THE SYNTHESIS AND STUDY OF SOME $(CH)_{14}$ HYDROCARBONS AND THEIR DERIVATIVES

by

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ABSTRACT

The $(CH)_n$ hydrocarbons have presented a challenge to the synthetic chemist to construct molecules of a wide variety of structural types, often with a high degree of symmetry and strain. The study of the thermal and photochemical rearrangements of polymethine hydrocarbons serve as a test of the Woodward-Hoffmann rules for conservation of orbital symmetry. The lower $(CH)_n$ homologues have been studied extensively, but the $(CH)_{14}$ set has been largely unexplored.

In this work the synthesis of two $(CH)_{14}$ hydrocarbons, bicyclo[4.4.4]tetradeca-2,4,7,9,11,13-hexaene (77) and *cis,transoid,cis*-tetracyclo[$8.2.2.0^{2,9}.0^{3,8}$]tetradeca-4,6,11,13-tetraene (78) was attempted.

The synthesis of 77 required that the unknown ring system bicyclo[4.4.4]tetradecane be prepared. The approach employed involved coupling reactions of symmetrical derivatives of 1,6-diethylidine cyclodeca-3,8-diones. The Grignard coupling reaction gave intramolecular cyclization products *cis*- and *trans*-9,10-divinyl hexalins (124) and (125) but did not give the desired ring system. The isomeric hydrocarbons 124 and 125 provided a unique insight into the mechanism of the Retro Diels-Alder reaction in the mass spectrometer.

Substituted derivatives of 78 were prepared and the products of their thermal and photochemical reactions were identified. A general synthesis of derivatives of barrelenes and cyclooctatetraenes was proposed.

The synthesis of 78 was accomplished in two steps from Nenitzescu's hydrocarbon (20). A Diels-Alder reaction with o-benzoquinone afforded

two isomeric α-diones 181 and 182. Photochemical bisdecarbonylation of the endo adduct 182 gave the $(CH)_{14}$ polymethine hydrocarbon. Two minor products form this reaction were also observed in the photochemical reaction of the dione 181. Mass spectral evidence suggested that they, too, may have been $(CH)_{14}$ hydrocarbons; 78 thus appeared a viable entry into the $(CH)_{14}$ energy surface.

GLOSSARY OF ABBREVIATIONS AND SYMBOLS

bp	boiling point
$(CH)_n$	polymethine hydrocarbon with n carbon and n hydrogen atoms
cmr	carbon magnetic resonance
d	doublet
DME	dimethoxyethane
DMSO	dimethyl sulfoxide
δ	chemical shift in parts per million downfield from TMS
Δ	thermal reaction
ΔH°	standard heat of formation
$\Delta\nu$	change in chemical shift
eV	electron Volt
ε	molar extinction coefficient
Hz.	Hertz
$h\nu$	photochemical reaction
IKE	Ion Kinetic Energy
ir	infrared
J	coupling constant in Hz.
K	equilibrium constant
λ	wavelength
m	multiplet
M^+	molecular ion
m/e	mass to charge ratio of an ion
mp	melting point
ms	mass spectrum

m_x	daughter ion x
N	the sum of the coupling constants J_{AX} plus $J_{AX'}$
nmr	nuclear magnetic resonance
NBS	N-bromosuccinimide
pmr	proton magnetic resonance
PIE	Precursor Ion Experiment
RDA	Retro Diels-Alder
s	singlet
t	triplet
tlc	thin layer chromatography
THF	tetrahydrofuran
TMS	tetramethylsilane
Ts	p-toluenesulfonyl
uv	ultraviolet
$\%\Sigma_{40}$	percentage of the total ion current above m/e 40
D_3 C_2 C_s	symmetry point groups
E Z	designation of stereochemistry about double bonds

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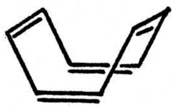
INTRODUCTION

The synthesis and study of neutral molecules comprised only of (CH) units has fascinated organic chemists for many years. From Willstätter's nonaromatic cyclooctatetraene (1)[1], through Schröder's fluxional bullvalene (2)[2], to the as yet unknown dodecahedrane (3)[3], $(CH)_n$ hydrocarbons have given rise to fundamental questions that have profoundly influenced modern organic chemistry.



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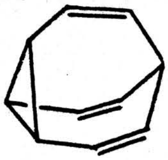

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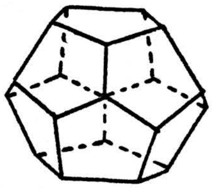

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Elegantly simple syntheses of many of the lower homologues have appeared in the literature beginning in the early 1960's. The larger molecules have received considerably less attention. The present work was undertaken to explore synthetic routes to the $(CH)_{14}$ hydrocarbons: in particular, to prepare a novel hydrocarbon that could be expected to lead to other $(CH)_{14}$ isomers.

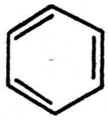
Herein follows an historical account of the development of the study of $(CH)_n$ hydrocarbons including what is presently known of the $(CH)_{14}$ series. A second part of this introduction surveys the synthetic methodology developed to handle the special problems that these strained and often labile compounds pose.

The Development of the Study of $(CH)_n$ Hydrocarbons

The most abundant $(CH)_n$ hydrocarbon (with the possible exception of acetylene) is as old as organic chemistry itself. In 1820 Michael Faraday began to study a liquid that was obtained on compression of illuminating gas made by the destructive distillation of whale oil. Five years later he reported the isolation by distillation and crystallization of bicarburet of hydrogen, now known as benzene. Mitscherlich prepared the same compound by the distillation of benzoic acid with lime in 1833.[4]

A variety of structures were proposed to account for the chemistry that benzene exhibited;[5] among them were those of Kekulé (1865) 4, of Ladenburg (1869) 8, and of Dewar (1867) 5. These, and the two remaining $(CH)_6$ hydrocarbons, or their derivatives, have been prepared and are shown in Figure 1.

Figure 1.



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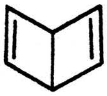
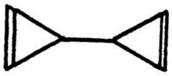
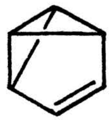


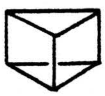
Dewar Benzene[6] (5)



Bicyclopropenyl[7] (6)



Benzvalene[8] (7)



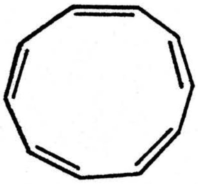
Prismane[9] (8)

The stability of the nonplanar $(CH)_6$ compounds are remarkable examples of the power of the rules of conservation of orbital symmetry.[10] (Hexamethyl) Dewar benzene has a half life at 120° of 105 hours[11] even though the enthalpy change for the isomerization to hexamethylbenzene is 60 Kcal/mole[12,13]. Similarly, the $\Delta H°$ for the conversion of benzvalene (7) to benzene (4) is 67.5 Kcal/mole.[14] Katz et al[15] commented however that they "were discouraged from investigating (benzvalene's) large scale isolation pure when the resonance energy of benzene and the strain energy of small ring compounds were called to our attention by the benzvalene exploding." Hexamethylprismane exhibits the same tendency at high temperatures.[16]

The $(CH)_6$ hydrocarbons, their synthesis and chemistry, sparked interest in the higher homologues where the variety of structural types was much richer and the attendant chemistry even more intriguing. Van Tamelen[17] said of the $(CH)_{10}$ series "The $(CH)_{10}$ system may serve as the ultimate testing ground for the Woodward-Hoffmann selection rules by helping set the limit in strain and helping gauge the influence of restrictive geometries on electrocyclic reactions."

Balaban[18] has made a compilation of all the possible $(CH)_{10}$ structural types, ignoring stereochemistry of ring junctions and about double bonds, predicting a total of 93 structures. The compounds that have been made to date are shown in Figure 2 which begins with the monocyclic isomers and proceeds through to the hexacyclic compounds.

Figure 2 The Known $(CH)_{10}$ Hydrocarbons



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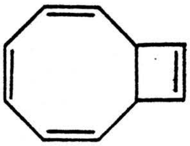

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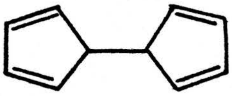

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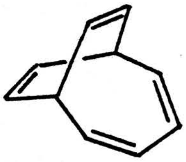

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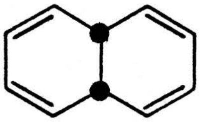

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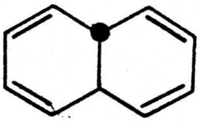

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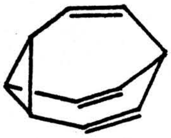

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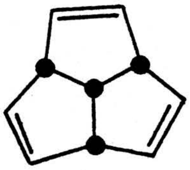

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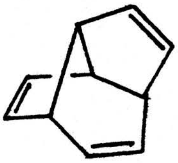

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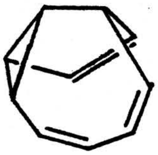

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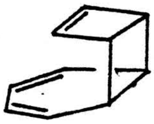

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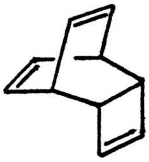

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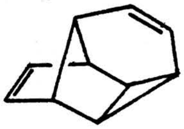

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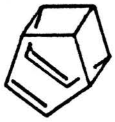

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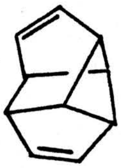
Figure 2 Continued



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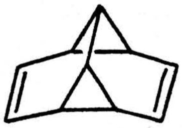

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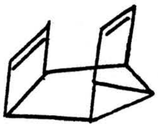

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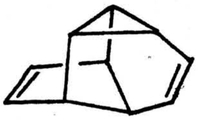

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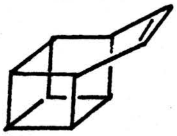

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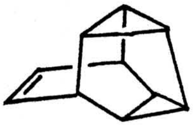

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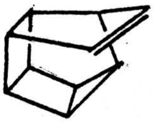

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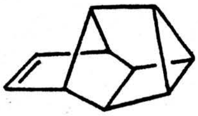

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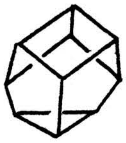

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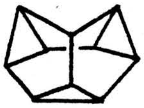

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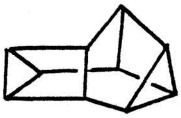

33 (37) *

The reference to the synthesis of the compound is in parentheses. * denotes that the compound was first prepared by irradiation of another $(CH)_{10}$ compound, and Δ denotes that the compound was first prepared by a thermal rearrangement of another $(CH)_{10}$ isomer.

The accompanying references pertain to the first synthesis of each compound. Improved syntheses, of some isomers by several groups, have rendered these compounds more accessible.

Perhaps the most exciting single advance in $(CH)_n$ hydrocarbon chemistry concerns the prediction and subsequent synthesis of molecules which undergo valence bond isomerization.* In 1962 Doering and Roth[39] proposed that the then unknown $(CH)_{10}$ bullvalene 2 would undergo a series of degenerate Cope rearrangements to give a completely fluxional structure. The following year Schröder[20] announced the synthesis of the compound and proved Doering and Roth correct: the nmr spectrum of bullvalene at 120° is one singlet.[40]

It is interesting to note that fully nine of the twenty-six known isomers were first synthesized by irradiation of another $(CH)_{10}$ compound while only one new isomer has been derived thermally. Studies of the thermochemistry of many of the $(CH)_{10}$'s have shown that the

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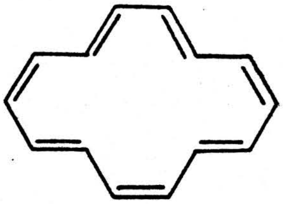
*Balaban[18] defines valence isomerism: "Valence-isomerism is a particular case of isomerism. Unlike ionotropic (e.g. prototropic) rearrangements, valence-isomerism is a concerted process involving only σ and π bonds of di-, tri-, or quadrivalent atoms, but leaving single bonded groups bonded to the same atoms as before. Valence isomers differ from one another by their σ and π framework, hence by the distances between atoms and by the bond angles. The reorganization of σ and π electrons is not accompanied by migrations of atoms or groups." Schröder et al[40] define valence isomerism: "It is an intramolecular rearrangement which obeys first order kinetics, is practically uncatalyzable, is independent of solvent, and is influenced only by temperature." Prior to the synthesis of bullvalene Doering and Roth[39] commented "It might be asked whether the borderline between mesomerism (or resonance) on the one hand and tautomerism on the other does not vanish in a molecule such as bullvalene. Group theory gives an unequivocal answer. Ten points cannot be arranged on the surface of a sphere so as to form a completely symmetrical three dimensional figure. Our phenomenon would therefore be one of tautomerism and not of mesomerism."

two dihydronaphthalenes 14 and 15 are minima on the thermal energy surface[19,20,22,26].

One would anticipate, by extrapolation from the $(CH)_{10}$ series, that the $(CH)_{14}$ hydrocarbons would comprise a set of compounds that might yield even greater and more varied synthetic challenges, and that these compounds might be induced to rearrange by thermal and photochemical treatment to other novel hydrocarbons. It is surprising how little explored the $(CH)_{14}$ set has been. A search through Chemical Abstracts revealed only five members. These are shown in Figure 3.

Figure 3 The Known $(CH)_{14}$ Hydrocarbons



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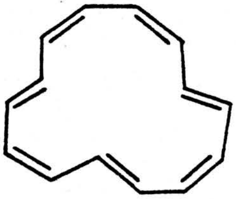

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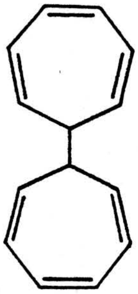

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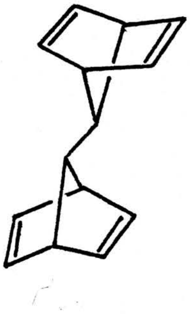

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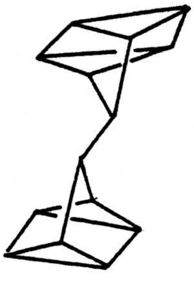


38

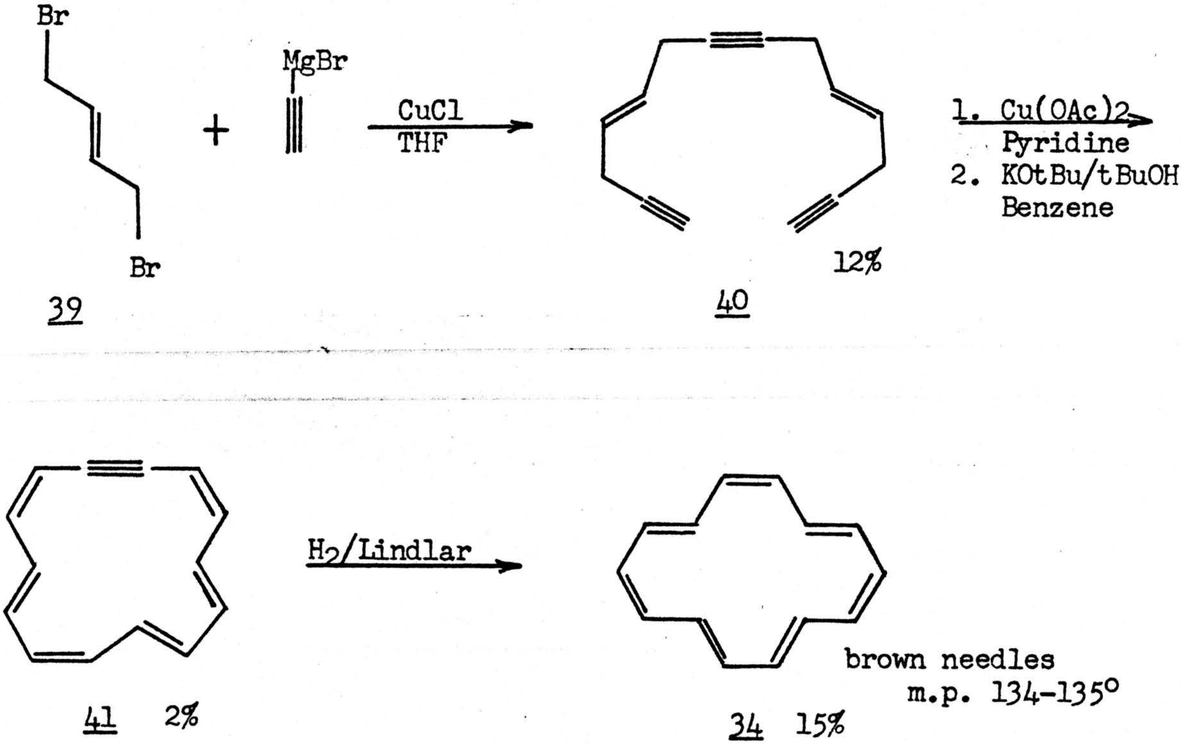
Bitropyl (36),[41] the first synthesized, was prepared in 97% yield by the coupling of tropylium bromide with zinc. Studies of the thermal and photochemistry of 36 while they have yielded interesting results, have not led to any other $(CH)_{14}$ isomers. Van Tamelen[42] and Givens[43] in the course of photochemical studies of 36 isolated bi(1,3,5-cycloheptatrien-1-yl), the product of two successive hydrogen migrations. Givens was able to isolate the intermediate (1,3,5-cycloheptatrien-1-yl)2,4,6-cycloheptatriene. Thermochemical studies[44] have shown that 36 cleaves readily to the stable cycloheptatrien-1-yl radical.

Like bitropyl, 37[45] was obtained by coupling of two seven carbon units. 7-Chloronorbornadiene coupled spontaneously when the Grignard reagent was prepared. Irradiation of this compound yielded the thermally stable fully saturated isomer 38.

Monocyclic $(CH)_n$ hydrocarbons[46] have been prepared, principally by Sondheimer, and their aromaticity studied mainly by nmr[47]. As predicted by Hückel's rule, those compounds with 4n + 2 pi electrons in a planar ring sustain diamagnetic ring currents in a magnetic field. Compounds with 4n pi electrons in the ring and those which are not planar were found not to sustain a ring current.

[14]-Annulene was prepared by Sondheimer and Gaoni[48] employing a Grignard coupling reaction, and a cupric acetate coupling of terminal acetylenes as key steps. The synthesis is outlined in Scheme 1.

Scheme 1.



The crystalline material[49] has been shown to have the structure 34. [14]-Annulene has been shown to undergo configurational isomerism in solution. The equilibrium mixture at -10° consists of 92% 34 and 8% 35. No reports of the isomerization of [14]-annulene to other $(CH)_{14}$ hydrocarbons have appeared.

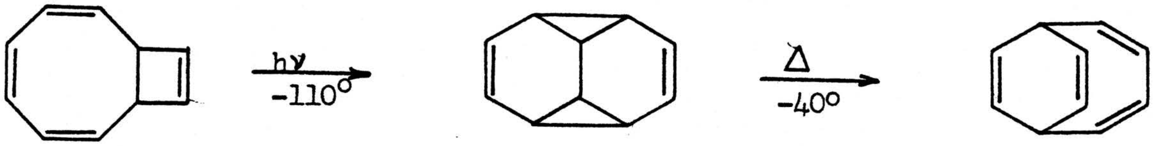
In fact, none of the five known hydrocarbons lead to other $(CH)_{14}$ compounds. The present work was undertaken to synthesize hydrocarbons which could rearrange thermally or photochemically to others of the series.

Synthetic Methodology

The fascination that $(CH)_n$ hydrocarbons hold for the chemist lies in their high degree of symmetry and in the strain imposed by their rigid framework. The synthetic chemist is challenged to devise and execute elegantly simple schemes to prepare these demanding molecules. The synthetic methodology must be powerful and specific, yet delicate enough so as not to rupture the strained bonds in the part of the molecule already constructed.

$(CH)_n$ hydrocarbons have frequently been prepared by photochemical and thermal rearrangements of other $(CH)_n$ precursors. Figure 2 illustrates this phenomenon for the $(CH)_{10}$ series. One third of all known $(CH)_{10}$ compounds were prepared by irradiation of others in the series. Masters in the application of this technique have been Masamune and coworkers[50] who have carried out photochemical reactions at temperatures at which thermal reactions are quenched. For example, they were able to obtain 24 in crystalline form by irradiation of 11 (or of 14 or 15) at -110° followed by chromatography at -80°. Irradiation at -40° yielded 13, the thermal rearrangement product of 24.[32]

Scheme 2.



11

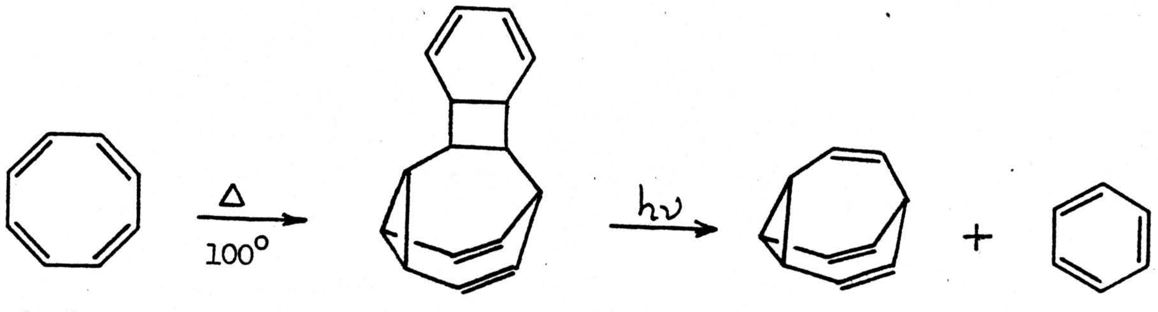
24 65%

+ 2 + 14 + 15

13

The first and "spectacular"* synthesis of bullvalene (2) demonstrates how a $(CH)_n$ hydrocarbon can be built up from other polymethine compounds and selectively cleaved yielding new $(CH)_n$ fragments. Cyclooctatetraene (1) was dimerized by heating at 100° giving the $(CH)_{16}$ hydrocarbon 42 (mp 76°) in 40% yield.[52,53] Photolysis in ether cleaved the cyclobutane ring, giving the two $(CH)_n$ fragments bullvalene (2) and benzene (1) in 75% yield.

Scheme 3.



$(CH)_8$ 1 $(CH)_{16}$ 42 $(CH)_{10}$ 2 $(CH)_6$ 4

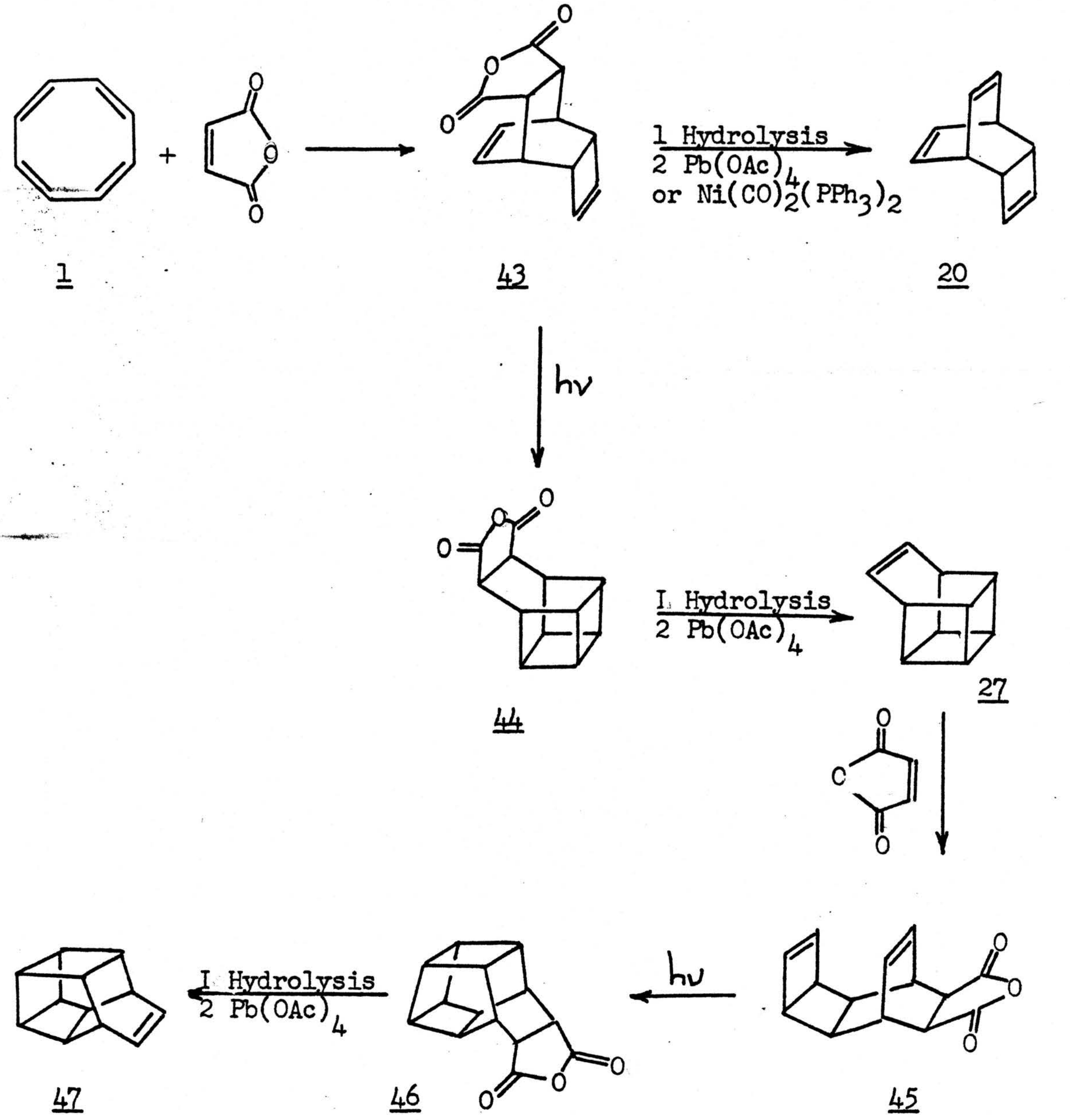
A general approach often employed for the construction of hydrocarbon skeleta is the addition of a masked or substituted $(CH)_n$ to an unsaturated molecule. Functional group manipulations are then required to give the desired $(CH)_n$ hydrocarbon.

---

*This synthesis is "spectacular" in its brevity and efficiency particularly when compared to the later "rational" synthesis of Doering[54] which involves nine steps.[55]

Masked $(CH)_2$ units that have been successfully employed to give entries into the $(CH)_n$ series are maleic anhydride and ethyl diazoacetate. Maleic anhydride was first used in the context of $(CH)_n$ hydrocarbons by Nenitzescu in the synthesis of hydrocarbon 20.[30] Hydrolysis

Scheme 4.

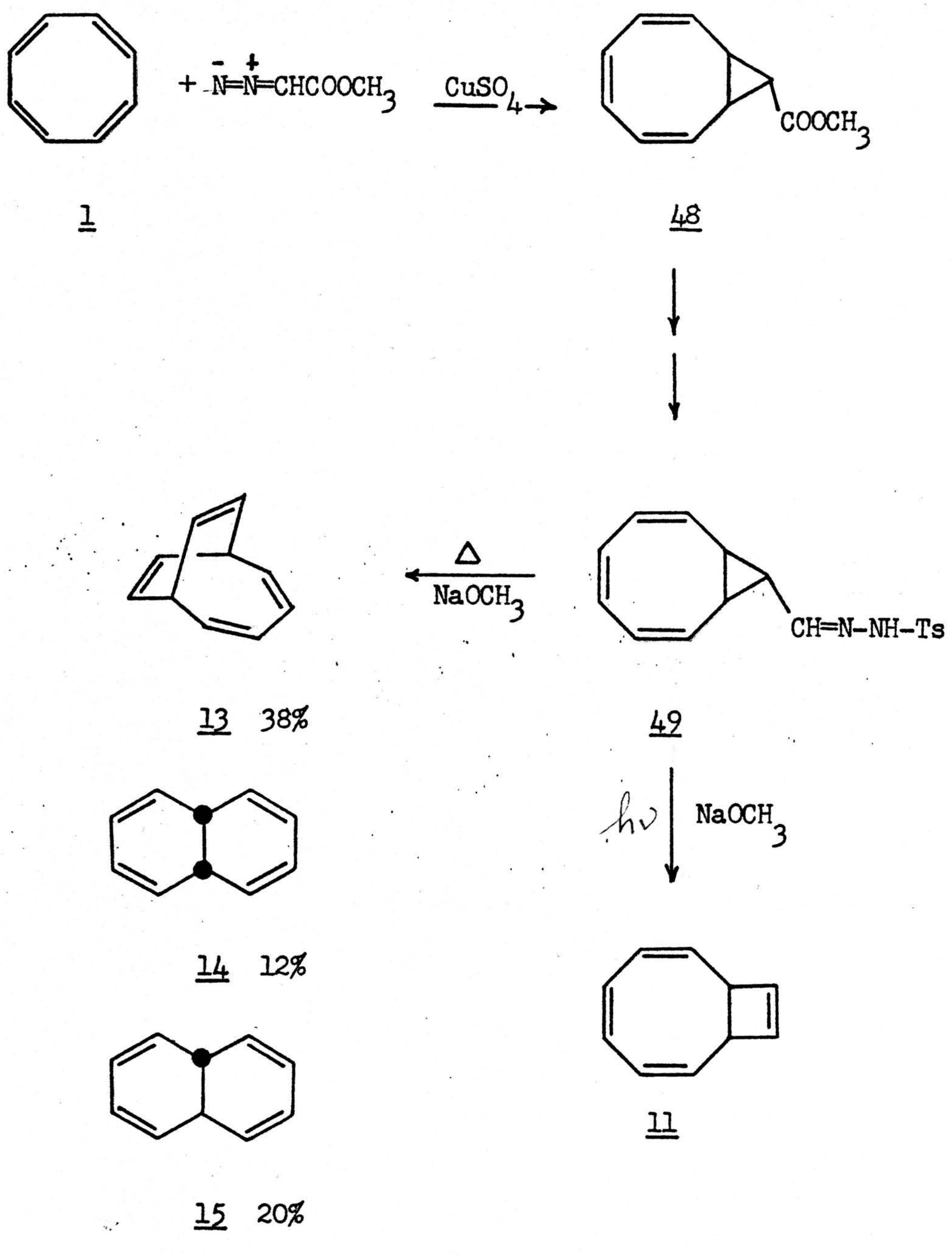


of 43, the adduct of cyclooctatetraene and maleic anhydride, and bisdecarboxylation with lead tetraacetate furnished the tricyclic triene 20. The yield of the bisdecarboxylation step using this method is poor. Dauben and coworkers[56] have recently developed the application of a nickel reagent to this reaction and have obtained greatly improved yields.

Photochemical closure and subsequent hydrolysis and bisdecarboxylation of 44 afforded basketene (27)[35]. Other workers extended the procedure beginning with basketene and obtained the $(CH)_{12}$ hydrocarbon 47 shown.[57]

Methyl diazocarboxylate has been added to cyclooctatetraene (1) in the presence of copper sulfate and the resulting ester 48 converted to the tosyl hydrazone 49. Pyrolysis of the sodium salt 49 gave three $(CH)_{10}$ compounds, 13, 14, and 15[34]. Low temperature photolysis of the salt led to the bicyclic hydrocarbon 11.[15] This sequence is shown in Scheme 5.

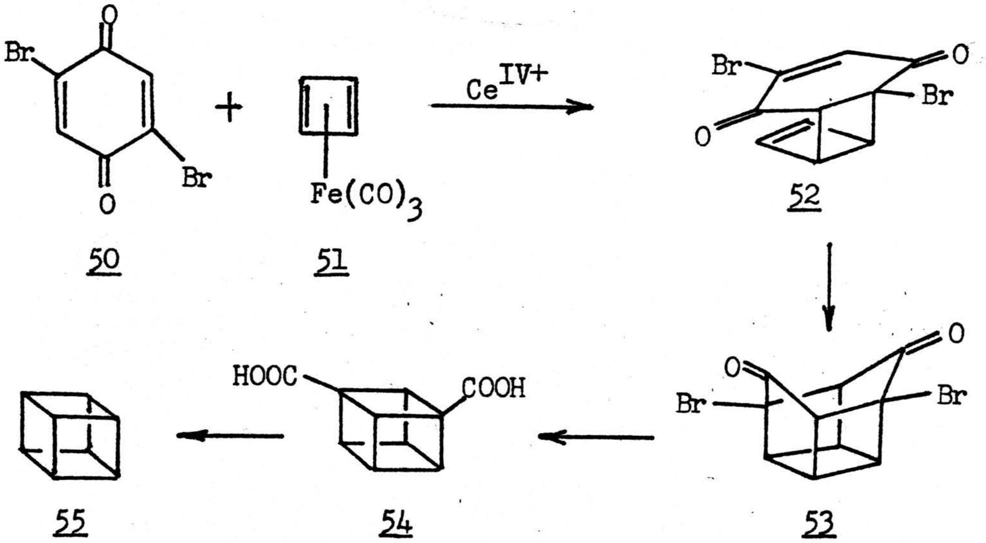
Scheme 5.



+ $\overset{-}{N}=\overset{+}{N}=CHCOOCH_3$
$CuSO_4$
$COOCH_3$
1
48
$CH=N-NH-Ts$
49
Δ
$NaOCH_3$
13 38%
14 12%
15 20%
hν
$NaOCH_3$
11

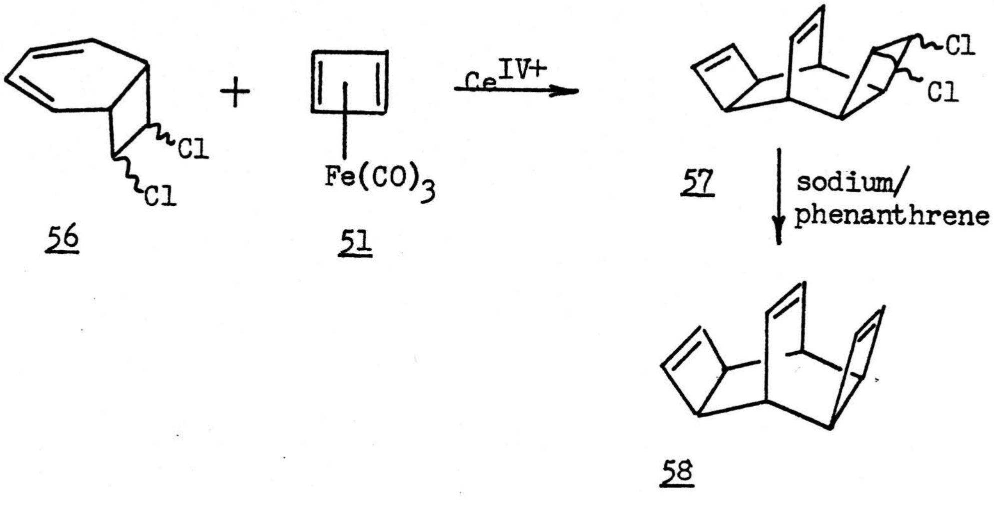
Masked $(CH)_4$ units have been added in several forms. Cyclobutadiene[58,59], generated by oxidation of its iron tricarbonyl complex 51, has been employed as either a diene or dienophile in Diels-Alder reactions. An efficient cubane synthesis has such an addition as a key step.[60]

Scheme 6.



Paquette and Stowell[61] prepared the tetracyclic $(CH)_{12}$ compound 58 by the use of the same reagent, and adding it to 56, itself a precursor

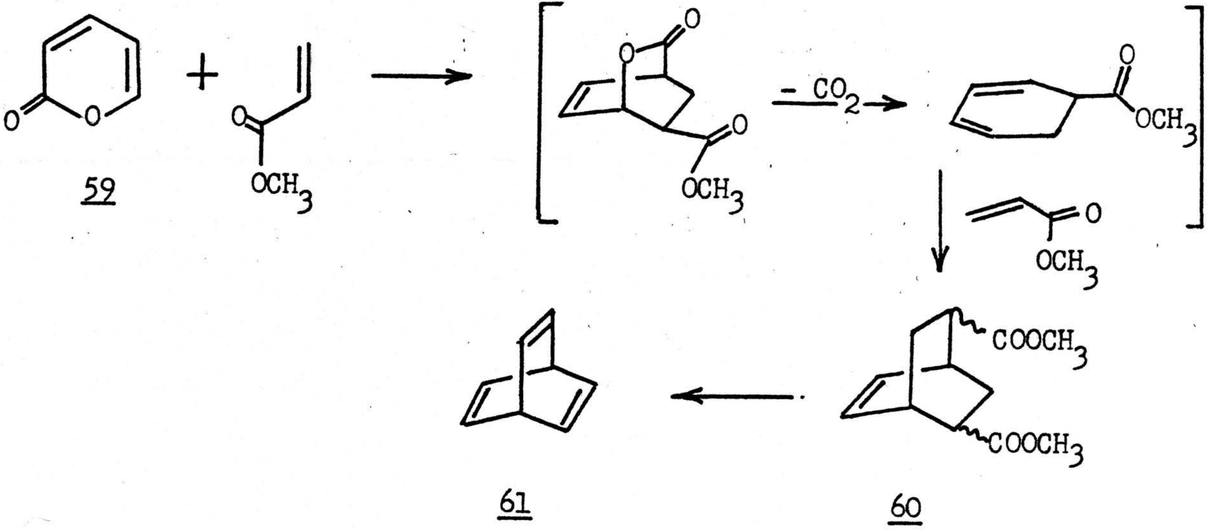
Scheme 7.



in the synthesis[62] of cyclobutadiene. The second step in this sequence is the dechlorination with sodium and phenanthrene to unmask the third double bond.

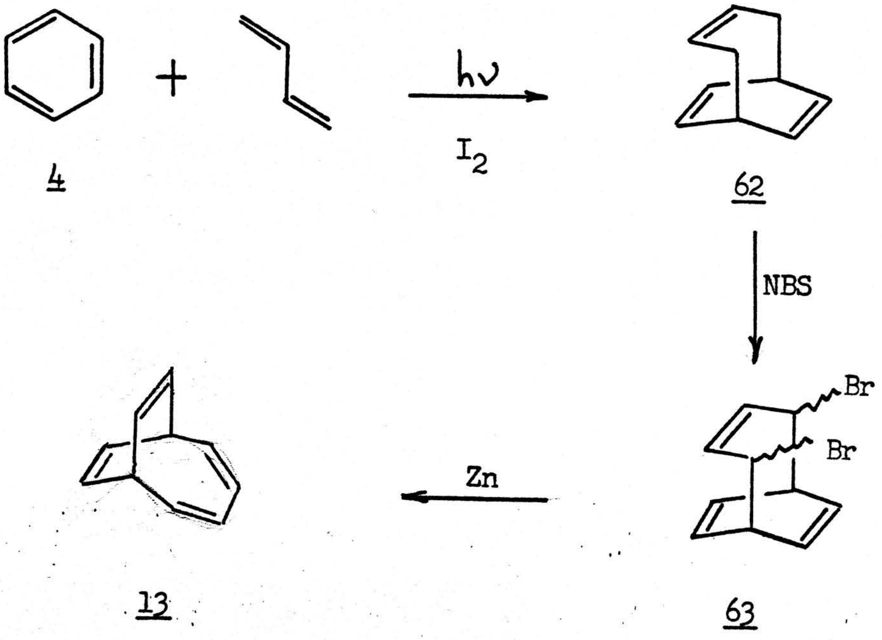
Another $(CH)_4$ source that has been used effectively is α-pyrone.[63] Barrelene 61 has been synthesized by double addition of either methyl vinyl ketone or methyl acrylate to coumalic acid; the latter process is shown below. Standard functional group manipulations give the $(CH)_8$ barrelene (61).

Scheme 8.



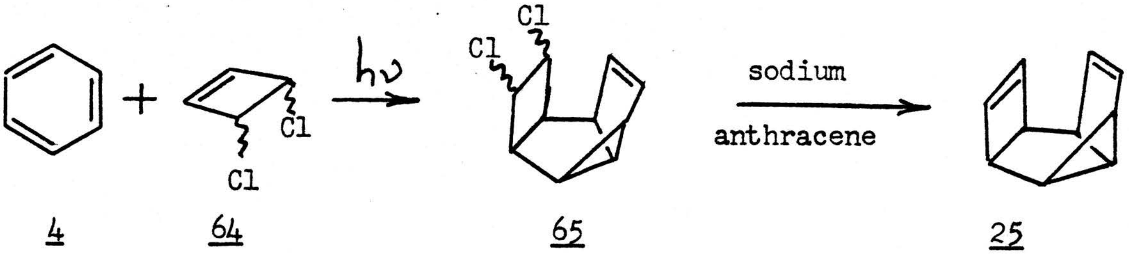
Butadiene has been added to benzene photochemically[64] in the presence of iodine to give the 1,4 adduct 62. Bromination with N-bromosuccinimide afforded the dibromide 63. The 1,4 elimination of bromine, a commonly used reaction in $(CH)_n$ syntheses, was accomplished with zinc. Lithium amalgam has also been used in other cases.

Scheme 9.



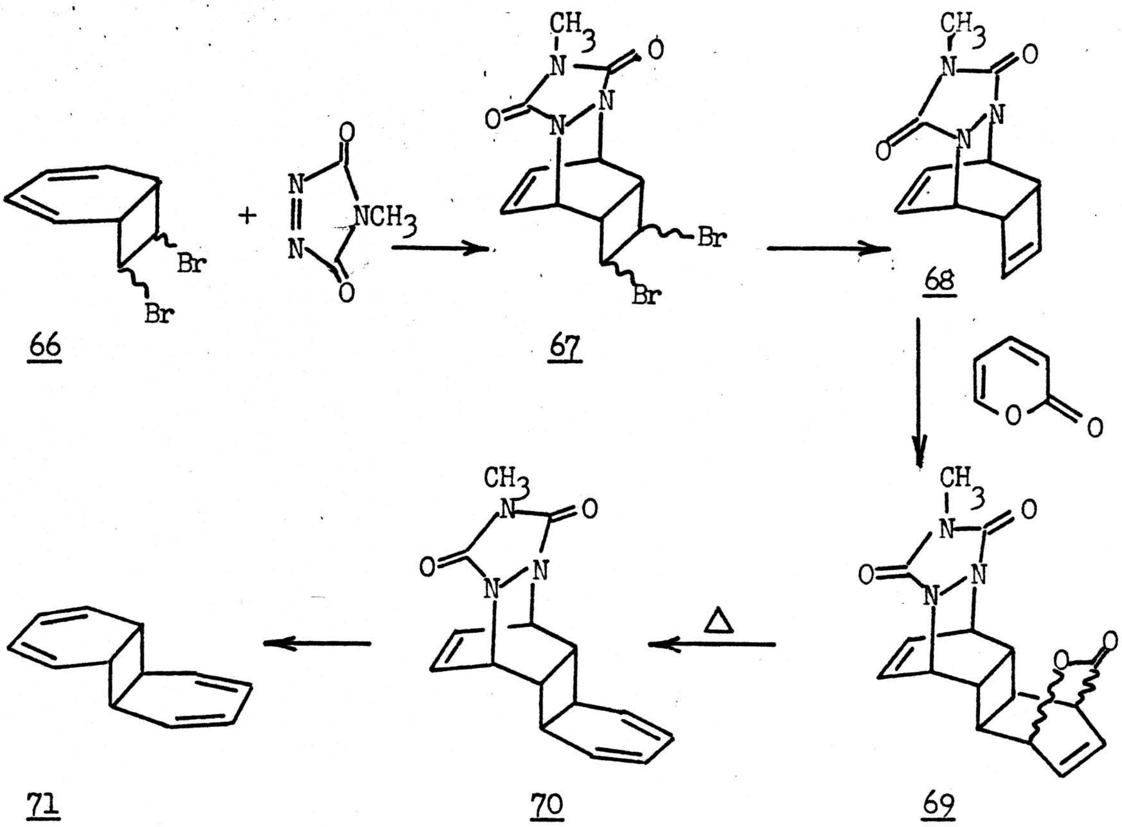
A photochemical addition to benzene has been effected using the masked $(CH)_4$ 64, a precursor in the synthesis of cyclobutadiene. The product 65 is the result of a 1,3 addition to benzene, presumably through the intermediacy of benzvalene.[65,66]

Scheme 10.



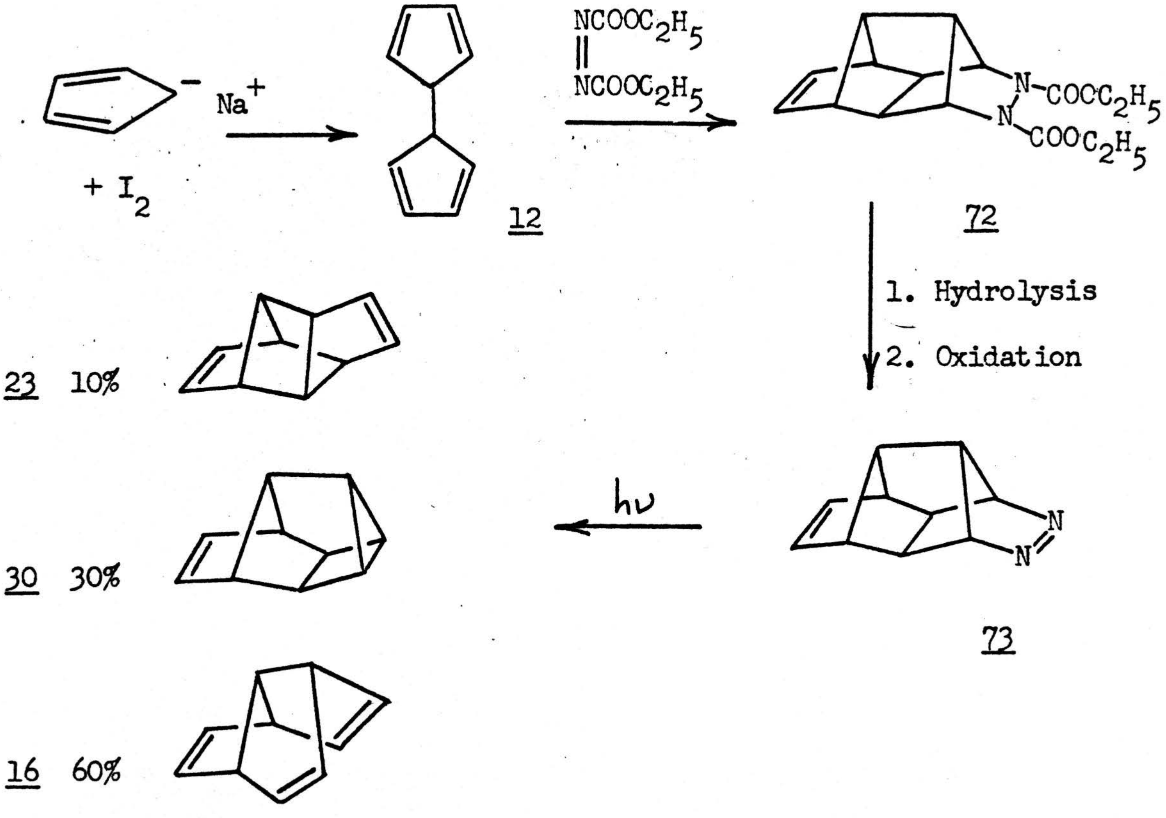
Berson and Davis[67] prepared the elusive benzene dimer 71 by an ingenious sequence. To brominated cyclooctatetraene 66 they added methyl triazolinedione to block the diene. Debromination to give 68, followed by a reverse electron demand Diels-Alder reaction[68,69] with α-pyrone gave, after expulsion of CO_2, the stable masked dimer of benzene 70. Gentle hydrolysis, then $CuCl_2$ oxidation with concomitant elimination of nitrogen gave the $(CH)_{12}$ product desired.

Scheme 11.



An elegant application of another diazo compound was made by Paquette and Wyvratt[70] in a simple and high yield synthesis of triquinacene (16). The unstable dimer of cyclopentadiene, 12[71], was trapped as 72 with diethyl azodicarboxylate in a Domino Diels-Alder reaction.[72] The tricyclic 16 was generated by photochemically induced elimination of nitrogen from 73.

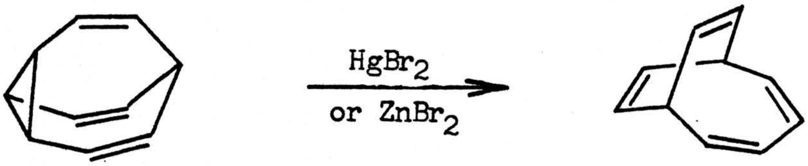
Scheme 12.



Metal salt catalyzed rearrangements make up a class of reactions that have generated new ring systems, and improved yields of compounds previously available.

For instance, bullvalene (2) on standing with mercuric or zinc bromide in ether at 22° for 24 hours is said to form a complex which gives in 90% yield the isomeric hydrocarbon 13.[73]

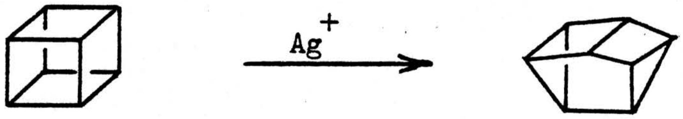
Scheme 13.



2 5 g. 13 4.5 g.

A new ring system was obtained when the isomerization of cubane (55) was carried out with silver or palladium salts giving cunaene (74).[74]

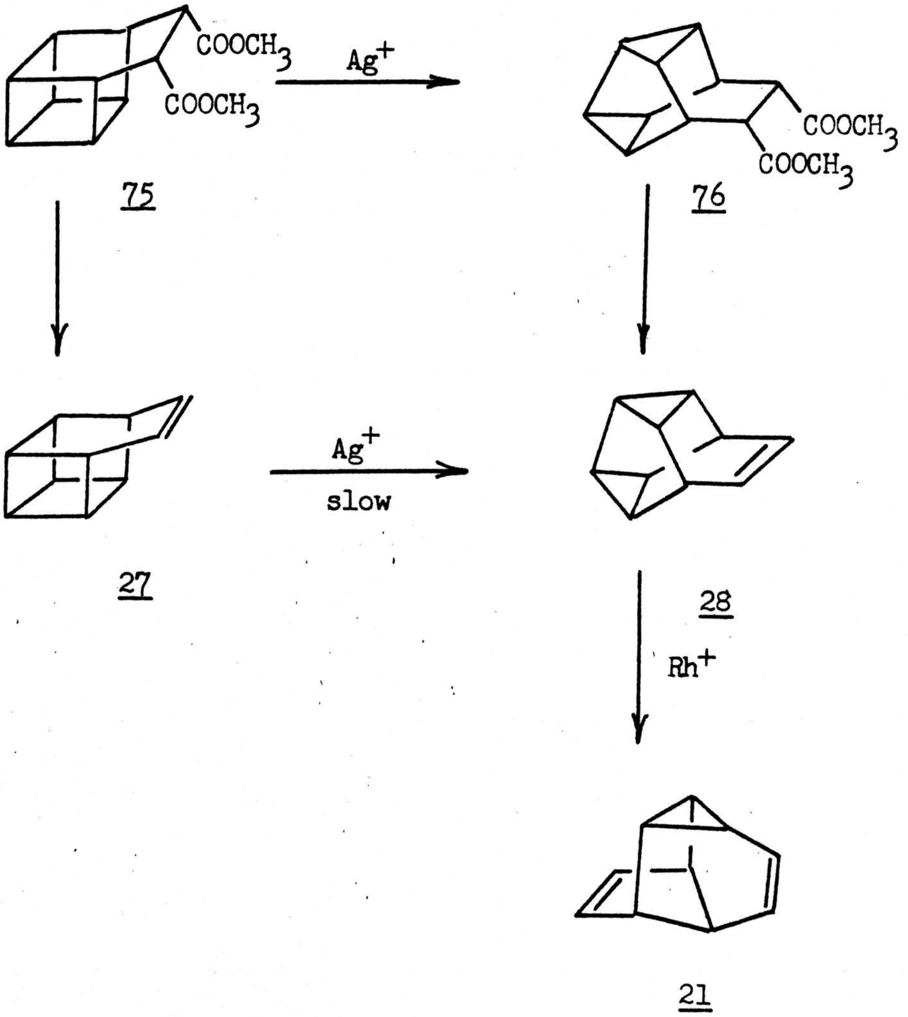
Scheme 14.



55 74

In fact, the effect of silver salts on molecules with strained sigma bonds was discovered by accident, when two French chemists who thought they had synthesized basketene[75] were shown to have obtained snoutene (28) instead.[76,77] A silver nitrate column, used to purify intermediate 76, had caused the isomerization to take place. Snoutene, while it is stable to silver salts, rearranges to another hydrocarbon 21 when rhodium salts are used.[78]

Scheme 15.

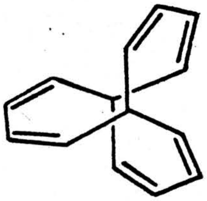


To summarize, the synthetic methodology in $(CH)_n$ hydrocarbon chemistry falls into two general categories. In the first rearrangements of the carbon frameworks have been induced with heat, light, or metal salts. In the second category fall the synthesis in which two (CH) units (often masked) are combined to construct a new larger hydrocarbon skeleton.

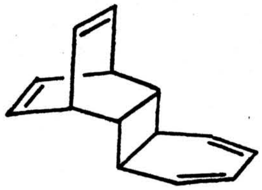
DISCUSSION

The goal of the present work was to synthesize a $(CH)_{14}$ hydrocarbon that would constitute an entry into the $(CH)_{14}$ series: i.e., to prepare a molecule that was reasonably stable, yet could be induced to rearrange, particularly by thermal or photochemical means, to other novel $(CH)_{14}$ isomers.

Part 1 of this Discussion describes the attempted synthesis of the first target molecule 77 and the results that were obtained. In Part 2 the successful synthesis of a second $(CH)_{14}$ hydrocarbon 78 is described.



77

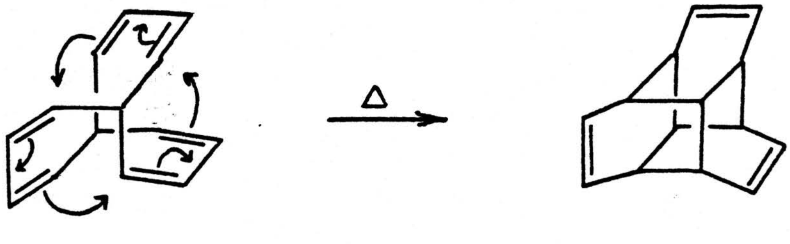


78

PART 1: THE ATTEMPTED SYNTHESIS OF BICYCLO[4.4.4]TETRADECA-2,4,7,9,11,13-HEXAENE (77)

The first hydrocarbon whose synthesis was undertaken was bicyclo[4.4.4]tetradeca-2,4,7,9,11,13-hexaene (77). This spherical molecule, with its D_3 symmetry and its helicity, seemed an interesting compound to synthesize for several reasons. First, from molecular models, 77 appeared to be strain free, and therefore, presumably stable. Secondly, although it has no asymmetric carbon atoms, the molecule itself is chiral. Thus, it would be of additional interest to resolve the racemic compound since conversion of the α to β helix without breaking and reforming bonds would appear to be a process with high activation energy. Thirdly, based on orbital symmetry considerations[10], allowed thermal and photochemical rearrangement products can be postulated. For instance, a possible photochemical product would be 79 which would result from a series of three intramolecular 2 + 2 additions. The report[79] of an unsuccessful attempt to synthesize 80, a possible thermal product, appeared during the course of this work.

77 79



77 80

While one can postulate that 79 and 80 might be derived from 77, only the synthesis and subsequent thermal and photochemical reactions of the parent compound would reveal the actual rearrangement products.

Synthetic Approaches to Bicyclo[4.4.4]tetradeca-2,4,7,9,11,13-hexaene (77)

The approach employed in this work to the synthesis of bicyclo[4.4.4]tetradeca-2,4,7,9,11,13-hexaene (77) divided the problem into two parts. The first task was to construct the unknown* bicyclo[4.4.4]-tetradecane skeleton, and the second was to manipulate functional groups to obtain the desired unsaturation.

Two approaches to the ring construction problem were explored. The first was based on a double Wittig reaction which, it was hoped, would give the carbon framework in one step. The second plan was a stepwise approach that had as the key step an intramolecular cyclization to give the same skeleton.

The Double Wittig Approach

In the Wittig reaction[81,82] an aldehyde or ketone is treated with a phosphorous ylid to form an intermediate betaine which can decompose to give an olefin and triphenylphosphine oxide. The reaction, which is performed under mild conditions, allows the double bond to be introduced in a regiospecific manner while elaborating the carbon skeleton of the molecule.

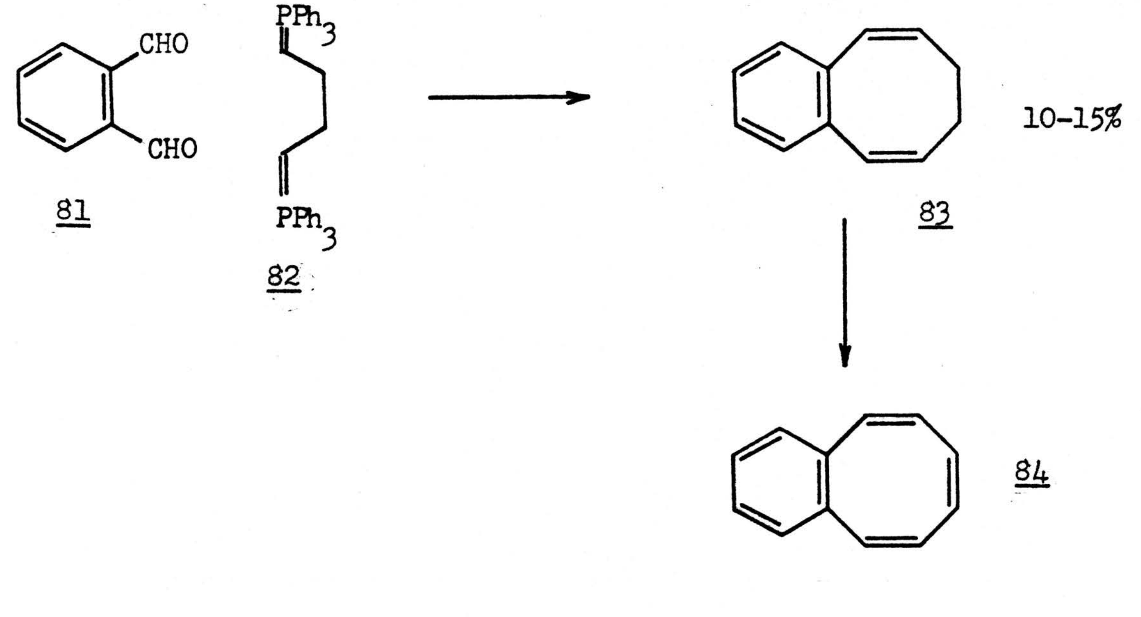
---

* P. v. R. Schleyer *et al*[80] have calculated that 1-bicyclo[4.4.4]tetradecyl chloride should display high solvolytic reactivity, and the difference in strain energy between the bridgehead carbenium ion and the corresponding hydrocarbon should be between -15 and -20 Kcal/mole.

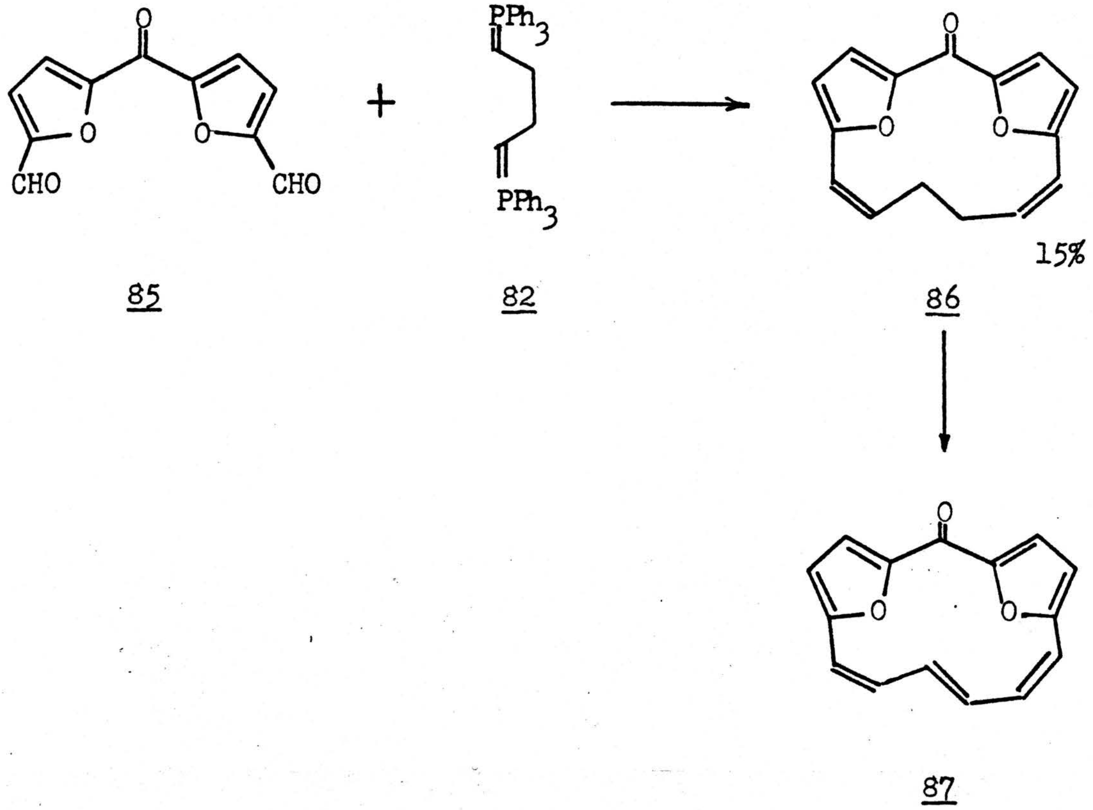
Double Wittig reactions,[83] in which a dialdehyde or diketone is treated with a bisylid, have been employed to synthesize cyclic hydrocarbons with two new double bonds. This reaction, which is a general method for the preparation of cyclic compounds of six members and larger, has been particularly effective in the synthesis of medium rings.[84-90]

The double Wittig reaction planned in the synthesis of the bicyclo[4.4.4]tetradecane skeleton required as a reagent the bisylid 82 that has been employed by several groups to give unsaturated cyclic hydrocarbons. Wittig *et al*[88] allowed 82 to react with phthalaldehyde (81) to obtain a 10% yield of 7,8-dihydrobenzocyclooctene (83). Allylic bromination with N-bromosuccinimide, followed by displacement with acetate, and pyrolysis, gave the further unsaturated benzocyclooctene (84). In another double Wittig reaction, the dialdehyde 85 was treated with the bisylid 82 to give the cyclic compound 86 in 15% yield.[89] This product, too, was converted to a further unsaturated compound 87 by a bromination -- dehydrobromination sequence.

Scheme 17.



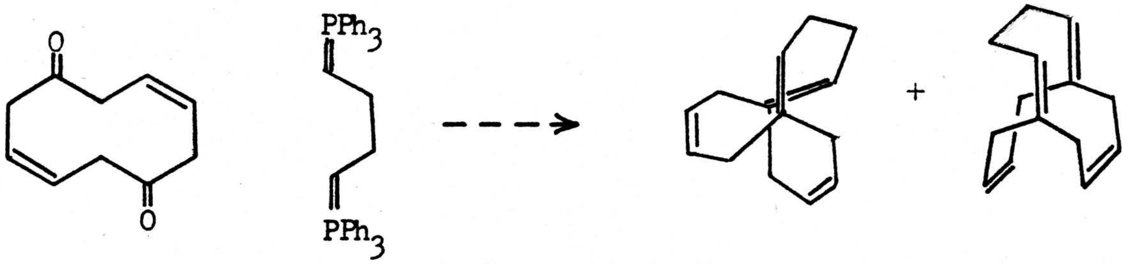
Scheme 18.



Although these precedents suggested that the yield of a similar reaction to prepare the bicyclo[4.4.4]tetradecane skeleton might also be low, the advantage that the new ring system might be constructed in one step with the introduction of two double bonds was considered to outweigh the disadvantage.

In the scheme to prepare the bicyclo[4.4.4]tetradecane skeleton, the bisylid 82 was to be treated with the known (*vide infra*) cyclodecadienedione 88 to produce the two bicyclic $C_{14}H_{18}$ isomers 89 and 90, which differ in the internal relative orientation about the new double bonds introduced. The tetraene 90 has a plane of symmetry; 89 has a C_2 axis, and closely resembles the $(CH)_{14}$ 77 in that it is chiral.

Scheme 19.



88 82 89 90

It is interesting to compare the racemization mechanism of the tetraene 89 and the hexaene 77. The conversion of optically active 89 would require that a bond or bonds be broken and then reformed to give the antipode with the opposite absolute stereochemistry. The hexaene 77 could be racemized simply by rotation about sigma bonds, even though because of strain, the activation energy for this process may be forbiddingly high. The designation of the molecular configuration of 90 as cis and 89 as trans was made according to the IUPAC rules for nomenclature in organic chemistry.[91] Little is known about the actual course of the double Wittig reaction.[83] Thus there is no precedent for favoring one particular relative stereochemistry over the other, and both tetraenes 89 and 90 must be anticipated.

A significant difference between the other double Wittig reactions discussed above and that at hand is that the double bonds to be introduced in this case are at bridgehead positions of a bridged ring system, and might add an element of strain. Becker,[92] and Dauben and Ipaktschi,[93] have employed intramolecular single Wittig reactions effectively to produce strained bridgehead double bonds. Dauben suggests that the bridgehead olefin product is formed in high yield because the reaction takes place in two steps. The initial betaine formation does not introduce much strain, and the loss of triphenylphosphine oxide, the driving force for the reaction, overcomes the strain introduced by the bridgehead double bond.

A bromination - dehydrobromination sequence was planned to convert the tetraenes 89 and 90 to the final $(CH)_{14}$ product 77.

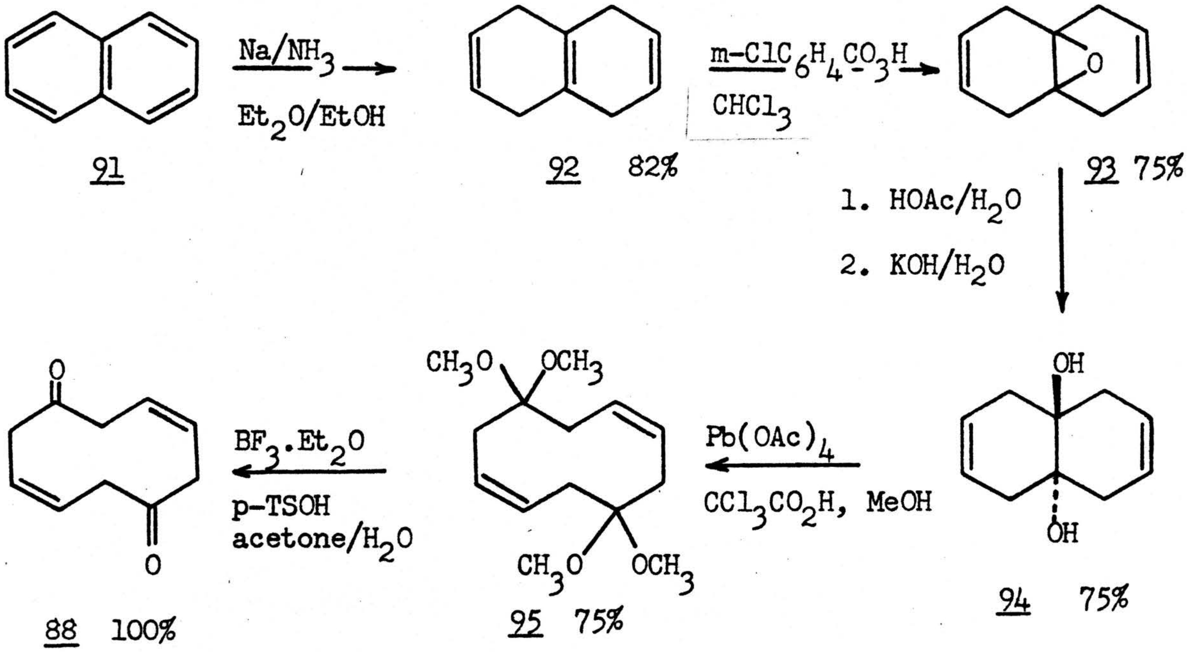
The Double Wittig Reaction

The precursor of the bisylid 82, the bisphosphonium salt of 1,4-dibromobutane, was prepared by the method of Horner *et al.*[94] The bright orange bisylid was most conveniently generated by treatment of a suspension of the bisphosphonium salt in tetrahydrofuran with n-butyllithium.

The other starting material, the dione 88, has been synthesized by Grob and Schiess.[95] A modification of their procedure, developed by Sondheimer,[96,97] was employed to prepare the dione, and as outlined on the next page.

The reaction between the bisylid 82 and the dione 88, did not yield observable quantities of 89 or 90. The conditions of the reaction were varied: the order of addition of the reagents was reversed; the reaction was carried out at higher dilution; the temperature that the reaction was allowed to reach, and the reaction time were varied; an attempt was made to isolate the intermediate bisbetaine with hydrogen bromide[98]. All these modifications were unsuccessful. No hydrocarbons were isolated.

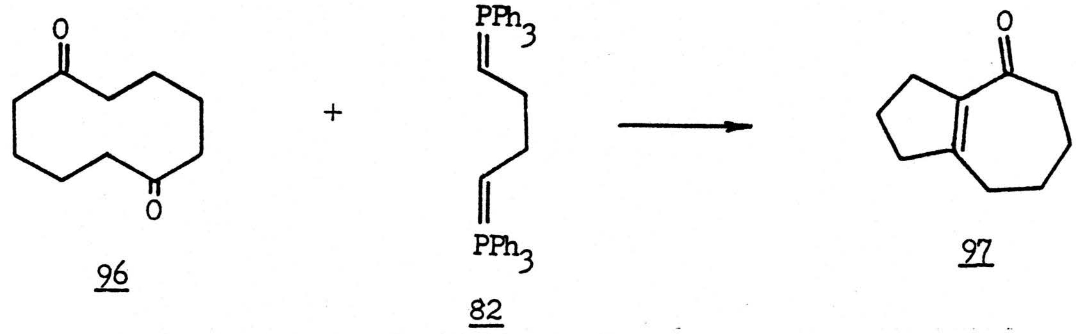
Scheme 20.



The double Wittig reaction was attempted using an alternate dione 96 obtained by hydrogenation of 88 at atmospheric pressure. Under the reaction conditions employed, the dione underwent an intramolecular aldol condensation giving a product whose infrared and nmr spectra were consistent with the structure 97.

This is a not unexpected result. Hückel *et al*[99] reported that heating an aqueous solution (either acidic or basic) of the dione 96 led to the formation of 97.

Scheme 21.

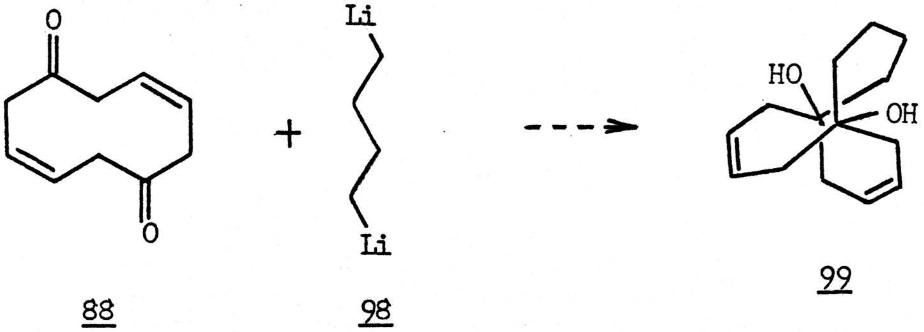


96 82 97

An Alternate Four Carbon Bridging Reaction

A different reaction, shown below, was carried out to add the four carbon bridge to the ten membered ring.

Scheme 22.



88 98 99

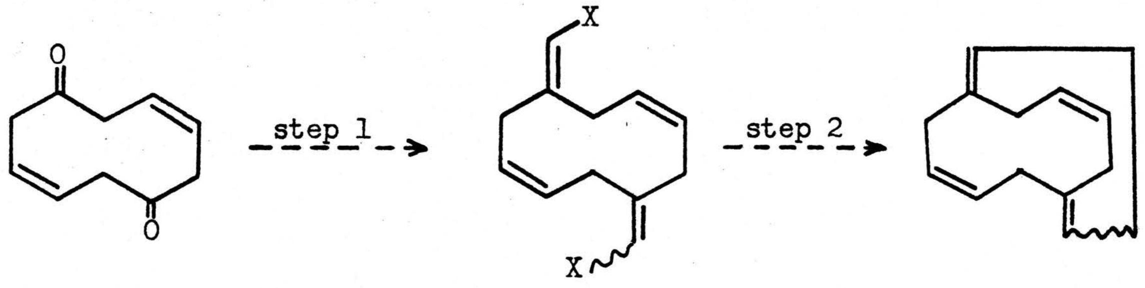
1,4-dilithiobutane (98) was prepared by the method of West and Rochow,[100,101] and added to the dione 88. All the products isolated showed carbonyl absorption in the infrared spectra.

At this point, the bridging of the ten membered ring with a four carbon unit reaction was abondoned, and a second approach to the ring construction problem was devised.

The Stepwise Approach to the Construction of the Bicyclo[4.4.4]tetradecane Skeleton.

In outline, the stepwise approach planned was to add two two-carbon units to the same ten membered ring 88, and then by some cyclization procedure, to join the termini of the two carbon units and thus form the bicyclo[4.4.4]tetradecane skeleton.

Scheme 23.



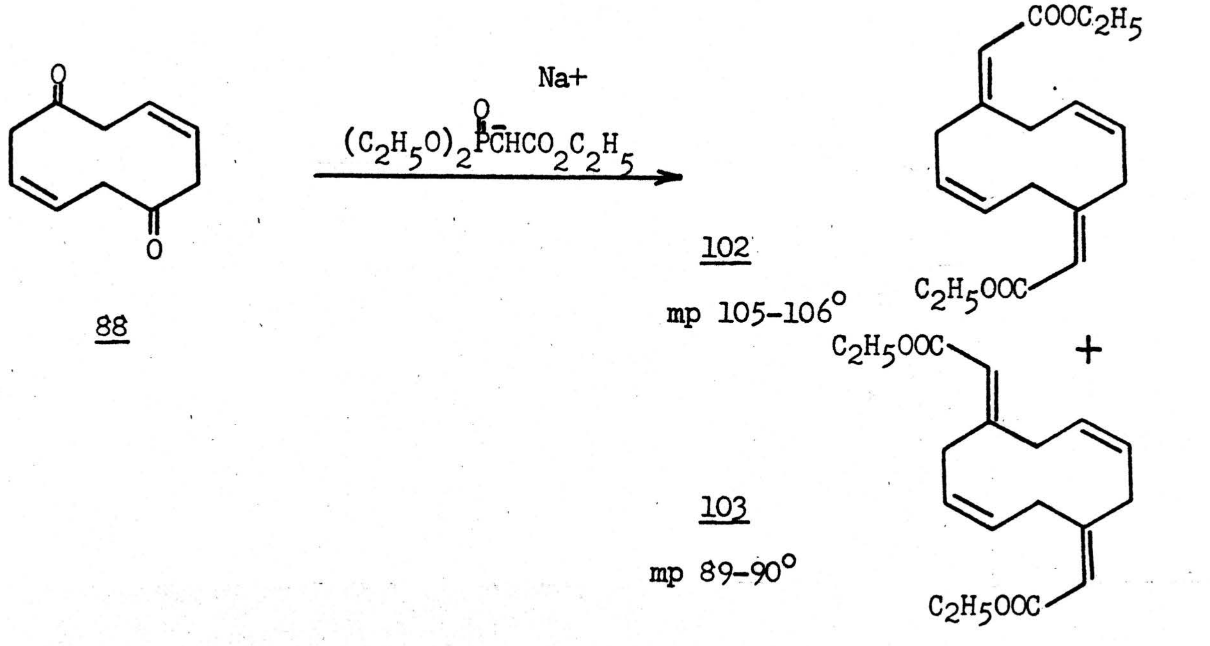
88 100 101

The number of methods available, depending on the nature of the variable x, made this route appear attractive.

Step 1: Addition of the Two-Carbon Bridges.

Step 1 was readily accomplished with the Wadsworth-Emmons[102,103] modification of the Wittig reaction, in which the sodium salt of triethyl phosphonoacetate was reacted with 88. Two products, 102 and 103, were obtained as a 1:1 mixture, in 86% isolated yield. Separation was achieved by a combination of column chromatography and fractional crystallization.

Scheme 24.



88

102

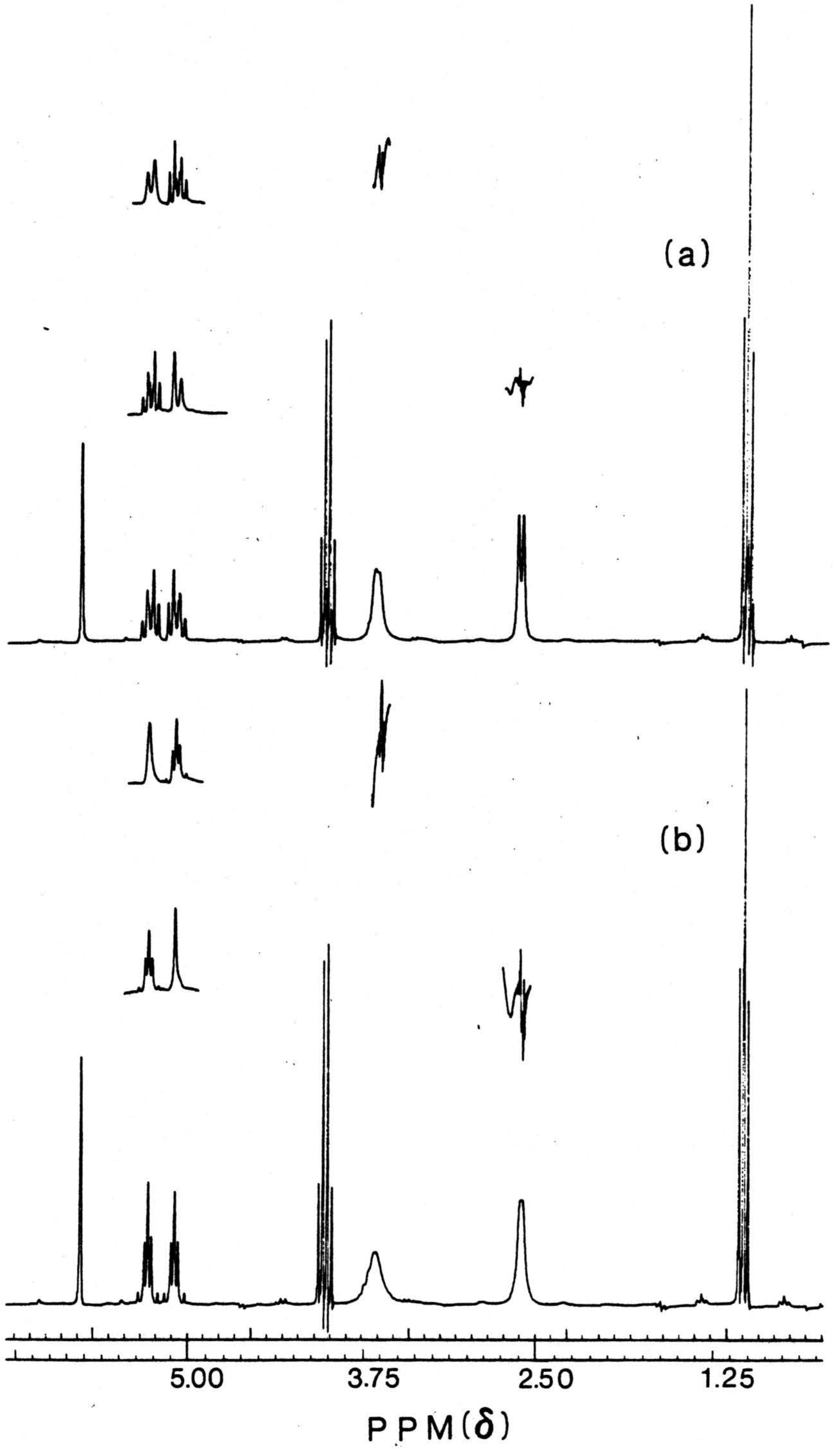
mp 105-106°

103

mp 89-90°

The infrared, mass spectra, and carbon magnetic resonance spectra of the two compounds were closely similar. The endocyclic vinyl patterns were superimposed in the deuterochloroform spectra. The structures were assigned on the basis of proton nmr decoupling experiments performed on deuterobenzene solutions at 220 MHz. The spectra are reproduced in Figure 4, and the chemical shifts are listed in Table 1.

Figure 4.



220 MHz NMR Spectrum of trans Diester <u>102</u> (a) and cis Diester <u>103</u> (b) in C_6D_6.

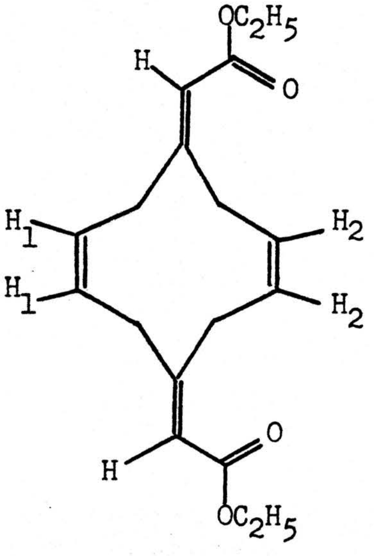
The deshielding effect of the carboethoxy group[104] causes the proximal methylene protons on the ring to be shifted downfield relative to the other ring methylenes. The endocyclic vinyl protons are subjected to the same effect, but more weakly. Two distinct carbocyclic methylene, and two endocyclic vinyl patterns are observed.

Table 1.

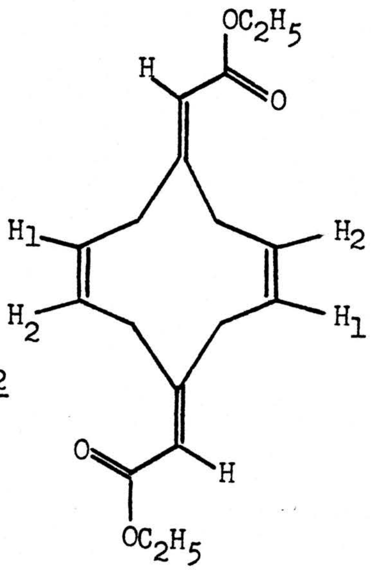
The Chemical Shifts of Diesters 102 and 103 in C_6D_6, 220 MHz NMR

	a	b
CH_3	δ 1.03	δ 1.03
CH_2O	4.03	4.03
CH_2	2.63	2.64
CH_2	3.65	3.67
=CH endo	5.14	5.11
=CH endo	5.27	5.30
-CH exo	5.79	5.79

If the structures are viewed as shown below, it is seen that the cis compound has a plane of symmetry and that the trans compound has a C_2 axis. In both cases, when the methylene protons that appear further upfield are irradiated, the endocyclic vinyl patterns are observed to change in a predictable manner. In the cis case, the upfield vinyl pattern appears as a singlet, the result of the two symmetry equivalent protons (H_1) on the double bond being decoupled from the rest of the molecule. In the trans compound, the upfield vinyl proton (H_1) is reduced to a doublet as it remains coupled to a non-equivalent proton (H_2) on each double bond. Irradiation of the downfield methylene protons causes the downfield vinyl protons (H_2) to be affected similarly. Thus, spectrum a is that of the trans isomer 102 and spectrum b is that of the cis isomer 103.



103

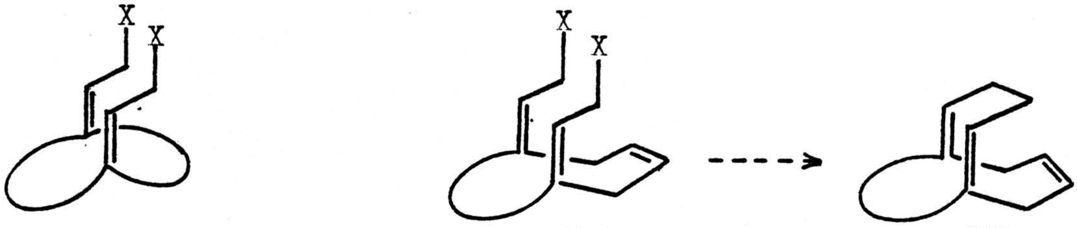


102

Step 2: The Cyclization Step

Molecules of the form 100 have two general features which can be taken into consideration when determining the method to be employed to synthesize the bicyclo[4.4.4]tetradecane skeleton.

Scheme 25.



100 a 100 b 101

First, as in 100 a, the problem can be considered as the coupling of two allyl units to give a substituted 1,5-hexadiene derivative. Reactions specifically designed for the purpose have been developed and extensively used, particularly in natural product syntheses.

Secondly, as in b, it can be seen that the cyclization gives a bicyclic system containing ten membered rings. The synthesis of ten membered rings has been difficult and, until recently, few methods for their construction had been developed.

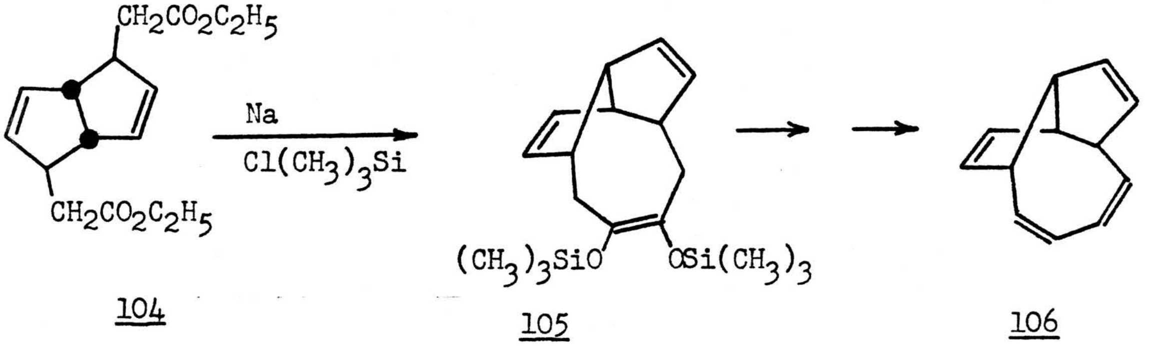
These general considerations are elaborated further below.

A: Attempted Coupling of the Allylic Diesters

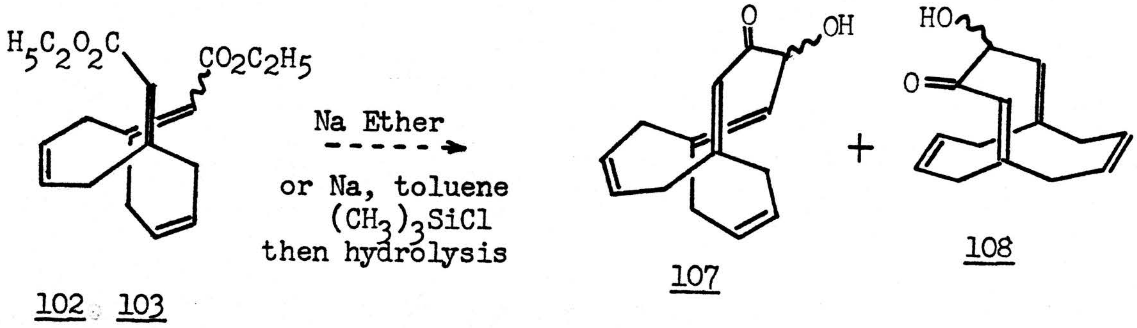
The first coupling reaction tried was the most direct one, the acyloin condensation[105,106,107]. Developed to prepare medium and large ring compounds, the acyloin has been the traditional method of preparation of ten membered rings.

A step in the synthesis[110] of the novel $(CH)_{12}$ hydrocarbon 106 was effected with this modification of the acyloin reaction.

Scheme 26.



Scheme 27.



Dimethyl decane-1,10-dicarboxylate has been cyclized under acyloin conditions to give 67 - 74% of the cyclized compound[106], 2-hydroxycyclododecanone. The yields of cyclization products have been much improved in some cases, by trapping the cyclized product as the bis silyl enol ether.[108,109] Prolonged reaction of a mixture of <u>102</u> and <u>103</u>, employing either the standard acyloin conditions or the modified ones, yielded only recovered starting material.

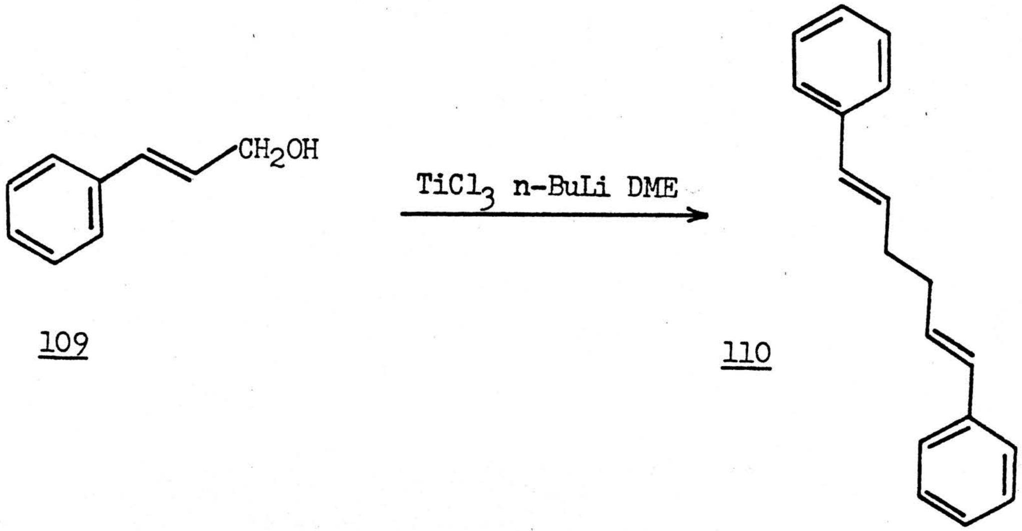
B: Attempted Coupling of the Allylic Diols

A method for coupling allylic alcohols developed by van Tamelen[111] was considered next. 1,5-Dienes have been synthesized by treatment of alkoxides of allylic alcohols with titanium trichloride and an alkyl lithium reagent. It has been suggested that the $TiCl_3$ may react with the alkoxide, then with the alkyl lithium to give a dialkoxyalkyl titanium compound. This compound then disproportionates and loses TiO_2 on heating resulting in the coupling of the alkyl residues.

$$\begin{tikzcd}
TiCl_3 + 2\ ROH \arrow[r, "2\ R'Li"] & \left[(RO)_2TiCl \right. \arrow[r, "R'Li"] & (RO)_2TiR' \arrow[d, "-R'\cdot"] \\
R_2 + TiO_2 & \left[(TiO_2)R_2 \right. \arrow[l] & (RO)_2Ti \arrow[l]
\end{tikzcd}$$

An intermolecular model reaction was first attempted using van Tamelen's conditions[112]. A 30% yield of the hydrocarbon 110 was obtained from cinnamyl alcohol (109).

Scheme 28.

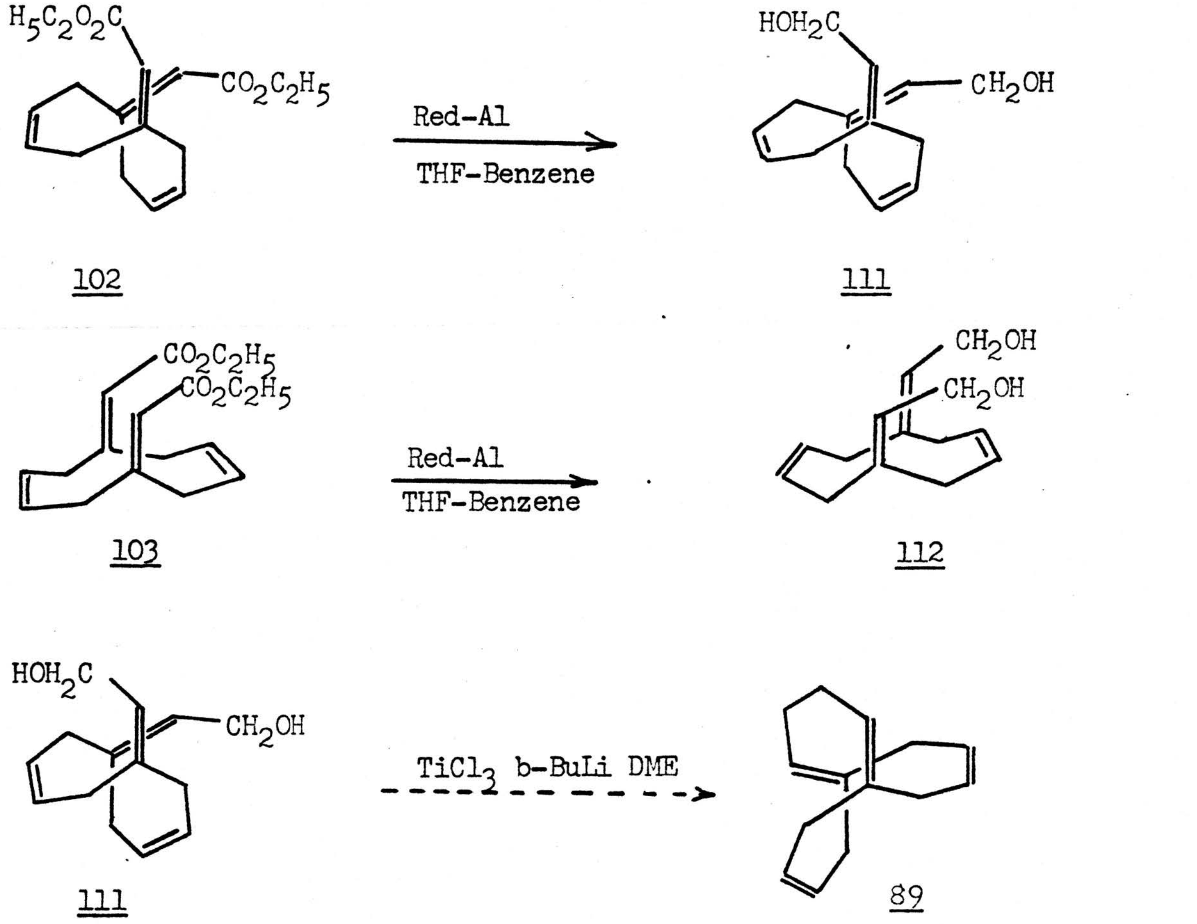


109

110

The diesters 102 and 103 were reduced to the corresponding allylic diols 111 and 112 by reaction with sodium-bis-(2-methoxyethoxy)aluminum hydride (Red-Al)[113] in tetrahydrofuran-benzene.

Scheme 29.



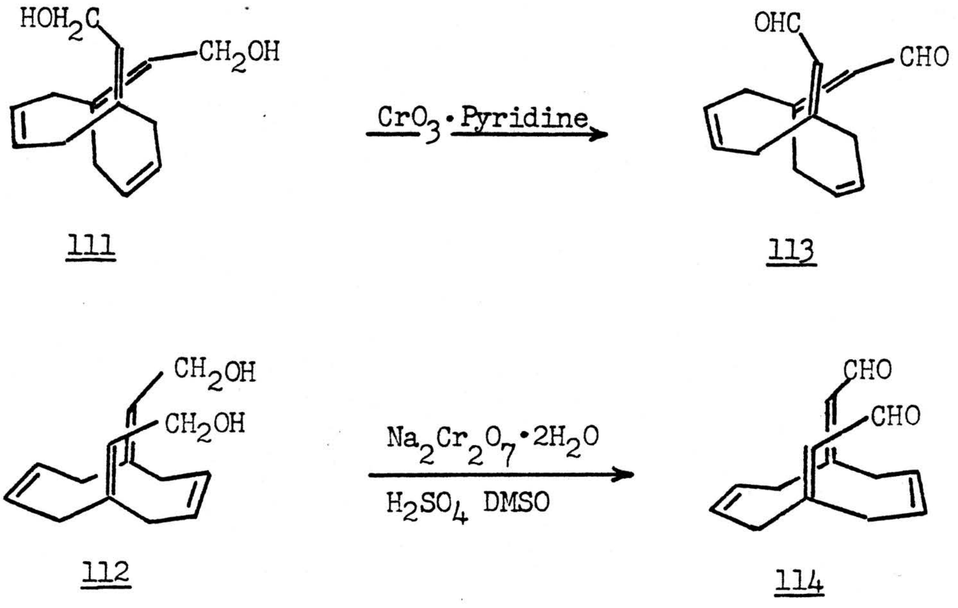
The diol <u>111</u> was subjected to van Tamelen's reaction conditions. Starting material was recovered. The failure of the reaction to take place was ascribed at least in part to the low solubility of the reactants in the ethereal solvent at -78°.

C: Attempted Coupling of the Allylic Dialdehydes

Two variants of the pinacol reaction were attempted to effect the intramolecular coupling of the allylic dialdehydes 113 and 114. The dialdehydes were prepared from the allylic diols by either Collins oxidation[114] which gave yields of 50%, or by an oxidation procedure developed by Rao[115] using sodium dichromate dihydrate and sulfuric acid in DMSO giving yields of 75%.

The first intramolecular reductive coupling attempted was based on a method developed by McMurry and coworkers.[116] Employing a 2:1 mixture of titanium trichloride and lithium aluminum hydride, they were able to effect the intermolecular coupling of a variety of carbonyl compounds. The α,β-unsaturated aldehyde retinal was coupled to give an 85% yield of β-carotene.[117] The intermediacy of pinacols was shown by their isolation and conversion under the reaction conditions to olefins.

Scheme 30.



111

113

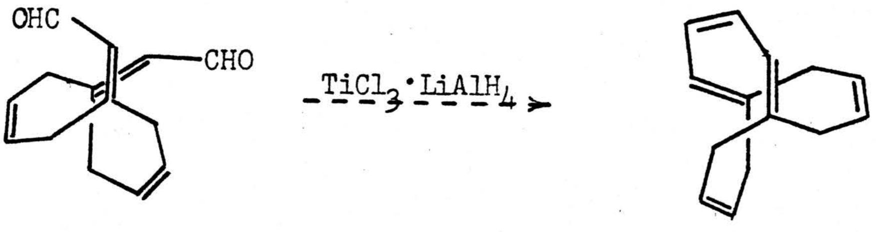
112

114

As a model study, the reductive coupling of benzophenone to tetraphenylethylene was carried out in 30% yield using McMurry's conditions.

The intramolecular coupling reaction was attempted on the trans dialdehyde 113.

Scheme 31



113 115

Only polymeric product was obtained.

One pinacol reduction of the dialdehyde with amalgamated aluminum was attempted using a system Schreibmann[118] has reported. He claimed to have obtained solutions of the pinacolates using THF or CH_2Cl_2 as solvents. The dialdehyde, in this instance, was recovered unchanged.

D: Coupling of the Allylic Halides

Extensive use of allylic halides has been made to prepare 1,5-dienes in coupling reactions mediated by metals. One such method that has long been known is the Grignard coupling of allylic halides with magnesium.[119] A more recent development is the reaction of allylic halides with zero valent nickel to give, *inter alia*, 1,5-dienes.[120]

The Grignard Coupling Reaction with Magnesium.

The Grignard reaction, which is experimentally more convenient, was investigated first. The nature of the Grignard coupling reaction is not well understood.[121] It has been suggested that the reaction may proceed at least partly by a free radical Wurtz type mechanism, and partly by formation of the allylic Grignard reagent which may then react with the remaining unreacted allylic halide.[122]

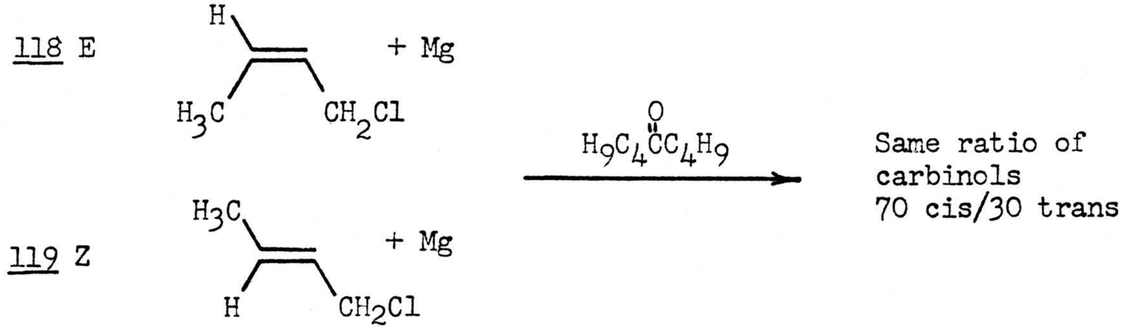
The structures of allylic Grignard reagents and the compositions of their ethereal solutions have received extensive study.[123,124,125] Grignard reagents are known to be in equilibrium in ether solutions with the dialkyl (or aryl) magnesium compound and dihalomagnesium. In the case of allylic Grignard reagents in ether, this "Schlenk equilibrium" favours the Grignard reagent with K approximately 50.[123]

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX$$

Studies have shown that the Grignard reagent, the dialkyl magnesium compound, and MgX_2 all occur in associated form in the reaction solution. The degree of association is dependent on the concentrations of the equilibrating species and the nature of the solvent. At concentrations of less than 0.05 molar in ether, the constituents of the equilibrium mixture are thought to be monomeric.

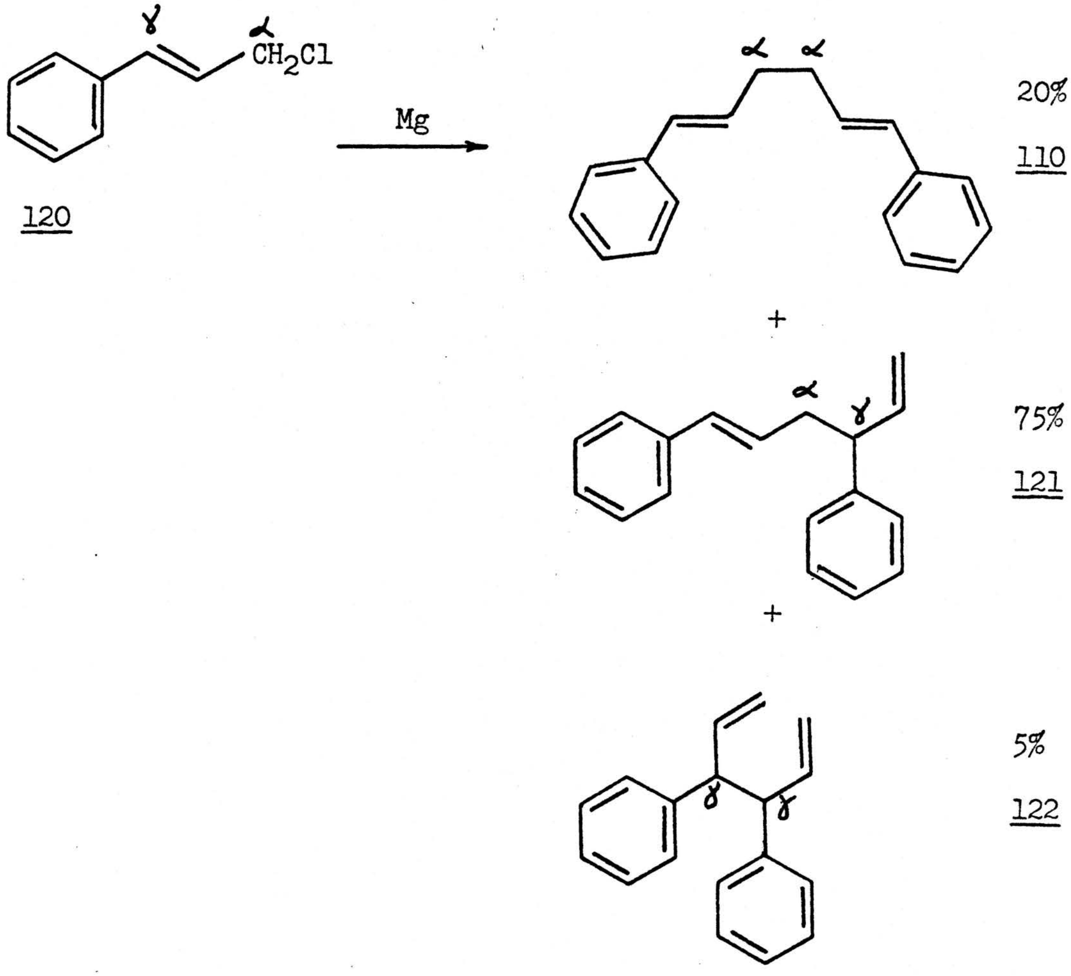
The structures of simple allylic Grignard reagents have been studied recently by nmr.[126] In a very few cases the Schlenk equilibrium could be determined, but generally it was found that the signals of the dialkyl magnesium compound and the Grignard reagent were superimposed. It has been shown that the magnesium is bound to the primary centre in allylic Grignard reagents such as those of 118 and 119. There is a rapid equilibrium between E and Z stereoisomers. The intermediacy of dialkyl magnesium compounds and the 1,3 shifted Grignard reagent have been postulated to account for the equilibrium. Low temperature nmr experiments did not lead to freezing out of the E to Z interconversion, suggesting that the barrier to interconversion is low. In fact, it has been shown that the Grignard reagents derived from 118 or 119 with symmetrical ketones gave the same ratio of stereoisomeric products.[127]

Scheme 32.



In spite of the uncertainty about the mechanism of the reaction Grignard couplings have been effected in high yield.[119,128,129] Typically, mixtures of hydrocarbons have been obtained with the predominant product that of the coupling of the α carbon of one allyl unit with the γ carbon of the other, as illustrated below for the case of cinnamyl chloride, where an 85% yield of coupled products was obtained.[128]

Scheme 33.



120

20% 110

75% 121

5% 122

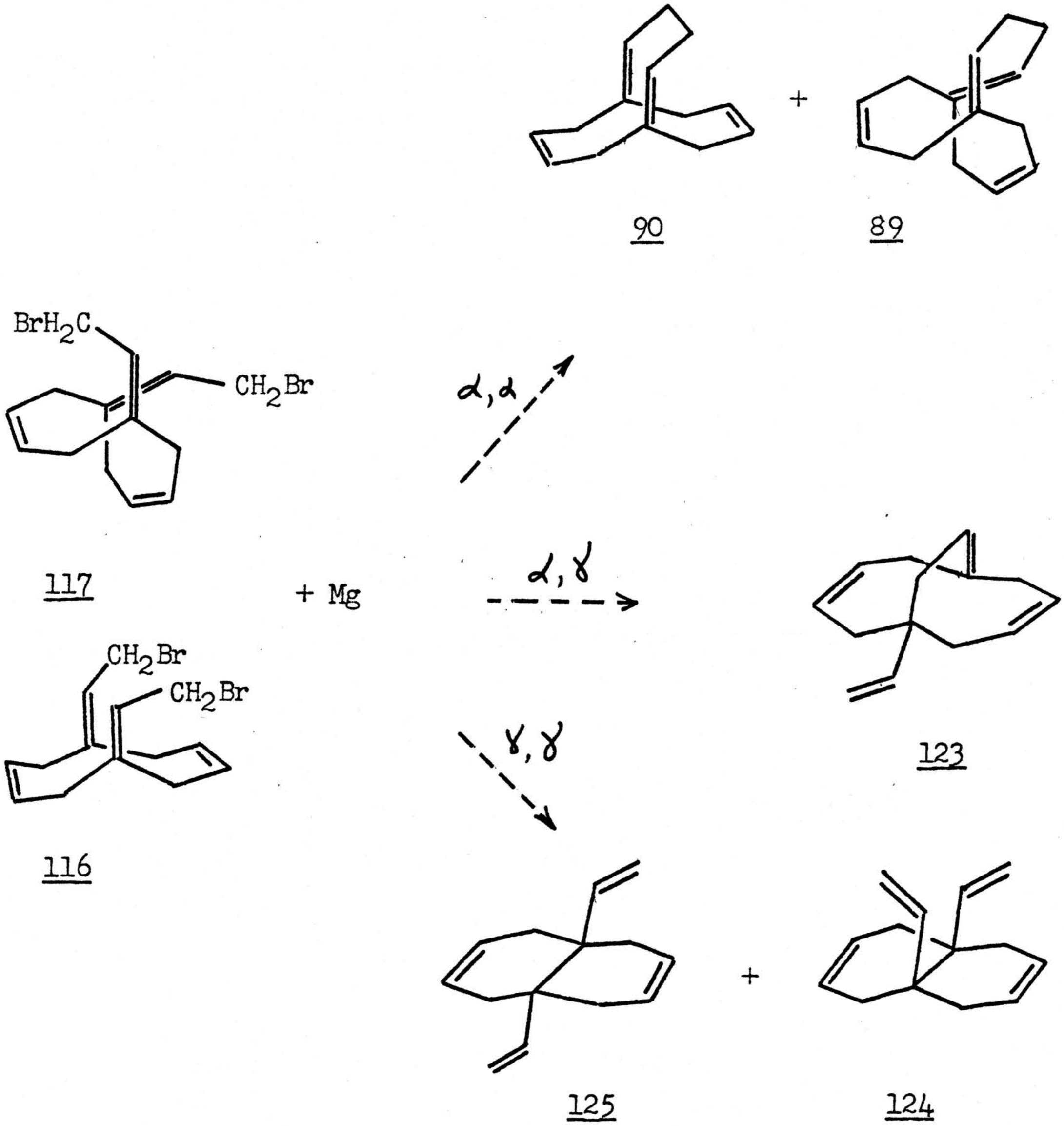
It was hoped that the allylic halides 116 and 117, prepared from the corresponding allylic alcohols 111 and 112 by treatment with phosphorus tribromide in ether,[130] could be induced to undergo analogous intramolecular cyclizations. The formation of the analogue of 121, the $\alpha\gamma$ cyclization product, 123, was thought to be unlikely. The steric constraints imposed by the ten membered ring could prevent the two carbon atoms from approaching close enough to react. The analogues of 110, derived from coupling of the primary termini, would give the desired bicyclo[4.4.4]tetradecane hydrocarbons 89 and 90. Because the stereochemical integrity of the allylic halide is lost during Grignard formation, both products must be anticipated from either allylic halide. Coupling of the γ carbon atoms would be expected to give two products, the cis and trans divinyl hexalins 124 and 125, depending on the conformation of the ten membered ring in the transition state.

The cis dibromide 116 was subjected to the Grignard reaction conditions, using slightly more than one equivalent of amalgamated magnesium in ether. Two coupled products, subsequently shown to be 124 and 125, were obtained in 30% overall yield, with a 6:4 ratio of cis to trans ring fused isomers. The divinyl hexalins were obtained as a mixture and the only non polar products of the reaction. The isomers were separated on silver nitrate impregnated thin layer plates.

The trans dibromide 117 gave the same two products in 15% yield with a ratio of cis to trans fused stereoisomers of 4:1.

It is tempting to speculate that the predominance of the cis isomer over the trans indicates that a cyclic transition state plays a role in determining the stereochemical ratio of products.

Scheme 34.



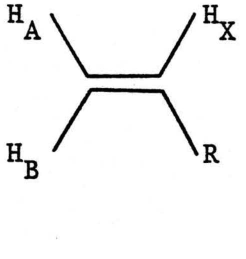
The ambient temperature 60 MHz nmr spectra presented in the Spectra section, as well as the infrared data, were consistent with the structures proposed, but did not allow the stereochemistry of the ring fusions to be deduced.

The chemical shifts and coupling constants of the exocyclic vinyl protons were obtained by matching computer calculated spectra with the experimental data*. The shifts and coupling constants are listed in Table 2 and the computer derived spectra of the exocyclic vinyl protons are shown with the spectra from which they were obtained in Figures 5 and 6.

Table 2.

The Chemical Shifts and Coupling Constants of the Exocyclic Vinyl Protons of 124 and 125, 60 MHz NMR.

	Trans 125	Cis 124
H_A	296.5 Hz	304.5 Hz
H_B	305.5	303.5
H_X	364.5	364.0
J_{AB}	1.8	1.8
J_{BX}	17.6	17.6
J_{AX}	11.0	11.0



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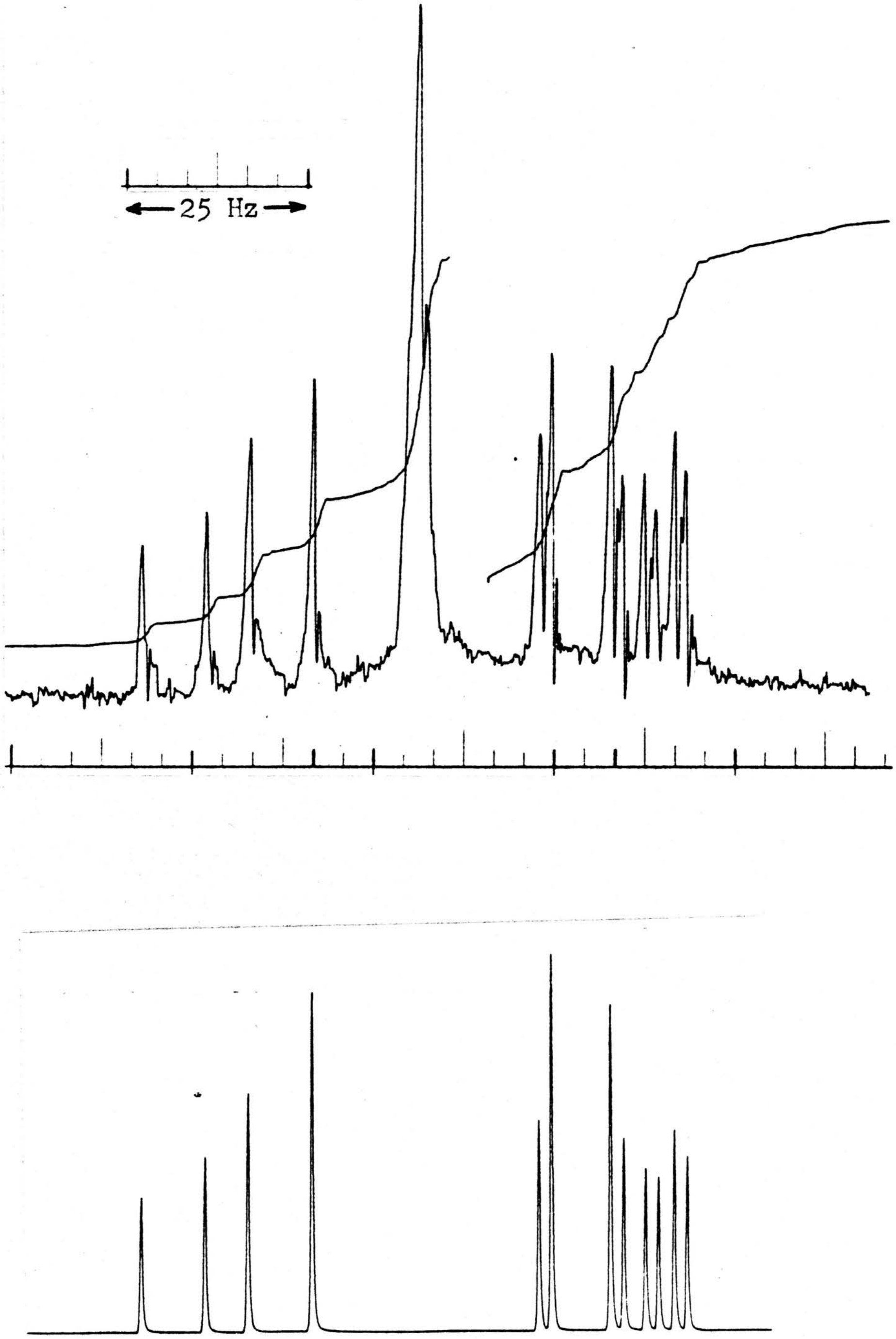
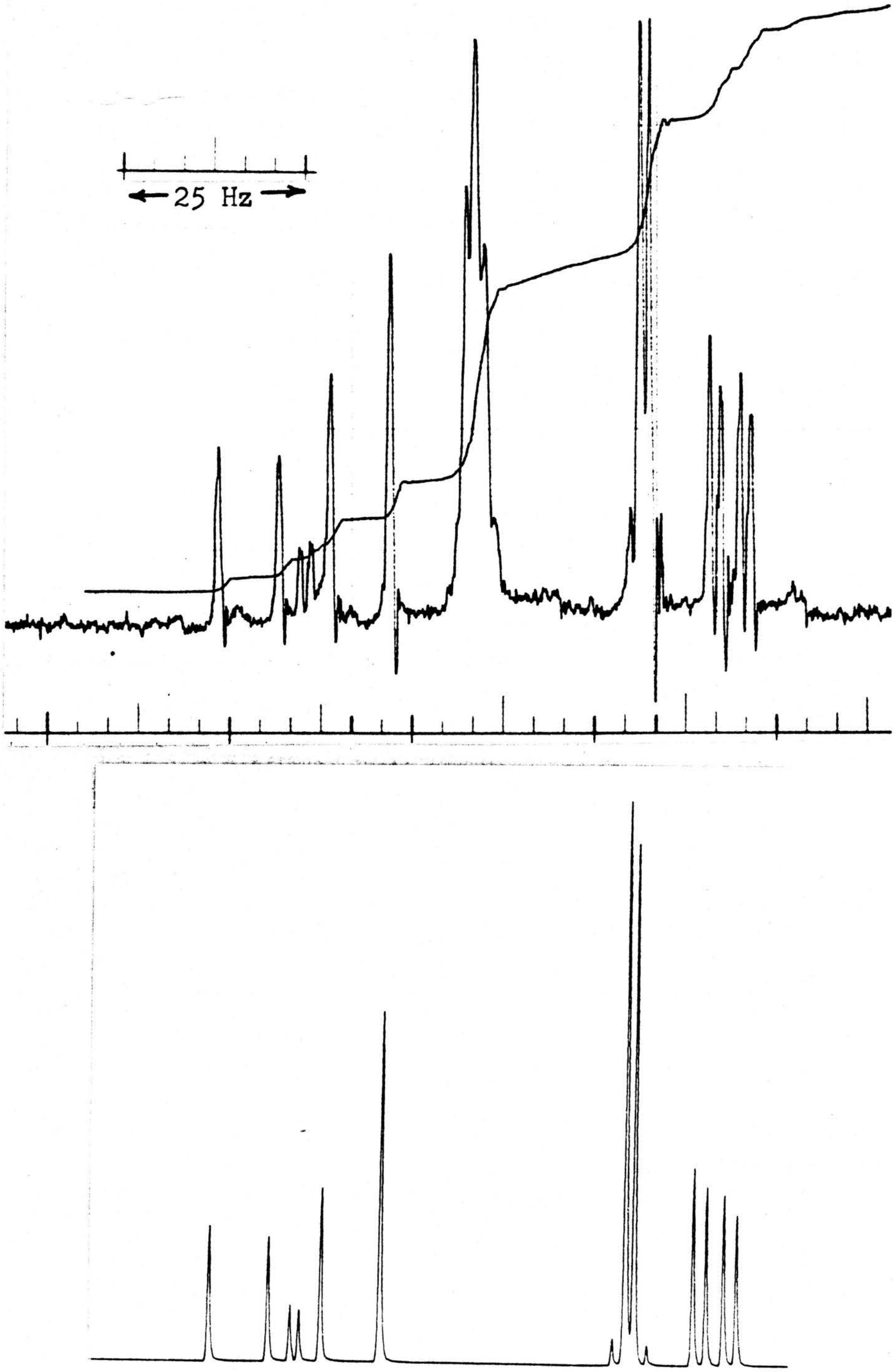
* The author wishes to express her thanks to Dr. A. G. McInnes, Mr. Don Smith and Mr. John van Ingen of the National Research Council for performing the nmr experiments. Mr. Smith did the computer simulations and Mr. van Ingen performed the variable temperature experiments.

Figure 5.



60 MHz NMR Spectrum of the Vinyl Region of trans-Divinyl Hexalin 125 250 Hz Sweep Width Shown with the Computer Derived X Portion of the ABX Pattern.

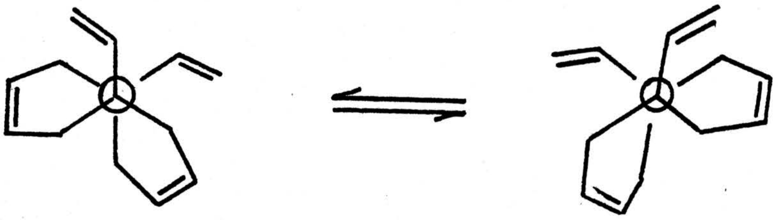
Figure 6.



60 MHz NMR Spectrum of the Vinyl Region of cis-Divinyl Hexalin 124 250 Hz Sweep Width Shown with the Computer Derived X Portion of the ABX Pattern.

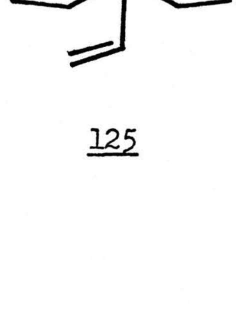
The stereochemistry of the ring fusion of the two hydrocarbons was deduced from variable temperature nmr studies.

The basis for the differentiation between the two stereoisomers was the conformational mobility of the cis fused compound and the comparative rigidity of the trans fused bicyclic system. An examination of molecular models suggests that the two degenerate conformers 124A and 124B are preferred for the cis compound, while the trans fusion in the other isomer prevents the rings from flipping.



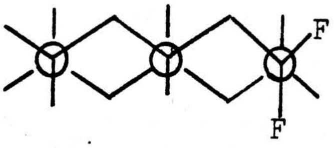
124 A

124 B

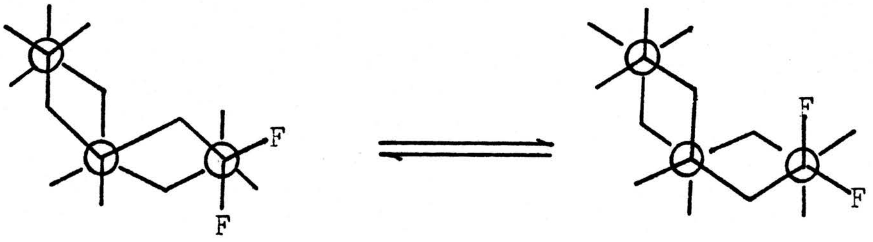


125

Similar reasoning has been used for the case of cis and trans fused decalins.[131,132,133] Roberts studied the substituted decalins 126 and 127. The F^{19} nmr spectrum of the trans isomer was invariant with temperature and showed an AB quartet for the two nonequivalent fluorines. The cis isomer gave at room temperature an AB quartet as well, but as the temperature was lowered two distinct AB quartets emerged.



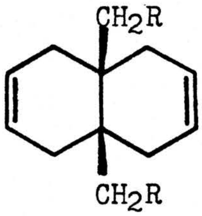
126



127 A

127 B

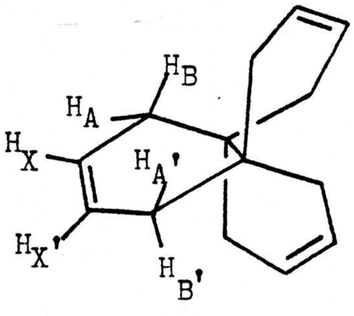
Gilboa and coworkers[134] have studied the temperature dependence of the nmr spectra of 128, 129, and 130, systems closely related to cis-9,10-divinyl hexalin.



128 R = Br
129 = CN
130 = $COOCH_3$

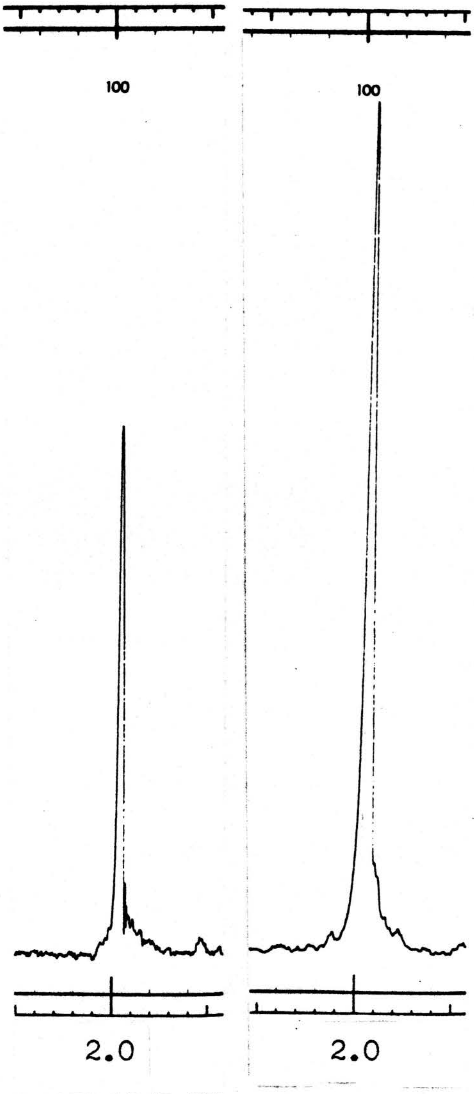
They found that at low temperatures, when the frequency of interconversion between conformers was low, the exocyclic methylene protons appeared as an AB quartet. With higher temperatures the frequency increased, the methylene protons became equivalent on the nmr time scale, and the quartet collapsed to a singlet.

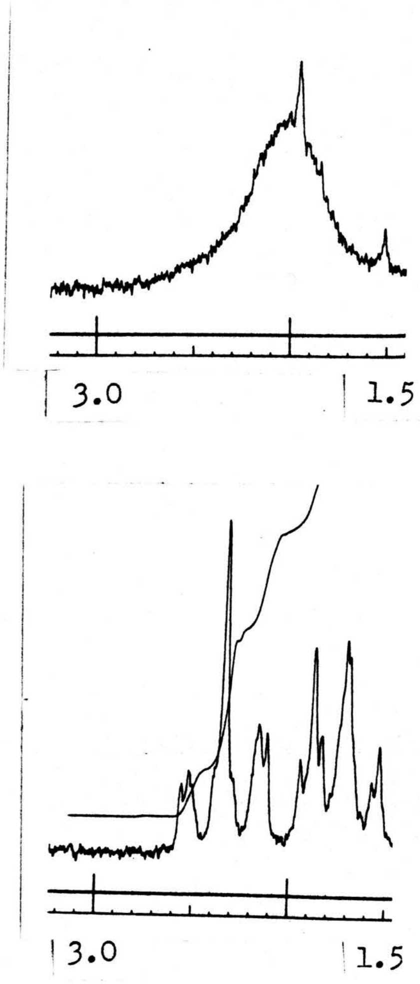
They also studied the propellatriene 131. The AA'BB'XX' system was simplified by irradiating the vinyl region so that an AA'BB' system resulted. At 90°C the allylic protons appeared as a singlet, but at -10° a quartet with further splitting resulted.



131

Figure 7.





100 MHz NMR Spectrum of the methylene protons of trans-divinyl hexalin 125 at ambient temperature (left) and -55^{o} (right). The two spectra were run at different amplitudes.

100 MHz NMR Spectrum of the methylene protons of cis-divinyl hexalin 124 at ambient temperature (upper) and at -55^{o}(lower).

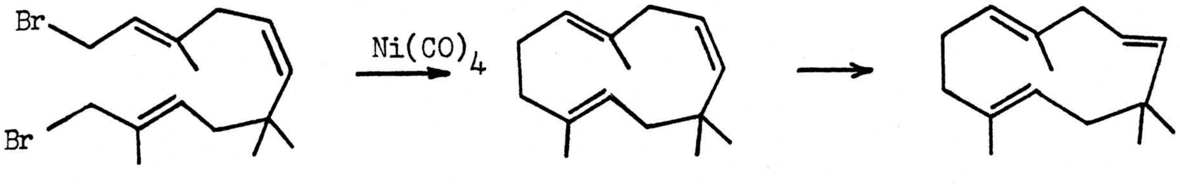
Observation of the methylene signals at δ 1 to 3 of the two isomers at variable temperatures allowed the stereochemistry of the ring fusions to be determined. The methylene signals of the cis compound <u>124</u> broadened as the temperature was lowered. At -40° a series of sharp peaks was observed, and no further change was noted as the temperature was decreased, suggesting that the conformational equilibrium was frozen. The sharp methylene signal of the trans compound was invariant with temperature. The methylene signals for the cis compound at ambient temperature and -55° are shown in Figure 7, as are the signals for the methylene protons in the trans compound.

Coupling Reactions Mediated by Nickel.

The Grignard reaction did give intramolecular coupled products but did not yield the desired hydrocarbons with the bicyclo[4.4.4]-tetradecane framework. It was thought, based on the precedents described below, that the desired coupling reaction might be effected with a zero valent nickel reagent.

Corey and coworkers have developed a synthesis of 1,5-dienes in which allylic halides are coupled with nickel reagents. This work has recently been reviewed by Semmelhack.[120] Particularly intriguing was the report that bis(allylic halides) could be coupled with nickel tetracarbonyl intramolecularly to give medium ring cyclic dienes in up to 75% yield. The synthesis of humulene (<u>134</u>) was achieved by such a cyclization although the yield of the cyclization step in this case was only 10%.[135]

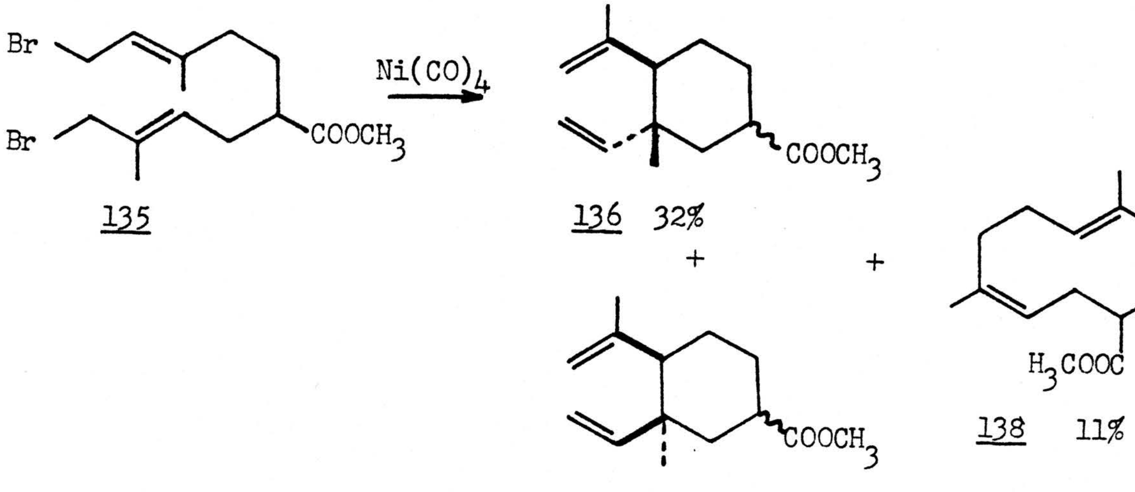
Scheme 35.



132 133 134

In another natural product synthesis, the bis(allylic halide) 135, under the Ni(CO)$_4$ coupling reaction conditions, gave as well as the divinyl derivatives 136 and 137, the ten membered cyclic diene 138 in 11% yield.[136]

Scheme 36.



135

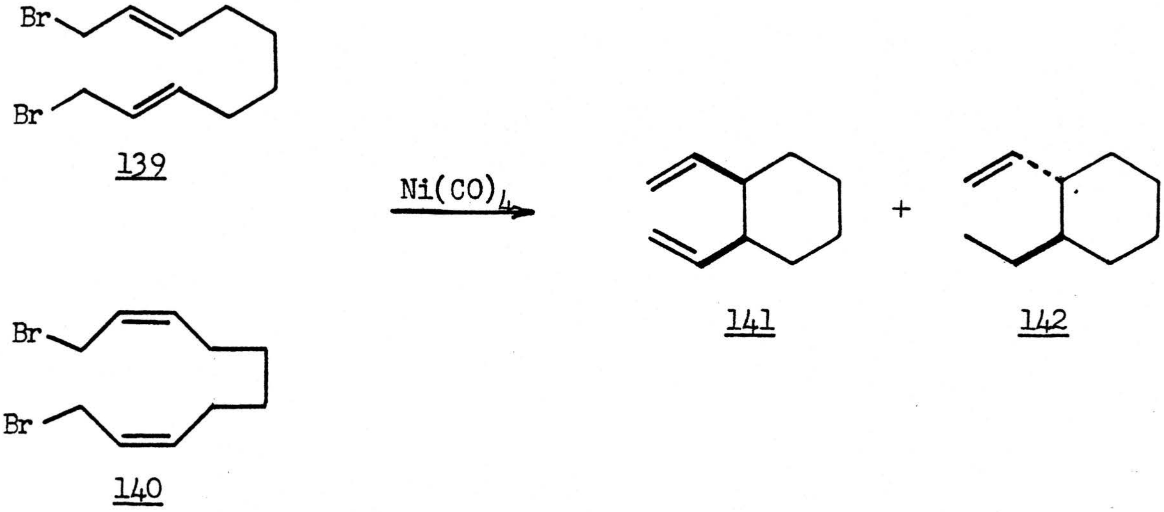
136 32%

137 23%

138 11%

However, the same reaction, carried out on the dibromides 139 and 140 yielded only the 1,2-divinyl cyclohexane derivatives 141 and 142.[137]

Scheme 37.



139

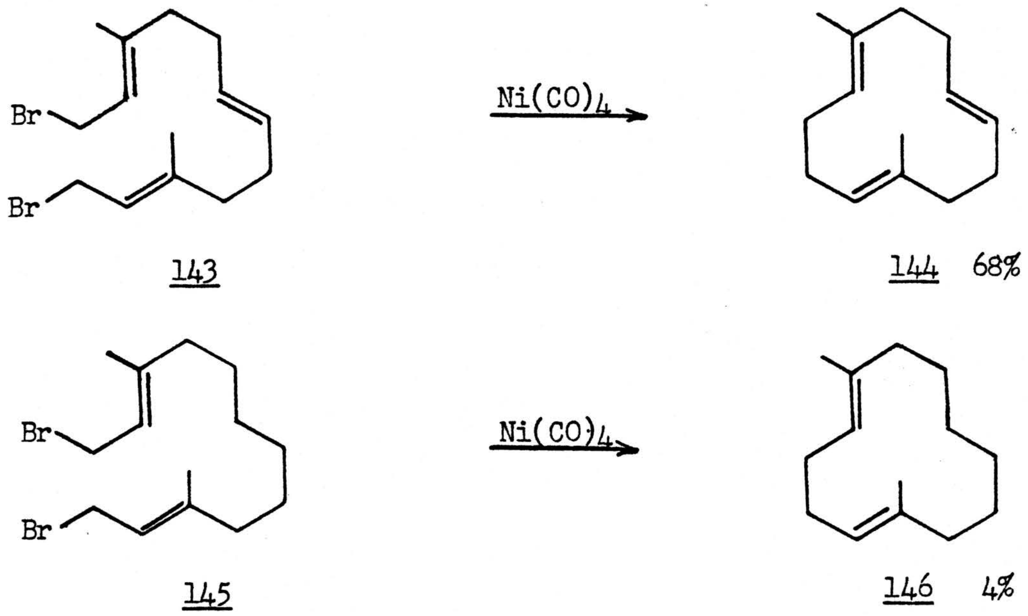
140

141

142

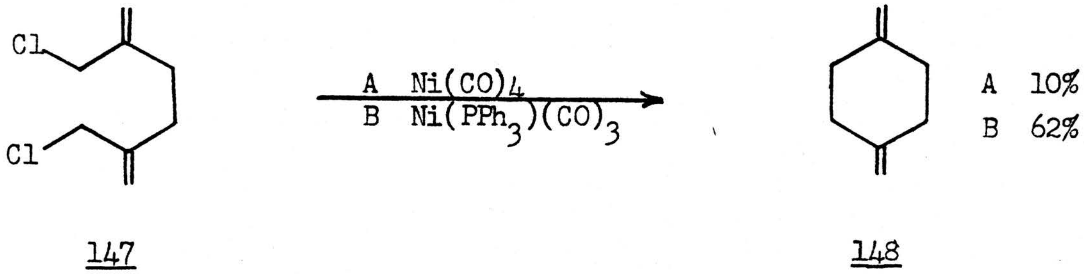
The nature of the ligands employed in the nickel reagent and the nature of the substrate have been shown in many cases to have a profound effect on the composition of the reaction products. A particularly dramatic example of the latter is the coupling of the dibromide 143. The intramolecular cyclization proceeded in 68% yield. When the same reaction was carried out on the dihydro compound 145 only a 4% yield was obtained.[138]

Scheme 38.



The effect of the ligands is demonstrated in the cyclization of 147.[139] With Ni(CO)$_4$ only a 10% yield of cyclized product was obtained, but with Ni(PPh$_3$)(CO)$_3$ a 62% yield of the monomeric cyclization product was isolated.

Scheme 39.

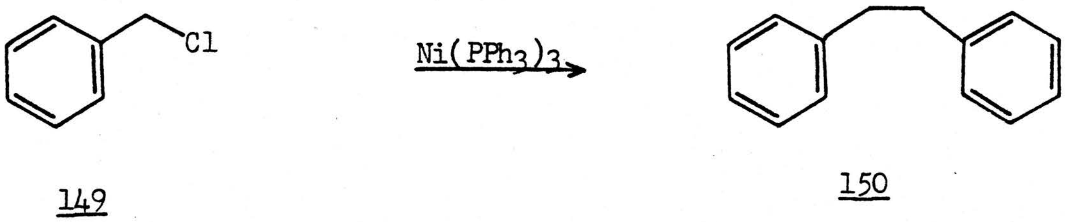


It appeared plausible, then, that a nickel reagent might yield the desired bicyclo[4.4.4]tetradecane derivative where magnesium had failed.

Because of the extreme toxicity of $Ni(CO)_4$ another nickel reagent was investigated first. Kende and coworkers developed a procedure, wherein tris(triphenylphosphine)nickel(0) could be generated *in situ* and employed for halide coupling.[140] They obtained a 50% yield of bicinnamyl (<u>110</u>) from cinnamyl chloride (<u>120</u>).

As a model reaction, benzyl chloride <u>149</u> was subjected to the reaction conditions of Kende *et al*, and a 46% yield of 1,2-diphenyl ethane (<u>150</u>) was isolated.

Scheme 40.



The same reaction conditions were employed in the coupling of a mixture of the cis and trans dibromides <u>116</u> and <u>117</u>. The only products isolated were the divinyl hexalins <u>124</u> and <u>125</u> in 10% total yield.

Because the nature of the ligand is critical in the yield and composition of the products of the coupling reaction, the nickel carbonyl reagent was also employed. A mixture of <u>116</u> and <u>117</u> was added over 15 hours to a solution of nickel carbonyl in N-methyl pyrrolidone at 50-52°. After workup a 24% yield of the divinyl hexalins was obtained.

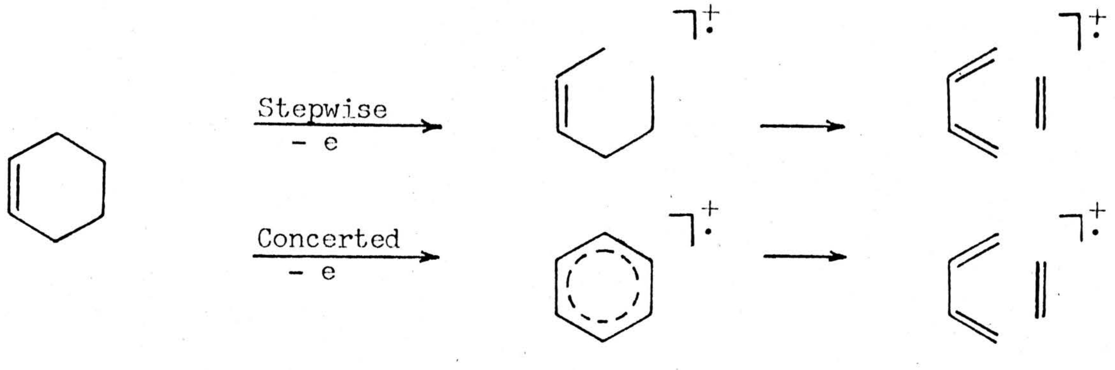
No further attempts were made to prepare the bicyclo[4.4.4]-tetradecane ring system, and the attempts to synthesize bicyclo[4.4.4]-tetradeca-2,4,7,9,11,13-hexaene (77) were reluctantly terminated.

A Digression from the Synthetic Scheme

In the course of the elucidation of the ring fusions of the divinyl hexalins 124 and 125 an interesting feature of the mass spectra of the two hydrocarbons was noted. The peak at 132 mass units, attributed to the loss of butadiene from the molecular ion, was much larger for the cis isomer than the trans. This Retro Diels-Alder reaction, a common fragmentation pattern in cyclohexene derivatives,[141] is a subject of controversy among mass spectroscopists. The mechanism of the fragmentation and the stereochemical dependence of the reaction in fused polycyclic systems are in question.

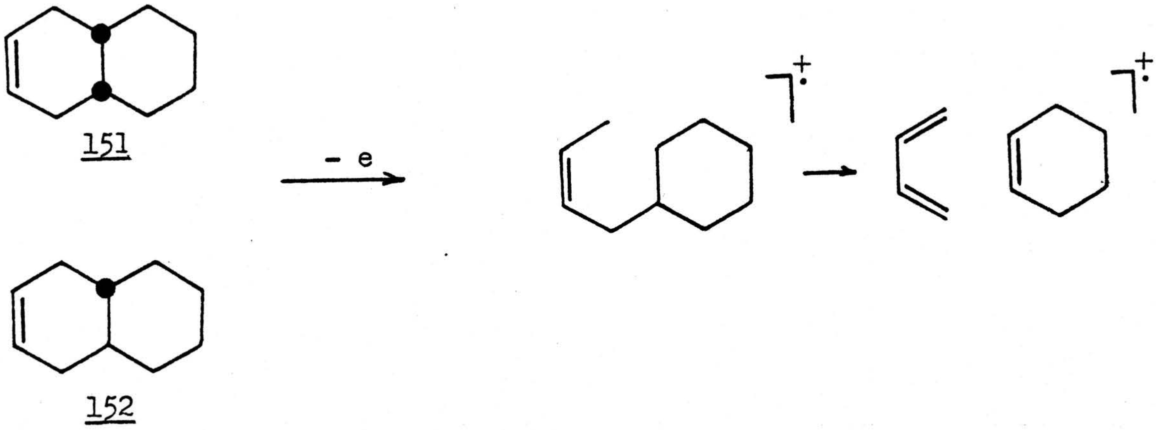
The fragmentation can take place by either a stepwise or a concerted process, in each case giving derivatives of ethylene and butadiene.

Scheme 41.



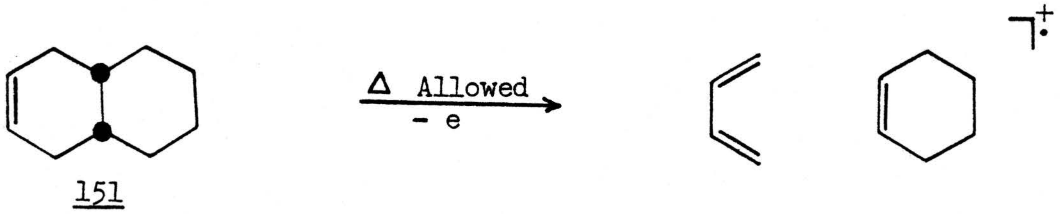
In the stepwise scheme the ring is opened and the fragmentation takes place in a second step, and is independent of the relative stereochemistry of substituents on the cyclohexene ring. This is illustrated for the case of the bicyclic olefins 151 and 152.

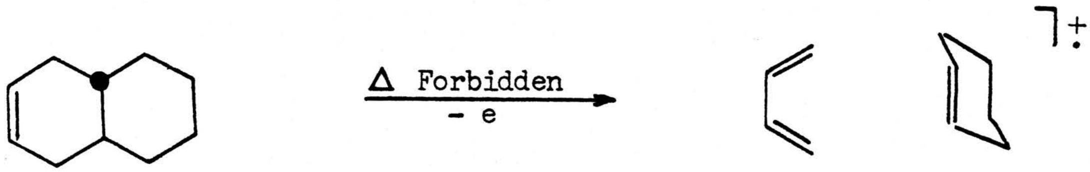
Scheme 42.



The concerted process can have a definite stereochemical requirement. For instance, in the bicyclic systems 151 and 152, a quasi thermal concerted process makes the Retro Diels-Alder reaction unfavourable where there is a trans ring fusion. The olefinic fragment would contain a highly strained trans double bond in a six membered ring.

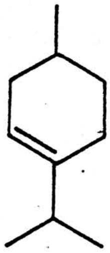
Scheme 43.



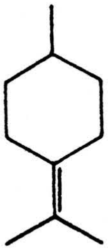


152

A complicating factor is the tendency of double bonds in simple cyclohexene systems to migrate before fragmentation of the ring. For instance, the M-43 peak is equally intense in the two olefins 153 and 154.



153

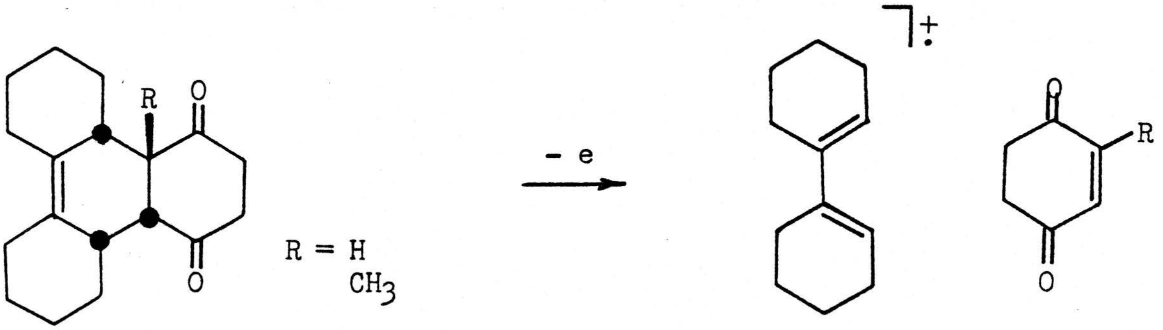


154

Djerassi[141] advocates the step-wise approach on energetic grounds. Djerassi and Hammerun[145] have compared the mass spectral fragmentations of 151 and 152 and found that the Retro Diels-Alder is not a favoured decomposition process. They found little dependence of the Retro Diels-Alder peak on the stereochemistry of the ring fusions. Djerassi and Hammerun were not able to detect a metastable ion for the Retro Diels-Alder process, and they concluded that double bond migrations and extensive decomposition were occurring in the source of the mass spectrometer.

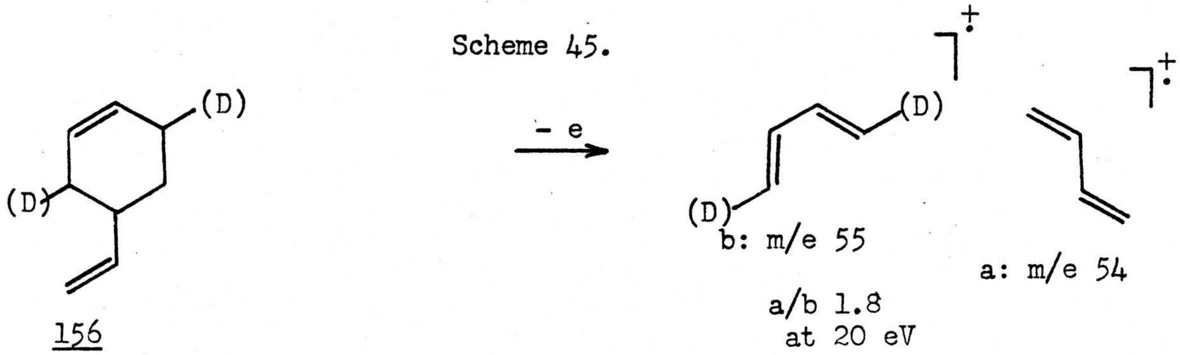
On the other hand, Mandelbaum and coworkers[146] have studied a series of diones of the general form 155 and found peaks corresponding to Retro Diels-Alder products only for the cis fused isomers.

Scheme 44.



155

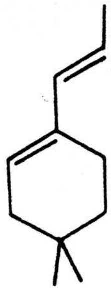
Scheme 45.



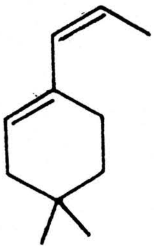
156

The case of 4-vinyl cyclohexene 156 may also support the concerted mechanism for the Retro Diels-Alder reaction. Smith and Thornton[142] prepared 156 labelled at C-3 or C-6, and observed the ratio of positively charged butadiene units in the mass spectrum. They found that the vinyl residue held almost twice as much positive charge as the ring butadiene. Dougherty's theoretical work supports a quasi thermal reaction mechanism for this reaction.[147,148]

Green,[149] in his recent review article, disagrees with Dougherty's view that Smith and Thornton's data necessarily require a concerted mechanism, and cites the case of Staley and Reichert[150] who obtained different fragmentation ratios for the terpenes 157 and 158.



157



158

Green comments that Mandelbaum's work where a stereochemical dependence is shown, is unique in that the molecules are "ornamented by oxygen and aromatic functionality", whereas the cases that demonstrate a stereochemical independence are simple olefins.

The hydrocarbons 124 and 125 appear to show a clear dependence of the Retro Diels-Alder reaction on the stereochemistry of the ring fusions. The $\%\Sigma_{40}$ data for both compounds is presented in Table 3, and the corresponding spectra are presented in the Spectra section. The difference in the 132 peaks, which is evident in the 70 eV spectra, is even more pronounced in the 10 eV spectra. In the cis compound the 132 peak becomes the base peak at 10 eV.

Table 3.

Mass Spectral Results for m/e 132 expressed as $\%\Sigma_{40}$.

	10 eV	70 eV
cis divinyl hexalin <u>124</u>	16.5	8.5
trans divinyl hexalin <u>125</u>	4.4	2.0

To ensure that the data obtained truly reflect the stereochemical requirements of the decomposition reaction, it is necessary to determine the origins of the daughter ion at m/e 132. Two mass spectrometric experiments based on observation of metastable ions were performed by Dr. W. Jamieson and Mr. Don Embree at the Atlantic Regional Laboratory of the NRC.

In the course of a normal mass spectral scan,[151,152] ions generated in the source are accelerated to a kinetic energy eV which is independent of the mass of the ions, and where $\frac{1}{2}mv^2 = eV$. Because of field inhomogenities in the source, and Boltzmann distribution of translational energies, an electrostatic analyzer is employed to allow only ions with a kinetic energy of eV to pass to be analyzed. The magnetic sector separates the ions on the basis of their mass by varying H, the strength of the magnetic field, according to the equation $m/e = \frac{H^2r^2}{2V}$ where r is the radius of the ion path in the magnetic sector, and V is the accelerating voltage. Mass analysis can also be achieved by holding H constant and varying V.

Metastable peaks normally are seen when an ion m_1 decomposes to daughter ions m_2, m_3 etc. after passing through the electrostatic analyzer and before mass analysis (the second field free region). The kinetic energy of the daughter ion m_2 is less than eV by a factor m_2/m_1. This ion appears on mass analysis at $m_2 \cdot m_2/m_1$. Examinations of metastable processes allow daughter and parent ions to be related and permit speculation to be made about decomposition pathways.

Ion kinetic energy (IKE) experiments[152] were performed on the divinyl hexalins <u>124</u> and <u>125</u>. This experiment shows the metastable transitions that the molecule undergoes. The experiment is performed by monitoring the metastable transitions that occur after the ions are accelerated and before they reach the electrostatic analyzer (the first field free region). The daughter ions will have a kinetic energy $m_2/m_1 \cdot eV$, $m_3/m_1 \cdot eV$, etc. The electrostatic analyzer is scanned down from V_o and the daughter ions m_2, m_3 etc., will be transmitted through the electric sector when $V_1 = V_o \cdot m_1/m_2$, $V_2 = V_o \cdot m_1/m_3$ etc., and be detected by the total ionization detector after the electric sector. A fingerprint-like spectrum of ion kinetic energies is obtained. The spectra obtained for the divinyl hexalins are presented in Figure 8. The transition for 186 to 132 should occur at .71 eV, and is evident in both spectra. The peak at .71 eV is not, however, necessarily unique to the transition of 186 to 132.

Perhaps more pertinent to the stereochemical question raised is the precursor ion experiment[152] (PIE). This experiment determines the precursor of a given daughter ion. To perform this experiment the field is adjusted in the magnetic sector so that only the daughter ion arrives at the collector. The ions are accelerated to a kinetic energy eV, and the electrostatic analyzer selects only ions with this kinetic energy. The electrostatic analyzer voltage is kept constant. Ions that decompose on the way to the electrostatic analyzer will have a lower kinetic energy

M_2/m_1 eV and will not be transmitted. However, if the accelerating voltage is increased the kinetic energy of the metastable ions will be greater, and, when $V_1 = V_o m_1/m_2$ the ion m_2 will be transmitted, and recorded at the collector. The spectrum obtained on scanning V will show all the precursors of the ion m_2.

The spectra of the divinyls 124 and 125 are presented in Figure 9. Both spectra show that the major precursor is most likely the molecular ion 186. In the trans compound there are three minor contributors to the 132 peak corresponding to the transitions 171 to 132, 157-8 to 132, and 143-145 to 132. It is interesting to note that the transition 171 to 132 is absent in the cis compound.

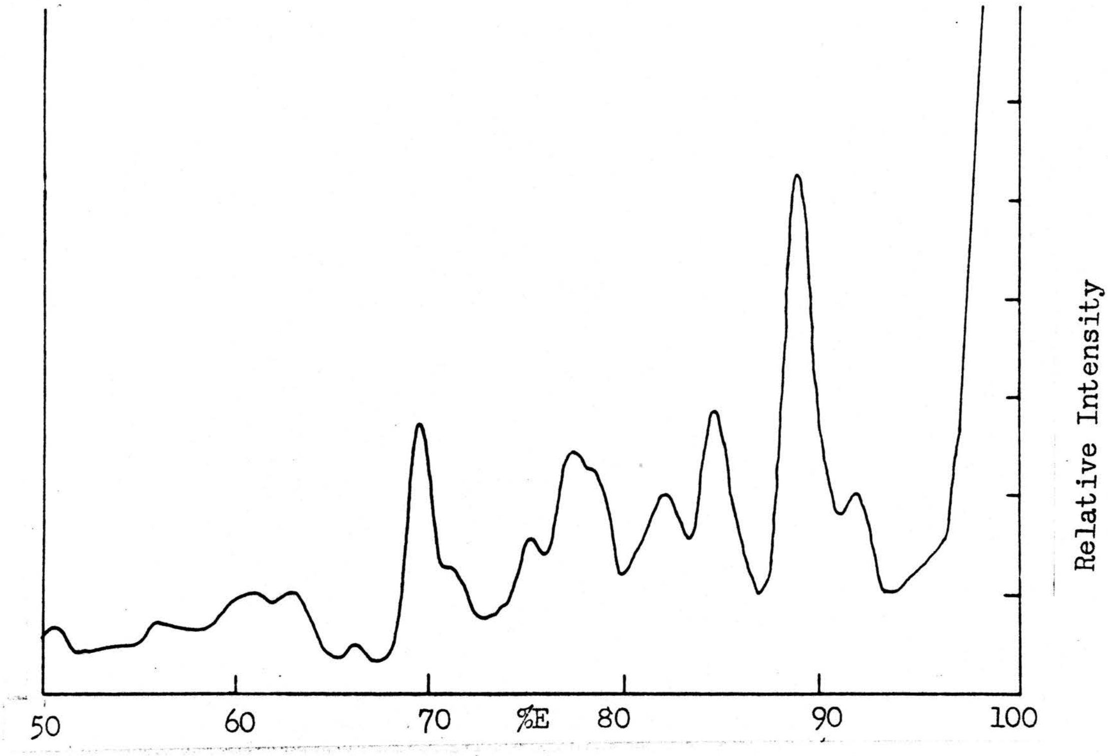
The experimental evidence can now be summarized. The molecular ions of the cis and trans hexalins both lose 54 mass units to give an ion m/e 132. The metastable peak corresponding to this transition is seen in both cases and the 186 ion is the primary parent.

What has not been experimentally determined is the structure or structures of the 132 species. The most likely fragmentation route is the loss of butadiene from the molecular ion. It is difficult to explain the loss of 54 mass units while maintaining the bicyclic skeleton. Stepwise loss of both vinyl groups would give the 132 ion; however, the peak corresponding to the loss of a single vinyl group is only a small peak, more significantly, the signal in the precursor ion experiment that would correspond to this transition is only a minor contributing parent to the 132 peak.

The only structural difference between the cis and trans divinyl hexalins is the stereochemistry of the ring fusion. It has been experimentally determined that the 132 peak is much more intense in the cis case than in the trans. The preferred loss of 54 mass units from the molecular ion of the cis isomer can be understood in terms of the concerted loss of butadiene in a thermally allowed Retro Diels-Alder reaction. If the loss of 54 mass units is an electronic ground state process, the analogous fragmentation in the trans case should be retarded.

In conclusion it appears that the divinyl hexalins are a unique example of a pair of stereoisomeric hydrocarbons that show a stereochemical dependence of the Retro Diels-Alder reaction in the mass spectrometer.

Figure 8.



IKE Spectra of cis-divinyl Hexalin 124 (above) and trans-divinyl Hexalin 125 (below).

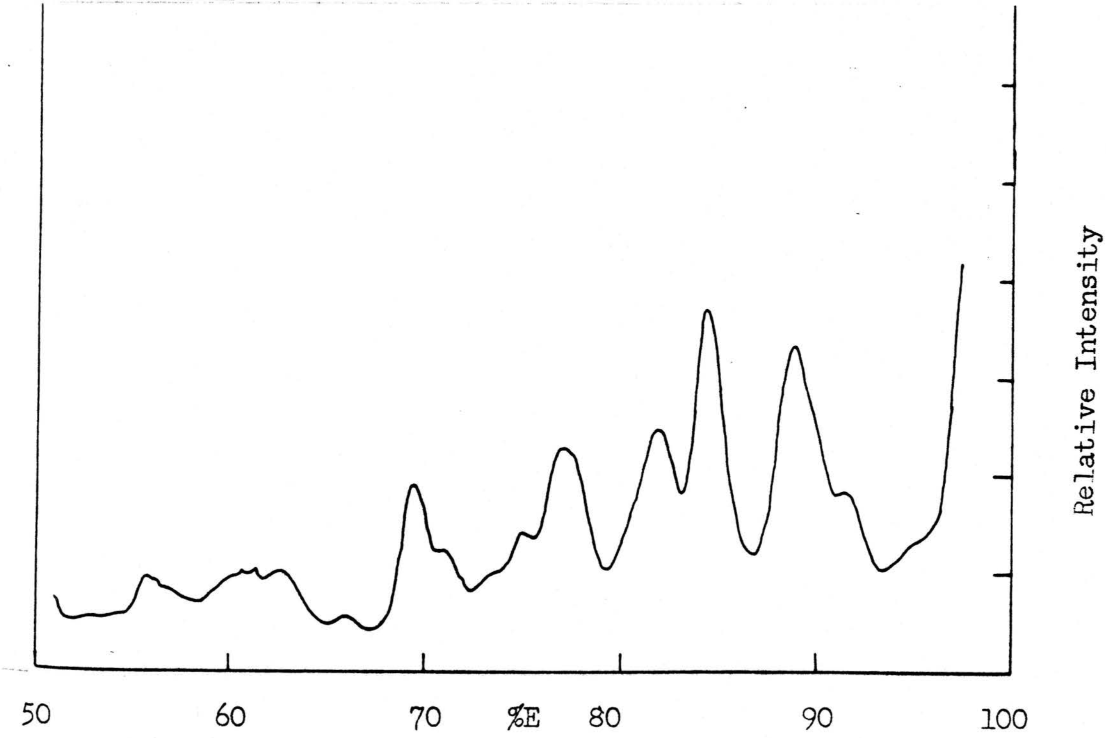
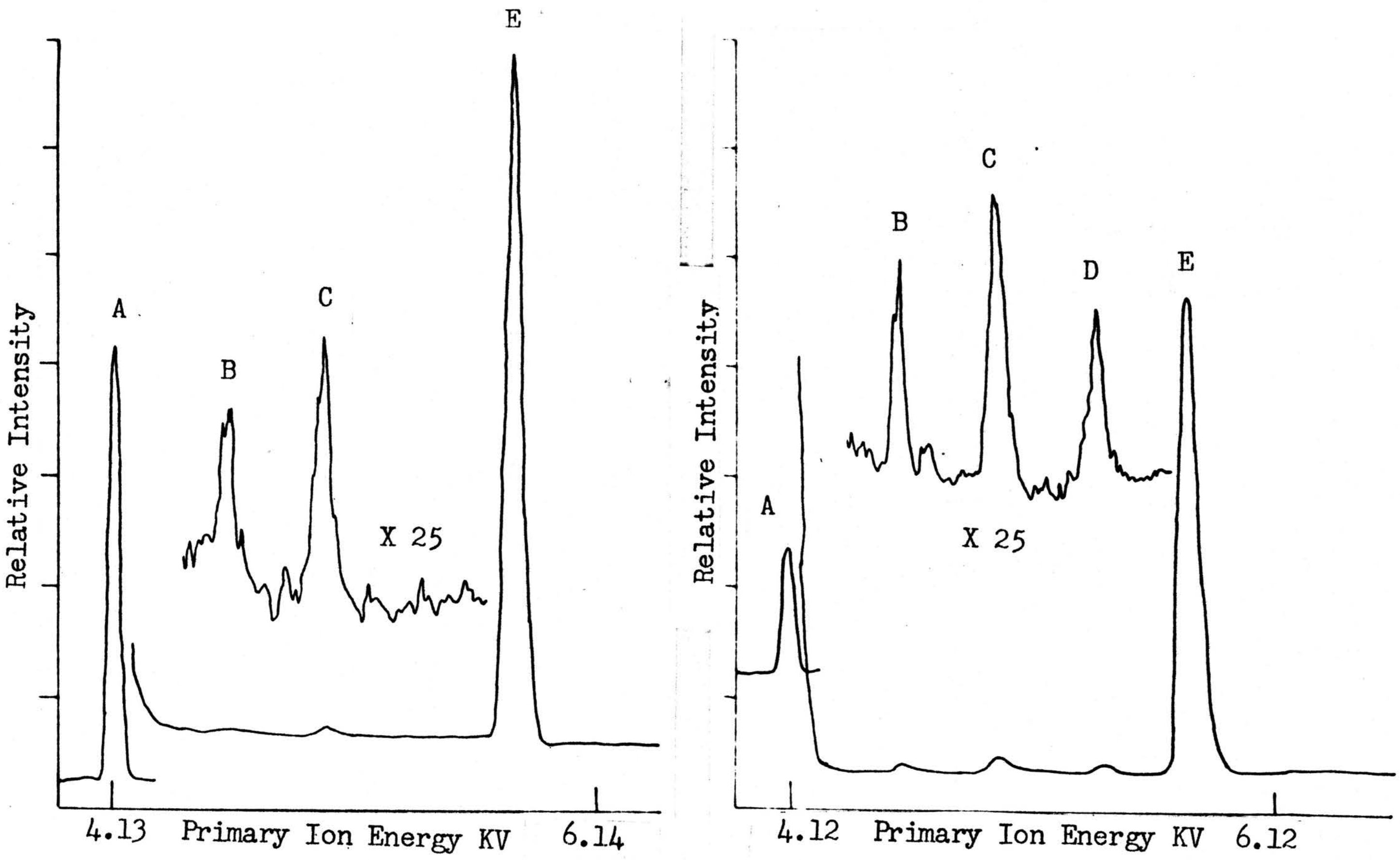


Figure 9.

PIE Spectra of cis-divinyl hexalin 124 (left) and trans-divinyl hexalin 125 (right).



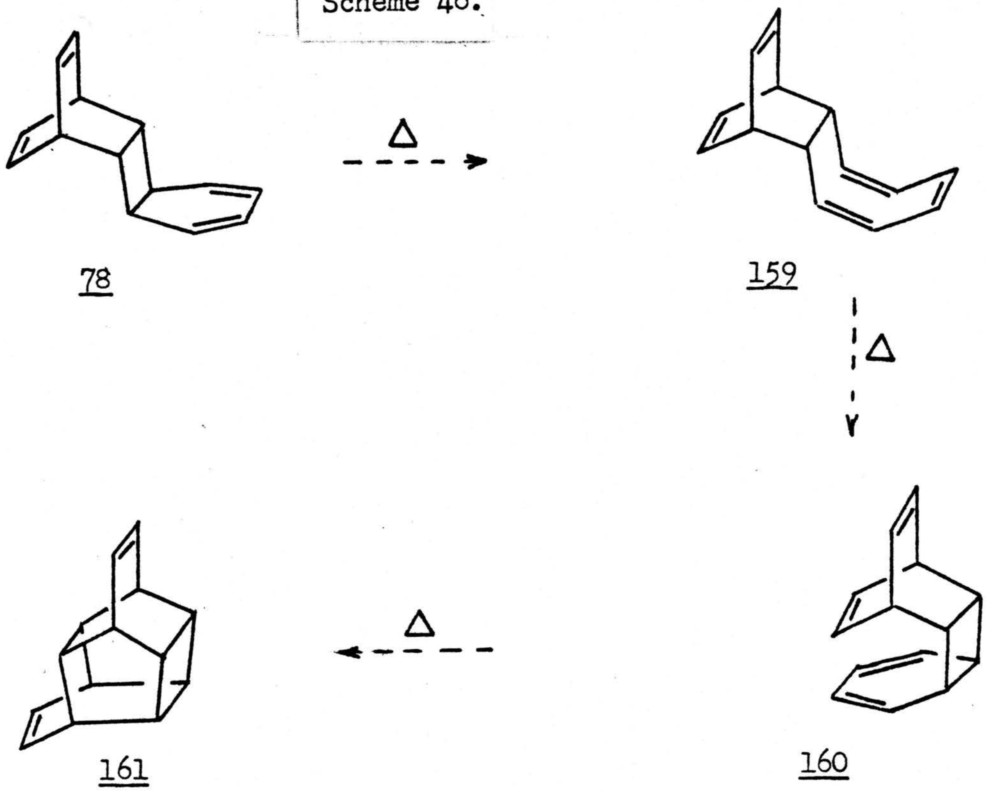
A.	Main Ion Beam m/e 132.	4.13 KV
B.	143-145 to 132.	4.60 KV
C.	157-158 to 132.	5.00 KV
D.	---	
E.	186 to 132.	5.78 KV

A.	Main Ion Beam m/e 132.	4.12 KV
B.	143-145 to 132.	4.57 KV
C.	157-158 to 132.	4.98 KV
D.	171 to 132.	5.40 KV
E.	186 to 132.	5.76 KV

PART 2: THE SYNTHESIS OF A $(CH)_{14}$ HYDROCARBON 78.

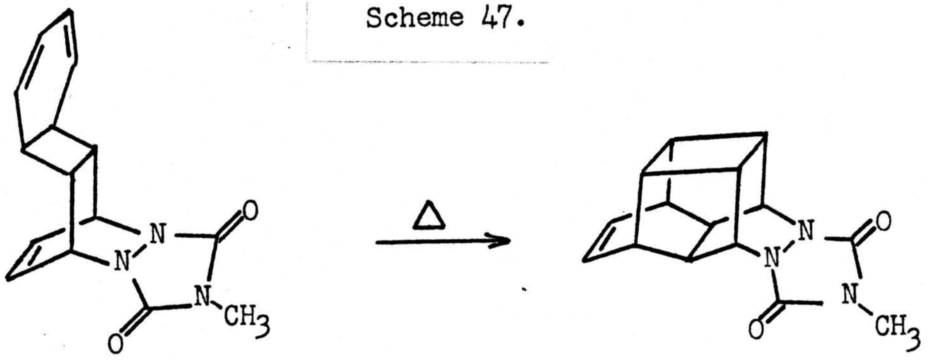
A second approach successfully afforded the $(CH)_{14}$ polymethine hydrocarbon *cis,transoid,cis*-tetracyclo$[8,2,2,0^{2,9},0^{3,8}]$tetradeca-4,6,11,13-tetraene (78). The tetracyclic tetraene was chosen as a possible entry into the $(CH)_{14}$ energy surface for two reasons. The synthetic scheme planned would render the hydrocarbon readily accessible to study, and thermal rearrangements might lead to other novel $(CH)_{14}$ compounds. In particular, the caged diene 161 might be obtained by a thermally allowed rearrangement sequence involving opening of the cyclohexadiene ring in 78 to give the cyclooctatriene 159. Subsequent reclosure to the cisoid stereoisomer 160 followed by intramolecular Diels-Alder reaction could afford the caged $(CH)_{14}$ hydrocarbon 161.

Scheme 46.



A closely parallel thermal rearrangement is reported in the literature. Berson and Davis[67] found that heating the masked dibenzene 70 afforded the caged derivative 162 which they postulate was formed by an analogous sequence.

Scheme 47.



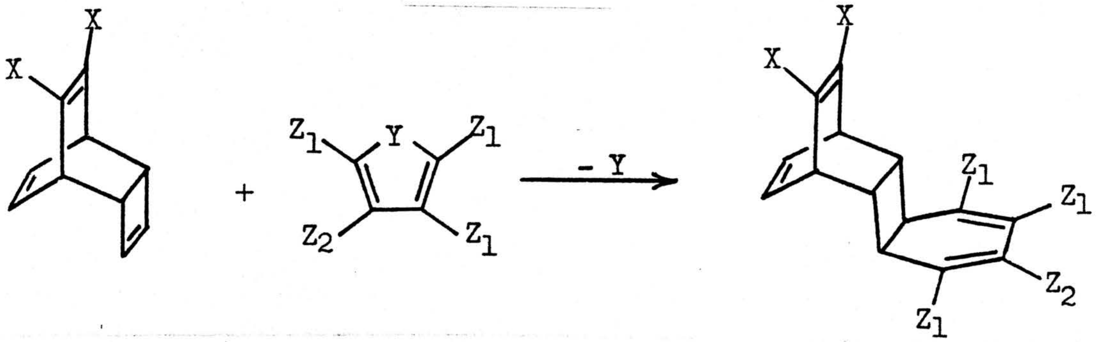
70

162

The Synthetic Plan

Construction of the skeleton of 78 was planned by addition of a masked four carbon unit in a Diels-Alder reaction to Nenitzescu's hydrocarbon 20 or a substituted analogue. The two carbomethoxy groups would provide a useful tool for determining the symmetry of any rearrangement products. The observation of two carbomethoxy groups in the nmr spectrum would indicate the lack of a plane of symmetry.

Scheme 48.



X=H 20

X=$COOCH_3$ 163

X=CF_3 164

Y=$\overset{O}{\overset{\|}{C}}$-O, Z_2=$COOCH_3$, Z_1=H 165

Y=$\overset{O}{\overset{\|}{C}}$-$\overset{O}{\overset{\|}{C}}$, Z_1=Z_2=Cl 166

Y=$\overset{O}{\overset{\|}{C}}$-$\overset{O}{\overset{\|}{C}}$, Z_1=Z_2=H 167

X=Z_1=Z_2=H 78

X=Z_2=$COOCH_3$, Z_1=H 168

X=$COOCH_3$, Z_1=Z_2=Cl 169

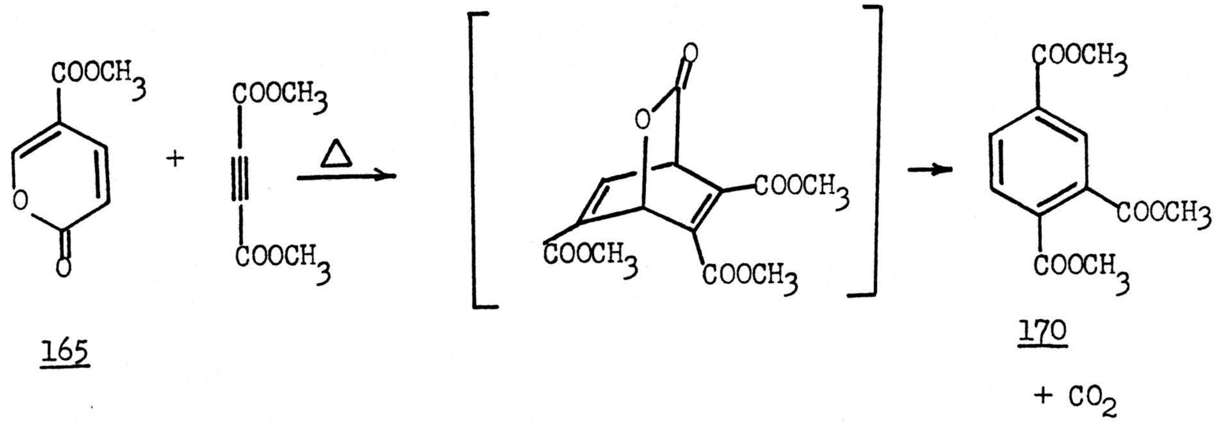
In parallel cases[155-156] electron deficient dienes add to the more reactive cyclobutene double bonds; the addition takes place on the less hindered face of the cyclobutene ring.

Model studies, described in the following two sections, were carried out with the triene 163 X=$COOCH_3$, prepared[157] by the addition of dimethyl acetylenedicarboxylate to cyclooctatetraene (1). The distilled product, contaminated with 25% dimethyl phthalate (as estimated by nmr) was used without further purification.

Methyl Coumalate as the Diene

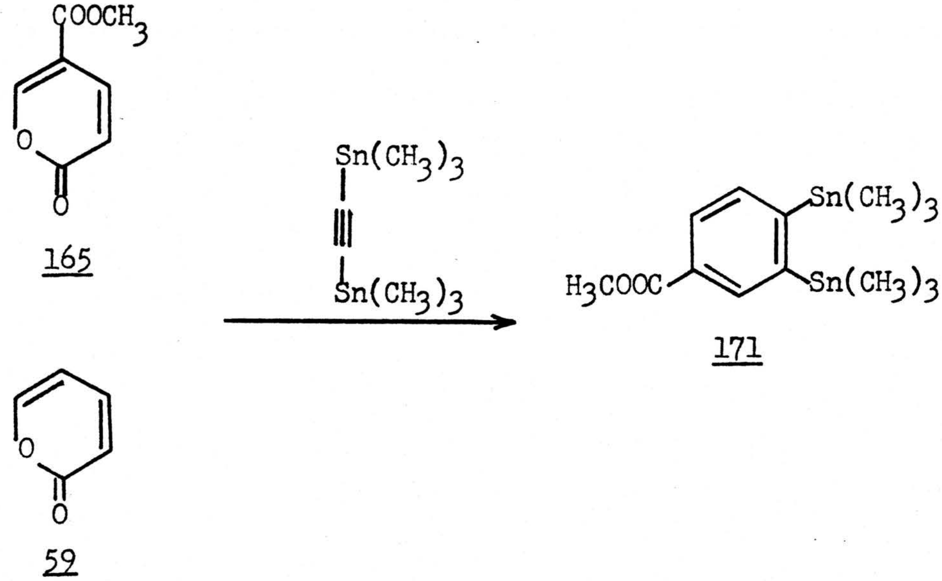
The first masked $(CH)_4$ unit investigated was 5-carbomethoxy-α-pyrone (165) (methyl coumalate), a diene that has been employed as a Diels-Alder addend since the discovery of the reaction[158,159]. An early example is the reaction of methyl coumalate with acetylenes[160]. Under the conditions employed to add methyl coumalate to dimethyl acetylenedicarboxylate the intermediate lactone suffers decarboxylation and the product isolated is 1,2,4-tricarbomethoxybenzene (170).

Scheme 49.



A similar addition of methyl vinyl ketone to unsubstituted α-pyrone formed the basis of Zimmermann's[63] synthesis of barrelene (61) *(vide supra)*. Evnin and Seyferth[161] carried out competition experiments with an electron rich dienophile, bis(trimethyltin)acetylene. Refluxing an equimolar mixture of α-pyrone, methyl coumalate, and bis(trimethyltin)acetylene in bromobenzene for 21 hours yielded only one product, the decarboxylated adduct of methyl coumalate and the acetylene, 171.

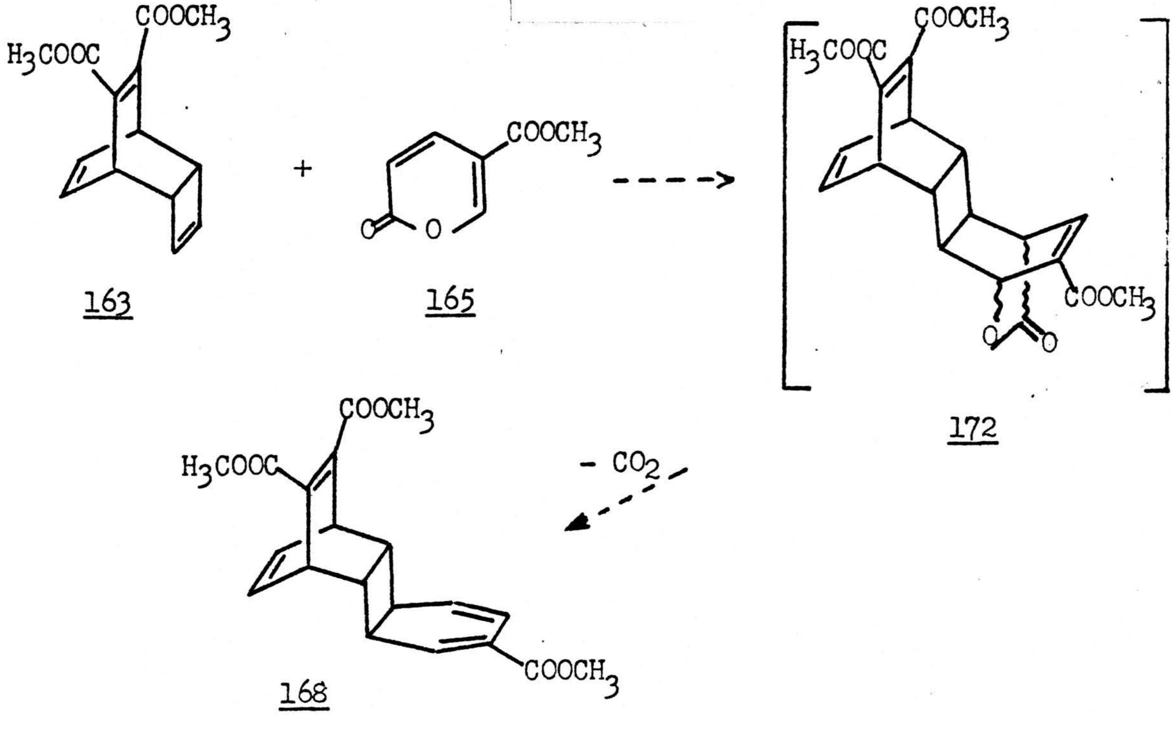
Scheme 50.



Thus, methyl coumalate is a much better diene in reverse electron demand Diels-Alder reactions than α-pyrone.

The sequence planned to prepare the skeleton of 78 is shown below.

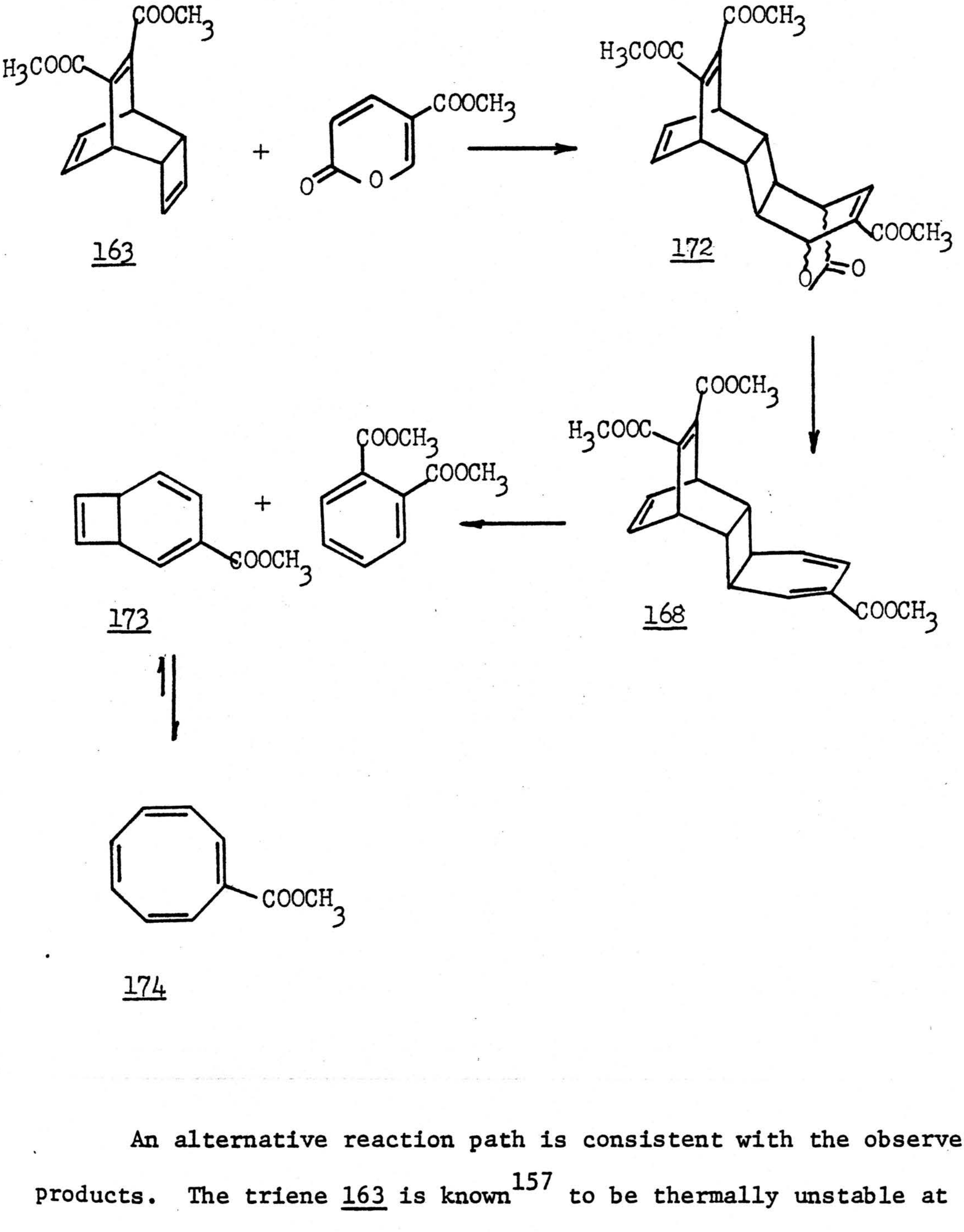
Scheme 51.



As indicated, two stereochemical isomers of the intermediate lactone 172 are possible, but the ambiguity is destroyed in the decarboxylation step in which both isomers should give the same cyclohexadiene derivative 168. Because of the symmetry of the starting cyclobutene derivative 163, the addition of the unsymmetrical diene unit from the less hindered face of the ring should give only one tricarbomethoxy tetraene derivative 168 as a racemic mixture.

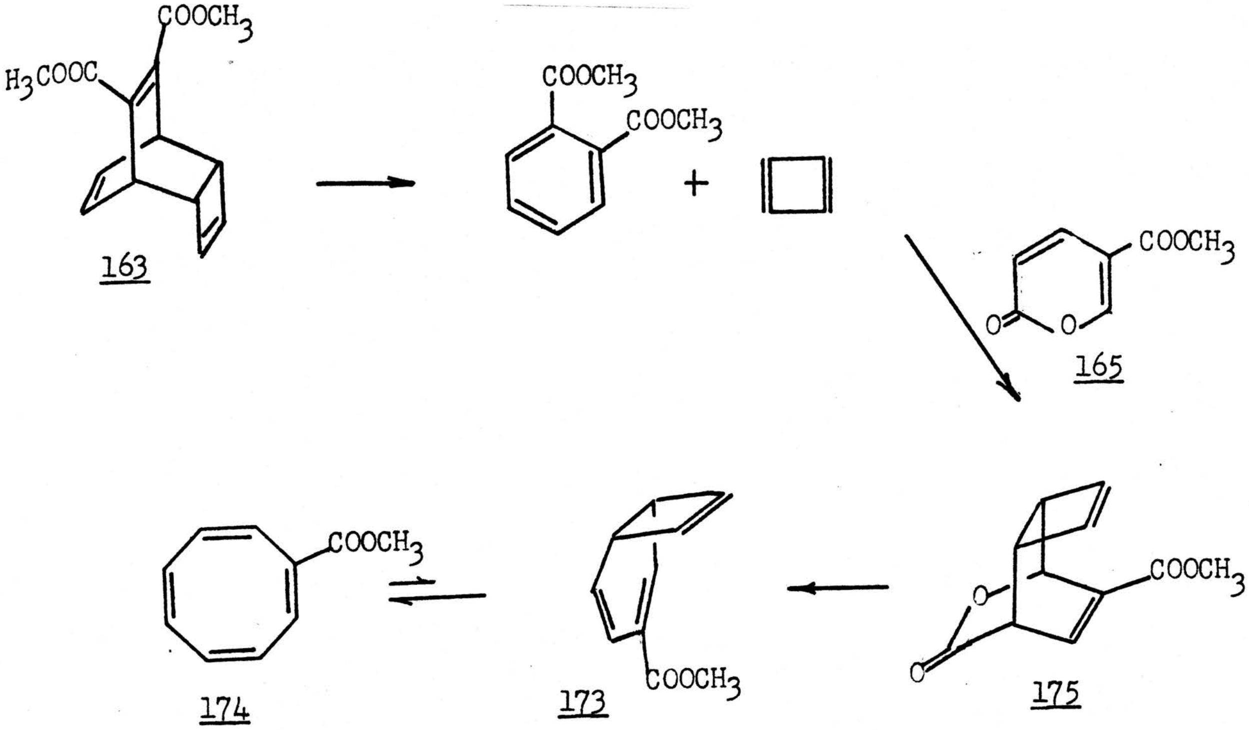
The reaction was carried out by heating an equimolar mixture of methyl coumalate (165) and 163 (contaminated with dimethyl phthalate) in deuterochloroform in a sealed nmr tube at 155°. The characteristic pmr signals of dimethyl phthalate grew with time; the signals for the starting materials decreased, and were no longer visible after 22 hours. No evidence for the product 168 was observed, however, carbomethoxycyclooctatetraene (174) was isolated and identified by comparison with published data.[162] It appeared that, if the cyclohexadiene derivative 168 was formed, it was thermally labile at the temperature necessary to carry out the Diels-Alder reaction. The reaction pathway shown below accounts for the products observed.

Scheme 52.



An alternative reaction path is consistent with the observed products. The triene 163 is known[157] to be thermally unstable at the temperature at which the reaction is carried out. Cyclobutadiene thus generated could add to methyl coumalate and subsequent loss of carbon dioxide would give carbomethoxycyclooctatetraene (174).

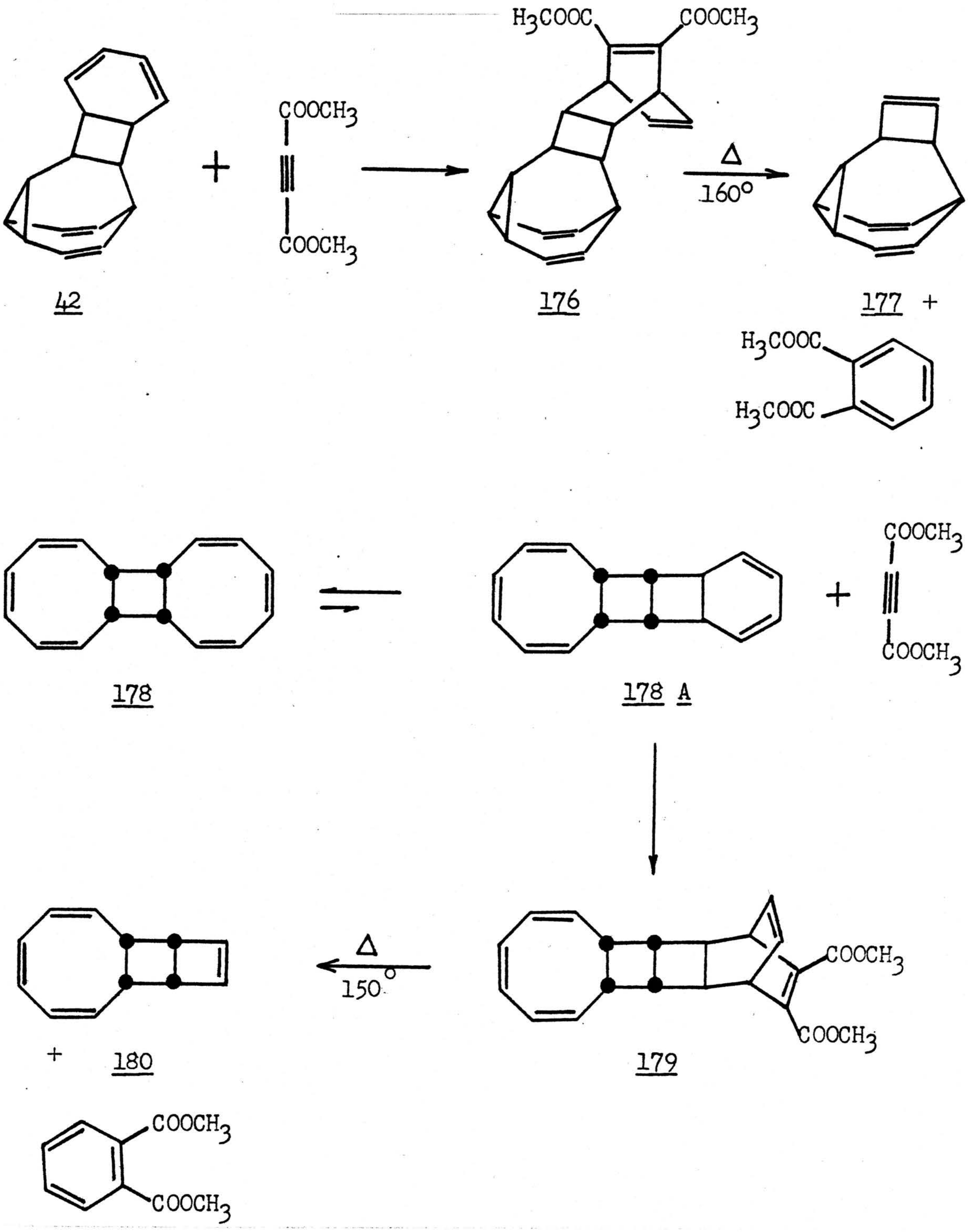
Scheme 53.



Because of the instability and reactivity of cyclobutadiene[11], in particular its tendency to dimerize, and because no cyclooctatetraene (1) or other cyclobutadiene adducts were isolated, this mechanism is not considered as likely.

The postulated decomposition of 168 is an example of a Retro Diels-Alder reaction[163], such as has been used to advantage in the synthesis of cyclobutene derivatives, as well as other labile compounds. Two hydrocarbons 177[164] and 180[165] were prepared by Retro Diels-Alder reactions in which precursors containing bicyclo[2.2.2]octan-2,5-diene units were heated to 150-160°.

Scheme 54.

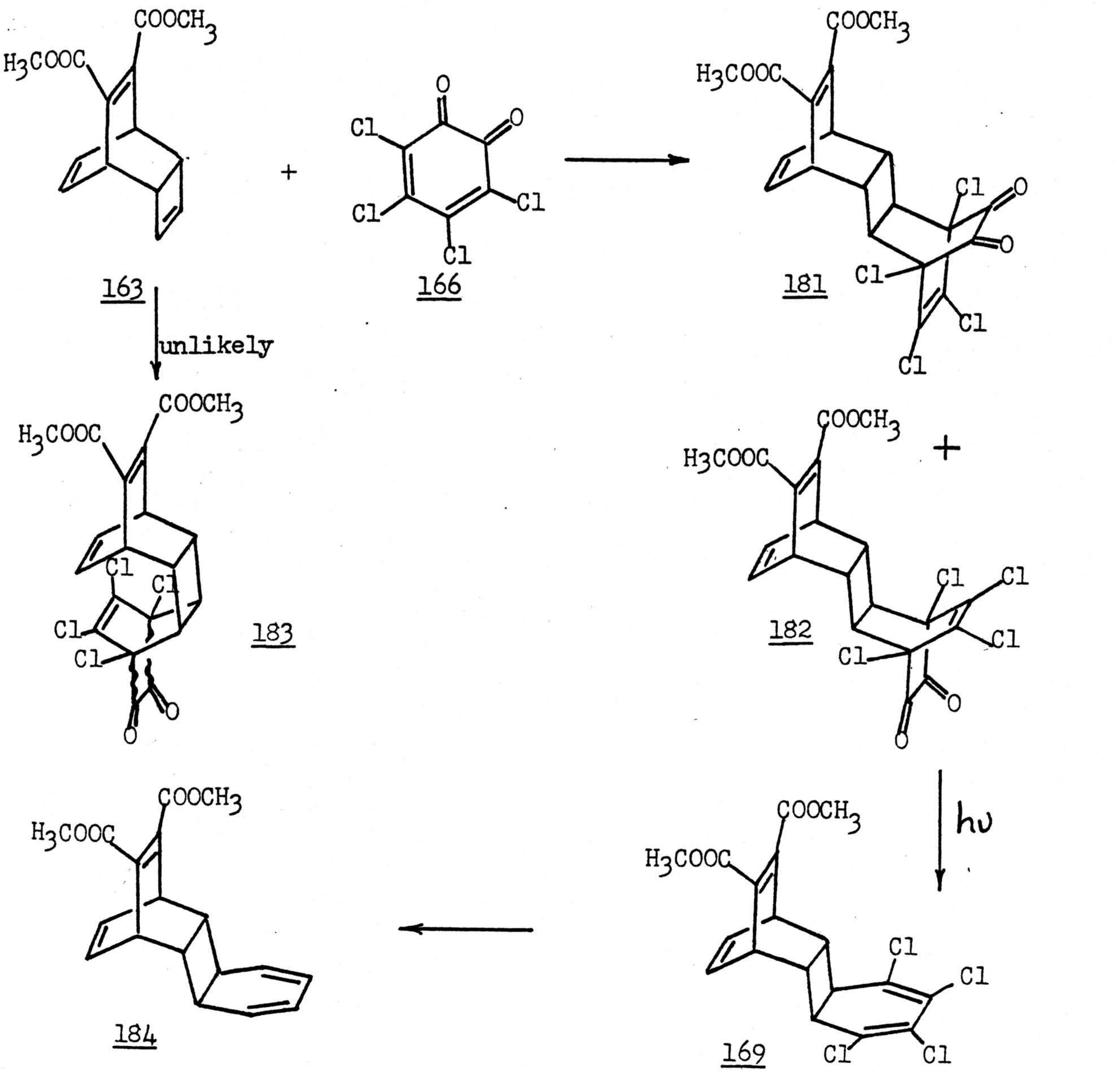


Whatever the mechanism of the reaction of 163 and 165, the carbon skeleton of 78 was not obtainable by this route. A new diene was sought that would react with the cyclobutene double bond at a lower temperature, and that would give a thermally stable adduct or pair of adducts.

Tetrachloro-o-benzoquinone as the Diene

The masked $(CH)_4$ unit next considered was the α-dicarbonyl compound tetrachloro-o-benzoquinone (166, o-chloranil). The sequence planned had as the first step an inverse electron demand Diels-Alder reaction[68,69] between o-chloranil and 163.

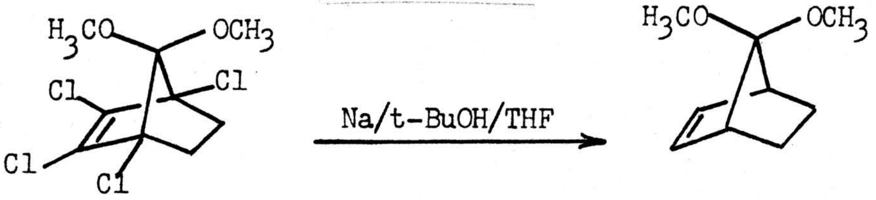
Scheme 55.



Reaction was expected to take place at the cyclobutene double bond from the less hindered side giving the isomeric diones 181 and 182. Endo attack was considered unlikely because of the severe steric interactions the etheno bridge would present to the approaching 1,3-diene. However dioxene formation from this side ought not to be completely impeded. Photochemical bisdecarbonylation was anticipated to give the cyclohexadiene derivative 169. This structure has the framework of the $(CH)_{14}$ hydrocarbon 78.

Transformation of a suitably protected derivative of 169 to the dicarbomethoxy derivative 184 (Z=H) might be effected by a dechlorination reaction with sodium and t-butanol in tetrahydrofuran. Gassman and co-workers[166,167] carried out such a dechlorination on the norbornene derivative 185 in 60% yield.

Scheme 56.



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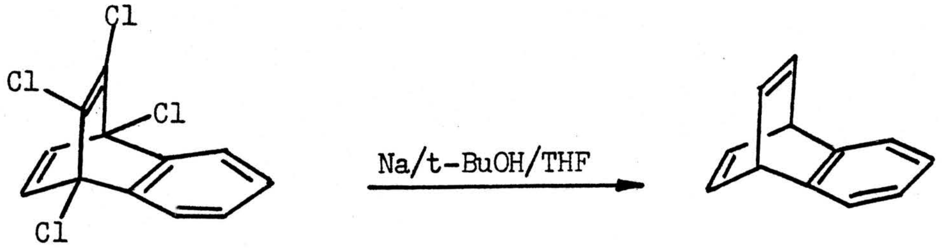
Heany *et al*[168] reported that employing a ratio of substrate to sodium of 4:1 gave essentially quantitative yields of benzobarrelene (188) starting from the tetrahalogenated compound 187.

Scheme 57.

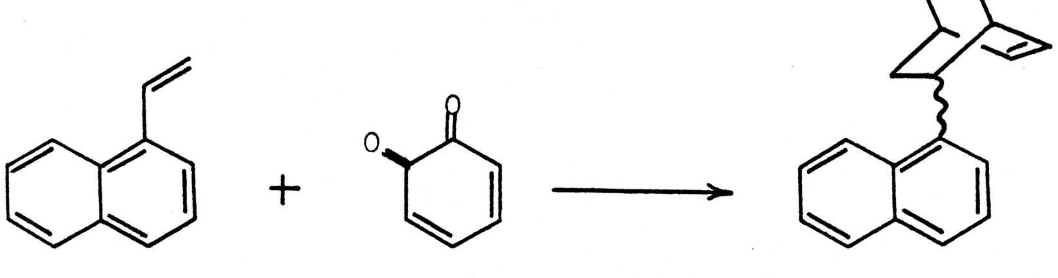


187

188

o-Benzoquinones are known[169] to react in cycloaddition reactions as 1,3-dienes, as dienophiles, and as heterodienes; dimerization is frequently encountered. The parent o-benzoquinone dimerizes readily, and few reactions are known where the major product is the result of o-benzoquinone adding as a 1,3-diene. One such example[170] is the addition of o-benzoquinone to 1-vinyl naphthalene (189) to give 190 in 12% yield after reaction for five days at ambient temperature.

Scheme 58.



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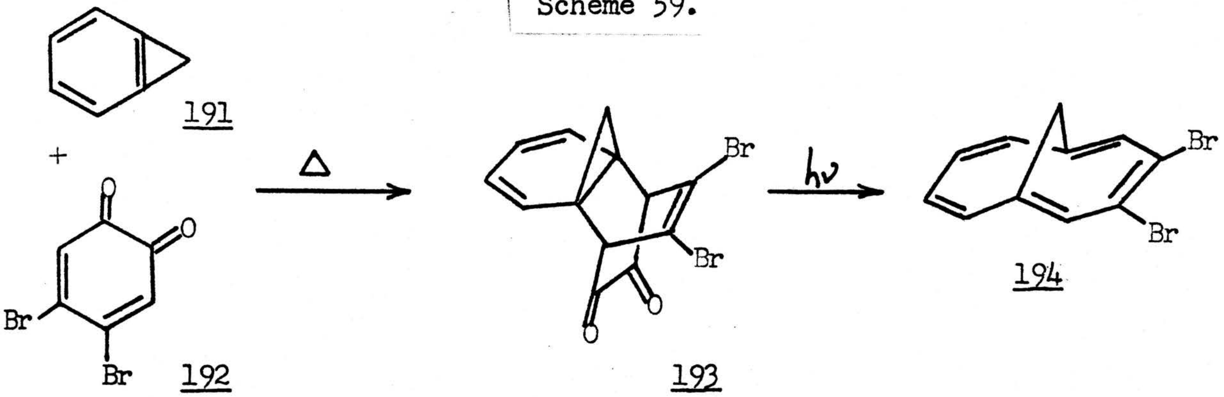
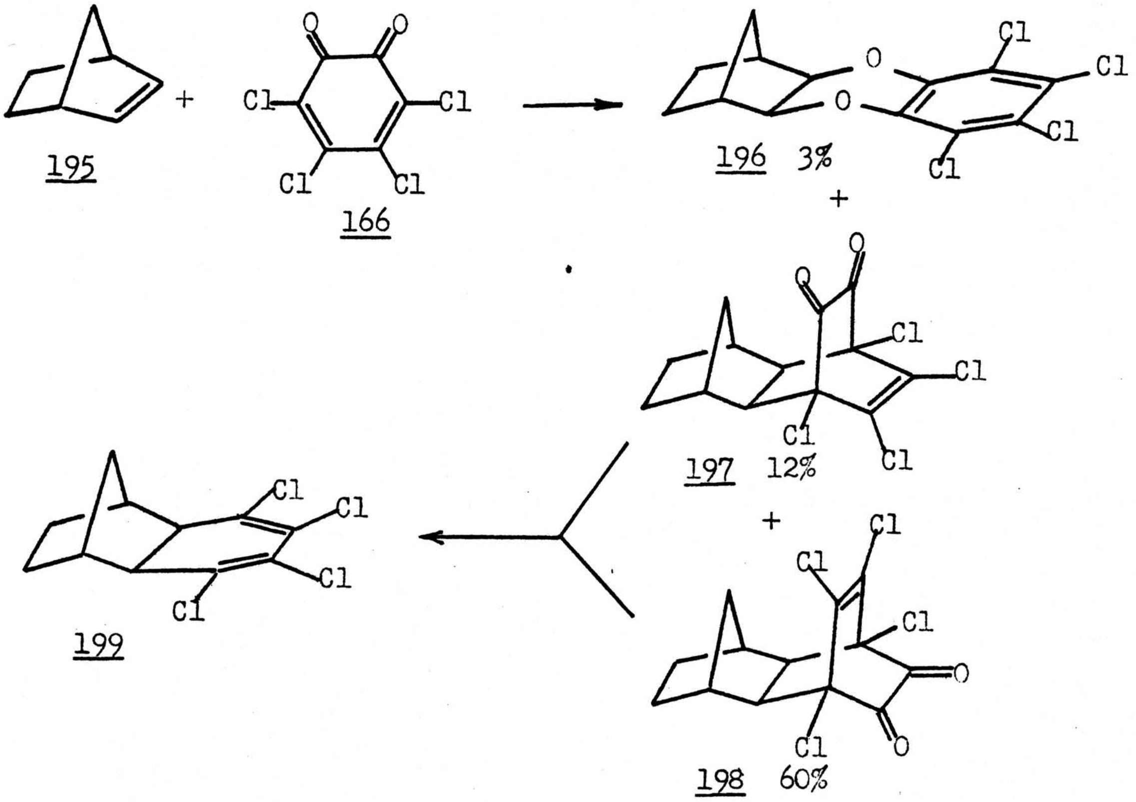
Halogen substituted o-benzoquinones tend to react as 1,3-dienes in cycloaddition reactions. An example is the synthesis of the bridged annulene 194 carried out by Vogel *et al.*[171] 4,5-dibromo-1,2-benzoquinone (192) was added to 191 in 65% yield giving only one stereoisomer 193. Photochemical bisdecarbonylation gave the annulene derivative 194.

Scheme 59.



The shelf stable tetrahalogenated o-benzoquinone 166, o-chloranil, has been studied as a reverse electron demand Diels-Alder addend by Sauer.[68] o-Chloranil does not react with the electron deficient olefin maleic anhydride, but does add to more electron rich olefins such as styrene. The major product isolated is normally the result of addition of o-chloranil as the 1,3-diene. The products of the reaction of norbornene (195) and o-chloranil[172] are shown on the next page.

Scheme 60.

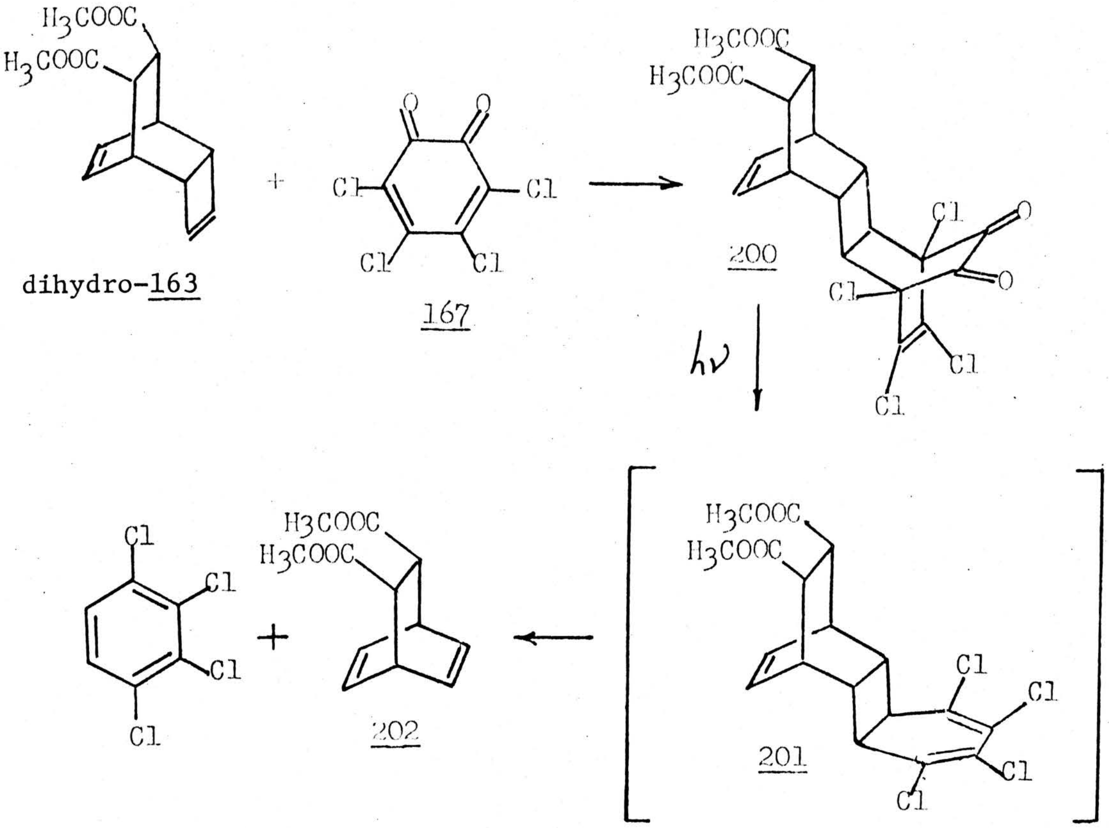


All three adducts are the result of attack of the electrophile from the exo side of the norbornene molecule, paralleling the usual observation[173] for the addition of electrophiles to norbornene. The reaction of o-chloranil as a heterodiene gives, as a minor product, the dioxene 196. Photochemical bisdecarboxylation of the two diones 197 and 198 gave the same cyclohexadiene 199.

o-Chloranil is reported[174] to react thermally with derivatives of acetylene to give bridged bicyclo[2.2.2]octane systems. A series of such bridged diones were examined by Strating *et al*[175] who reported that the compounds studied were thermally stable, but were readily converted to the corresponding cyclohexadiene derivatives by photolysis.

Warrener *et al*[153] reported the addition of o-chloranil to 199, a dihydro derivative of 163. They claimed that the addition to the cyclobutene double bond gave the single stereoisomer in 54% yield.

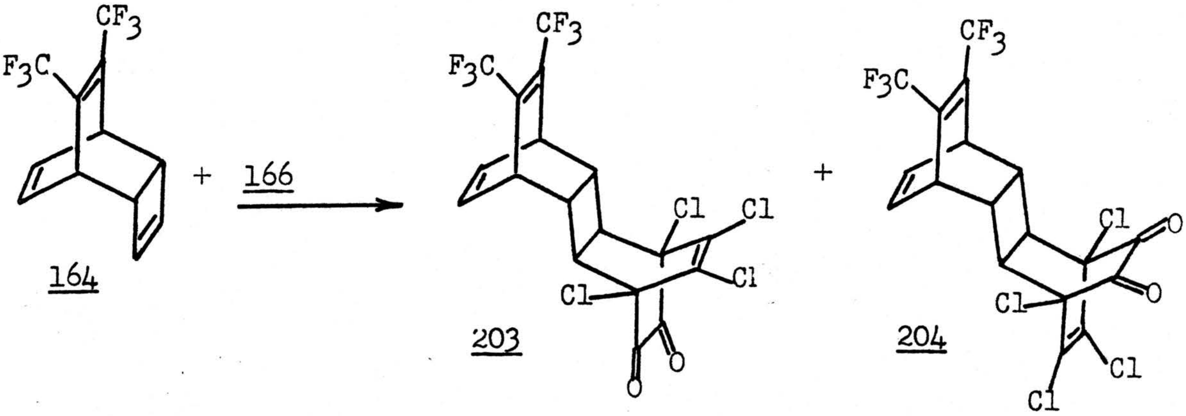
Scheme 61.



Irradiation of the dione in benzene through a pyrex filter yielded the dihydrobarrelene 202 and tetrachlorobenzene. They postulated, but did not isolate, the intermediate cyclohexadiene derivative 201.

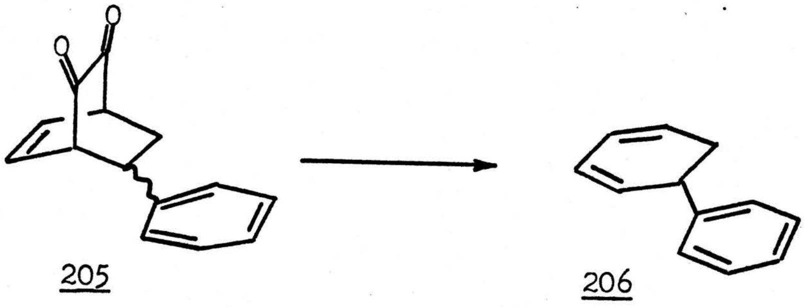
During the course of the present work Warrener *et al*[155] published a note in which the reaction of o-chloranil with the bistrifluoromethyl derivative 164 was described. In this case the ratio of addition products was 4 to 3. It is unclear, however, which isomer predominates.

Scheme 62.



It was anticipated from the reports of Warrener[153-156] and Friedrichschen[172] that the cycloaddition of o-chloranil to 163 should give the adducts 181 and 182 and that the diones should be stable up to the temperature at which dimethyl phthalate would be lost. The ratio of the α-diones and the possible formation of dioxenes could not be predicted. The photochemical transformation of the diones to the cyclohexadiene derivative 169 was thought possible even though Warrener *et al*[153] did not isolate their analogous intermediate 201. An encouraging precedent has been provided by Strating *et al*[175], who reported the isolation of the cyclohexadiene 206 by irradiation of 205.

Scheme 63.



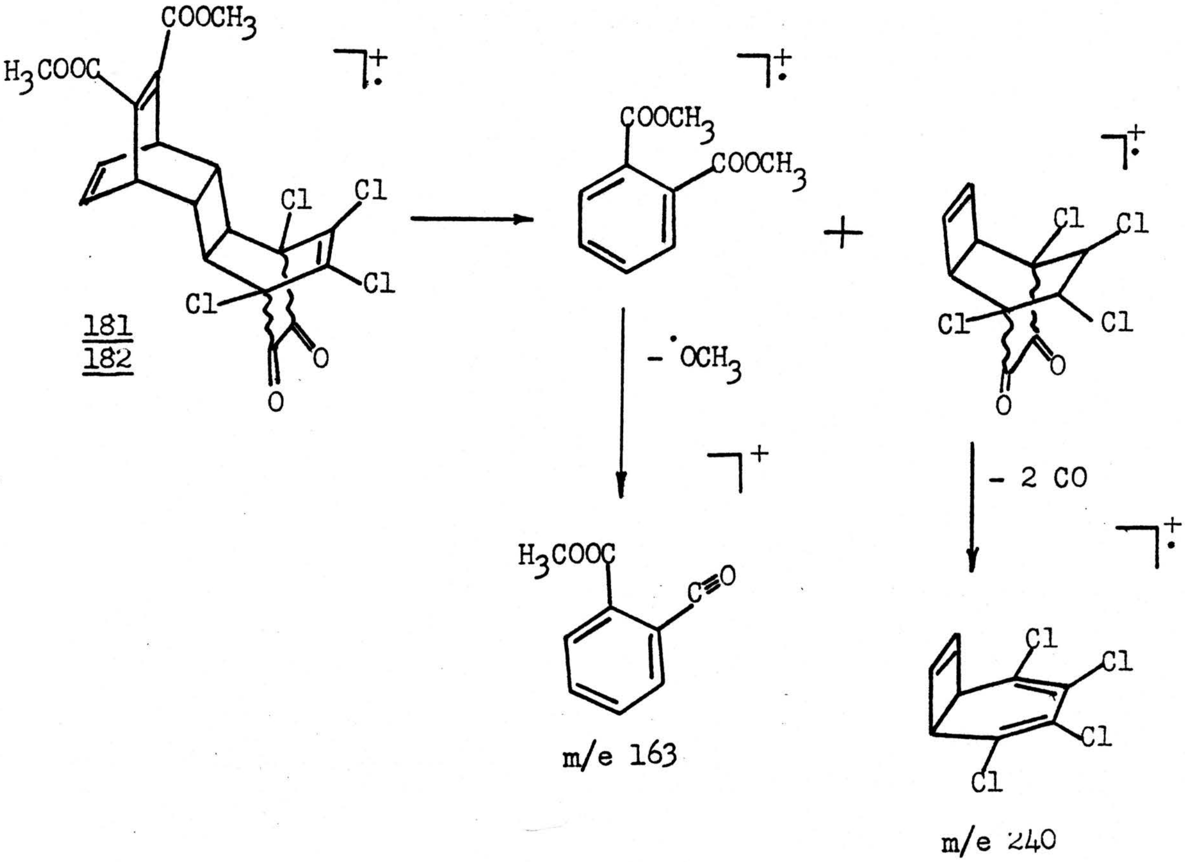
o-Chloranil was prepared by the oxidation of pentachlorophenol with nitric acid by the method of Rocklin.[176] The reaction of o-chloranil with 163 was carried out in chloroform solution at reflux. Chromatography of the crude reaction mixture yielded in equal amounts the two brilliantly yellow crystalline diones 181 and 182 in 86% combined yield. No other products were isolated.

For descriptive purposes, the adduct with the carbomethoxy groups on the same face of the molecule as the dione group will be designated as exo. The endo dione is the molecule having the dione and dicarbomethoxy groups on opposite faces.

The melting behaviour of the exo and endo diones depended on the rate of heating. The observed melting points taken at the same thermostat setting in sealed capillaries were 185-186° for the exo isomer 181, and 188-191° for the endo adduct 182, however, widely differing melting ranges were observed at other settings. The phase change may simply have been due to loss of dimethyl phthalate. Supporting this view is the vapour phase chromatographic behaviour of the diones. Two peaks were observed for each pure compound. The first in each case had the same retention time as dimethyl phthalate. It is likely that the second peak corresponded to the Retro Diels-Alder fragment in each case. The second from the endo dione had a slightly longer retention time than that from the exo isomer.

The mass spectra also parallel the thermal lability of the systems; molecular ions are not observed. The fragmentation pattern for both diones is a composite of the patterns observed for dimethyl phthalate and tetrachlorocyclooctatetraene (*vide infra*). The fragmentation patterns can be explained by an initial loss of dimethyl phthalate from the molecular ion by a Retro Diels-Alder (RDA) reaction. The base peak in the spectra of both diones occurs at m/e 163, corresponding to the loss of OCH_3 from dimethyl phthalate. The M^+ minus dimethyl phthalate ion occurs at m/e 296, 298, 300, and 302. Another grouping at m/e 240, 242, 244, 246, corresponds to the loss of dimethyl phthalate and two molecules of carbon monoxide from the molecular ion. The mass spectra of dimethyl phthalate, tetrachlorocyclooctatetraene and both diones <u>181</u> and <u>182</u> are presented in the Spectra section.

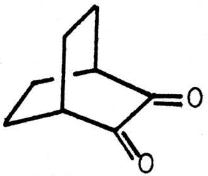
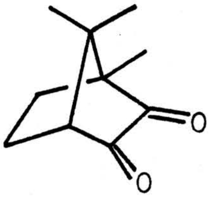
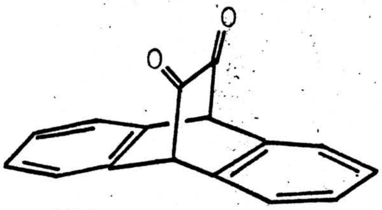
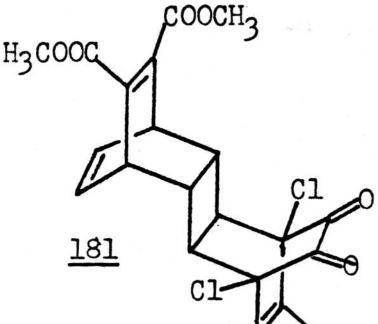
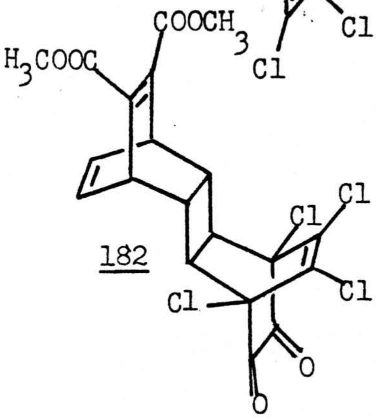
Scheme 64.



The carbonyl groups of 181 and 182 are constrained by the bicyclo[2.2.2]octane system to be cis and coplanar and are prevented from enolization in accordance with Bredt's rule.[177] This geometry gives rise to distinctive bands in the infrared and ultra violet spectra of the two diones. The high frequency positions of the two carbonyl bands observed in the infrared at 1780 and 1745 cm^{-1} are typical of similarly constrained diones.[178] The longer wavelength $n \rightarrow \pi^*$ band ("A" band) in the visible spectrum occurs between 445 and 490 nm in 2,3-diketo bicyclo[2.2.2]-octane systems. The extinction coefficients observed appear to depend on the substituents on the ring system. The "A" band $n \rightarrow \pi^*$ data for some representative α diones are shown below and with the values obtained for the diones 181 and 182.

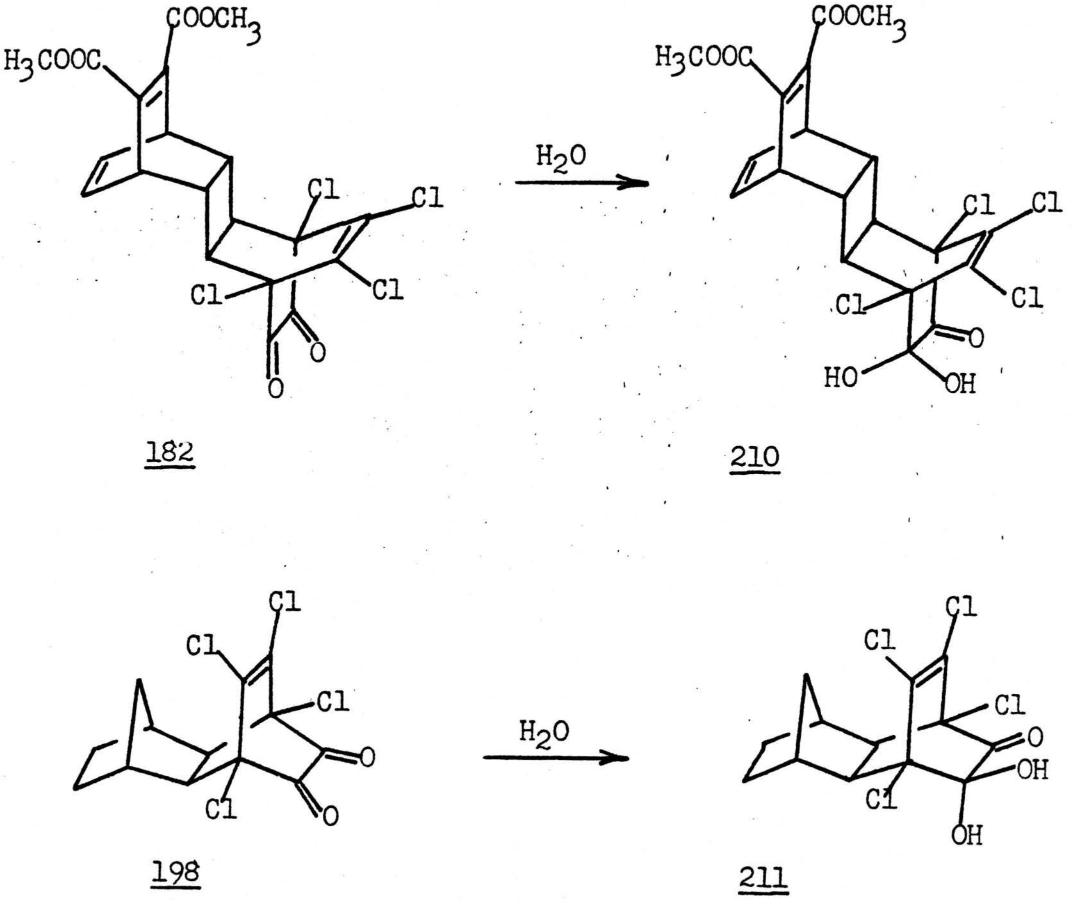
Table 4.

n→π* "A" Bands in the Ultraviolet Spectra of Some α Diones

	λ max. nm	ε	Solvent	Reference
 207	447-448	30	Cyclohexane	179
 208	468	30	Ethanol	180
 209	458	980	Cyclohexane	181
 181	445	430	Chloroform	this work
 182	445	175	Chloroform	this work

Yellow dilute chloroform solutions of the endo dione 182 lost colour rapidly (in 0.5 hour) on standing. This phenomenon is ascribed to the formation of 210, which is consistent with the observation of Friedrichschen and Epbinder[172] who reported the facile hydrate formation of the endo dione 198.

Scheme 65.

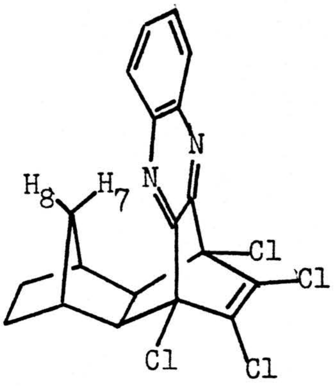


In the case at hand, the dione could be regenerated from the hydrate by refluxing a suspension of the colourless solid in benzene using a Dean

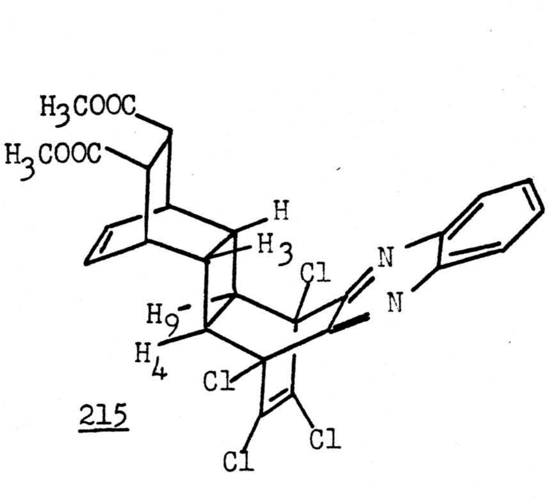
Stark trap. The lower extinction coefficient of the "A" band found for the dione 182 relative to the exo dione 181 may have been in part due to hydration by traces of water and acid present in the chloroform used as the solvent in the ultraviolet determination.

The hydration of one of the α-diones gave a clue to the relative stereochemistries of the adducts; further evidence was gathered from comparison of the nmr data of the quinoxaline derivatives 212 and 213 with the corresponding diketones 181 and 182. Examination of the changes of the chemical shifts of the protons that are shielded by the quinoxaline ring allow stereochemical assignments to be made.

Friedrichschen and Epbinder[172] assigned the stereochemistry of 197 by preparing the quinoxaline derivative 214 and noting a strong upfield shift for H_7. Warrener *et al*[153] prepared the quinoxaline of 215 and observed a shift upfield of .58 ppm for the protons assigned to C_3 and C_8 which are in the shielding cone of the quinoxaline ring. The protons of C_4 and C_9 of 215 should be less affected by the anisotropy of the quinoxaline ring.



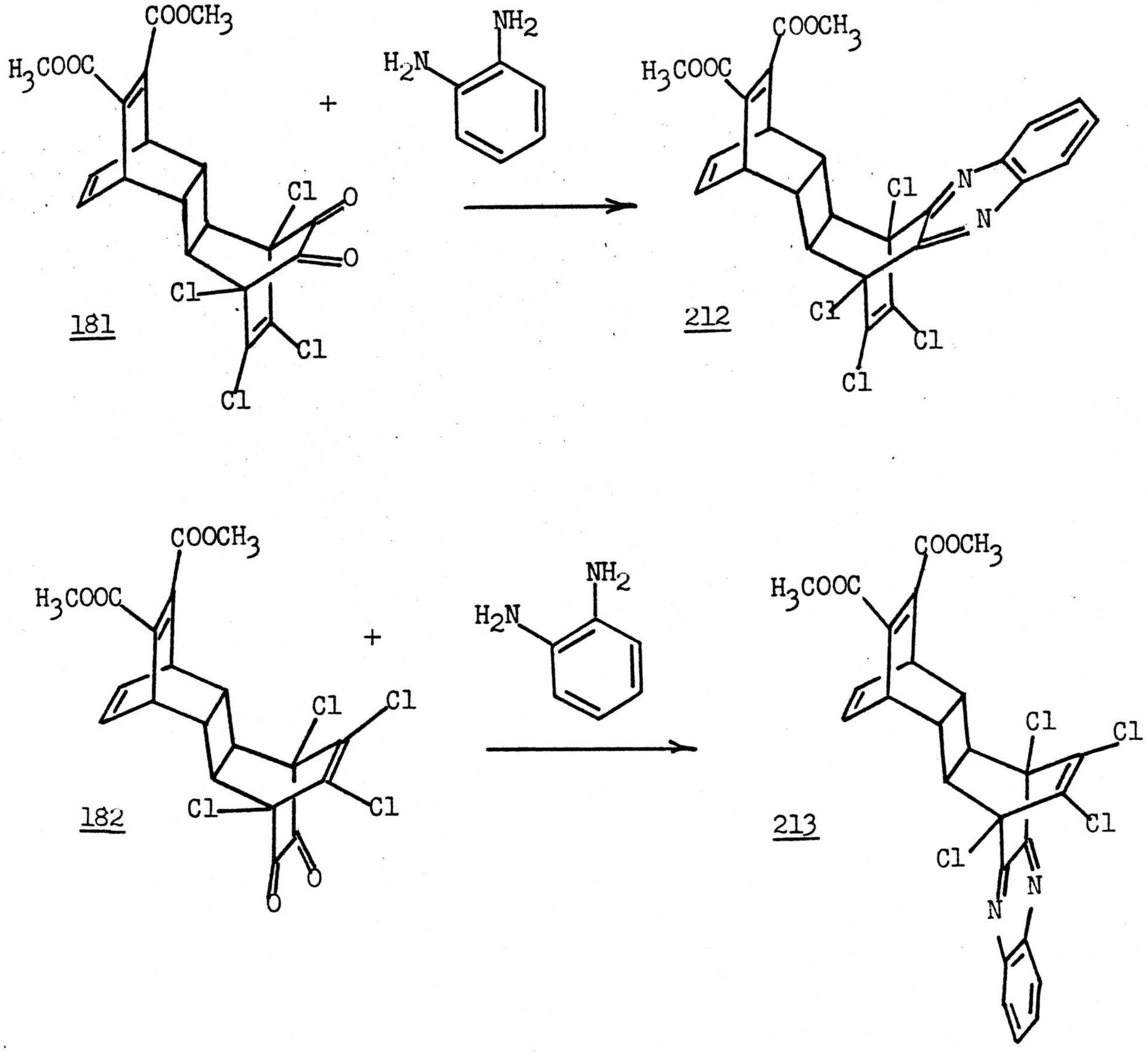
214



215

Brief heating of the endo dione, as the hydrate, with a molar equivalent of o-phenylenediamine in ethanol gave, on cooling of the solution a 50% yield of the crystalline quinoxaline 213. Similar treatment of the exo dione 182 resulted in a much lower yield (less than 20%) of the quinoxaline 212.

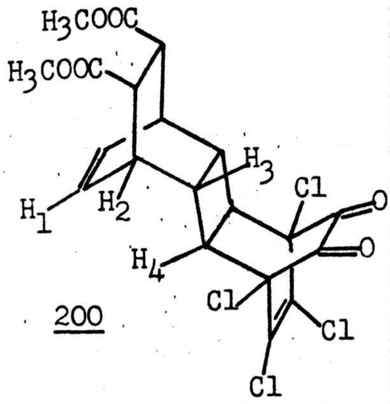
Scheme 66.



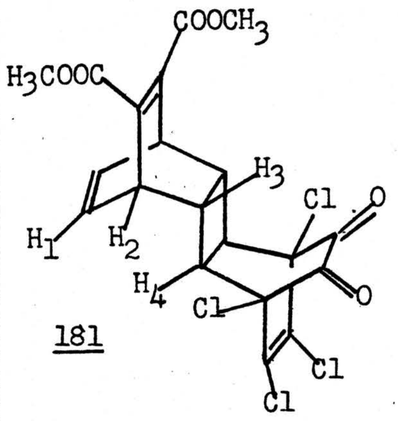
The chemical shifts and multiplicity of the protons of the two diones 181 and 182 are listed along with those of the dihydro derivative 200 of Warrener *et al*[153] in Table 5. The changes of the chemical shift of the H_3 proton in the quinoxaline derivatives are listed. The arbitrary numbering system is used for descriptive purposes only.

Table 5

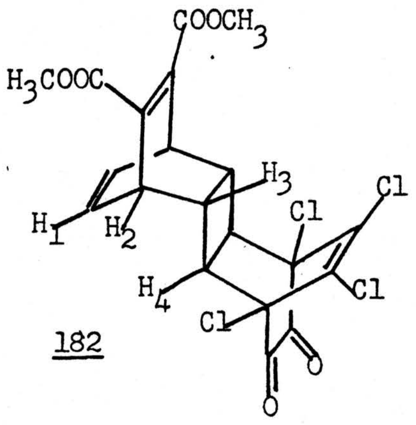
The chemical shifts of the methine protons of 200, 181, and 182, 80 MHz nmr



200



181



182

	200	181	182
H_1	6.55 2H t	6.57 2H dd	6.59 2H dd
H_2	3.13 2H m	4.13 2H m	4.22 2H m
H_3	1.97 2H m	1.94 2H m	2.33 4H m
H_4	2.62 2H d	2.43 2H m	

Δν in H_3 of quinoxaline

200	181	182
0.58 ppm	0.48 ppm	0.03 ppm

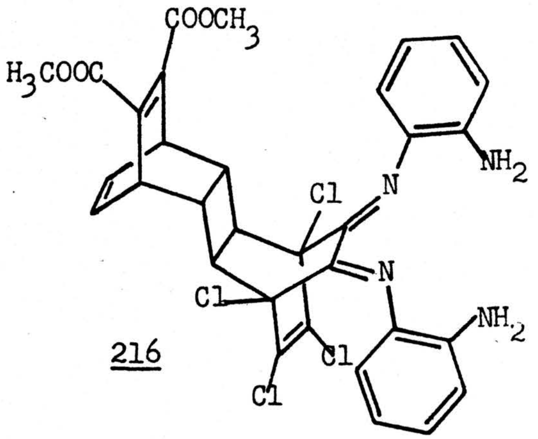
The proton signals of the exo dione were assigned on the basis of double irradiation experiments reproduced in the Spectra section. Irradiation of the signal at δ 4.13 caused the vinyl protons to collapse to a singlet. Thus the signal at δ 4.13 must be due to the bridgehead proton H_2. Irradiation of the furthest upfield signal at δ 1.94 caused the peak at δ 2.43 to collapse to a singlet. This signal at δ 2.43 which on irradiation at H_3 is decoupled from all the other protons of the molecule must be H_4. The signal irradiated at δ 1.94 must have been due to H_3.

The signals for the endo dione <u>182</u> were assigned by comparison with the exo dione <u>181</u>.

The chemical shifts of the protons of <u>181</u> and <u>182</u> are similar to those reported by Warrener *et al*[153] except, as anticipated, the bridgehead protons H_2 should be further downfield in <u>181</u> and <u>182</u>.

In large scale preparations of the exo quinoxaline derivative <u>212</u> a product precipitated from the reaction mixture that was insoluble in chloroform and gave one spot on tlc. Its nmr in deuteropyridine is reproduced in the Spectra section. On the basis of the nmr spectrum and thermolysis results obtained, the structure <u>216</u> is proposed. <u>216</u> is the result of attack of two molecules of o-phenylenediamine.

The nmr integration shows a ratio of aromatic and amine protons to vinyl, cyclobutane hydrogens H_3 and H_4, bridgehead H_3 and carbomethoxy methyl protons of 6:1:1:1:1:3.



216

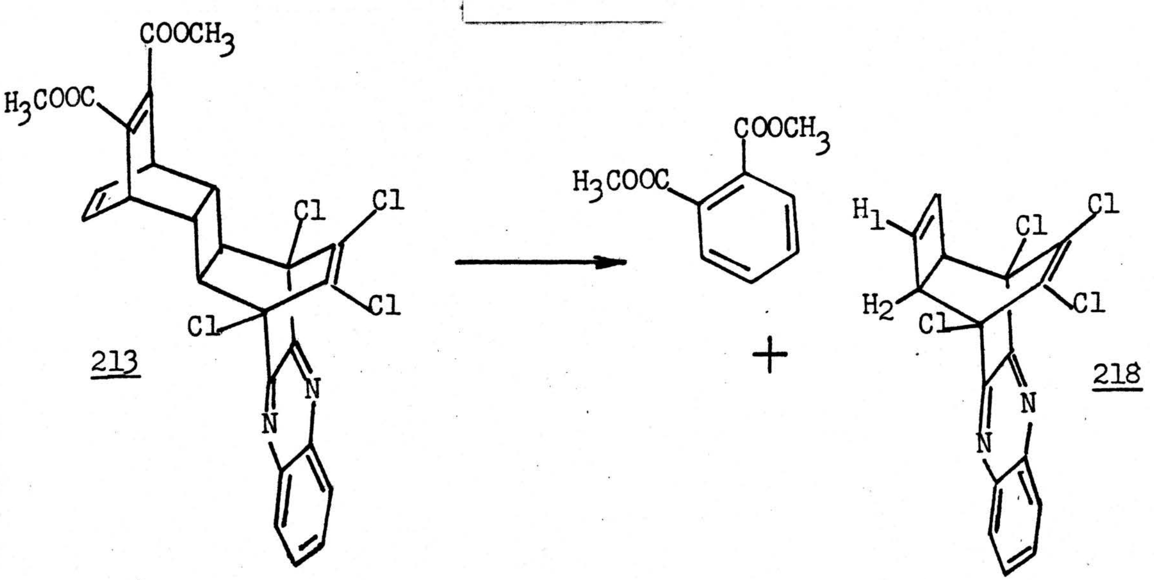
The mass spectrum of the abnormal adduct is consistent with the structure proposed. A molecular ion is not detected; however, the probe temperature required to provide detectable ion current was sufficient for the rearrangement proposed (*vide infra*) to take place. The o-phenylenediamine thus generated could have sublimed from the source of the mass spectrometer while the operator was searching for a molecular ion. The largest fragment observed has an m/e 368-372 corresponding to the Retro Diels-Alder loss of dimethyl phthalate from the quinoxaline 212.

The reluctance of the exo dione 181 to form a quinoxaline derivative may be related to the steric hindrance imposed by the H_3 protons on the cyclobutane ring. Severely hindered sterically α-diones have been reported[182,183] to give either anamolous adducts or not to react with o-phenylenediamine.

The stereochemical assignment of the diones 181 and 182 was further corroborated by comparison of the chemical shifts of the protons of the cyclobutenyl quinoxaline 218 derived from the endo quinoxaline 213 and the isomeric cyclobutenyl compound 217 prepared from the bisadduct of the exo dione 216.

The endo quinoxaline 213 was heated in a sealed nmr tube overnight at 155°. The Retro Diels-Alder products dimethyl phthalate and the cyclobutenyl quinoxaline 218 were isolated, the latter as a 45% yield of crystalline material.

Scheme 69.



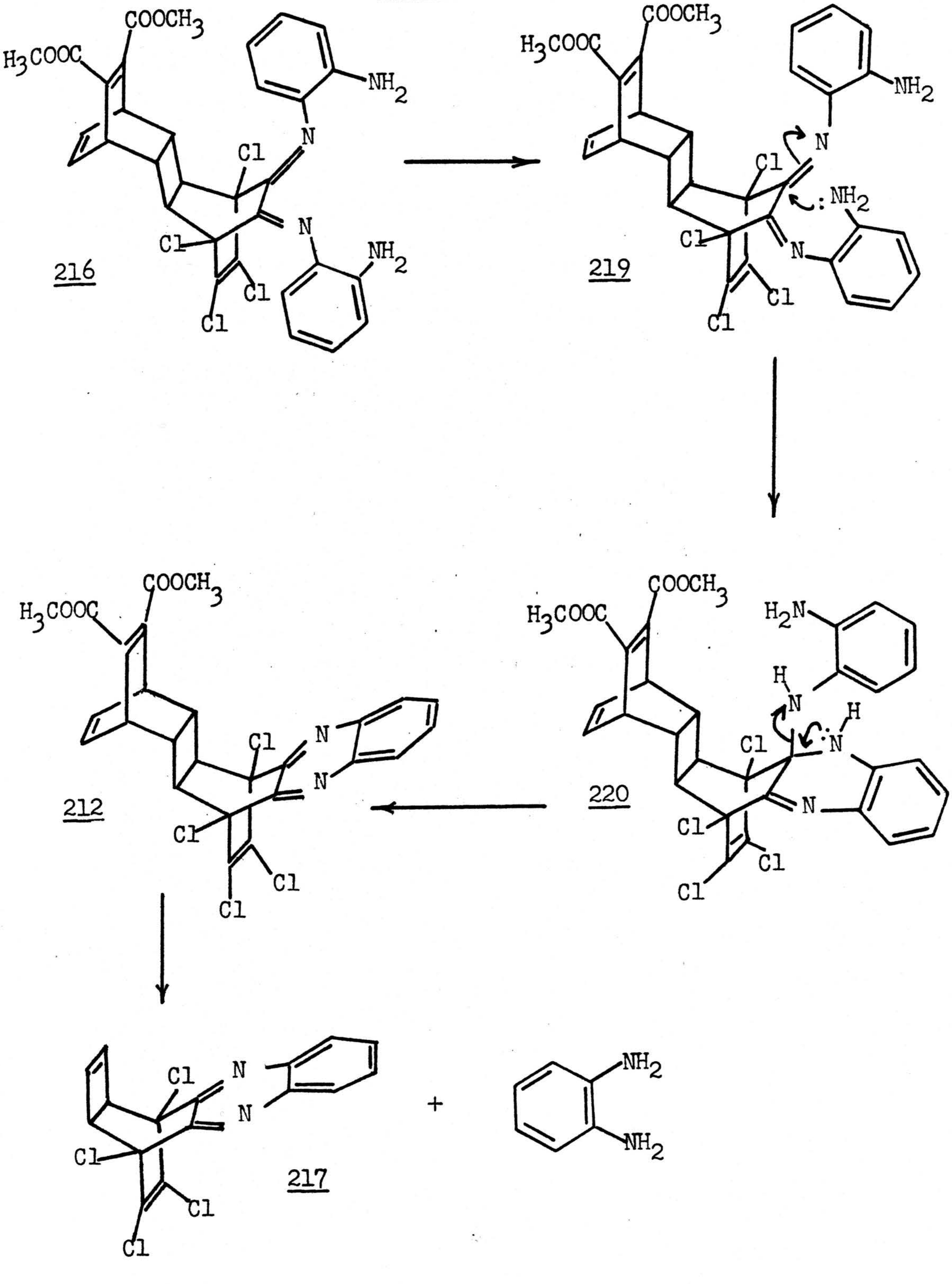
213

218

H_1 6.39
H_2 3.36 ($\Delta\nu$ .35 ppm)

Refluxing the bisadduct 216 overnight in xylene led to the isolation of very close to theoretical amounts of dimethyl phthalate and the cyclobutenyl quinoxaline 217. This remarkably efficient transformation is accounted for as following.

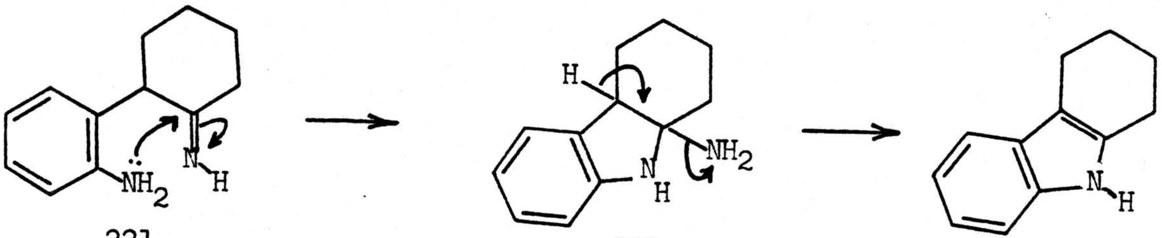
Scheme 67.



While the more stable configuration of the bisimine 216 is most likely the one in which the phenyl groups are directed away from each other, the isomerization[184,185] to the bisimine 219 should be facile at the temperature of the reaction. The lone pair of the amine can, by way of a six membered transition state, attack the carbon of the C=N double bond. Deprotonation and reprotonation of the appropriate nitrogen atoms would give the intermediate cyclized product 220. Expulsion of the elements of o-phenylenediamine would result in quinoxaline formation. A major driving force for this step is the formation of the aromatic system.

A similar cyclization mechanism has been invoked by Paquette[186] in a step of the Fischer indole synthesis, as shown below.

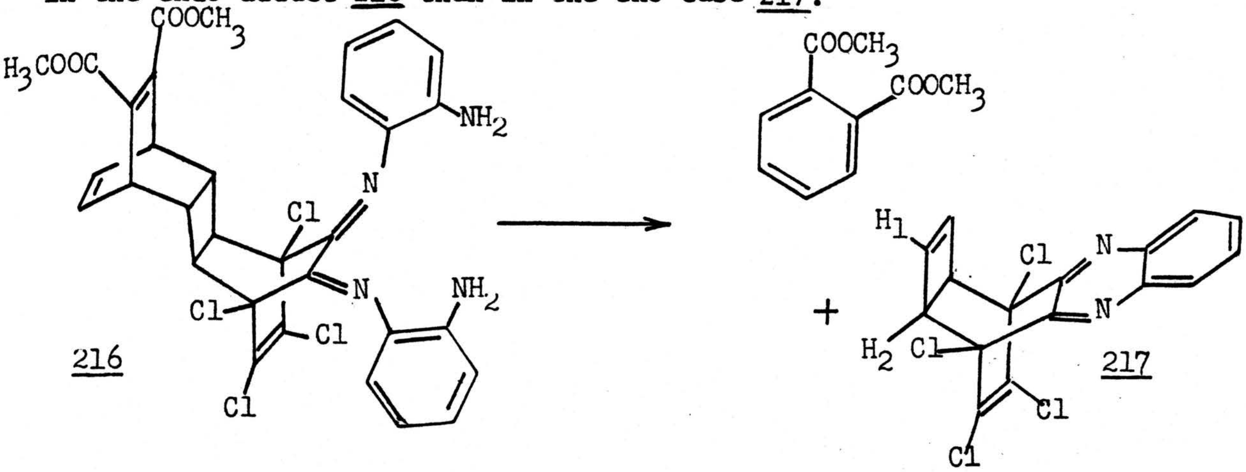
Scheme 68.



221 222 223

The Retro Diels-Alder loss of dimethyl phthalate has been shown as occuring as the last step. This need not be the case; the quinoxaline formation is removed from the site of the Retro Diels-Alder reaction.

If the stereochemical assignments made were correct, the vinyl protons in 217 should be shifted upfield relative to the vinyl protons in the isomeric 218 because of the shielding effect of the aromatic ring. Similarly, the bridgehead protons H_2 should be shifted further upfield in the endo adduct 218 than in the exo case 217.



H_1 6.04 ($\Delta\gamma$.35 ppm)
H_2 3.71

As predicted, the H_1 protons in the exo adduct 217 are shifted to higher field than the H_1 protons of the endo adduct. In agreement with expectation, the H_2 protons are shielded in the endo isomer 218 and not in the exo case.

The stereochemistry of the diones was thus firmly established for the highly substituted derivatives of the precursors of the skeleton of 78. It was hoped that comparison of the data obtained for less substituted compounds would allow the stereochemistries of the latter to be elucidated.

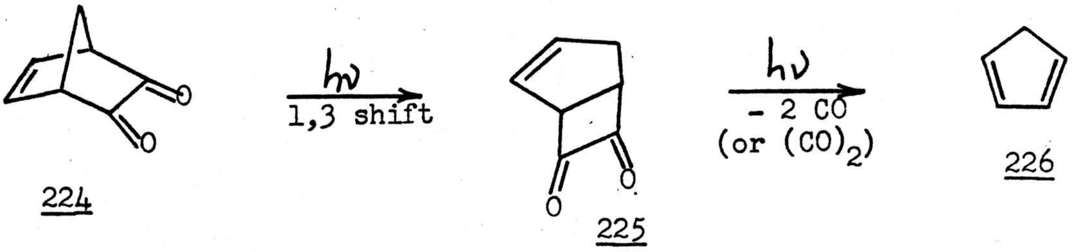
Irradiation of the diones 181 and 182

Vogel[171], Strating[175], and Warrener[153-156] and their coworkers, among others, have effected photochemical bisdecarbonylations of bicyclo-[2.2.2]octene-2,3-diones to give cyclohexadiene derivatives (*vide supra*).

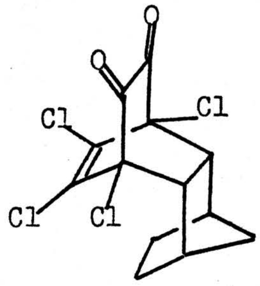
Irradiations have generally been carried out in benzene solutions through pyrex filters effectively eliminating light with a wavelength of less than 300 nm. The long wavelength "A" band of cisoid α-diones absorbs at *ca.* 460 nm and the cyclohexadiene products have maxima below 300 nm and should be photochemically stable.

Recently Rubin *et al*[187] reported a study on the mechanism of the photochemical bisdecarbonylation of bridged dione systems. They observed, and were able to isolate, intermediate cyclobutanedione compounds, the result of a 1,3 shift. These intermediates with maxima at 500 nm lost the elements of two molecules of carbon monoxide to give the diene 226.

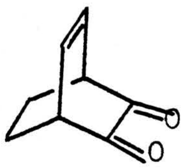
Scheme 70.



Among the bicyclo[2.2.2]octene systems they studied were 227 and 228.



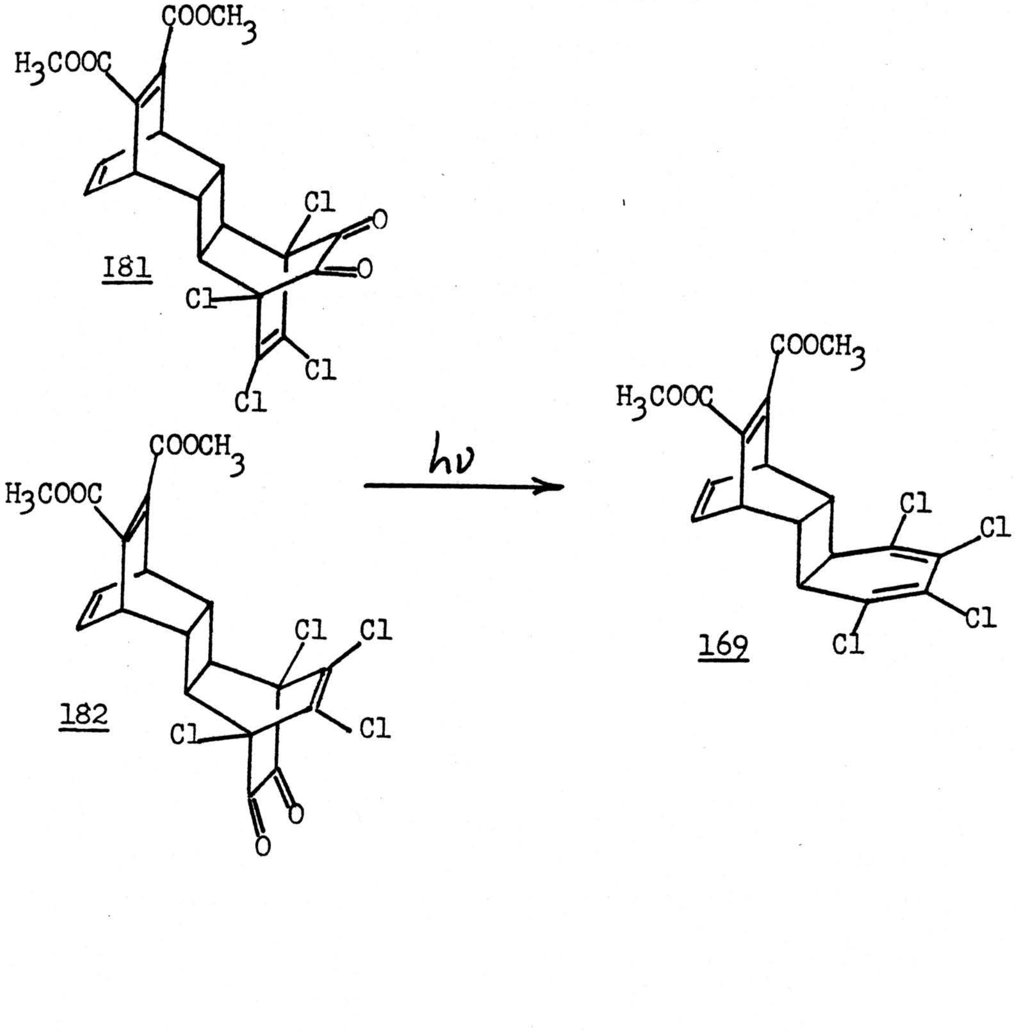
227



228

Based on these precedents the dicarbomethoxy tetrachlorinated diones 181 and 182 in benzene were irradiated with a sunlamp through pyrex in an ice bath. The reactions were followed by tlc. Irradiation of a mixture of diones gave after crystallization an 87% yield of the cyclohexadiene derivative 169, mp 192-193°. Irradiation of the separated diones also gave the same product.

Scheme 71.



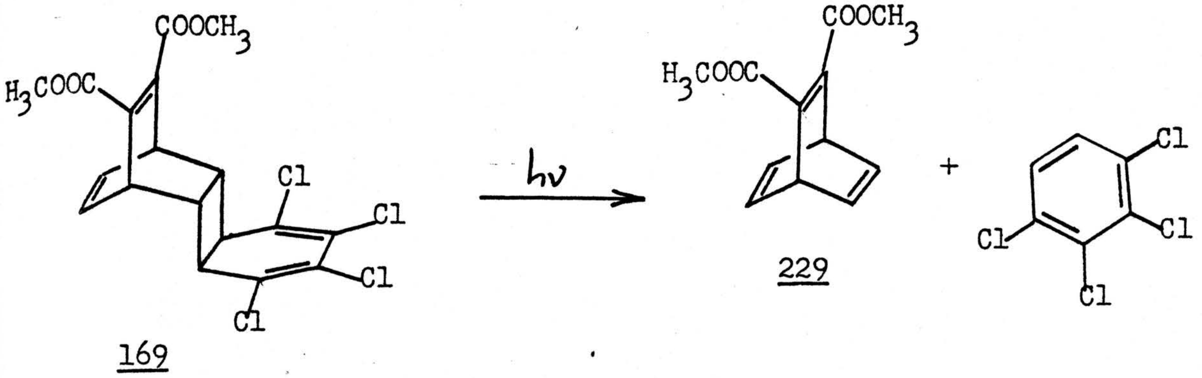
The pmr spectrum is reproduced in the Spectra section. An accurate mass measurement of the molecular ion was correct for the formula of 169. The fragmentation pattern of the mass spectrum of 169 is very similar to that of the diones 181 and 182. The base peak is the dimethyl phthalate base peak at m/e 163. The complete fragmentation pattern can be understood by comparison with the fragmentation patterns for dimethyl phthalate and tetrachlorocyclooctatetraene (*vide infra*). The mass spectrum of 169 is presented in the Spectra section.

The most intense maximum of the cyclohexadiene chromophore occurs at 293 nm with shoulders at 304 and 318 nm. It is significant that these last two bands extend beyond the cutoff of the filter. The possibility exists for photochemical reactions of the cyclohexadiene derivative.

In large scale photolyses, two minor products were observed to be formed. It was hoped that these minor and possibly secondary photoproducts might have rearranged $(CH)_{14}$ skeleta. The two compounds were obtained in pure form by preparative thin layer chromatography of the mother liquors of the crude reaction product.

One of these products, a pale yellow oil, was assigned the barrelene structure 229 on the basis of its nmr, ir, and mass spectrum. The chemical shifts observed for the methine protons for the dicarbomethoxybarrelene 229 were virtually identical to those reported[188] for 2,3-dicyanobarellene. A double irradiation experiment confirmed the assignment. When the bridgehead proton was irradiated, the vinyl doublet of doublets pattern collapsed to a singlet. The spectrum is reproduced in the Spectra section.

Scheme 72.



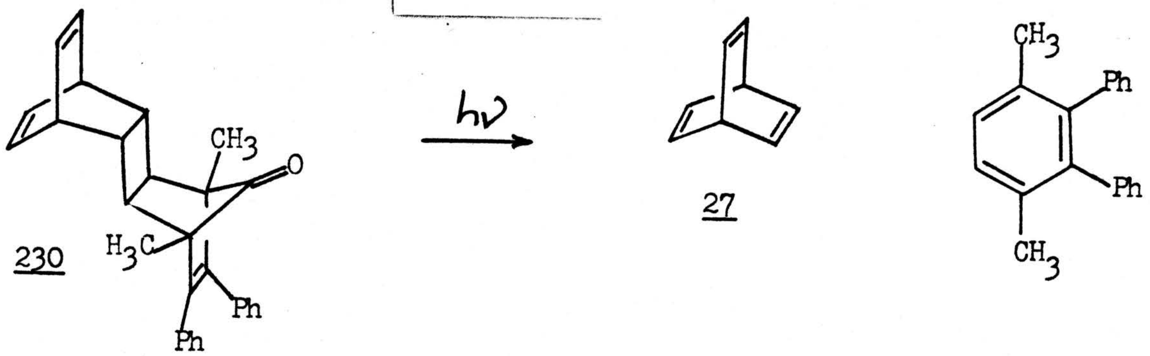
169

229

It is most likely that the barrelene 229 is formed by a photochemically allowed 2+2 cycloreversion reaction of the cyclohexadiene derivative 169.

During the course of this investigation Dauben *et al*[56] reported the efficient synthesis of unsubstituted barrelene by a similar photochemical reaction.

Scheme 73.

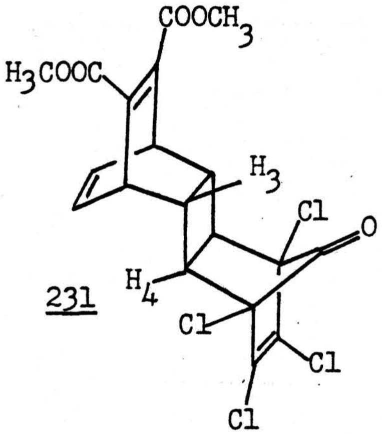


230

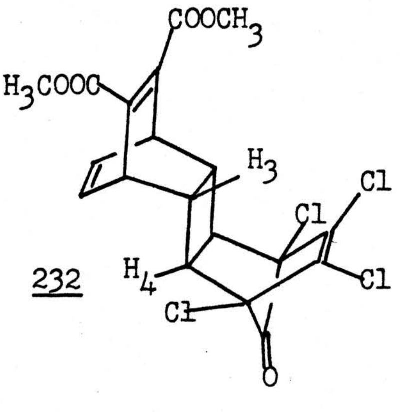
27

Several 2,3-disubstituted barrelenes have been reported in the literature. Ciganek[188] was able to obtain a 60% yield of 2,3-dicyanobarrelene by the $AlCl_3$ catalyzed Diels-Alder reaction of dicyanoacetylene with benzene. He reported, however, that the catalysis of the reaction of dimethyl acetylenedicarboxylate with benzene to give the barrelene 229 could not be effected. No reports of the synthesis of 2,3-dicarbomethoxybarrelene were found in the literature.

The other minor photoproduct was obtained as white crystals mp 168-172°. The pmr run in both deuterochloroform and deuterobenzene are reproduced in the Spectra section. The structure 232 is tentatively proposed on the basis of the spectra obtained.

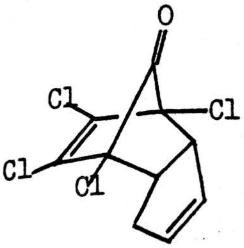


231

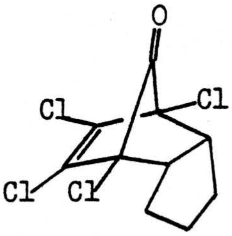


232

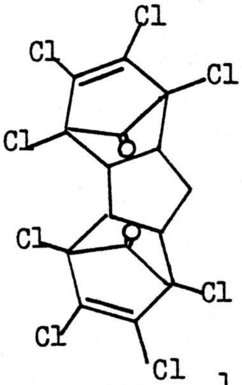
The infrared shows a strong carbonyl absorption at 1835 cm^{-1} ($CHCl_3$). This unusually high frequency absorption is typical of substituted 7-keto-norbornene systems. Yates and Eaton[189] reported that 233, 234, and 235 each had carbonyl bands in similar positions.



233 1830 cm^{-1}
1590 cm^{-1}



234 1830 cm^{-1}
1590 cm^{-1}



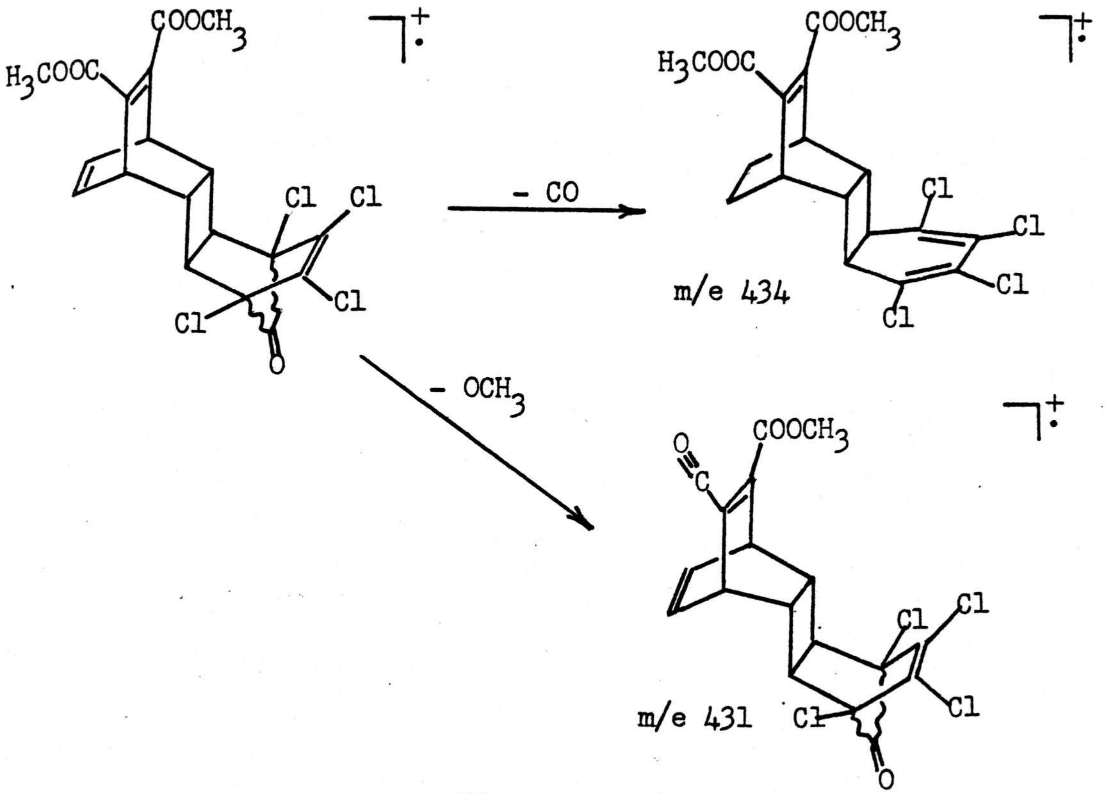
235 1820 cm^{-1}
1585 cm^{-1}

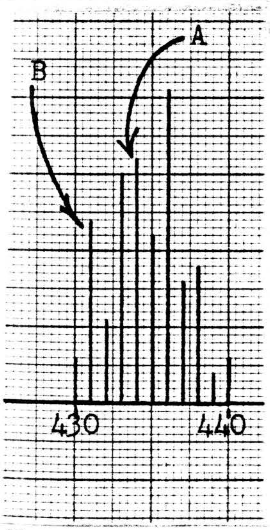
The Cl-C=C-Cl stretch in the compounds of Yates and Eaton occurred at 1585 and 1590 cm^{-1} and a band at 1590 cm^{-1} is observed in the minor photoproduct.

The pmr in both deuterobenzene and deuterochloroform are consistent with the original symmetry of the starting diones being maintained. The methyls of the carbomethoxy groups remain a singlet. In fact, the spectrum is reminiscent of the starting dione: the vinyl, bridgehead, carbomethoxy, and cyclobutane patterns are all retained. This suggests that the structure is closely similar to that of the starting material.

As well, the mass spectrum of the minor product, reproduced in the Spectra section, is very similar to that of the tetrachlorocyclohexadiene derivative 169. In fact, the spectra are superimposable except in the region m/e 430 to 440. The standard four chlorine pattern for the molecular ion of the major photoproduct is shown on the next page. The pattern for the minor photoproduct has in addition to those of the major photoproduct a pattern corresponding to the loss of OCH_3 from the postulated molecular ion. Accurate mass measurements were obtained for the peaks at m/e 431 and 434 corroborating the scheme shown below.

Scheme 74.





A

$C_{18}H_{14}O_4Cl_4$

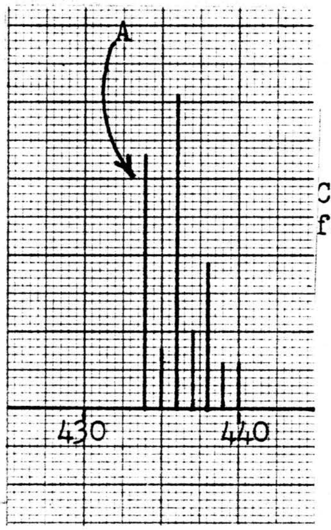
Calc. 433.9651
found 433.9642

B

$C_{18}H_{11}O_4Cl_4$

Calc. 430.9411
found 430.9427

Mass Spectral Fragmentation Pattern of Minor Photoproduct 232 in the Region m/e 430 to 440.



A

$C_{18}H_{14}O_4Cl_4$

Calc. 433.9651
found 433.9646

Mass Spectral Fragmentation Pattern for the Molecular Ion of Major Photoproduct 169.

Neither starting dione gave a molecular ion; the largest fragment observed was that for M^+-OCH_3. As previously discussed, the base peak for dimethyl phthalate occurs at M^+-OCH_3.

Because the starting material consisted of both diones 181 and 182, loss of one carbon monoxide molecule from the diones could result in two norbornene derivatives 231 and 232. The structure 232 was considered more likely than 231 based on nmr solvent shifts. In chloroform the cyclobutane protons are coincident; in deuterobenzene one set is shifted to higher field. The shape of the multiplets is similar to that observed for the exo dione in which the broader is due to H_3 (*vide supra*) and is more extensively coupled to other protons of the system. If the same assignments are made for the minor photoproduct, the proton labelled H_4 is shifted upfield. Jackmann[190] states that normally the benzene complex of a ketone results in shielding of the protons behind the carbonyl. Because the solvent must approach the carbonyl group from the less hindered side, the observed shift suggests that the correct structure is 232.

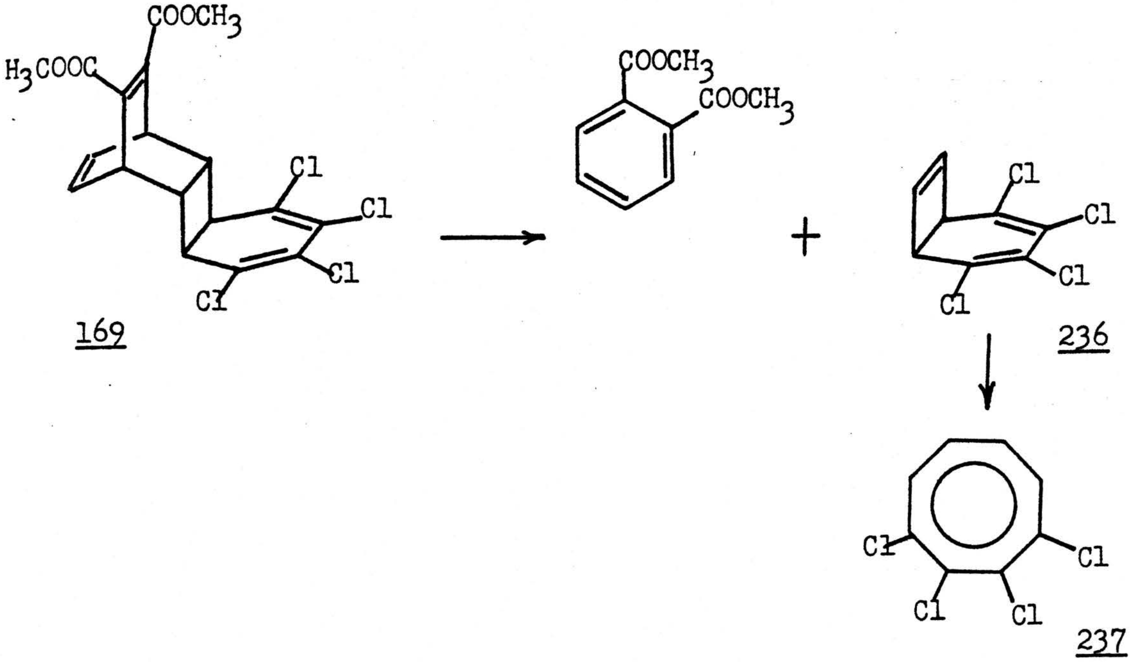
Although the minor photoproduct could not be induced to form a 2,4-dinitrophenyl hydrazone, on the basis of the spectral evidence just discussed, the structure 232 is tentatively proposed.

Thermochemistry of the Cyclohexadiene 169

In order to study possible thermal rearrangements that the $(CH)_{14}$ skeleton might undergo, the thermal reactions of the substituted derivative 169 were studied.

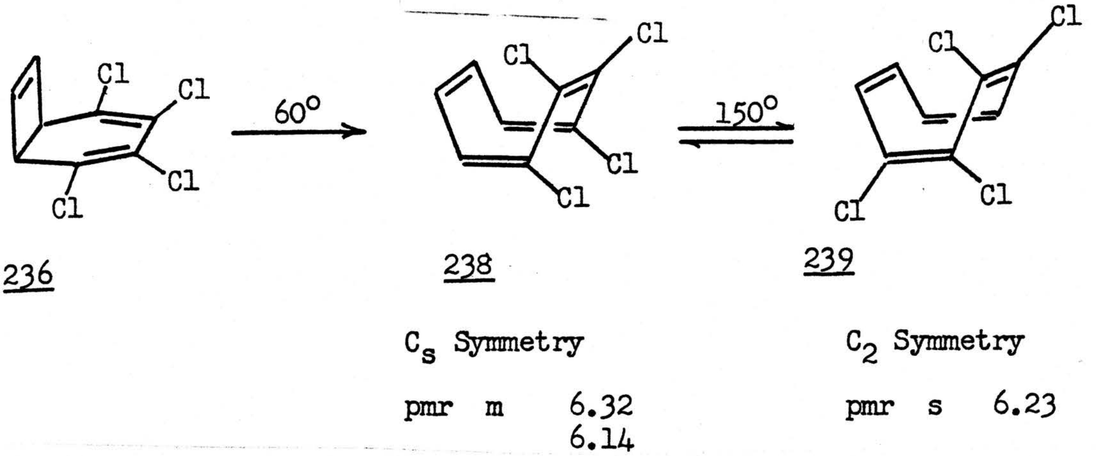
Deuterochloroform solutions of 169 were sealed in thick walled nmr tubes and the thermal reaction followed by nmr. No change was noted until the temperature was raised to 155°. At this temperature the peaks for the starting material began to disappear, and the characteristic pattern of dimethyl phthalate grew. A multiplet appeared in the region δ 6.1 to 6.3. This new product was assigned the gross structure of tetrachlorocyclooctatetraene 237, the product of the Retro Diels-Alder loss of dimethyl phthalate from the cyclohexadiene 169. Dimethyl phthalate and tetrachlorocyclooctatetraene 237 were the only observable products of the reaction.

Scheme 75.



While this work was being carried out Warrener *et al*[155] reported the preparation of the bicyclic compound 236, and described the thermal ring opening to the monocyclic cyclooctatetraene 238 by heating a solution of 236 to 60°. Further heating led to an equilibrium being set up between the two possible monocyclic cyclooctatetraenes, 238 and 239.

Scheme 76.



Warrener found that 238 showed two multiplets in the pmr spectrum at δ 6.32 and 6.14, and that the isomeric compound 235 displayed a singlet at δ 6.23. No comment was made about the position of the equilibrium.

Nmr data obtained from the isolated Retro Diels-Alder product 237 in this study suggested that a mixture was present.

The 80 MHz proton spectrum obtained in deuterobenzene, much different in appearance than that obtained in deuterochloroform, is reproduced in the Spectra section. From the 100 MHz spectrum also in the Spectra section in deuterobenzene a pattern corresponding to the sum of two separate AA'BB' systems could be inferred. Calculations by Professor T. B. Grindley of Dalhousie University, suggested that the two symmetrical inner patterns centred at δ 5.28 and 5.43 ($w_{\frac{1}{2}}$ *ca.* 6 Hz) might correspond to the pattern for 1,2,3,4-tetrachlorocyclooctatetraene 239. The chemical shifts and coupling constants obtained are shown on the next page.

Table 6. Calculated Chemical Shifts of Protons of <u>239</u> from 100 MHz Spectrum

H_5	5.25	$J_{5,6} = J_{7,8} =$	11.3 Hz
H_6	5.47	$J_{5,7} = J_{6,8} =$	- 0.9 Hz
H_7	5.47	$J_{5,8} =$	1.0 Hz
H_8	5.25	$J_{6,7} =$	4.0 Hz

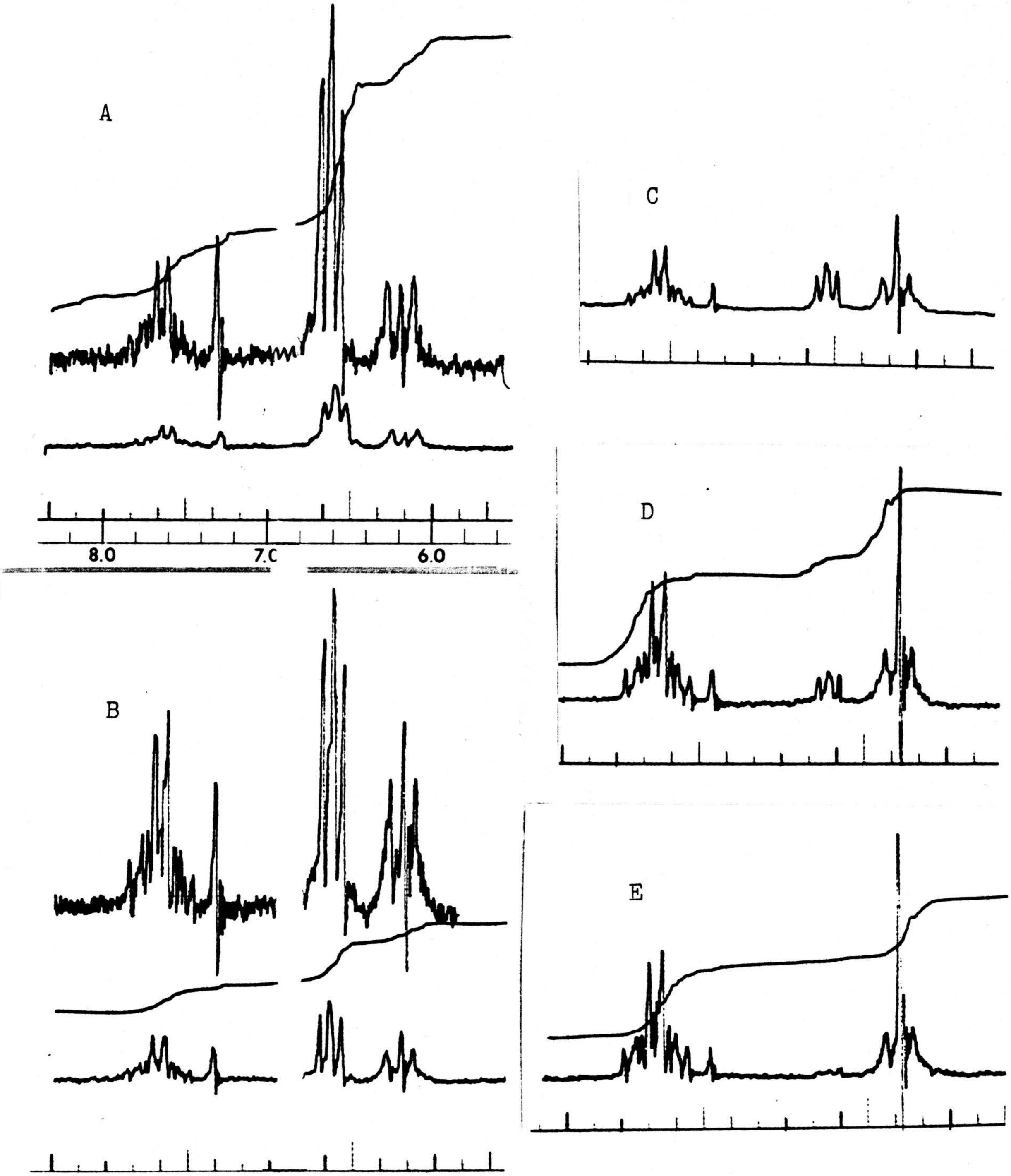
Good values could not be obtained for the other symmetrical AA'BB' pattern centred at δ 5.5 and 5.56 ($w_{\frac{1}{2}}$ *ca.* 9 Hz) of the monocyclic cyclooctatetraene <u>238</u>.

The proton decoupled ^{13}C nmr spectrum, obtained by Professor D. L. Hooper of Dalhousie University, has four signals at 131.64, 131.16, 131.01, and 129.89 ppm downfield from TMS. This spectrum is reproduced in the Spectra section. In the proton coupled spectrum, each of the peaks is found to be a doublet; thus there are four different C-H carbons present. Each of the tetrachlorocyclooctatetraenes <u>238</u> and <u>239</u> should have two C-H signals because of the symmetry of each molecule. 1,2,3,8-Tetrachlorocyclooctatetraene has a mirror plane, and C_s symmetry, so that $C_4 = C_7$ and $C_5 = C_6$, whereas 1,2,3,4-tetrachlorocyclooctatetraene has a C_2 axis, and C_2 symmetry, and $C_5 = C_8$, and $C_6 = C_7$.

It was not possible to observe signals for the carbons bound to chlorine with the sample size available, because of the long relaxation times of such carbon atoms in chlorocarbons. Roberts *et al*[191] have made ^{13}C assignments for a wide variety of chlorocarbons and reported that the chemical shifts of halogenated sp^2 carbons are in the range of 117 to 142 ppm downfield from TMS.

In the thermolysis study of this work it was noted that the ratio of the intensity of the peaks of the multiplet changes with time. After one hour of heating the ratio the outer multiplets (assigned to the structure <u>238</u> by Warrener) to the inner singlet (of <u>239</u>) was approximately 4:1. The singlet grew proportionally larger with time. After 16 hours of heating the ratio appeared to be 1:1. The figure on the following page shows the change of the vinyl protons in the pmr spectrum with time.

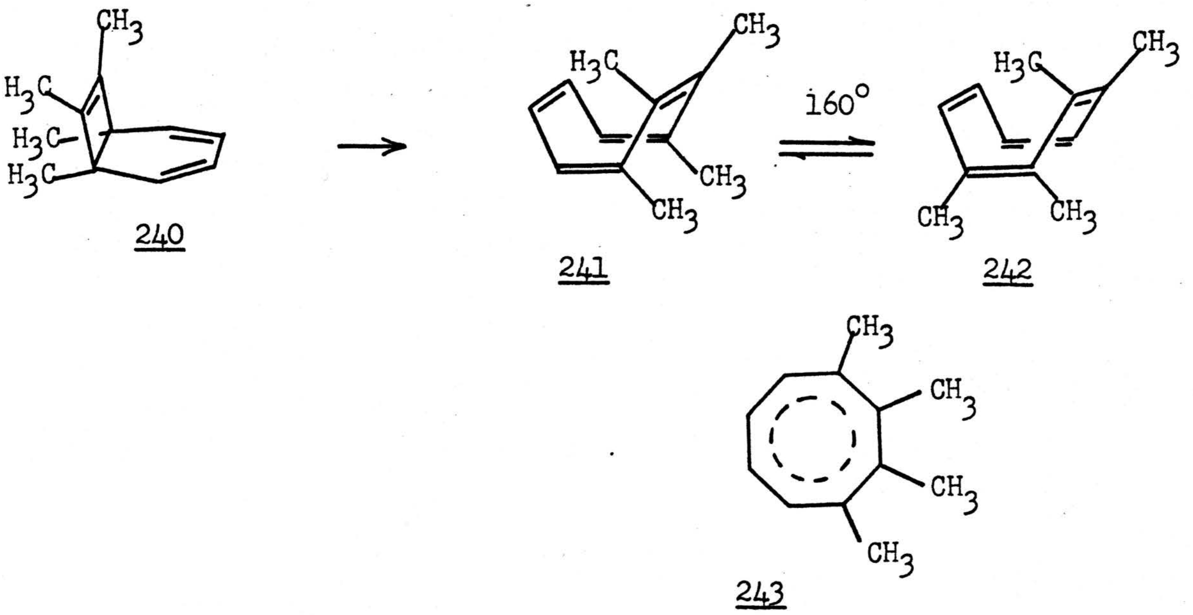
Figure 10.



T-60 NMR Spectra Monitoring the Thermolysis at 155° of <u>169</u> at times t = 1 h (A), 2 h (B), 4 h (C), 8 h (D), and 16 h (E).

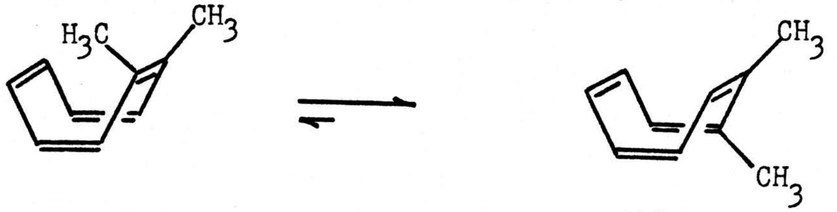
It is interesting to compare this result with those results obtained by Paquette *et al*[192-194] recently for the equilibrium of similarly substituted tetramethylcyclooctatetraenes. They observed that the 1,2,3,8-isomer 241 was preferred over the 1,2,3,4-compound 242 at 162°; the mixture consisted of 70% 1,2,3,8- and 30% 1,2,3,4-tetramethylcyclooctatetraene. The barrier to interconversion of the two tetramethyl isomers has been ascribed to van der Waals repusion of the methyl groups in the planar intermediate 243.

Scheme 77.



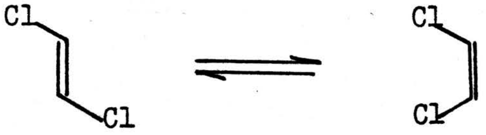
The increased stability of the 1,2,3,8-isomer[241] is due to the less severe methyl-methyl interactions in that isomer.

Indeed, Paquette[192] has noted that the equilibrium between the more simple 1,2-dimethyl- and 1,8-dimethylcyclooctatetraenes (244 and 245) favours the isomer with the methyl groups further away from each other.

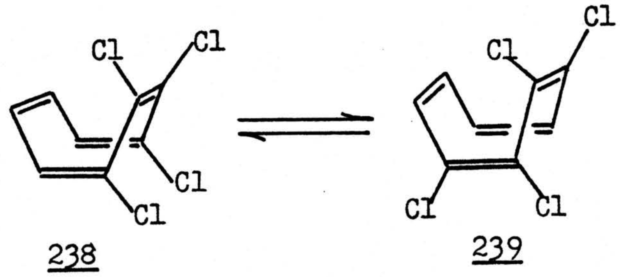


244 245

However, it is well known that cis-1,2-dichloroethylene is more stable than the trans isomer by approximately one Kcal/mole[195]. The reasons for this phenomenon are not well understood; Liberles[196] has suggested that

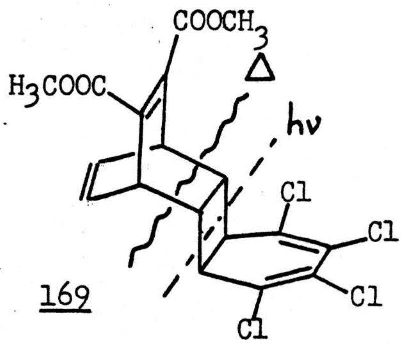


there is an attractive steric interaction between the halogens. Perhaps the same effect is operating in the case of the tetrachlorinated cyclooctatetraenes, and there is a net attraction between the halogens and thus, 1,2,3,4-tetrachlorocyclooctatetraene 239 is more stable than the corresponding 1,2,3,4-tetramethylcyclooctatetraene 242. Perhaps the tetrachlorinated derivatives 238 and 239 have similar stabilities, and the observed equilibrium (1 to 1 ratio at 155°) is understandable.



238 239

The thermal and photochemical reactions of the cyclohexadiene 169 did not lead to rearranged skeleta as was hoped; symmetry controlled fragmentation reactions intervened. Whereas photochemical reaction causes scission of the cyclobutane ring, thermal reaction causes the bicyclo-[2.2.2]octadiene moiety to be cleaved.

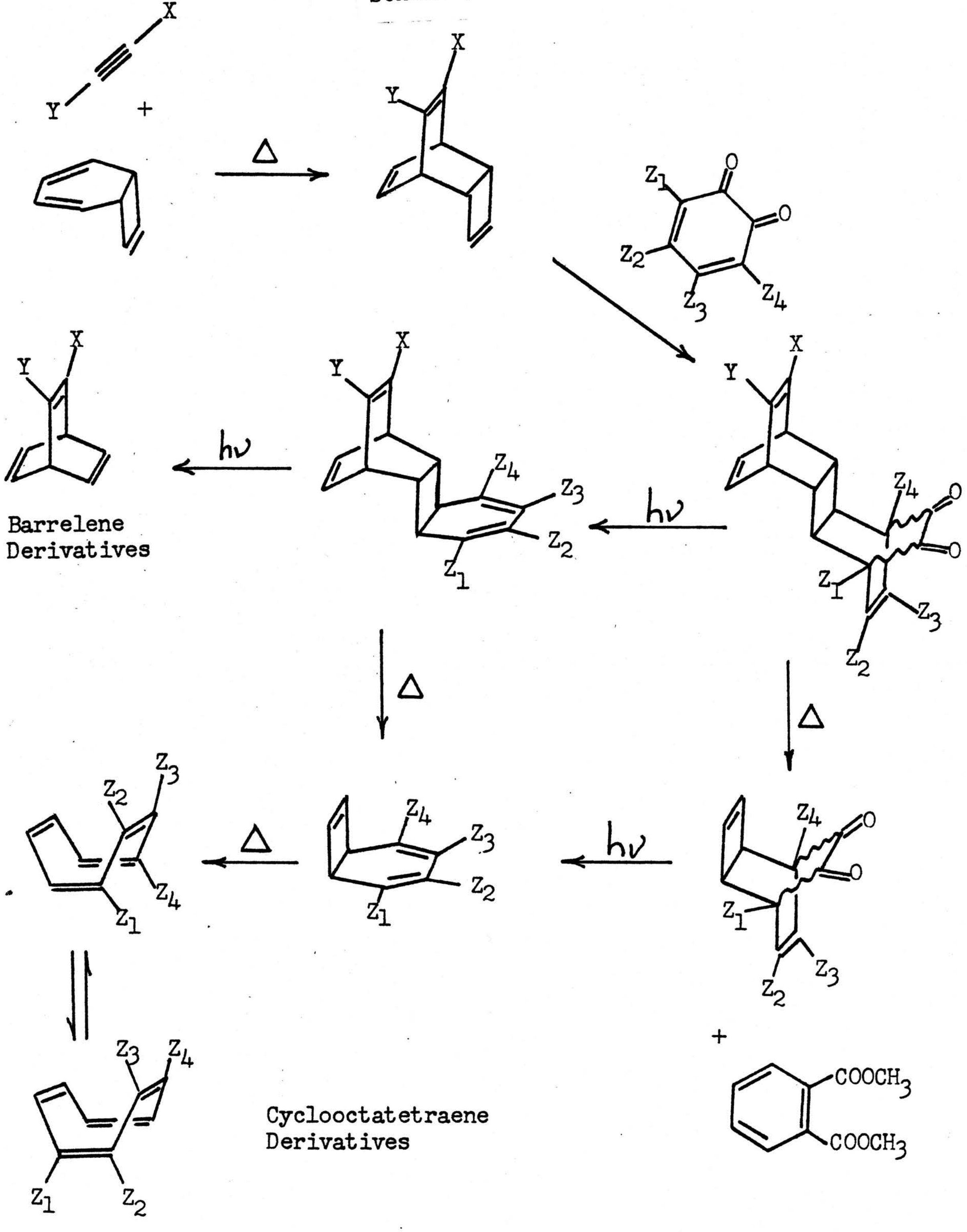


169

In principle, other substituted barrelenes and cyclooctatetraenes should be accessible by similar manipulations of the appropriately substituted skeleton.

By employing a different acetylene in the initial Diels-Alder reaction, a variety of mono or disubstituted barrelenes could be synthesized. Substitution of other groups for the chlorines of o-chloranil could lead to the ready availability of a wide variety of cyclooctatetraene derivatives. The synthetic scheme proposed is shown on the next page in Scheme 78.

Scheme 78.


X
Y
+
Δ
Z1
Z2
Z3
Z4
O
hν
Barrelene
Derivatives
Cyclooctatetraene
Derivatives
COOCH3
COOCH3

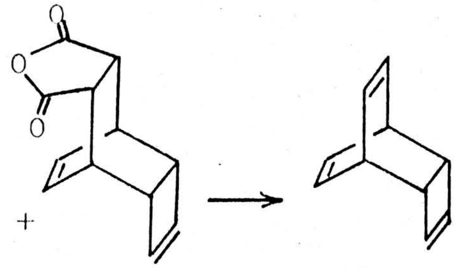
The Synthesis of the Polymethine Hydrocarbon 78

Having completed the synthesis, thermal, and photochemical studies of the highly substituted cyclohexadiene derivative 169, the conversion of 169 to the less substituted dicarbomethoxy derivative 184 was not pursued. Rather, the preparation of the unsubstituted $(CH)_{14}$ hydrocarbon 78 was undertaken.

Dauben's decarboxylation procedure to prepare the desired starting material 20 was modified. The nickel reagent for the reaction was prepared *in situ* by adding $Ni(CO)_4$ to a solution of triphenylphosphine in diglyme, a variation of the procedure of Statham and Rose.[197] To the cream coloured $Ni(CO)_2(PPH_3)_2$ was added the adduct[157] of maleic anhydride and cyclooctatetraene, 43. The published method of Dauben and coworkers[56] was followed from this point on. A total of 3.3 grams (66% yield) of Nenitzescu's hydrocarbon (20) was prepared by this method.

Scheme 79.

$$Ni(CO)_4 + 2\ P(Ph_3)_3 \rightarrow Ni(CO)_2(PPh_3)_2 \quad +$$

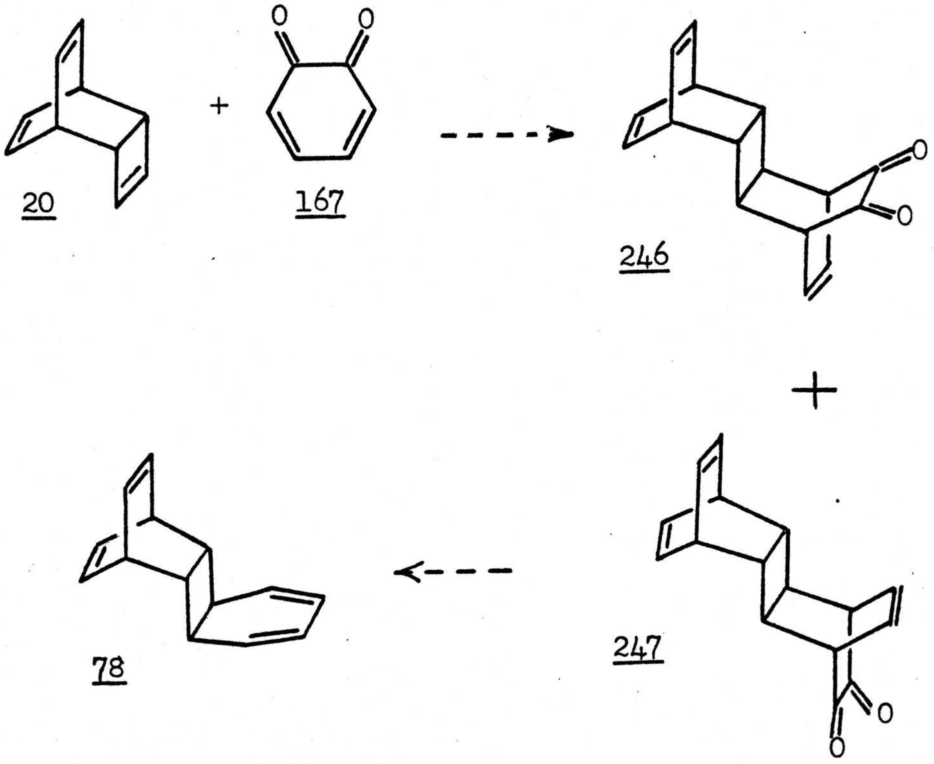


43

20

The synthetic plan was to carry out the same sequence which had been developed for the more substituted derivatives. It was thought that

Scheme 80.



Nenitzescu's hydrocarbon ought to be more reactive than 163 as an inverse electron demand Diels-Alder dienophile because the absence of the electron withdrawing carbomethoxy substituents. Indeed, an initial trial reaction between Nenitzescu's hydrocarbon (20) and o-chloranil carried out in an nmr tube proceeded so quickly at room temperature that the starting hydrocarbon was never observed in the pmr spectrum.

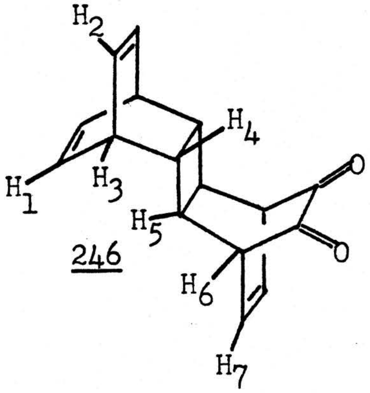
Thus it was anticipated that the poorer inverse electron demand Diels-Alder diene o-benzoquinone might be effective in adding to the reactive cyclobutenyl double bond of Nenitzescu's hydrocarbon as a 1,3-diene.

The successful reaction of the unsubstituted o-quinone with 20 would allow the desired $(CH)_{14}$ hydrocarbon to be obtained after only one further step - the photochemical bisdecarbonylation such as was employed in the more substituted series.

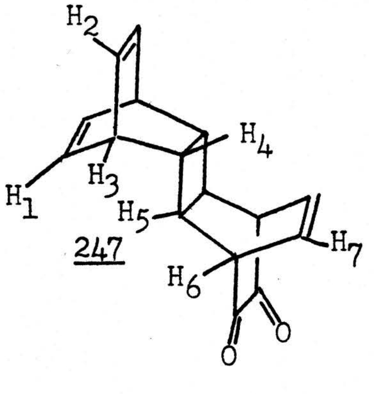
Accordingly, the air sensitive o-benzoquinone 167 was prepared by the oxidation of catechol by o-chloranil in ether at -25 to -30° by the method of Horspool.[198] The bright red needles were used without isolation as any manipulations in air caused rapid decomposition of the material.

Nenitzescu's hydrocarbon (20) was added to a benzene solution of an excess of o-benzoquinone and the reaction mixture was allowed to stand for 24 hours in the dark and under nitrogen. The orange benzene solution was decanted from a heavy black precipitate and on evaporation of the benzene the crude product was chromatographed on preparative thin layer plates. Two intensely yellow crystalline compounds 246 and 247 in a ratio of exo to endo of 3:2, were isolated in 10% yield (23% based on unrecovered starting material).

Double irradiation nmr experiments performed by Mr. J. van Ingen of the National Research Council, on an HA-100 spectrometer allowed the chemical shifts and coupling constants of the diones to be deduced. The relative stereochemistries were determined by comparison of the chemical shifts of the quinoxaline derivatives (*vide infra*).



246



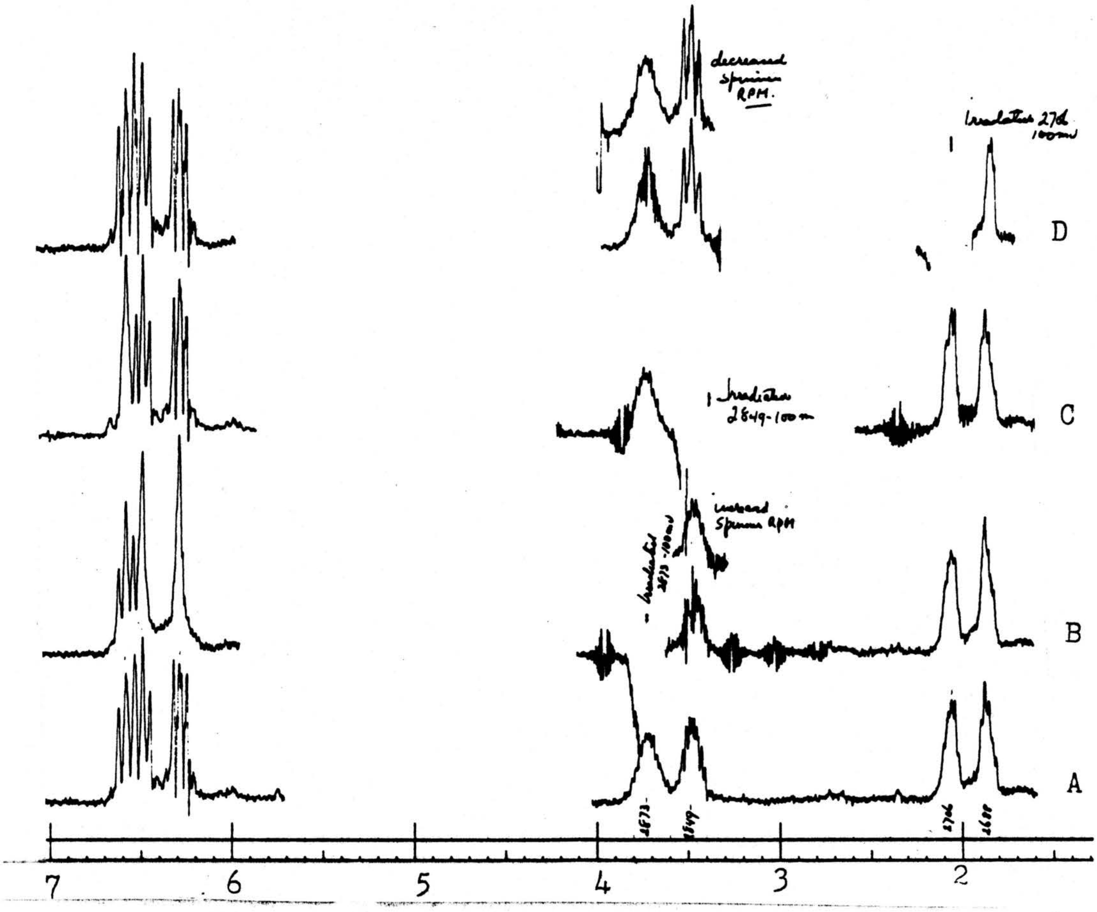
247

The patterns observed in the spectra, presented in Figures 11 and 12 are similar to the more substituted diones 181 and 182 except that the greater number of protons render the spectra more complicated. There are in each dione three different vinyl doublet of doublet patterns, (H_1, H_2, H_7), two different bridgehead multiplets (H_3, H_6), and the two cyclobutane signals (H_4, and H_5).

The chemical shifts and coupling constants obtained are shown in Table 7.

In the case of the endo dione 247, irradiation at the lower field bridgehead position at δ 3.72 caused two of the vinyl doublet of doublet patterns to collapse to singlets. Thus the lower field bridgehead signal δ 3.72 is that of H_3, and the two singlets generated at δ 6.30 and 6.50 must be of H_1 and H_2. Irradiation of the upfield bridgehead signal at δ 3.48 caused collapse of the remaining doublet of doublets δ 6.59 to a singlet, confirming that the upfield bridgehead proton was H_6. H_7, δ 6.59, can also be assigned on this evidence. Irradiation of the lower field cyclobutane signal at δ 2.06, due to H_5, caused the proton H_6 at δ 3.48 to

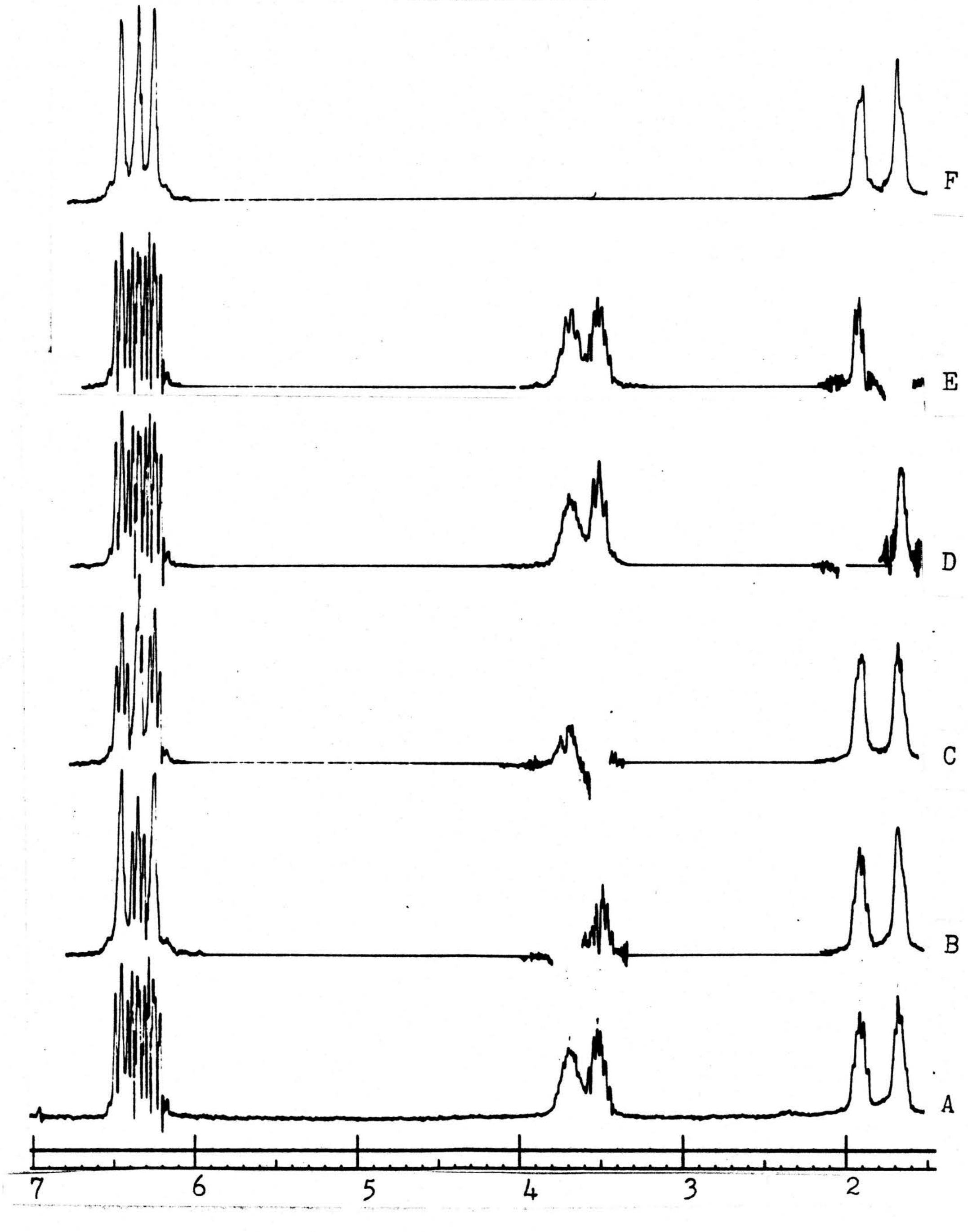
Figure 11.



100 MHz NMR Decoupling Experiments Performed on Endo Dione 247.

A. No irradiation.
B. Irradiation at δ 3.72.
C. Irradiation at δ 3.48.
D. Irradiation at δ 2.06.

Figure 12.



100 MHz NMR Decoupling Experiments Performed on the Exo Dione <u>246</u>.

A. No irradiation.
B. Irradiation at δ 3.72.
C. Irradiation at δ 3.52.
D. Irradiation at δ 1.92.
E. Irradiation at δ 1.68.
F. Irradiation at δ 3.72 and 3.52.

appear as a triplet or a collapsed doublet of doublets. The highest field signal at δ 1.88 is due to H_4.

Table 7

Chemical Shifts of Protons of Diones 246 and 247 100 MHz

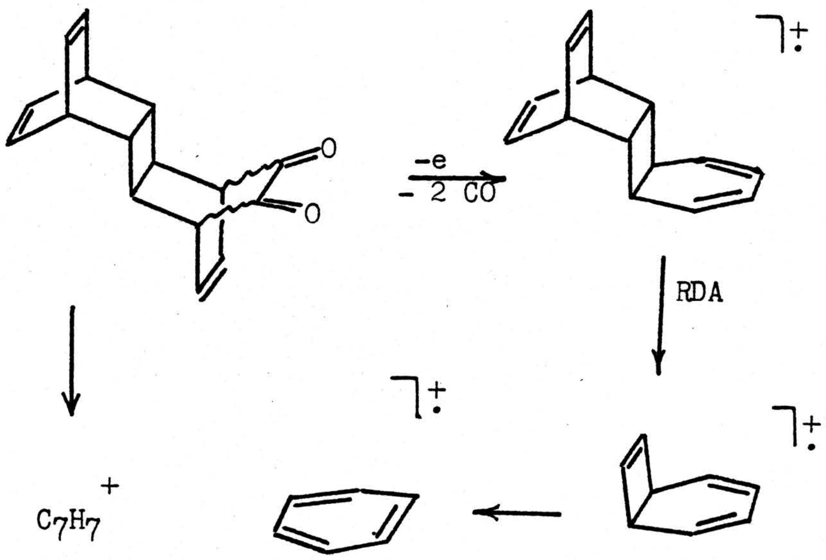
Proton	Endo Isomer 247	Exo Isomer 246
1	6.50 (N = 8.0 Hz)	6.47 (N = 7.6 Hz)
or		
2	6.30 (N = 7.4 Hz)	6.26 (N = 7.2 Hz)
3	3.72	3.70
4	1.88	1.68
5	2.06	1.92
6	3.48	3.52
7	6.59 (N = 9.0 Hz)	6.36 (N = 7.8 Hz)

Double irradiation experiments on the exo dione 246 led to similar conclusions. Irradiation of the lower field bridgehead signal δ 3.70 again led to collapse of two doublets of doublets δ 6.47 and 6.26, and irradiation of the higher field multiplet δ 3.52 caused the other doublet of doublets δ 6.36 to become a singlet. Irradiation of the lower field cyclobutane signal δ 1.92 causes the peak assigned to H_6 to sharpen to a triplet.

The $n \rightarrow \pi^*$ "A" band in the ultra violet spectra of both diones occurs at 448-449 nm which is consistent with the positions observed for other α-dione systems (*vide supra*).

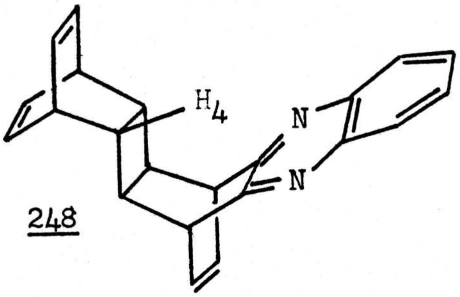
Correct mass measurements were obtained for the molecular ions of both diones. The decomposition patterns observed can readily be interpreted on the basis of those observed for the more substituted cases. The fragmentation patterns of the two diones are superimposable. The following mechanism is suggested: the loss of two molecules of carbon monoxide gives the ion corresponding to the $(CH)_{14}$ hydrocarbon 78. Further decomposition to C_6H_6 and C_8H_8 fragments in a Retro Diels-Alder process occurs as shown below.

Scheme 81.

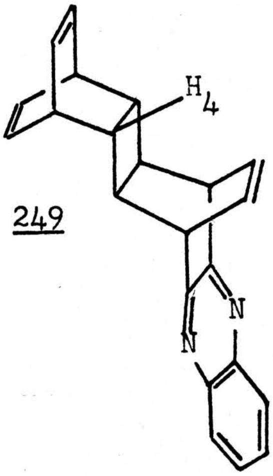


The other major fragment of the mass spectra of the diones is at m/e 91, ascribed to the tropylium ion, which may be formed from the molecular ion or 78 directly as the tropylium ion is not a known decomposition product of cyclooctatetraene (1)[199].

The quinoxaline derivative of each dione was prepared and the chemical shifts of H_4 compared to establish the relative stereochemistry of the α diones 246 and 247.



248



249

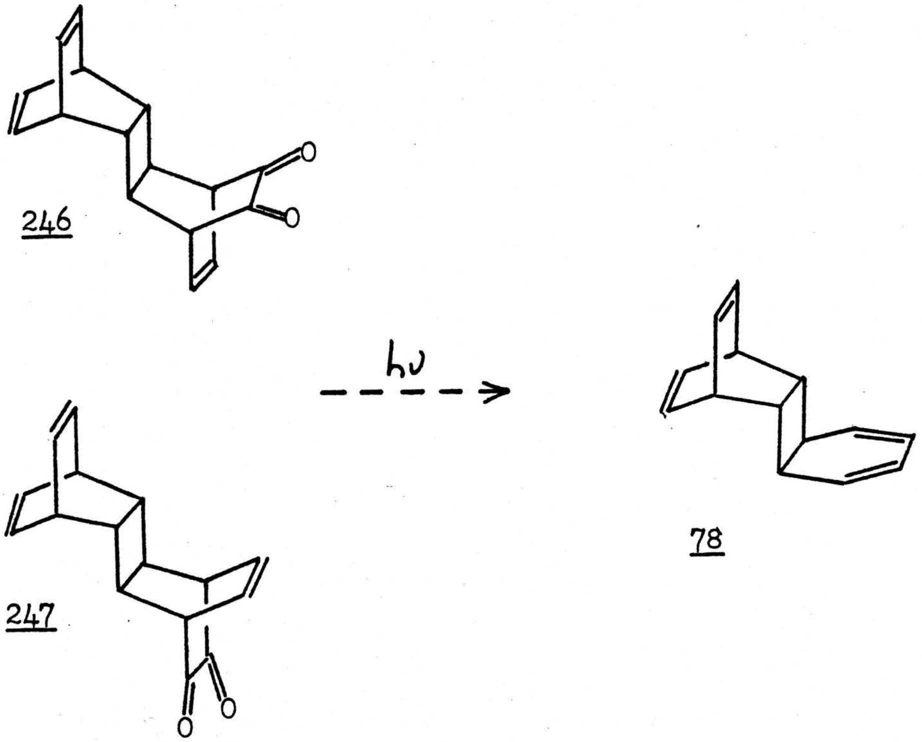
The quinoxaline condensation products were prepared by heating a solution of the dione with a molar equivalent of o-phenylenediamine in ethanol. The quinoxalines were isolated from the reaction mixtures by thin layer chromatography.

The observed chemical shift difference (0.6 ppm) of H_4 in the quinoxaline derivative 248 as opposed to H_4 of the dione 246 established that this isomer had the exo configuration shown. The chemical shift of H_4 of 249 and 247 differed only by .04 ppm, indicating that the quinoxaline ring was on the oposite face of the molecule.

On the basis of this evidence the relative configurations of the diones was established.

The final reaction in the sequence to prepare the $(CH)_{14}$ hydrocarbon 78 was the photochemical bisdecarbonylation of the diones 246 and 247.

Scheme 82.



The conditions initially used were the same as employed for the more substituted derivatives (*vide supra*). However, in the present case, irradiation of the unsubstituted diones 246 and 247 produced intractable mixtures of products. Successful preparation of the (CH)$_{14}$ hydrocarbon was effected by irradiation of benzene solutions of the diones through a filter of BiCl$_3$ in 10% HCl[200] which blocks light of less than 365 nm.

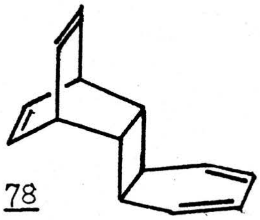
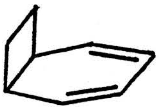
The yellow solution of the endo dione 247 was irradiated through the BiCl$_3$ filter for three hours. The reaction was monitored by tlc. After one hour of irradiation one nonpolar product was apparent (R$_f$ *ca.* .5).

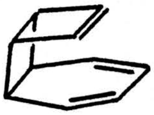
After two hours a second spot appeared (R_f *ca.* .6). After three hours the solvent was removed from the crude product. Chromatography on thick layer plates yielded three bands, two of which were visible with ultra violet light and one that was only detected on charring.

The middle band, visible with ultraviolet light, corresponded on tlc to the first observed photoproduct, yielded 6.3 mg (17%) of a white crystalline solid mp 50.5-51.0° (sealed capillary). This product was assigned the structure <u>78</u>, the $(CH)_{14}$ hydrocarbon desired, on the basis of its spectral characteristics, and a correct high resolution mass measurement for the molecular ion in the mass spectrum.

The ultraviolet spectrum has a broad maximum at 274 nm with an extinction coefficient of 2400. This is consistent with data observed for other hydrocarbons having a cyclohexadiene ring fused to a four membered ring, as shown in Table 8 below.

Table 8.

	λ max. nm	ϵ	Solvent	Reference
 <u>78</u>	274	2400	Cyclohexane	This Work
 <u>250</u>	274	3340	Cyclohexane	201

	λmax. nm.	ε	Solvent	Reference
 19	278	1750	—	29
 251	273 277	3000 3100	—	202

The infrared and pmr spectra are presented in the spectra section. The vinyl protons of the bicyclo[2.2.2]octadiene system appear as doublets of doublets. The cyclohexadiene protons are seen as a broad singlet at δ 5.65. Vedejs reported that the vinyl protons of 19 also occurred as a broad singlet at δ 5.52. The bridgehead multiplet H_3 has the same chemical shift as the bridgehead proton in the precursor 247. The chemical shifts of the cyclobutane protons are, in this case, coincident.

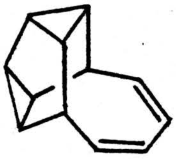
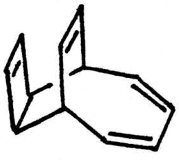
The Retro Diels-Alder fragmentation in the mass spectrometer for all the more substituted derivatives is observed for the $(CH)_{14}$ hydrocarbon 78. With the probe at low temperature (-15° C) the molecular ion appears as a major peak (17% of the base peak). The base peak occurs at m/e 104 and may correspond to the Retro Diels-Alder loss of benzene from the molecular ion. The tropylium ion m/e 91 (47% of the base peak) is not a known fragment of cyclooctatetraene, and may be formed by an alternate decomposition pathway from the molecular ion. The other major fragment is at m/e 78 corresponding to the loss of acetylene from cyclootatetraene.

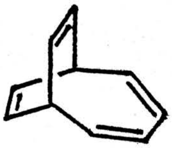
Mass measurement of the molecular ion of the least polar photoproduct, the second u.v. visible spot that appeared during the photolysis reaction, suggested that this product, too, could be a $(CH)_{14}$ hydrocarbon. In fact, although the sample contained obvious impurities, the ratio of the molecular ion and the peaks at m/e 104, 91, and 78 in the mass spectra were very similar to those of the major photoproduct 78.

Traces of impurities in the nmr solvent and in the sample, and the small amount of material available (less than 5 mg), prevented the determination of the ratio of vinyl protons to those on saturated carbon atoms. Two different vinyl multiplets were observed in a ratio of *ca.* 4:1 (see Experimental).

The ultraviolet spectrum of the compound, obtained in cyclohexane, exhibited maxima at 297 nm (ε 2700), 285 nm (ε 5000), 274 nm (ε 5000), 265 nm (ε 4200), 259 nm (sh, ε 3000). Few polycyclic $(CH)_n$ hydrocarbons have maxima at such high wavelength. Those that do, shown below, all contain eight membered rings with two double bonds in conjugation.

Table 9.

	λmax. nm	ϵ	Solvent	Reference
 252 $(CH)_{12}$	285 295 (sh)	2540 2250	Ethanol	203
 253 $(CH)_{12}$	280 268.5 258.5	2700 5000 4600	Hexane	165

	λmax. nm	ε	Solvent	Reference
 13 $(CH)_{10}$	280 268 258	2900 4200 4200	Ethanol	22

Perhaps this same chromophore is present in the minor photoproduct. Further speculation about the structure of this product will not be possible until more material is available for study.

The minor photoproduct that was not uv visible was also contaminated with hydrocarbon impurities. The sample (less than 5 mg) appeared to be a mixture of products; the nmr did show a distinctive doublet of doublet vinyl pattern (see Experimental). No structures could be postulated with the information available.

The photolysis reaction was carried out on the exo diene 246 using exactly the same conditions as for the endo dione 247. Two bands were isolated from the preparative thin layer plate. These corresponded to the minor photoproducts obtained in the previous reaction. None of the cyclohexadiene 78 was isolated. It is possible that the $(CH)_{14}$ hydrocarbon 78 was formed in the reaction and reacted further to give the two products isolated. Again neither was isolated in pure form, but high resolution mass measurements, carried out on the apparent molecular ions of both minor photoproducts, were correct for $C_{14}H_{14}$. It is interesting to note that the decomposition path of the non uv visible material is very different from that of the other two compounds. In this case, the peak at m/e 91 ascribed to the tropylium ion is the base peak and the C_8H_8 peak is a relatively minor fragmentation product. No structure for this product could be elucidated from the data available.

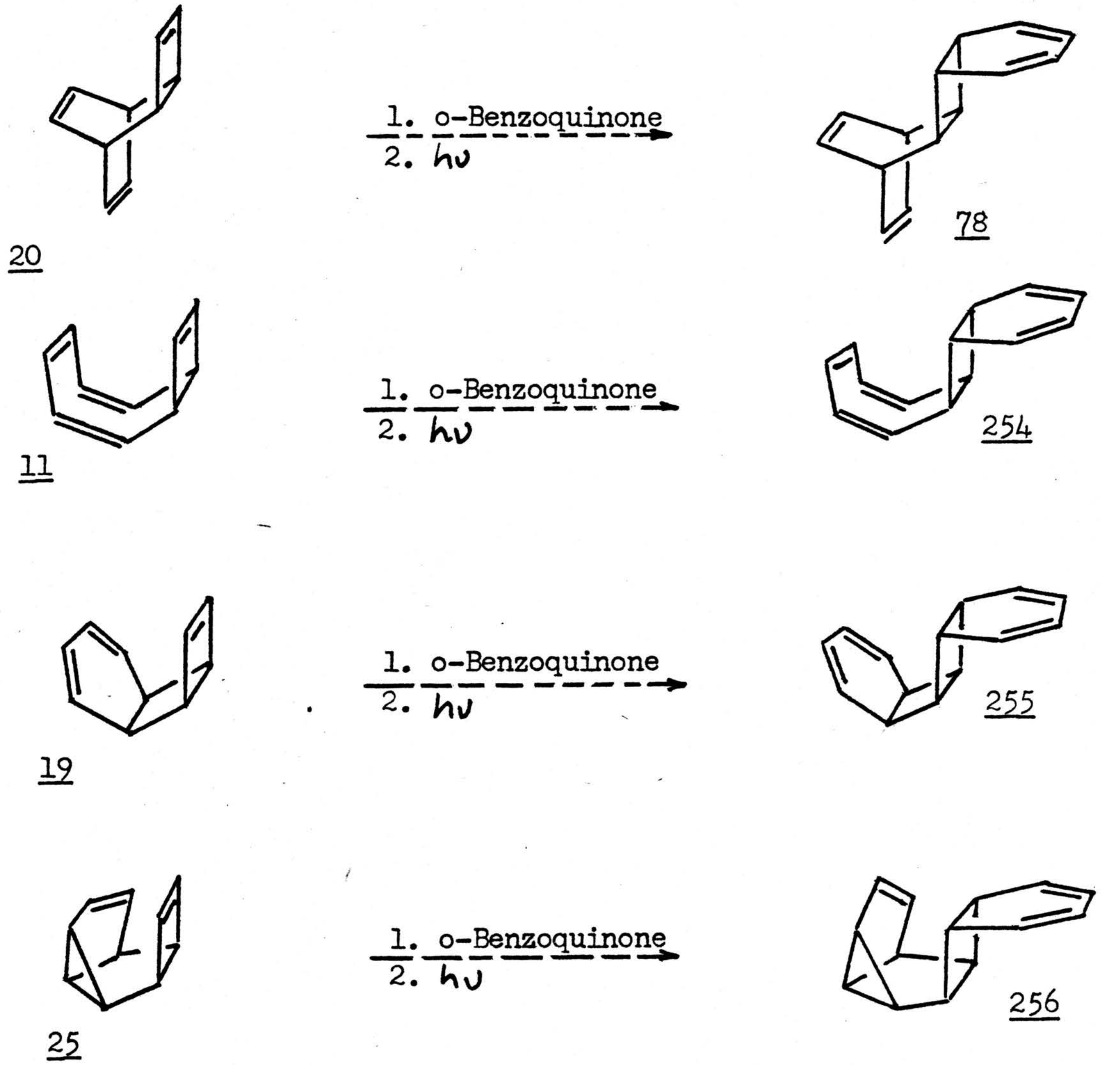
The photolysis reaction may have produced three $(CH)_{14}$ hydrocarbons. The structure of one of these could be rigourously proven. The other two hydrocarbons, obtained in small amounts and in impure form, could not be assigned structures with the limited data available.

CONCLUSIONS

The primary objective of this work was realized: a $(CH)_{14}$ hydrocarbon that would provide an entry into the $(CH)_{14}$ energy surface was synthesized. The polymethine hydrocarbon appeared sufficiently stable to be easily handled and tentative experimental results suggest that the hydrocarbon will be photochemically labile and will rearrange to other $(CH)_{14}$ isomers. The brevity of the synthetic scheme should render the $(CH)_{14}$ hydrocarbon 78 readily accessible so that thermal and photochemical studies could be undertaken.

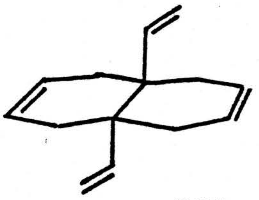
The reaction of o-benzoquinone with activated olefins (activated either by high electron density in the double bond, or by the relief of strain in proceeding from sp^2 to sp^3 carbon atoms) may find general utility in the synthesis of unsubstituted cyclohexadiene rings. In particular, this masked $(CH)_4$ unit may allow ready access to other $(CH)_{14}$ hydrocarbons from $(CH)_{10}$ precursors. In this work the reaction between o-benzoquinone and the cyclobutene double bond of Nenitzescu's hydrocarbon afforded, after photochemical removal of the thermally stable α-dione moiety, the $(CH)_{14}$ 78. Perhaps, then, other $(CH)_{14}$ hydrocarbons may be prepared from other $(CH)_{10}$ precursors. Three immediately analogous starting materials which contain cyclobutane rings, are shown on the next page.

Scheme 83.

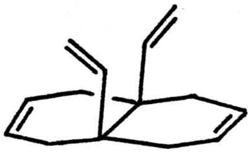


Other synthetically useful findings presented in this Thesis are the proposed general syntheses of substituted cyclooctatetraenes and barrelenes which could be conveniently realized by photochemical or thermal lysis of substituted derivatives of the $(CH)_{14}$ framework prepared in this work.

Finally, the divinyl hexalins 124 and 125 provided an interesting insight into the mechanism of Retro Diels-Alder fragmentations in the mass spectrometer.



125



124

EXPERIMENTAL

Melting points were determined on either a Kofler hot stage apparatus, or, for sealed capillary samples, on a "Mel-Temp" melting point apparatus, and are uncorrected.

Infrared spectra were recorded with a Unicam SP 1000 or a Perkin Elmer 237-B spectrophotometer. Band positions are reported in reciprocal centimeters (cm^{-1}); band intensities are denoted by s (strong), m (medium), w (weak) and br (broad).

Ultraviolet spectra were recorded with a Unicam SP 800A spectrophotometer using distilled or reagent grade solvents. Band positions are reported in nanometers (nm), together with their molar extinction coefficients (ε).

Proton magnetic resonance spectra were recorded on a Varian T-60 or CFT-20 spectrometer, and were run in deuterochloroform solutions with tetramethylsilane (TMS) as the internal standard, unless otherwise noted. Chemical shifts are reported on the delta scale (δ) in parts per million downfield from tetramethylsilane and are followed in parentheses by the signal multiplicity, coupling constant, relative intensity, and proton assignment. Signal multiplicities are denoted by the symbol s (singlet), d (doublet), t (triplet), and m (multiplet); values of the coupling constant J and N, the sum of coupling constants, $J_{AX} + J_{AX'}$, are given in Hertz (Hz).

Carbon magnetic spectra were recorded on a CFT-20 spectrometer in deuterochloroform solutions with tetramethylsilane as internal standard, and are reported in parts per million downfield from TMS, unless otherwise reported.

The mass spectra for Part I of this work were obtained on a CEC/Dupont 21-104 spectrometer, except for the spectra of the divinyl hexalins 124 and 125. The mass spectra of these compounds and all subsequent materials were obtained on a Dupont 491 or Dupont/CEC 21/110B spectrometer. High resolution measurements were performed on the Dupont/CEC 21-110B.

Gas chromatography was performed on a Varian Aerograph instrument equipped with a flame ionization detector. Helium was employed as the carrier gas, and two columns commonly used were a 6' 1/8" S.S. 3% OV-210 on 80-100 Chromasorb W, and a 5' X 1/8" S.S. 5% SE-30 on 60-80 AW DMCS Chromasorb W. Retention times of peaks are reported in minutes from the leading edge of the solvent peak.

Column chromatography was performed over Baker "Analyzed" reagent 60-200 mesh silica gel. Analytical 0.25 mm silica gel plates were prepared on glass from "Baker TLC" reagent silica gel 7GF or 7G. Silica gel (2.0 mm) precoated plates obtained from E.M. Reagents, 2 mm or 0.5 mm preparative plates prepared on glass from "Baker TLC" reagent silica 7G or 7GF were used for preparative thin layer chromatography.

Separations were visualized by ultraviolet light where applicable, or by spraying with 2% ceric sulfate in 2 N sulfuric acid, followed by heating of the plate to 150°. Silver impregnated thin layer plates were prepared from both analytical and preparative plates described above by preelution of the unspotted plates in the dark with a solution of 5 g of silver nitrate in 5 ml of water, diluted with 95 ml of acetonitrile. The plates were allowed to dry in the dark in the atmosphere, and were not further activated. All solvents used for column and thin layer chromatography were distilled before use.

Mass spectra are reported in mass to charge units (m/e) with the relative intensities as percentages of the most intense peak (base peak) in parentheses.

Unless otherwise stated, solvents were removed from solutions by evaporation at reduced pressure with a Büchi rotary evaporator.

Microanalyses were performed by Microanalyses Laboratories Limited, Toronto.

Butan-1,4-di(triphenylphosphonium) dibromide

The bis phosphonium salt was prepared by the method of Horner *et al*[94], mp 298-300°, yield 100%. Lit. mp 296-298°, yield 100%.

1,4,5,8-tetrahydronaphthalene (92)

Isotetralin (92) was prepared from naphthalene using the method of Grob and Schiess:[95] mp 53-55°, yield 80%. Lit. mp 55-57°, yield 82%.

9,10-epoxy-1,4,5,8,9,10-hexahydronaphthalene (93)

The epoxide was prepared by the method of Shani and Sondheimer.[97] The crude material, obtained in about 75% yield, was used in the next step without purification.

Trans-9,10-dihydroxy-1,4,5,8,9,10-hexahydronaphthalene (94)

The diol 94 was prepared according to the method of Grob and Schiess[95]; yield 54% from isotetralin (92), mp 82-83°. Lit. yield from the epoxide (93) 85%, mp 80-83°.

1,1,6,6-tetramethoxy-cyclodeca-3,8-dione (95)

The ketal was prepared by the method of Grob and Schiess[95]; yield 65% mp 186-190°. Lit. yield 75%, mp 197-200°.

Cis,cis-cyclodeca-3,8-diene-1,6-dione (88)

The dione 88 was prepared using a procedure of Grohmann and Sondheimer[96]. 4.0 g of ketal 95 was suspended in 100 ml reagent grade acetone. A solution of 0.8 g p-toluenesulphonic acid in 10 ml water was added followed by 0.4 ml $BF_3 \cdot Et_2O$. The mixture was allowed to stir for 2.5 hr. The acetone was removed at reduced pressure, and 100 ml water added. The resultant crystals were separated and washed with water until neutral. The solid was recrystallized from isopropanol: mp 179-181°, yield 85%. Sondheimer[204] reports mp 176-178° yield 100%.

The Double Wittig Reaction: Attempt to Prepare meso- and d,l-Bicyclo [4.4.4]tetradeca-1,5,8,12-tetraene (89) and (90)

To a stirred suspension of the bis phosphonium salt of 1,4-dibromobutane (452 mg; 0.61 mmol) in THF (25 ml; freshly distilled from $LiAlH_4$) at 0° under N_2 was added by syringe 0.6 ml n-BuLi in hexane (1.25 mmol). A dark orange colour appeared immediately. The bis phosphonium salt went into solution. The solution was stirred at 0° for 45 min to ensure complete formation of the bis ylid. The orange ylid solution was then added to a stirred solution of dione 88 (100 mg, 0.61 mmol) in 25 ml THF at -78° under N_2. At the beginning of the addition the orange colour disappeared, but recurred in the later stages of the addition. The orange solution was stirred for three hours at -78° and then allowed to warm to room temperature overnight. The brown solution was then poured into water. The aqueous mixture was extracted three times with ether. The combined ether extracts were washed with saturated sodium chloride solution, dried over anhydrous $MgSO_4$, and filtered. Evaporation of the solvent yielded 196 mg of purple oil. The oil was triturated with hexane to give 45 mg of hexane soluble material.

Preparative tlc (elution with 20% ether, 80% benzene) yielded 10.4 mg of a colourless oil which had a strong carbonyl absorption at 1720 cm^{-1}. No hydrocarbon products could be isolated.

1,6-Cyclodecadione (96)

The dione 88 (200 mg, 1.2 mmol) was stirred with 28 mg 10% Pd on C in 16 ml ethyl acetate under an atmosphere of hydrogen. 66 ml of H_2 was consumed (theoretical 60 ml). The suspension was filtered and the solution stripped of solvent to yield 219 mg (100%) of crystalline material: ir ($CHCl_3$) 2925 (s), 1680 (s) cm^{-1}; nmr ($CDCl_3$) δ1.9 (m, 4H), 2.4 (m, 4H). A sublimed sample melted at 93-97°, lit.[99] mp *ca.* 100.

Double Wittig Reaction: Attempt to prepare Bicyclo[4.4.4]tetradeca-1,5-diene

To a stirred suspension of the bisphosphonium salt of 1,4-dibromobutane (450 mg, 0.60 mmol) in THF (25 ml distilled from $LiAlH_4$) at 0° under N_2 was added by syringe 0.6 ml (1.25 mmol) of n-BuLi in hexane. The dione 96 (100 mg, 0.6 mmol) was added in 5 ml THF to the dark orange bis ylid. The yellow mixture was allowed to stir at 0° for 0.5 hr, then allowed to warm to room temperature and finally refluxed for one hr. Water was added and the organic layer separated. The aqueous layer was extracted with ether. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and taken down to yield an oil which was passed down a silica gel column using benzene as eluent. 60 mg of oil was obtained: ir (liq. film) 2930 (s), 1625 (s), 1635 (s) cm^{-1}, suggesting the structure 97. Lit.[99] mp 37°.

Attempted Coupling of 1,4-Dilithiobutane with Dione 88

A solution of the dialkyl lithium reagent 1,4-dilithiobutane was prepared by the method of West and Rochow[100] by the reaction of 1,4-dibromobutane with lithium in ether. The molarity of the dialkyl lithium solution was determined by titration of the alkyl lithium with 1 M sec-BuOH in xylene with 1,10-phenanthroline as the indicator.[205] A solution of the dilithiobutane reagent (7.2 ml, 1.0 mmol) was added by syringe to a stirred solution of dione 88 (165 mg, 1.0 mmol) in THF (125 ml, freshly distilled from $LiAlH_4$) at -78° for 0.5 h, then allowed to warm to room temperature. The colourless solution turned yellow, then orange on warming. When the solution had reached room temperature, water was added and the THF layer was separated. The aqueous layer was extracted three times with ether. The combined organic phases were washed once with sodium thiosulfate solution, once with saturated brine, and dried over anhydrous $MgSO_4$. On evaporation of the solvent 316 mg of a brown oil was obtained. This was chromatographed on preparative thin layer plates eluting with ether/benzene 1:4. All five of the bands obtained contained carbonyl absorption and were not further investigated.

Triethyl phosphonoacetate

Triethyl phosphonoacetate was prepared by the method of Wolisky and Erickson[206] in 91% yield, bp 92-95° (0.55 mm), $n_D^{28°}$ 1.4263. Lit. bp 109-109.5° (0.80 mm), $n_D^{20°}$ 1.4316, yield 88%.

trans and cis-Diethyl(E)-2,2'-[(Z,Z)-cyclodeca-1,6-diene-4,9-diylidene]-diacetate 102 and 103

The diesters were prepared by a variation of the Wadsworth-Emmons modification[102,103] of the Wittig reaction.

Sodium hydride dispersion (2.58 g, of 57% suspension in mineral oil; 61.5 mmol) was placed in a 250-ml three necked round bottom flask under N_2. The hydride was washed several times with dry benzene to remove the mineral oil. Anhydrous THF (20 ml freshly distilled from $LiAlH_4$) was added and the suspension cooled to 0°. A solution of triethyl phosphonoacetate (14.2 g, 63.2 mmol) in 50 ml THF was added slowly to avoid excessive frothing. The light brown solution was allowed to warm to room temperature and stirred for 0.5 hr. The dione 88 (2.00 g, 12 mmol) in 50 ml THF was added dropwise to the phosphonate salt solution. The reaction was allowed to stir for an additional hour then worked up by adding water, separating the organic layer, and washing the aqueous layer four times with ether. The combined organic phases were washed with saturated sodium chloride solution, dried over $MgSO_4$, and filtered. The solvent was removed to yield 5.69 g of a mobile brown oil.

Analytical tlc (benzene) indicated that approximately equal amounts of the diesters 102 and 103 were present in the reaction mixture.

The oil was chromatographed on a silica gel column (189 g, 2.8 X 87.5 cm) made up and eluted with a 1:1 mixture of low boiling petroleum ether and benzene. Twenty ml fractions were collected with the aid of a fraction collector. A total of *ca.* 7 l of solvent mixture was used, followed by 500 ml of benzene. The trans diester was eluted from the column first. The appropriate fractions were combined to give 612 mg of material rich in the trans diester 102, 1.58 g of a mixture of 102 and 103 and 1.03 g of material rich in 103. The total weight of diesters eluted was 3.22 g, corresponding to a yield for the reaction of 87%.

Recrystallization of the trans diester 102 from methanol, gave colourless square plates mp 105-106°.

pmr : see discussion

ir : ($CHCl_3$) 1720 (s), 1652 (ms) cm^{-1}.

ms : m/e 304 (M^+, 11%), 259 ($M^+-OC_2H_5$, 60%), 258 ($M^+-C_2H_5OH$, 100%).

cmr : Varian XL-100, ^{13}C, 25.2 MHz. The proton decoupled spectrum consisted of nine lines: 166.27, 158.98, 129.36, 128.04, 118.03, 59.75, 36.69, 28.26, and 14.34 ppm.

Repeated recrystallization from methanol gave an analytical sample mp 105.5-106°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C 71.02 H 7.95
found : C 70.77 H 8.25.

The cis diester 103 was crystallized from methanol to give colourless crystals mp 91-92°.

pmr : see discussion
ir : ($CHCl_3$) 1720 (s), 1652 (ms) cm^{-1}.
ms : m/e 304 (M^+, 9%), 259 ($M^+-OC_2H_5$, 60%), 258 ($M^+-C_2H_5OH$, 100%).
cmr : Varian XL-100 ^{13}C, 25.2 MHz. The proton decoupled spectrum consisted of nine lines: 166.16, 158.83, 128.97, 128.48, 118.12, 59.73, 36.70, 28.26, 14.35 ppm.

Repeated crystallization from methanol gave an analytical sample mp 90.0-90.5°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C 71.02 H 7.95
found C 71.21 H 8.03.

Attempted Acyloin Condensation of diesters 102 and 103

Sodium (30 mg, 1.32 mmol) in 8 ml toluene under N_2 was refluxed to give a fine sand. The mixture was cooled to room temperature and a solution of 100 mg of mixed diesters 102 and 103 (ca. 1:1) (0.3 mmol) and 163 mg (0.191 ml, 1.5 mmol) trimethylchlorosilane in 5 ml toluene was added by syringe to the reaction mixture. The reaction was refluxed for 24 hr, then cooled and filtered. The toluene was removed to give 86 mg of recovered diesters.

Trans-[4,9-di(2-hydroxyethylidine)](Z,Z)cyclodeca-1,6-diene 111

To a stirred solution of trans diester 102 (550 mg, 1.81 mmol) in THF (30 ml, freshly distilled from $LiAlH_4$) under nitrogen, was added a solution of 70% sodium bis(2-methoxyethoxy)aluminum hydride in benzene diluted with 30 ml of anhydrous THF. After 2.5 h, a further 1.0 ml of 70% sodium bis(2-methoxyethoxy)aluminum hydride in benzene (total dihydride 14 mmol) diluted with 10 ml THF. Stirring was continued for 45 minutes. A white suspended precipitate formed during the course of the reaction.

The reaction mixture was cooled in an ice bath and water was added cautiously with stirring. The organic phase was separated and the aqueous phase was washed four times with chloroform. The combined organic phases were washed three times with brine and dried over anhydrous $MgSO_4$. Removal of the solvent gave 398 mg (100%) of a white crystalline solid. The trans diol 111 could be recrystallized with difficulty from methanol mp 150-151°, however, for further reactions the material was used without further purification.

ir : ($CHCl_3$) 3640 (m), 3480 (br s), 1670 (s) cm^{-1}.

pmr : δ ca. 1.5 (br s, 2H, OH, concentration dependent), 2.7-3.0 (m, 8H, ring methylene protons), 4.25 (d, J = 7 Hz, 4H, $C\underline{H}_2OH$), 5.1-5.9 (m, 6H, vinyl protons).

ms : m/e 220 (M^+, 1%), 202 (M^+-H_2O, 12%), 184 ($M^+-2\,H_2O$, 14%).

Cis-[4,9-di(2-Hydroxyethylidene)](Z,Z)-cyclodeca-1,6-diene 112

To a stirred solution of the cis diester 103 (3.00 g, 9.87 mmol) in THF (100 ml, freshly distilled from $LiAlH_4$) under nitrogen was added a solution of 70% sodium bis(2-methoxyethoxy)aluminum hydride in benzene

(15 ml, 54 mmol dihydride) diluted with 150 ml anhydrous THF. After 2.5 h 20 ml water was added cautiously with stirring and the organic phase was decanted. White solid in the aqueous layer was dissolved with more water, and the aqueous was extracted three times with ether. The combined organic phases were washed with saturated brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the cis diol <u>112</u> as a colourless oil 2.13 g, 98% yield.

ir : (film) 3350 (s), 1668 (m) cm^{-1}.

pmr : δ ca. 1.5 (s, 2H, OH, concentration dependent), 2.7-3.0 (m, 8H, ring methylene protons), 4.23 (d, J = 7 Hz, 4H, $C\underline{H}_2OH$), 5.2-5.5 (m, 4H, ring vinyl protons), and 5.62 (br t, J = 7 Hz, 2H exocyclic vinyl protons.

ms : m/e 220 (M^+ 1%), 202 (M^+-H_2O, 6%), and 184 (M^+-2 H_2O, 11%).

The oil crystallized slowly on standing, but could not be crystalized from any solvent tried. The tlc in benzene/ether 7:3 indicated the presence of small amounts of polar impurities. From the pmr spectrum the material was considered pure enough for further use.

<u>Model $TiCl_3$ coupling reaction: Preparation of Bicinnamyl 110</u>

A stirred suspension of $TiCl_3$ (0.727 g, 4.71 mmol) in 30 ml dimethoxyethane (distilled from CaH_2) was cooled to -78° under argon. n-BuLi in hexane (7.44 ml, 14.1 mmol) was added slowly by syringe. A solution of cinnamyl alcohol (<u>109</u>) (1.36 g, 9.42 mmol) in 10 ml DME was added by syringe. The purple suspension was stirred at -78° for about 5 min, then allowed to warm to room temperature. The black solution was heated to reflux and maintained at that temperature for 15 min. The solution was cooled to room temperature and water was added. The black colour disappeared and a light yellow colour developed. The mixture was extracted five times with low boiling distilled petroleum ether. The petroleum ether extracts were washed once with saturated sodium chloride solution, dried over $MgSO_4$, and filtered. The solvent was removed at reduced pressure to yield 1.19 g of yellow oil (theoretical 1.10 g). A silica gel column was run of the mixture eluting with 50% petroleum ether, 50% benzene. Yellow crystals (420 mg) were obtained from nine fractions, representing a 38% yield of the hydrocarbon <u>110</u>.

ir : (CCl_4) 3090 (m), 3070 (m), 3020 (s), 2940 (s) 2850 (m) cm^{-1}.

pmr : δ 2.40 (m, $w_{\frac{1}{2}}$ 6 Hz, 4H, CH_2),

6.35 (m, $w_{\frac{1}{2}}$ 10 Hz, 4H, vinyl protons)

and 7.25 (m, $w_{\frac{1}{2}}$ 5 Hz, 10 H, aromatic).

<u>Attempted $TiCl_3$ coupling reaction of trans diol 111</u>:

$TiCl_3$ (170 mg, 1.1 mmol) was suspended in 25 ml DME (distilled from CaH_2) under argon and cooled to -78°. n-BuLi (1.75 ml, 3.3 mmol, in hexane) was added by syringe to the purple mixture. After several minutes trans diol <u>111</u> (242 mg, 1.1 mmol) in 25 ml DME was added over 5-10 minutes. White flakes appeared. The mixture was stirred at -78° for several hours then allowed to warm to room temperature and finally refluxed for 15 min. The mixture, containing blue, black, and white chunks was cooled, and water added. The reaction mixture was extracted four times with petroleum ether. The petroleum ether extracts were washed with saturated sodium chloride solution, dried over $MgSO_4$, and filtered. The solvent was removed at reduced pressure yielding 205 mg oil. The aqueous mixture was also extracted four times with $CHCl_3$. The combined

$CHCl_3$ extracts were washed with saturated sodium chloride solution, dried over anhydrous $MgSO_4$, and filtered. Material weighing 47.8 mg was obtained on evaporation of the solvent.

The material form the petroleum ether extracts was stirred with CCl_4 for about 10 min. The soluble portion, after removal of the solvent, weighed 79 mg. Analytical tlc (30% ether, 70% benzene) indicated that the $CHCl_3$ and CCl_4 insoluble materials were pure trans diol 111.

The remaining CCl_4 soluble material was chromatographed on a silica gel column packed in petroleum ether, and eluted with petroleum ether, with petroleum ether with increasingly larger proportions of benzene, then finally with ether. Fractions 1-10 appeared to contain octane. The other fractions all had carbonyl stretching absorption in the ir and were not further studied.

In all, 67% of the starting trans diol 111 was recovered. It was thought that, at -78° the diol never went into solution, and consequently, never reacted. The reaction was repeated by preforming the dialkoxide before cooling the reaction to -78°, but still 85% of the starting diol 111 was recovered.

Collins Oxidation of trans diol 111: Preparation of trans-2,2'[(Z,Z)-cyclodeca-1,6-diene-4,9-diylidene]-diacetaldehyde 113

To a stirred solution of pyridine (3.9 g, 49.6 mmol, distilled from BaO) in *ca.* 30 ml methylene chloride (distilled from P_2O_5) under N_2 at 0° was added CrO_3 (2.48 g, 24.8 mmol, previously stored over P_2O_5 overnight). After stirring the purple Collins reagent for 15 min, a solution of the trans diol 111 (0.400 g, 1.86 mmol) in *ca.* 50 ml methylene chloride was added dropwise. The reaction was allowed to stir at room temperature overnight. The methylene chloride was decanted and the residue was washed with additional CH_2Cl_2. The combined methylene chloride extracts were washed three times wtth 5% NaOH solution, once with 5% aqueous HCl solution, once with saturated sodium bicarbonate solution, twice with $CuSO_4$ solution, and once with saturated sodium chloride solution. The methylene chloride solution was dried over anhydrous $MgSO_4$, filtered and the solvent removed at reduced pressure to yield 192 mg trans dialdehyde 113 as an oil (*ca.* 50% yield).

ir : ($CHCl_3$) 2880 (w, br), 2790 (w, br) 1720 (w) 1680 (vs) 1635 (m) 1615 (w) cm^{-1}.

pmr : δ 10.13 (d, J = 7 Hz, 2H, CHO), 6.08 (br d, J = 7 Hz, 2H, exocyclic vinyl protons), 5.52 (br t, J = 5 Hz, 4H, endocyclic vinyl) 3.42 (br d, J = 5 Hz, 4H, CH_2) 3.02 (br d, J = 5 Hz, 4H, CH_2).

Rao oxidation of cis diol 112 Preparation of cis-2,2'[(Z,Z)-cyclodeca-1,6-diene-4,9-diylidene]-diacetaldehyde 114

$Na_2Cr_2O_7 \cdot 2H_2O$ (4.05 g, 13.5 mmol) was dissolved in DMSO (45 ml). The cis diol 112 (1.6 g, 7.44 mmol) was added to the stirring mixture. H_2SO_4 (2.9 ml, 55 mmol) was added by syringe over about 10 min. The deep orange colour deepened to red, then turned dark green. The temperature of the reaction mixture was maintained at about 30° by use of an ice salt bath. After 45 min a little isopropanol was added to destroy any unreacted oxidizing agent, then the solution was poured into water and extracted three times with $CHCl_3$. The $CHCl_3$ extracts were washed once with saturated sodium bicarbonate solution, once with water, then dried over anhydrous $MgSO_4$, and filtered. The solvent was removed at reduced pressure to yield 1.19 g of solid 114, *ca.* 75% yield.

ir : ($CHCl_3$) 2880 (w, br), 2795 (w, br) 1730 (m), 1680 (vs) 1640 (m) 1620 (w) cm^{-1}.

pmr : δ 10.13 (d, J = 8 Hz, 2H, CHO), 6.08 (br d, J = 8 Hz, 2H, exocyclic vinyl protons) 5.52 (br t, J = 5 Hz, 4H, endocyclic vinyl protons) 3.40 (br d, J = 5 Hz, 4H, CH_2), 3.05 (br d, J = 5 Hz, 4H, CH_2).

Model Coupling Reaction of Benzophenone with $TiCl_3/LiAlH_4$

To a stirred suspension of $TiCl_3$ (1.07 g, 6.94 mmol) in THF (20 ml, freshly distilled from $LiAlH_4$) cooled in an ice bath and under a nitrogen atmosphere was added all at once $LiAlH_4$ (132 mg, 3.47 mmol). The purple mixture turned dark brown and evolution of a gas was noted. The suspension was allowed to warm to room temperature and a solution of benzophenone (632 mg, 3.47 mmol) in THF (20 ml) was added dropwise. The mixture was refluxed for 4.5 h, then cooled in an ice bath. Water was added, and the yellow organic phase was separated from the black viscous aqueous layer. The organic phase was washed three times with saturated brine, dried over anhydrous $MgSO_4$, and the solvent removed to yield 510 mg of white crystalline solid which had carbonyl absorption in the ir. 295 mg of this material was chromatographed on a 2 mm preparative plate eluting with benzene. A fluorescent nonpolar band yielded ca. 80 mg of white solid whose ir was consistent with the published[207] spectrum of 1,2-diphenylethylene.

Attempted $TiCl_3/LiAlH_4$ coupling of trans dialdehyde 113

To a suspension of $TiCl_3$ (1.70 g, 11 mmol) in 125 ml THF (distilled from $LiAlH_4$) under N_2 at 0° was added $LiAlH_4$ (167 mg, 4.4 mmol). The black complex formed immediately. The THF mixture was heated to reflux and the trans dialdehyde 113 (240 mg, 1.1 mmol) in 20 ml THF was added dropwise over 20 min. Thin layer analysis performed shortly after the completion of the addition showed no starting material remaining. The reaction was refluxed for a further four hours, then allowed to stir at room temperature overnight. The reaction was worked up by adding water, and extracting three times with ether. The ether extracts were washed with water, dried over $MgSO_4$, and filtered. The solvent was removed at reduced pressure to give 200 mg of an oil. No material moved from the baseline of thin layer plates run of this product in benzene/ether, ether, or $CHCl_3$: ir 3600 cm^{-1}; nmr ($CDCl_3$) broad bands at δ 2.0 and 5.5. It was concluded that the material was polymeric.

Attempted Pinacol Coupling of the cis Dialdehyde 114

A mixture of cis dialdehyde 114 (290 mg, 1.3 mmol) and aluminum foil (33 mg, 1.2 mmol) in THF (150 ml, freshly distilled from $LiAlH_4$) was refluxed overnight according to the procedure of Schreibmann[118]. The mixture was cooled, and the solvent decanted and then removed to yield the dialdehyde 114 recovered unchanged.

cis[4,9-di(2-bromoethylidene)](Z,Z)cyclodeca-1,6-diene 116

To a stirred suspension of the cis diol 112 (500 mg, 2.27 mmol) in anhydrous ether (175 ml) under nitrogen and in the dark was added phosphorous tribromide (PBr_3, 160 μℓ, 1.7 mmol). The flask was heated to reflux for 1 h. The reaction mixture was poured into cold water. The phases were separated and the aqueous layer extracted twice with ether. The combined ether phases were washed with saturated bicarbonate solution, saturated brine solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the cis dibromide 116 as 597 mg 69% of a yellow oil that crystallized on standing. The material could be recrystallized from low boiling petroleum ether/benzene mp 129-131°.

ir : ($CHCl_3$) 1660 (s), 967 (s) cm^{-1}.

pmr : δ 2.6-3.2 (m, 8H, ring methylene protons), 4.03 (d, J = 8 Hz, 4H, CH_2Br), 5.2-5.5 (m approximating a triplet centred at 5.33, 4H, endocyclic vinyl protons), 5.72 (br t, J = 8 Hz, 2H exocyclic vinyl protons).

ms : m/e 344, 346, 348 (M^+, 1%, 2%, and 1%) 345, 347 (M^+-Br, 59% 57%).

anal : Calculated for $C_{14}H_{18}Br_2$ C 48.58 H 5.24 Br 46.17
found C 48.42 H 5.15 Br 45.97

trans-[4,9 Di(2-bromoethylidene)](Z,Z)cyclodeca-1,6-diene 117

To a stirred suspension of trans diol 111 (110 mg, .5 mmol) in anhydrous ether (35 ml) under a nitrogen atmosphere and in the dark was added PBr_3 (35 μℓ) and the mixture heated to reflux. After 2.5 h, a further 10 μℓ of PBr_3 (total PBr_3 0.47 mmol) was added and heating continued for a further .5 h. The reaction mixture was poured into cold water. The phases were separated and the acqueous phase extracted twice with ether.

The combined ether layers were washed with saturated sodium bicarbonate, with saturated brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded 170 mg (98%) of trans dibromide 117. The material was crystallized from petroleum ether benzene mp 133-136°.

ir : ($CHCl_3$) 1660 (ms), 970 (m), and 960 (m) cm^{-1}.

pmr : δ 2.6-3.2 (m, 8H ring methylene protons), 4.05 (d, J = 8 Hz, 4H, CH_2Br), 5.2-5.5 (m with a pronounced peak at 5.33, 4H, endocyclic vinyl protons), 5.72 (b t, J = 8 Hz, 2H, exocyclic vinyl protons).

ms : m/e 344, 346, 348 (M^+, 1%, 2%, 1%), 265, 267 (M^+-Br 94, 96%)

Anal	:	Calculated for $C_{14}H_{18}Br_2$	C 48.58	H 5.24	Br 46.17
		found	C 48.71	H 5.46	Br 45.98

Grignard Coupling Reaction of cis Dibromide 116: The Preparation of cis- and trans-9,10-divinyl-1,4,5,8,9,10-hexahydronaphthalene 124 and 125

To an amalgam prepared by stirring magnesium (65 mg, 2.7 mg-atom) with mercury (3 g) under nitrogen, was added a small portion of a concentrated solution of cis dibromide 116 in anhydrous ether. The reaction was initiated by the addition of a small crystal of iodine. The remaining dibromide solution (total of 920 mg, 2.66 mmol in 20 ml ether) was added slowly. The reaction was heated to reflux for 1 h, then allowed to stir at room temperature overnight. Saturated ammonium chloride solution was added, the phases were separated, and the organic phase washed with sodium thiosulfate solution, then with saturated brine and dried over anhydrous $MgSO_4$. On removal of the solvent 280 mg of a colourless oil was obtained. 200 mg was chromatographed on two 2 mm preparative plates yielding 110 mg of an oil consisting of cis divinyl hexalin 124 and trans divinyl hexalin 125 in a ratio of 3:2. The composition of the mixture was estimated by integration of the pmr signals attributed to H_x of the ABX pattern at δ 5.8 to 6.4.

Preparative tlc (1:1 ethyl acetate/benzene) of a 72 mg portion of this mixture on a 2-mm silver nitrate impregnated plate afforded 29 mg of cis divinyl hexalin <u>124</u> as an oil. On analytical tlc (silver nitrate plate eluting with benzene petroleum ether 1:1) the divinyl hexalin <u>124</u> appeared as one spot R_f .5. The ir, pmr, and mass spectra are reproduced in the Spectra section.

Final purification was effected by bulb to bulb distillation at 120° at 20 mm.

M^+ Calculated for $C_{14}H_{18}$: 186.14085
found : 186.1405

The trans divinyl hexalin <u>125</u> was also obtained from the silver nitrate preparative plate as an oil weighing 23 mg. Analytical tlc (silver nitrate impregnated plate eluted with a 1:1 mixture of petroleum ether and benzene) showed the trans divinyl hexalin as one spot R_f .3. The ir, pmr, and mass spectra are presented in the Spectra section.

Final purification of the trans divinyl hexalin was effected by bulb to bulb distillation at 120° at 20 mm. The purified material partially solidified at room temperature.

M^+ Calculated for $C_{14}H_{18}$: 186.14085
found : 186.1408

Grignard Coupling Reaction of trans Dibromide 117

To a stirred amalgam prepared from magnesium (37 mg, 1.5 mg-atom) and mercury (1 g) was added under nitrogen a concentrated solution of the trans dibromide 117 in anhydrous ether. The reaction was initiated by the addition of a small piece of magnesium that had been activated with methyl iodide. The remaining dibromide solution (total 490 mg, 1.42 mmol in 75 ml ether) was added slowly. The mixture was heated to reflux for 1 h, then allowed to stir at room temperature overnight.

The reaction was worked up as for the Grignard coupling reaction of the cis dibromide 116 to give 170 mg oil. Separation on perparative tlc gave 40 mg of a mixture of the divinyl hexalins 124 and 125 in a ratio of 4:1 as estimated by integration of the X portion of the ABX pattern at δ 5.8 to 6.4.

Model Coupling Reaction of Benzyl Chloride Mediated by $Ni(PPh_3)_3$

1,2-Diphenylethane was prepared according to the method of Kende, Liebenskind, and Braitsch.[140] Into a dry 25-ml round bottomed flask with stirring bar was placed triphenylphosphine (524 mg, 2.0 mmol), zinc powder (66 mg, 1.0 mg-atom, previously washed successively with dilute HCl, distilled water, methanol, and ether), and $Ni(PPh_3)_2Cl_2$ (653 mg, 1.0 mmol). Nitrogen was introduced into the flask by means of a syringe needle through a rubber septum. The needle was withdrawn and a syringe needle attached to the aspirator through a drying tube was used to evacuate the flask. The procedure was repeated three times. DMF (5 ml previously distilled from CaH_2, then flushed with nitrogen) was added by syringe. The colour of the solution quickly turned from blue to green. The flask was heated to 52-54°

for 1 h, at which time the reaction mixture was a red-brown slurry. The flask was cooled in a Dry Ice-acetone bath to just above the freezing point of DMF (m.p. -60°). Benzyl chloride (127 mg, 1.0 mmol) in DMF (2.0 ml) was added by syringe. The reaction was allowed to warm to room temperature overnight. The brown slurry was poured into 2% HCl (20 ml) and $CHCl_3$ (30 ml) was added. After extensive shaking the aqueous layer was light green. The organic phase was diluted with ether (50 ml), washed twice with distilled water and once with saturated sodium chloride solution, then was dried over $MgSO_4$, and filtered. The solvent was removed to yield 1.2 g of yellow partly crystalline material. The crude product was triturated with cold ether to remove a portion of the triphenylphosphine which was sparingly soluble in the cold solvent. The ether soluble material (586 mg) was separated on preparative thin layer plates by elution with low boiling petroleum ether. Two bands were visible by ultraviolet light. From the less polar band was isolated 43 mg (46%) of 1,2-diphenylethane whose infrared and n.m.r. spectra were identical with published data.[208]

Intramolecular Coupling of Dibromides 116 and 117 Mediated by $Ni(PPh_3)_3$

The slurry of $Ni(PPh_3)_3$ was prepared by the same procedure as in the preceding model coupling reaction of benzyl chloride, using $Ni(PPh_3)_2Cl_2$ (6.530 g, 10.0 mmol), zinc powder (660 mg, 10.0 mg-atom), and triphenylphosphine (5.240 g, 20.0 mmol) in DMF (50 ml). To the cold slurry (ca. -60°) was added slowly with stirring a solution of 116 and 117 (1.731 g, 5.00 mmol) in DMF (30 ml). The suspension was allowed to warm to room temperature overnight. The mixture was poured into 2% HCl (150 ml), and $CHCl_3$ (150 ml) was added. The light yellow organic phase was diluted with ether (250 ml), washed twice with distilled water, once with saturated sodium chloride solution, dried over $MgSO_4$, and the solvent was removed to yield 13.0 g of yellow oil. The oil was triturated with cold ether. The ether soluble material (7.25 g) was eluted with petroleum ether on a silica gel column (100 g). 20 ml fractions was collected. Fractions 11 through 19 yielded 93 mg (10%) of a mixture of divinyl hexalins 124 and 125. The subsequent fractions contained only triphenylphosphine.

Coupling of 116 and 117 Mediated by $Ni(CO)_4$

This reaction was carried out under nitrogen and in an efficient fume hood because of the extreme toxicity of $Ni(CO)_4$.

Into a dry 3 necked 100-ml round bottomed flask, cooled in a liquid nitrogen-toluene slush bath, (and equipped with a stirring bar, nitrogen inlet, rubber septum, and gas inlet tube, was condensed $Ni(CO)_4$ (1.1 to 1.2 ml, *ca.* .9 gm, 5.5 mmol). N-Methylpyrrolidone (35 ml, previously distilled from CaH_2 at reduced pressure and degassed before use) was added by syringe. The light yellow solution was heated to 50° and a solution of mixed dibromide 116 and 117 (500 mg, 1.45 mmol) in N-methyl pyrrolidone (3.0 ml) was added by motor-driven syringe over 20 h. The colour of the solution at the end of the addition was bright green. The reaction was cooled in an ice bath, and an equal volume of ether added. The ether and $Ni(CO)_4$ were co-distilled and the $Ni(CO)_4$ was destroyed by reaction with Br_2 in benzene. The residue was diluted with distilled water (150 ml) and extracted with pentane 5 times. The combined extracts were washed twice with distilled water, twice with saturated sodium chloride solution, and dried over $MgSO_4$. The solution was filtered and the pentane removed on the rotary evaporator giving 62 mg of a colourless oil. Nmr indicated that the mixture was composed of cis and trans divinyl hexalins <u>124</u> and <u>125</u> contaminated with a trace of N-methylpyrrolidone. By visual inspection it was estimated that the mixture was composed of over 95% <u>124</u> and <u>125</u> (24% yield). The mixture was not separated further.

Condensation Reaction of Methyl Coumalate and Dimethyl Tricyclo-[4.4.4.$0^{2,5}$]deca-3,7,9-triene-7,8-dicarboxylate

In a thick-walled nmr tube was sealed a degassed solution of methyl coumalate (165) (120 mg, 0.75 mmol), dimethyl tricyclo[4.2.2.$0^{2,5}$]-deca-3,7,9-triene-7,8-dicarboxylate (163) (185 mg, 0.75 mmol) and dimethyl phthalate (50 mg, 0.25 mmol) in $CDCl_3$ (1.0 ml). The tube was heated in a Kugelrohrofen at 155°. The sample was removed periodically and the reaction monitored by nmr. After 22 h heating was discontinued. The crude product (345 mg) was chromatographed by preparative tlc eluting with 2% ether, 98% benzene. A band with R_f 0.5 yielded 23 mg (19%) of a yellow oil whose ir was identical with the published spectrum[162] of methyl cyclooctatetraenecarboxylate.

nmr δ ($CDCl_3$) 6.0 (m, $w_{\frac{1}{2}}$ 10 Hz, 7H, vinyl H), 3.9 (s, 3H, OCH_3).
ms m/e 162 (M^+, 35%), 103 ($M-COOCH_3$, 100%).

Dimethyl Tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene-7,8-dicarboxylate

The adduct of cyclooctatetraene and dimethyl acetylenedicarboxalate, 163, was prepared according to the procedure of Avram, Nenitzescu, and Marica[157]. Integration of the nmr spectrum indicated that the product (b.p. 102-104° at 0.5 mm) was contaminated with 25% dimethyl phthalate. The mixture was used without further purification.

Tetrachloro-o-Benzoquinone

o-Chloranil was prepared in 33% yield by the oxidation of pentachlorophenol with nitric acid in CH_2Cl_2 according to the procedure of Rocklin. The product was crystallized from CCl_4 as red plates m.p. 126-129°. (Lit. m.p. 135°)

Diels-Alder Reaction Between o-Chloranil and Dimethyl Tricyclo[4.2.2.0^{2,5}] deca-3,7,9-triene-7,8-dicarboxylate 163

A solution of o-chloranil (500 mg, 2.0 mmol) and a mixture of diester (163) (450 mg, 1.8 mmol) and dimethyl phthalate (110 mg, 0.6 mmol) in $CHCl_3$ (15 ml) was allowed to stand at ambient temperature for 5 days. Tlc indicated that the reaction was not complete, so the mixture was heated at reflux overnight. The crude mixture, after evaporation of the solvent, was chromatographed on a column of silica gel (50 g made up in benzene) with the aid of a fraction collector. The products were eluted from the column with 6% ether, 94% benzene. A total of 788 mg (86%) of material was obtained and collected into three fractions: 213 mg of 181, 450 mg of a mixture of 181 and 182, and 125 mg of 182.

The exo dione 181 was recrystallized from benzene giving yellow crystals mp 185-186° (sealed capillary). The melting point was dependent on the rate of heating.

uv :($CHCl_3$) λ max 445 nm (ε 430)

ir :($CHCl_3$) 3080 (w, br), 2985 (m), 1775 (s), 1745 s(sh)i, 1730 (s), 1650 (m), 1610 (v), 1570 (w), 2085 (s) and 1070 (s) cm^{-1}.

vpc :(column at 185°) The pure compound had two peaks with retention times of 2.0 min. and 13.2 min. Dimethyl phthalate had a retention time of 2.0 min.

The pmr and mass spectra appear in the Spectra section.

M^+-OCH_3 calculated for $C_{19}H_{11}O_5Cl_4$ 458.93505

found 458.9361 ± .0014

The dione <u>182</u> was recrystallized from anhydrous benzene (see below) as yellow crystals mp 188-191° (sealed capillary).

uv :$CHCl_3$) λ max 445 nm (ε 175) (see discussion)

ir :($CHCl_3$) 3560 (w), 2985 (m), 1775 (s), 1730 (vs, br), 1650 (m), 1610 (w), 1590 (w), 1550, 1290 (s, br) and 1070 (s) cm^{-1}.

vpc :(column at 185°) The pure compound had two peaks with retention times of 2.0 min. and 14.4 min. Dimethyl phthalate had a retention time of 2.0 min.

The pmr and mass spectra are reproduced in the Spectra section.

M^+-OCH_3 calculated for $C_{19}H_{11}O_5Cl_4$ 458.93505
found 458.9366 ± .0014

The dione <u>182</u> readily formed a colourless hydrate on standing, mp *ca.* 170-175° (sealed capillary) with slow yellowing of the sample.

uv :(CH_3OH) no λ max above 220 nm end absorption 220 nm (ε 5000).

ir :($CHCl_3$) 3565 (w), 3100 (br, w), 2980 (w), 1780 (ms), 1745 (vs, sh), 1730 (vs), 1655 (m), 1615 (w), 1600 (w), 1290 (s), and 1075 (ms) cm^{-1}.

pmr :60 MHz ($CDCl_3$) δ 6.60 (m, $w_{1/2}$ 10 Hz, 2 vinyl H), 4.15 (m, $w_{1/2}$ 16 Hz, 2 bridgehead H), 3.75 (s, 6H, OCH_3), 2.33 (m, $w_{1/2}$ 12 Hz, 2H, cyclobutane), 2.10 (m, $w_{1/2}$ 15 Hz, 2H, cyclobutane).

The dione <u>182</u> could be regenerated from the hydrate by dissolving a sample in benzene and removing the water by distillation with a Dean Stark trap. The yellow dione crystallized from the anhydrous cooled solution.

Irradiation of Dione 181

A stirred solution of dione 181 (350 mg, 0.71 mmol) in benzene (150 ml, freshly distilled from CaH_2) was irradiated with a sunlamp (General Electric, 275 watt) with cooling (ice bath) under nitrogen for 2 h. The solvent was removed from the colourless solution to give 320 mg of off-white solid. Crystallization from ethanol and chromatography of the mother liquors gave 200 mg (65%) of material identical to cyclohexadiene 169 obtained from the photolysis of the mixed diones.

Irradiation of a Mixture of Diones 181 and 182

A mixture of 181 and 182 (1.38 g, 2.80 mmol) was dissolved in dry benzene (150 ml) in a 500-ml round bottomed flask. The stirred bright yellow solution was cooled in an ice bath and kept under nitrogen. Irradiation with a sunlamp (General Electric, 275 watt) was carried out for 5 h. The solvent was removed from the colourless solution to yield 1.24 g crude product. Crystallization from ethanol chloroform yielded the tetrachlorocyclohexadiene derivative 169 in 2 crops 1.060 g, (2.43 mmol, 87%) having a mp 192-193° (sealed capillary).

uv :(CH_3OH) λ max 318 (sh) (ε 1300), 304 (sh) (ε 2700), 293 (ε 3060), 282 (sh) (ε 2900), end absorption 225 (ε 5700).

ir :($CHCl_3$) 3060 (br w), 2980 (m), 1730 (br s), 1655 (m), 1625 (ms), 1608 (sh w), 1450 (m), 1290 (s), 1075 (s) cm^{-1}.

pmr :($CDCl_3$) 60 MHz: δ 6.60 (d of d, N = 8 Hz, 2 H), 4.22 (m, $w_{\frac{1}{2}}$ = 10 Hz, 2 H), 3.75 (s, 6 H), 2.55 (br s, $w_{\frac{1}{2}}$ = 4 Hz, 4 H).

cmr :($CDCl_3$) rel to TMS = 0.000 165.67, 140.61, 133.19, 131.00, 123.5, 52.29, 44.92, 42.81, 40.28 ppm.

ms :see Spectra section

M^+ calculated for $C_{18}H_{14}O_4Cl_4$ 433.96461

found 433.9651

In another run of the irradiation of the mixed diones <u>181</u> and <u>182</u> two minor products were obtained.

A *ca.* 1:1 mixture of dione <u>181</u> and <u>182</u> (1.35 g, 3.10 mmol) was dissolved in dry benzene (200 ml) and was irradiated for 5 h at 0° under nitrogen. Tlc indicated the presence of a small amount of material slightly more polar than the cyclohexadiene derivative <u>169</u>. This was isolated free of the major product from a silica gel column (100 g, made up in benzene) using benzene as the eluant. The fractions containing the minor component were combined and the solvent was removed to give 40 mg of material which was crystallized from ethanol. The colourless needles (14 mg) melted at 168-172°.

uv :(EtOH) λ max 302 (sh), end absorption

The ir, pmr, mass spectra are reproduced in the Spectra section.

The solvent was removed from the mother liquor to yield 23 mg of a yellow oil. This was chromatographed on a preparative tlc plate with 15% methyl acetate 85% carbon tetrachloride, yielding 14 mg of an oil which gave one spot on tlc (R_f .5) and was assigned the structure of the dicarbomethoxy barellene <u>229</u> on the basis of the spectral data presented on the next page.

ir :(neat film) 3090 (w), 3010 (mw), 2982 (m), 2860 (w), 1730 (vs br), 1650 (m br), 1608 (m), 1585 (w), 1440 (ms), 730 (ms) cm^{-1}.

pmr :see Spectra section

ms :m/e 220 (M^+, 27%)

Condensation of exo Dione 181 and o-Phenylenediamine

A solution of exo dione 181 (56 mg, .114 mmol) and o-phenylenediamine (13 mg, .114 mmol) in 95% ethanol (1.5 ml) was heated on a steam bath for 15 minutes. The solution was cooled, but no crystals could be obtained from the ethanol solution. The quinoxaline 212 (13 mg, .02 mmol, 20% yield) was obtained as white needles mp 195-199° (with decomposition) from methanol.

uv (CH_3OH) λ max 327 (sh) (ε 4300), 317 (ε 5300), 241 (ε 22,500) 210 (end absorption, ε 14,800)

ir ($CHCl_3$) 3050 (m br), 2985 (m), 1730 (vs br), 1650 (m), 1610 (w), 1580 (br w), 1070 (ms) cm^{-1}

pmr ($CDCl_3$) 80 MHz δ 7.89 (sym m, 4 aromatic H), 6.58 (d of d, N = 8 Hz, 2 vinyl H), 4.08 (m, $w_{1/2}$ = 12 Hz, 2 bridgehead H), 3.63 (s, 6 OCH_3), 2.52 (m, $w_{1/2}$ = 6 Hz, 2 cyclobutane H), 1.46 (m, $w_{1/2}$ = 10 Hz, 2 cyclobutane H).

vpc (column 258°) The pure compound gave two peaks with retention times 0.3 min, and 6.4 min. Dimethyl phthalate 0.3 min.

Reaction of exo Dione 181 with o-phenylenediamine

A solution of dione 181 (288 mg, 0.59 mmol) and o-phenylenediamine (65 mg, 0.6 mmol) in ethanol (25 ml) was heated on a steam bath briefly, then allowed to stand at room temperature overnight. Colourless crystals (136 mg) were obtained on filtration of the cold reaction mixture. The solid was insoluble in $CHCl_3$, and gave one spot on tlc (eluted in 25% methyl acetate - 75% carbon tetrachloride, R_f .45). The material could be recrystallized from acetonitrile as colourless thick plates which melted at 142-143°, resolidified in long needles and remelted at 202-205°.

uv ($CHCl_3$) λ max 332 (ε 1000), 295 (5200), end absorption 260 nm (10000)
(MeOH) 370 (5100), 331 (6500), 319 (6700), 242 (26,000), end absorption 215 nm (21,000).

ir ($CHCl_3$) 3300, (br, w), 1730 (br) cm^{-1}

pmr (C_5D_5N) 60 MHz δ 6.75 (unsymmetrical m, $w_{\frac{1}{2}}$ = 15 Hz, 12 H), 6.10 (br, s, 2 H), 4.39 (m, $w_{\frac{1}{2}}$ = 10 Hz, 2 H), 4.02 (m, $w_{\frac{1}{2}}$ = 8 Hz, 2 H), 3.60 (s, 6 H), 2.40 (m, $w_{\frac{1}{2}}$ = 6 Hz, 2 H).

The structure <u>216</u> was assigned to the product on the basis of the following:

A solution of the chloroform insoluble material was refluxed overnight in xylene (15 ml) using a Dean Stark trap. Tlc indicated that none of the original material remained. The crude product was eluted on a preparative tlc plate with ether carbon tetrachloride (1:3). Two bands were isolated: the more polar yielded dimethyl phthalate (18 mg, 0.1 mmol, identified by its nmr spectrum) and the less polar band gave the cyclobutene derivative <u>217</u> (34 mg, 0.95 mmol) as white solid mp 190-194° (recrystallized from ethanol mp 199.5-200° (sealed capillary).

uv (MeOH) λ max 326 (ε 5200), 316 (ε 5900), 306 (sh) (ε 5000), 239 nm (ε 31,000).

ir ($CHCl_3$) 3050 (ms br), 2995 (ms), 2980 (s), 2895 (m), 1730 (w), 1590 (ms), 1580 (ms), 1100 (s), 1050 (s), 1025 (s), 960 (s) cm^{-1}

pmr see Spectra section

ms :m/e 368, 370, 372 (M^+, 3%, 3%, 2%) 333, 335 (M^+-Cl, 100%, 93%)

M^+ calculated for $C_{16}H_8Cl_4N_2$ 367.94415

found 367.9437

Condensation of endo Dione 182 with o-Phenylenediamine, 213

The hydrated dione 182 (33 mg, .07 mmol) and o-phenylenediamine (7.3 mg, 0.07 mmol) were dissolved in 95% ethanol (1 ml) and heated on the steam bath briefly. From the cooled solution crystallized 18 mg (50%) of colourless adduct mp 208-212° (with decomposition).

uv (CH_3OH) λ max 327 (sh) (ε 3500), 316 (ε 4200), 240 (ε 23,000), end absorption 210 (ε 15,000)

ir ($CHCl_3$) 3050 (m br), 2980 (m), 1735 (vs br), 1655 (m), 1615 (w), 1600 (m), 1585 (w), 1075 (s), 1000 (ms) cm^{-1}.

pmr ($CDCl_3$) 80 MHz δ 7.97 (sym m 4 H, aromatic proton), 6.50 (d of d, N = 8 Hz, 2 H vinyl proton), 4.25 (m, $w_{\frac{1}{2}}$ = 12 Hz, 2 H bridgehead proton), 3.79 (s, 6H, OCH_3), 2.28 (m, $w_{\frac{1}{2}}$ = 4 Hz, 4 H cyclobutane).

ms m/e 368, 370, 372 (M^+-dimethyl phthalate = $M_{(1)}$ .5%, .8%, .5%), 333, 335 ($M_{(1)}$-Cl, 36%, 34%) 163 (dimethyl phthalate -OCH_3, 100%)

vpc (column 258°) The pure compound gave two peaks: 0.3 min, 7.2 minutes. Dimethyl phthalate 0.3 min.

Thermolysis of endo Quinoxaline 213. Preparation of 218

A degassed solution of the endo quinoxaline 213 (79 mg, .14 mmol), in $CDCl_3$ (.75 ml) was sealed in a thick-walled nmr tube and heated at 160° for 12 h. Proton nmr indicated that the thermolysis was complete. The crude product was separated on a preparative tlc plate eluting with 5% ether, 95% benzene. A band (R_f .75) yielded *ca.* 60 mg white semisolid, which was crystallized from ethanol (first crop 23 mg, 218 45%) mp 184.5-186°.

uv (MeOH) λ max 328 (ε 12,000), 316 (ε 15,700), 307 (sh) (ε 10,700), 241 nm (ε 56,000)

ir ($CHCl_3$) 3050 (w br), 2990 (w), 1600 (ms), 1582 (m), 1022 (s), 988 (ms), 955 (m) cm^{-1}.

pmr see Spectra section

ms m/e 368, 370, 372 (M^+, 2%, 2%, 1%) 333, 335 (M^+-Cl), 100%, 96%)

M^+ calculated for $C_{16}H_8Cl_4N_2$ 367.94415

found 367.9433

Thermolysis of Cyclohexadiene Derivative 169. Preparation of Tetrachlorocyclooctatetraene 237

A degassed solution of the cyclohexadiene derivative 169 (290 mg, .665 mmol) in $CDCl_3$ (1 ml) was sealed in a thick-walled nmr tube and heated in a Kugelrohrofen at 155°. The progress of the reaction was followed by nmr. The thermolysis appeared to be half complete after 4 h heating. After 12 h slight darkening of the sample was noted and the reaction was stopped. The crude reaction mixture was separated on a preparative tlc plate eluting with 2% ether, 98% petroleum ether. From a band with R_f .3 was isolated 103 mg (64%) of tetrachlorocyclooctatetraene 237.

uv (MeOH) λ max 229 (sh) nm (ε 7,700).

ir (neat film) 3050 (w), 2995 (w), 2880 (w), 2960 (w), 1630 (w), 1608 (s), 1382 (w), 1330 (w), 1195 (m), 1145 (ms), 1075 (ms), 1050 (w), 1040 (w), 958 (m), 900 (w), 870 (w), 860 (w), 845 (m), 795 (w), 765 (w), 725 (s), 715 (s) cm^{-1}.

pmr Given in the Spectra section

cmr Given in the Spectra section

ms m/e 240, 242, 244, 246 (M^+, 3%), 205, 207, 209, 211 (M - Cl, 65%), 170, 172, 174 (M - 2Cl, 100%).

Tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene 20

The oxidative bisdecarboxylation of the adduct of cyclooctatetraene and maleic anhydride, 43, using dicarbonyl bis(triphenylphosphine)-nickel was carried out by the procedure of Dauben *et al*[56] except that the nickel reagent was prepared *in situ* by a modification of the method of Rose and Statham[3]. Because of the toxicity of $Ni(CO)_4$ the reaction was carried out in an efficient fumehood.

In a dry 250-ml 3-necked round bottomed flask fitted with nitrogen inlet, condenser, gas inlet system connected to a pressure-equalized dropping funnel, and magnetic stirring bar was dissolved triphenylphosphine (36.8 g, 0.14 mol) in diglyme (95 ml, previously distilled from CaH_2). $Ni(CO)_4$ (9 ml, .07 mol) was added dropwise with stirring. A gas, in fine bubbles, began to be evolved immediately. After the addition was complete a light yellow precipitate formed. The mixture was stirred at room temperature overnight. The anhydride 43 (10.28 g, 0.05 mol) was then added all at once. The reaction mixture was heated and maintained at vigorous reflux for 4 h. The reaction was worked up using Dauben's procedure[56]. The ir and nmr spectra of the oil 3.36 g, 66% (bp 72-74° at 18 mm) were identical with the literature values[34].

Diels-Alder Reaction of Tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (20) and o-Benzoquinone Diones 246 and 247

o-Benzoquinone was freshly prepared by the oxidation of catechol with o-chloranil. Thus, in a dried, weighed 3-necked 100-ml round bottomed flask fitted with stirring bar and nitrogen inlet was dissolved o-chloranil (984 mg, 4.00 mmol) in anhydrous ether (30 ml). The red solution was cooled to -30° in a bath of CCl_4 - $CHCl_3$ (5:1) and dry ice, and catechol (440 mg, 4.00 mmol) was added all at once with stirring. The solution turned dark red immediately. Crystallization was induced by scratching then the reaction mixture was kept at -25° to -30° for 2 h. The liquid phase was removed by syringe and the residual ether evaporated at aspirator pressure (drying tube in the line). The dark red fine crystalline mass of o-benzoquinone (*ca.* 450 mg, 4.0 mmol) was dissolved in benzene (30 ml, distilled from CaH_2), and Nenitzescu's hydrocarbon (20) (260 mg, 2.00 mmol) in benzene (3 ml) was added by syringe. The mixture was kept at room temperature for 30 h. The resulting orange solution was decanted from a black residue, the solvent removed, and the crude mixture separated on preparative tlc plates eluting with 8% ether, 92% benzene. Two yellow bands yielded 49 mg (10%) of adducts, 30 mg from the less polar band and 19 mg from the more polar band. Unreacted Nenitzescu's hydrocarbon (20) (140 mg, R_f .9) was recovered; the combined yield of adducts based on unrecovered starting material was 22%. Each of the diones was recrystallized from benzene.

The less polar dione 246 (R_f .6) melted at 162-163.5° (sealed capillary).

uv :($CHCl_3$) λ max 448 nm (ε 200)

ir :($CHCl_3$) 3050 (br), 3000, 2980, 1775 (sh), 1750, 1615 (br), 1370, 1120 (w), 1100 (w), 1090 (w) cm^{-1}.

pmr :Data given in the Discussion.

ms :m/e 238 (M^+, 5%), 182 (M - 2 CO, 15%), 104 [M - (2 CO+C_6H_6), 100%], 91 (tropylium ion, 59%), 78 [M - (2 CO+C_8H_8), 74%].

Mass measurement: calc. for $C_{16}H_{14}O_2$ 238.09938
found 238.0993 ± .0007

The more polar dione 247 (R_f .5) melted at 165-167° (sealed capillary).

uv :($CHCl_3$) λ max 449 nm (ε 160).

ir :($CHCl_3$) 3050 (br), 2980 (br), 1760 (sh), 1750, 1615 (w), 1365, 1130 (w), 1110 (w), 1092 (w) cm^{-1}.

pmr :Data given in the Discussion.

ms :m/e 238 (M^+, 4%), 182 (M - 2 CO, 20%), 104 [M-(2 CO+C_6H_6), 100%], 91 (tropylium ion, 64%), 78 [M-(2 CO+C_8H_8), 70%].

Mass measurement: calc. for $C_{16}H_{14}O_2$ 238.09938
found 238.0986 ± .0007

Condensation of exo Dione 246 with o-Phenylenediamine, Preparation of 248

A solution of the exo dione 245 (3.4 mg, .014 mmol) and o-phenylenediamine (3 mg, .03 mmol) in 95% ethanol (1.0 ml) was heated on a steam bath for 15 min. The solvent was removed from the reaction mixture and the crude product was separated on a preparative tlc plate (5 x 20 cm, 1.0 mm in thickness) eluting with 5% ether and 95% benzene. A band that was visible with ultraviolet light gave *ca.* 1.0 mg of quinoxaline adduct 248 one spot on analytical tlc (5% ether, 95% benzene, R_f .55). The white solid was crystallized from ethanol to give colourless needles mp 181-182° (sealed capillary).

pmr : ($CDCl_3$) 80 MHz, δ 8.01-7.55 (symmetrical multiplet centred at 7.78, 4H, aromatic H), 6.53 (d of d, N = 7.3 Hz, 2H, vinyl H), 6.41 (d of d, N = 7.8 Hz, 2H, vinyl H), 6.03 (d of d, N = 7.7 Hz, 2H, vinyl H), 4.12 (m, $w_{1/2}$ = 10 Hz, 2H, bridgehead H), 3.56 (m, $w_{1/2}$ = 12 Hz, 2H, bridgehead H), 1.90 (m, $w_{1/2}$ = 8 Hz, 2H, cyclobutane H), 1.08 (m, $w_{1/2}$ 6 Hz, 2H, cyclobutane H); impurities were present at δ 1.54 and 1.25.

ms : Only a partial spectrum was obtained because the sample was consumed before the spectrum could be completed. The largest fragment observed occurred at m/e 232 ($M^+ - C_6H_6$, 5%), 78 (Retro Diels-Alder product, C_6H_6, 100%)

Condensation of endo Dione 247 with o-Phenylenediamine, Preparation of 249

A solution of endo dione 246 (5.1 mg, .02 mmol) and o-phenylenediamine (4 mg, .04 mmol) was heated on the steam bath for 10 min. The solvent was removed and the crude reaction product was separated on a preparative tlc plate (5 x 20 cm, 1.0 mm in thickness) eluting with 5% ether 95% benzene. A band visible by ultraviolet light yielded 3.9 mg (50%) of quinoxaline 249 which was crystallized from ethanol to give colourless clusters mp 177-180° (sealed capillary).

pmr : ($CDCl_3$) 80 MHz, δ 7.97-7.54 (multiplet centred at 7.74, 4H, aromatic H), 6.70 (d of d, N = 8 Hz, 2H, vinyl H), 6.33 (d of d, N = 5.9 Hz, 2H, vinyl H), 6.25 (d of d, N = 5.5 Hz, 2H, vinyl H), 4.14 (m,

$w_{\frac{1}{2}}$ = 12 Hz, 2H, bridgehead H), 3.68 (m, $w_{\frac{1}{2}}$ 12 Hz, 2H, bridgehead H), 1.84 (m, $w_{\frac{1}{2}}$ = 4 Hz, 2H, cyclobutane H), 1.57 (m, $w_{\frac{1}{2}}$ 8 Hz, 2H, cyclobutane H), impurity at δ 1.25.

ms :m/e 310 (M^+, 3%) 232 ($M^+ - C_6H_6$, 50%), 231 ($M^+ - (C_6H_6 + H)$, 100%) 78 (Retro Diels-Alder product C_6H_6, 68%).

Irradiation of Dione 246, Preparation of 78

A 10-mm pyrex tube containing a bright yellow solution of endo dione 247 (50 mg, 0.21 mmol) in benzene (10 ml, distilled from CaH_2) under nitrogen was placed inside a 25-mm pyrex tube filled with a solution of $BiCl_2$ (0.1 M in 10% HCl, cutoff 365 nm) and irradiated with a Hanovia 250 watt lamp for 3 h. The solvent was removed from the pale orange solution and the material separated on preparative tlc plates (Silica Gel 7GF, 0.5 mm) eluting with petroleum ether. A band that was visible under ultraviolet light (R_f .52) yielded 5.4 mg of a colourless oil that was one spot on analytical tlc (eluant petroleum ether, R_f .8).

uv :(Cyclohexane) assuming a molecular weight of 182: λ max 297 (ε 2700), 285 (ε 5000), 274 (ε 5200), 265 (ε 4200), 259 (sh) (ε 3000), end absorption 225 nm (ε 5200).

ir :(CCl_4) 3065 (s), 3040 (s), 2950 (s), 2900 (m), 1735 (w), 1655 (w) cm^{-1}.

pmr :The ratio of vinyl protons to those on saturated carbon atoms appeared to be 2:1. However impurities in the sample and solvent obscured the actual ratio of such protons in the photoproduct. There did appear to be two distinct vinyl multiplets at 6.0 (m, $w_{\frac{1}{2}}$ 25 Hz) and 5.5 (br t, $w_{\frac{1}{2}}$ 20 Hz) in a ratio of 4:1.

ms :Direct probe T -57° m/e 182 (M^+, 21%), 104 ($M^+ - C_6H_6$, 100%), 91 (tropylium ion, 32%), 78 ($C_6H_6^+$, 39%)

M^+ calculated for $C_{14}H_{14}$ 182.10955
found 182.1090

A second band, (R_f .45) visible under ultraviolet light yielded 6.3 mg of 78 as white crystals mp 50.5-51.0° (sealed capillary)

uv :(cyclohexane) λ max 274 (ε 2400), end absorption 225 nm (ε 3000).

ir :(CCl_4) 3050 (s), 3025 (s), 3000 (w), 2950 (s), 2925 (s), 2900 (s) (sh), 1730 (w), 1370 (br, m), 1350 (s), 1310 (m), 700 (m), 675 (s), 635 (w) cm^{-1}.

pmr :($CDCl_3$) 80 MHz 6.39 (d of d, N = 7.6 Hz, 2 H), 6.15 (d of d, N = 7.2 Hz, 2 H), 5.65 (br s, 4 H), 3.71 (m, $w_{1/2}$ = 11 Hz, 2 H), 2.07 (m, $w_{1/2}$ = 4 Hz, 4 H).

ms :see Spectra section.

M^+ calculated for $C_{14}H_4$ 182.10955
found 182.1093

A third band, (R_f .35) not visible by ultraviolet light, but observed by charring, yielded 4.0 mg of an off white semisolid which tlc indicated to be a mixture (analytical tlc R_f .42, .38). Further chromatography was attempted, but no pure products could be obtained. The pmr of the mixture contained two doublet of doublet patterns at δ 5.5 and 6.0. No ratio of vinyl to protons on saturated carbon atoms could be obtained.

Tlc showed the material at the baseline of the preparative plate (34 mg) to be a complicated mixture of products, which was not further investigated.

Irradiation of exo Dione 246

A 10-mm pyrex tube containing a yellow solution of exo dione 246 (35 mg, 0.15 mmol) in benzene (7.0 ml, distilled from CaH_2) under nitrogen was placed inside a 25-mm pyrex tube filled with a solution of $BiCl_2$ (0.1 M in 10% HCl, cutoff 365 nm) and irradiated with the Hanovia mercury lamp for 3 h. The solvent was evaporated from the solution and the crude product chromatographed on a preparative thin layer plate eluting with petroleum ether. A small amount of material was run on another preparative plate and was charred to show the positions of the bands. Two bands were thus obtained.

The less polar band (R_f *ca.* .8) yielded 2.3 mg of an oil whose spectra were similar to those obtained for the less polar photoproduct of the previous reaction.

uv :λ max (cyclohexane) qualitative 297, 285, 274, 265, 259 (sh) nm, in the same relative intensities as observed for the minor photoproduct obtained in the previous reaction.

ir :neat film 3065 (m), 3050 (ms), 2960 (s), 2900 (m), 1730 (w), 1635 (w), 1600 (w), 765 (ms), 750 (ms), 742 (s), 692 (s) cm^{-1}.

pmr :The sample appeared contaminated with hydrocarbon impurities. It was not possible to obtain a ratio of olefinic to aliphatic protons. However there appeared to be two distinct multiplets in the vinyl region - a broad multiplet $w_{\frac{1}{2}}$ *ca.* 25 Hz centred at δ 6.0, and a broad triplet $w_{\frac{1}{2}}$ *ca.* 20 Hz centred at δ 5.5 in a ratio of 1:4.

ms :m/e probe -57° 182 (M^+, 25%), 104 ($M^+ - C_6H_6$, 100%), 91 (tropylium ion, 30%) and 78 ($104 - C_2H_2$, 33%). The sample was contaminated with $CHCl_3$.

M^+ calculated for $C_{14}H_{14}$ 182.10955

found 182.1097

The more polar band yielded 5 mg of an oil:

ir :(film) 3080 (m), 3040 (m), 2960 (m), 2900 (m), 2840 (w), 1735 (w), 1600 (br, w), 730 (s), 705 (ms), and 680 (ms) cm^{-1}.

pmr :The sample was impure; no ratio of vinyl to protons on saturated carbon atoms could be obtained. Two clear doublet of doublets type patterns could be seen in the vinyl region centred at δ 5.5 and 6.0.

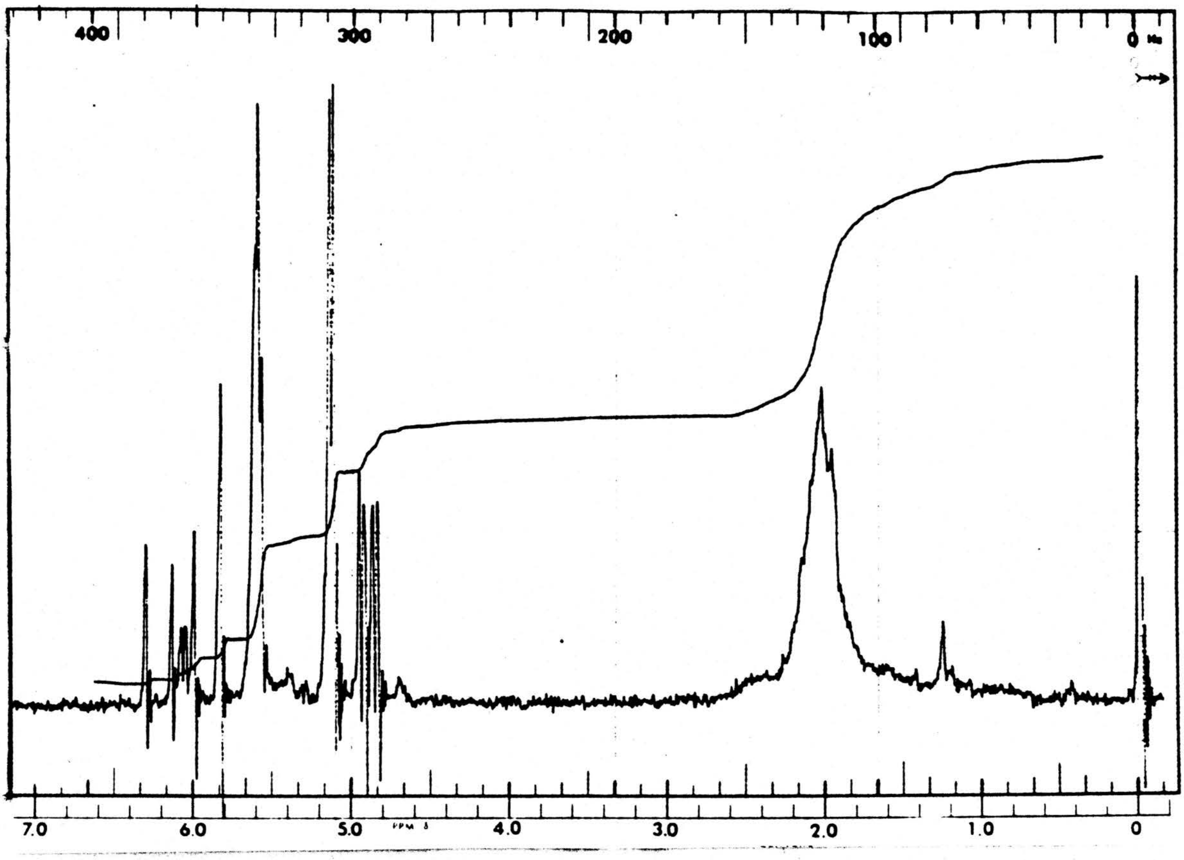
ms :Probe temperature -66°, m/e 182 (M^+, 40%), 104 ($M^+ - C_6H_6$, 34%), 91 (tropylium ion, 100%).

M^+ calculated for $C_{14}H_{14}$ 182.10955

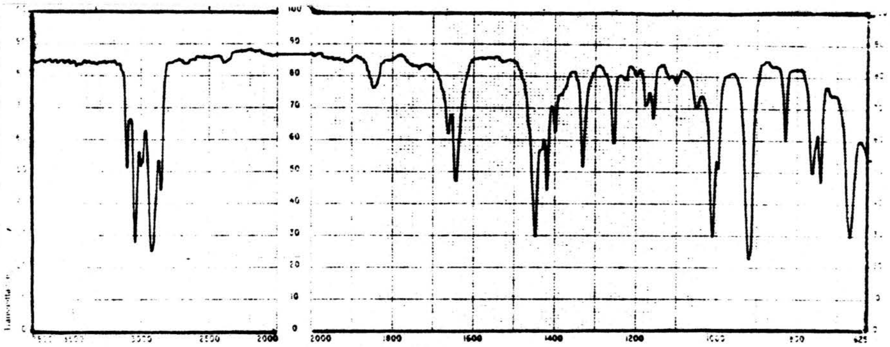
found 182.1093

SPECTRA

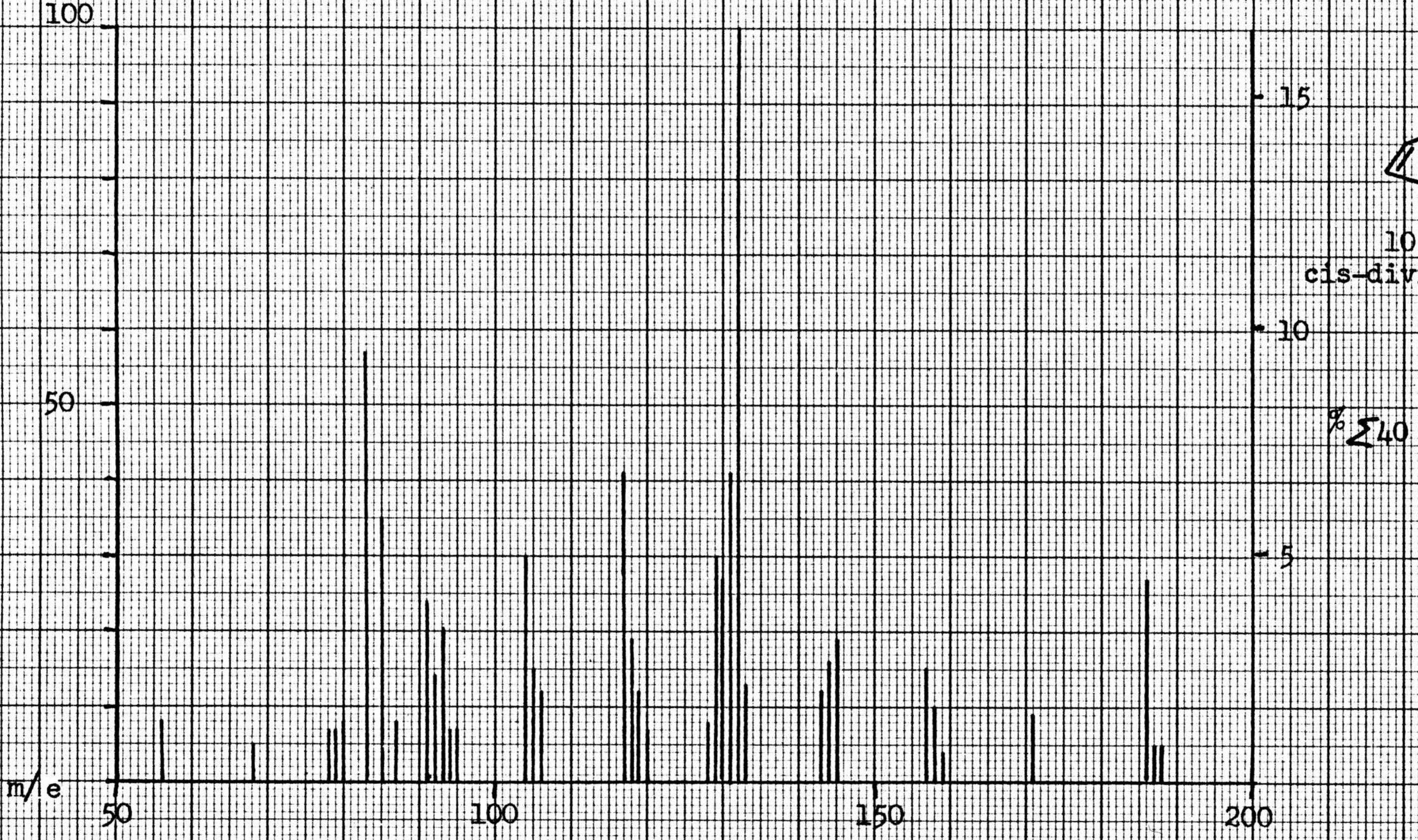
Index of Spectra

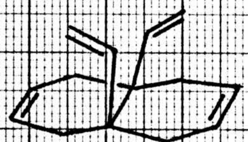


T-60 NMR Spectrum of cis-Divinyl Hexalin 124

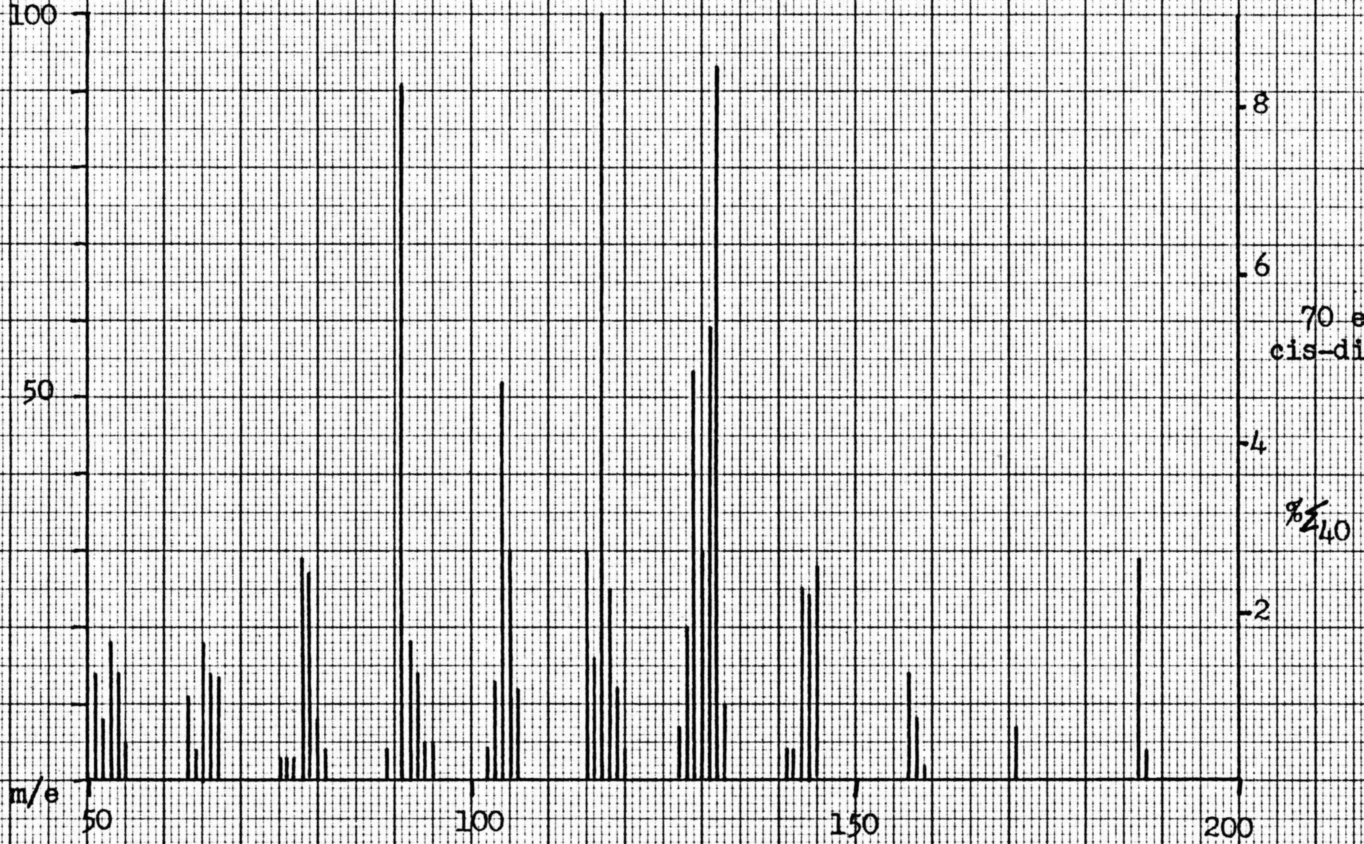


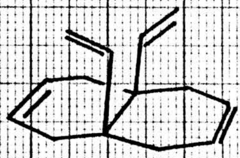
Infrared Spectrum of cis-Divinyl Hexalin 124 (film)



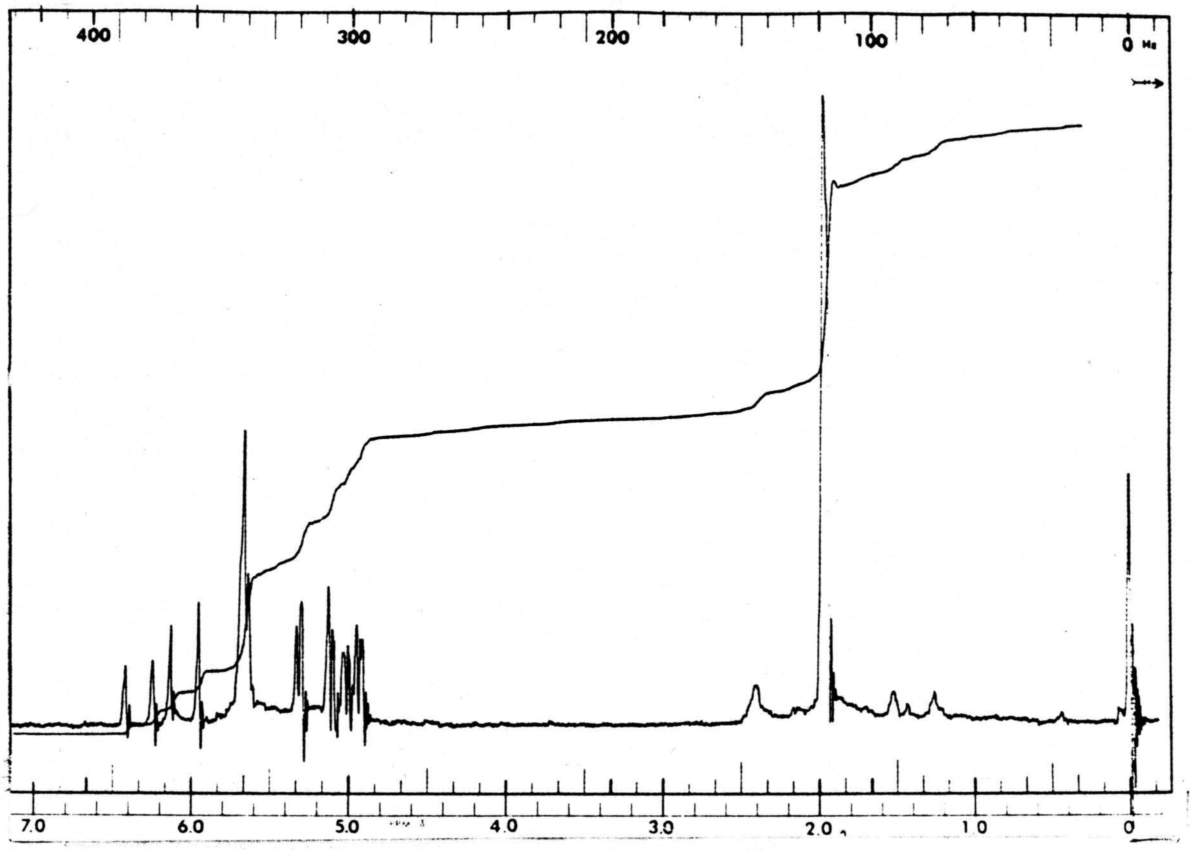


10 eV Spectrum of
cis-divinyl hexalin <u>124</u>

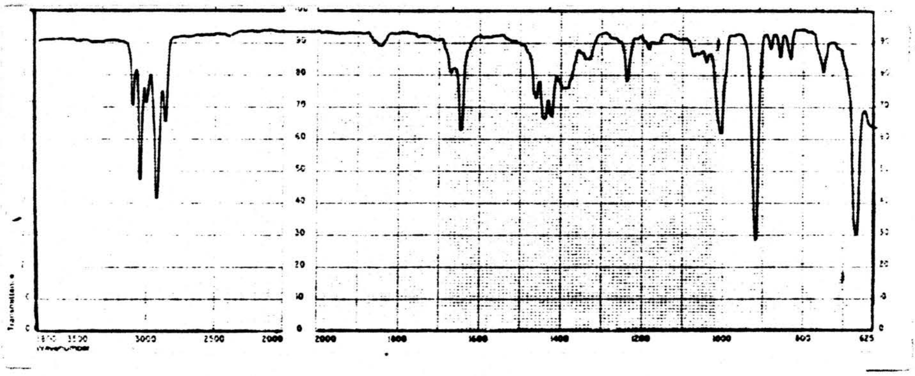




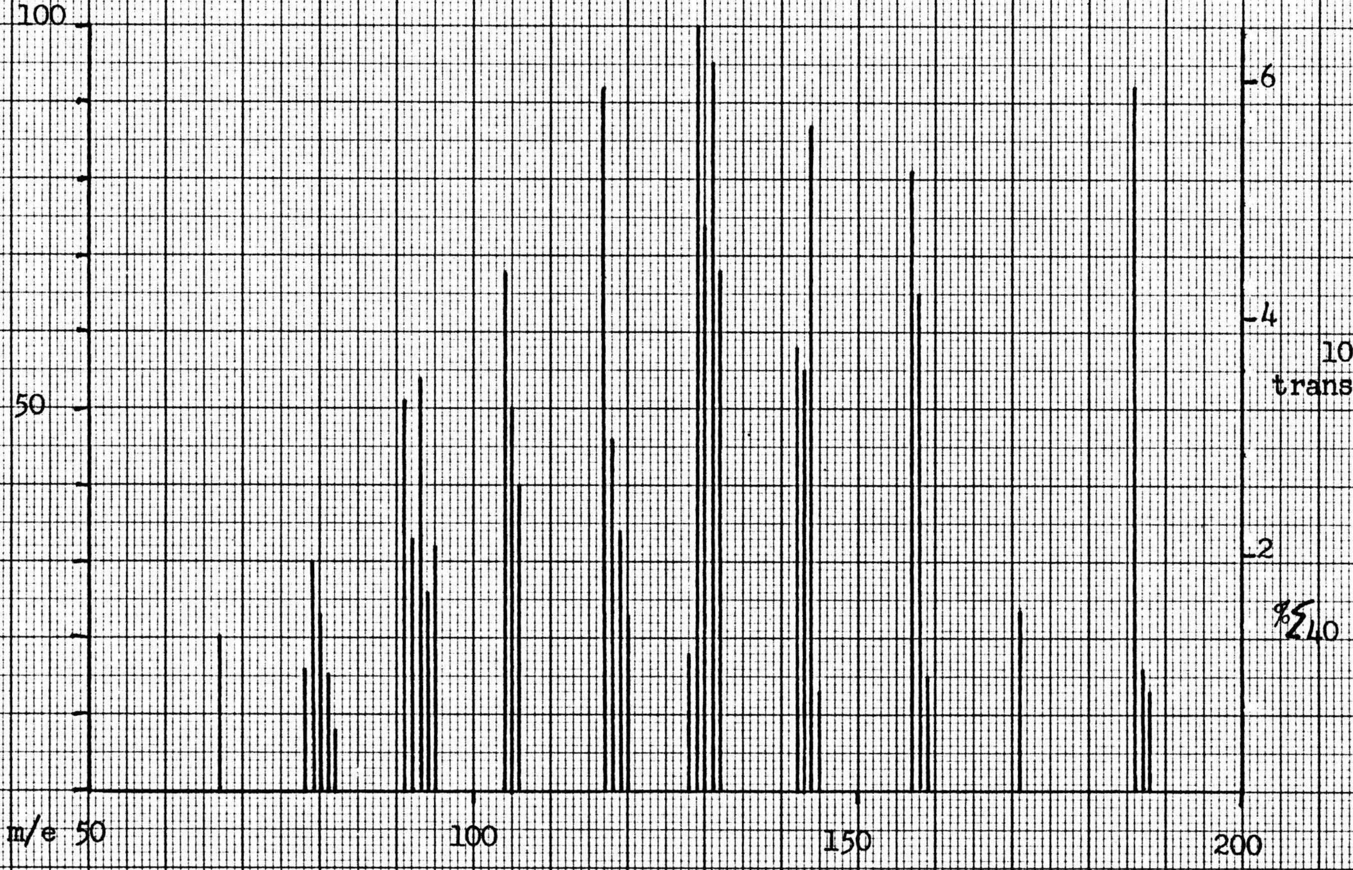
70 eV Spectrum of
cis-divinyl hexalin 124

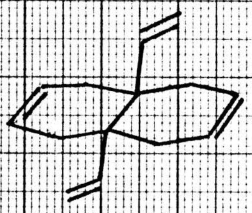


T-60 NMR Spectrum of trans-Divinyl Hexalin 125

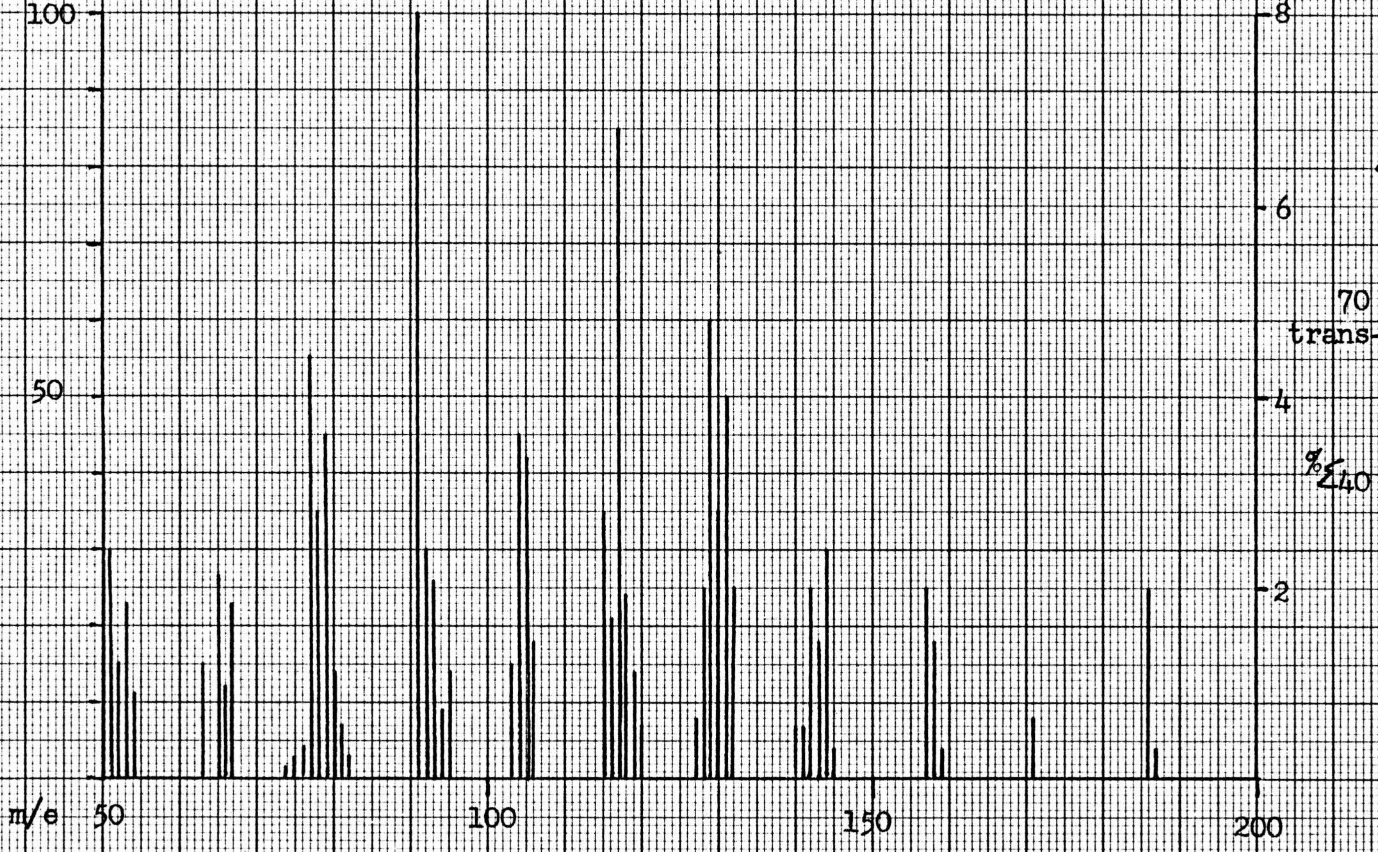


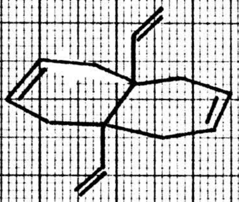
Infrared Spectrum of trans-Divinyl Hexalin 125 (film)





10 eV Spectrum of
trans-divinyl hexalin 125





70 eV Spectrum of
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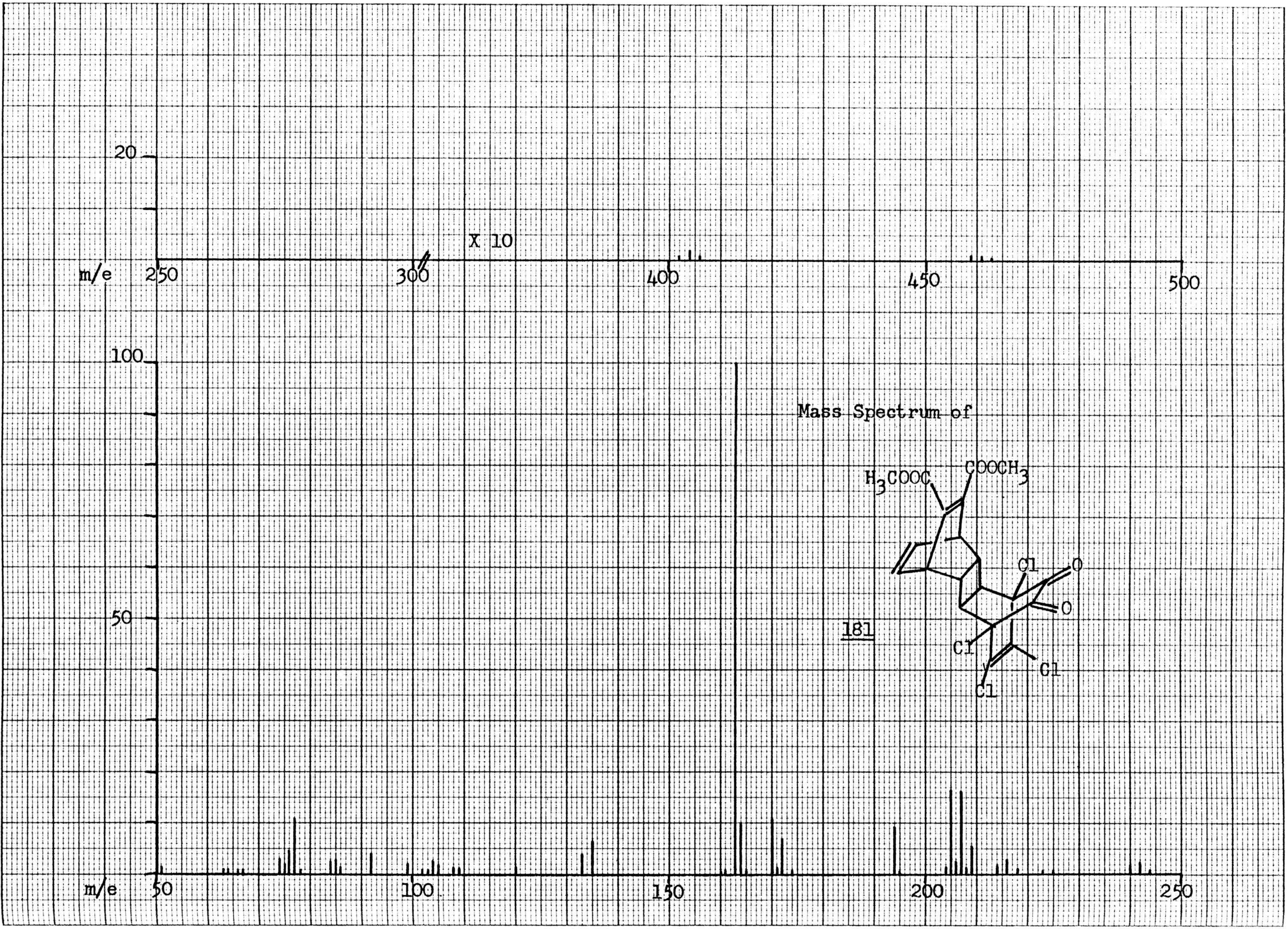
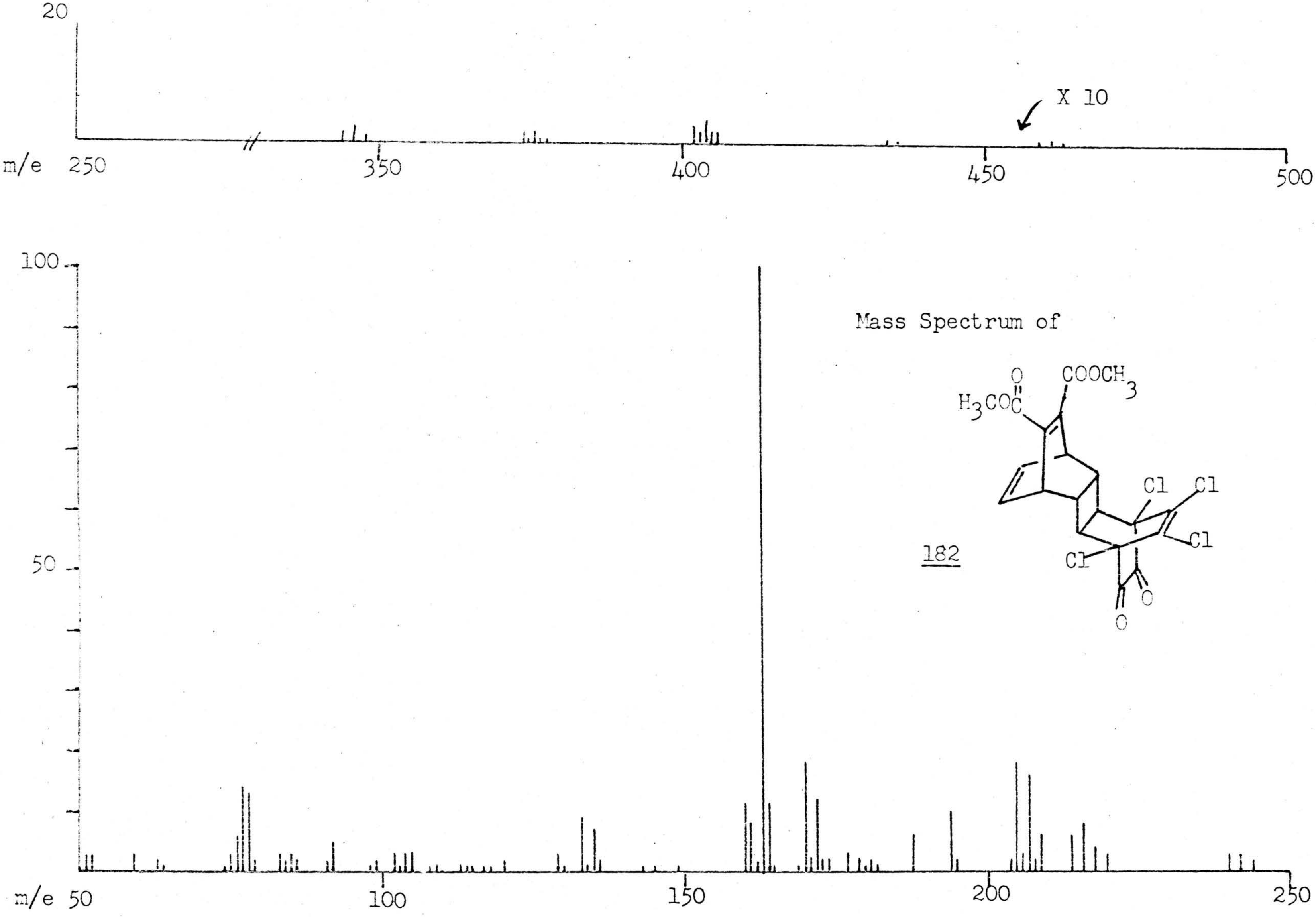


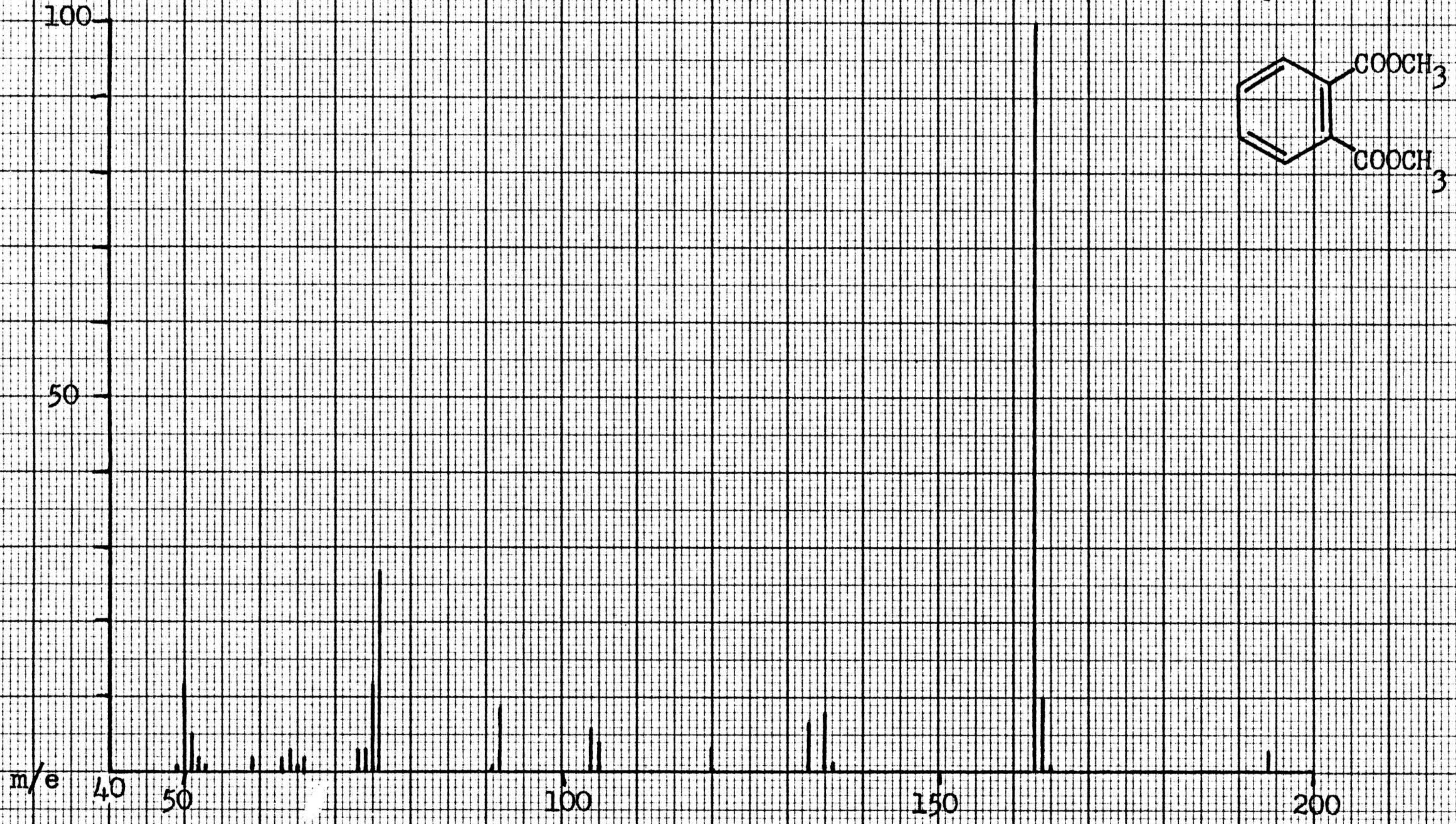
Mass Spectrum of

181

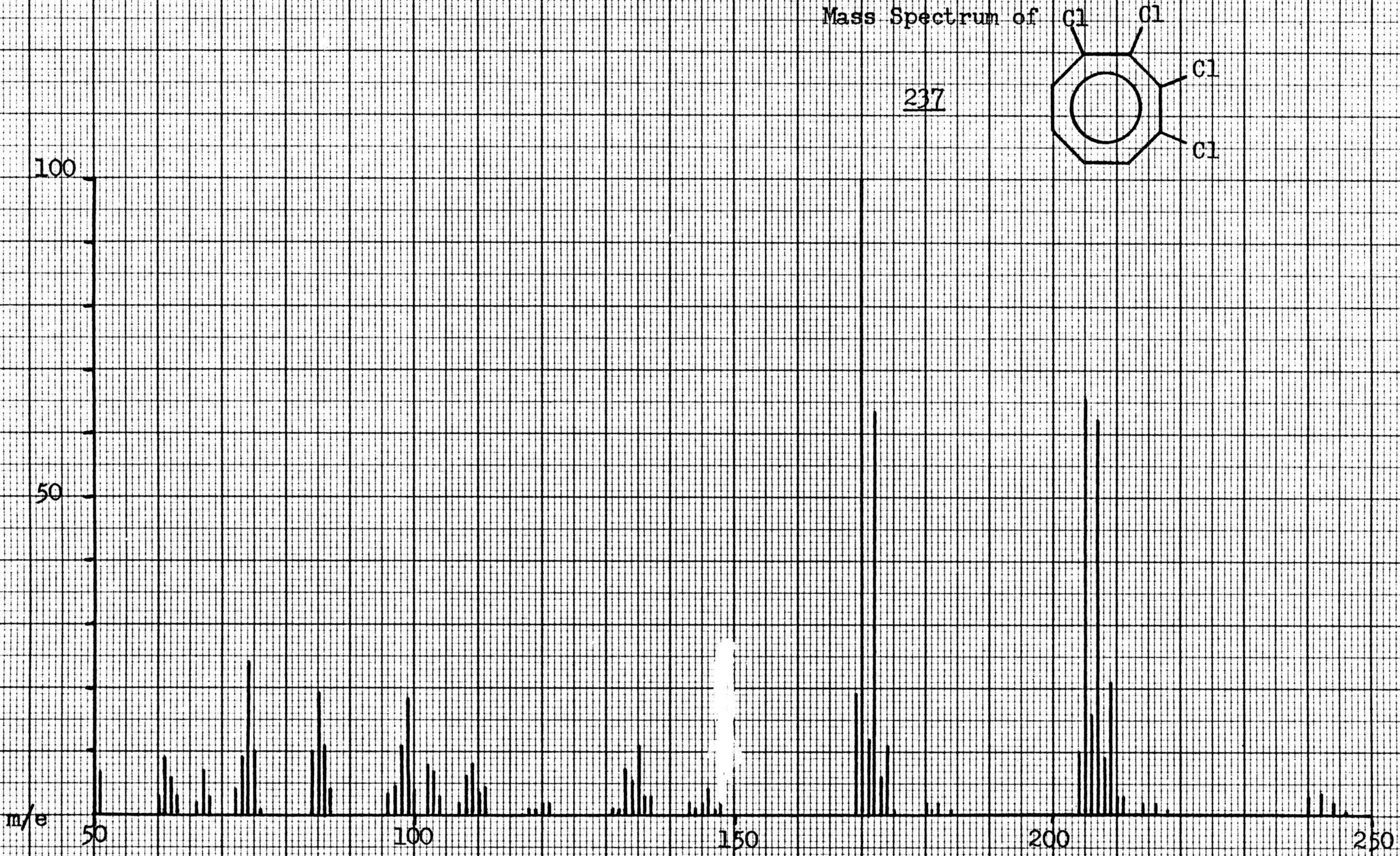


Mass Spectrum of

182

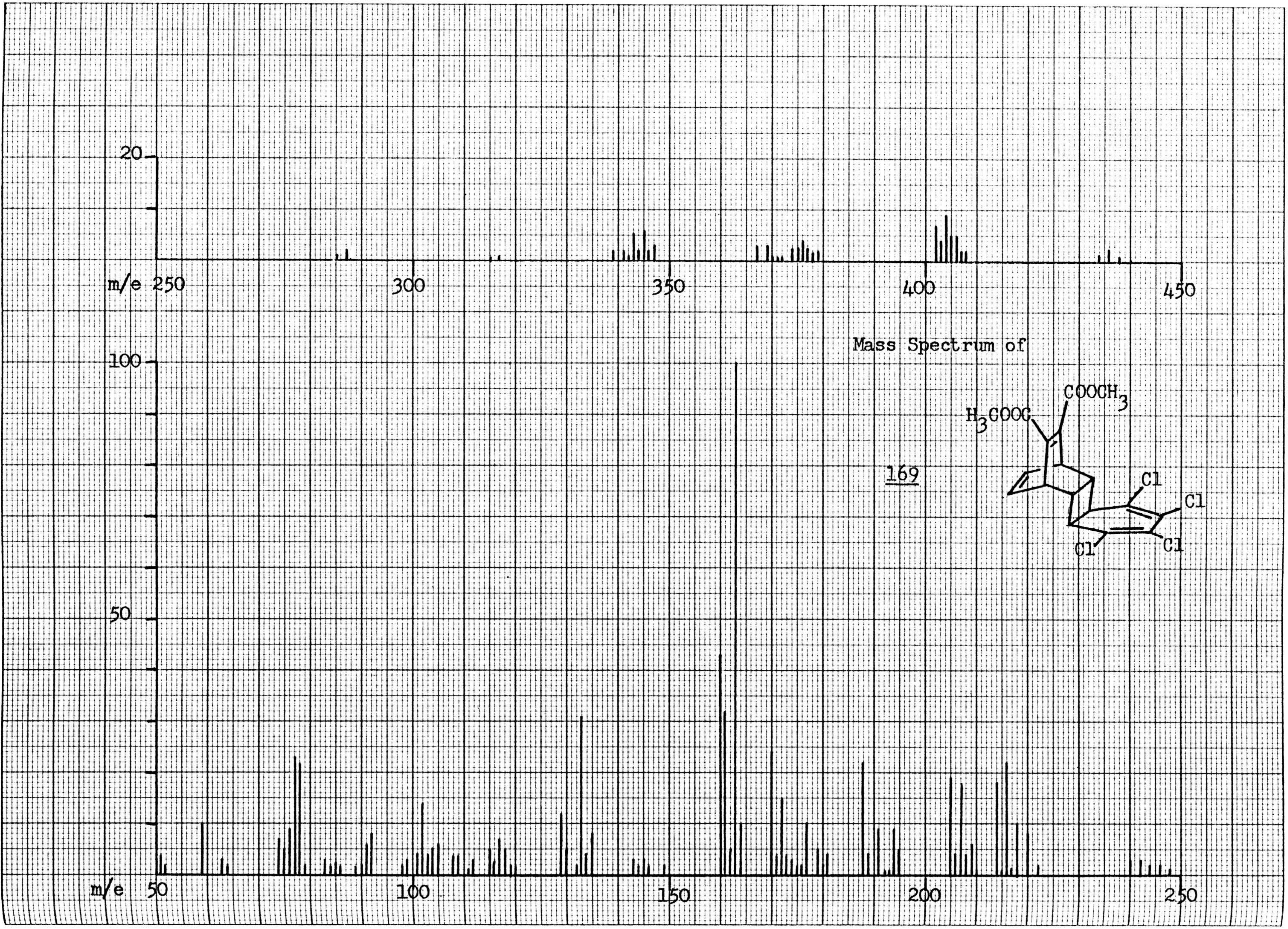


Mass Spectrum of



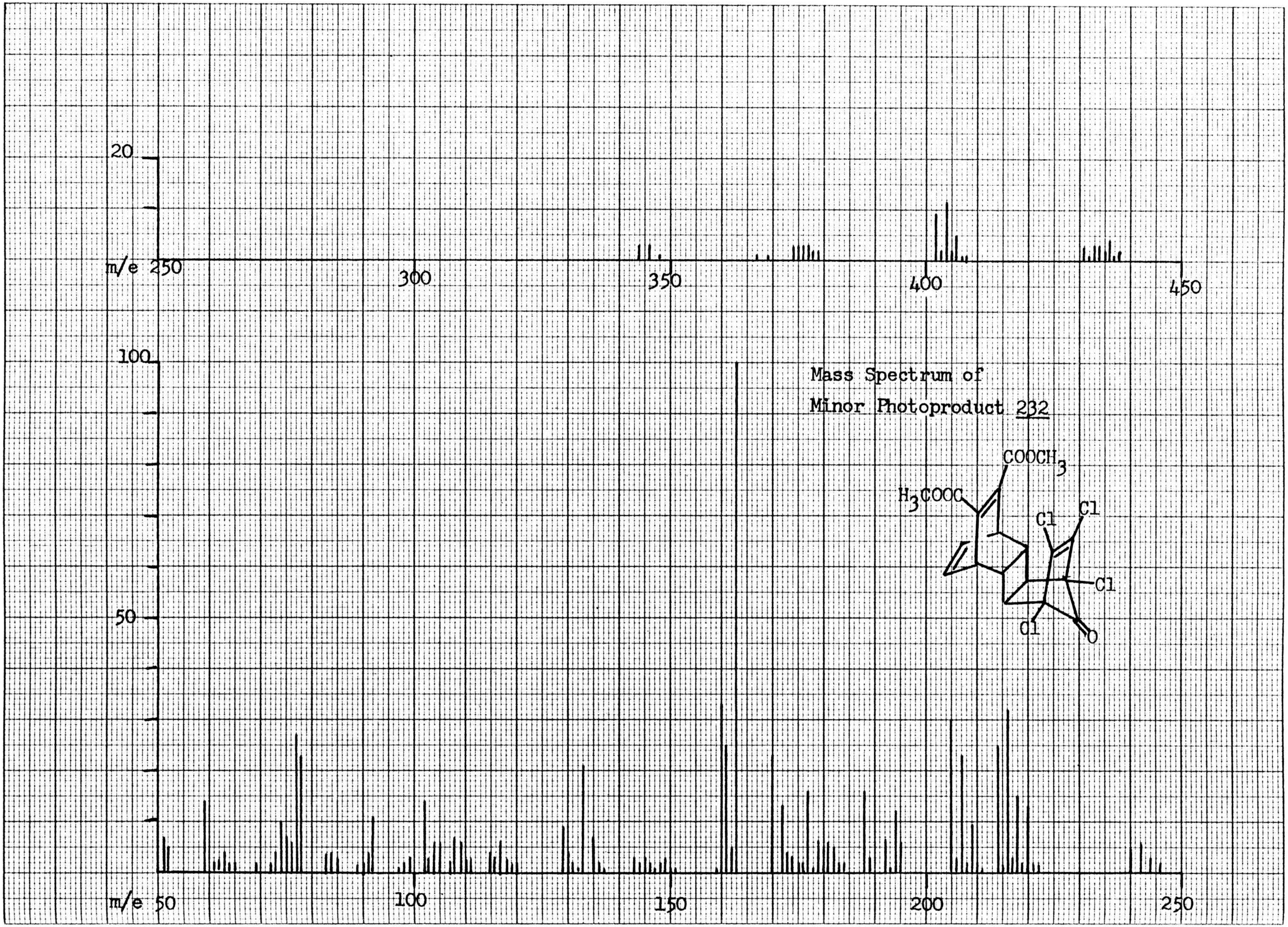
Mass Spectrum of

237

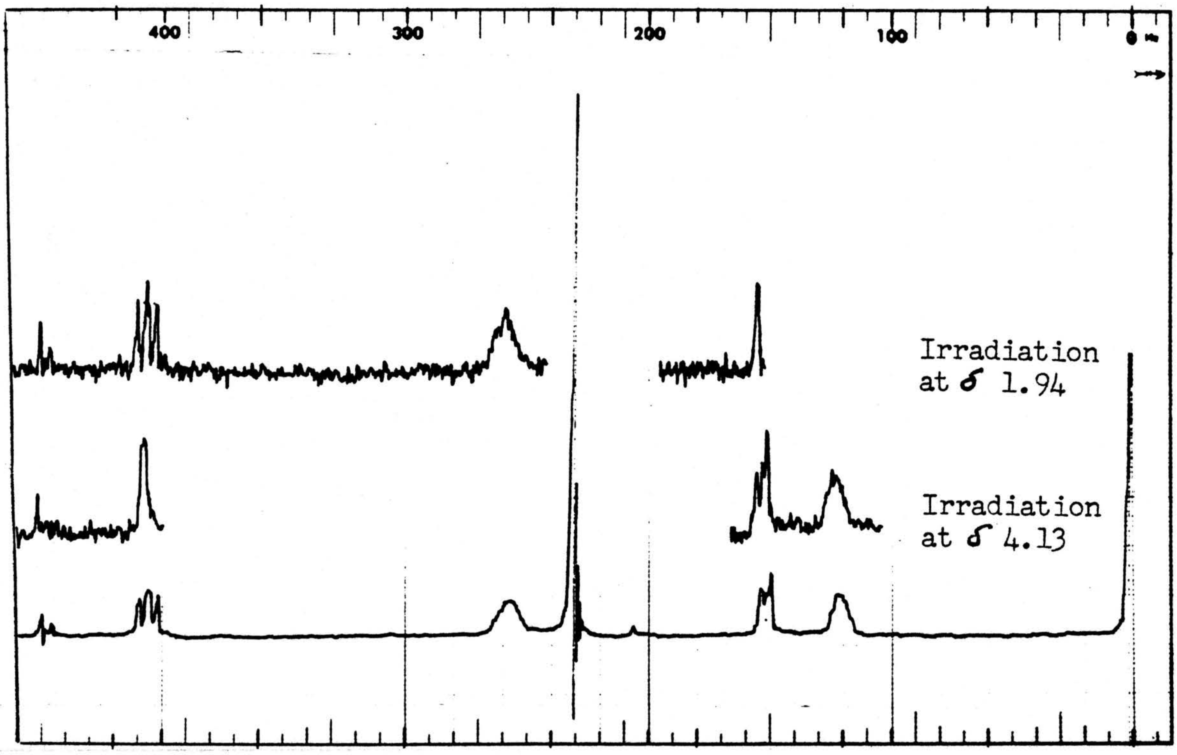


Mass Spectrum of

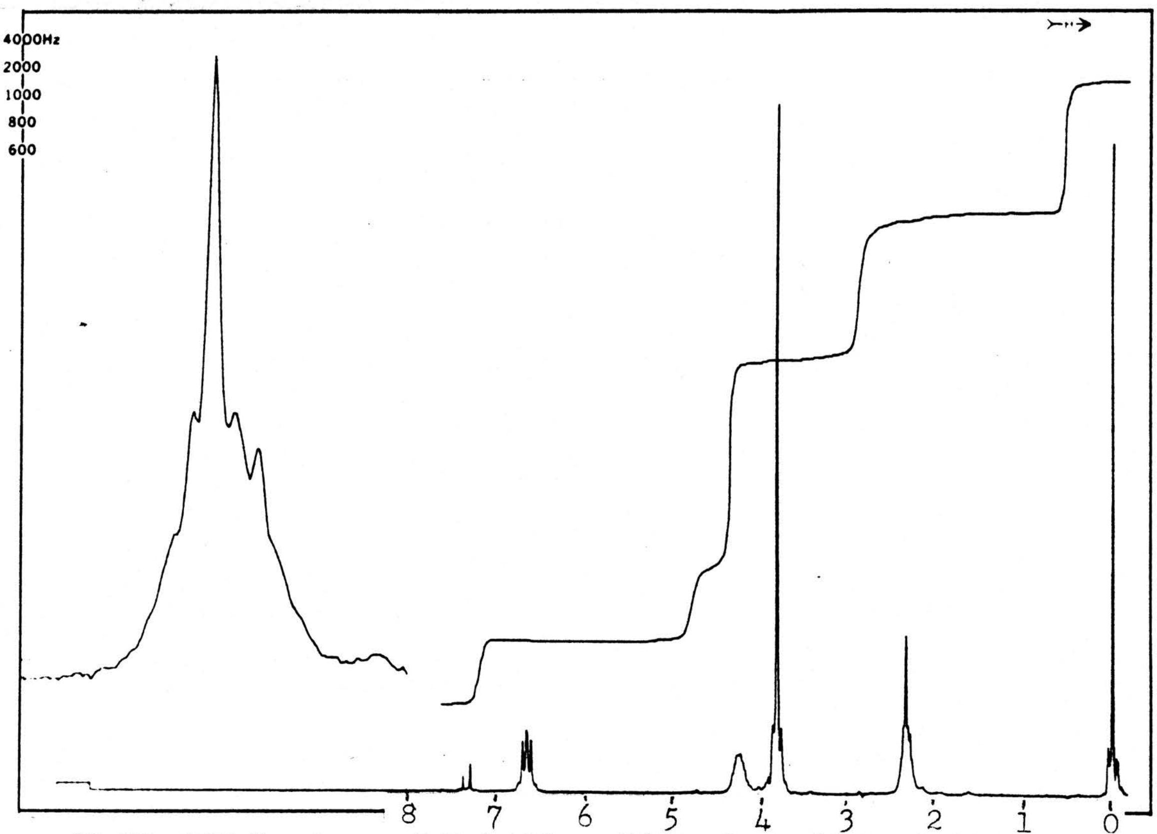
169



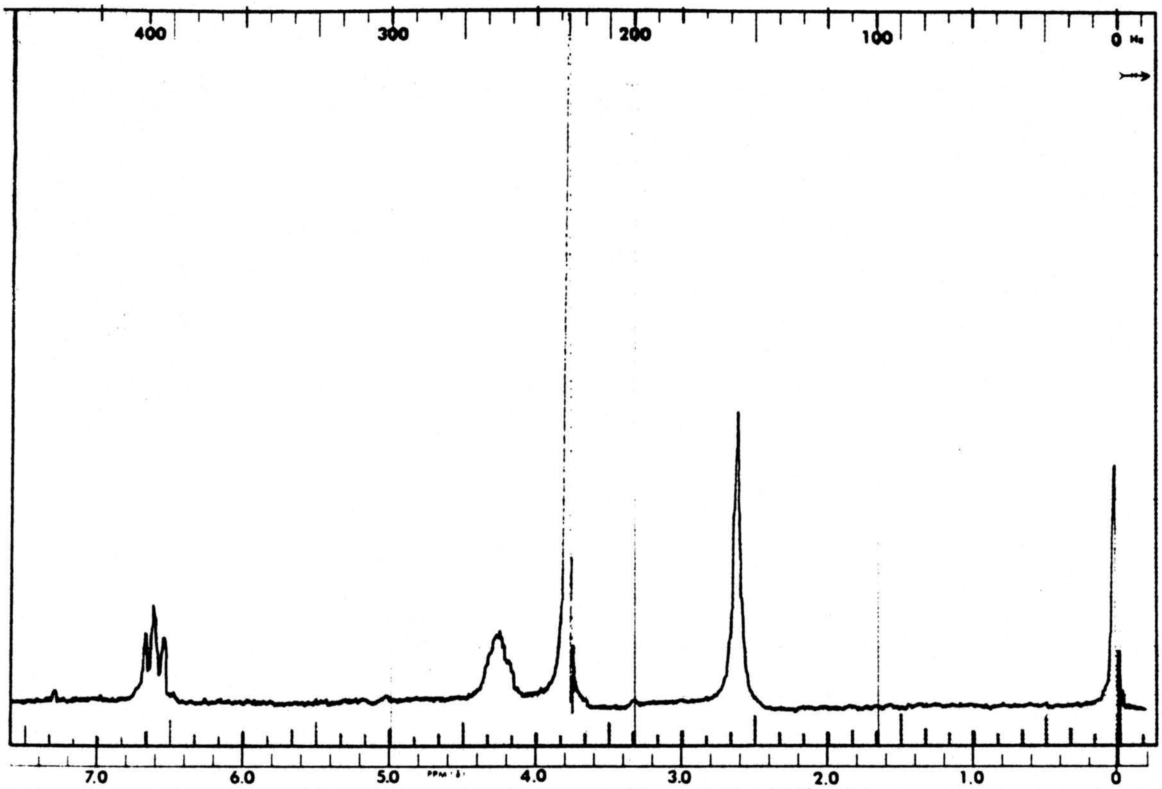
Mass Spectrum of Minor Photoproduct 232



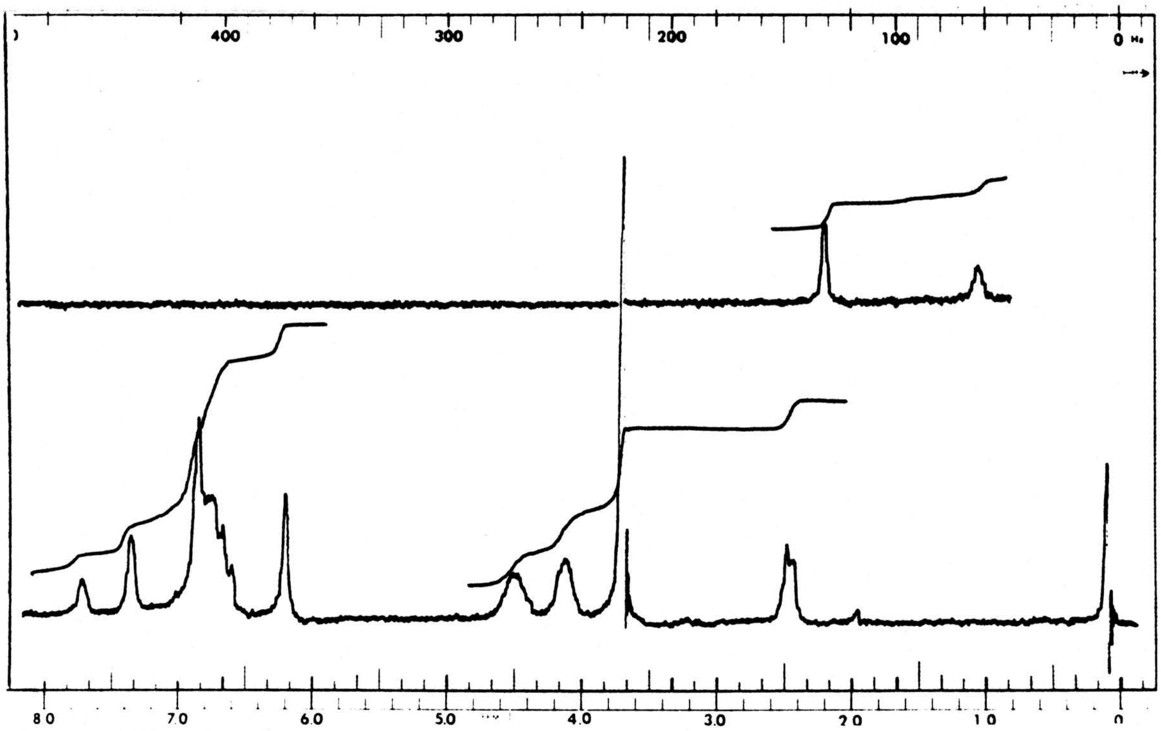
T-60 NMR Spectrum of Exo Dione 181; Sweep Width 500 Hz.



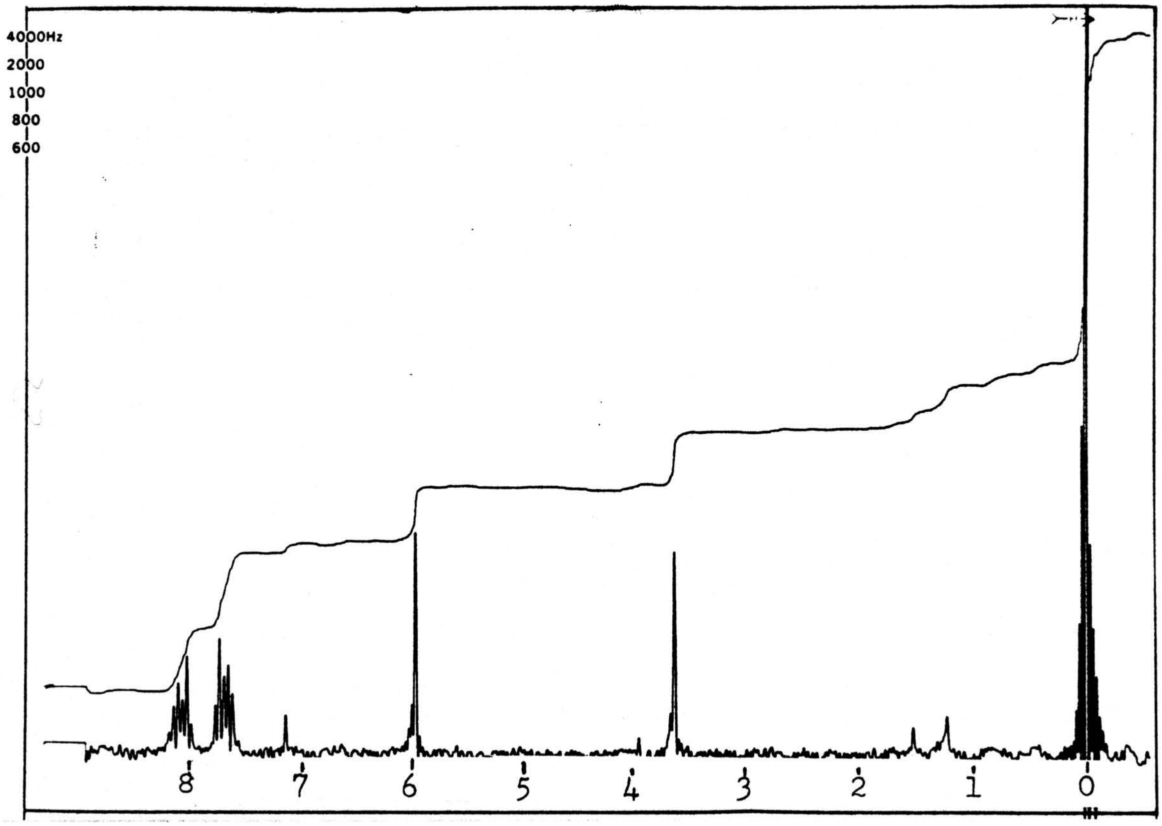
80 MHz NMR Spectrum of Endo Dione 182; Sweep Width 1000 Hz.



T-60 NMR Spectrum of Cyclohexadiene Derivative <u>169</u>; Sweep Width 500 Hz.

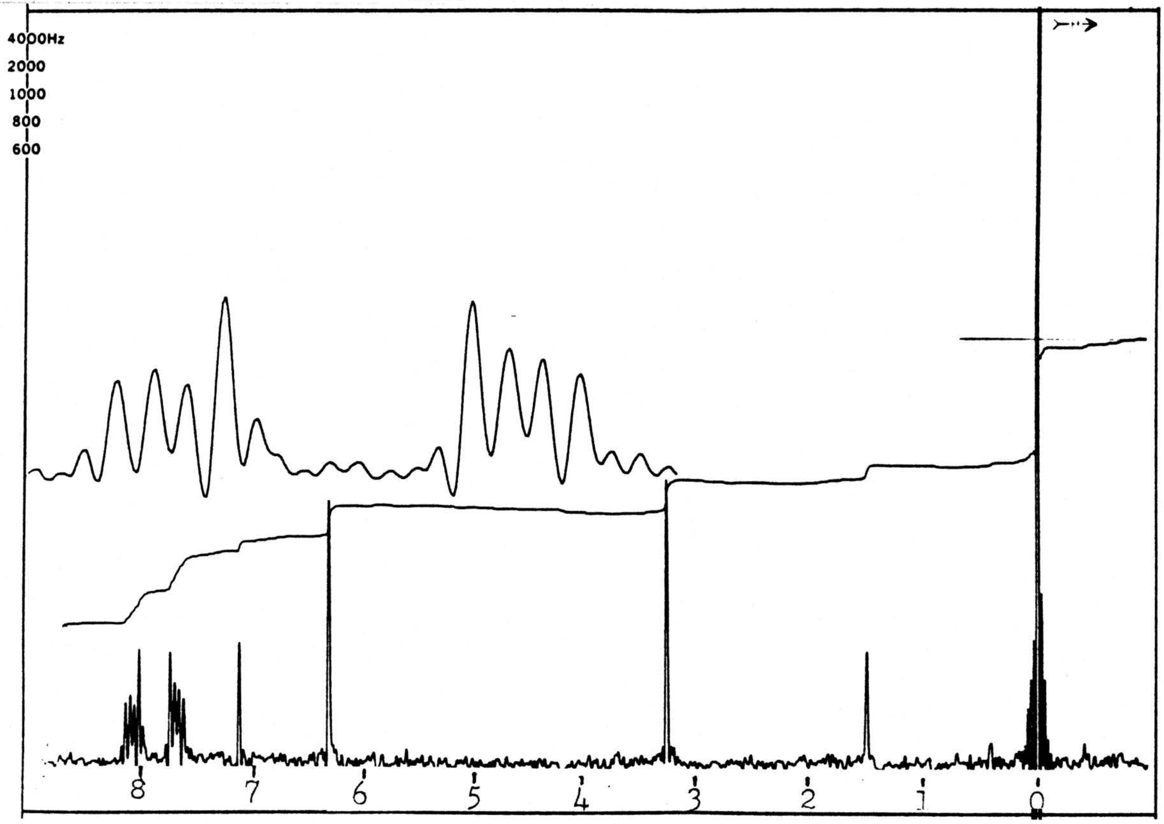


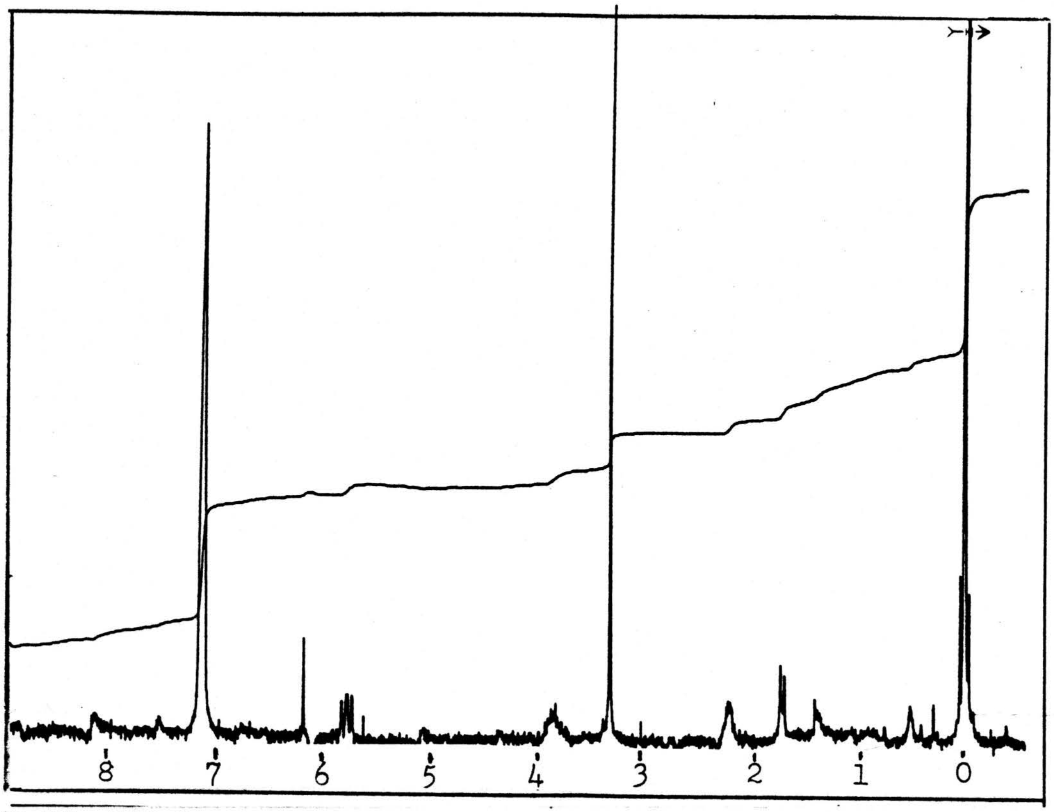
T-60 NMR Spectrum of Abnormal Quinoxaline Adduct <u>216</u>; Sweep Width 500 Hz. Insert offset 400 Hz; (C_5D_5N Solution).



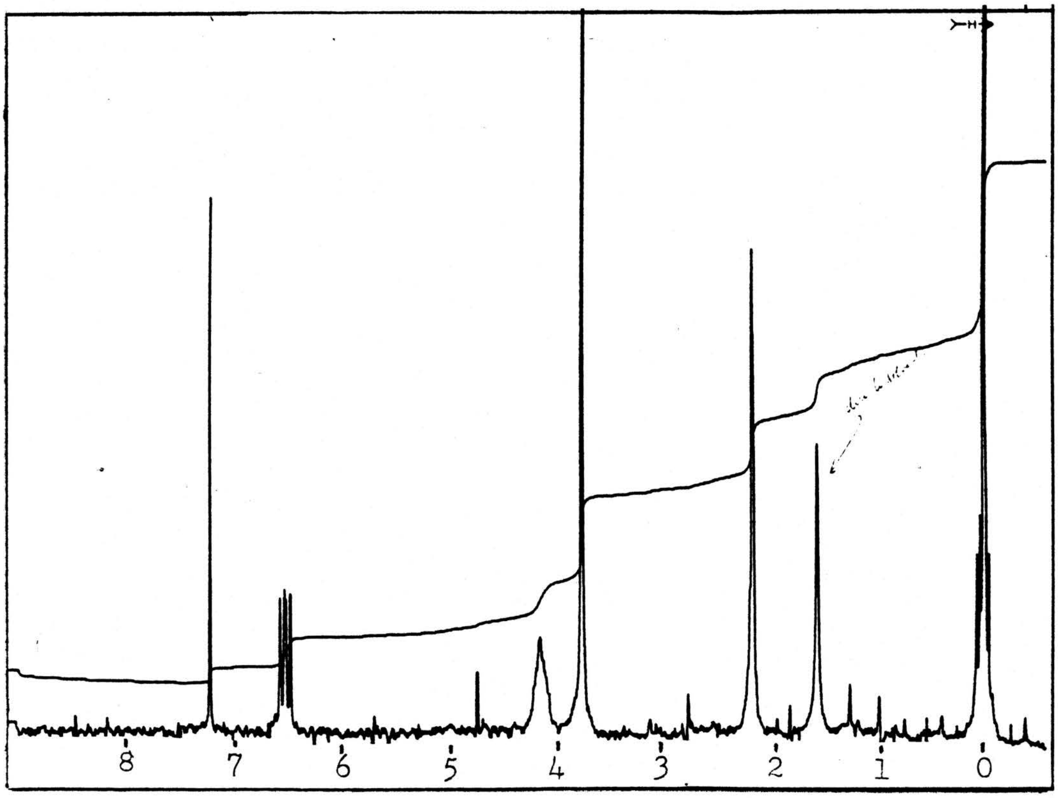
80 MHz NMR Spectrum of 217; Sweep Width 800 Hz.

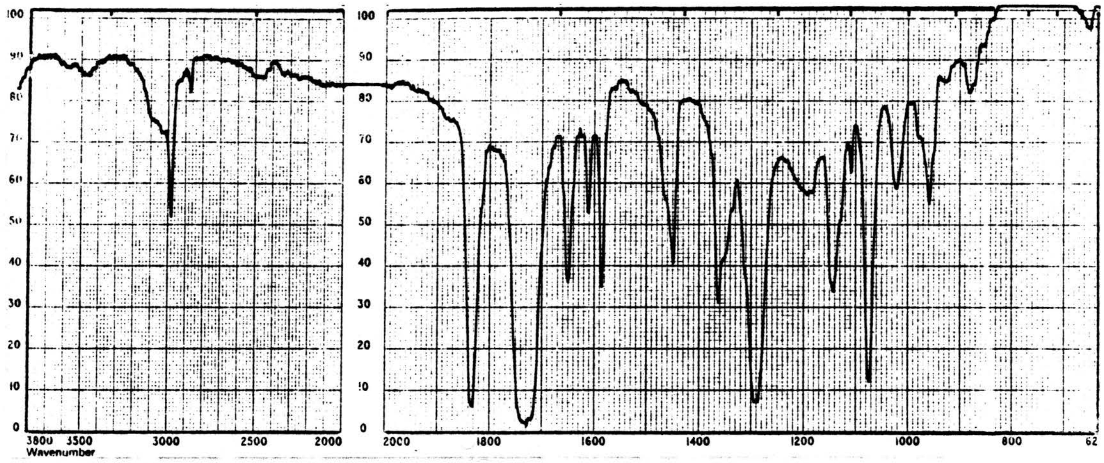
80 MHz NMR Spectrum of 218; Sweep Width 800 Hz.



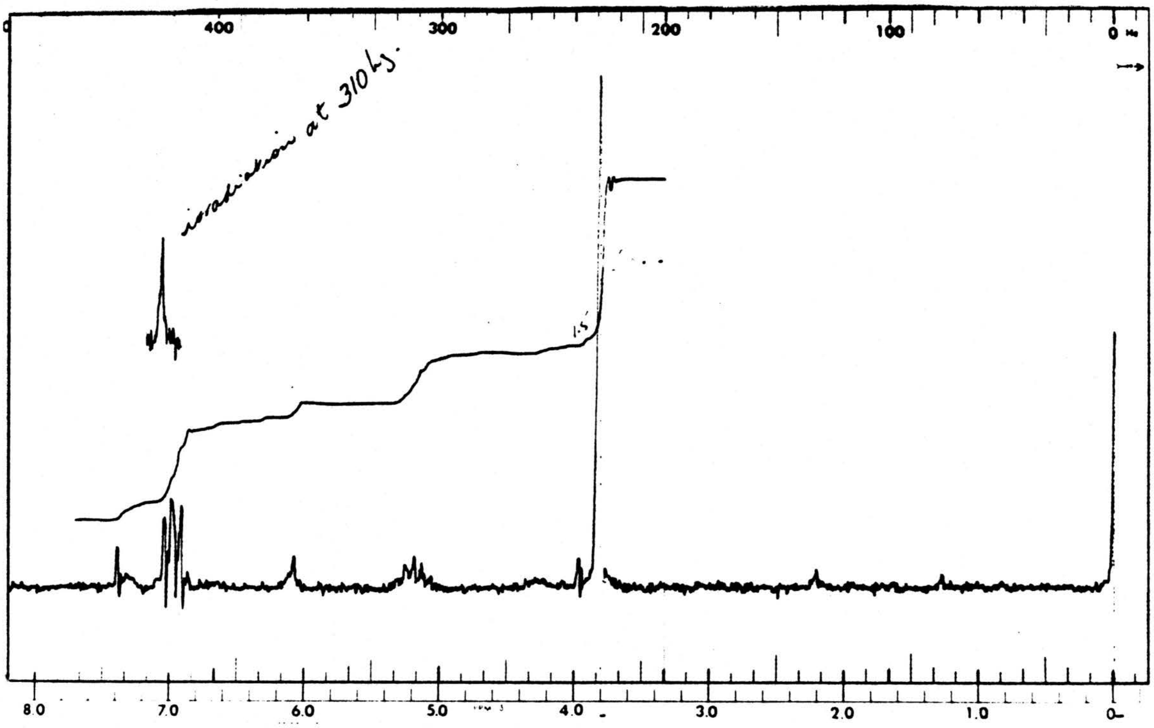


80 MHz NMR Spectra of Minor Photoproduct <u>232</u>; Sweep Width 800 Hz, in C_6D_6 (above) and $CDCl_3$ (below).

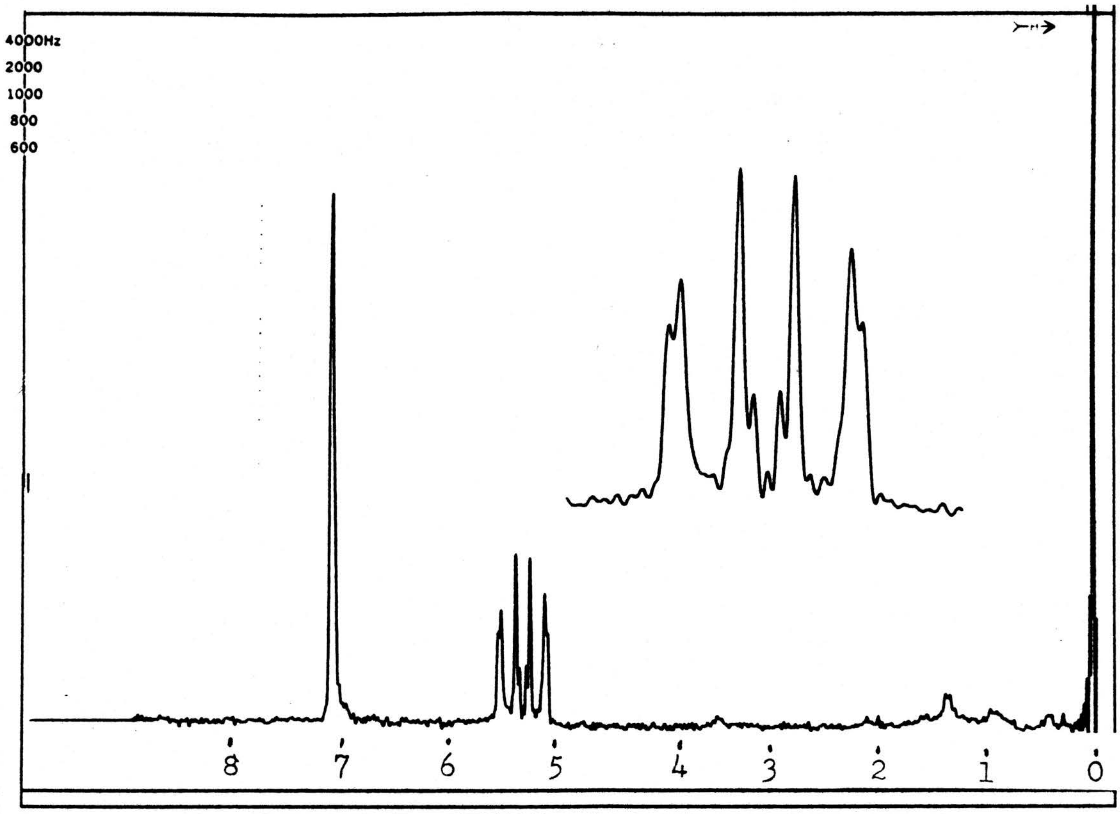




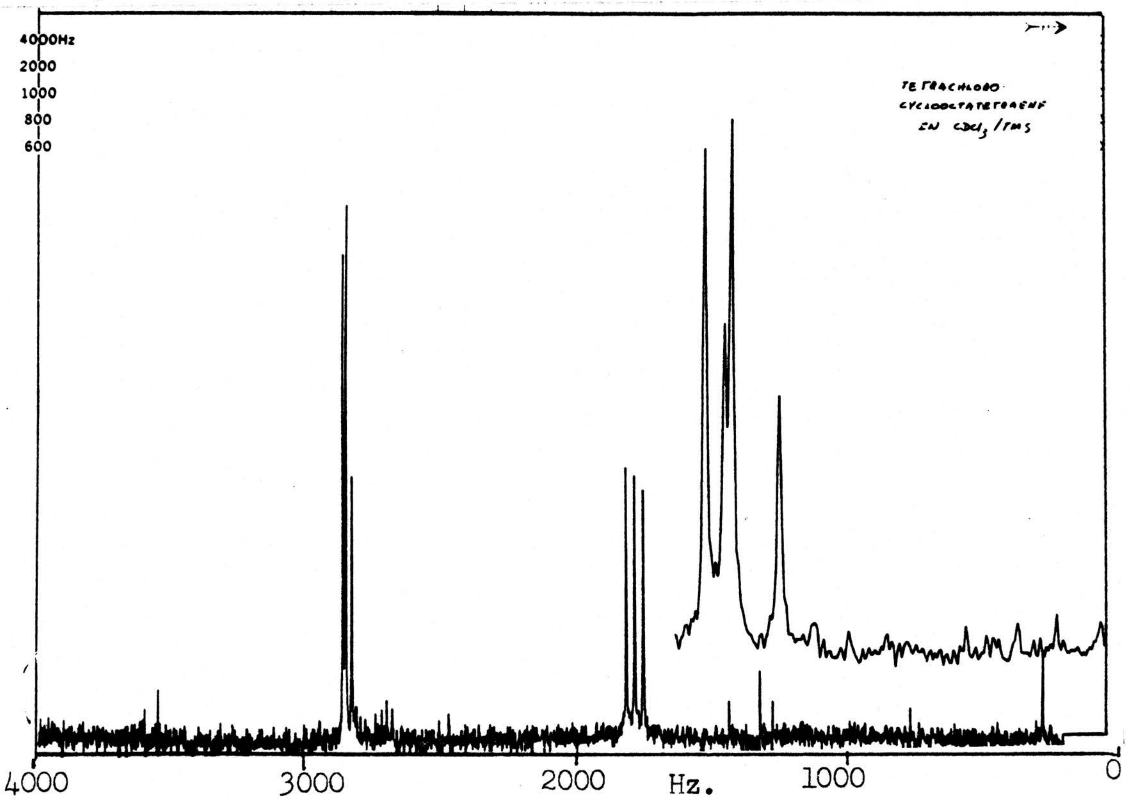
Infrared Spectrum of Minor Photoproduct 232 ($CHCl_3$).

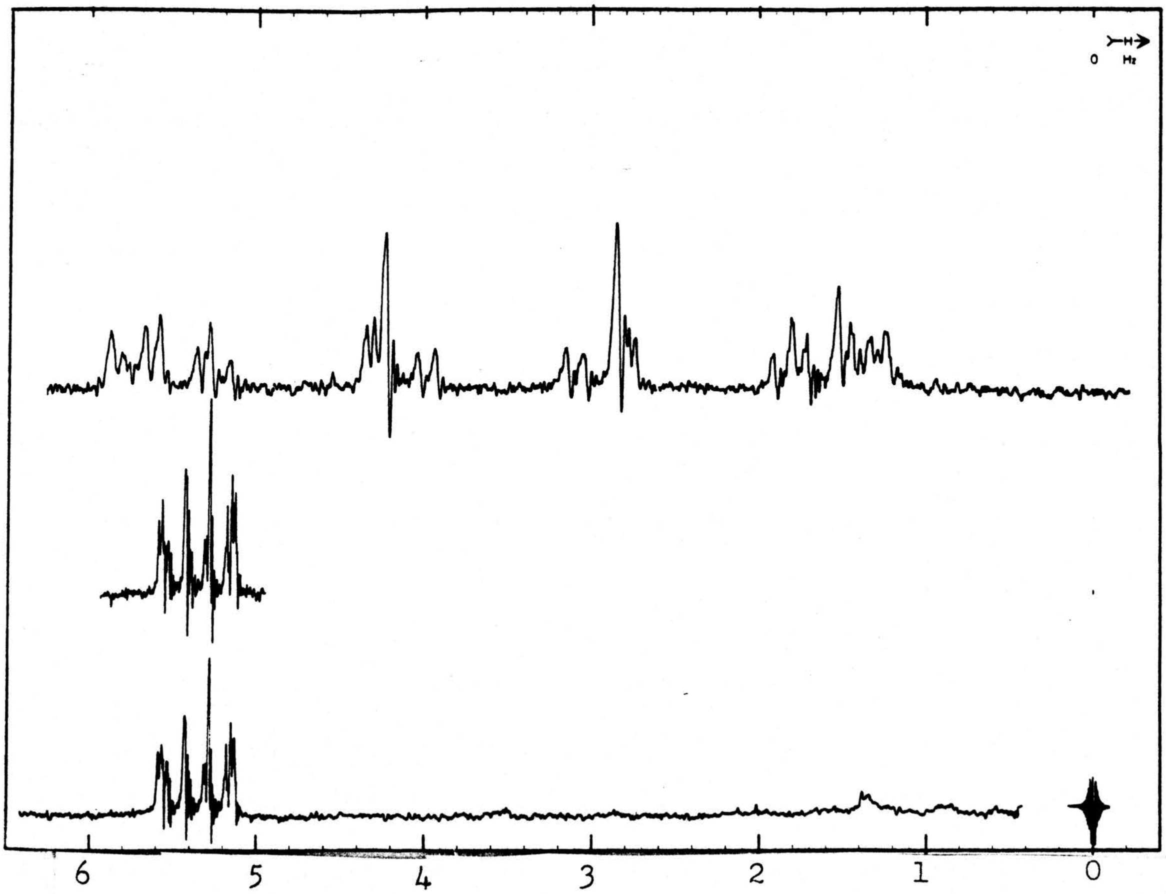


T-60 NMR Spectrum of Dicarbomethoxy Barrelene 229; Sweep Width 500 Hz.

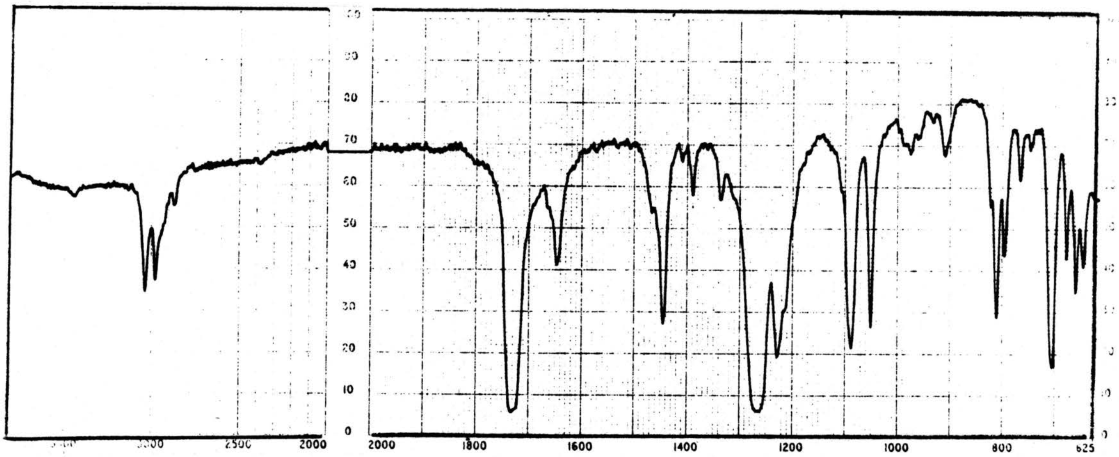


CFT-20 NMR Spectra of Tetrachlorocyclooctateraene <u>237</u>; Above 80 MHz Proton Spectrum; Sweep Width 800 Hz; Below 20 MHz Carbon Spectrum; Sweep Width 4000 Hz, insert 500 Hz.

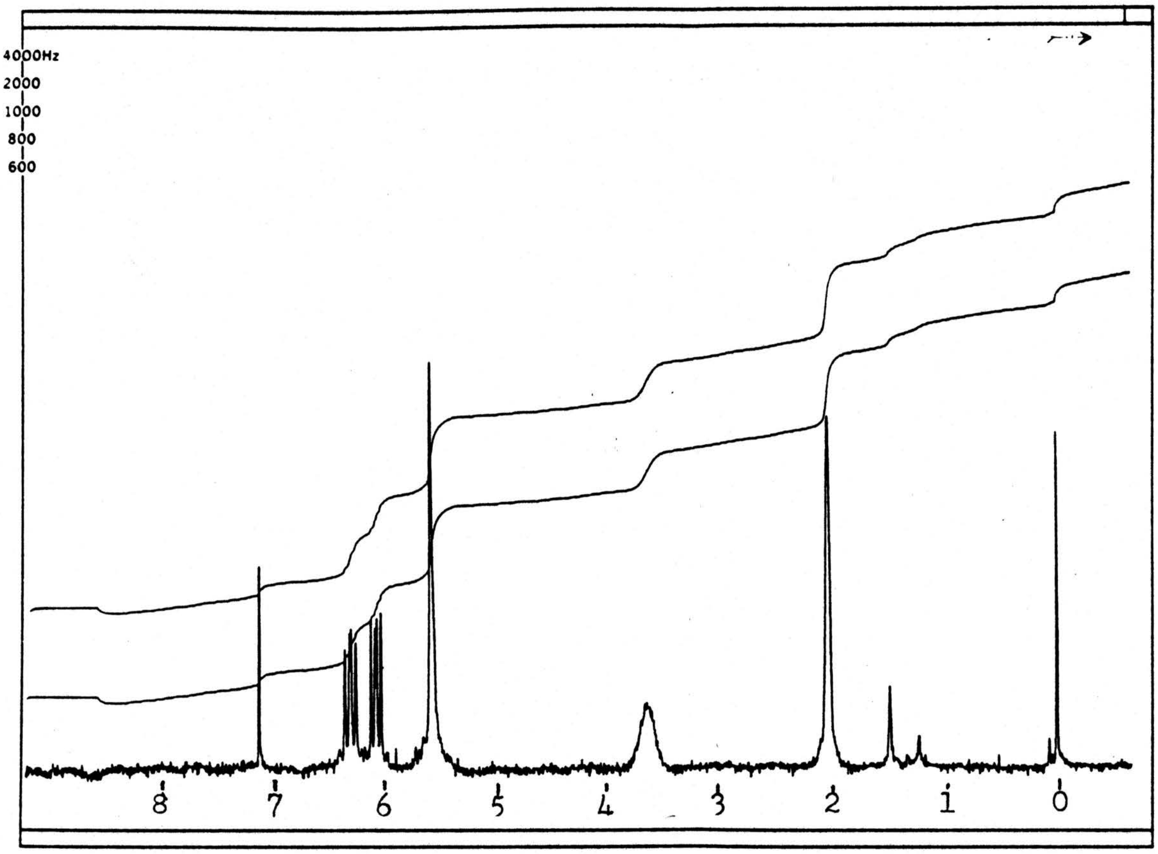




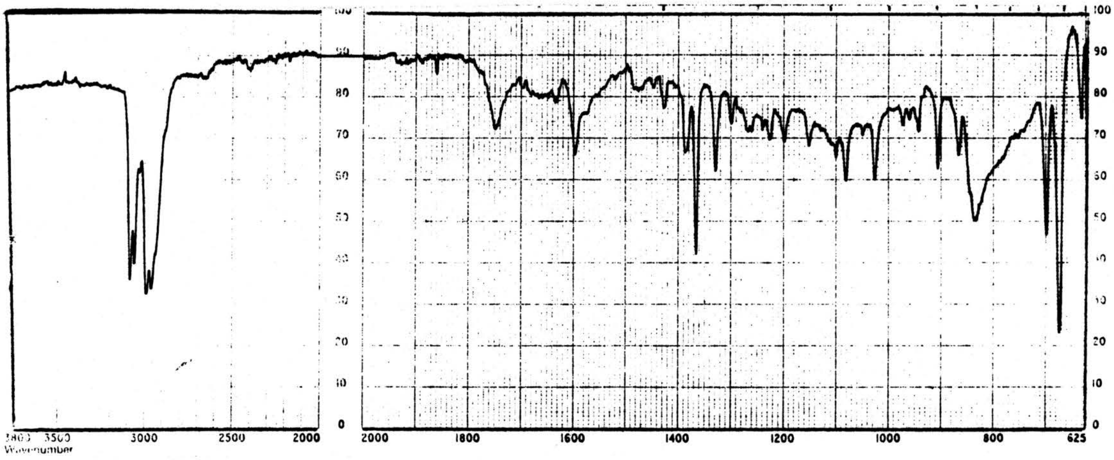
100 MHz NMR Spectrum of Tetrachlorocyclooctatetraene 237; Sweep Width 1000 Hz; insert Sweep Width 100 Hz.(C_6D_6).



Infrared Spectrum of Carbomethoxycyclooctatetraene 174 (film).



80 MHz NMR Spectrum of $(CH)_{14}$ Hydrocarbon <u>78</u>; Sweep Width 800 Hz.

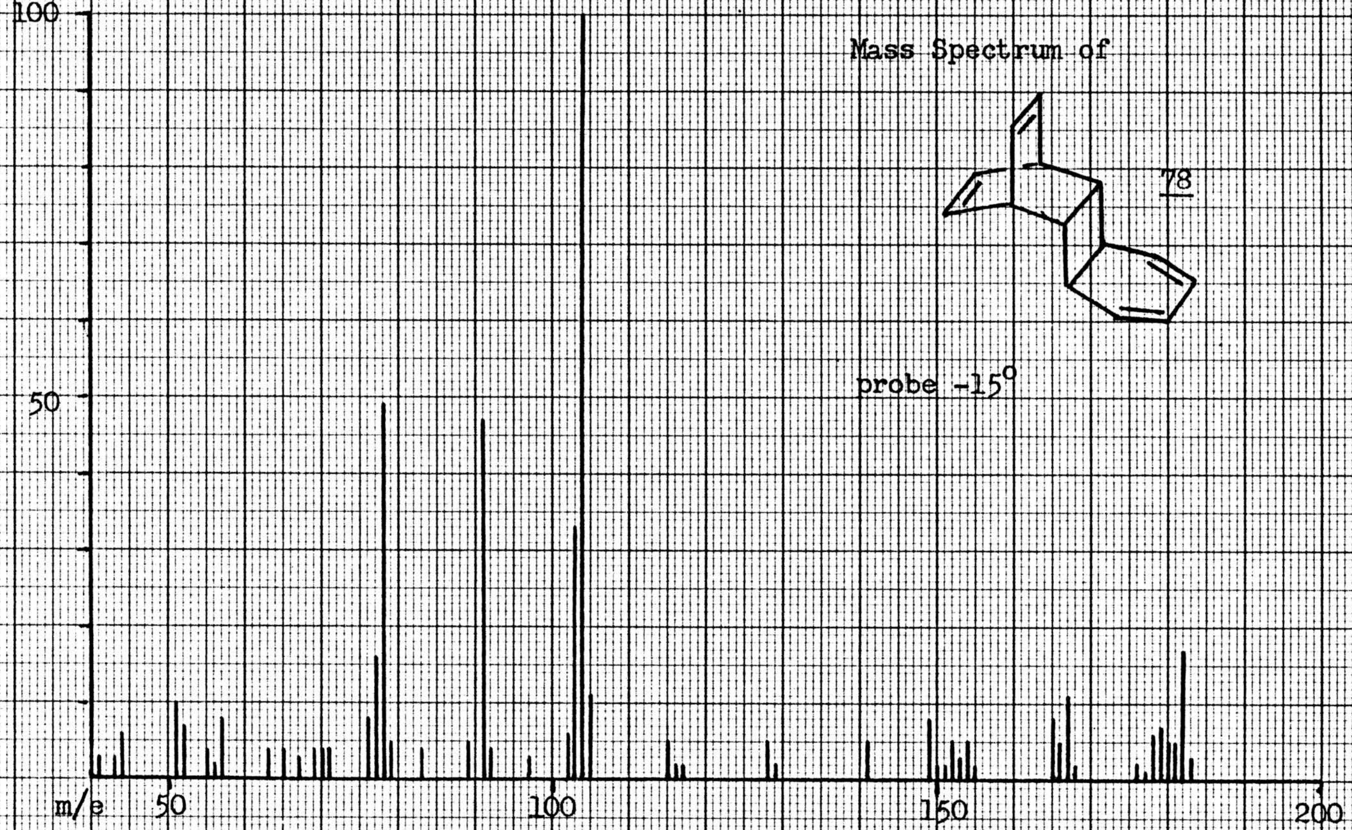


Infrared Spectrum of $(CH)_{14}$ Hydrocarbon <u>78</u> (CCl_4)

Mass Spectrum of

78

probe -15°



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