{C}$, and the resultant red-brown
solution was added dropwise during ten minutes to a briskly stirred, ice cooled solution of dibromo-N-methylmaleimide (12.5g; 0.046mol) in dimethylsulphoxide (30cm³) and dichloromethane (60cm³). Decomplexation was instantaneous, and a white precipitate formed. When addition was complete, the reaction mixture was poured into iced water (300cm³) and stirred gently until the dichloromethane phase clarified; this was then separated, washed with water, dried, and evaporated to a white solid which was recrystallised from methanol to afford 14.3g (82%) of the product as white plates.

M.p. 201-7° (dec.). Found: C, 41.38; H, 3.95; N, 3.57. Calc. for C₁₃H₁₅NO₂: C, 41.41; H, 4.01; N, 3.71.

¹H NMR δ 1.33, s, 6H, 2 x CH₃; 1.50, s, 6H, 2 x CH₃; 3.04, s, 3H, NCH₃. Mass spectrum m/z 299(79%), 297(80), 241(97), 239(100), 160(32), 132(24), 131(21), 117(33), 115(34), 91(36).

(3aa,4β,7β,7aa,8β,9β)-4,7,8,9-Tetrahydro-2,4,7,8,9,10,11-heptamethyl-5,6-diphenyl-3a,7a[1',2']-endo-cyclobuta-4,7-methano-1H-isooindole-1,3,12(2H)-trione (204)

A solution of the dibromide (199) (9.0g; 23.9mmol) and the cyclone dimer (381) (8.0g; 15.4mmol) in anhydrous tetrahydrofuran (30cm³) was heated under reflux for ten minutes, and then stirred under reflux for five hours, during which time granulated zinc/silver couple (4 x 0.5g) was added at hourly intervals. The reaction mixture was given the same work up as the adduct (153), and the crude crystalline product was dissolved in chloroform (40cm³) and heated under reflux for three hours
with maleic anhydride (1.0g; 10.2mmol). Solvent was then removed, and the residue was chromatographed on a column of activated alumina (16 x 4cm) using 20% dichloromethane in hexane as eluent. The product was isolated by recrystallisation from methanol, which afforded 8.6g (76%) of white crystals.

M.p. 195-6° (decarbonylation). Found: C, 80.24; H, 6.44; N, 2.64. Calc. for C32H31NO3: C, 80.48; H, 6.54; N, 2.93. 1H NMR δ 1.23, s, 6H, 2 x CH3; 1.49, s, 6H, 2 x CH3; 1.56, s, 6H, 2 x CH3; 2.96, s, 3H, NCH3; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 477(1%), 341(6), 262(22), 261(100), 233(24), 116(18), 108(98).

A second crop of crystals (1.3g) was contaminated with ca. 30% pentamethylphthalimide; a portion of this by-product was isolated by centrifugal layer chromatography (5% ethyl acetate in hexane), followed by recrystallisation from methanol, as white needles, m.p. 194-5° (lit. 180-1°). The 1H NMR spectrum of this product was identical to that reported in the literature.150

\[
(3\alpha,4\beta,7\beta,7\alpha,8\beta,9\beta)-4,7,8,9-Tetrahydro-2,8,9,10,11-pentamethyl-3\alpha,7\alpha[1',2']-endo-cyclobuta-4,7-epoxy-1H-isoindole-1,3(2H)-dione (202)
\]

A solution of the dibromide (199) (0.60g; 1.6mmol) and furan (ca. 1.5g) in anhydrous tetrahydrofuran (10cm³) was heated to reflux, treated with granulated zinc/silver couple (ca. 1g) and stirred under reflux for two hours. 1H NMR analysis of the white, crystalline
product (450mg; 99%) obtained after the usual work up procedure indicated a single component; this was recrystallised from hexane, affording 0.39g (86%) of small white crystals of the product.

M.p. 168-169°. Found: C, 71.82; H, 7.01; N, 4.80. Calc. for C_{17}H_{19}NO_{3}: C, 71.56; H, 6.71; N, 4.91. \(^1\)H NMR δ 1.16, s, 6H, 2 x CH\(_3\); 1.48, s, 6H, 2 x CH\(_3\); 2.76, s, 3H, NCH\(_3\); 5.01, t, J 1.1Hz, 2H, H4, H7; 6.43, t, J 1.1Hz, 2H, H5, H6. Mass spectrum m/z 217(100%), 173(12), 160(57), 68(11).

\((3aa,4B,7B,7aa,8B,9B)-4,7,8,9-Tetrahydro-2,8,9,10,11-pentamethyl-3a,7a[1',2']-endo-cyclobuta-4,7-imino-1H-isoindole-1,3(2H)-dione\) (203)

A solution of the dibromide (199) (0.20g; 0.53mmol) and freshly distilled pyrrole (1.0g) in anhydrous tetrahydrofuran (10cm\(^3\)) was stirred under reflux with granulated zinc/silver couple (ca. 1g) for two hours. The crude product obtained after neutral work up was analysed by \(^1\)H NMR and found to comprise dibromide (199), phthalimide (201) and adduct (203) in ca. 1:2:1 molar ratio. Acid extraction afforded the pyrrole adduct (203) as a white solid (17mg; 21%) which crystallised from hexane as white needles.

M.p. 173-5°. Found: C, 71.88; H, 7.14; N, 9.49. Calc. for C_{17}H_{20}N_{2}O_{2}: C, 71.81; H, 7.09; N, 9.85. \(^1\)H NMR δ 1.18, s, 6H, 2 x CH\(_3\); 1.46, s, 6H, 2 x CH\(_3\); 2.74, s, 3H, NCH\(_3\); 4.18, t, J 1.2Hz, 2H, H4, H7; 6.43, t, J 1.2Hz, 2H, H5, H6. Mass spectrum m/z 217(8%), 160(12), 67(100).
4,7,8,9-tetrahydro-2,4,7,8,9,10,11-heptamethyl-3a,7a[1',2']-endo-cyclobuta-4,7-epoxy-1H-isoindole-1,3(2H)-dione (205)/(206)

A solution of the dibromide (199) (0.20 g; 0.53 mmol) and 2,5-dimethylfuran (ca. 0.5 g) in anhydrous tetrahydrofuran (5 cm³) was stirred under reflux with zinc/silver couple (ca. 0.5 g) for two hours prior to the customary work up procedure. Products were isolated by centrifugal layer chromatography (5-15% ethyl acetate in hexane); first to elute was pentamethylphthalimide (201) (27 mg; 23%), followed by two adducts (57 mg; 34% and 54 mg; 33%), each of which was recrystallised from hexane.

Adduct # 1. M.p. 210-12° (sealed tube). Found: C, 73.12; H, 7.71; N, 4.29. Calc. for C₁₉H₂₃NO₃: C, 72.82; H, 7.40; N, 4.47. \(^1\text{H NMR}\) δ 1.29, s, 6H, 2 x CH₃; 1.45, s, 6H, 2 x CH₃; 1.79, s, 6H, 2 x CH₃; 2.73, s, 3H, NCH₃; 6.13, s, 2H, H5, H6.

Adduct # 2. M.p. 188-90°. Found: C, 72.98; H, 7.59; N, 4.20. Calc. for C₁₉H₂₃NO₃: C, 72.82; H, 7.40; N, 4.47. \(^1\text{H NMR}\) δ 1.03, s, 6H, 2 x CH₃; 1.44, s, 6H, 2 x CH₃; 1.63, s, 6H, 2 x CH₃; 2.91, s, 3H, NCH₃; 6.49, s, 2H, H5, H6.

Debromination of (199), with trapping by the model diene (207)

A solution of the dibromide (199) (80 mg; 0.21 mmol) and the trapping agent (207) (68 mg; 0.22 mmol) in anhydrous tetrahydrofuran (1 cm³) was heated under reflux with granulated zinc/silver couple (ca. 0.1 g) for one hour, and worked up in the usual way. The \(^1\text{H NMR}\) spectrum of the
crude product revealed the presence of two adducts in a ratio of ca. 7:1, together with traces of the phthalimide (201) and trapping agent (207). The adducts were isolated by preparative layer chromatography (50% dichloromethane in hexane), isomer (210) (9mg; 8%) eluting slightly more rapidly than isomer (209) (58mg; 55%).

(3aa, 8aa, 10a, 11b)-4, 8, 10, 11-Tetrahydro-2, 5, 8, 10, 11, 12, 13-heptamethyl-6, 7-diphenyl-3a, 8a[1', 2']-endo-cyclobuta-1H-benz[f]isoindole-1, 3(2H)-dione (209)

M.p. 240° (decomposition). Found: C, 83.96; H, 7.31; N, 3.03. Calc. for C_{35}H_{35}NO_{2}: C, 83.80; H, 7.03; N, 2.79. \^H NMR δ 1.03, s, 6H, 2 × CH₃; 1.50, s, 6H, 2 × CH₃; 2.06, s, 6H, 2 × CH₃; 2.90, s, 3H, NCH₃; 2.94, d, J 14.6Hz, 2H, H4, H9; 3.19, d, J 14.6Hz, 2H, H4, H9; 6.8-7.2, m, 10H, aromatic. Selective irradiation of the singlet at δ1.03 produced an 8% enhancement of the doublet at δ3.19 in the n.o.e. difference spectrum. Mass spectrum m/z 501(2%), 285(19), 284(100), 270(11).

(3aa, 8aa, 10a, 11a)-4, 8, 10, 11-Tetrahydro-2, 5, 8, 10, 11, 12, 13-heptamethyl-6, 7-diphenyl-3a, 8a[1', 2']-endo-cyclobuta-1H-benz[f]isoindole-1, 3(2H)-dione (210)

M.p. 235° (decomposition). Found: C, 83.68; H, 7.17; N, 3.00. Calc. for C_{35}H_{35}NO_{2}: C, 83.80; H, 7.03; N, 2.79. \^H NMR δ 1.08, s, 6H, 2 × CH₃; 1.71, s, 6H, 2 × CH₃; 1.98, s, 6H, 2 × CH₃; 2.63, d, J 14.6Hz, 2H, H4, H9; 2.89, s, 3H, NCH₃; 3.65, d, J 14.6Hz, 2H, H4, H9; 6.8-7.2, m, 10H, aromatic. No changes were evident in the nuclear Overhauser difference spectrum obtained from selective
irradiation of the singlet at $\delta$ 1.08. Mass spectrum $m/z$

501 (1%), 285 (22), 284 (100), 270 (12).

$2,3,4,5,8$-Pentamethyl-$8$-aza$\text{tricyclo}[4.3.-$

0^1,6_02,6^2]$nona-$1(6)_0,3$-diane-$7,9$-dione (200)

A solution of the dibromide (199) (0.30g; 0.8mmol) in anhydrous tetrahydrofuran ($10cm^3$) was heated to reflux, treated with powdered zinc/silver couple (ca. 1g), and stirred vigorously under reflux for three minutes. The reaction mixture was then poured into ice cold water, extracted with chloroform, washed with further iced water, and dried. The crude product was isolated as a white solid containing three components in roughly equal molar proportions. Two were recognised by $^1H$ NMR as unreacted dibromide (199) and pentamethylphthalimide (201); the third ($\delta$ 1.42, s, 6H, 2 x CH$_3$; 1.62, s, 6H, 2 x CH$_3$; 2.91, s, 3H, NCH$_3$) was assigned the Dewar benzene structure (200) following its instantaneous reaction with furan to form the previously characterised adduct (202).

The remainder of the crude product mixture was subjected to centrifugal layer chromatography (5% ethyl acetate in hexane). The first 15mg recovered were inspected by $^1H$ NMR without delay and found to comprise Dewar benzene (200) and its dibromo precursor (199), with very little of the phthalimide (201). This sample was maintained at probe temperature ($30^\circ C \pm 1^\circ C$) and the $^1H$ NMR spectrum was recorded at intervals for 90 minutes, during which time aromatisation of the Dewar benzene (200) took place. This reaction was monitored by $^1H$ NMR integration, using the
dibromide (199) as internal standard; the integrals obtained were then plotted, on a logarithmic scale, against time, providing a straight line from which the half life (44 ± 1 min) of (200) was measured.

Photolysis of tetramethylcyclobutadiene precursor (204)

(i) In solution of low temperature:

A solution of the adduct (204) (5mg) in anhydrous tetrahydrofuran (0.5cm³) was freeze-thaw degassed, sealed under argon, cooled to between -100° and -110° and irradiated (λ = 254nm) for two hours. The photolysate was analysed by ¹H NMR, following change of solvent to chloroform-d, and found to comprise unchanged (204), the phthalimide (157) and tetramethylcyclobutadiene dimer (212), in a molar ratio of ca. 2:4:1.

(ii) In a low temperature matrix:

A solution of the adduct (204) (2mg) in ether (3cm³), pentane (3cm³) and tetrahydrofuran (3cm³) was freeze-thaw degassed, sealed in vacuo, frozen in liquid nitrogen and irradiated (λ > 225nm) for fifteen hours. The glassy matrix turned slowly red, but decolourised instantaneously when warmed to the point where it began to thaw. The photolysate was analysed by ¹H NMR as above, and found to comprise the same three products in a molar ratio of ca. 4:4:1.

Pyrolysis of tetramethylcyclobutadiene precursor (204)

The adduct (204) (50mg) was added to boiling diglyme (0.5cm³), and the resultant solution was stirred under reflux for half an hour. The reaction mixture was poured
into water and the crude product was isolated from the chloroform extract in the usual way. Analysis of the crude mixture by $^1$H NMR revealed that the same three products were present as observed following photolysis, in a molar ratio of ca. 1:10:2.

$2a,8,8,8a$-Tetrahydro-1,2,2a,8a-tetramethyl-3,8-diphenyl-8,8-epoxycyclobuta[b]-naphthalene (215)/(216)

A solution of 1,3-diphenylisobenzofuran (0.35g; 1.3mmol) in diglyme (3cm$^3$) was heated to reflux, treated with the adduct (204) (0.43g; 0.9mmol) and stirred under reflux for one hour. Solvent was removed by carefully evaporating the boiling solution under a stream of nitrogen, and the two adducts were isolated by preparative layer chromatography (30% dichloromethane in hexane), the minor (0.06g; 17%) being slightly more mobile than the major (0.25g; 74%). Each adduct was recrystallized from methanol.

**Major isomer:** M.p. 144-5°. Found: C, 88.42; H, 7.16. Calc. for C$_{28}$H$_{26}$O: C, 88.85; H, 6.92. $^1$H NMR $\delta$ 1.04, s, 6H, 2 x CH$_3$; 1.10, s, 6H, 2 x CH$_3$; 7.0-7.9, m, 14H, aromatic. Mass spectrum m/z 379(31%), 378(100), 270(42), 108(97), 105(31), 93(30), 91(23), 77(36).

**Minor isomer:** M.p. 171-3°. Found: C, 88.41, H, 6.68. Calc. for C$_{28}$H$_{26}$O: C, 88.85; H, 6.92. $^1$H NMR $\delta$ 0.93, s, 6H, 2 x CH$_3$; 1.32, s, 6H, 2 x CH$_3$; 7.05, s, 4H, 7.3-7.8, m, 10H, aromatic. Mass spectrum m/z 379(30%), 378(100), 270(48), 108(98), 105(64), 93(30), 91(25), 77(44).
A solution of the adduct (204) (0.74g; 1.5mmol) and mCPBA (85%; 0.36g; 1.8mmol) in dichloromethane (20cm$^3$) was set aside at ambient temperature overnight, washed sequentially with 2M NaOH and water, dried, and evaporated to afford a white solid, which crystallised from methanol as white plates (0.68g; 89%).

M.p. 208-10° (decarbonylation). Found: C, 78.25; H, 6.36; N, 2.69. Calc. for C$_{32}$H$_{31}$N$_2$O$_4$: C, 77.87; H, 6.33; N, 2.84. $^1$H NMR δ 1.17, s, 6H, 2 x CH$_3$; 1.35, s, 6H, 2 x CH$_3$; 1.57, s, 6H, 2 x CH$_3$: 3.08, s, 3H, NCH$_3$; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 493(1%), 466(2), 345(5), 124(100), 110(15).

A solution of the cyclobutene (199) (1.0g; 2.6mmol) and mCPBA (85%, 0.6g; 3.0mmol) in dichloromethane (30cm$^3$) was boiled under reflux for fifteen hours and worked up as described above to afford a white solid which crystallised from methanol as white needles (0.97g; 93%).

Calc. for C_{13}H_{15}NO_{3}Br_{2}: C, 39.72; H, 3.85; N, 3.56.

\(^1\)H NMR δ 1.27, s, 6H, 2 × CH₃; 1.33, s, 6H, 2 × CH₃; 3.17, s, 3H, NCH₃. Mass spectrum m/z 315(13%), 314(14), 124(86), 123(18), 109(21), 44(100).

**Debromination and trapping of epoxide (217)**

A solution of the epoxide (217) (0.75g; 1.9mmol) and the cyclone dimer (381) (0.50g; 1.0mmol) in anhydrous tetrahydrofuran (15cm\(^3\)) was heated to reflux, treated with granulated zinc/silver couple (ca. 2g) and heated under reflux for half an hour. The crude products were isolated as usual and separated by preparative layer chromatography (50% dichloromethane in hexane). There was obtained 0.40g (43%) of a white crystalline solid, identified as the adduct (219), and 0.21g (47%) of an orange oil which slowly crystallised. This latter fraction was analysed by \(^1\)H NMR and found to contain three components in a molar ratio of ca. 3:2:5. These were subsequently identified as oxepins (222) and (224), and cyclo-hexadienone (226) respectively.

\((1a,2\beta,3\alpha,5\alpha,6\beta,7\alpha,8\beta,11\beta)-2,5,6,13-\)
\(Pentamethyl-4,16-dioxa-13-azahexacyclo-
\[5.4.3.1^8,11.0^1,7.0^2,6.0^2,5\]pentadeca-9-ene-
\(-12,14-dione\) (220)

A solution of the epoxide (217) (2.50g; 6.4mmol) in furan (10cm\(^3\)) and anhydrous tetrahydrofuran (20cm\(^3\)) was stirred under reflux with granulated zinc/silver couple (ca. 1g) for four hours and worked up as usual to afford a single crystalline
product, which was recrystallised from methanol. The yield was 1.78g (93%).

M.p. 208-10°. Found: C, 67.96; H, 6.48; N, 4.45. Calc. for C_{17}H_{19}NO_{4}: C, 67.76; H, 6.35; N, 4.65. \textsuperscript{1}H NMR \( \delta \) 1.11, s, 6H, 2 x CH\textsubscript{3}; 1.33, s, 6H, 2 x CH\textsubscript{3}; 2.85, s, 3H, NCH\textsubscript{3}; 5.08, t, J 1.1Hz, 2H, H8, H11; 6.38, t, J 1.1Hz, 2H, H9, H10. Mass spectrum m/z 259(11%), 233(21), 191(19), 190(18), 124(100), 123(12), 68(7).

(2\alpha,3\alpha,5\alpha,6\alpha)-2,3,5,6,9-Pentamethyl-4-oxa-9-azatetracyclo[5.3.0\textsuperscript{1},7.0\textsuperscript{2},6.0\textsuperscript{3},5]dec-1(7)-ene-8,10-dione (218)

The Dewar benzene oxide (218) was prepared from the dibromide (217) in the same way as the corresponding Dewar benzene (200). The presence of this compound in the crude product mixture was confirmed by addition of furan, whereupon the adduct (220) formed instantaneously. A pure sample of (218) (15mg; 8%) was isolated by centrifugal layer chromatography (10% ethyl acetate in hexane); subsequent fractions (128mg; 72%) were contaminated with its ring opened isomer, the oxepin (222). A trailing fraction (5mg; 3%) was identified by \textsuperscript{1}H NMR as the cyclohexadienone (226).

The pure sample of (218) was maintained at 30°C (± 1°) for three hours, and its \textsuperscript{1}H NMR spectrum (\( \delta \) 1.35, s, 6H, 2 x CH\textsubscript{3}; 1.41, s, 6H, 2 x CH\textsubscript{3}; 2.98, s, 3H, NCH\textsubscript{3}) was recorded at intervals. Fairly rapid isomerisation to the oxepin (222) was observed, and the rate of this isomerisation was monitored using \textsuperscript{1}H NMR integration, with
methylenedi bromide as internal standard. As before, the semi-logarithmic plot provided a straight line, confirming first order kinetics, from which the half life (77 ± 1 min) of (218) was readily obtained.

\[ 1,3,4,6,7\text{-Pentamethyl-1H-pyrrolo[d]oxepin} \]

\[ 2,8\text{-dione} \ (222) \]

This compound was isolated as orange crystals following recrystallisation from boiling hexane of the appropriate fractions from the previous experiment.

M. p. 164-5°. Found: C, 66.77; H, 6.59; N, 5.99. Calc. for \( C_{13}H_{15}N_2O_3 \): C, 66.94; H, 6.48; N, 6.00. \( ^1H \) NMR \( \delta \) 1.84, br.s, 6H, 2 x CH\(_3\); 2.34, br.s, 6H, 2 x CH\(_3\); 3.02, s, 3H, NCH\(_3\). \( ^13C \) NMR \( \delta \) 14.92, 17.16, 4 x CH\(_3\); 23.69, NCH\(_3\); 106.35, C4, C6; 129.86, C2a, C7a; 132.30, C3, C7; 168.78, 2 x CO. Mass spectrum \( m/z \) 233(65%), 218(19), 196(32), 195(41), 105(25), 77(49), 65(40), 63(31), 53(30), 51(48), 43(100).

Flash vacuum pyrolysis of the furan adduct (220)

The furan adduct (25mg) was subjected to FVP over a range of temperatures, and the pyrolysates were analysed by \( ^1H \) NMR. At lower temperatures, some of the adduct was recovered unchanged (60% at 390°, 10% at 440°) while at higher temperature (490°) the retro Diels-Alder cleavage of furan was quantitative. In each case the three isomers (222), (224) and (226) were observed as products, in a constant ratio of ca. 35:60:5. This ratio remained largely unaffected by repeated FVP, with only minor increases in the proportion of the cyclohexadienone (226).
Centrifugal layer chromatography (5-10% ethyl acetate in hexane) of the pyrolysate (450°C; 0.01 torr) from 150mg of the adduct (220) returned 108mg (93%) of C\textsubscript{13}H\textsubscript{15}NO\textsubscript{3} isomers, of which the final 2mg was pure cyclohexadienone (226). The remaining fractions contained the two oxepins in various ratios, the initial 17mg containing < 5% of the symmetrical isomer (222). The unsymmetrical oxepin (224) crystallised rapidly from a hexane solution of this fraction as yellow needles, which underwent partial melting and recrystallisation between 95°C and 100°C.

\textit{1,3,4,5,7-Pentamethyl-1H-pyrrolo[c]oxepin-2,8-dione} (224)

M.p. 119-20°C. Found: C, 66.98; H, 6.65; N, 6.02. Calc. for C\textsubscript{13}H\textsubscript{15}NO\textsubscript{3}: C, 66.94; H, 6.48; N, 6.00. \textsuperscript{1}H NMR δ 1.79, q, J 1.2Hz, 3H, CH\textsubscript{3}; 2.01, q, J 1.2Hz, 3H, CH\textsubscript{3}; 2.37, br.s, 6H, 2 x CH\textsubscript{3}; 3.00, s, 3H, NCH\textsubscript{3}. The signal at δ 2.37 resolved into two broad singlets on addition of benzene-\textit{d}\textsubscript{6}. \textsuperscript{13}C NMR δ 15.46, 16.88, 19.15, 19.63, 4 x CH\textsubscript{3}; 23.85, NCH\textsubscript{3}; 116.07, C7a, 122.38, C4; 123.70, C2a, 147.81, 147.99, C5, C7; 162.69, C3; 166.92, 167.90, 2 x CO. Mass spectrum \textit{m/z} 233(100%), 218(18), 190(79), 189(84), 161(16), 133(21), 105(20), 77(34).

\textit{Solution thermolyis of oxepin} (222)

A solution of the symmetrical oxepin (222) (15mg) in freshly opened chloroform-\textit{d} (0.3cm\textsuperscript{3}) was sealed, under nitrogen, in a \textsuperscript{1}H NMR tube, and heated at 100°C for 600 hours. The \textsuperscript{1}H NMR spectrum was recorded and integrated at intervals, and the ratios of the various components to an internal standard (methylene bromide) were calculated.
Isomerisation to the unsymmetrical oxepin was initially fairly rapid, but after approximately 100 hours the two oxepins reached equilibrium with the molar ratio of (222):(224) stabilising at ca. 1:4. Thereafter both isomers underwent first order decay \( (t_\frac{1}{2} \approx \text{ca.} 290 \text{ hrs}) \) with the formation of the cyclohexadienone (226).

Similar results were obtained using pure unsymmetrical oxepin (224).

**Acid catalysed solution thermolysis of oxepin (222)**

A solution of the symmetrical oxepin (222) (5mg) in stale chloroform-\( d \) (0.3cm\(^3\)) was heated at 85°C in a sealed \( ^1\text{H} \) NMR tube. After six hours, ca. 40% of the oxepin had isomerised to the cyclohexadienone (226), and after 24 hours this isomerisation was essentially quantitative.

A solution of hydrogen chloride in chloroform-\( d \) was prepared by bubbling the gas through the solvent for one minute. This solution was set aside in a stoppered vial for three hours, and then used to prepare a solution of the symmetrical oxepin, which was set aside at ambient temperature. The orange colour of the oxepin slowly faded, and after two days, isomerisation to the cyclohexadienone (226) was complete and quantitative. Solvent was removed, and the cyclohexadienone crystallised from hexane as pale yellow crystals.

\begin{center}
\textbf{2,4,6,6',7-Pentamethyl-1H-isoindole-1,3,5(2H,6H)-trione (226)}
\end{center}

M.p. 101-2°. Found: C, 67.29; H, 6.51; N, 6.31. Calc. for C\(_{13}\)H\(_{15}\)NO\(_3\): C, 66.94; H, 6.48;
Acid catalysed hydrolysis of oxepin (222)

A solution of the two oxepins (222) and (224) (100mg; ratio 7:3) in tetrahydrofuran (5cm$^3$) was treated with 0.5M sulphuric acid (3cm$^3$) and set aside at ambient temperature. The orange colour of the oxepin solution faded to a lemon yellow within one hour. After a total of two days, the reaction mixture was poured into water and extracted with chloroform, and the crude product mixture was isolated, after a bicarbonate wash, as a pale yellow solid. Analysis by $^1$H NMR revealed three products: the unsymmetrical oxepin (224), the cyclohexadienone (226) and a major component with spectral features characteristic of the 1,2-diol (229). The first two components were isolated following centrifugal layer chromatography (10% ethyl acetate in hexane): the oxepin (224) (17mg; 17%) crystallised slowly from hexane in the new form of chunky orange crystals, m.p. 119-20°, and the cyclohexadienone (226) (7mg; 7%) as pale yellow crystals, m.p. 101-2°. The major component was then isolated, following elution with ethyl acetate, as a clear, colourless oil (69mg; 64%), the $^1$H NMR spectrum of which ($\delta$ 1.28, br.s, 6H, 2 x CH$_3$; 2.37, s, 6H, 2 x CH$_3$; 2.87, br.s, 2H, 2 x OH; 2.97, s, 3H, NCH$_3$), while still consistent with the diol structure (229), differed from that of the original product. This fraction was recrystallised from hexane, affording white plates of
the original product. The differences in the $^1$H NMR spectra presumably reflect *cis/trans* isomerisation during chromatography, particularly since the crystalline product, when again subjected to centrifugal layer chromatography, returned its oily isomer.

$5,6$-Dihydro-5,6-dihydroxy-2,4,5,6,7-pentamethyl-1H-isoindole-1,3(2H)-dione

(229)

M.p. 140-1°. Found: C, 62.28; H, 6.90; N, 5.49.
Calc. for $\text{C}_{13}\text{H}_{17}\text{N}_4$: C, 62.14; H, 6.82; N, 5.57.

$^1$H NMR $\delta$ 1.30, br.s, 6H, 2 x CH$_3$; 2.40, s, 6H, 2 x CH$_3$; 3.04, s, 3H, NCH$_3$. Mass spectrum $m/z$ 251(21%), 209(14), 208(100), 166(15), 151(16), 123(12).

**Acid catalysed hydrolysis of oxepin (224)**

A sample of the unsymmetrical oxepin (224) (4mg) was subjected to the above hydrolysis conditions for four days. Analysis of the crude product mixture by $^1$H NMR revealed traces of residual oxepin (224) and cyclohexadienone (226), with the major product being the symmetrical 1,2-diol (229).

Heptamethyl-9,10-diphenyl-4-oxa-13-azapentacyclo[5.4.3.0$^1$.7$^0$.6$^2$.0$^3$.5$^5$.]-tetradeca-8,10-diene-12,14-dione

(237)

A solution of the cyclone adduct (219) (0.68g; 1.46mmol) in diglyme (2cm$^3$) was stirred under reflux for one hour. Solvent was removed by careful
evaporation of the boiling solution under a stream of nitrogen, and the residue was recrystallised from methanol to afford 0.58g (90%) of the product as white crystals.

M.p. 201-2°. Found: C, 80.08; H, 6.87; N, 3.28. Calc. for C$_{31}$H$_{31}$N0$_3$: C, 79.97; H, 6.71; N, 3.01. $^1$H NMR $\delta$ 1.19, s, 6H, 2 x CH$_3$; 1.36, s, 6H, 2 x CH$_3$; 1.71, s, 6H, 2 x CH$_3$; 3.11, s, 3H, NCH$_3$; 6.7-7.1, m, 10H, aromatic. Mass spectrum m/z 465(1%), 340(12), 124(100), 123(15), 109(21), 81(8).

Low temperature photolysis of tetramethylfuran

A solution of tetramethylfuran (12mg) in acetone-$d_6$ (0.3cm$^3$) was cooled to -80° and irradiated ($\lambda$ = 254 nm) for 90 minutes. No changes were evident from the $^1$H NMR spectrum. However, after a further 30 minutes irradiation, four new resonances could be discerned: $\delta$ 1.07, s, 3H; 1.40, s, 3H; 1.54, q, $J$ 1.0 Hz, 3H; 1.74, q, $J$ 1.0 Hz, 3H.

A second such solution (5mg/0.3cm$^3$) was distilled in vacuo and transferred, under argon, to a quartz $^1$H NMR tube where it was irradiated (-90°; $\lambda$ = 254nm) for twenty minutes. Nearly all the tetramethylfuran was consumed, and the new resonances listed above were supplemented by two singlets ($\delta$ 1.30, 1.51). This sample proved stable at ambient temperature for three days, with only a small increase in tetramethylfuran content. However, an identical sample, prepared simultaneously but without distillation prior to photolysis, reverted
completely to tetramethylfuran within one day.

Solvent and tetramethylfuran were removed from the stable solution by evaporation in vacuo, and replaced by chloroform-\textit{d}. The same two products were observed by $^1$H NMR: (233) $\delta$ 1.08, s, 3H; 1.50, s, 3H; 1.53, q, $J$ 1.0Hz, 3H; 1.82, q, $J$ 1.0Hz, 3H and (235) $\delta$ 1.29, s, 6H; 1.64, s, 6H. After two hours, complete reversion to tetramethylfuran had occurred.

The above procedure was repeated using acetone in place of acetone-\textit{d}_6, and a chloroform-\textit{d} solution containing predominantly the bis oxetan (236) (new resonances at $\delta$ 1.30, s, 6H; 1.45, s, 6H) was obtained. After ninety minutes, this had largely reverted to tetramethylfuran and acetone, but small residual quantities of the two oxetans allowed assignment of the two new resonances ($\delta$ 1.27, s, 3H; 1.36, s, 3H) of the mono adduct (234). After six hours, only tetramethylfuran and acetone remained.

\textit{Low temperature photolysis of tetramethyl Dewar furan precursor} (237)

A solution of the epoxide (237) (5mg) in acetone-\textit{d}_6 (0.3cm$^3$) was freeze-thaw degassed, sealed under argon, cooled to $-90^\circ$C and irradiated ($\lambda$ = 254 nm) for ten minutes. The photolysate was frozen in liquid nitrogen and allowed to warm to $-80^\circ$C in a pre-cooled $^1$H NMR probe. The $^1$H NMR spectrum contained resonances for three compounds: unreacted precursor (237), the phthalimide (157) and the cyclopropene (238), in a molar ratio of
Small temperature dependences of the chemical shifts were observed, e.g. (238) (-80°C: δ 1.07, s, 3H; 1.75, s, 3H; 2.11, s, 6H. -40°C: δ 1.08, 1.73, 2.07. 20°C: δ 1.09, 1.71, 2.04).

A solution of the epoxide (237) (0.43g; 0.92mmol) in acetone (12cm³) was freeze-thaw degassed, sealed in vacuo, cooled to -50° and irradiated (λ = 254nm) for 90 minutes. Solvent was removed at ambient temperature under reduced pressure (17 torr) and the residue was distilled in vacuo (bath temperature 40°). The final crystalline residue was analysed by ¹H NMR and found to comprise unreacted precursor (237) and phthalimide (157) (molar ratio 1:4). The cyclopropene (238) was isolated in a cold trap as a crystalline solid which melted below 0° to a clear, colourless, fragrant oil (72mg; 79%).

¹H NMR δ 1.17, s, 3H, CH₃; 1.80, s, 3H, COCH₃; 2.02, s, 6H, 2 x CH₃. ¹³C NMR (5% C₅D₅N/CDC1₃) δ 8.66, q, J 130.0Hz, 2 x CH₃; 16.54, q, J 125.8Hz, CH₃; 25.73, q, J 126.8Hz, COCH₃; 37.26, s, Cl; 110.16, s, C2,C3; 213.86, s, CO. Mass spectrum m/z 124 (6%), 123(6), 81(100), 53(18), 43(23), 41(21), 39(16).

Methano photolysis of tetramethyl Dewar furan precursor (237)

A solution of the epoxide (237) (100mg) in methanol (10cm³) was freeze-thaw degassed, cooled to -20°, and irradiated (λ = 254nm) for one hour, during which time the phthalimide (157) crystallised as white needles.
Solvent was removed under reduced pressure (17 torr) and the volatile products (11mg; 30%) were isolated by distillation in vacuo (bath temperature 40°/0.01 torr). \(^1\)H NMR analysis indicated the presence of two components, the cyclopropene (238) and the cyclobutene (242), in ca. 1:2 ratio.

**4-Methoxy-1,2,3,4-tetramethyl-2-cyclobuten-1-ol**

(242)

A solution of the cyclopropene (238) (5 mg) in chloroform-\(d\) (0.3cm\(^3\)) was treated with methanol (1cm\(^3\)) and set aside for thirty minutes at ambient temperature. Solvent was removed under reduced pressure, and the oily residue was identified by \(^1\)H NMR as pure (242).

\(^1\)H NMR \(\delta\) 1.33, s, 3H, 1.36, s, 3H, 1.55, q, \(J\ 1.2\text{Hz}\), 3H, 1.60, q, \(J\ 1.2\text{Hz}\), 3H, 4 x CH\(_3\); 3.32, s, 3H, OCH\(_3\).

\(^13\)C NMR \(\delta\) 7.01, 8.76, 16.06, 19.46, 4 x CH\(_3\); 52.72, OCH\(_3\); 81.44, 85.69, Cl,C4; 142.01, 142.41, C2,C3.

**FVP of cyclopropene** (238)

Solutions of the epoxide (237) (15mg) in anhydrorous ether (1cm\(^3\)) were cooled to -40° and irradiated (\(\lambda = 254\text{nm}\)) for 40 minutes. Solvent was removed as usual, and the residue was cooled in liquid nitrogen and allowed to warm to room temperature under vacuum (0.01 torr). Volatile materials passed through the pyrolysis tube and were collected in a cold trap containing chloroform-\(d\) (0.3cm\(^3\)). The single product (247) resulting from FVP at 400° was identified by comparison with the published
$^1$H NMR spectrum. Pyrolysis at 280° produced two products, (247) and (245), in ca. 1:2 ratio.

A second procedure did not give rise to significant amounts of the dehydrated product (247). A solution of the cyclopropene (238) (70mg), in 5% pyridine-$d_5$/95% chloroform-$d$ was frozen in liquid nitrogen and allowed to warm to ambient temperature under vacuum (0.01 torr). Solvent and solute distilled gently through the pyrolysis tube and were collected in a cold trap. Sequential pyrolyses at 220°, 280°, 350° and 400° produced a roughly equimolar mixture of the cyclobutene (245) and unchanged (238).

$1,2,3$-Trimethyl-4-methylene-2-cyclobuten-1-ol (245)

$^1$H NMR (5% C$_5$D$_5$N/CDC$_3$) δ 1.41, s, 3H, 1.62, q, J 1.2Hz, 3H, 1.74, q, J 1.2Hz, 3H, 3 x CH$_3$; 4.28, s, 1H, 4.51, s, 1H, CH$_2$. $^{13}$C NMR (5% C$_5$D$_5$N/CDC$_3$) δ 8.28, q, J 126.7Hz, 8.94, q, J 126.5Hz, 20.82, q, J 126.0Hz, 3 x CH$_3$; 80.31, s, Cl; 87.72, t, J 157.6Hz, CH$_2$; 141.99, s, 154.41, s, 160.02, s, C2,C3,C4.

(1α,2α,5α,6α)-1,6-Dibromo-2,3,5,8-tetramethyl-8-azatri cyclo[4.3.0]$^{1,6}$,8$^{1,5}$-non-3-ene-7,8-dione (252)

Aluminium tribromide (2.7g; 10mmol) was cooled to -90° and stirred while dichloromethane (15cm$^3$), and a cold (-78°) solution of propyne (0.4g; 10mmol) and 2-butyne (0.5g; 9.3mmol) in dichloromethane (8cm$^3$), were added in sequence dropwise. Fifteen minutes after
addition was complete an orange precipitate formed, which redissolved on warming slightly to produce a dark orange/brown solution. This was cooled to -90°, whereupon crystallisation again occurred, and stirred for a further five minutes before again being warmed slightly. The resultant dark solution was then added dropwise to a briskly stirred, dry ice cooled solution of dibromo-\(N\)-methylmaleimide (148) (1.0g; 3.7mmol) in dichloromethane (15cm\(^3\)) and dimethylsulphoxide (5cm\(^3\)). The dark colour of the complex vanished immediately and a white suspension was formed. This was worked up in the same way as the permethyl derivative (199) to afford a dark green oil, from which 1.1g (82%) of small white crystals were isolated after chromatography (alumina/hexane/dichloromethane) and recrystallisation (hexane).


\(^1\)H NMR δ 1.50, s, 3H, 1.55, m, 6H, 3 x CH\(_3\); 3.05, s, 3H, NCH\(_3\); 3.42, m, 1H, H5. Mass spectrum m/z 283 (97%), 281(100), 226(62), 224(64), 199(18), 197(19), 118(29), 117(28), 115(21).

Debromination and trapping of dibromide (252)

A solution of the dibromide (252) (0.60g; 1.65mmol) and the cyclone dimer (381) (0.50g; 0.96mmol) in anhydrous tetrahydrofuran (10cm\(^3\)) was heated to reflux, treated with granulated zinc/silver couple (ca. 0.5g), stirred under reflux for one hour, and worked up as usual. Products were separated by preparative layer chromatography (dichloromethane); the adduct (253) (0.57g; 75%)
crystallised from methanol as white plates, and the more polar phthalimide (383) (19mg; 6%) from the same solvent as white needles.

\[(3aa,4B,7B,7aa,8B,9B)-4,7,8,9-Tetrahydro-2,4,7,8,10,11-hexamethyl-5,6-diphenyl-3a,7a-[1',2']-endo-cyclobuta-4,7-methano-1H-isoxindole-1,3,12(2H)-trione\] (253)

M.p. 158-60°. Found: C, 80.65; H, 6.32; N, 3.12. Calc. for C\(_{31}\)H\(_{29}\)N\(_{2}\)O\(_{3}\): C, 80.32; H, 6.31; N, 3.02.

\(^1\)H NMR 5 1.37, s, 3H, 1.49, s, 3H, 1.54, br.s, 9H, 5 x CH\(_{3}\); 2.80, br.s, 1H, H9; 2.96, s, 3H, NCH\(_{3}\); 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 463(4%), 260(100), 232(27), 94(98).

\[2,4,5,6-Tetramethyl-1H-isoxindole-1,3(2H)-dione\] (383)

M.p. 106-7°. Found: C, 70.92; H, 6.45; N, 6.88. Calc. for C\(_{12}\)H\(_{13}\)N\(_{2}\)O\(_{2}\): C, 70.92; H, 6.45; N, 6.89.

\(^1\)H NMR 5 2.27, s, 3H, 2.39, s, 3H, 2.65, s, 3H, 3 x CH\(_{3}\); 3.12, s, 3H, NCH\(_{3}\); 7.46, s, 1H, H7. Mass spectrum m/z 203(100%), 146(47).

\[(1a,2B,3a,5a,6B,7a,8B,11B)-2,3,5,8,11,13-Hexamethyl-9,10-diphenyl-4-oxa-13-aza-hexacyclo[6.4.3.1,8,11.0,0^2,6,0^3,5]-pentadeca-9-ene-12,14,15-trione\] (254)

A solution of the cyclobutene (253) (0.40g; 0.86mmol) and mCPBA (85%; 0.19g; 0.94mmol) in dichloromethane (10cm\(^3\)) was set aside at ambient temperature for eight
hours, and worked up in the same way as the permethyl derivative (219) to afford a white solid which crystallised from methanol as white plates (0.37g; 89%).

M.p. 199-201°. Found: C, 77.95; H, 6.07; N, 2.99.
Calc. for C$_{31}$H$_{29}$N$_{2}$O$_{4}$: C, 77.64; H, 6.09; N, 2.92.

$^1$H NMR δ 1.32, s, 3H, 1.38, s, 3H, 1.40, s, 3H, 1.48, s, 3H, 1.56, s, 3H, 5 x CH$_3$; 2.59, s, 1H, H6; 3.07, s, 3H, NCH$_3$; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 479 (1%), 451(4), 340(11), 110(100), 109(14), 95(15).

(1α,2β,3α,6α,6β,7α)-2,3,5,8,11,12-
Hexamethyl-9,10-diphenyl-4-oxa-13-
aza-pentacyclo[5.4.3.0$^2$.0$^2$.0$^3$.5]-
tetradeca-8,10-diene-12,14-dione (255)

A solution of the ketone (254) (200mg) in diglyme (2cm$^3$) was boiled under reflux for one hour. Solvent was removed from the boiling solution by careful evaporation under a stream of nitrogen, and the product was isolated, by recrystallisation from methanol, as white needles (177mg; 94%).

Calc. for C$_{30}$H$_{29}$N$_{2}$O$_{3}$: C, 79.80; H, 6.47; N, 3.10.

$^1$H NMR δ 1.37, s, 3H, 1.39, s, 3H, 1.44, s, 3H, 1.71, s, 3H, 1.79, s, 3H, 5 x CH$_3$; 2.80, s, 1H, H6; 3.16, s, 3H, NCH$_3$; 6.7-7.1, m, 10H, aromatic. Mass spectrum m/z 451(4%), 340(17), 110(100), 109(18), 95(20).
Low temperature photolysis of trimethyl Dewar furan precursor (255)

A solution of the epoxide (255) (7mg) in acetone-$d_6$ (0.3cm$^3$) was freeze-thaw degassed, sealed under argon, cooled to -85° and irradiated ($\lambda = 254$nm) for 40 minutes. The photolysate was frozen in liquid nitrogen and allowed to warm to -80° in a pre-cooled $^1$H NMR probe. The spectrum recorded at this temperature contained signals for three compounds, namely phthalimide (157), precursor (255) and cyclopropene (259), in a ca. 2:1:2 ratio; however, the corresponding ratio at room temperature was ca. 5:1:2, because of crystallisation of the phthalimide (157) at low temperature.

Distillation (20°/0.01 torr) of the photolysate afforded an acetone-$d_6$ solution of 1-(1,2-dimethyl-2-cyclopropen-1-yl)ethanone (259) ($\delta$ 1.14, s, 3H, CH$_3$; 1.73, s, 3H, COCH$_3$; 2.17, d, $J$ 1.3Hz, 3H, CH$_3$; 6.82, q, $J$ 1.3Hz, 1H, H3), containing no other detectable products.

Preparation of labelled tetramethyl Dewar furan precursor (265)

A solution of the exocyclic diene (263) (150mg) in ethyl acetate (15cm$^3$) was stirred for two days with 5% palladium on charcoal (30mg) under an atmosphere of 98% deuterium (ca. 50cm$^3$), and then filtered through celite and evaporated to afford a white solid. $^1$H NMR spectroscopic analysis indicated that the labelled cyclobutene (264), identified by comparison with unlabelled (204), which differs only in its more intense
δ 1.49 resonance, was the major product, but centrifugal layer chromatography failed to remove trace impurities. Accordingly, the mixture was epoxidised in the same way as (204), and the labelled epoxide (265) was isolated by centrifugal layer chromatography (10-15% ethyl acetate in hexane) followed by recrystallisation (methanol) as white plates, m.p. 205-7° (decarbonylation). The overall yield was 118mg (75%). Integration of the 1H NMR spectrum indicated a deuterium content of ca. 35% in the methyl groups resonating at δ 1.35.

The deuterium content was measured more accurately using mass spectroscopic analysis of the C₄(CH₃)₄O fragment, since its intensity was much greater than that of the parent molecular ion. Measured intensities for d₀ (27%), d₁ (77), d₂ (100), d₃ (45), d₄ (24), d₅ (8) and d₆ (4) species were corrected for ¹³C natural abundance, and the following distribution of deuterium was calculated: d₀ (10.3%), d₁ (28.7), d₂ (35.6), d₃ (13.8), d₄ (8.0), d₅ (2.3) and d₆ (1.1). From this information, the percentage of deuterium in the terminal methyl groups of (265) was calculated to be 31.9%, or 98% of the theoretical figure.

The labelled epoxide (265) was decarbonylated to (266) (label at δ 1.36) in the same way as unlabelled material and isolated in 96% yield as white crystals, m.p. 199-200°. Both this and the precursor (265) were used to prepare labelled cyclopropenes (273) and (275), and these were isolated by vacuum distillation and analysed in chloroform-d solution, since the acetone-d₅
peak was shift equivalent with their vinylic methyl resonances. The proton ratios observed are tabulated in the text of this thesis (page 59).

\[(1a,2a,5a,6a)-1,2,5,4,6,7,8\text{-Octamethyl-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene}\] (212)

A solution of the AlCl₃-cyclobutadiene \(\pi\)-complex (190) was prepared from 10.0g but-2-yn, as described previously, and cooled in dry ice for approximately 10 minutes. A solution of DMSO (40cm³) in dichloromethane (60cm³) was stirred vigourously, with dry ice/acetone cooling, until the DMSO began to crystallise, at which point the solution of the organometallic complex was added, by pouring, during 1-2 minutes. The reaction mixture was worked up in the same way as that for the adduct (199) to afford a sweet smelling, greenish solid which turned crimson on addition of methanol. The product was isolated by crystallisation from methanol as white plates, m.p. 198-9° (sealed tube; lit. 151 198-9°). The yield was 5.4g (54%).

**Pyrolysis of Cookson's diester** (280)

The diester (280) (30mg) was heated at 330-40°, under nitrogen, for ten minutes. Three of the products, namely unchanged diester (280), Cope rearranged diester (284) and the phthalate (282), were recognised in the \(^1\)H NMR spectrum of the pyrolysate, but many others were not.

**FVP of Cookson's diester** (280)

The diester (280) (15mg) was subjected to FVP
(470°/0.01 torr) and afforded a colourless oily pyrolysate. Three products only, unchanged (280), rearranged (284) and aromatised (282), in a molar ratio of ca. 3:6:1, were observed in the $^1$H NMR spectrum. Identical results were obtained from pure, rearranged diester (284).

Partial separation of the two diesters was possible by repetitive centrifugal layer chromatography (5% ethyl acetate in hexane), Cookson's diester being marginally more mobile, and a small amount of pure, rearranged diester (284) was isolated, by crystallisation from methanol, as white rods. With the aid of these seed crystals it proved possible to isolate further samples of (284) by fractional crystallisation of the mixture from methanol at ambient temperature.

(1α,2β,5β,6β)-Dimethyl-2,3,4,5,6,7,8,10-octamethyltricyclo[4.2.2.0$^{2,6}$]deca-3,7,9-triene-1,8-dicarboxylic acid (284)

M.p. 131-2°. Found: C, 73.74; H, 8.47.
Calc. for C$_{22}$H$_{30}$O$_4$: C, 73.71; H, 8.43.
$^1$H NMR δ 0.84, s, 3H, 1.19, s, 3H, 1.29, s, 3H, 1.39, q, $\ J$ 1.3Hz, 3H, 1.52, q, $\ J$ 1.3Hz, 3H, 1.64, q, $\ J$ 1.2Hz, 3H, 1.71, q, $\ J$ 1.2Hz, 3H, 1.92, s, 3H, 8 x CH$_3$; 3.66, s, 6H, 2 x COOCH$_3$. Mass spectrum m/z 358 (3%), 109(10), 108(100).

Epoxidation of Cookson's diester (280)

A solution of mCPBA (ca. 85%, 0.45g; 0.22mmol) in chloroform (10cm$^3$) was added dropwise during fifteen minutes to a stirred, ice cooled solution of the diester
(0.85g; 0.24mmol) in chloroform (15cm³). The resultant chloroform solution was washed with saturated sodium bicarbonate solution and water, and the products were isolated by centrifugal layer chromatography (5-20% ethyl acetate in hexane). First to elute was unchanged (280) (0.15g); this was followed by the epoxides (285) (0.26g; 36%) and (286) (0.46g; 63%), each of which was recrystallised from methanol.

(1α,2β,3α,5α,6β,7α)-Dimethyl-1,2,3,5,6,7,10,11-octamethyl-4-oxatetraacyclo[5.2.2.0²,6.0³,5]-undeca-8,10-diene-8,9-dicarboxylic acid (285)

M.p. 114-5°. Found: C, 70.28; H, 8.32. Calc. for C₂₂H₃₀O₅: C, 70.56; H, 8.07. ¹H NMR δ 0.88, s, 6H, 1.21, s, 6H, 1.46, s, 6H, 1.84, s, 6H, 8 x CH₃; 3.68, s, 6H, 2 x COOCH₃. Mass Spectrum m/z 374 (< 1%), 219(4), 125(9), 124(100), 123(9), 109(14).

(1α,2α,5α,6α,7β,9β)-Dimethyl-1,2,3,4,5,6,7,8-octamethyl-8-oxatetraacyclo-[4.3.2.0²,5.0³,9]-undeca-3,10-diene-10,11-dicarboxylic acid (286)

M.p. 145-6°. Found: C, 70.55; H, 8.40. Calc. for C₂₂H₃₀O₅: C, 70.56; H, 8.07. ¹H NMR δ 0.94, s, 6H, 1.26, s, 6H, 1.31, s, 6H, 1.60, s, 6H, 8 x CH₃; 3.69, s, 6H, 2 x COOCH₃. Mass spectrum m/z 374(19%), 240(94), 196(30), 151(53), 124(28), 108(100).

Epoxidation of rearranged diester (284)

A solution of the diester (284) (40mg; 0.11mmol) was treated with mCPBA (85%; 20mg; 0.10mmol) and set
aside for ten minutes. The reaction mixture was worked up as before, and centrifugal layer chromatography (10-30% ethyl acetate in hexane) returned 12mg of unchanged (284), followed by epoxides (287) (21mg; 72%), (288) (6mg; 21%) and (289) (2mg; 7%), each of which crystallised from methanol.

\[(1a,2a,3a,5a,6\theta,7\theta)-\text{Dimethyl-2,3,5,6,7,8,10,11-octamethyl-4-oxatetraacyclo}[5.2.2.0^{2\theta},6.0^{5\theta},8\theta]\text{-undeca-8,10-diene-1,9-dicarboxylic acid (287)}\]

M.p. 143-5°. Found: C, 70.78; H, 8.31. Calc. for C_{22}H_{30}O_5: C, 70.56; H, 8.07. \textsuperscript{1}H NMR δ 0.72, s, 3H, 0.97, s, 3H, 1.20, s, 3H, 1.38, s, 3H, 1.45, s, 3H, 1.65, q, J 1.3Hz, 3H, 1.73, q, J 1.3Hz, 3H, 2.08, s, 3H, 8 x CH₃; 3.70, s, 3H, 3.73, s, 3H, 2 x COOCH₃. Mass spectrum m/z 374(1%), 219(5), 125(9), 124(100), 123(12), 109(17).

\[(1a,2a,5a,6\theta,7\theta,9\theta)-\text{Dimethyl-2,3,4,5,6,7,8,9,11-octamethyl-8-oxatetraacyclo}[4.3.2.0^{2\theta},5\theta,0^{7\theta},9\theta]\text{undeca-3,10-diene-1,10-dicarboxylic acid (288)}\]

M.p. 151-2°. Found: C, 70.65; H, 8.34. Calc. for C_{22}H_{30}O_5: C, 70.56; H, 8.07. \textsuperscript{1}H NMR δ 1.09, s, 3H, 1.23, s, 3H, 1.36, s, 6H, 1.38, q, J 1.3Hz, 3H, 1.41, s, 3H, 1.50, q, J 1.3Hz, 3H, 1.88, s, 3H, 8 x CH₃; 3.67, s, 6H, 2 x COOCH₃. Mass spectrum m/z 374 (7%), 240 (61), 196(100), 151(72), 124(23), 108(84).

\[(1a,2a,3\theta,5\theta,6\theta,7\theta,8\theta,10\alpha)-\text{Dimethyl-2,3,5,6,7,8,10,12-octamethyl-4,8-dioxapentacyclo}[5.3.2.0^{2\theta},6.0^{3\theta},5\theta,10\theta]\text{-dodeca-11-ene-1,11-dicarboxylic acid (289)}\]
M.p. 160-1°. Found: C, 67.73; H, 8.09. Calc. for C\textsubscript{22}H\textsubscript{30}O\textsubscript{6}: C, 67.67; H, 7.74. \textsuperscript{1}H NMR δ 0.95, s, 3H, 1.14, s, 3H, 1.16, s, 3H, 1.31, s, 3H, 1.33, s, 3H, 1.37, s, 3H, 1.42, s, 3H, 2.02, s, 3H, 8 x CH\textsubscript{3}; 3.70, s, 3H, 3.74, s, 3H, 2 x COOCH\textsubscript{3}. Mass spectrum m/z 360(5%), 192(9), 124(8), 123(100), 122(8).

Flash vacuum pyrolysis of tetramethyl Dewar furan precursor (285)

Samples of the epoxide (ca. 15mg) were subjected to FVP (0.01 torr). The extent of aromatisation was measured by \textsuperscript{1}H NMR analysis of the oil which collected at the exit from the pyrolysis tube, and varied from ca. 40% at 440° to ca. 70% at 470°. Volatile materials were recovered from a cold trap, containing 5% pyridine-\textsubscript{d}\textsubscript{5} in chloroform-\textsubscript{d} (0.35cm\textsuperscript{3}) and methylene bromide (5\textmu l) as internal standard. Yields were essentially quantitative, and in each case three products were observed. The methylene cyclobutene (245) was only present in small amounts (ca. 5%); the ratio of the remaining two products, cyclopropene (238) and bicyclobutane (248), depended on temperature, with the formation of (248) varying from ca. 70% at 440° to ca. 30% at 470°.

Larger scale FVP (ca. 200mg at 450°) resulted in only ca. 30% aromatisation and provided a roughly equimolar mixture of cyclopropene (238) and bicyclobutane (248), with the usual trace of cyclobutene (245). The \textsuperscript{13}C NMR spectrum of this mixture, recorded in 5% C\textsubscript{5}D\textsubscript{5}N/CDCl\textsubscript{3},
contained 13 lines, of which six were assigned to the cyclopropene (238), and one to the methylene carbon of (245). The remaining six were assigned to the bicyclobutane (248), and had intensities corresponding to those for the equimolar amount of cyclopropene (238) present. Lack of sample precluded observation of the quaternary resonances in the proton coupled spectrum.

Repetition of this experiment provided a ca. 1:2 mixture of bicyclobutane (248) and cyclopropene (238), from which the $^{13}$C NMR spectrum of (248) in benzene-$d_6$ was obtained.

$1,2,3$-Trimethyl-4-methylene-bicyclobutan-2-ol (248)

$^1$H NMR δ 1.74, br.s, 6H, 2 x CH$_3$; 1.98, br.s, 3H, CH$_3$; 4.14, br.s, 2H, CH$_2$. $^{13}$C NMR (5%C$_5$D$_5$N/CDC$_3$) δ 12.9, q, J 126.5Hz, 2 x CH$_3$; 16.5, q, J 127.7Hz, CH$_3$; 89.5, t, J 157.2Hz, CH$_2$; 109.2, C2; 138.7, C1, C3; 145.7, C4. $^{13}$C NMR (C$_6$D$_6$) δ 13.3, 16.6, 90.7, 110.0, 139.2, 145.8.

Radical bromination of tetramethylecyclobutadiene adduct (199)

A solution of the adduct (199) (3.0g; 8mmol) in carbon tetrachloride (50cm$^3$) was heated under reflux with $N$-bromosuccinimide (3.5g; 20mmol) and a catalytic amount of benzoyl peroxide for one hour. Succinimide was removed by filtration and the residue from evaporation of the filtrate was applied to an alumina column.
(4 x 16cm). Gradient elution with dichloromethane (0-40%) in hexane afforded tetrabromide (314) (0.52g; 12%) followed by its symmetrical isomer (313) (1.43g; 34%), each of which was recrystallised from hexane.

(1a,2a,5a,6a)-1,6-Dibromo-3,4-bis(bromo-methyl)-2,5,8-trimethyl-8-azatriyclo-[4.3.0]1,6,02,5]non-3-ene-7,9-dione (314)

M.p. 152-4°. Found: C, 29.16; H, 2.43; N, 2.68.
Calc. for C13H13NO2Br4: C, 29.19; H, 2.45; N, 2.62.
1H NMR δ 1.50, s, 6H, 2 x CH3; 3.08, s, 3H, NCH3;
3.76, d, J 12.0Hz, 2H, 3.99, d, J 12.0Hz, 2H, 2 x CH2Br.
Mass spectrum m/z 535 (<1%), 457(8), 455(25), 453(26),
451(9), 400(20), 398(52), 396(54), 394(21), 215(32),
214(28), 129(100), 128(68), 115(73).

(1a,2a,5u,6a)-1,6-Dibromo-3-dibromomethyl-2,4,5,8-tetramethyl-8-aza-tricyclo[4.3.0]1,6,02,5]non-3-ene-7,9-dione (314)

Calc. for C13H13NO2Br4: C, 29.19; H, 2.45; N, 2.62.
1H NMR δ 1.39, s, 3H, 1.49, s, 3H, 1.92, s, 3H, 3 x CH3;
3.08, s, 3H, NCH3; 3.84, s, 1H, CHBr2. Mass spectrum
m/z 535(1%), 459(17), 457(74), 455(72), 453(14),
399(47), 397(48), 215(51), 214(70), 129(93), 115(100).

Debromination and trapping of tetrabromide (313)

A solution of the tetrabromide (313) (100mg; 0.19mmol) and the cyclone dimer (381) (50mg; 0.10mmol) in anhydrous tetrahydrofuran (1cm3) was heated to
reflux, treated with zinc-silver couple (ca. 0.1g) and heated under reflux for one hour. After standard work up, the two isomeric products were isolated by preparative layer chromatography (50% dichloromethane/hexane), the major isomer being slightly more mobile, followed by recrystallisation from hexane. Isolated yields were 8mg (20%) of minor dimer (319) and 22mg (55%) of major dimer (321).

(3aa, 10aa, 11a, 12a)-4, 10, 11, 12-Tetrahydro-2, 5, 7, 9, 11, 12-hexamethyl-13, 14-bis(methylene)-3a, 10a[1', 2']-endo-cyclobuta-1H, 6H-isoindolo[5, 6-f]isoindole-1, 3, 6, 8(2H, 7H)-tetraone (321)

M.p. 165° (decomposition). Found: C, 72.68; H, 6.33; N, 6.36. Calc. for C26H26N2O4: C, 72.54; H, 6.09; N, 6.51. 1H NMR δ 1.20, s, 6H, 2.61, s, 6H, 4 x CH3; 2.82, s, 3H, 3.07, s, 3H, 2 x NCH3; 2.75, d, J 15.1Hz, 2H, 3.49, d, J 15.1Hz, 2H, H4, H10; 5.00, s, 2H, 5.44, s, 2H, 2 x CH2. Selective irradiation of the singlet at δ 1.20 produced a 5% enhancement of the singlet at δ 5.00 in the nuclear Overhauser difference spectrum. Mass spectrum m/z 430(16%), 216(14), 215(100).

(3aa, 10aa, 11b, 12b)-4, 10, 11, 12-Tetrahydro-2, 5, 7, 9, 11, 12-hexamethyl-13, 14-bis(methylene)-3a, 10a[1', 2']-endo-cyclobuta-1H, 6H-isoindolo[5, 6-f]isoindole-1, 3, 6, 8-(2H, 7H)-tetraone (319)
M.p. 157° (decomposition). Found: C, 72.62; H, 6.22; N, 6.44. Calc. for C_{26}H_{26}N_{2}O_{4}: C, 72.54; H, 6.09; N, 6.51. ¹H NMR δ 1.16, s, 6H, 2.70, s, 6H, 4 x CH₃; 2.77, s, 3H, 3.11, s, 3H, 2 x NCH₃; 2.95, d, J 15.2Hz, 2H, 3.20, d, J 15.2Hz, 2H, H4, H10; 4.87, s, 2H, 5.25, s, 2H, 2 x CH₂. Selective irradiation of the singlet at δ 1.16 produced a 5% enhancement of the singlet at δ 4.87 and an 8% enhancement of the doublet at δ 2.95 in the nuclear Overhauser difference spectrum. Mass spectrum m/z 430(18%), 216(13), 215(100).

\( \text{(1a,2a,5a,6a)} - \text{1,6-Dibromo-2,5,8-trimethyl-3,4-bis(methylene)-8-azatriacyclo[4.3.0]^{1,6.0^{2,5}}-nona-7,9-dione} \) (315)

A solution of the tetrabromide (313) (0.30g; 0.56mmol) in anhydrous ether (15cm³) was stirred vigourously under reflux with zinc powder (4.0g) for twelve minutes, quenched with water, and worked up as usual. Preparative layer chromatography (dichloromethane) returned 7mg of unchanged starting material, followed by the dibromide (315) (131mg; 64%) and the Dewar o-xyylene dimer (319) (36mg; 31%). The dibromide (315) crystallised from hexane as white plates.

M.p. 147-9°. Found: C, 41.69; H, 3.49; N, 3.71. Calc. for C_{13}H_{13}NOBr₂: C, 41.63; H, 3.49; N, 3.73. ¹H NMR δ 1.45, s, 6H, 2 x CH₃; 2.99, s, 3H, NCH₃; 4.97, d, J 1.2Hz, 2H, 5.33, d, J 1.2Hz, 2H, 2 x CH₂. Mass spectrum m/z 296(12%), 294(12), 239(8), 237(8), 215(100), 214(31).
A solution of the 1,3-diene (315) (53mg; 0.14mmol) and the triazolinedione (316) (27mg; 0.14mmol) in dichloromethane (2cm³) was set aside at ambient temperature. The red colour of the triazolinedione faded within a few minutes. Solvent was removed, and the residue was recrystallised from hexane, affording the adduct (317) as white needles (61mg; 77%).

M.p. 234° (decomposition). Found: C, 46.94; H, 3.52; N, 9.65. Calc. for C_{22}H_{20}N_{4}O_{4}Br_{2}: C, 46.83; H, 3.57; N, 9.93. 1H NMR δ 1.52, s, 6H, 2 x CH₃; 2.37, s, 3H, CH₃; 3.07, s, 3H, NCH₃; 4.05, m, 4H, 2 x CH₂; 7.30, d, J 1.2Hz, 4H, aromatic. Mass spectrum m/z 566(7%), 564(14), 562(7), 404(100), 403(42), 227(53), 215(52), 133(80), 132(59), 105(42), 91(47).

The 1,3-diene (315) (105mg; 0.28mmol) was treated with a solution of the 7-oxanorbornadiene (322) (ca. 60%; 0.10g; 0.29mmol) in chloroform (10cm³) and set aside for
twenty minutes. A portion of the reaction mixture was then evaporated to dryness and examined by $^1H$ NMR; none of the 1,3-diene (315) remained, and a single adduct (323) had formed ($\delta$ 1.31, s, 6H, 1.57, s, 6H, 4 x CH$_3$; 2.78, s, 3H, 3.05, s, 3H, 2 x NCH$_3$; 6.15, s, 2H, olefinic). This $^1H$ NMR sample was analysed the following day, and found to contain dimethylfuran (65) and the new adduct (324) in place of the old. The maleimide (324) was isolated by preparative layer chromatography (40% ethyl acetate in hexane) and crystallised from hexane as white needles (111mg; 82%).

M.p. 343-7°. Found: C, 44.23; H, 3.32; N, 5.71. Calc. for C$_{18}$H$_{16}$N$_2$O$_4$Br$_2$: C, 44.66; H, 3.33; N, 5.79.

$^1H$ NMR $\delta$ 1.45, s, 6H, 2 x CH$_3$; 2.90, s, 4H, 2 x CH$_2$; 2.96, s, 3H, 2.99, s, 3H, 2 x NCH$_3$. Mass spectrum m/z 406(7%), 404(6), 348(98), 346(100), 324(21), 182(23), 153(28), 152(27).

**Debromination and trapping of adduct (324)**

A solution of the adduct (324) (40mg; 0.08mmol) and the cyclone dimer (381) (50mg; 0.10mmol) in anhydrous tetrahydrofuran (1cm$^3$) was heated to reflux, treated with zinc-silver couple (ca. 0.2g) and stirred under reflux for one hour. The clear orange solution turned rapidly cloudy. Products were isolated by preparative layer chromatography (chloroform) after standard work up. The adduct (327) (3mg; 6%) was trailed by the phthalimide (326), much of which remained at the base line. A portion of this by-product was recovered, and crystallised from chloroform/hexane as white needles.
144.

4,10-Dihydro-2,5,7,9-tetramethyl-1H,6H-isoindolo[5,6-f]isoindole-1,3,6,8(2H,7H)-tetraone (326)

M.p. 323-5° (sublimation). Found: C, 66.92; H, 4.93; N, 8.43. Calc. for C_{18}H_{16}N_{2}O_{4}: C, 66.66; H, 4.97; N, 8.64. ¹H NMR δ 2.68, s, 6H, 2 x CH₃; 3.07, s, 3H, 3.14, s, 3H, 2 x NCH₃; 3.71, s, 4H, 2 x CH₂. Mass spectrum m/z 324(100%), 322(35), 268(92), 240(51), 182(59), 153(34), 152(32).

**Radical bromination of adduct (204)**

A solution of the cyclobutene (204) (2.0g; 4.2mmol) in carbon tetrachloride (40cm³) was heated under reflux with N-bromosuccinimide (1.7g; 9.5mmol), over a sun lamp, for eighteen hours. Succinimide was removed by filtration and the products were isolated by centrifugal layer chromatography (30% dichloromethane in hexane), the tribromide eluting first. Following recrystallisation from hexane, the yield of tribromide (329) was 0.7g(23%), and that of dibromide (328) 1.5g (56%).

(3aa,4B,7B,7aa,8B,8B)-10,11-bis(Bromomethyl)-4,7,8,9-tetrahydro-2,4,7,8,9-pentamethyl-5,6-diphenyl-3a,7a[1',2']-endo-cyclobuta-4,7-methano-1H-isoindole-1,8,12(2H)-trione (328)

M.p. 185-7° (decarbonylation). Found: C, 60.80; H, 4.50; N, 2.13. Calc. for C_{32}H_{29}NO_{3}Br_{2}: C, 60.49;
H, 4.60; N, 2.20. $^1$H NMR δ 1.40, s, 6H, 1.57, s, 6H, 4 × CH₃: 2.98, s, 3H, NCH₃: 3.80, d, $J$ 11.7Hz, 2H, 4.05, d, $J$ 11.7Hz, 2H, 2 × CH₂Br; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 475(4%), 342(12), 341(21), 340(30), 261(19), 260(87), 215(42), 106(100).

$(3\alpha, 4\beta, 7\beta, 7aa, 8\beta, 8\beta)-11$-Bromomethyl-10-dibromomethyl-4,7,8,9-tetrahydro-2,4,7,8,9-pentamethyl-5,6-diphenyl-3a,7a[1',2']-endo-cyclobuta-4,7-methano-1H-isoindole-1,3,12(2H)-trione (329)

M.p. 207-9° (decarbonylation). Found: C, 54.04; H, 3.91; N, 1.77. Calc. for C₃₂H₂₈N₂O₃Br₃: C, 53.81; H, 3.95; N, 1.96. $^1$H NMR δ 1.44, s, 3H, 1.48, s, 3H, 1.57, s, 3H, 1.58, s, 3H, 4 × CH₃: 2.99, s, 3H, NCH₃: 3.82, d, $J$ 11.2Hz, 4.59, d, $J$ 11.2Hz, 2H, CH₂Br, 5.96, s, 1H, CHBr₂. Mass spectrum m/z 474(1%), 342(18), 341(22), 340(31), 261(14), 260(64), 214(28), 187(100), 185(100), 105(19).

Debromination of tribromide (329)

A solution of the tribromide (329) (15mg) in anhydrous tetrahydrofuran (4cm³) and anhydrous ether (2cm³) was stirred under reflux with zinc powder (1g) for one hour. Neutral work up provided a white crystalline solid (10mg; 100%), identified by $^1$H NMR spectroscopy as the 1,3-diene (263).
A similar solution in ether alone was heated under reflux with zinc powder for thirty minutes, affording a mixture of the 1,3-diene (263) and a second component (aa. 2 eq), assigned structure (330) on the basis of its $^1$H NMR spectrum ($\delta$ 1.35, s, 3H, 1.37, s, 3H, 1.59, s, 3H, 1.60, s, 3H, 4 x CH$_3$: 2.91, s, 3H, NCH$_3$: 5.19, t, $J$ 1.3Hz, 1H, 5.99, t, $J$ 1.1Hz, 1H, 6.14, t, $J$ 1.2Hz, 1H, olefinic) but not isolated. The stereochemistry of this intermediate can be assigned on the basis of the two low field olefinic resonances, one of which is deshielded by the geminal bromine and the other by steric compression. 153

A solution of the dibromide (328) (1.40g; 2.20mmol) in anhydrous ether (40cm$^3$) was stirred, under reflux, with zinc powder (10g) for one hour, quenched with water, extracted into chloroform, and purified by centrifugal layer chromatography (50% dichloromethane in hexane). The product crystallised from methanol as white plates (0.74g; 71%).
M.p. 182-3° (decarbonylation). Found: C, 80.45; H, 5.99; N, 3.12. Calc. for C_{32}H_{29}NO_3: C, 80.82; H, 6.15; N, 2.95. 

1H NMR δ 1.35, s, 6H, 1.60, s, 6H, 4 x CH_3; 2.88, s, 3H, NCH_3; 4.93, d, J 0.9Hz, 2H, 5.28, d, J 0.9Hz, 2H, 2 x CH_2; 6.8-7.2, m, 10H, aromatic. 

13C NMR δ 9.60, 14.48, 4 x CH_3; 24.54, NCH_3; 50.15, 57.05, 57.49, C3a,C4,C7,C7a,C8,C9; 106.64, 2 x CH_2; 127.52, 127.85, 129.83, 133.02, aromatic; 143.84, 151.34, C5,C6,C10,C11; 175.74, 2 x CO; 202.07, CO. Mass spectrum m/z 475(7%), 342(9), 341(9), 340(16), 262(23), 261(84), 232(17), 215(28), 106(100).

Cycloaddition of (263) with the 7-oxanorbornadiene (322)

A solution of the 1,3-diene (263) (29mg; 0.06mmol) in chloroform-d (0.2cm³) was titrated with a solution of the dienophile (322) (80%; 23mg; 0.09mmol) in chloroform-d (0.3cm³) until a slight excess had been added. Formation of the initial cycloadduct (331) (δ 1.23, s, 6H, 1.56, s, 6H, 1.58, s, 6H, 6 x CH_3; 2.79, s, 3H, 2.99, s, 3H, 2 x NCH_3; 6.14, s, 2H, olefinic) was complete in 20 minutes, but thereafter new signals for dimethylfuran (65) and the maleimide (327) appeared as the first formed (331) decomposed (t_½ = ca. 4 hrs at 30°C). The stable maleimide (327) (24mg; 67%) was isolated by preparative layer chromatography (20% ethyl acetate in hexane) followed by recrystallisation (hexane).
A solution of the dibromide (328) (100mg; 0.16mmol) in anhydrous tetrahydrofuran (4cm$^3$) was heated to reflux, treated with zinc/silver powder (ca. 0.5g), stirred vigorously for two minutes, treated with the dibromide (357) (80mg; 0.22mmol) and stirred under reflux for ten minutes before being quenched with water. The product was isolated from the chloroform extract by preparative layer chromatography (chloroform) and crystallised from hexane as white needles (68mg; 74%).

M.p. 212-4° (decarbonylation). Found: C, 76.22; H, 5.41; N, 5.12. Calc. for C$_3$H$_{3}$_{2}N$_{2}$O$_{5}$: C, 76.01; H, 5.52; N, 4.79. $^1$H NMR $^\delta$ 1.36, s, 6H, 1.59, s, 6H, 4 x CH$_3$; 2.86, s, 3H, NCH$_3$; 2.89, s, 4H, 2 x CH$_2$; 2.99, s, 3H, NCH$_3$; 6.8-7.2, m, 10H, aromatic. Mass spectrum $m/z$ 342(30%), 341(42), 281(19), 261(31), 216(16), 208 (100).

(4aa,4ba,4cB,5a,8a,8aB,8ba,8ca)-4,4b,5,-
8,8b,8-Hexahydro-2,4b,5,8,8b,11-hexamethyl-
6,7-diphenyl-4a,8a-epoxy-4a,8a-
(methaniminomethano)-5,8-methano-1H-
benzo[3',4']cyclobuta[1',2':3,4]cyclobuta-
[1,2-f]isoindole-1,3,10,12,13(2H)-pentaone (332)

A solution of the cyclobutene (327) (100mg) and
mCPBA (ca. 7 eq) in dichloromethane (5 cm$^3$) was set aside at ambient temperature for three days. Acid by products were removed with aqueous NaOH and the product was isolated by preparative layer chromatography (chloroform) followed by recrystallisation (dichloromethane) as white plates (59 mg; 57%).

M.p. 229-231° (decarbonylation). Found: C, 73.59; H, 5.34; N, 4.68. Calc. for C$_{37}$H$_{32}$N$_2$O$_6$: C, 73.99; H, 5.37; N, 4.66. $^1$H NMR $\delta$ 1.32, s, 6H; 1.60, s, 6H; 1.37, s, 6H; 4 x CH$_3$; 2.84, s, 3H, NCH$_3$; 2.89, m, 4H, 2 x CH$_2$; 2.95, s, 3H, NCH$_3$; 2.90, s, 3H, NCH$_3$; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 574 (5%), 282 (21), 210 (20), 209 (24), 208 (100), 173 (47).

(4aa,4ba,4cβ,8aβ,8ba,8ca)-4,4b,-
8b,9-Tetrahydro-2,4b,5,8,8b,11-
hexamethyl-6,7-diphenyl-4a,8c-epoxy-
4c,8a-(methaniminomethano)-1H-
benzo[3',4']cyclobuta[1',2':3,4]-
cyclobuta[1,2-f]-isoindole-1,3,10,12(2H)-tetraone (333)

A solution of the ketone (332) (31 mg) in diglyme (1 cm$^3$) was heated under reflux for an hour. The product was recovered by centrifugal layer chromatography (20% ethyl acetate in hexane) followed by recrystallisation (same solvent) as white needles (17 mg; 58%).

M.p. 271-3°. Found: C, 75.16; H, 5.76; N, 4.92. Calc. for C$_{36}$H$_{32}$N$_2$O$_5$: C, 75.51, H, 5.63, N, 4.89. $^1$H NMR (acetone-$d_6$) $\delta$ 1.37, s, 6H; 1.75, s, 6H; 4 x CH$_3$; 2.79, s, 4H; 2 x CH$_2$; 2.88, s, 3H, 2.90, s, 3H; 2 x NCH$_3$; 6.7-7.1, m, 10H, aromatic. Mass spectrum m/z
Low temperature photolysis of the bridged Dewar furan precursor (332)

A solution of the epoxide (332) (7 mg) in acetone-$d_6$ (0.35 cm$^3$) was sealed under argon, cooled to -85° and irradiated ($\lambda = 254$ nm) for 50 minutes. The $^1$H NMR spectrum of the photolysate indicated the presence of unreacted epoxide (332) and phthalimide (157) (molar ratio ca. 1:3). The only other significant component had methyl resonances at $\delta$ 1.44 and 1.54, together, integrating to roughly the same value as the $\delta$ 2.87 resonance of (157). Three components were detected by analytical layer chromatography: two were identified as the epoxide (332) and the phthalimide (157), but the third, recovered as a mixture with the slightly more mobile (157) following centrifugal layer chromatography (dichloromethane), differed from the third component detected by $^1$H NMR. Traces of this third isolated component were detectable in the original NMR spectrum ($\delta$ 2.79, s, 6H; 3.23, s, 3H; 7.7-8.7, m, 4H).

Analysis of the photolysate from an identical experiment by $^1$H NMR at -80°C provided a spectrum identical to that obtained at 30°C, except for a slight broadening of the resonance at $\delta$ 1.54 belonging to the major unknown product.
A solution of the 7-oxanorbornadiene (338) (29.4g; 0.13mol), dimethylacetylenedicarboxylate (18.2g; 0.13mol) and RuH$_2$(CO)(PPh$_3$)$_3$ (0.3g; 2.5 x 10$^{-3}$ eq) in benzene (70cm$^3$) was heated at 80°, under nitrogen, for 16 hours. The product was isolated by distillation (b.p.98-102°/0.01 torr) as a white crystalline solid, m.p.66-7° (lit. 154° 70°). The yield was 43.2g (91%).

A solution of the tricyclic diester (339) (20.0g; 53.8mmol) and the maleimide (148) (16.0g; 59.5mmol) in acetone (300cm$^3$) was cooled in an ice/salt bath and irradiated (λ>225nm), under a nitrogen atmosphere, for three hours, with constant stirring. The resultant suspension was filtered, and the filtrate was evaporated to an orange oil which was chromatographed on an alumina column (4 x 16cm), with dichloromethane elution, to afford a single lachrymatory product which crystallised from hexane (15.6g; 45%).

M.p. 161-2°. Found: C, 35.74; H, 2.06; N, 1.95. Calc. for C$_{19}$H$_{13}$NO$_7$Br$_2$F$_6$: C, 35.60; H, 2.04; N, 2.18.
152.

$^1$H NMR $\delta$ 3.08, s, 2H, H3c,H7a; 3.18, s, 3H, NCH$_3$; 3.75, s, 6H, COOCH$_3$; 5.72, s, 2H, H4, H7. Mass spectrum m/z 643(1%), 641(2), 639(1), 562(18), 560(17), 530(20), 528(19), 358(20), 356(21), 314(39), 312(37), 301(99), 299(100), 247(77), 59(89).

**Flash vacuum pyrolysis of photoadduct (340)**

Samples of the photoadduct (340) (ca. 10mg) were subjected to FVP at 0.01 torr. Bromine was seen and smelt in the cold trap, and the less volatile fragments that collected at the exit from the pyrolysis tube were analysed by $^1$H NMR. Pyrolysis at 400° produced a single such product, the phthalimide (344), while at 350° a binary mixture (ca. 1:1) of this same product and unchanged photoadduct (340) was obtained.

Preparative FVP (400°; 0.01 torr) of the photoadduct (340) (50mg) provided 19mg (88%) of phthalimide (344) which crystallised from methanol as needles.

**Dimethyl-2-methyl-1H-isoindole-1,3(2H)-dione-4,7-dicarboxylic acid (344)**

M.p. 124-5°. Found: C, 56.25, H, 3.96; N, 4.84. Calc. for C$_{13}$H$_{11}$NO$_6$: C, 56.32; H, 4.00; N, 5.05.

$^1$H NMR $\delta$ 3.18, s, 3H, NCH$_3$; 4.02, s, 6H, 2 x COOCH$_3$; 7.92, s, 2H, aromatic. Mass spectrum m/z 277(43%), 247(100), 219(31), 175(38), 162(27), 161(30), 104(42), 103(49), 102(41), 77(30), 76(29), 75(78), 74(69).
Dimethyl-1,4,4c,6,8,8a-hexahydro-10-methyl-6,7-bis(trifluoromethyl)-1,4:5,8-diepoxo-4a,8aa-
(methaniminomethano)benzo[3',4'-]cyclobuta[1',2':3,4]cyclobutabenzen-9,11-dione-4b,8b-dicarboxylic acid (346)

A solution of the photoadduct (340) (0.40g; 0.62mmol) in furan (1cm³) and anhydrous tetrahydrofuran (9cm³) was heated, under reflux, with zinc/silver couple (ca. 1g) for two hours, and worked up as usual. Products were recovered by preparative layer chromatography (dichloromethane), the phthalimide (344) (0.12g; 69%) eluting first. The adduct (346) (31mg; 9%) crystallised from methanol.

M.p. 244-7° (sublimation). Found: C, 50.35; H, 3.04; N, 2.43. Calc. for C₂₃H₁₇NO₈F₆: C, 50.28; H, 3.12; N, 2.55. 1H NMR δ 2.46, s, 2H, H₄c,H₈a; 2.89, s, 3H, NCH₃; 3.86, s, 6H, 2 x COOCH₃; 5.30, t, J 1.1Hz, 2H, H₁,H₄; 5.33, s, 2H, H₂, H₅, H₈; 6.45, t, J 1.1Hz, 2H, H₂, H₃. Mass spectrum m/z 549 (<1%), 246(4), 68(100).

1,5-Dibromo-3,6,7-trimethyl-3-azabicyclo-[3.2.0]hept-6-ene-2,4-dione (348)

A solution of the maleimide (148) (10.0g; 37mmol) and but-2-yne (25.0g; 460mmol) in acetone (120cm³) was maintained at 0°C during 11 hours irradiation (λ>225nm). Distillation (bath temperature 60°) returned a 30% solution of but-2-yne in acetone (54g; ca. 70% recovery). The remaining solvent was
removed under reduced pressure, and the dark oily residue was chromatographed on a silica column (30x4cm; 10-30% dichloromethane in hexane), returning 0.8g of the maleimide (148) followed by 5.5g (50%) of the photoadduct (348), which was recrystallised from hexane.

M. p. 94-5°. Found: C, 33.42; H, 2.86; N, 4.09.
Calc. for C₉H₉NO₂Br₂: C, 33.47; H, 2.81; N, 4.34.

¹H NMR δ 1.79, s, 6H, 2 x CH₃; 3.03, s, 3H, NCH₃.
¹³C NMR δ 10.76; 2 x CH₃; 25.82, NCH₃; 62.13, Cl,C5; 143.13, C6,C7; 170.05, C2,C4. Mass spectrum m/z 325(24%), 323(59), 321(24), 244(68), 242(71), 240(53), 238(100), 236(52), 78(76), 77(42).

1,5-Dibromo-2,4,7-trimethyl-8-oxa-7-azatricyclo[3.3.0.0³⁴]octa-6,8-dione (349/350)

A solution of the cyclobutene (348) (0.30g; 0.93mmol) and mCPBA (ca. 5 eq) in ethanol free chloroform (15cm³) was heated at 60° in a stoppered flask for four days. The solution was washed with NaOH and the products were isolated by preparative layer chromatography (dichloromethane). Two isomeric epoxides (ca. 3:1; 0.25g; 79%) were isolated; pure samples of the major and minor isomers were obtained from the leading and trailing edge, respectively, of the chromatographed mixture, and each was recrystallised from hexane.

¹H NMR δ 1.71, s, 6H, 2 x CH₃; 3.07, s, 3H, NCH₃. Mass spectrum m/z 260(7%), 258(7), 254(9), 203(98), 201(100), 43(88).
Minor isomer: M.p. 172-3°. Found: C, 31.68; H, 2.68; N, 4.27. Calc. for C₉H₉NO₃Br₂: C, 31.89; H, 2.68; N, 4.13. ¹H NMR δ 1.54, s, 6H, 2 x CH₃; 3.13, s, 3H, NCH₃. Mass spectrum m/z 260 (4%), 258 (4), 254 (3), 203 (62), 201 (61), 43 (100).

4,7-Dihydro-2,8,10-trimethyl-4,7-epoxy-3a,7a-endo-oxirano-1H-isouindole-1,3(2H)-dione (352a,b)

A solution of the above dibromide (major isomer) (100mg; 0.3mmol) in furan (3cm³) and anhydrous tetrahydrofuran (3cm³) was stirred vigourously with zinc powder (1g) while being treated with titanium tetrachloride (4 drops), and then heated under reflux for two hours before the usual aqueous quench and work up. A single adduct (352a) (22mg) was isolated by preparative layer chromatography (40% hexane in ethyl acetate), together with a less mobile fraction (9mg) containing (352a) and two other components. These were resolved by HPLC (20% ethyl acetate in hexane; 2cm³/min) with the following retention times: (352a), 7; (352b), 14; (353) 20 min. Isolated yields were: (352a), 25mg, 34%; (352b), 3mg, 4%; (353), 3mg, 4%. Each component was recrystallised from hexane.

Major adduct (352a): M.p. 155-7°. Found: C, 62.99; H, 5.46; N, 5.99. Calc. for C₁₃H₁₃NO₄: C, 63.15; H, 5.30; N, 5.66. ¹H NMR δ 1.58, s, 6H, 2 x CH₃; 2.81, s, 3H, NCH₃; 5.10, t, J 1.0Hz, 2H, H₄, H₇; 6.46, t, J 1.0Hz, 2H, H₅, H₆. ¹³C NMR δ 9.75, 2 x CH₃; 24.89, NCH₃; 63.93, C₃a, C₇a; 65.76, C₈; 77.65, C₄, C₇; 135.74, C₅, C₆; 171.43, C₁, C₃. Mass spectrum m/z 179 (100%), 135 (33), 93 (20), 80 (29), 68 (22), 43 (77).
Minor adduct (352b): M.p. 188-9°. Found: C, 63.60; H, 5.45; N, 5.89. Calc. for C_{13}H_{13}NO_{4}: C, 63.15; H, 5.30; N, 5.66. 1H NMR δ 1.41, s, 6H, 2 x CH₃; 2.97, s, 3H, NCH₃; 5.14, t, J 1.0Hz, 2H, H₄, H₇; 6.68, t, J 1.0Hz, 2H, H₅, H₆.

Mass spectrum m/z 179(100%), 135(42), 93(18), 80(21), 68(17), 43(84).

9-Chloro-4,7-dihydro-8-hydroxy-2,8,9-trimethyl-4,7-epoxy-3a,7a-ethano-1H-isoindole-1,3(2H)-dione (353)

A solution of the dibromides (349/50) (ca. 70% major isomer; 0.16g) in furan (6cm³) and anhydrous tetrahydrofuran (12cm³) was stirred vigorously with zinc powder (3g) while being treated with titanium tetrachloride (12 drops), and then heated under reflux for four hours before the usual aqueous quench and work up. Preparative layer chromatography (40% hexane in ethyl acetate) returned a mixture of unreacted dibromides (349/50) (ca. 90% minor isomer; 0.03g) followed by a single product, the chlorohydrin (353) (11mg; 10%), which crystallised from chloroform/hexane as white plates.

The chlorohydrin (353) was also the only product, in low yield, from treatment of the furan adducts (352a,b) with zinc and titanium tetrachloride as described above.

M.p. 227-9°. Found: C, 55.14; H, 4.95; N, 5.23; Cl, 13.18. Calc. for C_{13}H_{14}NO_{4}Cl: C, 55.04; H, 4.97; N, 4.94; Cl, 12.50. 1H NMR δ 1.53, s, 3H, 1.86, s, 3H, 2 x CH₃; 2.86, s, NCH₃; 5.16, t, J 1.0Hz, 1H, 5.20, t, J 1.0Hz, 1H, H₄, H₇; 6.39, t, J 1.0Hz, 2H, H₅, H₆. 13C NMR δ 18.53, 21.77, 2 x CH₃; 25.15, NCH₃; 60.90, 61.84,
C3a, C7a; 70.95, C9; 73.74, C8; 79.20, C4 or C7; 135.34, 135.86, C5, C6; 172.81, 172.88, C1, C3. Mass spectrum m/z 240 (5%), 202 (9), 201 (100).

4,7-Dihydro-2,8,9-trimethyl-4,7-epoxy-3a,7a-etheno-1H-isoindole-1,3(2H)-dione (356)

A solution of the dibromide (348) (100mg) in furan (2cm³) and anhydrous tetrahydrofuran (1cm³) was stirred vigourously with zinc powder (1g) while being treated with titanium tetrachloride (2 drops), heated under reflux for one hour, and worked up as usual. A binary mixture of products was isolated by preparative layer chromatography (chloroform) and resolved using HPLC (10% ethyl acetate in hexane). The major component (r.t. 11 min; 19mg; 37%) crystallised from hexane as white plates, m.p. 59-60°, and was identified as (354). The furan adduct (356) (r.t. 14 min; 9mg; 13%) crystallised from hexane as white needles.

M.p. 161-6° (sublimation). Found: C, 67.33; H, 5.82; N, 6.03. Calc. for C₁₃H₁₃NO₃: C, 67.52, H, 5.67; N, 6.06. ¹H NMR δ 1.64, s, 6H, 2 x CH₃; 2.95, s, 3H, NCH₃; 5.10, t, J 1.1Hz, 2H, H4, H7; 6.29, t, J 1.1Hz, 2H, H5, H6. Mass spectrum m/z 231 (43%), 216 (29), 202 (47), 174 (34), 112 (36), 110 (40), 91 (55), 77 (100), 76 (54).

3,6,7-Trimethyl-3-azabicyclo[3.2.0]hept-6-ene-2,4-dione (354)

A solution of N-methylmaleimide (0.50g; 45mmol) in 30% but-2-yne/acetone (10cm³) was irradiated (λ>225nm) at 0° for six hours. The photolysate
was filtered and the photoadduct (354) was isolated from the filtrate as a pale yellow oil (0.34g; 46%) by centrifugal layer chromatography (dichloromethane). Recrystallisation from hexane produced white plates.

\[
\text{M. p. 59-60°. Found: C, 65.06; H, 6.70; N, 8.40. Calc. for C}_{9}\text{H}_{11}\text{N}_{2}O_{2}: \text{C, 65.44; H, 6.71, N, 8.48.} \]

\[
\begin{align*}
\text{IH NMR} & \quad \delta 1.75, \text{br.s, 6H, } 2 \times \text{CH}_3; 2.92, \text{s, 3H, } \text{NCH}_3; 3.51, \text{br.s, 2H, } \text{H1, H5. Mass spectrum } m/z 165 (61%), 112(13), 90(100), 89(52). \\
\end{align*}
\]

**Flash vacuum pyrolysis of the Dewar furan adduct (352a)**

The adduct (352a) (10mg) was subjected to FVP (500°; 0.01 torr). The pale yellow, crystalline pyrolysate was identified by \(^1\text{H NMR}\) as the bicyclic furan (360). Pyrolysis at 450° produced only this product and unreacted adduct (352a), in ca. 1:2 ratio.

\[
\text{3a,7a-Dibromo-3a,4,6,7a-tetrahydro-2,4,7-trimethyl-4,7-epoxy-1H-isoindole-1,3(2H)-dione (357)}
\]

A solution of the dibromomaleimide (148) (3.3g; 12.3mmol) and 2,5-dimethylfuran (3.8g; 39.6mmol) in carbon tetrachloride (10cm\(^3\)) was stirred at 70° for five hours and at 50° for two hours. The white crystalline product was isolated by hot filtration, washed with carbon tetrachloride (10cm\(^3\)) and recrystallised from chloroform/hexane as white needles (2.2g; 49%). Recrystallisation of the combined residues from filtration provided a further 1.7g of an equimolar mixture of adduct (357) and maleimide (148).
M.p. 158-61° (decomposition). Found: C, 36.60; H, 3.01; N, 3.95. Calc. for C_{11}H_{11}NO_{3}Br_{2}: C, 36.20; H, 3.04; N, 3.84. \(^1\)H NMR \(\delta\) 1.74, s, 6H, 2 x CH\(_3\); 3.07, s, 3H, NCH\(_3\); 6.41, s, 2H, H5, H6. Mass spectrum m/z 286(100%), 284(100), 91(36).

\[3a,7a\text{-Dibromo-3a,4,5,6,7,7a-hexahydro-2,4,7-trimethyl-4,7-epoxy-1H-isoindole-1,5(2H)-dione (358)}\]

A solution of the alkene (357) (1.0g) in ethyl acetate (40cm\(^3\)) was stirred under an atmosphere of hydrogen, with a 10% palladium on charcoal catalyst (15mg), for twenty four hours. Solvent removal from the filtrate afforded a white solid which was recrystallised from hexane (0.97g; 97%).

M.p. 131-3°. Found: C, 36.17; H, 3.56; N, 3.64. Calc. for C_{11}H_{13}NO_{3}Br_{2}: C, 36.00; H, 3.57; N, 3.82. \(^1\)H NMR \(\delta\) 1.59, s, 6H, 2 x CH\(_3\); 1.70, d, \(J\) 7.8Hz, 2H, H5, H6; 2.57, d, \(J\) 7.8Hz, 2H, H5, H6; 3.08, s, 3H, NCH\(_3\). Mass spectrum m/z 287 (100%), 285(100), 251(22), 249(22), 178(18).

\[4,5,6,7\text{-Tetrahydro-2,4,7-trimethyl-4,7-epoxy-1H-isoindole-1,5(2H)-dione (359)}\]

A solution of the dibromide (358) (0.35g) in anhydrous ether (15cm\(^3\)) was stirred under reflux with zinc dust (2g) for two hours, and worked up as usual. Preparative layer chromatography (chloroform) returned 0.06g of dibromide (358), followed by the alkene (359), a white solid which crystallised from
hexane as white needles (0.13g; 79%).

M.p. 113-5°. Found: C, 63.50; H, 6.39; N, 6.65.
Calc. for C_{11}H_{13}NO_{3}: C, 63.76; H, 6.32; N, 6.76.

^{1}H NMR δ 1.46-1.66, m, 2H, H5, H6; 1.78, s, 6H, 2 x CH\textsubscript{3};
1.88-2.08, m, 2H, H5, H6; 2.94, s, 3H, NCH\textsubscript{3}. Mass
spectrum m/z 207(8%), 179(100), 134(26), 93(14), 79(13).

Addition of furan to a ^{1}H NMR sample of the alkene
(359) led to the formation of two adducts (ca. 3:2)
within one hour at ambient temperature. (Major adduct:
δ 2.94, s, 3H; 5.14, t, 2H; 6.55, t, 2H. Minor adduct:
δ 2.77, s, 3H; 6.30, t, 2H; 6.46, t, 2H).

4,7-Dihydro-2,4,7-trimethyl-4,7-epoxy-
1H-isoindole-1,3(2H)-dione (322)

A solution of the dibromide (357)
(20mg) in anhydrous ether (6cm\textsuperscript{3}) was
stirred under reflux with zinc powder (ca. 5g) for one
hour, and worked up as usual. ^{1}H NMR analysis of the
crystalline product indicated that two compounds were
present, in ca. 4:1 ratio. The major component was
recognised as unchanged (357), while the minor (δ 1.87,
s, 6H; 2.92, s, 3H; 6.97, s, 2H) was assigned structure
(322). This latter component reacted completely within
five minutes with furan to form two adducts (ca. 5:1).
(Major adduct: δ 1.53, s, 6H; 2.88, s, 3H; 5.08, t, 2H;
6.60, t, 2H. Minor adduct: δ 1.76, s, 6H, 2.71, s, 3H;
5.27, t, 2H).

A more reliable debromination procedure follows:
a solution of the dibromide (357) (0.10g) in anhydrous
tetrahydrofuran (5 cm$^3$) was heated to reflux, treated with zinc/silver powder (ca. 0.5 g), stirred vigourously for three minutes, quenched with water, and worked up as usual to afford a pale yellow solid (ca. 45 mg). $^1$H NMR analysis indicated that the oxanorbornadiene (322) was the major component; also present were the dibromide (357) (10%), the phthalimide (362) (5%) and traces of the bis-adduct (361). Recrystallisation from hexane afforded white crystals, m.p. ca. 110°, of the oxanorbornadiene (322), contaminated slightly with dibromide (357) (< 5%), which yellowed rapidly on exposure to the air.

1,3,5-Trimethyl-4H-furo[3,4-c]pyrrole-4,6(5H)-dione (360)

The oxanorbornene (359) (50 mg) was subjected to FVP (550°/0.01 torr), affording a white, crystalline pyrolysate, which recrystallised from hexane as white needles (39 mg; 90%).

M.p. 185-6° (sealed tube). Found: C, 60.43; H, 5.07; N, 7.59. Calc. for C$_9$H$_9$NO$_3$: C, 60.33; H, 5.06; N, 7.82. $^1$H NMR $\delta$ 2.45, s, 6H, 2 x CH$_3$; 3.03, s, 3H, NCH$_3$. Mass spectrum m/z 179(100%), 163(12), 134(27), 93(34), 79(47).

Tetrahydro-1,4,5,8,10-pentamethyl-1,4:5,8-diepoxy-4a,8a-(methanimino-methano)naphthalene-9,11-dione (361)

A solution of the dibromide (357) (200 mg; 0.55 mmol) and 2,5-dimethylfuran (200 mg; 2.1 mmol) in anhydrous tetrahydrofuran (10 cm$^3$) was stirred with zinc powder
(ca. 1g) while being treated with titanium tetrachloride (4 drops), and stirred for a further three hours at ambient temperature under a nitrogen atmosphere. The bis-adduct (361) was isolated by preparative layer chromatography (30% hexane in ethyl acetate) following the usual aqueous quench and work up, and was recrystallised from hexane (84 mg; 53%).

M.p. 169-71°. Found: C, 66.74; H, 6.54; N, 4.63. Calc. for C_{16}H_{19}NO_{4}: C, 66.42; H, 6.62; N, 4.84. 

^1H NMR δ 1.53, s, 6H, 2 x CH₃; 1.64, s, 6H, 2 x CH₃; 2.85, s, 3H, NCH₃; 6.30, s, 2H, H2, H3; H6, H7. Mass spectrum m/z 259(12%), 258(58), 216(11), 96(100), 95(31).

Flash vacuum pyrolysis (400°/0.01 torr) of the adduct (361) afforded the bicyclic furan (360) as sole product. At 300°, 20% of the adduct (361) underwent fragmentation, producing an equimolar mixture of the same furan (360) and the intermediate 7-oxanorbornadiene (322).

Exclusion of dimethylfuran from the above procedure resulted in the isolation of a pale yellow solid, which was recrystallised from methanol to afford 47mg (45%) of the phthalimide (362) as white needles, m.p. 168-70° (lit. 152 176-7°). 

^1H NMR δ 2.64, s, 6H, 2 x CH₃; 3.13, s, 3H,
NCH₃; 7.29, s, 2H, H5, H6.

\((1a, 4a, 5b, 6a)-5, 6\text{-bis(Bromomethyl)}-1, 4\text{-dimethyl}-2, 3\text{-diphenylbicyclo[2. 2. 1]}\text{-hept-2-ene-7-one} \) (367)

A solution of the cyclone dimer (381) (5.0g; 10mmol) and E-bis(bromomethyl)ethylene (366) (20.0g; 93mmol) in benzene \((100\text{cm}^3)\) was heated at \(105^\circ\) in a sealed tube for 36 hours. Polymeric by products were removed by filtration and the filtrate was evaporated at 17 torr. Unreacted alkene (366) was recovered by vacuum distillation (0.01 torr) and the residue was chromatographed on a silica column \((20 \times 3\text{cm})\), using gradient elution with dichloromethane \((0-50\%)\) in hexane. The adduct (367) crystallised from methanol as white needles \((1.07g; 12\%)\).

M.p. 170-2°. Found: C, 58.06; H, 4.58. Calc. for \(C_{23}H_{22}Br_2O\): C, 58.25; H, 4.68. \(^1\)H NMR \(\delta\) \(1.29, s, 3H, 1.43, s, 3H, 2 \times \text{CH}_3; 2.1-2.3, m, 1H, 2.4-2.7, m, 1H, H5, H6; 3.4-3.9, m, 4H, 2 \times \text{CH}_2\text{Br}; 6.9-7.3, m, 10H, aromatic. Mass spectrum \(m/z\) 474 (1%), 448(50), 447(31), 446(100), 444(50), 367(18), 365(18), 352(23), 350(23), 273(24), 272(79), 260(18), 259(26), 256(21), 242(23), 215(22), 116(22), 115(29), 91(27).

\(1, 4\text{-Dimethyl-5, 6-bis(methylene)-2, 3-diphenylbicyclo[2. 2. 1]}\text{-hept-2-ene-7-one} \) (207)

A solution of the dibromide (367) \((0.80g)\) in anhydrous dimethylformamide
(12cm$^3$) was stirred at 80° under a nitrogen atmosphere, with anhydrous potassium fluoride (2g), for thirty-six hours. The reaction mixture was then poured into water and extracted with chloroform; the white solid isolated crystallised from methanol as white plates (0.49g; 93%).

M.p. 160-1° (decarbonylation). Found: C, 88.75; H, 6.55. Calc. for C$_{23}$H$_{20}$O: C, 88.43; H, 6.45. $^1$H NMR $\delta$ 1.32, s, 6H, 2 x CH$_3$; 5.03, s, 2H, 5.54, s, 2H, 2 x CH$_2$; 6.9-7.3, m, 10H, aromatic. $^{13}$C NMR $\delta$ 8.47, 2 x CH$_3$; 59.42, Cl,C4; 101.43, 2 x CH$_2$; 127.41, 127.91, 128.95, 134.14, aromatic; 143.59, C2,C3; 147.14, C5,C6; 204.52, C7. Mass spectrum m/z 285 (28%), 284(100), 269(27), 253(23).

2,5-Dimethyl-3,4-diphenylbicyclo-[4.2.0]octa-1,3,5-triene (369)

The ketone (207) (20mg) was subjected to FVP (350°/0.01 torr), affording a white pyrolysate which crystallised as needles from methanol (16mg; 88%).

M.p. 118-9°. Found: C, 93.25; H, 7.14. Calc. for C$_{22}$H$_{20}$: C, 92.91; H, 7.09. $^1$H NMR $\delta$ 1.90, s, 6H, 2 x CH$_3$; 3.15, s, 4H, H7,H8; 6.8-7.2, m, 10H, aromatic. Mass spectrum m/z 284(100%), 78(34), 77(32), 73(61).
A solution of the 1,3-diene (207) (70mg; 0.22mmol) in chloroform-\(d\) (1cm\(^3\)) was cooled to -40° and treated with a solution of the triazolinedione (316) (43mg; 0.23mmol) in the same solvent (1cm\(^3\)), in small portions. The red colour of the triazolinedione faded to a pale pink within five minutes. The solution was frozen in dry ice and allowed to warm to -40° in a precooled NMR probe, whereupon its spectrum was recorded. No decomposition was detectable during three hours at -40°.

\[ ^1\text{H NMR} \delta 1.52, \text{s, 6H, } 2 \times \text{CH}_3; \ 2.41, \text{s, CH}_3; \ 4.56, \text{s, H5,H10; } 7.0-7.2, \text{ m, 14H, aromatic.} \]
\[ ^{13}\text{C NMR} \delta 7.85, \text{ 2 x CH}_3; \ 21.33, \text{ CH}_3; \ 42.74, \text{ C5,C10; } 61.58, \text{ C6, C9; } 125.55, 127.41, 127.63, 128.22, 128.81, 130.06, 133.09, 136.54, \text{ aromatic; } 138.87, \text{ C7,C8; } 145.76, \text{ C5a,C9a; } 152.54, \text{ C1,C3; } 187.35, \text{ C12.} \]

The solution of the norbornadien-7-one (370), prepared above, was allowed to warm to ambient temperature. Carbon monoxide was evolved vigorously, but ceased within five minutes. The solution was cooled to -40°, and the
13C NMR spectrum was recorded. Solvent was then removed and the residue crystallised from methanol as white needles (99mg; 93%).

M.p. 231-5°. Found: C, 79.04; H, 5.91; N, 8.86.
Calc. for C31H27N3O2: C, 78.62; H, 5.75; N, 8.87.

1H NMR δ 2.02, s, 6H, 2 x CH3; 2.41, s, 3H, CH3; 4.79, s, 4H, H5, H10; 7.0-7.5, m, 14H, aromatic. 13C NMR δ 16.55, 2 x CH3; 21.35, CH3; 44.89, C5, C10; 125.62, 126.23, 127.48, 127.60, 129.84, 130.06, 130.63, 138.80, 139.77, 140.89, aromatic; 153.44, CI, CI3. Mass spectrum m/z 474(37%), 473(100), 472(21), 459(11), 283(12).
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175.


