PART I
STUDIES CONCERNED WITH THE SYNTHESIS OF OCTALENE AND BICYCLO [6.2.0] DECA-1,3,5,7,9-PENTAENE

PART II
THE REARRANGEMENTS OF MONOSUBSTITUTED CYCLOOCTATETRAENES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY

Greg A. Bullock

1968

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Part I: STUDIES CONCERNED WITH THE SYNTHESIS OF OCTALENE AND BICYCLO[6.2.0]DECA-1,3,5,7,9-PENTAENE
Part II: THE REARRANGEMENTS OF MONOSUBSTITUTED CYCLOOCTATETRAENES

presented by

Greg A. Bullock

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Eugene LeGoff
Major professor

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ABSTRACT

PART I

STUDIES CONCERNED WITH THE SYNTHESIS OF
OCTALENE AND BICYCLO[6.2.0]DECA-1,3,5,7,9-PENTAENE

PART II

THE REARRANGEMENTS OF
MONOSUBSTITUTED CYCLOÖCTATETRAENES

by Greg A. Bullock

The initial goal of this investigation concerned the synthesis of bicyclo[6.6.0]tetradeca-1,3,5,7,9,11,13-heptaene (octalene). Several synthetic approaches leading to the preparation of octalene were attempted. None of these approaches, however, was successful. During the course of this investigation a new synthetic route to [2.2]paracyclophanes was discovered. 4,5,12,13-Tetracarbomethoxy[2.2]paracyclophane was synthesized from dimethyl 3,6-bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate di-p-toluenesulfonate by solvolysis in buffered acetic acid. The bis(hydroxymethyl)cyclohexadiene was prepared from a Diels-Alder reaction between trans,trans-2,4-hexadiene-1,6-diol and dimethyl acetylenedicarboxylate.

The synthesis of bicyclo[6.2.0]deca-1,3,5,7,9-pentaene was also attempted. Synthetic approaches to the bicyclic decapentaene involved the attempted condensation of both dehydrocycloöctatetraene and N,N-diethylaminocycloöctatetraene with substituted acetylenes. The condensation of N,N,diethylaminocycloöctatetraene with dimethyl

acetylenedicarboxylate yields dimethyl 1,2-naphthalenedicarboxylate as the only isolable product. A logical proposal for the formation of this product is that the condensation product, dimethyl 1-N,N-diethylaminobicyclo[6.2.0]deca-2,4,6,9-tetraene-9,10-dicarboxylate, ring opens to produce dimethyl 1-N,N-diethylaminocyclodecapentaene-2,3-dicarboxylate. The [10]annulene could then cyclize accompanied by the loss of diethyl amine to yield the observed product. The preparation of bicyclo[6.2.0]decapentaene was attempted also from tetramethyl tricyclo[$6.2.0.0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate without success. The stereochemical configuration of tetramethyl tricyclo[$6.2.0.0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate was established from its nmr spectrum and from the configuration of tetramethyl 11-oxatetracyclo[$4.4.1.0^{2,5}.0^{7,10}$]undecane-3,4,8,9-tetracarboxylate, one of its reaction products. The cyclohexadione ring of the tetramethyl dione exists in a boat form with the two cyclobutane rings <u>cis</u> fused to the pseudoequatorial positions. The carbomethoxy groups are believed to be <u>cis</u> to each other and <u>trans</u> to the cyclohexadione-cyclobutane ring junction.

Chloro- and bromocycloöctatetraene thermally rearrange to <u>trans</u>-β-chloro- and <u>trans</u>-β-bromostyrene, respectively. The solvolysis of chlorocycloöctatetraene in methanolic solutions containing various nucleophiles is also discussed. Methanolysis of chlorocycloöctatetraene yields a mixture of

trans-β-chlorostyrene, trans-β-methoxystyrene, and phenylacetaldehyde dimethyl acetal. If methanol-d is used as the solvent, the phenyacetaldehyde dimethyl acetal is labeled in the benzylic position. Methanolysis of chlorocycloöctatetraene in the presence of sodium methoxide produces, along with trans-β-chlorostyrene and trans-β-methoxystyrene, methoxycycloöctatetraene whereas methanolysis in the presence of lithium bromide yields trans-β-chlorostyrene, trans-β-methoxystyrene, and trans-β-bromostyrene. These results are compatible with the view that the valence tautomer of chlorocycloöctatetraene, 1-chlorobicyclo[4.2.0]octa-2,4,7-triene, ionizes to the corresponding bicyclic octatrienyl carbonium ion. A mechanism for the formation of the products in these reactions is discussed. The rearrangement takes a different pathway when diethylamino- or t-butoxycycloöctatetraene are heated. In both of these cases the α-substituted styrenes are produced. A mechanism for the latter rearrangement is proposed.

PART I

STUDIES CONCERNED WITH THE SYNTHESIS OF OCTALENE AND BICYCLO[6.2.0]DECA-1,3,5,7,9-PENTAENE

PART II

THE REARRANGEMENTS OF MONOSUBSTITUTED CYCLOÖCTATETRAENES

By

Greg A. Bullock

A THESIS

Submitted to
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Department of Chemistry

1968

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To Lisa

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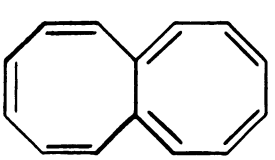
PART I

STUDIES CONCERNED WITH THE SYNTHESIS OF OCTALENE AND BICYCLO[6.2.0]DECA-1,3,5,7,9-PENTAENE

HISTORICAL AND INTRODUCTION

Until recently the term "aromatic" as applied to organic compounds was considered synonymous with "benzenoid" (meaning derived from benzene). The ability of these compounds to undergo substitution reactions had long been considered as a principle criterion of aromaticity. However, as a result of the investigations into the chemical reactions of azulene, chemists recognized that cyclic compounds other than benzene derivatives can undergo substitution reactions instead of addition reactions. These observations led to such compounds being classified as "non-benzenoid aromatics".

This thesis, in part, will concern the attempted synthesis of two such non-benzenoid aromatic compounds: octalene 1 and bicyclo[6.2.0]deca-1,3,5,7,9-pentaene 2.



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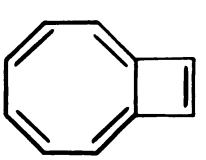


2

The synthesis of either of these two compounds and the study of their physical and chemical properties would serve to support existing theories dealing with the criteria for aromaticity or cause them to be substantially modified.

The most straightforward manner of detecting aromaticity in either of these two compounds would be by obtaining their

nuclear magnetic resonance spectrum. The magnetic field which is applied in obtaining such spectra causes an induced circulation of the delocalized pi-electrons of an aromatic molecule and, therefore, ring currents are established in the molecule. This "ring current effect" is responsible for the deshielding of the protons or any other groups oriented such that they are contained outside of and in the plane of the aromatic ring. Based on this method of experimental investigation, the following definition of an aromatic compound has been suggested: "The essential feature is a ring of atoms so linked that pi-electrons are delocalized right round the ring. We can define an aromatic compound, therefore, as a compound which will sustain an induced ring current. The magnitude of the ring current will be a function of the delocalization of pi-electrons around the ring and therefore a measure of aromaticity."(1).

Although the increased stability of benzene has been recognized for many years, it was not until the 1930's when Hückel, Pauling and others developed the molecular orbital (MO) and valence bond (VB) methods that a theoretical basis for this stability was established (2,3). The most important contributions of these theories were that they proved to be well founded from a physical point of view and they allowed the calculation of the thermochemical resonance energy, a measurable quantity. The change in emphasis of aromaticity from chemical behavior to physical properties illustrates the great success of semiquantitative

calculations of ground states compared with that of chemical reactivity.

The delocalization energy and resonance energy of a molecule are generally used as a criterion for aromaticity. Delocalization energy differs from resonance energy in that the latter has been corrected for strain energy. Thus, delocalization energy is calculated from theoretical treatments and is adjusted by accounting for strain energy to give the resonance energy.

Simple Hückel molecular orbital theory has been used to calculate the delocalization energy of both octalene and bicyclo[6.2.0]decapentaene. In these procedures overlap was neglected, all coulomb integrals were considered equal and all resonance integrals between adjacent carbon atoms were considered equal. The delocalization energy of octalene was calculated (5) to be 4.19β (0.30β per pi-electron), but the delocalization energy is found to be much less (0.28β) when a more sophisticated treatment (6) is used. Allinger and Gilardeau (7) have performed calculations that indicate that the non-planar form of octalene is more stable than the planar form by over 50 kcal/mole. They predict that the molecule will exist in a non-planar configuration with alternating long and short bonds (similar to the tub configuration of two fused cyclooctatetraene molecules). Allinger and Gilardeau (7) have also calculated the expected electronic spectrum for both the planar and non-planar forms of octalene. The calculated delocalization energy of

bicyclo[6.2.0]decapentaene (8) was 2.84β (0.28β per pi-electron) which is somewhat less than delocalization energies of benzenoid aromatics of comparable size (naphthalene is 0.37β per pi-electron). Although the pi-electron delocalization energy provides a measure of the overall stability of a molecule, other contributing factors may in some instances lower or cancel its calculated effect. In each of the above individual cases, the possibility must be taken into account of a reduction in stability due to the considerable angle strain which may be present or due to the possible non-coplanarity of eight-membered rings. Bicyclo[6.2.0]decapentaene, at least, may be more stable in this respect than octalene since the fused four-membered ring should help to flatten out the eight-membered ring.

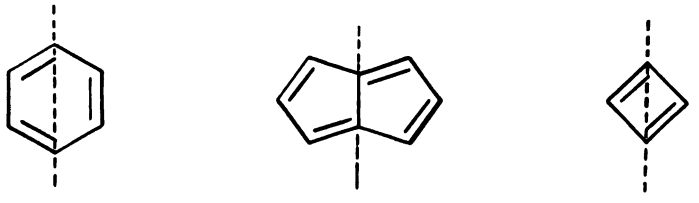
The fundamental concept underlying current ideas on aromaticity is known as Hückel's rule (3). In its general form, the rule derived by Hückel states that "amongst fully conjugated, planar, monocyclic polyolefins only those possessing (4n + 2) pi-electrons, where n is an integer, will have special aromatic stability."

In its earliest form, Hückel's rule was stringently restricted to monocyclic hydrocarbons. Examination of numerous experimental results has indicated that it is also applicable to bicyclic fused systems. This liberalization of the "4n + 2" rule is readily understood if it is assumed that the bridging bond does not introduce any noticeable change in the aromatic character of the molecule but acts

only to preserve the coplanarity of the system. Such a simplification is made more admissible since calculations show that the perturbation caused by the bridging bond in both naphthalene and azulene is small and that it cannot affect the general aromatic nature of the system. If the bridge bond is disregarded in this manner, naphthalene and azulene would be derivable from the ten-membered cyclic hydrocarbon, cyclodecapentaene, which contains ten pi-electrons (i.e. n = 2 in the Hückel 4n + 2 formula) so these compounds should possess aromatic character. In its general form the rule may be stated as "any plane (or nearly plane) fused system containing no atoms common to more than two rings will be aromatic if the number of pi-electrons in it is equal to 4n + 2 (where n is a whole number)" (4).

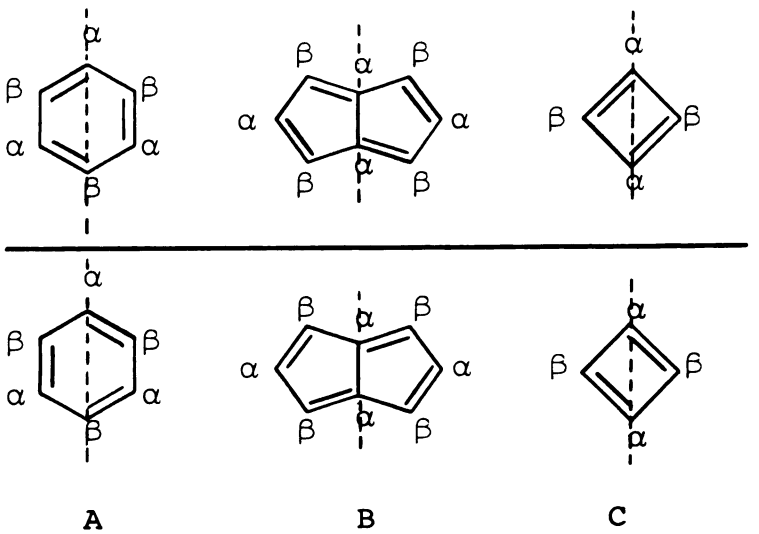
According to the generalized rule, octalene (14 pi-electrons; n = 3) and bicyclo[6.2.0]decapentaene (10 pi-electrons; n = 2) would both be expected to exhibit aromatic character.

Another proposal which has been used to distinguish between normal aromatics and pseudoaromatics (polyolefins) is "Craig's rule". This distinction, as developed by Craig (9), is based on symmetry and applies only to molecules having an axis passing through at least two pi-centers as illustrated by the following molecules.



A molecule such as bicyclo[6.2.0]decapentaene that does not fulfill the symmetry requirement cannot be characterized by this method.

The rule is applied by first labeling each carbon atom of one of the Kekulé-type structures with an <u>alpha</u> or a <u>beta</u> (spin symbols) alternately as far as possible so that each end of a double bond has opposite spins. The molecule is then rotated 180^0 about its axis of symmetry to give another canonical form.



A B C

There are two symbols associated with this operation: p and q. P is equal to the number of <u>pi</u>-centers affected by the rotation and q is equal to the number of <u>alphas</u> and <u>betas</u> which must be interchanged so that the original labeling scheme is restored.

The values of p and q are then applied to the following equation:

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

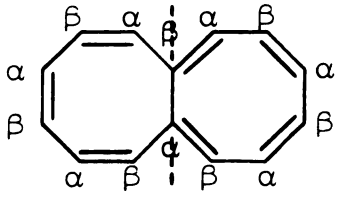
If chi is odd, the molecule has a nontotally symmetrical ground state and is a pseudoaromatic (polyolefin). If chi is even, the molecule has a totally symmetrical ground state and is a normal aromatic.

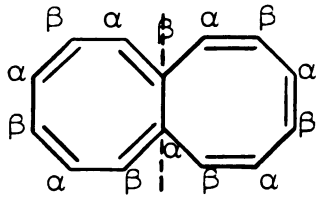
A) Benzene: $p = 2$ because two pi-centers have been interchanged (molecule has been transformed into a Kekulé isomer); $q = 0$ since no change in the labeling system has occurred; $p + q = 2$ and therefore benzene is a normal aromatic since chi is even.

B) Pentalene: $p = 3$ since three pi-centers have been affected in the 180^0 rotation procedure; $q = 0$ for no change in the labeling has occurred; $p + q = 3$ and chi is odd so pentalene is a pseudoaromatic.

C) Cyclobutadiene: $p = 1$ because one carbon atom has been interchanged; $q = 0$ since no change in the alpha and beta labeling has occurred; $p + q = 1$ and cyclobutadiene is a pseudoaromatic.

Since octalene possesses the necessary symmetry requirements (an axis passing through two pi-centers), Craig's rule can be applied.

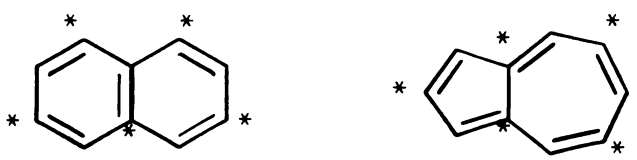




For octalene, $p = 6$ since six pi-centers have been interchanged in going from one Kekulé-type form to the other and $q = 0$ because the alpha and beta labeling system has

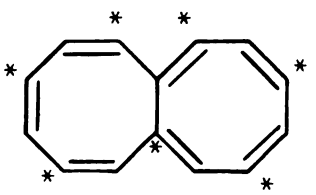
remained unchanged. The value of chi is even and therefore octalene has a symmetrical ground state and should be a normal aromatic.

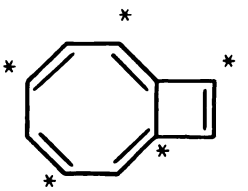
Another classification that has been used to predict aromatic character is the alternant or nonalternant character of a molecule. Coulson and Rushbrooke (10) proposed that alternant or starrable compounds would be aromatic whereas nonalternant compounds would be pseudoaromatic. To be an alternant molecule it is meant that if alternant carbon atoms around the ring are starred no two starred carbon atoms will be adjacent; otherwise it is a nonalternant molecule. Naphthalene would be an example of an alternant molecule while azulene is nonalternant.



The underlying importance of this process is that in an alternant molecule the signs of the atomic orbitals will alternate about the carbon atoms and there can be complete delocalization over the entire molecule. A nonalternant molecule, however, will have at least one position at which the sign of the atomic orbitals on adjacent carbons will be the same and there should be little, if any, pi-electron overlap across this position. Therefore, azulene should show reduced pi-electron overlap across the 9,10-bond and the resonance energy would be expected to be reduced due to this factor.

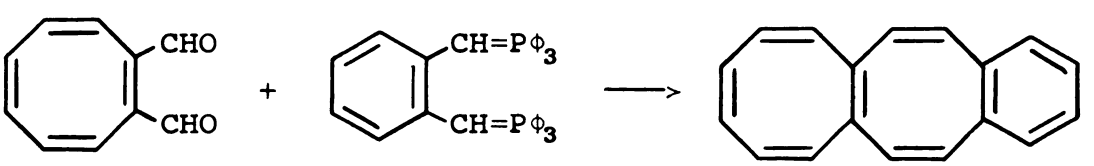
Application of this process to octalene and bicyclo-[6.2.0]decapentaene reveals that both molecules are alternant and should therefore show aromatic character.





Previous Approaches to Octalene

To date, there has been only one report in the chemical literature concerning a successful synthesis of an octalene derivative. Breslow and coworkers (11) prepared benzo[c]octalene 5 in a 1-2% yield from the reaction of 1,8-diformylcyclooctatetraene 3 with the bisphosphorane 4. This octalene derivative was not particularly stable, being

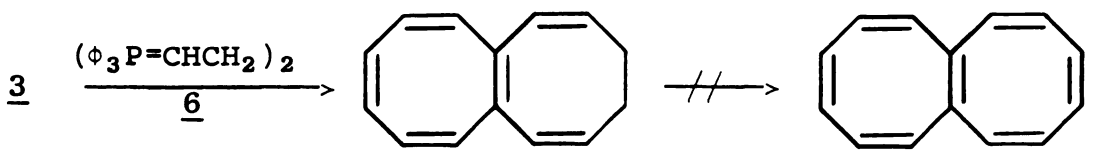


3 4 5

destroyed on exposure to air and, in part, by heat. The octalene protons are unshifted (τ 4.30) from normal cyclooctatetraene protons (τ 4.31). The ultraviolet spectrum (λ max 328 mμ) resembles that of benzocyclooctatetraene (12) (in which the eight-membered ring is in a tub conformation). This data would seem to indicate that the eight-membered

rings exist in an ordinary tub conformation and that benzo-octalene is not aromatic.

Related evidence comes from the reaction (11) of 1,8-diformylcyclooctatetraene 3 with bisphosphorane 6. The product isolated from this reaction in 10% yield, dihydrooctalene 7, resisted all attempts at dehydrogenation to octalene. This would suggest that octalene does not have any striking stability.



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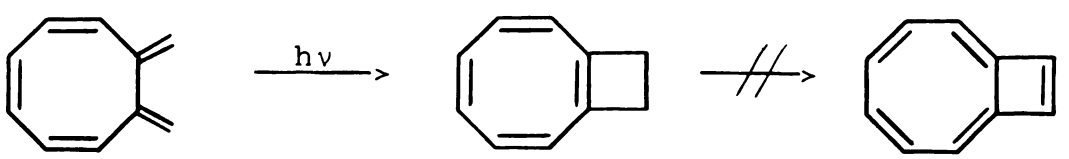
Previous Approaches to Bicyclo[6.2.0]deca-1,3,5,7,9-pentaene

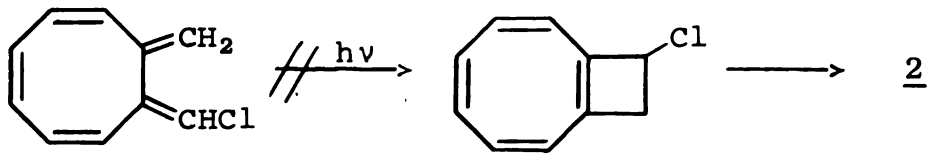
A few unsuccessful attempts to prepare bicyclo[6.2.0]-decapentaene have appeared in the literature. Elix, Sargent and Sondheimer (13) have prepared bicyclo[6.2.0]deca-1,3,5,7-tetraene 9 by the photochemical cyclization of 7,8-dimethyleneecycloocta-1,3,5-triene 8. However, all attempts to con-



8 9 2

vert 9 to the bicyclic decapentaene 2 were unsuccessful. These same authors (14) attempted to prepare a precursor of

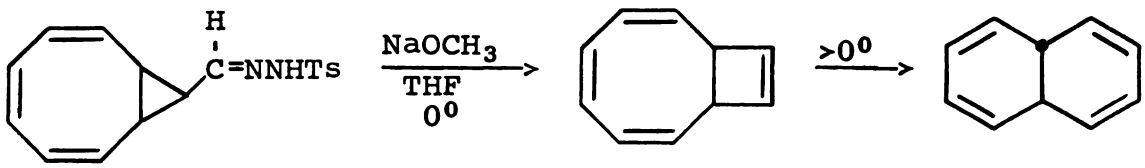
2, 9-chlorobicyclo[6.2.0]deca-1,3,5,7-tetraene 11, by irradiation of 7-methylene-8-chloromethylenecyclooöcta-1,3,5-triene 10. They found, however, that substitution of a chlorine



10 11

atom for a methylene hydrogen in 8 deactivates the exocyclic diene system and causes the endocyclic double bonds to become more photolabile.

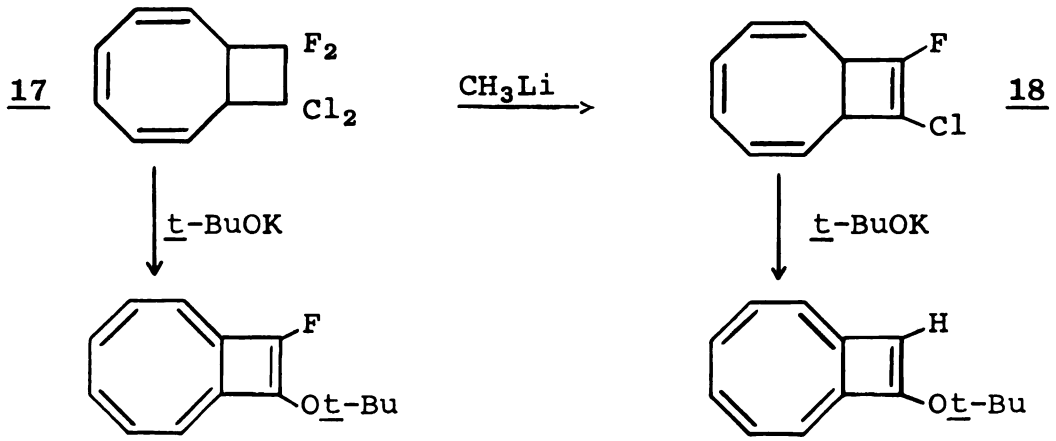
Masamune and co-workers (15) synthesized bicyclo[6.2.0]-deca-2,4,6,9-tetraene 15 by irradiating a solution of bicyclo[6.1.0]nona-2,4,6-triene-trans-9-carboxaldehyde tosylhydrazone 14 in tetrahydrofuran containing an equivalent amount of sodium methoxide at 0°C. However, 15 readily isomerized to trans-9,10-dihydronaphthalene 16 at temperatures above 0°.



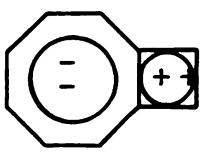
14 15 16

During the preparation of this thesis, Schroder (16) reported the successful synthesis of two substituted bicyclo[6.2.0]deca-1,3,5,7,9-pentaenes. Thus, treatment of the cycloadduct 17 with potassium t-butoxide resulted in

the formation of deep red 8-fluoro-9-t-butoxybicyclo[6.2.0]-decapentaene 19, an extremely air-sensitive but thermally stable compound. In an analogous fashion, 8-t-butoxybicyclo-



19 20

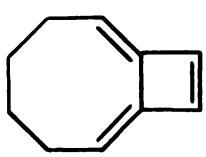


21

[6.2.0]deca-1,3,5,7,9-pentaene 20 could be obtained from 18. The nmr spectrum of 20 showed a multiplet around τ4.0 for the six olefinic eight-membered ring protons while the cyclobutenyl proton absorbs at surprisingly low field (τ2.9).[1]

Schroder has offered the suggestion, based on the nmr data, that 19 and 20 may be best represented by a structure

[1]The cyclobutenyl protons of bicyclo[6.2.0]deca-1,7,9-triene i appear (15) at τ3.40.



i

such as 21. He has also pointed out, however, that additional experiments are required to decide if bicyclo[6.2.0]-decapentaene displays delocalization of the pi-electrons analogous to the isomeric naphthalene and azulene systems.

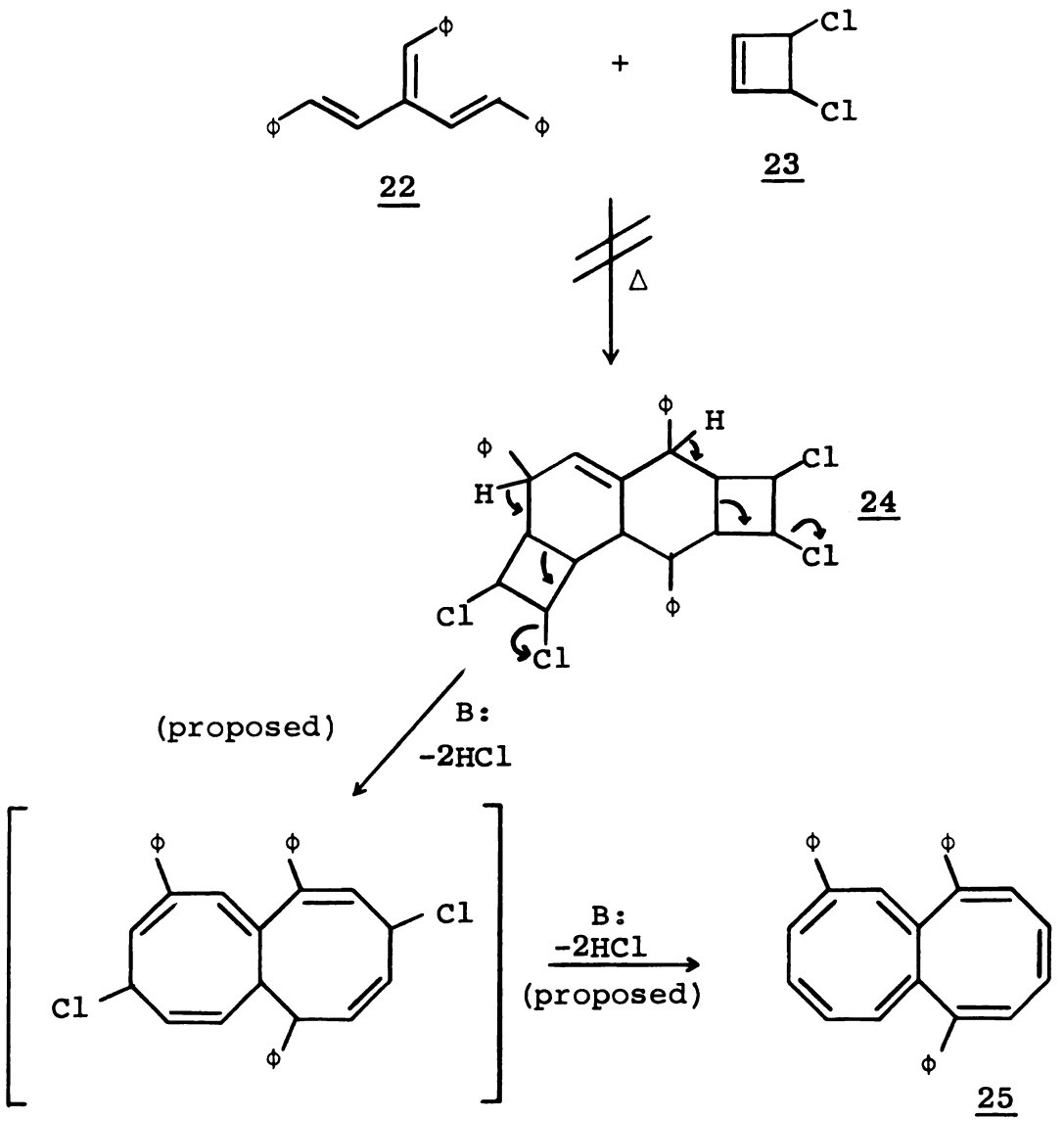
RESULTS AND DISCUSSION

Octalene

The initial goal of this investigation concerned the synthesis of bicyclo[6.6.0]tetradeca-1,3,5,7,9,11,13-heptaene (octalene). The first approach directed toward the synthesis of octalene involved a double Diels-Alder reaction between 1,4-diphenyl-2-styryl-1,3-butadiene 22 and cis-3,4-dichlorocyclobutene 23 (Scheme I). Treatment of the product of this reaction 24 with base was expected to result in the elimination of four moles of hydrochloric acid yielding the desired product, triphenyloctalene 25.

To ascertain if 1,4-diphenyl-2-styryl-1,3-butadiene 22 would enter into a double Diels-Alder reaction, the reaction of 22 with maleic anhydride was performed as a model reaction. The 1,4-diphenyl-2-styryl-1,3-butadiene was synthesized by the method of Bohlman (17). Heating 22 and an excess of maleic anhydride at 120° afforded a 68% yield of the desired double Diels-Alder adduct 26. The Diels-Alder reaction between 22 and cis-3,4-dichlorocyclobutene was then attempted in refluxing xylene. A brown viscous material was isolated, which would not solidify or distill. Attempted purification by column chromatography produced a yellow glassy material, which again would not crystallize. The Diels-Alder reaction was also tried in refluxing benzene and toluene. In both cases, a yellow, presumably polymeric, glassy material was isolated after column chromatography. A possible

Scheme I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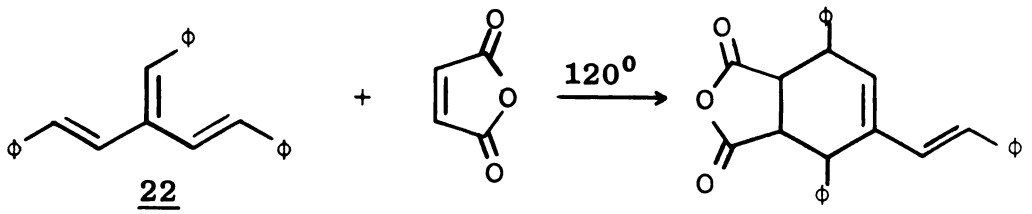
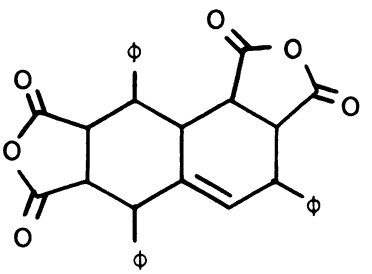
Φ
25

explanation for the failure of this Diels-Alder reaction to occur could be that the rate of thermal isomerization (18)



22



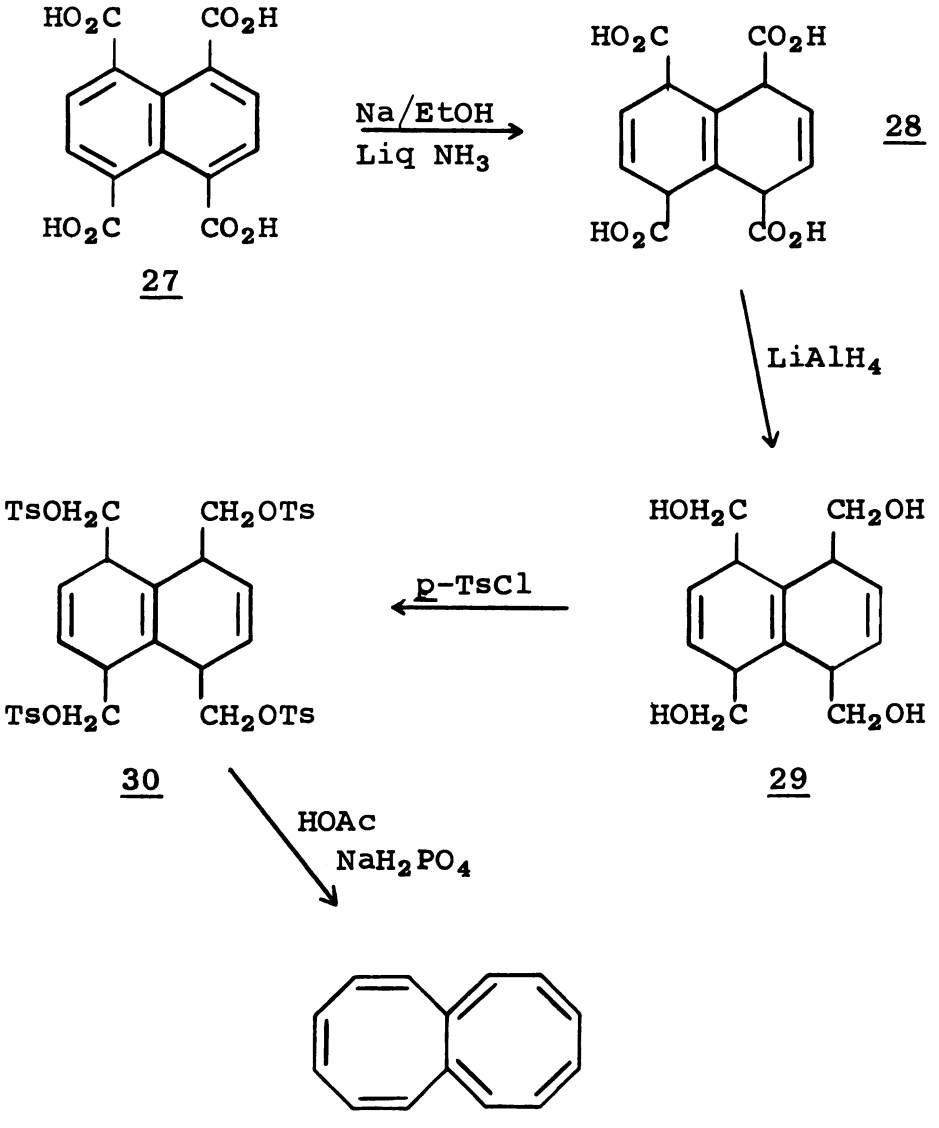
26

of cis-3,4-dichlorocyclobutene to cis, trans-1,4-dichloro-1,3-butadiene is faster than the rate of the Diels-Alder reaction between 22 and cis-3,4-dichlorocyclobutene. The resultant cis, trans-1,4-dichloro-1,3-butadiene could then copolymerize with 1,4-diphenyl-2-styryl-1,3-butadiene 22.

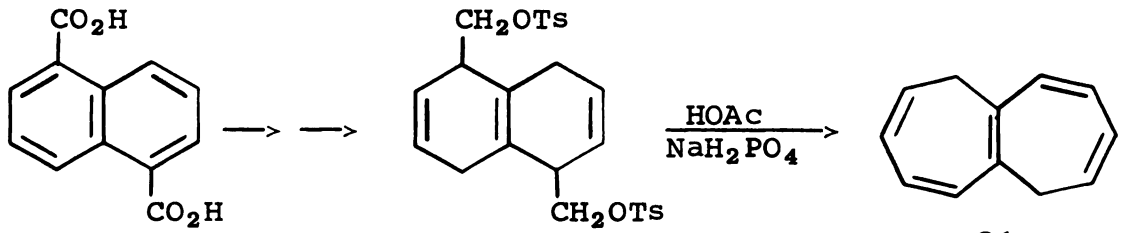
At this point, an alternate pathway for the synthesis of octalene was considered (Scheme II).

This reaction sequence would involve the Birch reduction of 1,4,5,8-naphthalenetetracarboxylic acid 28. Lithium aluminum hydride could then be used to reduce the tetra-acid 28 to the corresponding tetraol 29. The tetratosylate 30, prepared from the tetraol 29, hopefully would ring expand directly to octalene by solvolysis in sodium dihydrogenphosphate-acetic acid solution.

Scheme II


HO2C
CO2H
HO2C
CO2H
27
Na/EtOH
Liq NH3
HO2C
CO2H
HO2C
CO2H
28
LiAlH4
TsOH2C
CH2OTs
TsOH2C
CH2OTs
30
p-TsCl
HOH2C
CH2OH
HOH2C
CH2OH
29
HOAc
NaH2PO4

This reaction sequence is similar to that employed by Dauben and Bertelli (19) for the synthesis of dihydroheptalene 31.



31

There were two main uncertainties connected with this proposed path (Scheme II) to octalene. First, the Birch reduction of 1,4,5,8-naphthalenetetracarboxylic acid was not a known reaction and may be a difficult step to accomplish; second, the ring expansion of a non-benzenoid fused six-membered ring to an eight-membered ring had not been reported.[2]

The Birch reduction of 27 to 1,4,5,8-tetrahydro-1,4,5,8-naphthalenetetracarboxylic acid, as previously mentioned, was not a known reaction. There are no reports of a tetracarboxylic acid successfully undergoing the Birch reduction.

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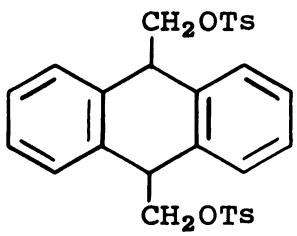
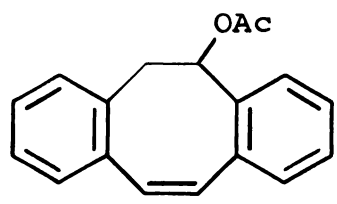
[2] Cis-9,10-bis(hydroxymethyl)-9,10-dihydroanthracene distosylate i has been shown to give mainly the cyclooctatrienol derivative ii on solvolysis with acetic acid buffered with sodium acetate; E. Cioranescu, A. Bucur, M. Banciu and C. D. Nenitzescu, Rev. Roumaine Chim., 10, 141 (1965) (Chem. Abstr., 63, 11456 (1965)).

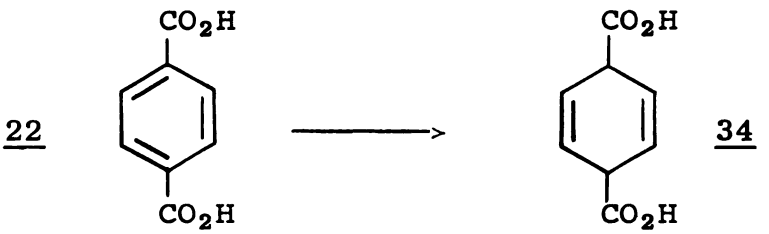


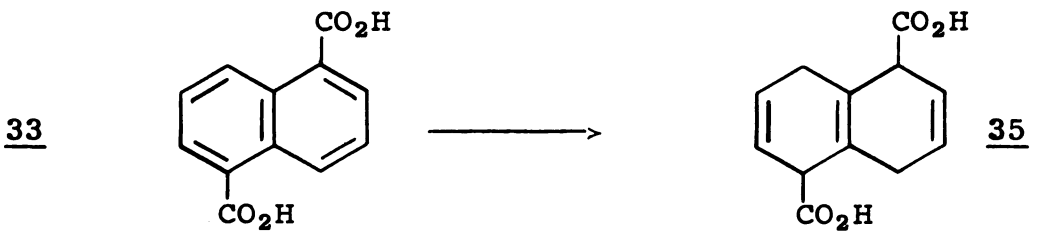
i



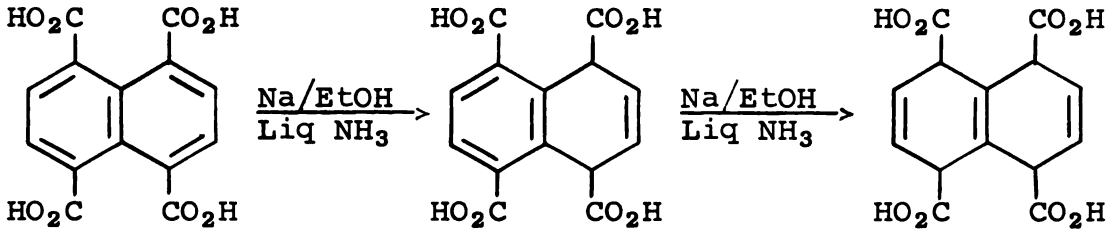
ii

Sodium in liquid ammonia will reduce aromatic para-dicarboxylic acids to give dihydro diacids and in all cases the diacids are non-conjugated, being reduced at the 1,4-position with respect to the carboxyl groups. Thus, terephthalic acid 32 and 1,5-naphthalenedicarboxylic acid 33 were reduced to 1,4-dihydroterephthalic acid 34 (20) and 1,4,5,8-tetrahydro-1,5-naphthalenedicarboxylic acid 35, (19) respectively.





Birch reduction of 1,4,5,8-naphthalenetetracarboxylic acid 27 would be expected to yield the intermediate acid 36, which should undergo further reduction to furnish the desired product 28. Sodium in liquid ammonia does not reduce isolated double bonds so the 2,3-double bond in 36 would be expected to be stable under the reaction conditions (21).

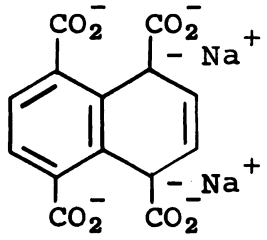


36 28

In initial attempts to carry out the above reduction, crude commercially available 1,4,5,8-naphthalenetetracarboxylic acid 27 was used as the starting material. In all cases, only starting material was recovered. At this point, we concluded that possibly the impurities in the crude tetra-acid were preventing the reduction from occurring. To circumvent this problem the tetra-acid was converted to the tetramethyl ester (22). The ester was a tractable compound that could easily be recrystallized from ethanol-water. The pure tetra-acid 27 could then be regenerated almost quantitatively by saponification in a mixture of methanol and water with potassium hydroxide.

The Birch reduction was attempted on purified 1,4,5,8-naphthalenetetracarboxylic acid 27. The procedure involved the addition of tetra-acid 27 to a solution of six equivalents of sodium ethoxide in liquid ammonia at -78°C (this allowed conversion of tetra-acid 27 to the slightly soluble tetra-sodium salt). Ethanol (12 equivalents) was added as a source of protons (23) to react with the proposed intermediate 37 in the sodium-liquid ammonia reduction. Eight equivalents of sodium were then added in small pieces over an eight

hour period to accomplish the reduction. Since the tetrasodium salt was only slightly (if at all) soluble in the



37

reaction medium, the sodium was added over a long period of time so that equilibrium could be established between additions. After all the sodium had reacted, the ammonia was evaporated with a stream of nitrogen. Acidification of the resultant tan solid produced a solid material which could be recrystallized from boiling water. Analysis showed that the composition of the product agreed with the empirical formula for 1,4,5,8-tetrahydronaphthalene-1,4,5,8-tetracarboxylic acid. A neutralization equivalent on this purified acid with standardized sodium hydroxide gave values of 76.7 and 77.3, both in close agreement to the calculated value of 77.1.

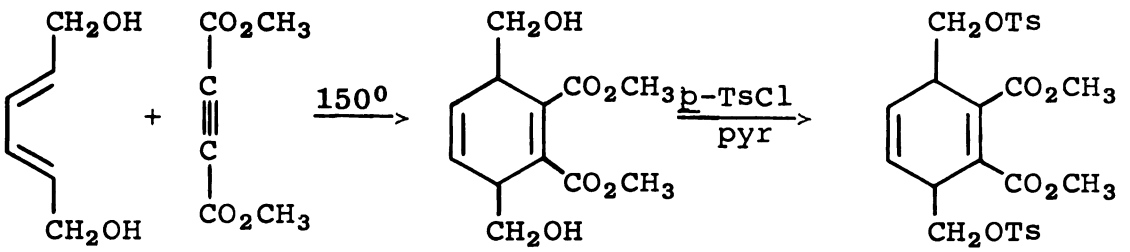
The data indicated that the product had the desired empirical formula and there only remained the problem of establishing its structure. The proof of the structure of the reduced acid was based mainly on the nmr spectrum. The desired product would be expected to show two absorptions in the ratio of 1:1. The observed spectrum showed a one proton singlet at τ5.32 and a one proton singlet at τ7.81 and was consistent with the expected spectrum for 1,4,5,8-tetrahydronaphthalenetetracarboxylic acid 28. The singlet at

τ5.32 was assigned to the olefinic protons, whereas the singlet at τ7.81 would correspond to the allylic protons. Evidently the dihedral angle between the allylic and olefinic protons is about 90^0 since coupling was not observed between the two different protons (24). The protons appearing at τ7.81 underwent deuterium exchange with basic deuterium oxide at 100^0, which would be expected for protons alpha to a carboxylic acid group. From this data, the structure of the reduced acid was assumed to be correct.

Later attempts to prepare the reduced acid 28 occasionally yielded only starting material. An investigation, therefore, was undertaken into possible modifications of the reduction step. Varying the concentration of all reagents revealed that the volume of ammonia employed was critical for the successful Birch reduction of the tetra-acid 27. A successful reduction required at least 100 ml of ammonia per gram of tetra-acid 27. Using the modified procedure, 40-50% yields of 1,4,5,8-tetrahydro-1,4,5,8-naphthalenetetracarboxylic acid 28 could be obtained.

Having successfully accomplished the Birch reduction of 1,4,5,8-naphthalenetetracarboxylic acid 27, the next obstacle involved the ring expansion of a six-membered ring to an eight-membered ring. The ring expansion was attempted on the model compound dimethyl 3,6-bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate di-p-toluenesulfonate 39 (Scheme III). The acetolysis of 39, however, did not yield dimethyl cyclooctatetraene-1,2-dicarboxylate 40, the compound

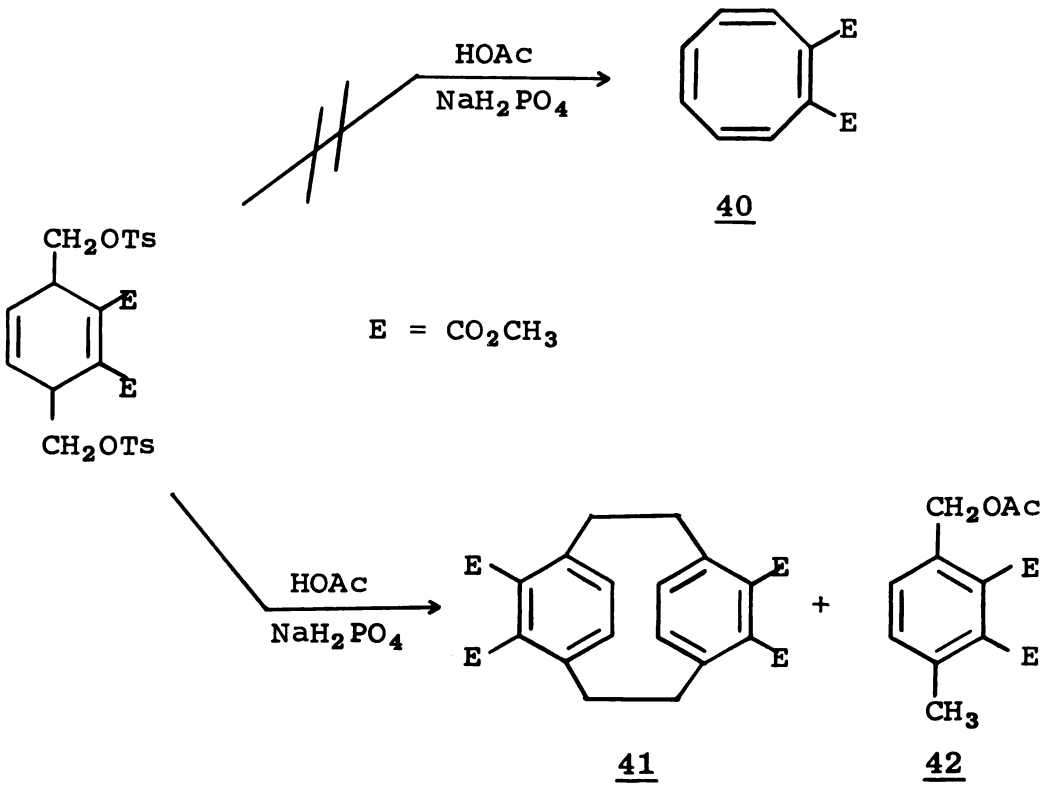
Scheme III



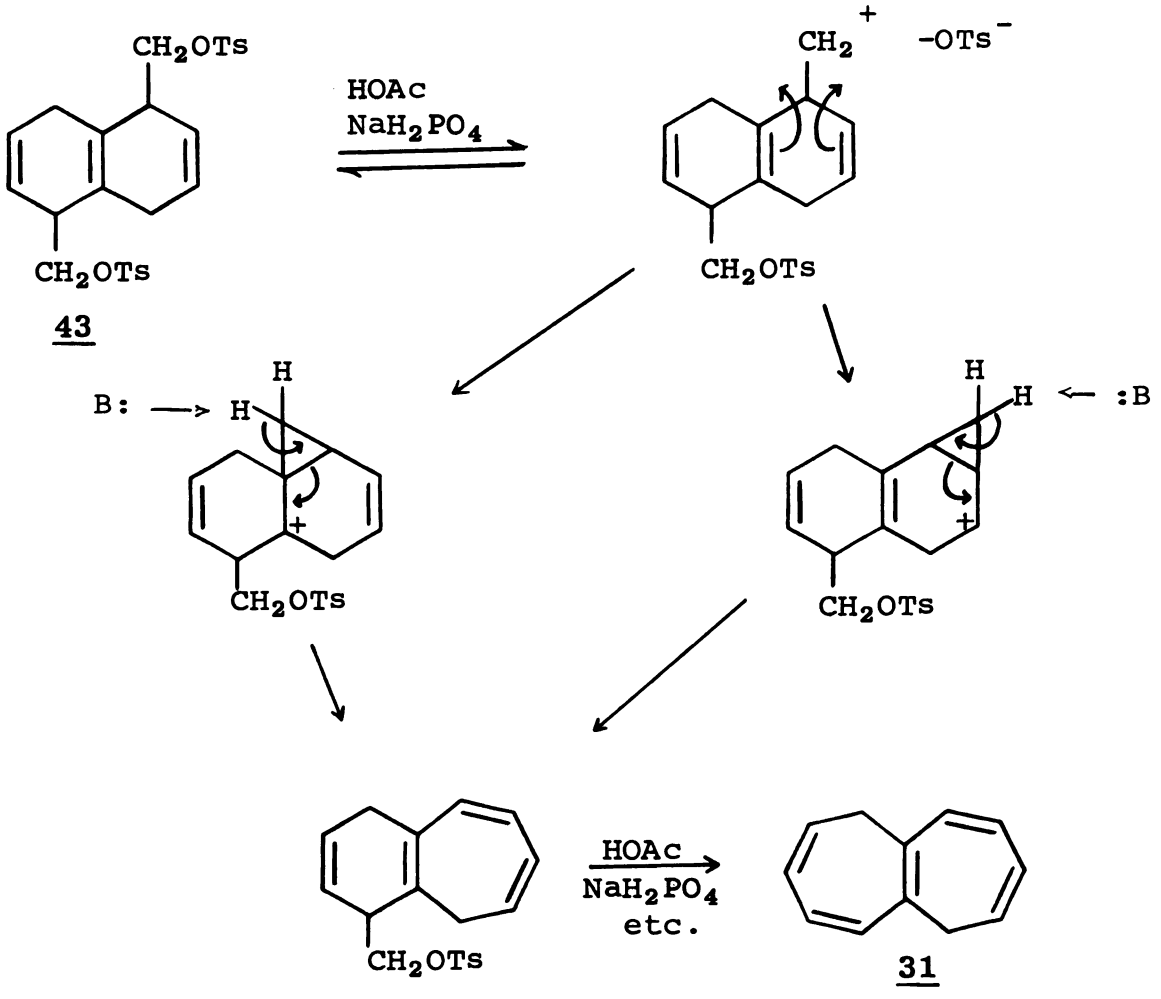
38 39

expected from a double ring expansion. Instead, two new products were isolated: 4,5,12,13-tetracarbomethoxy[2.2]-paracyclophane 41 and what is believed to be 2,3-dicarbomethoxy-4-methylbenzyl acetate 42. The latter compound was not characterized but its structure was consistent with its nmr spectrum, which consisted of a 2H AB quartet (J = 8Hz) centered at τ2.46 (aromatic protons), a 2H singlet at τ5.94 (methylene protons), a 3H singlet at τ6.72 (methyl ester protons), a 3H singlet at τ6.83 (methyl ester protons), a 3H singlet at τ7.82 (methyl group) and a 3H singlet at τ8.21 (acetate protons).

The structure of the paracyclophane 41 was established from its uv and nmr spectra. The uv spectrum of 41 was very similar to that reported (25) for [2.2]paracyclophane. The nmr spectrum of 41 showed a singlet at τ2.93 (4H) for the aromatic ring protons, a singlet at τ6.15 (12H) for the carbomethoxy protons and an A_2B_2 multiplet centered at τ6.80 (8H) for the benzylic protons.

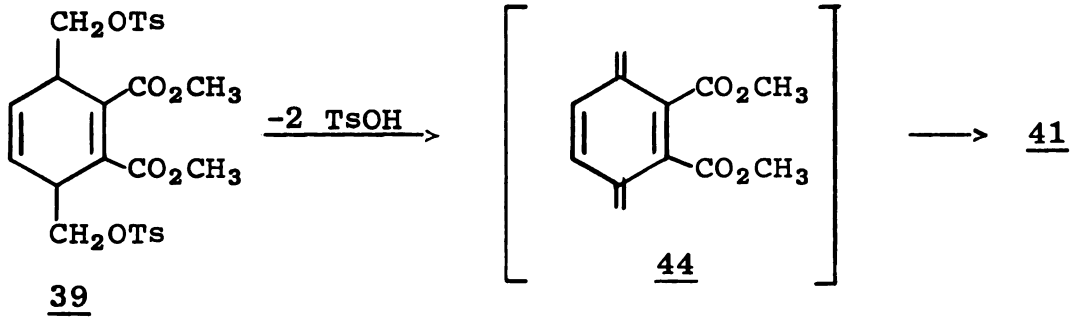


The failure of 39 to undergo a double ring expansion can be explained by considering the mechanism that Dauben and Bertelli (19) have proposed for the ring expansion of 1,5-bis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene di-p-toluenesulfonate 43 to dihydroheptalene 31. Because one of the double bonds in 39 is incorporated into an α,β-unsaturated diester system, this double bond would not participate in the formation of a cyclopropyl carbonium ion. The lack of availability of one of the two double bonds to stabilize the incipient carbonium ion may slow down the rate of ring expansion enough so that elimination of p-toluenesulfinic acid to yield dicarbomethoxy-p-xylylene 44 becomes



the major reaction. Elimination of two p-toluenesulfinic acid molecules would certainly be favored in this case due to the acidity of the 3 and 6 ring protons (γ-protons in an α,β,Δ,ϵ-unsaturated system).

As has been previously pointed out for a similar reaction (26), the dimerization of **44** to **41** must involve a multistep process since the Woodward-Hoffmann selection rules (27) do not allow a direct thermal 6 + 6 electrocyclic reaction.



39 44

This method of preparation of paracyclophanes may have some synthetic utility since the starting bis(hydroxymethyl)-cyclohexadienes can be easily prepared by either of two methods:

a) A Diels-Alder reaction between trans, trans-2,4-hexadiene-1,6-diol and an appropriate acetylene.

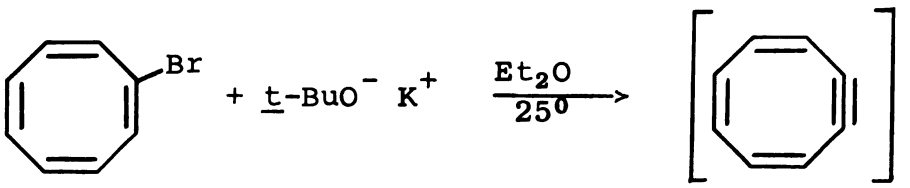
b) Birch reduction of an appropriately substituted aromatic para-dicarboxylic acid followed by hydride reduction to the corresponding diol.

The failure of a six-membered ring to expand to an eight-membered ring coupled with Breslow's (11) publication concerning the preparation of benzo[c]octalene induced us to abandon the synthesis of octalene in favor of bicyclo-[6.2.0]deca-1,3,5,7,9-pentaene.

Bicyclo[6.2.0]deca-1,3,5,7,9-pentaene

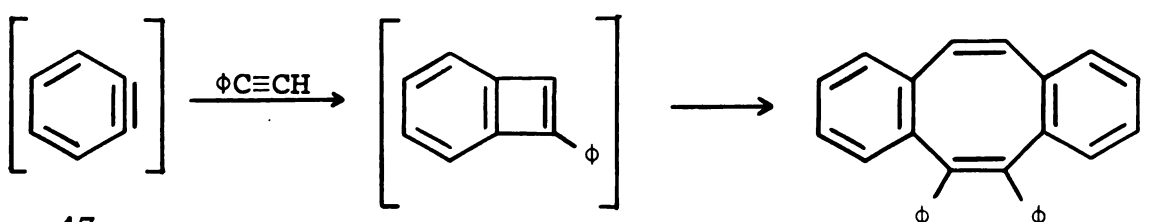
Krebs (28) has reported that treatment of bromocyclo-öctatetraene 45 with an ethereal suspension of potassium t-butoxide yields 1,2-dehydrocycloöctatetraene 46 as a

transient intermediate. The chemical reactivity of 1,2-dehydrocycloöctatetraene (Scheme IV) is very similar to that of benzyne 47 (Scheme V). The chemical similarity of 1,2-



45 46

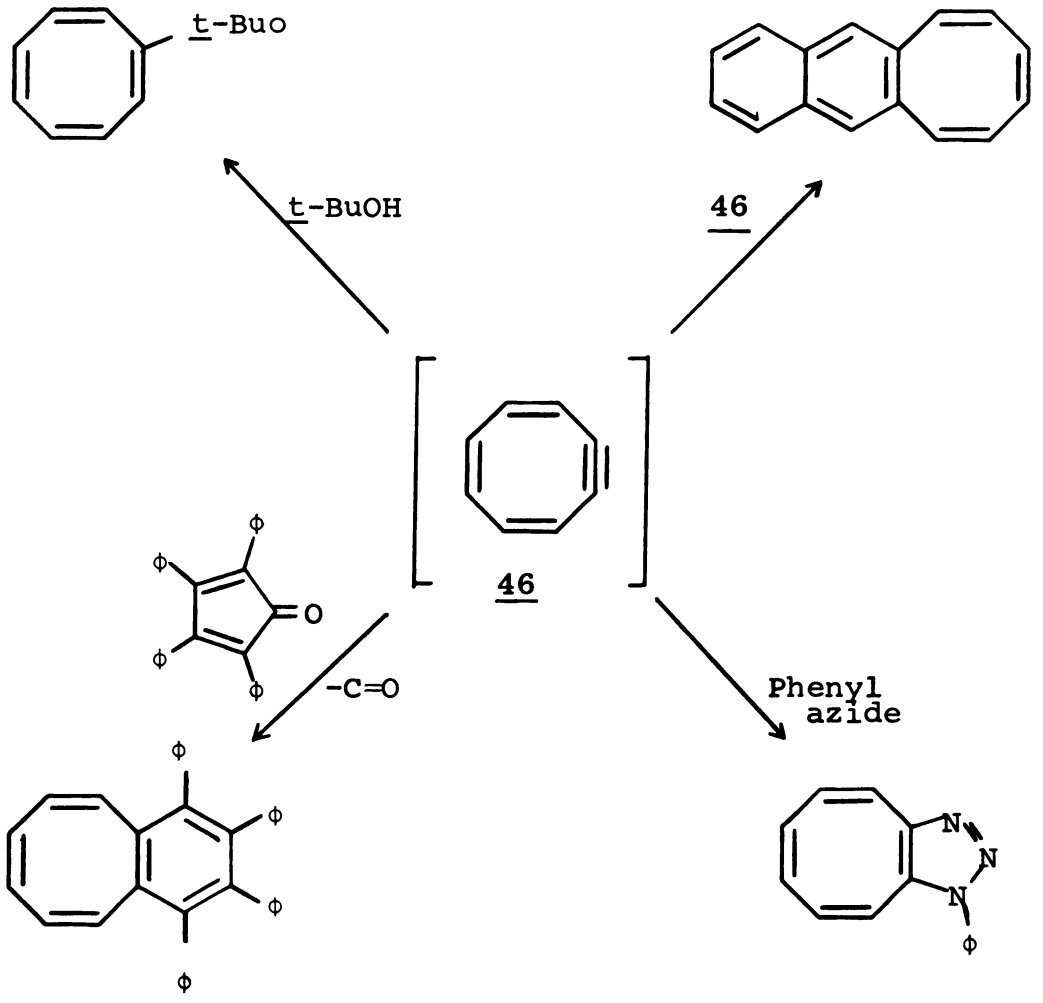
dehydrocycloöctatetraene and benzyne suggested the direct synthesis of a substituted bicyclo[6.2.0]deca-1,3,5,7,9-pentaene 48 by condensation of 1,2-dehydrocycloöctatetraene with a substituted acetylene. This type of reaction has been successfully accomplished with benzyne (29).



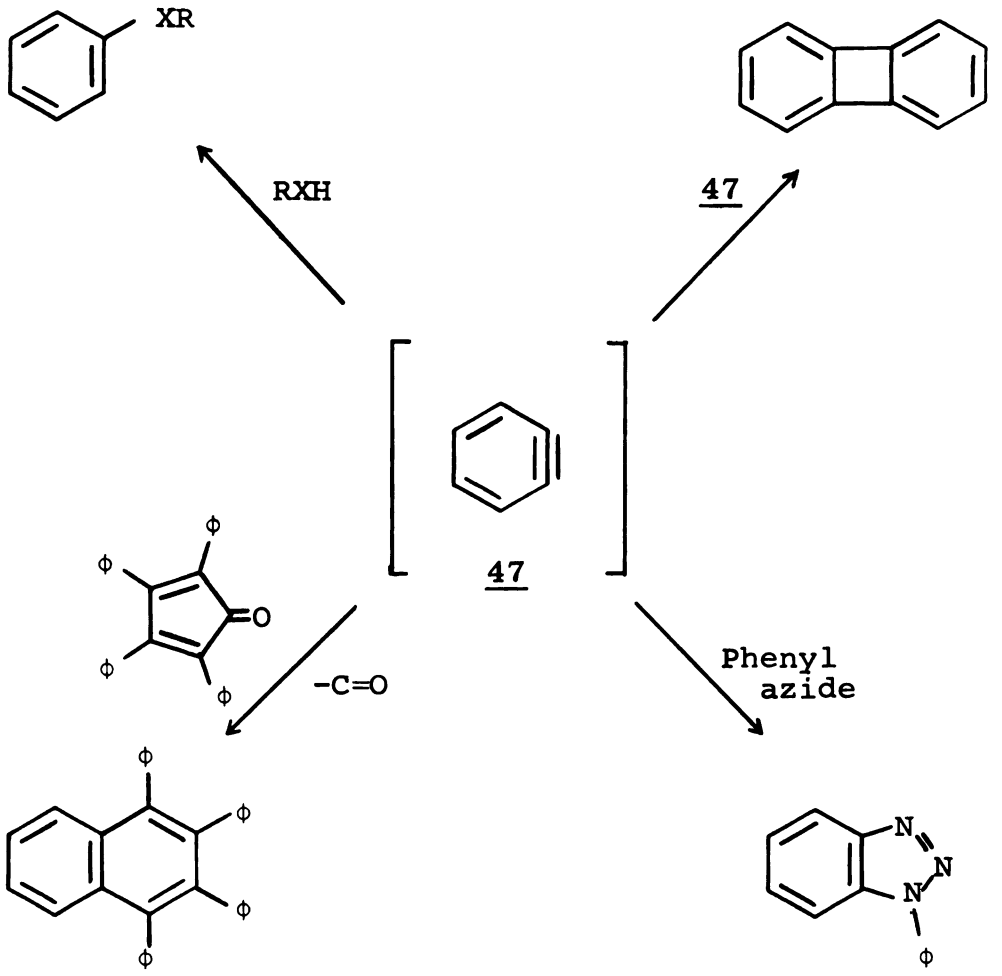
47

1,2-Dehydrocycloöctatetraene was prepared in the presence of a large molar excess of either tolane, 3-hexyne, or 1-methoxy-1-butyne. The only products isolated from these reactions were t-butoxycycloöctatetraene 49 and naphtho-2,3-cycloöctatetraene 50. These two products result from the reaction of 1,2-dehydrocycloöctatetraene with t-butyl alcohol (to form 49) and with itself (to form 50). Potassium t-amylate was also employed as a base to generate 1,2-dehydrocycloöctatetraene. Potassium t-amylate rather than

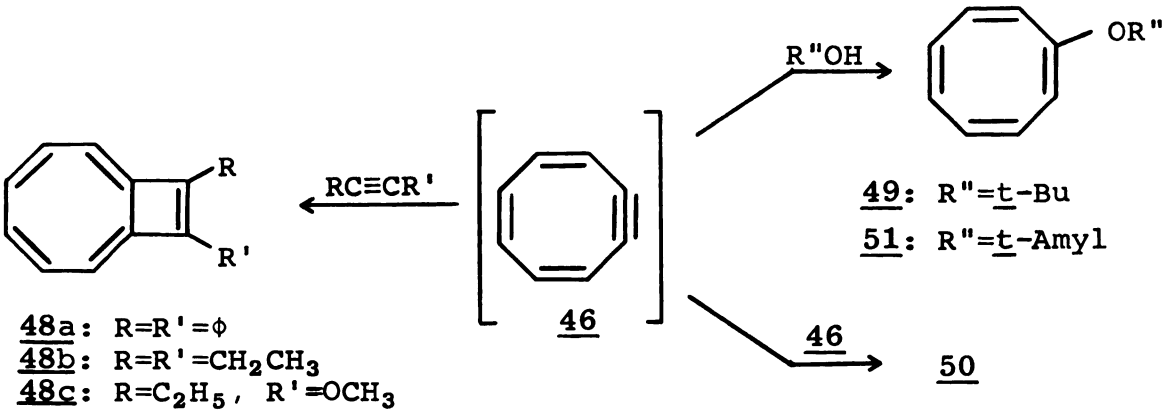
Scheme IV



Scheme V

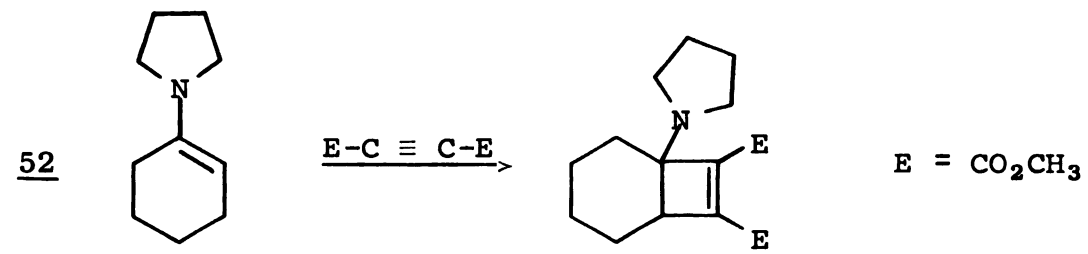


potassium t-butoxide would seem to be the preferred base

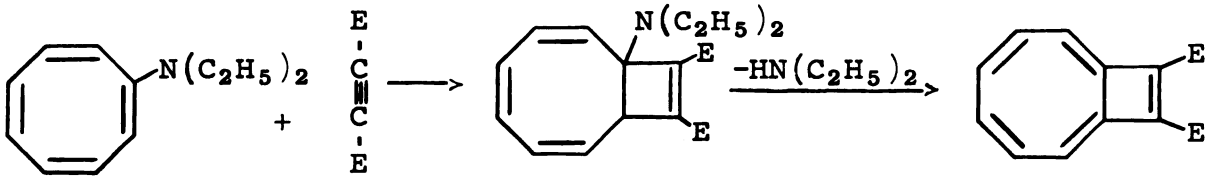


for this reaction because it is soluble in tetrahydrofuran and can be prepared from stoichiometric amounts of potassium and t-amyl alcohol. Preparation in this manner allows the use of an alcohol-free base. Generation of 1,2-dehydrocycloöctatetraene in the presence of 1-methoxy-1-butyne using potassium t-amylate as the base produced only t-amyloxycycloöctatetraene 51 and naphtho-2,3-cycloöctatetraene 50.

The previously reported (30) condensation of N-(1-cyclohexenyl)-pyrrolidine 52 with dimethyl acetylenedicarboxylate appeared to be adaptable to the synthesis of 9,10-dicarbomethoxybicyclo[6.2.0]deca-1,3,5,7,9-pentaene 55. Condensation

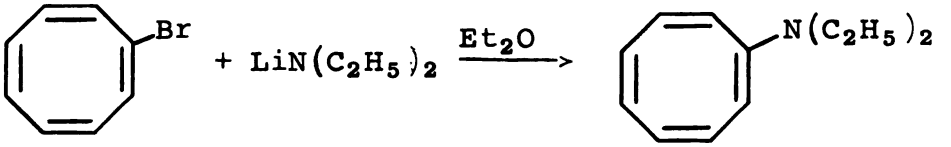


of N,N-diethylaminocycloöctatetraene 53 with dimethyl acetyenedicarboxylate followed by deamination should yield the desired product 55.



53 54 55

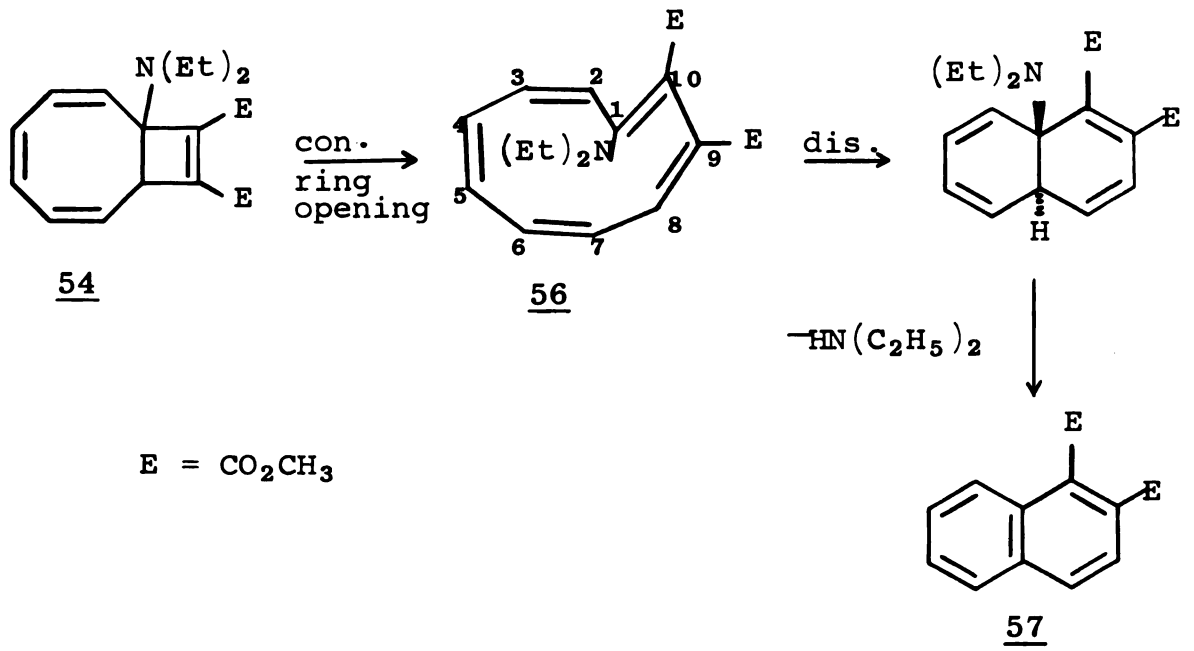
The first step in this synthesis involved the preparation of the previously unknown N,N-diethylaminocycloöctatetraene 53. This synthesis was accomplished by the reaction of bromocycloöctatetraene with lithium diethylamide in



53

refluxing diethyl ether. The structure of 53 was established by the nmr spectrum and hydrolysis in 30% acetic acid to cycloöcta-1,3,5-triene-7-one (isolated as the 2,4-dinitrophenylhydrazone).

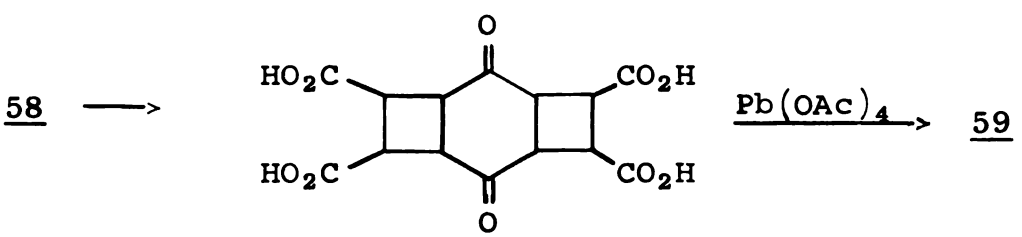
The condensation of 53 with dimethyl acetylenedicarboxylate yielded, instead of 54 or 55, dimethyl naphthalene-1,2-dicarboxylate 57. A logical proposal for this reaction is that the C_1-C_8 bond in 54 opens in a conrotatory process to produce the unstable intermediate 56, which cyclizes in a disrotatory process at C_1 and C_6 accompanied by elimination of diethyl amine to yield the observed product 57.



54 56 57

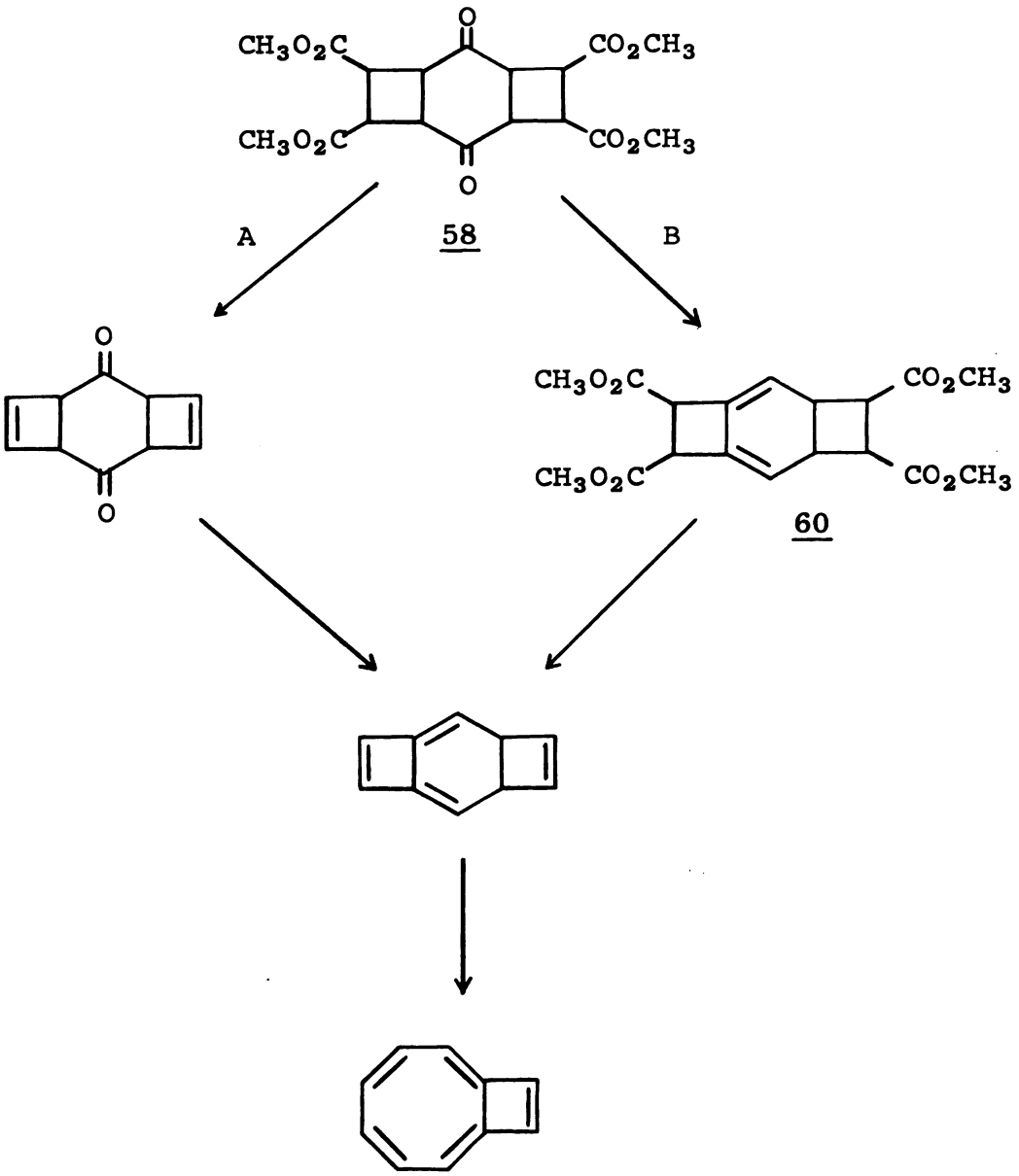
The next approach to the synthesis of bicyclo[6.2.0]-decapentaene utilized tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58 (31). Two possible synthetic approaches to the bicyclic decapentaene were possible (Scheme VI).

Path A would involve the saponification of 58 to the corresponding tetracarboxylic acid 61. Bisdecarboxylation of the tetra-acid 61 should yield tricyclo[6.2.0.$0^{3,6}$]deca-4,9-diene-2,7-dione 59. The synthesis of the tetracarboxylic



61

Scheme VI

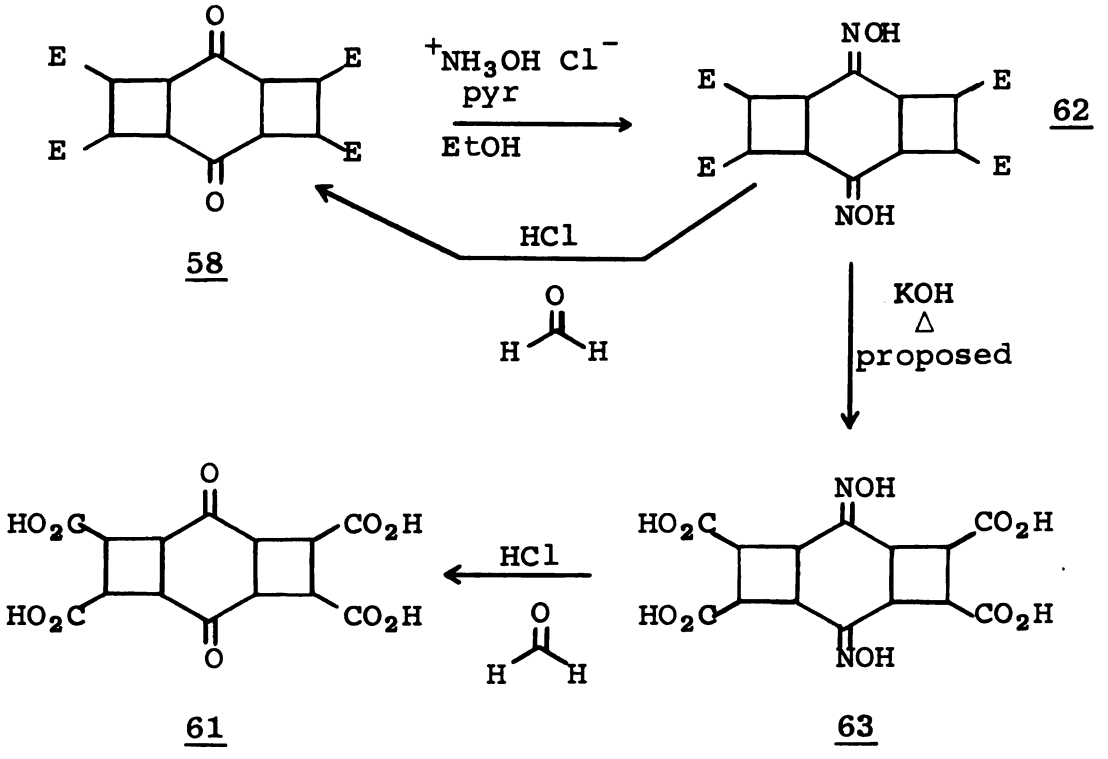

CH3O2C
CO2CH3
CH3O2C
CO2CH3
O
O
58
A
B
O
O
CH3O2C
CO2CH3
CH3O2C
CO2CH3
60

acid 61 has appeared in the literature (32) but all attempts to repeat the reported work failed. Saponification of the tetramethyl ester 58 in either refluxing aqueous potassium hydroxide or dilute hydrochloric acid produced only a glassy polymeric material. The tetramethyl ester 58 and tetracarboxylic acid 61 contain hydrogens α to a keto group. The acidity of these hydrogens could have caused an aldol condensation to occur under the saponification conditions, therefore producing polymeric material. To circumvent this problem, the reaction sequence in Scheme VII was attempted.

The bisoxime derivative 62 of the tetramethyl ester 58 is easily prepared by reaction of 58 with hydroxylamine hydrochloride in refluxing ethanol. The bisoxime derivative can be readily converted to the starting dione by oxime exchange in 40% formalin. Difficulty was encountered in the attempted saponification of bisoxime 62. The product expected from this reaction would be the bisoxime tetracarboxylic acid 63. The acid 63 could not be isolated from the saponification product because of the apparent high water solubility of the product. Structure determination under these conditions was not possible. Attempts to remove the oxime groups from the crude tetra-acid by the formalin method produced only one isolable compound in a poor yield. The structure of this compound was not determined but is is not the reported tetra-acid 61.

At this point, the alternate reaction sequence (Scheme VI; Path B) to tetramethyl tricyclo[6.2.0.$0^{3,6}$]deca-1,7-diene-4,5,9,10-tetracarboxylate 60 was employed. The

Scheme VII

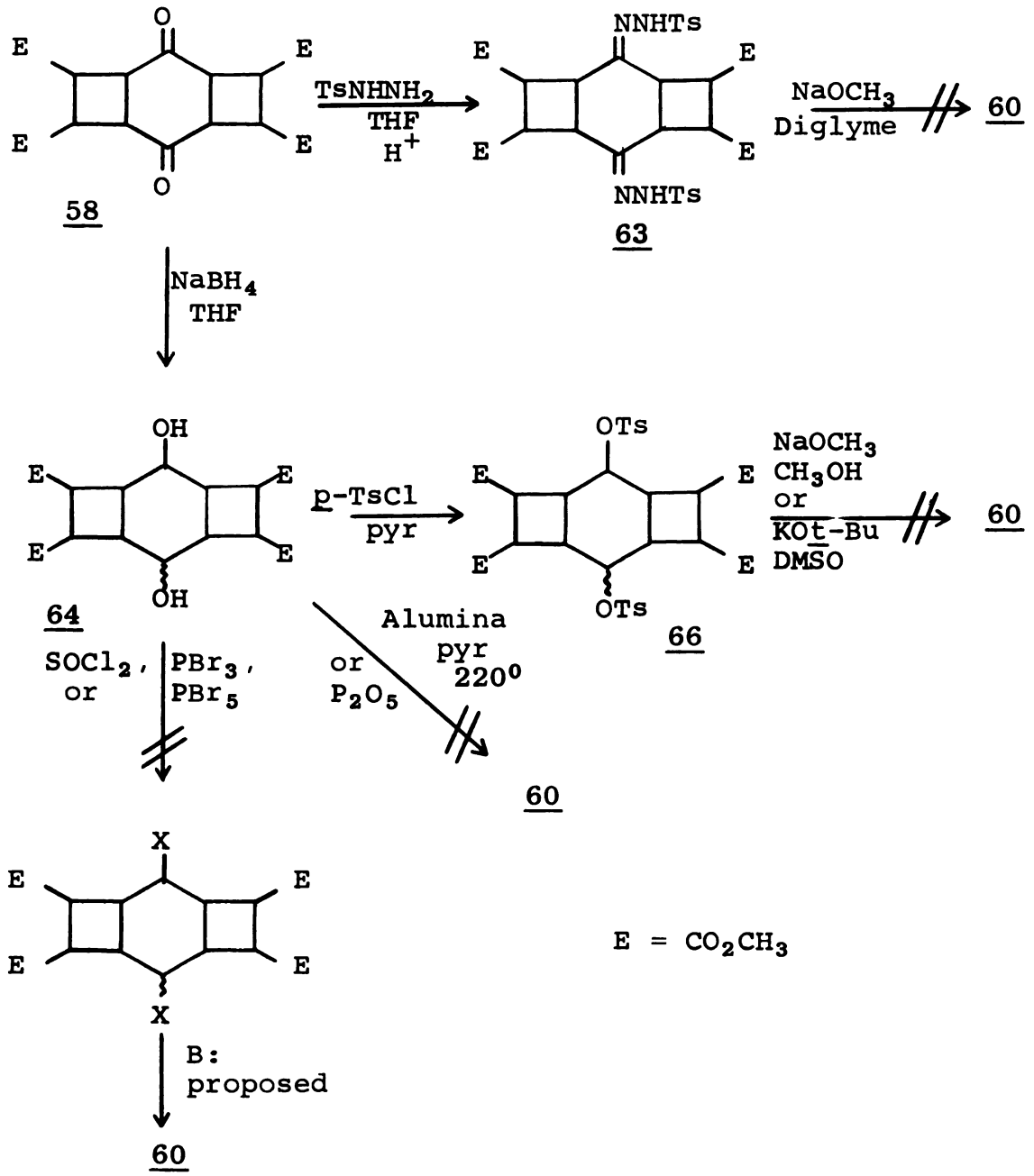

E
E
E
E
O
O
58
+NH3OH Cl-
pyr
EtOH
NOH
NOH
62
HCl
O
H
H
KOH
Δ
proposed
HO2C
HO2C
CO2H
CO2H
O
O
61
HCl
O
H
H
NOH
NOH
63

attempted preparations of 60 are outlined in Scheme VIII.

The preparation of the bistosylhydrazone 63 proceeded smoothly. Attempted formation of the tetramethyl diene ester 60 by reaction of 63 with sodium methoxide in diglyme yielded three products (separated by column chromatography). None of the isolated products showed the presence of olefinic protons in their nmr spectrum so they were not further investigated.

Tetramethyl 2,7-dihydroxytricyclo[6.2.0.$0^{3,6}$]decane-4,5,9,10-tetracarboxylate 64 is obtained in high yield by reduction of the dione 58 with sodium borohydride in tetrahydrofuran at room temperature. The diol is isolated as a viscous oil that presumably contains the three diastereomeric diols possible from the reduction of the dione. Conversion of the diol to the corresponding dichloride or dibromide was attempted with thionyl chloride, phosphorous tribromide, and phosphorous pentabromide. Hydrolysis of the reaction products with dilute hydrochloric acid yielded only the starting diol. Direct dehydration of the diol with a catalytic amount of pyridine absorbed on Woehlm alumina was tried at 220^0. This method has been successfully employed (33,34) for the dehydration of terpenes. However, only starting diol was isolated from this reaction. The failure of the latter two reactions to occur may be due to steric factors encountered in the diol. The six-membered ring of the diol 64 is believed to be in the boat conformation (this assignment will be explained later) with the cyclobutane rings cis fused

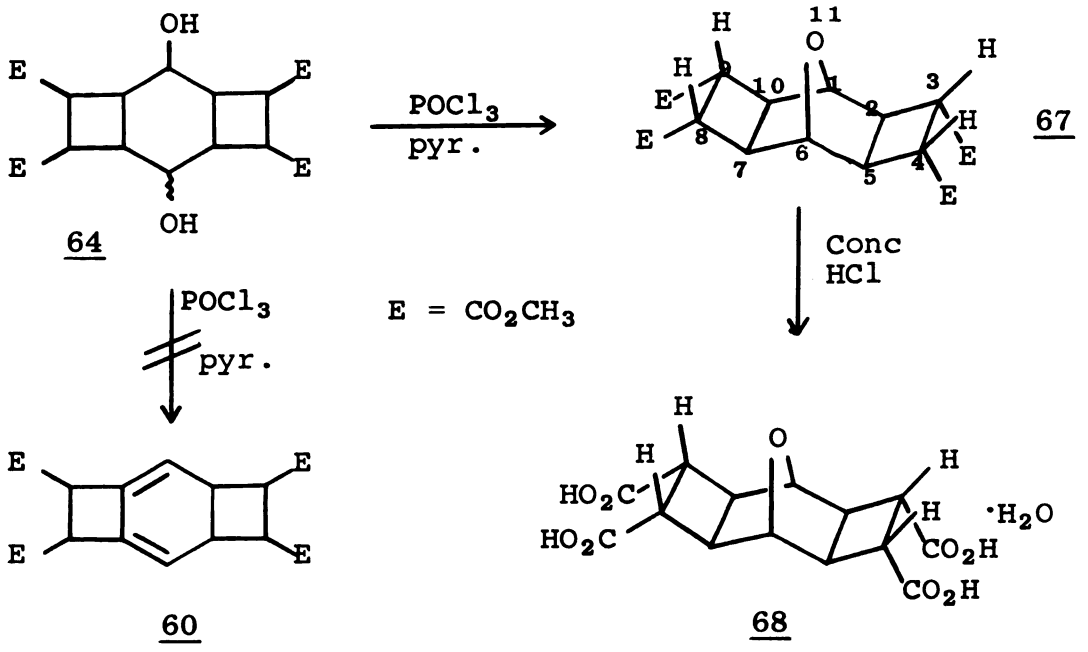
Scheme VIII



to the pseudo-equatorial positions. Molecular models strongly suggest that attack at C_2 or C_7 (carbons at which the hydroxyl groups are attached) will be very unlikely because of shielding of these carbons by either the adjacent hydrogens or the backside of the molecule.

The ditosylate 66 could be obtained by reaction of the diol 64 with p-toluenesulfonyl chloride in chloroform. Formation of the tricyclic decadiene 60 from the ditosylate was attempted using both sodium methoxide in methanol and potassium t-butoxide in dimethyl sulfoxide. Both reaction products yielded one major product (isolated by column chromatography), which did not contain olefinic protons in the nmr spectrum.

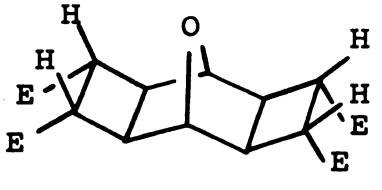
The dehydration of the tricyclic decanediol 64 was also attempted with phosphoryl chloride in pyridine. This reagent has been found (35,36) to be particularly effective for the dehydration of alcohols. The product isolated from the reaction in 16% yield was tetramethyl 11-oxatetracyclo-[4,4,1,$0^{2,5}$.$0^{7,10}$]undecane-3,4,8,9-tetracarboxylate 67. A substantial quantity (75%) of unaltered diol was also recovered. The structure of 67 was established from the elemental analysis and the nmr spectrum, which showed a singlet for the 1 and 6 hydrogens at τ5.65, a singlet for the 12 methyl hydrogens at τ6.32 and a symmetrical A_2B_2 multiplet centered at τ7.0 for the 2,3,4,5,7,8,9, and 10 hydrogens. The A_2B_2 multiplet consists of a multiplet for the 2,5,7,



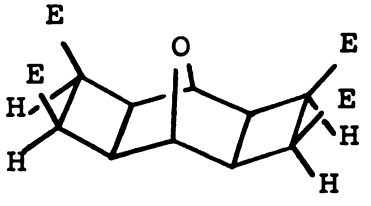
and 10 hydrogens at τ6.78 and a multiplet for the protons (3,4,8, and 9) alpha to the carbomethoxy groups at τ7.22. The assignment for the A_2B_2 multiplet was substantiated by partially exchanging the 3,4,8, and 9 hydrogens of tetra-acid 68 with deuterium using basic deuterium oxide. The nmr spectrum of the partially deuterated tetra-acid 68 showed a decrease in intensity for the low field A_2B_2 absorption as compared to the high field portion of the A_2B_2 multiplet.

The stereochemistry of 67 was assigned by the use of the nmr spectrum, molecular models, and the method of formation of tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58. The simplicity of the nmr spectrum of 67 indicated that the molecule was quite symmetrical. The oxa-bridgehead hydrogens, 1 and 6, are not

split signifying that the dihedral angle between these hydrogens and the 2,5,7, and 10 hydrogens is about 90^0 (24). To meet this requirement, the cyclobutane rings must be cis exo-fused. If the cyclobutane rings were cis endo-fused, models show that the angle between H_1 and H_5, H_7 would be approximately 40^0. In the latter case, a coupling constant of about 5 Hz would be expected. Steric crowding would also preclude the assignment of two cis endo-fused cyclobutane rings in 67. The appearance of the A_2B_2 multiplet in the nmr spectrum of 67 narrows the structure of 67 to two possible stereochemical configurations, 67a and 67b.



67a

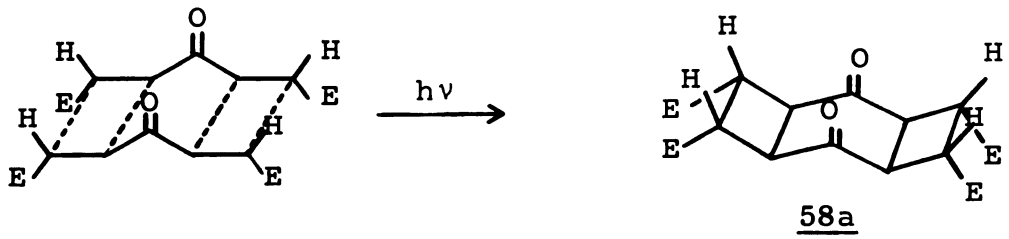


67b

Since the cyclohexane ring of 67 is in the boat conformation, the cyclohexadione ring of tetramethyl tricyclo-[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58, the precursor to 67, should also be in the boat conformation assuming that the stereochemistry of the tricyclic dione 58 has remained unchanged throughout the reaction sequence. The sodium borohydride reduction of the dione 58 should not have altered the stereochemistry of the cyclobutane rings because the low base strength of the borohydride anion usually permits the reduction of a carbonyl function without

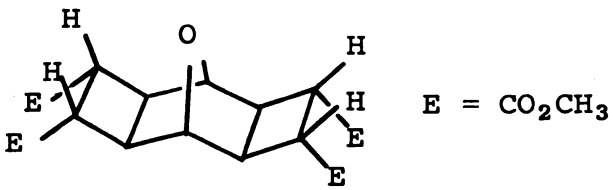
racemization of an adjacent center of asymmetry (37). Since no protonic solvents were present during the reduction, the enolate anion of the dione should not have been produced. Reaction of the reduction product, the tricyclic diol 64, with phosphoryl chloride in pyridine should also proceed without altering the stereochemistry about the cyclobutane rings. When the tricyclic dione 58 was refluxed with pyridine for 2 hours, only the unaltered dione 58 was recovered. This indicates that a basic reagent will not change the stereochemistry of the starting material, the tricyclic dione 58.

Assuming then that the cyclohexadione ring of the tricyclic dione 58 is in the boat conformation and that the stereochemistry has remained unaltered throughout the reaction scheme, the stereochemistry of the cyclobutane rings would follow from the manner of preparation of the tricyclic dione 58. The tricyclic dione 58 was prepared by the photochemical dimerization of dimethyl trans, trans-1,4-pentadiene-3-one-1,5-dicarboxylate (32). Dimerization in a head to head fashion would produce the tricyclic dione 58, which contains the cyclohexadione ring in a boat conformation. The carbomethoxy groups would then be cis to each other and trans to the cyclohexadione-cyclobutane ring junction. The stereochemistry of tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58 would therefore be as shown for 58a. The cyclobutane rings of tetramethyl 11-oxatetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]undecane-3,4,8,9-tetracarboxylate



58a

67 should also possess this stereochemistry and structure 67a would appear to be correct.

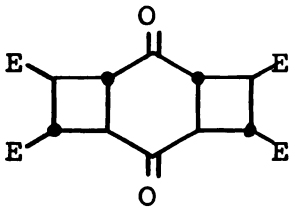


67a

Corse, Finkle and Lunkin (38) have reported that the configuration of the tricyclic dione 58 consists of the cyclobutane rings being joined by trans fusions to the cyclohexadienone ring and the protons alpha to the carbomethoxy groups on the same four-membered ring must be trans to each other and trans to the adjacent protons on the junction carbon atoms. Their assignment was based solely on the nmr spectrum (taken in trifluoroacetic acid), which showed a pair of incompletely resolved multiplets centered at τ5.30 and τ5.80 and a single methoxyl resonance at τ6.09. The configuration 58a would also be in agreement with this nmr spectrum.

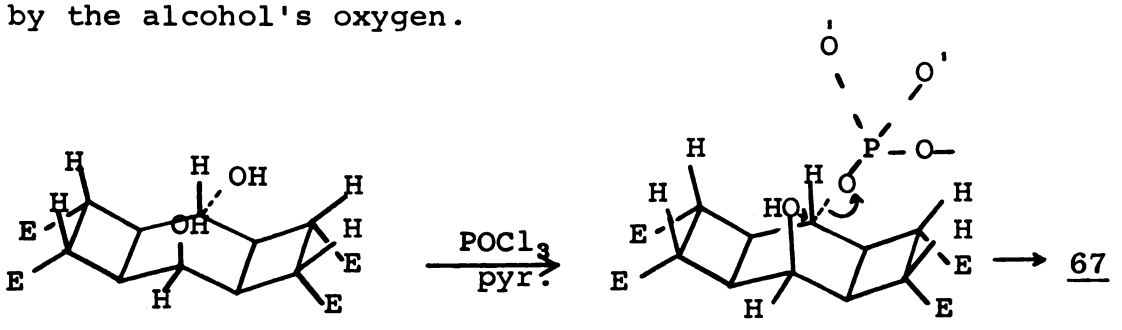
The configuration 58b of the tricyclic dione, as proposed by Corse and co-workers, contains two cyclobutane rings trans fused to the cyclohexadione ring. It would be expected

that under the influence of a mild base (pyridine) the junction carbon atoms adjacent to the carbonyl groups would be

58b  E = CO_2CH_3

epimerized to the more stable cis fused cyclobutane rings. This type of transformation has been reported by Corey and co-workers (57). Since only the unaltered tricyclic dione was recovered after refluxing in pyridine, the stereochemical assignment 58a rather than 58b would seem to be preferred.

Only one of the three possible diastereomeric diols, 69, can yield the observed tetracyclic ester 67. The other two diastereomeric diols probably do not react under the reaction conditions and are therefore recovered after hydrolysis. The mechanism of formation of 67 from 69 most likely occurs through an SN_2 displacement of the phosphate group by the alcohol's oxygen.



69 E = CO_2CH_3

EXPERIMENTAL

General Procedures

All infrared spectra were obtained on a Perkin-Elmer Model 237B recording spectrophotometer, using sodium chloride cells. The nmr spectra were obtained with a Varian A-60 or Jeolco C-60H spectrometer. Chemical shifts are reported as τ values measured from either tetramethylsilane or, when D_2O was used as the solvent, sodium 2,2-dimethyl-2-silapentane-5-sulfonate. All ultraviolet spectra were measured with a Unicam Model SP-800 using 1 cm quartz cells. Mass spectra were obtained by M. Petschel of this department with a consolidated Electrodynamics Corp. Mass Spectrometer Type 21-103C. Analysis by vpc was carried out on an Aerograph A-90-P3 instrument with a thermal conductivity detector using a 15% carbowax 20M column, 5' x $\frac{1}{4}$".

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected.

All microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

The molecular models used were Framework Molecular Models by Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Diels-Alder Reaction of 22 with Maleic Anhydride

1,4-Diphenyl-2-styryl-1,3-butadiene, 1 g (0.00325 mole), and an excess (3 g) of maleic anhydride were dissolved in

5 ml of anhydrous toluene. The mixture was refluxed for 48 hr under an atmosphere of nitrogen. The toluene was evaporated under reduced pressure and the unreacted maleic anhydride was removed by sublimation at 90° under reduced pressure. The resulting brown oil solidified on cooling. The solid material was refluxed with chloroform and the insoluble white crystalline material was removed by filtration. The Diels-Alder adduct was dissolved in acetone and freed of insoluble material by filtration. Evaporation of the acetone produced 1.109 g (68%) of the dianhydride 26 as a white crystalline solid: m; 305-308°; uv(CH_3CN) 230 (ϵ 1650), 253 (910), 259 (870), 265 (695), and 310mμ (520).

Anal. Calcd for $C_{32}H_{24}O_6$: C, 76.18; H, 4.79. Found: C, 76.26; H, 4.90.

1,4,5,8-Tetrahydro-1,4,5,8-naphthalenetetracarboxylic Acid 28

A 1-l., three-necked, round-bottomed flask was equipped with a mechanical stirrer, dry ice condensor and dropping funnel and cooled in a dry ice-acetone bath. Ammonia (700 ml) was distilled into the flask and 23 ml (0.39 mole) of absolute ethanol was added dropwise with stirring. Sodium, 3 g (0.1305 mole), was then added in 0.1 g pieces. After the sodium had dissolved (30 min), 7 g (0.0232 mole) of 1,4,5,8-naphthalenetetracarboxylic acid was added and the suspension was stirred for 30 min. Sodium, 4.5 g (0.191 mole), was added in small pieces (0.2 g) over an 8 hr period maintaining the temperature at -80°. After the complete

addition and reaction of the sodium, the ammonia was allowed to evaporate. The resulting tan solid was dissolved in 150 ml of water, filtered free of insoluble material, and acidified to pH 1 with 6N hydrochloric acid. The solution was evaporated to dryness under reduced pressure and the tan residue was diluted with 100 ml of cold water. The crude tetra-acid was removed by filtration. Two recrystallizations from boiling water produced 2.8 g (40%) of 1,4,5,8-tetrahydro-1,4,5,8-naphthalenetetracarboxylic acid as colorless plates: mp 228-229°; ir (Nujol) 3300-2500 (s, broad), 1700 (s, broad), 1330 (s), 1273 (m), 1198 (s), 920 (w), and 773 (w) cm^{-1}; nmr (NaOD in D_2O) τ5.32 (s, 4), and τ7.81 (s, 4).

Anal. Calcd for $C_{14}H_{12}O_8$: C, 54.55; H, 3.92. Found: C, 54.53; H, 4.05.

Dimethyl 3,6-Bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate 38

2,4-Hexadiene-1,6-diol (39), 0.8 g (0.007 mole), was combined with 2.5 g (0.014 mole) of dimethyl acetylenedicarboxylate and the resulting semisolid was heated at 150° for 24 hr under an atmosphere of nitrogen. The unreacted dimethyl acetylenedicarboxylate was removed under reduced pressure at 90°. The orange residue was dissolved in a minimal amount of boiling ethyl acetate and cooled to 0° producing 0.338 g (19%) of the diol 38 as a yellow crystalline solid: mp 99.5-102°; ir (Nujol) 3300 (m, broad), 1702 (s),

1628 (w), 1270 (s), 1068 (m), and 823 (m) cm^{-1}; nmr ($CDCl_3$) τ4.16 (m, 2), 6.62 (m, 2), and 6.21 (m 12).

Dimethyl 3,6-Bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate Di-p-toluenesulfonate 39

p-Toluenesulfonylchloride, 2.7 g (0.014 mole), recrystallized from 90-120° petroleum ether (mp 64-65°), was dissolved in 10 ml of dry pyridine (distilled from potassium hydroxide). This solution was added dropwise to 0.83 g (0.0065 mole) of dimethyl 3,6-bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate 38 dissolved in 5 ml of dry pyridine at a temperature of -6 to 0°. The mixture was kept overnight at 0°. The pyridine was removed under reduced pressure at room temperature and the dark red residue was dissolved in 50 ml of chloroform. The chloroform solution was washed with 50 ml of ice cold 10% hydrochloric acid and 50 ml of 5% sodium bicarbonate. The chloroform extract was separated, dried ($MgSO_4$), and concentrated producing a dark red oil: ir (Neat) 2945 (m), 1710 (s), 1595 (m), and 1365 (s) cm^{-1}. All attempts to crystallize the ditosylate failed so the crude ditosylate was used for the following ring expansion.

Attempted Ring Expansion of 39

Acetic acid (100 ml) was combined with acetic anhydride (20 ml) and refluxed overnight. The acetic acid used for the following solvolysis was obtained from this mixture by distillation through a 12 inch Vigreaux column (bp 117-118°).

Crude dimethyl 3,6-bis(hydroxymethyl)-1,4-cyclohexadiene-1,2-dicarboxylate di-p-toluenesulfonate 39, 1.65 g (0.00293 mole), was added to a solution of sodium dihydrogenphosphate monohydrate, 1.8 g (0.013 mole), in dry acetic acid (20 ml) in a 100-ml, three-necked, round-bottomed flask, fitted with a mechanical stirrer, reflux condensor, nitrogen inlet and outlet and thermometer. The mixture, blanketed with dry nitrogen, was heated to 90^0 with an oil bath for 22 hr. The dark brown solution was transferred to a 400 ml beaker. The glassware was rinsed with water and ether and combined with the original solution. Ether (150 ml) was added and the two-phase system was cooled to 6^0 in an ice bath. Next, a solution prepared by dissolving 24 g of potassium hydroxide in 400 ml water was added dropwise with stirring at $6\text{-}12^0$ until the pH of the aqueous layer was 14. The ethereal extract was separated, washed with water, dried ($MgSO_4$) and concentrated producing a yellow semisolid. The crude semisolid was dissolved in hot methanol and upon cooling white crystals formed. Two recrystallizations from methanol produced 0.134 g (21%) of 4,5,12,13-tetracarbomethoxy-2,2-paracyclophane 41 as colorless needles: mp $203\text{-}204.5^0$; uv (ethanol) 215 (ϵ 2,260), 270 (170) and 302 mμ (170); ir (Nujol) 1717 (s), 1188 (s), 1164 (m), 1128 (m), 1104 (m), 1004 (w), 873 (w), and 800 (w) cm^{-1}; nmr ($CDCl_3$) τ2.93 (s, 4), 6.15 (s, 12), and 6.80 (m, 8).

Anal. Calcd for $C_{24}H_{24}O_8$: C, 65.45; H, 5.49. Found: C, 65.46; H, 5.40.

Distillation of the crude methanol solution produced what is believed to be 2,3-dicarbomethoxy-4-methylbenzyl acetate 42: bp 70-74° (3 mm); ir ($CHCl_3$) 2946 (m), 1747 (s), 1712 (s), 1600 (w), 1375 (s), 1221 (s), 1177 (m), 1050 (m), 1009 (m), and 922 (m) cm^{-1}; nmr ($CDCl_3$) τ2.29 (d, 1, J = 8 Hz), 2.71 (d, 1, J = 8 Hz), 5.94 (s, 2), 6.72 (s, 3), 6.83 (s, 3), 7.82 (s, 3), and 8.21 (s, 3).

9,10-Diethylbicyclo[6.2.0]deca-1,3,5,7,9-pentaene 48b (Attempted)

Bromocyclooctatetraene (48), 5 g (0.0273 mole), in 10 ml ether was added dropwise over a period of 1.5 hr to a stirred suspension of 75 ml (54.2 g; 0.66 mole) of 3-hexyne, 75 ml of ether and 4 g of potassium t-butoxide under nitrogen. The dark brown suspension was stirred at room temperature for 20 hr. The suspension was hydrolyzed with 100 ml of deoxygenated water. The ethereal layer was separated, dried (Na_2SO_4), and concentrated to a volume of 10 ml by evaporation under reduced pressure at room temperature. The residue was column chromatographed under an atomosphere of nitrogen on silicic acid (100 g) eluting with deoxygenated carbon tetrachloride-benzene (15% benzene). Evaporation of the eluents with a stream of nitrogen produced 0.729 g (15%) of t-butoxycyclooctatetraene: bp 38-39° (0.55 mm) [lit. (28) bp 37-38° (0.05 mm)] and 0.458 g (7%) of naphtho-2,3-cyclooctatetraene: mp 109-112° [lit.(28) mp 113-114°].

9-Ethyl-10-methoxybicyclo[6.2.0]deca-1,3,5,7,9-pentaene 48c (Attempted); Preparation of t-Amyloxycyclooctatetraene 51

A solution of potassium t-amylate in tetrahydrofuran was prepared by adding 2 g (0.05 mole) of potassium to a solution of 2.64 g (0.03 mole) of t-amyl alcohol (distilled from sodium) in 50 ml of dry (distilled from calcium hydride) tetrahydrofuran and refluxing with stirring under nitrogen for 90 hr. The solution was cooled and the unreacted potassium was removed by fitration under nitrogen. The potassium t-amylate solution was found to be 1.075 molar by titration of a 2-ml aliquot with 0.0983N hydrochloric acid.

A solution of potassium t-amylate in tetrahydrofuran, 27 ml (0.029 mole), was added dropwise over a 30 min period to a solution containing 10 ml of dry tetrahydrofuran, 20.4 g (0.25 mole) of 1-methoxy-1-butyne (40), and 5 g (0.0273 mole) of bromocyclooctatetraene with stirring under nitrogen at room temperature. The solution immediately turned brown and warmed slightly. Stirring was continued for 42 hr. The suspension was hydrolyzed with 50 ml of deoxygenated distilled water and 150 ml of ether was added. The ethereal layer was separated, washed with two 50-ml portions of saturated sodium chloride and concentrated under reduced pressure at room temperature. The residue was chromatographed under nitrogen on silicic acid (100 g) eluting with carbon tetrachloride-methylene chloride (23% methylene chloride). Evaporation of the eluents with a stream of nitrogen produced

0.339 g (6%) of naphtho-2,3-cyclooctatetraene: mp 110-112° [lit. (28) mp 113-114°] and 1.27 g (21%) of t-amyloxycyclooctatetraene: bp 46-48° (0.15 mm); ir (Neat) 3000 (s), 2979 (s), 2940 (m), 2880 (w), 1633 (s), 1460 (m), 1398 (w), 1369 (m), 1224 (m), 1139 (s), 927 (w), 833 (m), 802 (m), and 790 (s) cm^{-1}; nmr ($CDCl_3$) τ3.72-4.70 (m, 7), 8.39 (q, 2, J = 7 Hz), 8.77 (s, 6), and 9.12 (t, 3, J = 7 Hz); mass spectrum (56 eV) m/e (rel intensity) 190 (5), 175 (4), 161 (5), 120 (95), 91 (100), 78 (95), and 70 (90).

Stirring 0.40 g (0.0021 mole) of t-amyloxycyclooctatetraene in a solution consisting of 23 ml of 95% ethanol, 4 ml of water, and 3 ml of concentrated sulfuric acid for 2 hr under nitrogen at room temperature produced cycloocta-1,3,5-triene-7-one. The cyclooctatrienone was identified as its 2,4-dinitrophenylhydrazone: mp 155.5-157° [lit. (41) mp 158-159°].

N,N-Diethylaminocyclooctatetraene 53

Into a dry 250-ml Erlenmeyer flask equipped with a condensor, dropping funnel, and magnetic stirring bar was placed 4.11 g (0.057 mole) of diethyl amine in 50 ml of dry ether under nitrogen. To this stirred solution was added 34 ml of n-butyllithium in hexane (1.6M; 0.0546 mole) dropwise over a period of 10 min. The resulting opaque solution of lithium diethylamide was cooled to -4° in an ice-95% ethanol bath and 5 g (0.0273 mole) of bromocyclooctatetraene in 15 ml of dry ether was added dropwise over a period of 15 min. The dark

red solution was stirred at -4° for 10 min, allowed to warm to room temperature over a period of 20 min, and then refluxed for 92 hr. The resulting suspension was hydrolyzed by cooling to -10° in an ice-95% ethanol bath and adding 50 ml of deoxygenated water dropwise over a period of 15 min. The ethereal layer was separated, washed twice with 100-ml portions of cold deoxygenated water and dried ($MgSO_4$) under nitrogen. Evaporation of the solvent at room temperature afforded 4.2 g (88%) of N,N-diethylaminocyclooctatetraene as a deep red liquid: ir (Neat) 2960 (s), 2935 (m), 2855 (w), 1612 (s), 1379 (m), 1250 (m), 1126 (m), and 672 (m) cm^{-1}; nmr (Neat) τ3.9-4.6 (m, 6) 5.52 (d, 1, $\underline{J}$ = 4 Hz), 6.99 (q, 4, $\underline{J}$ = 7 Hz), and 9.01 (t, 6, $\underline{J}$ = 7 Hz).

Stirring N,N-diethylaminocyclooctatetraene with 30% acetic acid for 30 min at room temperature and 20 min at 35° furnished cycloocta-1,3,5-triene-7-one. The cyclooctatrienone was identified as its 2,4-dinitrophenylhydrazone derivative: mp 156-157 [lit. (41) mp 158-159°].

Dimethyl 1-N,N-Diethylaminobicyclo[6.2.0]deca-2,4,6,9-tetraene-9,10-dicarboxylate 54 (Attempted); Preparation of Dimethyl 1,2-Naphthalenedicarboxylate 57

Dimethyl acetylenedicarboxylate, 1.20 g (0.00845 mole), in 10 ml of ether was added dropwise over a period of 15 min to a solution of 1.48 g (0.00845 mole) of N,N-diethylaminocyclooctatetraene in 40 ml of ether under nitrogen with stirring at 0°. The solution was allowed to warm to room

temperature and was then refluxed for 5 hr. The resulting solution was washed twice with water, dried ($MgSO_4$), and concentrated. The red oily residue was chromatographed on 50 g of silicic acid eluting with chloroform. Evaporation of the eluent and recrystallization from methanol afforded 0.441 g (21%) of dimethyl 1,2-naphthalenedicarboxylate as colorless needles: mp 82-82.5° [lit. (42) mp 82-83°]; ir ($CDCl_3$) 2948 (s), 2880 (m), 1725 (s), 1435 (s), 1293 (s), 1270 (s), 1248 (s), 1141 (s), 1043 (m), and 852 (s) cm^{-1}; nmr ($CDCl_3$) τ1.61-2.30 (m, 6), 5.85 (s, 3), and 5.97 (s, 3).

Tetramethyl Tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58

Dimethyl trans-trans-1,4-Pentadiene-3-one-1,5-dicarboxylate (32), 4.1 g (0.021 mole), was slurried in methylene chloride (25 ml) and deposited on the walls of a 4-l. beaker. The methylene chloride was allowed to evaporate and the ketone was then irradiated for 8 hr with a Hanovia Type L, 450 watt ultraviolet lamp using a vycor filter. The photolyzed material was washed with hot chloroform and removed by filtration yielding 2.8 g (69%) of the tricyclic ester 58: mp 242-243° [lit. (32) mp 242-243°].

Tetramethyl Tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-2,7-bisoxime-4,5,9,10-tetracarboxylate 62

Tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58, 1 g (0.00252 mole), was combined with

10 ml of ethanol, 5 ml of pyridine and 0.8 g (0.012 mole) of hydroxylamine hydrochloride and refluxed with stirring for 2 hr. The reaction mixture was cooled and concentrated to a yellow oil. The oil was crystallized by addition of 20 ml of water. Two recrystallizations from ethanol-water afforded 0.763 g (71%) of the bisoxime 62 as colorless plates: mp 223-224°; ir (Nujol) 3400 (s, broad), 1730 (s), 1638 (w), 1275 (m), 1200 (m), 947 (m), and 830 (w) cm^{-1}; nmr (DMSO-d_6) τ5.80-6.78 (m).

Anal. Calcd for $C_{18}H_{22}O_{10}$: C, 50.70; H, 5.20. Found: C, 50.90; H, 5.25.

Bisoxime 62, 0.22 g (0.516 mmol), was combined with 2 ml of 40% formalin and 0.4 ml of 2N hydrochloric acid and heated on a steam bath for 20 min. The bisoxime immediately dissolved and a white solid started to precipitate out of the solution. The resulting suspension was cooled, diluted with water, and filtered producing 0.2039 g (100%) of the tricyclic dione 58: mp 242-243° [lit. (32) mp 242-243°].

Bisoxime 62, 0.2 g (0.5 mmol), was heated with 1 ml of acetic anhydride on a steam bath for 5 min. The solution was cooled and diluted with 2 ml of water. The resulting white solid was removed by filtration. Two recrystallizations from ethanol produced 0.215 g (85%) of the bisoxime diacetate 62a: mp 178.5-179°; ir (Nujol) 1774 (s), 1727 (s), 1640 (w), 1279 (s), 1200 (s, broad), and 887 (m) cm^{-1}; nmr (DMSO-d_6) τ5.70-6.70 (m, 20), and 8.10 (s, 6).

Anal. Calcd for $C_{22}H_{26}O_{12}$: C, 51.76; H, 5.13. Found: C, 51.80; H, 5.06.

Tetramethyl Tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-2,7-bistosylhydrazone-4,5,9,10-tetracarboxylate 63

Tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate 58, 0.76 g (1.92 mmol), was combined with 0.94 g (5 mmol) of 4-toluenesulfonylhydrazine in 50 ml of tetrahydrofuran containing 1 ml of concentrated hydrochloric acid and stirred for 24 hr under nitrogen at room temperature. The tetrahydrofuran solution was concentrated and the resulting yellow oil was crystallized by adding 10 ml of ethanol. Two recrystallizations from chloroform-ethanol afforded 1.207 g (86%) of the bistosylhydrazone 63 as long, colorless needles: mp 208-209.5°; ir ($CHCl_3$) 3130 (w, broad), 3010 (w, broad), 2950 (w), 1725 (s), 1600 (w), 1440 (m), 1350 (m), 1273 (m), 1168 (s), 1065 (m), and 960 (w) cm^{-1}; nmr ($CDCl_3$) τ1.82 (d, 4, J = 8 Hz), 2.42 (d, 4, J = 8 Hz), 5.74-7.0 (m, 20), and 7.61 (s, 6).

Anal. Calcd for $C_{32}H_{36}N_4O_{12}S_2$: C, 52.45; H, 4.95. Found: C, 52.30; H, 5.02.

Tetramethyl 2,7-Dihydroxytricyclo[6.2.0.$0^{3,6}$]decane-4,5,9,10-tetracarboxylate 64

Tetramethyl tricyclo[6.2.0.$0^{3,6}$]decane-2,7-dione-4,5,9,10-tetracarboxylate, 3 g (7.56 mmol), was dissolved in 350 ml of dry tetrahydrofuran containing 0.3 g (8 mmol)

of sodium borohydride and stirred at room temperature for 48 hr. The yellow solution was diluted with 100 ml of anhydrous methanol and allowed to stand for 12 hr at room temperature with occasional stirring. The solution was concentrated, 100 ml of water was added and the solution, containing a small quantity of undissolved oil, was acidified to pH 1 with 6N hydrochloric acid. Chloroform (100 ml) was added and the resulting two-phase system was allowed to stand for 12 hr with occasional agitation. The chloroform layer was separated and the aqueous extract was saturated with sodium chloride and extracted with three additional 50-ml portions of chloroform. The chloroform extracts were combined, dried ($MgSO_4$), and concentrated affording 2.177 g (72%) of the crude diol as a pale yellow, viscous liquid. Crystallization could be accomplished from chloroform-hexane. Five crystallizations produced 0.6366 g (21%) of the diol 64 as small colorless needles: mp 239.5-242°; ir (Nujol) 3450 (s, broad), 1725 (s, broad), 1440 (s), 1255 (s), 1200 (m), 1173 (m), 1100 (w), 1056 (w), 948 (m), and 891 (w) cm^{-1}; nmr (DMSO-d_6) 3.93 (m, 2) and 5.91-6.96 (m, 22).

Anal. Calcd for $C_{18}H_{24}O_{10}$: C, 54.00; H, 6.04. Found: C, 54.09; H, 5.79.

Tetramethyl 2,7-Dibromotricyclo[6.2.0.$0^{3,6}$]decane-4,5,9,10-tetracarboxylate 65 (Attempted)

Bromine, 4.64 g (0.028 mole), dissolved in 6 ml of methylene chloride was slowly added to a cooled (ice bath)

solution of 7.59 g (0.029 mole) of phosphorous tribromide in 8 ml of methylene chloride with stirring. A yellow precipitate of phosphorous pentabromide formed. Diol 64, 5.1 g (0.0128 mole), dissolved in 10 ml of methylene chloride was added over a period of 1 hr to the well stirred and cooled mixture. An additional 5 ml of methylene chloride was added and the suspension was stirred for 3 hr. Ice water (25 ml) was added; the methylene chloride layer was separated, washed with water, 10% sodium bicarbonate and saturated sodium chloride. Concentration of the methylene chloride extract afforded only 4.86 g (95%) of the starting diol (by ir).

Tetramethyl 2,7-Dihydroxytricyclo[6.2.0.$0^{3,6}$]decane-4,5,9,10-tetracarboxylate Di-p-toluenesulfonate 66

Diol 64, 14.7 g (0.037 mole), was dissolved in 100 ml of pyridine at 0^0 and treated with a solution of 21 g (0.111 mole) of p-toluenesulfonylchloride dissolved in 100 ml of chloroform. After standing at 0^0 for 8 days, the solution was poured into 450 ml of ice cold 2N hydrochloric acid. An additional 100 ml of chloroform was added, the organic phase was separated, washed with 300 ml of 1N hydrochloric acid (0^0), 300 ml of water, and 300 ml of saturated sodium chloride solution. Concentration of the chloroform extract under reduced pressure at room temperature afforded 17.2 g (65%) of the crude ditosylate 66 as a pale yellow liquid. All attempts to crystallize the ditosylate 66 were unsuccessful so the crude ditosylate was used directly in all reactions: ir

($CHCl_3$) 3130 (w), 2995 (m), 2950 (s), 1735 (s, broad), 1600 (m), 1437 (s), 1375 (s), 1280 (s), 1169 (s), 1080 (m), 1008 (m), and 915 (m) cm^{-1}; nmr ($CDCl_3$) τ2.19 (d, 4, $\underline{J}$ = 8 Hz), 2.72 (d, 4, $\underline{J}$ = 8 Hz), 5.72-7.35 (m, 22) and 7.57 (s, 6).

Tetramethyl 11-Oxatetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]undecane-3,4,8,9-tetracarboxylate 67

Phosphoryl chloride, 5 g (0.33 mole), was added dropwise with stirring to a solution of 3.305 g (8.3 mmol) of diol 64 dissolved in 24 ml of pyridine at 0^0. The resulting suspension was stirred at room temperature for 21 hr and at 100^0 for 1.5 hr. The reaction mixture was cooled in an ice bath and poured over 100 g of ice. The aqueous solution was extracted with three 70-ml portions of chloroform. The chloroform extracts were combined, washed with four 100-ml portions of 2N hydrochloric acid and two 100-ml portions of water. The chloroform extract was dried ($MgSO_4$) and concentrated to a brown oil. Addition of 20 ml of methanol caused the tetracyclic ester 67 to crystallize. Two recrystallizations from hot methanol produced 0.446 g (16%) of the tetracyclic ester 67 as colorless needles: mp 209.5-210.5^0; ir (Nujol) 1740 (s), 1350 (m), 1300 (m), 1232 (m), 1177 (m), 1154 (m), 1056 (w), 1031 (w), 860 (w), and 826 (w) cm^{-1}; nmr ($CDCl_3$) τ5.65 (s, 2), 6.32 (s, 12), 6.78 (m, 4), and 7.22 (m, 4).

Anal. Calcd for $C_{18}H_{22}O_9$: C, 56.54; H, 5.80. Found: C, 56.26; H, 5.65.

11-Oxatetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]undecane-3,4,8,9-tetracarboxylic Acid Monohydrate 68

Tetracyclic ester 67, 0.030 g (0.0784 mmol), was combined with 15 drops of dioxane, 15 drops of water and 5 drops of 6N hydrochloric acid and heated on a steam bath for 15 hr. The resulting suspension was diluted with water and the tetra-acid was removed by filtration. Two recrystallizations from boiling water followed by drying under reduced pressure at 100^0 afforded 0.025 g (92%) of the tetra-acid monohydrate 68 as a colorless crystalline solid: mp 340^0; ir (Nujol) 3475 (m, broad), 3300-2500 (m), 1710 (s), 1635 (w), 1350 (w), 1282 (m), 1245 (m), 950 (w), 922 (w), and 742 (w) cm^{-1}; nmr (NaOD in D_2O) τ5.64 (s, 2), 7.09 (m, 4), and 7.40 (m, 4).

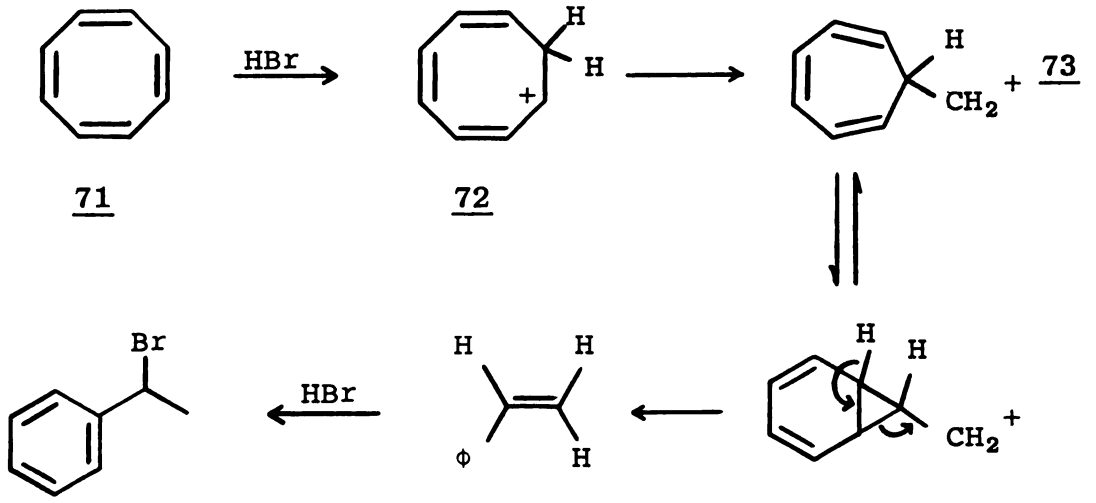
Anal. Calcd for $C_{14}H_{16}O_{10}$: C, 48.84; H, 4.68. Found: C, 48.77; H, 4.50.

PART II

THE REARRANGEMENTS OF MONOSUBSTITUTED CYCLOÖCTATETRAENES

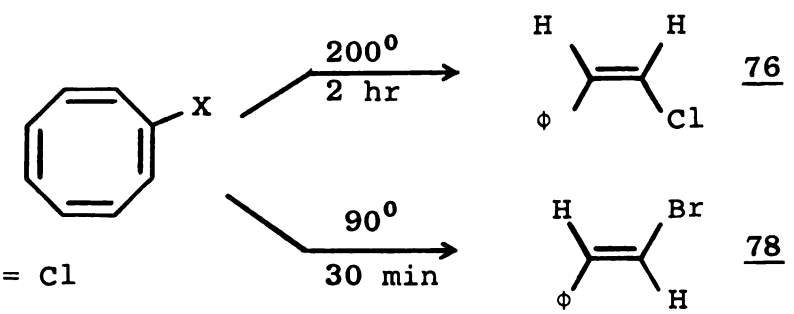
Cycloöctatetraene and its derivatives undergo both acid catalyzed and thermal rearrangements.

The acid catalyzed rearrangements have attracted by far the most attention in the literature (43,44,45,46). A mechanism for this type of rearrangement has been postulated (46). For example, Willstatter and Heidelberger (47) treated cycloöctatetraene 71 with hydrogen bromide, Reppe and his coworkers (43) identified the product as α-bromoethylbenzene and Ganellin and Pettit (46) proposed the following mechanism for the rearrangement:



The rearrangement presumably involves addition of a proton to cycloöctatetraene yielding the cycloöctatrienyl carbonium ion 72 which undergoes a Wagner-Meerwein rearrangement to the carbonium ion 73. Further rearrangement of the valence tautomer of 73 and the addition of hydrogen bromide yields the observed product.

Thermal rearrangements of cycloöctatetraenes, on the other hand, have received very little attention to date. In the only reported paper dealing with this subject, Cope and Burg (48) noted that during the preparation of bromo- and chlorocycloöctatetraene, considerable amounts of the corresponding β-halostyrenes were isolated. Further studies indicated that chlorocycloöctatetraene 75 readily rearranged to cis-β-chlorostyrene 76 at 200° and bromocycloöctatetraene 77 to trans-β-bromostyrene 78 at 90°.



75: X = Cl
77: X = Br

A mechanism for this type of rearrangement has so far not been proposed.

RESULTS AND DISCUSSION

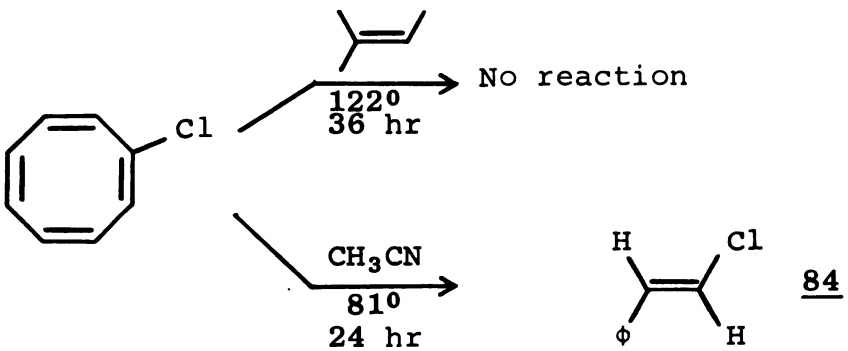
Thermal rearrangements of cycloöctatetraenes have commanded only minor research interest in the past; therefore, this type of rearrangement was studied in order to establish a possible mechanism.

As mentioned previously, Cope and Burg (48) reported that chloro- and bromocycloöctatetraene thermally rearranged to cis-β-chloro- and trans-β-bromostyrene, respectively. Since the work of Cope and Burg on the thermal rearrangement of chloro- and bromocycloöctatetraene had been reported before the advent of nuclear magnetic resonance spectroscopy, the products from the thermal rearrangements were reinvestigated to determine if the assigned structures were indeed correct. The styrene isolated from the thermal rearrangement of bromocycloöctatetraene was shown by its nmr spectrum to be the reported trans-β-bromostyrene **78**, but the product from the thermal rearrangement of chlorocycloöctatetraene was proved by nmr and ir (51) to be trans-β-chlorostyrene **84** instead of the reported cis isomer **76**. Both trans-β-halostyrenes showed a typical trans vicinal olefinic coupling (50) of 13.7 Hz.

The thermal rearrangement of both chloro- and bromocycloöctatetraene appeared to be stereospecific. Analysis of the halostyrene from either thermal rearrangement by vapor phase chromatography (vpc) or nmr showed the presence of only the

trans isomer. There appeared to be no detectable amount of cis isomer present.

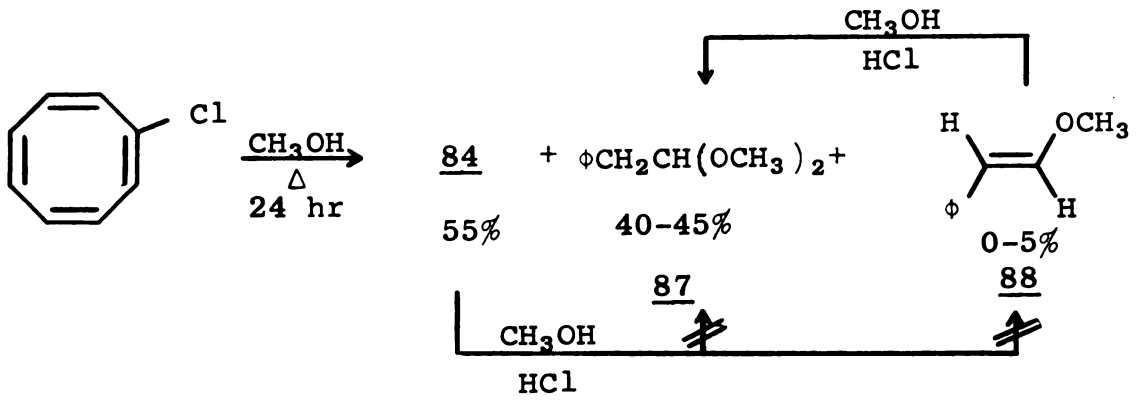
The rate of the rearrangement of chlorocycloöctatetraene and presumably bromocycloöoctatetraene noticeably increased in polar solvents. For example, heating chlorocycloöctatetraene for 36 hours at 122° in a sealed tube with 2-methyl-2-



84

butene produced only unaltered starting material. In refluxing acetonitrile (bp 81°), however, chlorocycloöctatetraene was completely converted to trans-β-chlorostyrene in 24 hours. This suggests that the rearrangement is proceeding through a polar intermediate.

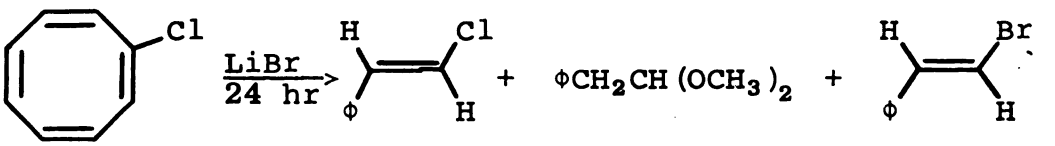
Rearrangement of chlorocycloöctatetraene in refluxing methanol produced besides trans-β-chlorostyrene, two additional products, phenylacetaldehyde dimethyl acetal **87** and trans-β-methoxystyrene **88**. trans-β-Chlorostyrene would not convert to either the acetal **87** or the methoxystyrene **88** under the reaction conditions, whereas trans-β-methoxystyrene **88** is readily transformed (46) into phenylacetaldehyde dimethyl acetal **87**. Phenylacetaldehyde dimethyl acetal **87**



and trans-β-methoxystyrene **88** were identified by comparison of their infrared spectra with their reported spectra (52).

The rearrangement of chlorocycloöctatetraene was performed in methanol-d to determine the extent of deuterium incorporation. The trans-β-chlorostyrene isolated from the reaction product was found to be free of deuterium (by nmr), but the phenylacetaldehyde dimethyl acetal contained two deuterium atoms, both on the benzylic carbon. The location of the deuteriums at the benzylic position followed from the nmr spectrum, which showed the signal of the methine proton as a singlet at τ5.56 rather than the triplet characteristic of the undeuterated compound and the disappearance of the doublet for the benzylic protons. The deuterium content of trans-β-methoxystyrene was unfortunately not determined because the reaction product contained only a small amount of this compound. Since trans-β-methoxystyrene converts to phenyacetaldehyde dimethyl acetal under the reaction conditions, if the methoxystyrene is labeled, the deuterium must be present at the α position.

Rearrangement of chlorocycloöctatetraene in refluxing methanol containing an excess of sodium methoxide altered the products and product distribution. Thus, methoxycycloöctatetraene 89 was isolated along with trans-β-chlorostyrene and trans-β-methoxystyrene. Methoxycycloöctatetraene was found to be stable under the reaction conditions. Phenylacetaldehyde dimethyl acetal would not be expected to be present in the reaction mixture because the addition of methanol to trans-β-methoxystyrene is catalyzed only by acid. Methoxycycloöctatetraene 89 was identified by its mass spectrum, its rapid hydrolysis in dilute alcoholic sulfuric acid to cycloöctatrienone (characterized as its 2,4-DNP) and the nmr spectrum, which showed a multiplet for six cycloöctatetraene hydrogens at τ3.93-4.41, a multiplet for the cycloöctatetraene hydrogen α to the methoxy group at τ5.05-5.15, and a three proton singlet for the methoxy group at τ6.42. The rearrangement of chlorocycloöctatetraene in refluxing methanol containing a fifteen mole excess of lithium bromide dramatically illustrates the effect of a strong nucleophile on the reaction. The products obtained from the reaction were trans-β-chlorostyrene (14%), phenylacetaldehyde dimethyl acetal (3%), and trans-β-bromostyrene (83%). The large yield



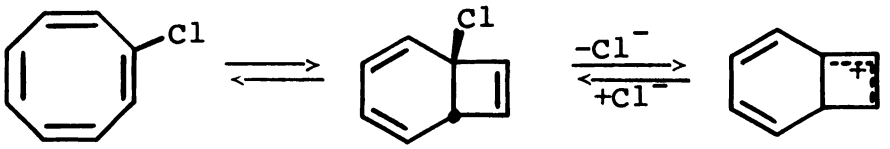
14% 3% 83%

of trans-β-bromostyrene indicates that the nucleophilic

bromide ion is successfully competing with chloride ion and methanol in the trapping of the rearrangement intermediate.

A possible mechanism for the rearrangement of chlorocycloöctatetraene in polar solvent, which is consistent with all the acquired data, is proposed in Scheme IX for methanol solution, in Scheme X for methanolic sodium methoxide and in Scheme XI for methanolic lithium bromide.

This mechanism proposes initial ionization in the polar methanol solutions of 1-chlorobicyclo[4.2.0]octa-2,4,7-triene 90, one of four possible valence tautomers of chlorocycloöctatetraene, to the bicyclic octatrienyl carbonium ion 91.

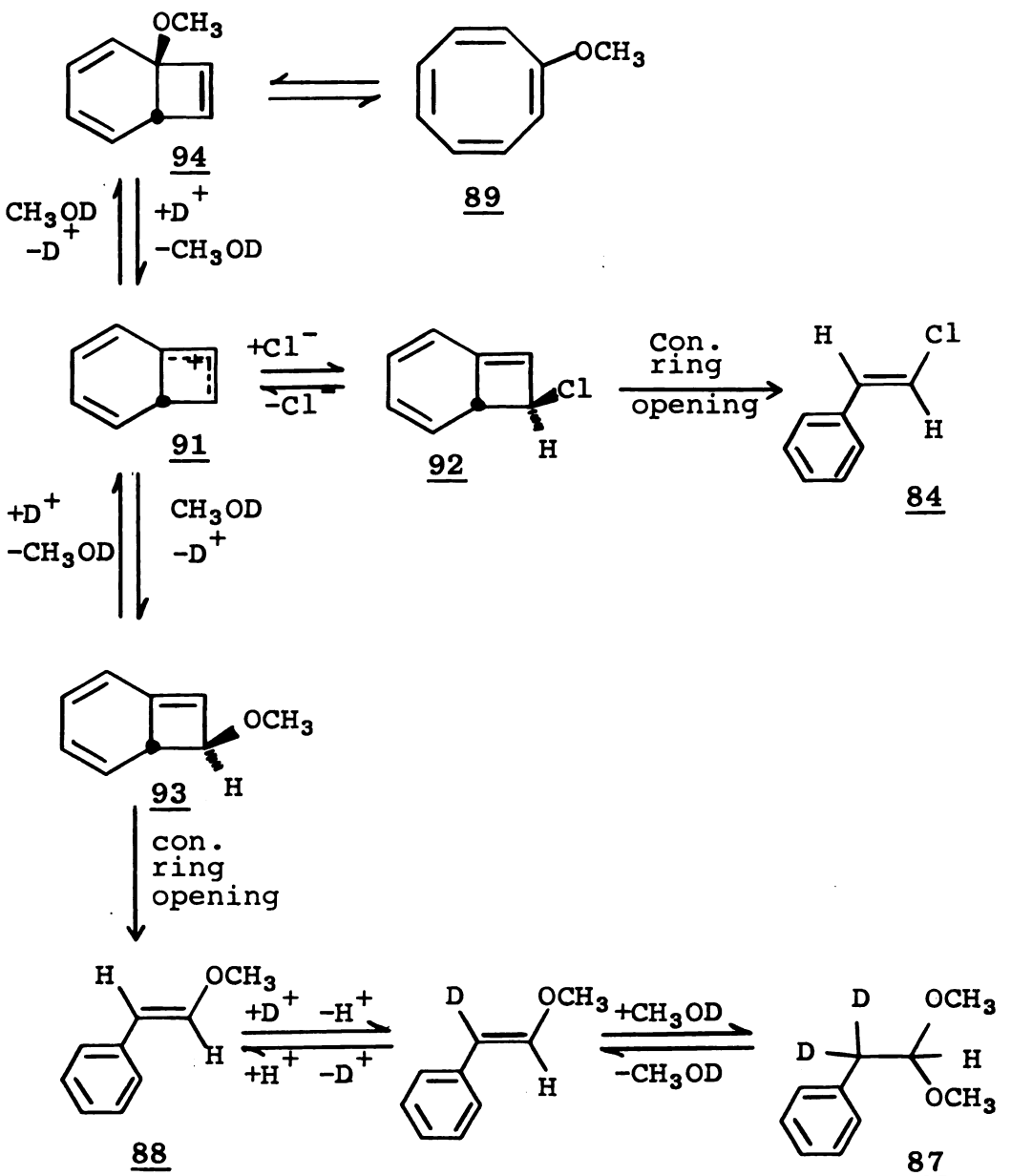


90 91

The stereospecific formation of exo-8-substituted bicyclo[4.2.0]octa-2,4,6-triene 97, the precursor to trans-β-substituted styrene 98, is rationalized by assuming that the approaching nucleophile only attacks from the exo side of 91 because of the greater steric accessibility of the exo face and the steric difficulties involved in approaching the endo face. A molecular model of the bicyclic octatrienyl carbonium ion 91 supports this assumption by revealing that the C_2 pi-orbital effectively prevents attack by a nucleophile from the endo face by shielding the endo face of the

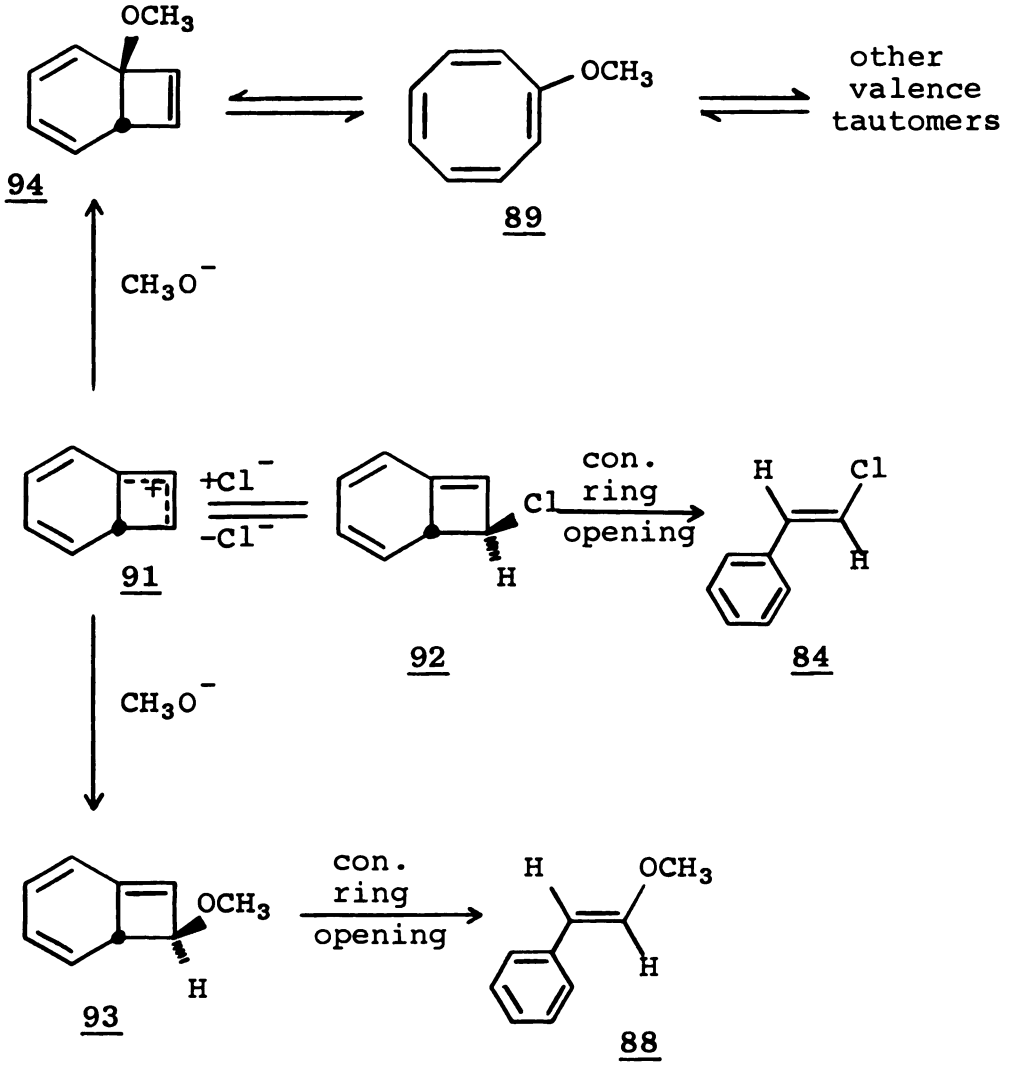
Scheme IX

Chlorocycloöctatetraene and Methanol-d



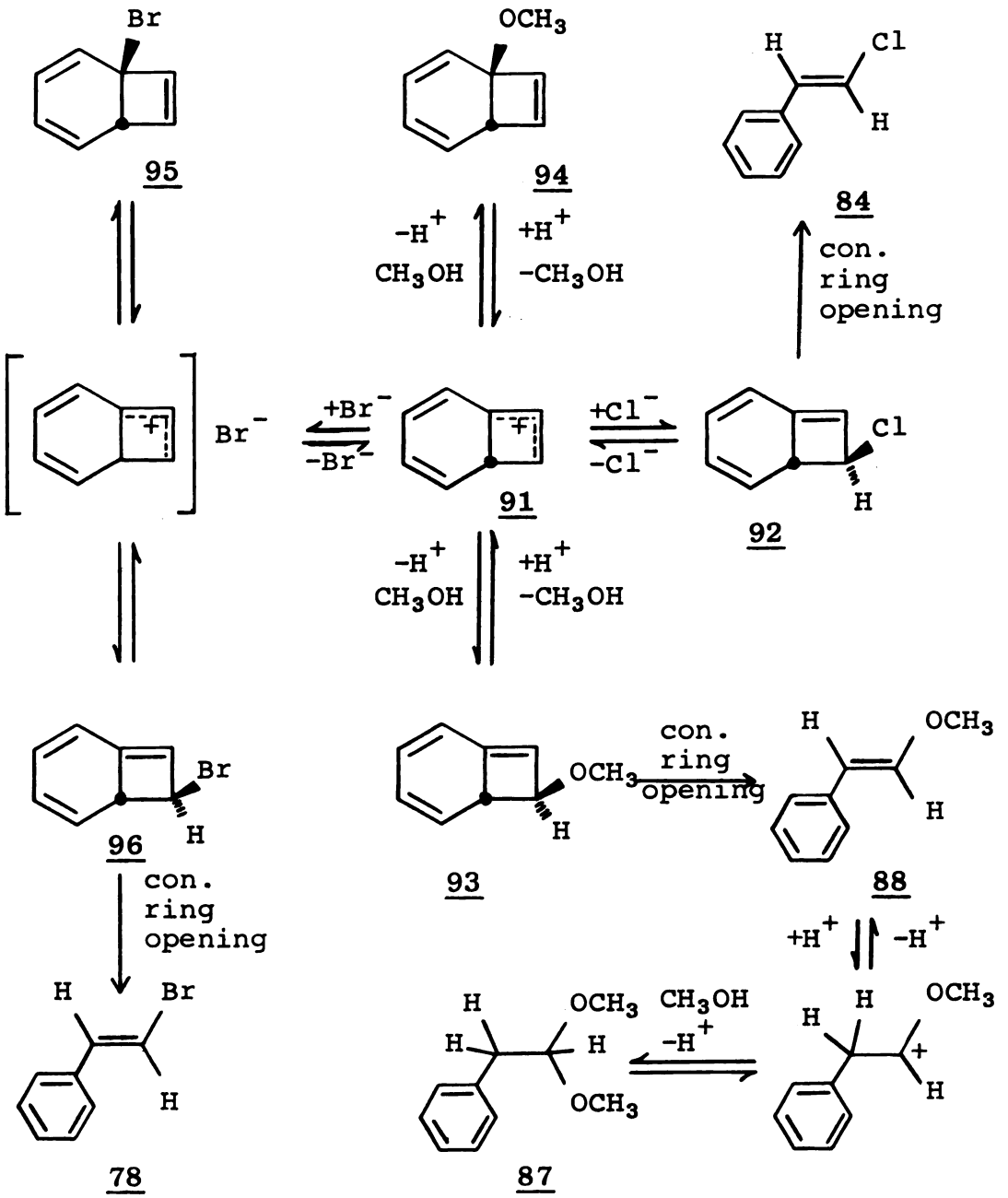
Scheme X

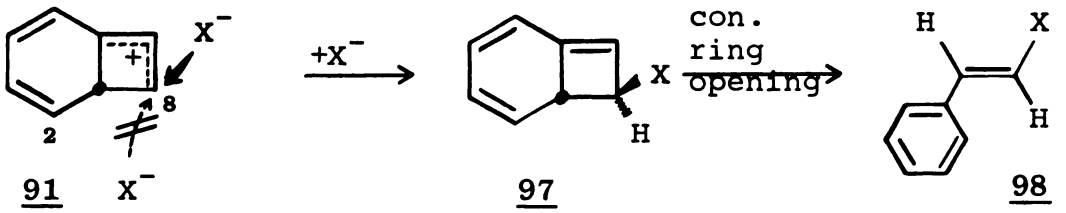
Chlorocyclooctatetraene and Methanolic Sodium Methoxide



Scheme XI

Chlorocyclooctatetraene and Methanolic Lithium Bromide





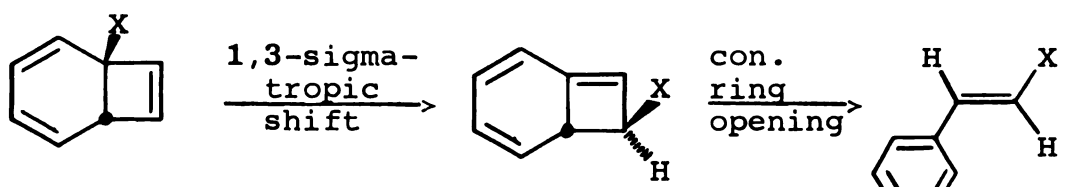
vacant pi-orbital on C_8. Once the exo-8-substituted bicyclo-[4.2.0]octa-2,4,6-triene 97 has been formed, a thermally allowed conrotatory opening (53) of the cyclobutene ring would stereospecifically yield the trans-β-substituted styrene 98.

The absence of methoxycycloöctatetraene 89 as a product in Scheme IX is also consistent with the proposed mechanism. Methoxycycloöctatetraene 89 would be in equilibrium with its valence tautomer, 1-methoxybicyclo[4.2.0]octa-2,4,7-triene 94, which would be formed by the addition of methanol-d to the bicyclic octatrienyl carbonium ion 91. However, since the addition of methanol-d to the carbonium ion 91 is a reversible reaction in an acidic medium, any product formed by an irreversible reaction would deplete the reaction mixture of methoxycycloöctatetraene. Since both trans-β-chlorostyrene 84 and trans-β-methoxystyrene are formed by a conrotatory ring opening, in this case an essentially irreversible reaction, the presence of methoxycycloöctatetraene 89 in any detectable amount would not be expected. Subjecting methoxycycloöctatetraene to the reaction conditions (refluxing methanol containing a catalytic amount of dry hydrochloric acid) established the reversibility of the reaction sequence 89 $\rightleftharpoons$ 94 $\rightleftharpoons$ 91. The products obtained from this reaction

were phenylacetaldehyde dimethyl acetal (97%), trans-β-methoxystyrene (3%), and a trace of trans-β-chlorostyrene. The presence of unreacted methoxycycloöctatetraene was not detected.

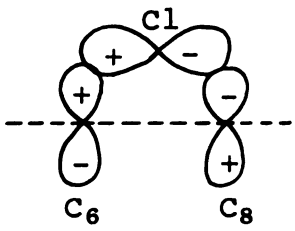
The formation of methoxycycloöctatetraene 89, however, would be expected in basic solution (Scheme X), as was observed, since the addition of methoxide ion to the bicyclic octatrienyl carbonium ion 91 would be an irreversible reaction.

An alternative mechanism for the thermal rearrangement of neat chlorocycloöctatetraene and neat bromocycloöctatetraene to the corresponding trans-β-halostyrenes is possible. This mechanism involves the stereospecific formation of exo-8-halobicyclo[4.2.0]octa-2,4,6-triene 97 by a 1,3-sigmatropic suprafacial shift (49) of the halogen atom in the valence tautomer 90. The suprafacial sigmatropic shift is



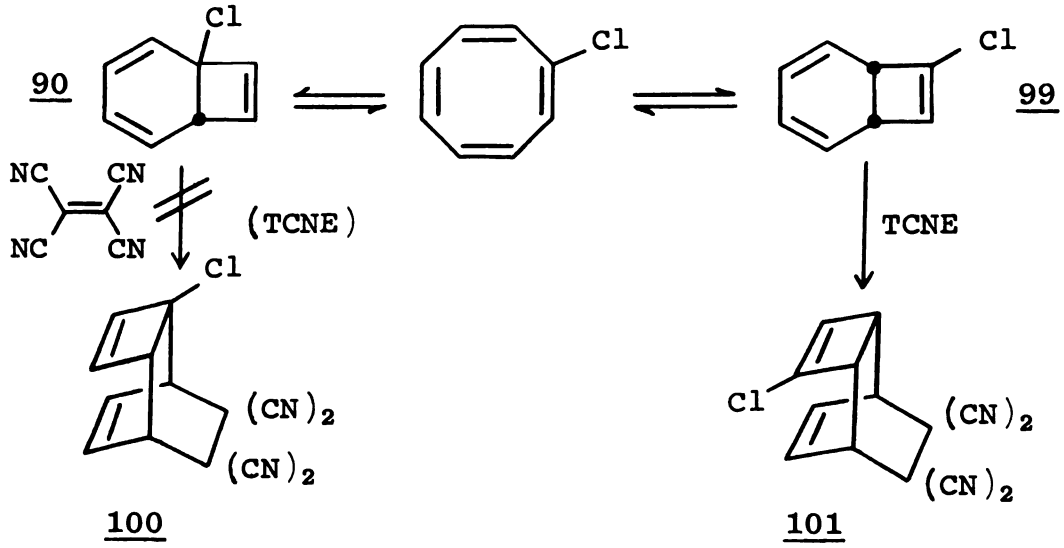
90 97 98

allowed because the migrating halogen atom possesses an available p-orbital that can interact with the pi system in the transition state (49). Conrotatory ring opening of 97 would yield the trans-β-halostyrene 98.



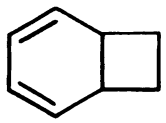
Differentiation between the two possible mechanisms (ionization vs. 1,3-sigmatropic shift) for the neat rearrangements was not attempted. The rearrangement of chlorocycloöctatetraene in refluxing methanolic solutions most likely does not proceed by the latter mechanism because a 1,3-sigmatropic shift should not be favored by increasing the solvent polarity.

An attempt was made to trap 1-chlorobicyclo[4.2.0]octa-2,4,7-triene 90 by preparing a Diels-Alder adduct of chlorocycloöctatetraene. The isolated Diels-Alder adduct was found to be derived from valence tautomer 99 rather than 90.



The tub conformation of chlorocycloöctatetraene contains no 1,3-diene system providing the approximately planar

configuration essential for a Diels-Alder reaction. On the other hand, the valence tautomers 90, 99 of chlorocycloöcta-tetraene do offer a planar diene system, particularly since incorporation of the cyclobutene ring causes further flattening of the 1,3-cyclohexadiene system. Neither 1,3-cycloöctadiene (54) nor 1,3,5-cycloöctatriene reacted with maleic anhydride to form a Diels-Alder adduct, but bicyclo[4.2.0]-octa-2,4-diene 102 (55) was able to do so. These facts suggest that a moderate equilibrium concentration of the valence

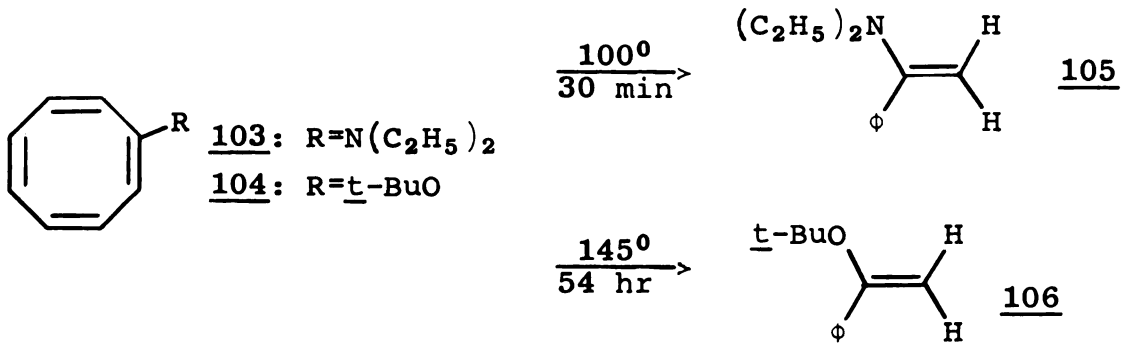


102

tautomers rather than chlorocycloöctatetraene may enter into the Diels-Alder reaction.

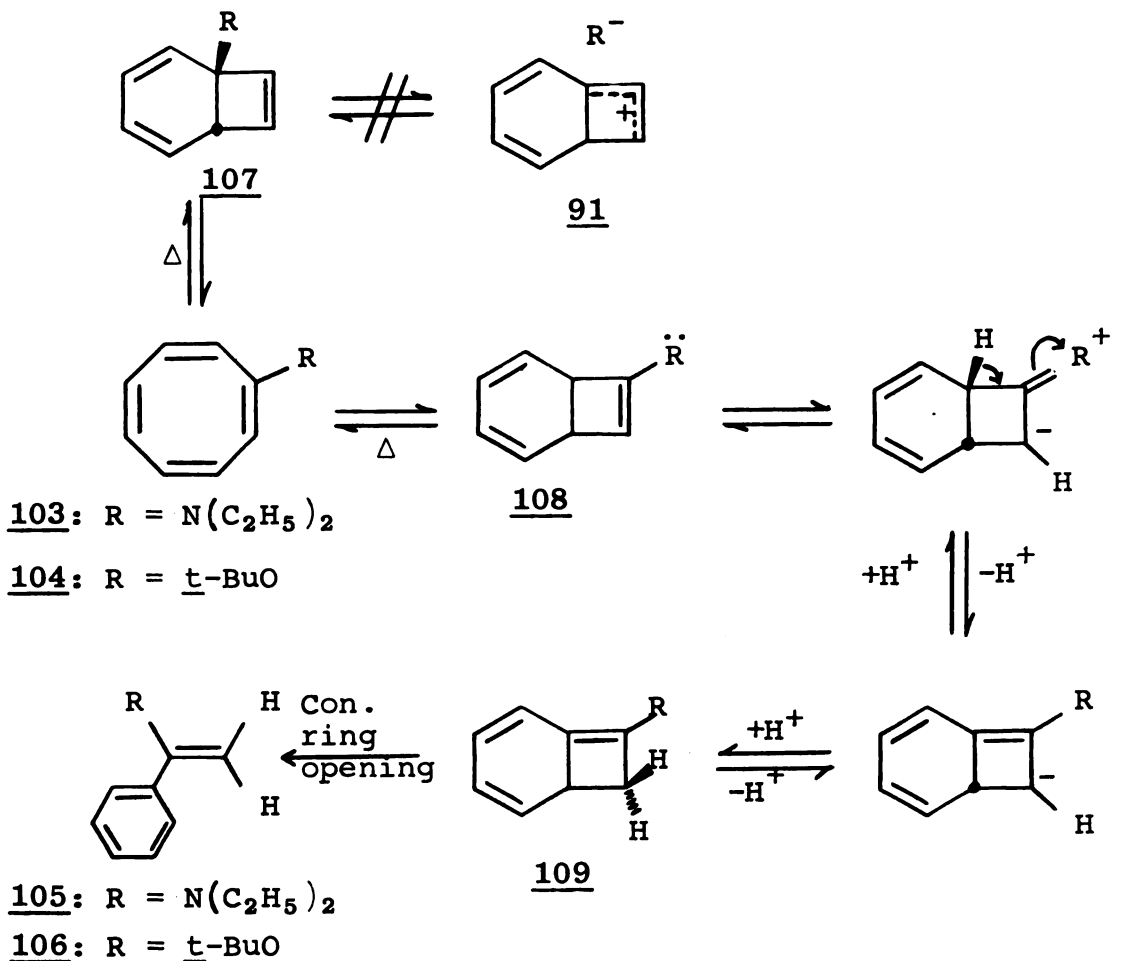
The failure of valence tautomer 90 to react with tetracyanoethylene can be rationalized by assuming that the chlorine atom of 90 repels the cyano groups of tetracyanoethylene through electron-electron repulsion. Therefore, the essential pi-overlap required for a Diels-Alder reaction would not be present. A molecular model of the transition state expected from the reaction of 90 and tetracyanoethylene substantiates this assumption. The structure of 99, on the other hand, does not permit this type of electron-electron repulsion and formation of the Diels-Alder transition state can easily occur.

The rearrangement takes a different pathway when diethylaminocycloöctatetraene **103** or t-butoxycycloöctatetraene **104** (28) are heated. In both of these cases the α-substituted styrenes, **105** and **106**, are produced cleanly. Chemical evidence for the structures of **105** and **106** was obtained by their rapid hydrolysis as an enamine and vinyl ether, respectively, by dilute acid forming acetophenone (isolated as the semicarbazide or 2,4-DNP).



A possible mechanism for the rearrangement of diethylamino- and t-butoxycycloöctatetraene is proposed in Scheme XII. This mechanism involves the formation of 7-substituted bicyclo[4.2.0]octa-2,4,7-triene **108**, a valence tautomer of the substituted cycloöctatetraene. The valence tautomer could then rearrange to 7-substituted bicyclo[4.2.0]octa-2,4,6-triene **109** followed by a conrotatory ring opening to the α-substituted styrene. An alternate pathway available would be the formation of 1-substituted bicyclo[4.2.0]octa-2,4,7-triene **107**, another valence tautomer of the substituted cycloöctatetraene. This valence tautomer, however, would not ionize to the carbonium ion **91** because of the strong

Scheme XII



103: R = $N(C_2H_5)_2$

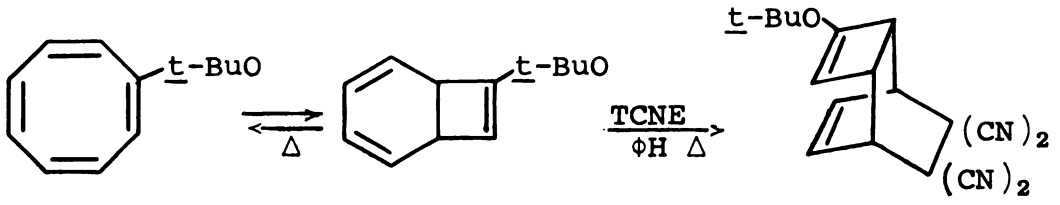
104: R = t-BuO

105: R = $N(C_2H_5)_2$

106: R = t-BuO

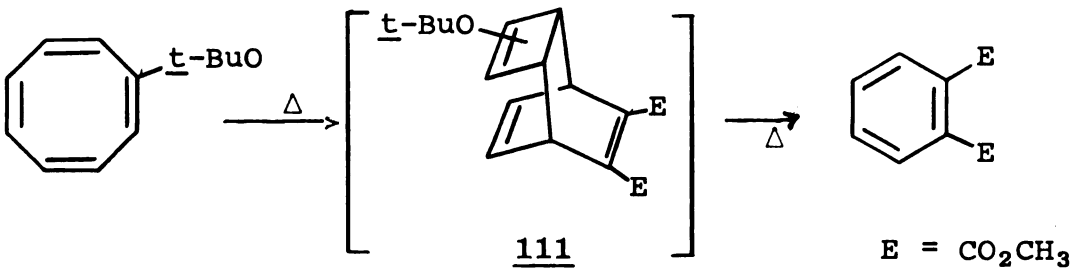
basicity of the leaving group.

Preparation of the Diels-Alder adduct **110** of t-butoxycyclooctatetraene established the intermediacy of 7-t-butoxybicyclo[4.2.0]octa-2,4,7-triene **108**. The structural assignment of **110** follows from the nmr spectrum which shows three olefinic protons and four bridgehead protons. The Diels-Alder reaction between t-butoxycyclooctatetraene and dimethyl acetylenedicarboxylate forms the basis for the assignment of the t-butoxy group in **110** to the cyclobutene double bond. The latter Diels-Alder reaction yielded not



108 **110**

the expected product, but instead its thermal degradation product, dimethyl phthalate. If the t-butoxy group had been situated on the cyclohexadiene ring of **111** rather than the cyclobutene ring, the product of the reaction would have been a t-butoxy substituted phthalate rather than the observed dimethyl phthalate. This fact coupled with the nmr spectrum's integral ratio suggested that the t-butoxy group in **110** was located on the double bond of the cyclobutene ring.



111

E = CO_2CH_3

EXPERIMENTAL

Thermal Rearrangement of Chlorocycloöctatetraene 75 to trans-β-Chlorostyrene

Chlorocycloöctatetraene (48), 3 g (0.0217 mole), was combined with 10 mg of hydroquinone and refluxed at 200° in a nitrogen atmosphere for 2 hr. Distillation of the brown reaction product yielded 0.873 g (29%) of trans-β-chlorostyrene: bp 61-62° (4.5 mm); ir (neat) (51) 1609 (m), 1498 (w), 1448 (m), 1248 (m), 1071 (w), 939 (s), 859 (m), 814 (m), 741 (s), and 695 (s) cm^{-1}; nmr (neat) τ2.7-3.1 (m, 5), 3.32 (d, 1, J = 13.7 Hz), 3.67 (d, 1, J = 13.7 Hz).

Rearrangement of Chlorocycloöctatetraene in Refluxing Methanol

Chlorocycloöctatetraene, 0.5 g (2.89 mmol), was combined with 2.5 ml of methanol and refluxed for 24 hr under nitrogen. The reaction mixture was concentrated to a volume of about 0.5 ml. The product was analyzed by vpc, using a 15% Carbowax 20M column (5 ft x $\frac{1}{4}$ in) at 100°. There were three components, the ratio from faster to slower was 55:45:5. The materials were separated by vpc. The products were trans-β-chlorostyrene (55%) (retention time, 26 min), identified by the infrared spectrum (51), phenylacetaldehyde dimethyl acetal (45%) (retention time, 34 min), identified by the infrared spectrum and the nmr spectrum ($CDCl_3$)

τ2.67-2.95 (m, 5), 5.52 (t, 1, J = 6 Hz), 6.84 (s, 6) and 7.16 (d, 2, J = 6 Hz), and trans-β-methoxystyrene (5%) (retention time, 44 min), identified by its infrared spectrum (52) and the nmr spectrum ($CDCl_3$) τ2.55-2.8 (m, 5), 2.89 (d, 1, J = 13.7 Hz), 4.16 (d, 1, J = 13.7 Hz) and 6.33 (s, 3).

Rearrangement of chlorocycloöctatetraene in refluxing methanol-d produced trans-β-chlorostyrene, trans-β-methoxystyrene (position of deuterium is uncertain), and 2,2-dideutero-2-phenylacetaldehyde dimethyl acetal (separated by vpc): nmr ($CDCl_3$) τ2.70-3.04 (m, 5), 5.56 (s, 1), and 6.82 (s, 6).

Rearrangement of Chlorocycloöctatetraene in Methanolic Sodium Methoxide

Chlorocycloöctatetraene, 0.320 g (1.85 mmol), was combined with sodium methoxide (from 0.12 g (0.52 mmol) of sodium) dissolved in 2.5 ml of methanol and refluxed for 20.5 hr under nitrogen. The reaction product was diluted with 20 ml of water and extracted with two 10-ml portions of ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Three compounds were isolated by the use of vpc (15% Carbowax 20M, 5 ft x $\frac{1}{4}$ in, 106°, retention times, 16, 24, and 37 min). The slower moving fraction (37 min) and the next slowest moving fraction (24 min) were shown to be trans-β-methoxystyrene (30%) and trans-β-chlorostyrene (31%), respectively, by their infrared spectra (52,51). The fastest moving fraction

(16 min) was identified as methoxycyclooctatetraene: ir (CCl_4) 3005 (s), 2953 (m), 2904 (w), 2840 (w), 1662 (m), 1641 (s), 1465 (m), 1452 (m), 1443 (m), 1403 (m), 1379 (m), 1231 (s), 1202 (s), 1163 (s), 1020 (s), 835 (m), 800 (s), and 756 (s) cm^{-1}; nmr ($CDCl_3$) τ3.93-4.41 (m, 6), 5.05-5.15 (m, 1), and 6.42 (s, 3); mass spectrum (62.5 eV) m/e 134.

Stirring methoxycyclooctatetraene with a solution containing 2 ml of ethanol, 1 ml of water, and 0.5 ml of concentrated sulfuric acid yielded cycloocta-1,3,5-triene-7-one. The cyclooctatrienone was identified as its 2,4-dinitrophenylhydrazone derivative: mp 153-156° [lit. (41) mp 158-159°].

Rearrangement of Chlorocyclooctatetraene in Methanolic Lithium Bromide

Chlorocyclooctatetraene, 0.250 g (1.445 mmol), was combined with 2 g (20 mmol) of lithium bromide and 5 ml of methanol and refluxed for 24 hr under nitrogen. The pale yellow solution was diluted with 40 ml of water and extracted with 25 ml of ether. The ethereal layer was separated, dried ($MgSO_4$), and concentrated by evaporation under reduced pressure. The reaction product upon vpc, after a small solvent peak, showed three peaks (15% Carbowax 20M, 93°, retention times, 22, 30, and 46 min). The two faster moving peaks were trans-β-chlorostyrene (14%) and trans-β-methoxystyrene (3%), respectively (by infrared). The slowest moving peak was identified as trans-β-bromostyrene (83%)

by comparison of its infrared spectrum with that of an authentic sample (48).

Tetracyanoethylene Diels-Alder Adduct of Chlorocycloöcta-tetraene

Tetracyanoethylene, 0.93 g (7.26 mmol), was combined with 1 g (7.26 mmol) of chlorocycloöctatetraene dissolved in 3 ml of benzene and allowed to stand at room temperature for 129 hr under nitrogen. The insoluble material (TCNE) was removed by filtration and washed with 3 ml of benzene. The benzene solution was concentrated to a brown semisolid under reduced pressure. Two recrystallizations from hot methanol yielded 0.057 g (3%) of the Diels-Alder adduct 101 as colorless needles: mp 235-235.5°; ir (KBr) 2950 (w), 2920 (w), 1587 (s), 1270 (m), 1228 (m), 1136 (m), 1090 (m), 920 (m), 798 (m), 745 (s), and 699 (w) cm^{-1}; nmr (DMF) τ3.58-3.71 (m, 2), 4.03-4.21 (m, 1), and 5.81-6.05 (m, 4).

Anal. Calcd for $C_{14}H_7ClN_4$: C, 63.05; H, 2.65. Found: C, 62.75; H, 2.72.

Thermal Rearrangement of N,N-Diethylaminocycloöctatetraene 103

N,N-Diethylaminocycloöctatetraene (2.0 g) was heated under an atmosphere of nitrogen at 100° for 0.5 hr. Distillation of the reaction product produced 1.63 g (81%) of α-N,N-diethylaminostyrene 105: bp 47-48° (0.15 mm); nmr (Neat) τ2.45-2.90 (m, 5), 5.75 (s, 1), 5.90 (s, 1), 7.06 (q, 4, J = 7 Hz), and 9.03 (t, 6, J = 7 Hz).

α-N,N-Diethylaminostyrene was hydrolyzed to acetophenone by stirring with 30% acetic acid at 90° for 15 min under nitrogen. The acetophenone was isolated as the semicarbazide derivative: mp 196-198° [lit. (56) mp 198°].

Thermal Rearrangement of t-Butoxycycloöctatetraene 104

t-Butoxycycloöctatetraene (28), 1.3 g (7.4 mmol), was heated at 144-147° for 45 hr under an atmosphere of nitrogen. The nmr spectrum of the crude material indicated that approximately 25% of the t-butoxycycloöctatetraene had rearranged to α-t-butoxystyrene 106: nmr (Neat) τ2.69-2.81 (m, 5), 6.43 (s, 1), 6.54 (s, 1), and 8.70 (s).

The t-butoxy ether was hydrolyzed by dissolving the crude material in 10 ml of 95% ethanol and then adding 20 ml of 15% sulfuric acid solution. This solution was stirred under nitrogen for 2 hr at room temperature. Water (45 ml) was added and the solution was neutralized with sodium carbonate. The aqueous solution was extracted with four 10-ml portions of ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The reaction product was analyzed by vpc, using a 15% Carbowax 20M column (5 ft x $\frac{1}{4}$ in) at 121° and there were two components. The ratio of the faster to the slower moving material was approximately 3:1. The material appearing at 14 min was identified as cycloöcta-1,3,5-triene-7-one by its infrared spectrum (41). The minor, slower moving material (30 min) was acetophenone. The infrared spectrum of

the collected acetophenone was identical in all respects to the infrared spectrum of commercially available acetophenone. A 2,4-dinitrophenylhydrazone derivative was made of the collected acetophenone: mp 247.5-248.5° [lit. (56) mp 250°].

Tetracyanoethylene Diels-Alder Adduct of t-Butoxycyclooctatetraene 104

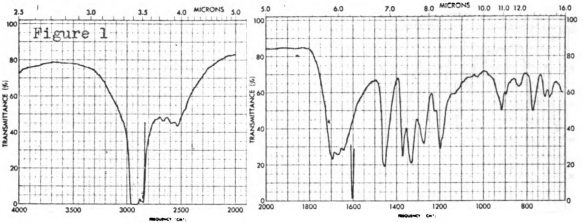
t-Butoxycyclooctatetraene, 1 g (5.7 mmol), was combined with 0.726 g (5.7 mmol) of tetracyanoethylene in 3 ml of benzene and refluxed for 19 hr under nitrogen. The benzene was removed under reduced pressure producing a dark brown oil, which slowly solidified on standing. Two recrystallizations from boiling methanol produced 1.12 g (65%) of the Diels-Alder adduct 110 as a beige crystalline solid: mp 159.5-161°; ir (KBr) 2985 (m), 2940 (w), 1627 (m), 1590 (s), 1367 (m), 1300 (m), 1243 (m), 1200 (m), 849 (m), 728 (m), and 699 (w) cm^{-1}; nmr ($CDCl_3$) τ3.86-4.52 (m, 3), 6.2-6.54 (m, 4), and 8.53 (s, 9).

Anal. Calcd for $C_{18}H_{16}N_4O$: C, 71.03; H, 5.30. Found: C, 70.81; H, 5.34.

The Diels-Alder Reaction of t-Butoxycyclooctatetraene with Dimethyl Acetylenedicarboxylate

t-Butoxycyclooctatetraene, 2.0 g (11.3 mmol), was combined with 1.612 g (11.3 mmol) of dimethyl acetylenedicarboxylate in 4 ml of dry toluene under an atmosphere of nitrogen and refluxed for 23 hr. The dark brown solution was

vacuum distilled through a semimicro column. The distillation separated a forerun of 0.32 g of t-butoxycycloöctatetraene, bp 47-52° (0.2 mm), from 1.2 g (49%) of dimethyl phthalate: bp 90-94.5° (0.2 mm). The infrared and nmr spectra of the isolated dimethyl phthalate were identical in all respects to those of commercially available dimethyl phthalate.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5.0 6.0 7.0 8.0 MICRONS 10.0 11.0 12.0 16.0
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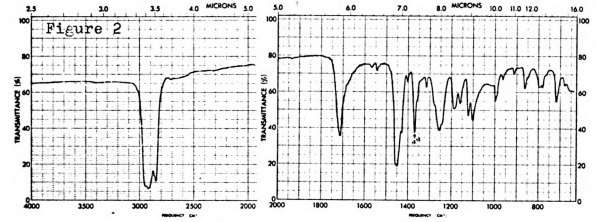
2000 1800 1600 1400 1200 1000 800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TRANSMITTANCE (%)
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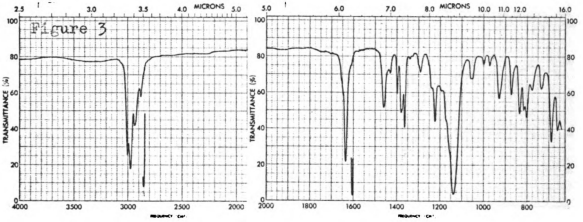
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TRANSMITTANCE (%)
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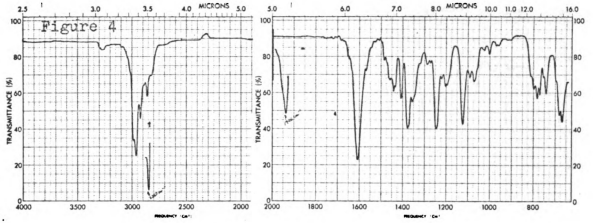
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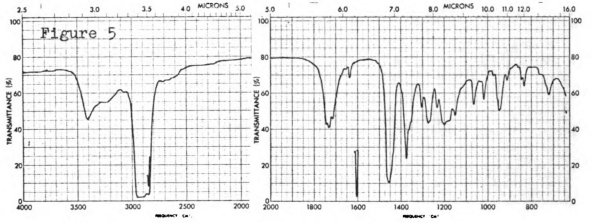
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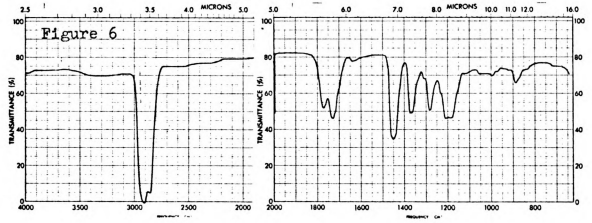
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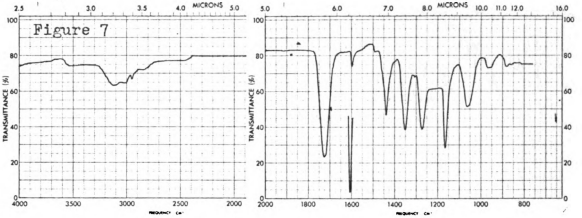
2000 1800 1600 1400 1200 1000 800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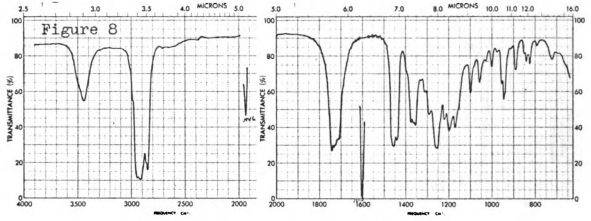
MICRONS
TRANSMITTANCE (%)
FREQUENCY CM-1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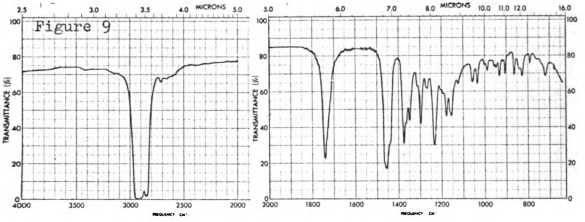
MICRONS
TRANSMITTANCE (%)
FREQUENCY CM-1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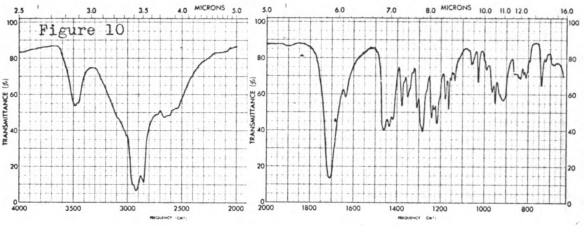
MICRONS
TRANSMITTANCE (%)
FREQUENCY CM-1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4.0
MICRONS
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5.0
6.0
7.0
8.0
MICRONS
10.0
11.0
12.0
16.0
TRANSMITTANCE (%)
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40
20
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1000
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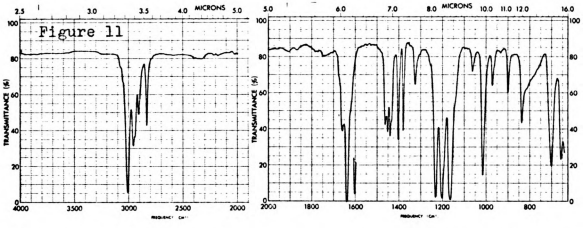
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4.0
MICRONS
5.0
5.0
6.0
7.0
8.0
MICRONS
10.0
11.0
12.0
16.0
TRANSMITTANCE (%)
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40
20
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3500
3000
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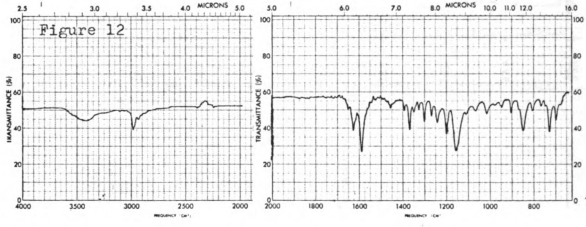
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4.0
MICRONS
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5.0
6.0
7.0
8.0
MICRONS
10.0
11.0
12.0
16.0
TRANSMITTANCE (%)
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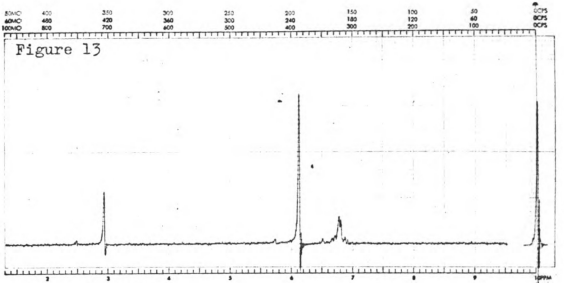

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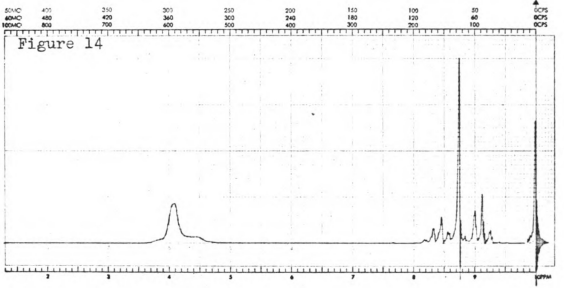

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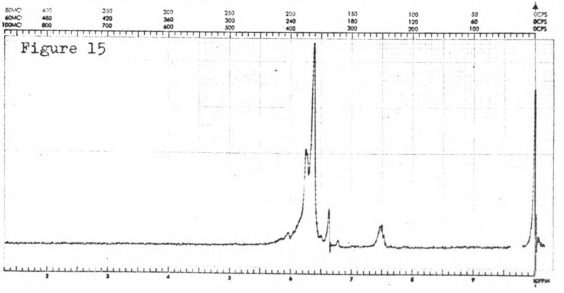

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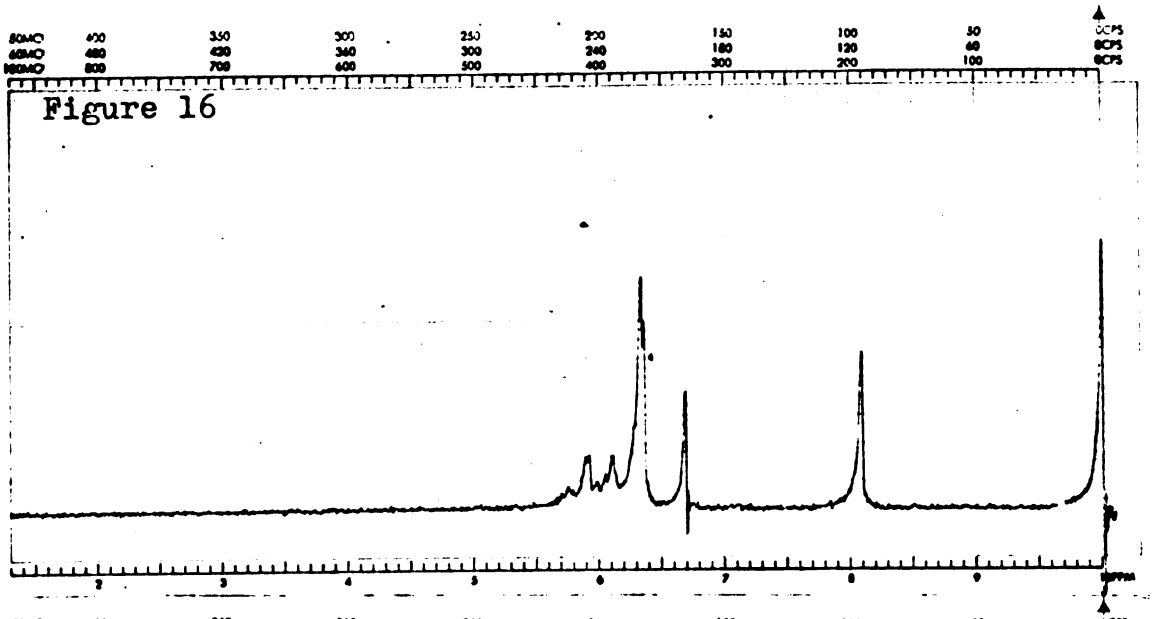

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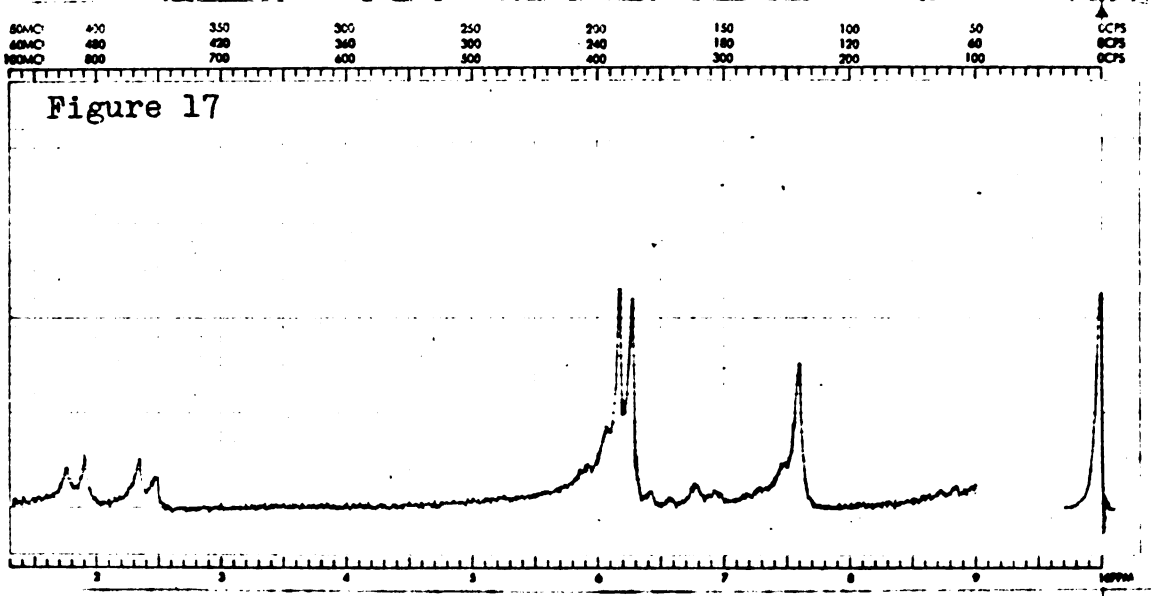

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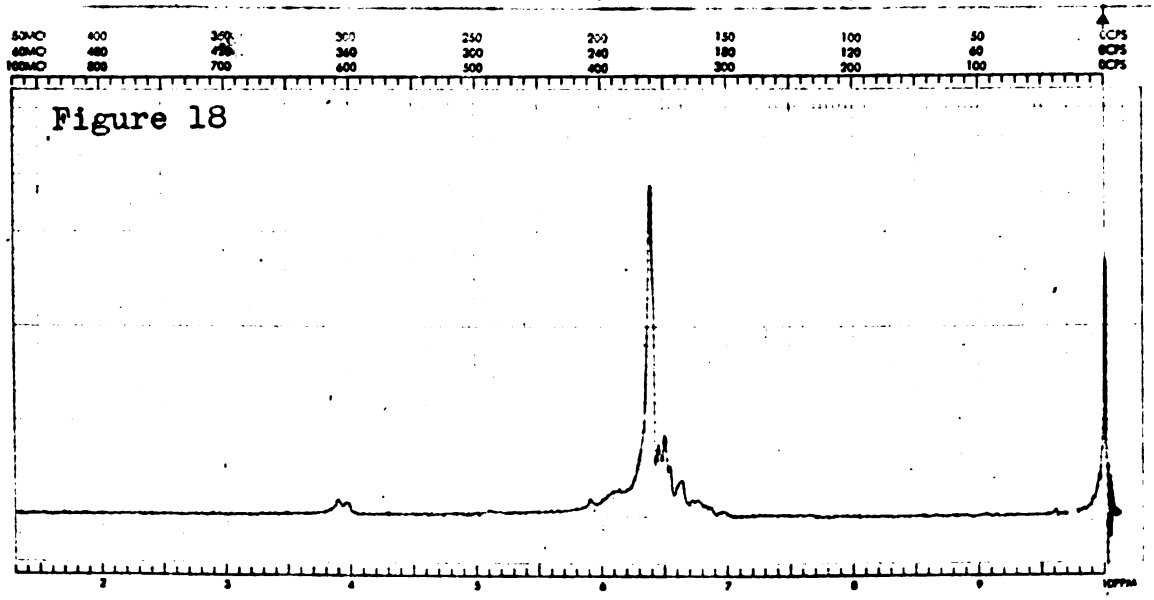
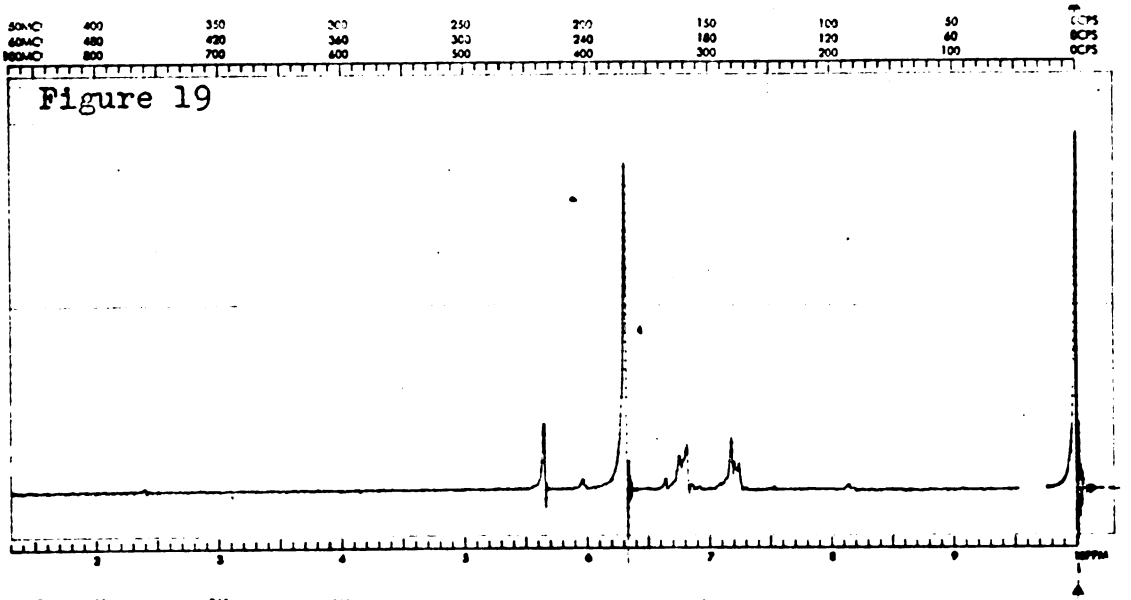


Figure 18

Figure 19



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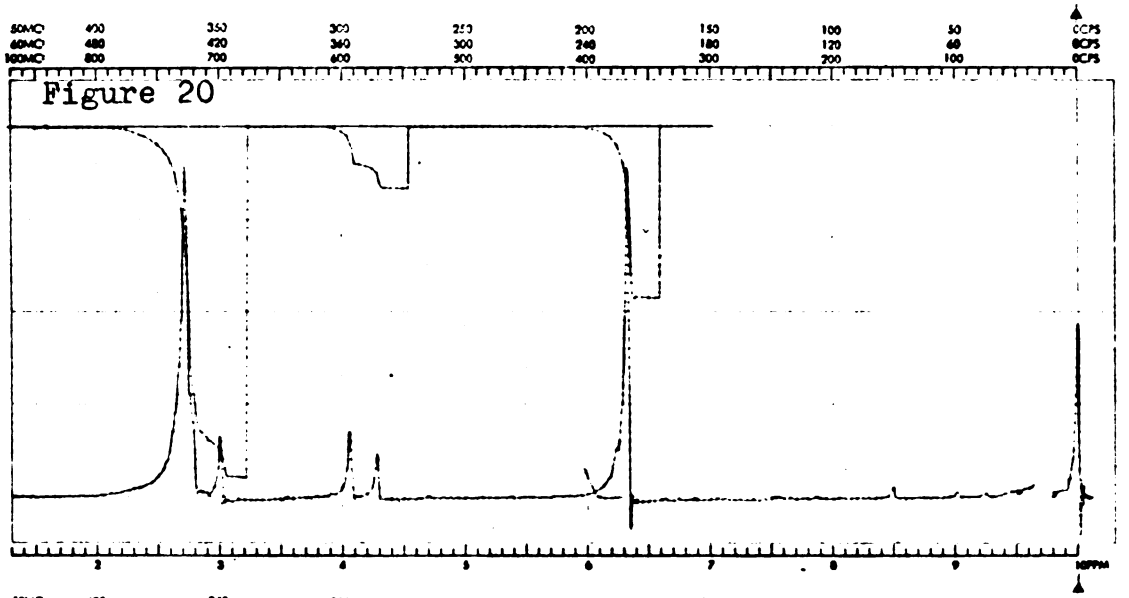

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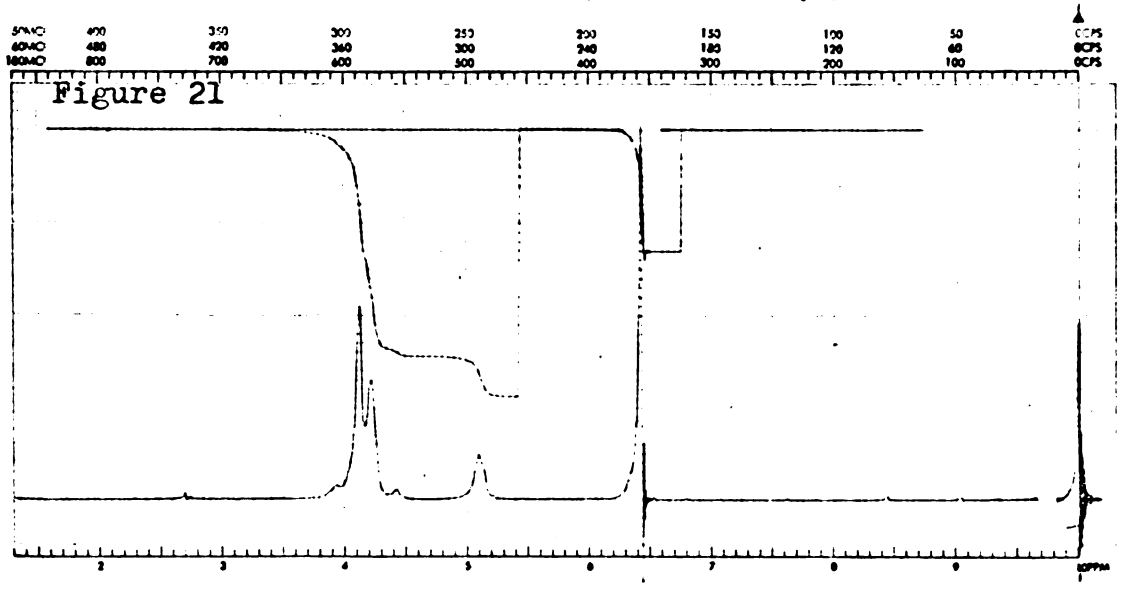

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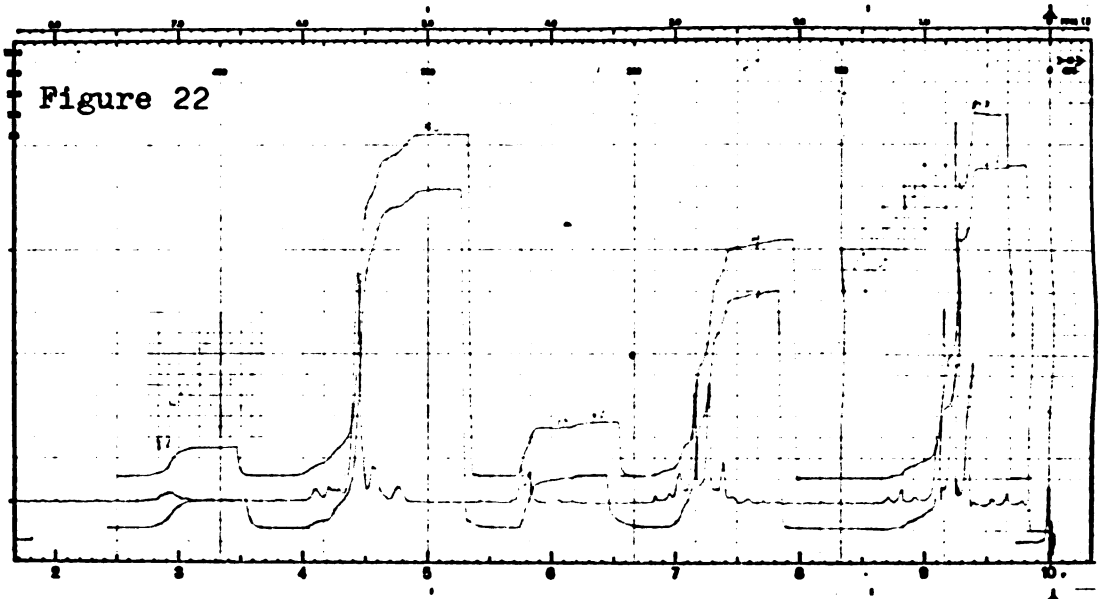

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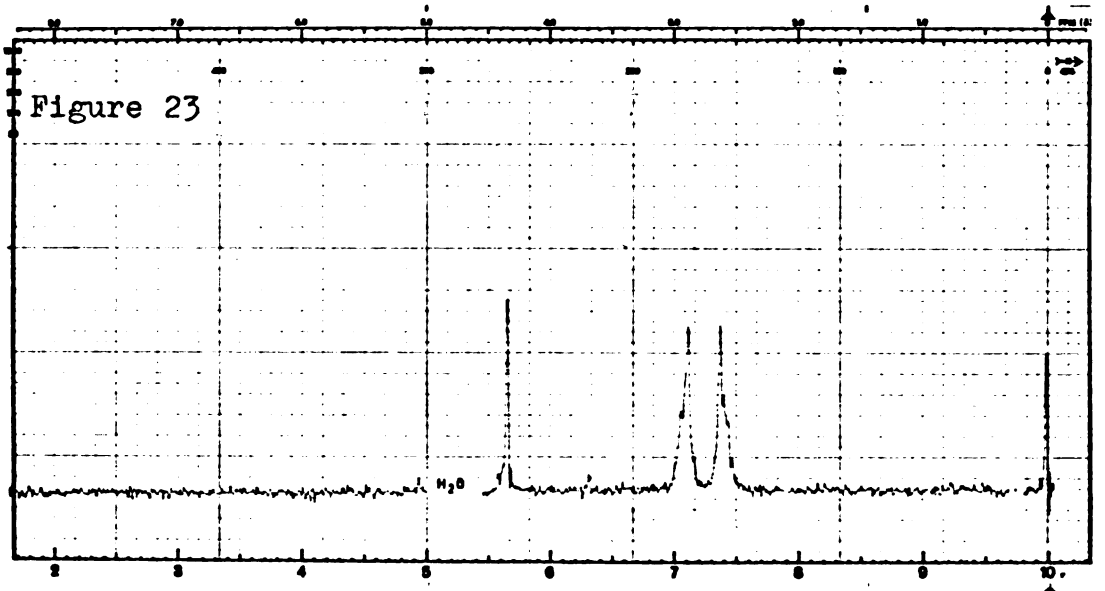

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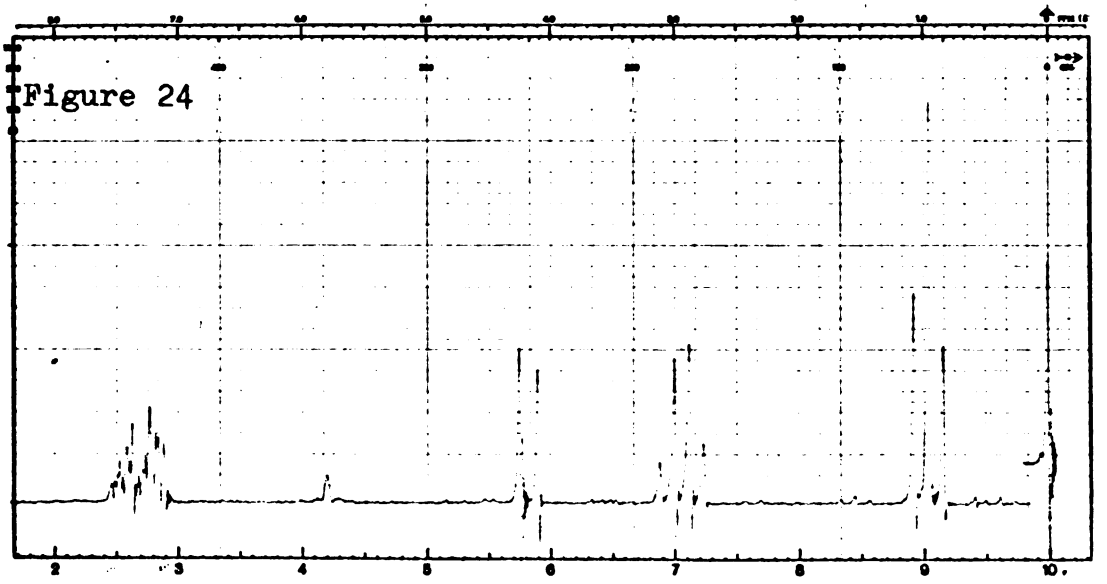

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