SOME ASPECTS OF THE CHEMISTRY OF CYCLOOCTATETRAENE AND ITS DERIVATIVES

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SUMMARY

This thesis is divided into four chapters.

Chapter 1 deals with the syntheses and cycloaddition reactions (in general, with tetracyanoethylene and N-phenyltriazolinedione) of the following olefins: 7-methylenecycloocta-1,3,5-triene; 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene; 7-isopropylidenecycloocta-1,3,5-triene; (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-trienes; (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)cycloocta-1,3,5-trienes; (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-trienes; 7-benzhydrylidenecycloocta-1,3,5-triene; 7-dicyanomethylenecycloocta-1,3,5-triene. In all but two cases (7-dicyanomethylenecycloocta-1,3,5-triene, which did not undergo cycloaddition, and 7-benhydrylidenecycloocta-1,3,5-triene), the olefins produce $\pi 8 + \pi 2$ adducts; details of the cycloaddition mechanism are presented. In addition to $\pi 8 + \pi 2$ adducts, the 7-arylidenecycloocta-1,3,5-trienes form (*E*)- "3,6" adducts. A mechanism for this mode of addition is proposed and the origin of the observed stereospecificity is discussed.

The addition of bromine to 7-methylenecycloocta-1,3,5-triene is examined.

In Chapter 2, the cycloaddition reactions (with tetracyanoethylene, N-phenyltriazolinedione and maleic anhydride)

of isopropenyl- and vinylcyclooctatetraenes with one and more than one equivalent of dienophile are investigated.

As a route to bicyclo[6,5,0]trideca-2,4,6,8(9)-tetraene, the solvolysis of 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (in 1,1,1,3,3,3-hexafluoropropan-2-ol) is discussed in Chapter 3; the desired bicyclic tetraene was not isolated, however.

The final Chapter describes unsuccessful attempts to prepare dichloroketene adducts of cyclooctatetraene and some of its derivatives.

STATEMENT

This thesis contains no material previously submitted for a degree or diploma in any University, and to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference is made in the text.

P.K. Kirkbride

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I would like to express my sincere gratitude to my parents who, during my years at university, have provided warmth, encouragement and support. Finally, Julie Gardner has been an untiring source of affection and patient reassurance and to her I extend my warmest thanks.

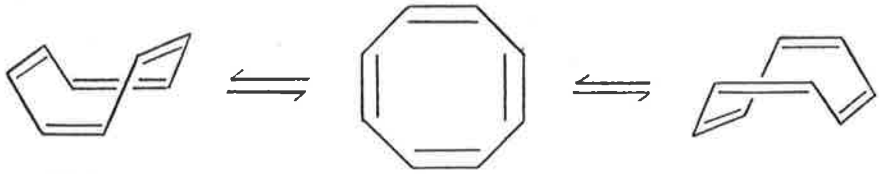
CHAPTER 1

THE SYNTHESES AND CYCLOADDITION REACTIONS OF 7-ALKYLIDENE- AND 7-ARYLIDENECYCLOOCTA-1,3,5-TRIENES

1.1 INTRODUCTION

Although cyclooctatetraene was first prepared in 1911,[1] growth in the knowledge of its chemistry only became rapid after 1948 when this intriguing olefin became available in large quantities.[2] Such has been the progress since 1965 that three major reviews[3,4,5] and two books[6,7] dealing with the chemistry of cyclooctatetraene and its derivatives have been published.

An important point to emerge has been the unusual reactions cyclooctatetraene and its derivatives enter into as a consequence of being non-planar annulenes containing eight π electrons. One of the most interesting attributes of these olefins is their ability to enter into cycloaddition reactions and the manners in which they do so. Cyclooctatetraene (1), which is "tub" shaped,[8] is able to undergo three fundamental structural changes, namely ring inversion (Equation 1), valence tautomerization (Equation 2) and bond shifting (Equation 3). The barrier to ring inversion and the extent of valence tautomerization are important factors controlling the outcome of cycloaddition reactions because the tub shaped cyclooctatetraene molecule cannot enter

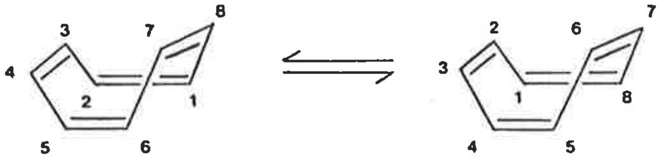


(1)

EQUATION 1

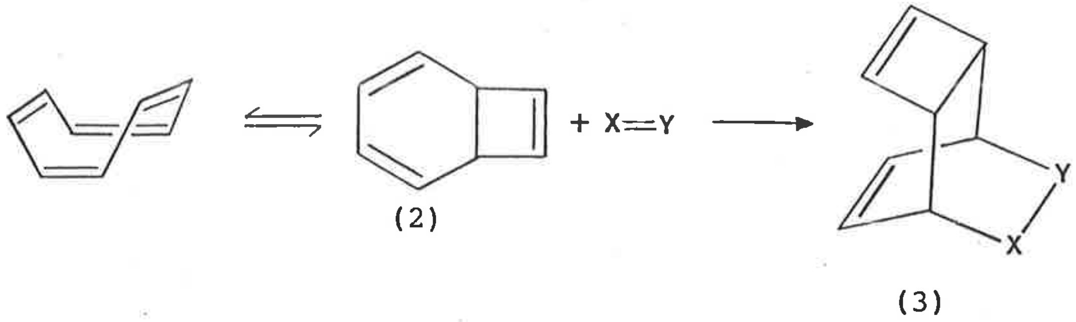
(2)

EQUATION 2



EQUATION 3

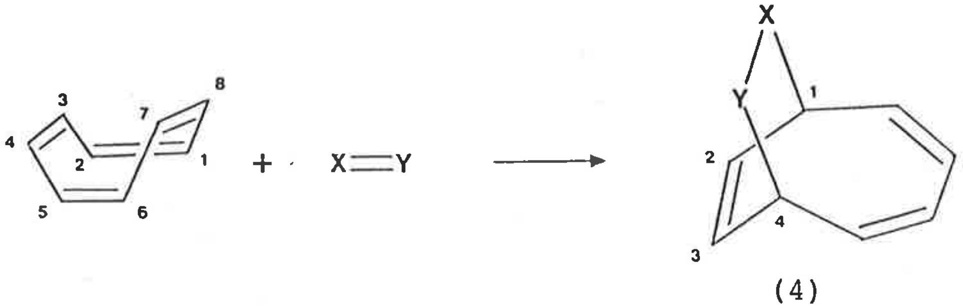
directly into concerted cycloadditions. Instead, the bicyclic valence tautomer (2) of cyclooctatetraene, which is present in rapid[9] equilibrium with cyclooctatetraene to the extent of 0.01% at 100°C,[9] acts as a 4π electron donor and tricyclic adducts (3) are formed with a wide variety of dienophiles (Scheme 1).[10] Most adducts of cyclooctatetraene and its derivatives which have been reported are Diels-Alder adducts of this type and they are usually prepared by



SCHEME 1

treating cyclooctatetraene with the dienophile at a temperature which is high enough to provide a serviceable concentration of (2).[10]

In addition, there are other cycloaddition reactions between cyclooctatetraene and certain 2π electron donors which proceed along multi-step reaction pathways and lead to the formation of 1,4* adducts (4) (Scheme 2).[11,12,13,14]



SCHEME 2

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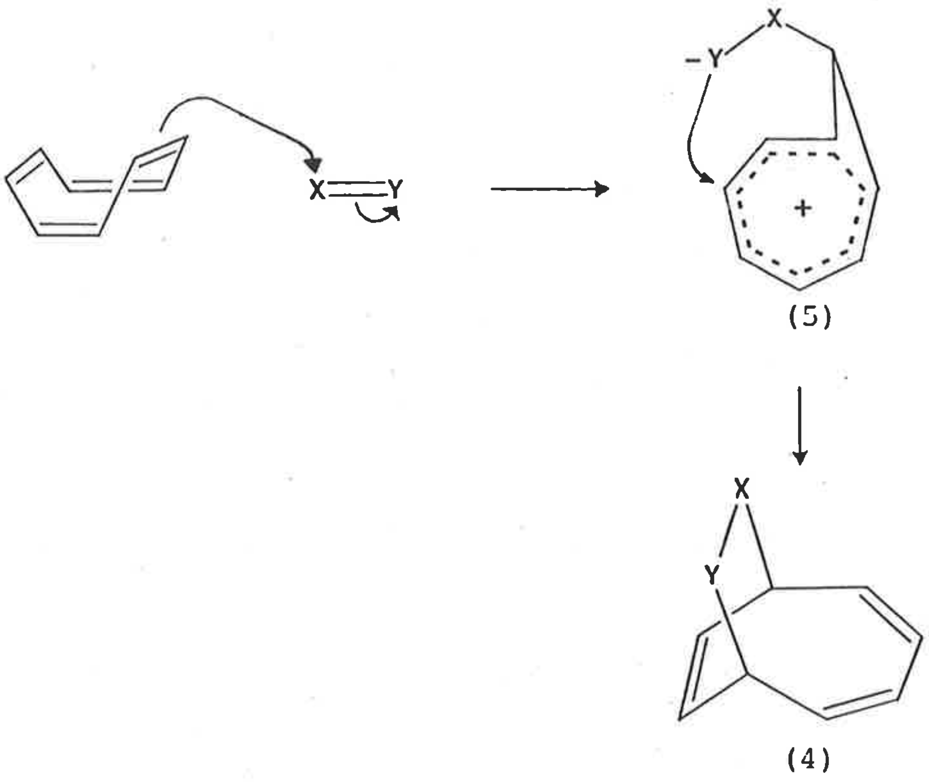
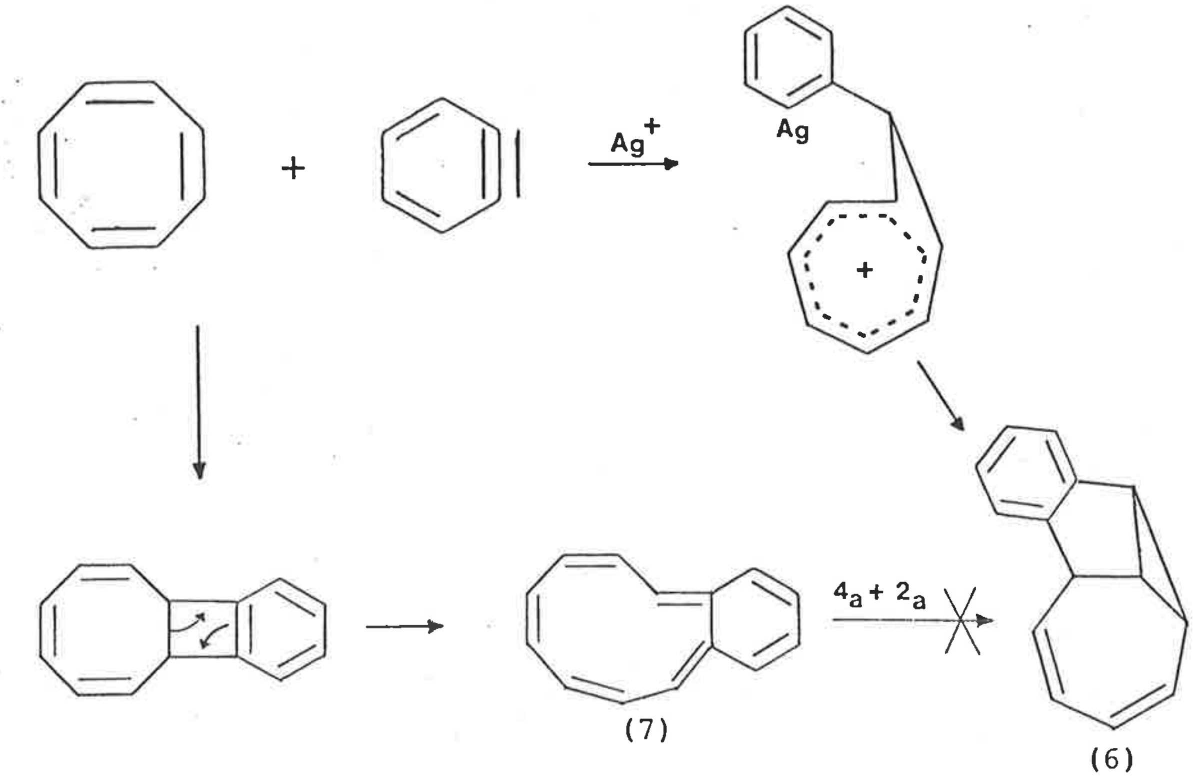
* The 1,4 terminology is used to describe adducts which are formed when a 2π donor forms bonds with carbon atoms 1 and 4 of cyclooctatetraene.

Early investigators,[15] and in particular Huisgen and his co-workers,[16,24] suggested that these 1,4 adducts were the result of two-step reactions which involved electrophilic attack on cyclooctatetraene, formation of a zwitterion (5) and then charge annihilation (Scheme 3). The cationic portion of this zwitterion, they argued, was a homotropylium cation which is known to be a stable, aromatic species.[17,18] Cycloaddition reactions which proceed through a dipolar intermediate usually show a marked rate dependence upon solvent polarity and it is unfortunate that these early workers failed to report upon this aspect of the 1,4 cycloadditions to cyclooctatetraene. In addition, under conditions which allow 1,4 cycloaddition, no other adducts



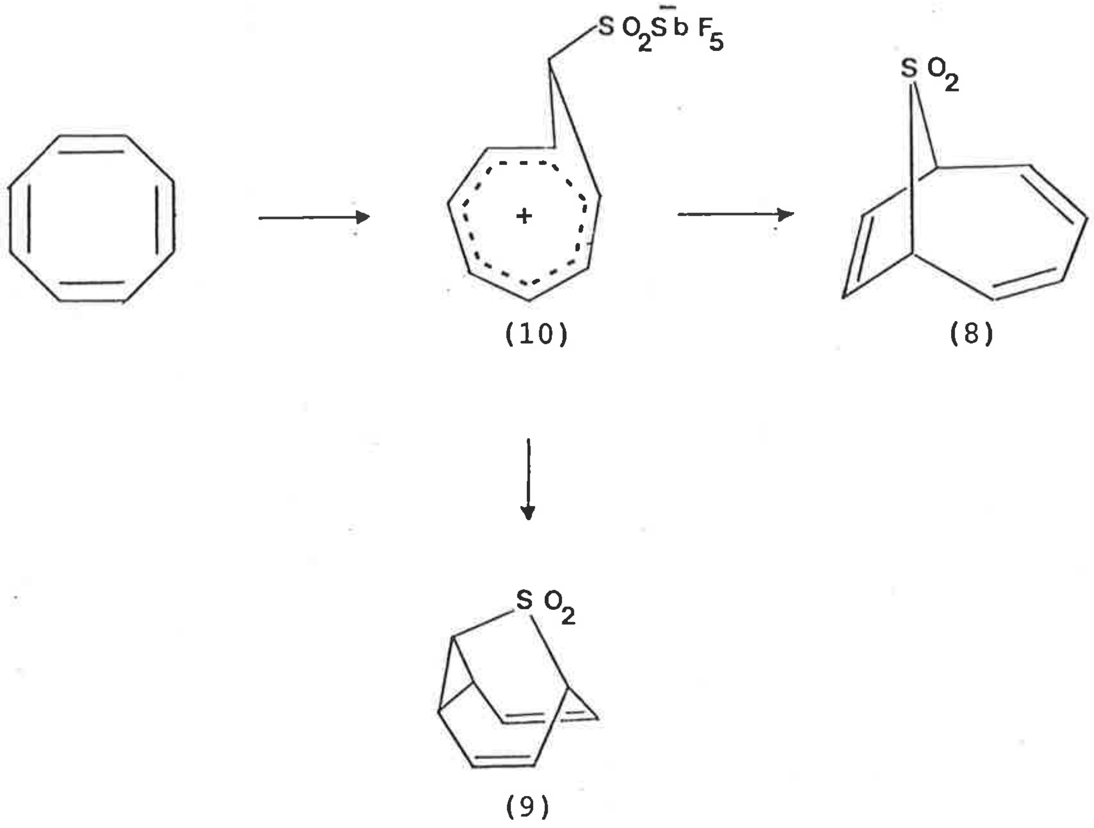
SCHEME 3

are obtained which have structures that convincingly point to the intermediacy of homotropylium cations. The benzyne adduct (6) of cyclooctatetraene, for example, possesses a structure which implicates the involvement of homotropylium cations in its formation (Scheme 4).[19,20] In this case, an alternate mechanism involving pericyclic reactions must be ruled out; the geometry required for an intramolecular $\pi 4_a + \pi 2_a$ cycloaddition, which might generate the cyclopropyl ring, cannot be readily achieved by the *trans* 10-[annulene] (7) (Scheme 4).[19,20] Other genuine, non-concerted



SCHEME 4

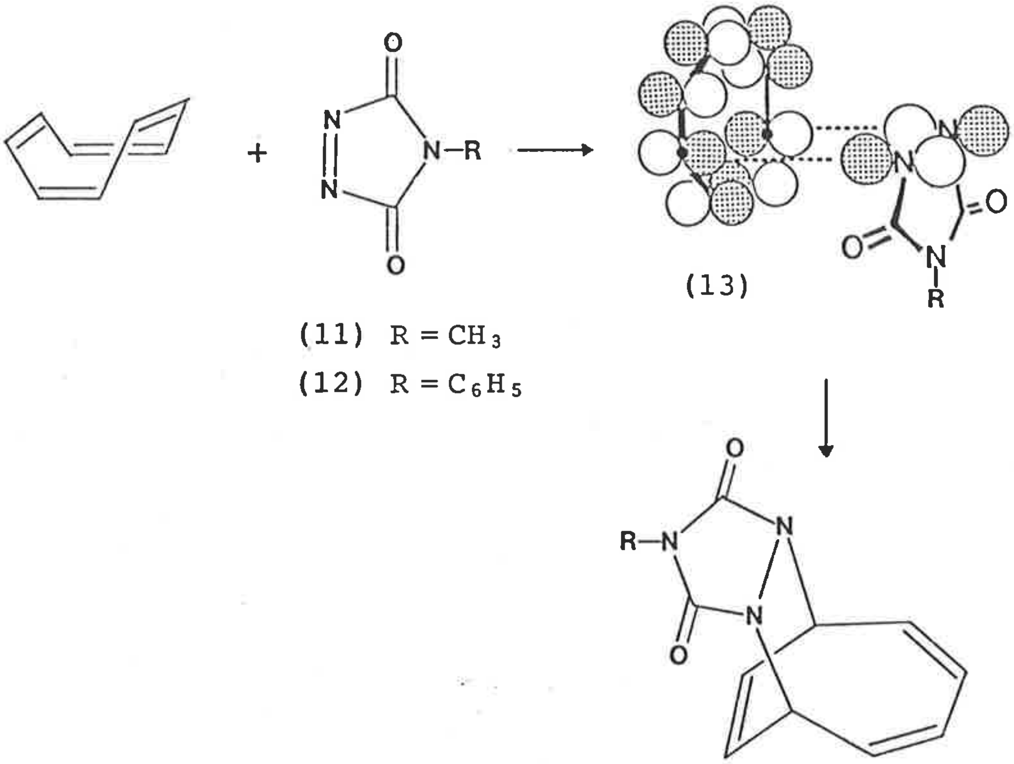
electrophilic cycloadditions to cyclooctatetraene, such as that of sulphur dioxide in the presence of antimony pentafluoride,[21] lead to mixtures of adducts such as (8) and (9) which are formed by charge annihilations at various carbon atoms of the homotropylium species (10) (Scheme 5).



SCHEME 5

It would thus appear that the exact mechanism responsible for the formation of most reported 1,4 adducts is at present uncertain.

Snyder[14] proposed that some 1,4 adducts might be obtained from concerted reactions, which proceed *via* *bis*-pericyclic transition states (13) (the two pericyclic fragments in this case containing six and eight π electrons) (Scheme 6), and that these reactions can be distinguished by



SCHEME 6

the independence of their rates upon solvent polarity. The reaction between N-methyltriazolinedione (11), an extremely reactive dienophile, and cyclooctatetraene is cited by Snyder as an example of a *bis*-pericyclic process and the second order rate constants for this reaction in various solvents are listed in Table 1.

Although the relative extents of Diels-Alder and 1,4 cycloadditions to cyclooctatetraene vary markedly with temperature and the nature of the dienophile, it is nevertheless possible to make some broad generalizations.

TABLE 1

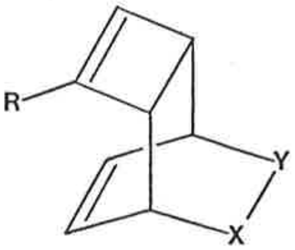
Second order rate constants of cycloaddition of N-methyltriazolinedione to cyclooctatetraene as a function of solvent (20°C)

Solvent	Rate Constant
Benzene	0.28
Chlorobenzene	0.63
Dichloromethane	1.2
Acetone	0.35
Acetonitrile	0.19

At high temperatures (above 80°C), the amount of bicyclo[4,2,0]octa-2,4,7-triene (2) in equilibrium with cyclooctatetraene is sufficient to enable even sluggish dienophiles such as maleic anhydride to react and form Diels-Alder adducts. Only the most reactive dienophiles such as the triazolinediones (11) and (12) react with cyclooctatetraene near room temperature; in these cases 1,4 adducts are formed slowly and in low yields. Mixtures of 1,4 and Diels-Alder adducts are obtained if cyclooctatetraene is allowed to react with powerful dienophiles at elevated temperatures.[10]

The addition of a substituent to the cyclooctatetraene molecule can have a profound effect upon the course of its cycloaddition reactions. The cycloaddition reactions of monosubstituted cyclooctatetraenes usually have been performed at high temperature and in the presence of poor to only moderately reactive dienophiles. These reactions have led, with a few interesting exceptions, to formation of

Diels-Alder adducts (14) substituted at the 3 position.[22] Paquette[23] concluded that ring closure of mono-alkylated and phenylcyclooctatetraenes gives 7-substituted bicyclo[4,2,0]-octa-2,4,7-trienes (15) as the kinetically favoured isomer and that it is this particular triene that is trapped by most dienophiles.



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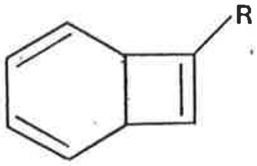
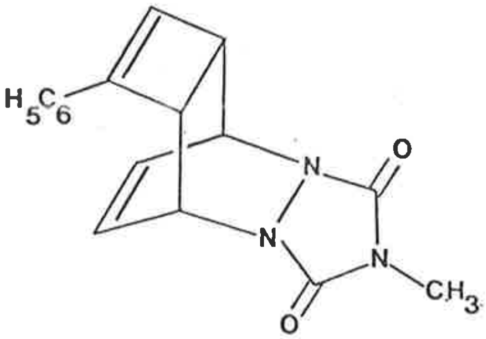


(15)

Addition of electron withdrawing substituents to the cyclooctatetraene molecule accelerates the rate of its ring closure to such an extent that the cycloaddition step now becomes rate determining and adducts derived from 4-,5-,6- and 7-substituted bicyclo[4,2,0]octa-2,4,7-trienes are obtained. This subtle changeover in mechanism induced by the nature of the substituent, is demonstrated by the reactions of triazolinediones with phenyl and cyanocyclooctatetraenes. The 3-substituted tetracyclic adduct (16) was the sole product (84%) of the reaction between N-methyltriazolinedione (11) and phenylcyclooctatetraene in boiling ethyl acetate;[23] on the other hand, under similar conditions N-phenyltriazolinedione (12) adds to cyanocyclooctatetraene to give all four possible Diels-Alder adducts (17), (18), (19) and (20).[23]



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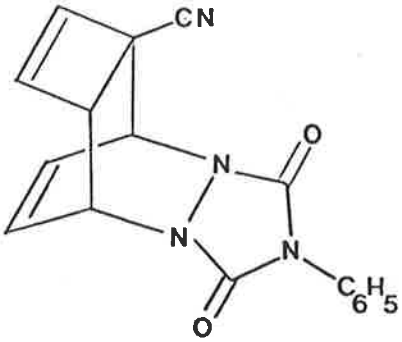

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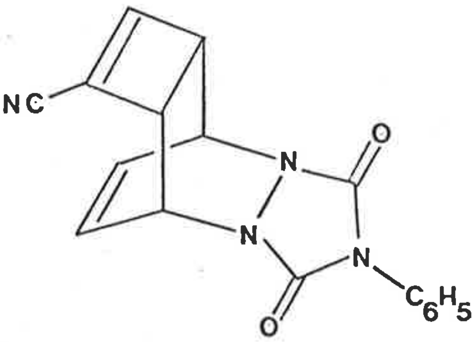

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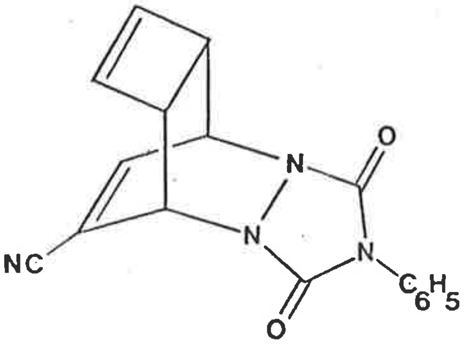

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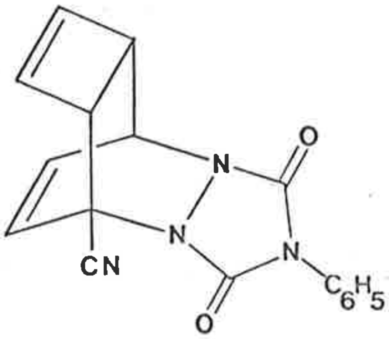
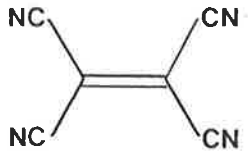


(20)

In contrast, Diels-Alder, 1,4 and 1,2 adducts can be obtained from cycloadditions to a cyclooctatetraene bearing an electron releasing substituent. For example, the action of tetracyanoethylene (21) upon methoxycyclooctatetraene in benzene at room temperature gives a mixture of the two 1,4 adducts (22) and (23).[24] Intriguingly, under similar



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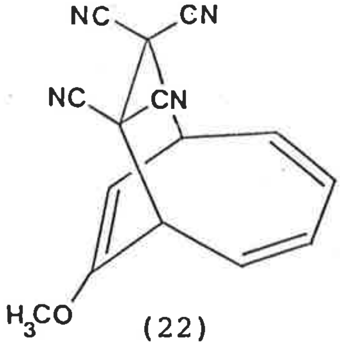

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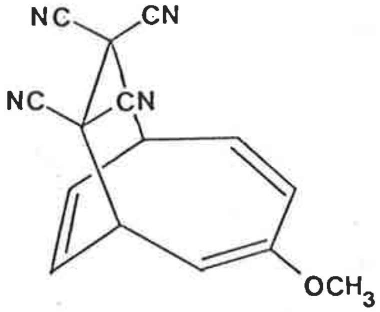
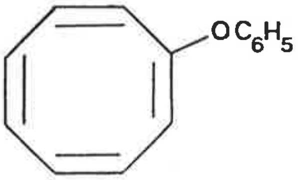


(23)

conditions tetracyanoethylene reacts with phenoxycyclooctatetraene (24) to produce adduct (25) and a small amount of (26).[24] Unfortunately, corresponding cycloadditions were



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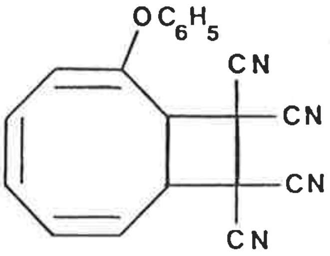

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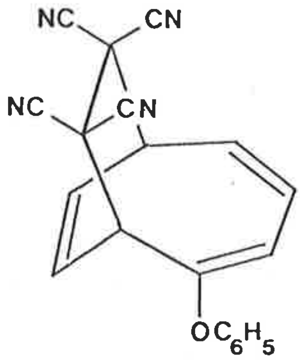
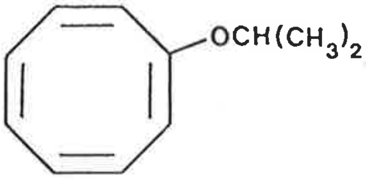


(26)

not performed under conditions of high temperature to establish whether Diels-Alder addition of tetracyanoethylene to these alkoxycyclooctatetraenes could be induced. Sluggish dienophiles, such as maleic anhydride, produce Diels-Alder adducts upon reaction with alkoxycyclooctatetraenes.[24]

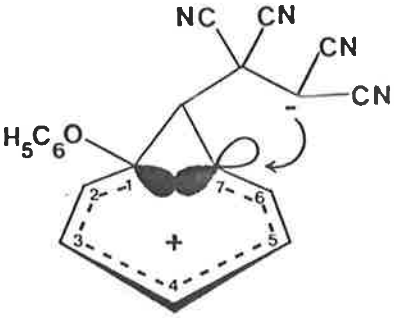
It is interesting to note that tetracyanoethylene forms 1,4 (or 1,2) adducts with alkoxycyclooctatetraenes but Diels-Alder adducts with cyclooctatetraene; the 1,4 cycloaddition mechanisms proposed by Snyder[14] and Huisgen[16] (discussed previously) can both accommodate this changeover in the mode of cycloaddition. Huisgen[24] suggested that 1,4 cycloaddition occurs *via* homotropylium zwitterions and therefore factors which act to stabilise the zwitterion will enhance 1,4 addition. Due to the electron releasing property of alkoxyl groups, the zwitterions derived from alkoxycyclooctatetraenes are stable compared to that derived from cyclooctatetraene.

Snyder suggested that 1,4 cycloaddition of tetracyanoethylene to alkoxycyclooctatetraenes occurs because addition of electron releasing substituents to cyclooctatetraene enhances its capacity for *bis*-pericyclic cycloadditions. It has been demonstrated by Oth[25] that the barriers to ring inversion of ethoxycyclooctatetraene and isopropoxycyclooctatetraene (<u>27</u>) are lower than for cyclooctatetraene;[26] it is therefore reasonable to assume that it is easier for some alkoxycyclooctatetraenes to attain the planarity required for a *bis*-pericyclic transition state than it is for cyclooctatetraene. In addition, Snyder mentions that electron releasing substituents might decrease the amount of bicyclo[4,2,0]octa-2,4,7-triene in equilibrium with cyclooctatetraene thereby decreasing the likelihood of Diels-Alder reactions.



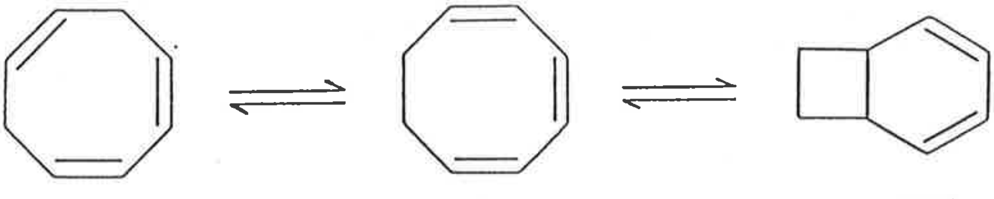
(27)

It would appear that except for two cases, the exact mechanism responsible for the formation of cycloadducts of alkoxycyclooctatetraenes is uncertain. Evanega[27] has shown that the rate of 1,4 cycloaddition of N-phenyltriazolinedione to methoxycyclooctatetraene is not dependent on solvent polarity; in this case at least, the adduct must be considered as the product of a concerted cycloaddition. In the case of cycloadditions of tetracyanoethylene to methoxy- and phenoxycyclooctatetraenes, the independence of reaction rate on solvent polarity has not been demonstrated and, as a consequence, the dipolar mechanism of Huisgen cannot be discounted. The 1,2 adduct (<u>25</u>) is of particular interest as it could not have arisen from a concerted, thermal pericyclic process. Since the most electrophilic carbon atoms of a homotropylium cation appear to be C_1 and C_7,[28] it is reasonable to suggest that (<u>25</u>) arises from (<u>28</u>) by the favourable charge annihilation process depicted.



(28)

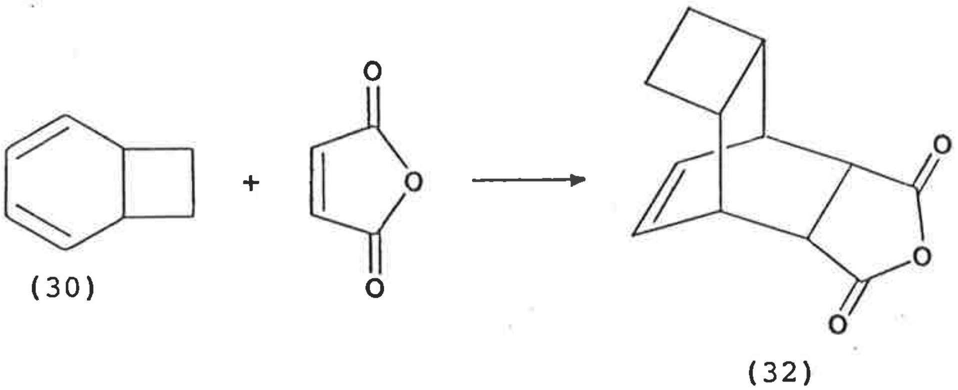
Cycloocta-1,3,5-triene (29) is in equilibrium with its bicyclic valence tautomer (30) but, unlike cyclooctatetraene, the rate of this equilibrium is so slow that the valence tautomer can be separated from cycloocta-1,3,5-triene by careful fractional distillation.[29] In addition, cycloocta-1,3,5-triene is converted into the 1,3,6-triene (31) by reversible 1,5 hydrogen shifts but at 100°C the equilibrium concentration of (31) is only 0.5% (Scheme 7).[30]



(31) (29) (30)

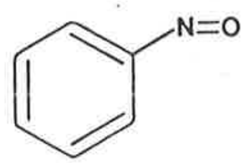
SCHEME 7

Not surprisingly, bicyclo[4,2,0]octa-2,4-diene (30) enters into Diels-Alder reactions with dienophiles such as maleic anhydride to form adducts such as (32);[31] when (31) is treated with maleic anhydride, (32) is also formed (Scheme 8).[32] Different types of adducts are obtained when (29) and



SCHEME 8

(30) are treated with electrophilic 2π donors such as nitrosobenzene and chlorosulphonylisocyanate. Nitrosobenzene (33) reacts with bicyclo[4,2,0]octa-2,4-diene (30) to form a Diels-Alder adduct (34) but with cycloocta-1,3,5-triene it gives the 1,4 adduct (35).[33] On the other hand, chlorosulphonylisocyanate (36) forms six different but related adducts with (29) and (30). To triene (29), it adds to form zwitterion (37) which collapses reversibly to give (38) and (39) and irreversibly to give (40) (Scheme 9).[34] Addition to diene (30) produces the zwitterion (41) which undergoes charge annihilation to give (42), (43), (44) and (45) (Scheme 10).[35] A qualitative dependence of the rate of cycloaddition of chlorosulphonylisocyanate to cycloocta-1,3,5-triene upon solvent polarity has been demonstrated and this evidence supports the mechanistic proposals outlined in Schemes 9 and 10.[34,35]



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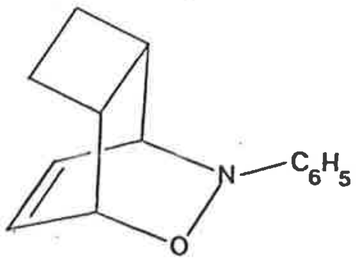

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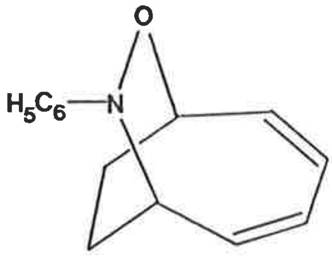

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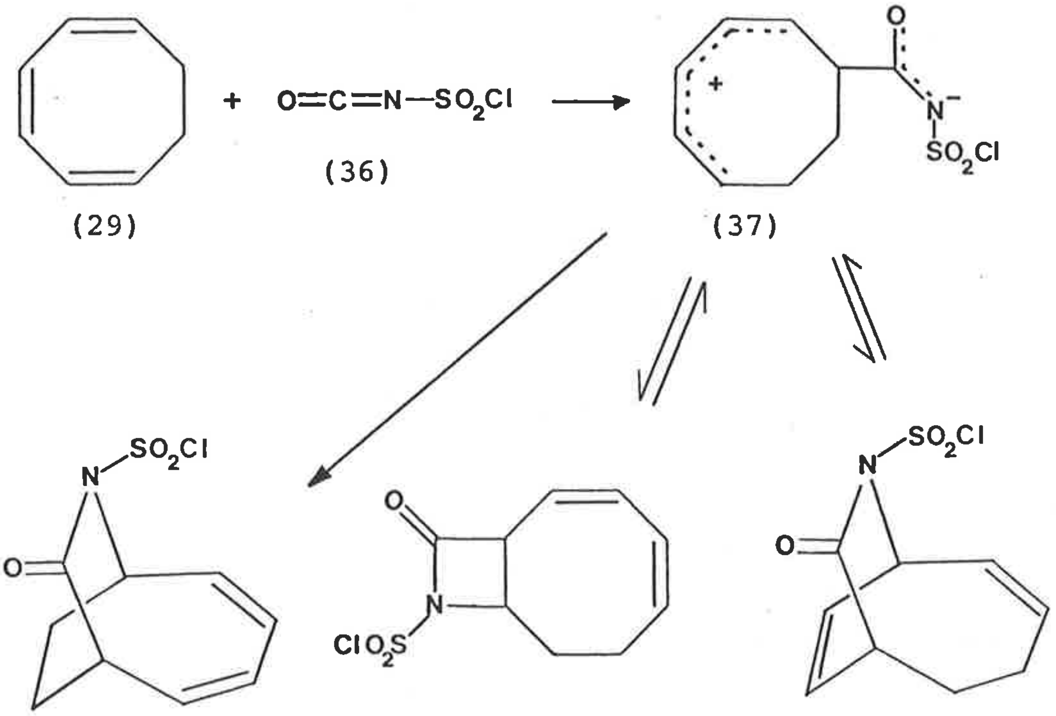
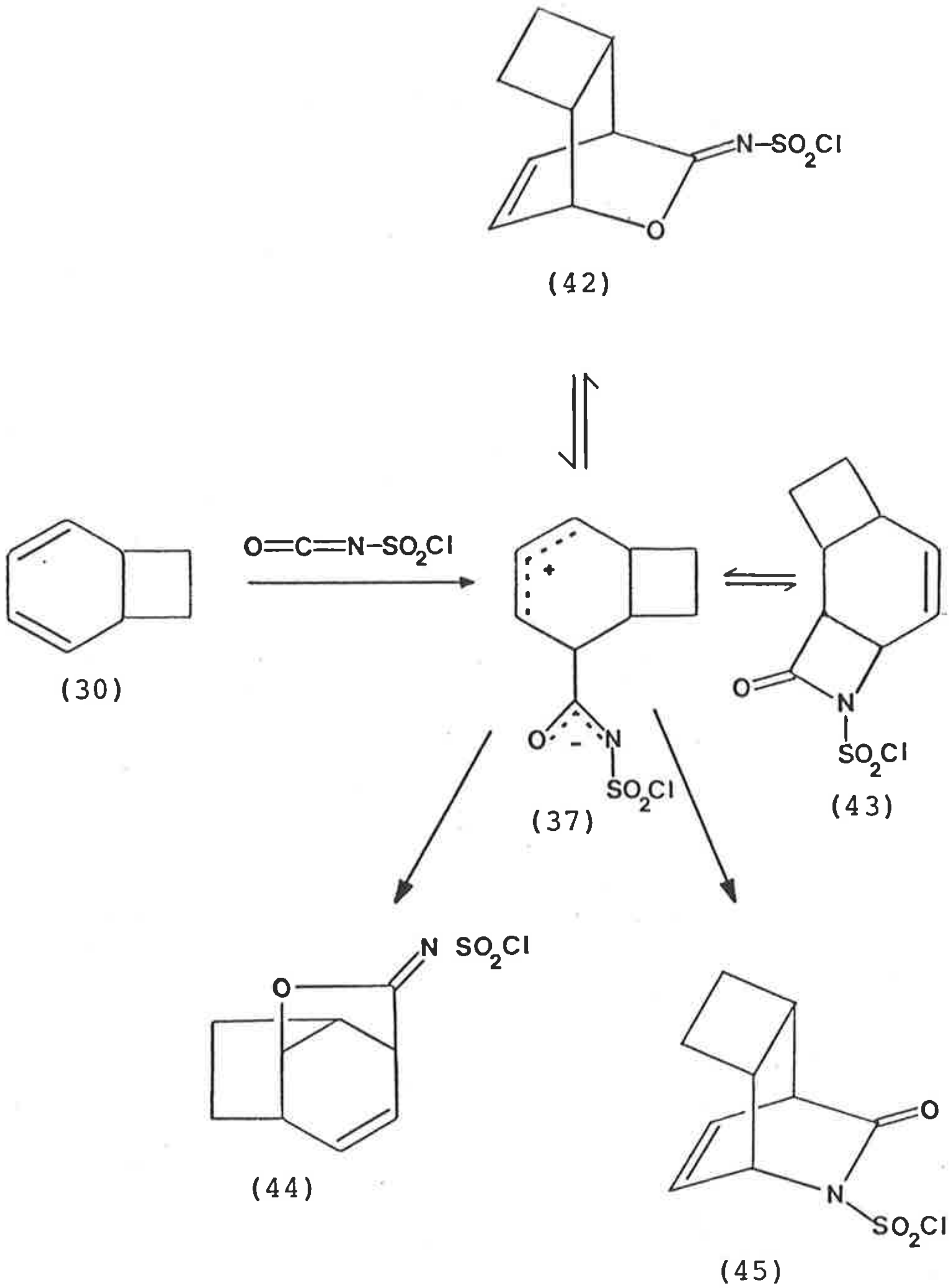
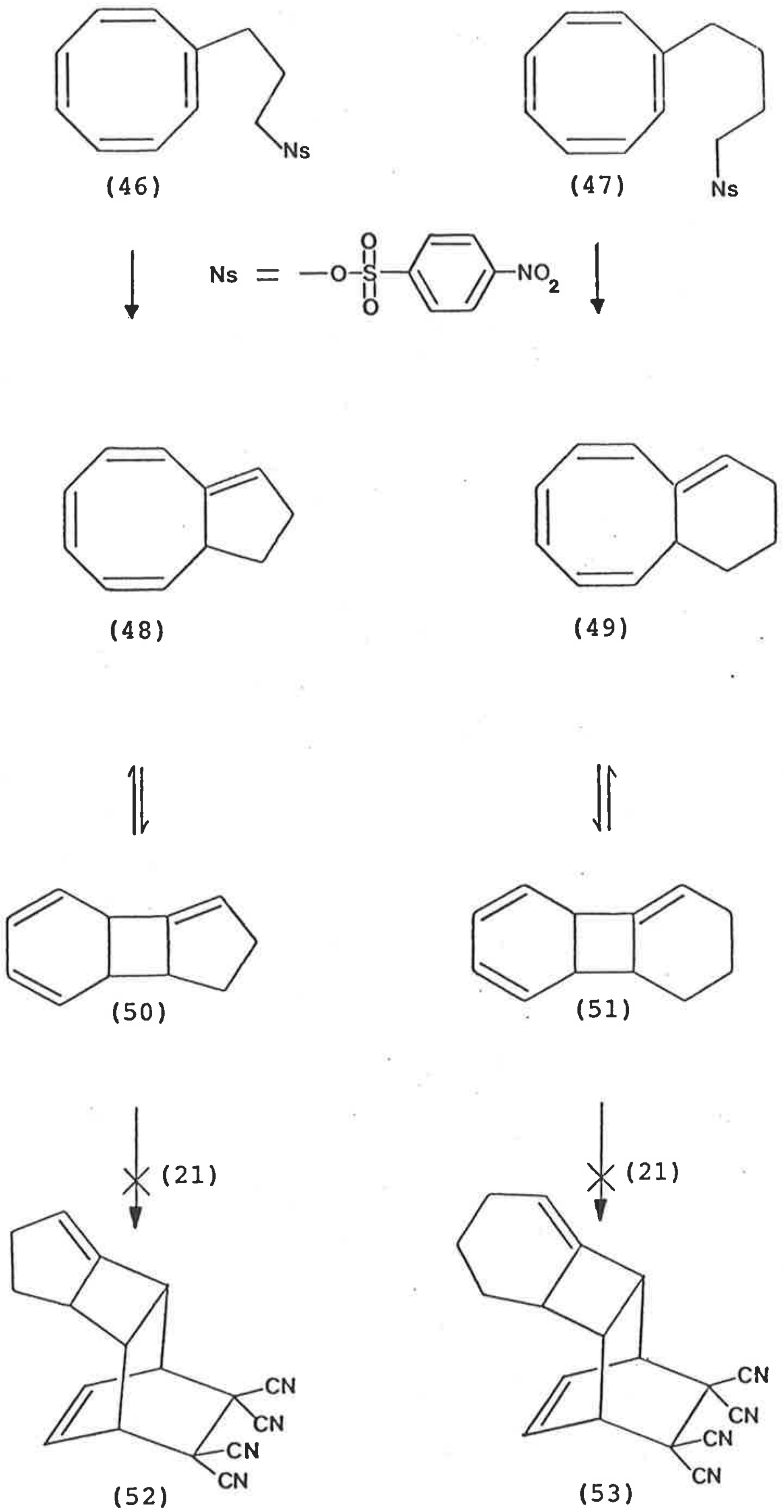


SCHEME 9



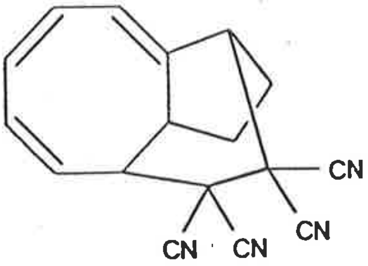
SCHEME 10

Work in this department by Ferber and Gream[36] has led to the discovery of novel cycloadducts of 7-alkylidenecycloocta-1,3,5-trienes (48) and (49). It was hoped that the identification of these olefins, which were prepared by the solvolyses of *p*-nitrobenzenesulphonate esters (46) and (47)[37],

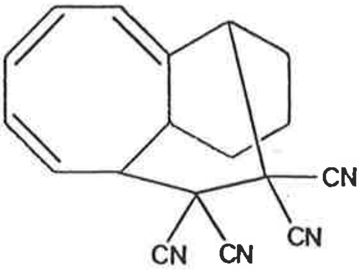

Ns
(46)
(47)
Ns
Ns = —O-SO2-C6H4-NO2
(48)
(49)
(50)
(51)
(21)
(21)
CN
CN
CN
CN
(52)
CN
CN
CN
CN
(53)

SCHEME 11

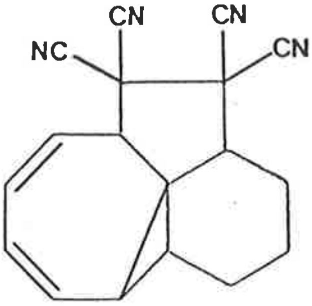
might have been facilitated by the preparation of their tetracyanoethylene adducts which were expected to be those, (52) and (53), resulting from Diels-Alder addition of tetracyanoethylene to the valence tautomers (50) and (51) (Scheme 11). In the event, however, the novel tricyclic and tetracyclic adducts (54), (55) and (56), which are all formally π8 + π2 adducts, were obtained. Only one other π8 + π2 adduct of a 7-alkylidenecycloocta-1,3,5-triene has been reported in the chemical literature. In 1978, Lagowski^{38} reported that tetracyanoethylene was rapidly consumed by a mixture of 1,3,5,7-tetramethylcyclooctatetraene (57) and other oligomers of propyne and that the π8 + π2 adduct (59) was formed. It was suggested by Lagowski that (59) might have been formed by a π8 + π2 cycloaddition reaction between tetracyanoethylene and 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (58) which was itself derived from (57) by a base catalysed isomerization process (Scheme 12). Ferber^{36} suggested that homotropylium zwitterions (60) produced (54), (55) and (56) upon charge



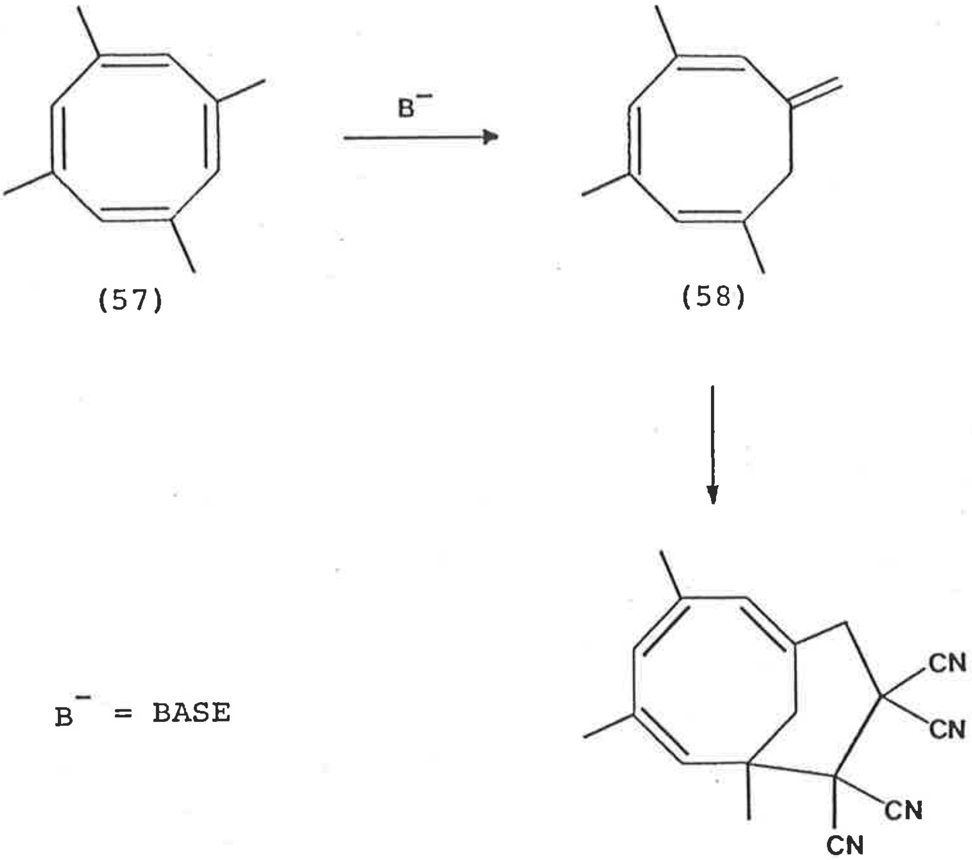
(54)



(55)



(56)



(57)

(58)

(59)

B$^-$ = BASE

SCHEME 12

annihilations at C_2 (by a "6,7'" addition process*) and C_7 (a "1,7'" process*) (Scheme 13).

The discoveries made by Ferber and Lagowski indicated that a closer examination of the cycloaddition reactions of 7-alkylidenecycloocta-1,3,5-trienes and 7-arylidenecycloocta-1,3,5-trienes was warranted.

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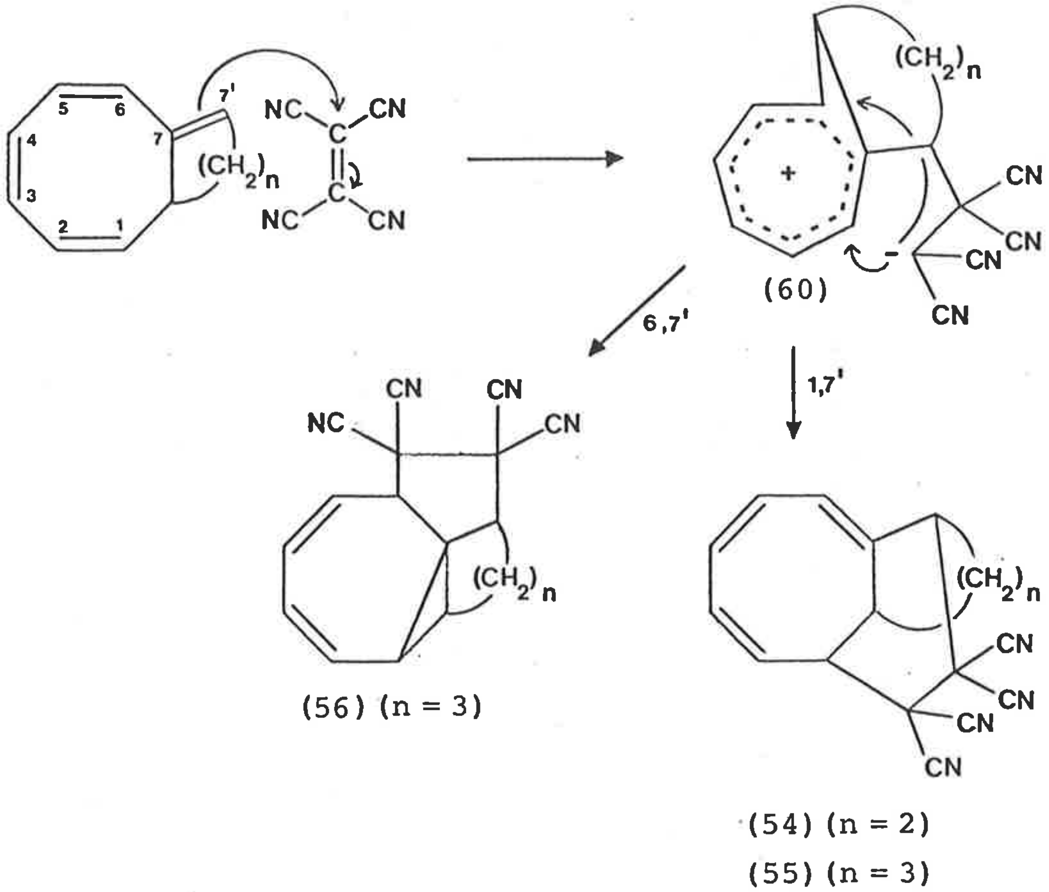
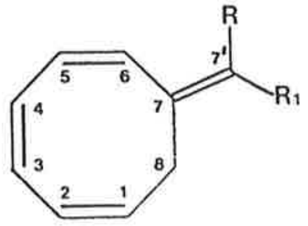
* The terminology is used to describe processes whereby the 2π donor forms bonds with atoms C_7' and either C_6 or C_1, respectively, of a 7-alkylidenecycloocta-1,3,5-triene.


5
6
4
7
3
2
1
7'
(CH2)n
NC
CN
C
C
NC
CN
(CH2)n
+
CN
CN
CN
CN
(60)
6,7'
1,7'
CN
CN
NC
CN
(CH2)n
(56) (n = 3)
(CH2)n
CN
CN
CN
CN
(54) (n = 2)
(55) (n = 3)

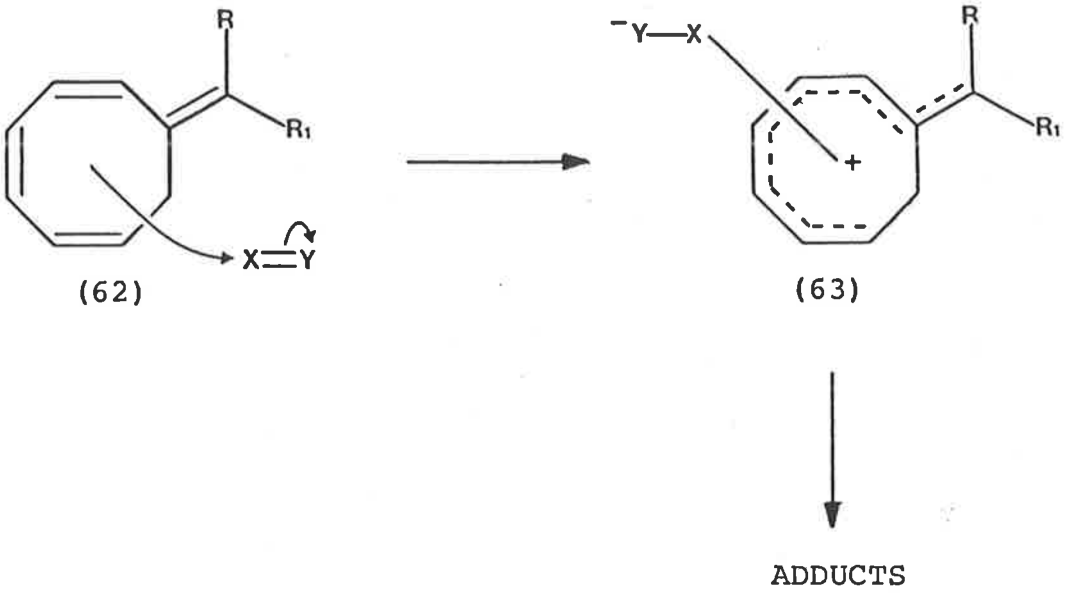
SCHEME 13

1.2 SYNTHESIS OF 7-ALKYLIDENE- AND 7-ARYLIDENECYCLOOCTA-1,3,5-TRIENES

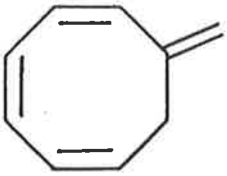
The cycloaddition reactions of a range of 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes (62) were examined in an effort to establish whether the $\pi 8 + \pi 2$ mode of cycloaddition observed by Ferber[36] and Lagowski[38] is a general process. These olefins contain seven carbon atoms which are at least potential sources of electrons for electrophilic dienophiles; Ferber and Lagowski, however, have only obtained adducts resulting from electrophilic attack on C_7'. It was hoped that attack on atoms other than C_7', leading to the formation of novel adducts, could be induced by selecting groups R and R_1 which have the ability to stabilise zwitterions such as (63) which bear a partial positive charge on C_7' (Scheme 14). The following olefins were prepared and their cycloaddition reactions were examined: 7-methylenecycloocta-1,3,5-triene (64), 7-isopropylidenecycloocta-1,3,5-triene (65), (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-triene (66), (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)cycloocta-1,3,5-triene (67), (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-triene (68) and 7-benzhydrylidenecycloocta-1,3,5-triene (69).

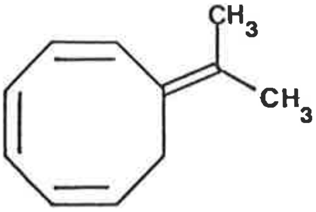


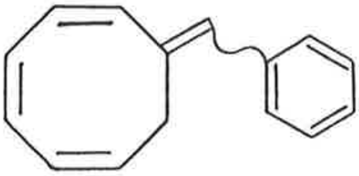
(62)

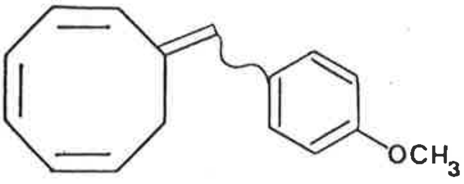


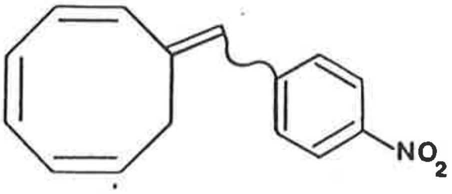
SCHEME 14

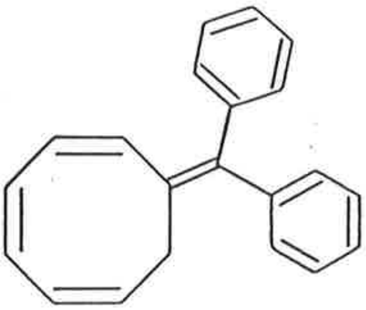

(64)


(65)


(66)

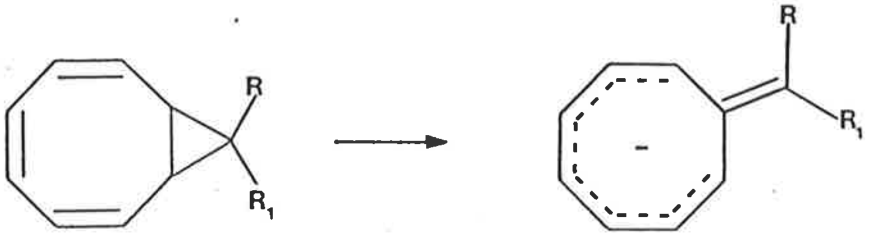

(67)


(68)


(69)

Routes to a number of substituted 7-alkylidenecycloocta-1,3,5-trienes have been reported.[37,39,40,41,42] However, in general, none of these was applicable to the syntheses of the olefins required for the present work.

Staley[43,44,45,46] reported that bicyclic olefins (70) undergo deprotonation and rearrangement in the presence of strong base to give cycloocta-1,3,5-trienyl anions (71) (Scheme 15). In one case,[43] where $R_1 = R_2 = H$, Staley reported that a mixture of tetraenes (64), (72) and (73) was

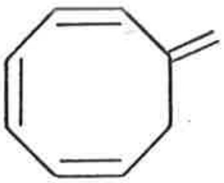


(70)

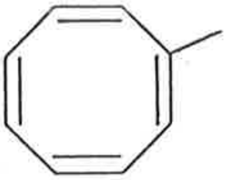
(71a), $R = H$, $R_1 = C_6H_5$
(71b), $R = H$, $R_1 = C_6H_4OCH_3$
(71c), $R = R_1 = C_6H_6$
(71d), $R = R_1 = H$

SCHEME 15

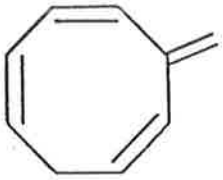
obtained on quenching the anion (71d) with water. Equilibration of these olefins under basic conditions gave a mixture containing (64) (31%), (72) (67%) and (73) (2%).[43] Although Staley prepared (71 a, b, c), he failed to report on their conversions into (66), (67) and (69). It was felt that, although (65), (66), (67), (68) and (69) might be prepared by quenching an appropriate anion (71), complex



(64)



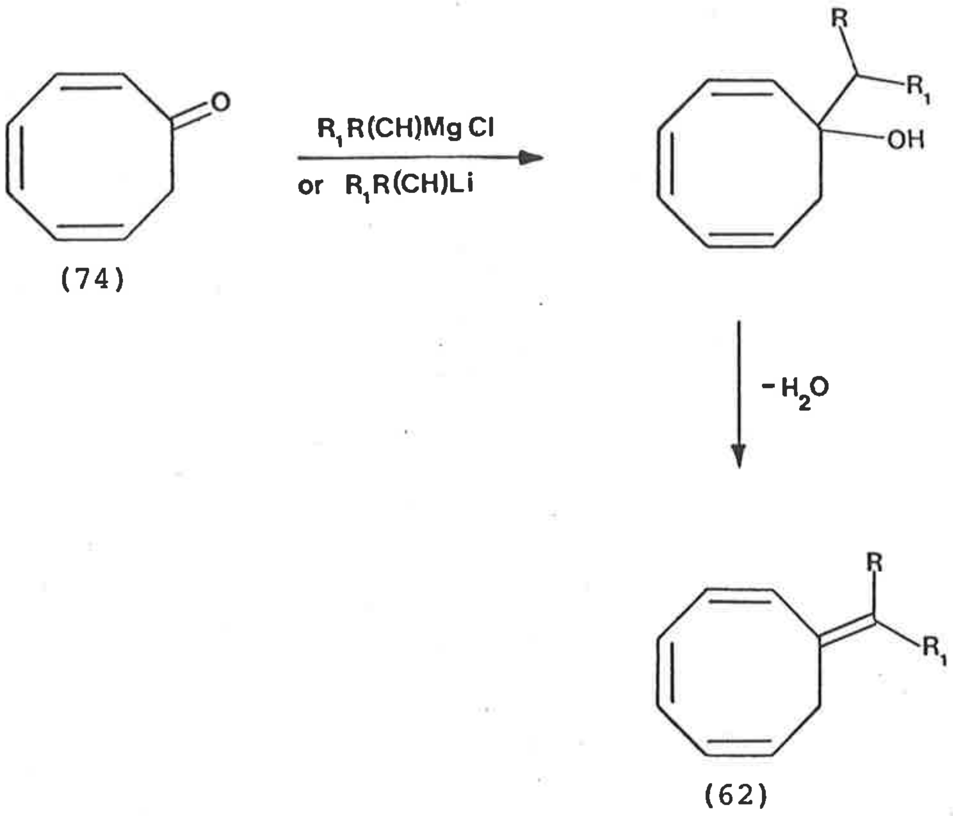
(72)



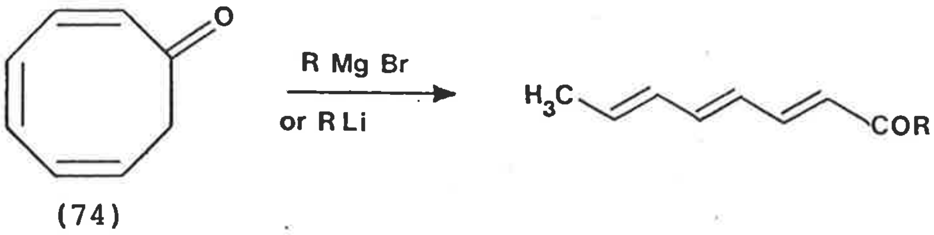
(73)

mixtures of tetraenes would be isolated. In addition, it was anticipated that the bicyclic olefins (70) would be difficult to prepare in synthetically useful amounts; for these reasons, other general routes to 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes were sought.

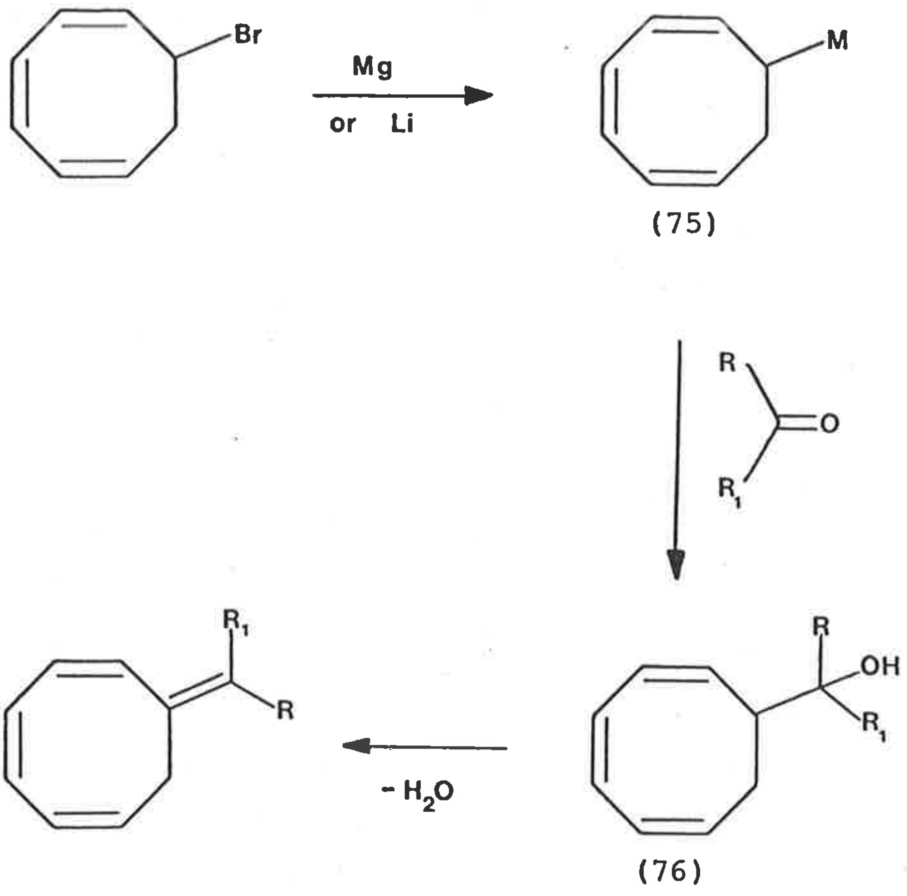
Several possible routes to these olefins, which involved conventional carbocyclic chemistry, were not investigated because of anticipated difficulties arising from the unusual properties of cyclooctatetraenyl derivatives. For example, the work of Kroner[47] and Ogawa[48] suggested that attempts to prepare cyclooctatrienyl derivatives by a sequence involving the action of organometallic reagents upon cycloocta-2,4,6-trienone (74) (Scheme 16) should fail because acyclic products generally are formed on treatment of (74) with these reagents (Scheme 17).[47,48] A synthetic sequence (Scheme 18) combining alkylation of a suitable ketone by a cyclooctatrienylmetal species (75) with subsequent dehydration of the alcohol (76) thus produced, was not investigated because (75) is likely to undergo disproportionation[49] (Scheme 19).



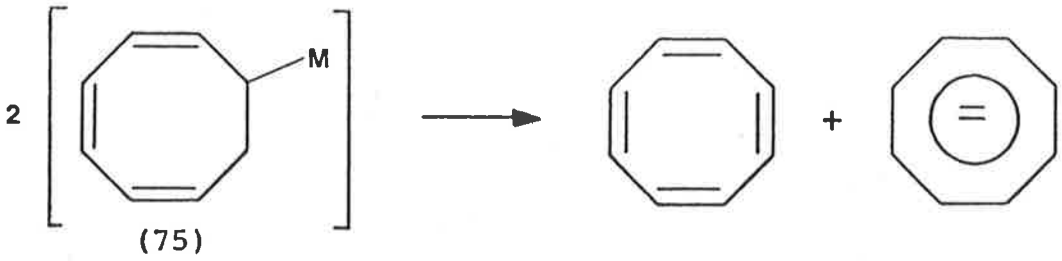
SCHEME 16



SCHEME 17

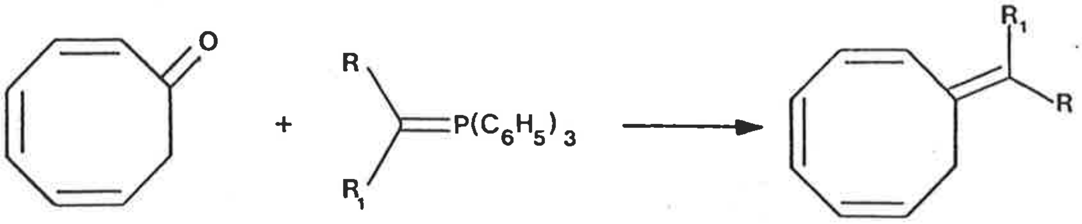


SCHEME 18



SCHEME 19

An obvious, although hitherto unreported, route to 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes which warranted investigation involved a Wittig reaction between cycloocta-2,4,6-trienone (74) and a suitable phosphorane (77) (Scheme 20). The simplest 7-alkylidenecycloocta-1,3,5-triene (64), which is an unstable and air sensitive oil, was prepared in low yields (20 - 35%) by the action of methylenetriphenylphosphorane (77a) on cycloocta-2,4,6-trienone[50] in dimethylsulphoxide. Material prepared in this manner had infra-red, p.m.r. and electronic spectral characteristics identical to those reported by Gardner[51] for 7-methylenecycloocta-1,3,5-triene (64) which he prepared unambiguously *via* another route (the details of which were not mentioned). An increased yield (78%) of (64) was observed in one case using the modified Wittig procedure of Aldercruetz;[52] this procedure was not used routinely because it was described only after the bulk of the work involving (64) was completed. Mixtures,



(74)

(77a), $R = R_1 = H$
(77b), $R = R_1 = CH_3$
(77c), $R = H$, $R_1 = C_6H_5$

SCHEME 20

containing traces of material which might have been the desired olefins (p.m.r. spectroscopy), were obtained from the Wittig reactions between (77b), (77c) and cycloocta-2,4,6-trienone under the conditions outlined in Table 2.

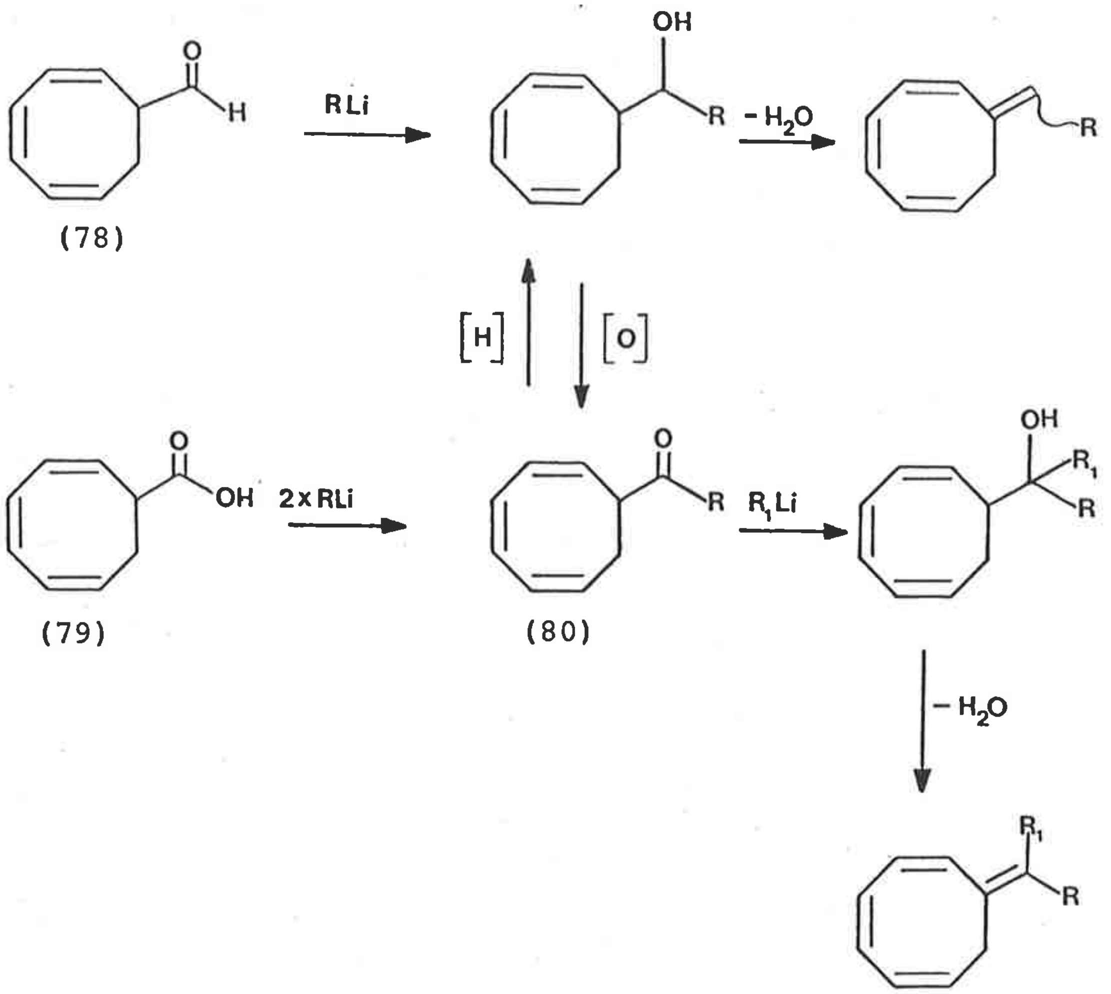
TABLE 2

Conditions used for the Wittig reactions between cycloocta-2,4,6-trienone, triphenylisopropylidenephosphorane (77b) and benzylidenetriphenylphosphorane (77c) at 25°C

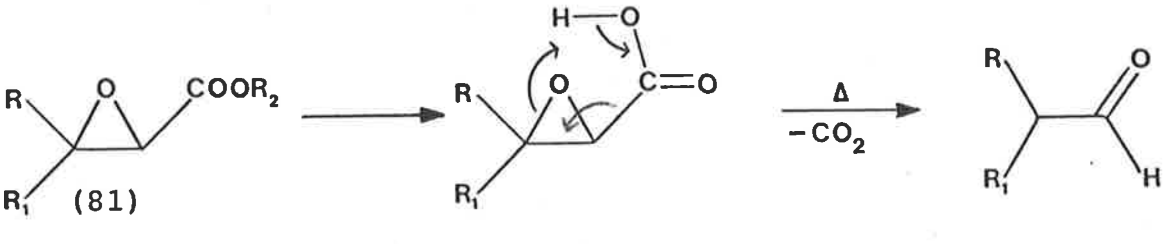
Phosphorane	Base used to generate phosphorane	Solvent
77b	n-butyllithium	ether
77b	n-butyllithium	dimethylsulphoxide
77b	potassium t-butoxide	tetrahydrofuran
77c	n-butyllithium	ether
77c	n-butyllithium	dimethylsulphoxide
77c	sodium ethoxide	ethanol
77c	potassium t-butoxide	tetrahydrofuran

In view of the limited success of the Wittig reaction, other routes to the cycloocta-1,3,5-trienes, which proceed *via* key intermediate (78) or the corresponding acid (79), (Scheme 21) were investigated.

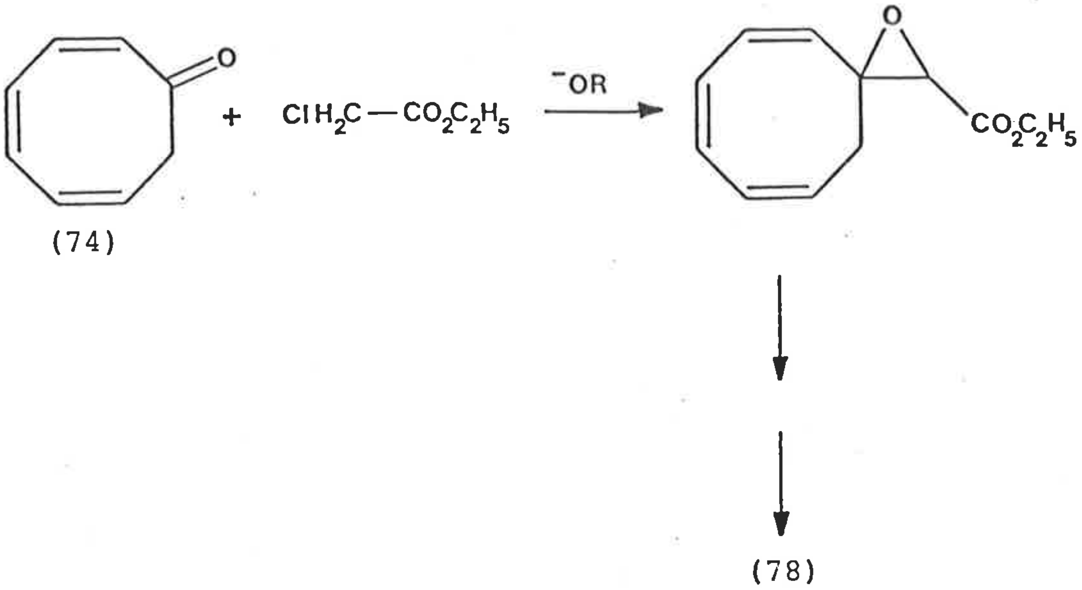
A wide variety of glycidic esters (81) yield aldehydes on hydrolysis and decarboxylation[53] (Scheme 22). As a route to (78), the proposed sequence (Scheme 23) was abandoned when it was found that the Darzens condensation between ethyl chloroacetate and cycloocta-2,4,6-trienone gave a mixture of at least six components containing unchanged ketone (determined by analytical thin layer chromatography (t.l.c.)).



SCHEME 21



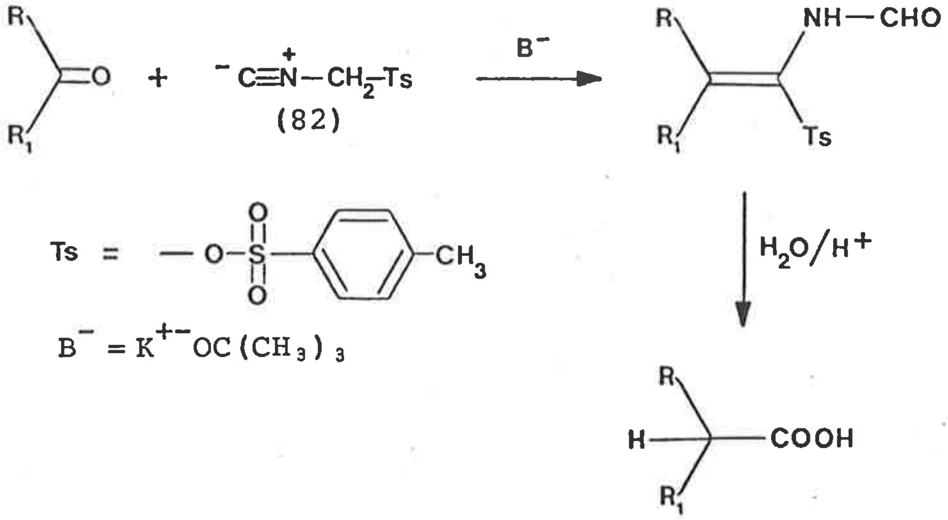
SCHEME 22



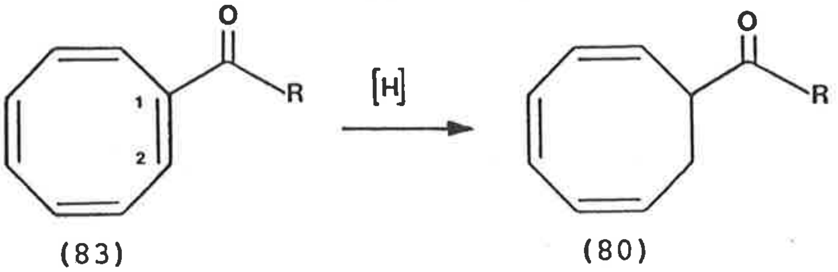
SCHEME 23

The products of condensation between *p*-toluenesulphonylmethylisocyanide (82) and ketones often yield carboxylic acids on hydrolysis[54] (Scheme 24). The action of (82) on cycloocta-2,4,6-trienone, followed by acid hydrolysis of the reaction mixture, led to a complex mixture (t.l.c.) which did not appear to contain (79) (p.m.r. and infra-red spectroscopy).

In addition, a direct preparation of (80) (R = aryl) was attempted. It was hoped that reduction of the C_1-C_2 carbon-carbon double bond of aroylcyclooctatetraenes (83) (Scheme 25) could be accomplished and that the resulting 7-aroylcycloocta-1,3,5-trienes (80) might be converted into (66), (67), (68) and (69). In the event, benzoylcyclooctatetraene[40] (83) (R = phenyl) yielded a complex mixture (t.l.c.) of ketones (p.m.r. and infra-red spectroscopy) on treatment with lithium

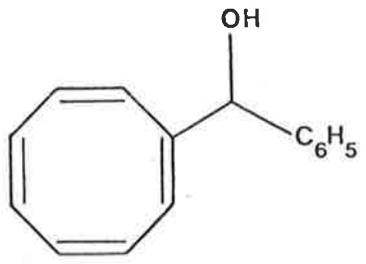


SCHEME 24



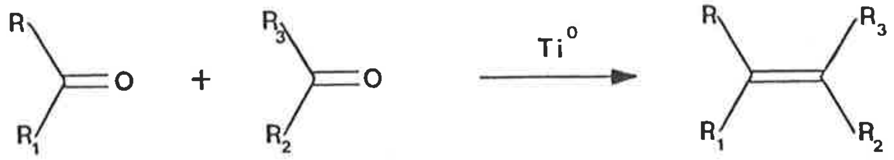
SCHEME 25

aluminiumhydride - cuprous iodide complex.[55] Sodium borohydride is capable of converting α,β-unsaturated ketones into saturated alcohols;[56] however, cyclooctatetraenylphenylmethanol (84) appeared to be formed (p.m.r. spectroscopy) by the action of sodium borohydride on (83).



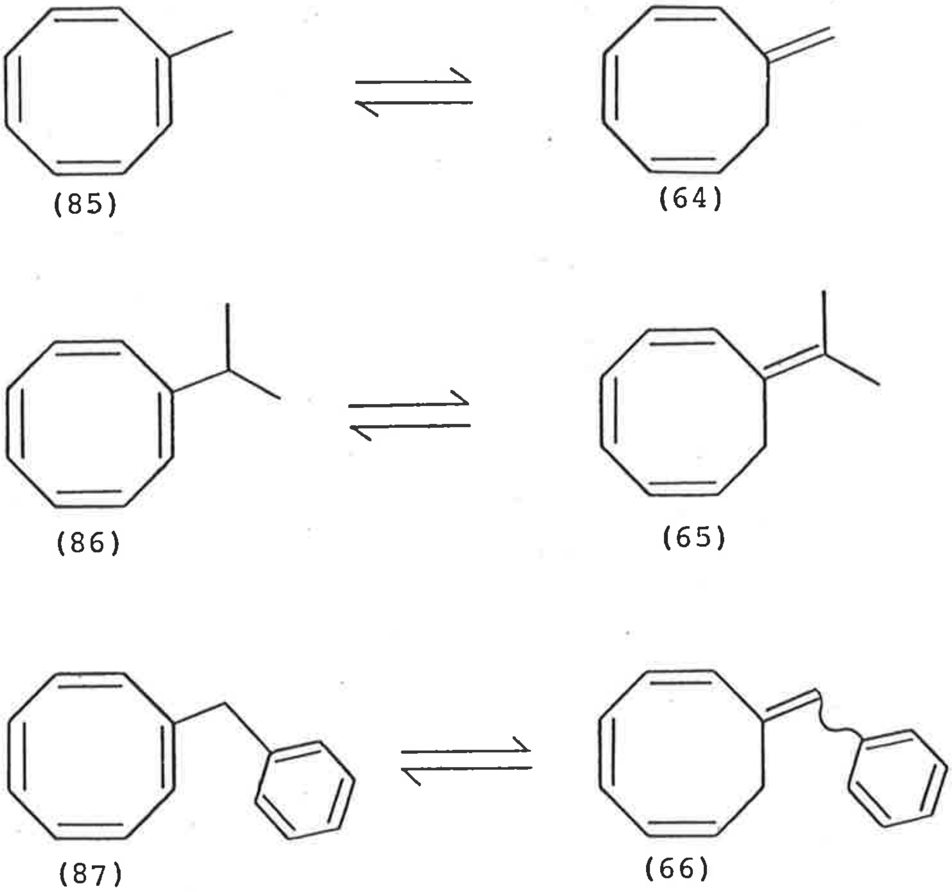
(84)

McMurry[57] reported that a range of tetrasubstituted olefins could be prepared by coupling ketones in the presence of zerovalent titanium (Scheme 26). The couplings of acetone and benzophenone with cycloocta-2,4,6-trienone, which were expected to produce (65) and (69), respectively, were unsuccessful. In both cases, very complex mixtures (t.l.c.), which contained unchanged cycloocta-2,4,6-trienone and traces of material which might have been the desired tetraenes (p.m.r. spectroscopy), were obtained.



SCHEME 26

A successful route to some 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes involved isomerization of cyclooctatetraenes (85), (86) and (87) (Scheme 27). Although rhodium trichloride[58] did not catalyse the transformation of



SCHEME 27

(86) into (65), it was found that potassium t-butoxide effected conversion of the cyclooctatetraenes (85), (86) and (87) into (64), (65) and (66) under the conditions outlined in Table 3. In all three cases, mixtures containing the two isomers were obtained (Table 3); however, it was found that when solutions of (85) and (64) or (87) and (66) in ether were washed with aqueous solutions of silver nitrate (20%),

TABLE 3

Isomerizations of alkylcyclooctatetraenes

Isomerization	Solvent	Temp.	Product Distribution	Yield of cycloocta-1,3,5-triene
(85)-(64)	tetrahydrofuran	25°	(85),73%; (64),27%	17%
(86)-(65)	dimethylsulphoxide	70-90°	(86),15%; (65),85%	74%
(87)-(66)	tetrahydrofuran	25°	(87), 6% (66),94%	86%

most of the alkylcyclooctatetraene contaminant was removed. Concentration of the organic phase afforded samples of (64) and (66) in high isomeric purity (>98% by gas-liquid chromatography (g.l.c.) analyses). The base catalysed isomerization of (86) was a highly capricious process. 7-Isopropylidenecycloocta-1,3,5-triene (65), which was identified by its p.m.r. spectral characteristics and as its N-phenyltriazolinedione adduct (see Section 1.4), was prepared in highly variable absolute yields (0 - 74%)* and was often obtained contaminated by unidentified compounds. Very high purity of reagents and solvent was necessary to effect a smooth isomerization of (86). In addition, the temperature at which the reaction was conducted was a crucial factor; prolonged or vigorous heating (at greater than 90°) led to an unacceptable level of polymerization of (86) whereas its isomerization did not occur below 70°. In one experiment, the isomerization was attempted in boiling tetrahydrofuran and, instead of (65), isoproprpenyl-

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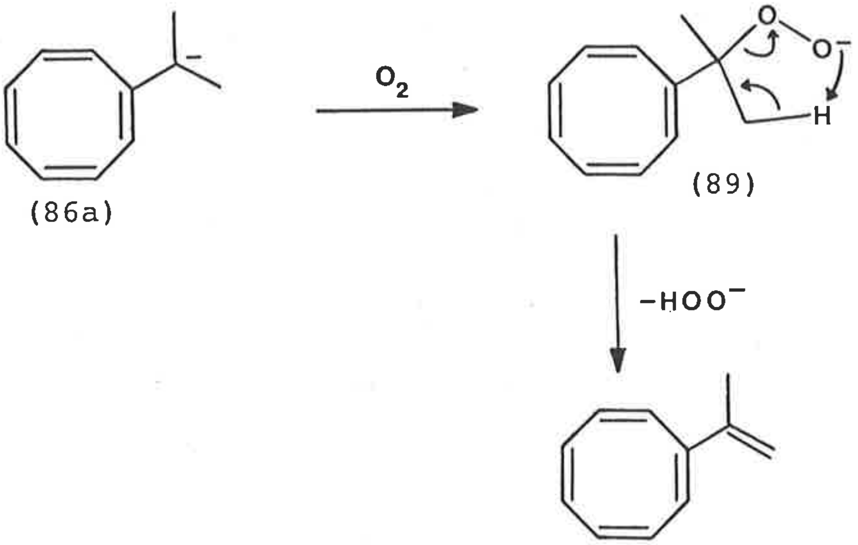
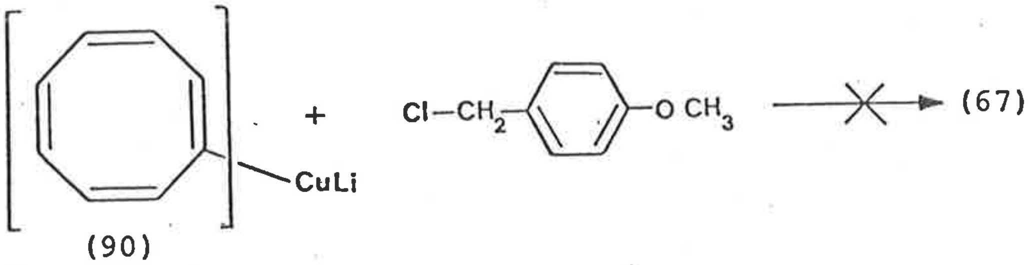
* Out of 15 attempts at the conversion of (86) into (65), only 3 were successful; varying amounts of unchanged (86) were obtained from the other twelve experiments.

cyclooctatetraene (88) (83%) was obtained. This olefin was identified by comparison of its p.m.r. spectral characteristics and g.l.c. properties with those of authentic material prepared by coupling 2-propenylmagnesium bromide with bromocyclooctatetraene in the presence of ferric chloride.[103] Carbanions are known to undergo peroxidation with oxygen;[59] perhaps the peroxide (89), derived from (86a) by the action of adventitious oxygen, undergoes elimination of hydroperoxide ion to give (88) (Scheme 28).

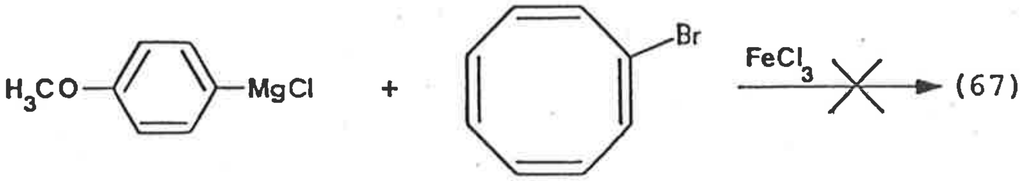


SCHEME 28

The preparation of (67) and (69) could not be accomplished using a route similar to those shown in Scheme 27 because the appropriate alkylcyclooctatetraenes could not be prepared. Under standard conditions, lithium dicyclooctatetraenylcuprate[60] (90) failed to couple with *p*-methoxybenzylchloride (Scheme 29); moreover, the highly reactive Grignard reagent, *p*-methoxybenzylmagnesium chloride,[61] could not be coupled with bromocyclooctatetraene (Scheme 30). In addition, cyclooctatetraenyllithium[62] and cyclooctatetraenylmagnesium bromide[63] failed to couple with benzhydrylchloride

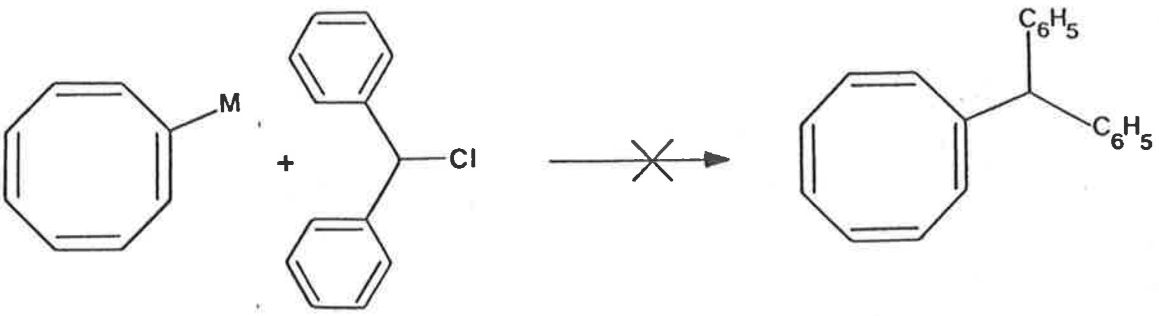


SCHEME 29

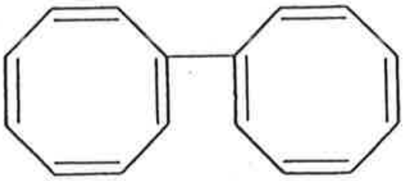


SCHEME 30

(Scheme 31). In all cases, varying amounts of cyclooctatetraene and *bis*-cyclooctatetraene (91)[64] were obtained.

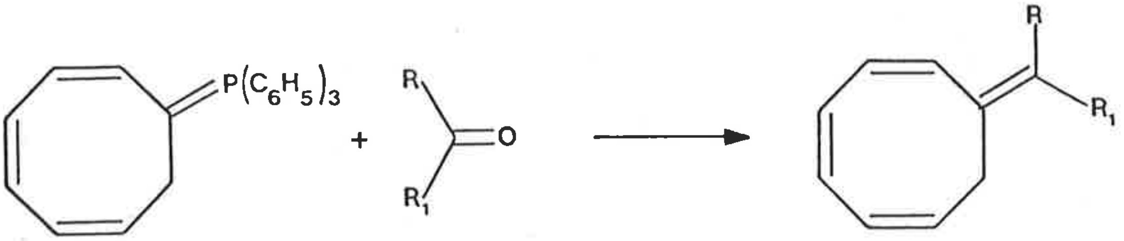


SCHEME 31



(91)

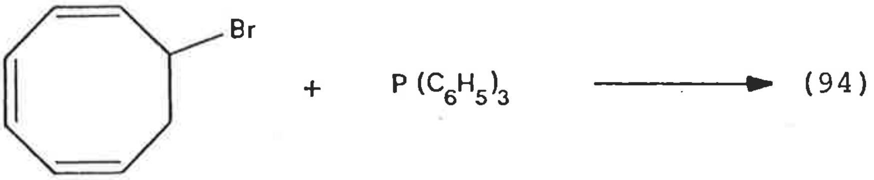
The 7-arylidenecycloocta-1,3,5-trienes (66), (67), (68) and (69) were prepared by the Wittig reactions between 7-cycloocta-1,3,5-trienylidenetriphenylphosphorane (92) and the appropriate carbonyl compound (Scheme 32).



(92)

SCHEME 32

Phosphorane (92) was prepared, in ether, by the action of n-butyllithium on 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide (94) which was itself derived from 7-bromocycloocta-1,3,5-triene (93)[65] (Scheme 33). The phosphonium salt (94) was found to be comparatively acidic. It was deprotonated rapidly by n-butyllithium and sodium ethoxide (in ethanol); moreover, it was noticed that the signal due to the acidic methine proton in the p.m.r. spectrum of (94) disappeared on treatment with deuterium oxide.

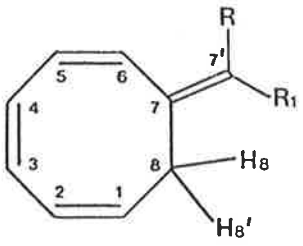


(93)

SCHEME 33

Compound (94) was also very air sensitive and could not be recrystallized. Based on the amounts of crude (94) used in the Wittig reactions (Scheme 32), yields of olefins (66), (67), (68) and (69) were 73%, 52%, 32% and 27% respectively; in the cases of (66), (67) and (68), mixtures of (*E*) and (*Z*) geometrical isomers were obtained.

Structures (65), (66), (67), (68) and (69) were assigned to the olefins on the basis of their p.m.r. (and in some cases, c.m.r.) spectral characteristics. The p.m.r. spectrum of 7-methylenecycloocta-1,3,5-triene (64) contained a broad signal centred at δ 5.90 (6H), two singlets at δ 4.93 and 4.73 (2H) and a doublet at δ 3.14 (2H, J 7.5 Hz). Olefins (65) - (69) gave rise to broad signals near δ 5.9 and doublets (2H, J *ca.* 7.5 Hz) between δ 3.0 and 3.5; the doublets were assigned to the doubly allylic methylene protons H_8 and H_8' (62). For (66), (67) and (68), which

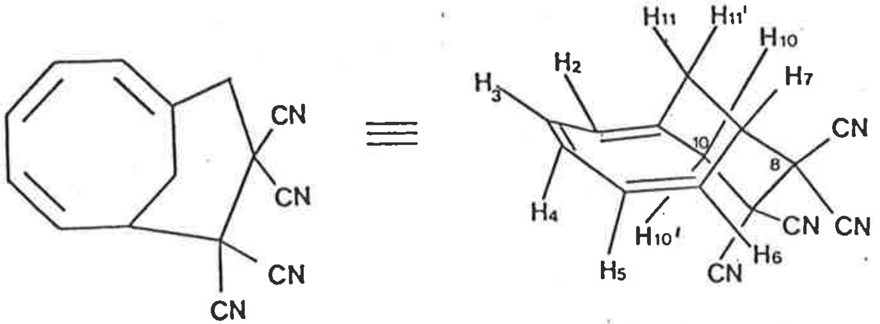


(62)

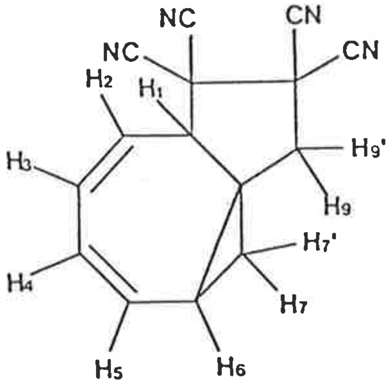
were obtained as mixtures of (*E*) and (*Z*) geometric isomers, two doublets, one for each of the geometric isomers, were observed between δ 3.0 and 3.5. Although the areas of these doublets enabled the proportions of the geometric isomers of (66), (67) and (68) to be calculated, c.m.r. spectroscopy was used to assign configurations to the predominant isomer. The c.m.r. spectra of (66) and (67) contained an intense, high field (*ca.* δ 30) triplet and a weaker, lower field (*ca.* δ 38) triplet. Because H_8 and H_8' are compressed by the aryl group in the (*E*) configurations of (66) and (67), it was assumed that the frequencies at which C_8 in (*E*)-(66) or (67) resonate were lower than those for C_8 in (*Z*)-(66) or (67).[66] As a consequence, the higher field triplets, which correspond to the major isomers, were assigned to (*E*)-(66) and (67). In the p.m.r. spectra of (66), (67) and (68), it was therefore assumed that the doublets of greater intensity in the region between δ 3.0 and 3.5 corresponded to the (*E*)-isomer (these doublets were invariably observed at a field lower than the doublets of lesser intensity). In all cases, the (*E*):(*Z*) ratio was calculated from the areas of these doublets (determined by triangulation); in the case of (67), the value obtained (87%) for the abundance of the (*E*) isomer was in good agreement with that (90%) obtained by c.m.r. spectroscopy. This value was determined from the ratio of the areas of the signals assigned to C_8 (complete relaxation of the carbon atoms in (67) was achieved during the acquisition of the c.m.r. spectrum and the carbon atoms did not receive nuclear overhauser enhancement). Unfortunately, (*E*) and (*Z*) isomers could not be separated by g.l.c. or t.l.c.

1.3 CYCLOADDITION REACTIONS OF 7-METHYLENECYCLOOCTA-1,3,5-TRIENE

Tetracyanoethylene (21) reacts rapidly with 7-methylenecycloocta-1,3,5-triene (64) in ethyl acetate at room temperature to give two adducts (95) (43%) and (96) (11%).[36] Polymeric material derived from (64)* was also obtained and it was assumed that consumption of (64) by this side reaction prevented the achievement of a higher yield of adducts.



(95) (95)



(96)

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*7-Methylenecycloocta-1,3,5-triene even polymerizes appreciably in dilute ether solutions kept at -15° for 12 h.

The structures (95) and (96) were assigned to the adducts, which were separated by high performance liquid chromatography (h.p.l.c.), on the basis of their spectral characteristics. The $\pi 8 + \pi 2$ adduct (95), which will be referred to as a "1,7'" type (see page 20), exhibited in its p.m.r. spectrum (Figure 1) a broad, complex signal between δ 6.4 and 5.9 (due to five protons) and singlets at δ 3.73 and 3.15 (due to one and two protons, respectively). The singlet at δ 3.15 obscured the low field "wings" of an ABX system in which the AB part was centred at δ 3.12 and 2.20 (2H). Protons H_2, H_3, H_4, H_5 and H_6 were assigned to the broad lowest field signal while the singlets at δ 3.73 and 3.15 were assigned to H_7, H_{10} and H_{10}'. It was assumed that H_{10}, H_{10}', H_7 and H_{11}', whose resonances were found at fields lower than is usual for alicyclic and allylic protons, were deshielded by the nitrile groups.[67] Partial ring flipping of the flexible bicyclo[5,3,1]undecane skeleton (of (95)), which was shown by molecular models to contain a six membered ring in a chair conformation, is invoked to explain the degeneracy of H_{10} and H_{10}'. Protons H_{11} and H_{11}' were assigned to the ABX system centred at δ 3.12 and 2.20. There is a slight difference between the values (2.5 Hz and 3 Hz) of the $J_{11'7}$ and $J_{11,7}$ coupling constants and it was assumed, after an examination of molecular models, that a 1,3 diaxial interaction between H_{11}' and a nitrile group attached to C_8 decreased the dihedral angle between H_7 and H_{11}' compared to the corresponding angle in cyclohexane. Therefore, because the dihedral angles between H_{11}, H_{11}' and H_7 are not equal, $J_{11',7}$ is not expected to equal $J_{11,7}$. For

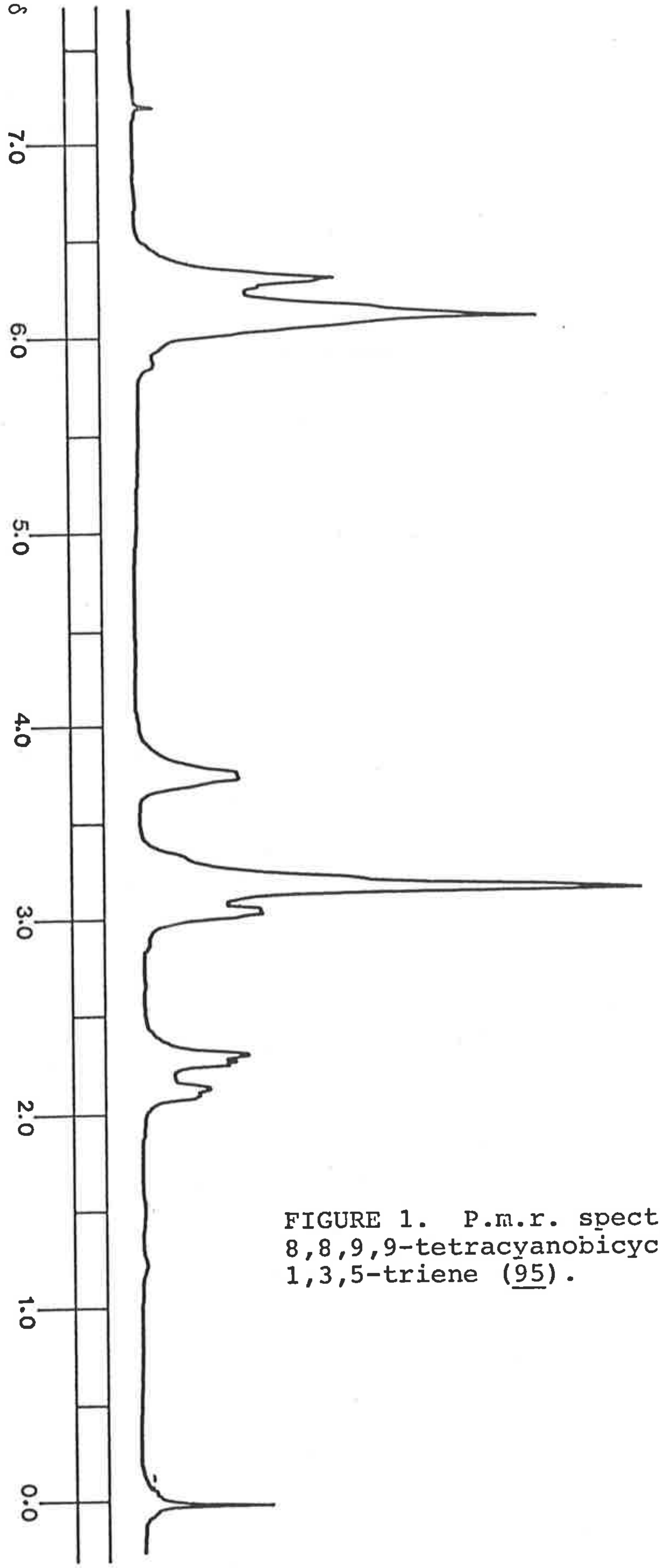


FIGURE 1. P.m.r. spectrum (80 MHz) of 8,8,9,9-tetracyanobicyclo[5,3,1]undeca-1,3,5-triene (95).

other "1,7'" adducts, especially those bearing substituents on C_{10} (see Sections 1.5 - 1.8), larger differences between the magnitude of $J_{11',7}$ and $J_{11,7}$ are observed. The c.m.r. spectrum of (95) contained six signals in the region (δ 110 - 150) where SP^2 carbon atoms might be expected to resonate[68] and three in the region (δ 10 - 50) expected[68] for SP^3 carbon atoms; importantly, all these signals were characterized by multiplicities expected for structure (95) (see Experimental section). Under the conditions which were used to obtain c.m.r. spectra, signals due to quaternary atoms bearing nitrile substituents and the nitrile groups themselves were not detected. It is important to note that the p.m.r. spectral characteristics of (95) closely resemble those obtained for (59) by Lagowski[69] (the structure (59) was confirmed by x-ray crystallography).[38] The electronic spectrum of (95), in ethanol, contained a strong absorption at 218 nm ($\varepsilon = 3.1 \times 10^3$) and a shoulder at 257 nm; this spectrum is somewhat similar to that of cycloocta-1,3,5-triene (29) (λ_{max} 265 nm, cyclohexane).[70] From comparison of molecular models, it can be seen that these two trienes can attain similar "tub" conformations.

The p.m.r. spectrum of the minor adduct of 7-methylene-cycloocta-1,3,5-triene contained a broad signal (4H) between δ 6.5 and 5.5, a doublet (1H, J 2 Hz) at δ 3.78, an AB "quartet" centred at δ 2.95 and 2.62 and a complex envelope (3H) between δ 1.90 and 0.77. Structure (96) was assigned to this adduct with the four olefinic protons H_2, H_3, H_4 and H_5 being responsible for the lowest field signal, the doublet at δ 3.78 being attributed to H_1 and the AB system was assigned to protons H_9 and H_9'. H_1 is strongly deshielded by the α cyclopropyl ring,[71] the α double bond and the nitrile groups while H_9 and H_9' are deshielded by nitrile groups. Importantly, the chemical shifts of H_1, H_2, H_3, H_4, H_5 and H_6 are very similar to those reported by Ferber[72] for corresponding protons in (56); however, Ferber reported that H_1 was observed as a doublet of larger coupling constant (7.6 Hz). Evidence that (56), unlike (96), exists in a conformation which allows strong coupling between H_1 and H_2 is provided by the electronic spectra of these two, and model, compounds. The electronic spectrum of (96), in ethanol solutions, exhibited an absorption maximum at 258 nm ($\varepsilon = 2.9 \times 10^3$) which is very close to the values (258 nm[73] and 263 nm[74]) reported for bicyclo[5,1,0]octa-2,4-diene (97). For comparison, spectral characteristics of (96) and structurally related olefins are shown in Table 4.

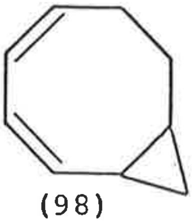
TABLE 4

Electronic Spectral Characteristics of Olefins

Olefin	Absorption Maximum Wavelength (nm)	Solvent	Refernece
(96)	258	ethanol	
(97)	258,263	ethanol	73,74
(98)	234	ethanol	75
(99)	248	isooctane	76
(100)	228	cyclohexane	77
(56)	280	ethanol	72

As can be seen from the Table, there is a considerable wavelength difference between the absorption maxima of (56) and (96) or (97). From a comparison of the absorption

(97)



(98)

(99)

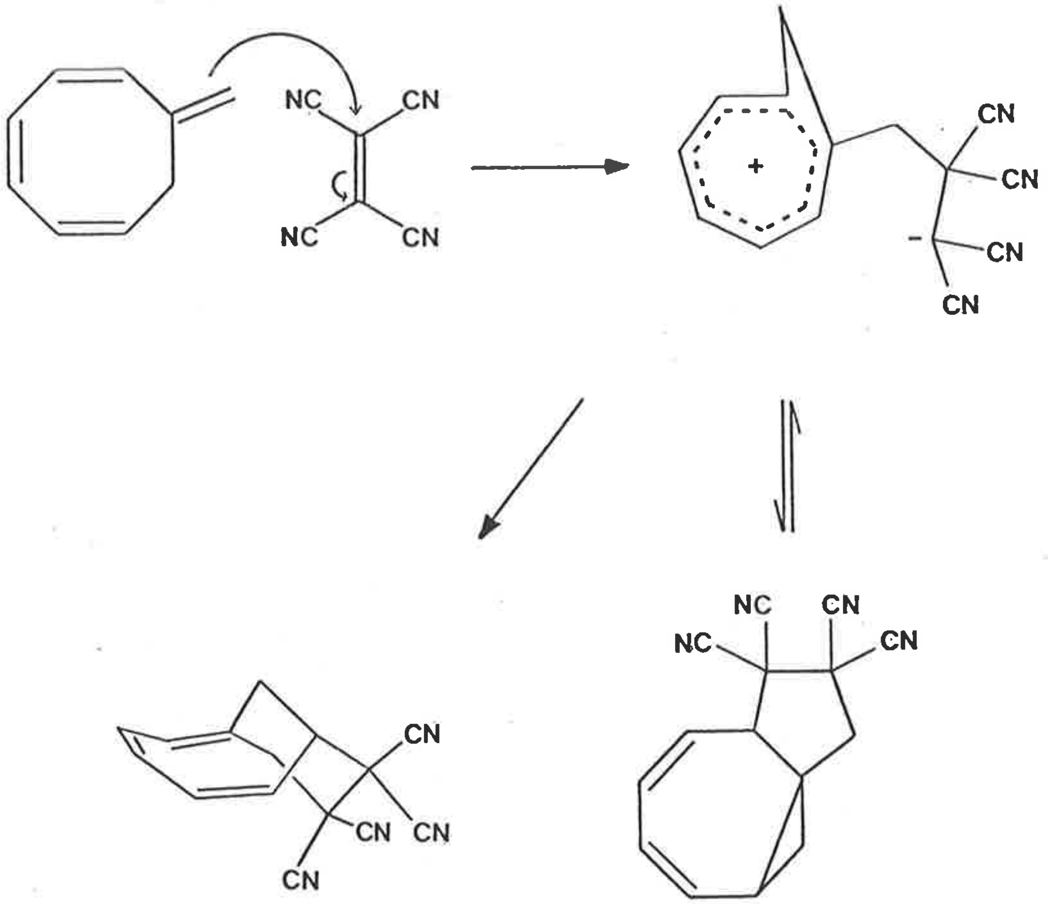
(100)

maxima wavelengths for (97) and (98), it can be seen that slightly different geometries, and therefore slightly different extents of orbital overlap, greatly affect the wavelength of the absorption maxima of the cyclopropyl-diene chromophore. It is suggested that, compared to (96) and (97), (56) enjoys considerable overlap of the diene and cyclopropyl moeities; molecular models of (56) indicate that upon achieving a high degree of orbital overlap, the dihedral angle between H_1 and H_2 approaches 0°. From Karplus' equation, it is predicted that $J_{1,2}$ for (56) should be larger than $J_{1,2}$ for (96).

Further evidence for the "conjugated" diene-cyclopropyl system was provided by the c.m.r. spectrum of (96) which contained: four doublets between δ 123 and 136, a triplet at 45.9, a doublet at 55.7, a singlet at 35.35, a doublet at 23.5 and a triplet at 21.0. The resonances at δ 45.9 and 55.5 exhibited ^{13}C-H coupling constants within the range expected[78] (*ca*. 130 Hz) for medium sized ring, aliphatic carbon atoms; the signals at δ 21.0 and 23.5, however, had ^{13}C-H coupling constants of 163 and 169 Hz, respectively. The low chemical shift (δ 35.35) for the quaternary carbon atom in addition to the magnitudes of these coupling constants provides strong evidence for the cyclopropyl ring.[78]

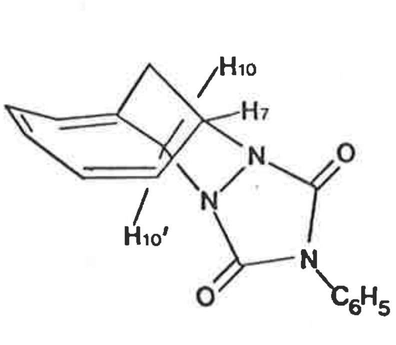
It was found that pure (96) was converted, in quantitative yield, into (95) by simply heating it in ethyl acetate at 100°C for 12 h. Consequently, the step involving charge annihilation (Scheme 34) must be reversible and the $\pi 8 + \pi 2$ adduct (95) is the product of thermodynamic control.

N-Phenyltriazolinedione (12) reacted extremely rapidly (within 1 min) with a solution of 7-methylenecycloocta-1,3,5-triene in acetone at room temperature to give a white, crystalline product (100%) which was shown by t.l.c. to be homogeneous. The p.m.r. spectrum of this adduct (Figure 2), to which was assigned structure (101), was similar to that obtained for the corresponding adduct (95). As was the case with (95), the p.m.r. spectrum of (101) contained a broad, complex signal between δ 6.0 and 6.5 (which was assigned to the five olefinic protons) and an ABX system (with the AB part centred at δ 3.06 and 2.21) which was assigned to the two methylene protons attached to the main bridge. For adduct (95), flipping of flexible bicyclic skeleton made H_{10} and H_{10}' degenerate; for (101), however, no such ring flipping is



(95) (96)

SCHEME 34



(<u>101</u>)

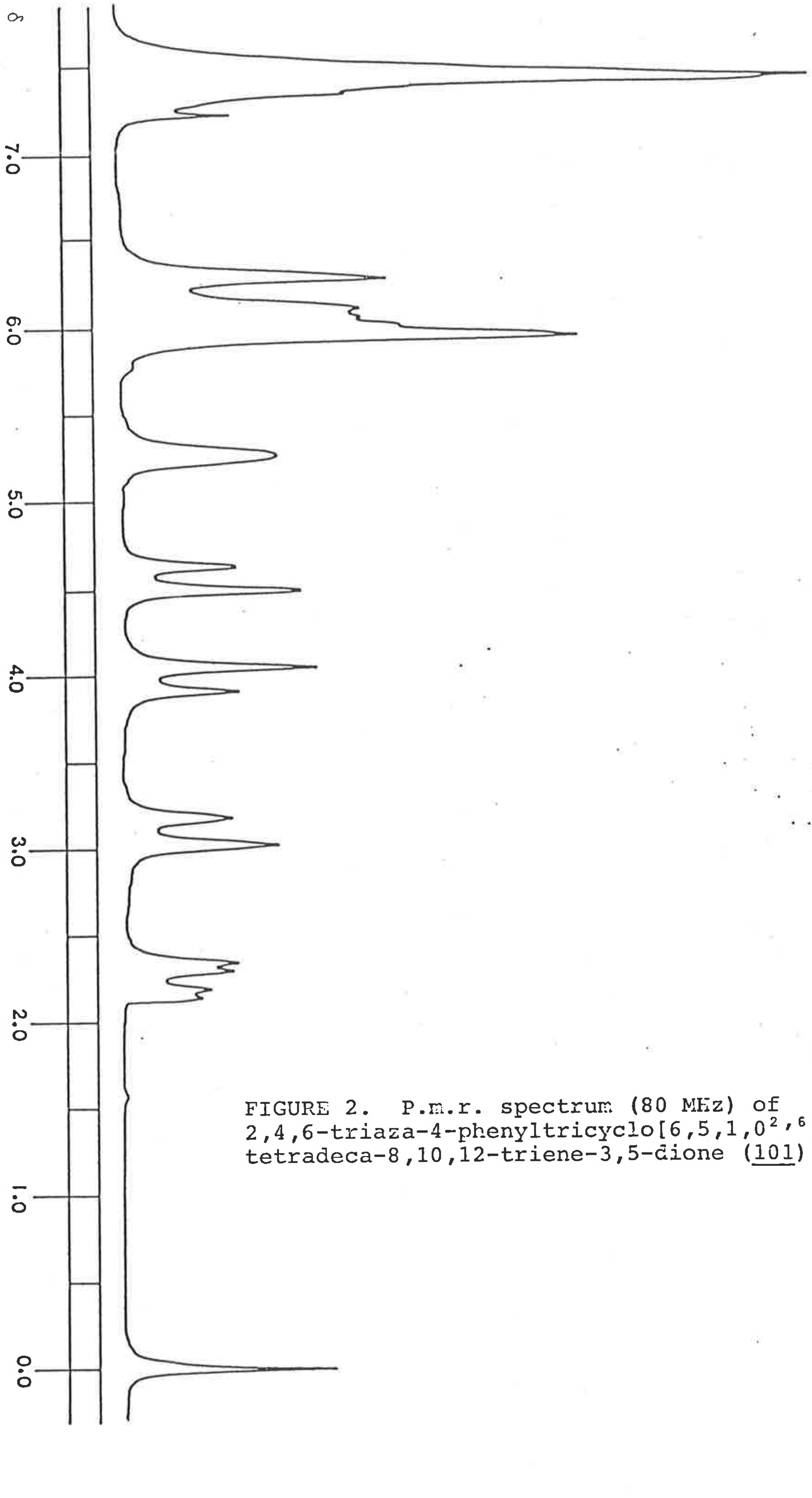
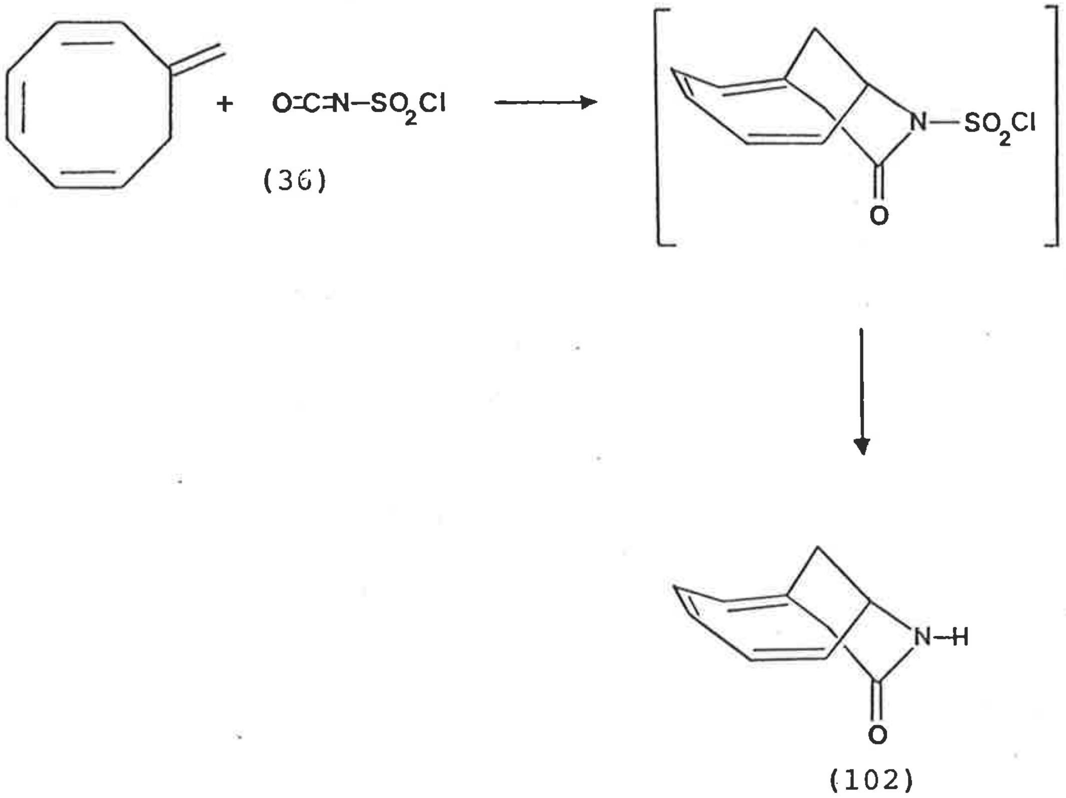


FIGURE 2. P.m.r. spectrum (80 MHz) of 2,4,6-triaza-4-phenyltricyclo[6,5,1,$0^{2,6}$] tetradeca-8,10,12-triene-3,5-dione (<u>101</u>).

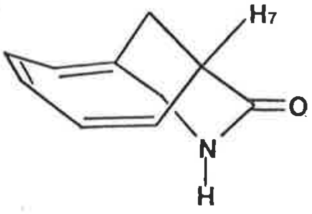
possible and as a consequence H_{10} and H_{10}' are observed as an AB quartet (centred at δ 4.53 and 3.97). Because H_{10}, H_{10}' and H_7 are attached to carbon atoms bearing nitrogen, their signals are detected at a frequency much higher than the signals assigned to corresponding protons of adduct (95). Electronic, infra-red, c.m.r. and mass spectral characteristics (see Experimental) for this adduct are consistent with the assigned structure.

The reaction between chlorosulphonylisocyanate (36) and 7-methylenecycloocta-1,3,5-triene at room temperature yielded a product which gave, on treatment with an alkaline (pH 8) solution of sodium bisulphite at room temperature,[79] the lactam (102) (29%) as the only product (t.l.c.) (Scheme 35).



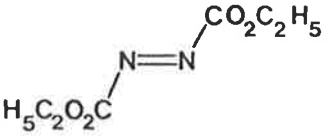
SCHEME 35

Infra-red spectral characteristics (ν_{max} 3431 cm^{-1} and 1658) and the presence of an exchangeable (D_2O) signal in the p.m.r. spectrum of this adduct confirmed that cycloaddition had occurred with the carbon and nitrogen atoms (and not the carbon and oxygen atoms) of the isocyanate moeity. As was the case with (101) and (95), the p.m.r. spectrum of (102) contained a broad signal between δ 6.1 and 5.5 (5H) and an ABX system (2H, J_{AB} 10 Hz) with the AB part centred at δ 3.20 and 2.22. In addition, the p.m.r. spectrum contained a singlet (2H) at δ 3.08 and a singlet (1H) at δ 4.32; these signals confirm the assignment of structure (102) to the adduct. In the p.m.r. spectrum of the isomeric adduct (103), the singlet due to H_7 is expected to be found at a frequency much lower than δ 4.32.[80]

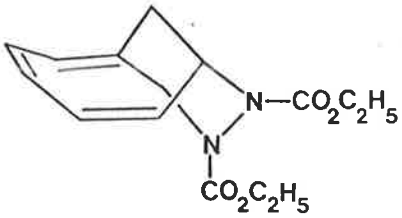


(103)

Diethyl azodicarboxylate (104) reacted slowly with 7-methylenecycloocta-1,3,5-triene in acetone to form a mixture of two compounds (t.l.c.) in low yield (30%). The major product (20%), which was separated by h.p.l.c., was a stable, crystalline solid identified as (105) by its spectral characteristics which were very similar to those obtained for (101) (see Experimental).



(104)



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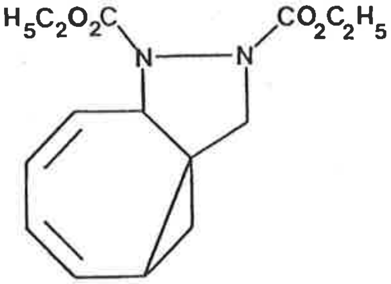

(106)

Structure (106) was tentatively assigned to the minor adduct on the basis of its p.m.r. and c.m.r. spectral properties; insufficient compound, and its instability, prevented a pure sample of (106) being obtained.* The p.m.r. spectrum contained a complex signal between δ 6.43 and 5.45 (4H), a singlet at δ 4.55 (1H), quartets at δ 4.16 and 4.13 (both 3H, J 7 Hz), AB "quartets" centred at δ 3.55 and 3.40, and 3.40 and 3.06, a triplet at δ 1.26 (6H, J 7 Hz) and a complex signal between δ 2.12 and 0.4 (3H). The c.m.r. spectrum was complex and contained doublets between δ 140

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*Chromatography of this material upon silica gel yielded various amounts of (104), (105) and (106).

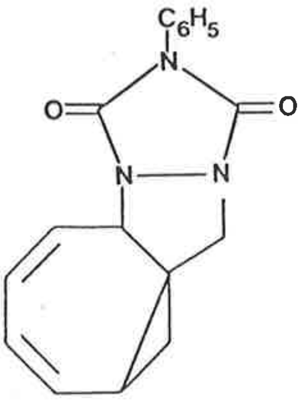
and 120, four triplets, two doublets and a singlet between δ 65 and 50, a triplet at δ 31 and a quartet at δ 14.5. The complexity of the c.m.r. and p.m.r. spectra suggest that the carbethoxy groups are attached to (<u>106</u>) in a mixture of *cis* and *trans* configurations. In addition, the c.m.r. spectrum was further complicated by signals which could be attributed to (<u>105</u>) that formed during the time required to obtain the spectrum; this latter problem could not be circumvented because 14 h of continuous data acquisition was required to obtain a spectrum.

Attempts to form adducts of 7-methylenecycloocta-1,3,5-triene with either maleic anhydride or dimethyl acetylenedicarboxylate (<u>107</u>) at room temperature or in boiling solvents failed. Low yields of unchanged starting material and large amounts of intractable material were obtained. It is suggested that polymerization of the tetraene might be occurring before reactions with these sluggish dienophiles could take place.

$$H_5C_2O_2C{-}C\equiv C{-}CO_2C_2H_5$$

(<u>107</u>)

Addition of reactive or moderately reactive dienophiles to 7-methylenecycloocta-1,3,5-triene yields adducts which are structurally related to those obtained by Ferber[36] and Lagowski;[38] it would appear from the structures of these adducts, and the rapidity of their formation, that addition of the dienophile occurs *via* homotropylium zwitterions. The more reactive dienophiles (chlorosulphonylisocyanate and N-phenyltriazolinedione)* enter into reactions with (64) from which are isolated only one type of $\pi 8 + \pi 2$ cycloadduct and it is not immediately apparent whether these reactions yield other, unstable adducts. For example (107) might be formed from the reaction between N-phenyltriazolinedione and (64) and, by analogy with other adducts of its type, might be converted rapidly and irreversibly into (101) under the reaction conditions. The exact mechanism involved in these selective reactions might remain uncertain until further work is carried out to establish whether adducts such as (107) and (108) are formed. This question might be resolved by monitoring the reaction between (64) and the dienophile at low temperature by p.m.r. spectroscopy.



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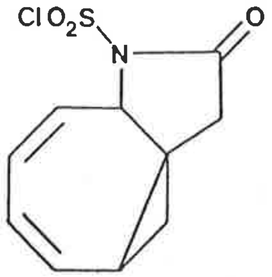

(108)

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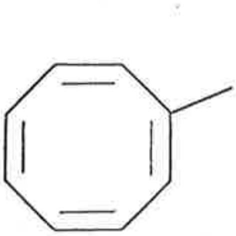
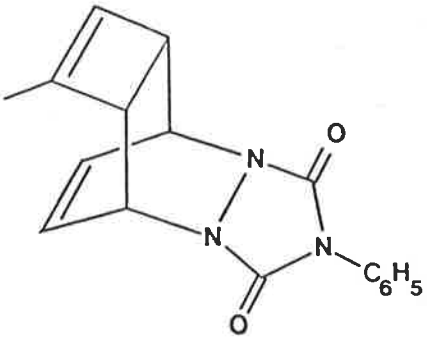
*Interestingly, Hogeveen[81] states that the rates of electrophilic cycloaddition to polyenes decreases in the order chlorosulphonylisocyanate > tetracyanoethylene > N-phenyltriazolinedione. With (64), however, the order appears to be (36) $\simeq$ (12) > (21).

From the reaction between N-phenyltriazolinedione and methylcyclooctatetraene (85), the expected adduct (110) is obtained in low yield (22%) while a large amount of high molecular weight material is produced.[22] Paquette[22] suggested

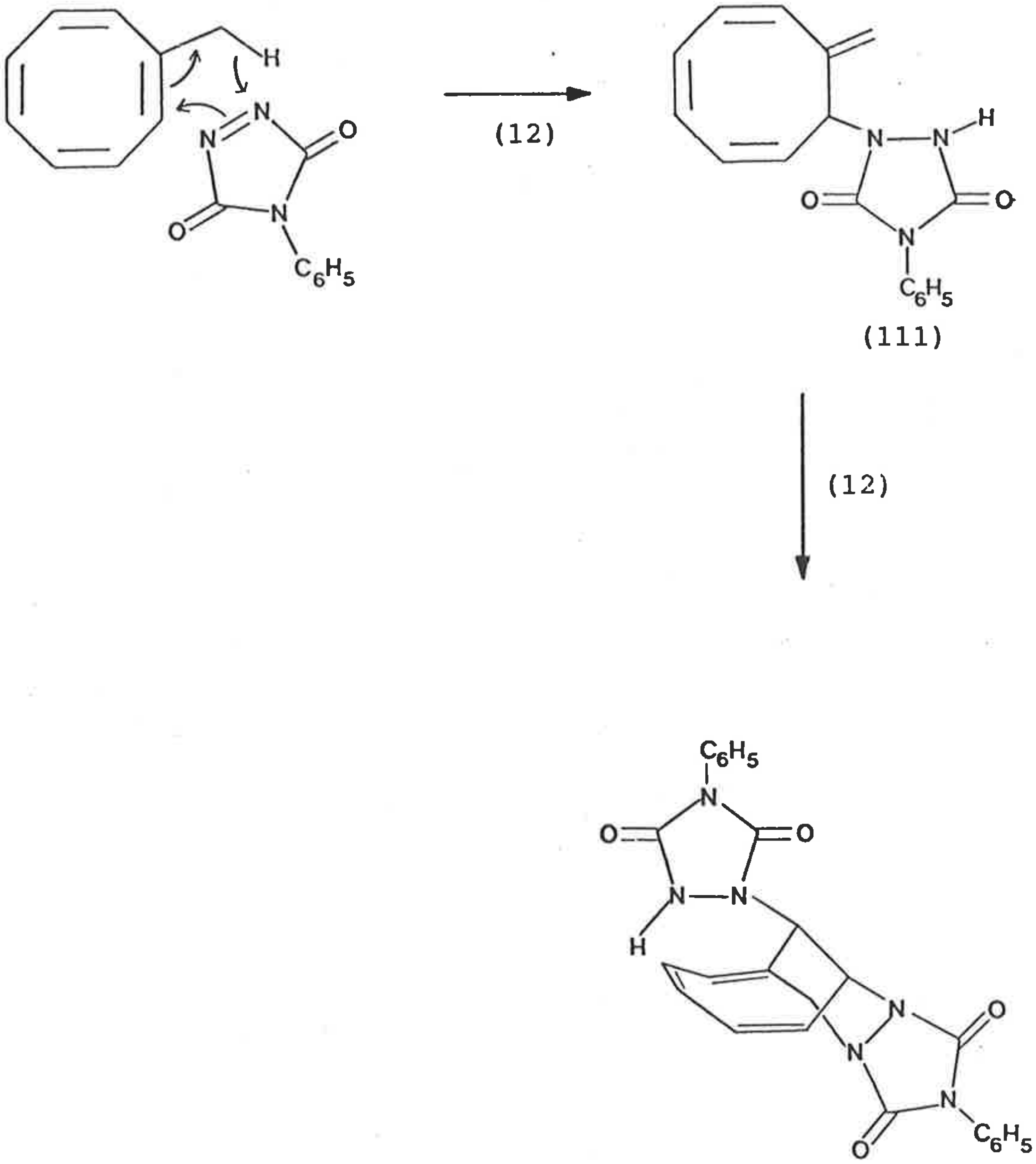


(85)



(110)

that N-phenyltriazolinedione enters into an "ene" reaction with (85) to form an adduct (111) which suffers attack by the dienophile, in an unknown manner, to yield the high molecular weight material. Bearing in mind the observed preference of 7-methylenecycloocta-1,3,5-triene to enter into $\pi 8 + \pi 2$ cycloaddition reactions, a feasible route to this high molecular weight material might involve addition of N-phenyltriazolinedione in a $\pi 8 + \pi 2$ manner to (111) (Scheme 36).



SCHEME 36.

1.4 THE CYCLOADDITION REACTIONS OF 1,3,5,7-TETRAMETHYLCYCLOOCTATETRAENE AND 7-METHYLENE-1,3,5-TRIMETHYLCYCLOOCTA-1,3,5-TRIENE

In view of the ability of 7-methylenecycloocta-1,3,5-triene (64) to form $\pi 8 + \pi 2$ adducts, it was decided to investigate the conditions under which the related $\pi 8 + \pi 2$ adduct (59), described previously by Lagowski[38] (see page 19), is formed. In dioxane/ether solutions, Lagowski reported that tetracyanoethylene reacted rapidly with a mixture of 1,3,5,7-tetramethylcyclooctatetraene (57), other tetramers of propyne and trimer of propyne at room temperature to form a mixture containing (59), unchanged tetramers and an adduct of the trimer. Significantly, p.m.r. and c.m.r. spectroscopy indicated that only 1,3,5,7-tetramethylcyclooctatetraene and the trimer had been consumed by tetracyanoethylene. Lagowski proposed that tetracyanoethylene radical anions converted (57) into 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (58) which entered into a $\pi 8 + \pi 2$ cycloaddition reaction with tetracyanoethylene to form (59) (Scheme 12).

Lagowski's proposal was tested by treating pure (57), which was prepared by the pyrolysis of photodimers of 1,4-dimethylpyrone[82] as described by De Mayo,*[83] with tetracyanoethylene. Even after two weeks at room temperature, tetracyanoethylene did not produce any adducts with (57) in ether-dioxane solutions. Cycloaddition of tetracyanoethylene to (57) was, however, achieved in boiling ethyl

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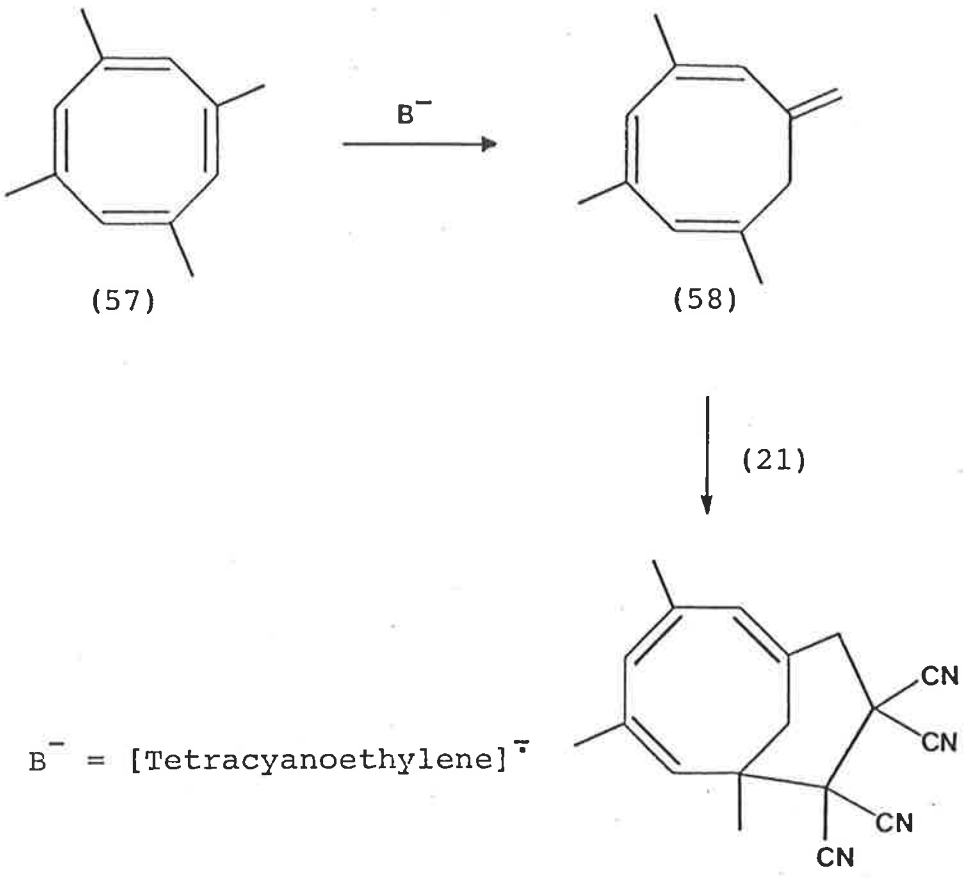
* Contrary to the findings of Maier,[84] the p.m.r. spectrum of the material obtained from the pyrolysis did not indicate that 1,2,4,7-tetramethylcyclooctatetraene[85] had been formed.

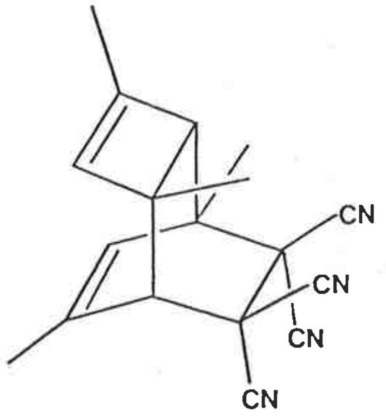


B⁻ = [Tetracyanoethylene]$^{\overset{\cdot}{-}}$

(59)

SCHEME 12

acetate; in addition to the $\pi 8 + \pi 2$ adduct (59) (10%), the Diels-Alder adduct (112) (90%) was obtained. In agreement with the findings of Criegee,[85] who showed that tetramethylcyclooctatetraenes reluctantly enter into Diels-Alder reactions with tetracyanoethylene at room temperature, adduct (112) was not obtained from the reaction between (57) and (21) in ethyl acetate at room temperature. Under these conditions, the $\pi 8 + \pi 2$ adduct (59) (5%), was the sole product.

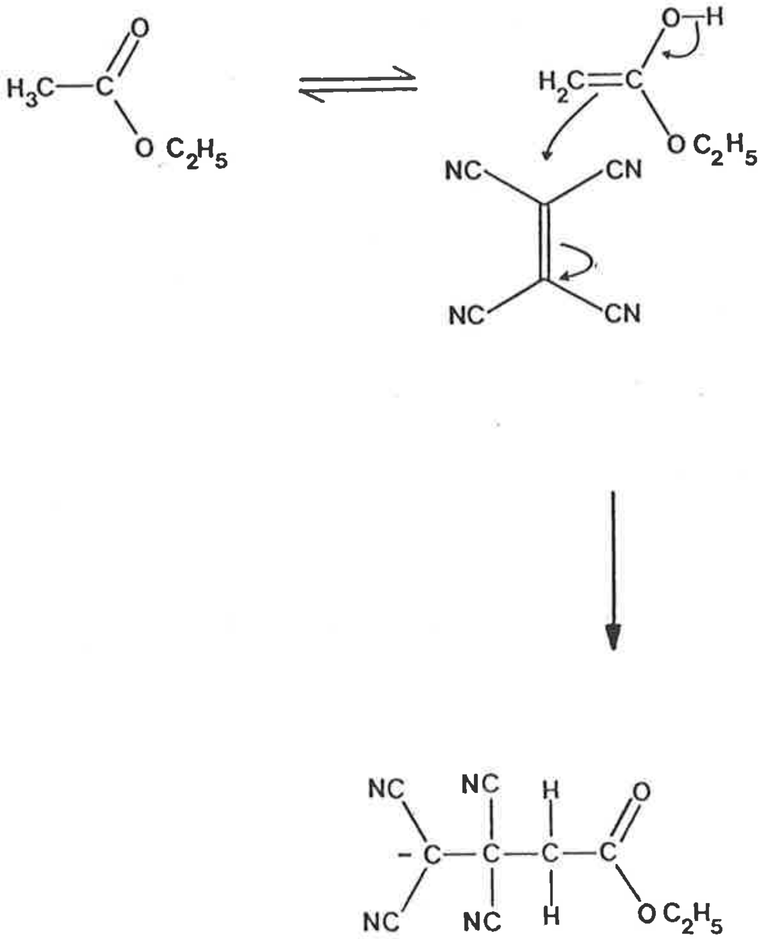


(112)

To confirm that (58) is indeed a precursor to (59), (58) was prepared and treated with tetracyanoethylene. It was found that potassium t-butoxide was capable of converting (57) into (58) in boiling tetrahydrofuran; under these conditions, a mixture containing (57) (58% by p.m.r. spectroscopy) and (58) (42%) was obtained (cf. Table 3, page 35). When this mixture, in ethyl acetate, was treated with tetracyanoethylene, a quantitative yield (based upon the amount of (58)) of (59) and unchanged (57) (95%) were obtained after 15 min.

Clearly, in ether-dioxane solutions at least, tetracyanoethylene alone cannot convert (57) into (58); moreover, the formation of (59) is contingent on this isomerization. Lagowski[69] has subsequently suggested that the agent responsible for the isomerization of (57) into (58) in his experiments might have been a zwitterion (for which no structure was suggested) formed by the electrophilic attack on the trimer by tetracyanoethylene.

The formation of (59) from (57) in ethyl acetate is intriguing. Tetracyanoethylene is known to form charge transfer complexes and zwitterions with enol ethers;[86,87] perhaps tetracyanoethylene reacts with the enol tautomer of ethyl acetate to form the anion (113) which acts to convert (57) into (58) (Scheme 37).



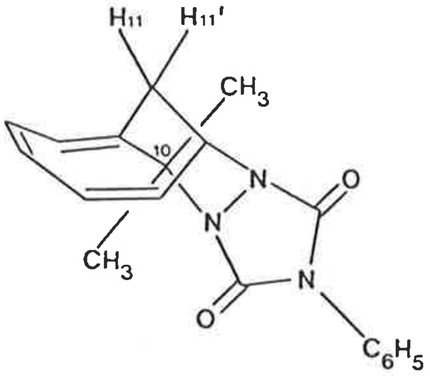
(113)

SCHEME 37

1.5 REACTION OF 7-ISOPROPYLIDENECYCLOOCTA-1,3,5-TRIENE WITH N-PHENYLTRIAZOLINEDIONE

Upon treatment with potassium t-butoxide, a solution of isopropylcyclooctatetraene (86) in anhydrous, de-gassed dimethylsulphoxide yielded a complex mixture of olefins containing 7-isopropylidenecycloocta-1,3,5-triene (65) (*ca.* 27%) (g.l.c.).* This mixture was allowed to react with N-phenyltriazolinedione (12) and the consumption of (65) was followed by g.l.c. From this reaction, an adduct was formed very rapidly and in a quantitative yield (based on the amount of (65) calculated from the g.l.c. trace of the olefin mixture). Isopropylcyclooctatetraene and other compounds in the reaction mixture were not observed to react with the triazolinedione (g.l.c.).

Based on its spectral characteristics, which were very similar to those obtained for (101), structure (114) was assigned to the adduct. Its p.m.r. spectrum contains a



(114)

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* See page 35 for a discussion relating to this conversion.

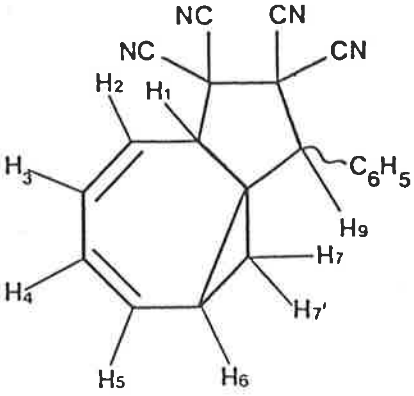
signal between δ 7.2 and 7.5 (5H), a signal between δ 5.88 and 6.13 (5H), a broad singlet at δ 5.0 (1H) and an ABX system with the AB part centred at δ 2.69 and 2.88 (2H); as is to be expected, the spectrum of (114) contained two singlets (each 3H) which were attributed to the two methyl groups and did not contain signals corresponding to H_{10} and H_{10}' of (101). Compared to the signal ascribed to H_{11}' in (101), that for H_{11}' in (114) suffered a paramagnetic shift. Since it is known that compression of a proton leads to it being deshielded,[80] it was assumed that a 1,3-diaxial interaction between H_{11}' and the methyl group attached to C_{10} in (114) was responsible for the observed shift.

C.m.r. and electronic spectral characteristics of the adduct are consistent with the assigned structure and also are very similar to those recorded for (101) (see Experimental).

1.6 REACTION OF 7-BENZYLIDENECYCLOOCTA-1,3,5-TRIENE WITH TETRACYANOETHYLENE

When a mixture of (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-triene (66), containing 66% of the (*E*)-isomer (p.m.r. spectroscopy), was treated with tetracyanoethylene in boiling ethyl acetate, a mixture (t.l.c.) of four compounds (94%) was obtained. Through h.p.l.c., this mixture was separated into three fractions.

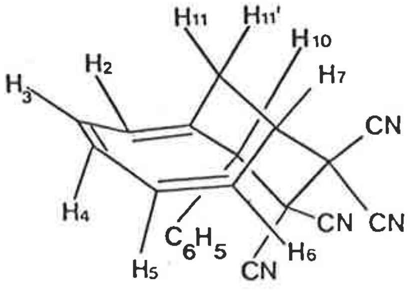
(1) The fraction of shortest retention time (comprising 14% of the mixture) contained an adduct which was identified as (115) on the basis of its p.m.r., c.m.r. and electronic spectral characteristics. Signals due to H_1, H_2, H_3, H_4, H_5, H_6, H_7 and H_7' in (115) were found at chemical shifts similar to those for the corresponding protons in (96); as is to be expected, H_9 in (115) was found as a singlet at a field lower than either H_9 or H_9' in (96). Compared to the doublets observed for (56) and (96),



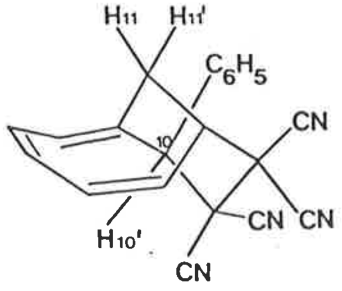
(115)

H_1 in (115) was observed as a broadened singlet; the dependency of the magnitude of the $J_{1,2}$ coupling constant on the conformation of the bicyclo[5,3,1]octa-2,4-dienyl skeleton has been discussed previously. Both the c.m.r. and electronic spectra are consistent with the assigned structure. The absence of additional signals in the p.m.r. and c.m.r. spectra of (115) suggested that a single diastereomer might have been obtained; the exact stereochemistry was, however, not deduced.

(2) The second fraction, which amounted to 68% of the adduct mixture, consisted of a 1:1 mixture of the two epimeric $\pi 8 + \pi 2$ adducts (116) and (117). An epimerically pure adduct (116) was separated from the mixture by



(116)



(117)

fractional crystallization. Its p.m.r. spectrum (Figure 3) showed the presence of five aromatic (δ 7.53) and five olefinic hydrogen atoms (δ 6.21). The broad singlets at δ 4.25 and 3.88, each of which corresponded to one proton, were assigned to H_{10} and H_7 while the complex ABX system (J_{AB} 13.8 Hz) with the AB part centred at δ 3.34 and 2.46 was assigned to H_{11}

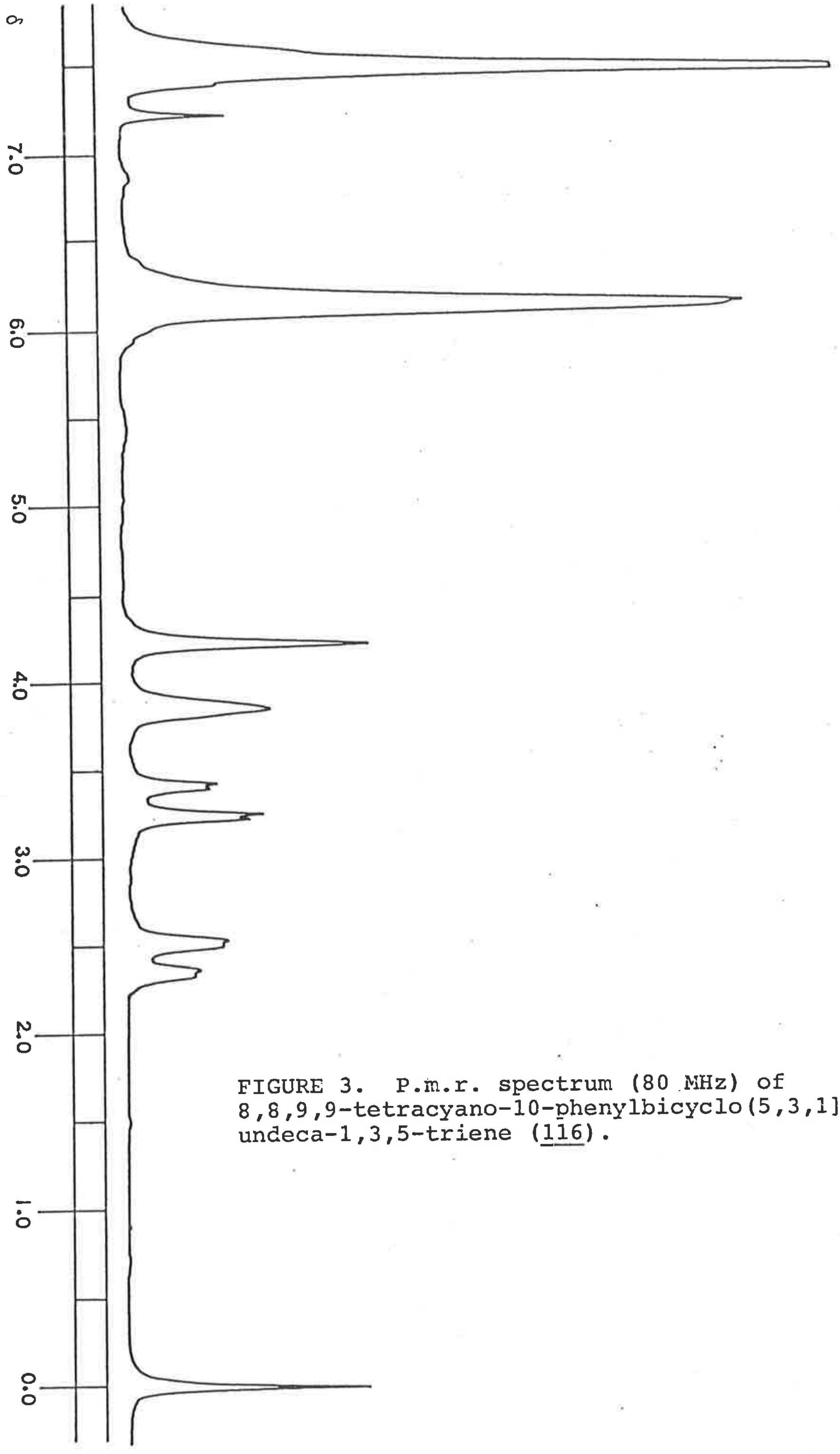


FIGURE 3. P.m.r. spectrum (80 MHz) of 8,8,9,9-tetracyano-10-phenylbicyclo(5,3,1]-undeca-1,3,5-triene (116).

and H_{11}'. As can be seen from Figure 4, the p.m.r. spectrum of (116) closely resembles that of (95); as is to be expected, replacement of H_{10}' in (95) by a phenyl group resulted in a paramagnetic shift in the frequency of H_{10}.

The assignment of structure (116) to the epimerically pure adduct was based primarily on these p.m.r. spectral characteristics. In addition to the signals mentioned, the p.m.r. spectrum of a mixture of (117) and (116) contained a singlet at δ 4.70 and an ABX system (J_{AB} 14 Hz) with the AB part centred at δ 3.05 and 2.91. From molecular models, it was determined that H_{10}' was in an "equatorial" environment with respect to the six membered ring of (117) and was, therefore, in close proximity to two nitrile groups. From a molecular model of (116), it was seen that H_{10} was in an "axial" environment and was affected by only one nitrile group; therefore the singlet at δ 4.70 was assigned to (117) and the singlet at δ 4.25 was assigned to (116). Previously (page 63) it was noted that H_{11}' in (114) was deshielded by a Van Der Waals interaction with the methyl group attached to C_{10}; as a consequence, the AB part of the ABX system due to H_{11} and H_{11}' in (114) was much "narrower" than the corresponding system for (101). From molecular models of (117) it was determined that H_{11}' interacts with the phenyl group attached to C_{10}; therefore, by analogy, the "narrow" AB part of the ABX system (centred at δ 3.05 and 2.91) was assigned to (117) and the "wide" system (centred at δ 3.34 and 2.46) to (116). As is to be expected, compared to that present in the p.m.r. spectrum of (117), the AB part of the ABX system due to H_{11} and H_{11}' in (95) more closely resembles that assigned to H_{11} and H_{11}' in (116).

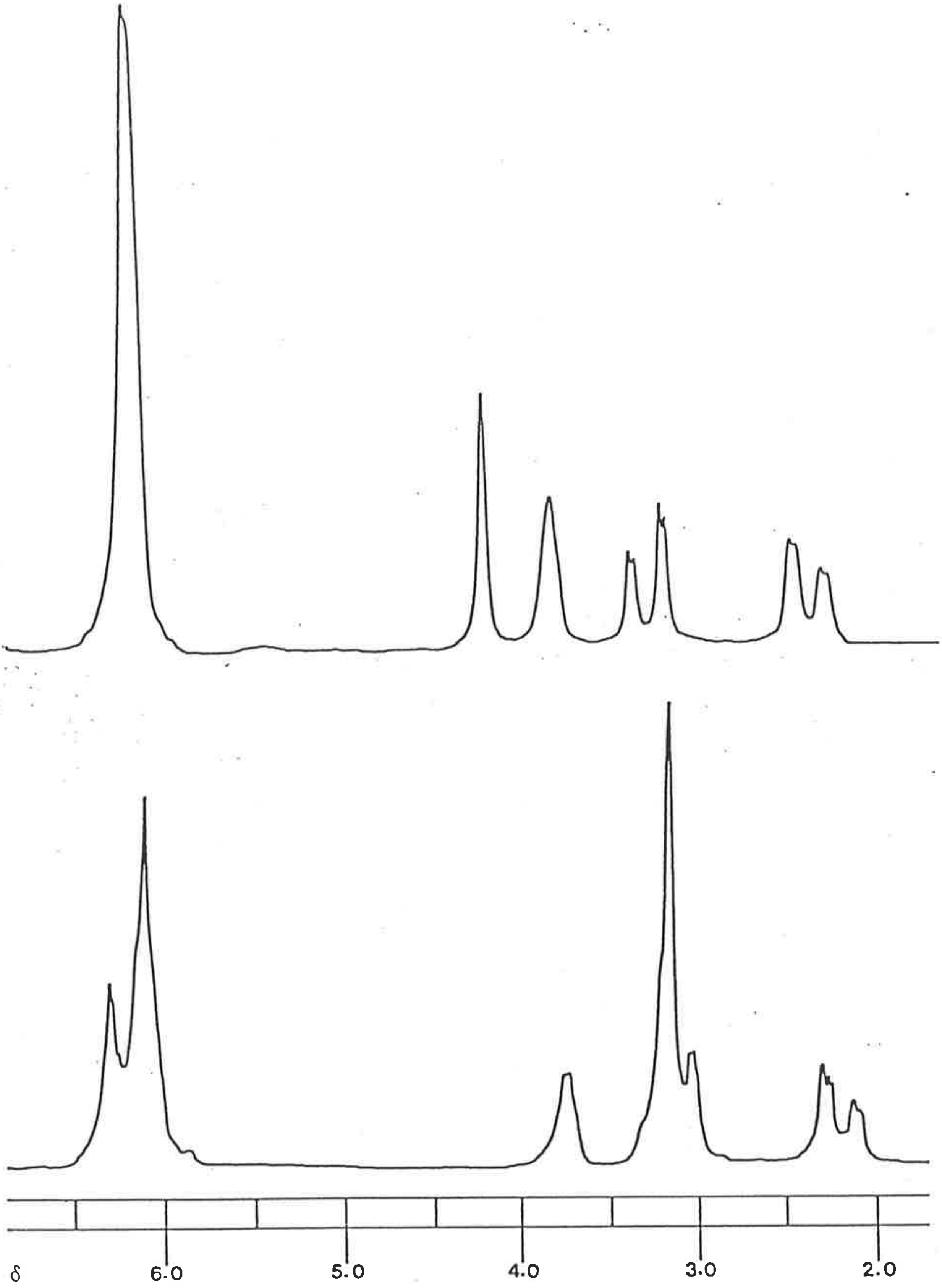
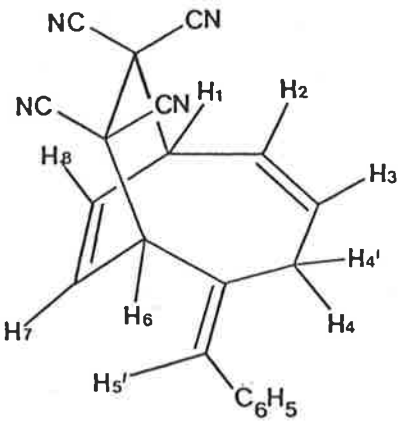


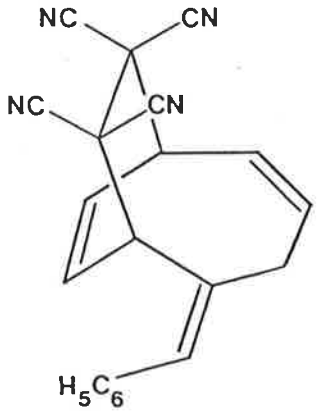
FIGURE 4. P.m.r. spectral characteristics (80 MHz) of 8,8,9,9-tetracyano-10-phenylbicyclo[5,3,1]undeca-1,3,5-triene (<u>116</u>) (top) and 8,8,9,9-tetracyanobicyclo[5,3,1]undeca-1,3,5-triene (<u>95</u>) (bottom).

C.m.r. and electronic spectral characteristics of (116) and (117) are similar to those obtained for (95) (see Experimental).

(3) The fraction of longest retention time yielded an adduct (17%), which, on the basis of its p.m.r., c.m.r. and electronic spectral characteristics, was identified as (118). Under the reaction conditions (118) is not converted into any of the $\pi8+\pi2$ adducts; in addition, the sharp melting point of (118) and its p.m.r. and c.m.r. spectral characteristics indicated that it was not contaminated with (119).



(118)



(119)

The p.m.r. spectrum of (118) (Figure 5) contains a signal at δ 7.33 (5H) due to the aromatic protons, a singlet at δ 6.89 (which was assigned to H_5') and a very complex signal between δ 6.56 and 5.7 (4H). This signal was assigned to H_7 and H_8, which were observed as a complex multiplet, and H_2 and H_3 which were observed as the very complex "AB system" centred at δ 6.24 and 5.81 (the low field "wings" are

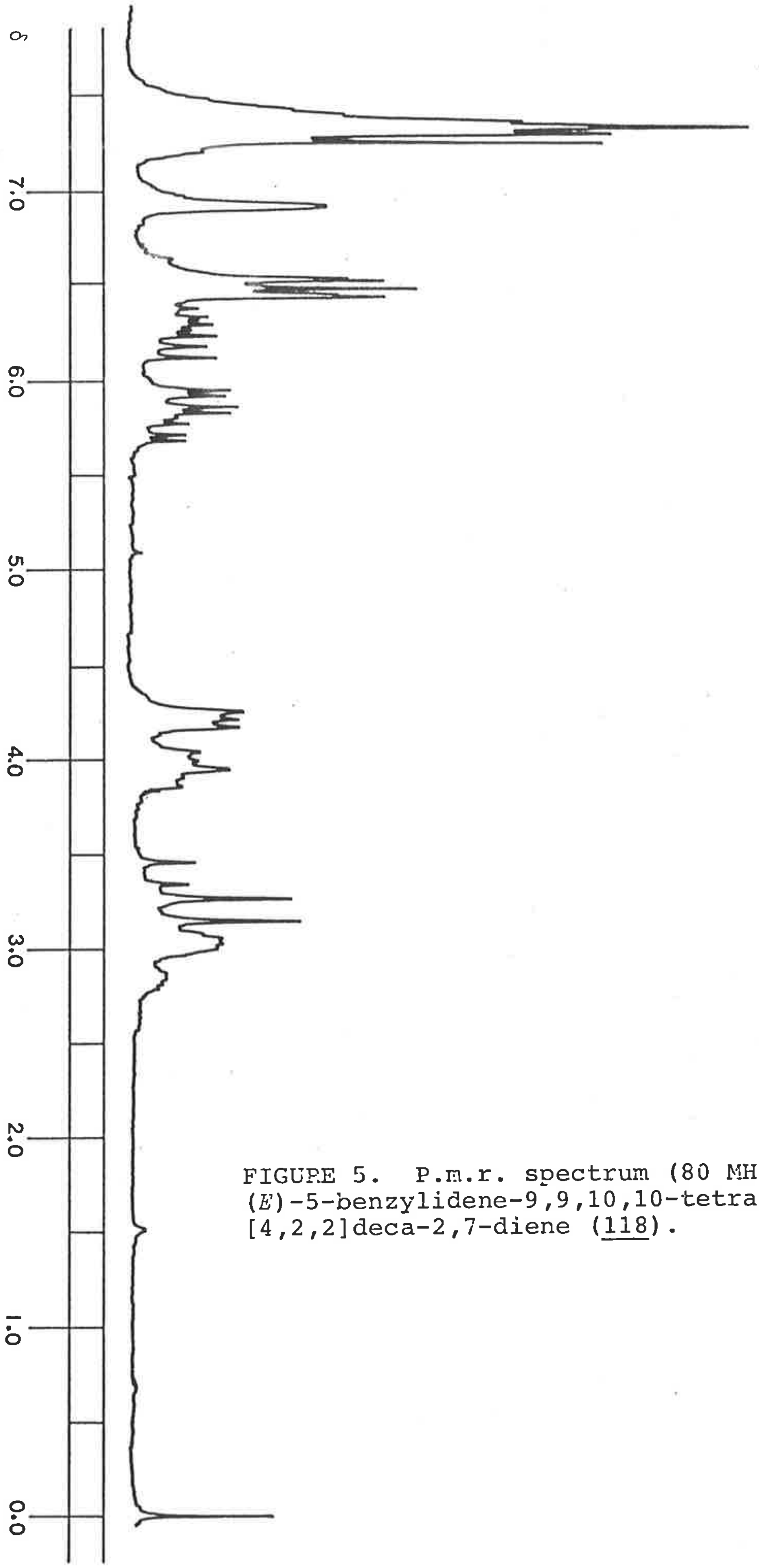
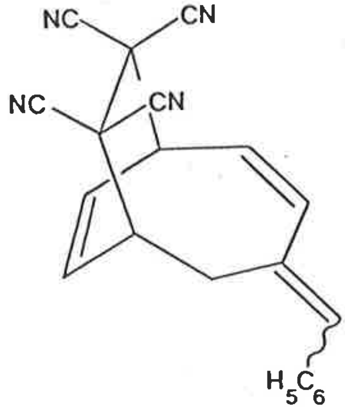


FIGURE 5. P.m.r. spectrum (80 MHz) of (*E*)-5-benzylidene-9,9,10,10-tetracyanobicyclo-[4,2,2]deca-2,7-diene (118).

partially obscured by the multiplet due to H_7 and H_8). H_1 and H_6 were found, as complex multiplets, at δ 4.21 and 3.91, respectively, while H_4 and H_4' gave rise to the very complex "AB system" centred at δ 3.27 and 2.96. Double irradiation of the alicyclic protons H_4 and H_4' revealed that they are not coupled to H_1 or H_6. Of the three possible structures containing five olefinic and four aliphatic hydrogen atoms, (<u>118</u>), (<u>119</u>) and (<u>120</u>), the latter must be ruled out because it contains contiguous SP^3 carbon atoms. Moreover, the small difference between the chemical shifts of H_1 and H_6 suggests that (<u>118</u>), and not (<u>119</u>), was obtained. In section 1.9, an adduct similar to (<u>118</u>) is discussed; for this adduct,



(120)

which contains a (Z)-phenyl group, the signals due to protons analogous to H_1 and H_6 are separated by approximately δ 0.7.

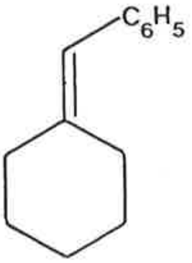
The c.m.r. spectrum of (<u>118</u>) was complex in the region between δ 130 and 128 but three signals, characterized by the multiplicities expected for (<u>118</u>) were present between δ 52 and 26 (see Experimental).

Further evidence for structure (118) was provided by electronic spectroscopy. The spectral characteristics of (118) closely resemble those reported for some structurally related derivatives of styrene (Table 5); again, structure (120) can be ruled out because its electronic spectrum should resemble that of phenylbutadiene to some extent.

TABLE 5

Electronic spectral characteristics of (118) and some structurally related olefins

Olefin	λ_{max} (nM)	Solvent	Reference
(118)	249	ethanol	
styrene	245	ethanol	88
β,β-dimethyl-styrene	245	isooctane	89
(121)	*ca.* 245	cyclohexane	90
phenylbutadiene	306	isooctane	88

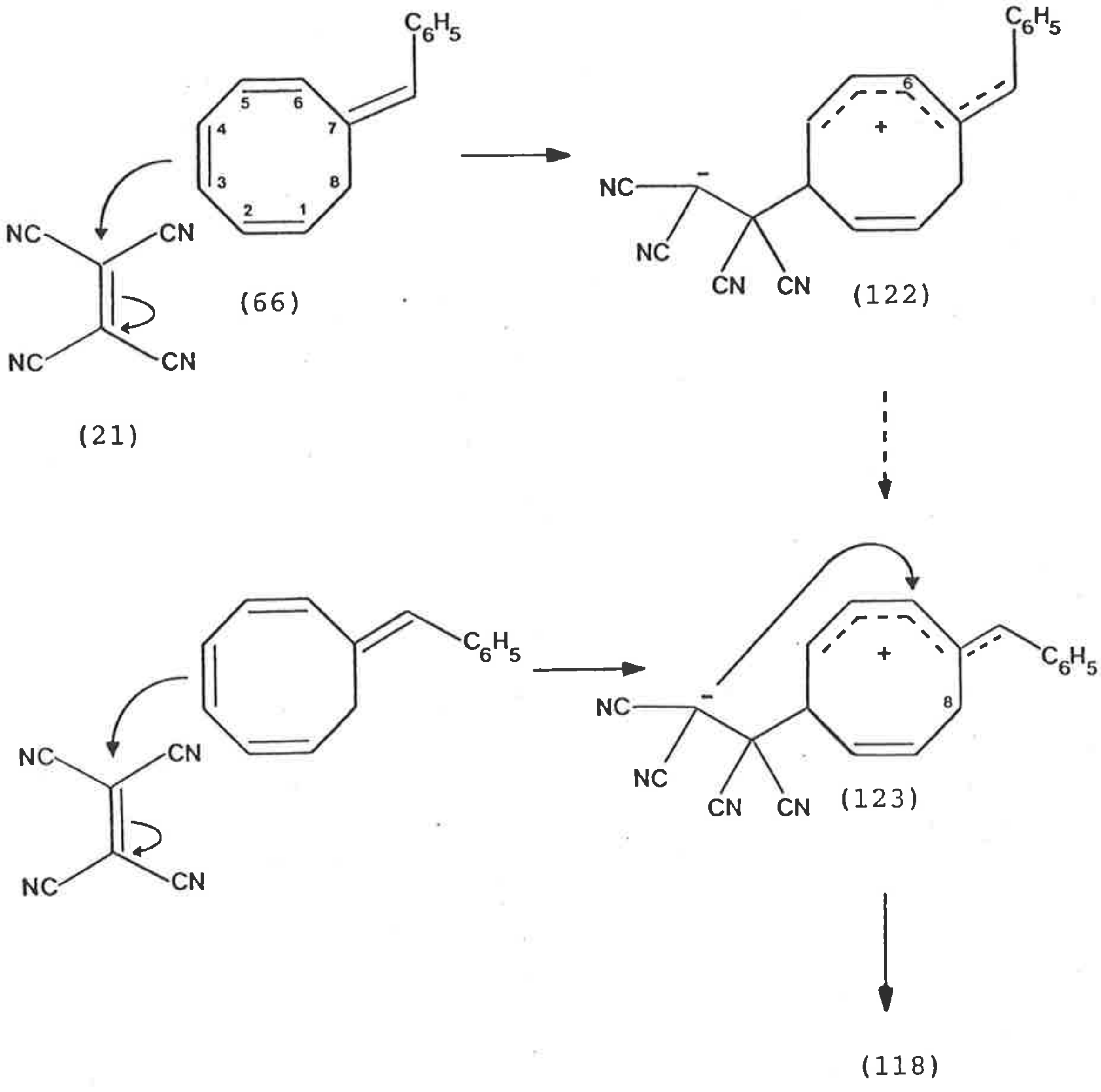


(121)

To account for the formation of (118), two mechanisms can be considered.

(1) A stepwise mechanism:

The addition of tetracyanoethylene to (66) might proceed *via* zwitterionic intermediates (122) and (123) (Scheme 38); the formation of (118) to the exclusion of (119) implies, however, that only (123) undergoes charge annihilation. It is possible to show, with molecular models, that the



SCHEME 38

configuration (122) is of higher energy than (123) because unfavourable steric interactions between the aryl moeity and the hydrogen atom attached to C_6 prevent the aryl and pentadienyl moeities from achieving coplanarity. In configuration (123), however, extensive overlap between the aryl and pentadienyl fragments is possible because C_8 and its hydrogen atoms lie above the plane containing the carbon atoms $C_3 - C_7$' and the aryl group. On the basis of the information obtained from the reaction between (66) and tetracyanoethylene, it is not possible to decide whether (122) undergoes bond rotation to give (123) or reverts to starting material.

Tetracyanoethylene might form a π complex with the aryl moeity in (66).*[91] If the complex formed with (*E*)-(66) adopts a conformation similar to that depicted in Figure 6, then tetracyanoethylene is close to the $C_3 - C_4$ double bond and might, therefore, be favourably disposed to react with it. In the corresponding complex derived from (*Z*)-(66), tetracyanoethylene is not as close to the $C_3 - C_4$ double bond; it is therefore reasonable to propose that, in addition to being more stable than (122), the zwitterion (123) might be formed more rapidly than it.

It is important to note that the 7-alkylidenecycloocta-1,3,5-trienes (48), (49), (58) and (64) cannot produce stabilized pentadienyl cations analogous to (122) or (123). Therefore these olefins are not expected to yield adducts

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* Immediately on treatment with tetracyanoethylene, solutions of the olefins (48),[72] (49),[72] (64), (66), (67), (68) and (69) became highly coloured; the intensity of these colours faded as the adducts were produced (see Experimental).

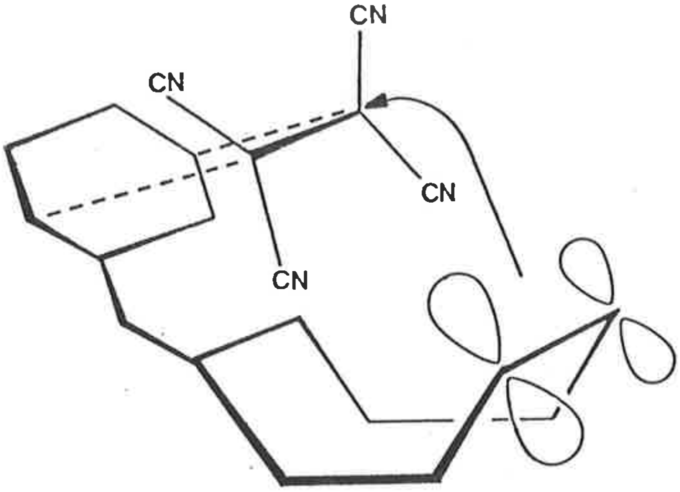
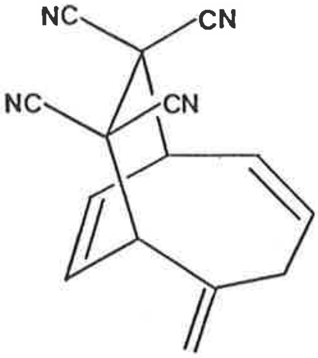


FIGURE 6

analogous to (118) with tetracyanoethylene; significantly, no such adducts have been found.

(2) A concerted $\pi 4 + \pi 2$ mechanism can also account for the formation of (118). In order to enter into a concerted reaction, the "tub" shaped ring of (66) must at least partially flatten to achieve adequate overlap of the appropriate diene segment. Because concerted 1,4 additions to cyclooctatetraene proceed very slowly and are inefficient,[14] it is reasonable to assume that such additions to (66) might also be slow. It is unlikely that this process could compete with the rapid $\pi 8 + \pi 2$ cycloadditions even to the extent indicated by the yield of (118). Moreover, if (66) were able to achieve some degree of planarity, then "1,4" and "3,6" (for an explanation of the terminology, see page 20) additions should occur and mixtures of (118), (119) and (120) should be formed. Since (64) should attain planarity with

at least the same ease as (66), adducts such as (124) and (125) should have been formed by the action of tetracyanoethylene on (64).



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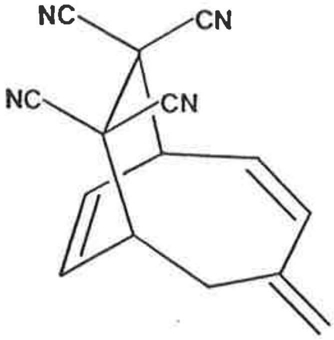
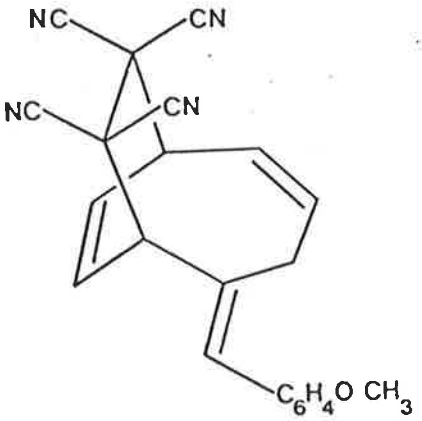


(125)

The "3,6" adduct (118) is, therefore, thought to be formed by the non-concerted pathway.

1.7 THE CYCLOADDITION REACTIONS OF 7-(*p*-METHOXYBENZYLIDENE)-CYCLOOCTA-1,3,5-TRIENE

In boiling ethyl acetate, tetracyanoethylene reacted with a mixture of (*E*)-(77%) and (*Z*)-7-(*p*-methoxybenzylidene)-cycloocta-1,3,5-triene (67) to give a mixture of three compounds (65%). Through h.p.l.c., this mixture was separated into two fractions. The fraction of longer retention time (comprising 59% of the adduct mixture) contained (126); the p.m.r. (Figure 7) and c.m.r. spectral characteristics of this adduct were very similar to those of (118). The other fraction contained a mixture of adducts identified as (127) and (128) on the basis of their p.m.r., c.m.r. and electronic spectral characteristics which were very similar to those of (116) and (117). Adduct (128) was separated from the mixture by fractional crystallization; compared to those for (127) and (116), the p.m.r. spectrum of (128) contains the characteristics (discussed on page 67) expected for an "axially" substituted π8 + π2 adduct. In



(126)

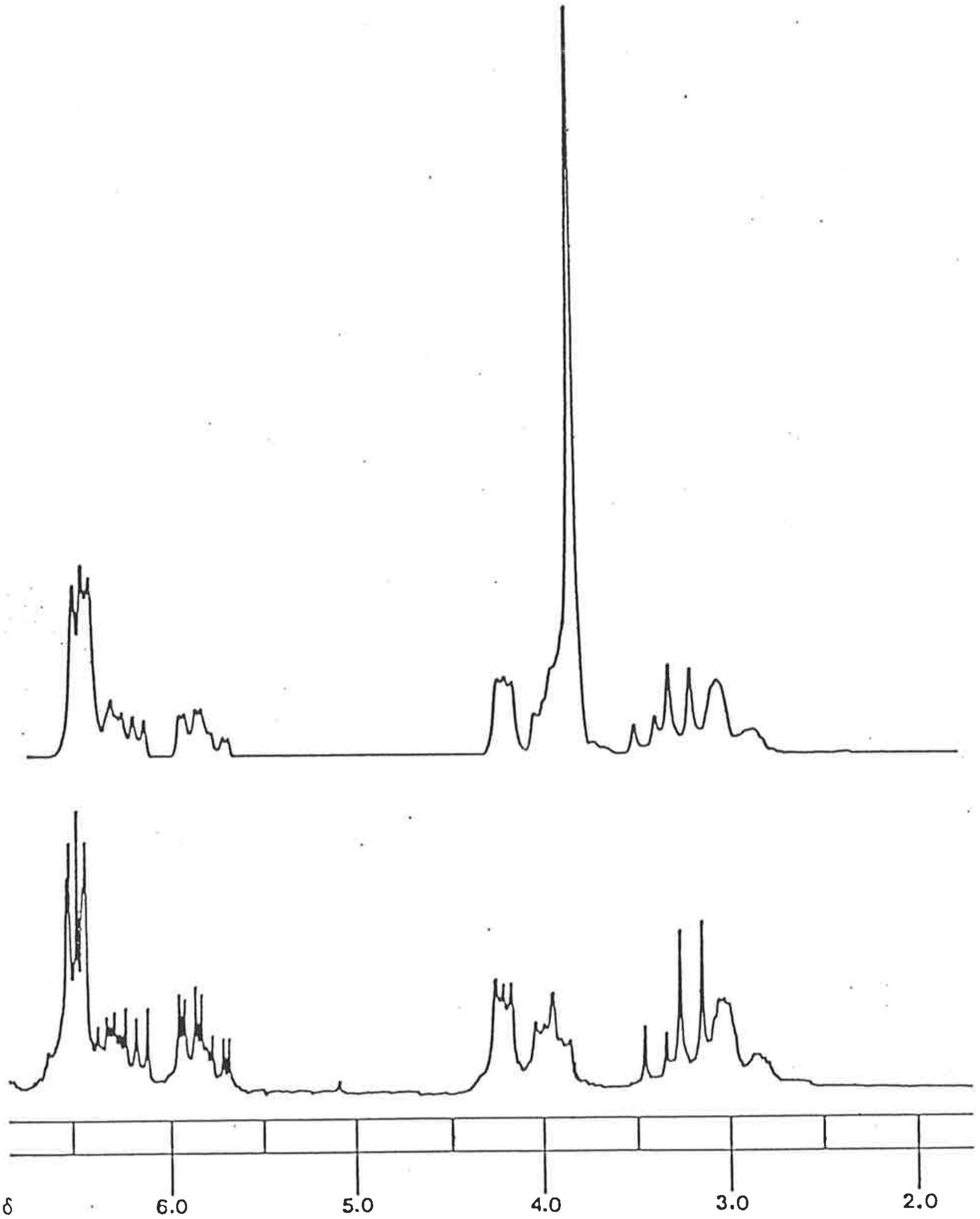
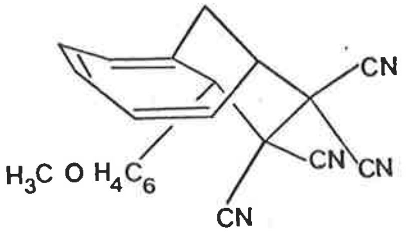
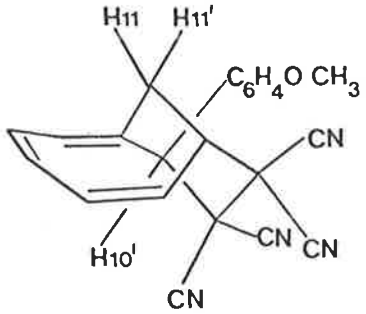


FIGURE 7. P.m.r. spectral characteristics (80 MHz) of (*E*)-5-benzylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (118) (bottom) and (*E*)-5-(*p*-methoxybenzylidene)-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (126).

FIGURE 8. P.m.r. spectral characteristics (80 MHz) of 8,8,9,9-tetracyano-10-phenylbicyclo[5,3,1]undeca-1,3,5-triene (116) (bottom) and 8,8,9,9-tetracyano-10-(*p*-methoxyphenyl)bicyclo-[5,3,1]undeca-1,3,5-triene (128) (top).



(127)



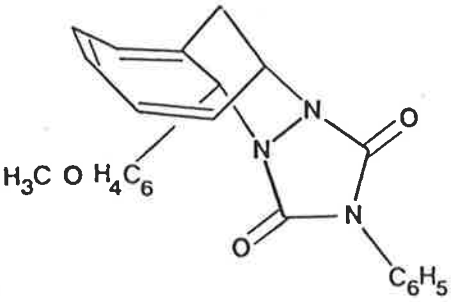
(128)

particular, the "narrow" ABX system of H_{11}' and H_{11} in (128) and the high frequency of the signal due to H_{10}' are evident in Figure 8.

With tetracyanoethylene, a mixture of (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-trienes, of which 66% was in the (*E*) configuration, yielded a mixture of adducts containing the "3,6" adduct (118) to the extent of 17%. The mixture of (*E*)- and (*Z*)-(67), however, which contained 77% in the (*E*) form, reacted with tetracyanoethylene to give a mixture of adducts of which 59% was the "3,6" adduct (126). Since (67) polymerized to a greater extent than did (66) during the course of their cycloaddition reactions, the total yield of adducts derived from (67) (65%) was lower than the yield of adducts arising from (66) (95%). Absolute yields notwithstanding, the yields of (126) and (118), relative to those of the appropriate $\pi 8 + \pi 2$ adducts, indicate that the electron releasing nature of the methoxyl group enhanced addition in the "3,6" mode. It is thought that (126) is produced by the non-concerted pathway outlined in

Scheme 38 and that the zwitterion produced from (67) is stabilized (relative to (123)) by the methoxyl group.

An examination of the reaction between (*E*)- and (*Z*)-(67) and N-phenyltriazolinedione furnished additional information concerning the mechanisms of $\pi 8 + \pi 2$ and "3,6" cycloadditions. This reaction proceeded rapidly at room temperature and gave, in quantitative yield, a mixture of two adducts (t.l.c.). Fractional crystallization* of this adduct mixture afforded a pure sample of the "equatorially" substituted $\pi 8 + \pi 2$ adduct (129) and a mixture containing a small amount of (129) and some unidentified material. The p.m.r. spectral



(129)

characteristics of (129) were very similar to those of (101); in particular, the methylene protons attached to the main bridge of (129) gave rise to a "wide" AB part of an ABX system (see Experimental). Since the yield of (129) (82%) corresponded

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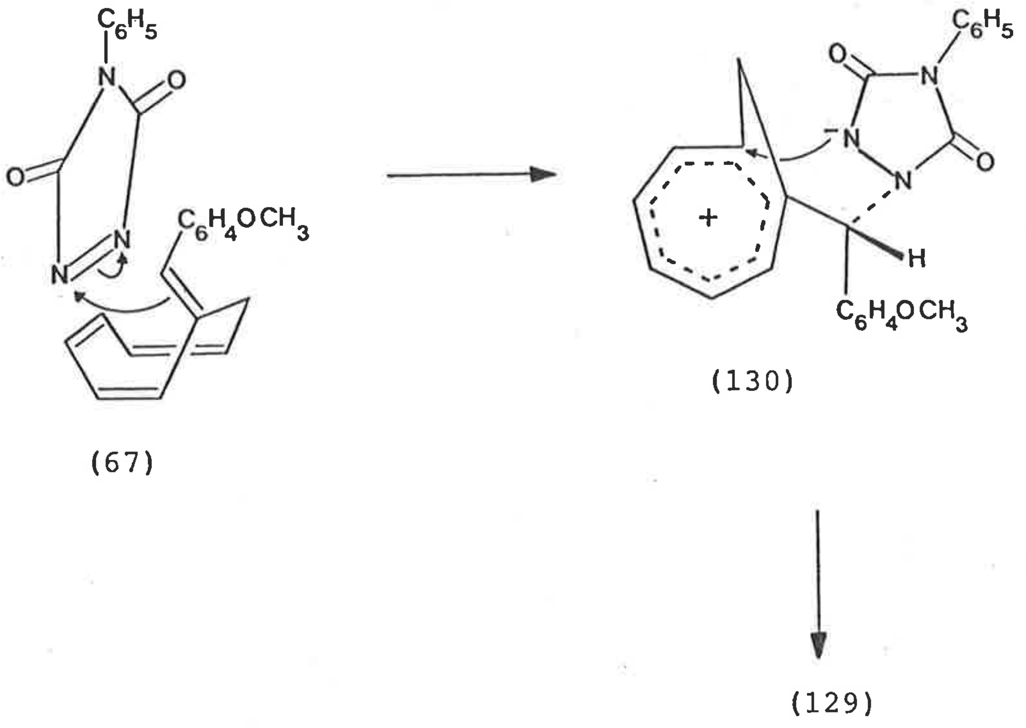
* In one experiment, separation of the adducts was attempted on silica gel but a poor recovery of adducts was the result.

approximately to the amount of (*E*)-(67) (*ca.* 90%)* which was present in the mixture of (*E*)- and (*Z*)-(67), it is reasonable to assume that the "equatorial" $\pi 8 + \pi 2$ adduct (129) was derived from the (*E*)- olefin. The above result suggests that electrophilic attack on (*E*)-(67) (and its enantiomer which is generated by ring flipping) occurred exclusively on its "upper" face to give zwitterion (130) (and its enantiomer) which formed the "equatorial" adduct (129) (Scheme 39). Attack on the "bottom" face of (*E*)-(67),



SCHEME 39

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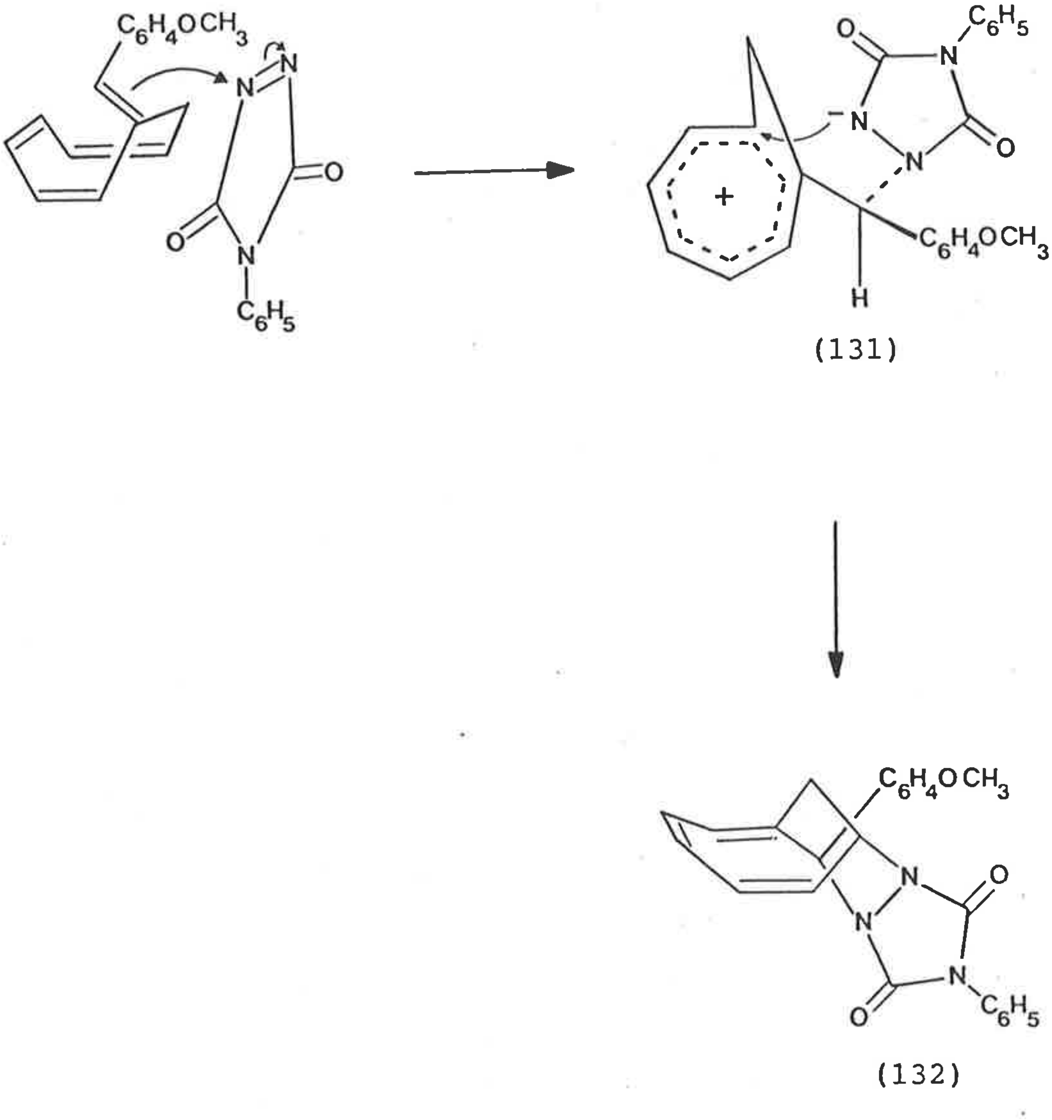
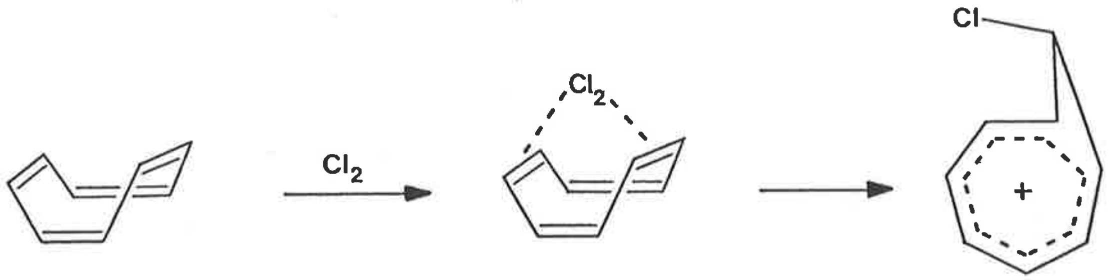
* See page 41 and Experimental.

which leads to the zwitterion (131) (a diastereomer of (130)) and, ultimately, the "axially" substituted $\pi 8 + \pi 2$ adduct (132) (Scheme 40), must be ruled out. Attack on the "upper" face of (*Z*)-(67) would produce (132).



SCHEME 40

Huisgen[92] has reported that *endo*-halohomotropylium cations (133) were produced by the attack of halogens on cyclooctatetraene. To account for the high stereoselectivity, it was suggested that π-complexation of the halogen preceded formation of (133) (Scheme 41). Perhaps the stereospecific formation of (130) was also contingent on the generation of a π-complex (such as that depicted in Figure 9).



(133)

SCHEME 41

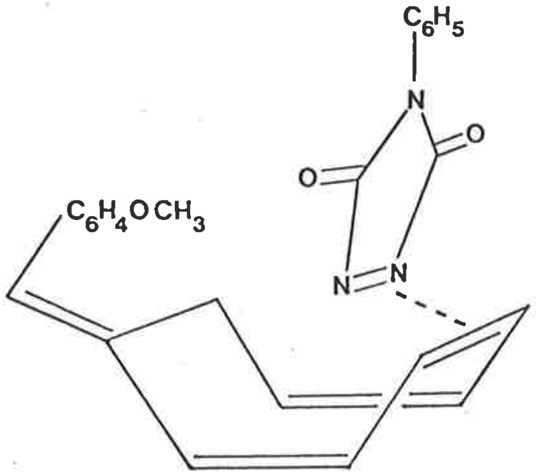


FIGURE 9

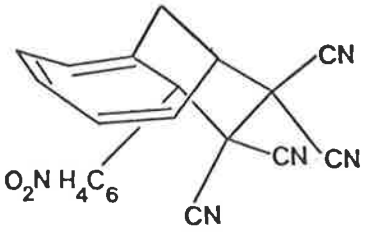
An examination of the absolute yields of adducts derived from (66) reveals that if π8 + π2 cycloadditions of tetracyanoethylene are stereospecific, as found for those of N-phenyltriazolinedione, then "3,6" cycloaddition of tetracyanoethylene must also be stereospecific. A mixture of (*E*)-(66%) and (*Z*)-7-benzylidenecycloocta-1,3,5-triene reacted with tetracyanoethylene to give the "3,6" adduct (118) (15.5%), the "equatorial" $\pi 8 + \pi 2$ adduct (116) (32%), the "axial" $\pi 8 + \pi 2$ adduct (117) (32%) and an $\pi 8 + \pi 2$ adduct (115) (13%) of unknown stereochemistry. If (*Z*)-(66) is converted exclusively into the "axial" $\pi 8 + \pi 2$ adduct (117), then the yield of this adduct implies that virtually all of the (*Z*)-(66) present in the original olefin mixture was consumed to give (117). As a consequence, (118) can only have arisen from "3,6" cycloaddition to (*E*)-(66). Presumably, if any (122) was formed, it reverted to starting materials and did not isomerize to (123) (Scheme 38). Unfortunately, in its reaction with tetracyanoethylene, large amounts of (67) were destroyed by polymerization; as a consequence, further evidence of the stereospecific nature of cycloadditions to 7-arylidenecycloocta-1,3,5-trienes cannot be obtained.

1.8 THE CYCLOADDITION REACTIONS OF 7-(*p*-NITROBENZYLIDENE)-CYCLOOCTA-1,3,5-TRIENE

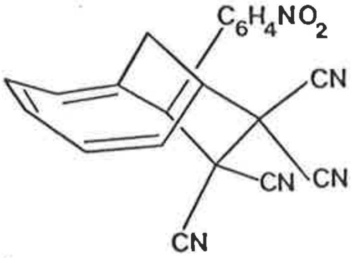
It has been established that the yield of the "3,6" adduct derived from 7-(*p*-methoxybenzylidene)cycloocta-1,3,5-triene (67) exceeds that of the "3,6" adduct derived from 7-benzylidenecycloocta-1,3,5-triene (66) and it was assumed that the electron releasing nature of the methoxyl group was responsible for this enhancement. Consistent with this observation, it was found that 7-(*p*-nitrobenzylidene)cycloocta-1,3,5-triene (68) entered almost exclusively into $\pi 8 + \pi 2$ cycloaddition with tetracyanoethylene and N-phenyltriazolinedione.

In boiling ethyl acetate, a mixture of (*E*)- and (*Z*)-(68) reacted with tetracyanoethylene to form a mixture of adducts (41%) containing (134), (135) (91% combined) and an unidentified adduct. Structures (134) and (135) were assigned to the adducts on the basis of their spectral characteristics; the lack of material, and their instability, prevented a satisfactory elemental analysis being obtained (see experimental).

It is therefore confirmed that the stepwise process (page 73) is involved in the formation of the "3,6" adducts of 7-arylidenecycloocta-1,3,5-trienes; from Table 6 it can be clearly seen that the extent of "3,6", compared to $\pi 8 + \pi 2$ cycloaddition, is highly dependent on the ability of the aryl moeity to stabilize the adjacent positive charge.



(134)



(135)

TABLE 6

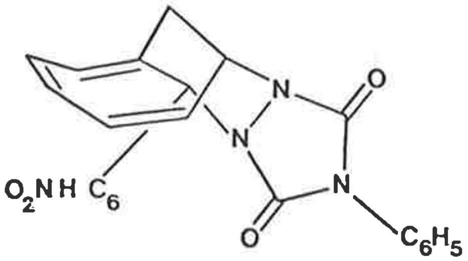
Relative extents of "3,6" and $\pi 8 + \pi 2$ cycloadditions to 7-arylidenecycloocta-1,3,5-trienes

Olefin	Adduct Ratio $\pi 8 + \pi 2$: "3,6"
(<u>67</u>)	0.7 : 1
(<u>66</u>)	4.8 : 1
(<u>68</u>)	10.1 : 1*

*Assuming the unidentified material is the "3,6" adduct.

It should be noted that when a mixture of (*E*)- and (*Z*)-(<u>68</u>) was heated briefly with tetracyanoethylene in ethyl acetate, the mixture of unchanged olefins was noticeably (p.m.r. spectroscopy) diminished in the amount of (*E*)-(<u>68</u>). Presumably, the (*E*)-olefin is consumed more rapidly by the dienophile.

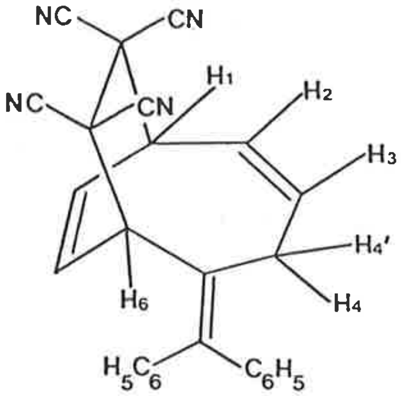
When a mixture of (*E*)- and (*Z*)-(<u>68</u>), containing only a trace (p.m.r. spectroscopy) of the (*Z*)-olefin, was treated with N-phenyltriazolinedione, a quantitative yield of adducts containing the "equatorial" π8 + π2 adduct (136) (*ca.* 90%) was obtained. This result suggests that (136), in a manner similar to (129) (page 82), is produced stereospecifically. Moreover, it should be noted that in all cases examined, N-phenyltriazolinedione has produced only one type of π8 + π2 adduct (i.e. "1,7'" types) on reaction with the 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes. Factors responsible for this behaviour are not obvious, however.



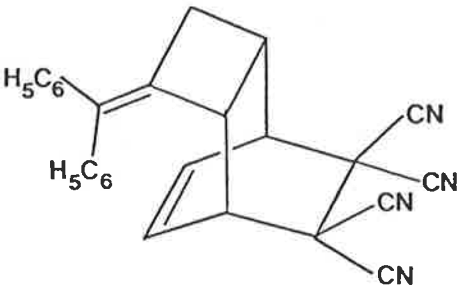
(136)

1.9 REACTION OF 7-BENZHYDRYLIDENECYCLOOCTA-1,3,5-TRIENE WITH TETRACYANOETHYLENE

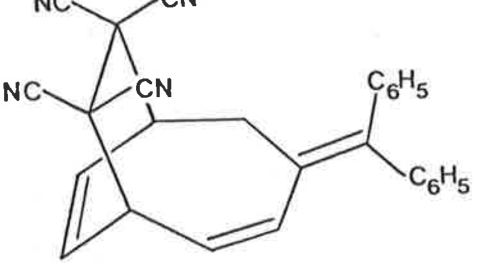
7-Benzhydrylidenecycloocta-1,3,5-triene (69) reacted with tetracyanoethylene in boiling ethyl acetate to give a mixture of two compounds (t.l.c.) (57%) which contained the "3,6" adduct (137) (22%) and, unexpectedly, the Diels-Alder adduct (138) (78%).



(137)



(138)



(139)

The structures were deduced from the p.m.r. (Figures 10 and 11), c.m.r. and electronic spectral characteristics of these adducts. The p.m.r. spectral characteristics of (137) were similar to those of (118) (Figure 12) but a striking difference between them arises from the apparent magnetic equivalence of H_4 and H_4' in (137) and the reduced magnitude of long range coupling. It was found by spin decoupling that H_4 and H_4' are coupled only to H_3 (the possibility that (139) was obtained is, therefore, ruled out) while H_2 is coupled only to H_1 and H_3; as a consequence, the signal due to

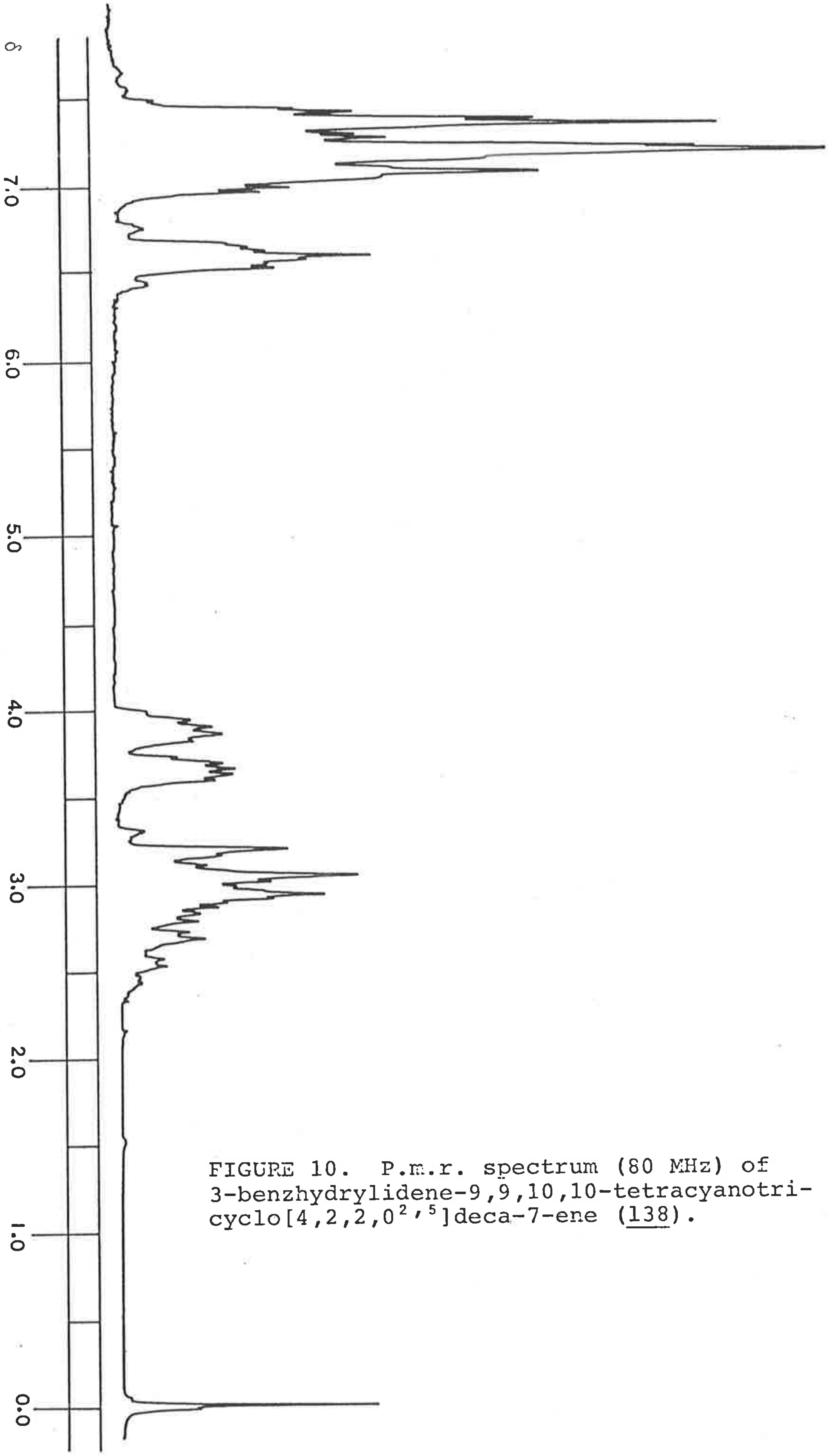


FIGURE 10. P.m.r. spectrum (80 MHz) of 3-benzhydrylidene-9,9,10,10-tetracyanotricyclo[$4,2,2,0^{2,5}$]deca-7-ene (<u>138</u>).

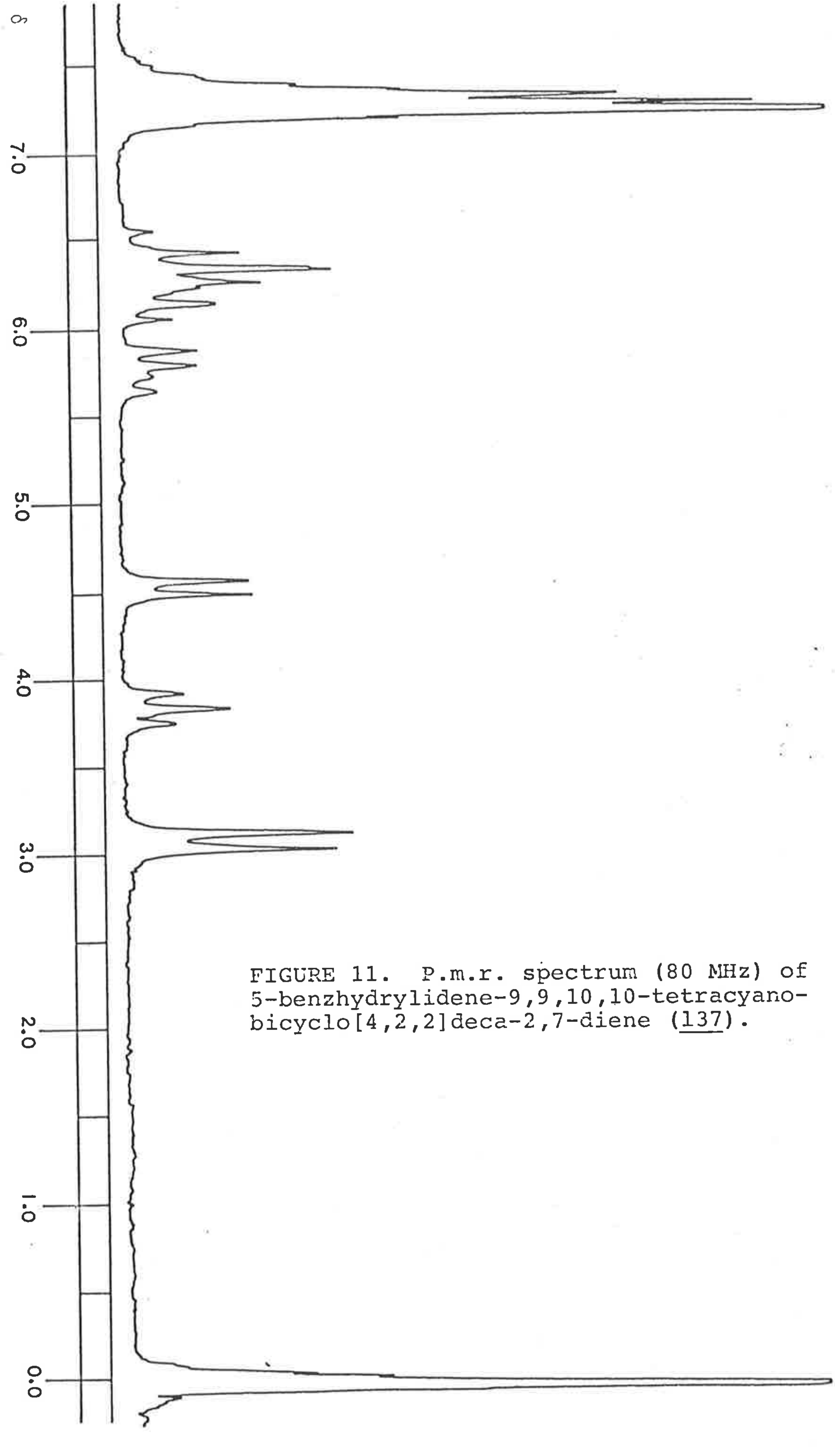


FIGURE 11. P.m.r. spectrum (80 MHz) of 5-benzhydrylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (<u>137</u>).

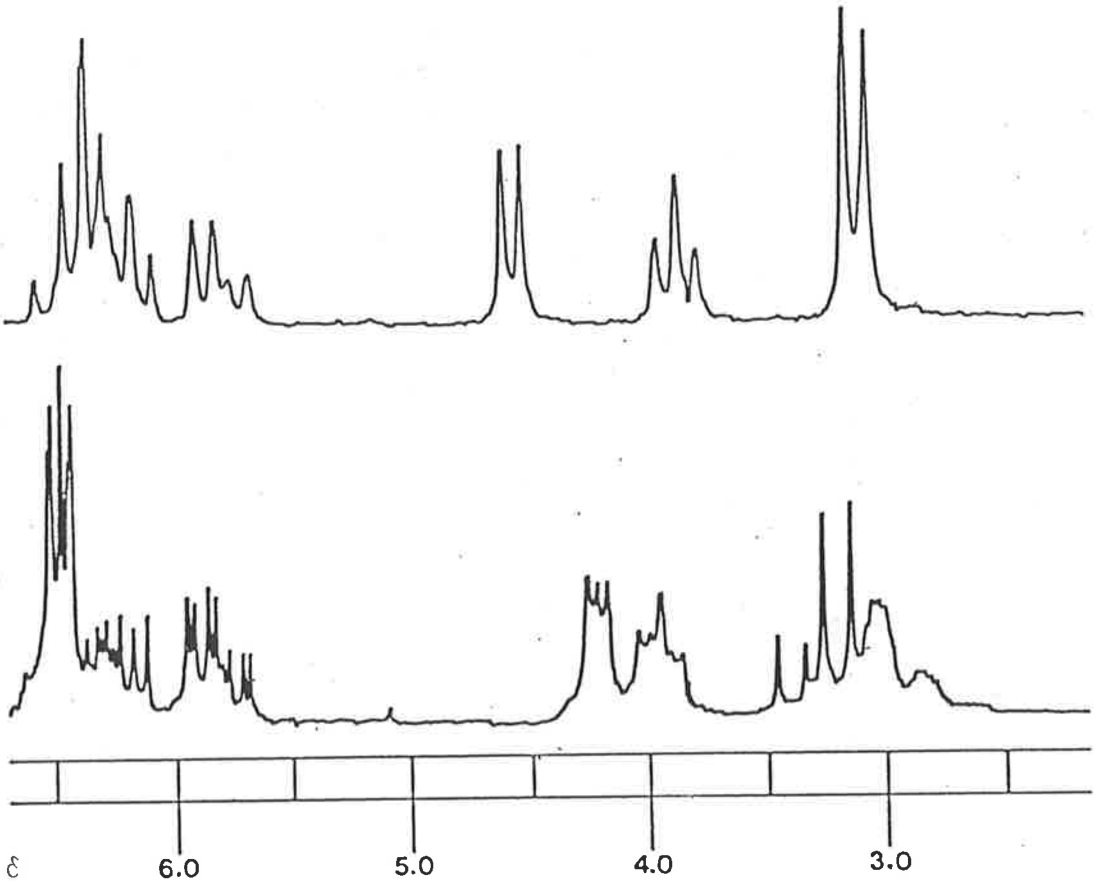


FIGURE 12. P.m.r. spectral characteristics (80 MHz) of 5-benzhydrylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (<u>137</u>) (top) and (*E*)-5-benzylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (<u>126</u>) (bottom).

H_3 (δ 6.26) is observed as a doublet of triplets, H_4 and H_4' are observed as doublets and H_2 is observed as a doublet of doublets (δ 5.86). Furthermore, it should be noted that the magnitudes of $J_{3,4}$, $J_{1,8}$ and $J_{1,2}$ are all 7.5 Hz. The reason for the chemical equivalence of H_4 and H_4' is not immediately apparent. It is possible, however, that (137) exists in a conformation approaching that depicted in Figure 13 in which the chemical shifts of H_4 and H_4' are made equivalent by the proximities of the (*Z*)-phenyl ring and the nitrile groups. The p.m.r. spectrum of (137) provided confirmation of the assignment of (*E*)-stereochemistry to the "3,6" adducts (118) and (126). That H_6 was not adjacent to the aryl group in (118) and (126) was suggested by the similarity in chemical shifts of the signals due to H_1 and H_6. From Figure 12 it can be seen that a large paramagnetic shift in the signal due

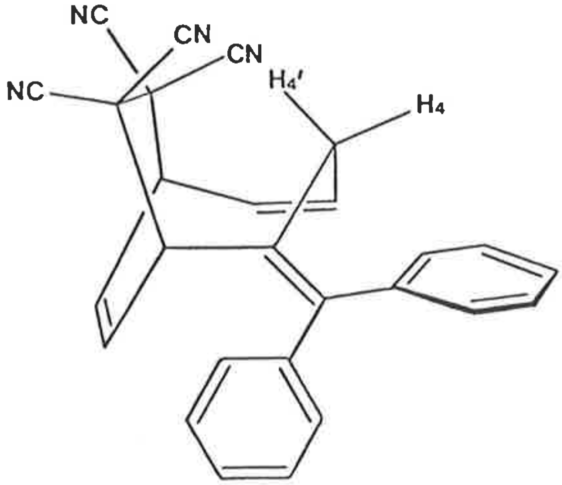
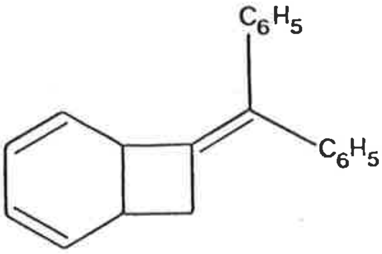


FIGURE 13

to H_6 is brought about by the (Z)-phenyl group. In addition, a signal which was assigned to C_6 in the c.m.r. spectrum of (137) suffered a diamagnetic shift relative to the signal assigned to C_6 in (118); this shift is to be expected because C_6 in (137) bears a hydrogen atom compressed by the (Z)-phenyl group.

The electronic spectrum of (137), in ethanol, contains an absorption at 248 nM which, because of its similarity to that of (118) and those reported for derivatives of styrene (Table 5), suggests that only one of the two phenyl groups overlaps effectively with the exocyclic double bond. Molecular models indeed indicate that a structure bearing "skewed" phenyl groups (Figure 13) contains fewer unfavourable steric interactions than a structure bearing these groups in a coplanar arrangement.

Presumably, the Diels-Alder adduct (138) arises from the reaction between 7-benzhydrylidenebicyclo[4,2,0]undeca-2,4-diene (140), a bicyclic valence tautomer of (69), and tetracyanoethylene. This hitherto unobserved mode of



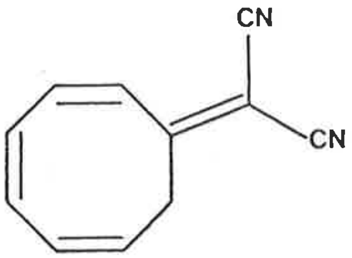
(140)

cycloaddition to 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes might be a preferred reaction simply because $\pi 8 + \pi 2$

and "3,6" cycloadditions with (69) are impeded. Since the formation of a zwitterion analogous to (123) from (69) would be inhibited by the presence of the (Z)-phenyl group (see page 73), "3,6" cycloaddition to (69) is not expected to predominate. Moreover, the size of the two phenyl groups attached to (69) might prevent electrophilic attack on C_7' thereby suppressing $\pi 8 + \pi 2$ cycloaddition. With its two major competing processes thus curtailed, Diels-Alder addition to (69) might become the predominant process.

1.10 THE CYCLOADDITION REACTIONS OF 7-(DICYANOMETHYLENE)-CYCLOOCTA-2,4,6-TRIENE

In connection with the investigation into the cycloaddition reactions of 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes, 7-(dicyanomethylene)cycloocta-1,3,5-triene (141)[93] was treated with a range of dienophiles. Even under forcing conditions (see Experimental), (141) did not yield any adducts with N-phenyltriazolinedione, chlorosulphonylisocyanate, tetracyanoethylene and dimethyl acetylenedicarboxylate; in all cases, high yields of unchanged (141) were obtained.



(141)

7-Isopropylidenecycloocta-1,3,5-triene (65) enters into $\pi 8 + \pi 2$ cycloaddition with N-phenyltriazolinedione. Since accurately scaled molecular models* show that the Van Der Waals radius of a nitrile group is smaller than that of a methyl group, it can be seen that the size of the nitrile group cannot be responsible for inhibiting the electrophilic attack (on C_7') necessary for $\pi 8 + \pi 2$ cycloaddition.

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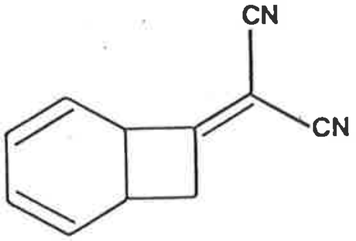
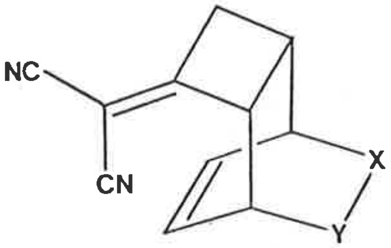
* Manufactured by Catlin Ltd., England.

Presumably, the nitrile groups reduce the electron density around C_7' to such an extent that π8 + π2 addition does not take place.

Importantly, in addition to being deactivated towards π8 + π2 cycloaddition, (141) did not yield any Diels-Alder adducts (143) with the dienophiles mentioned. This observation suggests that the rate of establishment of the equilibrium between (141) and its bicyclic valence tautomer (142) is very slow. No cycloadducts of (141) have been described in the chemical literature.



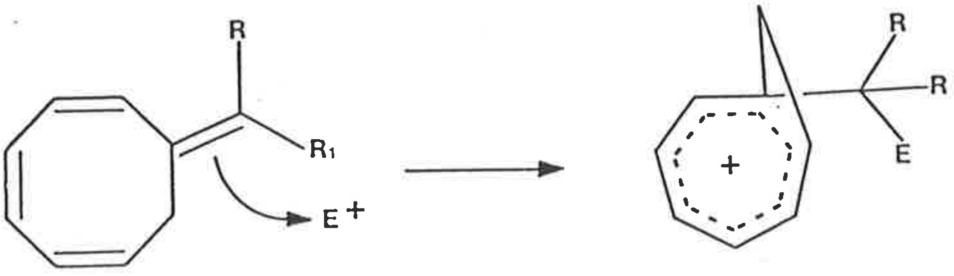
(142)



(143)

1.11 THE REACTIONS BETWEEN BROMINE AND 7-METHYLENECYCLOOCTA-1,3,5-TRIENE

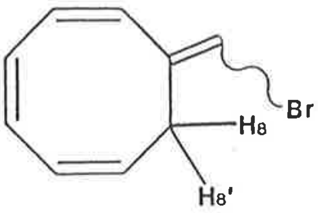
It has been established that, as the first step of cycloaddition, 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes suffer electrophilic attack by dienophiles to form zwitterions containing homotropylium cations. These olefins have the potential to generate homotropylium cations (144) on attack by other types of electrophiles (Scheme 42); bearing in mind that Huisgen[28,92,94] discovered some interesting processes involving the formation of homotropylium cations from the reaction between halogens and cyclooctatetraene, it was decided to investigate the reaction between (64) and bromine.



(144)

SCHEME 42

Bromination of (64) at low temperature gave a mixture of bromides; it was found, however, that the composition of this mixture was dependent on the rapidity with which bromine was added. At -78° in dichloromethane, slow addition of one equivalent of bromine to (64) gave a mixture of (*E*)- and (*Z*)-7-(bromomethylene)cycloocta-1,3,5-trienes (145) (27%). The assignment of the structure was based on the



(145)

p.m.r., c.m.r., electronic and mass spectral characteristics of the bromide. Its molecular formula, arrived at by elemental analysis and high resolution mass spectrometry, confirmed that only one atom of bromine had been incorporated into (64). Similar to the p.m.r. spectra of (66), (67) and (68), that of (145) contained a broad envelope (7H) between δ 6.83 and 5.47 and two overlapping doublets (2H, J 7.5 Hz) at δ 3.23 and 3.09 (assigned to H_8 and H_8'). In contrast to the case observed for (66), (67) and (68), the doublet at high field was more intense than that at low field; it was therefore concluded that (*Z*)-(145) was the major reaction product (see page 40 for a discussion dealing with the identification of geometrical isomers of 7-arylidenecycloocta-1,3,5-trienes). The c.m.r. spectrum of (145) was similar to those of (66), (67) and (68) and contained two high field triplets, δ 31.09 and 35.35, which were assigned to the SP^3 carbon atoms in (*E*)- and (*Z*)-(145), respectively; the triplet at lowest field, and of highest intensity, was assigned to the (*Z*)-isomer on the basis of a model discussed previously (page 40). In addition, the electronic spectrum of (145) (λ_{max} 281 and 231 nM) is very similar to that obtained for (64) (λ_{max} 270 and 223 nM). It should be noted that the wavelength of the absorption maximum of the bromo-olefin (145) should be longer than that of the olefin (64).[95]

When a concentrated solution of bromine (one equivalent) was added rapidly to a solution of (64) at -78°, a mixture containing (*E*)- and (*Z*)-(145) (21%), a tetrabromide (16%) and traces of other compounds (t.l.c.) was obtained. Preparative t.l.c. of the mixture afforded a homogeneous (t.l.c.) sample of the tetrabromide. Since this compound was too unstable for satisfactory elemental analysis, high resolution mass spectrometry was used to confirm that it had the molecular formula $C_9H_{10}Br_4$. The presence of two high field triplets (δ 30.01 and 39.37) in the c.m.r. spectrum of the tetrabromide suggested that, during the course of its dibromination, (64) had become attached to a bromine atom through C_7'. Moreover, the presence of three doublets (δ 127, 131 and 133) and a singlet (δ 135) indicated that the tetrabromide contained a disubstituted and a trisubstituted double bond. Of three structures (146), (147) and (148) suggested by these spectral characteristics, (146) and (147) were eliminated as possibilities after an examination of the p.m.r. spectrum of the tetrabromide. This spectrum contained a signal at δ 6.42 (1H), a complex multiplet (2H) between δ 6.09 and 5.72, a doublet (2H) at δ 4.81, a complex signal centred at δ 4.65, an AB "quartet" (2H, J_{AB} 10 Hz) centred at δ 4.39 and 4.11 and the AB part of an ABX system (2H, J_{AB} 15 Hz, J_{AX} 7.5 Hz) at δ 2.93 and 2.74 (see Figure 14); double irradiation at δ 4.65 caused the AB part of the ABX system to collapse into a simple AB "quartet". For each of the structures (146),

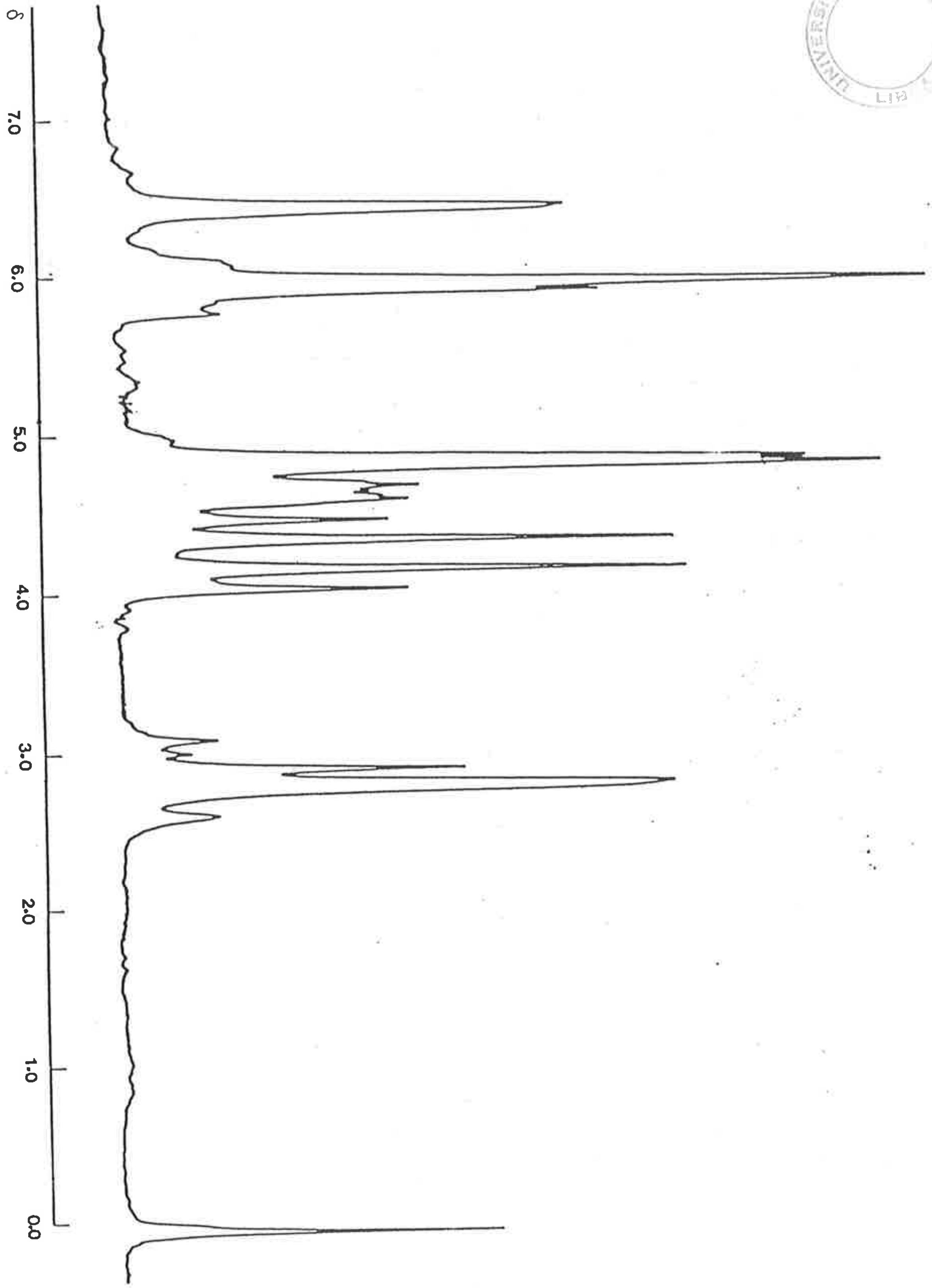
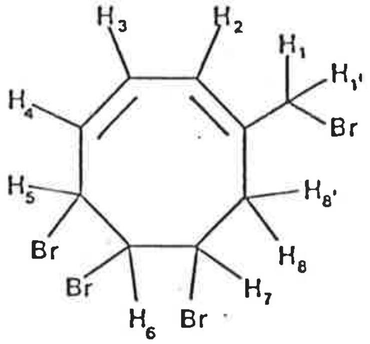
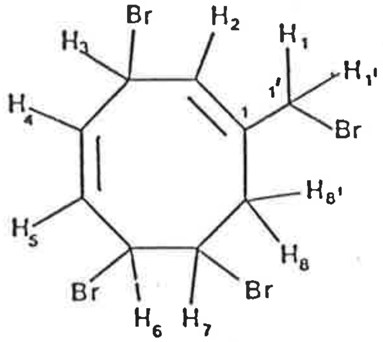


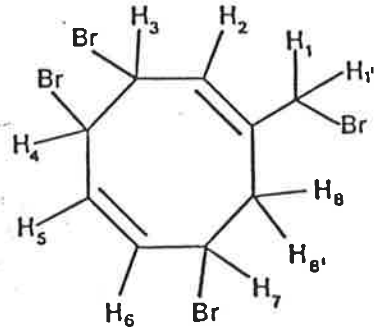
FIGURE 14. P.m.r. spectrum (80 MHz) of bromomethyl-3,4,7-tribromocycloocta-1,5-diene (<u>148</u>)



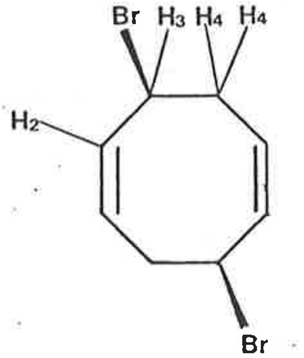
(146)



(147)



(148)



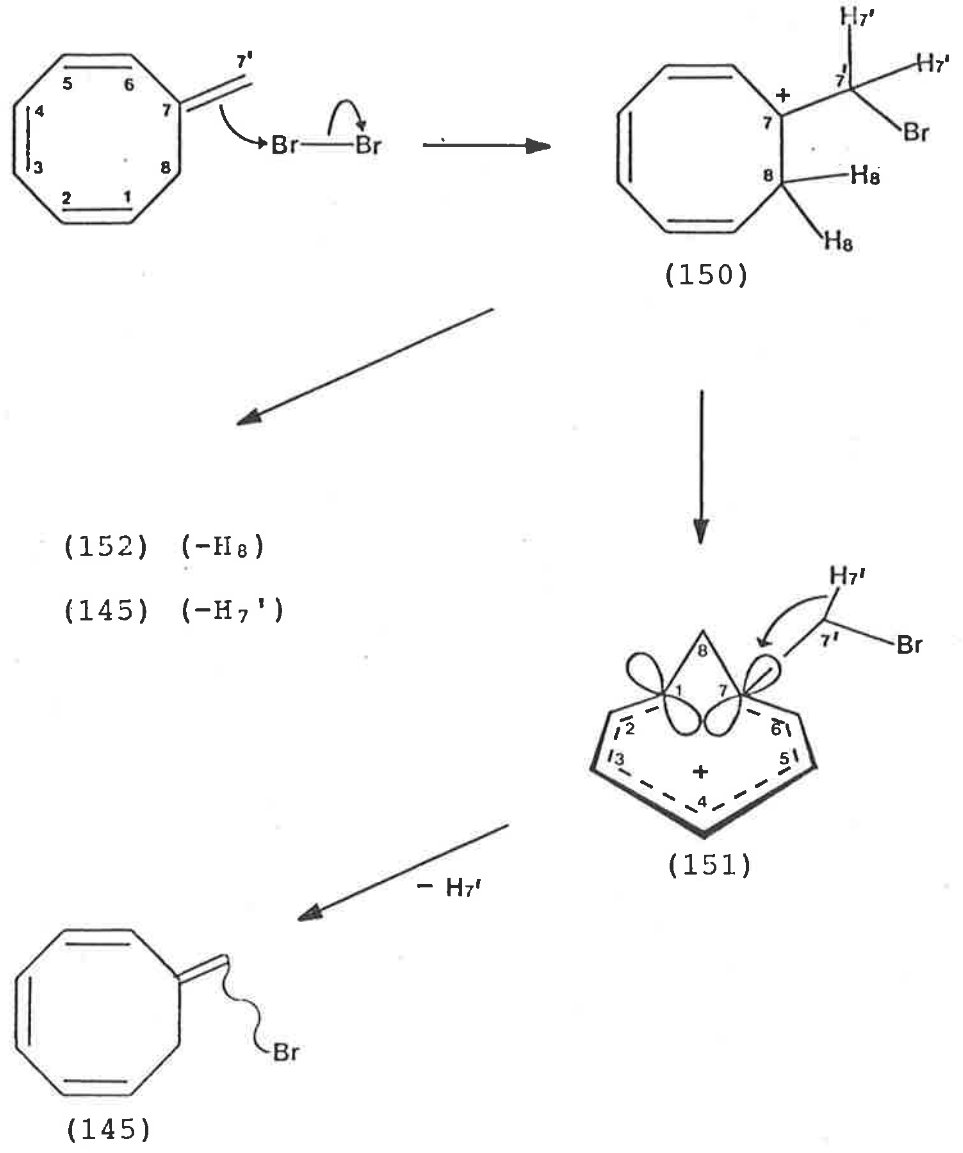
(149)

(147) and (148) the ABX system must be assigned to H_8 and H_8' and it follows from the double resonance experiment that the signal at δ 4.65 must be assigned to H_7. For structure (146), it was assumed that the signal for H_6 would be found at a frequency similar to that for H_7 and that the signal for H_5, due to the deshielding effect of the α double bond, would be found at a frequency higher than that for H_7. Such a pattern of signals which could be ascribed to H_5, H_6 and H_7 was not observed in the p.m.r. spectrum of the tetrabromide. The signals due to H_6 and H_3 in (147) must occur at higher and much higher frequencies, respectively, than those due

to H_7. Signals corresponding to one proton each which could be assigned to H_3 and H_6 in (<u>147</u>) were not present in the p.m.r. spectrum of the tetrabromide. In structure (<u>148</u>), H_7, H_3 and H_4 are expected to have similar chemical shifts; H_3 and H_4 were assigned to the "doublet" at δ 4.81. It was assumed that restricted rotation of the C_1-C_1' bond, brought about by the size of the bromine atom (verified by molecular models), was responsible for the magnetic non-equivalence of the protons attached to C_1'. Importantly, the signals due to H_8, H_8', H_7, H_6, H_5, H_4 and H_3 were found at chemical shifts similar to those reported[96] for the corresponding protons in (<u>149</u>). Since the magnitudes reported[96] for $J_{3,4}$ and $J_{2,3}$ for (<u>149</u>) were larger than the corresponding coupling constants ($J_{7,8}$ and $J_{2,3}$) for (<u>148</u>), it was assumed that the bromo and bromomethyl groups in (<u>148</u>) enforce a conformation slightly different to the twist boat form postulated for (<u>149</u>). The exact conformation of (<u>148</u>), however, cannot be deduced until the relative stereochemistry about C_4, C_5 and C_7 is determined. Unfortunately, this relative stereochemistry could not be deduced from the p.m.r. spectrum of (<u>148</u>) and a lack of material prevented a stereochemical determination based on Huisgen's method.[94] Using this method, the isolation of *meso*-dibromosuccinic acid, for example, from the oxidative ozonolysis of (<u>148</u>) would have shown that it existed as the *cis*-3,4-tetrabromide.

Protons at
C' are
iastereotopic

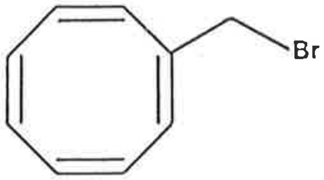
To account for the exclusive formation of (<u>145</u>) by the "slow bromination" of (<u>64</u>), it is proposed that (<u>64</u>) suffered electrophilic attack on its exocyclic double bond and formed a cation (<u>150</u>) which rearranged to the bromomethylhomotropylium cation (151). In the presence of a low concentration of nucleophile (slow addition of bromine), deprotonation of (151) occurred before it could capture a bromide ion (Scheme 43). That deprotonation of the intermediate occurred exclusively at C_{7}' (and not at C_{8}) is



SCHEME 43

evidence for the involvement of homotropylium cations. From a molecular model of (150), it can be seen that both the

C_7'-H_7' and C_8-H_8 bonds can achieve coplanarity with the vacant *p* orbital of the carbonium ion; as a consequence, both C_7' and C_8 might be expected to suffer deprotonation. On the other hand, a molecular model of (151) shows that only the C_7'-H_7' bond can achieve coplanarity with the *p* orbital of C_7;[97,98,99,100] from the homotropylium cation (151), exclusive deprotonation of C_7' is expected.*,[101] The origin of the slight stereoselectivity observed in the formation of (*E*)- and (*Z*)-(145) is not obvious.



(152)

Under conditions where there was a high concentration of bromine (i.e. rapid addition of bromine), it is proposed that (151) could capture a bromide ion to produce a dibromide which could undergo further bromination to give (148). Two mechanisms for the conversion of (151) into (148) can be considered:

(1) attack on C_5 in (151) by a bromide ion to form the intermediate dibromide (153) which suffers a 1,4 addition of bromine to give (148) (Scheme 44).

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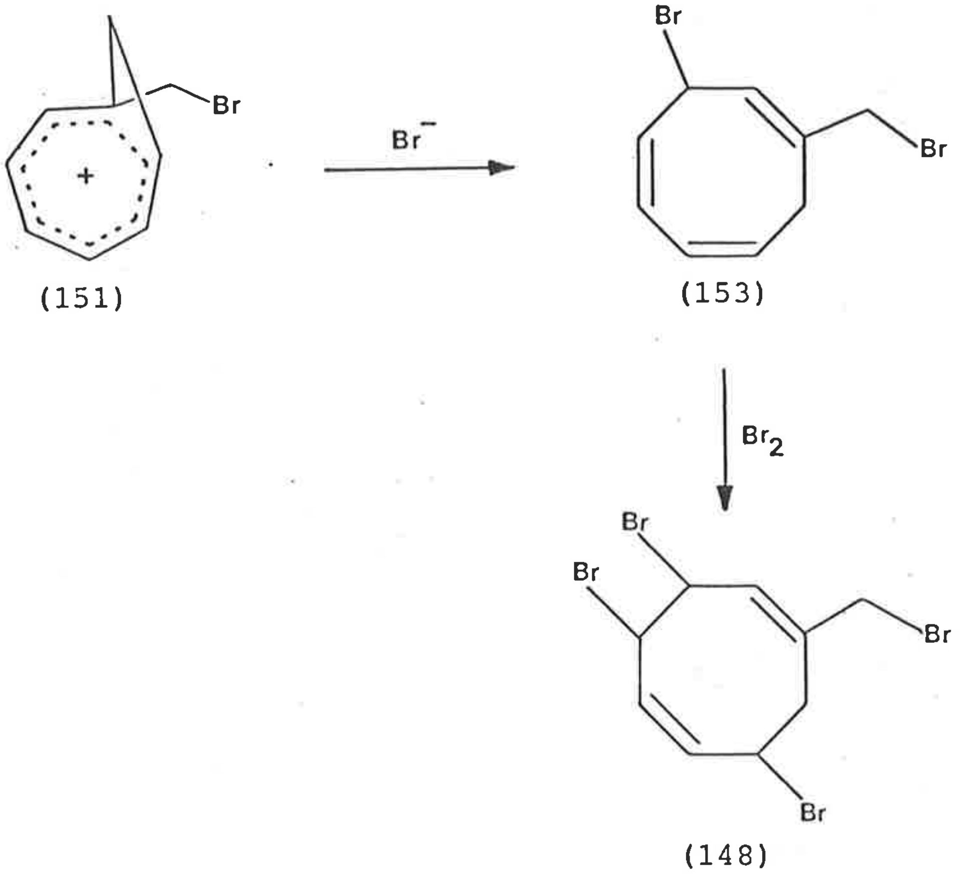
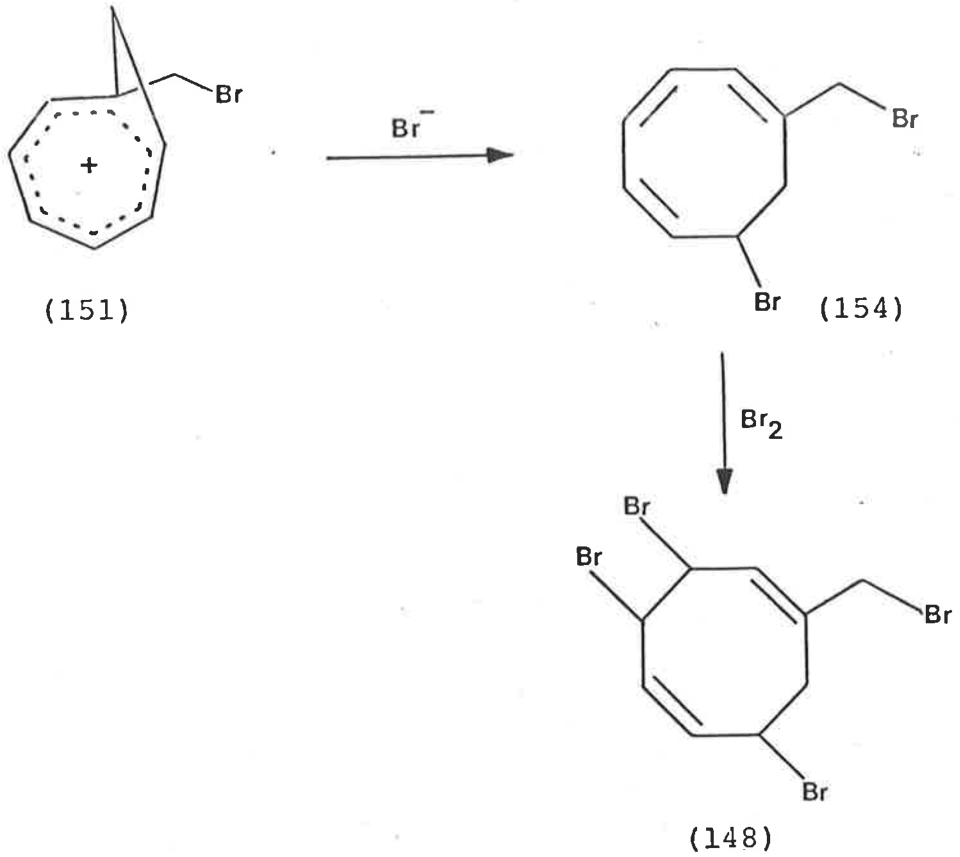
* Evidence that bromomethylcyclooctatetraene (152)[102] was not formed was supplied by the p.m.r., c.m.r. and electronic spectra of the monobromide (see Experimental).

(2) attack on C_1 in (151) by a bromide ion to form the intermediate dibromide (154) which suffers a 1,2 addition of bromine to give (148) (Scheme 45).

In general, nucleophiles have not been observed to attack C_5 of homotropylium cations. Moreover, since the results obtained by Huisgen^{28} and Haddon^{99} suggest that of the carbon atoms $C_1 - C_7$ in (151), C_1 should possess the highest charge density, it is reasonable to suggest that process (2) was involved in the formation of (148).



SCHEME 44



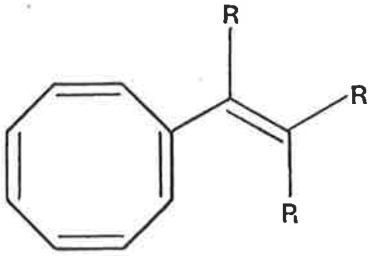
SCHEME 45

CHAPTER 2

THE CYCLOADDITION REACTIONS OF SOME ALKENYLCYCLOOCTATETRAENES

2.1 INTRODUCTION

Of the numerous investigations dealing with the cycloaddition reactions of mono-substituted cyclooctatetraenes, only one has dealt with the reactions of an alkenylcyclooctatetraene (155). In 1952, Withey[104] reported that a mixture of acetylene oligomers, which was shown to contain vinylcyclooctatetraene (156),[105,106] reacted vigorously with an excess of maleic anhydride at 160° to form a single product. Although elemental analysis suggested that this compound was a *bis*-adduct of (156), its structure was not determined.



(155)

(156) $R = R_1 = R_2 = H$

(88) $R = CH_3$ $R_1 = R_2 = H$

As a result of obtaining isopropenylcyclooctatetraene (88) by the action of potassium t-butoxide on isopropylcyclooctatetraene (see page 36), the cycloaddition reactions of this alkenylcyclooctatetraene with one and two equivalents of dienophiles were investigated. In addition, the *bis*-adduct reported by Withey was prepared and its structure deduced.

2.2 THE CYCLOADDITION REACTIONS OF ISOPROPENYLCYCLOOCTATETRAENE

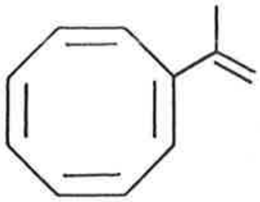
Isopropenylcyclooctatetraene (88), which was prepared from isopropylcyclooctatetraene (see page 36) or by coupling[103] isopropenylmagnesium bromide with bromocyclooctatetraene (page 36 and Experimental), reacted extremely rapidly with one equivalent of N-phenyltriazolinedione at room temperature to give a 1:1 adduct (mass spectrometry and elemental analysis) in quantitative yield. In principle, any one of three types of 1:1 adducts might have been formed:

(1) A Diels-Alder adduct (158) which might arise from a concerted addition of (12) to the bicyclic valence tautomer (157) of (88),

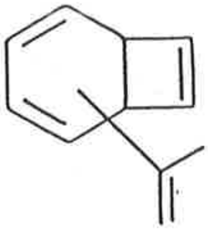
(2) A Diels-Alder adduct (159),

(3) A 1,4 adduct (160).

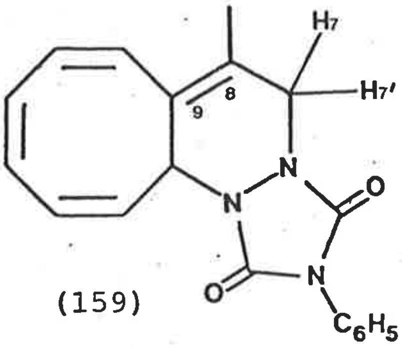
The structure (159) was assigned to the adduct primarily on the basis of its c.m.r. spectral characteristics which included a quartet (δ 16.29), a triplet (δ 44.87) and a doublet (δ 54.43). The most diagnostic feature of the c.m.r. spectrum was the triplet; adducts (158) and (160) do not possess an SP^3 carbon atom bearing two hydrogens. In addition, the p.m.r. spectrum of the adduct was consistent with the structure (159). An AB "quartet" was present in the spectrum at δ 4.24 and 4.03 and this signal, which was assigned to H_7 and H_7', cannot arise from adducts (158) and (160). The remaining p.m.r. and c.m.r. spectral characteristics (see Experimental) were also consistent with the structure (159).



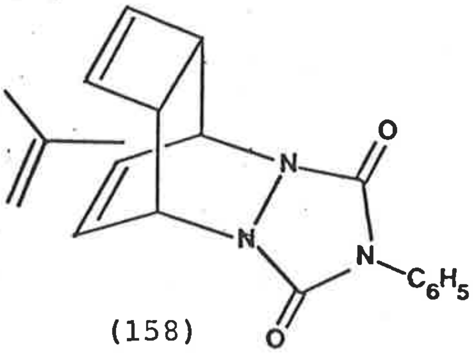
(88)



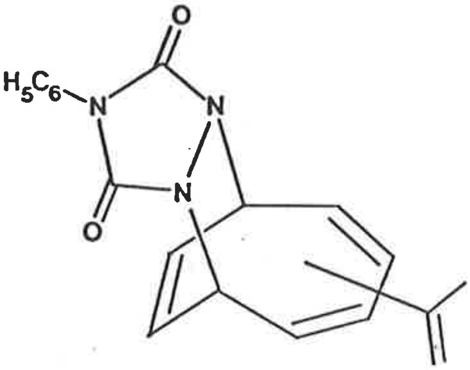
(157)



(159)

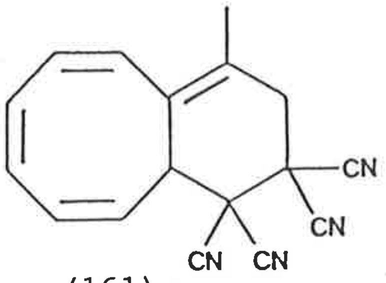


(158)



(160)

In a similar manner, tetracyanoethylene reacted with an equimolar amount of isopropenylcyclooctatetraene in ethyl acetate to give the Diels-Alder adduct (161) (93%). The possibility that adducts analogous to (158) and (160) were formed was ruled out after an examination of the c.m.r. spectrum of the product. In addition to containing signals at high field similar to those observed for (158), the c.m.r. spectrum of (161) contained two additional, but very



(161)

weak, singlets at δ 37.17 and 43.12. The origin of these signals was attributed to the two quaternary carbon atoms bearing nitrile substituents. Signals due to such carbon atoms, although not observed in the c.m.r. spectra of the π8 + π2 or "3,6" adducts described in Chapter 1, have been reported to occur in the vicinity of δ 43 - 53.[81]

It has been shown that 1,4 cycloaddition to (88) and Diels-Alder addition to its bicyclic valence tautomer (157) do not occur. The concentration of (157), it should be noted, is likely to be very low compared to that of (88).[107] Moreover, it has been shown[107] that the rate-limiting step in the Diels-Alder additions of reactive dienophiles to the bicyclic valence tautomers of cyclooctatetraenes is the formation of these tautomers. Therefore, bearing in mind the relative rates of addition of dienophiles to butadienes[108] and the valence tautomerization of cyclooctatetraenes,[107] it can be seen that the rates of formation of (159) and (161) should exceed the rate of formation of Diels-Alder adducts such as (158). Tetracyanoethylene, except in special cases,[24] does not enter into 1,4 cycloadditions with cyclooctatetraenes[107,22] and such additions of N-phenyltriazolinedione are inefficient;[14,16,23] therefore, 1,4 cycloaddition is unlikely to compete effectively with Diels-Alder additions to (<u>88</u>).

The Diels-Alder adduct (<u>159</u>), which contains a 7-alkylidenecycloocta-1,3,5-trienyl moeity similar to those possessed by the olefins discussed in Chapter 1, reacted with an excess of N-phenyltriazolinedione in boiling dichloromethane to give a *bis*-adduct (mass spectrometry) in quantitative yield. Although high resolution mass spectrometry confirmed that this adduct had a molecular formula of $C_{27}H_{22}N_6O_4$, a satisfactory elemental analysis could not be obtained;* as a consequence, any assignment of a structure to this adduct must be considered tentative. Its p.m.r. spectrum contained a singlet (3H) at δ 2.19 which can be attributed to a methyl group attached to a double bond. The presence of such a methyl group implies that the second equivalent of dienophile did not add to the C_8-C_9 double bond of (<u>159</u>), i.e. not in an $\pi 8+\pi 2$ manner. Although the *bis*-adducts (<u>162</u>), (<u>163</u>) and (<u>164</u>), which might be generated from (<u>159</u>) by $\pi 4+\pi 2$, processes ** all contain a methyl group attached to a double bond, the possibility that (<u>162</u>) had been obtained was eliminated after a closer examination of the p.m.r. spectrum of the compound. In addition to the

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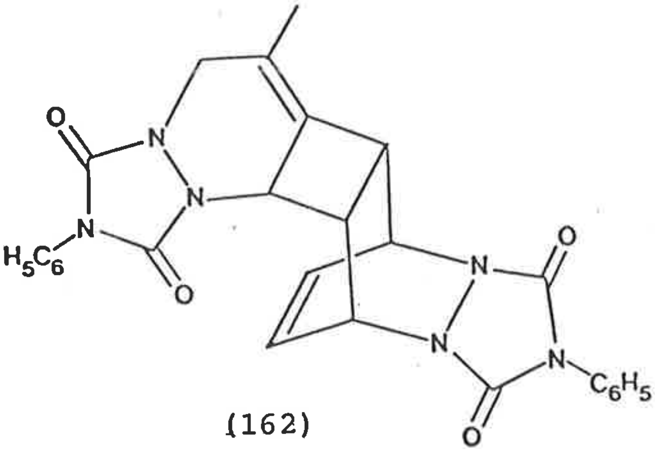
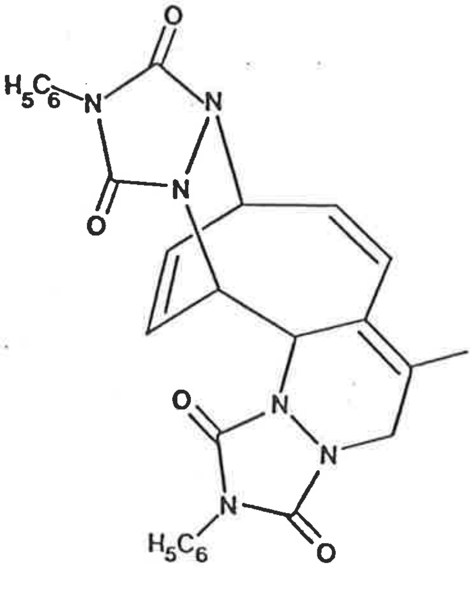
* Recrystallization of this substance to a constant melting point yielded a substance which gave an elemental analysis corresponding to $C_{27}H_{22}N_6O_4 \cdot 2(H_2O)$ (see Experimental).

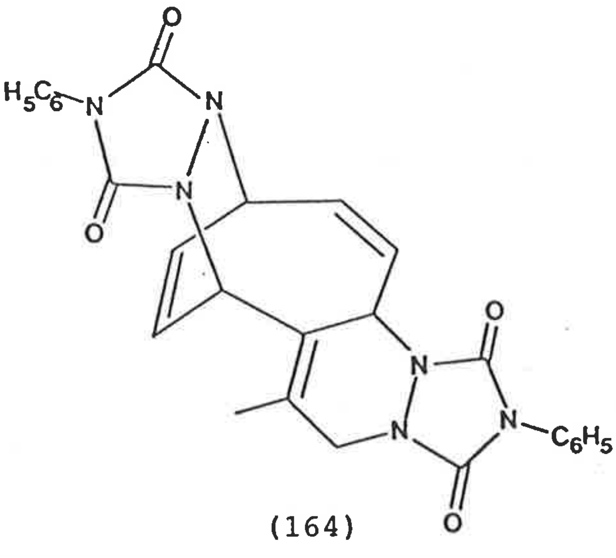
** *bis*-Adducts generated from (<u>159</u>) by a $\pi 2+\pi 2$ process were not considered because addition of N-phenyltriazolinedione in this manner to a polyolefin is unlikely.[109,110]


O
N
N
N
H_5C_6
O
N
O
N
N
C_6H_5
O

(162)


O
H_5C_6
N
N
N
O
O
N
N
N
H_5C_6
O

(163)


O
H_5C_6
N
N
N
O
O
N
N
N
C_6H_5
O

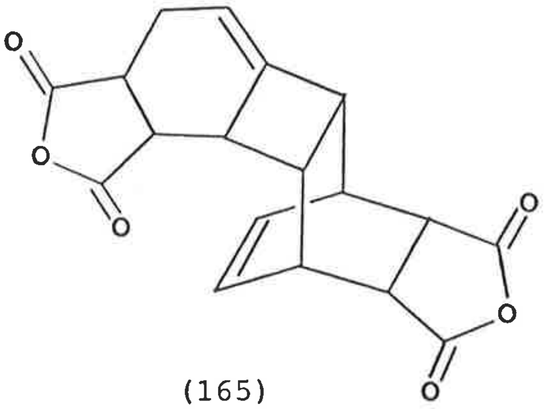
(164)

singlet at δ 2.19, the spectrum contained an AB "quartet" (2H, J_{AB} 16.5 Hz) centred at δ 4.26 and 3.96, a complex system of two multiplets between δ 6.84 and 5.29 (2H and 5H) and a broad singlet at δ 7.48 (10H). Protons which could give rise to the AB "quartet" (H_A and H_B) are possessed by (162), (163) and (164) but it was expected that (162) would give rise to signals (5H) at a field higher than the AB "quartet"; a signal due to the cyclobutyl protons (2H) as well as the singlet due to the vinylic methyl group should be observed. The spectral characteristics of the *bis*-adduct are not consistent with those expected for (162). Unfortunately, homonuclear decoupling of the complex signals between δ 6.84 and 5.29 was not possible and, therefore, p.m.r. spectroscopy could not be used to differentiate between (163) and (164).

Due to the low solubility of this *bis*-adduct, a meaningful c.m.r. spectrum of it could not be obtained; due to the similarity of (163) to (164), however, c.m.r. spectroscopy might be a tool of limited application in this case. Since N-methyltriazolinedione (11) adducts often are more soluble than analogous N-phenyltriazolinedione adducts,[23] the assignment of a structure to the *bis*-adduct might be facilitated by preparing and identifying (principally with the aid of x-ray crystallography) an analogous N-methyltriazolinedione adduct.

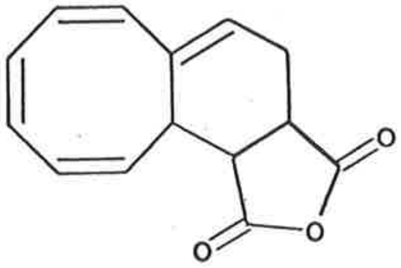
2.3 THE REACTION OF VINYLCYCLOOCTATETRAENE WITH AN EXCESS OF MALEIC ANHYDRIDE

Vinylcyclooctatetraene, which was prepared by coupling either vinyllithium[111] or vinylmagnesium bromide with bromocyclooctatetraene, was treated with an excess of maleic anhydride in the manner described by Withey.[104] The product from this reaction, m.p. 302 - 304°C (lit.[104] 303 - 305), was confirmed to be a *bis*-adduct by mass spectrometry. C.m.r. and p.m.r. spectroscopy indicated that it contained only two double bonds, one of which was trisubstituted. A large and complex signal (9H) was observed between δ 2.88 and 0.93 in the p.m.r. spectrum and c.m.r. spectroscopy showed that the *bis*-adduct contained at least eight non-equivalent SP³ carbon atoms all of which, except one, were tertiary. On the basis of these spectral characteristics, structure (165) was assigned to the *bis*-adduct.



(165)

It is obvious, then, that the alkenylcyclooctatetraenes (88) and (156) yield different types of *bis*-adducts with maleic anhydride and N-phenyltriazolinedione. Moreover, if it is assumed that (166) is a precursor to (165), then from the above and the results obtained by Ferber,[36] it can be seen that the three structurally related olefins (166), (159) and (49) give three different types of adduct (1,4, Diels-Alder, and $\pi 8 + \pi 2$) with (12), maleic anhydride and (21), respectively. The differing behaviours of maleic anhydride and N-phenyltriazolinedione towards the olefins (166) and (159), respectively, may be due to the reluctance, compared to the triazolinedione, of maleic anhydride to enter into dipolar cycloaddition reactions.[81]



(166)

Factors which might have been responsible for preventing the formation of $\pi 8 + \pi 2$ adducts from (166) and (159) are not obvious; a subtle interplay of steric and electronic factors (such as the ability of the nitrogen atoms and carbonyl groups in (159) to reduce the nucleophilicity of the $C_8 - C_9$ double bond) may play an important role.

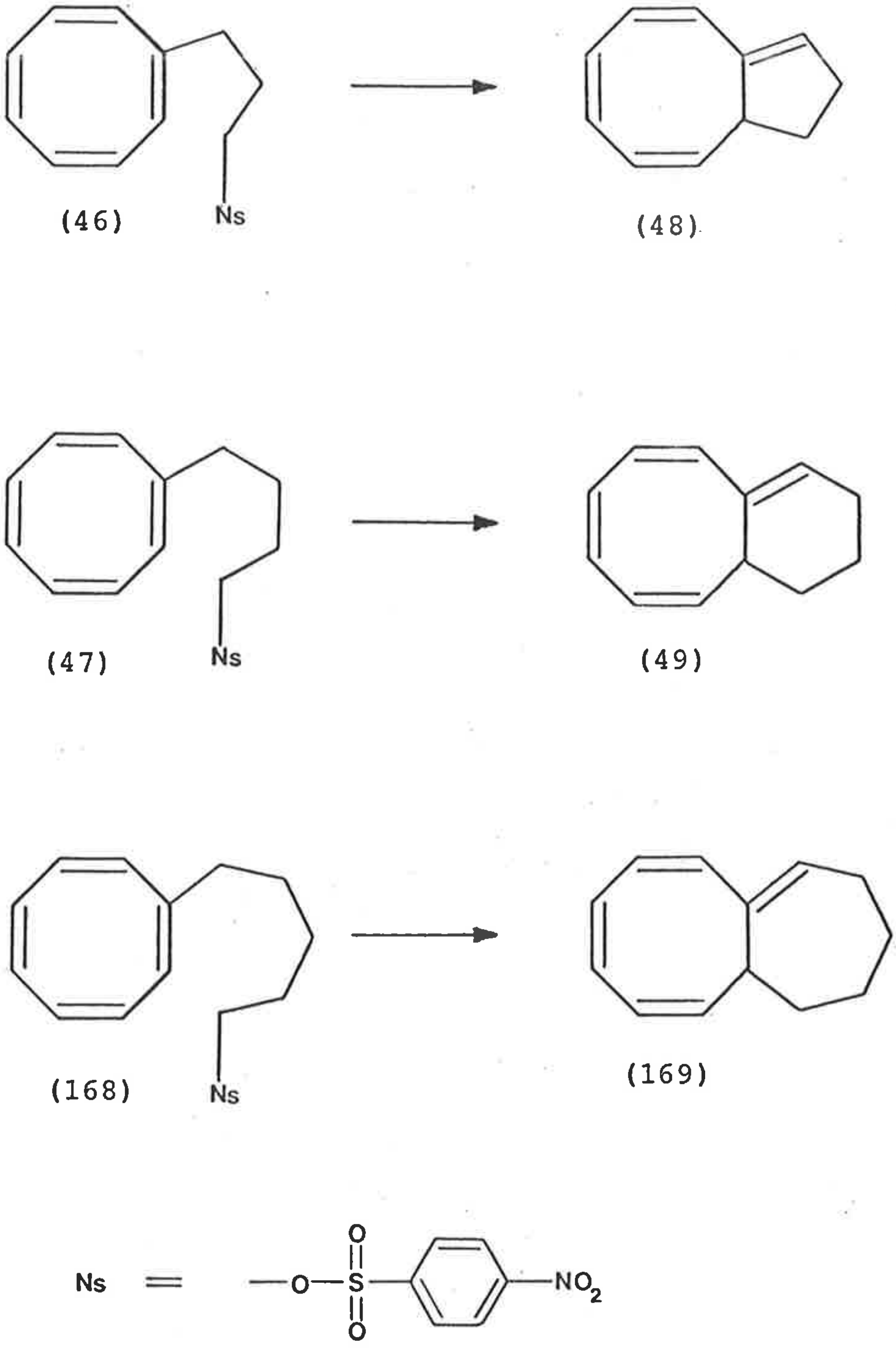
CHAPTER 3

THE SOLVOLYSIS OF 5-CYCLOOCTATETRAENYLPENTYL *p*-NITROBENZENESULPHONATE

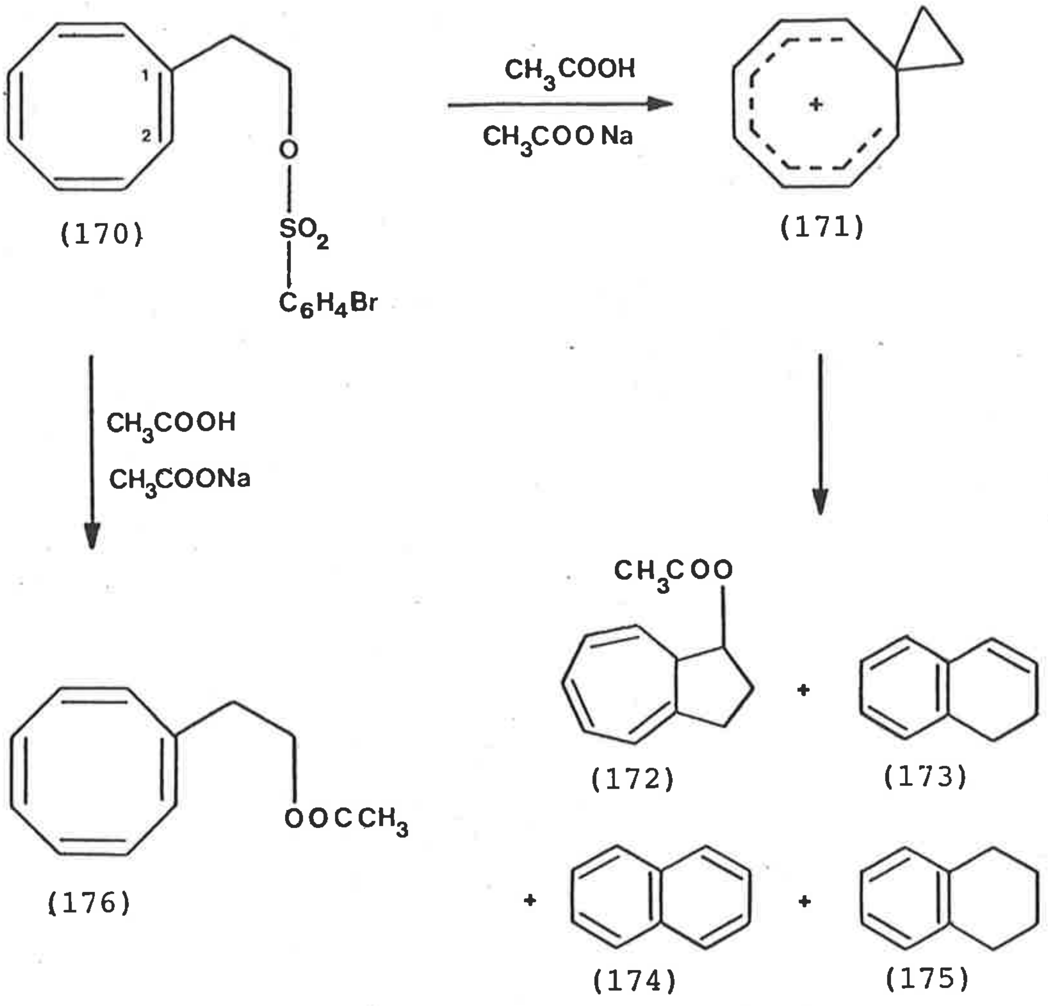
3.1 INTRODUCTION

As mentioned in Section 1.1, Gream and coworkers[37,112] have shown that the cyclooctatetraenylalkyl *p*-nitrobenzenesulphonate esters (46) and (47) produce the "annelated 7-alkylidenecycloocta-1,3,5-trienes" (48) and (49) on solvolysis (Scheme 47). It was therefore decided to examine the solvolysis of 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (168) to determine whether it might provide an efficient route to bicyclo[6,5,0]trideca-2,4,6,8(9)-tetraene (169) (Scheme 47).

Evidence that the π bonds in the cyclooctatetraenyl moeity provide assistance to the solvolyses of some cyclooctatetraenylalkyl arenesulphonate esters has been provided by Paquette[113,114] and Gream[37,112] and their coworkers. Paquette[114] has shown that the C_1C_2 double bond of (170), through a homoallylic interaction, assists in the displacement of the arenesulphonate group and that the cation (171) thus produced undergoes various rearrangements to give, ultimately, the azulene and naphthalene derivatives (172), (173), (174) and (175) (Scheme 48). Only a modest degree, however, of anchimeric assistance is rendered by the cyclooctatetraenyl



SCHEME 47



SCHEME 48

moeity. From Table 7 , it is evident that although (170) solvolyses more rapidly than its saturated analogue (177), neither of these rates approaches that of the solvolysis of the cyclooctenyl sulphonate ester (178).[114]

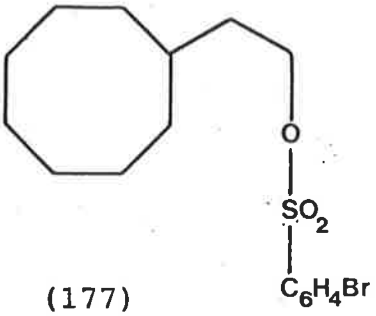
TABLE 7

Rates of acetolysis (65°) of various *p*-bromobenzenesulphonates

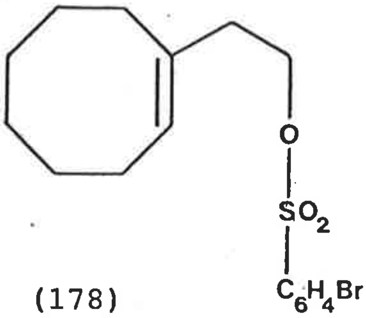
Substrate	Rate of Solvolysis** (sec^{-1})	Relative Rate[114]
(170)	6.58×10^{-6}	5
(178)	3.74×10^{-4}	260
(177)	1.43×10^{-6}*	1

* *extrapolated value*

** *with sodium acetate buffer*



(177)



(178)

Gream and coworkers[37] have shown that 3-cyclooctatetraenylpropyl and 4-cyclooctatetraenylbutyl *p*-nitrobenzenesulphonates (46) and (47) solvolyse in 1,1,1,3,3,3-hexafluoropropan-2-ol* to give a range of products (Scheme 49). Since the saturated analogues (187) and (188) solvolyse more slowly than (46) and (47), the participation of the cyclooctatetraenyl moeity in the ionizing step has been unequivocally demonstrated (Table 8).

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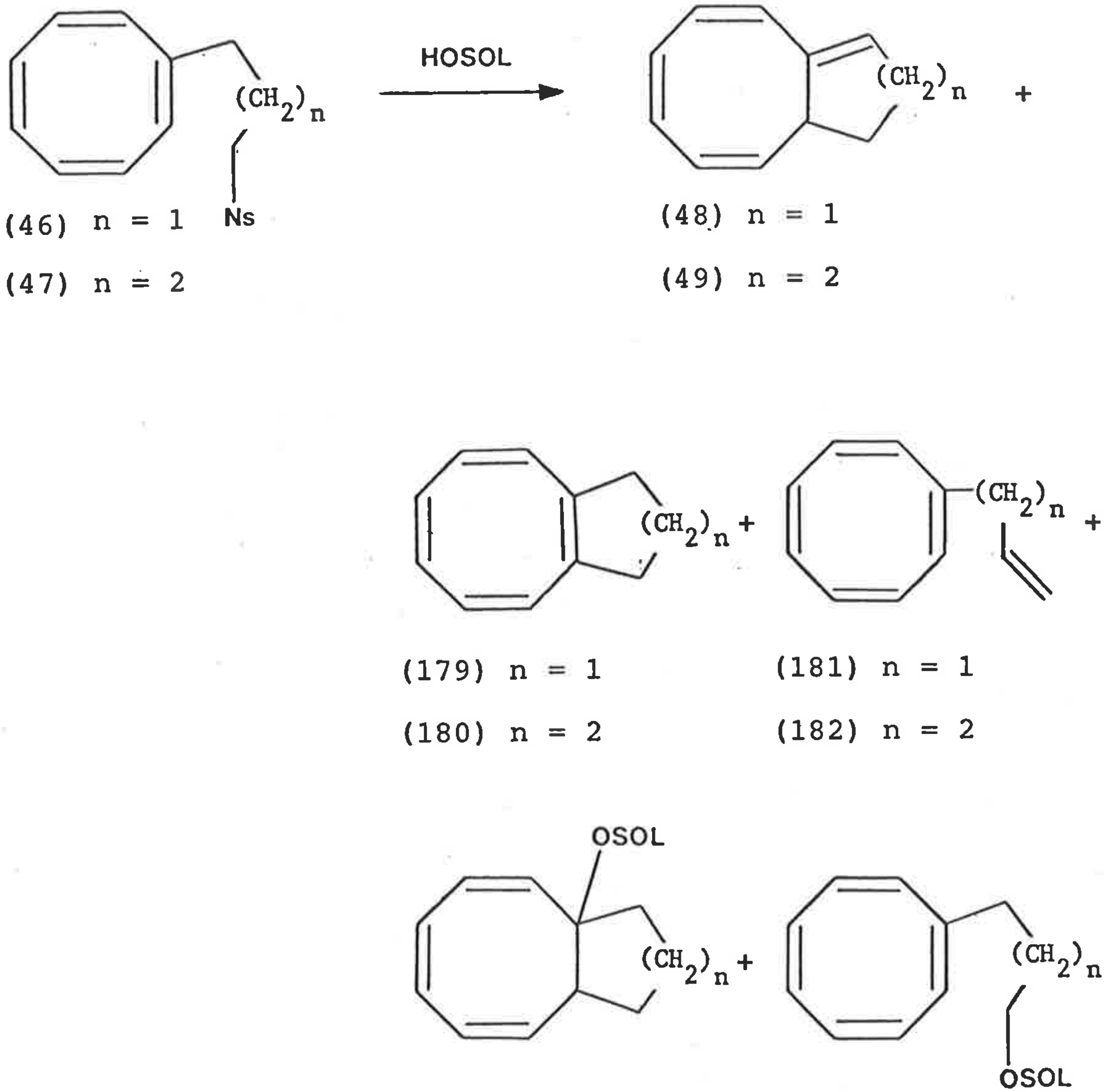
* Referred to as hexafluoropropan-2-ol hereafter.



(46) n = 1
(47) n = 2

(48) n = 1
(49) n = 2

(179) n = 1
(180) n = 2

(181) n = 1
(182) n = 2

(183) n = 1
(184) n = 2

(185) n = 1
(186) n = 2

HOSOL = CF_3-CHOH-CF_3

SCHEME 49

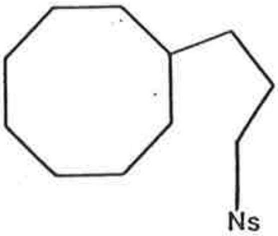
TABLE 8

Rates of solvolysis (in hexafluoropropan-2-ol at 100°) of various *p*-nitrobenzenesulphonates

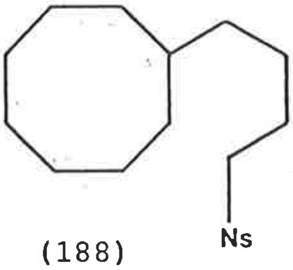
Substrate	Rate of solvolysis** (10^5 k, sec^{-1})	Rate Enhancement k *saturated*/k *unsaturated*
(46)	32.3; 33.2	5.49
(187)	5.89; 6.05	
(47)	467*	151
(188)	3.09; 3.10	

* *with extrapolated value*

** *with triethylamine buffer*



(187)



(188)

The work of Paquette[114] and Gream[37,112] and their coworkers has shown that the concentrations of buffer and sulphonate ester and the nature of the solvent are important factors influencing the outcome of these solvolytic reactions. It can be seen (Table 9) that at low concentrations of buffer and substrate, the solvolysis of (170) exclusively produces cyclized products. In common with many solvolyses, at progressively higher concentrations it is evident that competition from Sn2 displacement of the leaving group increases; interestingly, a comparatively high concentration of buffer and ester is required to induce the formation of the azulene derivative (172).

TABLE 9

Products of acetolysis of (170) as a function of concentration

Buffer Conc. (M)	Ratio [Buffer]: [(170)]	Product Composition (%)				
		(172)	(173)	(174)	(175)	(176)
0.1	1:1		86	7	7	
0.2	10:1	69	12			19
2.0	10:1	48	3			49

Gream and coworkers[37] have found that the use of hexafluoropropan-2-ol (and, to a lesser extent, 1,1,1-trifluoroethanol) compared to acetic acid as solvent leads to a remarkably high yield of cyclized products (Table 10). It is important to note that significant π bond participation in the solvolyses of other pent-4-enyl* derivatives has been previously observed only in special cases;[115,116] pent-4-enyl *p*-nitrobenzenesulphonate (189), for example, cyclizes to the extent of only 1.5% even in hexafluoropropan-2-ol.[117] It has been suggested[37,117,118,119] that the high ionizing capacity[120] and low nucleophilicity[120] of hexafluoropropan-2-ol is responsible for its extraordinary ability to induce cyclization of substrates which have been previously regarded as incapable of displaying such behaviour.

---

* That is, compounds with the double bond in the 4,5 position to the carbon atom bearing the leaving group.

TABLE 10

Products (%) from the solvolyses of (46) and (47) (100°) as a function of solvent

Substrate	Solvent (HOSOL, Scheme 49)	Product Distribution (48)	(179)	(181)	(183)	(185)	Cyclization (%)
(46)	acetic acid[A]	1.6		1.0		97.4	1.6
(46)	CF_3CH_2-OH [B]	39(73)		trace		27	39(73)[C]
(46)	CF_3-CHOH-CF_3[B]	67(99.5)[C]		trace		0.5	67(99.5)[C]
		(49)	(180)	(182)	(184)	(186)	
(47)	acetic acid[A]	40.3	2.6	0.9		56.2	43
(47)	CF_3-CH_2-OH[B,D]	28.9	3.5		61.7	5.9	94.1
(47)	CF_3-CHOH-CF_3[B,E]	98.8	1.2				100

A *Buffer, 0.02 m sodium acetate.*

B *Buffer, 0.02 m triethylamine.*

C *Yield in parentheses is based on the assumption that (48) is the only product that is not stable to the reaction conditions.*

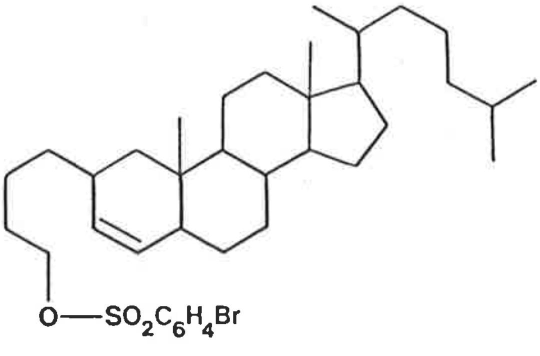
D *Solvolysis conducted at 80°.*

E *Solvolysis conducted at 40°.*

(189)

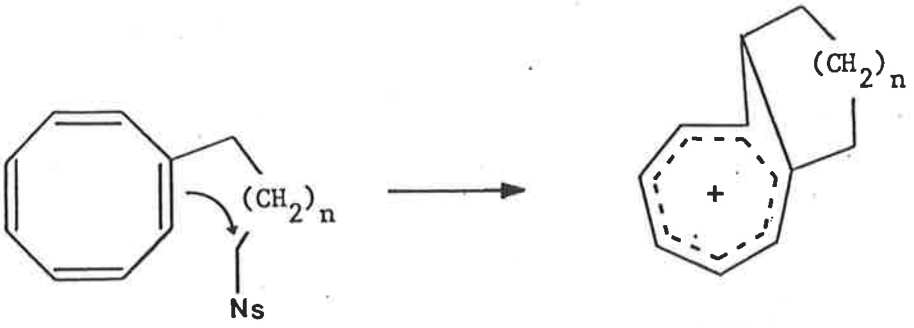
3-Cyclooctatetraenylpropyl *p*-nitrobenzenesulphonate (46), compared to the behaviour of the analogous pent-4-enyl derivative pent-4-enyl *p*-nitrobenzenesulphonate (189), solvolyses in hexafluoropropan-2-ol with substantial π bond participation and since the hept-6-enyl derivatives (190)[121] and (191)[122] cyclize to a significant extent even in 1,1,1-trifluoroethanol, it was felt that 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (168), also a hept-6-enyl derivative, should cyclize to an appreciable extent in hexafluoropropan-2-ol.

(190)



(191)

It has been convincingly argued by Gream and Ferber[37] that homotropylium cations (192) are generated by the solvolyses of (46) and (47) (Scheme 50). Whereas (168) might



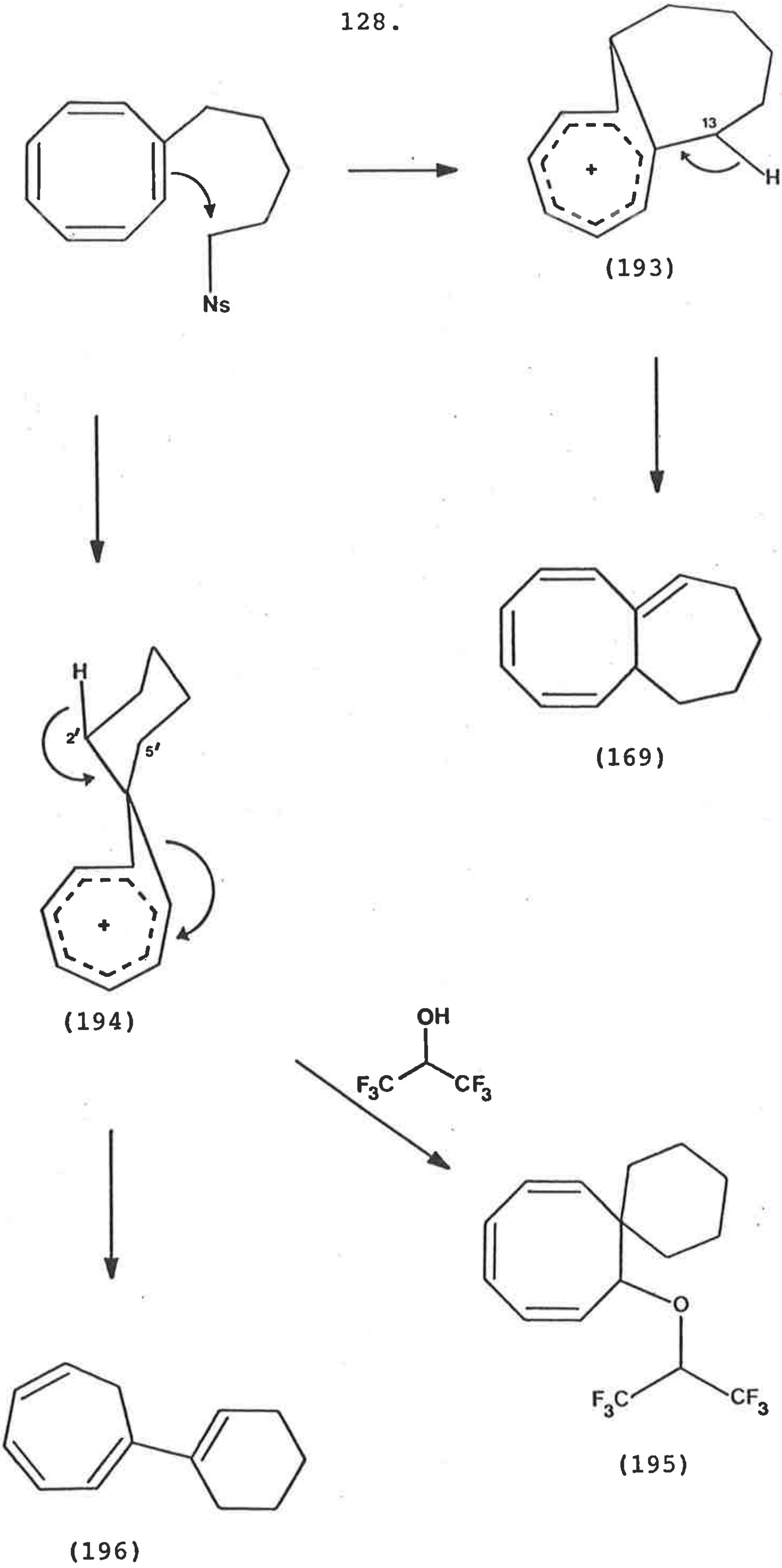
(46) n = 1

(47) n = 2

(192)

SCHEME 50

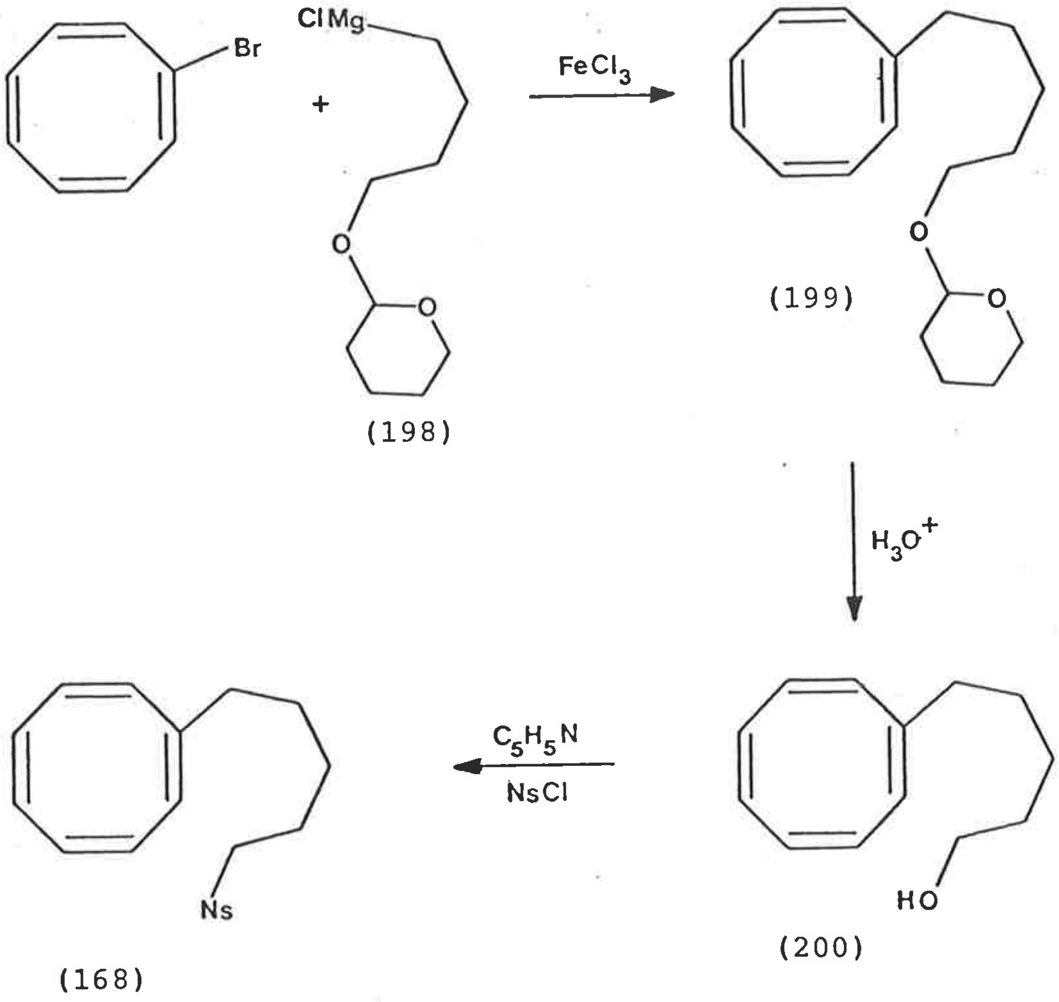
produce an analogous homotropylium cation (193) which should suffer deprotonation at C_{13}[37] to give the desired tetraene (169), it might also give the spirohomotropylium cation (194) by a six atom cyclization process (Scheme 51).[121] The fate of (194) is open to conjecture; it is possible that (194) might rearrange to (193), for example, suffer nucleophilic attack to give spiro compounds such as (195) or yield the cycloheptatrienyl derivative (196) on deprotonation at C_2' or C_5' (Scheme 51).



SCHEME 51

3.2 RESULTS AND DISCUSSION

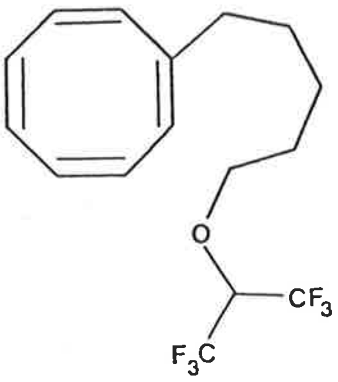
The coupling of bromocyclooctatetraene with the Grignard reagent (198) derived from 5-chloropentyl tetrahydropyran-2-yl ether (197) in the presence of ferric chloride produced 5-cyclooctatetraenylpentyl tetrahydropyran-2-yl ether (199) which gave, after acid hydrolysis, 5-cyclooctatetraenylpentanol (200) (38% based on the amount of bromocyclooctatetraene used) (Scheme 52). In the presence of a slight excess of pyridine,[112] the reaction between *p*-nitrobenzenesulphonyl chloride and (200) furnished 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (168) (Scheme 52).



SCHEME 52

The solvolysis of (168) was carried out under two sets of conditions:

(1) A relatively concentrated solution of (168) (0.125 M) and triethylamine (as buffer, 0.33 M) in hexafluoropropan-2-ol was heated at 85°. Unexpectedly, work-up of the reaction mixture (when p.m.r. spectroscopy indicated that (168) had been totally consumed) yielded a mixture containing 5-cyclooctatetraenylpentyl 1,1,1,2,2,2-hexafluoroprop-2-yl ether (201) (*ca.* 88% by g.l.c.). The assignment of structure (201) to the product was based on its p.m.r. and mass spectral characteristics; the possibility that the isomeric compounds (202) and (195) were obtained was ruled out by the presence of a triplet (2H) at δ 3.86 in the p.m.r. spectrum and a peak at *m/e* 117 (due to loss of $-CH_2-CH_2-CH_2-CH_2-O-CH-(CF_3)_2$)[123] in the mass spectrum.



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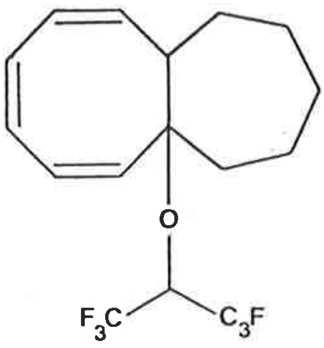
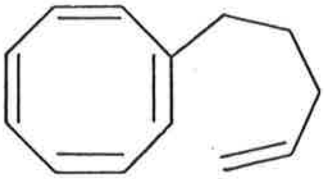


(202)

(2) Since triethylamine is sufficiently basic (pk_a 11.0)[124] to abstract a proton from hexafluoropropan-2-ol (pk_a 9.3)[125] (thereby giving rise to the nucleophilic hexafluoroprop-2-oxide ion) a relatively dilute solution of triethylamine (0.02 M) and (168) (0.01 M) was solvolysed at 85° for 22 h. A mixture of eight compounds (g.l.c.) was formed with the most abundant component, the ether (201) (identified by g.l.c. peak enhancement), present to the extent of approximately 23% (g.l.c.), apart from (201), none of the other components was identified. Since it is known that 7-alkylidene- and 7-arylidenecycloocta-1,3,5-trienes are prone to polymerization, a solvolysis of a mixture (0.01 M in (168) and 0.02 M in triethylamine) that had been degassed thoroughly by freeze-thaw cycles under a reduced pressure of nitrogen was carried out. Again, the mixture of eight components was formed; because unchanged (168) was not obtained, it was felt that its solvolysis had produced a large amount of unstable material. If it is assumed, on the basis of the results of Gream and Ferber,[37] that only two monocyclic products (*i.e.* (201) and (203)) were formed by the solvolysis of (168) and that (169) is not stable under the reaction conditions, it can be concluded that the extent of cyclization of (168) might be approximately 65% (100% - 23% - 12%; the latter figure represents the yield of the second most abundant component of the mixture).



(203)

After solvolysis for 4 h at 85°, a similar mixture of eight compounds, together with some unchanged (168), was obtained.

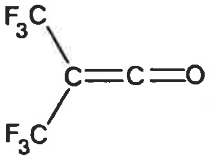
Synthesis of (169) by this route, therefore, does not appear to be feasible.

CHAPTER 4

THE TREATMENT OF CYCLOOCTATETRAENE AND ITS DERIVATIVES WITH DICHLOROKETENE

4.1 INTRODUCTION

Only one example of the addition of a ketene to cyclooctatetraene has been reported. England,[126] who was investigating the scope and limitations of cycloaddition reactions between olefins and *bis*-(perfluoromethyl)ketene (204), treated this ketene with cyclooctatetraene and obtained a $\pi 4 + \pi 2$ adduct (205) instead of the expected $\pi 2 + \pi 2$ adduct (206),



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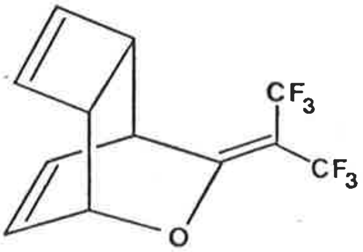

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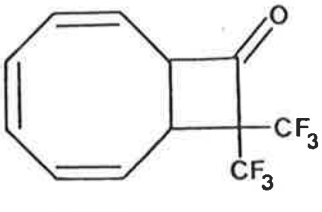
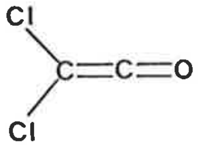


(206)

It was hoped that cyclooctatetraene would enter into $\pi 2 + \pi 2$ cycloaddition with dichloroketene (207) to produce 1:1, 1:2 and 1:3 adducts (208), (209) and (210). Dichloroketene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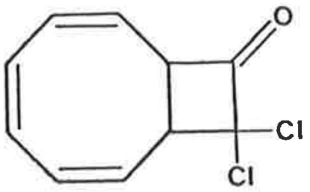
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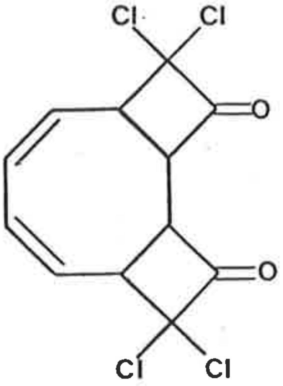
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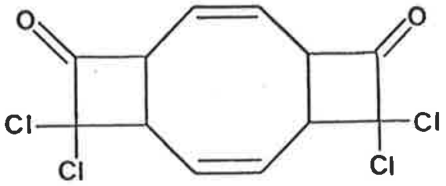
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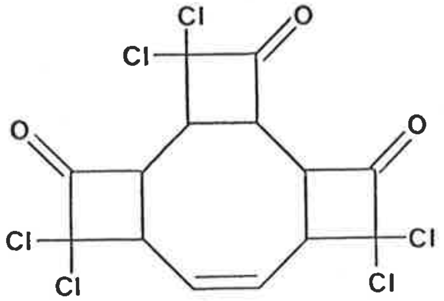
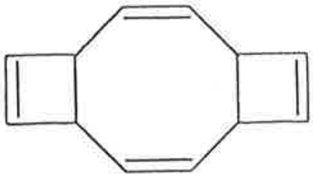

(210)

was chosen as the ketene with which to examine the cycloaddition reactions of cyclooctatetraene for two reasons:

(1) Compared to other ketenes, (207) exhibits a high reactivity towards olefins;[127] in the presence of

phosphorus oxychloride[128] (and under conditions of high dilution)[129,130] dichloroketene has been shown to enter into $\pi 2 + \pi 2$ cycloadditions with poor "ketenophiles" such as norbornenes.

(2) The α,α-dichlorocyclobutanones produced by $\pi 2 + \pi 2$ cycloaddition of (207) to olefins are able to be converted into a diverse range of compounds.[127] Therefore, in addition to being products of a hitherto unreported cycloaddition reaction of cyclooctatetraene, the adducts (208), (209) and (210) might be versatile synthetic intermediates. In particular, it was thought that these adducts might be converted into annulenes. Using a process similar to that devised by Gream and Meinwald,[131] (209) and (210) might yield the olefins (211) and (212) which are likely to undergo cycloreversion to give 12- and 14-annulenes, respectively. On similar treatment, (208) might give (213) which is thought to produce 10-annulene on cycloreversion.[132]



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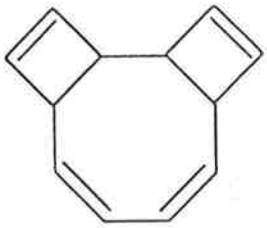

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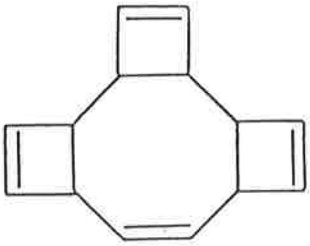

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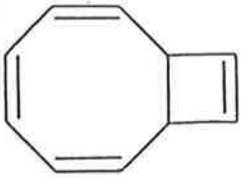


(213)

4.2 RESULTS AND DISCUSSION

Under the conditions outlined in Table 11, dichloroketene did not form an adduct with cyclooctatetraene; in all cases, cyclooctatetraene (>85%) was the only identifiable compound obtained.

TABLE 11

Conditions for reactions between cyclooctatetraene and dichloroketene

Run	Solvent	Reaction		Molar Equivalents		Method(s)
		Time	Temp.	Ketene	Cycloocta-tetraene	
1	Ether	2 h	25°	1	1	1[A], 2[B]
2	Ether	2 h	34°	1	1	1,2
3	Ether	12 h	25°	1	1	1,2
4	Ether	12 h	34°	1	1	1
5	T.H.F.[D]	2 h	65°	1	1	1,2
6	T.H.F.	12 h	65°	1	1	1,2
7	Benzene	2 h	25°	1	1	1,2
8	Benzene	2 h	80°	1	1	1
9	Benzene	2 h	80°	1	1	1
10	Benzene	12 h	80°	2	1	1
11	Benzene	12 h	80°	1	2	1
12	Hexane	2 h	25°	1	1	3[C]
13	Hexane	2 h	69°	1	1	3
14	Hexane	2 h	69°	1	1	3

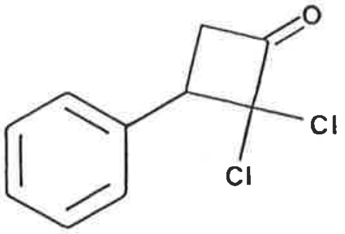
A Dechlorination of trichloroacetyl chloride by zinc.

B Dechlorination of trichloroacetyl chloride by zinc in the presence of 1 molar equivalent of phosphorus oxychloride.

C Dehydrochlorination of dichloroacetyl chloride by triethylamine.

D Tetrahydrofuran.

In Table 11, method 1 refers to that described by Brady.[129] This process involves the generation of dichloroketene, by the action of activated zinc upon trichloroacetyl chloride, *in situ* with the olefin. In this manner, Brady was able to achieve high yields of $\pi2+\pi2$ adducts even with poor "ketenophiles" such as norbornene (64%) and 2,3-dimethyl-2-butene (75%). In boiling ether (the conditions recommended by Brady), dichloroketene did not add to cyclooctatetraene. Compound (214)[128] (74%) was obtained from a control experiment in which the acid chloride was treated with zinc in the presence of styrene; it was therefore assumed that dichloroketene was indeed being generated under the conditions used. The key feature of Brady's method is that loss of ketene by polymerization is reduced. This is achieved by generating the ketene under conditions which approximate to high dilution, that is, the acid chloride is added as a dilute solution (*ca*. 0.05 M) at a very slow and continuous rate to a boiling suspension of activated zinc in ether. It was felt that the failure of dichloroketene to add to cyclooctatetraene in runs 1 and 2 (Table 11) might have been due to the rate of polymerization of the ketene being greater



(214)

than the rate of its cycloaddition to cyclooctatetraene. For this reason, experiments were conducted in which the ketene was generated even more slowly (over 12 h).* In addition, experiments were conducted at higher temperatures in polar (tetrahydrofuran) and non-polar solvents (benzene) (runs 5 to 11, Table 11). It was felt that the rate of cycloaddition to cyclooctatetraene at these higher temperatures might have been fast enough to compete effectively with the polymerization of the ketene. In the event, it was found that none of these experiments was successful.

Method 2 (Table 11) refers to that developed by Krepski[128] which entails the generation of the ketene (from trichloroacetyl chloride and zinc) *in situ* with the olefin and an equimolar amount of phosphorus oxychloride. Although Krepski has shown that this method leads to good yields of ketene adducts, unchanged starting material (greater than 85% recovery) was the only identifiable material obtained when the ketene was generated in the presence of cyclooctatetraene.

Dichloroketene can also be prepared under mild conditions by the action of triethylamine on dichloroacetyl chloride (Method 3, Table 11).[130] Although the ketene was generated (as evidenced by the isolation of (<u>214</u>) from a control experiment) in the presence of cyclooctatetraene, no adducts were obtained; again, only unchanged cyclooctatetraene (greater than 90% recovery) could be isolated.

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* For this purpose, a motor driven syringe (Perfusor) was employed to add the acid chloride.

Cycloaddition of dichloroketene to the cyclooctatetraene molecule was not enhanced by activating it[130] with a methoxyl group. The only identifiable material obtained from the reaction between methoxycyclooctatetraene and dichloroketene (which was prepared by method 3) contained unchanged starting material and cycloocta-2,4,6-trienone (74) (combined yields greater than 90%).* Additional experiments employing methods 1 and 2 were not attempted because it was felt that phosphorus oxychloride and zinc chloride (which is a by-product of methods 1 and 2) might induce polymerization of methoxycyclooctatetraene.[128]

Dichloroketene is thought to add to olefins in a concerted $\pi 2_s + \pi 2_a$ manner in which the carbon-carbon double bonds of the ketene and the olefin, and the nodal planes of these π bonds, must attain the mutually perpendicular arrangement depicted in Figure 15.[129,130] It was thought that unfavourable interactions between the π systems of cyclooctatetraene and the non bonding orbitals on the oxygen atom of the ketene (a situation represented in Figure 16) prevented the attainment of this demanding transition state. Significantly, cycloocta-1,5-diene, which exists in a tub shape similar to that of cyclooctatetraene[133] but does not possess π systems which can inhibit the attack of dichloroketene, forms a $\pi 2 + \pi 2$ adduct with (207).[134]

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* Presumably, hydrolysis of methoxycyclooctatetraene to give (74) occurs during the aqueous (and slightly acidic) work-up of the reaction.

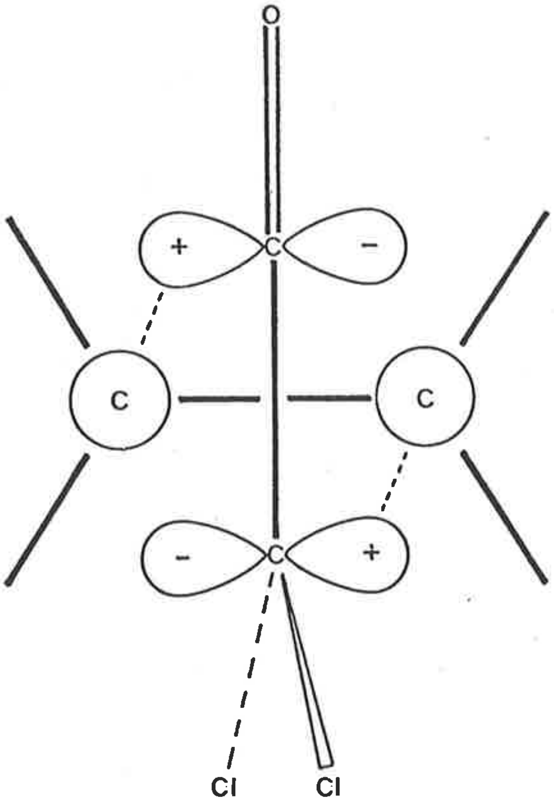
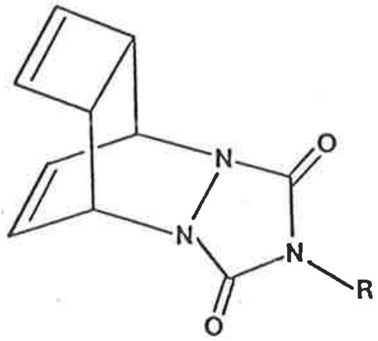


FIGURE 15

To circumvent this problem, the additions of dichloroketene to masked cyclooctatetraene species containing carbon-carbon double bonds suitably disposed for ketene attack were examined. Cyclohexenes[128,129,134] and the cyclobutenyl moeity in (215)[135] form adducts with dichloroketene and therefore it seemed reasonable to expect (216), (217) or (2) to form adducts. Compounds such as (218) (derived from (216)) might be converted into (208) by the procedures reported by Snyder[136] and Adam[137] (Scheme 53).



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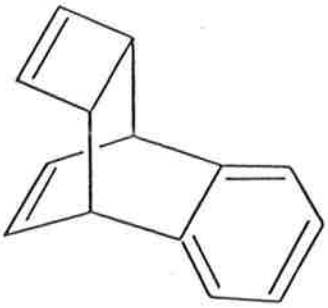

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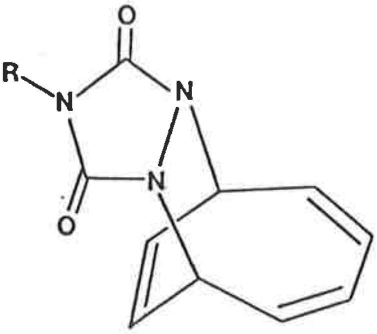

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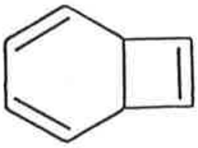

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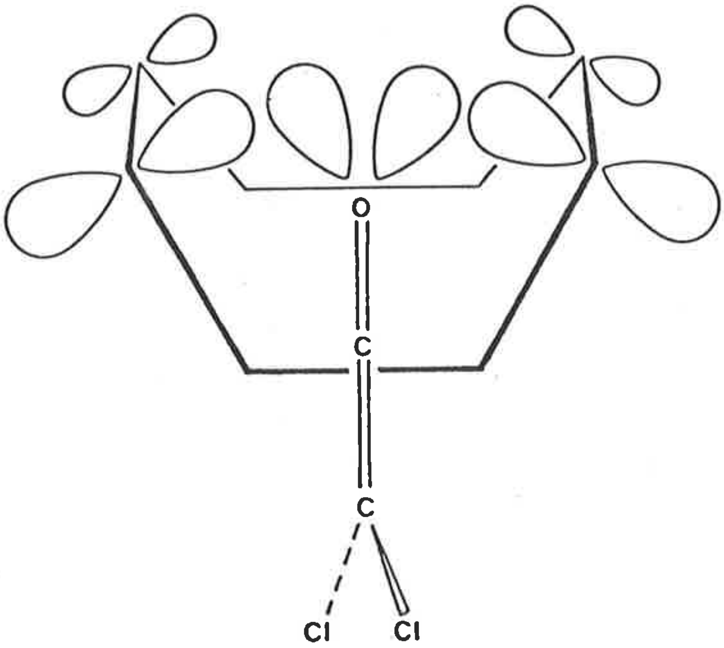
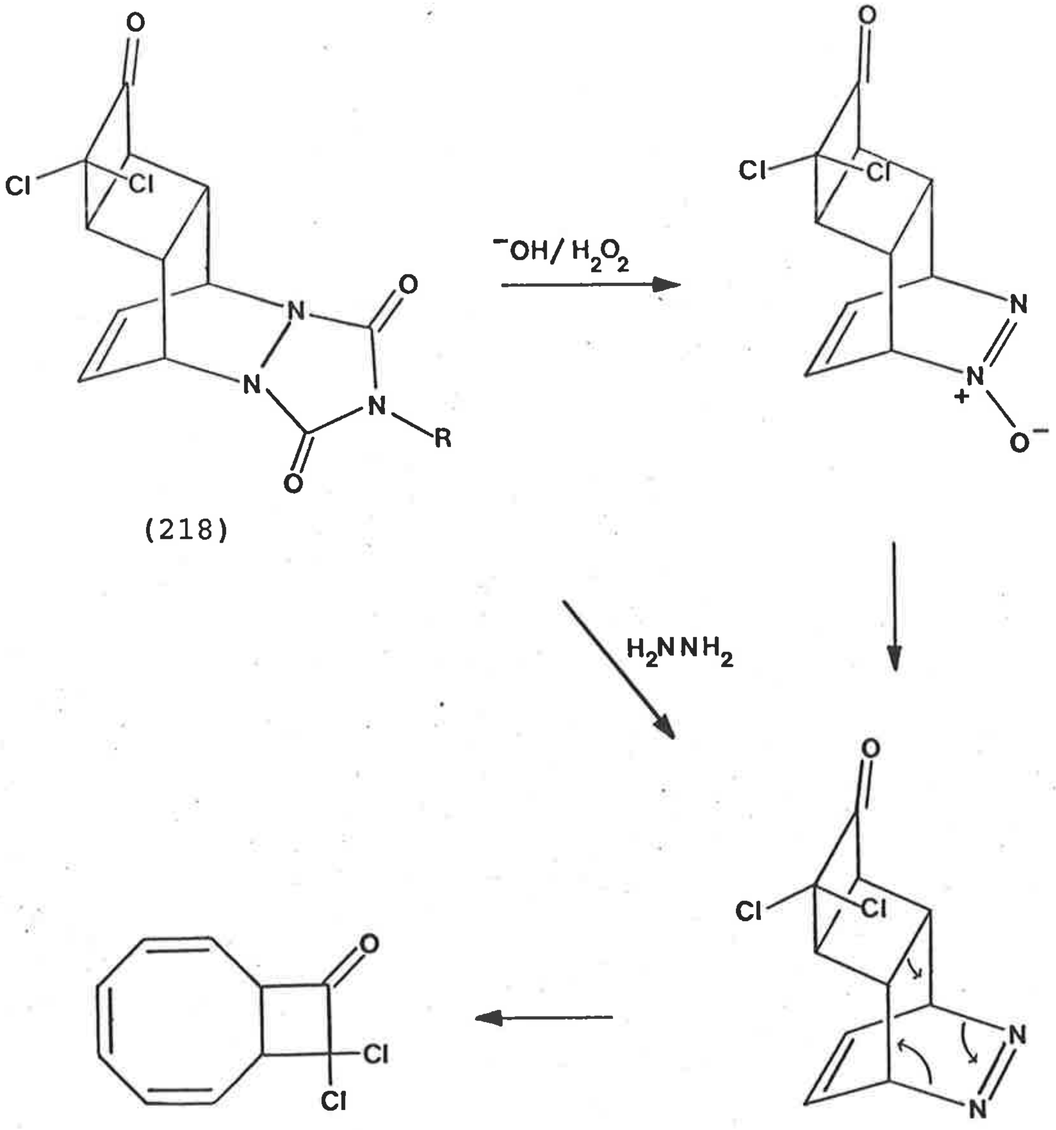


FIGURE 16



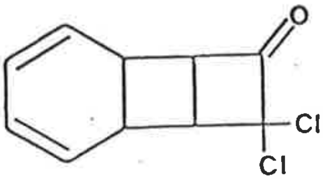
(218)

(208)

SCHEME 53

When (216) (R = phenyl)[11,16,138] was treated with dichloroketene (prepared by method 2) in boiling ether or tetrahydrofuran, the only isolable product was a white solid. This substance was shown by p.m.r. spectroscopy to be predominantly unchanged (216) but weak signals, which could be due to (218), were detected. When mixtures of (216) and (217)[11,16,138] were treated with dichloroketene (methods 1 and 2), the material isolated from the reaction mixture was shown by p.m.r. and mass spectroscopy to contain unchanged starting material and a trace of a substance with a molecular weight of approximately 500; this compound might be a 1:2 adduct.

At 100°, bicyclo[4,2,0]octa-2,4,7-triene (2) is in rapid equilibrium with cyclooctatetraene to the extent of 0.01%,[9] and, therefore, under the conditions outlined in Table 11, the probability of (2) entering into cycloaddition with dichloroketene would have been exceedingly small. To establish whether (219) or (220), which would probably be isolated as (208), could be prepared, (2) was generated at low temperature[139] and treated with dichloroketene (method 3). At temperatures between -40°C and -10°, a range over which (2) has a half life of some hours,[140] dichloroketene did not add to (2).



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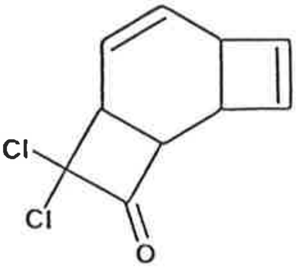
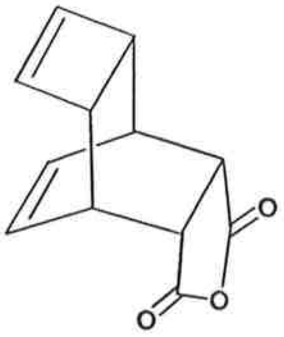


(220)

In only one instance did a reaction between dichloroketene and a derivative of cyclooctatetraene give an adduct in a significant amount. The addition of dichloroketene to the maleic anhydride adduct (222)[2] of cyclooctatetraene, which only proceeded in the presence of phosphorus oxychloride, yielded a solid (31%) which was tentatively identified as (223) on the basis of its p.m.r. and mass spectral characteristics. Unfortunately, a method for the simple conversion of (223) into (208) is not available.



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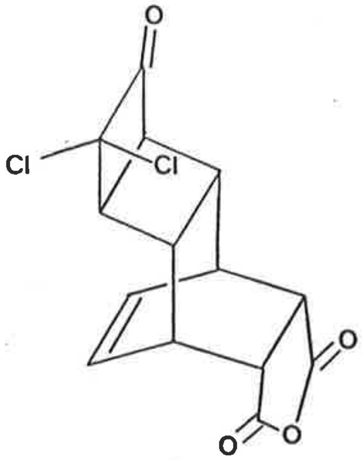
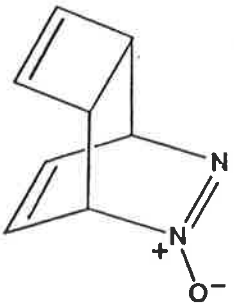


(223)

From the examples discussed above, it would appear that the cyclobutenyl fragment of Diels-Alder adducts of cyclooctatetraene is capable of entering into cycloaddition with dichloroketene. It might be possible, therefore, to find conditions under which the reaction between (216) (or other masked cyclooctatetraenes such as (224)) and dichloroketene produces the desired adduct (218) in a quantity which is sufficient to allow its conversion into (208).



(224)

EXPERIMENTAL

GENERAL

Proton magnetic resonance (p.m.r.) spectra were recorded at 80 MHz (unless stated otherwise) with a Bruker W.P.80 spectrometer using deuterochloroform as solvent (unless stated otherwise) and tetramethylsilane as internal standard; spectra were recorded at 60 MHz with a JEOLCO JNMPMX60 spectrometer.

Carbon magnetic resonance (c.m.r.) spectra were recorded with a Bruker W.P.80 spectrometer operating at 20.1 MHz. Chemical shifts were determined relative to the signal obtained for deuterated solvent (deuterochloroform unless stated otherwise). Signal multiplicities, for both ^{13}C and ^{1}H nuclei, are given in brackets (following the magnitude of the chemical shift) and are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet.

Infra-red spectra were determined as liquid films for liquids and in chloroform solutions for solids unless stated otherwise. The spectra were recorded on a Jasco IRA-1 grating spectrometer, the absorption frequencies (ν_{max}) are given in cm^{-1} and the intensities of the absorptions are expressed as follows: s, strong; m, medium; w, weak; b, broad; sh, shoulder.

Electronic spectra were recorded in ethanol solutions (unless stated otherwise) on a UNICAM SP8-100 spectrophotometer.

Mass spectra were determined with an AEI-GEC MS 3074 spectrometer operating at 70 eV.

Melting points were obtained with a Koffler hot stage microscope and are uncorrected.

Analytical gas-liquid chromatography (g.l.c.) was carried out with either a Pye 104 gas chromatograph or a Perkin-Elmer Sigma 3B instrument connected to a Perkin-Elmer PE M2 calculating integrator. Both chromatographs were equipped with flame ionization detectors. The following columns were used (flow rate of carrier gas (nitrogen) is shown in parentheses):

(a) 5% A piezon M on Varaport 30, (100 - 120 mesh), 3 m × 2 mm, (30 ml/min),

(b) 3% OV17 on Gas Chrom Q (100 - 120 mesh), 2 m × 2 mm, (30 ml/min),

(c) 15% SE-30 on Varaport 30 (100 - 120 mesh), 2 m × 2 mm, (40 ml/min),

(d) 5% OV17 on Varaport 30, (80 - 100 mesh), 3 m × 2 mm, (30 - 40 ml/min),

(e) 5% A piezon M on Varaport 30, (80 - 100 mesh), 3.5 m × 2 mm.

Analytical and preparative high performance liquid chromatography (h.p.l.c.) was carried out with either Spectra-Physics Chromatronix 3500 or Waters Associates liquid chromatographs. The latter was equipped with a differential refractometer while the Chromatronix instrument was connected to an absorbance detector (254 nm). The following columns were used:

with the Chromatronix instrument, 10 μm silica gel (Lichrosorb), 350 mm × 2 mm (analytical work); 350 mm × 10 mm (preparative work);

with the Waters instrument, 10 μm silica gel (Radial Pak B, Waters Associates), 100 mm × 10 mm (preparative and analytical work).

All organic extracts were dried over anhydrous magnesium sulphate unless stated otherwise.

Light petroleum refers to the fraction of boiling point 55 - 70°; anhydrous organic solvents were prepared according to Burfield[141] or Perrin.[142]

Elemental analyses were performed by the Australian Microanalytical Service, Melbourne.

7-Methylenecycloocta-1,3,5-triene (64)

(a) A solution of n-butyllithium in hexane (6.25 mmol, 4.46 ml) was added dropwise to a stirred solution of methyltriphenylphosphonium bromide (2.22 g, 6.25 mmol) in anhydrous dimethylsulphoxide (25 ml) at room temperature under a nitrogen atmosphere. The resulting yellow phosphorane solution was stirred at room temperature for 10 - 15 min. and then treated dropwise with a solution of cycloocta-2,4,6-trienone[50] (750 mg, 6.25 mmol) in anhydrous ether (5 ml). After the opaque brown solution had been stirred at room temperature for 3 h, it was diluted with water (400 ml) and extracted with pentane (4 × 50 ml). The combined organic extracts were dried ($MgSO_4$) and carefully concentrated (below 30°) to a yellow oil which yielded, after chromatography on silica gel (pentane), 7-methylenecycloocta-1,3,5-triene (147 - 218 mg, 20 - 35%). Material prepared in this manner had p.m.r., infra-red and electronic spectral characteristics identical to those reported for (<u>64</u>) by Gardner;[51] it was, however, too unstable for elemental analysis (Found: $M^{+\cdot}$, 118.0783. C_9H_{10} requires $M^{+\cdot}$ 118.0783). Due to the unstable nature of (<u>64</u>), further purification was not attempted.

(b) Preparation of (<u>64</u>) by the "cyclic" Wittig procedure.[52]

An aliquot (15 ml) of a solution of methylenetriphenyl phosphorane (prepared in ether (80 ml) from methyltriphenyl-phosphonium bromide (4.65 g, 12.5 mmol) and a solution of n-butyllithium in hexane (13.9 ml, 12.5 mmol)) was added *via* syringe to a stirred solution of cyclooctatrienone (270 mg, 2.25 mmol) in anhydrous ether (10 ml) under an atmosphere of nitrogen. After 20 min., the resulting brown suspension was treated with water (225 µl, 2.25 mmol), stirred for a further 10 min. and then treated with another aliquot (15 ml) of the phosphorane solution. The above cycle was repeated until all the phosphorane solution had been added and then the reaction mixture was treated with water (100 ml). The organic phase was separated, washed successively with water (3 × 50 ml) and brine (50 ml), dried ($MgSO_4$) and carefully concentrated at room temperature to a yellow oil. Chromatography on silica gel (pentane) yielded (64) (210 mg, 78%).

Attempted preparations of 7-isopropylidenecycloocta-1,3,5-triene (65)

(a) Wittig route (in ether).

A solution of cycloocta-2,4,6-trienone (260 mg, 2.2 mmol) in anhydrous ether (5 ml) was added dropwise to a stirred solution of triphenylisopropylidenephosphorane (prepared, in ether (50 ml), from triphenylisopropylphosphonium bromide (802 mg, 2.1 mmol) and a solution of n-butyllithium in hexane (1.53 ml, 2.1 mmol)) under a nitrogen atmosphere. After the brown solution had been stirred at room temperature for 2 h, it was filtered to remove triphenylphosphonium oxide. The clear yellow filtrate was concentrated to a yellow oil which was chromatographed on silica gel. Elution with light petroleum yielded a mixture of compounds (t.l.c., p.m.r. spectroscopy); signals in the p.m.r. spectrum of this mixture near δ 2.0 and 3.0 suggested that some (65) might have been formed. Separation of this mixture was not achieved with preparative t.l.c. (silica gel, light petroleum).

(b) Wittig route (in tetrahydrofuran).

On treatment with a solution of cycloocta-2,4,6-trienone (260 mg, 2.2 mmol) in anhydrous tetrahydrofuran (10 ml), triphenylisopropylidenephosphorane (prepared from a solution of potassium t-butoxide (250 mg, 2.2 mmol) in tetrahydrofuran (20 ml) and the phosphonium salt (802 mg, 2.1 mmol)) gave a dark brown solution. After the solution had been stirred at room temperature for 2 h it was concentrated *in vacuo* and then diluted with light petroleum (50 ml) and water (100 ml). The organic phase was removed, washed with water (3 × 100 ml), dried and concentrated to a yellow, oily mixture similar to that obtained by route (a) (p.m.r. spectroscopy and t.l.c.).

(c) Wittig route (in dimethylsulphoxide).

After aqueous work-up and chromatography on silica gel, a yellow, oily mixture (similar to those obtained by routes a and b) was obtained from the reaction between cycloocta-2,4,6-trienone (260 mg, 2.2 mmol) and triphenylisopropylphosphorane (prepared, in dimethylsulphoxide (25 ml), by the action of n-butyllithium in hexane (1.6 ml, 2.2 mmol) on the phosphonium salt (810 mg, 2.2 mmol)).

(d) Crossed pinacol coupling route.[57]

A stirred suspension of lithium shavings (450 mg, 65 mmol) and anhydrous titanium trichloride (2.87 g, 18.6 mmol) in anhydrous 1,2-dimethoxyethane (30 ml) in a nitrogen atmosphere was boiled under reflux for 6 h. After the resulting black suspension had been cooled to room temperature, it was treated with a solution of cycloocta-2,4,6-trienone (280 mg, 2.33 mmol) and acetone (133 mg, 2.33 mmol) in anhydrous 1,2-dimethoxyethane (5 ml) and stirred for a further 2 h. The solution was diluted with light petroleum (100 ml), filtered through a pad of Florisil and the clear, yellow filtrate was concentrated to a yellow oil. Analytical t.l.c. showed that this oil was a complex mixture containing some unchanged starting material while p.m.r. spectroscopy indicated that a trace of (65) might have been formed.

Attempted preparations of 7-benzylidenecycloocta-1,3,5-triene (66)

(a) Wittig route (in ether).

n-Butyllithium as a solution in hexane (4.6 ml, 6.2 mmol) was added under an atmosphere of nitrogen to a stirred suspension of benzyltriphenylphosphonium chloride[153] (2.43 g, 6.2 mmol) in anhydrous ether (75 ml). The vivid orange coloured phosphorane solution was stirred at room temperature for 5 min. and treated dropwise with a solution of cycloocta-2,4,6-trienone (750 mg, 6.2 mmol) in anhydrous ether (10 ml); on addition of the ketone the colour of the solution changed to a deep tan. After the solution had been stirred at room temperature for 4 h, it was filtered to remove triphenylphosphine oxide. The filtrate, after concentration and chromatography on silica gel (light petroleum), yielded a yellow oil containing, amongst other components (t.l.c.), unchanged starting material and a trace of material which might have been (66) (p.m.r. spectroscopy).

(b) Wittig route (in dimethylsulphoxide, ethanol and tetrahydrofuran).

When solutions of benzylidenetriphenylphosphorane in dimethylsulphoxide (20 ml), ethanol (30 ml) or tetrahydrofuran (prepared by the actions of n-butyllithium (2 mmol), sodium ethoxide (2 mmol) or potassium t-butoxide (2 mmol) on benzyltriphenylphosphonium chloride (810 mg, 2 mmol), respectively) were treated with cycloocta-2,4,6-trienone (250 mg, 2 mmol), a yellow oil was obtained after work-up. P.m.r. spectroscopy and t.l.c. indicated that this oil, in addition to containing unchanged starting material, contained only a trace of material which might have been 7-benzylidenecycloocta-1,3,5-triene.

Attempted preparation of cycloocta-1,3,5-triene-7-carboxaldehyde (78)

A solution of potassium t-butoxide (419 mg, 3.7 mmol) in anhydrous t-butanol (10 ml) was added dropwise under a nitrogen atmosphere to a stirred solution of cycloocta-2,4,6-trienone (650 mg, 3.7 mmol) and ethyl chloroacetate (450 mg, 3.7 mmol) in anhydrous t-butanol (20 ml). After the solution had been stirred at room temperature for 70 h, it was diluted with water (100 ml) and extracted with ether (3 × 25 ml). The combined organic extracts were dried, concentrated and adsorbed onto a column of silica gel. Elution with a solution of ether (20%) in light petroleum afforded unchanged cycloocta-2,4,6-trienone (140 mg). A yellow oil containing at least six components (t.l.c.) was obtained on elution with a solution of ethanol (20%) in light petroleum.

Attempted synthesis of cycloocta-1,3,5-triene-7-carboxylic acid (79)[54]

A suspension of potassium t-butoxide (1.12 g, 10 mmol) in anhydrous tetrahydrofuran (20 ml) stirred under an atmosphere of nitrogen was treated at 8° with a solution of *p*-toluenesulphonylmethylisocyanide (1.95 g, 10 mmol) in anhydrous tetrahydrofuran. The red solution was cooled to -10°, treated with a solution of cycloocta-2,4,6-trienone (1.2 g, 10 mmol) in anhydrous tetrahydrofuran (10 ml) and then stirred at -10° for 1 h. After the resulting brown suspension had been treated with glacial acetic acid (0.57 ml, 1.0 mol), it was concentrated *in vacuo* (below 25°), diluted with water (25 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were dried and concentrated to a brown oil which was shown by t.l.c. to be a complex mixture. Separation by preparative t.l.c. (20% ether in light petroleum, light petroleum) afforded other mixtures which did not appear to contain (79) (p.m.r. spectroscopy).

Attempted conjugate reduction of benzoylcyclooctatetraene (83)

(a) With lithium aluminiumhydride - cuprous iodide.[55]

A stirred suspension of cuprous iodide (3.7 g, 19.4 mmol) in anhydrous tetrahydrofuran (10 ml) was treated at 0° with a solution of lithium aluminiumhydride (182 mg, 4.8 mmol) in tetrahydrofuran (7.3 ml). After the black suspension had been stirred for 15 min. at 0°, it was treated dropwise with a solution of benzoylcyclooctatetraene (1.0 g, 4.8 mmol) in anhydrous tetrahydrofuran. The solution was stirred for 1 h at room temperature, treated with sodium sulphate decahydrate (5 g) and filtered to give a clear yellow solution. T.l.c. indicated that a complex mixture had been obtained. Preparative t.l.c. (20% ether in light petroleum) yielded mixtures of compounds which did not appear to contain the desired keto-olefin (infra-red spectroscopy).

(b) With sodium borohydride.[56]

A solution of benzoylcyclooctatetraene (1 g, 4.8 mmol) in ethanol (5 ml) was added dropwise to a stirred suspension of sodium borohydride (181 mg, 4.8 mmol) in water (15 ml) and ethanol (15 ml) at 0°. After being stirred at room temperature for 3 h, the mixture was diluted with ether (40 ml) and washed successively with saturated brine (3 × 20 ml) and water (3 × 20 ml), dried and concentrated to a yellow oil (780 mg, 78%). This material was tentatively identified as cyclooctatetraenylphenylmethanol on the basis of its p.m.r. spectral characteristics: (CCl_4, 60 MHz) δ 7.13 (5H, s), 5.62 (7H, broad s), 4.93 (1H, s), 2.62 (1H, broad s, exchangeable with D_2O).

Preparations of 7-methylenecycloocta-1,3,5-triene (<u>64</u>), 7-isopropylidenecycloocta-1,3,5-triene (<u>65</u>) and 7-benzylidenecycloocta-1,3,5-triene (<u>66</u>) by base catalysed isomerization.

(a) 7-methylenecycloocta-1,3,5-triene (<u>64</u>)

A solution of methylcyclooctatetraene[144] (50 mg, 0.4 mmol), undecane (as an internal standard, *ca.* 80 μl) and potassium t-butoxide (10 mg, 0.09 mmol) in anhydrous tetrahydrofuran (7 ml) was stirred at room temperature under an atmosphere of nitrogen. Over the course of 40 h, samples (*ca*. 5 µl) of the reaction mixture were withdrawn and examined by g.l.c. (column A, 140°); the percentages, relative to undecane, of methylcyclooctatetraene and 7-methylenecycloocta-1,3,5-triene (determined by peak enhancement on "spiking" with authentic material prepared by the Wittig reaction, page 149), were as follows:

(a) After 2.5 h; methylcyclooctatetraene (97.3%); (<u>64</u>) (2.7%) (material balance is 94%); 2.5% absolute yield of (<u>64</u>).

(b) After 20 h; methylcyclooctatetraene (78%); (<u>64</u>) (22%) (material balance is 81%); 17.9% absolute yield of (<u>64</u>).

(c) After 40 h; methylcyclooctatetraene (73%); (<u>64</u>) (27%) (material balance is 65%); 17.5% absolute yield of (<u>64</u>).

A similar isomerization conducted under reflux conditions gave side products and a greatly reduced absolute yield of (<u>64</u>). The response ratio of (<u>64</u>) to (<u>85</u>) was assumed to be 1:1.

After 40 h, the isomerized mixture was diluted with ether (40 ml), washed with water (2 × 20 ml), dried and extracted with an aqueous solution (20%) of silver nitrate (3 × 20 ml). The organic phase contained (<u>64</u>) contaminated to only a small extent (2%) by (<u>85</u>).

(b) 7-Isopropylidenecycloocta-1,3,5-triene (65).

A solution of freshly distilled isopropylcyclooctatetraene[143] (160 mg, 1.1 mmol) and undecane* (as internal standard, 50 μl) in anhydrous dimethylsulphoxide (5 ml) was frozen and thawed three times under a reduced pressure of nitrogen. Solid potassium t-butoxide (10 mg, 0.09 mmol) was added and the solution was heated at *ca.* 70-90° under an atmosphere of nitrogen. G.l.c. (column B, 110°) indicated that a complex mixture of compounds, including unchanged isopropylcyclooctatetraene* and (65)* in the ratio 15:85,** was obtained. 7-Isopropylidenecycloocta-1,3,5-triene was identified as its N-phenyltriazolinedione adduct (page 173) and by its p.m.r. spectral characteristics (CCl_4, 60 MHz) δ 6.73 - 5.33 (6H, complex), 3.20 (2H, d, J 7.5 Hz), 1.80 (3H, s) and 1.75 (3H, s); no other component of the mixture reacted with N-phenyltriazolinedione.

In one experiment, isopropylcyclooctatetraene (100 mg, 0.69 mmol) in a saturated solution of potassium t-butoxide in tetrahydrofuran (10 ml) was boiled under reflux for 72 h in a nitrogen atmosphere. The cooled solution was then diluted with water (100 ml) and extracted with ether (3 × 20 ml). The combined organic extracts yielded isopropenylcyclooctatetraene (88) (83 mg, 83%), b.p. 60° (block)/35mm (Found: C, 91.3%; H, 8.4. $C_{11}H_{12}$ requires C, 91.6%; H, 8.6%). P.m.r. (CCl_4, 60 MHz) δ 6.02 - 5.60 (7H, complex), 4.82 (2H broad s) and

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* Assumed to have equal response ratios.

** This isomerization was extremely capricious; out of 15 attempts, only 3 were successful and in these cases the absolute yields of (65) were 74%, 27% and 21%.

1.90 (3H, s); λ_{max} (ethanol) 207 nm ($\varepsilon = 2.45 \times 10^4$), 225 nm ($\varepsilon = 1.19 \times 10^4$); mass spectrum: *m/e* 144 (27%), 143 (17%), 129 (100), 117 (13), 91 (20); $M^{+\cdot}$ 144.0938. $C_{11}H_{12}$ requires 144.0939. The g.l.c. (column B, 110°) and p.m.r. characteristics of this product were identical to those of authentic (88) prepared by the coupling between isopropenylmagnesium bromide and bromocyclooctatetraene.[103]

(c) 7-Benzylidenecycloocta-1,3,5-triene (66).

A solution of bromocyclooctatetraene[144] (1.0 g, 5.47 mmol) in anhydrous tetrahydrofuran (10 ml) was added rapidly under a nitrogen atmosphere to a stirred solution of benzylmagnesium bromide (prepared from benzyl bromide (961 mg, 5.6 mmol) and magnesium turnings (200 mg, 8.2 mmol)) in anhydrous tetrahydrofuran (25 ml) at -10°. The solution was immediately treated with a solution of ferric chloride (20 mg) in anhydrous tetrahydrofuran (1 ml) whereupon it changed colour to a deep red/black. After it had been stirred at -10° for 2 h, the solution was allowed to warm to room temperature over 1 h. After this period, the solution was treated with saturated aqueous ammonium chloride (100 ml) and extracted with ether (3 × 50 ml). The combined organic phases were washed with water (3 × 50 ml), then brine (1 × 50 ml), dried and carefully concentrated to a yellow oil which yielded benzylcyclooctatetraene[44] (210 mg, 19%), b.p. 79°/0.01 mm.

A solution of benzylcyclooctatetraene (210 mg, 1.1 mmol), undecane (66 mg, as internal standard) and potassium t-butoxide (10 mg, 0.09 mmol) in anhydrous tetrahydrofuran (10 ml) was stirred under a nitrogen atmosphere for 10 min. at room temperature. The resulting brown solution was shown by g.l.c. (column C, 130 - 200° at 10°/min.) to contain a mixture of (66) and benzylcyclooctatetraene* (91% combined) in the ratio of 95:5. The solution of olefins was diluted with ether (25 ml), washed with water, dried and then washed with an aqueous solution (20%) of silver nitrate (3 × 20 ml) to remove unchanged benzylcyclooctatetraene. 7-Benzylidenecycloocta-1,3,5-triene,* as a mixture of (*E*)- and (*Z*)-isomers, was obtained as a clear yellow liquid, b.p. 105° at 0.03 mm (Found: C, 92.4; H, 7.1. $C_{15}H_{14}$ requires C, 92.7; H, 7.3%). ν_{max} (film) 3029 (s), 1602 (m), 753 (m), 711 (s); λ_{max} 209 nm ($\varepsilon = 1.80 \times 10^4$), 252 nm ($\varepsilon = 1.57 \times 10^4$) and 306 nm ($\varepsilon = 1.20 \times 10^4$); p.m.r. ($CCl_4$, 60 MHz) δ 7.13 (5H, s), 6.86 - 5.66 (6H, complex), 6.42 (1H, s), 3.3 and 3.18 (2H combined, 2 × d, J 6 Hz); c.m.r. δ 29.15 (t), 37.65 (t), 124.62 (d), 126.08 (d), 126.81 (d), 127.90 (d), 128.51 (d), 128.87 (s), 129.60 (d), 130.82 (d), 136.52 (d), 137.98 (s), 138.83 (d), 139.32 (d), 139.68 (d); mass spectrum: *m/e* 194 (52%), 165 (100), 115 (45), 91 (19), 78 (23).

Attempted preparation of *p*-methoxybenzylcyclooctatetraene.

(a) Reaction between lithium dicyclooctatetraenylcuprate (91) and *p*-methoxybenzylchloride.

A solution of lithium dicyclooctatetraenylcuprate (prepared, according to Paquette,[60] from t-butyllithium

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* The response ratio of these two olefins was found to be 1.0:1.05.

(32 mmol), bromocyclooctatetraene (2.0 g, 11 mmol) and cuprous iodide (3.0 g, 16 mmol)) in ether (50 ml) was treated at -78° with a solution of *p*-methoxybenzylchloride[145] (6.3 g, 40 mmol) in ether. After the solution had been stirred at -78° for 2 h and room temperature for 2 h, work-up[60] afforded cyclooctatetraene (p.m.r. spectroscopy) (930 mg, 81%).

(b) Reaction between *p*-methoxybenzylmagnesium chloride and bromocyclooctatetraene.

A solution of ferric chloride (5 mg), bromocyclooctatetraene (1.0 g, 5.5 mmol) and *p*-methoxybenzylmagnesium chloride (prepared, according to Van Campen,[61] from *p*-methoxybenzylchloride (1.1 g, 7 mmol), magnesium turnings (97 mg, 4 mmol) and magnesium powder (97 mg, 4 mmol)) in tetrahydrofuran (70 ml) was stirred under nitrogen for 1 h at -10° and then at 0° for 1 h. Work up, following the procedure outlined on page 158,afforded cyclooctatetraene (154 mg, 27%) and bromocyclooctatetraene (640 mg, 64%).

Attempted preparation of benzhydrylcyclooctatetraene.

(a) Reaction between cyclooctatetraenylmagnesium bromide and benzhydrylchloride.

A solution of benzhydrylchloride[146] (2.6 g, 13 mmol), cyclooctatetraenylmagnesium bromide (prepared, according to Schroder,[63] from magnesium turnings (300 mg, 12.3 mol) and bromocyclooctatetraene (1.0 g, 5.5 mmol)), lithium chloride (17 mg, 0.4 mmol) and cuprous chloride (27 mg, 0.27 mmol) in anhydrous tetrahydrofuran was stirred at room temperature for 3 h. Work-up (using the procedure outlined by Gream and

Mular)[112] afforded *bis*-cyclooctatetraene (<u>91</u>) (500 mg, 89%), m.p. 123 - 125° (lit.[64] 125.4 - 126.5°), and some cyclooctatetraene.

(b) Reaction between cyclooctatetraenyllithium and benzhydrylchloride.

A solution of benzhydrylchloride (2.0 g, 10 mmol) and cyclooctatetraenyllithium (prepared, using the procedure outlined by Paquette,[62] from n-butyllithium (6 mmol) and bromocyclooctatetraene (1.1 g, 6 mmol)) in ether was stirred at room temperature for 15 h. After this time, work-up in the described manner[62] afforded cyclooctatetraene (595 mg, 95%).

<u>Preparation of 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide (94).</u>

A solution of triphenylphosphine (9.0 g, 34 mmol) in anhydrous benzene (30 ml) was treated dropwise at room temperature with 7-bromocycloocta-1,3,5-triene[65] (6.2 g, 33.5 mmol). After the solution had been kept at 5° under an atmosphere of nitrogen for 3 h, it was filtered and washed with anhydrous benzene (4 × 50 ml) and ether (4 × 50 ml) (both operations being performed under an atmosphere of nitrogen) to give the phosphonium salt (15 g, 100%) as a white, air sensitive powder. P.m.r. (60 MHz) δ 7.63 (15H, complex), 6.5 - 5.03 (6H, complex), 3.23 (1H, broad s, exchangeable with D_2O), 2.65 (2H, complex). Compound (<u>94</u>) was too unstable for elemental analysis and could not be recrystallized; samples which had been kept for periods greater than one week, even under nitrogen at -15°, required washing (successively with benzene, ethyl acetate and ether) prior to use.

Preparations of 7-benzylidenecycloocta-1,3,5-triene (66), 7-(*p*-methoxybenzylidene)cycloocta-1,3,5-triene (67), 7-(*p*-nitrobenzylidene)cycloocta-1,3,5-triene (68) and 7-benzhydrylidenecycloocta-1,3,5-triene (69).

(a) 7-benzylidenecycloocta-1,3,5-triene (66).

A stirred suspension of freshly prepared 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide (2.1 g, 4.7 mmol) in anhydrous ether (50 ml) was treated dropwise under a nitrogen atmosphere with a solution of n-butyllithium in hexane (4.7 mmol, 5 ml). The colour of the suspension changed to a deep red on addition of the alkyllithium; after it had been stirred at room temperature for 15 min., the phosphorane solution was treated dropwise with a solution of benzaldehyde (500 mg, 4.7 mmol) in anhydrous ether (5 ml) and stirred at room temperature for 3 h.* The solution was washed with water (5 × 50 ml), dried and concentrated to a yellow oil which yielded, after chromatography on silica gel (light petroleum) (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-triene (66) (665 mg, 73%).

(b) 7-(*p*-methoxybenzylidene)cycloocta-1,3,5-triene (67).

A stirred solution of 7-cycloocta-1,3,5-trienylidene-triphenyl phosphorane (prepared from n-butyllithium (4.0 mmol) and 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide

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* Shown by g.l.c. (column C, 130 - 220°, 10°/min), to be the optimum reaction period.

(2.0 g, 4.4 mmol)) in ether (50 ml) was treated under a nitrogen atmosphere with a solution of *p*-methoxybenzaldehyde (650 mg, 4.7 mmol) in ether (5 ml). The mixture was stirred at room temperature for 3 h, diluted with ether (50 ml), washed with water (3 × 50 ml), dried and concentrated to yield a mixture of (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)cycloocta-1,3,5-trienes (67) (465 mg, 52%) as a yellow oil, b.p. 112°/0.01 mm (Found: $M^{+\cdot}$ 224.1200, $C_{16}H_{16}O$ requires $M^{+\cdot}$ 224.1201). P.m.r. (CCl_4, 60 MHz) δ 7.28 - 6.25 (4H, AA'BB' system), 6.60 - 5.68 (7H, complex), 3.75 (3H, s), 3.37 and 3.30 (2H combined, 2 × d, J 8 Hz); c.m.r. ($CDCl_3$) δ 29.16 (t), 37.67 (t), 55.40 (q), 114.07 (d), 124.15 (d), 125.61 (d), 127 - 133 complex, 136.66 (d), 137.87 (s), 139.70 (d), 139.94 (d); λ_{max} 217 nm ($t = 1.60 \times 10^4$), 261 nm ($\varepsilon = 1.51 \times 10^4$) and 298 nm ($\varepsilon = 1.22 \times 10^4$); mass spectrum, *m/e* 224 (100%), 209 (15), 193 (25), 115 (50), 91 (22), 78 (23), 77 (41).

This material was unstable; indeed, it was indicated by g.l.c. (column C, 180°) that the yield of (67) decreased if the Wittig reaction was allowed to proceed for periods longer than 3 h. Compound (67) was always used immediately after preparation.

(c) 7-(*p*-nitrobenzylidene)cycloocta-1,3,5-triene (68).

A solution of *p*-nitrobenzaldehyde (640 mg, 4.2 mmol) in dimethylsulphoxide (5 ml) was added carefully,* under nitrogen, to a stirred solution of 7-cycloocta-1,3,5-

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* An exothermic reaction ensues; the reaction is kept at room temperature by cold water.

trienylidenetriphenylphosphorane which was prepared, in ether (50 ml), by the action of a solution of n-butyllithium (4.47 ml, 4.47 mmol) in hexane on 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide (2.0 g, 4.47 mmol). After the solution had been stirred at room temperature for 3 h, it was diluted with ether (100 ml), extracted with water (4 × 50 ml), dried and concentrated to a yellow oil. Chromatography on silica gel (1% ether in light petroleum) afforded a mixture of (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)-cycloocta-1,3,5-trienes (68) (335 mg, 32%) as a brilliant yellow oil, b.p. 140° (block)/0.1 mm (Found: $M^{+\bullet}$ 239.0940. $C_{15}H_{13}NO_2$ requires $M^{+\bullet}$ 239.0946). P.m.r. (60 MHz, CCl_4) δ 8.02 and 7.23 (4H, AA'BB' system J_{AB} 8 Hz), 6.41 (1H, s), 6.31 - 5.46 (6H, complex), 3.28 and 3.23 (2H combined, 2 × d J 7 Hz); λ_{max} 367 nm ($\epsilon = 1.26 \times 10^4$), 240 nm ($\epsilon = 1.53 \times 10^4$), 222 nm ($\epsilon = 1.67 \times 10^4$), *ca.* 205 nm strong end absorption; mass spectrum, *m/e* 277 (12%), 262 (47), 239 (100), 178 (94), 165 (95), 152 (46). This material was unstable and was used immediately after preparation.

(d) 7-Benzhydrylidenecycloocta-1,3,5-triene (69).

A solution of benzophenone (1.4 g, 7.7 mmol) in ether (5 ml) was added under nitrogen to a stirred solution of 7-cycloocta-1,3,5-trienylidenetriphenylphosphorane (prepared, in ether (50 ml), by the action of a solution of n-butyllithium (8.35 ml, 8.4 mmol) in hexane on 7-cycloocta-1,3,5-trienyltriphenylphosphonium bromide (3.75 g, 8.4 mmol)). After the solution had been stirred at room temperature for 8 h, it was diluted with ether (75 ml), washed with water (5 × 50 ml), dried and concentrated to a yellow oil.

Chromatography on silica gel (light petroleum) afforded 7-benzhydrylidenecycloocta-1,3,5-triene (69) (560 mg, 27%) as a yellow oil, b.p. 110°/0.3 mm (Found: $M^{+\cdot}$ 270.1405. $C_{21}H_{18}$ requires $M^{+\cdot}$ 270.1408). P.m.r. δ 7.31 (10H, broad s), 6.89 - 5.54 (6H, complex), 3.28 (2H, d, J 8 Hz); mass spectrum, *m/e* 270 (91%), 191 (70), 179 (53), 167 (100), 129 (43), 115 (55), 91 (60), 78 (36). This compound was very unstable and was used immediately after preparation.

WORK DESCRIBED IN SECTION 1.3

Addition of tetracyanoethylene to 7-methylenecycloocta-1,3,5-triene.

Tetracyanoethylene (330 mg, 2.54 mmol), that had been sublimed through a column of activated charcoal, was added at room temperature to a solution of 7-methylenecycloocta-1,3,5-triene (300 mg, 2.54 mmol) in ethyl acetate (10 ml) under an atmosphere of nitrogen. The colour of the solution immediately changed to a deep magenta; after 3 h at room temperature, the solution was diluted with ether (30 ml), washed successively with an aqueous solution of sodium metabisulphite (20%, 3 × 20 ml) (to remove unchanged tetracyanoethylene), water (20 ml) and brine (20 ml). The dried organic phase was concentrated to an off-white solid (340 mg, 54%) which was shown by t.l.c. (silica gel, 50% ether in light petroleum) to contain two compounds. These two compounds, identified as (95) (80% of mixture) and (96) (20%) were separated by h.p.l.c. (10 µm silica gel, 20% ether in light petroleum):

8,8,9,9-tetracyanobicyclo[5,3,1]undeca-1,3,5-triene (95).

m.p. 141.5 - 143 (after sublimation at 120°/0.01 mm) (Found: C, 73.1; H, 4.1; N, 22.6. $C_{15}H_{10}N_4$ requires C, 73.2; H, 4.1; N, 22.8%); p.m.r. (60 MHz), δ 6.4 - 5.9 (5H, complex), 3.73 (1H, broad s), 3.15 (2H, s) 3.12 and 2.20 (2H, AB part of an ABX system, J_{AB} 14 Hz, J_{AX} 2 Hz, J_{BX} 3 Hz) (double irradiation at *ca.* δ 3.1 caused the doublet of doublets at 2.20 to collapse to a broad singlet); c.m.r. δ 27.8 (t, J_{CH} 137 Hz), 42.9 (d, 131), 47.8 (d, 137), 125.5 (d, 163), 128.2 (d, 169), 128.8 (d, 169), 131.1 (d, 156), 131.6 (d, 156), 132.5 (s); λ_{max} 218 nm ($\varepsilon = 3.1 \times 10^4$), shoulder at 257 nm; mass spectrum, *m/e* 246 (8%) 118 (75), 117 (100), 91 (31), 78 (29).

10,10,11,11-tetracyanotricyclo[6,3,0,$0^{6,8}$]undeca-2,4-diene (96).

m.p. 126 - 127.5 (after repeated recrystallizations from mixtures of ether and pentane) (Found: C, 73.0; H, 4.2. $C_{15}H_{10}N_4$ requires C, 73.2; H, 4.1%); p.m.r. (60 MHz), δ 5.5 - 6.5 (4H, complex), 3.78 (1H, d, J 2 Hz), 2.95 and 2.62 (2H, AB q, J_{AB} 14 Hz), 0.77 - 1.90 (3H, complex); c.m.r., δ 21.01 (t, J_{CH} 163 Hz), 23.56 (d, 169), 35.35 (s), 45.91 (t, 138), 55.75 (d, 138), 123.04 (d, 163), 124.38 (d, 163), 132.03 (d, 155), 135.78 (d, 163); λ_{max} 258 nm ($\varepsilon = 2.95 \times 10^3$) and 203 nm ($3.94 \times 10^3$); mass spectrum, *m/e* 246 (6%), 117 (100), 91 (20), 78 (27).

A solution of (96) (30 mg) in ethyl acetate (2 ml) under nitrogen in a sealed ampoule was heated at 100° for 12 h. After this time, h.p.l.c. (20 μm silica gel, 20% ether in light petroleum) indicated that (96) had been converted completely into (95).

Addition of N-phenyltriazolinedione to 7-methylenecycloocta-1,3,5-triene.

7-Methylenecycloocta-1,3,5-triene (200 mg, 1.7 mmol) was treated at room temperature with a solution of N-phenyltriazolinedione (260 mg, 1.64 mmol) (prepared by the action of dinitrogen tetroxide on N-phenylurazole[147]) in acetone (5 ml). The red colour of the dienophile faded rapidly on addition to the olefin and after 5 min, a white solid precipitated from the reaction mixture. This solid was collected and recrystallized from ethyl acetate to yield 2,4,6-triaza-4-phenyltricyclo[6,5,1,$0^{2,6}$]tetradeca-8,10,12-triene-3,5-dione (<u>101</u>) (420 mg, 92%), m.p. 213 - 214° (Found: C, 69.8; H, 5.1; N, 14.5. $C_{17}H_{15}N_3O_2$ requires C, 69.6; H, 5.1; N, 14.3%). P.m.r. (60 MHz) δ 7.40 (5H, s), 6.40 - 5.77 (5H, complex), 5.23 (1H, s), 4.53 and 3.97 (2H, AB q, J_{AB} 11 Hz), 3.06 and 2.21 (2H, AB part of an ABX system, J_{AB} 11 Hz, J_{AX} 4 Hz); c.m.r. δ 30.24 (t), 51.14 (t), 56.6 (d), 125.71 (d), 128.4 - 129.1 complex, 134.68 (s); ν_{max} 1773 (m), 1718 (s), 1499 (m), 1383 (m), 1298 (m), 1148 (m), 741 (m), 702 (m); λ_{max} 216 nm ($\varepsilon = 2.5 \times 10^4$), shoulders at 206 and 255 nm; mass spectrum, *m/e* 293 (17%), 117 (100%), 91 (58), 78 (12).

Concentration of the acetone filtrate and mother liquor from the recrystallization afforded additional (<u>101</u>) (30 mg, 7%).

Addition of chlorosulphonylisocyanate to 7-methylenecycloocta-1,3,5-triene.

Chlorosulphonylisocyanate (240 mg, 1.69 mmol) was added under a nitrogen atmosphere to a stirred solution of

7-methylenecycloocta-1,3,5-triene (200 mg, 1.7 mmol) in anhydrous dichloromethane (5 ml) at room temperature. The colour of the solution immediately changed to a deep, emerald green; after it had been stirred at room temperature for 10 min., the solution was diluted with ether (50 ml) and washed with ice-water (2 × 50 ml). The organic extract was then added dropwise to a stirred suspension of ether (100 ml) in an aqueous solution of sodium metabisulphite (20%) (100 ml); during the course of the addition, the pH of the solution was maintained between 7 and 8 by the addition of an aqueous solution of potassium hydroxide (1 M).[79] After the suspension had been stirred at room temperature for 15 min., the organic phase was removed, dried and concentrated to a yellow solid (88 mg, 27%) which was shown to be homogeneous by t.l.c. (silica gel, 50% ether in light petroleum). Recrystallization of this solid (from ether/pentane mixtures) followed by sublimation (100°/0.05 mm) afforded pure 8-azabicyclo[5,3,1]undeca-1,3,5-triene-9-one (<u>102</u>) as a white solid, m.p. 141-142.5, (Found: C, 74.6; H, 7.0; N, 8.7. $C_9H_{10}NO$ requires C, 74.5; H, 6.8; N, 8.7%). P.m.r. (60 MHz), δ 7.20 (1H, broad, exchangeable with D_2O), 6.13 - 5.47 (5H, complex), 4.32 (1H, broad s) 3.20 and 2.22 (2H, AB part of an ABX system, J_{AB} 10 Hz, J_{AX} 5 Hz), 3.08 (2H, s); c.m.r. 30.49, 43.24, 53.08, 123.28, 124.74, 127.29, 129.48, 133.61, 135.07; ν_{max} 3431 (m), 3029 (m), 1658 (s), 1628 (sh); λ_{max} 210 nm ($\varepsilon = 1.09 \times 10^4$) shoulder at 262 nm; mass spectrum, *m/e* 161 (75%), 118 (100), 117 (80), 91 (52), 78 (18).

Addition of diethyl azodicarboxylate to 7-methylenecycloocta-1,3,5-triene

A solution of diethyl azodicarboxylate (210 mg, 1.40 mmol) (prepared by the actions of silver carbonate[148] or fuming nitric acid[149] on diethyl hydrazodicarboxylate[149]) and 7-methylenecycloocta-1,3,5-triene (170 mg, 1.40 mmol) in anhydrous acetone (10 ml) was boiled under nitrogen for 12 h. The solution was concentrated *in vacuo* to a yellow oil which was shown by t.l.c. (50% ether in light petroleum) to contain unchanged diethyl azodicarboxylate, polymeric material and two adducts of (64). Chromatography of this oil on silica gel (50% ether in light petroleum) yielded a mixture of adducts (114 mg, 30%) which were separated by h.p.l.c. (10 μm silica gel, 35% ether in light petroleum). The major component (66%) of the adduct mixture, after recrystallization from ether/pentane mixtures, was identified as 8,9-dicarbethoxy-8,9-diazabicyclo[5,3,1]undeca-1,3,5-triene (105), m.p. 116 - 118° (Found: C, 61.8; H, 6.8; N, 9.3. $C_{15}H_{20}N_2O_4$ requires C, 61.6; H, 6.9; N, 9.6%). P.m.r. (60 MHz), δ 5.5 - 6.20 (5H, complex), 5.33 (1H, broad s), 4.66 and 3.43 (2H, AB q, J_{AB} 12 Hz), 4.13 (2H, q, J 7 Hz), 4.00 (2H, q, J 7 Hz), 2.82 and 1.98 (2H, AB part of an ABX system, J_{AB} 12 Hz, J_{AX} 4 Hz), 1.27 (3H, t, J 7 Hz), 1.15 (3H, t, J 7 Hz); c.m.r. δ 14.35 (q), 14.53 (q), 32.32 (t), 53.27 (t), 54.91 (t), 59.89 (d), 62.20 (t), 64.45 (t), 124.33 (d), 124.75 (d), 128.22 (d, 2 × C), 130.89 (d), 138.82 (s); ν_{max} 3010 (m), 2960 (w), 1713 (s), 1379 (m), 1251 (m), 1233 (m), 1191 (m); λ_{max}, 209 nm ($\varepsilon = 8.21 \times 10^3$) shoulder at 220 nm; mass spectrum, *m/e* 292 (28%), 130 (17), 118 (100), 117 (85), 91 (36), 78 (17).

The minor component of the adduct mixture was an unstable compound which isomerized to (<u>105</u>) and decomposed on recrystallization (ether/pentane) or preparative t.l.c. on silica gel (50% ether in light petroleum). This substance was tentatively identified as a mixture of 10,11-*cis*- and 10,11-*trans*-10,11-dicarbethoxy-10,11-diazatricyclo[6,3,0,$0^{6,8}$]undeca-2,4-diene (<u>106</u>) on the basis of its p.m.r. and c.m.r. spectral characteristics. P.m.r. (60 MHz), δ 6.43 - 5.45 (4H, complex), 4.55 (1H, s), 4.16 (2H, q, J 7 Hz), 4.13 (2H, q, J 7 Hz), 3.55 and 3.23, 3.40 and 3.06 (2H combined, AB q, J_{AB} 13 and 9 Hz, respectively), 2.12 - 0.4 (3H, complex), 1.26 (6H, 2 × t, J 7 Hz); c.m.r. 14.6 (q), 31.7 (t), 50.52 (t), 52.10 (s), 53.3 (t), 56.4 (d), 59.5 (d), 62.4 (t), 62.8 (t), 124 - 130 complex, 135.2 (d).

WORK DESCRIBED IN SECTION 1.4

Addition of tetracyanoethylene to 1,3,5,7-tetramethylcyclooctatetraene (57)

(a) Under Lagowski's conditions.[38]

A solution of tetracyanoethylene (270 mg, 2.18 mmol), and 1,3,5,7-tetramethylcyclooctatetraene (<u>57</u>)[83] (340 mg, 2.18 mmol) in dioxane (10 ml) and ether (10 ml) was kept at room temperature under a nitrogen atmosphere for 20 days. After this time, the solution was diluted with ether (50 ml), washed with an aqueous solution of sodium metabisulphite (20%, 3 × 20 ml), dried and concentrated to a colourless oil. Preparative t.l.c. (silica gel, 50% ether in hexane) afforded unchanged (<u>57</u>) (335 mg, 98%).

(b) In ethyl acetate at room temperature.

The above procedure was followed except that ethyl acetate (10 ml) was used as solvent; after 24 h unchanged tetracyanoethylene was removed and preparative t.l.c. (silica gel, 50% ether in hexane) afforded unchanged (57) (323 mg, 95%) and 8,8,9,9-tetracyano-3,5,7-trimethylbicyclo[5,3,1]undeca-1,3,5-triene (59) (31 mg, 5%), m.p. 182 - 185° (lit.[38] 184 - 186°) after sublimation (75°/0.01 mm). P.m.r.* (60 MHz), δ 6.15 (1H, s), 5.67 (1H, s), 5.43 (1H, s), 3.10 (2H, s), 3.08 and 2.07 (2H, partially obscured AB system, J_{AB} 13 Hz), 1.92 (3H, s), 1.78 (3H, s), 1.97 (3H, s).

(c) In boiling ethyl acetate.

A solution of tetracyanoethylene (270 mg, 2.18 mmol) and 1,3,5,7-tetramethylcyclooctatetraene (340 mg, 2.18 mmol) in ethyl acetate (20 ml) was boiled under reflux in an atmosphere of nitrogen for 4 h. After this time, the reaction mixture was washed with an aqueous solution of sodium metabisulphite (20%, 2 × 10 ml), dried and concentrated to yield a white solid. Preparative t.l.c. (silica gel, 50% ether in hexane) yielded (59) (10%) and 9,9,10,10-tetracyano-1,3,5,7-tetramethyltricyclo[4,2,2,$0^{2,5}$]undeca-3,7-diene (112) (90%) as a white solid, m.p. 173.5 - 174.5 after sublimation at 120°/0.1 mm (Found: C, 74.7; H, 5.9. $C_{18}H_{16}N_4$ requires C, 75.0; H, 5.6%). P.m.r. (60 MHz) 5.67 (1H, s), 5.40 (1H, s), 2.98 (1H, s), 2.63 (1H, broad s), 2.00 (3H, s), 1.65 (9H, s); c.m.r., δ 16.03 (q), 20.16 (2 × q), 22.35 (q), 41.18 (s), 48.10 (s), 51.74 (d), 53.20 (d), 123.77 (d),

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* Identical to that recorded by Lagowski.[69]

137.37 (d), 145.75 (s), 145.88 (s); λ_{max}, 209 nm ($\varepsilon = 3.4 \times 10^3$); mass spectrum, *m/e* 288 (5%), 273 (8), 246 (15), 160 (45), 145 (100), 117 (27), 91 (25), 78 (20).

Preparation of 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (58) and its reaction with tetracyanoethylene

A solution of 1,3,5,7-tetramethylcyclooctatetraene (57) (100 mg, 0.63 mmol) and potassium t-butoxide (20 mg, 0.18 mmol) in anhydrous tetrahydrofuran (10 ml) was boiled under reflux in an atmosphere of nitrogen for 3 h. After this time, the mixture was diluted with ether (50 ml), washed with water (3 × 20 ml), dried and concentrated to a colourless oil. By p.m.r. spectroscopy, this oil was shown to be a mixture of unchanged (57) (58%) and 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (58) (42%); the mixture was not separated. P.m.r. (60 MHz, CCl_4), δ 5.91 (1H, s), 5.56 (1H, s) 5.45 (1H, s) 5.27*, 4.71 (1H, s showing evidence of fine coupling), 4.52 (1H, s), 2.73 (2H, s), 1.80 (6H, s), 1.67 (3H, s), 1.67.*

The mixture of (57) and (58) (80 mg, 0.49 mmol) was dissolved in ethyl acetate (10 ml) and treated with tetracyanoethylene (39 mg, 0.3 mmol) under an atmosphere of nitrogen. After the solution had been stirred at room temperature for 15 min., it was diluted with ether (20 ml), washed with an aqueous solution of sodium metabisulphite (20%, 2 × 10 ml), dried and concentrated to a white solid. This solid was extracted with hexane (5 × 0.5 ml) to give

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* Peaks due to 1,3,5,7-tetramethylcyclooctatetraene.

(59) (100% based on the amount of (58) present in the mixture of olefins) and, on concentration of the hexane extract, (57) (95%).

WORK DESCRIBED IN SECTION 1.5

Addition of N-phenyltriazolinedione to 7-isopropylidenecycloocta-1,3,5-triene (65)

The mixture containing (65) (*ca.* 43 mg, 0.29 mmol, estimated by g.l.c.)prepared by the base catalysed isomerization of isopropylcyclooctatetraene (see page 157) was diluted with ether (30 ml), washed with water (3 × 20 ml), dried and concentrated under reduced pressure (*ca.* 100 mm) to a brown oil. The oil was dissolved in acetone (5 ml) and treated dropwise with a solution of N-phenyltriazolinedione (200 mg, 1.26 mmol) in acetone (5 ml) until the red colour of the dienophile persisted. At this instant, g.l.c. (column B, 110°) indicated that 7-isopropylidenecycloocta-1,3,5-triene had been entirely consumed while the other components were not diminished. The reaction mixture was concentrated to an oil which, on preparative t.l.c. (50% ethyl acetate in light petroleum), yielded 2,4,6-triaza-7,7-dimethyl-4-phenyltricyclo[6,5,1,$0^{2,6}$]tetradeca-8,10,12-triene-3,5-dione (114) (94 mg, 100%), m.p. 193 - 195 (*ex* mixtures of ethyl acetate and light petroleum) (Found: C, 70.9; H, 5.7. $C_{19}H_{19}N_3O_2$ requires C, 71.0; H, 6.0%). P.m.r. (60 MHz), δ 7.5 - 7.2 (5H, complex), 6.13 - 5.88 (5H, complex), 5.00 (1H, broad s) 2.88 and 2.69 (2H, AB part of an ABX system), J_{AB} 11.5 Hz, J_{AX} 6 Hz), 1.75 (3H, s), 1.65 (3H, s); c.m.r.

δ 21.63 (q), 24.43 (q), 26.37 (t), 59.77 (d), 66.21 (s), 122.81 (d), 123 - 133 complex, 151.99 (s), 152.45 (s); λ_{max} 202 nm ($\varepsilon = 2.06 \times 10^4$) shoulders at 214 nm and 255 nm; mass spectrum, *m/e* 321 (64%), 145 (92), 131 (100), 119 (93), 91 (86), 78 (14), 76 (25).

WORK DESCRIBED IN SECTION 1.6

Addition of tetracyanoethylene to (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-triene (66)

A solution of (*E*)- and (*Z*)-7-benzylidenecycloocta-1,3,5-triene (1.34 g, 6.9 mmol) (of which 66% was in the (*E*)-configuration) and tetracyanoethylene (883 mg, 6.9 mmol) in ethyl acetate (25 ml) was boiled under reflux in a nitrogen atmosphere for 12 h. The solution was then diluted with ethyl acetate (50 ml), washed successively with an aqueous solution of sodium metabisulphite (20%, 3 × 20 ml), water (20 ml) and brine (50 ml), dried and concentrated to a yellow oil. This oil was separated into a mixture of four adducts (2.1 g, 94%) and polymeric material by chromatography on silica gel (30% ethyl acetate in light petroleum). By h.p.l.c. (10 µm silica gel, 10% ethyl acetate in light petroleum) the adduct mixture was separated into three fractions.

(a) The fraction of shortest retention time, which accounted for 14% of the adduct mixture, yielded 10,10,11,11-tetracyano-9-phenyltricyclo[6,3,0,$0^{6,8}$]undeca-2,4-diene (115), m.p. 187 - 192 (*ex* ether/light petroleum), (Found: C, 77.9; H, 4.6; N, 17.7. $C_{21}H_{15}N_4$ requires C, 78.2;

H, 4.4; N, 17.4%). P.m.r. δ 7.43 (5H, s), 6.55 - 5.73 (4H, complex), 4.11 (1H, s), 3.67 (1H, s), 1.56 - 0.75 (3H, complex); c.m.r. δ 20.78 (d), 23.09 (t), 36.79 (s), 56.13 (d), 60.42 (d), 125.97 (d), 126.94 (d), 129.74 (d), 130.34 (d), 130.71 (d), 131.63 (d), 136.29 (d); λ_{max} 257 nm ($\varepsilon = 4.97 \times 10^3$), 208 nm ($\varepsilon = 1.60 \times 10^4$); mass spectrum, *m/e* 322 (6%), 194 (100), 179 (70), 168 (34), 116 (58), 91 (35), 78 (22), 77 (35).

(b) The fraction of intermediate retention time, which contained material amounting to 68% of the adduct mixture, yielded a 1:1 mixture of $\pi 8 + \pi 2$ adducts (116) and (117). Fractional crystallization of this mixture, from ether/light petroleum, gave another mixture of (116) and (117) and epimerically pure 8,8,9,9-tetracyano-10-phenylbicyclo[5,3,1]-undeca-1,3,5-triene (116), m.p. 221.5 - 222.5° (after sublimation, 100°/0.1 mm), (Found: C, 78.3; H, 4.2. $C_{21}H_{15}N_4$ requires C, 78.2; H, 4.4%). P.m.r. δ 7.53 (5H, d, J 2 Hz), 6.21 (5H, broad envelope), 4.25 (1H, s), 3.88 (1H, broad s), 3.34 and 2.46 (2H, ABX system, J_{AB} 13.8 Hz, J_{AX} 2.4 Hz, J_{BX} 3.0 Hz), (double irradiation at δ 3.8 caused the ABX system to collapse into an AB "quartet") (in addition to the signals mentioned above, the p.m.r. spectrum of a mixture of (116) and (117) contained a singlet (1H) at δ 4.70 and a "narrow" (see page 67) ABX system centred at δ 3.05 and 2.91 (J_{AB} 14 Hz, J_{AX} 6 Hz)); c.m.r. δ 30.61 (t), 47.86 (d), 55.99 (d), 126.32 (d), 128.39 (d), 128.75 (d), 129.72 (d), 130.09 (d), 130.45 (d), 131.54 (d), 135.07 (s), 136.65 (s) (in addition to these signals, the c.m.r. spectrum of a mixture of (116) and (117) contained a triplet at δ 25.02, and doublets at δ 47.01 and 55.27); λ_{max} 260 nm (ε = 2.31 × 10^3), 211 nm (ε = 2.59 × 10^4); mass spectrum, *m/e* 322 (7%), 194 (100), 179 (30), 116 (30), 91 (15).

(c) The fraction of longest retention time, 17% of adduct mixture, yielded (*E*)-5-benzylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (118), m.p. 170.5 - 172° (*ex* chloroform (light petroleum), (Found: C, 78.1; H, 4.4. $C_{21}H_{15}N_4$ requires C, 78.2; H, 4.4%). P.m.r. δ 7.33 (5H, "d", J 2.5 Hz), 6.89 (1H, s), 6.56 - 6.36 (2H, complex), 6.24 and 5.81 (2H, AB "q", J_{AB} 12 Hz, split into dd, J 2.5 and 7 Hz at δ 5.81 and into dd, J 9 and 4.5 Hz at 6.24), 4.31 - 4.08 (1H, complex), 4.08 - 3.75 (1H, complex), 3.27 and 2.96 (2H, AB "q", J_{AB} 15 Hz, split into d, J 9 Hz at δ 3.27 and complex multiplets at 2.96) (double irradiation at δ 3.8 simplified the complex AB system at δ 6.24 and 5.81 but did not simplify the AB system centred at δ 3.27 and 2.96; double irradiation at δ 3.27 and 2.96 did not cause the multiplets between δ 4.31 and 3.75 to collapse); c.m.r. δ 26.11 (t), 42.66 (d), 52.11 (d), 121.22 (d), 127.78 (d), 128 - 130 complex, 137.25 (d), 139.56 (d); λ_{max} 249 nm (ε = 1.56 × 10^4), 210 nm (ε = 1.73 × 10^4); mass spectrum, *m/e* 322 (3%), 194 (100), 179 (33), 116 (37), 91 (17).

A solution of (118) (50 mg) in ethyl acetate was heated in a sealed tube at 120° for 5 days. After this period, no conversion of (118) into (115), (116) or (117) was evident (h.p.l.c.).

WORK DESCRIBED IN SECTION 1.7

Addition of tetracyanoethylene to (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)cycloocta-1,3,5-trienes (67)

A solution of (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)-cycloocta-1,3,5-trienes (350 mg, 1.5 mmol), of which 77% was the (*E*)- olefin, and tetracyanoethylene (190 mg, 1.5 mmol) in ethyl acetate (10 ml) was boiled under nitrogen for 2 h. The mixture was then diluted with ethyl acetate (40 ml), washed successively with an aqueous solution of sodium metabisulphite (20%, 2 × 20 ml), water (2 × 20 ml) and brine (20 ml). The dried organic extract was concentrated to a yellow oil which was subjected to chromatography on silica gel; gradient elution with mixtures of ether (20 - 50%) in light petroleum yielded polymeric material, a mixture of $\pi 8 + \pi 2$ and "3,6" adducts (172 mg) and then pure "3,6" adduct (126) (131 mg). Through h.p.l.c. (10 μm silica gel, 15% ethyl acetate in hexane), the mixture yielded pure (126) (48 mg; in total, 179 mg obtained, 38%) and a 1:1 mixture of the $\pi 8 + \pi 2$ adducts (127) and (128) (124 mg, 27%).

The "3,6" adduct, (*E*)-5-(*p*-methoxybenzylidene)-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (126), recrystallized from mixtures of ether/light petroleum, had a melting point of 195 - 197°, (Found: C, 74.7; H, 4.7. $C_{22}H_{16}N_4O$ requires C, 75.0; H, 4.6%). P.m.r. δ 7.23 and 6.92 (4H, AA'BB' system, J_{AB} 8.5 Hz), 6.86 (1H, s), 6.65 - 6.43 (2H, complex), 6.36 and 5.87 (2H, AB part of an AB system, J_{AB} 11.5 Hz, split into dd, J 7 and 2.5 Hz at δ 5.87 and dd, J 10 and 5 Hz at δ 6.36), 4.27 - 4.08 (1H, complex), 4.08 - 3.77 (1H, complex), 3.82 (3H, s), 3.31 and

2.95 (2H, AB system, J_{AB} 14.5 Hz, split into d, J 10 Hz, at δ 3.31 and complex multiplets at 2.95); c.m.r. (hexadeuteroacetone) δ 26.89 (t), 42.31 (d), 51.79 (q), 55.67 (d), 114.95 (d), 128.55 (d), 129.64 (s), 130.62 (s), 131.10 (d; 2 × C?), 136.93 (d), 139.85 (d); λ_{max} 269 nm ($\varepsilon = 1.59 \times 10^4$), 203 nm ($\varepsilon = 2.71 \times 10^4$); mass spectrum, *m/e* 352 (10%), 234 (100), 209 (40), 193 (35), 178 (21), 146 (73), 121 (58), 115 (36), 91 (17), 78 (15), 76 (43).

Epimerically pure (<u>128</u>), m.p. 192 - 193°, was obtained from the mixture of (<u>127</u>) and (<u>128</u>) by fractional crystallization from mixtures of dichloromethane and light petroleum (Found: C, 74.7; H, 4.7. $C_{22}H_{16}N_4O$ requires C, 75.0; H, 4.6%). P.m.r. δ 7.45 and 7.03 (4H, AB system, J_{AB} 8 Hz), 5.89 - 6.65 (5H, complex), 4.66 (1H, s), 4.11 - 3.75 (1H, complex), 3.86 (3H, s), 3.03 and 2.93 (2H, ABX system, J_{AB} 13.5 Hz, J_{AX} 7.5 Hz) (in addition to the signals mentioned above, the p.m.r. spectrum (60 MHz) of a mixture of (<u>127</u>) and (<u>128</u>) contained a singlet (1H) at δ 4.16 and a "wide" (see page 67) AB part of an ABX system (J_{AB} 13 Hz, J_{AX} 2 Hz, J_{BX} 4 Hz) centred at δ 3.27 and 2.38); c.m.r. δ 25.03 (t), 47.14 (d), 54.91 (q), 55.64 (d), 115.40 (d), 125 - 130 complex, 125.97 (s), 130.59 (s), 134.11 (d); λ_{max} 281 nm ($\varepsilon = 4.25 \times 10^3$), 274 nm ($\varepsilon = 4.61 \times 10^3$), 227 nm ($\varepsilon = 1.23 \times 10^4$), 209 nm ($\varepsilon = 1.98 \times 10^4$); mass spectrum, *m/e* 352 (5%), 224 (100), 209 (18), 193 (18), 146 (32), 121 (31), 115 (25).

Addition of N-phenyltriazolinedione to (*E*)- and (*Z*)-7-(*p*-methoxybenzylidene)cycloocta-1,3,5-trienes (67)

A solution of N-phenyltriazolinedione (70 mg, 0.4 mmol) in acetone (10 ml) was added, under an atmosphere of nitrogen, to 7-(*p*-methoxybenzylidene)cycloocta-1,3,5-triene (67) (83 mg, 0.36 mmol) (containing the (*E*) olefin to the extent of 90% (c.m.r.) or 87% (p.m.r.); see page 40). After 10 min at room temperature, t.l.c. (30% light petroleum in dichloromethane) indicated that the olefin had been consumed entirely and two products, one in a trace amount, had been formed. The solution was concentrated, diluted with dichloromethane (20 ml), washed with an aqueous solution of sodium metabisulphite (20%, 2 × 10 ml), dried and concentrated to a yellow oil. The oil was crystallized by the addition of light petroleum and then fractionally crystallized twice* (dichloromethane, light petroleum) to yield epimerically pure 2,4,6-triaza-7-(*p*-methoxyphenyl)-4-phenyltricyclo[6,5,1,$0^{2,6}$]-tetradeca-8,10,12-triene-3,5-dione (129) (120 mg, 82%), m.p. 193 - 195°, (Found: C, 72.2; H, 5.2. $C_{24}H_{17}N_3O_3$ requires C, 72.2; H, 5.3%), and a mixture (23 mg, 16%) of (129) and an unidentified adduct. P.m.r. δ 7.69 - 6.57 (9H, complex), 6.57 - 5.89 (6H, complex), 5.25 (1H, broad s), 3.79 (3H, s), 2.85 and 2.27 (2H, AB part of an ABX system, J_{AB} 13 Hz, J_{AX} 4 Hz).

From the mixture of compounds was obtained additional (129) (*ca.* 5 mg, 4%) and the unidentified adduct (9 mg, 6%) (preparative t.l.c., 30% dichloromethane in light petroleum).*

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* A poor recovery results from separation on silica gel.

C.m.r. δ 25.63 (t), 55.51 (q), 57.45 (d), 62.43 (d), 114.66 (d), 137.50 (s), 125 - 135 complex; mass spectrum, *m/e* 399 (100%), 384 (2), 264 (15), 223 (90), 197 (61), 115 (22), 91 (24), 78 (8), 77 (16).

WORK DESCRIBED IN SECTION 1.8

Addition of tetracyanoethylene to (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-triene (68)

A solution of (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-trienes (68) (166 mg, 0.7 mmol) and tetracyanoethylene (128 mg, 1.0 mmol) in ethyl acetate (20 ml) was boiled under nitrogen for 12 h. After this time, the solution was diluted with dichloromethane (20 ml), washed successively with aqueous sodium metabisulphite (20%, 2 × 20 ml) and water (20 ml), dried and concentrated to an oily, yellow solid. This solid yielded a white powder (105 mg, 41%) on trituration (20% ether in light petroleum) which was shown by t.l.c. (70% dichloromethane in light petroleum) to be composed of three compounds, one present in a trace amount. The mixture was separated by chromatography on silica gel (50% dichloromethane in light petroleum) into a mixture of $\pi 8 + \pi 2$ adducts (134) and (135) (96 mg, 91% of adduct mixture) and an unidentified adduct (9 mg, 9%). Fractional crystallization (dichloromethane/ether/light petroleum) of the $\pi 8 + \pi 2$ adduct mixture gave epimerically pure 8,8,9,9-tetracyano-10-(*p*-nitrophenyl)-bicyclo[5,3,0]undeca-1,3,5-triene (135), m.p. 218 - 220°, (Found: $M^{+\cdot}$ 367.1074. $C_{21}H_{13}N_5O_2$ requires $M^{+\cdot}$ 367.1069) (this material was relatively unstable). P.m.r. δ 8.43 and

7.76 (4H, AA'BB' system, J_{AB} 8.5 Hz), 6.65 - 5.96 (5H, complex), 4.79 (1H, s), 3.93 (1H, complex), 3.14 and 2.89 (2H, ABX system, J_{AB} 14.5 Hz, J_{AX} 7.5 Hz) (the p.m.r. spectrum (60 MHz) of a mixture of (134) and (135) contained, in addition to the resonances mentioned above, a singlet at δ 4.63 and a "wide" ABX system (see page 67) due to (134)); λ_{max} 261 nm ($\varepsilon = 1.07 \times 10^4$), 206 nm ($1.54 \times 10^4$); mass spectrum *m/e* 367 (4%), 239 (100), 192 (33), 178 (25), 165 (22), 115 (23), 103 (25), 91 (10), 78 (10).

Addition of N-phenyltriazolinedione to (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-trienes (68)

A solution of N-phenyltriazolinedione (85 mg, 0.5 mmol) and a mixture of (*E*)- and (*Z*)-7-(*p*-nitrobenzylidene)cycloocta-1,3,5-trienes (68) (100 mg, 0.4 mmol; containing a trace of the (*Z*) isomer) in acetone (10 ml) was stirred at room temperature for 1 h. After this time, the reaction mixture was diluted with dichloromethane (50 ml), washed with aqueous sodium metabisulphite (20%, 2 × 10 ml), dried and concentrated to a yellow solid (180 mg, 100%). Fractional crystallization (dichloromethane/light petroleum) afforded a mixture of (136) and an unidentified adduct (23 mg, 13%) and epimerically pure 2,4,6-triaza-4-phenyl-7-(*p*-nitrophenyl)-tricyclo[6,5,1,$0^{2,6}$]tetradeca-8,10,12-triene-3,5-dione (136) (156 mg, 87%), m.p. 212 - 213, (Found: C, 66.5; H, 4.7. $C_{23}H_{18}N_4O_4$ requires C, 66.7; H, 4.4%). P.m.r. δ 8.38 - 7.30 (9H, complex), 6.62 (1H, s), 6.36 - 5.97 (5H complex), 5.29 (1H, broad s), 2.92 and 2.12 (2H, AB system, J_{AB} 13 Hz, J_{AX} 4 Hz); mass spectrum, *m/e* 414 (41%), 397 (20), 238 (92), 192 (52), 178 (52), 165 (62), 119 (100), 91 (86), 78 (44), 77 (29).

WORK DESCRIBED IN SECTION 1.9

Addition of tetracyanoethylene to 7-benzhydrylidenecycloocta-1,3,5-triene (69)

A solution of 7-benzhydrylidenecycloocta-1,3,5-triene (69) (400 mg, 1.49 mmol) and tetracyanoethylene (500 mg, 3.9 mmol) in ethyl acetate (20 ml) was boiled under nitrogen for 12 h. After this time, the solution was diluted with dichloromethane (50 ml), washed successively with aqueous sodium metabisulphite (20%, 2 × 20 ml) and water (20 ml), dried and concentrated to a yellow solid. Chromatography of this material on silica gel (gradient elution with ethyl acetate (initial concentration, 5%) in light petroleum) afforded a yellow fore-run (containing polymeric material) the Diels-Alder adduct (138) (262 mg, 78%), m.p. (after sublimation 120°/0.1 mm) 245 - 246°, (Found: C, 81.1; H, 4.7. $C_{27}H_{18}N_4$ requires C, 81.4; H, 4.6%) and the "3,6" adduct (137) (74 mg, 22%) m.p. 211 - 212.5 (*ex* dichloromethane/light petroleum) (Found: C, 81.1; H, 4.4. $C_{27}H_{18}N_4$ requires C, 81.4; H, 4.6%).

3-benzhydrylidene-9,9,10,10-tetracyanotricyclo[4,2,2,$0^{2,5}$]-deca-7-ene (138): p.m.r. δ 7.58 - 6.93 (10H, complex), 6.93 - 6.42 (2H, complex), 3.92 (1H, complex), 3.67 (1H, complex), 3.38 - 2.40 (4H, complex); c.m.r. δ 26.61 (d), 34.51 (t), 40.70 (d), 42.40 (d), 42.40 (s), 132.89 (s), 133.87 (d), 139.57 (s), 125 - 132 complex; λ_{max} (acetonitrile) 263 nm ($\varepsilon = 1.92 \times 10^4$) shoulders at 257, 233 and 224 nm, 195 nm

($\varepsilon = 4.28 \times 10^4$); mass spectrum, *m/e* 398 (67%), 371 (6), 271 (25), 256 (27), 219 (100), 206 (40), 193 (91), 166 (39), 129 (31), 115 (42), 91 (39), 77 (23).

5-benzhydrylidene-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,7-diene (137): p.m.r. δ 7.55 - 7.18 (10H, complex), 6.42 (2H, complex), 6.26 and 5.86 (2H, AB q, J_{AB} 12 Hz split into t, J 7.5 Hz, at δ 6.26 and d, J 7.5 Hz, at 5.86), 4.55 (1H, d, J 5.1 Hz), 3.88 (1H, dd, J 7.5 Hz), 3.11 (2H, d, J 7.5 Hz); c.m.r. δ 28.07 (t), 42.65 (d), 46.05 (d), 120.75 (d), 127 - 130 complex, 136.29 (d), 140.42 (d), 141.27 (s), 148.93 (s); λ_{max} 248 nm ($\varepsilon = 1.04 \times 10^4$), shoulder at 225 nm, 203 nm ($\varepsilon = 3.64 \times 10^4$); mass spectrum, *m/e* 398 (2%), 270 (100), 255 (25), 204 (32), 192 (77), 179 (32), 165 (38), 128 (15), 115 (14), 91 (16).

WORK DESCRIBED IN SECTION 1.10

Attempted addition of dienophiles to 7-(dicyanomethylene)cycloocta-1,3,5-triene (141)

7-(Dicyanomethylene)cycloocta-1,3,5-triene (141) did not produce any adducts with the following dienophiles under the following conditions:

(a) tetracyanoethylene in ethyl acetate, either at room temperature or reflux (reaction time of up to 2 days);

(b) N-phenyltriazolinedione in acetone, either at room temperature (for 2 days) or reflux (3 h);

(c) chlorosulphonylisocyanate in dichloromethane at room temperature for 2 days;

(d) dimethyl acetylenedicarboxylate in boiling ethyl acetate for 2 days.

In all cases, unchanged 7-(dicyanomethylene)cycloocta-1,3,5-triene (>77%) and polymeric material was obtained.

WORK DESCRIBED IN SECTION 1.11

Addition of bromine to 7-methylenecycloocta-1,3,5-triene (64)

(a) Slow addition of bromine.

A solution of bromine (677 mg, 4.23 mmol) in anhydrous dichloromethane (5 ml) was added dropwise, over a period of 3 min, to a stirred solution of 7-methylenecycloocta-1,3,5-triene (64) (500 mg, 4.23 mmol) in anhydrous dichloromethane (10 ml) at -78° under an atmosphere of nitrogen. After the solution had been stirred at -78° for 15 min, it was passed, while still cold, down a column of dry, activated neutral alumina (10 g). The alumina was washed with ether (15 ml) and the combined eluants were concentrated to a yellow oil (214 mg, 25%) which yielded (*E*)- and (*Z*)-7-(bromomethylene) cycloocta-1,3,5-triene (145), b.p. 80 - 90° (oven)/4.5 mm, (Found: C, 54.8; H, 4.9; Br, 40.8. C_9H_9Br requires C, 54.8; H, 4.6; Br, 40.5%).

P.m.r. δ 6.83 - 5.47 (7H, complex), 3.23 and 3.09 (2H combined, 2 × d, J 7.5 Hz); c.m.r. δ 31.09 (t), 35.35 (t), 105.79 (d), 110.05 (d), 124 - 136 complex; λ_{max} 281 nm ($\varepsilon = 4.08 \times 10^3$), 231 nm ($\varepsilon = 1.59 \times 10^4$) shoulder at 205 nm; mass spectrum, *m/e* 198 (17%), 196 (17), 117 (100), 115 (91), 91 (61).

(b) Rapid addition of bromine.

A solution of bromine (420 mg, 2.6 mmol) in dichloromethane (1 ml) was added all at once under an atmosphere of nitrogen to a stirred solution of 7-methylenecycloocta-1,3,5-triene (<u>64</u>) (310 mg, 2.6 mmol) in dichloromethane (10 ml) at -78°. The solution was stirred at -78° for 15 min and then passed, while still cold, down a column of dry, activated neutral alumina (10 g). The alumina was washed with ether (20 ml) and the combined eluants were concentrated to a yellow oil which was shown by t.l.c. (silica gel, light petroleum) to be a complex mixture containing (<u>145</u>) and another major component. Preparative t.l.c. (silica gel, light petroleum) afforded (<u>145</u>) (175 mg, 21%) and bromomethyl-3,4,7-tribromocycloocta-1,5-diene (<u>148</u>) (295 mg, 16%), (Found: $M^{+\bullet}$, 435.7503. $C_9H_{10}Br_4$ requires $M^{+\bullet}$, 435.7498).

P.m.r. δ 6.42 (1H, complex), 6.09 - 5.72 (2H, complex), 4.81 (2H, d, J 3 Hz), 4.75 - 4.55 (1H, complex), 4.39 and 4.11 (2H, AB q, J_{AB} 10 Hz), 2.74 and 2.93 (2H, AB part of an ABX system, J_{AB} 15 Hz, J_{AX} 7.5 Hz) (on double irradiation at δ 4.65, the ABX system collapses into a simple AB "quartet"); c.m.r. δ 30.01 (t), 39.37 (t), 46.41 (d), 49.69 (d), 59.53 (d), 127.18 (d), 131.07 (d), 133.87 (d), 135.20 (s); λ_{max} 238 nm ($\varepsilon = 9.95 \times 10^3$); mass spectrum, *m/e* 442 (0.2%), 440 (0.7), 438 (1), 436 (0.7), 434 (0.2), 361 (7), 359 (18), 357 (18), 355 (7), 279 (20), 277 (40), 275 (20), 199 (20), 198 (20), 197 (40), 196 (20), 118 (100), 91 (93).

WORK DESCRIBED IN CHAPTER 2

WORK DESCRIBED IN SECTION 2.2

Preparation of isopropenylcyclooctatetraene (88)

(a) From isopropylcyclooctatetraene.

See page 157.

(b) From the coupling[103] of bromocyclooctatetraene with isopropenylmagnesium bromide.

A solution of bromocyclooctatetraene (7.7 g, 41.8 mmol), isopropenylmagnesium bromide (prepared from 2-bromopropene (15.2 g, 126 mmol) and magnesium turnings (3.0 g, 123 mmol)) and anhydrous ferric chloride (50 mg) in anhydrous tetrahydrofuran (100 ml) was stirred under a nitrogen atmosphere at -78° for 1 h and then at room temperature for 24 h. The brown solution was then diluted with ether (100 ml), washed successively with saturated aqueous ammonium chloride (2 × 100 ml), water (5 × 100 ml) and brine (1 × 100 ml), dried and then washed with aqueous silver nitrate solution (20%, 5 × 50 ml). The aqueous phases were combined, washed with ether (20 ml) and then treated with concentrated aqueous ammonium hydroxide until the brown precipitate ("silver hydroxide") dissolved. The solution was then extracted with ether (3 × 50 ml) and the combined organic extracts were dried and concentrated carefully under reduced pressure (*ca.* 100 mm) to a yellow oil. Distillation afforded isopropenylcyclooctatetraene (1.5 g, 25%), b.p. 60°/33 mm, (Found: C, 91.2; H, 8.4. $C_{11}H_{12}$ requires C, 91.6; H, 8.6%). P.m.r. δ 6.02 - 5.60 (7H, complex), 4.82 (2H, broad s), 1.90 (3H, s); c.m.r. δ 20.83 (q), 114.74 (t), 128.42 (d), 131 - 135 complex, 144.28 (s); λ_{max} 225 nm ($\varepsilon = 1.19 \times 10^4$), 207 nm ($\varepsilon = 2.45 \times 10^4$); mass spectrum, *m/e* 144 (27%), 143 (17), 129 (100), 128 (82), 117 (13), 115 (31), 91 (20).

Addition of tetracyanoethylene to isopropenylcyclooctatetraene (88)

A solution of tetracyanoethylene (60 mg, 0.46 mmol) and isopropenylcyclooctatetraene (88) (70 mg, 0.48 mmol) in ethyl acetate (5 ml) was stirred at room temperature under a nigrogen atmosphere for 5 min (the solution became deep red-brown coloured immediately on mixing the reagents). The solution was diluted with ether (20 ml), treated with an aqueous solution of sodium metabisulphite (20%, 10 ml) and concentrated to a yellow oil which yielded pure 11,11,12,12-tetracyano-9-methylbicyclo[6,4,0]undeca-2,4,6,8(9)-tetraene (161) (120 mg, 93%) on preparative t.l.c. (silica gel, 50% ether in light petroleum), m.p. 126 - 127 (*ex* ether/light petroleum), (Found: C, 75.0; H, 4.20. $C_{17}H_{12}N_4$ requires C, 75.0; H, 4.4%). P.m.r. δ 6.92 - 5.71 (6H, complex), 4.53 (1H, multiplet), 3.13 (2H, broad s), 1.93 (3H, s); c.m.r. δ 19.27 (q), 37.17 (s), 38.14 (t), 43.12 (s), 44.46 (d), 125.15 (s), 127.17 (d), 127.41 (d), 128.39 (d), 128.75 (d), 131.54 (d), 134.95 (d); λ_{max} 224 nm ($\varepsilon = 1.53 \times 10^4$), 261 nm ($\varepsilon = 5.46 \times 10^3$); mass spectrum, *m/e* 272 (39%), 256 (17), 144 (100), 129 (97), 78 (89).

Addition of N-phenyltriazolinedione to isopropenylcyclooctatetraene (88)

A solution of N-phenyltriazolinedione (960 mg, 5.5 mmol) in acetone (10 ml) was added dropwise to a stirred solution of isopropenylcyclooctatetraene (88) (800 mg, 5.5 mmol) in acetone (20 ml); the bright red colour of the dienophile faded immediately on addition to the olefin. The solution was stirred at room temperature for 10 min (by which time crystals had precipitated) and filtered to yield crude 2,4,6-triaza-8-methyl-4-phenyltricyclo[7,6,0,$0^{2,6}$]pentadeca-8,10,12,14-tetraene-3,5-dione (159) (1.32 g, 75%); concentration of the filtrate afforded additional (159) (422 mg, 24%). Sublimation *in vacuo* (160°/0.01 mm) yielded (159) as white needles m.p. 185 - 186°, (Found: C, 71.4; H, 5.3; N, 13.3. $C_{19}H_{17}N_3O_2$ requires C, 71.5; H, 5.4; N, 13.2%). P.m.r. δ 7.67 - 7.23 (5H complex), 6.74 - 5.52 (7H, complex), 4.24 and 4.03 (2H, AB q, J_{AB} 17.5 Hz), 1,89 (3H, s); c.m.r. δ 16.29 (q), 47.87 (t), 54.43 (d), 131.5 - 124 complex, 134.35 (d), 151.96 (s), 153.05 (s); λ_{max} 300 nm ($\varepsilon = 3.14 \times 10^3$), 260 nm ($\varepsilon = 4.57 \times 10^3$), 224 nm ($\varepsilon = 3.68 \times 10^4$), 200 nm ($\varepsilon = 2.31 \times 10^4$); ν_{max} 3029 (w), 2986 (w), 2874 (w), 1782 (s), 1726 (s), 1611 (w), 1512 (s), 1289 (m), 1139 (m), 912 (s); mass spectrum, *m/e* 319 (100%), 304 (33), 241 (28), 172 (33), 143 (71), 129 (61), 119 (76), 91 (38), 78 (57).

Addition of N-phenyltriazolinedione to 2,4,6-triaza-8-methyl-4-phenyltricyclo[7,6,0,$0^{2,6}$]pentadeca-8,10,12,14-tetraene-3,5-dione (159)

A solution of (159) (55 mg, 0.17 mmol) and N-phenyltriazolinedione (80 mg, 0.46 mmol) in dichloromethane (20 ml) was boiled under reflux in a nitrogen atmosphere for 2 h during which time the red solution faded somewhat and a white precipitate formed. The cooled solution was filtered to give a *bis*-adduct (73 mg, 87%) and a red filtrate which was washed with aqueous sodium metabisulphite (20%, 2 × 10 ml), dried and concentrated to yield additional material (11 mg, 13%). The *bis*-adduct samples were combined and recrystallized from a large volume of 1,4 dioxan to give a white powder, m.p. 274° (dec.), (Found: C, 60.9; H, 4.7. $C_{27}H_{22}N_6O_4$ requires C, 65.6; H, 4.5%. Found: $M^{+\cdot}$ 494.1710. $C_{27}H_{22}N_6O_4$ requires $M^{+\cdot}$ 494.1702). P.m.r. δ 7.48 (10H, broad s), 6.84 - 6.32 (2H, complex), 6.32 - 5.29 (5H, complex), 4.26 and 3.96 (2H, AB q, J_{AB} 16.5 Hz), 2.19 (3H, s).

Recrystallizations from ethyl acetate and chloroform to a constant melting point (274 - 275° and 276 - 276.5°, respectively) afforded white needles, (Found: C, 61.3; H, 4.6; N, 16.0, and C, 61.7; H, 4.6%, respectively. *N.b.* $C_{27}H_{22}N_6O_4 \cdot 2(H_2O)$ requires C, 61.1; H, 4.9%).

WORK DESCRIBED IN SECTION 2.3

Addition of maleic anhydride to vinylcyclooctatetraene (156)

The *bis*-adduct described by Withey[104] was prepared from vinylcyclooctatetraene (156)[111] (100 mg, 0.77 mmol) and maleic anhydride (274 mg, 2.7 mmol) at 140°, m.p. 302 - 304° (dec.) (lit.[104] 303 - 305 (dec.)), (80 mg, 30%); structure (165) was assigned to this compound. P.m.r. (*ca.* 5% deuterochloroform in hexadeuterodimethylsulphoxide) δ 5.54 (2H, broad s), 4.89 (1H, complex), 2.88 - 0.93 (11H, complex); c.m.r. (hexadeuterodimethylsulphoxide) 23.54 (t), 34.59 (2 × d), 34.83 (d), 35.92 (d), 39.20 (d), 41.15 (d), 41.88 (d), 43.21 (2 × d?), 118.03 (d), 131.76 (d), 132.97 (d), 145.48 (s), 173.30 (s), 173.78 (2 × s?), 175.85 (s); mass spectrum, *m/e* 327 ($M^{+\cdot}$ + 1, 8%), 326 ($M^{+\cdot}$, 5), 298 (8), 280 (5), 254 (27), 227 (14), 181 (45), 155 (100), 128 (23), 100 (45), 91 (58), 78 (56).

WORK DESCRIBED IN CHAPTER 3

WORK DESCRIBED IN SECTION 3.2

Preparation of 5-chloropentyl tetrahydropyran-2-yl ether (197)

5-Chloropentanol[150] (25 g, 0.2 mol) was added to stirred solution of *p*-toluenesulphonic acid (10 mg) in dihydropyran (17.1 g, 0.2 mol) under a nitrogen atmosphere. The solution was then boiled under reflux for 8 h, washed with aqueous sodium carbonate (10%, 5 ml), dried and distilled to yield the ether (37 g, 87%), b.p. 74 - 77°/0.2 mm. P.m.r. (60 MHz, CCl_4) δ 4.45 (1H, broad multiplet), 3.88 - 3.00 (6H, complex), 2.0 - 1.26 (12H, complex).

Preparation of 5-cyclooctatetraenylpentanol (200)

A solution of redistilled 5-chloropentyl tetrahydropyran-2-yl ether (6.4 g, 31.0 mmol) and 1,2-dibromoethane* (500 mg, 2.6 mmol) in anhydrous tetrahydrofuran (35 ml) was added under a nitrogen atmosphere to magnesium turnings (800 mg, 32.9 mmol) and a crystal of iodine at such a rate that gentle reflux was maintained. The solution was then boiled under reflux for a further 30 min and transferred, with the aid of tetrahydrofuran (30 ml), to a flask containing bromocyclooctatetraene (5.7 g, 31.2 mmol). This mixture was cooled to -10° under an atmosphere of nitrogen, treated with a solution of anhydrous ferric chloride (10 mg) in anhydrous tetrahydrofuran (1 ml) and then stirred at 0° for 4 h. After this time, the solution was treated with saturated aqueous

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* Considerable difficulty was encountered in the preparation of the Grignard reagent; it was found that addition of the chloride and dibromoethane to magnesium and iodine gave the best results.

ammonium chloride (20 ml), diluted with ether (125 ml), washed with water (5 × 50 ml) and concentrated to a brown oil. The oil was added to dilute hydrochloric acid (50 ml), treated with tetrahydrofuran (an amount sufficient to give a homogeneous solution) and then stirred at room temperature for 2 h. After this time the mixture was neutralized with sodium carbonate, the layers were separated and the aqueous phase extracted with ether (3 × 50 ml). The combined organic phases were washed with water (5 × 30 ml), dried and concentrated to a red-brown oil. Chromatography (silica gel, 0 - 5% ether in light petroleum, gradient elution) followed by distillation afforded 5-cyclooctatetraenylpentanol (2.2 g, 38%), b.p. 105° (oven)/0.1 mm, (Found: C, 81.8; H, 9.5. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%). P.m.r. (60 MHz, CCl_4) δ 5.95 - 5.30 (7H, complex), 3.50 (2H, poorly resolved t, $J \approx 5$ Hz), 2.00 (2H, poorly resolved t, $J \approx 6$ Hz), 1.78 - 1.13 (7H, complex); ν_{max} 3380 (s,b), 3020 (s), 2960 (s), 2883 (s), 1653 (w,b), 1447 (w,b), 1044 (m,b), 801 (m), 684 (m); mass spectrum, *m/e* 190 (13%), 131 (25), 117 (100), 91 (34), 85 (30), 78 (17).

Preparation of 5-cyclooctatetraenyl *p*-nitrobenzenesulphonate (168) (based on the procedure described by Mular).[112]

A solution of *p*-nitrobenzenesulphonyl chloride (1.25 g, 6.6 mmol) and 5-cyclooctatetraenylpentanol (200) (730 mg, 3.8 mmol) in pyridine (0.7 mmol) was stirred under nitrogen at 0° for 2 h. After this time, the mixture was treated with water (2 drops), stirred for a further 10 min and then diluted with a mixture of ether (50 ml) and ice-cold water (50 ml).

The organic layer was separated, washed with dilute hydrochloric acid (5%, 2 × 20 ml), aqueous sodium bicarbonate (2 × 20 ml), dried and concentrated to a yellow powder. Recrystallization (light petroleum/ether) afforded pure 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (168) 1.1 g, 76%) as pale yellow needles, m.p. 57 - 58.5°, (Found: C, 61.0; H, 6.0. $C_{19}H_{21}NO_5S$ requires C, 60.8; H, 5.6%). P.m.r. (60 MHz, CCl_4) δ 8.22 and 7.91 (4H, AA'BB' system, "J_{AB}" 9 Hz), 5.76 - 5.30 (7H, complex), 4.06 (2H, t, J 6 Hz), 1.96 (2H, poorly resolved t), 1.78 - 1.13 (6H, complex); mass spectrum, *m/e* 375 (7%), 129 (33), 117 (100), 91 (37).

Solvolysis of 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (168)

(a) Relatively high concentration of (168).

A solution of 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (35 mg, 9.4×10^{-5} mol) and triethylamine (35 µl, 2.5×10^{-4} mol) in anhydrous[37] hexafluoropropan-2-ol (0.75 ml) was heated at 85° (constant temperature bath) under nitrogen in a sealed p.m.r. spectroscopy tube. By observing the disappearance of the AA'BB' system due to the aromatic protons in 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate and the appearance of an AA'BB' system (*ca.* δ 8.1 and 7.8, "J_{AB}" 11 Hz; AA'BB' system due to (168) used as calibrant) due to *p*-nitrobenzenesulphonate anion, the progress of the solvolysis was monitored by p.m.r. spectroscopy. By this method, the half-life of the ester (168) under these solvolysis conditions was estimated to be approximately 2 - 3 h. After 22 h at 85°, the reaction mixture was diluted with ether (20 ml). An accurately weighed sample of undecane (7.74 mg, 4.96 × 10 mol) was added (quantitatively, with the aid of ether) and the solution was washed successively with aqueous sodium hydroxide (10%, 3 × 15 ml), water (10 ml) and brine (10 ml) and then dried. G.l.c. (column e, 120 - 210° at 7°/min) indicated that a mixture of nine compounds had been obtained; the major component* (produced in approximately 88% yield from the starting material) was identified, after purification by preparative t.l.c. (10% ether in light petroleum), as 5-cyclooctatetraenylpentyl 1,1,1,3,3,3-hexafluoroprop-2-yl ether (<u>201</u>), (Found: $M^{+\cdot}$ 340.1273. $C_{16}H_{18}OF_6$ requires 340.1262). P.m.r. δ 6.01 - 5.47 (7H, complex), 4.04 (1H, septet, J_{HF} 6.25 Hz), 3.86 (2H, t, J 7.5 Hz), 2.06 (2H, poorly resolved t), 1.89 - 0.76 (6H, complex); mass spectrum, *m/e* 340 (11%), 131 (20), 117 (100), 104 (18), 91 (27), 78 (12).

(b) Low concentration of (<u>168</u>).

A solution of 5-cyclooctatetraenylpentyl *p*-nitrobenzenesulphonate (<u>168</u>) (40 mg, 1.07 × 10^{-4} mol) and triethylamine (28 μl, 2 × 10^{-4} mol) in anhydrous hexafluoropropan-2-ol (10 ml) was frozen, under nitrogen, and then thawed three times under a reduced pressure of nitrogen (*ca.* 60 mm). The solution was then heated under nitrogen in a sealed ampoule at 85° for 22 h. After this period, t.l.c. (silica gel, 10% ether in light petroleum) indicated that the starting material had been consumed entirely; the reaction mixture was diluted

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* The response ratio of undecane : major product was calculated to be approximately 1 : 1.16.

with ether (20 ml) and to this solution was added (quantitatively, with the aid of ether) an accurately weighed sample of undecane (internal standard, 9.67 mg, 6.19×10^{-5} mol). The solution was washed successively with aqueous sodium hydroxide (10%, 3 × 30 ml) and water (3 × 20 ml), dried and then shown by g.l.c. (column e, 120 - 210° at 7°/min) to contain the ether (201) (5.6 mg, 23%) and seven other compounds.

WORK DESCRIBED IN CHAPTER 4

WORK DESCRIBED IN SECTION 4.2

Attempted addition of dichloroketene to cyclooctatetraene

(a) Procedure of Brady.[129]

A solution of trichloroacetyl chloride (910 mg, 4.8 mmol) in anhydrous ether (50 ml) was added dropwise over a 2 h* period (*via* a Perfusor) to a stirred suspension of activated zinc (prepared from zinc dust (1.0 g, 15.3 mmol) and cuprous iodide (140 mg, 0.74 mmol))[151] and cyclooctatetraene (500 mg, 480 mmol) in anhydrous ether (50 ml) under nitrogen. The solution was then stirred for a further 12 h, filtered through a pad of Celite and concentrated (*ca.* 40°/100 mm) to *ca.* 10 ml. The yellow solution was treated with light petroleum (75 ml) (to precipitate zinc salts), decanted from the granular precipitate and then washed successively with water (3 × 50 ml), aqueous sodium bicarbonate (10%, 2 × 50 ml) and brine (20 ml), dried and concentrated (*ca.* 40°/100 mm) to a deep yellow oil. From this oil, the only identifiable material to be obtained was unchanged cyclooctatetraene (460 mg, 92%). Further experiments, carried out under the conditions outlined in Table 11, gave unchanged cyclooctatetraene (>85%).

Since 2,2-dichloro-3-phenylbutanone (214)[128] (74%) was obtained when the above procedure was carried out in the presence of styrene, it was ascertained that dichloroketene

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* This period is the "reaction time" referred to in Table 11; in procedures (a), (b) and (c) this period was invariably followed by a further 12 h of reaction time during which the reaction mixture was stirred at the specified temperature (Table 11).

was being generated under the conditions described.

(b) Procedure of Krepski.[128]

A solution of trichloroacetyl chloride (910 mg, 4.8 mmol) and phosphorus oxychloride (750 mg, 5.0 mmol) in anhydrous ether (50 ml) was added (*via* a Perfusor) over a period of 2 h to a stirred suspension of activated zinc dust (prepared from zinc dust (1.0 g, 15.3 mmol) and cuprous iodide (140 mg, 0.74 mmol))[151] and cyclooctatetraene (500 mg, 4.8 mmol) in anhydrous ether (50 ml) under nitrogen. The suspension was stirred at room temperature for 12 h and then filtered through Celite. The filtrate was concentrated carefully to *ca.* 10 ml, treated with light petroleum (75 ml) to precipitate zinc salts and then filtered once more. The yellow filtrate was washed successively with water (2 × 100 ml), aqueous sodium bicarbonate (10%, 2 × 50 ml) and brine (2 × 50 ml), dried and concentrated carefully (*ca.* 40°/100 mm) to a yellow oil. Chromatography on silica gel (light petroleum) afforded only unchanged cyclooctatetraene (430 mg, 86%) and polymeric material. T.l.c. (silica gel; light petroleum/ether) did not indicate the presence of other compounds in the reaction mixture. Polymeric material and unchanged cyclooctatetraene ($>$85%) were the only isolable products obtained from the addition of dichloroketene to cyclooctatetraene using the procedure described above and the conditions outlined in Table 11.

2,2-Dichloro-3-phenylcyclobutanone (<u>214</u>)[128] (68%) was obtained when dichloroketene was generated, *via* a procedure identical to that described above, in the presence of styrene.

(c) Procedure of Ghosez.[130]

A solution of triethylamine (1.0 g, 9.9 mmol) in anhydrous hexane (50 ml) was added dropwise (*via* a Perfusor) over a period of 2 h to a stirred solution of cyclooctatetraene (1.06 g, 10.2 mmol) and dichloroacetyl chloride (1.5 g, 10.1 mmol) in anhydrous hexane (100 ml) under nitrogen. After the amine was added, the solution was stirred for a further 12 h and treated with water (100 ml). The organic phase was separated, washed successively with dilute hydrochloric acid (2 × 50 ml), aqueous sodium bicarbonate (10%, 2 × 50 ml) and water (50 ml), dried and concentrated to a yellow-orange oil. From this oil, the only identifiable product to be obtained was cyclooctatetraene (996 mg, 94%). Unchanged cyclooctatetraene (>92%) was the only isolable compound when the above procedure was performed under the conditions outlined in Table 11; again, 2,2-dichloro-3-phenylcyclobutanone (<u>214</u>) (67%) was produced by the control experiment.

<u>Attempted addition of dichloroketene to methoxycyclooctatetraene</u>

A solution of triethylamine (183 mg, 1.8 mmol) in benzene (20 ml) was added dropwise over a period of 3 h to a stirred solution of methoxycyclooctatetraene[144] (250 mg, 1.9 mmol) and dichloroacetyl chloride (275 mg, 1.9 mmol) in boiling benzene (50 ml) under nitrogen. The solution was then stirred and boiled for a further 12 h and worked up in the manner described in (c) above to yield a mixture of cycloocta-2,4,6-trienone and methoxycyclooctatetraene (combined yield 93%).

Addition of dichloroketene to Diels-Alder adduct (216)

A stirred suspension of the Diels-Alder adduct (216)[11,16,138] (155 mg, 0.55 mmol) and activated zinc (prepared from zinc powder (111 mg, 1.69 mmol) and cuprous iodide (20 mg, 0.1 mmol)) in anhydrous ether (20 ml) was treated dropwise over a period of 3 h (Perfusor) with a solution of trichloroacetyl chloride. The solution was then stirred for 14 h and filtered, the residue being washed exhaustively with ethyl acetate (3 × 20 ml). The combined filtrates were washed with water (3 × 20 ml), dried and concentrated to a white powder (92 mg, 59%). P.m.r. spectroscopy indicated that this material was predominantly unchanged (216) but additional resonances in the region δ 3 - 4 were observed; these signals could be due to a ketene adduct.[128,129,130] Similar results were obtained when the above procedure was followed with tetrahydrofuran as solvent.

Addition of dichloroketene to a mixture of (216) and (217)

A stirred suspension of (216) and (217)[138] (100 mg, 0.38 mol combined) and activated zinc (prepared from zinc powder (140 mg, 2.1 mmol) and cuprous iodide (25 mg, 0.13 mmol)) in anhydrous ether (20 ml) was treated dropwise over a period of 3 h (Perfusor) under an atmosphere of nitrogen with a solution of trichloroacetyl chloride (130 mg, 0.71 mmol) in anhydrous ether. After the addition of the acid chloride was completed, the suspension was boiled for 12 h, cooled and filtered (the residue was washed with ethyl acetate (3 × 25 ml)). The combined filtrates were washed with water (3 × 50 ml), dried and concentrated to a white solid (82 mg, 82%). P.m.r. spectroscopy indicated that this substance was composed predominantly of (216) and (217). Weak signals in the p.m.r. spectrum between δ 3 and 4 and peaks at *m/e* 503, 504 and 505 (corresponding to a molecular formula of $C_{16}H_{13}N_3O_2 \cdot 2\ (C_2OCl_2)$) in the mass spectrum suggest that a small amount of ketene adduct might have been formed.

Attempted addition of dichloroketene to bicyclo[4,2,0]octa-2,4,7-triene (2)

A stirred solution of bicyclo[4,2,0]octa-2,4,7-triene (2) (prepared, according to Adam,[139] from *trans*-7,8-dibromo-bicyclo[4,2,0]octa-2,4-diene[152] (1.0 g, 3.8 mmol) and a solution of n-butyllithium (4.2 ml, 3.8 mmol) in hexane), undecane (as internal standard, 250 µl) and triethylamine (362 mg, 3.5 mmol) in anhydrous ether (50 ml) was treated dropwise over a period of 1 h (Perfusor) at -40° with a solution of dichloroacetyl chloride (529 mg, 3.2 mmol) in anhydrous ether (20 ml) under an atmosphere of nitrogen. The consumption of bicyclo[4,2,0]octa-2,4,7-triene, relative to the internal standard, was monitored by g.l.c. (column d, 100°). After addition of the acid chloride was completed, g.l.c. indicated that most of the olefin was still unchanged; the solution was allowed to warm to -25°, treated with triethylamine (362 mg, 3.5 mmol) and, over a period of ½ h (Perfusor), a solution of dichloroacetyl chloride (529 mg, 3.2 mmol) in anhydrous ether (10 ml). After being stirred at -20° for 45 min, the solution was allowed to warm to room temperature over a period of 2 h and was then stirred at this temperature for 10 h. The solution was then washed with water (4 × 50 ml) and dried. G.l.c. indicated that 88% of the starting material had remained unchanged; material other than cyclooctatetraene was not identifiable, however.

Addition of dichloroketene to (222)

A solution of trichloroacetyl chloride (270 mg, 1.56 mmol) and phosphorus oxychloride (226 mg, 1.56 mmol) in anhydrous tetrahydrofuran (10 ml) was added over a period of 4 h (Perfusor) to a boiling solution of activated zinc (prepared from zinc dust (102 mg, 1.56 mmol) and cuprous iodide (18 mg, 0.1 mmol)) and (222) (120 mg, 0.6 mmol) in anhydrous tetrahydrofuran (20 ml) stirred under a nitrogen atmosphere. After addition was completed, the solution was boiled for a further 12 h, filtered, diluted with ether (100 ml) and washed with water (3 × 100 ml). The dried organic phase was concentrated to a yellow oil which yielded a white solid (58 mg, 31%) on trituration (carbon tetrachloride). This solid, which was difficult to recrystallize, was washed several times with ether to give a white solid m.p. 179 - 181°. P.m.r.* (60 MHz, hexadeuteroacetone) δ 6.46 (2H, complex), 3.68 - 3.28 (6H, complex), 3.03 - 2.61 (2H, complex); mass spectrum showed peaks at *m/e* 312, 313, 314, 164 (100%), 162 (100%).

Attempts to repeat this preparation were unsuccessful.

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* The tentative assignment of structure (223) to this substance was based on the similarity of these p.m.r. spectral characteristics to those of (222) and, in particular, (32).[107]

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