INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

THE SYNTHESIS OF 1,2-DIMETHYLENECYCLOOCTATRIENE AND SOME BICYCLO[6.2.0]DECANES

by

Basil V. Gregorovich

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
in the
Department of Chemistry
University of Ottawa
Ottawa, Canada

August, 1966

Candidate

B.V. Gregorovich

Supervisor

Professor F.A.L. Anet
D.Phil. (Oxon.)

Université d'Ottawa
BIBLIOTHÈQUES
LIBRARIES
University of Ottawa

UMI Number: DC52443

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

UMI Microform DC52443
Copyright 2007 by ProQuest LLC
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

To

VERA

and

Pheidippides

Roman Law and Greek Art,

the legacy of

Organic Chemistry

Preface

Part I

The structure of benzene was established in the latter half of the nineteenth century. Long standing interest in other fully unsaturated carbocycles developed since it was thought they might have properties related to those of benzene. The application of quantum physics to the motion of electrons, which led to the development of molecular orbital theory, gave renewed impetus to the study of such systems. Molecular orbital calculations have been applied to a remarkable variety of unsaturated cyclic molecules including many with exocyclic double bonds. There has been great interest in the comparison of calculated and measured properties of such molecules and as a result their synthesis has been of great importance. In the series of unsaturated carbocycles which contain an even membered ring and two adjacent exocyclic double bonds those with four and six carbons in the ring are known. It was of interest to synthesize the third member 1,2-dimethylenecyclooctatriene.

Part II

Bicyclic compounds which contain a cyclobutane ring have been known since the turn of the century and those in which the second ring contains four, five or six carbons are now readily accessible. Those with a larger

second ring are relatively rare. The addition of ketene to cis,trans-1,3-cyclooctadiene proved to be a feasible entry into such a system.

Acknowledgments

It was a privilege for the author to work under the supervision of Dr. F. A. L. Anet. His enthusiasm, interest, and originality have been instrumental in the completion of this research. The author wishes to thank Dr. R. R. Fraser for the use of facilities in his laboratory and Dr. M. C. Cook for the personal interest he has shown. Fellowships awarded to the author by Canadian Industries Limited are gratefully acknowledged.

Table of Contents

List of Tables

List of Figures

Abstract

Part I

2-Butynoic acid, which was synthesized by the reaction of carbon dioxide with lithio methylacetylide, was converted to the methyl ester with diazomethane. This ester, when photolysed in benzene, gave 2-carbomethoxy-1-methylcyclo"octatetraene. Hydrogenation of 2-carbomethoxy-1-methylcyclo"octatetraene confirmed the presence of four double bonds and gave a single product, cis-2-carbomethoxy-1-methylcyclo"octane. 2-Carbomethoxy-1-methylcyclo"octatetraene was converted to the alcohol by metal hydride in ether. It was found that aluminum hydride gave better yields than lithium aluminum hydride. The reaction of phosphorus tribromide with this alcohol gave the bromo compound which, when treated with trimethylamine in methanol-hexane, gave 1-methyl-2-N,N,N-trimethylaminomethylcyclo"octatetraene bromide. This quaternary bromide on treatment with an aqueous slurry of silver oxide gave the quaternary hydroxide, which was readily converted to 1,2-dimethylenecyclo"octatriene by pyrolysis at reduced pressure.

The mass spectra of 2-carbomethoxy-1-methylcyclo"octatetraene, 2-hydroxymethyl-1-methylcyclo"octatetraene, and 1,2-dimethylenecyclo"octatriene were obtained and breakdown patterns were proposed.

1,2-Dimethylenecyclooctatriene was shown to be monocyclic by the n.m.r. spectrum, although the possibility that the monocyclic form is in equilibrium with a small amount of a bicyclic form is not excluded. An attempt to obtain a bicyclic form by photolysis was unsuccessful.

1,2-Dimethylenecyclooctatriene was shown to be fairly stable thermally but extremely sensitive to oxygen. The infrared spectrum indicated that the molecule is not highly strained. Molecular orbital calculations were performed on planar 1,2-dimethylenecyclooctatriene. The total π energy, the delocalization energy, the bond orders and the free valences were calculated. Despite a high calculated delocalization energy for the planar form, the molecule apparently prefers a less strained non-planar shape as is shown by the ultraviolet spectrum.

The reactions of a variety of π systems with dienophiles were compared with the reaction of 1,2-dimethylenecyclooctatriene with tetracyanoethylene.

Part II

The addition of ketene to cis,trans-1,3-cyclooctadiene gave trans-bicyclo[6.2.0]dec-2-en-9-one. Arguments were presented supporting the assignment of the position of the double bond as $\gamma\delta$ to the carbonyl group and the fusion of the rings as trans. The reduced product, bicyclo[6.2.0] dec-9-one was prepared. The reduction confirmed that the original product had only one double bond. cis-Bicyclo

[6.2.0]dec-2-en-9-one was obtained by passing a dilute solution of trans-bicyclo[6.2.0]dec-2-en-9-one in pentane through an alumina column. Wolff-Kishner reduction gave bicyclo[6.2.0]dec-2-ene which was used for dehydrogenation studies. Dehydrogenation by rhodium on alumina gave a small amount of azulene but none of the desired bicyclo [6.2.0]decapentaene.

PART I

SYNTHESIS OF 1,2-DIMETHYLENECYCLOÖCTATRIENE

INTRODUCTION

A. General

Kekulé's proposal (1) for the structure of benzene encouraged speculation about the stability and reactivity of the higher and lower analogues cyclooctatetraene and cyclobutadiene. Early attempts to synthesize cyclobutadiene failed while cyclooctatetraene, which was synthesized by Willstätter (2) in 1911 from the alkaloid pseudo-pelletierine, was found to be typically olefinic in behaviour. It was thus seen that a simple correspondence between structure and benzene-like behaviour did not exist.

Aromaticity, a term which is derived from the odorous character of many natural product derivatives of the benzene series, began to mean a stability and reactivity associated with a benzene type structure. It was soon realized that pyridine fitted this classification and also that five membered heterocycles with two double bonds could be designated as aromatic. A logical development of these observations was the concept of the aromatic sextet (3) which became a useful guide to aromatic character. The application of electronic theory to the concept of aromaticity led to the formulation by Ingold of the theory of mesomerism (resonance) (4) which dealt with the distinct chemical reactivity of benzene-type molecules. The theories of mesomerism and the aromatic sextet were shown to be

compatible with the quantum physics of electrons by Hückel (5) and others. Two quantitative descriptions of aromatic systems developed, the valence bond (VB) and molecular orbital (MO) methods, which permitted the calculation of the thermochemical resonance energy, which can be measured experimentally.

Benzene is thermochemically more stable and much less reactive than molecules with alternate double and single bonds are expected to be. The resonance energy of benzene, the difference in energy between the benzene structure as it exists and the energy if its π bonds were of the cyclohexene type, amounts to 36 kcal per mole. Since the development of quantum methods it is the possession of a large resonance energy, rather than the tendency towards particular types of reactivity, that has become diagnostic of the aromatic compound.

B. Classification of Conjugated Systems

Hückel (5) in his π electron theory of aromaticity suggested that there is a fundamental difference between molecules with 4n and 4n + 2 π electrons. This is because the bonding molecular orbitals, which can be calculated, are filled in the case of molecules with 4n + 2 π electrons, with no electrons in non-bonding or antibonding orbitals, whereas for molecules having 4n π electrons this is not the case. His arguments referred to molecules with π electrons arranged on a circle. Stabilizing delocalization of electrons

occurs only in molecules having 4n + 2 π electrons and hence completed molecular orbital configurations.

Conjugated π electron systems can also be classified as to their alternant or non-alternant character (6). An alternant molecule can have its π centers divided into two sets such that each center is next to a center of the other set and never to a member of its own set. In a non-alternant molecule the electronic charge in the ground state is displaced from a distribution of one π electron per carbon. Among non-alternant molecules which are known there are many with substantial resonance energies so that the alternant character of a molecule is not closely connected with its aromaticity.

A classification, aimed at predicting the conditions for appreciable resonance energy, was proposed by Craig (7) and has become known as Craig's rules. To apply this criterion a molecule must have one or more twofold axes passing through at least two π centers. The molecule is labelled with the symbols α and β placing different symbols at the ends of all the double bonds of one Kekulé structure and applying them alternately as far as possible. The following expression is then evaluated:

$$\chi = (-1)^{p+q}$$

where p is the number of interchanges of π electron centers affected by rotation about the twofold axis and q is the number of interchanges of spin symbols required to restore

the original labelling scheme. π electron systems with totally symmetrical ground states give χ positive and those with unsymmetrical ground states give χ negative. A π system with an unsymmetrical ground state apparently does not have a type of π electron interaction which leads to large resonance energies and for such molecules the name pseudoaromatic has been suggested. It should be noted that monocyclic molecules with $4n$ π electrons are all pseudoaromatics.

C. Bond Strain

A major assumption of π electron theories of aromaticity is that the σ and π electrons do not interact so that study can be confined to the behaviour of the π electron system. This simplification must become less valid when the σ bonding in the molecule under study differs from that in the reference molecule used to determine standard values of bond heats of formation. Cyclobutane has interior angles of 90° while the normal C-C-C bond angle for sp^3 hybridized carbon is 109.5°. This angle strain renders cyclobutane thermochemically less stable than if it were constructed of normal C-C and C-H bonds. The greater energy of the cyclobutane molecule, reflected in the increased heat of combustion relative to a normal system, is called the strain energy and amounts to 27 kcal per mole (8). If angle strain occurs in a π electron molecule, then the observed resonance energy will be less than that predicted for the system by the amount of the strain energy. Cyclobutadiene, like cyclobutane, has

interior angles of 90° but since the normal C-C-C bond angle for sp^2 hybridized carbon is 120° cyclobutadiene must have substantially more strain than cyclobutane. The resonance energy of biphenylene is 22 kcal per mole (9) while that of biphenyl is 81 kcal per mole. Assuming equal π energies for the two molecules one gets a strain energy of 59 kcal per mole for cyclobutadiene (10). However, since biphenylene is a distorted 4n π electron system it is probable that its resonance energy would be less than that of biphenyl even if it were strain free. Consequently the actual value is probably lower than the 59 kcal per mole obtained by the above method. It is generally true that calculated values of strain energy are higher than observed values because it has not been possible to evaluate the reduction in strain brought about by electronic adjustments such as σ-π interactions (11).

In contrast to cyclobutane the strain energy in five and seven membered rings amounts to only about 5 kcal per mole. We thus have a variety of situations depending on the magnitude of strain and resonance energies.

Cyclobutadiene is a pseudoaromatic and hence would have no resonance stabilization but it should have substantial strain. It is, in fact, an extremely unstable molecule, which apparently has only a short lifetime. Cyclooctatetraene, though also a pseudoaromatic, can attain a strain free configuration. It is relatively stable and polyolefinic in behaviour.

Biphenylene has substantial resonance energy but because of severe strain the observed resonance energy is only 1.9 kcal per mole per π electron, compared to 6.7 kcal per mole per π electron for biphenyl.

Finally we have a situation such as that in tropolone where resonance is substantial, though less than in benzenoid systems, and strain is not extensive giving an observed resonance energy of 3 kcal per mole per π electron.

D. Monocyclic Pseudoaromatics

a. Cyclobutadiene

The high strain energy and lack of resonance stabilization (see Section C.) predicted for cyclobutadiene suggest that it is incapable of existence or has a very short life. The first recorded attempt at the synthesis of a cyclobutadiene derivative was that of Perkin (12) who tried to prepare cyclobutadiene-1,2-dicarboxylic acid by the action of alkali on 1,2-dibromobutane-1,2-dicarboxylic acid. He obtained 1-bromo-2-carboxycyclobutene-1 instead.

The first derivative to be prepared was biphenylene which was synthesized by Lothrup (13) by the action of cuprous oxide on 2,2'-dibromobiphenyl. Better yields (15%) were obtained using biphenyleneiodonium iodide in place of 2,2'-dibromobiphenyl. Wheland supports the view that biphenylene is essentially two benzene rings linked by single bonds (14). The ultraviolet spectrum (15) and orientation effects in Friedel-Crafts acylation (16) which gives a single

product, 2,6-diacetylbiphenylene, show that some interaction between the benzene rings must exist. However the calculated π bond order for the bonds joining the two rings is only 0.263 and a recent X-ray study by Mark and Trotter (17) gives the length of this bond as 1.52Å. Thus the interaction between the rings must be small and biphenylene displays little cyclobutadienoid character.

Another successful approach to cyclobutadiene synthesis has been the preparation of metal complex stabilized compounds. A share in two electrons with a metal having suitably orientated orbitals would give cyclobutadiene a closed shell and so would enhance its stability. The first of such compounds, synthesized by Criegee and Schröder, was a nickel chloride - 1,2,3,4-tetramethylcyclobutadiene complex prepared by the action of $Ni(CO)_4$ on 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (18). The iron carbonyl complex of unsubstituted cyclobutadiene was synthesized by Pettit and co-workers by the reaction of $Fe_2(CO)_9$ with 3,4-dichlorocyclobutene (19). Decomposition of this complex with ceric ammonium sulfate in the presence of methyl propynoate trapped the cyclobutadiene as 2-carbomethoxybicyclo[2.2.0]-2,5-hexadiene (20) which readily converts to methyl benzoate. Pettit also was able to distill the cyclobutadiene, as it was formed, into a trap cooled in liquid nitrogen, and then add methyl propynoate in ether to get methyl benzoate, thus providing strong evidence for the formation of free cyclobutadiene.

b. Cyclooctatetraene

Cyclooctatetraene (COT) has 4n π electrons and so is a pseudoaromatic which would be expected to have little resonance stabilization. One might expect the same synthetic difficulties as are found with cyclobutadiene. However, in contrast to cyclobutadiene, cyclooctatetraene can attain a non-planar, essentially strain free configuration. A wide variety of cyclooctatetraenes have been prepared and their chemical and physical properties have been extensively studied. Interestingly, pentalene which can be considered a cross-linked COT but which is restricted from attaining a strain free configuration, has not itself been synthesized although the pentalene dianion (21) and the hexaphenyl derivative (22) have been recently prepared.

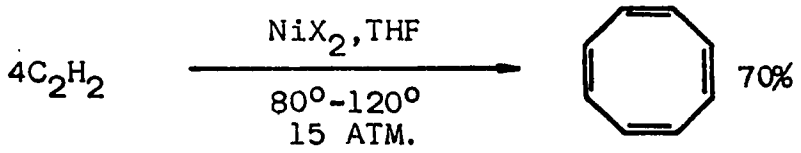
The first synthesis of COT was accomplished by Willstätter (2) who in 1911 converted pseudopelletierine (I) into COT(II) by a thirteen step sequence.

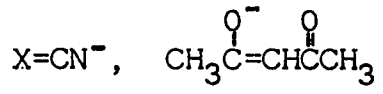
I II

Another synthesis which also uses the pyrolysis of quaternary hydroxides to introduce the final double bonds is that of Cope (23). 2-Chloro-1,3-butadiene was dimerized to yield a cyclobutane which on heating gave 1,6-dichloro-1,5-cyclooctadiene. The two vinyl chlorine groups were removed using sodium in liquid ammonia and 5,8-dibromo,1,3-cyclo-

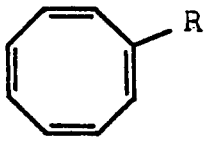
"octadiene was formed on treatment with N-bromosuccinimide. The bromine atoms were replaced with dimethylamine and the dimethylamino compound thus formed was quaternized, converted to the hydroxide and pyrolyzed to give COT in low yield.

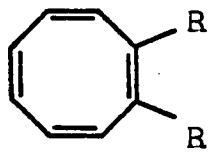
The first synthesis of COT to provide substantial quantities for detailed study was that of Reppe (24). He was able to convert acetylene into COT using a suitable nickel catalyst.



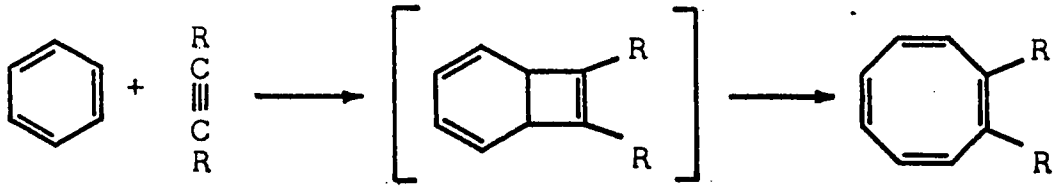


By using mono and disubstituted acetylenes with acetylene Cope (25,26) was able to make a variety of substituted cyclo"octatetraenes of the following type:



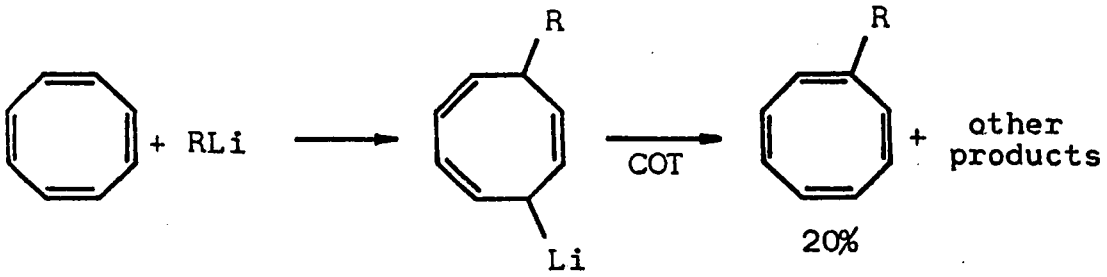


A more recent synthesis of COT is the photolysis of a solution of a substituted acetylene in benzene (27,28).



At least one of the R groups must be an ester or phenyl group. An alkyl substituted acetylene can be used if benzene is replaced by benzonitrile (29).

Substituted cyclooctatetraenes can be prepared by direct substitution using organo lithium compounds (30,31).



R = ϕ, p-dimethylaminophenyl,
$n\text{-}C_4H_9$, C_2H_5

Unfortunately yields are low and mixtures of cyclooctatrienes are obtained which complicate purification.

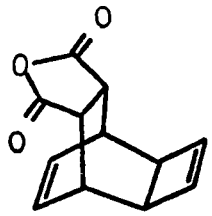
A wide variety of cyclooctatetraenes have been obtained by reactions of the side chain (32,33).

Cyclooctatetraene is a yellow liquid with b.p. 141°C/760 mm pressure. The structure was shown to be monocyclic (II_A) rather than bicyclic (II_B) by Willstätter (2).

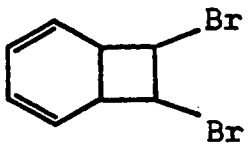
II_A II_B

However in many of its reactions COT behaves as though it were in the bicyclic form as for example in the Diels-Alder addition to maleic anhydride (24) (III) and the

addition of bromine (IV).

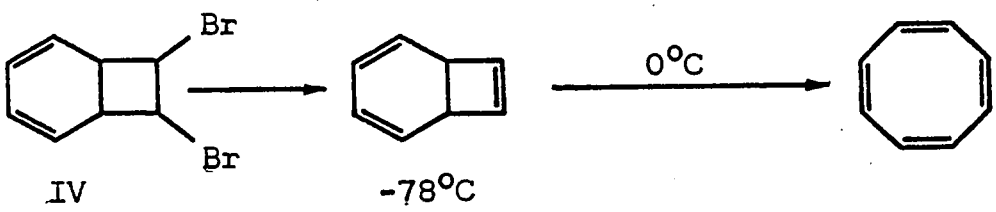


III



IV

It is possible that there is an equilibrium mixture between the monocyclic and bicyclic forms with only a very small concentration of the bicyclic form present. On the other hand bridging to the bicyclic form could occur during or subsequent to the reaction. The bicyclic form has in fact been prepared by the treatment of 7,8-dibromobicyclo [4.2.0]-2,4-octadiene (IV) with 9,10-disodiophenanthrene (34).

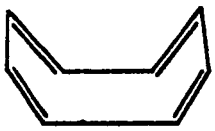


IV -78°C

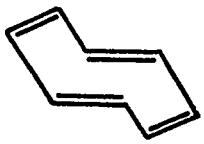
It is stable at -78°C but passes quickly and smoothly into the monocyclic form at 0°C. Its half life at 0°C is fourteen minutes. Since the tub form of COT does not provide the necessary planar 1,3-diene system needed for Diels-Alder reaction it is reasonable to assume that a small concentration of the bicyclic form is present and undergoes the reac-

tion. Huisgen and Mietzsch (35) by rate studies of Diels-Alder addition using a variety of dienophiles have shown that this is in fact the case. They estimated that at 100°C in dioxan the concentration of the bicyclic form was 0.01%. In the case of halogenation, however, there is no requirement for coplanarity. Also the reaction occurs rapidly at 0°C whereas the Diels-Alder addition of maleic anhydride requires several hours refluxing in benzene to go to completion. For these reasons it is likely that halogen reacts with the monocyclic form (36).

Although the monocyclic form of COT was established by Willstätter the conformation of the ring as the tub form was not accepted until quite recently. Three possible conformations were proposed:



TUB



TRANS

CROWN

The <u>trans</u> conformation is unlikely because of the very high strain energy associated with two <u>trans</u> double bonds in an eight membered ring. The crown conformation would have substantial strain associated with twisting of the double bonds.

Arguing from all available physical data and con-

sideration of angle strain Person, Pimentel and Pitzer (37) concluded that COT has the tub conformation. A later X-ray diffraction study (38) gave the following values:

	COT	NORMAL (39)
C=C	1.334 ± 0.001 Å	1.35 Å
C-C (sp^2-sp^2)	1.462 ± 0.001 Å	1.48 Å
C-H	1.090 ± 0.005 Å	1.086 Å
∢ C=C-C	126.46° ± 0.23°	120°
∢ C=C-H	118.3° ± 5.9°	120°

This clearly establishes the tub conformation and the alternate double bond-single bond nature of COT. Although there are four double bonds alternating with four single bonds in COT π overlap between neighbouring double bonds is sterically inhibited. The C=C stretching vibration in the infrared lies at 1635 cm^{-1}, a typical value for a non-conjugated aliphatic carbon-carbon double bond (40).

The ultraviolet spectrum (41) has two broad inflections with tailing into the visible region. This is in marked contrast to both the fine structure of benzene and the intense distinct absorptions of a conjugated polyolefin. 1,3,5-Hexatriene, for example, has three intense absorptions at 248 mμ , 258 mμ and 268 mμ (42).

The n.m.r. spectrum (43) has a single absorption at 4.32 τ (60 Mc/sec.), TMS internal standard, showing that all protons are equivalent and that no delocalization of elec-

trons occurs.

An interesting consequence of the tub shape of cyclooctatetraene is that monosubstitution results in an asymmetric molecule which should thus be optically active. An attempt to separate carboxycyclooctatetraene into its optically active components using quinine hydrate failed (44). It has recently been shown by Anet (45,46) that two rate processes, bond shift and ring inversion, both of which result in racemization, take place in cyclooctatetraenes. These processes occur at a fast enough rate to preclude the separation of monosubstituted cyclooctatetraenes into their optically active forms.

E. Exomethylene Compounds

a. General

A simple resonance picture does not predict substantial delocalization energy for unsaturated compounds with exocyclic methylene groups because no unexcited structural alternatives can be written. MO theory, however, does not suffer from this restriction and in fact predicts substantial delocalization energies for these molecules.

For the first three members of this series, methylenecyclopropene, fulvene and heptafulvene, the calculated delocalization energies are 0.96β, 1.47β and 1.99β respectively (47). This is a delocalization energy of about 0.24β per π electron in all three cases. Craig's rules give χ positive for the three molecules, again suggesting

substantial delocalization. However the free valence of the exocyclic methylene group is 0.97 which would make these molecules very reactive in free radical reactions. These compounds are all non-alternant and so have a displacement of charge from one π electron per carbon. The charge density of the methylene carbon of fulvene is 0.622 so that fulvene should have a dipole moment with the ring at the negative end. Methylenecyclopropene and heptafulvene, on the other hand, have charge densities on the methylene carbon of 1.488 and 1.311 respectively. They would be expected to have the ring at the positive end of the dipole.

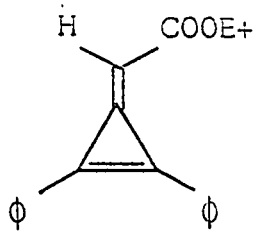
A study of the chemistry of these molecules (see below) shows fair agreement with MO predictions, which however, do not explain the much greater stability of fulvene relative to the other two. Methylenecyclopropene would, of course, have a very high strain energy, but the strain in heptafulvene should be of the same order as that in fulvene.

b. Methylenecyclopropene

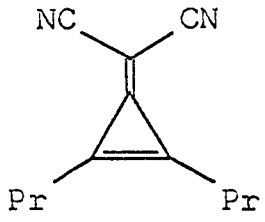
The parent hydrocarbon, which is a cross conjugated analogue of cyclobutadiene, has never been prepared. The high charge density of 1.49 predicted for the terminal exomethylene carbon atom suggests that a dipolar resonance form should make a substantial contribution. Thus electronegative groups on the methylene carbon should stabilize

the molecule.

Several such substituted compounds have recently been synthesized of which the two prepared by Battiste (V) (48) and Kende and Izzo (VI) (49) offer an interesting comparison.



V



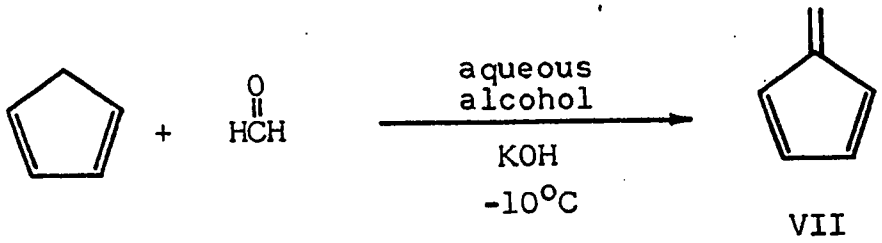
VI

The ester (V) reacted immediately with tetracyanoethylene in acetonitrile at 25°C and slowly polymerized at room temperature. The methylenecyclopropene (VI) was inert to tetracyanoethylene in acetonitrile at 25°C and did not react with bromine in methylene chloride. It has very strong stabilization of the dipolar form because of two electron donating groups which stabilize the positively charged ring and two electron withdrawing groups which stabilize the negatively charged exocyclic carbon so that its inertness to olefinic reagents

is not surprising.

c. Fulvene

In sharp contrast to methylenecyclopropene fulvene derivatives are known to occur in nature (50) and the first derivative, dibenzofulvene was prepared by De La Harpe and van Dorp (51) eighty years ago. Thiele (52) prepared a variety of fulvenes by the condensation of aldehydes and ketones with cyclopentadiene in the presence of base. These included dimethylfulvene and fulvene which however he was unable to isolate. Unsubstituted fulvene (VII) was prepared in 1956 by the condensation of formaldehyde with cyclopentadiene (53).

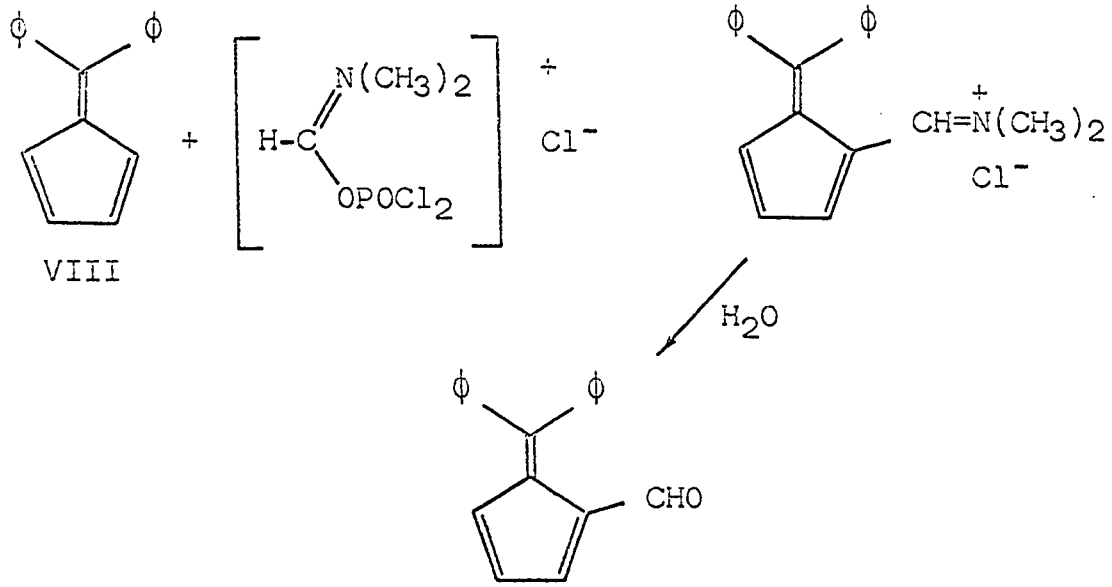


VII

A recent synthesis giving fulvene in good yield is the treatment of 6-N,N-dimethyl-aminofulvene with lithium aluminum hydride (54).

Since fulvene has a cross conjugated structure of the same number of π electrons as benzene it might be expected to show some aromatic properties. As predicted by MO calculations fulvene has a dipole moment, although the experimental value of 1.2D (55) (extrapolated from the

value for 6,6-dimethylfulvene) is much less than the 4.7D calculated from MO theory. The DE calculated using β = -18 kcal is 23 kcal per mole. With a predicted strain of 10 kcal per mole this gives a RE of 13 kcal per mole which compares favourably with the experimental value of 11 kcal per mole (56). This resonance energy of about 2 kcal per mole per π electron suggests that fulvene should show both olefinic and aromatic properties. The olefinic character of fulvene seems to predominate. It polymerizes within a few hours at room temperature, although it can be stored under inert atmosphere at -78°C for several days. Fulvenes add bromine readily, are prone to autoxidation and undergo Diels-Alder addition demonstrating their olefinic nature. However they also react with nucleophilic and electrophilic reagents. For example, 6,6-diphenylfulvene (VIII) can be readily formylated with Vilsmeir's complex (57).

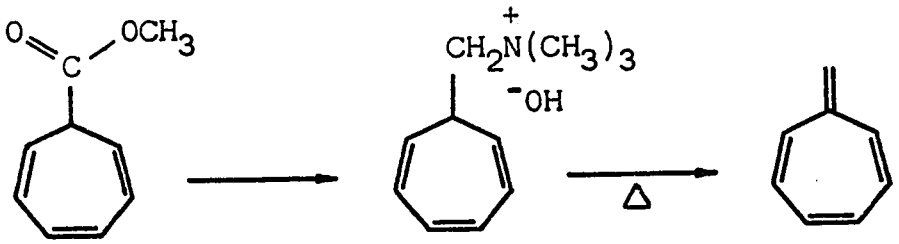


VIII

d. Heptafulvene

Heptafulvene might be expected to have a stability of the same order as fulvene since they have the same delocalization energy per π electron and the strain energy in five and seven membered rings is considered to be about the same. In fact heptafulvene is substantially less stable than fulvene.

The parent hydrocarbon (IX) was first prepared by Doering (58) from 7-carbomethoxycycloheptatriene (X). Treatment of the ester with aqueous ammonia gave the amide which was reduced to 7-aminomethylcycloheptatriene by lithium aluminum hydride. Exhaustive methylation followed by treatment with silver oxide gave the quaternary hydroxide which was pyrolyzed to yield heptafulvene.



X IX

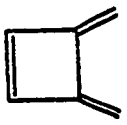
Attempts to isolate pure heptafulvene from a propane solution by removing solvent at -60°C were unsuccessful. A dilute solution (0.1%) has a half life of four days if the solution contains trimethylamine. A washed hexane solution (0.3%) decomposes in 30-40 min. at -60°C.

Heptafulvene is typically olefinic in character readily adding bromine and undergoing 1,3 addition with dimethylacetylene to give, after oxidation, a disubstituted azulene.

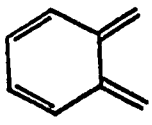
The dipole moment of 8,8-dicyanoheptafulvene is 7.49D (59) with the ring positive. From the value for the dicyano derivative, heptafulvene was estimated to have a dipole moment of 3.07D which compares favourably with the value of 2.35D obtained by MO calculations (60). This dipole moment is the highest observed, so far, for any hydrocarbon.

F. Di-exomethylene Compounds

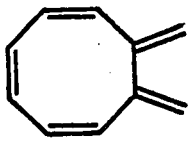
Discussion will be limited to those compounds having the exomethylene groups on adjacent carbons. The first members of this series are 1,2-dimethylenecyclobutene (XI), 1,2-dimethylenecyclohexadiene (XII), and 1,2-dimethylenecyclooctatriene (XIII).



XI



XII



XIII

These are alternant hydrocarbons so there will be no displacement of charge from one π electron per carbon and consequently these molecules will display no dipole moment. Unfortunately these π systems lack sufficient

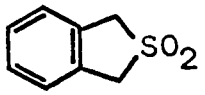
symmetry to permit the application of Craig's rules. The delocalization energies of XI and XII are 1.21β and 1.95β respectively giving a delocalization energy per π electron of 0.20β for XI and 0.24β for XII. The free valence of the exomethylene groups is 0.96 for XII which is very close to the value for monoexomethylene compounds. The calculated free valence for XI is lower at 0.86 (61).

Thus molecules in this series would be expected to be highly reactive and rather unstable. 1,2-Dimethylenecyclobutene should be more stable than 1,2-dimethylenecyclohexadiene. 1,2-Dimethylenecyclobutene (62) has been prepared from 1,2-dibromo-3,4-dicarboxycyclobutane. Treatment of 1,2-dibromo-3,4-dicarboxycyclobutane with phosphorus pentachloride followed by dimethylamine gave a diamide which on reduction with lithium aluminum hydride gave a mixture of two amines 1,2-N,N-dimethylaminomethylcyclobutene and 1,2-dibromo-3,4-N,N-dimethylaminomethylcyclobutane. The latter amine was converted to the former in good yield by reaction with zinc in methanol. Quaternization of the two amino groups with methyl iodide followed by treatment with silver oxide gave a diquaternary hydroxide which could be pyrolyzed to 1,2-dimethylenecyclobutene (XI) in about 1% overall yield. 3,4-Diphenyl-1,2-dimethylenecyclobutene was similarly prepared by the pyrolysis of the corresponding bis-quaternary hydroxide (63). 3,4-Dimethyl-1,2-dimethylenecyclobutene was synthesized independently by two groups of workers. In both cases the product was obtained by dehydro-

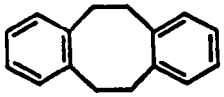
halogenation of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene. Criegee and co-workers used quinoline (64) and Griffin and Peterson used potassium t-butoxide in t-butyl alcohol (65) to perform the dehydrochlorination.

1,2-Dimethylenecyclohexadiene has not been isolated and studied in the pure state but excellent evidence for its formation has been obtained.

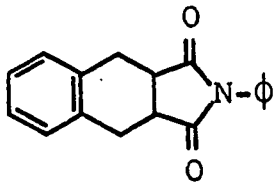
Pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide (XIV) (66) at 280-300°C gave 1,2,5,6-dibenzocyclooctadiene (XV), a dimer of 1,2-dimethylenecyclohexadiene. If the pyrolysis is done in the presence of N-phenylmaleimide then a Diels-Alder adduct (XVI) can be obtained.



XIV

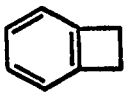


XV

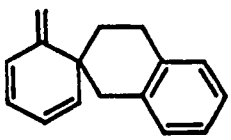


XVI

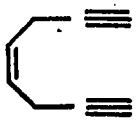
Pyrolysis in the gas phase above 460°C gave benzcyclobutene (XVII) the valence bond isomer of 1,2-dimethylenecyclohexadiene.



XVII



XVIII



XIX

Apparently the high strain associated with the cyclobutene ring is compensated for by the formation of the benzene ring. This isomerization to benzcyclobutene demonstrates the extreme reluctance of the molecule to retain the dimethylene structure.

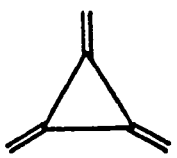
At low temperature a different dimer, spiro-di-o-xylylene (XVIII) is obtained (67). More recently XVIII was obtained in 25% yield by the treatment of cis-4-octene-1,7-diyne (XIX) with potassium t-butoxide in t-butanol at 65°C (68). This compound polymerizes readily at room temperature to give a poly-o-xylylene.

Since the third member of this series (XIII) is a subject of this research, further discussion of these compounds will be reserved for a later part of the thesis.

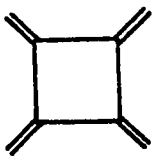
G. Fully Cross Conjugated Systems

a. General

Molecular orbital calculations predict a delocalization energy of 1.30β or 0.22β per π electron for trimethylenecyclopropane (XX) the first member of the series and 1.66β or 0.21β per π electron for tetramethylenecyclobutane (XXI).



XX



XXI

The free valence for the methylene groups is similar being 0.90 for XX and 0.88 for XXI. Since these molecules would have very high strain associated with the C-C-C angle deformation and they have high values for the free valence of the methylene groups they would be expected to be unstable and reactive.

b. Trimethylenecyclopropane

Several interesting approaches to the synthesis of trimethylenecyclopropane have been reported. Waitkus, Peterson and Griffin obtained the compound by the Hofmann pyrolysis of tris-N,N,N-trimethylaminomethylcyclopropane hydroxide and by dehydrohalogenation of 1,2,3-trisiodomethylcyclopropane (69). Dorko obtained trimethylenecyclopropane by dehydrohalogenation of 2,3-dibromomethylmethylenecyclopropane using potassium hydroxide at 150°C (70). Blomquist was actually the first to prepare trimethylenecyclopropane but he was unable to fully characterize it (see reference 69).

The n.m.r. spectrum exhibits a single absorption at 4.86 τ (in carbon disulfide) which is in the olefinic region and indicates no delocalization. The absorption slowly diminishes and disappears after 45 minutes if the sample is not kept cool and free of oxygen (69). Trimethylenecyclopropane is stable for several days at -78°C in the absence of oxygen but warming to room temperature results in polymerization to a viscous oil which slowly converts to a yellow solid. A yellow polymer also precipitates from a carbon tetrachloride solution kept at 0°C (70).

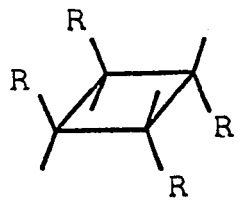
We thus see a range of properties for the three conjugated isomers benzene, fulvene, and trimethylene-cyclopropane. Benzene is very stable, undergoes substitution reactions, and has a high resonance energy, all properties typical of aromatic character. Fulvene, the intermediate member of the series, is only moderately stable, undergoes mainly olefinic type reactions but does undergo so substitution reactions and has a moderate resonance energy. Trimethylenecyclopropane because of very high strain energy is very unstable and behaves in general as a very reactive olefin.

c. Tetramethylenecyclobutane

Despite high delocalization energy calculated for tetramethylenecyclobutane, the high strain energy expected, coupled with a free valence of 0.88 obtained from MO theory suggest an unstable species capable at best of only precarious existence. This is found to be the case.

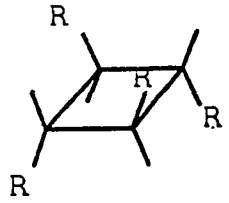
Tetramethylenecyclobutane was prepared by Griffin and Peterson by three routes (65). Ultraviolet irradiation of fumaronitrile in the crystalline state gave a tetracyanocyclobutane (XXII) of configuration cis, trans, cis. This was readily converted to cis, trans, cis-1,2,3,4-tetra-(N,N-dimethylaminomethyl)-cyclobutane tetra-oxide (XXIII) which gave tetramethylenecyclobutane in 1-2% yield on pyrolysis at 250°C in a nitrogen atmosphere at

reduced pressure. Yields of 50% were subsequently obtained by treatment of trans,trans,trans-1,2,3,4-tetrabromomethylcyclobutane (XXIV) with sodium ethoxide in ethanol.



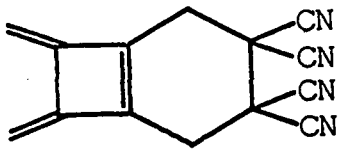
R=CN XXII

R=$CH_2\overset{\downarrow}{N}(CH_3)_2$ XXIII
O



XXIV

R=CH_2Br



XXV

Tetramethylenecyclobutane is stable in dilute solution at -78°C, but dimerizes readily on warming to room temperature. It is characterized by extreme sensitivity to oxygen, yielding, on even brief exposure to air, an insoluble polymer containing up to 40% oxygen. Treatment with tetracyanoethylene at 25°C gave the Diels-Alder adduct 3,3,4,4-tetracyano-7,8-dimethylenebicyclo[4.2.0] octa-1(6)-ene (XXV).

The n.m.r. spectrum of tetramethylenecyclobutane has a single peak at 4.81τ which is in the olefinic region but since 1,2-dimethylene-3,4-dimethyl-3-cyclobutene has its exomethylene absorption at 5.45τ the shift of 0.64 p.p.m. might be attributed to some delocalization of the π electrons. Despite the possibility of slight electron delocalization, however, it appears that it

behaves as a very reactive polyolefin as expected from the high value of the free valence of the exocyclic methylene groups.

Experimental

A. Analytical Instruments

1) Melting points were determined on a Thomas-Hoover Capillary Melting Point Apparatus model 6406-K manufactured by A. H. Thomas Co., Philadelphia.
2) Infrared spectra were measured as films or nujol mulls on a Beckman IR-8 Infrared Spectrophotometer manufactured by Beckman, Fullerton, California.
3) Ultraviolet spectra were obtained on a Model 202 Ultraviolet-Visible Spectrophotometer supplied by Perkin-Elmer, Norwalk, Conn.
4) Nuclear magnetic resonance spectra were obtained as 20% solutions in a solvent as noted. The instrument, a Varian V-4302 high resolution spectrometer operating at 60 Mc/s, was modified to HA-60/DA-60 specifications. The manufacturer was Varian Associates, Palo Alto, California.
5) Refractive indices were measured on an Abbé refractometer manufactured by Carl-Zeiss, Germany.
6) Mass spectra were determined on a model RMV-6D Mass Spectrometer manufactured by Hitachi, Tokyo, Japan.
7) Analyses were obtained from two sources:
   a) Mr. Hector Seguin, National Research Council,

Ottawa, Canada. b) Midwest Microlab Inc., Indianapolis, Indiana.

8) Vapour Phase Chromatography was performed using a variety of columns as noted. Two instruments were used a) Vapour Fractometer model 154, Perkin-Elmer Corporation, Norwalk, Conn. b) Aerograph-Autoprep model A-700, manufactured by Wilkins Instrument and Research Inc., Walnut Creek, Calif.

B. Preparative Instruments

1) The photolyses were performed on a Rayonet Photochemical reactor supplied by the Southern N.E. Ultraviolet Co., Middleton, Connecticut.

2) For the high pressure reaction a Magne-Dash, floor model autoclave manufactured by Autoclave Engineers, Erie, Pennsylvania, was used.

C. Synthetic Procedures

2-Butynoic Acid

The method of preparation used was a modification of the synthesis of Kauer and Brown (71). Anhydrous tetrahydrofuran (200 ml.) and anhydrous ethyl ether (100 ml.) were placed in a glass liner of the correct size to fit a one liter autoclave. The glass liner was sealed with a rubber stopper which contained holes to accommodate a calcium chloride drying tube and a gas inlet tube which

extended to the bottom of the vessel. Methylacetylene (13.4 g., 0.335 moles) was condensed in the tetrahydrofuran-ethyl ether solution which was cooled to -80°C in a dry ice-acetone bath during the addition. The glass liner was then fitted with a magnetic stirrer, a dry ice condenser and a dropping funnel containing a hexane solution (210 ml.) of butyl lithium (21.4 g., 0.335 moles). The butyl lithium-hexane solution was added dropwise to the stirred solution of methylacetylene in tetrahydrofuran-ethyl ether over a period of 45 minutes. On completion of the addition the glass liner was placed in a one liter bomb; the bomb was sealed and the stirrer started. Carbon dioxide was introduced cautiously at such a rate that the reaction temperature did not rise above 55°C. Finally full cylinder pressure (850 p.s.i.) was used and the reaction stirred for six hours. The liner was taken from the autoclave and the combined solvents were removed on a flash evaporator. Water (200 ml.) was added to dissolve the lithium 2-butynoate, the solution was filtered to remove remaining solids and the filtrate was extracted with two portions of ethyl ether (100 ml. each) which were discarded. The filtrate was acidified with 5N sulphuric acid (100 ml.) and continuously extracted with ethyl ether (500 ml.) for 24 hours. The ether extracts were dried over magnesium sulfate and the ether was removed on a flash evaporator to give a syrup, which was dried in a vacuum desiccator over sulfuric acid. It was then dissolved in

benzene, treated with activated charcoal, and finally recrystallized from benzene. The yield was 13.5 g. (48%), m.p. 75-77°C. Literature m.p. 77-78°C.

Methyl 2-butynoate

A solution of diazomethane in ethyl ether (72) was slowly added to a shaken solution of 2-butynoic acid (11.0 g., 0.131 moles) in ethyl ether (150 ml.) until diazomethane was in excess (this was determined by placing a rod, dipped in acetic acid, into the solution; an excess of diazomethane was indicated by bubbles formed around the rod). The ether solution was dried over magnesium sulfate, filtered, and the ether removed by distillation. The product was purified by distillation at reduced pressure through a Podbielniak column (0.5 x 20 cm.). The yield was 9.11 g. (71%), b.p. 44°C at 15 m.m. pressure. An analytical sample was purified by vapour phase chromatography giving n_D^{25} = 1.4348. (See Table I).

Calculated for $C_5H_6O_2$: C, 61.21 H, 6.17

Found : C, 61.22 H, 6.08

2-Carbomethoxy-1-methylcyclooctatetraene

a. Methyl 2-butynoate (0.98 g., 0.010 moles) was dissolved in dry benzene (130 ml.) and the solution was placed in a photochemical cell (2.2 x 37 cm.) made from Vycor #7910 glass. The cell was installed in a Rayonet photochemical reactor and a slow stream of oxygen-free nitrogen was bubbled through the solution during the

period of irradiation. On completion of irradiation (12 hours) the benzene and remaining methyl-2-butynoate were removed on the flash evaporator (bath temperature 50°C). The cell was cleaned with chlorosulfonic acid in preparation for the next photolysis. The crude products from 15 such photolyses were combined and distilled at reduced pressure through a short Vigreux column (1 x 5 cm.) to give the yellow, liquid product (13.78 g., 52%) b.p. 38°C at 0.010 m.m. pressure. A redistilled analytical sample gave $n_D^{25} = 1.5308$.

Calculated for $C_{11}H_{12}O_2$	:	C,74.97	H,6.86
Found	:	C,74.83	H,6.89

b. Methyl-2-butynoate (0.98 g., 0.010 moles) dissolved in dry benzene (130 ml.) was photolyzed as in procedure (a.) for 36 hours. The cell was cleaned at 12 hour intervals with chlorosulfonic acid. The yield of ester obtained was 1.04 g., (59%).

c. Methyl-2-butynoate (4.90 g., 0.050 moles) dissolved in dry benzene (130 ml.) was photolyzed as in procedure (b.) for 36 hours. The yield of ester obtained was 3.48 g., (39%).

d. 2-Carbomethoxy-1-methylcyclooctatetraene (2.16 g., 0.012 moles) dissolved in dry benzene (130 ml.) was photolyzed as in procedure (a.) for 12 hours. The photolyzed solution was analyzed for the presence of methyl-2-butynoate by infrared spectroscopy and vapour phase chromatography. The solution was placed in a 0.201 m.m. infrared cell and the spectrum examined for the characteristic C≡C stretching frequency at 2245 $c.m.^{-1}$.

The vapour phase chromatography was accomplished using a Carbowax 1500 (on teflon) column at 104°C, and a flow rate of 60 ml./min. The retention time of methyl-2--butynoate under those conditions was 4.4 minutes. The size of the sample injected was 0.20 ml. Solutions of known concentration of methyl-2-butynoate in benzene were prepared and analyzed by both methods. It was possible to detect methyl-2-butynoate in a solution of 9.0 mg. of the ester in 10 ml. of benzene by infrared spectroscopy and in a solution of 15.0 mg. of the ester in 10 ml. of benzene by vapour phase chromatography.

Both analytical methods showed that no methyl-2--butynoate was formed in the photolysis of 2-carbomethoxy-1--methylcyclooctatetraene in benzene.

2-Carbomethoxy-1-methylcyclooctane

2-Carbomethoxy-1-methylcyclooctatetraene (0.469 g., 2.66 millimoles), dissolved in glacial acetic acid (15 ml.), was hydrogenated in the presence of prereduced platinum oxide (0.25 g.). The hydrogenation was complete after 6 hours when 99.4% of four molar equivalents of hydrogen had been absorbed. The solution was filtered and chloroform (40 ml.) was added. The acetic acid was removed by extraction with water (3 x 10 ml.), 10% sodium bicarbonate (3 x 10 ml.), and again water (3 x 10 ml.). The chloroform solution was dried over anhydrous magnesium sulfate, filtered, and the chloroform removed on the flash

evaporator. Purification by evaporative distillation at 40°C and 0.025 m.m. pressure gave the product (0.360 g., 73%), b.p. 251°C at 761 m.m., and n_D^{25} = 1.4641.

Calculated for $C_{11}H_{20}O_2$: C,71.69 H,10.94

Found : C,71.97 H,10.82

2-Hydroxymethyl-1-methylcyclooctatetraene

Method A.

A solution of 2-carbomethoxy-1-methylcyclo-octatetraene (8.94 g., 0.0508 moles) in ethyl ether (500 ml.) was placed in a one liter three-necked flask equipped with a calcium chloride drying tube, a dropping funnel, and a paddle stirrer with a ground glass seal. A solution of lithium aluminum hydride (1.93 g., 0.0508 moles) in anhydrous ethyl ether (150 ml.) was added dropwise over a period of one hour to the cooled (0°C), stirred solution. On completion of addition the reaction was stirred for one hour at 0°C. Water (10 ml.) was added dropwise, the ether solution was decanted and the remaining solids were extracted in a Soxhlet extractor for 6 hours. The ether solutions were combined, dried over magnesium sulfate, filtered, and the ether was removed on the flash evaporator. Evaporative distillation at 55°C, 0.020 m.m., gave a yellow viscous liquid, (4.01 g., 53%) b.p. 252°C at 756 m.m., and n_D^{25} = 1.5503.

Calculated for $C_{10}H_{12}O$: C,81.04 H,8.16

Found : C,80.20 H,8.08

Method B.

To a solution of lithium aluminum hydride (79 millimoles) in ether (150 ml.) was added anhydrous aluminum chloride (3.52 g., 26.3 millimoles). After stirring for one hour the suspension was cooled to -75°C and a solution of 2-carbomethoxy-1-methylcyclooctatetraene (5.56 g., 31.6 millimoles) in ether (150 ml.) was added over a period of 15 minutes. The reaction was stirred for two hours at room temperature and then a saturated solution of aqueous ammonium chloride (150 ml.) was added over a period of 15 minutes. The ether layer was separated, combined with ether extractions of the aqueous layer (2 x 100 ml.) and dried over anhydrous magnesium sulfate. The ether was removed on the flash evaporator and the crude alcohol purified by evaporative distillation at 55°C, 0.020 m.m. to give the product (3.36 g., 72%).

Vapour phase chromatography was successfully used for analytical purposes (see Table I). Purification on a preparative scale was unsuccessful, however, because partial decomposition occurred at temperatures needed to give a reasonable retention time even when very short columns were used.

Thin layer chromatography using silica gel and a variety of solvents (benzene, chloroform, carbon tetrachloride) did not remove the major impurity (see Table I).

Purification through the silver nitrate complex was attempted as follows. A solution of the alcohol

(0.148 g., 1.00 millimoles) in hexane (30 ml.) was shaken with 50% aqueous silver nitrate solution (30 ml.). The hexane was discarded. The aqueous solution was extracted with ether (2 x 50 ml.), and then slowly added to concentrated aqueous ammonia (25 ml.) containing crushed ice. The alcohol was extracted with hexane (2 x 25 ml.); the hexane solution was dried over anhydrous magnesium sulfate, filtered, and the hexane removed on the flash evaporator to give the alcohol (0.118 g., 80%). V.P.C. showed that the major impurity had not been removed (see Table I).

2-Bromomethyl-1-methylcyclooctatetraene

2-Hydroxymethyl-1-methylcyclooctatetraene (1.74 g., 0.0118 moles), pyridine (0.35 g.) and hexane (13.0 ml.) were placed in a three-necked flask (50 ml. capacity) equipped with a magnetic stirrer, a nitrogen inlet, a water cooled condenser and a dropping funnel. Phosphorus tribromide (1.23 g., 0.0045 moles) in hexane (20.0 ml.) was added dropwise to the cooled (0°C), stirred solution which was kept under a slow stream of nitrogen. On completion of addition the reaction mixture was stirred for 4 hours at room temperature and then filtered through glass wool. The filtrate was extracted with two portions of water (15 ml.), dried for one-half hour over anhydrous magnesium sulfate, filtered, and the solvent removed on the flash evaporator. Spectral data only were obtained for this compound.

1-Methyl-2-N,N,N-trimethylammoniomethylcyclooctatetraene bromide

2-Bromomethyl-1-methylcyclooctatetraene was prepared as outlined above using 2-hydroxymethyl-1-methylcyclooctatetraene (4.01 g., 0.0271 moles), pyridine (0.84 g.) and hexane (60 ml.) to which was added phosphorus tribromide (2.84 g., 0.0104 moles) in hexane (60 ml.) over a period of one half hour. After completion of the 4 hour reaction period the mixture was filtered through glass wool into a one necked flask; it was cooled to 0°C and trimethylamine (16 g., 0.27 moles) in methanol (120 ml.), also at 0°C, was added. The air in the flask was displaced with nitrogen, the flask was sealed and kept refrigerated (2°C) for three days. Pale yellow plate-like crystals, which crystallized from the reaction, were filtered off to give the product (3.09 g., m.p. 219-221°C). Recrystallization from ethanol gave greenish-yellow, needle-like crystals (2.80 g., 38%) m.p. 225-226°C.

Calculated for $C_{13}H_{20}BrN$:	C,57.78	H,7.46	N,5.18
Found :	C,57.64	H,7.27	N,5.38

1,2-Dimethylenecyclooctatriene

1-Methyl-2-N,N,N-trimethylammoniomethylcyclooctatetraene bromide (0.20 g., 0.74 millimoles) was stirred with a slurry of silver oxide (0.50 g.) in water (15 ml.) for one hour. The solids were filtered off and the filtrate concentrated to 2 ml. This quaternary hydroxide solution

was pyrolyzed at 25 m.m. pressure under a stream of argon using a free flame (micro burner) and the product was collected in hexane at -80°C. Purification was by vapour phase chromatography using a column, 30 cm. in length, of 20% Silicon Gum Rubber SE 30, on 30/60 mesh Chromosorb, a flow rate of 100 ml/min and a column temperature of 50°C. For a sample size of 0.20 ml. (about 25% 1,2-dimethylene--cyclo$\ddot{o}$ctatriene in hexane) the retention time of the product collected was 9-16 min.; collection was in an oxygen free atmosphere at -80°C. The yield obtained was 35 mg. (36%).

Calculated for $C_{10}H_{10}$	:	C,92.26	H,7.74
Found	:	C,91.31	H,8.04

The extreme sensitivity to oxygen of 1,2-dimethylenecyclo$\ddot{o}$ctatriene, particularly when neat, necessitated careful manipulation when obtaining physical data.

The infrared plates were prepared in a dry box swept with Argon. The weight of the sample used to get the ultraviolet spectrum was obtained as follows. The product was weighed in the V.P.C. tube in which it had been collected, it was taken up in hexane which was diluted to a known volume, and the V.P.C. tube. which contained a white polymer, was dried and weighed.

The analytical sample remained in the V.P.C. collection tube at -80°C until just prior to weighing.

Sensitivity of 1,2-Dimethylenecyclo^{11}octatriene to Oxygen

1,2-Dimethylenecyclo^{11}octatriene placed on infrared salt plates was exposed to air for intervals of 15 sec. and 5 minutes. An infrared spectrum was taken after each exposure. The colourless, mobile 1,2-dimethylene-cyclo^{11}octatriene on exposure to air changes to a heavy oil after a few minutes, and then rapidly converts (less than 10 minutes) to an insoluble white solid polymer.

Thermal Stability of 1,2-Dimethylenecyclo^{11}octatriene

A 3-neck flask (250 ml.) was equipped with a gas inlet tube, a rubber septum and a water cooled condenser sealed at the top with a mercury bubbler. A hexane solution of 1,2-dimethylenecyclo^{11}octatriene of the proper concentration to give an on-scale reading on the ultra-violet spectrometer at 272 mμ was placed in the flask. The system was flushed with argon until the hexane (b.p. 68°C) began to reflux. After steady reflux was attained the argon flow was stopped. Aliquots were removed at suitable intervals for a period of eight hours and the absorbances of the solutions at 272 mμ were measured. The initial absorbance, A_o = 0.96, represented a concentration of 0.011 millimoles per liter (see Table III). The absorbance after 8 hours reflux remained at 0.96.

Photolysis of 1,2-Dimethylenecyclo^{11}octatriene

A solution of 1,2-dimethylenecyclo^{11}octatriene (40 mg) in carbon tetrachloride (1.0 ml.) was placed in a

quartz ultraviolet cell (0.5 x 15 cm.) and photolysed for one half hour. The cell wall was coated with a yellow insoluble polymer.

The n.m.r. spectrum of the carbon tetrachloride solution showed only unchanged starting material.

The Reaction of 1,2-Dimethylenecyclooctatriene with Tetracyanoethylene

A. 1,2-Dimethylenecyclooctatriene prepared from 0.203 g. (0.752 millimoles) of 1-methyl-2-N,N,N-trimethylaminomethylcyclooctatetraene bromide and collected in hexane (1 ml.) at -80°C was placed in a flask equipped with a gas inlet tube and a reflux condenser. A solution of tetracyanoethylene (0.096 g., 0.75 millimoles) in benzene (4 ml.) was added and the reaction was refluxed for 15 minutes during which the system was swept with argon. A dark coloured precipitate formed immediately on addition of the tetracyanoethylene. During the reflux period the reaction mixture lightened in colour until at the end of 15 minutes the solution was a clear, pale yellow and some dark coloured material adhered to the sides of the vessel. The clear solution was decanted and the benzene removed on the flash evaporator to give the crude product (0.143 g., 74%). The n.m.r. spectrum of the crude product was obtained. Attempted purification by thin layer chromatography using several coatings (silica gel, neutral alumina and magnesium silicate) and a

variety of solvents (ethanol, chloroform, benzene) led to decomposition.

B. The above reaction was repeated using 0.150 g. (0.56 millimoles) of the quaternary bromide and 0.036 g. (0.28 millimoles) of tetracyanoethylene. The n.m.r. of the crude sample was taken.

Purification by sublimation for 24 hours at room temperature and 0.010 m.m. pressure, onto a surface cooled to 3°C gave 2 mg. of a white crystalline product m.p. 145-146°C.

C. An attempt was made to monitor the reaction of 1,2-dimethylenecyclooctatriene with tetracyanoethylene by letting the reaction take place in an n.m.r. tube. This would have permitted n.m.r. spectra to be taken at suitable intervals. This was not possible, however, because the reaction was extremely fast even at 0°C.

Physical Data

Table I: Vapour Phase Chromatography

Compound	Column				Flow Rate (ml./min)	Retention Time (minutes)
	Liquid Phase	Solid Support	Length (m.)	Temperature (°C)		
methyl-2-butynoate	Apiezon (20%)	Chromosorb	1.1	86	60	8.4
2-carbomethoxy-1-methylcyclooctatetraene	Versamid (20%)	Chromosorb 30/60 mesh	3.0	150	100	32.9
"	Carbowax 1500	Teflon (powdered)	2.0	144	60	8.6
2-carbomethoxy-1-methylcyclooctane	Silicon Gum Rubber SE 30 (20%)	Chromosorb 30/60 mesh	3.0	150	100	34.7
"	Versamid (20%)	Chromosorb 30/60 mesh	3.0	150	100	29.2
"	Carbowax 1500	Teflon (powdered)	2.0	115	60	21.8
2-hydroxymethyl-1-methylcyclooctatetraene	Carbowax 1500	Teflon (powdered)	2.0	144	60	(1)29.6* (2)19.6
1,2-dimethylene-cyclooctatriene	Silicon Gum Rubber SE 30 (20%)	Chromosorb 30/60 mesh	0.3	50	100	9.5

*The ratio of the two peak areas 1. to 2. was 18.5 to 1.

Table II: Infrared Spectra

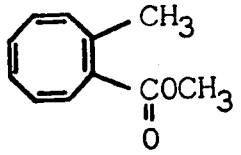
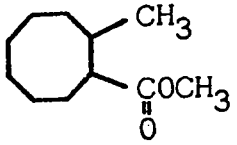
Compound	Function	Type of Vibration	Absorption cm^{-1}	Remarks	Spectrum Page Number
$CH_3-C\equiv C-\overset{\overset{O}{\|}}{C}-O-CH_3$	C-H	stretch	2960	The spectrum	57
	C≡C	"	2245	was taken	
	C=O	"	1710	neat as a	
	C-O-C	"	1265	thin film.	
	C-H (C=C-H)	stretch	2995	The spectrum	57
	C-H (CH_3)	asymmetric stretch	2970	was taken	
	C-H (CH_2)	" "	2940	neat as a	
	C=O		1712	thin film.	
	C=C		1650		
	C-O-C		1245		
	C-H (C=C-H)	bend, planar	1200		
	ring	distortion	812		
	ring	"	782		
	C-H (C=C-H)	bend	700		
	C-H (C=C-H)	"	630		
	C-H (CH_3)	asymmetric stretch	2960	The spectrum	57
	C-H (CH_2)	" "	2920	was taken	
	C-H (CH_3)	symmetric stretch	2880	neat, as a	
	C-H (CH_2)	" "	2860	thin film.	

Table II (continued): Infrared Spectra

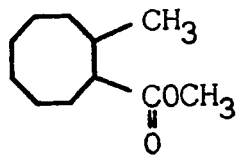
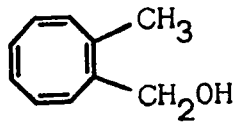
Compound	Function	Type of Vibration	Absorption cm^{-1}	Remarks	Spectrum Page Number
cont'd 	C=O	symmetric stretch	1730		
	CH_2	scissor	1458		
	CH_3	asymmetric bend	1465		
	CH_3	symmetric bend	1360		
	C-O-C	stretch	1170		
	O-H	stretch	3350	The spectrum	
	C-H (C=C-H)	stretch	3005	was taken	58
	C-H (CH_3)	asymmetric stretch	2988	neat as a	
	C-H (CH_2)	" "	2945	thin film.	
	C-H (CH_3)	symmetric stretch	2880		
	C-H (CH_2)	" "	2860		
	C=C	stretch	1645		
	C=C	"	1623		
	C-H (C=C-H)	bend, planar	1210		
	C-O-C	stretch	1008		
	ring	distortion	820		
	ring	"	795		
	C-H (C=C-H)	bend	710		
	C-H (C=C-H)	bend	640		

Table II (continued): Infrared Spectra

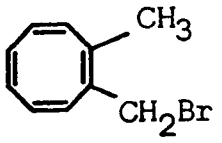
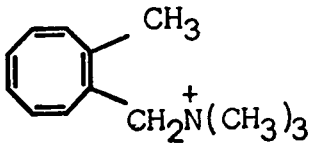
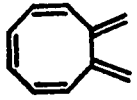
Compound	Function	Type of Vibration	Absorption cm^{-1}	Remarks	Spectrum Page Number
	C-H (C=C-H)	stretch	2998	The spectrum	
	C-H (CH_3)	asymmetric stretch	2965	was taken	
	C=C	stretch	1625	neat as a	58
	C-H (C=C-H)	bend, planar	1200	thin film.	
	C-H (C=C-H)	bend	705		
	C-H (C=C-H)	"	635		
	C=C	stretch	1625	The spectrum	
	ring	distortion	835	was taken as	
	ring	"	783	a Nujol mull.	58
	C-H (C=C-H)	bend	700		
	C-H (C=C-H)	bend	642		
	C-H ($C=CH_2$)	stretch	3075	The spectrum	
	C-H (C=C-H)	stretch	3000	was taken	
	C=C	stretch	1630	neat as a	59
	C=C	stretch	1585	thin film.	
	C=C	stretch	1560	Peaks at 735,	
	C-H ($C=CH_2$)	bend	880	660 and	
	ring	distortion	770	622 cm^{-1} were	
	C-H (C=C-H)	bend	710	not assigned.	
	C-H (C=C-H)	bend	640		

Table II (continued): Infrared Spectra

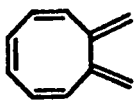
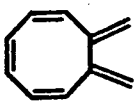
Compound	Function	Type of Vibration	Absorption cm^{-1}	Remarks	Spectrum Page Number
 + O_2	All functions shown before exposure plus	-	-	The salt plates were exposed to air for 15 sec.	
	C-H (aliphatic)	stretch	2960		
	C-H (")	"	2930		
	C-H (")	"	2860		
	C=O	stretch	1725		
	C-O-C	stretch	1260 1115		
	C-O-C	stretch	1065 1015		
 + O_2	C-H (aliphatic)	stretch	2960	The salt plates were exposed to air for 5 minutes.	59
	C-H (")	stretch	2925		
	C-H (")	"	2860		
	C=O	"	1720		
	C-O-C	"	1255 1115		
	C-O-C	"	1065 1030		
	CH (CHO)		785		

Table II (continued): Infrared Spectra

Compound	Function	Type of Vibration	Absorption cm^{-1}	Remarks	Spectrum Page Number
1,2-dimethylene-cyclooctatriene-tetracyanoethylene derivative	C=C-H	stretch	3010	The spectrum was run in $CHCl_3$ solution using compensated 0.1 m.m. cells. The product used was unpurified material from preparation A.	59
	C-H	stretch	2960		
	C≡N	stretch	2260		
	C≡N	stretch	2205		
	C=C	stretch	1630, 1580		
	$-CH_2-$	scissors	1475		
	C=C-H	bend	860		

Table III: Ultraviolet Spectra

Compound	Solvent	Absorption mμ	log ε	Spectrum Page Number
methyl 2-butynoate	Hexane	220	1.88	60
2-carbomethoxy-1-methyl-cyclooctatetraene	Hexane	224 292	3.94 2.64	60
2-hydroxymethyl-1-methyl-cyclooctatetraene	Hexane	223 269	3.56 2.60	61
1-methyl-2-N,N,N-trimethylammonio-methylcyclooctatetraene bromide	Ethanol	203 279	4.32 2.49	61
1,2-dimethylenecyclooctatriene	Hexane	228 272	4.23 3.96	62
1,2-dimethylenecyclooctatriene-tetracyanoethylene derivative (sublimed)	Ethanol	209	3.69	62

Table IV: Nuclear Magnetic Resonance Data

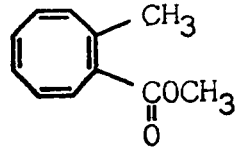
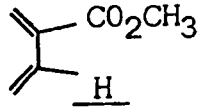
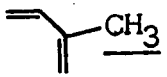
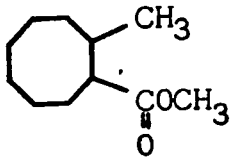
Compound	Function	Chemical Shift	Multiplicity	Splitting c.p.s.	Integrated area	Remarks Spectrum Page No.
$CH_3C\equiv C\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$	$\overset{O}{\overset{\|}{C}}\text{-}OCH_3$	6.34	S		3.1	Solvent: CCl_4
	$CH_3C\equiv C$	8.02	S		3.0	Page 63
		3.08	D	2.0	1.0	Solvent: CCl_4
	Other Ring Protons	4.23	M		5.3	
	$\overset{O}{\overset{\|}{C}}\text{-}OCH_3$	6.33	S		3.0	
		8.19	T	1	2.8	Page 63
	$\overset{O}{\overset{\|}{C}}\text{-}OCH_3$	6.44	S		3.0	Solvent: CCl_4
	Other Ring Protons	7.40 8.45	M S		1.8 12.3	Broad based singlet

Table IV (continued): Nuclear Magnetic Resonance Data

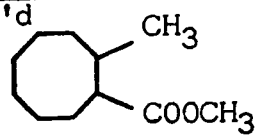
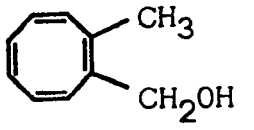
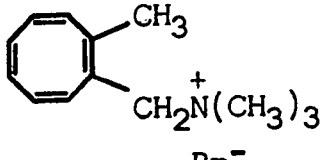
Compound	Function	Chemical Shift	Multiplicity	Splitting c.p.s.	Integrated area	Remarks / Spectrum Page No.
cont'd 		9.19	D	6	3.0	Page 64
	Ring Protons	4.33	S		5.6	Solvent: CCl_4
	$-\underline{CH_2}-OH$	6.04	S		2.0	On shaking with D_2O the absorption at 7.31 disappears
	$-CH_2-\underline{OH}$	7.31	S		1.1	
	$-CH_3$	8.24	S		3.0	Page 64
	Ring Protons	4.09	M		5.8	Solvent: D_2O
	H-O-H	5.40	S			
	$-CH_2-$	6.06	Q	13.5	2.0	
	$-\overset{+}{N}(CH_3)_3$	6.93	S		8.7	
	$-\underline{CH_3}$	8.17	S		3.0	Page 65

Table IV (continued): Nuclear Magnetic Resonance Data

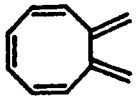
Compound	Function	Chemical Shift	Multiplicity	Splitting c.p.s.	Integrated area	Remarks Spectrum Page No.
	Ring Protons	3.70	M		2.1	Solvent: CS_2
		3.90	M			
		4.18	M			
		4.30	S			
		4.33	S		4.0	
		4.37	S			
		4.39				
	Inner Methylene Protons	5.02	M		2.0	
	Outer Methylene Protons	5.27	M		2.0	Page 65
1,2-Dimethylene-cyclooctatriene-tetracyanoethylene derivative	Ring Protons	4.09	M		4.1	Solvent: $CDCl_3$
		6.90	S		1.0	Preparation A.
		7.01	S		1.8	Page 66
1,2-Dimethylene-cyclooctatriene-tetracyanoethylene derivative	Ring Protons	4.10	M		11.3	Solvent: $CDCl_3$
	Inner Methylene Protons	4.89	M		1.0	Preparation B.
	Outer Methylene Protons	5.14	M		1.0	
		6.90	S		2.2	
		7.02	S		3.8	Page 66

Table V

Mass Spectral Data

2-Carbomethoxy-1-methylcyclooctatetraene

The mass spectrum was obtained at an ionization potential of 50 volts. The table contains all peaks with a % Σ_{39} (the contribution to the spectrum of each peak as a percentage of the total ionization between m/e 39 and the molecular ion) 1% and larger.

m/e	% Σ_{39}	m/e	% Σ_{39}	m/e	% Σ_{39}
17.6	6.4	117	17.5	78	2.4
161	1.3	116	8.8	77	2.0
148	1.0	115	12.6	65	2.7
145	2.2	105	1.9	63	2.0
144	1.7	102	1.9	59	1.0
133	1.9	91	6.1	51	2.5
118	2.5	89	1.9	39	3.9

Table V (continued)

Mass Spectral Data

2-Hydroxymethyl-1-methylcyclooctatetraene

The mass spectrum was obtained at an ionization potential of 10 volts. The table contains all peaks with a $\% \Sigma_{79}$ greater than 1%.

m/e	$\% \Sigma_{79}$	m/e	$\% \Sigma_{79}$	m/e	$\% \Sigma_{79}$
148	37.8	131	3.8	118	2.7
147	1.9	130	17.1	117	2.5
146	1.6	129	1.4	106	1.4
134	1.9	120	1.6	105	1.4
133	13.1	119	3.3	91	1.6

Mass Spectral Data

1,2-Dimethylenecyclooctatriene

The mass spectrum was obtained at an ionization potential of 20 volts. The table contains all peaks with a $\% \Sigma_{52}$ greater than 0.5%.

m/e	$\% \Sigma_{52}$	m/e	$\% \Sigma_{52}$	m/e	$\% \Sigma_{52}$
130	28.65	117	0.53	103	0.98
129	23.53	116	5.55	91	1.53
128	8.56	115	13.68	78	4.50
127	2.56	105	0.53	52	7.56

Table V (continued)

Mass Spectral Data

1,2-Dimethylenecyclooctatriene-Tetracyanoethylene Derivative

The mass spectrum was obtained at an ionization potential of 50 volts. The table contains all peaks with a $\% \mathcal{E}_{50}$ greater than 0.36%.

m/e	$\% \mathcal{E}_{50}$	m/e	$\% \mathcal{E}_{50}$	m/e	$\% \mathcal{E}_{50}$
258	0.36	114	0.51	76	2.57
155	0.40	113	0.40	75	1.77
153	0.54	104	1.48	74	0.69
152	0.40	103	1.12	66	0.47
141	1.05	102	2.03	65	2.97
140	0.51	101	0.72	64	2.64
131	1.05	100	0.54	63	3.98
130	9.48	91	1.27	62	0.80
129	8.90	90	0.54	57	0.47
128	2.28	89	2.32	55	0.43
127	1.16	88	0.80	53	0.80
126	0.58	87	0.51	52	4.20
125	0.40	79	0.54	51	5.65
116	2.14	78	3.51	50	2.24
115	12.78	77	3.66		

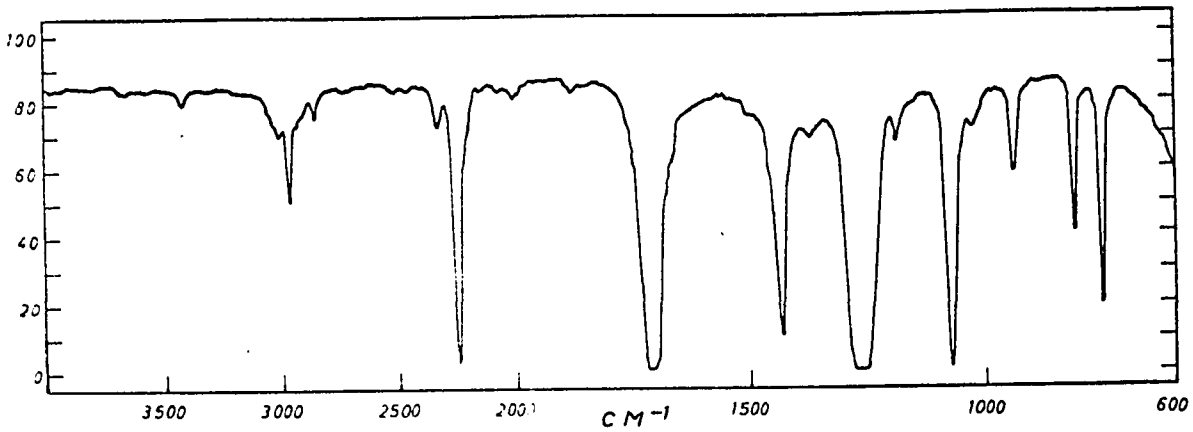


Fig. 1 The infrared spectrum of methyl 2-butynoate.

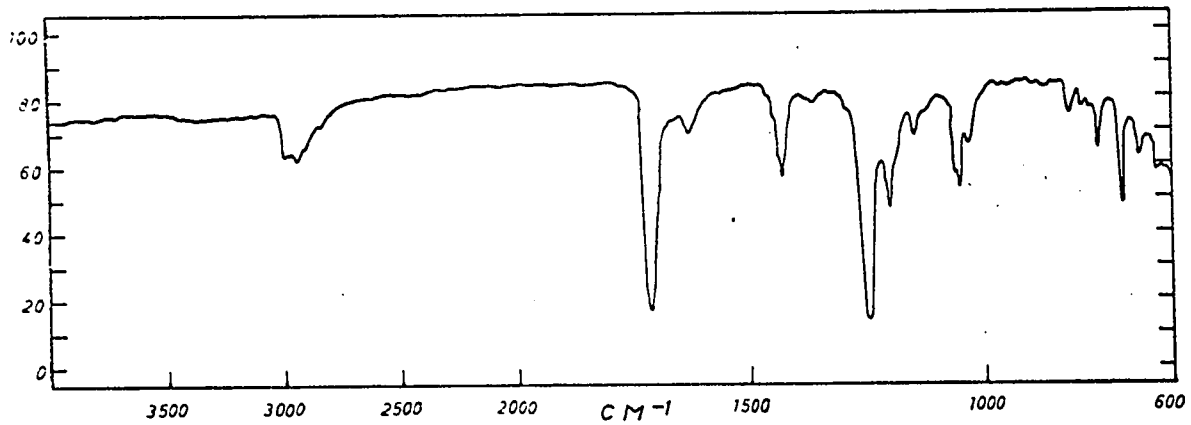


Fig. 2 The infrared spectrum of 2-carbomethoxy-1-methylcycloöctatetraene.

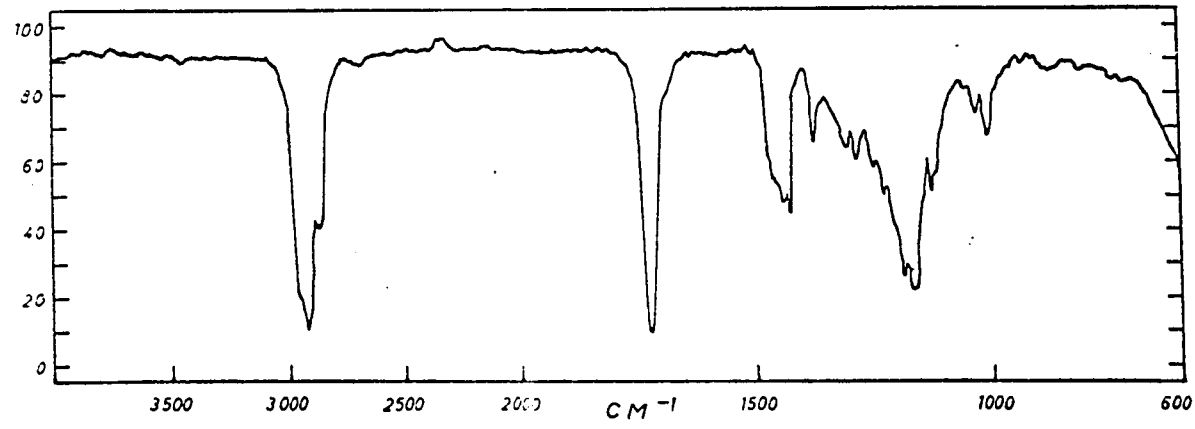


Fig. 3 The infrared spectrum of 2-carbomethoxy-1-methylcycloöctane.

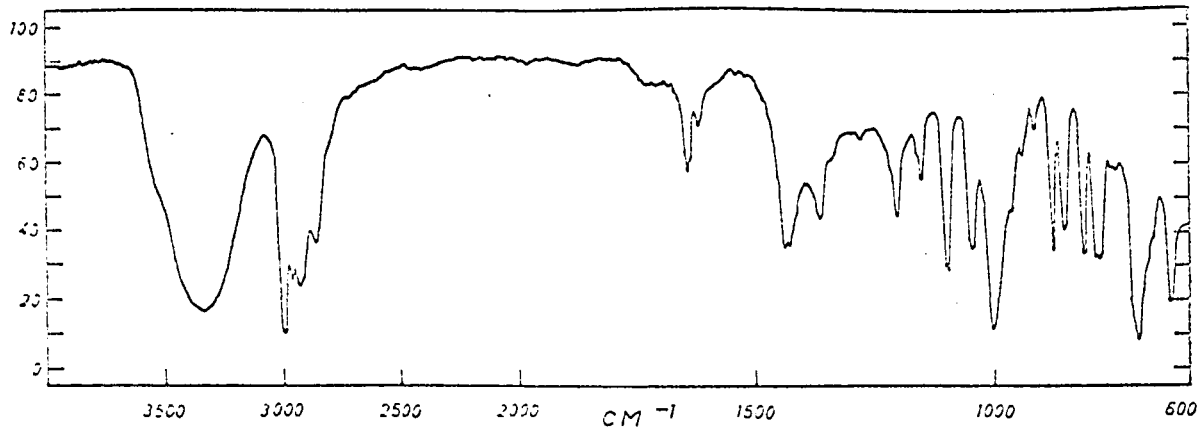


Fig. 4 The infrared spectrum of 2-hydroxymethyl-1-methylcyclooctatetraene.

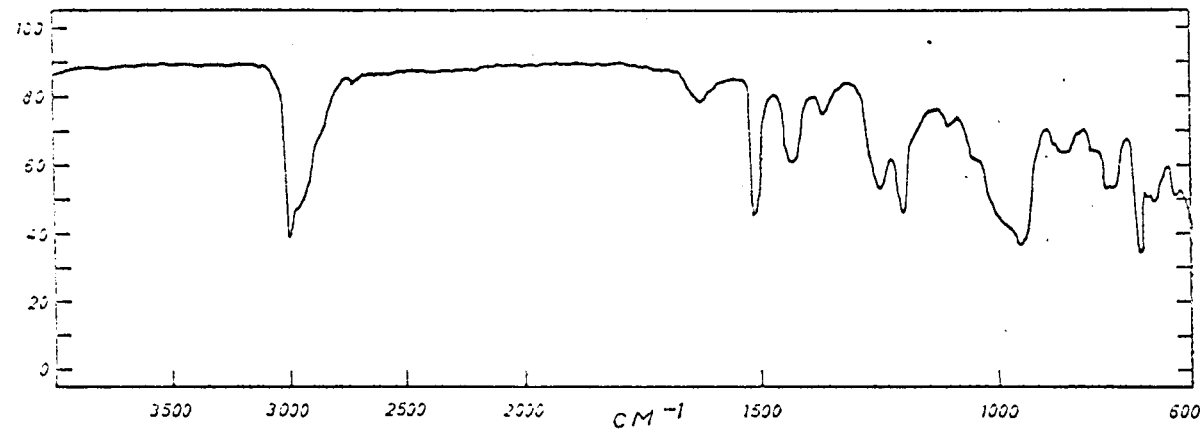


Fig. 5 The infrared spectrum of 2-bromomethyl-1-methylcyclooctatetraene.

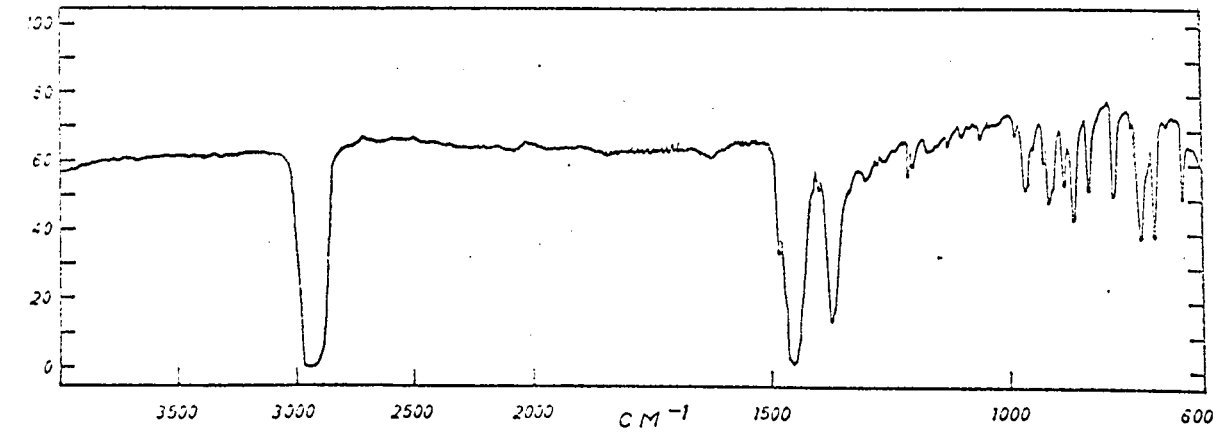


Fig. 6 The infrared spectrum of 1-methyl-2-N,N,N-trimethylammoniomethylcyclooctatetraene bromide.

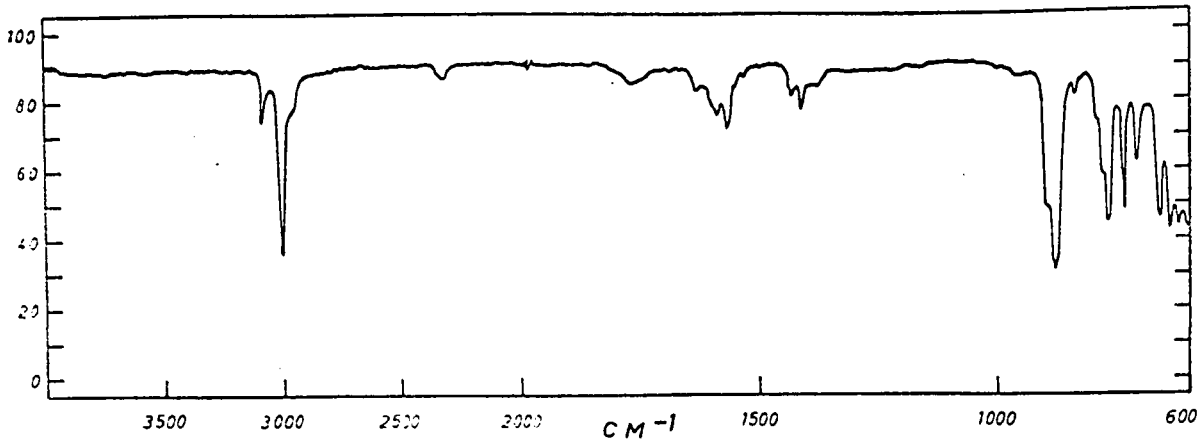


Fig. 7 The infrared spectrum of 1,2-dimethylene-cyclooctatriene.

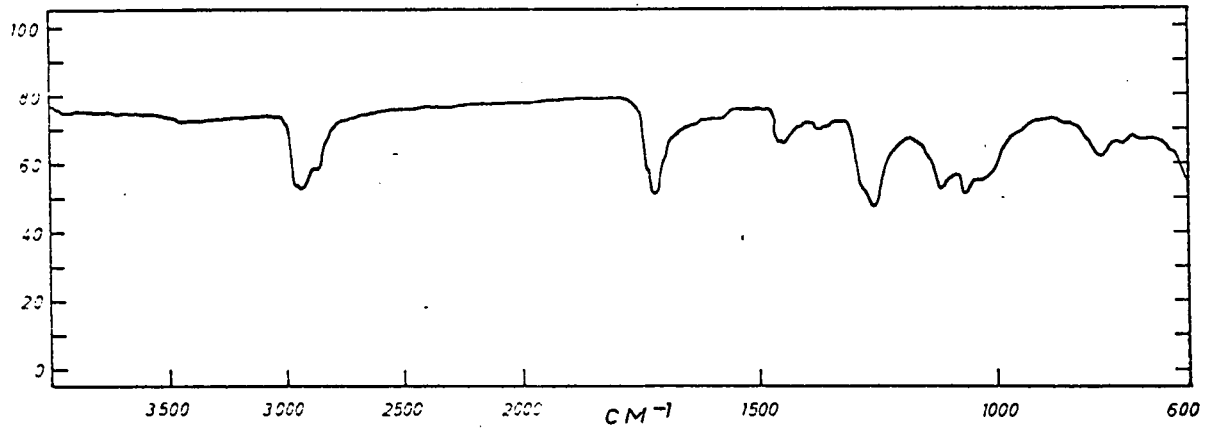


Fig. 8 The infrared spectrum of 1,2-dimethylene-cyclooctatriene after exposure to air on the infrared salt plates for 15 seconds.

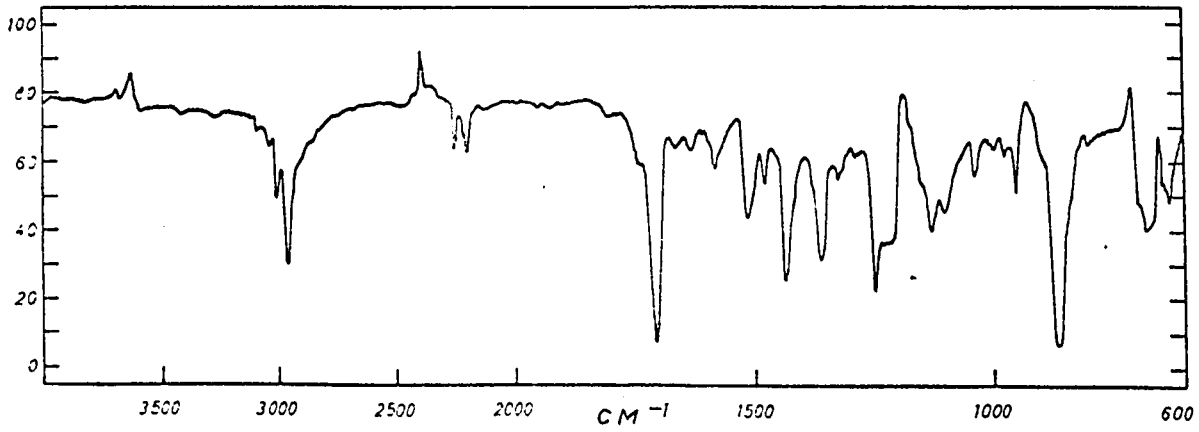


Fig. 9 The infrared spectrum of 1,2-dimethylene-cyclooctatriene after exposure to air on the infrared salt plates for 5 minutes.

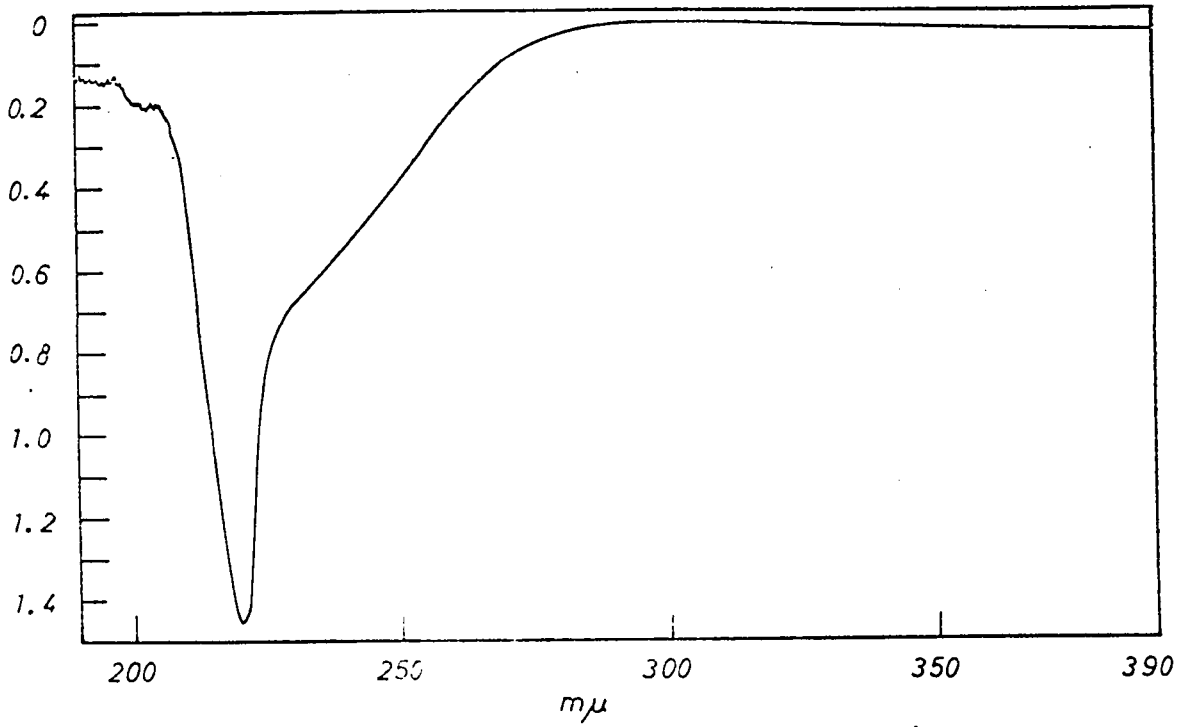


Fig. 10 The ultraviolet spectrum of methyl 2-butynoate.

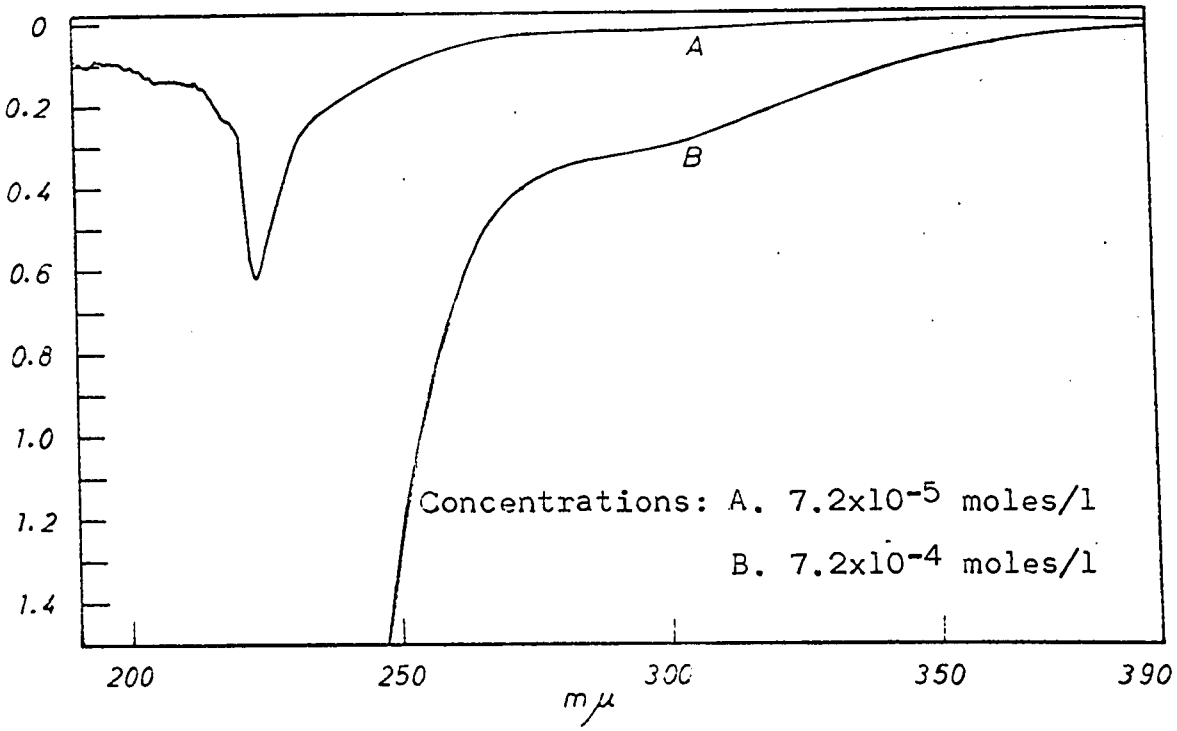


Fig. 11 The ultraviolet spectrum of 2-carbomethoxy-1-methylcycloöctatetraene.

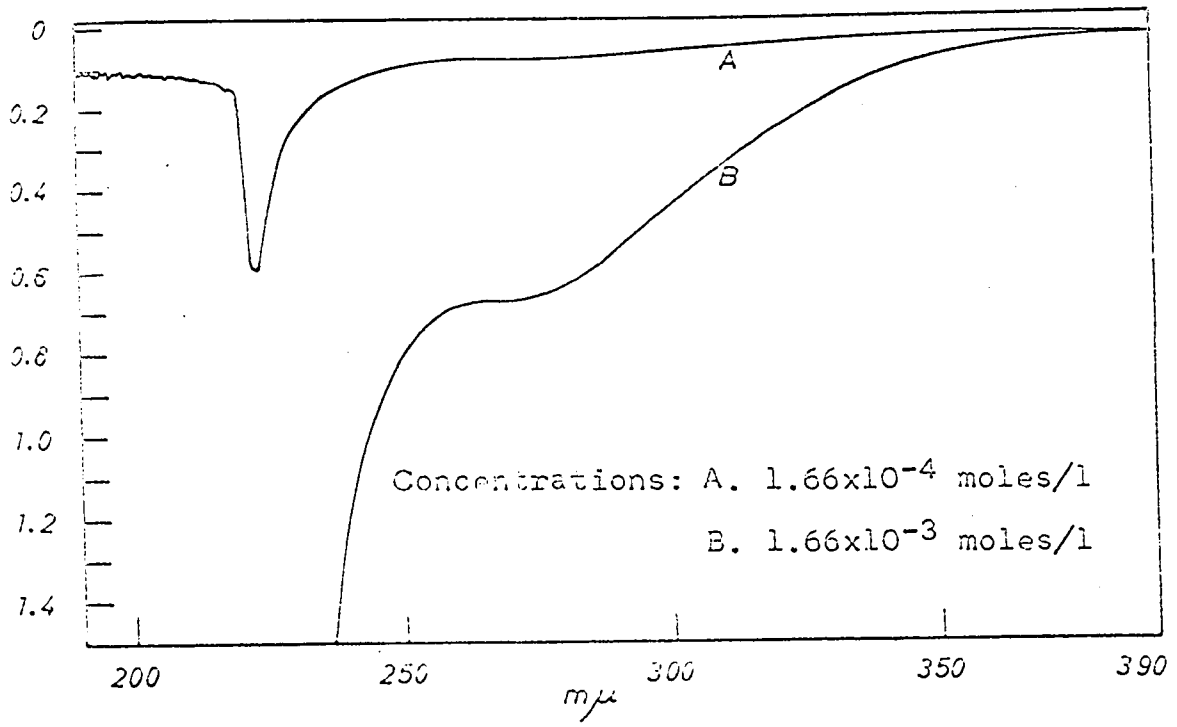


Fig. 12 The ultraviolet spectrum of 2-hydroxymethyl-1-methylcyclo̤octatetraene.

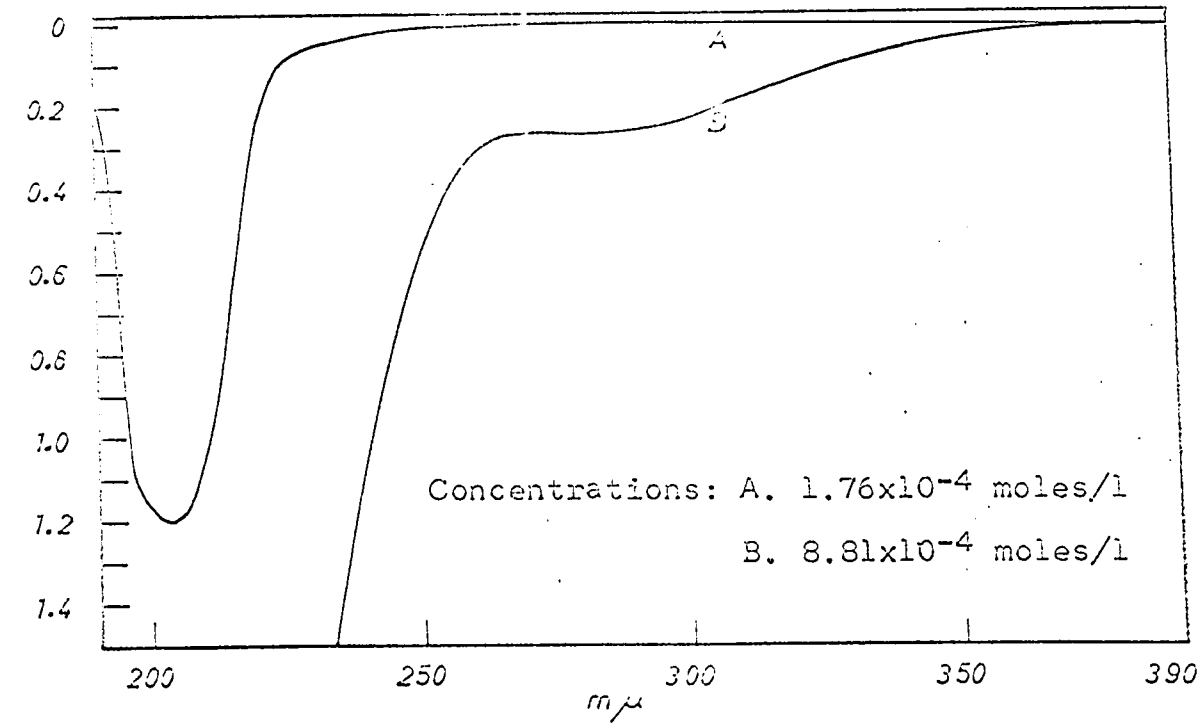


Fig. 13 The ultraviolet spectrum of 1-methyl-2-N,N,N-trimethylammoniomethylcyclo-o̤ctatetraene bromide.

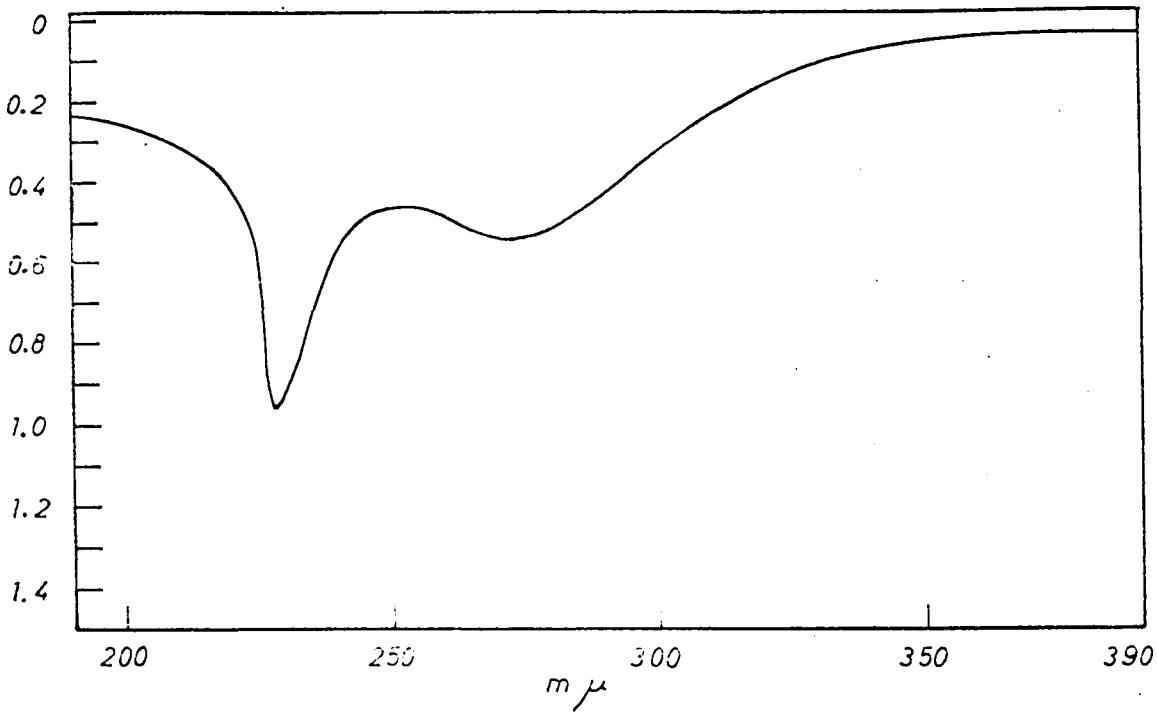


Fig. 14 The ultraviolet spectrum of 1,2-dimethylenecycloöctatriene.

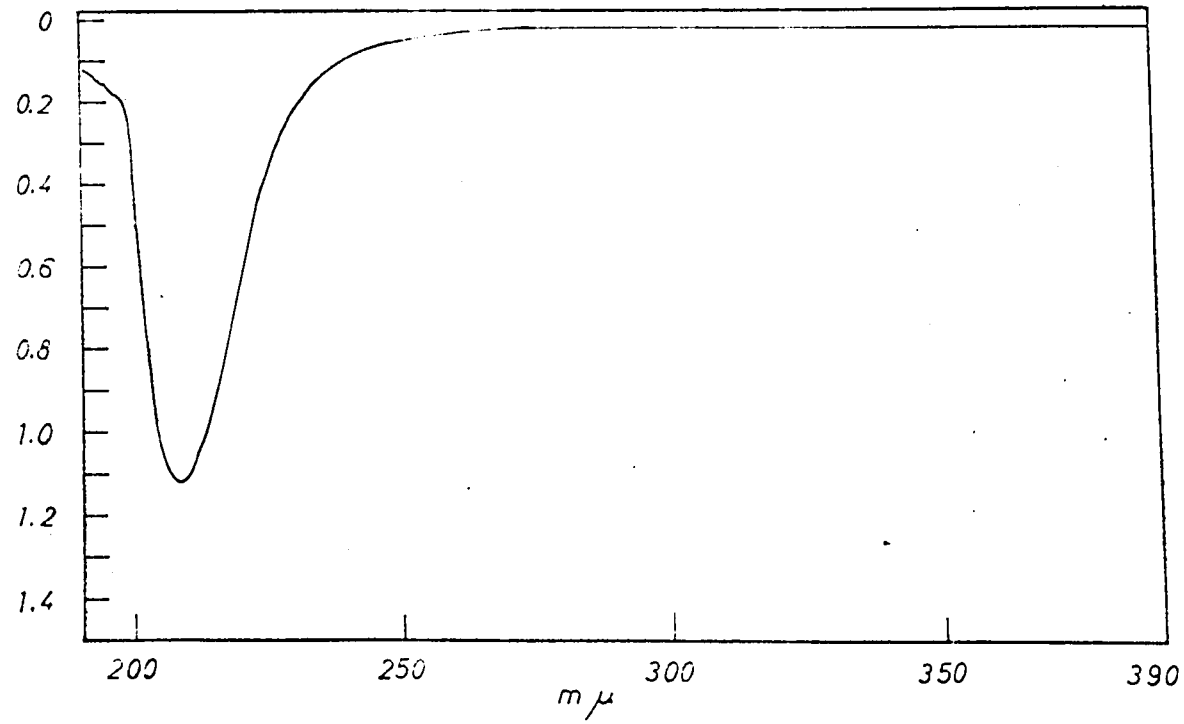


Fig. 15 The ultraviolet spectrum of a 1,2-dimethylenecycloöctatriene-tetracyanoethylene derivative.

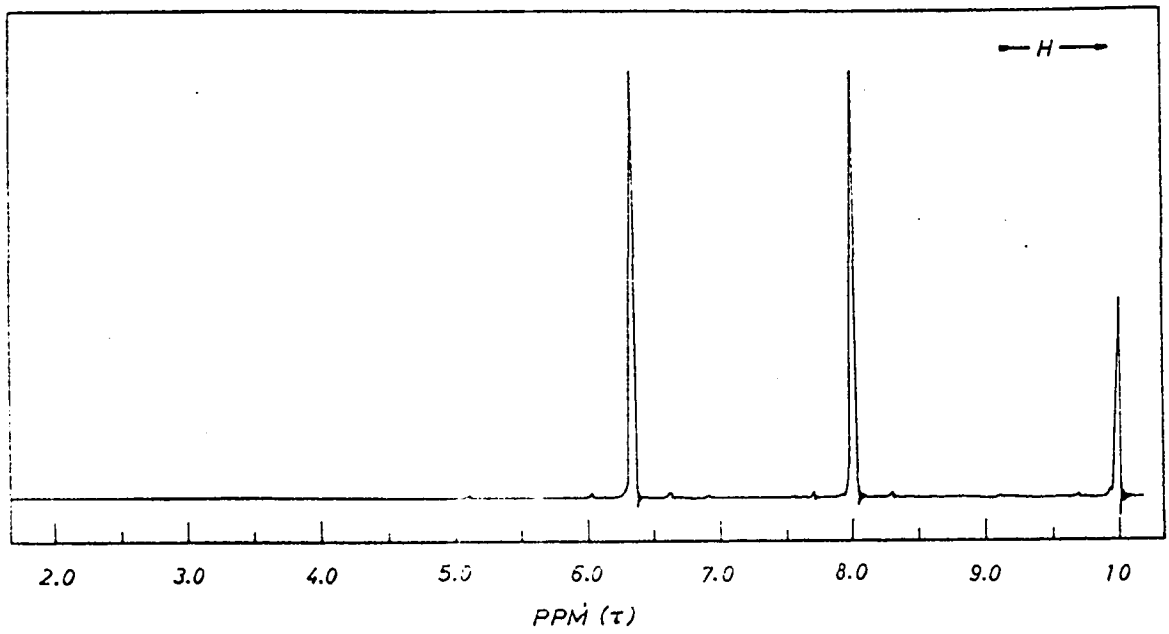


Fig. 16 The n.m.r. spectrum of methyl 2-butynoate.

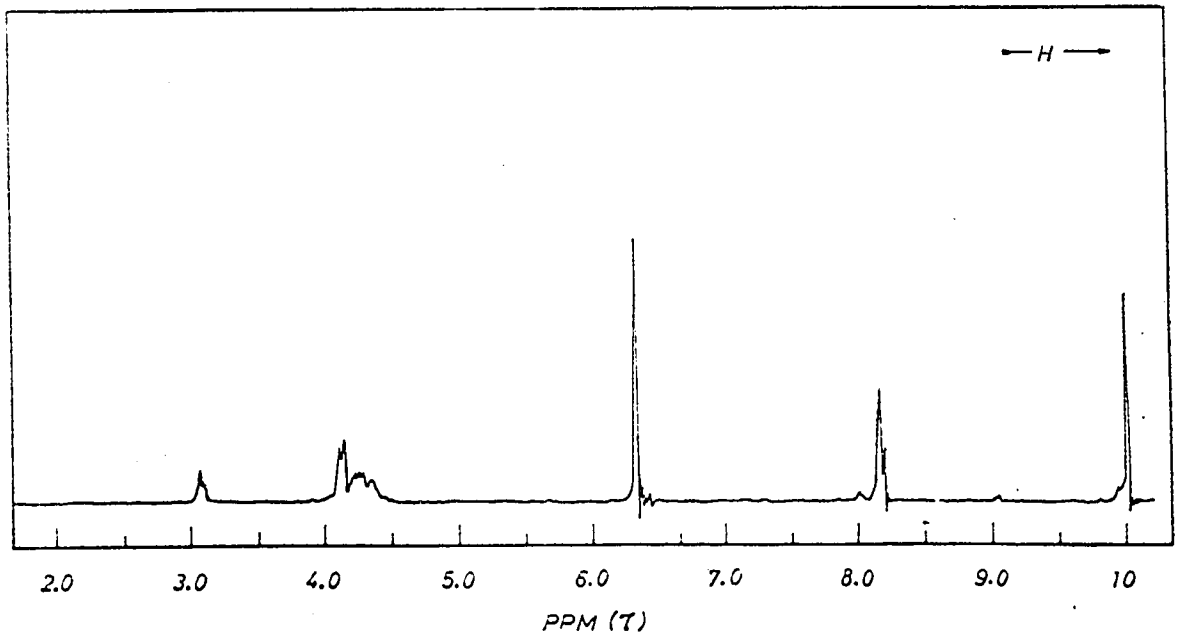


Fig. 17 The n.m.r. spectrum of 2-carbomethoxy-1-methylcycloöctatetraene.

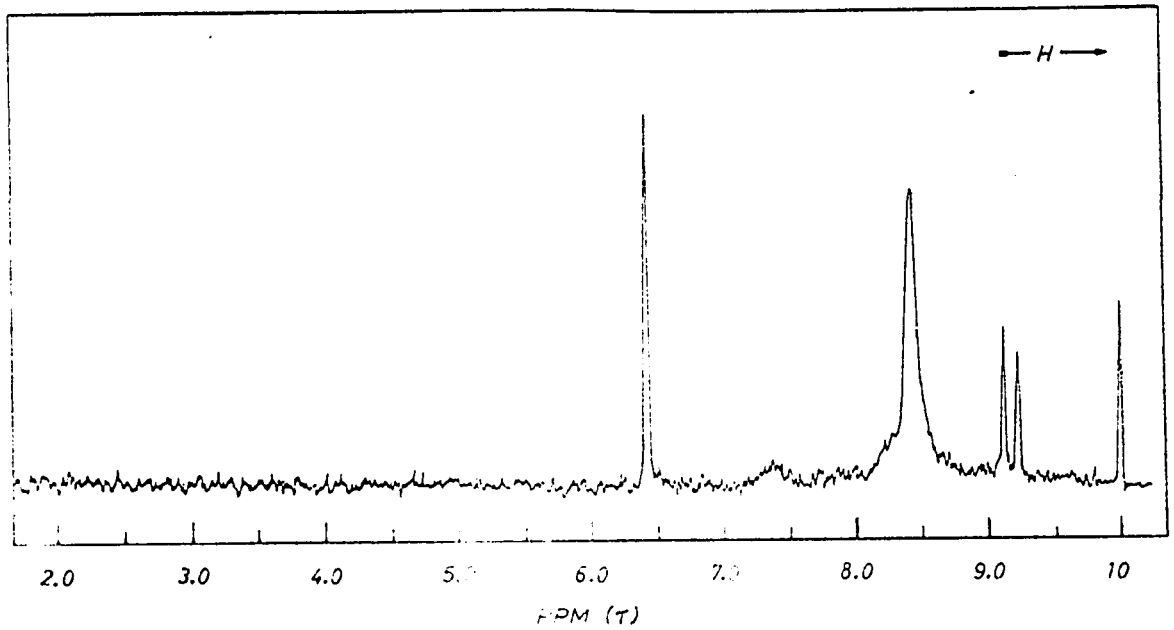


Fig. 18 The n.m.r. spectrum of 2-carbomethoxy-1-methylcyclooctatetraene.

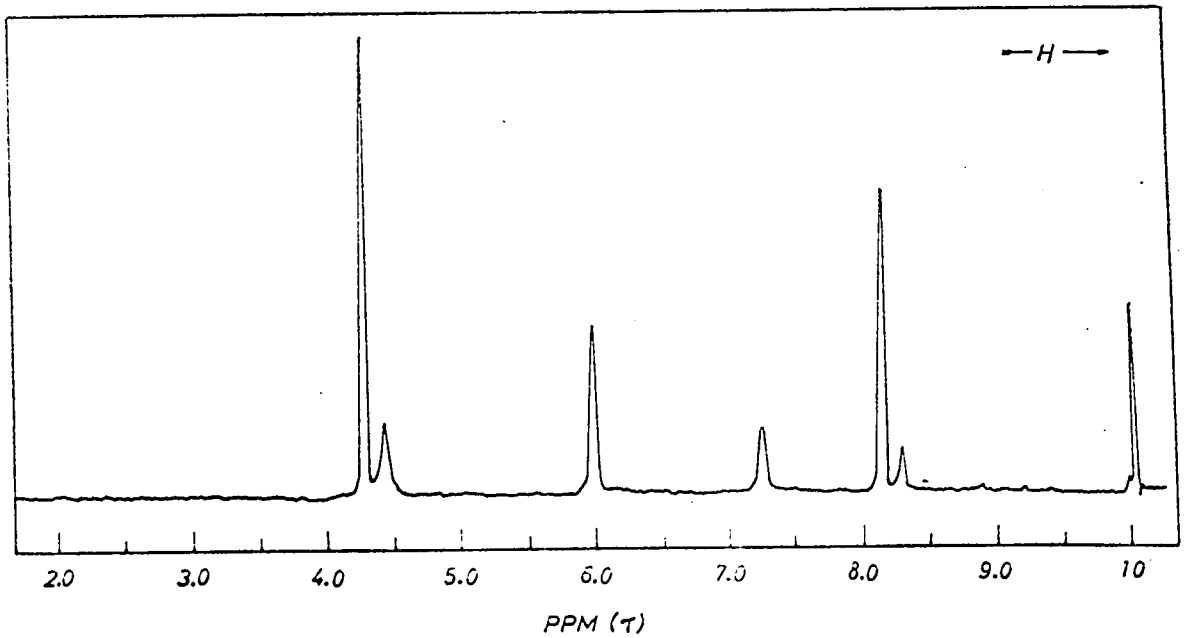


Fig. 19 The n.m.r. spectrum of 2-hydroxymethyl-1-methylcyclooctatetraene.

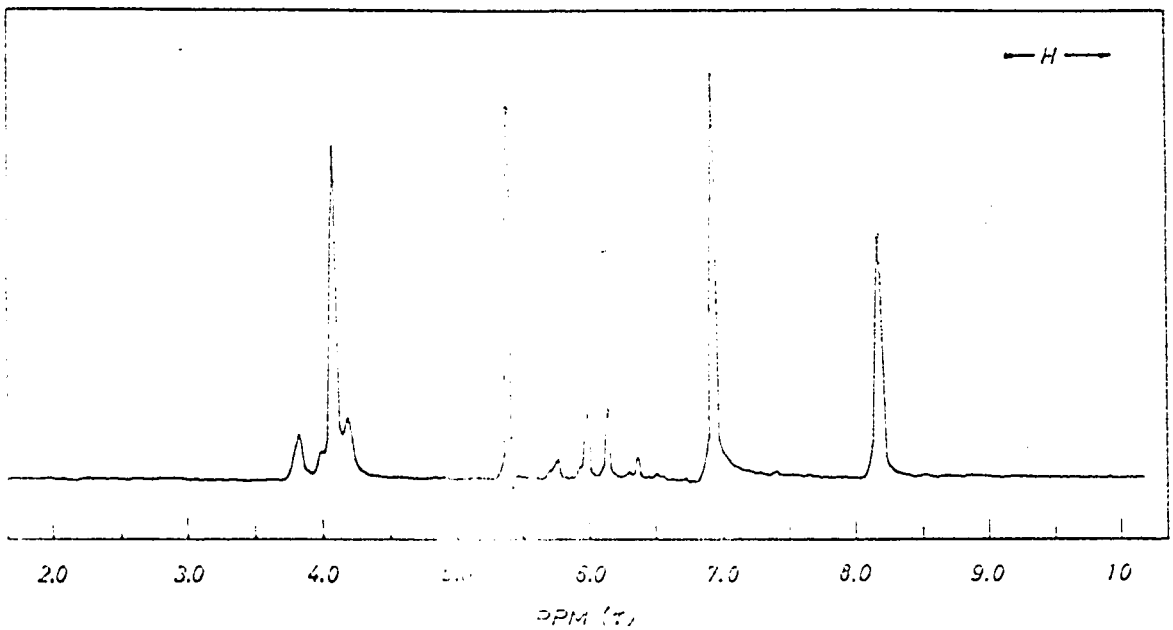


Fig. 20 The n.m.r. spectrum of 1-methyl-2-N,N,N-trimethylammoniomethylcyclooctatetraene bromide.

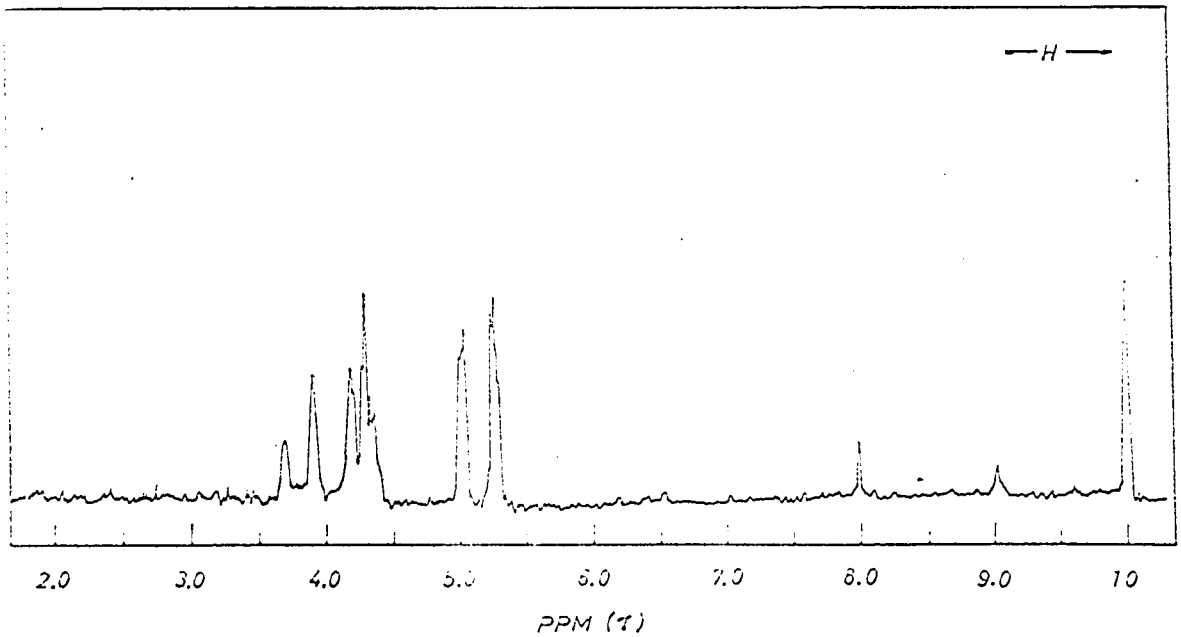


Fig. 21 The n.m.r. spectrum of 1,2-dimethylene-cyclooctatriene.

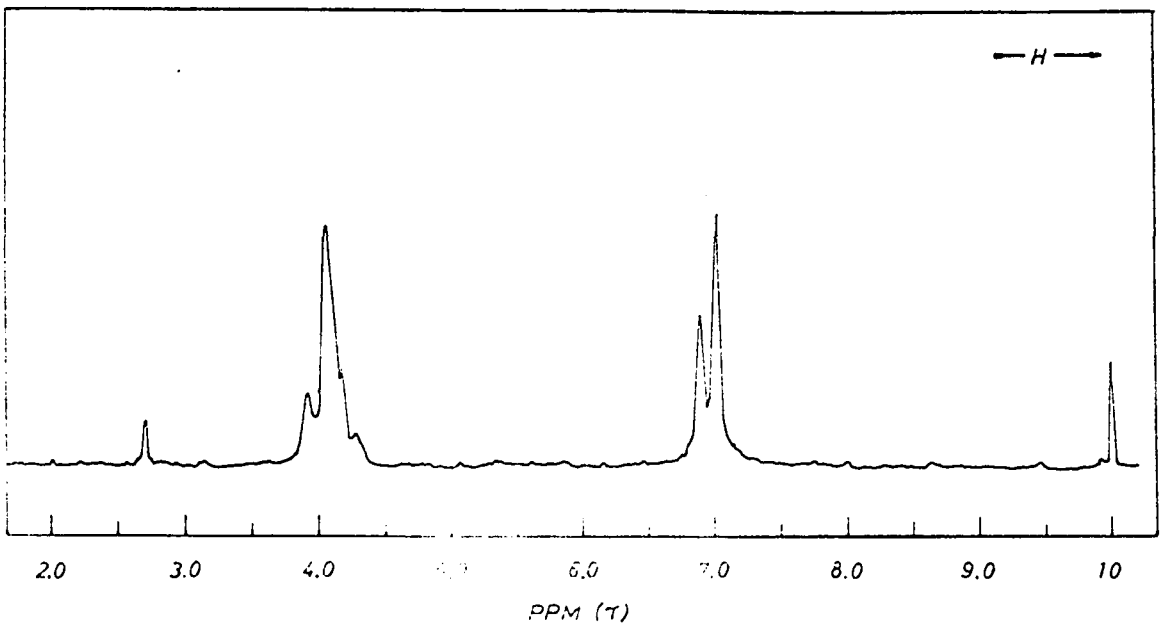


Fig. 22 The n.m.r. spectrum of a 1,2-dimethylenecyclo-öctatriene-tetracyanoethylene derivative (preparation A.).

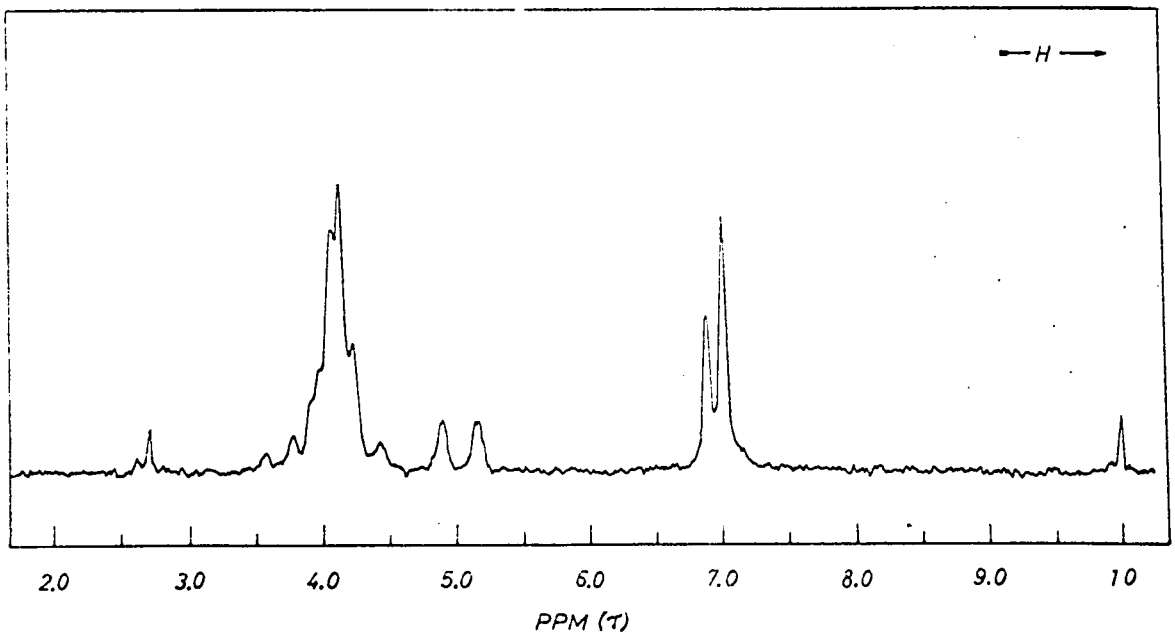
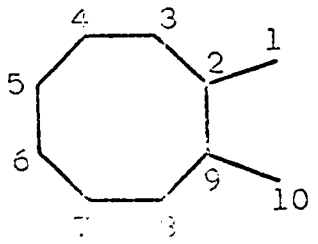


Fig. 23 The n.m.r. spectrum of a 1,2-dimethylenecyclo-öctatriene-tetracyanoethylene derivative (preparation B.).

Molecular Orbital Calculations

Simple Hückel molecular orbital calculations were performed on 1,2-dimethylenecyclooctatriene. The calculations were carried out as outlined by Streitweiser (56) and the format is similar to that in "Dictionary of π-Electron Calculations" (47).

1,2-Dimethylenecyclooctatriene



Energy	E
1	2.17009
2	1.61796
3	1.48119
4	0.61802
5	0.31111

The total π energy E_π = 12.39674 β

The delocalization energy D.E. = 2.39674 β

The delocalization energy per π electron is 0.23967 β

COEFFICIENTS

E	2.17009	1.61796	1.48119	0.61802	0.31111
1	-0.21877	0.19582	-0.16899	0.51169	-0.35154
2	-0.47474	0.31618	-0.25032	0.31621	-0.10937
3	-0.33672	0.00001	-0.45210	0.00001	0.42685
4	-0.25597	-0.31617	-4.41932	-0.31621	0.24217
5	-0.21876	-0.51158	-0.16900	-0.19543	-0.35154

CHARGE-BOND ORDER MATRIX

	1	2	3	4	5
1	1.0003	0.8166	0.0000	-0.3640	-0.0004
2	0.8166	0.9999	0.4527	0.0001	-0.0779
3	0.0000	0.4527	1.0000	0.7583	0.0000
4	-0.3640	0.0001	0.7583	0.9999	0.5306
5	0.0004	-0.0779	0.0000	0.5306	0.9998
6	0.2850	0.0001	-0.3056	-0.0001	0.7328
7	-0.0004	-0.0198	-0.0000	-0.1034	-0.0001
8	-0.3056	0.0000	0.1824	0.0000	-0.3056
9	0.0005	0.3493	0.0000	-0.0261	0.0001
10	-0.1612	0.0000	-0.3056	-0.0000	0.2858

FREE VALENCES

1	0.915
2	0.113
3	0.521
4	0.443
5	0.469

Discussion

The development of quantum mechanical treatments of π electron systems has led to a strong interest in the synthesis and properties of such systems. One series of π electron molecules is that in which there is a ring containing an even number of carbon atoms with two exocyclic methylene groups on adjacent carbons. Of the first three members of this series 1,2-dimethylenecyclobutene has been prepared and its properties studied (62) and 1,2-dimethylenecyclohexadiene has been prepared but not isolated (66). It was of interest to prepare the third member of this series, 1,2-dimethylenecyclooctatriene.

A. 1,2-Disubstituted Cyclooctatetraenes

The proposed synthetic sequence, which proved successful, is given in Figure 24. Of the available cyclooctatetraene syntheses there are two which are suitable for the preparation of 1,2-disubstituted-cyclooctatetraenes: the co-polymerization of disubstituted acetylenes with acetylene under pressure (25,26) and the irradiation of suitable disubstituted acetylenes in benzene (27,28). The photochemical and pressure reactions were examined concurrently.

As a trial run an attempt was made to polymerize acetylene to cyclooctatetraene using nickel cyanide as a catalyst, tetrahydrofuran as solvent, a pressure of 150 p.s.i. acetylene, and sufficient nitrogen to give a total pressure of 850 p.s.i. The reaction was performed in the Magne-Dash autoclave at a temperature of 80°C. Several

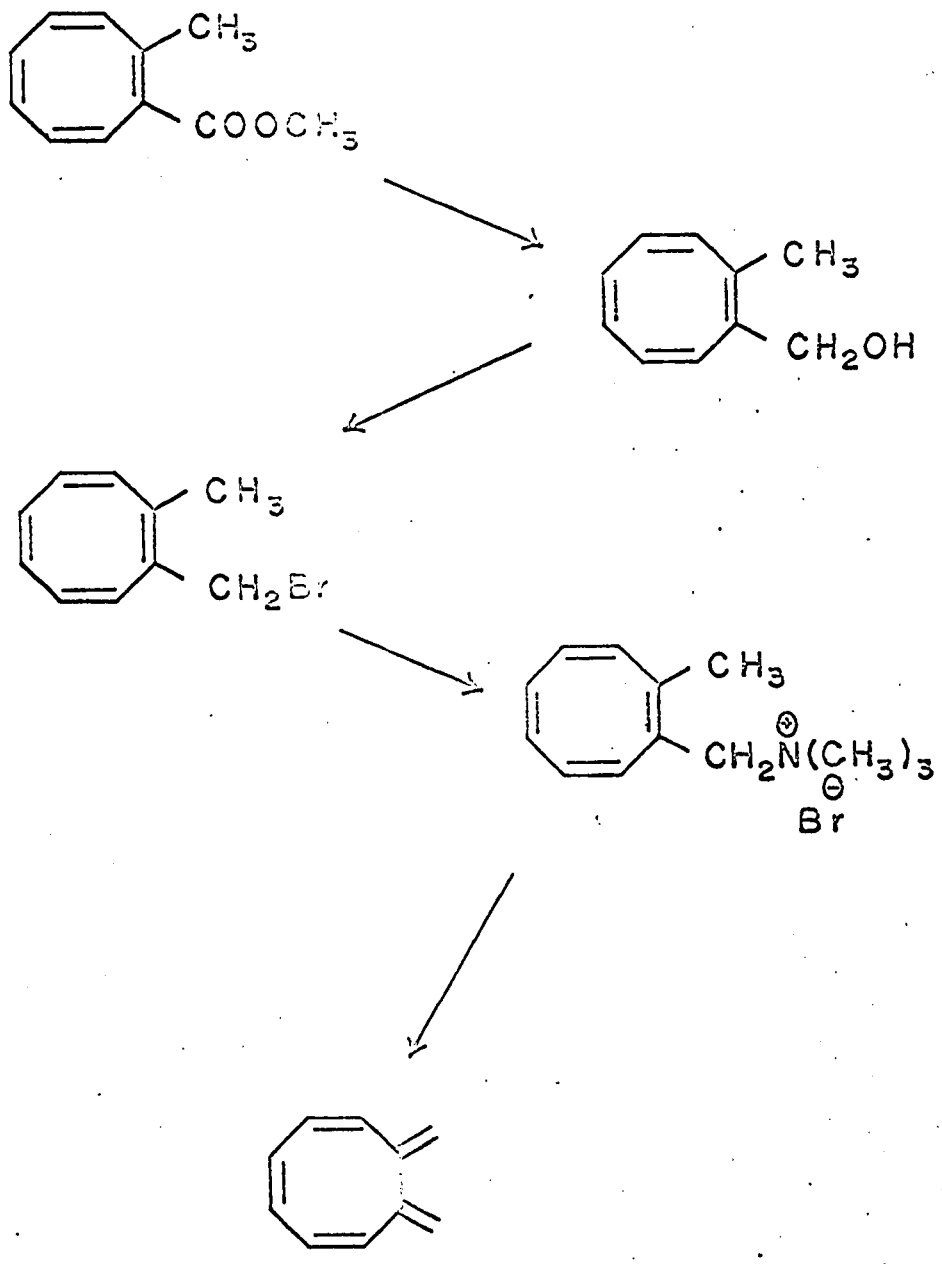


Figure 24. Reaction sequence showing the conversion of 2-carbomethoxy-1-methylcyclooctatetraene to 1,2-dimethylenecyclooctatriene.

explosions soon resulted in a loss of interest in this approach. It is possible that the Magne-Dash autoclave is not suited for this type of reaction since the stirring system involves the use of a solenoid which may have resulted in local overheating.

The photochemical reaction proved successful and so it was used to prepare the required cyclooctatetraene. The starting material for the photochemical reaction, 2-butynoic acid, has been prepared by the treatment of sodio methylacetylide with carbon dioxide (71). Since butyl lithium is now available commercially the use of the lithio derivative, which can easily be formed from butyl lithium and methylacetylene, was preferred. The reaction of carbon dioxide, under pressure, with lithio methylacetylide proceeded smoothly to give a 48% yield of 2-butynoic acid, compared to the 60% yield obtained using the sodio derivative. The somewhat lower yield obtained using lithio methylacetylide probably resulted from its lower solubility in the solvent system used.

Conversion to methyl 2-butynoate was accomplished using diazomethane. The low yield obtained (71%) compared to the almost quantitative yield usually obtained in this reaction resulted from the use of unpurified starting material. It was found to be more convenient to use the 2-butynoic acid in crude form and to purify at the ester stage.

The infrared spectrum of methyl 2-butynoate had absorptions at 2245 cm^{-1} and 1710 cm^{-1} which were assigned to the C≡C and the C=O stretching vibrations respectively. The C=O absorption was lowered from its usual position at 1750-1735 cm^{-1} (73) by conjugation with the triple bond. The ultraviolet spectrum showed a single absorption at 220 mμ with low intensity (log ϵ = 1.88) as would be expected for this compound. The n.m.r. spectrum had two peaks of equal intensity. The peak at 6.34τ was assigned to the protons of the methoxyl group (6.23τ in methyl formate (74) and the peak at 8.02τ to the proton on the carbon having the triple bond (8.20τ in methyl acetylene (74)).

Methyl 2-butynoate was irradiated in benzene to give a yellow viscous product. Microanalysis of the photoproduct gave the empirical formula $C_{11}H_{12}O_2$, and mass spectral analysis gave the molecular weight as 176. These correspond to the values expected for 2-carbomethoxy-1-methylcyclo-ö̈ctatetraene. The mass spectrum confirmed the presence of a methyl group by a peak at m/e = 161 (m-15) and the presence of a carbomethoxy group by a peak at m/e = 117 (m-59). The intense molecular ion (% Σ_{39} = 6.4%) is consistent with a structure having all vinyl bonds (75a). The ultraviolet spectrum had the two absorptions indicative of cyclo-ö̈ctatetraenes at 224 mμ (log ϵ = 3.94) and 292 mμ (log ϵ = 2.64). Unsubstituted cyclo-ö̈ctatetraene has absorptions at about 200 mμ (log ϵ = 3.06) and 274 mμ (log ϵ = 2.55).

The infrared spectrum had bands at 1712 cm^{-1}, 1650 cm^{-1} and 1245 cm^{-1} which could be assigned to the C=O, C=C, and C-O-C stretching vibrations, respectively. The ester band is lowered from its usual position by conjugation with the cyclooctatetraene ring (73). In the n.m.r. spectrum the peak at 8.19 τ (relative intensity 2.8) can be assigned to the methyl group attached to the ring and the peak at 6.33 τ (relative intensity 3.0) can be assigned to the methoxyl methyl. The bulk of the ring protons occurred as a multiplet centered at 4.23 τ (relative intensity 5.3) which is close to the value of 4.3 τ for unsubstituted cyclooctatetraene (74). The peak at 3.08 τ (relative intensity 1.0) can be assigned to the proton which is on the carbon adjacent to the carbon bearing the carbomethoxy group.

Bryce-Smith and Lodge (28) obtained an 8% yield of carbomethoxycyclooctatetraene when they photolyzed a 0.06 molar solution of methyl propynoate in benzene in a quartz cell for 20 hours. Initial experiments carried out under similar conditions using a 0.05 molar solution of methyl 2-butynoate in benzene and a 24 hour photolysis period gave a 16% yield of 2-carbomethoxy-1-methylcyclooctatetraene. It was possible, however, to obtain a marked improvement in the yield from this reaction. Cleanliness of the photolysis cell was found to be of great importance since during the reaction a tough polymeric film coats the cell wall and thus decreases the ultraviolet transmission.

Chlorosulfonic acid was suitable for removing this coating, which was found to be impervious to organic solvents, nitric acid and chromate-sulfuric acid.

The use of a cell made from Vycor #7910 (Corning Glass) rather than quartz increased the yield to 34% (for a 24 hour photolysis period). This glass has 70% transmission at 250 mμ and zero transmission below 220 mμ (76). Since methyl 2-butynoate has a maximum absorption at 220 mμ with tailing towards longer wavelengths the region needed for activation of the molecule is still available. Apparently, however, the removal of the higher energy radiation which can pass through quartz (220-180 mμ) results in a decrease in the rate of polymerization of the cyclooctatetraene.

A further increase in yield resulted when more dilute solutions were used. Irradiating a 0.01 molar solution of methyl 2-butynoate in benzene, using a Vycor #7910 cell, gave, after 12 hours irradiation, a 52% yield. Although further dilution would probably have resulted in further improvement in percentage yield, since a batch process was used, the 0.01 molar solution was considered the minimum suitable for preparative purposes.

Increasing the irradiation time to 36 hours (with cleaning of the cell every 12 hours) gave a 59% yield which is only 7% greater than that obtained with a 12 hour irradiation period. This sharp decrease in the apparent rate of formation of the product could be due to several factors.

a. An equilibrium exists between methyl 2-butynoate and 2-carbomethoxy-1-methylcyclo^{1,3,5}octatetraene.

b. A high concentration of 2-carbomethoxy-1-methylcyclo^{1,3,5}octatetraene effectively filters the incident ultraviolet light and so prevents activation of the methyl 2-butynoate.

c. Once a certain relative ratio of product to starting material is obtained the loss of product through polymer formation is about equal to its rate of formation.

To determine whether an equilibrium exists between the cyclo^{1,3,5}octatetraene and the acetylenic esters, pure 2-carbomethoxy-1-methylcyclo^{1,3,5}octatetraene in benzene was photolyzed under the same conditions as its formation. The photolyzed solution was then analyzed for the presence of methyl 2-butynoate by infrared and vapour phase chromatographic methods. Standard solutions of methyl 2-butynoate in benzene were run to determine the sensitivity of the analytical methods. The infrared method (the C≡C peak was used) was capable of detecting 9 mg. of methyl 2-butynoate in 10 milliliters of benzene which corresponded to 3% conversion of 2-carbomethoxy-1-methylcyclo^{1,3,5}octatetraene into methyl 2-butynoate. The vapour phase chromatographic method was capable of detecting 15 mg. of methyl 2-butynoate in 10 milliliters of benzene which corresponded to 5% conversion of the cyclo^{1,3,5}octatetraene ester into the acetylenic ester. No methyl 2-butynoate was detected by either method so

that an equilibrium mixture, if it exists, contains less than 3% methyl 2-butynoate.

The irradiation of a 0.05 molar solution of methyl 2-butynoate for 36 hours gave a 39% yield. The concentration of 2-carbomethoxy-1-methylcyclo^{11}octatetraene in the solution at the end of the photolysis was 0.015 molar. In the photolysis of the dilute solution (0.01 molar) the concentration of the cyclo^{11}octatetraene ester at the end of the photolysis was 0.0045 molar. If the filtering action of the product were the important factor in the apparent decrease in its rate of formation then this decrease should occur when solutions have the same concentration of product, regardless of the amount of methyl 2-butynoate present. Since this is not the case, possibility (b) is not the main factor involved.

It would appear then that possibility (c) is the most important factor involved. This was confirmed by the observation that the rate of disappearance of methyl 2-butynoate, as determined by noting the disappearance of the C $\equiv$ C stretching vibration in the infrared, remained fairly constant until the end of the photolysis period when about 80% had been consumed.

2-Carbomethoxy-1-methylcyclo^{11}octatetraene absorbed four moles of hydrogen to give 2-carbomethoxy-1-methylcyclo^{11}octane. The infrared spectrum showed four absorptions in the C-H stretch region (2960, 2920, 2880 and 2860 cm^{-1}) consistent with a compound having both CH_3 and CH_2 groups.

The C=O stretch absorption occurred at 1730 cm^{-1} which is higher than that for the cyclo̤octatetraene ester (1712 cm^{-1}) because the carbonyl group is no longer conjugated with a double bond. In the n.m.r. spectrum the absorption, which was a doublet, centered at 9.19 τ (relative intensity 3.0), was assigned to the methyl group attached to the ring. The methyl group couples with the hydrogen on the same ring carbon which bears the methyl group with a coupling constant of 6 c.p.s. This is a reasonable value for vicinyl coupling (77). The ring protons are centered at 8.45 τ (relative intensity 12.3) and at 7.40 τ (relative intensity 1.8) and the methoxyl protons are at 6.44 τ (relative intensity 3.0).

The vapour phase chromatographic behaviour of 2-carbomethoxy-1-methylcyclo̤octane was carefully studied on three columns as noted in Table I. These data suggest that a single hydrogenation product was formed. If the double bonds in 2-carbomethoxy-1-methylcyclo̤octatetraene were reduced in a completely random fashion then one would expect a 50:50 mixture of <u>cis</u> and <u>trans</u> cyclo̤octane. It appears, however, that the two substituents are very effective in blocking the approach of the catalyst so that 2-carbomethoxy-1-methylcyclo̤octene is formed. Reduction of this cyclo̤octene would give the <u>cis</u> product only so that it is possible to assign this <u>cis</u> configuration to the 2-carbomethoxy-1-methylcyclo̤octane that was prepared.

The 2-carbomethoxy-1-methylcyclooctatetraene obtained photochemically was reduced by metal hydride to the alcohol. The ultraviolet spectrum had the expected cyclooctatetraene absorptions at 223 mμ ($\log \epsilon$ = 3.56) and 269 mμ ($\log \epsilon$ = 2.60). The infrared showed bands at 3350 cm^{-1} (OH), 3005 cm^{-1} (C=C-H), 1645, 1623 cm^{-1} (C=C), and 1008 cm^{-1} (C-O-C). Completeness of reduction was indicated by the lack of a band at 1712 cm^{-1} (C=O). In the n.m.r. spectrum the peak at 8.24 τ (relative intensity 3.0) was assigned to the methyl group, the peak at 6.04 τ (relative intensity 2.0) to the methylene group and the broad singlet at 4.33 τ (relative intensity 5.6) to the ring protons. The peak at 7.31 τ (relative intensity 1.1) was assigned to the OH proton on the basis of deuterium exchange. Peaks at 8.33 τ and 4.47 τ are due to impurity. The mass spectrum gave a molecular weight of 148, as required for 2-hydroxymethyl-1-methylcyclooctatetraene, and also confirmed the presence of a methyl group by a peak at m/e = 133 (m-15) and a hydroxymethyl group by a peak at m/e = 117 (m-31). The molecular ion was particularly intense (% Σ_{79} = 37.8) as would be expected for this compound.

The major impurity which is evident in both the n.m.r. and the v.p.c. analyses was not starting material, as shown by infrared and v.p.c., and was not a styrene which would have been removed in the silver nitrate treatment since it does not form a complex.

The reduction using inverse addition of lithium aluminum hydride in ether at 0°C gave a reasonable yield (53%) of the alcohol. Using aluminum hydride, which is considered more suitable for compounds containing double bonds (78), the yield was raised to 72%. This is far below that reported by Le Goff and La Count who obtained a 94% yield in the conversion of 1,2-dicarbomethoxycyclooctatetraene to the diol (79). They published n.m.r. data only, however, so the purity of their product was not established.

2-Hydroxymethyl-1-methylcyclooctatetraene was converted to the bromide by phosphorus tribromide in hexane. The infrared spectrum of the product showed bands at 2993 cm^{-1} (C=C-H) and 1625 cm^{-1} (C=C). The absence of bands at 3350 cm^{-1} (OH) and 1008 cm^{-1} (C-O-C) was noted. Shaking with aqueous silver nitrate produced an immediate precipitate. Concentration of the hexane solution resulted in rapid darkening. Because of its instability the bromide was not further characterized but was used directly in the next preparation. Since the bromo group is allylic and strong steric interaction occurs with the nearby methyl group the instability of this compound is not surprising.

Conversion of 2-bromomethyl-1-methylcyclooctatetraene to the quaternary bromide was accomplished using trimethylamine. Since the reaction involves the formation of a charged product and presumably has a charged transition state, the use of a polar solvent was deemed desirable.

Since the bromo compound is rather unstable, however, it appeared best to leave it in the hexane solution and to increase the polarity of the solvent system by adding methanol. A 50% methanol-hexane solution gave suitable results.

The quaternary bromide is a stable, high melting solid (m.p. 225-226°C) which crystallizes as green-yellow needles from ethanol. In the infrared spectrum there was a band at 1625 cm^{-1} which was assigned to the C=C stretching vibration and in the ultraviolet there are absorptions at 203 mμ ($\log \epsilon = 4.32$) and at 279 mμ ($\log \epsilon = 2.49$). In the n.m.r. spectrum the peak at 8.17 τ (relative intensity 3.0) was assigned to the methyl group attached to the ring and the peak at 6.93 τ (relative intensity 8.7) to the methyl groups on the nitrogen. The ring protons occurred as a multiplet centered at 4.09 τ (relative intensity 5.8). The methylene protons were centered at 6.06 τ (relative intensity 2.0). They occurred as an AB quartet with a coupling constant of 13.5 c.p.s., a reasonable value for geminal coupling (80), and a relative chemical shift (calculated) of 18.6 c.p.s. (77). It is possible for the methylene protons to have different chemical shifts because of the asymmetry of the cyclooctatetraene ring. In a particular conformation one of the protons of the methylene group will lie closer to the π system of the ring and so will be shifted to lower field. The environments of the two protons could be averaged by rotation but the bulky

N,N,N-trimethyl group on the methylene and the nearby methyl group prevent this.

The infrared absorptions of cyclooctatetraene in the lower region of the spectrum (below 1500 cm^{-1}) have been assigned by the calculation of energies of possible vibrations (40). It has been found that these peaks can also be assigned in monosubstituted cyclooctatetraenes (81). The origins of the infrared bands in the disubstituted cyclooctatetraenes were assigned (Table II) by comparison with these cases.

The ultraviolet spectra of the compounds prepared all had the two peaks expected for cyclooctatetraenes (Table III). The lower transition (about 200 mμ in cyclooctatetraene) which is a $\pi \longrightarrow \pi^*$ transition shows a shift to 224 mμ for the ester prepared and 223 mμ for the alcohol. Only the quaternary bromide had its absorption at about the same position as cyclooctatetraene (203 mμ) presumably because the non-bonding electrons on the nitrogen are not available for interaction with the ring. The longer wavelength absorption which occurs at 280 mμ (log ϵ = 2.64) (41) in cyclooctatetraene also was not shifted in the quaternary bromide (279 mμ, log ϵ = 2.49). Both the alcohol and the ester showed substantial shifts although in opposite directions. The alcohol absorption was shifted to shorter wavelength (269 mμ) and the ester to longer wavelength (292 mμ).

The mass spectra of 2-carbomethoxy-1-methyl-cyclo$^{\text{II}}$octatetraene and 2-hydroxymethyl-1-methylcyclo-$^{\text{II}}$octatetraene as well as providing direct evidence of the nature of the groups attached to the cyclo$^{\text{II}}$octatetraene ring also show the wealth of breakdown pathways available for these molecules. The breakdown sequences shown on the following pages only intend to show that the major peaks can be accounted for in a reasonable manner. There are, of course, in some cases alternate ways of formulating the breakdown sequences and the structures of the products.

Figure 25. THE MASS SPECTRAL BREAKDOWN PATTERN OF 2-CARBOMETHOXY-1-METHYLCYCLOOCTATETRAENE

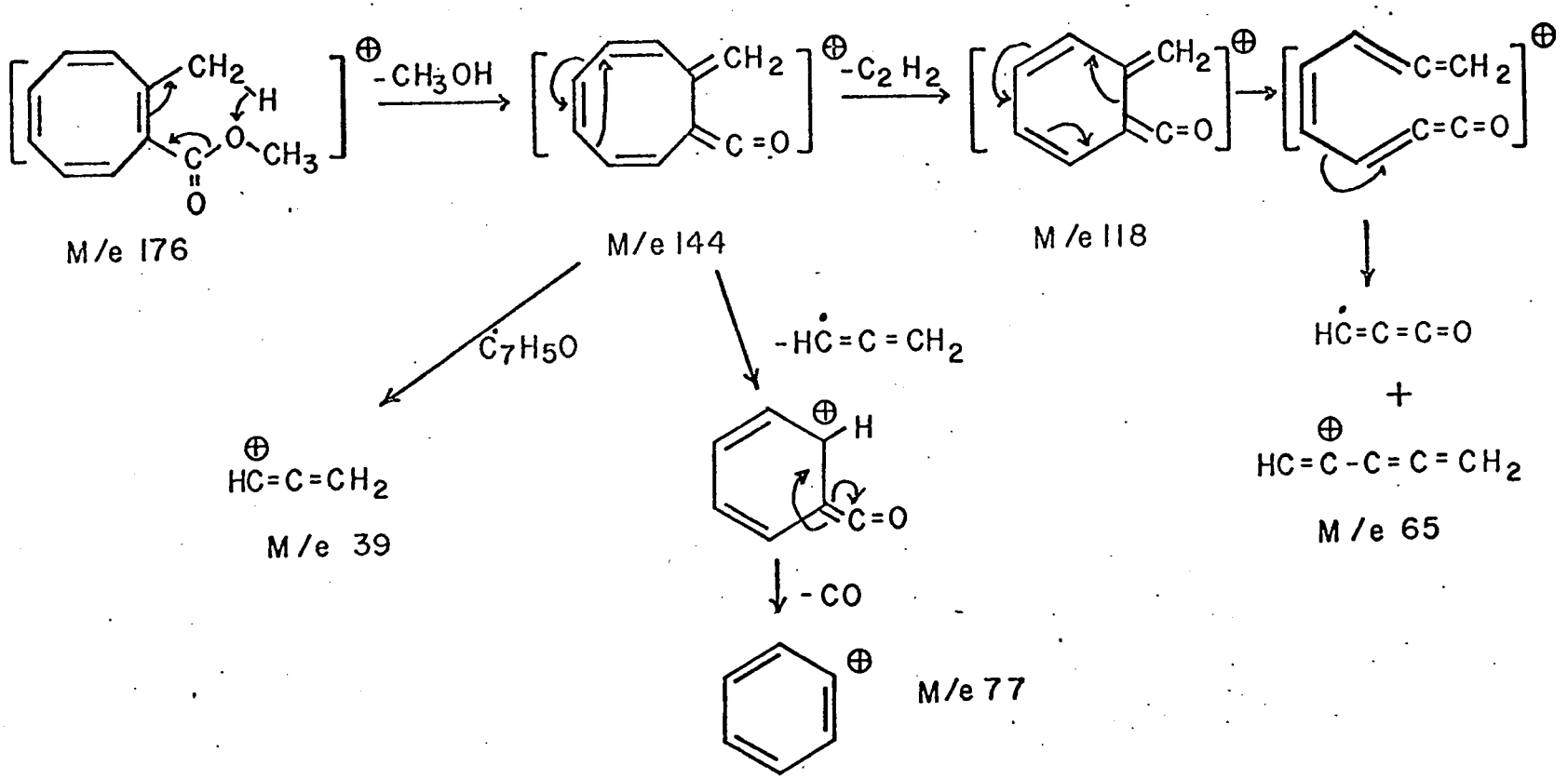


Figure 25. (continued)

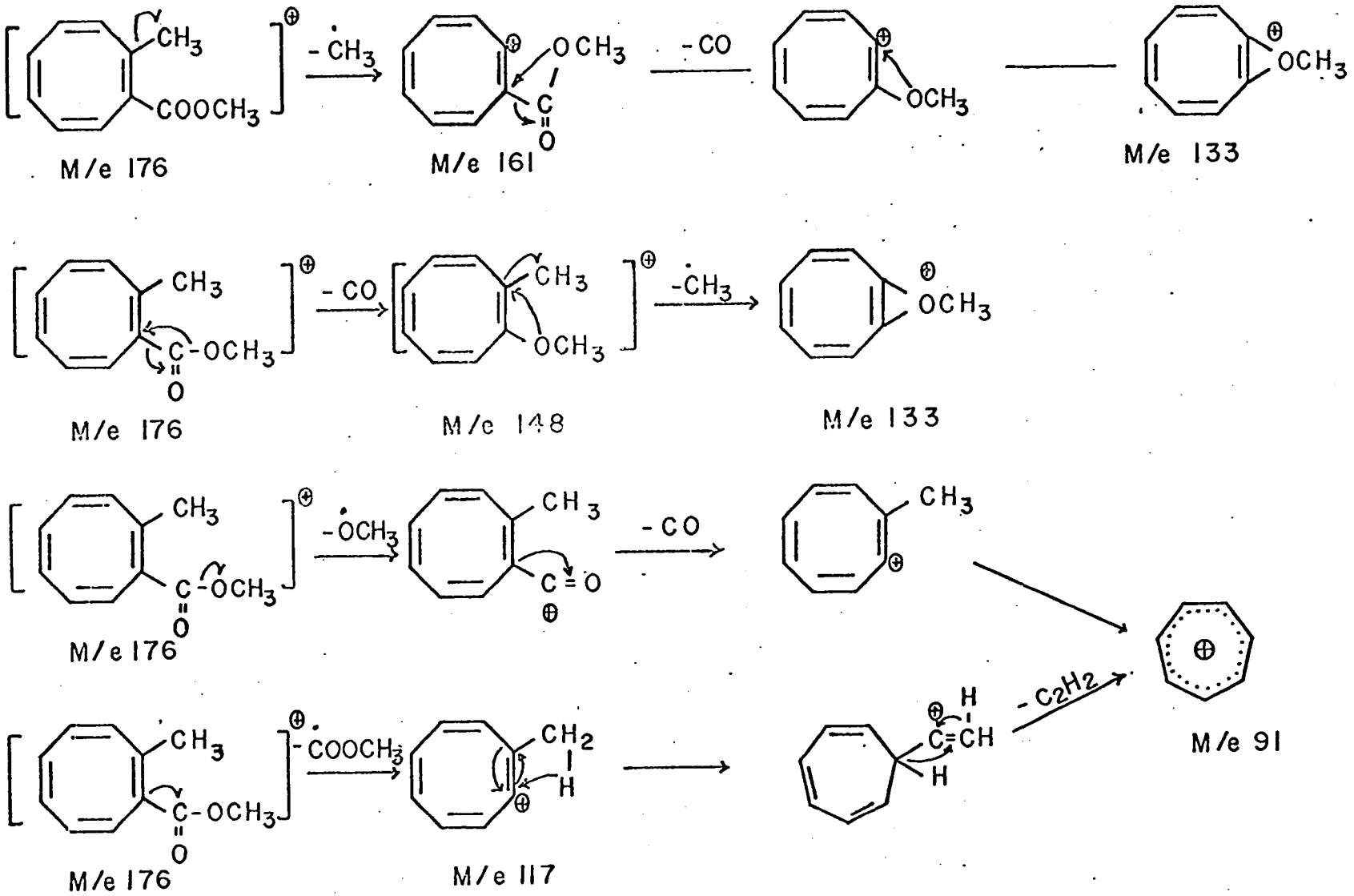
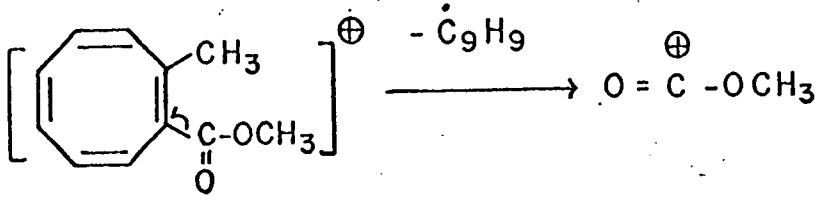
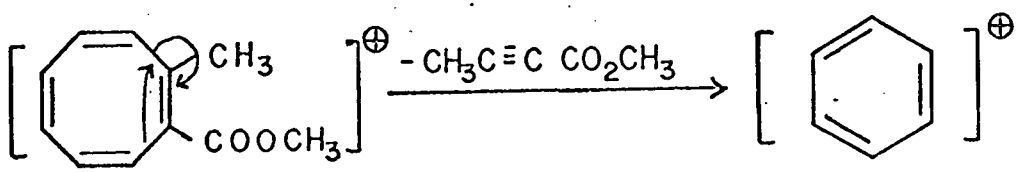


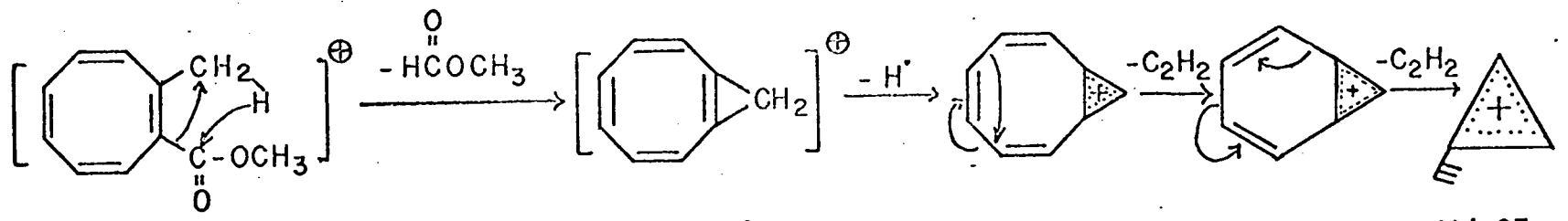
Figure 25. (continued)



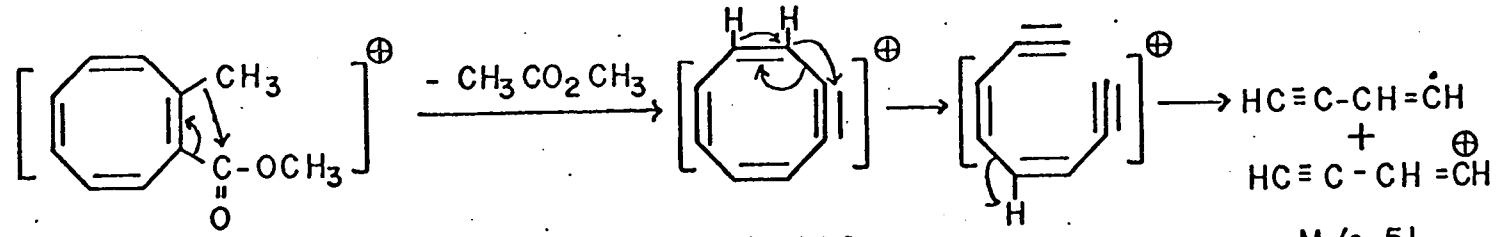
M/e 176 M/e 59



M/e 176 M/e 78



M/e 176 M/e 116 M/e 115 M/e 89 M/e 63



M/e 176 M/e 102 M/e 51

Figure 26. THE MASS SPECTRAL BREAKDOWN PATTERN OF 2-HYDROXYMETHYL-1-METHYLCYCLOOCTATETRAENE

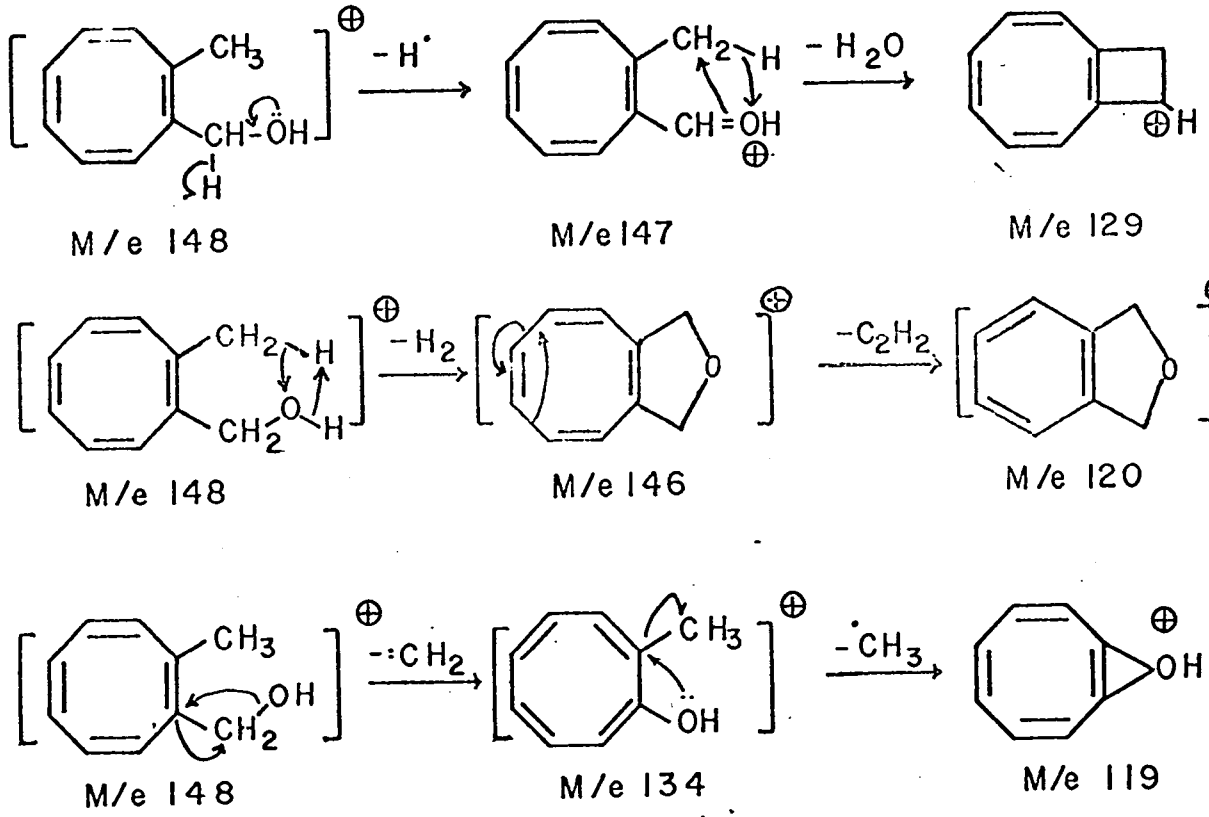
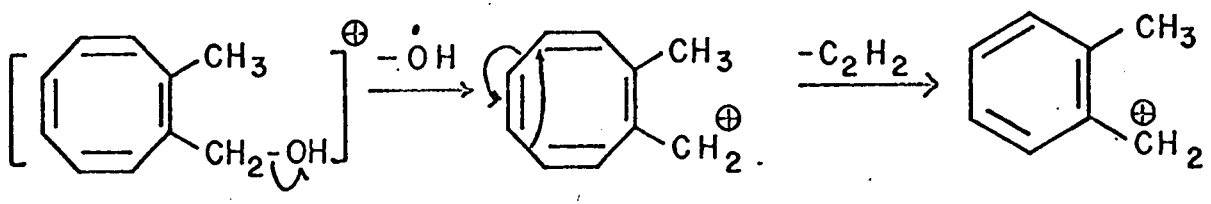
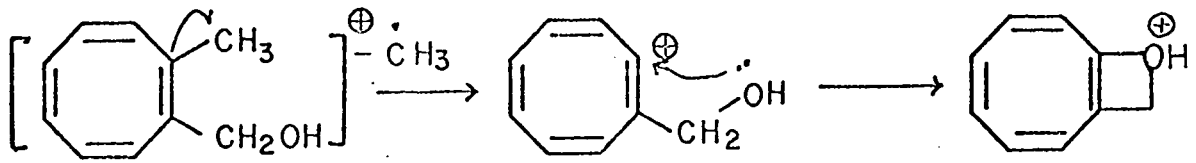


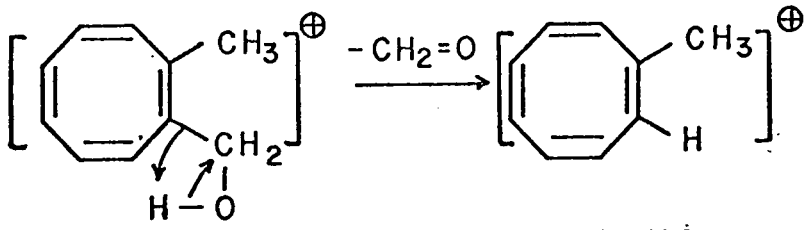
Figure 26. (continued)



M/e 148 M/e 131 M/e 105

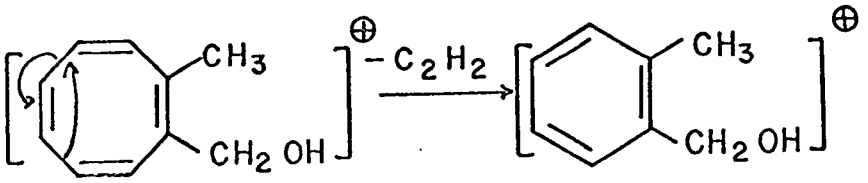


M/e 148 M/e 133

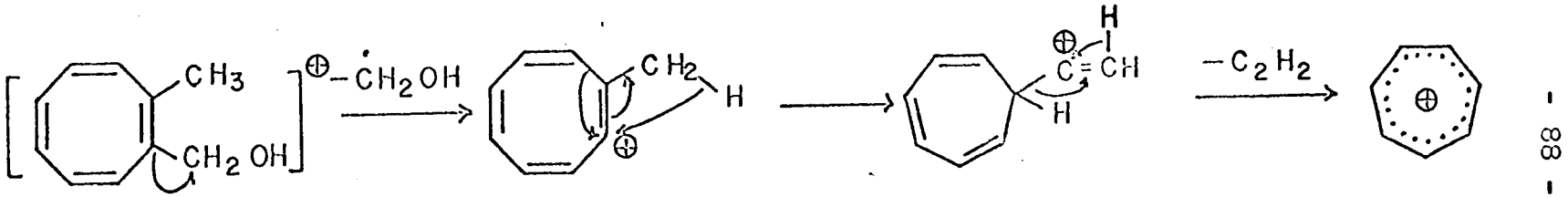


M/e 148 M/e 118

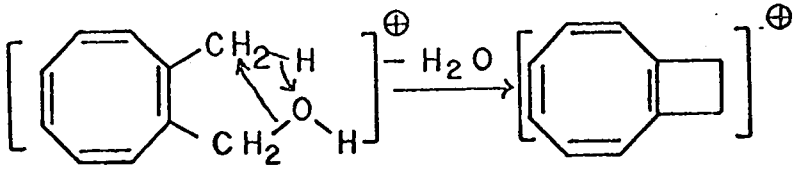
Figure 26. (continued)



M/e148 M/e 106



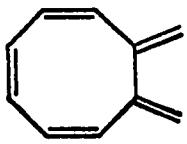
M/e 148 M/e 117 M/e 91



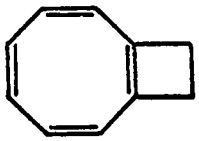
M/e 148 M/e 130

B. 1,2-Dimethylenecyclooctatriene

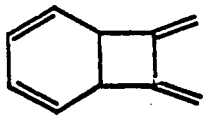
Pyrolysis of the quaternary hydroxide obtained from 1-methyl-2-N,N,N-trimethylaminomethylcyclooctatetraene bromide gave, after purification, a colourless, oxygen sensitive compound. Microanalysis and the molecular weight obtained from the mass spectrum showed it to be a $C_{10}H_{10}$ hydrocarbon. Even if it is assumed that the reaction proceeds without rearrangement of atoms (an assumption later shown to be correct) it is still possible for the product to exist in several forms, of which three of the more likely ones are shown below.



XIII



XXVI

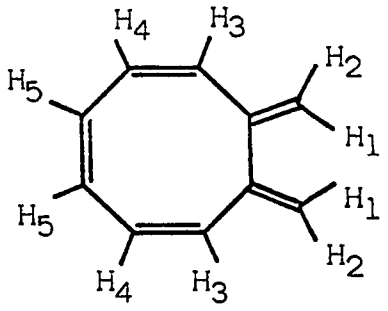


XXVII

These structures are valence bond tautomers which result from the rearrangement of double bonds. The product could have any one of these structures or it could exist as an equilibrium mixture of two or more of them.

The structure of the product as XIII was convincingly proved by the n.m.r. spectrum. It showed only two very small peaks in the aliphatic region at 7.98 τ and 9.02 τ. Each of these peaks had an integrated intensity of less than 0.2 protons. The peak at 7.98 τ was due to a

small amount of trimethylamine which was not removed by the v.p.c. purification. Since the rest of the spectrum consisted of peaks in the olefinic region only, the product must have the monocyclic dimethylene structure.



The peaks at 5.02 τ (relative intensity 2.0) and 5.27 τ (relative intensity 2.0) were assigned to the methylene protons H_1 and H_2 respectively. The inner protons H_1 are shifted downfield relative to the outer protons H_2 because of the influence of the other nearby exocyclic double bond. The coupling constant J_{12} is about 1 c/s. The protons H_3 are shifted downfield relative to H_4 and H_5 by the influence of the exocyclic double bonds. Although H_4 and H_5 are not appreciably chemically shifted they can be distinguished by virtue of the coupling of H_4 with H_3. Coupling of this type has been observed to be 11.8 c/s in cyclooctatetraene (45). The coupling constant of H_4 with H_5 would be small (0 - 1 c/s) because the dihedral angle would be in the region of 90°. The peaks at 3.70 τ and 3.90 τ can thus be assigned to H_3 and those at 4.18 τ and 4.39 τ to H_4. They form an AB system with a coupling of 12 c/s

and a relative chemical shift (calculated)(77) of 31.7 c/s. The remaining peaks (4.30τ , 4.33τ and 4.37τ) were assigned to H_5.

The n.m.r. spectrum shows unequivocally that the product exists mainly as structure XIII. It does not, however, preclude the possibility that it is in equilibrium with one or more other structures which are present in small amount only, as in the case of cyclooctatetraene which has been shown to be in equilibrium with its bicyclo form (35).

The ultraviolet spectrum of 1,2-dimethylenecyclooctatriene is reminiscent of cyclooctatetraene though somewhat more intense with absorptions at 228mμ(log ϵ = 4.23) and 272mμ(log ϵ = 3.96) compared to cyclooctatetraene which has absorptions at about 200mμ and 280mμ(log ϵ = 2.64) (41). These spectra are in sharp contrast to those of linear polyenes which can easily assume the planar configuration necessary for good π overlap. Octatetraene, for example, has four peaks at 268mμ, 278mμ, 291mμ and 304mμ (82). This suggests that 1,2-dimethylenecyclooctatriene, like cyclooctatetraene, has limited overlap of its π bonds and so is not planar. It is probable that it is tub shaped like cyclooctatetraene.

The infrared spectrum of 1,2-dimethylenecyclooctatriene had bands at 3075cm^{-1} (C=$\underline{CH_2}$ stretch), 3000cm^{-1} (C=$\underline{C}$-H stretch), 880cm^{-1} (C=$\underline{CH_2}$ bend), 710cm^{-1} and 640cm^{-1} (C=$\underline{C}$-H bend) which compare favourably with assignments for 1,2-dimethylenecyclobutene of 3040cm^{-1} (C=$\underline{CH_2}$ stretch),

2950cm^{-1} (C=C-H stretch) and 870cm^{-1} (C=CH_2 bend) (62). The bands at 710cm^{-1} and 640cm^{-1} were assigned on the basis of comparison with disubstituted cyclooctatetraenes. Since there are many other peaks in the region 800-600cm^{-1}, this assignment cannot be considered a firm one.

It has been noted that strain in a molecule can affect the position of infrared bands. In the C=C stretch region, if the double bond is exocyclic to a ring, the frequency of absorption increases as the size of the ring decreases, that is, as strain in the ring increases. Thus the C=C stretch absorption band of methylenecyclohexane is at 1651cm^{-1}, that of methylenecyclopentane is at 1657cm^{-1} and that of methylenecyclobutene is at 1678cm^{-1}. On the other hand, if the double bond is in the ring, the position of the C=C absorption band decreases with increasing ring strain. Thus the C=C stretch absorption band of cyclohexene is at 1646cm^{-1}, that of cyclopentene is at 1611cm^{-1} and that of cyclobutene is at 1566cm^{-1}. A complicating factor which must be considered is conjugation which lowers the infrared frequency. It has been found that 1,2-dimethylene compounds can achieve sufficient coplanarity to conjugate. For example, the C=C stretch band of 1,2-dimethylenecyclopentane is at 1626cm^{-1}, a drop of 31cm^{-1} from methylenecyclopentane, and that of 1,2-dimethylenecyclobutane is at 1650cm^{-1}, a drop of 28cm^{-1} from methylenecyclobutane (83). This complication can be ignored, however, as long as all the compounds compared have two adjacent

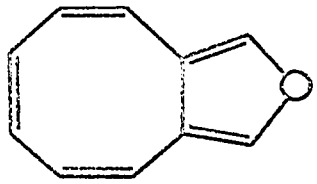
exocyclic double bonds which can conjugate. The double bonds in the ring are restricted from strong interaction by molecular geometry so that conjugation effects need not be considered for them.

An examination first of the C=C stretch band of the methylene groups of 1,2-dimethylenecyclooctatriene which occurs at 1630cm^{-1} suggests a completely different degree of strain compared to such molecules as trimethylenecyclopropane which absorbs at 1750cm^{-1} (70) and tetramethylenecyclobutane which has bands at 1760cm^{-1} and 1710cm^{-1} (65). The infrared suggests very severe strain in these two molecules. In fact the infrared band of the methylene groups in 1,2-dimethylenecyclooctatriene is very close to that of 1,2-dimethylenecyclopentane (1626cm^{-1}) in which strain should not be extensive.

The infrared bands of the double bonds in the ring, which occur at 1585cm^{-1} and 1560cm^{-1}, are substantially shifted from those of cyclooctatetraene which has its bands at 1635cm^{-1} and 1609cm^{-1} (40) and cyclooctatriene which has its bands at 1638cm^{-1} and 1610cm^{-1} (84). Apparently some strain has been introduced into these bonds presumably because of a change in ring geometry resulting from the presence of the two exocyclic double bonds. Of course the lowering of the infrared frequency could be due to conjugation but the ultraviolet spectrum seems to exclude this possibility. It appears then that the above correlation of the infrared evidence suggests that in 1,2-dimethylene-

cyclo"octatriene the exocyclic methylene groups are probably close to coplanar, that the ring geometry is slightly changed from that in cyclo"octatetraene and that the ring possesses only moderate strain.

A molecule very close in structure to 1,2-dimethylenecyclo"octatriene, cyclo"octa[c]furan (XXVIII) (79) has C=C stretch absorptions at 1645 cm^{-1} for the exocyclic



XXVIII

bonds and 1533 cm^{-1} for the interior bonds which suggests that it has a somewhat higher strain energy than 1,2-dimethylenecyclo"octatriene.

The mass spectrum of 1,2-dimethylenecyclo"octatriene proved unique in the extreme ease with which one and two protons were lost. The intensity of the species m/e = 129 is 23.5 per cent Σ_{52} compared to 28.6 for the molecular ion suggesting that there must be excellent stabilization of this species. Loss of a proton from 1,2-dimethylenecyclo-"octatriene does not lead to a stabilized ion, if the structure is retained, so that it seems necessary to postulate that breakdown can occur through other structures. The most likely ones are 1(8),2,4,6-bicyclo[6.2.0]decatetraene (XXVI) and 7,8-dimethylene-2,4-bicyclo[4.2.0]octadiene (XXVII) which were mentioned previously (p. 89).

Figure 27. THE MASS SPECTRAL BREAKDOWN PATTERN OF 1,2-DIMETHYLENECYCLOOCTRIENE

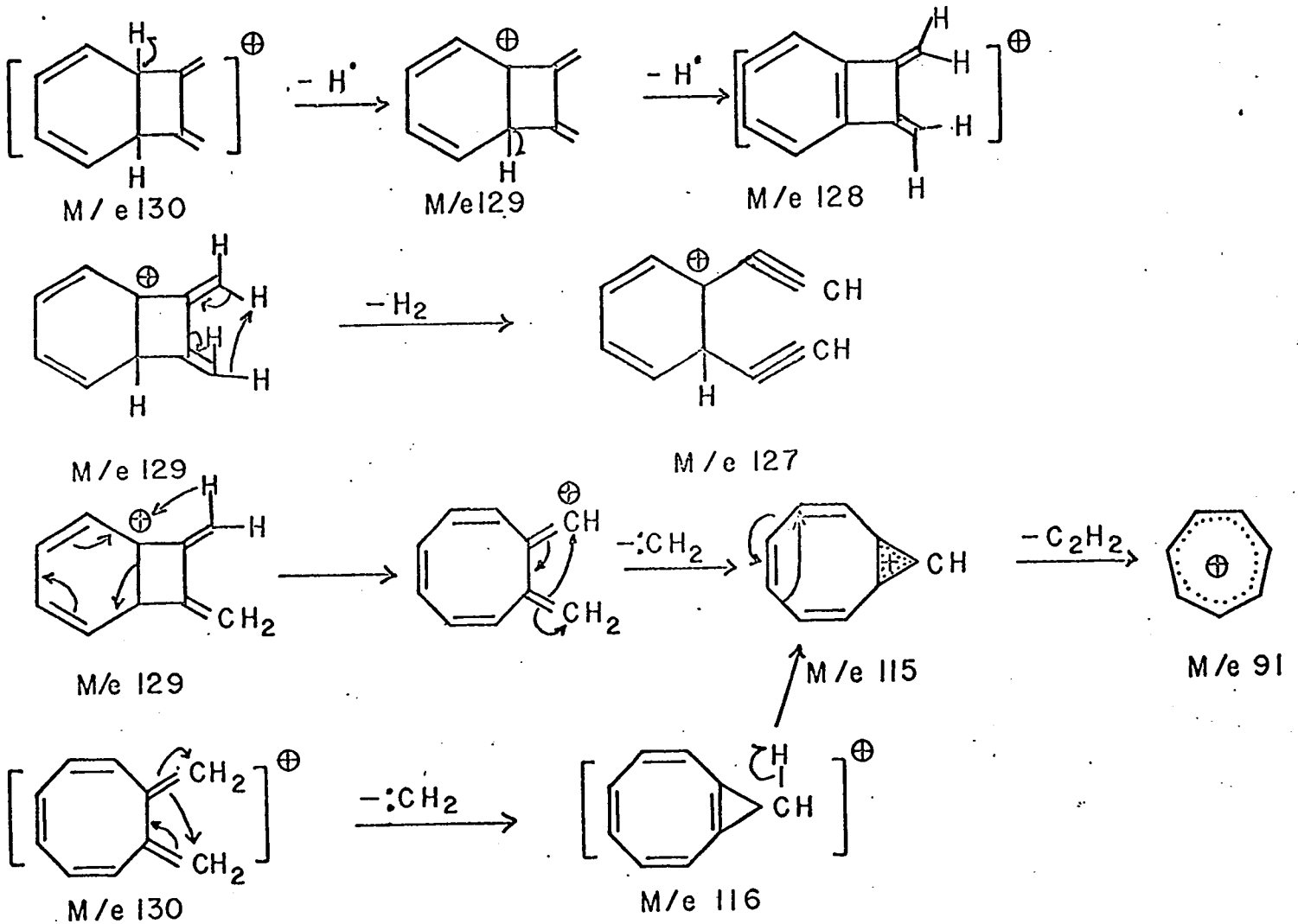
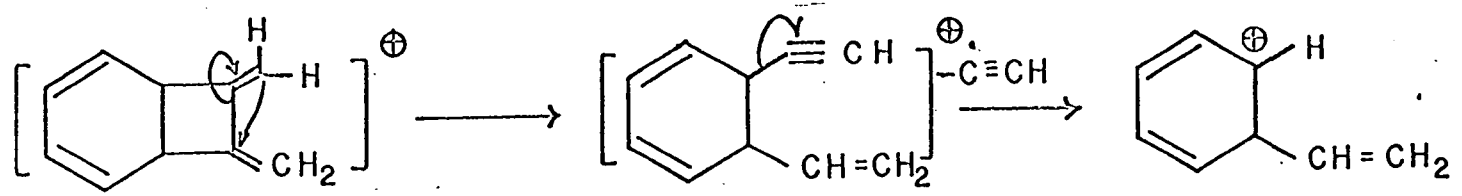
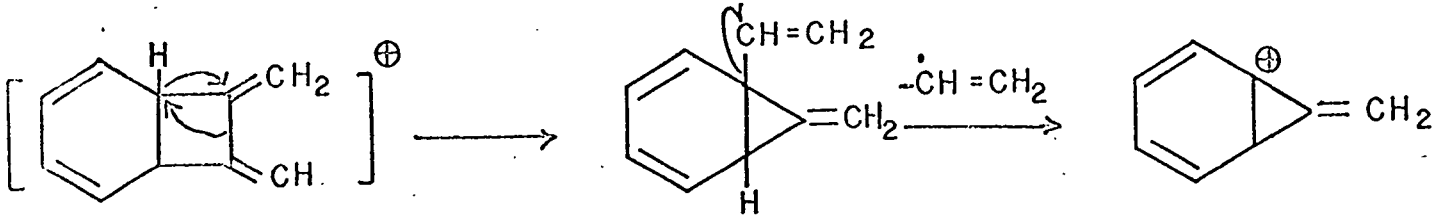


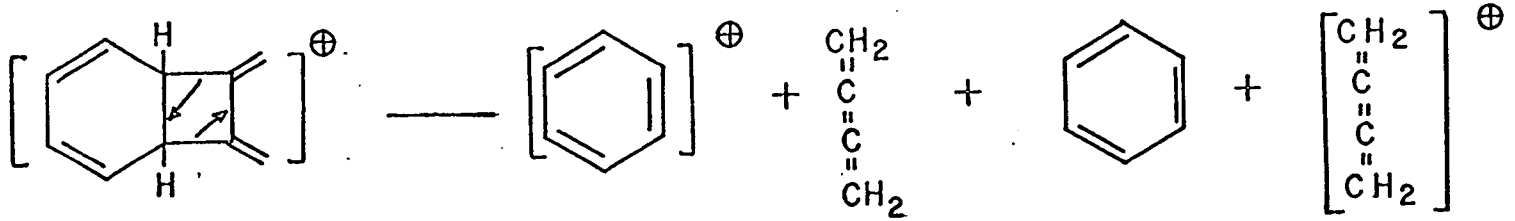
Figure 27. (continued)



M/e 130 M/e 105



M/e 130 M/e 103



M/e 130 M/e 78 M/e 52

Loss of water from 2-hydroxymethyl-1-methylcyclo-octatetraene gave a species of m/e 130 which could have been formulated as XIII or XXVI. A comparison of the mass spectrum of 1,2-dimethylenecyclooctatriene with that of 2-hydroxymethyl-1-methylcyclooctatetraene below m/e 130 shows little in common. The peak at m/e 129 is very small in the alcohol and peaks at m/e 128, 127, 116, 115 and 103 all present in 1,2-dimethylenecyclooctatriene were absent in the alcohol. It seems reasonable then to postulate that the species of m/e 130 in the mass spectrum of 2-hydroxy-methyl-1-methylcyclooctatetraene has the structure XXVI and that the breakdown of 1,2-dimethylenecyclooctatriene involves only the structures XIII and XXVII. It should be noted that XXVII need not be present in equilibrium with XIII under ordinary conditions but could be formed in the mass spectrometer only. Although for convenience almost all of the breakdown patterns are shown starting from structure XXVII, the change to this structure could also occur during the initial breakdown.

It has been shown that 1,3,5-cyclooctatriene when heated to 100°C forms an equilibrium mixture containing 30% of the bicyclo form, 2,4-bicyclo[4.2.0]octadiene (84,85). In 1,2-dimethylenecyclooctatriene, however, the exocyclic methylene groups would tend to destabilize the bicyclo form.

Loss of a hydrogen from structure XXVII gives an allylically stabilized ion and loss of a second proton gives a benzene ring thus accounting satisfactorily for the high

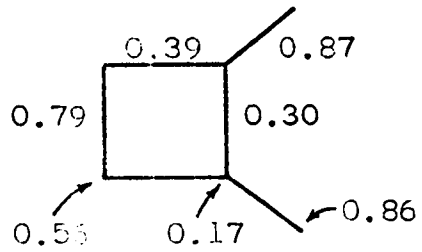
intensity of the peaks at m/e 129 and m/e 128.

An additional piece of evidence regarding the breakdown pattern is a metastable peak (75b) at about m/e 102.6 which shows that the ion of m/e 129 loses CH_2 to give the ion of m/e 115. This does not exclude the formation of the ion of m/e 115 in other ways, however, and a second pathway, starting with the molecular ion is shown.

Molecular orbital calculations on 1,2-dimethylenecyclooctatriene gave the delocalization energy, bond orders and free valences and these are compared with calculations on 1,2-dimethylenecyclobutene and 1,2-dimethylenecyclohexadiene in Fig. 28. These molecules all have substantial delocalization energies which suggests that stabilization through π electron delocalization can occur in the planar form of these structures. On the other hand the high values for the free valences of the exocyclic methylene groups indicates a very high reactivity for these positions. An examination of corresponding bond orders and free valences places 1,2-dimethylenecyclooctatriene in an intermediate position between 1,2-dimethylenecyclobutene and 1,2-dimethylenecyclohexadiene.

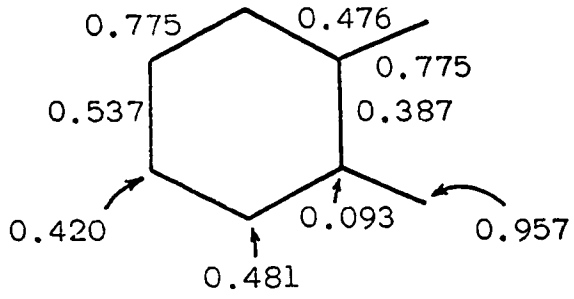
1,2-Dimethylenecyclobutene has the lowest calculated value for the free valence of the exocyclic methylene groups (0.86) so that these positions should be less reactive than the methylene positions in the other two molecules. However,the large angle deformation associated with changing the normal trigonal bond angles of 120° to form a four

D.E.=1.21 β



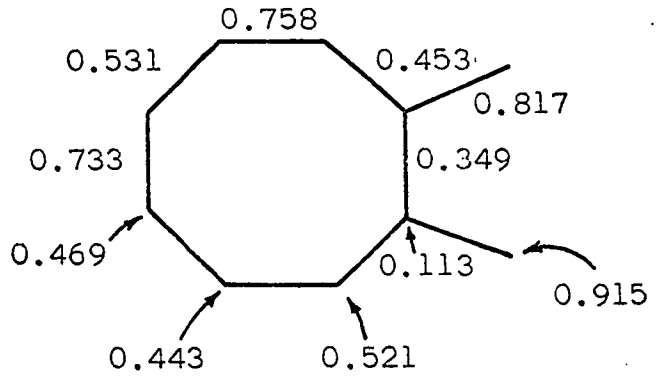
Roberts(61)

D.E.=1.954β



Coulson and Streitwieser(47)

D.E.=2.397β



The numbers opposite bonds are π bond orders.

The arrows designate free valences.

Figure 28. Data from molecular orbital calculations on 1,2-dimethylenecyclobutene, 1,2-dimethylenecyclohexadiene and 1,2-dimethylenecyclooctatriene.

membered ring which has interior angles of 90° would result in a high strain energy. A high degree of thermal stability would thus not be expected. 1,2-Dimethylenecyclobutene was prepared by Blomquist and Maitlis (62) and proved to be sufficiently stable to be isolated in a pure state. However it reacted with air to give a solid oxygen containing polymer and at room temperature it darkened and polymerized rapidly even when kept under nitrogen. In contrast to this behaviour 1,2-dimethylenecyclobutane formed a polymer only after standing several months at room temperature (86).

1,2-Dimethylenecyclohexadiene has an extremely high value for the free valence of the exocyclic methylene groups (0.957) indicating extreme reactivity for this molecule. This is borne out by the fact that although there is good evidence for its formation in several reactions it has never been isolated (66).

Planar 1,2-dimethylenecyclooctatriene has a value of 0.915 for the free valence of the exocyclic methylene groups, a value which is intermediate between 1,2-dimethylenecyclohexadiene (0.957) and 1,2-dimethylenecyclobutene (0.86). In contrast to 1,2-dimethylenecyclobutene, however, which is very strained 1,2-dimethylenecyclooctatriene should be able to attain a structure of much lower strain by buckling of of the ring.

In extremely dilute solution 1,2-dimethylenecyclooctatriene shows no detectable decomposition even after refluxing for eight hours in hexane (b.p. 68°C) provided

that oxygen is vigorously excluded. In the absence of solvent, however, polymerization occurs slowly at -15°C and very rapidly at room temperature to give a glassy insoluble polymer. The reaction with oxygen (air) is very fast giving first a heavy oil and then a white solid polymer. The infrared spectrum of a sample on salt plates, which was exposed to air for 15 seconds, contained a major peak at 1725cm^{-1} (C=O). Exposure to air for 5 minutes resulted in the complete disappearance of all olefinic peaks in the infrared spectrum.

The π system of 1,2-dimethylenecyclooctatriene offers a wide range of possibilities for attack by a dienophile such as tetracyanoethylene. A variety of products resulting from 1,2 addition, 1,4 addition and 1,6 addition can be formulated.

It is of interest to compare 1,2-dimethylenecyclooctatriene with other π systems in their behaviour toward dienophiles. The products obtained from the reaction of a number of unsaturated systems with a variety of dienophiles is shown in Fig. 29.

1,2-Dimethylenecyclobutane reacts readily with N-phenylmaleimide and maleic anhydride to give the normal Diels-Alder products XXIX and XXX respectively (86). 1,2-Dimethylenecyclobutene could give the Diels-Alder adduct in the same way but the product would then be a highly strained cyclobutadiene. With the very reactive tetracyanoethylene a product is obtained, with some difficulty. This product results from 1,2 addition across one of the exocyclic

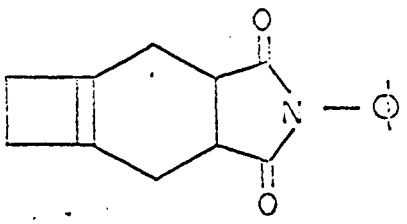
double bonds and gives the spiro structure XXXI with 3,4-diphenyl-1,2-dimethylenecyclobutene (63) and XXXII with 3,4-dimethyl-1,2-dimethylenecyclobutene (65,87).

Tetramethylenecyclobutane possesses a very attractive structure for 1,4 addition and in fact gives a normal Diels-Alder product XXXIII which is a dimethylenecyclobutene (65). This product could not, however, be induced to add another molecule of tetracyanoethylene.

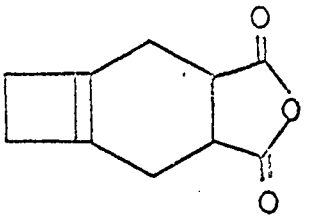
In contrast to 1,2-dimethylenecyclobutene, the 1,2-dimethylenecyclohexadiene structure is particularly favourable for 1,4 addition across the exocyclic methylene groups because the resulting product would have a benzene ring. The reaction of N-phenylmaleimide with 1,2-dimethylenecyclohexadiene gives XXXIV (66).

A rather surprising adduct is the one obtained from the reaction of tetracyanoethylene with cyclo$^{\text{II}}$octa[c]furan (XXXV) (79). The ultraviolet spectrum of cyclo$^{\text{II}}$octa[c]furan indicates a lack of conjugation which is probably a result of buckling of the ring in a manner similar to cyclo$^{\text{II}}$octatetraene. This structure does not offer the coplanarity of two double bonds usually considered necessary for Diels-Alder addition to occur. It is possible that some loose association or π complex of tetracyanoethylene with cyclo$^{\text{II}}$octa[c]furan results in a geometry change in the latter.

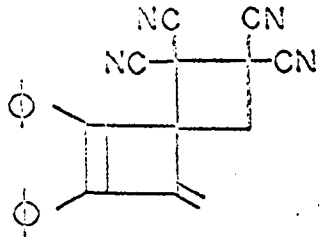
The reaction of tetracyanoethylene with 1,2-dimethylenecyclo$^{\text{II}}$octatriene gave a brown solid material in good yield (74%). Unfortunately decomposition occurred



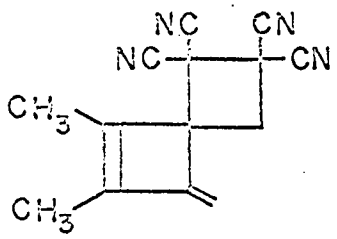
XXIX



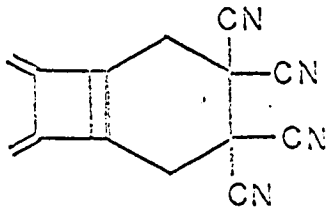
XXX



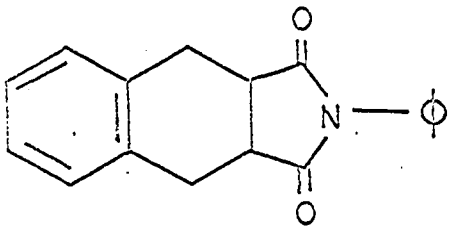
XXXI



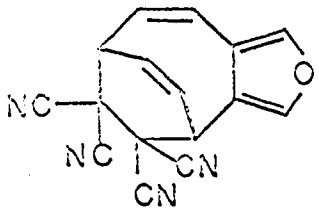
XXXII



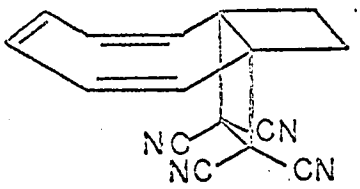
XXXIII



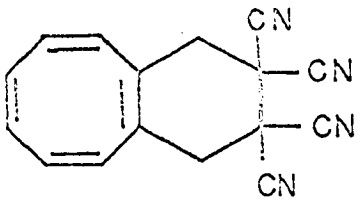
XXXIV



XXXV



XXXVI



XXXVII

Figure 29. A series of dienophile-diene adducts.

on attempted purification using thin layer chromatography. so that some data, principally the n.m.r. spectrum was obtained on the unpurified material only. The structural evidence obtained seems to be best explained by the formation of two products XXXVI and XXXVII. The product, from a preparation in which 1,2-dimethylenecyclooctatriene was in excess, was sublimed to give a small amount of a white crystalline material with m.p. 145°C. The ultraviolet spectrum had a single absorption at 209mμ. This suggests that neither a cyclooctatriene nor a cyclooctatetraene structure is present although conversion to a bicyclo form might have occurred during sublimation. The mass spectrum gave a very weak peak at m/e 258 consistent with a 1:1 adduct and the bulk of the spectrum consisted of peaks below m/e 130. This is expected for any adduct which has two allylic bonds. These bonds should rupture easily giving the original reactants. The spectrum below m/e 130 contained all of the peaks present in the mass spectrum of 1,2-dimethylenecyclooctatriene and with about the same relative intensities. Thus the nature of the product as an adduct of tetracyanoethylene and 1,2-dimethylenecyclooctatriene is confirmed.

The infrared spectrum obtained on unpurified product had bands at 2260cm^{-1}, 2205cm^{-1} (C≡N stretch), 3010cm^{-1} (C=CH stretch), 1630cm^{-1}, 1580cm^{-1} (C=C stretch) and 860cm^{-1} (C=C-H bend). The C=C stretch region is similar to that in cyclooctatriene and cyclooctatetraene.

The n.m.r. spectrum taken on unpurified product showed that the exocyclic methylene groups were no longer present. This does not require that reaction occur only at these positions, however, since a change in the geometry of the ring could destabilize the dimethylene form resulting in formation of a four membered ring. An attempt to determine if the addition of tetracyanoethylene occurred at the same rate as the disappearance of the exocyclic methylene groups was unsuccessful because the reaction was extremely fast, even at 0°C.

In the n.m.r. spectrum the olefinic region consisted of a multiplet centered at 4.09τ (relative intensity 4.1). There were two peaks, both singlets, which can be assigned to allylic protons, at 6.90τ (relative intensity 1.0) and at 7.01τ (relative intensity 1.8). The intensity of the olefinic region relative to the sum of the intensities of the two peaks in the allylic region is 6.0 to 4.1.

It appears difficult to accommodate all of the data in one structure and so it was concluded that the two products XXXVI and XXXVII were formed.

Compound XXXVII results from the 1,4 addition of tetracyanoethylene to the two exocyclic double bonds of 1,2-dimethylenecyclooctatriene. This is the most favourable mode of reaction since the two exocyclic double bonds form a planar or almost planar system necessary for reaction with a dienophile and the product formed has a cyclooctatetraene ring which should be fairly strainless. The fusion of a six

membered ring to cyclo[8]octatetraene should result in little additional strain. For these reasons this structure was assigned to the major component which consisted of about 60% of the material isolated, as shown by the n.m.r. integration.

The methylene groups have the highest calculated free valences and so these positions are the most reactive and XXXVII would again be the expected product. However the MO calculations were performed on planar 1,2-dimethylene-cyclo[8]octatriene and spectral data show that it is not planar. It is not known whether a valid analogy can be drawn in such a case.

The second product obtained, XXXVI, results from the 1,2 addition of tetracyanoethylene to the carbons bearing the dimethylene groups. Such a product could arise in various ways. One possibility is that there is a mobile equilibrium between the 1,2-dimethylenecyclo[8]octatriene structure and a small amount of the bicyclo structure 1 (8), 2,4,6-bicyclo [6.2.0]decatetraene XXVI. XXXVI is a likely product from the reaction of tetracyanoethylene with compound XXVI. Attempts to prepare XXVI by the irradiation of 1,2-dimethylenecyclo-[8]octatriene were unsuccessful. This could be because structure XXVI is so unfavourable that it is not formed on photolysis or if it is formed it quickly polymerizes. On the other hand it could be because when formed it rapidly reverts to the 1,2-dimethylenecyclo[8]octatriene structure thus supporting the mobile equilibrium idea.

Unfortunately the mass spectral evidence suggests that 1,2-dimethylenecyclo"octatriene and XXVI do not readily interconvert. Structure XXVI, which was postulated to have been formed by loss of water from 2-hydroxymethyl-1-methyl-cyclo"octatetraene, has a totally different breakdown pattern from 1,2-dimethylenecyclo"octatriene. This would be unlikely to occur if the two structures were in equilibrium with each other.

There is a feature of the reaction of tetracyanoethylene with 1,2-dimethylenecyclo"octatriene which was not previously mentioned. Even when the reactants were added together at -80°C a deep green colour and a solid suspension were immediately produced. After standing for a short time at room temperature or warming for a few minutes the reaction mixture changed to a clear yellow solution. This immediate colouration indicates that a π complex may be first formed in the reaction. If this is the case then the two products could arise from one intermediate. The tetracyanoethylene could interact with the two exocyclic double bonds forming a complex which would break down to give the two products. The more stable product XXXVII would be expected to be formed in larger yield.

Part II

The Synthesis of Some Bicyclo[6.2.0]decanes

Introduction

A wide variety of synthetic methods is available for the preparation of cyclobutanes. Many of these methods can be applied to the synthesis of bicyclic compounds containing a four membered ring. Bicyclic compounds in which a four membered ring is fused to a four, five or six membered ring are, in fact, readily accessible. However, those compounds which have a cyclobutane ring fused to a ring containing seven or more carbons are uncommon.

Since the various general methods of synthesis have had wide application only a few examples will be used to illustrate each method.

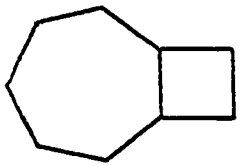
A. Ring Closure

Cycloalkanes with two suitable groups on adjacent carbon atoms can be cyclized to give bicyclic structures having a fused cyclobutane ring. Either the cyclobutane ring or the other ring can be formed by the ring closure.

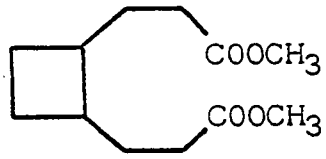
Allinger and co-workers prepared bicyclo[5.2.0] nonane (XXXVIII) with both *cis* and *trans* ring fusions, using a ring closure method (88).

The *trans* compound was prepared by the treatment of 1,2-bis(3-methylpropanoate) cyclobutane (XXXIX) with sodium hydride to give 3-carbomethoxy-4-keto-bicyclo [5.2.0]nonane. This was hydrolyzed to the keto acid,

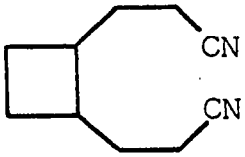
decarboxylated, and the keto group removed by the Wolff-Kishner reaction to give the parent hydrocarbon. The cis compound was obtained by cyclization of 1,2-bis(2-cyanoethyl)) cyclobutane (XL). Treatment with lithium methylphenylamide gave the imino nitrile which could be hydrolyzed to the keto acid and then converted to cis-bicyclo[5.2.0] nonane by the same sequence used for the trans compound.



XXXVIII



XXXIX

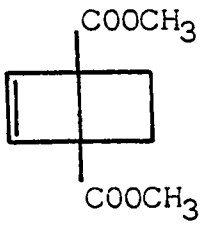


XL

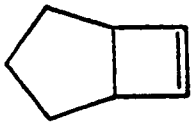
B. Photochemical Reactions

Many cyclic olefins isomerize to bicyclic forms when irradiated with ultraviolet light. For example 1,4-dicarbomethoxy-1,2-hexadiene in the presence of diazomethane is readily converted into 1,4-dicarbomethoxybicyclo[2.2.0]hex-2-ene (XLI) (89). Bicyclo[3.2.0]hept-6-ene (XLII) can be obtained in 42% yield by the irradiation of 1,2-cycloheptadiene (90) and bicyclo[4.2.0]oct-7-ene (XLIII) can be obtained in 9% yield from 1,3-cyclooctadiene (91).

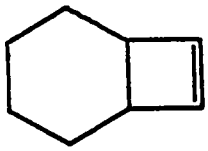
The photolysis of some cyclic ketones also results in the formation of bicyclic compounds.



XLI

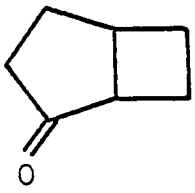


XLII

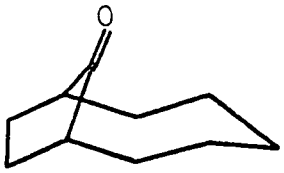


XLIII

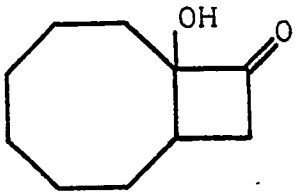
Some bicyclic ketones lose carbon monoxide on irradiation. Bicyclo[3.2.0]pentan-3-one (XLIV) loses carbon monoxide to give bicyclo[2.2.0]hexane (92) and bicyclo[5.2.1] decan-10-one (XLV) gives bicyclo[5.2.0]nonane (93).



XLIV



XLV

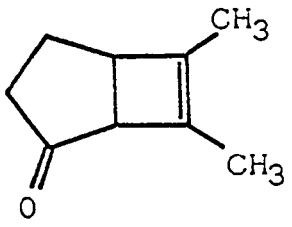


XLVI

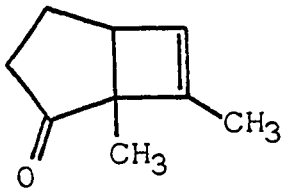
Photolysis of 1,2-decanedione gives a 74% yield of 1-hydroxybicyclo[6.2.0]decan-10-one (XLVI) (94). The high yield in this reaction makes it an excellent entry into the bicyclo[6.2.0]decane system.

Many unsaturated cyclic ketones can be sufficiently activated by ultraviolet radiation so that simple unsaturated compounds will add to them. Cyclopenten-3-one on ultraviolet

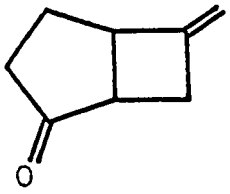
irradiation will add 2-butyne to give 6,7-dimethylbicyclo [3.2.0]hept-6-en-2-one (XLVII) along with some of the rearranged product 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one (XLVIII) (95).



XLVII



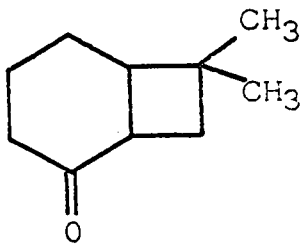
XLVIII



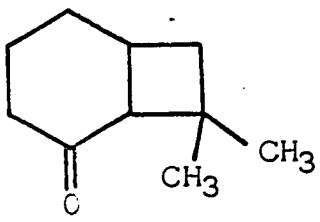
XLIX

Allene also adds to cyclopenten-3-one under photo excitation to give 6-methylenebicyclo[3.2.0]heptan-2-one (XLIX) as well as a small amount of the isomeric 7-methylene-bicyclo[3.2.0]heptan-2-one (95).

Another reaction of this type is the one used by Corey, Mitra and Uda in the synthesis of caryophyllene (96). This involved the addition of isobutylene to cyclohexen-3-one at -40°C under ultraviolet radiation to give 7,7-dimethyl-bicyclo[4.2.0]octan-2-one (L). None of the isomeric 8,8-dimethylbicyclo[4.2.0]octan-2-one (LI) was obtained.



L

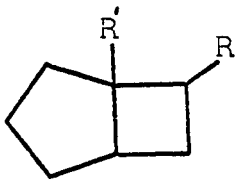


LI

Later ring expansion gave the bicyclo[7.2.0]undecane structure possessed by caryophyllene and isocaryophyllene.

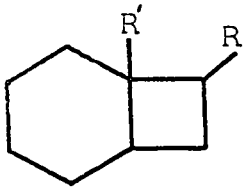
C. Thermal Cycloadditions

A new and quite versatile thermal cycloaddition reaction is that between unsaturated compounds and enamines. Enamines can be easily prepared by the reaction of secondary amines with ketones under suitable conditions, usually acid catalysis with some provision for removing water as it is formed (97). Methyl propenoate readily adds to the dimethylamine enamines of cyclopentanone and cyclohexanone to give 1-N,N-dimethylamino-7-carbomethoxybicyclo [3.2.0]heptane (LII) and 1-N,N-dimethylamino-8-carbomethoxybicyclo[4.2.0]octane (LIII) respectively (98).

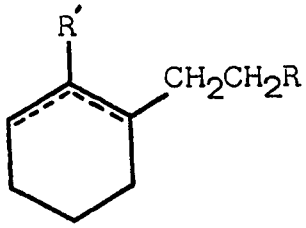


LII

R = $COOCH_3$



LIII



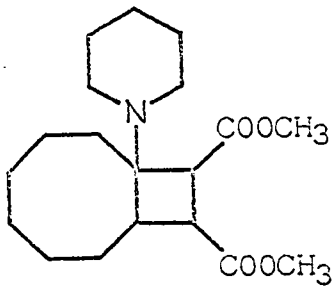
LIV

R' = $N(CH_3)_2$

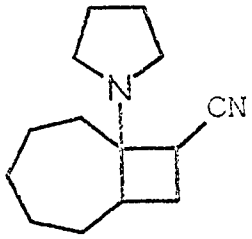
The reaction is readily reversible, but the products can be converted to stable alcohols with lithium aluminum hydride. Some of the Stork alkylation product, for example LIV, is also formed, but after reduction with lithium aluminum hydride it can be hydrolyzed in aqueous acid to the keto alcohol which can then be easily separated.

Piperidine enamines prepared from various cyclic ketones were found to add diethyl maleate rapidly in acetonitrile to give cyclobutane adducts. Ketones with ring sizes up to eight were used to get adducts of the type LV shown for the product obtained from cyclooctanone (98).

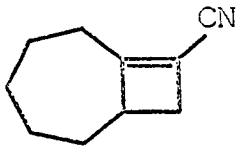
Fleming and Harley-Mason were able to add acrylonitrile to the pyrrolidine enamines prepared from cyclopentanone, cyclohexanone and cycloheptanone to get products of the type LVI shown for cycloheptanone (99).



LV



LVI



LVII

In the case of the bicyclo[5.2.0]nonane and the bicyclo[4.2.0]octane derivatives they were able to remove the amine with a Hofmann pyrolysis reaction and so get an unsaturated nitrile of the type LVII obtained from LVI.

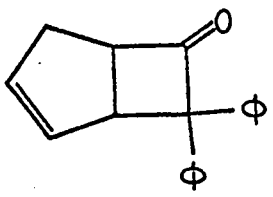
Although fluorinated unsaturated compounds have been used in the synthesis of large numbers of cyclobutanes (100) there has been little application to the synthesis of bicyclic compounds because many of the products are not useful for further synthetic work. A reaction which is of

importance is the addition of tetrafluoroethylene to cyclopentadiene to give 6,6,7,7-tetrafluorobicyclo[3.2.0] hept-2-ene. This product is of particular interest because of its easy conversion to tropolone (101).

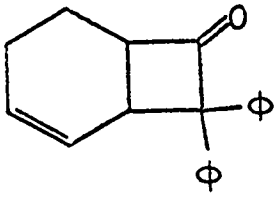
Historically the most important of the thermal cycloaddition reactions is the addition of ketenes to cyclic olefins. In fact, until the recent development of photochemical methods, this could be considered the most important synthesis of bicyclic compounds containing cyclobutane rings.

Staudinger and Suter obtained 7,7-diphenylbicyclo [3.2.0]hept-2-en-6-one (LVIII) by the addition of diphenylketene to cyclopentadiene (102) although the complete structure was not established until later (103). Diphenylketene also adds to 1,3-cyclohexadiene to give the corresponding adduct 8,8-diphenylbicyclo[4.2.0]oct-2-en-7-one (LIX). Reaction with cyclopentene (103) and cyclohexene (102) occurs to give products which are the reduced forms of LVIII and LIX respectively.

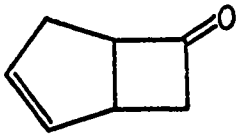
Unsubstituted ketene is less reactive to addition reactions and has a greater tendency to dimerize than the diphenyl derivative. Ketene does react at elevated temperature (100°C) in toluene to give cyclobutanones with cyclopentadiene (LX) (104) and cyclohexadiene (105). The yield from the reaction of ketene with cyclohexadiene is very low (3%), however, so that this is not a good method for the preparation of this bicyclic system.



LXVIII



LIX



LX

Experimental

A. Analytical Instruments

1) Melting points were determined on a Gallenkamp Capillary Melting Point apparatus model MF-370, manufactured by A.C. Gallenkamp and Company Ltd., London, England.

2) Infrared spectra were measured as liquid films on the Infracord Spectrometer Model 137, manufactured by Perkin-Elmer, Norwalk, Connecticut.

3) Nuclear magnetic resonance spectra were obtained in solution as noted, using tetramethylsilane as an internal standard. The instrument was a Varian V-4302 high resolution spectrometer operating at 60 Mc/s. The manufacturer was Varian Associates, Palo Alto, California.

4) Analyses were performed by Midwest Microlab Inc., Indianapolis, Indiana.

5) The Vapour Phase Chromatograph Instruments used were the following:

a) Vapor Fractometer Model 154, Perkin-Elmer Corporation, Norwalk, Connecticut.

b) Pye-Argon Chromatograph, N.G. Pye and Company Limited, Cambridge, England.

B. Preparative Instrument

Ketene was prepared by the pyrolysis of acetone vapour by a hot wire. The apparatus was patterned after

that shown in a ketene review article by Hanford and Sauer (106). An important modification was the use of quartz rods in the center of the wire coils to keep them in place.

C. Synthetic Procedures

3-Bromocyclooctene

Anhydrous hydrogen bromide was bubbled slowly through 1,3-cyclooctadiene (278.8 g., 2.58 moles) until 202.8 g. (2.50 moles) was absorbed. The product, purified by distillation through a Vigreux column (2.5 cm. x 35 cm.), amounted to 378.0 g. (80%) with b.p. 84-87°C at 9 mm. pressure.

The boiling point reported in the literature was 79° at 5 mm. (107).

The product gave an immediate precipitate when shaken with aqueous silver nitrate solution.

3-Dimethylaminocyclooctene

To 3-bromocyclooctene (378 g., 2.00 moles) in toluene (600 ml.), cooled to -78°C, was added dimethylamine (270 g., 6.0 moles). The solution was permitted to warm to room temperature and it was left at this temperature for 48 hours. The toluene solution was extracted with 3N hydrochloric acid (3 x 300 ml.), the combined extracts were warmed for five minutes and then extracted with ether (3 x 200 ml.) which was discarded. The aqueous solution was made basic with 6N sodium hydroxide solution and then

extracted with ether (3 x 300 ml.). The combined ether extracts were dried over sodium hydroxide, filtered, and the ether removed on the flash evaporator. The product was purified by distillation through a Vigreux column (2.5 cm. x 35 cm.) to give the amine (233 g., 76%) b.p. 70.5-71.5°C at 5 mm.

The picrate, recrystallized from methanol-acetone had m.p. 211-212°C. The melting point reported in the literature was 208.6-209°C d.(107).

3-N,N,N-trimethylaminocyclooctene iodide

To 3-dimethylaminocyclooctene (230 g., 1.50 moles) in cyclohexane (1.0 l.) was added, with rapid stirring, methyl iodide (213 g., 1.50 moles). After one hour the product was collected on a Buchner funnel and washed with cyclohexane (2 x 250 ml.). To the combined cyclohexane solution and washings was added additional methyl iodide (71 g., 0.50 moles) and the solution was refluxed for three hours. The product which separated was filtered off and combined with the first portion to give a total yield of 407 g. (92%) m.p. 190-192°C. The reported melting point was 184.2-185°C (107).

cis,trans-1,3-Cyclooctadiene

A solution of 3-N,N,N-trimethylaminocyclooctene iodide (35 g., 0.12 moles) in water (200 ml.) was stirred one hour with silver oxide (32.4 g., 0.12 moles). The mixture was filtered and the filtrate was concentrated to 50 ml.

on the flash evaporator using a bath temperature of 45°C. The quaternary base was decomposed under nitrogen at 35 mm. pressure using a free flame and the distillate was collected in a trap cooled in dry ice-acetone. Pentane (100 ml.) was added to the distillate; the pentane layer was isolated and washed with 10% hydrochloric acid (75 ml.), 5% sodium bicarbonate (75 ml.) and water (75 ml.). The pentane solution was then shaken for 5 minutes with 100 g. of 20% aqueous silver nitrate solution. The aqueous layer was separated and kept at 0°C overnight. A few crystals of the complex formed; these were separated and the melting point was found to be 127-129°C (sealed tube). The melting point reported in the literature was 126-127.5°C (108).

To the cooled silver nitrate solution was added concentrated ammonium hydroxide (25 ml.) and the product was extracted with pentane (2 x 25 ml.). The pentane extracts were dried over magnesium sulfate for one hour, filtered, and the pentane removed by distillation. The residue was distilled to give the product (0.92 g., 7%), b.p. 32°C at 4 mm. pressure.

When cis,trans-1,3-cyclooctadiene was prepared for use in the reaction with ketene it was not separated from the cis,cis-1,3-cyclooctadiene. The amount of cis, trans-1,3-cyclooctadiene in the mixture was roughly estimated from the infrared spectrum of the mixture. cis, trans-1,3-Cyclooctadiene has a distinctive peak at 955 cm^{-1} and cis,cis-1,3-cyclooctadiene has a distinctive peak at 915 cm^{-1}.

trans-Bicyclo[6.2.0]dec-2-en-9-one

3-N,N,N-trimethylaminocyclooctene iodide (40.0 g., 0.136 moles) was converted to the quaternary hydroxide using silver oxide (36.7 g., 0.136 moles) and the quaternary hydroxide was then pyrolyzed to cis,trans-1,3-cyclooctadiene following the procedure previously described. In a typical reaction the yield of combined dienes was 11.3 g. (77%). The amount of 1,3-cyclooctadiene in this mixture was about 4.6 g. (40% of the mixture) as estimated from the infrared spectrum. The yield of cis,trans-1,3-cyclooctadiene, based on the iodide, was about 30%. The mixed 1,3-cyclooctadienes dissolved in nitromethane (80 ml.) were placed in a glass pressure bottle (soda bottle) equipped with a drying tube and cooled to -78°C in dry ice-acetone. To the cooled pressure bottle twice distilled ketene (2.5 ml.) dissolved in ether (20 ml.), also at -78°C, was added. The bottle was sealed, allowed to warm to room temperature, shaken well, and then allowed to stand overnight. The yield from five reactions was combined, the ether was removed on the flash evaporator, and the residue was extracted with pentane (500 ml.) in a continuous extractor for 48 hours. The pentane solution was extracted with water (3 x 200 ml.), dried over anhydrous magnesium sulfate, and the pentane removed by distillation through a glass helix packed column (1.3 x 6.0 cm.) to give the product (14.90 g., 23% based on cis,trans-1,3-cyclooctadiene or 7% based on the iodide), b.p. 74-76°C at 0.5 mm. pressure,

n_D = $1.5023^{20°}$ and specific gravity 1.0127.

Calculated for $C_{10}H_{14}O$: C, 79.95; H, 9.39.

Found: C, 80.13; H, 9.04.

The analytical sample was obtained by decomposition of the semicarbazone derivative and was actually a mixture of cis and trans fused ketones. The semicarbazone derivative was prepared by a standard procedure and purified by recrystallization from ethanol, giving m.p. 212-213°C (dec).

Calculated for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27.

Found: C, 63.94; H, 8.36.

cis-Bicyclo[6.2.0]dec-2-en-9-one

trans-Bicyclo[6.2.0]dec-2-en-9-one (2.08 g., 0.138 moles) dissolved in pentane (400 ml.) was passed through a water cooled (5°C) column (2 x 26 cm.) packed with basic alumina (Merck, pH 10.0-10.5). This was followed by pure pentane (400 ml.). The pentane was removed from the combined eluate by distillation through a column (2.5 x 15 cm.) packed with glass helices. Evaporative distillation of the residue at 100°C and 8 mm. pressure gave the product (1.54 g., 74%), n_D = $1.5028^{20°}$ and specific gravity 1.0137. The semicarbazone, purified by recrystallization from ethanol, had m.p. 200-201°C.

Calculated for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27.

Found: C, 63.87; H, 8.40.

The mixed melting point of the semicarbazone of the cis and trans ketones was 178-182°C.

Bicyclo[6.2.0]dec-9-one

A solution of trans-bicyclo[6.2.0]dec-2-en-9-one (3.70 g., 0.0246 moles) in ethanol (20 ml.) was added to prereduced platinum oxide (0.125 g.) in ethanol (10 ml.). Hydrogen was introduced and the mixture was shaken until uptake of hydrogen stopped. 102% of one molar equivalent of hydrogen was absorbed. The catalyst was filtered off, the ethanol was removed on the flash evaporator, and the residue was distilled to give the product (2.96 g., 80%) b.p. 70-72°C at 0.9 mm. pressure.

Calculated for $C_{10}H_{16}O$: C, 78.89; H, 10.59.

Found: C, 78.82; H, 10.30.

Bicyclo[6.2.0]dec-2-ene

trans-Bicyclo[6.2.0]dec-2-en-9-one (2.28 g., 0.0152 moles), potassium hydroxide (2.53 g.) and 85% hydrazine hydrate (2.03 ml.) were dissolved in bis(2-hydroxyethyl) ether (20 ml.). This solution was refluxed for ½ hour and then material was distilled off until the internal temperature rose to 230°C. The distillate was extracted with pentane (10 ml.) and the extracts were retained. The reaction was refluxed for 1½ hours after which water (50 ml.) was added and the product was extracted with pentane (2 x 25 ml.). These pentane extracts were combined with the extract from the distillate and passed through a column (1.0 x 10 cm.) packed with neutral alumina (Fluka) which was further eluted with pentane (25 ml.).

The pentane solution was dried over anhydrous magnesium sulfate, filtered, the pentane removed by distillation and the product obtained by evaporative distillation at 45°C at 10 mm. pressure into a cooled (0°C) receiver. The yield was 1.14 g. (55%).

Calculated for $C_{10}H_{16}$: C, 88.16; H, 11.84.
Found: C, 88.06; H, 11.77.

Dehydrogenation of Bicyclo[6.2.0]dec-2-ene

The dehydrogenation apparatus operated at reduced pressure (30 mm.) with the reactant swept through by nitrogen and the product collected in a receiver cooled in dry ice-acetone. The catalyst bed was 1.5 x 5.0 cm. and consisted of rhodium (0.5%) on alumina pellets. Bicyclo[6.2.0]dec-2-ene (0.10 g., 0.74 millimoles) was swept through the catalyst, which was heated to 400°C, and the product was collected in the cooled (-78°C) receiver. The product consisted mainly of unchanged starting material and a small amount of an intense blue substance.

Table VI: Infrared Spectra

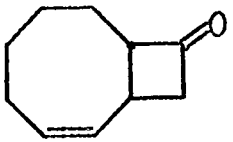
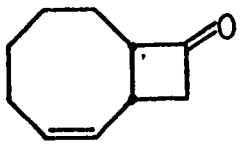
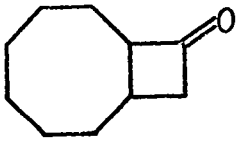
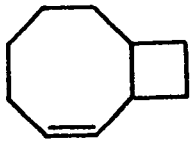
Compound	Function	Type of Vibration	Absorption cm-1	Remarks	Spectrum Page Number
 (trans)	C=C-H	stretch	3005	The spectrum was taken neat as a thin film	127
	C-H(CH_2)	stretch	2930		
	C-H(CH_2)	stretch	2880		
	C=O	stretch	1770 1700		
	C=C	stretch	1650		
			1445, 1185 1145, 1125 1015, 788 742, 726 680		
 (cis)	C=C-H	stretch	3005	The spectrum was taken neat as a thin film	127
	C-H	stretch	2940		
	C-H	stretch	2870		
	C=O	stretch	1775 1700		

Table VI (continued): Infrared Spectra

Compound	Function	Type of Vibration	Absorption cm-1	Remarks	Spectrum Page Number
(cont'd)	C=C	stretch	1650 1450, 1105 1075, 960 865, 842 820, 785 750, 700		
	C-H C-H C=O	stretch stretch stretch	2985 2860 1170	The spectrum was taken neat as a thin film	128
	C=C-H C-H C-H C=C	stretch stretch stretch stretch	3030 2920 2880 1650 1445, 1255 1090, 1020 805, 755 745, 702	The spectrum was taken neat as a thin film	128

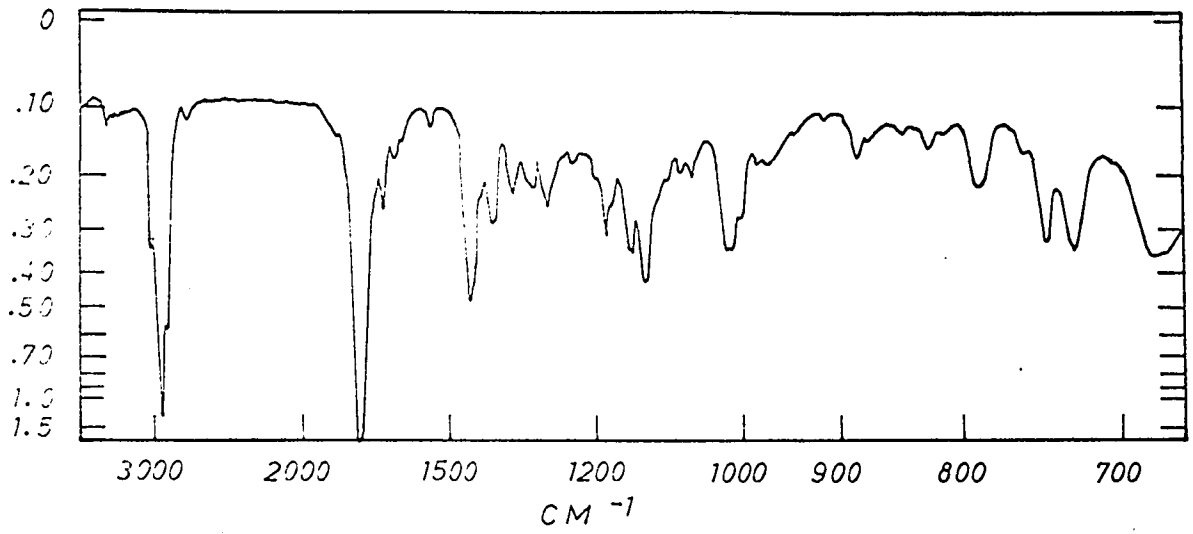


Figure 30. The infrared spectrum of trans-bicyclo[6.2.0] dec-2-en-9-one.

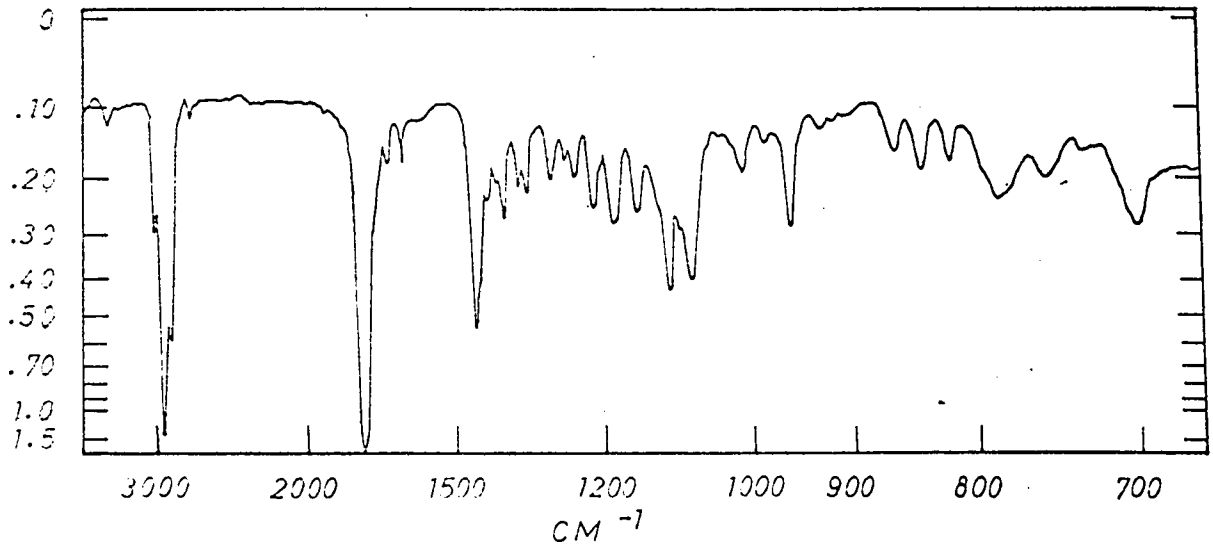


Figure 31. The infrared spectrum of cis-bicyclo[6.2.0] dec-2-en-9-one.

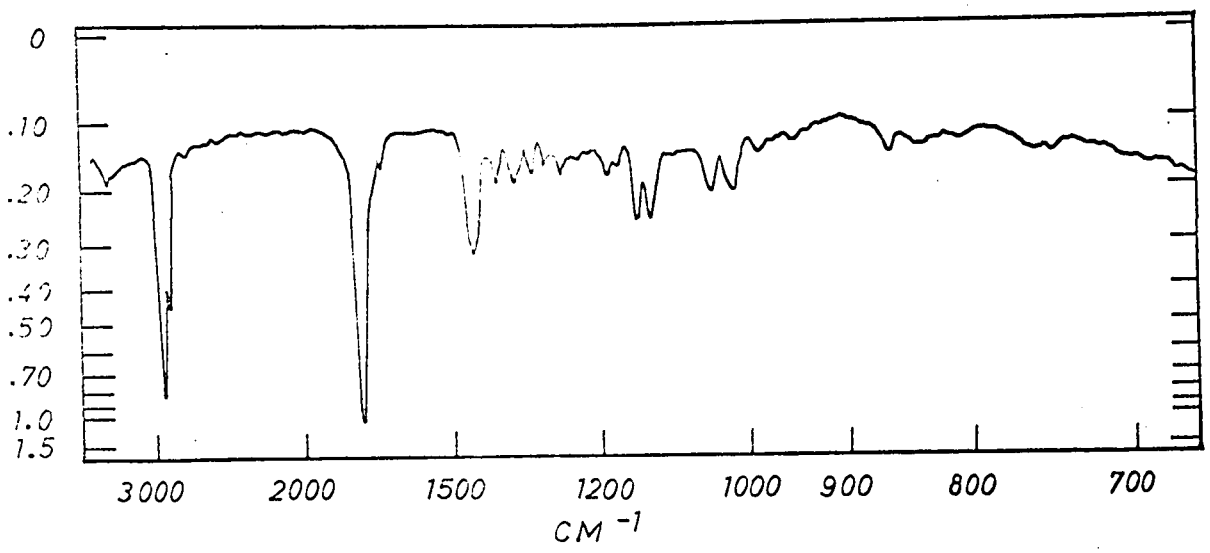


Figure 32. The infrared spectrum of bicyclo[6.2.0] dec-9-one.

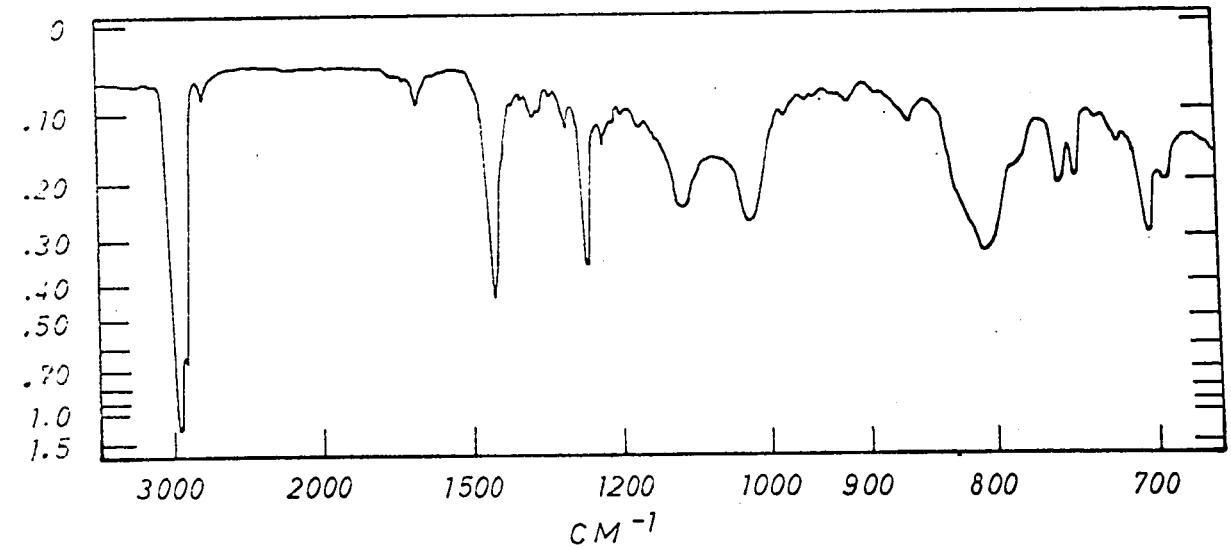
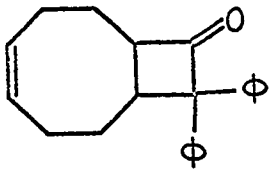


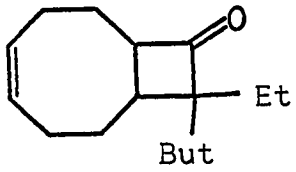
Figure 33. The infrared spectrum of bicyclo[6.2.0] dec-2-ene.

Discussion

At the time this work was started only one synthesis of a fused eight and four membered ring system had been achieved. Ziegler and co-workers treated cis,trans-1,5-cyclooctadiene with diphenylketene at -40°C to get 10,10-diphenylbicyclo[6.2.0]dec-4-en-9-one (LXI) (109).



LXI



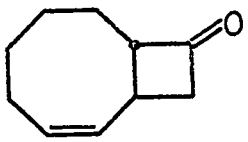
LXII

More recently it has been found that butylethylketene adds, at elevated temperatures (150-180°C), to cyclooctene and to cis,cis-1,5-cyclooctadiene to give adducts of the type (LXII) shown for cis,cis-1,5-cyclooctadiene (110). Under the same conditions cis,cis-1,5-cyclooctadiene also gave some product in which addition took place to both double bonds. Only the di-adduct was obtained when cis,cis-1,3-cyclooctadiene was treated with butylethylketene at 150°C.

The addition of unsubstituted ketene to an unsaturated eight membered ring might appear to be a suitable means of synthesizing an unsubstituted bicyclo[6.2.0]decane ring system. Unfortunately ketene readily dimerizes and is much less reactive in addition reactions than its dialkyl and diphenyl analogues. The attempted addition of ketene to cis, cis-1,3-cyclooctadiene at 100°C in toluene failed. This is

not surprising since addition to 1,3-cyclohexadiene under the same conditions gave only a 3% yield (105). Apparently dimerization of the ketene proceeds at a faster rate than addition. An attempt to induce addition by photo-excitation also was unsuccessful. The reaction was performed by bubbling ketene through an ethyl ether solution of cis,cis-1,3-cyclooctadiene as it was being irradiated by ultraviolet light. One difficulty may have been the possibility that the concentration of ketene present in the solution at a given time was very low.

It seemed that a very reactive olefin would be necessary, so cis,trans-1,3-cyclooctadiene was synthesized and in fact was found to react with ketene. The product, as will be subsequently shown, can be best formulated as trans-bicyclo[6.2.0]dec-2-en-9-one (LXIII).



LXIII

The cis,trans-1,3-cyclooctadiene used in the reaction was prepared from 3-bromocyclooctene by the same procedure used by Cope and co-workers (107,108). 3-Bromocyclooctene was converted to 3-N,N-dimethylaminocyclooctene, which was subjected to Hofmann degradation to give the cis, trans diene. The 3-bromocyclooctene was prepared by the addition of hydrogen bromide to cis,cis-1,3-cyclooctadiene,

using a procedure patterned after the preparation of 3-chloropentene from cyclopentadiene (111). Vapour phase chromatography indicated that a single product had been formed. When the product was shaken with aqueous silver nitrate a precipitate formed immediately. This indicated that bromine had entered at the allylic 3-position.

For the reaction with ketene the cis,trans-1,3-cyclooctadiene was not separated from the cis,cis-1,3-cyclooctadiene also formed in the Hofmann degradation but the amount was roughly estimated from the infrared spectrum of the mixture. The reaction was performed by adding ketene in ether at -80°C to a cooled nitromethane solution of the two dienes. Nitromethane was chosen as a solvent because it had been shown that in the reaction of tetracyanoethylene with 4-methyl-1,3-pentadiene the formation of a cyclobutane structure was favoured by polar solvents. In fact in nitromethane the reaction gave only cyclobutane formation and no product resulting from 1,4 addition (112). It was more convenient, however, to add the ketene (b.p. -56°C) in ether solution since nitromethane freezes at -29°C. The product was first isolated through the semicarbazone derivative which was decomposed in aqueous solution with phthalic acid. However, vapour phase chromatography showed that two components were present in the product and it was suspected that isomerization might have occurred during isolation. Consequently the product was instead isolated by continuous extraction with pentane. The product obtained in this manner

showed only one of the two components previously observed by vapour phase chromatography.

Microanalysis showed that one molecule of ketene added to the 1,3-cyclooctadiene. Attempts to add ketene to cis,cis-1,3-cyclooctadiene under identical conditions and under more vigorous conditions (100° in toluene) failed, so it seems likely that addition took place to the trans double bond in cis,trans-1,3-cyclooctadiene.

The infrared spectrum showed peaks at 3005 cm^{-1} for C=C-H stretch and 1650 cm^{-1} for C=C stretch. The presence of a cyclobutanone moiety was confirmed by the carbonyl frequency at 1770 cm^{-1} which compares favourably with that of cyclobutanone which occurs at 1775 cm^{-1} (67). Hydrogenation using platinum oxide as a catalyst resulted in the absorption of one molar equivalent of hydrogen. The infrared spectrum of the reduced product retained the cyclobutanone absorption at 1770 cm^{-1} but lost the characteristic double bond absorptions at 3005 cm^{-1} and 1650 cm^{-1} so the molecule has only one double bond.

Two other features of the structure which remain to be established are the position of the double bond and the ring fusion. That the ring fusion must be trans will be evident from the following argument. When the product, obtained from the reaction of ketene with cis,trans-1,3-cyclooctadiene, was passed through a column containing basic alumina a new substance was formed. Microanalysis showed that this compound, which was a colourless liquid, had the

same empirical formula as the original product. That the compound had a double bond was shown by the infrared spectrum in which peaks at 3005 cm^{-1} and 1650 cm^{-1} were assigned to the C=C-H and C=C stretching vibrations respectively. A peak at 1775 cm^{-1} showed that the cyclobutanone moiety was still intact. That a new substance was indeed formed was shown by the infrared spectra of the two compounds which showed many differences in the region 1200 cm^{-1} to 650 cm^{-1} (See Table VI). Also the semicarbazone derivative of the original product had a melting point of 211-212°C whereas the semicarbazone derivative of the compound derived from it had a melting point of 200-201°C. A mixture of the two semicarbazones showed melting point depression. Ketones are known to exchange protons in the α positions under basic conditions. If a keto group is adjacent to a ring junction then such exchange can result in isomerization at this center, depending on the relative stability of the cis and trans fused ring systems. It is reasonable to propose, then, that the two compounds obtained differ only in their ring junction.

As was pointed out previously, (page 132) it is likely that the ketene adds to the trans double bond. Since ketene adds in a cis manner we have cis addition to a trans double bond which should result in a product with trans fused rings. Isomerization might occur during the reaction, however, so we have the following possibilities.

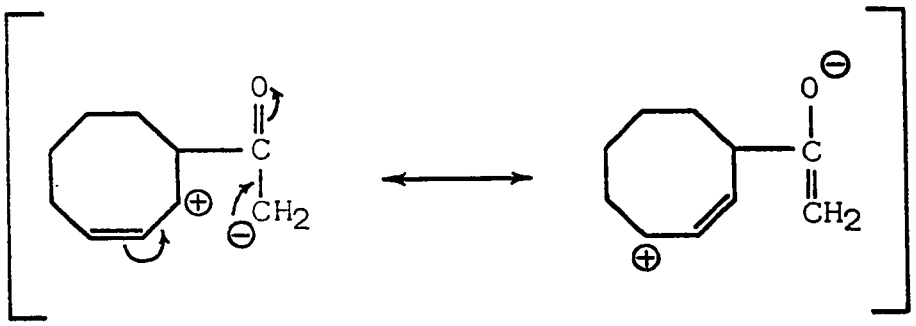
If the trans fused ring system is more stable than the cis fused system no isomerization would occur during the

reaction and no subsequent isomerization under acidic or basic conditions would be possible. If the cis fused system is more stable than the trans fused system, then the addition could give either the cis or trans fused product depending on whether or not isomerization occurs during the reaction. If isomerization to give the cis ring fusion does occur during the reaction, then no subsequent isomerization is possible. If there is no isomerization during the reaction, then subsequent isomerization with acid or base can occur. Since this is the case, the product obtained from the reaction of ketene and cis,trans-1,3-cyclooctadiene must have its ring system fused in a trans manner and the substance derived from it by passage through basic alumina must have a cis fused ring system.

It has been reported that dimethylketene adds to cis and trans butenylethyl ethers in a stereospecific manner. Addition to the trans ether gives a trans adduct and addition to the cis ether gives a cis adduct (113). It should be pointed out that vapour phase chromatography showed that isomerization of the pure trans compound to the cis compound was virtually complete, so that the situation arising from partial isomerization did not have to be considered. Such a situation would arise if the relative stabilities of the two isomers were close. Since the chromatograph which was used did not have a heated injection port, peaks obtained were quite broad. It is estimated that 3-4% of the trans compound could still be present after isomerization, but this does not affect the overall argument.

Unfortunately the position of the double bond was not rigorously established, but the position as shown (LXIII) seems to be the most suitable. If ketene were to add in the opposite direction, the product would have the double bond in a position $\beta\gamma$ to the carbonyl group. Normally such bonds isomerize to the $\alpha\beta$ position fairly readily and this isomerization can be detected by a lowering of the carbonyl frequency. Since isomerization of the ring junction involves proton exchange in a position which would be allylic to a double bond in the $\beta\gamma$ position, one might have expected that migration of the double bond to the $\alpha\beta$ position would have occurred. Since the carbonyl frequency for the cis compound is 1775 cm^{-1}, no such migration of the double bond occurred and it can be concluded that ketene probably added in the opposite direction to give a structure having the double bond in a position $\gamma\delta$ to the carbonyl group.

It has been established that diphenylketene adds to cyclopentadiene and to 1,3-cyclohexadiene to give products having the double bond in a position $\gamma\delta$ to the carbonyl group (103). Mechanistically, addition in this direction is favoured because of greater stabilization of the intermediate formed. Assuming for the moment that the mechanism is ionic and involves complete separation of charge, then addition which results in a $\gamma\delta$ double bond in the product has stabilization of the positive charge by the double bond and of the negative charge by the carbonyl group.



If addition were to occur in the opposite direction, only the negative charge would be stabilized. It should be pointed out that complete separation of charge could not in fact take place since this would permit free rotation and the reaction would no longer be stereospecific. It has been suggested that the two bonds form simultaneously but that one bond forms faster than the other. If the reaction proceeds through a free radical mechanism, then a similar argument can be applied and the same orientation is favoured. A critical discussion of the mechanism of four center addition reactions can be found in Breslow and in references contained therein (114).

Wolff-Kishner reduction of trans-bicyclo[6.2.0]dec-2-en-9-one gave two products. These products were separated on a small scale by preparative vapour phase chromatography. The product with shorter retention time (25.9 min) present as 27% of the mixture was probably the alcohol, as shown by a peak in the infrared spectrum at 3450 cm^{-1} which can be assigned to the -OH stretch frequency. The major product (retention time 29.2 min) which consisted of 73% of the mixture was the desired bicyclo[6.2.0]dec-2-ene. The alcohol

could be easily removed from the mixture by passing the product through an alumina column. This product probably has cis ring fusion since the reaction involves the use of strong base. It would be of interest to confirm this by preparation of the trans hydrocarbon. If the two hydrocarbons were available, they would also be useful for equilibration studies. Cyclobutanes with two adjacent alkyl substituents are more stable when these substituents are trans to each other rather than cis. However, if the cyclobutane is fused to a small ring, the cis form will be more stable than the trans form because of ring strain produced by fusion in a trans manner. If the second ring is large enough, however, the trans compound will be more stable. Thus we will have a ring size at which the "crossover" point lies (88). Allinger prepared the cis and trans bicyclo[5.2.0]nonanes but was unable to equilibrate them. The cis and trans bicyclo[6.2.0]dec-2-enes should equilibrate easily since the ring fusion is allylic to a double bond.

Unfortunately, attempts to prepare trans-bicyclo [6.2.0]dec-2-ene were unsuccessful. Treatment of 9-tosyl-bicyclo[6.2.0]dec-2-ene with lithium aluminum hydride under a variety of conditions gave only the alcohol back. The reaction of tosylhydrazones with sodium borohydride showed some promise (115) but extremely poor yields were obtained in this case. Vapour phase chromatography showed that this reaction gave a single product which differed from the product obtained by the Wolff-Kishner reaction. Unfortunately

the small amount of material available did not permit further investigation.

An attempt was made to dehydrogenate bicyclo[6.2.0] dec-2-ene in the vapour phase using rhodium on alumina support as the catalyst. Preliminary experiments indicated that some azulene was formed although it was identified only by its deep blue colour. The bulk of the material was recovered unchanged. Although studies were not continued because of lack of time and material, it would be fruitful to find conditions under which most of the starting material reacted. This could involve the use of a higher temperature, a longer catalyst bed and an improved catalyst. A catalyst such as 10% platinum or palladium on asbestos fibre would be suitable. It is best to avoid carbon support for the catalyst since materials are very strongly adsorbed on carbon and so are likely to rearrange. Under such conditions it may be possible to obtain, along with the azulene, some of the desired bicyclo[6.2.0]decapentaene.

REFERENCES

1. P. E. Verkade, The Kekulé Symposium, September, 1958, Butterworths, London, p.1ff.
2. R. Willstätter and E. Waser, Ber. Dtsch. Chem. Ges. 44, 3423, (1911).
3. J. W. Armit and R. Robinson, J. Chem. Soc., 121, 827, (1922); 127, 1604, (1925).
4. C. K. Ingold and E. H. Ingold, J. Chem. Soc., 1310, (1926).
5. E. Hückel, Z. Physik, 70, 204, (1931).
6. C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc., 36, 193, (1940).
7. D. P. Craig, J. Chem. Soc., 3175, (1951).
8. J. Coops and S. Kaarsemaker, Rec. Trav. Chem., 69, 1364, (1950).
9. R. C. Cass, H. D. Springall and P. G. Quincey, J. Chem. Soc., 1188, (1955).
10. D. P. Craig, Non-Benzenoid Aromatics, D. Ginsburg Ed., Interscience, New York, (1959) p.21.
11. C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1, (1949).
12. W. H. Perkin Jr., J. Chem. Soc., 65, 967, (1894).
13. W. C. Lothrup, J. Amer. Chem. Soc., 63, 1187, (1941).
14. G. W. Wheland, Resonance in Organic Chemistry, Wiley, New York, (1955).
15. E. P. Carr, L. W. Pickett and D. Voris, J. Amer. Chem. Soc., 63, 3231, (1941).

16. W. Baker, M. P. V. Boarland and J. F. W. McOmie, J. Chem. Soc., 1476, (1954).

17. T. C. W. Mark and J. Trotter, Proc. Chem. Soc., 163, (1961).

18. R. Criegee and Gerhard Schröder, Ann., 623, 1, (1959).

19. G. F. Emerson, L. Watts and R. Pettit, J. Amer. Chem. Soc., 87, 131, (1965).

20. L. Watts, J. D. Fitzpatrick and R. Pettit, J. Amer. Chem. Soc., 87, 3253, (1965).

21. T. J. Katz and M. Rosenburger, J. Amer. Chem. Soc., 84, 865, (1962).

22. E. LeGoff, J. Amer. Chem. Soc., 84, 3975, (1962).

23. A. C. Cope and W. I. Bailey, J. Amer. Chem. Soc., 70, 2305, (1948).

24. W. Reppe, O. Schlichting, K. Klager and T. Toepel, Liebigs Ann. Chem., 560, 1, (1948).

25. A. C. Cope and H. Campbell, J. Amer. Chem. Soc., 74, 179, (1952).

26. A. C. Cope and D. S. Smith, J. Amer. Chem. Soc., 74, 5136, (1952).

27. E. Grovenstein Jr., and D. V. Rao, Tet. Letters, 148, (1961).

28. D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., 326, (1959); J. Chem. Soc., 695, (1963).

29. J. G. Atkinson, D. E. Ayer, G. Buchi and E. W. Robb, J. Amer. Chem. Soc., 85, 2257, (1963).

30. A. C. Cope and M. R. Kiuter, J. Amer. Chem. Soc., 72, 630, (1950).

31. A. C. Cope and H. O. van Orden, J. Amer. Chem. Soc., 74, 175, (1952).

32. A. C. Cope and D. F. Rugen, J. Amer. Chem. Soc., 75, 3215, (1953).

33. A. C. Cope, R. M. Pike and D. F. Rugen, J. Amer. Chem. Soc., 76, 4945, (1954).

34. E. Vogel, H. Kieter and W. R. Roth, Angew. Chem. (Int.) 3, 442, (1964).

35. R. Huisgen and F. Mietzsch, Angew. Chem. (Int.), 3, 83, (1964).

36. G. Schröder, Cyclooctatetraen, Monograph, Verlag Chemie, Weinheim, (1965) p.47.

37. W. Person, G. Pimentel and K. Pitzer, J. Amer. Chem. Soc., 74, 3437, (1952).

38. O. Bastiansen, L. Hedberg and K. Hedberg, J. Chem. Phys., 27, 1311, (1957).

39. M. J. S. Dewar and H. N. Schmeising, Tet., 166, (1959); Tet., 96, (1960).

40. E. R. Lipincott, R. C. Lord and R. S. McDonald, J. Amer. Chem. Soc., 73, 3370, (1951).

41. S. Miyakawa, I. Tanaka and T. Uemura, Bull. Jap. Chem. Soc., 24, 136, (1951).

42. G. F. Woods and L. H. Schwartzman, J. Amer. Chem. Soc., 70, 3394, (1948).

43. J. S. Waugh and R. W. Fessenden, J. Amer. Chem. Soc., 79, 846, (1957).

44. A. C. Cope, M. Burg and S. W. Fenton, J. Amer. Chem. Soc., 74, 173, (1952).

45. F. A. L. Anet, J. Amer. Chem. Soc., 84, 671, (1962).

46. F. A. L. Anet, A. J. R. Bourn and Y. S. Lin, J. Amer. Chem. Soc., 86, 3576, (1964).

47. C. A. Coulson and A. Streitwieser Jr., Dictionary of π electron Calculations, Freeman, San Francisco, (1965).

48. M. A. Battiste, J. Amer. Chem. Soc., 86, 942, (1964).

49. A. S. Kende and P. T. Izzo, J. Amer. Chem. Soc., 86, 3587, (1964).

50. E. D. Bergmann in J. W. Cook, Progress in Organic Chemistry, Vol. 3, Butterworths, London, 1955.

51. C. De La Harpe and W. A. van Dorp, Ber. Dtsch. Chem. Ges., 8, 1048, (1875).

52. J. Thiele, Ber., 33, 666, (1900).

53. J. Thiec and J. Wiemann, Bull. Soc. Chem. Fr., 177, (1956).

54. E. Sturm and K. Hafner, Angew. Chem. (Int.), 3, 749, (1964).

55. G. W. Wheland and D. E. Mann, J. Chem. Phys., 17, 264, (1949).

56. A. Streitwieser, Molecular Orbital Theory, John Wiley, New York, (1961).

57. K. Hafner et al., Angew. Chem. (Int.), 2, 123, (1963).

58. W. von E. Doering and D. W. Wiley, Tet., 183, (1960).

59. M. Yamakawa, H. Watanabe, T. Mukai, T. Nozoe and M. Kubo, J. Amer. Chem. Soc., 82, 5665, (1960).

60. G. Berthier and B. Pullman, Trans. Far. Soc., 45, 484, (1949).

61. J. D. Roberts, A. Streitwieser Jr., and Clare M. Regan, J. Amer. Chem. Soc., 74, 4579, (1952).

62. A. T. Blomquist and P. M. Maitlis, Proc., 332, (1961).

63. A. T. Blomquist and Y. C. Meinwald, J. Amer. Chem. Soc., 79, 5316, (1957).

64. R. Criegee et al., Ber., 96, 2362, (1963).

65. G. W. Griffin and L. I. Peterson, J. Amer. Chem. Soc., 85, 2268, (1963).

66. M. P. Cava and A. A. Deana, J. Amer. Chem. Soc., 81, 4266, (1959).

67. L. A. Errede, J. Amer. Chem. Soc., 83, 949, (1961).

68. D. A. Ben-Efraim and F. Sondheimer, Tet. Letters No. 5, 313, (1963).

69. P. A. Waitkus, L. I. Peterson and G. W. Griffin, J. Amer. Chem. Soc., 88, 181, (1966).

70. E. A. Dorko, J. Amer. Chem. Soc., 87, 5518, (1965).

71. J. C. Kauer and M. Brown, Organic Syntheses, 42, 97, (1962).

72. A. I. Vogel, Practical Organic Chemistry, Longmans, 1956, p.969.

73. R. N. Jones, Infrared Spectra of Organic Compounds, NRC Bulletin #6, Ottawa, (1959).

74. Varian Nuclear Magnetic Resonance Spectra Catalog, Varian Associates, Palo Alto, California.

75. K. Biemann, Mass Spectrometry, McGraw-Hill, New York, (1962). a. p.51; b. p.153ff.

76. Personal Communication, Corning Glass Works, Corning, N.Y., U.S.A.

77. J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, McGraw-Hill, Toronto, (1959), p.119ff.

78. M. J. Jorgenson, Tet. Letters, #13, 559, (1962).

79. E. LeGoff and R. B. LaCount, Tet. Letters, #32, 2787, (1965).

80. L. M. Jackman, Nuclear Magnetic Resonance Spectroscopy, London, (1959), p.85.

81. A. C. Cope and D. F. Rugen, J. Amer. Chem. Soc., 75, 3215, (1953).

82. G. F. Woods and L. H. Schwartzman, J. Amer. Chem. Soc., 71, 1396, (1949).

83. L. J. Bellamy, The Infrared Spectra of Complex Molecules, London, (1958), p.387ff.

84. K. Alder and H. A. Dortmann, Chem. Ber., 87, 1492, (1954).

85. A. C. Cope et al., J. Amer. Chem. Soc., 74, 4867, (1952).

86. A. T. Blomquist and J. A. Verdol, J. Amer. Chem. Soc., 77, 1806, (1955).

87. R. Criegee, J. Dekker, W. Engel, P. Ludwig and K. Noll, Ber., 96, 2362, (1963).

88. N. L. Allinger, M. Nakazaki and V. Zalkow, J. Amer. Chem. Soc., 81, 4074, (1959).

89. M. Prinzbach and J. M. Hartenstein, Angew. Chem. 75, 639, (1963).

90. W. G. Dauben and R. L. Cargill, Tet., 186, (1961).

91. S. F. Chapell III and R. F. Clark, Chem. and Ind., 1198, (1962).

92. S. Cremer and R. Srinivasan, Tet. Letters No. 21, 24, (1960).

93. C. D. Gutsche and C. W. Armbuster, Tet. Letters No. 26, 1297, (1962).

94. W. H. Urry, D. J. Trecker and D. A. Winey, Tet. Letters No. 14, 609, (1962).

95. P. E. Eaton, Tet. Letters No. 48, 3695, (1964).

96. E. J. Corey, R. B. Mitra and H. Uda, J. Amer. Chem. Soc., 86, 485, (1964).

97. C. Mannich and H. Davidson, Ber., 69, 2106, (1936).

98. K. C. Brannock, R. B. Burpitt, V. W. Goodlett, and J. G. Thweatt, J. Org. Chem., 29, 813, (1964).

99. I. Fleming and J. Harley-Mason, J. Chem. Soc., 2165, (1964).

100. J. D. Roberts and C. M. Sharts, Organic Reactions Vol. XII, (1962), p.1.

101. J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, J. Amer. Chem. Soc., 80, 3672, (1958).

102. H. Staudinger and E. Suter, Ber., 53, 1092, (1920).

103. E. H. Farmer and M. O. Farooq, J. Chem. Soc., 1925, (1938).

104. B. T. Brooks and G. Wilbert, J. Amer. Chem. Soc., 63, 870, (1941).

105. A. T. Blomquist and J. Kwiatek, J. Amer. Chem. Soc., 73, 2098, (1951).

106. W. E. Hanford and J. C. Sauer, Organic Reactions Vol. III (1946), pp.132-135.

107. A. C. Cope and L. L. Estes Jr., J. Amer. Chem. Soc., 72, 1128, (1950).

108. A. C. Cope and C. L. Bumgardner, J. Amer. Chem. Soc., 78, 2812, (1956).

109. K. Ziegler et al., Ann., 589, 122, (1954).

110. J. C. Martin, P. G. Gott, V. W. Goodlett and R. H. Hasek, J. Org. Chem., 30, 4175, (1965).

111. R. R. Moffett, Organic Syntheses, 32, 41, (1952).

112. C. A. Stewart, J. Amer. Chem. Soc., 84, 117, (1962).

113. J. C. Martin, V. W. Goodlett and R. D. Burpitt, J. Org. Chem., 30, 4309, (1965).

114. R. Breslow, Organic Reaction Mechanisms, W. A. Benjamin, New York, (1965), p.127.

115. L. Caglioti and P. Grasselli, Chem. and Ind., 153, (1964).

Claims to Original Research

Part I

1. The following new compounds were synthesized:
   a. Methyl 2-butynoate
   b. 2-Carbomethoxy-1-methylcyclo[8]octatetraene
   c. 2-Carbomethoxy-1-methylcyclo[8]octane
   d. 2-Hydroxymethyl-1-methylcyclo[8]octatetraene
   e. 2-Bromomethyl-1-methylcyclo[8]octatetraene
   f. 1-Methyl-2-N,N,N-trimethylammoniomethylcyclo-[8]octatetraene bromide
   g. 1,2-Dimethylenecyclo[8]octatriene
2. A marked improvement in the yield of a substituted cyclo[8]octatetraene from the photolysis of a substituted acetylene in benzene was obtained. This was accomplished by cleaning the photolysis cell with chlorosulfonic acid, by using dilute solutions, and by performing the photolysis in a cell made from Vycor #7910.
3. A vapour phase chromatographic study of the reduction product from 2-carbomethoxy-1-methylcyclo[8]octatetraene showed that only one product was formed. It is proposed that this is cis-2-carbomethoxy-1-methylcyclo-[8]octane.
4. Mass spectral breakdown patterns are proposed for 2-carbomethoxy-1-methylcyclo[8]octatetraene, 2-hydroxymethyl-1-methylcyclo[8]octatetraene and 1,2-dimethylenecyclo[8]octatriene.
5. It is proposed that 1,2-dimethylenecyclo[8]octatriene is

monocyclic and not in equilibrium with an appreciable amount of a bicyclic form. It is further proposed that it is not planar and that it is not highly strained.

6. The photolytic behaviour of 1,2-dimethylenecyclooctatriene was studied with a view to preparing a bicyclic form.
7. The thermal stability and oxygen sensitivity of 1,2-dimethylenecyclooctatriene were determined.
8. The reaction of 1,2-dimethylenecyclooctatriene with tetracyanoethylene was studied.
9. Molecular orbital calculations were performed on planar 1,2-dimethylenecyclooctatriene. The total π energy, delocalization energy, free valences, and bond orders were calculated.

Part II

10. The following new compounds were synthesized:
    a. trans-Bicyclo[6.2.0]dec-2-en-9-one
    b. trans-Bicyclo[6.2.0]dec-2-en-9-one semicarbazone
    c. cis-Bicyclo[6.2.0]dec-2-en-9-one
    d. cis-Bicyclo[6.2.0]dec-2-en-9-one semicarbazone
    e. Bicyclo[6.2.0]dec-9-one
    f. Bicyclo[6.2.0]dec-2-ene
11. The product of addition of ketene to cis,trans-1,3-cyclooctadiene (10a.) was shown to have trans ring fusion.
12. Dehydrogenation studies were carried out on bicyclo [6.2.0]dec-2-ene. Azulene was obtained in low yield.