

Synthesis and reactions of Dewar furans (5-oxabicyclo[2.1.0]pent-2-enes)

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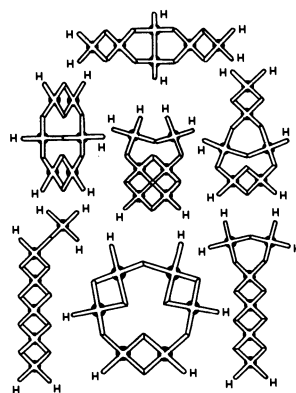
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Abstract – The first preparation of Dewar furan (cyclobutadiene epoxide) is reported. This species is too unstable to be isolated and is characterised by trapping it in adduct form with isobenzofuran. Dewar furan is readily isomerised to cyclopropene aldehyde even at -80°C . Several substituted Dewar furans have been prepared and the mechanism of their rearrangement investigated. Current evidence does not support the presence of a carbene intermediate and alternative mechanisms are discussed.

1 INTRODUCTION

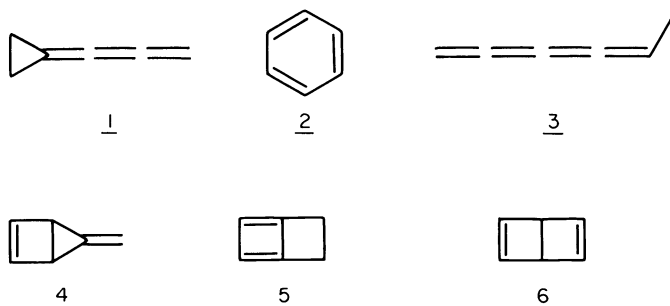
It seems appropriate that this lecture open with a reference to Sir James Dewar since it was in Scotland, in the "Proceedings of the Royal Society of Edinburgh", that the Dewar isomer story began. He reported in 1867 "a mechanical arrangement adapted to illustrate structure in the non-saturated hydrocarbons" and demonstrated its application with the construction of several hypothetical isomers of benzene (ref. 1) (Scheme 1). The Dewar selection corresponds to structures (1)–(7) in Scheme 2, and the omission of prismane (8) and benzvalene (9) reflects the limitations of "his little device" rather than Dewar's lack of appreciation of the existence of such structures. Indeed Dewar accepted the Kekulé structure (2) for benzene, and never proposed the bicyclic representation (6), which bears his name, any more than the other structures shown in Scheme 1. Rightly, or wrongly (ref. 3), this association has passed into the folklore of aromatic chemistry. Its use is retained in this article since the Dewar nomenclature draws together specific valence bond isomers of a whole series of aromatic and pseudoaromatic molecules not otherwise possible.

Scheme 1

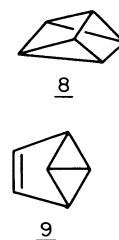


Scheme 2

Original Dewar selection

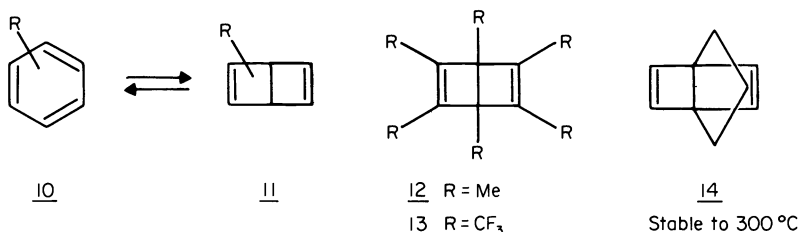


New additions



The Dewar forms (11) of the benzenoid aromatics (10) are now recognised chemical systems and the hexamethyl derivative (12) is even commercially available. Heavily substituted aromatics are known in which the Dewar form is the more stable structure (ref. 4), and when part of a propellane structure, e.g. (14), they are also extremely stable (Scheme 3) (ref. 5).

Scheme 3

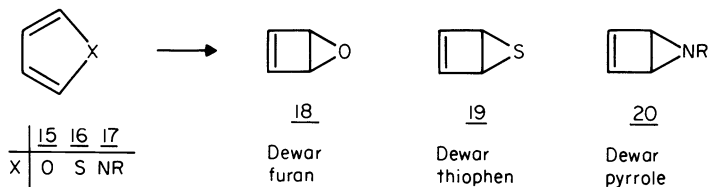


The synthesis of the parent system was received with a mixture of awe and scepticism when first reported by van Tamelen and Pappas in 1963 (ref. 6). It is now well established that this early report was correct and that the unsubstituted Dewar valence isomer (6) is a stable, but reactive, chemical entity. That it exists at all, has been attributed to the non-allowed nature of the 4π disrotatory process involved in its conversion back into the highly stable aromatic system (ref. 7).

2 THE DEWAR FORMS OF 5-MEMBERED HETEROCYCLES

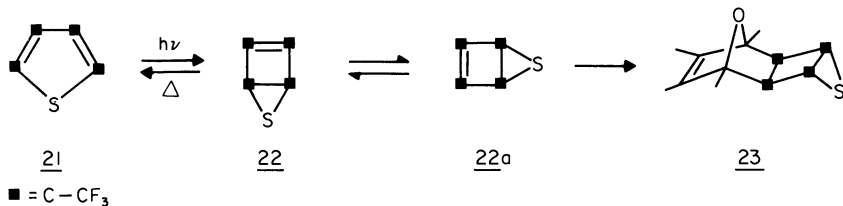
The Dewar forms (18), (19) and (20) (Scheme 4) of the parent 5-membered heterocycles, furan (15), thiophen (16) and pyrrole (17) can also be formulated, but their synthesis has lagged far behind that of the isoelectronic benzenoid aromatics. Indeed it was only this year (1985) that Dewar thiophen (19), the first member of this series, was reported by Strausz (ref. 8); a lag period of 22 years over the parent Dewar benzene. Like the history of the Dewar benzenes, the substituted members of the Dewar heterocycles also preceded the appearance of the parent isomers; moreover the synthetic strategy of the early approaches for the preparation of such valence isomers, namely photoisomerisation, also paralleled that of the benzenoid aromatics.

Scheme 4



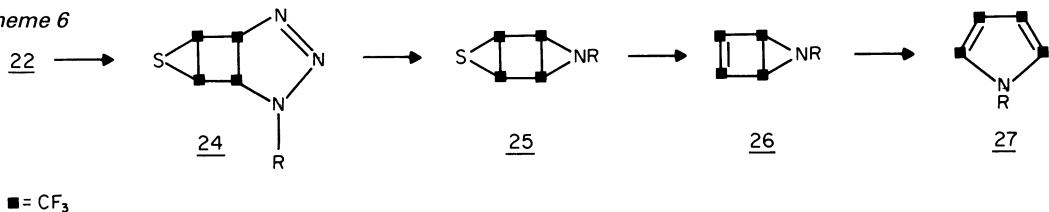
Heicklen reported the first such Dewar structure, the tetrakis (trifluoromethyl) Dewar thiophen (22) in 1970, formed by vapour phase irradiation of the corresponding thiophen (21) (ref. 9). Some equivocation surrounded the early structural assignment, but this was resolved by 19-F nmr spectroscopy (ref. 10). Kobayashi and his coworkers have subsequently improved the synthesis of (22) and studied the reactions of this unusual molecule (Scheme 5) (ref. 11). The π-bond of (22) exhibits high dienophilicity and an adduct (28) forms even

Scheme 5



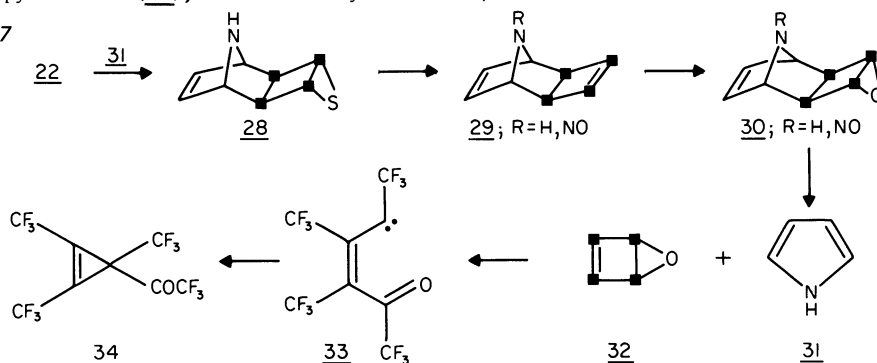
with the normally unreactive pyrrole (ref. 12); the crystal structure of the tetramethyl-furan adduct (23) has been reported and this offers further proof of the Dewar structure of (22). Degenerate rearrangement of (22) ↔ (22a) has been observed by 19-F nmr above 100°, and a concerted pseudopericyclic mechanism, involving the d-orbitals of sulfur, proposed to account for the formal [1,3] migration of sulfur around the ring (sulfur walk) (ref. 13). Isomerisation of (22) to the thiophene (21) occurs at 160° (t_{1/2} = 5.1 hr).

Scheme 6



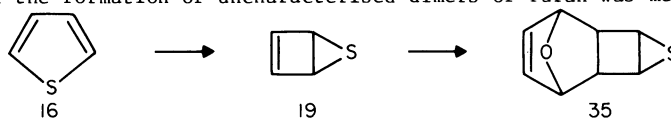
Dewar thiophen (22) has served a key role in the synthesis of other Dewar heterocycles. Thus Kobayashi has converted it in 3-steps to the Dewar pyrrole (26) as outlined in Scheme 6 (ref. 14), while Lemal has prepared the only stable Dewar furan (32) in 6-steps also starting from (22) (see Scheme 7) (ref. 15). The Dewar furan (32), in contrast to (22), does not display degenerate rearrangement but undergoes facile isomerisation to the perfluoro cyclopropyl ketone (34), considered by Lemal to proceed via the intermediate carbene (33).

Scheme 7



The stability of pertrifluoromethyl Dewar furan ($t_{1/2} = \text{ca } 20 \text{ min}/95^\circ$) is much less than that of the pertrifluoromethyl Dewar benzene (13) ($t_{1/2} = \text{ca } 135 \text{ hr}/170^\circ$) and this set the stage for a real synthetic challenge for those wanting to synthesise the parent Dewar furan, given that the stability of the parent Dewar benzene ($t_{1/2} = \text{ca } 50 \text{ hr}/20^\circ$) was already low. Furan trapping and photoisomerisation were the key ingredients of Strausz's approach to the parent Dewar thiophene (19) (Scheme 8) (ref. 8). Thus irradiation of a mixture of thiophen in furan resulted in the formation of the *exo* and *endo* adducts (35), albeit in low yield (<5%). Dewar thiophen can be detected in a glassy matrix at -170°C using this irradiation technique and trapped with furan. Significantly no corresponding adduct of Dewar furan was reported although the formation of uncharacterised dimers of furan was mentioned.

Scheme 8



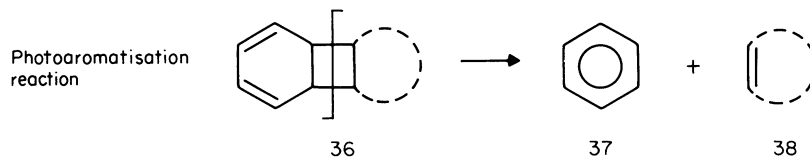
Furans, unlike their heterocyclic analogues, the thiophenes and substituted pyrroles, do not form Dewar isomers upon irradiation. The furans are certainly photolabile, but despite a plethora of products being produced and characterised (ref. 16), no evidence for the intermediacy of Dewar furans has been forthcoming.

3 THE SYNTHESIS OF DEWAR FURAN

3.1 General strategy: use of the 1,2-photoaromatisation reaction

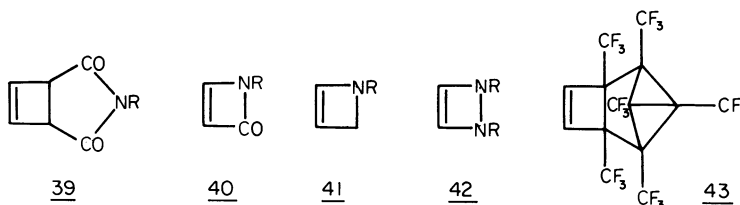
Not all the information mentioned above was available to us at the commencement of our work in this area, but we had decided that a special approach would be needed to prepare Dewar furan, the target of our research programme. We elected to utilise the 1,2-photoaromatisation reaction (ref. 17,18), (Scheme 9), to introduce the π -bond into a preformed dihydro

Scheme 9



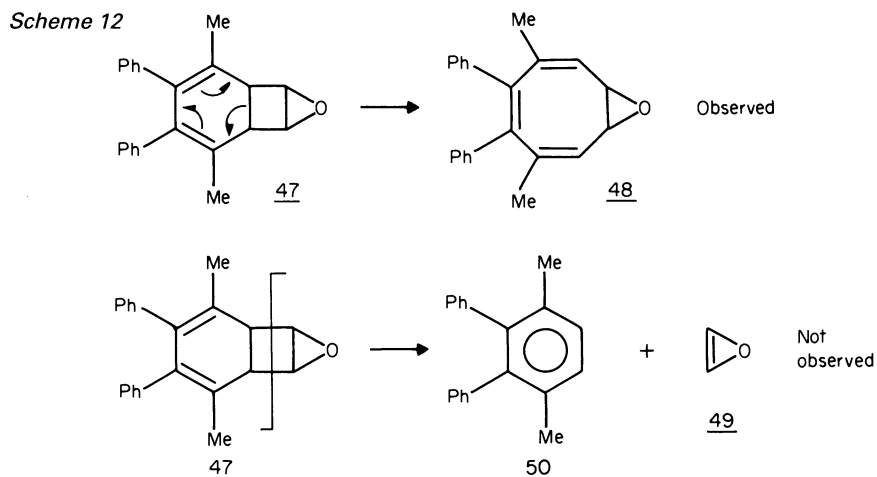
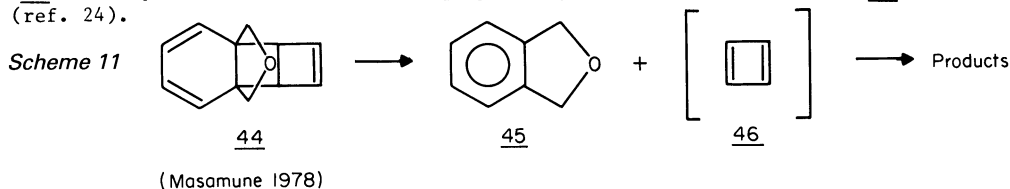
Dewar furan, since there was good precedent for this approach. Some early examples [(39) (ref. 18), (40) (ref. 19), (41) (ref. 20), (42) (ref. 21) and (43) (ref. 22)] of the application of this photofragmentation reaction are shown in Scheme 10.

Scheme 10

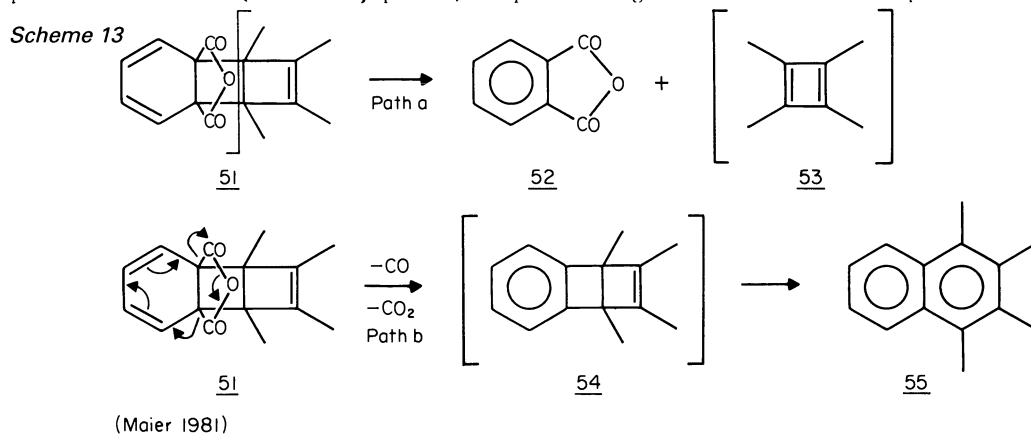


These results confirm the ability of this reaction to generate unsaturated heterocyclic compounds and, in particular, to introduce a π -bond into the 4-membered ring of a strained system, e.g. (43). We were also able to take advantage of some elegant contributions by Masamune and Maier in this field.

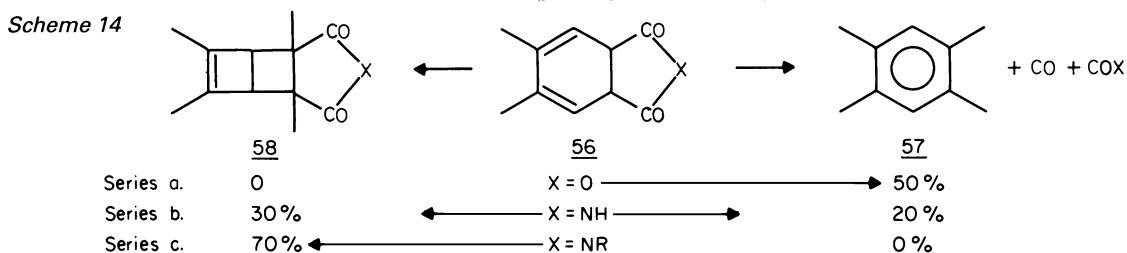
Masamune showed (ref. 23) that irradiation of propellane (44) (Scheme 11) yielded cyclobutadiene (46), a high energy species, and in so doing established the beneficial role that a pinching group played in directing the photofragmentation route, over the alternative 6π -disrotatory ring opening process; the latter had caused us concern when attempting to use the 1,2-photoaromatisation reaction for the generation of oxirene (49) from the diene epoxide (47) which preferred to form the ring-opened cyclooctatetraene epoxide (48) (Scheme 12) (ref. 24).



Maier (ref. 25) used this reaction to produce tetramethylcyclobutadiene (53). As part of that study he employed the anhydride as a pinching group, but this suffered competitive photoaromatisation (Scheme 13, path b) to produce significant amounts of naphthalene (55).



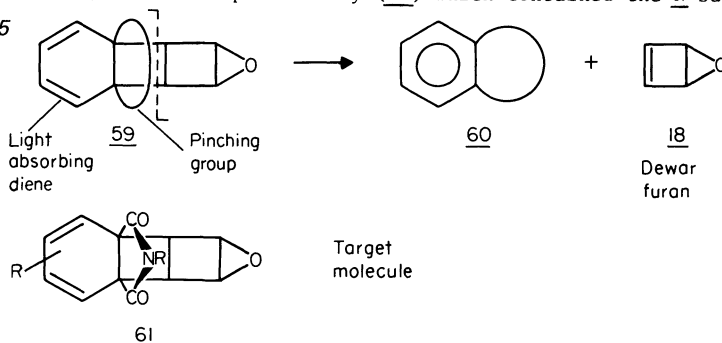
The use of the anhydride group offered synthetic advantages over the oxadimethylene bridge used by Masamune. First it can be introduced in cyclic form and advantage taken of the dienophilicity it bestows on a π -bond; in contrast the related 2,5-dihydrofuran moiety lacks dienophilicity and the ring must be constructed at a later stage in the synthesis. In resolving this concern of the balance of photostability over ease of synthetic introduction, we drew on some of our earlier work involving the photochemistry of substrates containing



the imide group (ref. 26). Irradiation of the *N*-substituted imide (56c) (Scheme 14) produced exclusively the valence isomer (58c) whereas the anhydride (56a) yielded entirely the aromatic hydrocarbon (57); the unsubstituted imide (56b) was more ambivalent and both isomerisation and fragmentation was observed to occur. Clearly the *N*-substituted imide bridge did not enter into the photoaromatisation process with the same ease as the anhydride, and since it retained the synthetic advantages of the anhydride group, it appeared very suitable for our synthetic requirements.

We formulated a propellane (59) as a general substrate suitable for the production of Dewar furan (Scheme 15) and more specifically (61) which contained the *N*-substituted imide bridge.

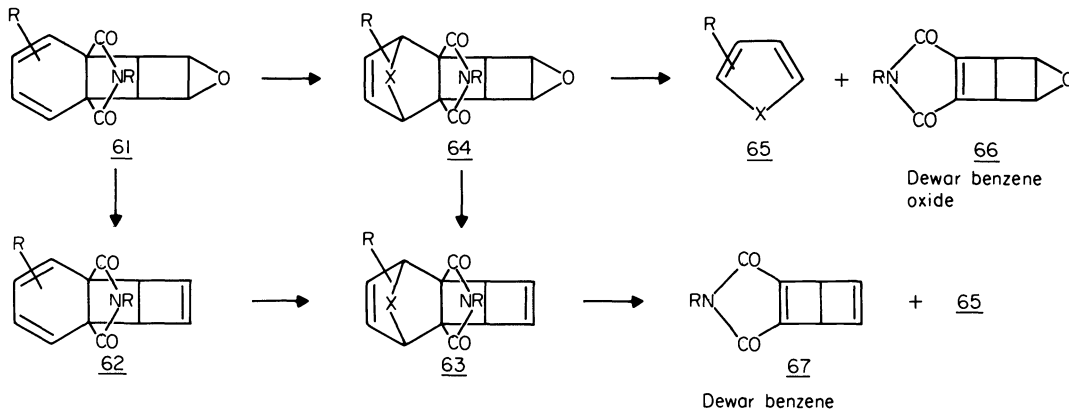
Scheme 15



3.2 Retrosynthesis of target molecule

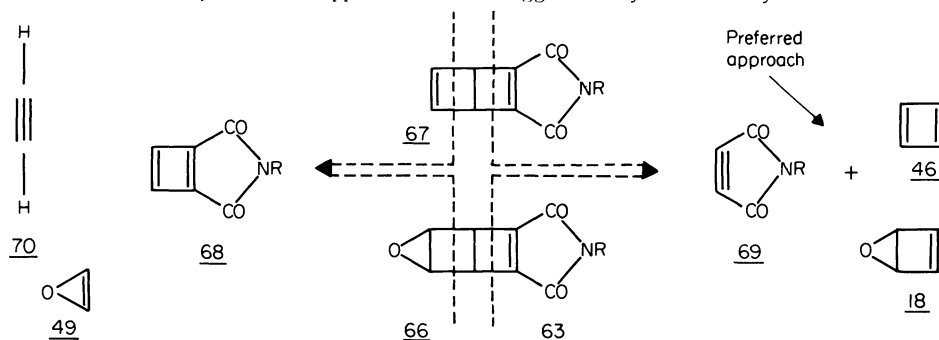
Having agreed on the structure of the target molecule as (61) we subjected it to partial retrosynthetic analysis as shown in Scheme 16. It was obvious that highly reactive intermediates such as the Dewar benzene (67) and the related epoxide (66), would need to be involved in its synthesis and some preliminary work was required to establish the viability of such an approach.

Scheme 16



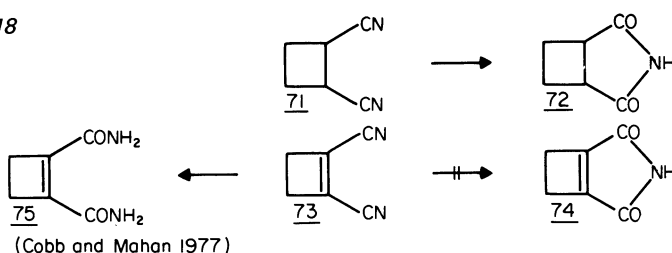
A second requirement became apparent in the retrosynthesis of Dewar benzene (67) (Scheme 17). This was the need to develop a synthetic equivalent of didehydromaleimide (69) for reaction with cyclobutadiene in the "preferred approach" mode suggested by this analysis.

Scheme 17



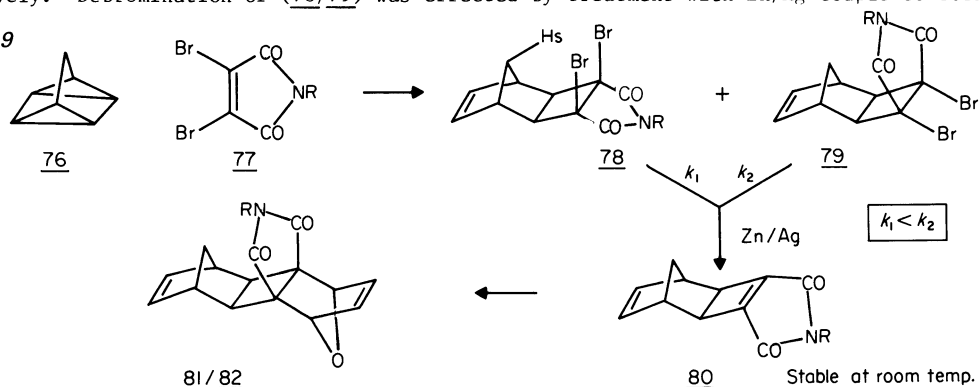
A particular concern relating to the synthesis of Dewar benzene (67) was raised in some work reported by Cobb and Mahan who stated that cyclobutanomaleimides related to (74) (see Scheme 18) "were too unstable for normal existence" (ref. 27). Their evidence was based on the hydrolysis study of nitriles (71) and (73), where the inclusion of the π -bond in (73) no longer led to a cyclic product. This proposal challenged the idea of using an intermediate Dewar benzene (67) or the related oxide (66) which each contained a cyclobutanomaleimide moiety.

Scheme 18



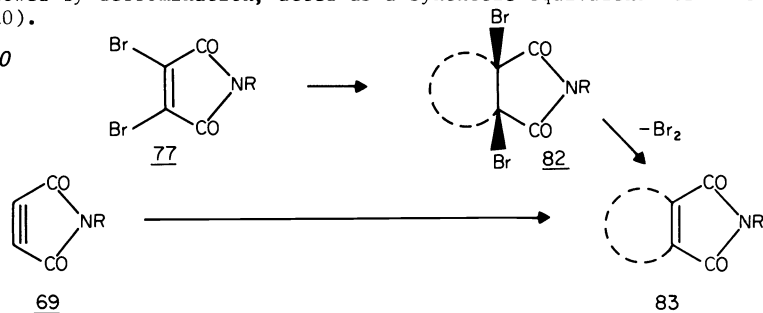
3.2.1 Preparation of first stable cyclobutanomaleimide. In the event, each of these factors could be evaluated at the same time. Thus reaction of *N*-methyl 3,4-dibromomaleimide (77) with quadricyclane (76) (Scheme 19) yielded a 4:1 mixture of adducts (78) and (79) respectively. Debromination of (78/79) was effected by treatment with Zn/Ag couple to form

Scheme 19



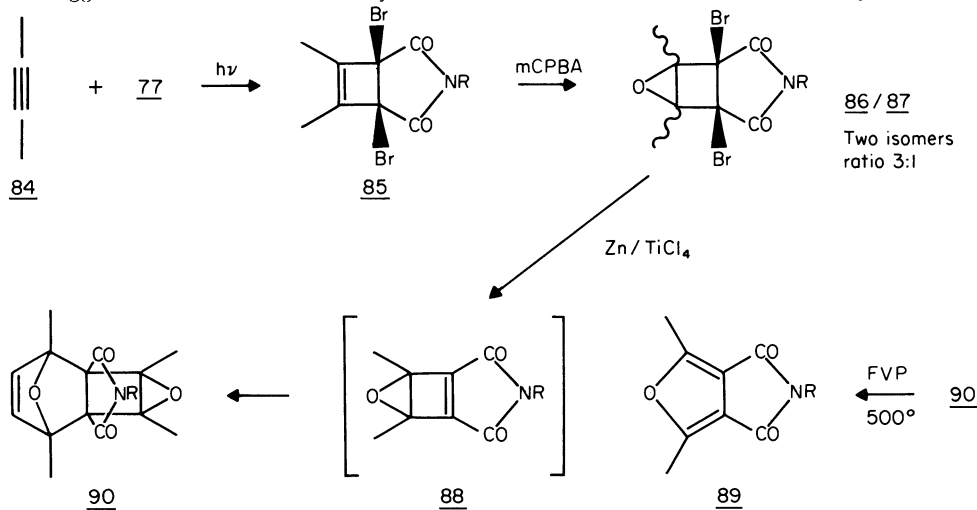
cyclobutanomaleimide (80). This was sufficiently stable at room temperature to be isolated, but its high reactivity required that it be characterised in adduct form, e.g. furan produced (81/82). Clearly cyclobutanomaleimides could be produced and the cycloaddition of (77) followed by debromination, acted as a synthetic equivalent for didehydromaleimide (69) (Scheme 20).

Scheme 20



3.2.2 Diversion: synthesis of the novel Dewar furan (88). Having gained the necessary information to allow us to proceed with our synthesis of the Dewar furan photosubstrate (61) we did not travel that path immediately. This decision was made in view of the above results which suggested a more direct entry into substituted Dewar furans. As only a single

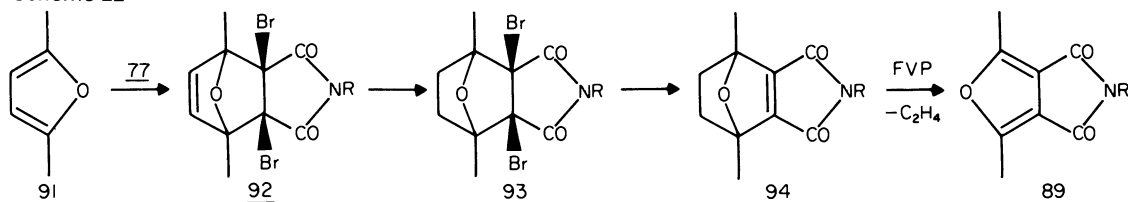
Scheme 21



Dewar furan, namely (32), had been reported at that time, we considered that the information so gleaned could be useful for our major study.

The reaction sequence, shown in Scheme 21 (ref. 28), proved to be straightforward and involved initial photocycloaddition of but-2-yne (84) onto the dibromomaleimide (77) to yield the cyclobutene (85). Epoxidation with mCPBA yielded a 3:1 mixture of the dibromo epoxides (86) and (87). Debromination of these compounds was difficult and required treatment with the more powerful Zn/TiCl₄ reagent. The Dewar furan (88) was too reactive to detect and was characterised by trapping with furan which produced a mixture of adducts (90) in moderate yield. Attempts to generate the Dewar furan by FVP of (90) were also unsuccessful and the isolated product was the related succinimidofuran (89). The structure of (89) was confirmed by separate synthesis as outlined in Scheme 22 (ref. 29).

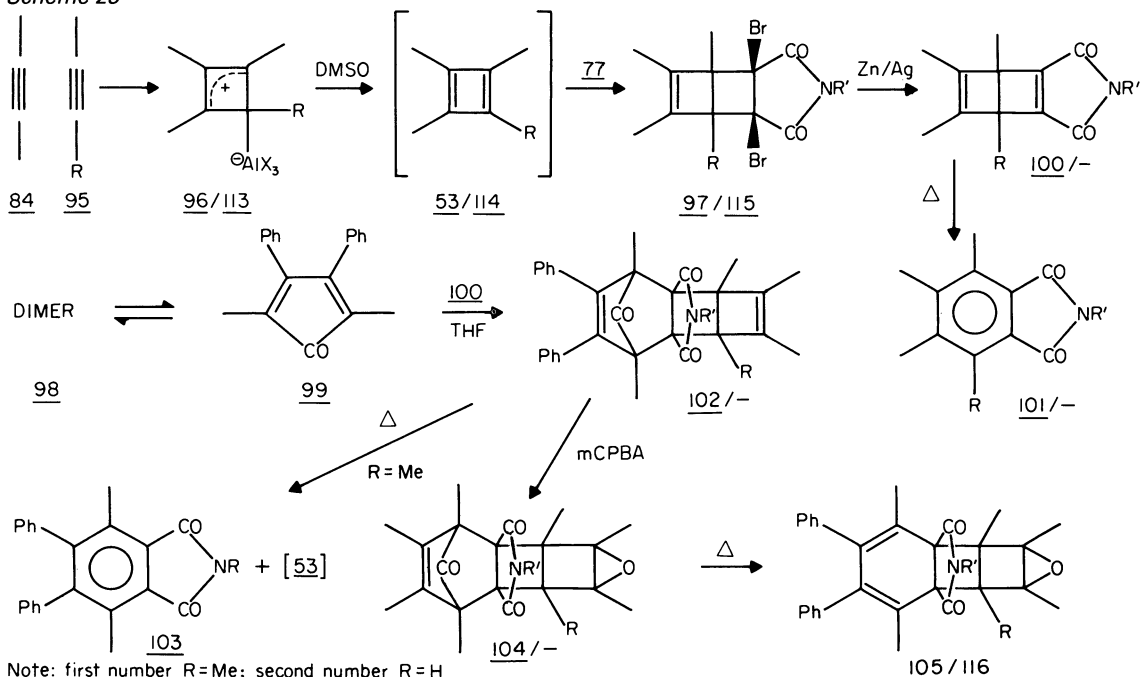
Scheme 22



3.3 Synthesis of the methyl substituted Dewar furan precursors

In the tetramethyl series the reaction commenced with tetramethyl cyclobutadiene (53) produced from the crystalline salt (96) by treatment with DMSO according to van Bekkum's method (Scheme 23) (ref. 30). Trapping of (53) *in situ* with *N*-methyl 3,4-dibromomaleimide (77) yielded adduct (97) in excellent yield. Debromination of (97) to form the Dewar benzene intermediate (100) was effected by treatment with Zn/Ag couple (ref. 31). The conditions for this debromination were critical: the mild granular form of Zn/Ag couple was employed and this was added batchwise in THF at reflux. The Dewar benzene so formed was trapped *in situ* by the dienone (99), and in the time interval between additions more dienone (99) was formed from its dimer (98). Following this method a high yield of the site selective adduct (102) could be obtained. The Dewar benzene (100) was sufficiently stable to be isolated ($t_{1/2} = 44$ min at 30°C) and for this purpose was produced from (97) by reaction with the more efficient debrominating agent, Zn/Ag powder.

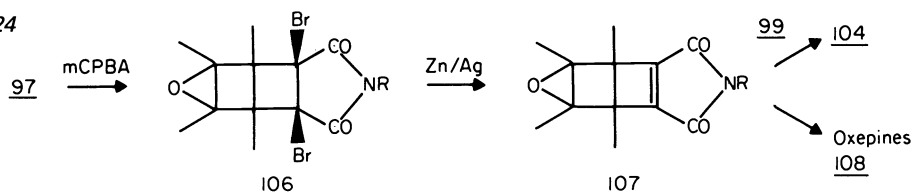
Scheme 23



Note: first number R=Me; second number R=H

Subsequent site selective oxidation of (102) with mCPBA formed the epoxide (104). An alternative route to (104) was to introduce the epoxide ring at an earlier stage, by reaction of the cyclobutene (97) with mCPBA (see Scheme 24). Treatment of the resultant epoxide (106) with Zn/Ag couple yielded the Dewar benzene epoxide (107) ($t_{1/2} = 77$ min/30°C). Repetition of this reaction in the presence of the dienone (99), as above, formed an adduct identical with (104). In this case significant ring opening of the intermediate Dewar benzene epoxide (107) occurred to form a mixture of oxepines (108) and related products (ref. 32). This method is only used for preparation of the parent substrate (see later).

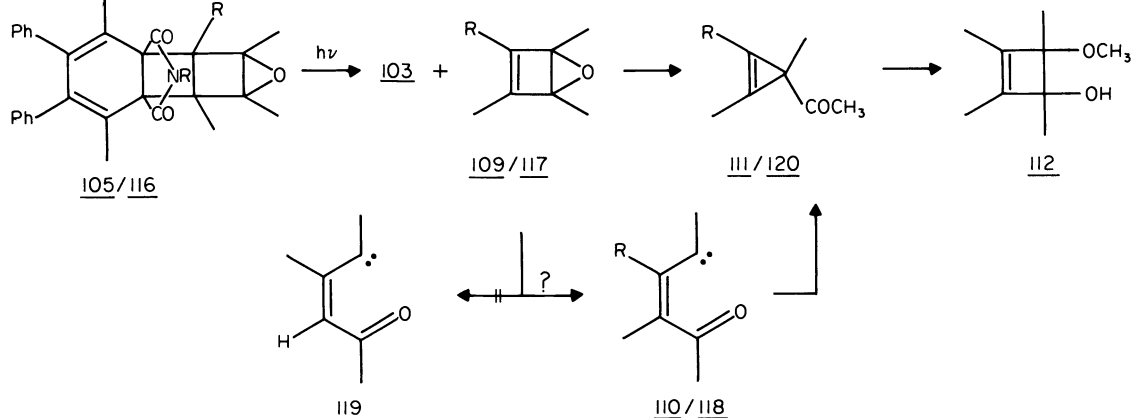
Scheme 24



Thermal decarbonylation of adduct (104) (Scheme 23) yielded the required diene (105) in excellent yield (ref. 33). In contrast, attempts to thermally decarbonylate the related cyclobutene (102) led immediately to fragmentation of the first formed cyclohexadiene and formation of the aromatic phthalimide (103), together with the transient tetramethylcyclobutadiene (53).

3.3.1 Photochemical breakdown of propellane (105). Irradiation of propellane (105) was effected in acetone solution using a low pressure Hg lamp (254 nm). Rapid reaction occurred to produce the phthalimide (103) together with a $C_4(Me)_4O$ fragment (see Scheme 25). ^{13}C nmr spectroscopy showed the presence of a carbonyl group and this ruled out the Dewar furan structure (109) for this new product. The C_s symmetry of its nmr spectra and comparison of chemical shift data with that of model compounds (ref. 34) allowed the cyclopropenyl methyl ketone structure (111) to be assigned to it. Cyclopropenyl ketone (111) is considered to be formed by rearrangement of the preformed tetramethyl Dewar furan (109), possibly via the carbene intermediate (110). In an attempt to confirm the presence of the carbene (110), the photolysis of (105) was carried out in methanol solution. A new product (112) was isolated but it was shown subsequently to be formed from reaction of methanol with cyclopropenyl ketone (111); the latter was a coproduct when irradiation of (105) was conducted at low temperature. No carbene derived products were obtained by irradiation of (105) in the presence of olefin containing solvents, and so the presence of carbene (110) remains unconfirmed.

Scheme 25



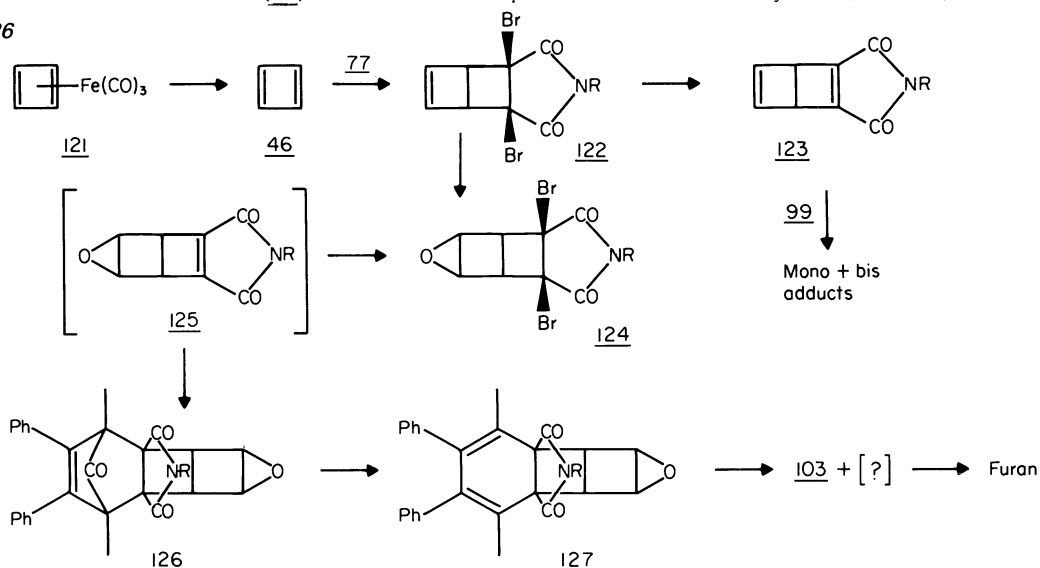
The trimethyl Dewar furan precursor (116) was prepared in a similar way (the second set of numbers in Scheme 23 apply to the trimethyl series) (ref. 33). In this case the trimethyl cyclobutenyl cation (113) was prepared by $AlBr_3$ induced condensation of but-2-yne with propyne (ref. 35). This salt (113) served as the precursor to trimethyl cyclobutadiene (114). No previous use of (114) in cycloadditions had been reported and so it was of interest to note that complete site selectivity to form (115) occurs in its reaction with dibromo maleimide (77). The remaining steps to the photosubstrate (116) were analogous to those discussed for the tetramethyl compound (see Scheme 23). Irradiation of (116) (Scheme 25; second set of numbers apply) proceeded smoothly to produce phthalimide (103) and the cyclopropenyl ketone (120), again presumed to arise by rearrangement of preformed Dewar furan (117). That only a single cyclopropene was formed is indicative of the selectivity in the bond breaking occurring in (117), and this is discussed later.

3.4 The parent Dewar furan

The propellane (127) required as the photosubstrate for the production of the parent Dewar furan was prepared as outlined in Scheme 26. Thus cycloaddition of cyclobutadiene, generated by Ce^{4+} oxidation of the iron carbonyl complex (121) (ref. 36) onto the dibromomaleimide (77) was readily achieved and the resultant adduct (122) converted to the epoxide (124) by treatment with mCPBA. Conversion to the transient Dewar benzene oxide (125) was again achieved by reaction with the Zn/Ag couple in THF and trapped in the usual way with cyclopentadienone (99) to form adduct (126). Thermal decarbonylation of (126) occurred cleanly to produce the desired propellane (127) in fine yield. This route to (127) is preferred to one involving the trapping of the Dewar benzene (123), since a mixture of mono and bisadducts is formed upon reaction with dienone (99).

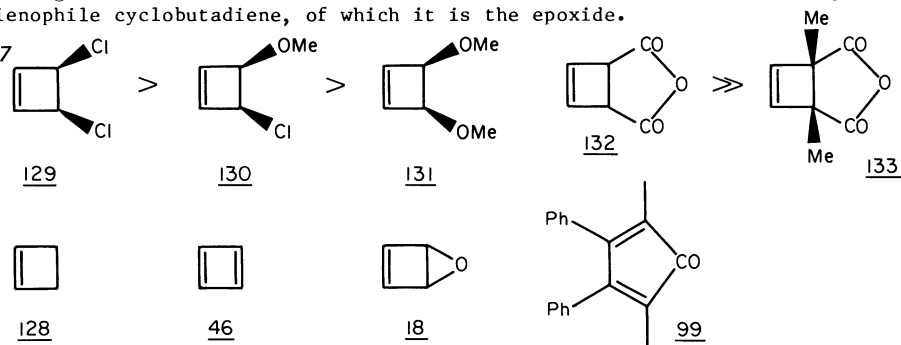
Irradiation of propellane (127) was again efficient and quantitative breakdown was achieved after brief irradiation. The surprising fact, however, was the absence of any significant product other than the phthalimide (103). Irradiations of (127) were conducted in various solvents and at temperatures down to -80° and monitored by pmr spectroscopy. The only small fragment identified was furan (15) which formed in poor and inconsistent yield (max 15%).

Scheme 26



Attempts to trap transient intermediates from this irradiation proved to be difficult even when conducted in the presence of d_2 -furan (used successfully by Strausz to capture Dewar thiophen) (ref. 8) or 1,3-diphenylisobenzofuran (used to trap 2-cyano 3-methyl-Dewar thiophen (ref. 37)). A question which caused some uncertainty related to the potential dienophilicity of Dewar furan. How would the epoxide ring affect the proximate π -system? Cyclobutene (128) and its β -substituted derivatives are known to be moderately reactive dienophiles but to be affected by orbital interactions, electronic effects and steric factors. A decrease in dienophilicity, as judged by reaction with dienone (99), occurred with increasing oxygen substitution at the β -position, e.g. (129) > (130) > (131) (see Scheme 27) being a key observation; the steric contribution being illustrated well by the marked decrease in reactivity of (133) over (132) (ref. 38). On the other hand the presence of the epoxide ring was expected to increase the dienophilicity of the π -bond owing to the increased ring strain introduced into the Dewar furan and also its relationship with the active dienophile cyclobutadiene, of which it is the epoxide.

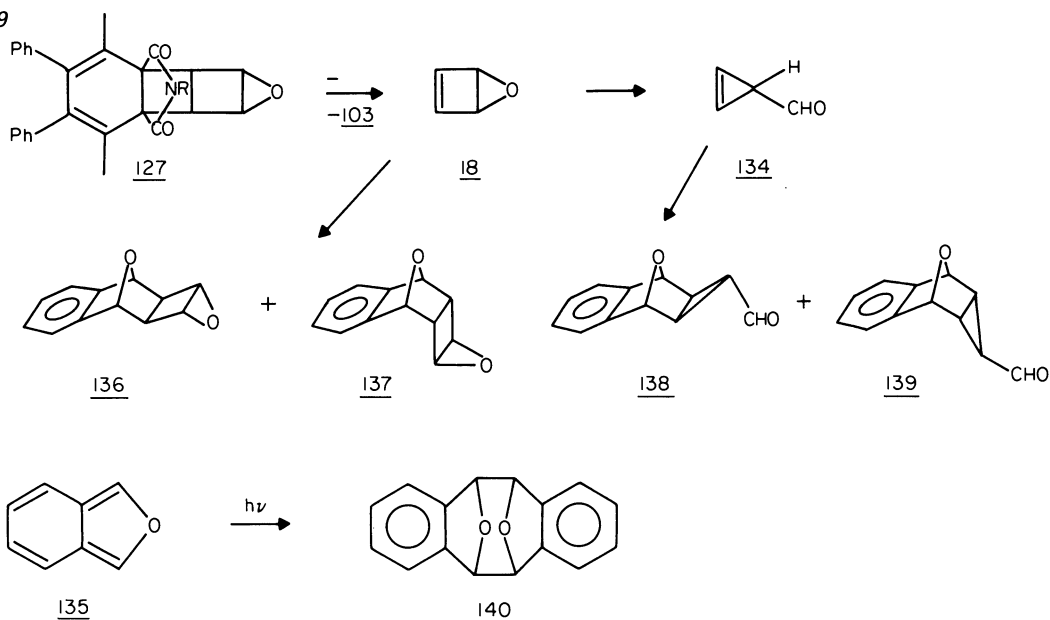
Scheme 27



The question remained: what could be used as a suitable trapping agent? The trap had to satisfy certain criteria (a) it had to be stable under the irradiation conditions, (b) it must not quench the 1,2-photoaromatisation reaction, (c) it must be an active diene in Diels-Alder reactions.

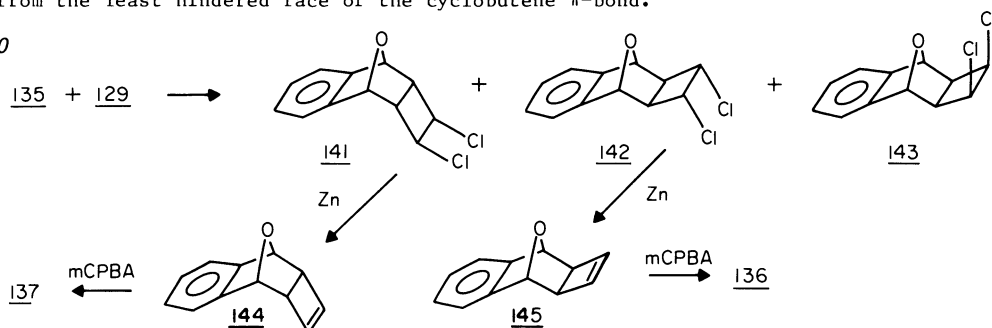
3.4.1 Trapping of Dewar furan (18) with isobenzofuran. On the principle that it "takes a thief to catch a thief" we set up an experiment using the highly reactive isobenzofuran (IBF)(135)(ref. 39) as trap. Thus irradiation of (105) in THF containing excess isobenzofuran gave rise to a mixture of four C_4H_4O /IBF cycloadducts together with phthalimide (103) and the isobenzofuran dimer (140) (Scheme 29). The C_s -symmetry of the nmr spectra and the presence of a carbonyl group supported that the adducts were derived from cyclopropene aldehyde (134) and were a mixture of *endo*- and *exo*-isomers (138/139). The structures were confirmed by separate reaction of cyclopropene aldehyde with isobenzofuran. The other two IBF adducts also had C_2 -symmetry yet contained no carbonyl group, which is consistent with the Dewar furan/IBF adducts (137) and (138). Again an *endo/exo* relationship was deduced from the pmr spectral data. The structures were confirmed by separate synthesis as outlined in Scheme 30. Thus reaction of IBF (135) with *cis*-3,4-dichlorocyclobutene (129) produced a mixture of three 1:1 adducts (141)-(143). Spectral data, especially LIS spectroscopy, allowed stereochemical assignments to be made. Dechlorination (Zn/EtOH) formed the related cyclobutene, *endo*-isomer (144) from (141) and *exo*-isomer (145) from

Scheme 29



(**142**), which yielded the corresponding epoxides (**137**) and (**136**) respectively, on treatment with mCPBA. The structural assignments for these epoxides is made on the basis that mCPBA attacks from the least hindered face of the cyclobutene π -bond.

Scheme 30



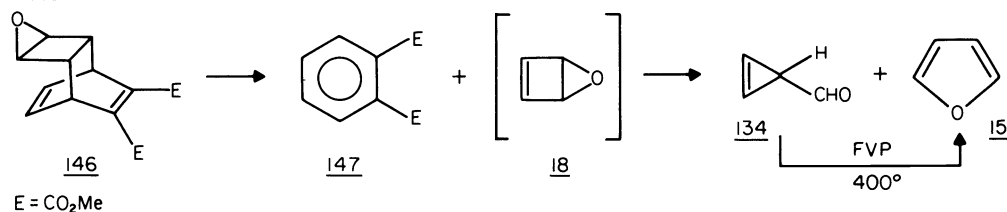
Significantly the proportion of IBF Dewar furan adducts (**136/137**) was increased while that for the cyclopropene aldehyde adducts (**138/139**) was decreased as the temperature of the photolysis was lowered (see Table 1). The increased lifetime of Dewar furan (**18**) at lower temperature, as reflected in the increased formation of adducts (**136/137**), indicates that (**18**) is the primary photoproduct. The cyclopropene aldehyde (**134**) is derived from (**18**) under the reaction conditions and that this still occurs at -65° is a clear indication that the activation energy for the transformation of (**18**) into (**134**) is indeed low.

Table 1

Photolysis temperature	(136) %	(137) %	(138) %	(139) %
-5°	10	5	65	20
-25°	20	15	50	15
-45°	35	20	35	10
-65°	45	30	20	5

A question which remained unanswered in this study was the origin of furan in the direct irradiation of (**127**). Was furan derived from cyclopropene aldehyde (**134**) or from Dewar furan (**18**) itself? Certainly furan was absent from the irradiation experiments when components (**134**) and (**18**) were removed by trapping with IBF.

Scheme 31

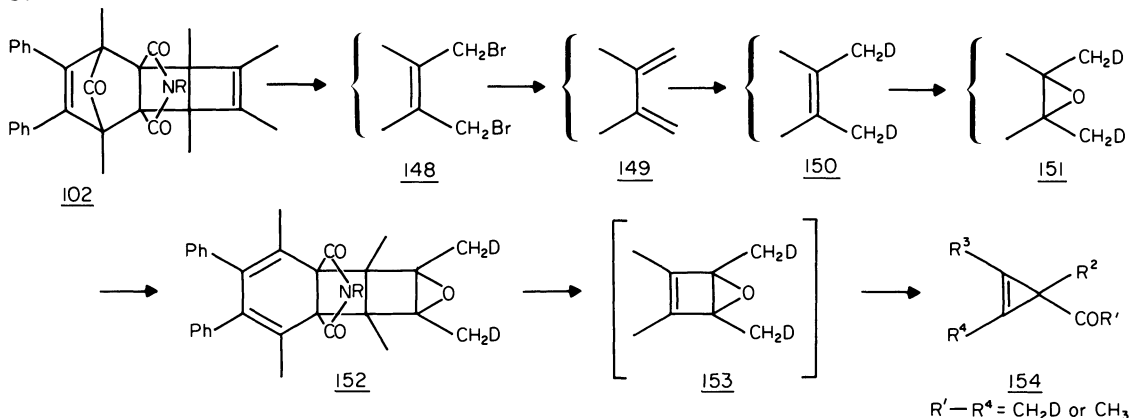


In helping to decide this question we prepared cyclopropene aldehyde (134) separately by pyrolysis of (146) (ref. 40), see Scheme 31, and subjected it to the irradiation conditions. No formation of furan was observed although the aldehyde (134) was rapidly destroyed. This accounts for the absence of this aldehyde in the initial irradiation experiments but the exact source of furan remains undetermined (tentatively assigned to inefficient photorearrangement of Dewar furan).

4 MECHANISTIC STUDIES

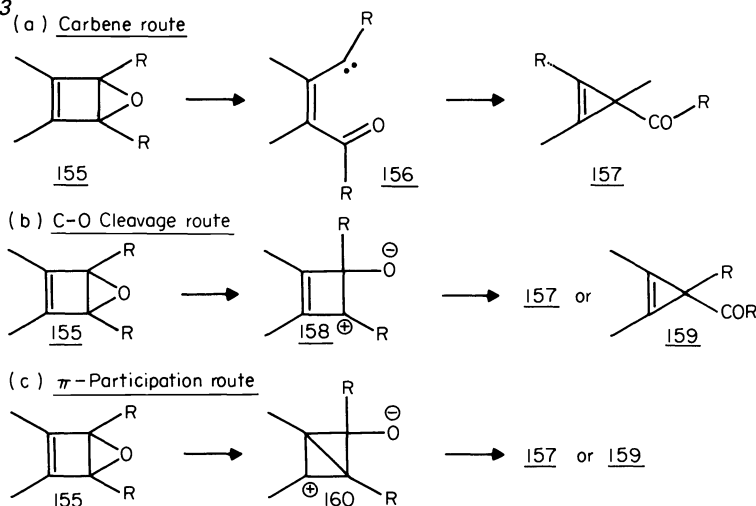
In order to study the mechanism of the rearrangement of Dewar furans into cyclopropenes in more detail, the symmetrically labelled Dewar furan (153) was investigated. The photosubstrate (152) used to generate this Dewar furan was synthesised from the related tetramethyl Dewar furan precursor (102) as outlined in Scheme 32. The resultant cyclopropenyl ketone (154) was isolated and the distribution of the deuterated methyl groups

Scheme 32



evaluated by pmr spectroscopy. The results, presented in Table 2, compare the experimental values with the theoretical values calculated for the three mechanistic pathways outlined in Scheme 33. This type of labelling does not allow a clear distinction to be made between the

Scheme 33



C-O bond cleavage and the π -participation routes, but it does separate them from the carbene route. Indeed the experimental results support a mechanism other than the carbene route being operational in this rearrangement.

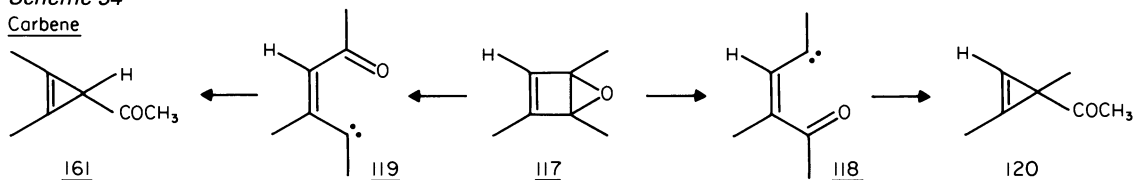
Table 2

Mechanism	Product	Proton ratio (0.96D/CH ₃)	
		Allylic : acetyl	Aliphatic : acetyl
Carbene	(176)	2.47	1.47
C-O cleavage π -participation	(176)/(178)	2.70	1.24
Experimental values		2.9 ± 0.3	1.25 ± 0.15

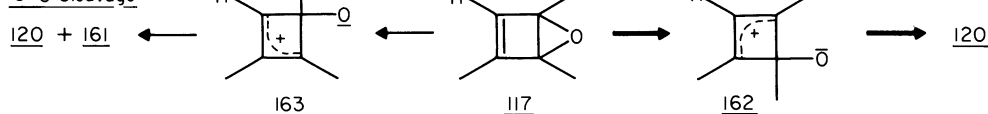
Fortunately the selectivity noted in the rearrangement of the trimethyl Dewar furan (117) to the cyclopropenyl ketone (120) held additional information on the nature of the rearrangement. Thus analysis of the three reaction pathways in this less symmetrical Dewar furan (see Scheme 34) clearly distinguishes between the C-O bond cleavage and π -participation routes. This distinction rests on accepting a zwitterionic intermediate and comparing the stability of the alternative zwitterionic species. In each case, the stability of the carbonium ion moiety offers a clear preference: (162) over (163) in the cyclobutenyl series, and (165) over (164) in the bicyclobutanyl series. As intermediate (162) leads exclusively to the observed cyclopropenyl ketone (120), the C-O bond cleavage route appears to be the favoured process.

Scheme 34

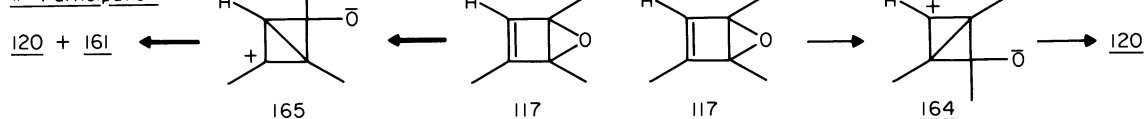
Carbene



C-O Cleavage



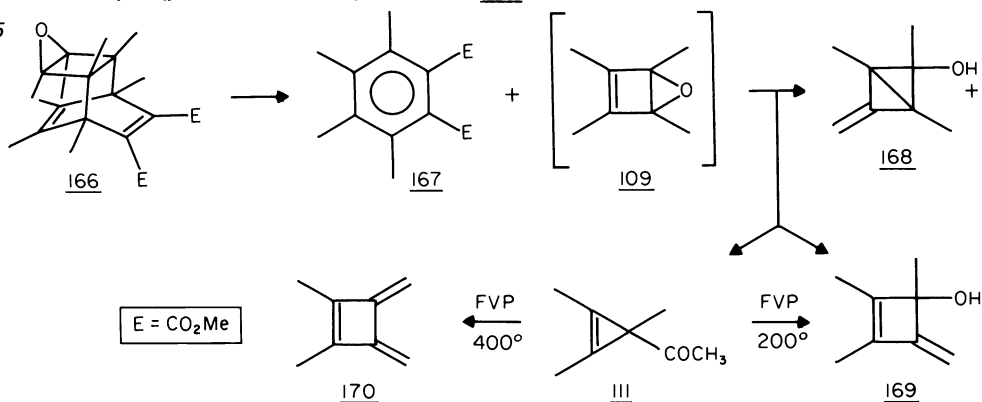
π -Participation



4.1 Flash vacuum pyrolysis studies

Further information was gleaned from flash vacuum pyrolysis (FVP) studies on a series of formal Diels-Alder adducts of Dewar furans. The most significant result was obtained by FVP of the tricyclic epoxide (166) available by epoxidation of the related olefin (ref. 41) (Scheme 35). In this case cyclopropene (111) and two other olefinic products (168) and (169) were obtained, together with the phthalate (167).

Scheme 35



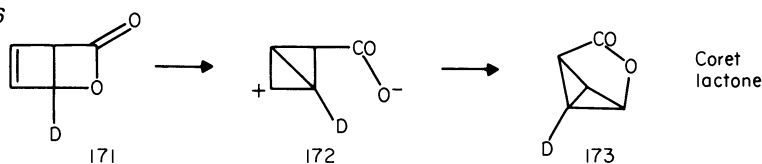
Separate FVP of cyclopropenyl ketone (111) was shown to produce the methylene cyclobutenol (169) at 280°; at 400° the bismethylene cyclobutene (170) was formed. No evidence for the production of either tetramethyl furan or the bicyclobutane (168) was found.

Formation of the bicyclobutane (168) offers firm support for a bicyclic zwitterion of type (160). In addition, the co-formation of the methylene cyclobutenol (169) has significance since it is derived from the isomeric cyclobutenyl zwitterionic species of type (158). As the above reactions occur in the gas phase, whereas the specificity noted in the rearrangement of trimethyl Dewar furan occurs in solution we have some difficulty in comparing this evidence directly. The following information from the literature was used to help us reach our mechanistic conclusion (see 4.2.3).

4.2 Mechanism of Dewar furan rearrangement

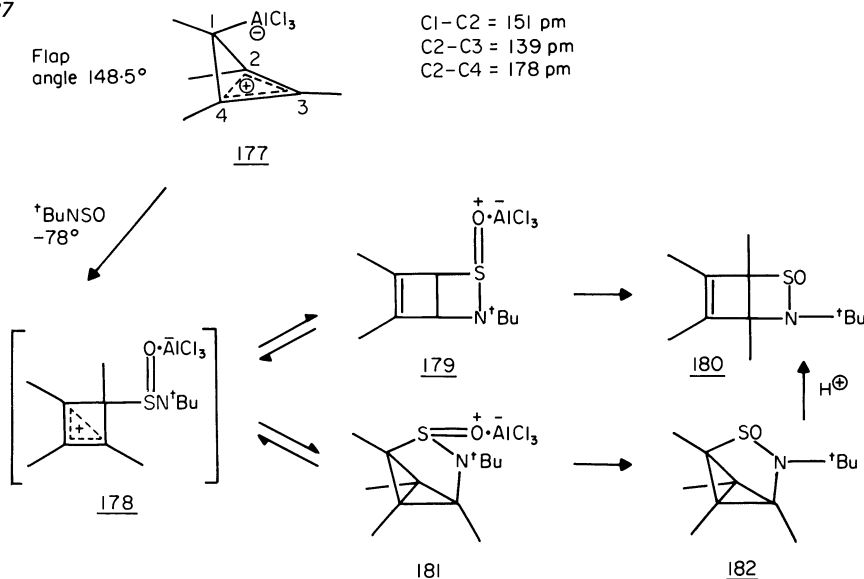
4.2.1 Literature analogues. An example which supports the π -participation route is available from the work of Corey and Pirkle (Scheme 36) (ref. 42). They found that Dewar α -pyrone (171) readily rearranged thermally to a tricyclic lactone (173). Using deuterium labelling they were able to find support for the bicyclic intermediate (172). This zwitterionic species (172) is very similar to that, e.g. (160), proposed in Scheme 33. Each is formed by C-O bond cleavage of a heterocyclic ring fused to a cyclobutene.

Scheme 36



Another relevant study is the work of Hogeveen and his coworkers (Scheme 37) (ref. 43). They report treating the aluminium chloride complex (177) with *N*-tertiarybutylsulfanylamine at low temperature and detecting a pair of equilibrating complexes (179) and (181), which can be converted to a mixture of isomeric heterocyclic compounds (180) and (182). These heterocyclic compounds are related in structure to their progenitor aluminium chloride complexes, which themselves are interrelated by a third complex (178).

Scheme 37

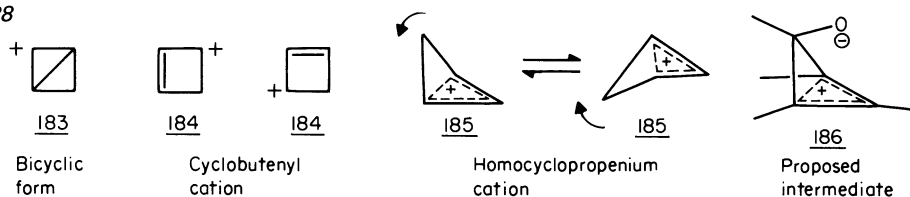


Some information regarding the nature of the common intermediate (178) proposed by these workers is offered by an X-ray structure determination of their starting aluminium chloride complex (177) (ref. 44). This structure is clearly non planar (flap angle 148.5°), yet the C2-C4 bond length of 178 pm does not support full bonding between these positions. Should a similar structure be acceptable for (178), and later for (186), then collapse to either the bicyclobutyl system or cyclobutenyl system is readily appreciated. Thus (178) yields (181) by bond formation across the C2-C4 positions favoured by reduction in the flap angle; increasing the flap angle causes separation of C2 and C4 and yields the cyclobutenyl species (179).

4.2.2 The homocyclopropenium cation. The structure of the homocyclopropenium cation is relevant to the present investigation yet it remains an unresolved problem.

Olah and coworkers (ref. 45) have studied this topic and unite the planar bicyclobutyl cation form (183) and the cyclobutenyl cation (resonance hybrids 184a,b) via a homocyclopropenium cation (185) (Scheme 38). On the basis of ¹H nmr spectroscopy in super acid solution they proposed that this species is an equilibrating one comprising of the two ring inverted isomers (185a) and (185b). The activation energy of this interconversion was determined to be only 8.4 Kcal/mol.

Scheme 38



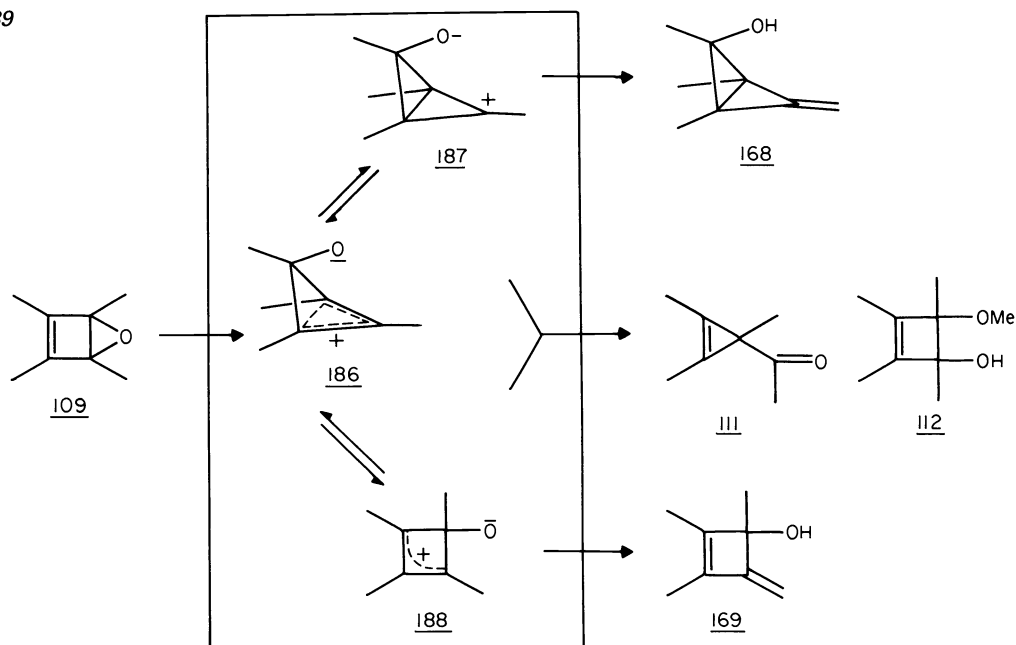
Theoreticians continue to differ on the question of whether (185) is homoaromatic. Haddon has recently summarised the various molecular orbital calculations reported for this species and the planar cyclobutenyl cation (184), which is the presumed transition state for ring-inversion of (185). The experimentally determined structure and homoaromatisation energy

are successfully reproduced by semi-empirical treatments [MINDO 2 (ref. 46), MINDO 3 (ref. 47)] while *ab initio* calculations [STO-2G (ref. 48), STO-3G (ref. 49)] tend towards a planar cyclobutenyl structure with very little barrier to ring inversion. However, the most recent *ab initio* calculations (ref. 50), 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 (ref. 51) take an opposing view, claiming that the 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.

4.2.3 Mechanistic Proposal: a working hypothesis. It is now clear that our earlier division of the mechanism into discrete intermediates may have been an oversimplification. Notwithstanding we can offer a working hypothesis for the rearrangement of tetramethyl Dewar furan (109). This is outlined in Scheme 39 where we propose that the first step is the formation of the bicyclobutyl species (187). In the gas phase, this is interrelated with the homocyclopropenium species (186) and thereby with (188): the bicyclic olefin (168) being derived from (187), the methylene cyclobutene (169) from (188). The cyclopropene (111) is related to the system but it may be derived from either (187) or (188). In solution the relative lifetimes of (187) and (188) may well change, and so explain the exclusive formation of (111).

A similar scheme may be appropriate for trimethyl Dewar furan, in which case an intermediacy like (188) is favoured, however no corresponding gas phase study has yet been performed. The parent Dewar furan question is fully open and must await labelling studies. The key to these rearrangements is held in the nature of the intermediates related to (186)-(188) which appear in the boxed area of Scheme 41. As such intermediates can be accessed by both gas phase and solution techniques we are hopeful of further developments in this area.

Scheme 39



5 ACKNOWLEDGEMENTS

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