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The approaches to 13-methylphenalene system and the studies of aromaticity and antiaromaticity

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THE APPROACHES TO 13-METHYLPHENALENE SYSTEM AND THE STUDIES OF AROMATICITY AND ANTIAROMATICITY

by

WOLIN HUANG

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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ABSTRACT

THE APPROACHES TO 13-METHYLPHENALENE SYSTEM AND THE STUDIES OF AROMATICITY AND ANTIAROMATICITY

by

Wolin Huang

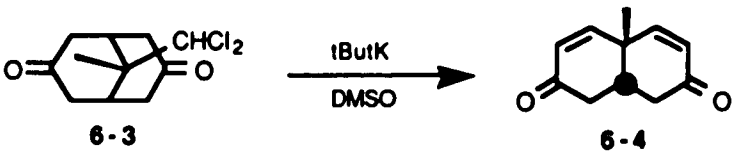
Adviser: Professor Klaus G. Grohmann

An important precursor to the long sought 13-methylphenalene system, dihydro-13-methylphenalene (pentaene) **10-4**, has been synthesized. Dehydrobromination of the hexabromides gave **10-4** and bromopentaenes, which convert to the **10-4** through a lithium-bromo exchange followed by protonation. **10-4** might undergo an unusual solvent-dependent hydrogen [1,11] σ shift.

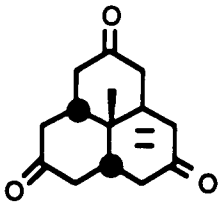
10-4 was treated with DDQ at 80 °C giving perinaphthenone, and treated with sodium dimsyl at room temperature furnishing phenalenyl anion. In both cases, the stable planar high conjugated phenalene system were formed. As a result, the central methyl has lost.

The interesting known conversion of dione **6-3** into dienedione **6-4** was investigated in detail. The reaction conditions have been optimized, and the yield has been improved to 52 %.

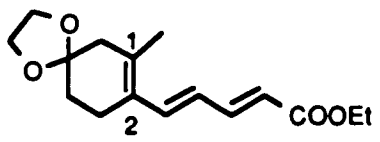
The stereochemistry of the tricyclic trione **VI** was investigated. After an base-catalyzed hydrogen-deuterium exchange, the NOE spectrum undoubtedly points out that **VI** is cis, cis, trans.



6-3 6-4



VI



VII

An unusual epoxidation at C1 and C2 in the triene VII has been found, just open to air in solid form for 24 hours, in 80 % yield.

For concentrating air sensitive compounds, a modified rotatory evaporator was designed and made. For the very air-sensitive reactions, an all-in-one apparatus was designed and made, in which a reaction container, a filter and a NMR tube are connected safely into a very tiny space.

A quite detailed up-date review of aromaticity and annulene is provided.

AM1 calculation for 13-methylphenalene showed the following. The bond dissociation energy of carbon-carbon bond of the methyl in 13-methylphenalene is as low as 8.71 kcal/mol; *Y-hyperconjugation* (a new type conjugation) might occur; And methyl-group shift would take place at temperature above -111 °C.

The (4n+2) π electron monocyclic aromaticity rule is explained by group theory. A new aromatic system possessing D_{3h} symmetry and 6n π electron rule is proposed. MO studies, resonance energy per atom (REPA) and ^1H NMR data of the parent members of this system support that 6n π electron aromatic compounds show higher aromaticity than (4n+2) π electron monocyclic compounds. This notion may be significant to understand the nature of general aromaticity and to predict some stable compounds especially poly-ionic compounds.

ACKNOWLEGEMENT

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CHAPTER ONE. BACKGROUND

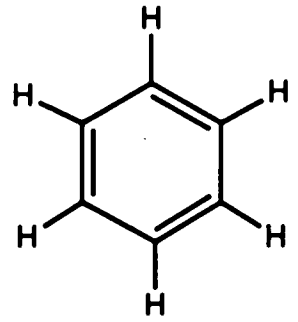
1.1 Aromaticity And Antiaromaticity

A. History

Since the discovery of benzene by Faraday in 1825 in the condensate of an illuminating gas obtained from the pyrolysis of whale oil, millions of aromatic compounds have been discovered or synthesized, and the notion of aromaticity has been generated and continuously deepened. The concepts of aromaticity and antiaromaticity have evolved dramatically into a cornerstone for modern theories of chemical structure and reactivity.[1,2,3]

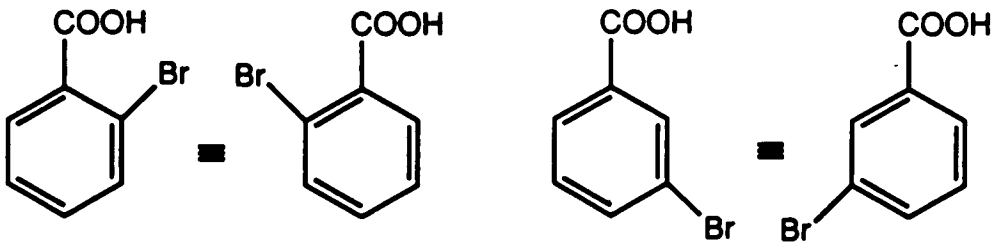
To understand and develop these stimulating concepts, a brief review of the history is necessary. The important discoveries are listed chronologically, as well as logically because any discovery must be based on its predecessors, as following.

In 1865, Kekulé proposed his famous formula for benzene. He also introduced the words "aromatic" and "aromaticity" to describe structural characteristics of cyclic conjugation in six membered rings. His treatise of organic chemistry is based on the dichotomy aliphatic-aromatic.



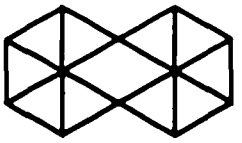
Kekulé's benzene structure

The objections raised by Ladenburg that always one, not two, ortho-(or meta-) disubstituted isomers may be isolated, were countered in 1872 by Kekulé with his oscillating bond hypothesis.



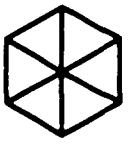
1,2 1,6 1,3 1,5

Erlenmayer was the fist proponent of a generalizing trend which was to continue afterwards, by proposing that the concept of aromaticity should be associated with similar reactivity rather than similar structure. This generalization, which encompassed Erlenmayer's naphthalene and Victor Meyer's thiophen, enabled Bamberger in 1891-3 to recognize the importance of the six free valencies by adapting it to five-membered heterocycles, the Armstrong-Baeyer central formula (1), Dewar's "para bonded" formula (2), and Claus's diagonal formula (3).

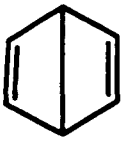


Erlenmayer's naphthalene

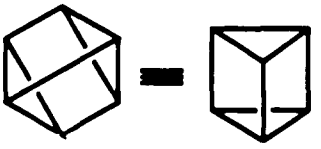
Victor Meyer's thiophene



1.



2.



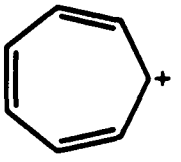
3.

A blind alley was Thiele's explanation (1899) of the apparent saturation of benzene through the "residual valency" hypothesis. In 1911, Willstätter, prompted by Thiele's ideas, prepared cyclooctatetraene and disproved thereby Thiele's hypothesis that all conjugated cyclopolyenes were aromatic.

Kossel's and Lewis's electronic theory of valency in 1916 was applied to benzene by Armit and Robinson. They reinterpreted Bamberger's theory in terms of the "aromatic sextet" of electrons which, like the octet in atoms, was presumed to have a closed configuration, but they could not answer the following question: Why does six rather than eight electrons form a stable shell?

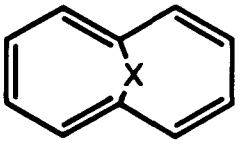
During the 1920's quantum mechanics was developed, it was Erich Hückel's merit to propose the first, quantum mechanical approximate model for aromatic compounds and to obtain thereby the magic (4n+2) electron rule and resonance energy in 1930's, although its importance was not recognized immediately, (Hückel's theory

will be discussed in detail in the next section.) M. J. S. Dewar elucidated the tropolone structure in 1945[4], restated Hückel's prediction that tropylium should be aromatic (as was indeed proven later by Doering) and led to a better standard than Hückel's for the conjugation energy in aromatics, leading to the Dewar resonance energy (DRE)[5]. To prove the DRE, he gave experimental evidence for borazaro and boroxaro aromatics.



Tropylium

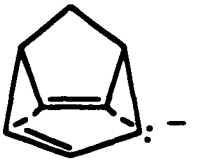
Base on Hückel's theory, many exciting compounds such as bridged 10-, 14- and 18-π-electron systems by Vogel, 14-π-electron systems by Boekelheide, large annulenes and dehydroannulenes by Sondheimer, cyclopropenylium systems by Breslow, $(CH)_9^-$ and $(CH)_8^{2-}$ by Katz, Sydnones and Münchrones were discovered.



X=CH_2,O,NH

Vogel's bridged 10-π-electron system

The Hückel rule has been applied not only to planar continuous conjugated systems, but also to homoaromatic systems where one or more out-of-plane CH_2 groups are intercalated.



In 1937, using a quantum mechanical treatment and the earlier observations of Hückel and Pauling, London[6] developed a theory to explain the high diamagnetism in (4n+2) systems.

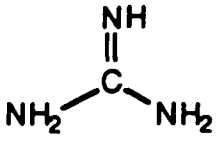
In 1951, Berthier, Mayot and Pullman showed that application of the London theory to certain hydrocarbons of the 4n type led to a positive contribution to the diamagnetic (paramagnetic) susceptibility[7].

In 1961, Elvidge and Jackman[8] put forward the very plausible proposal that a compound should be defined as aromatic if it "... will sustain an induced [π-electron] (diamagnetic) ring current" and that the magnitude of this "ring current" may be taken to be a quantitative measure of the systems "aromaticity".

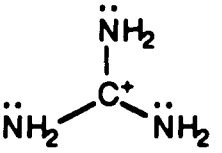
In ca. 1966, five groups[9,10,11,12,13] independently gave prominence to the observation that paramagnetic "ring-current" are to be expected in the (4n)-annulenes. In these systems, shielding occurs in outside the ring and deshieding occurs inside or above the ring.

In 1972, P. J. Gund[14] introduced the notions of "Y-delocalization" and "Y-aromaticity" in order to explain the unique properties of guanidine and guanidinium ion and as a basis for the

following prediction: acyclic compounds with closed shell Y-delocalized 6-electron configuration should possess "aromatic" stability.



guanidine



guanidinium ion

After Bagus and Ladic discussed the stability of polygonal H_N hydrogen chain systems (HCS) in 1982,[15] Ichikawa,[16] Dewar[17] and Haddon[18] introduced this notion into σ-aromaticity.

Historically, the concept of aromaticity went through several distinct phases:

from structural characteristics to reactivity
from carbocycles to heterocycles
from reactivity to resonance energy
from the number of carbons to the number of electrons
from 6 electrons to (4n+2) electrons
from neutral to ionic compounds
from monocyclic to multicyclic and bridged
from continuous conjugated to homo conjugated
from resonance energy to diamagnetism/paramagnetism
from aromatic to antiaromatic
from π bonds to σ bonds
from cycles to Y-shapes

It can be seen that the term "aromaticity" has broadened and differs considerably from Kekelé's original definition. Some scientists (Binsch[19], Heilbronner[20], Lloyd[21], Labarre[22]), playing possibly "devils advocates", questioned provocatively, if aromaticity is outmoded.

Since polycyclic aromaticity, ionic aromaticity, Y-aromaticity and σ-aromaticity have been introduced, difficulties have been raised both scientifically and philosophically. Labarre and Crasnier described this with a very striking and poetic fashion in the following terms:[23]

"Chemists and Physicists are at present in the middle of a cavern which Plato would not have disavowed; they observe on the walls of the cavern *certain shadows* resulting from the lighting of an unknown subject (aromaticity) by the different sources of light represented by their various chemical or physical techniques of observation: an agreeable odor, an aptitude to nitration and sulphonation, a ring current, a magneto-optical excess, a diamagnetic anisotropy, a resonance energy, a U. V. bathochromic effect, and even a mathematical term. The question is: Do these shadows all belong to the *same* invisible myth (or reality)? and the answer is 'Nobody knows at present'."

The definitions of "aromaticity" and "antiaromaticity" are now more and more concentrating on the question that is associated with *resonance energy* (*lowered molecular energy*)[24] or with *ring current*[25], or with *both*.[26] A unifying definition (or the nature) of aromaticity becomes more and more challenging.

B. Resonance Energy And Ring Current

a. Resonance Energy

For monocyclic polyenes, Hückel's rule stated in an extended and more modern version is as follows:

"For polyenes with 4n+2 C-atoms in the path of conjugation, the π-electron energies of the annulenes, $C_{(4n+2)}H_{(4n+2)}$, will be lower (more stable) than those of the linear polyenes, $C_{(4n+2)}H_{(4n+4)}$, whereas the reverse is true for the annulenes, $C_{4n}H_{4n}$, which have π-electron energies greater than those of the corresponding linear polyenes, $C_{4n}H_{(4n+2)}$ (less stable)."[27]

Hükel's rule as originally formulated only mentioned the extra stability of systems with (4n+2) π-electrons. Systems with 4n π-electrons are now known to be less stable than the analogous 4n+2 π-electron system and this observation has been incorporated into the Hückel theory.

According to the simple Hückel theory the annulenes, if planar, should all have their total π-energy less than m times that of the ethylene molecules. The resulting stability gain is defined as the delocalization energy (DE),[28] (eq 1)

$$DE = -(E_{\pi\ total} - mE_{\pi\ ethylene}) \qquad (1)$$

Where $E_{\pi\ total}$ is the total π-energy and $E_{\pi\ ethylene}$ is the π-energy in the ethylene molecule. According to this simple Hückel approach (see Figure 1.1-1), the (4n+2) π-electron systems will have closed electron shells, whereas those with 4n will not, and that there will be a gradual increase in DE with increasing ring size. The smaller

(4n+2) π-electron systems are predicted to be more stable than the neighboring 4n π-electron systems, but this difference in stability virtually disappears for the larger rings. This approach specifically predicts that cyclobutadiene will be a square planar, triplet diradical with zero DE, that benzene will be a symmetrical hexagon with considerable DE, and that cyclooctatetraene will be a planar, octagonal triplet diradical, again with considerable DE.

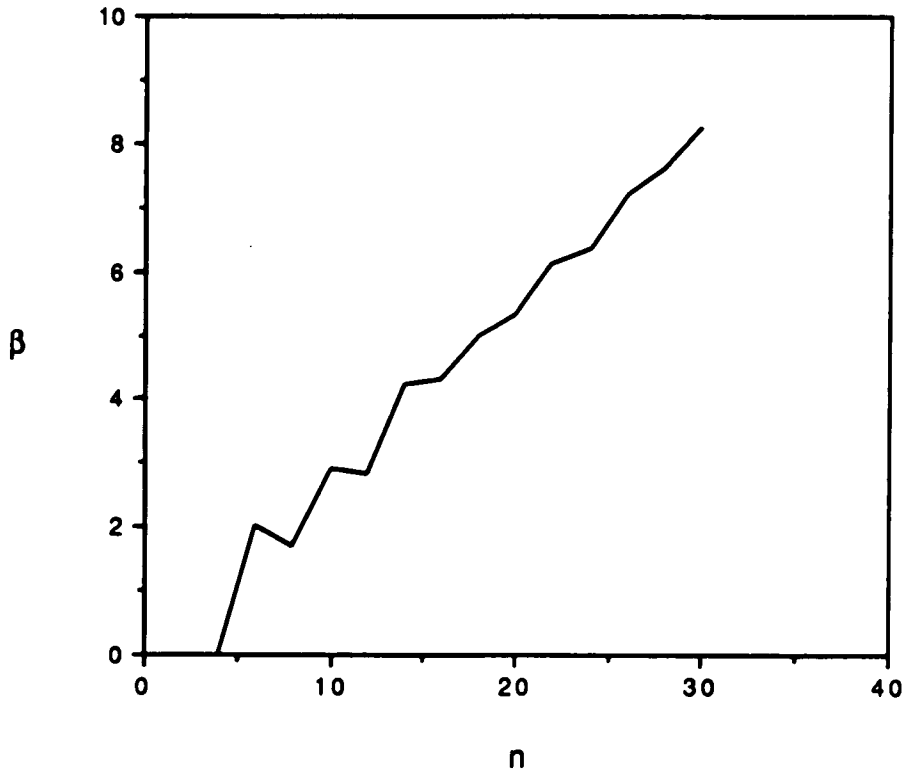


Figure 1.1-1. Delocalization (HMO) energy of the annulenes[28]

Although the simple Hückel theory predicts extra stability for 4n systems when n > 1, this is not confirmed by experimental

facts, (vide infra) (Figure 1.1-1). Annulenes with 4n π-electrons are less stable chemically than annulenes with (4n+2) π-electrons. More elaborate π-energy calculations, using the Pople-Pariser-Parr (PPP) approximation, by Dewar and Gleicher have shown that the resonance energy (RE) (defined as the difference between the calculated heat of formation of a given molecule and heat of formation calculated for a single classical structure using empirical bond energies[29]) for 4n+2 annulenes is positive and the RE for 4n annulenes is negative in some cases (n = 1,2) (Figure. 1.1-2). The HMO method, using polyene reference structure, thus gives reasonable DE values (Figure 1.1-2).[30]

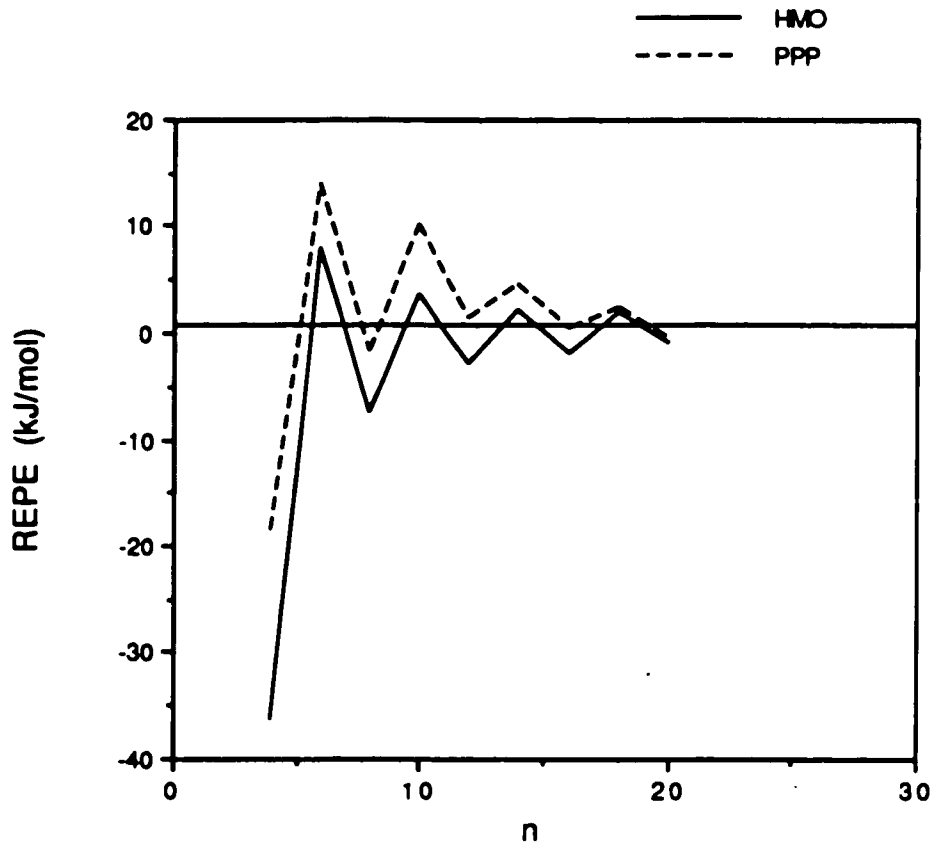


Figure 1.1-2. The resonance energy per electron, REPE (PPP and HMO)

A planar molecule possessing cyclic delocalization is considered aromatic if its RE is greater than zero. (Figure 1.1-2). Figure 1.1-2 shows that only 4n+2 annulenes possess positive RE (HMO), while the 4n annulenes possess negative or zero RE (HMO). Therefore, these 4n systems are termed antiaromatic[31].

Unfortunately, the determination of aromaticity or antiaromaticity can not be solely based on the number of π-electrons, and the resonance energy, an experimental quantity, is very difficult to obtain. Other factors which are important include

the strain energy associated with the molecule, especially when considered in its planar conformation, and the degree of bond alternation.

b. Ring Current

Experimentally, molecules of the (4n+2) type like benzene were observed to possess unusually high diamagnetism when placed in an external magnetic field perpendicular to the plane of the molecule. Pauling developed a semi-classical theory to explain the diamagnetic anisotropy in some aromatic molecules. The impression of an external magnetic field causes a flow of the π-electrons around the ring.[32]

Using a quantum mechanical treatment and the earlier theoretical approximations by Hückel and Pauling, London, in 1937, developed a theory to explain the high diamagnetism in (4n+2) systems which gave good correlation with experimental observation.[33] In qualitative terms London's theory concluded that for molecules possessing 4n+2 π-electrons in a planar cyclic conjugated array, a negative contribution to the diamagnetic susceptibility could be expected. Jackman and Elvidge used the term diamagnetic ring current to explain this phenomenon.[34] As consequence of a diamagnetic ring current, one observed is considerable deshielding in the molecular plane outside the ring, and even larger shielding inside or above the molecular plane,(Figure 1.1-3).

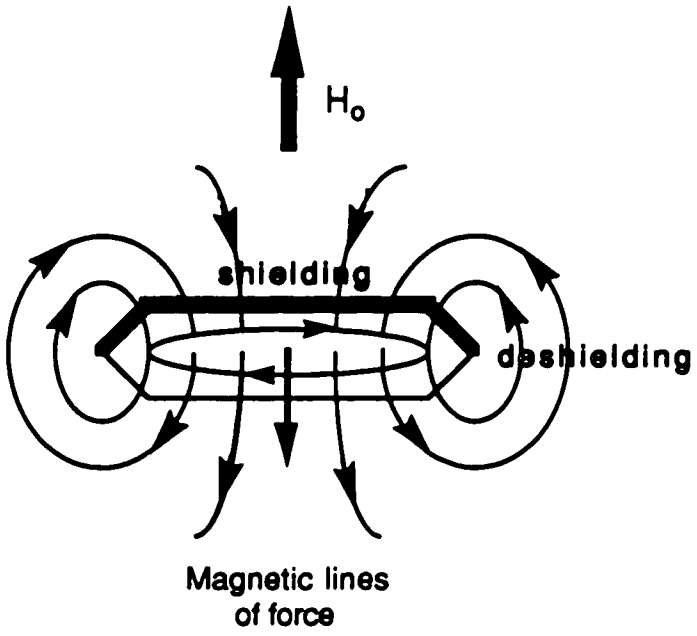


Figure 1.1-3. Current and magnetic lines of induced in benzene by a primary field, H_o[35]

In 1951 Berthier, Mayot, and Pullman showed that application of the London theory to certain hydrocarbons of the 4n type led to a positive contribution to the diamagnetic susceptibility.[36] Thus the impression of an external magnetic field on 4n systems results in the formation of a paramagnetic ring current. The previously stated shielding effects are reversed in a paramagnetic ring current. Thus there is considerable shielding in the molecular plane and even more deshielding inside or above the molecular plane.

In 1966 Pople and Untch further examined induced ring currents in 4n versus (4n+2) systems and made the following observations:[37]

1. For all degrees of bond alternation the London theory always predicts a negative contribution to the diamagnetic

susceptibility (diamagnetic ring current) when there are (4n+2) π-electrons. When there are 4n π-electrons the theory predicts a positive contribution to the diamagnetic susceptibility (paramagnetic ring current).

2. For all sizes of rings the degree of the induced ring current effect is quenched with bond alternation. Larger rings are affected more by a given amount of bond alternation. Qualitatively, the induced ring current in 4n systems is quenched more by a given amount of bond alternation than in (4n+2) systems.

3. For 4n systems the London theory predicts infinite paramagnetism when there is no bond alternation. However, in practice all 4n systems show some bond alternation and thus converge towards zero resonance energy (Figure 1.1-2). At that point both series should behave as typical reactive polyolefins. The previously stated degeneracy is removed and the paramagnetic effect takes on a finite value.

Point 3 is very important. The London theory predicts infinite paramagnetism when there is no bond alternation, but in reality all 4n systems exhibit some bond alternation. In 4n systems when there is no bond alternation the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are degenerate, (Figure 1.1-4). This degeneracy leads to infinite paramagnetism. This degeneracy in the ground state is removed by the process of bond alternation. The ground state is now in a non-degenerate singlet state (Figure 1.1-4). This is an example of the Jahn-Teller effect.[38] As Figure 1.1-4 shows once the ground state of a 4n system is no longer degenerate, a small HOMO-LUMO gap is created. This small energy gap accounts for the relative instability of systems

because the energy required to raise a ground state electron to an excited state (the LUMO) is small. In addition, since the ground state is now non-degenerate the paramagnetism in 4n systems becomes finite.

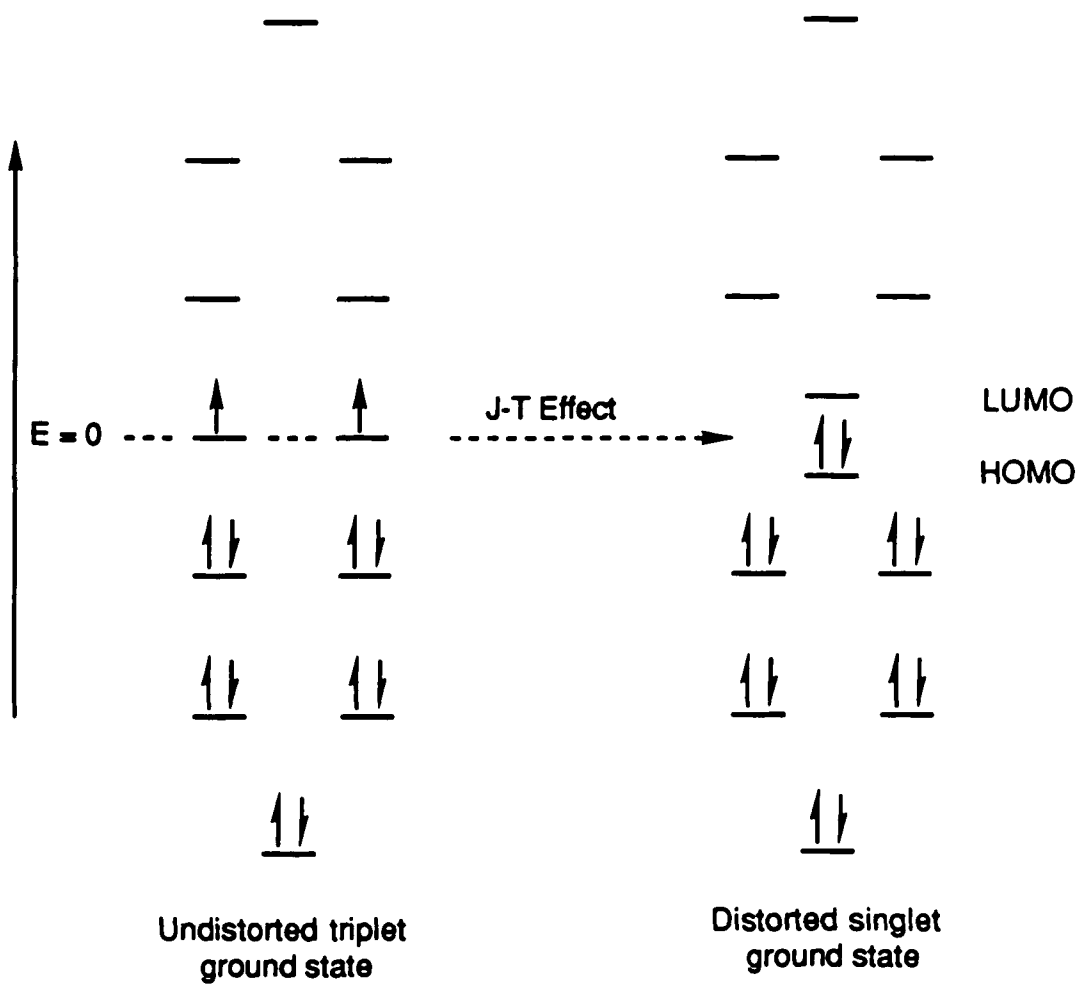


Figure 1.1-4. The Jahn-Teller Effect on The Molecular Orbitals of A Generalized [12]Annulene.

The Jahn-Teller distortion becomes very important for small 4n annulenes and is still important in larger 4n+2 annulenes. The

calculations of Dewar and Gleicher[39] predict that at a ring size of 26 C-atoms bond alternation begins for (4n+2)-π-electron systems. Consequently, [26]annulene is predicted to be non-aromatic (RE=0), (Figure 1.1-2).

The previously stated shielding effects for diatropic (4n+2 systems) and paratropic (4n systems) molecules have been measured most accurately by ^{1}H-NMR spectroscopy. Some examples are shown in section 1.2.

c. Resonance Energy And Ring current

Haddon has presented a unified theory linking resonance energy (RE) to induced ring current (RC).[40] The relationship of RE to RC for the (4n+2) annulenes is given by

$$RC = 3S\ RE/\pi^2$$

Where S is the area of the ring and RE is the Dewar resonance energy, because RE and RC are both related to p_{rs} (bond order) and β (resonance integral) as follows:

$$RC = p_{rs}S\beta/N$$

$$RE = \pi^2 p_{rs}\beta/3N$$

The REs derived in this way are in good accord with those observed by the PPP and modified HMO methods. A similar theoretical treatment has been presented by Aihara.[41]

C. Criteria

Theory and experiment have provided a number of criteria for aromaticity and antiaromaticity.

a. Resonance Energies Expanding from Dewar's original Pariser-Parr-Pople (PPP) calculation, a variety of other approaches to the resonance energies have been reported. Schaad and Hess gave a reparameterization of the Hückel method with the reference energies obtained by summing individual bond energies.[42] Aihara and Gutman[43], Milum and Trinajstic[44] used an infinitely large cyclic polyene as reference structure. Herndon introduced a valence bond method.[45] The agreement on the calculated resonance energy for the various methods and models is good, and the calculated energies do appear to provide a reliable index of stability and reactivity for the compounds for which calculations have been made. The occurrence of a positive calculated resonance energy, presumably above a prescribed limit, could then be used to classify aromatic, antiaromatic or nonaromatic compounds.

Among the above methods and models, Schaad and Hess's REPE is the most widely accepted over the last decade. Single and double bonds in hydrocarbons have been classified into eight types according to the number of attached hydrogen atoms as in Table 1.1-1. Total HMO π energies of acyclic polyenes, calculated in the usual way, have been found to be linear functions of the number of each type of bond. This allows the assignment of an empirical π-bond energy to each bond type, such that the total HMO energy of acyclic polyenes is simply a sum of these bond-energy terms. HMO π-energies of cyclic hydrocarbons are not linear functions of the numbers of bonds and hence are not obtainable as a sum of bond-

energy terms. Therefore resonance energies are defined as the difference between HMO π-energy and the additive contribution obtained by summing individual bond energies. For example, the RE and REPA of benzene are easily obtained by use of eq 1-5.

$$E_{loc} = 3E_{22} + 3E_{12} = 7.61\beta \quad (1)$$

$$RE = E_{HMO} - E_{loc} \quad (2)$$

$$RE = (8.00 - 7.61)\beta = 0.39\beta \quad (3)$$

$$REPA = RE/n \quad (4)$$

$$REPA = 0.39\beta/6 = 0.065\beta \quad (5)$$

Table 1.1-1. Calculated Hückel π-Bond Energies of Carbon-Carbon Double and Single Bonds of Acyclic Polyenes[46]

Designation[a]	Type of bond	Calculated π-Bond Energy, (β)
23	$H_2C{=}CH$	2.0000[b]
22	HC=CH	2.0699
22'	$H_2C{=}C$	2.0000[b]
21	HC=C	2.1083
20	C=C	2.1716
12	HC-CH	0.4660
11	HC-C	0.4362
10	C-C	0.4358

[a] The first index gives the bond order, the second the number of attached hydrogens. [b] Arbitrarily assigned.

For ion and radical bond energies, a similar calculation method has been applied with the terms in Table 1.1-2.

Table 1.1-2. Ion and Radical Bond Energy Terms[47]

bond type[a]	designation	bond π-energy (β)
$HC\text{-}CH_2^{\bullet}$	$E_3^{\bullet}$	0.6632
$HC\text{-}CH^{\bullet}$	$E_2^{\bullet}$	0.5996
$C\text{-}CH_2$	$E_2'^{\bullet}$	0.5950
$HC\text{-}C^{\bullet}$	$E_1^{\bullet}$	0.5480
$C\text{-}CH^{\bullet}$	$E_1'^{\bullet}$	0.5697
$C\text{-}C^{\bullet}$	$E_0^{\bullet}$	0.5430
$HC^{\bullet}\text{-}CH_2^{\bullet}$	$E_3^{\bullet\bullet}$	0.7967
$HC^{\bullet}\text{-}CH^{\bullet}$	$E_2^{\bullet\bullet}$	0.7330
$C^{\bullet}\text{-}CH_2^{\bullet}$	$E_2'^{\bullet\bullet}$	0.7067
$C^{\bullet}\text{-}CH^{\bullet}$	$E_1^{\bullet\bullet}$	0.6815
$C^{\bullet}\text{-}C^{\bullet}$	$E_0^{\bullet\bullet}$	0.6570

a. The asterisks refer to positive or negative charges or in the first six bond energy terms to single electrons. Only monoradicals are treated, and the last five bond energies do not apply to these systems.

b. NMR The most widely used method for determining aromaticity and antiaromaticity has been the observation of diatropicity or paratropicity in the ^1H NMR spectrum. This technique is easy to apply, is nondestructive, and requires only small quantities of compound.

Haddon has applied a simple model to the calculation of ring currents in annulenes using the previously reported application of the Biot-Savart law for the calculation of special magnetic fields.[48] Model chemical shifts were assigned to different environments while geometries were obtained from x-ray crystallographic analyses wherever possible and a ring current geometric factor (RCGF) was derived. Two parameterizations were made, the most satisfactory being that in which the magnetic resonance integral β_M was estimated from the ring current of trans-15,16-dimethyl-dihydropyrene. A measure of the aromatic character (AC) of the system was taken from the value of k necessary to reproduce the ring current. The constant k relates to the resonance integral and measures the degree of bond alternation in the system. A value of k = 1 occurs if all the bonds are of equal length and k tends toward zero as bond alternation increases. For the model system 15,16-dimethyl-dihydropyrene k = 1.000; this and the values for other compounds are shown in Table 1.1-3.

Table 1.1-3. Calculated Ring Currents and Aromatic Character by Haddon's Method

Compound	Ring Current RC ($cm^2\ t^{-1}$ ppt)	Aromatic Character k
Benzene	-1.1861	1 +
Naphthalene	-1.1247	1 +
1,6-Methano[10]annulene	-0.7622	0.768
[12]Annulene	0.2137	0.582

Tridehydro[12]annulene	1.1811	0.749
[14]Annulene	-0.7451	0.779
15,16-dimethyl-dihydropyrene	-1.5495	1.000
[16]Annulene	0.6288	0.729
[16]Annulenyl dianion	-1.7861	0.937
[18]Annulene	-1.2043	0.837
[24]Annulene	0.8862	0.805

From the table it can be seen that aromatic (4n+2) annulenes have values of $k > 0.75$, whereas antiaromatic 4n annulenes have values of $k < 0.75$. [12]annulene is considerably more antiaromatic than [16]annulene. This is in accord with the observed physical and chemical properties. The higher k value for tridehydro[12]annulene compared to [12]annulene probably reflects the steric nonbonded destabilization in the latter compound.

c. Hardness The term absolute hardness is defined by Pearson and Parr[49]. A finite approximation is

$$\eta = (I - A)/2$$

Where I and A are the ionization potential and electron affinity, respectively. The value η is known to be an index of stability and reactivity. In molecular orbital theory, e.g., Hartree-Fock theory or Hückel theory, there results

$$\eta = (E_{LUMO} - E_{HOMO})/2$$

as first emphasized by Pearson.[50] This is the working definition of absolute hardness. In 1989, Zhou and Parr defined the relative hardness[51]

$$\eta_r = \eta - \eta_a$$

Where η_a is the hardness of hypothetical acyclic reference structure by means of a graphical method, following Aihara,[52] and Gutman, Milun, and Trinajstic.[53]

Compounds with large η values are expected to have high stability and hence to be aromatic. From 216 calculated samples we can see that the dividing line between aromatic and antiaromatic species is around -0.2β (approximately $-0.15\beta \leq \eta \leq -0.25\beta$) for a Hückel hardness and around zero ($0.08\beta \leq \eta_r \leq -0.08\beta$) for Hückel relative hardness.[54]

d. Bond Lengths In 1971, Julg applied the C-C bond length to be a criterion of aromaticity in annulenes.[55] Aromatic system should have equal bond lengths, which should be the average between carbon-carbon single bonds and double bonds, (approach 139 pm, the benzene C-C bond) whereas nonaromatic or antiaromatic annulenes should have bonds of alternating length. Since 1985, Bird has taken this approach further to five-membered ring,[56] six-membered ring,[57] and bicyclic[58] heterocycles.

The bond orders, N, were calculated from the bond length, R, using the Gordy relationship[59]:

$$N = a/R^2 - b$$

Constant *a* and *b* is listed upon the atoms bonded, e.g., 6.80 and 1.71 for C-C bond; 6.48 and 2.0 for C-N bond. The coefficients of variation for the bond orders of a particular heterocycle are given by the expression:

$$V = 100/\tilde{N}\ [\Sigma(N-\tilde{N})^2/n]^{1/2}$$

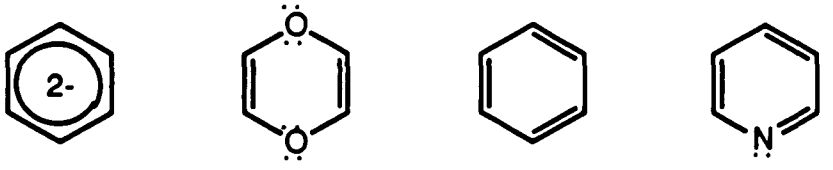
Where $\tilde{N}$ is the arithmetic mean of the various bond orders, N, and n is the number of bonds. In the case of a fully delocalized heterocycle V will have the value 0, whereas for a non-delocalized Kekulé form with alternating single and double bonds the value depends upon the type of ring system. Thus for a five-membered ring heterocycle V_k = 35, for a six-membered ring heterocycle V_k = 33.3, and for systems consisting of a five-membered and a six-membered ring fused together V_k = 35. In order to place the values of V on a more convenient scale than 0 to 35, the calculated V is substituted into the equation:

$$\text{Aromaticity Index, } I = 100(1-V/V_k)$$

e. First- or second-order double bond fixation Binsch has suggested as a criterion for aromaticity that the compound should not show strong first- or second-order double bond fixation. To determine these parameters, the planar sp^2 σ framework is set up with equal bcnd lengths (e.g., 150 pm), and the geometry is then examined after the π electrons are introduced. The total energy is

developed as a Taylor series, which can be interrupted to give first-order terms (dependent upon ∂E) or second-order terms (dependent upon $\partial^2 E$). The bond orders can be derived from the first-order terms, and the difference in bond order between adjacent bonds measures the first-order double bond fixation. For second-order terms, a critical value was determined above which second-order bond fixation occurred. Benzene exhibits neither first- nor second-order bond fixation.

f. Conformation Podlogar et al. recently suggested a conformational criterion for aromaticity and antiaromaticity.[60] This idea is based on the known results: a planar ring system maximizes overlap of the atomic p orbitals contributing to the π-system. This π-interaction is highly stabilizing for aromatic systems but destabilizing for antiaromatic systems. Deviation from planarity of the molecular framework will disrupt the π-overlap and consequently arrect the energy. Therefore probing the potential energy hypersurface for various geometries should permit determination of the aromatic or antiaromatic nature of a species.



1 **2** **3** **4**

For example, The compounds **1**, **2**, **3** and **4** were investigated with an ab initio (Hartree-Fock) molecular orbital study. The energy differences between folding angle (the 2-1-4-5 dihedral angle) from

180° to 160° are -20.2, 0.8, 15 and 9 kcal/mol, which implies antiaromatic, nonaromatic, strong aromatic and weak aromatic, respectively.

1.2 Annulenes

A. Annulenes

The term annulene has been given to a series of monocyclic polyolefins, $C_{2m}H_{2m}$ (m=2,3,4...), containing a complete contiguous set of double bonds.[61,62] All C-atoms are sp^2-hybridized. Benzene, [6]annulene, is the most common member of this class of compounds. Much interest has been devoted to the higher homologous.

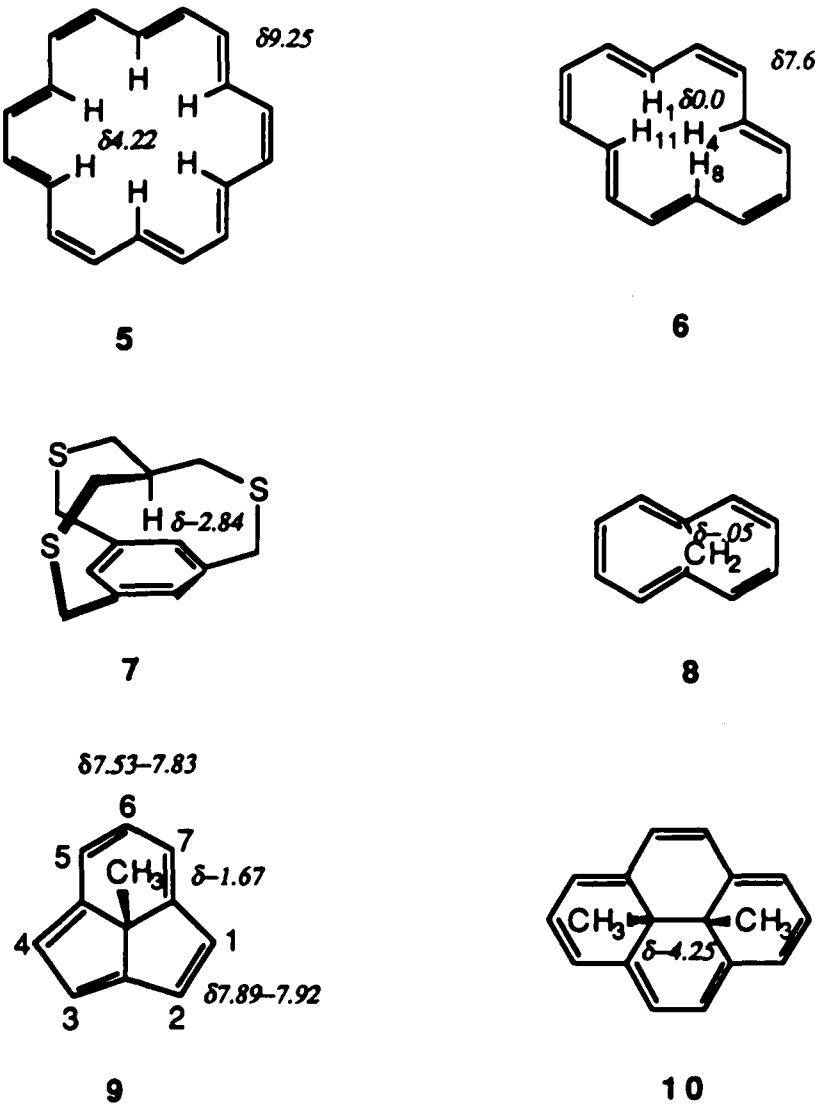


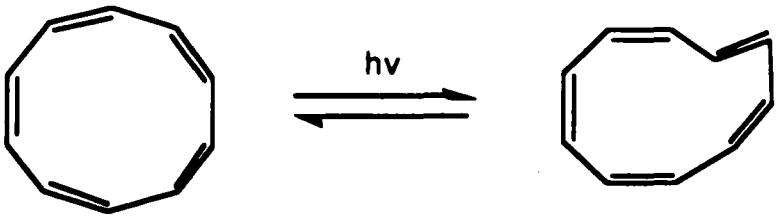
Figure 1.2-1. Some Selected (4n+2) π-Electron Systems

[18]Annulene **5**[63] shows a temperature dependent ^{1}H-NMR spectrum. At -60 °C the ^{1}H-NMR shows two signals, one set of six protons at δ -4.22[64] and the other set of 12 protons at δ 9.25. The structure as written in Figure 1.2-1 has been verified by a X-ray analysis.[65] The six inner protons are shielded and the 12 outer protons are deshielded in complete agreement with a diamagnetic

ring current.

[14]Annulene **6**[66] exists in two major conformations. One conformation has H_1 and H_4 above H_8 and H_{11}, and the other has H_1 and H_8 above H_4 and H_{11}. The X-ray analysis supports this conclusion.[67] The temperature dependent ^{1}H-NMR spectrum at -60 °C shows two sets of signals. The four internal protons resonate at δ 0.0, while the ten external protons resonate at δ 7.6. These results are fully consistent with a diamagnetic ring current.

The remaining examples in Figure 1.2-1 illustrate the use of some bridging groups in diatropic molecules. These bridging groups add rigidity to the illustrated molecules. The central proton in 2,6,15-trithia-*in*-[3^{4,10}][7]metacyclophane **7**[68] resonates at δ -2.84, a clear manifestation of the diamagnetic ring current above the benzene ring. X-ray crystallographic analysis revealed the hydrogen-to-ring distance of 1.69 Å. 1,6-Methano-[10]annulene **8**[69] shows a resonance for the bridging methylene protons at δ -0.5. The bridging group not only adds rigidity to the system, but also adds stability to the system. 1,6-Methano-[10]annulene can be contrasted with the unbridged [10]annulene **8'**, synthesized by Masamune and coworkers.[70] **8'** is a very unstable molecule. It behaves as a reactive polyolefin and can be only isolated at low temperature. In addition, **8'** shows no evidence of a diamagnetic current. The molecule can not assume a planar conformation because of strain factors. (eq. 2)



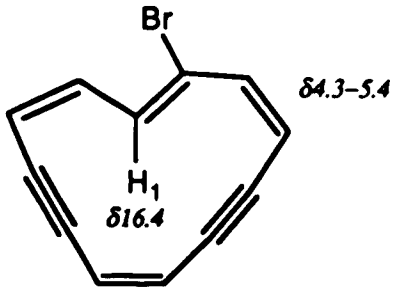
eq. 2

8'

The ^{1}H NMR of 7b-methyl-7b*H*-cyclopent[cd]indene **9**[71], a tricyclic aromatic [10]annulene, is consistent with a symmetrical structure and the existence of a diamagnetic ring current. It shows a signal at δ-1.67 for the central methyl group. The peripheral protons are at δ 7.53-7.83 (AB_2 system, 5-, 6-, and 7-H) and 7.89-7.92 (AB system, 1-, 2-, 3-, and 4-H).

Another example of a bridged diatropic molecule is trans- 15, 16-dimethyldihydropyrene **10**.[72] The methyl groups are within the cavity of the molecule and show a ^{1}H-NMR signal at δ-4.25.

Clearly, ^{1}H-NMR accurately determines the shielding effects in diatropic molecules. The shielding effects in paratropic molecules have also be measured accurately by ^{1}H NMR. Figure 1.2-2 illustrates some selected 4n systems.



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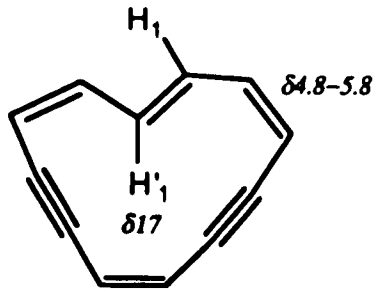

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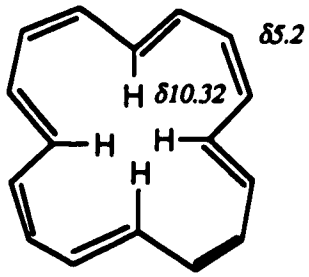

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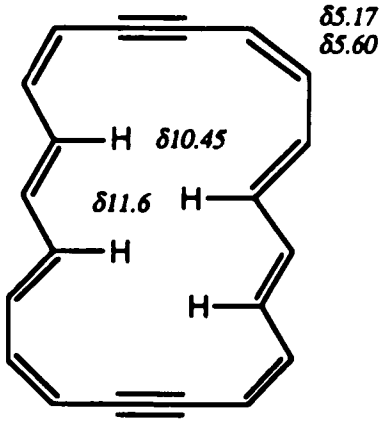

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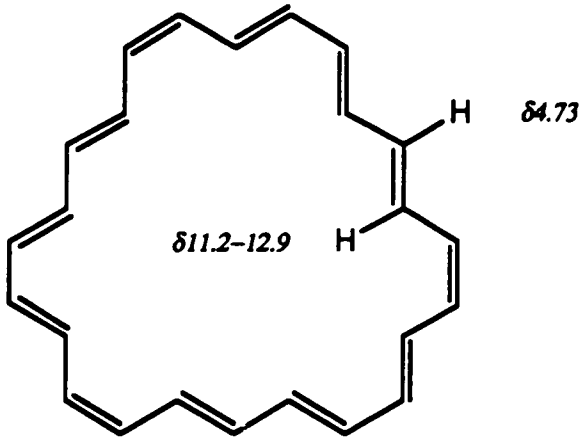


15

Figure 1.2-2. Some Selected 4n π-Electron Systems

One of the first experimental observations of a paramagnetic ring current effect was in 5-bromo-1,9-didehydro-[12]annulene **11** and 1,5-didehydro-[12]annulene **12**.[73] The internal proton (H_1) in **2-11** resonates at δ 16.4 and the internal proton (H'_1) in **12** resonates at ca. δ17. The external protons in **11** resonate at δ4.3-5.4 and the external protons in **12** resonate at δ 4.8-5.8. These data are in complete agreement with a paramagnetic ring current.

[16]Annulene **13**[74] shows a temperature dependent ^{1}H-NMR spectrum. At -120 °C the four internal protons resonate at δ10.32 (triplet) and the external protons resonate at δ 5.2 (multiplet). The torsional strain angle in [16]annulene is only approximately 20°. This means the four internal protons do not suffer a severe steric interaction when the molecule assumes a planar conformation.

1,11-Didehydro-[20]annulene **14**, synthesized by Sondheimer,[75] shows typical properties of a 4n system. The internal protons resonate (-80 °C) at δ11.6 (2H) and 10.45 (2H). The external protons show signals at δ 5.17 and 5.60.

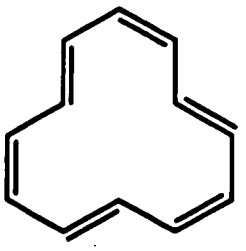
The final example in Figure 1.2-2 is [24]annulene **15**, synthesized by Sondheimer and Calder.[76] This molecule also exhibits a temperature dependent ^{1}H-NMR spectrum. At -80°C the internal protons resonate a δ11.2-12.9, while the external protons resonate at δ 4.73.

It is interesting to note that as the ring size increases from **13** through **15** the internal protons are deshielded by approximately 2.6 ppm. This may mean that the larger [24]annulene is sterically less crowded than **13** or **14** and that **15** can assume a more favorable planar geometry, thus maximizing the paramagnetic ring

current. The external protons remain relatively insensitive to increasing ring size in going from **13** to **15**. These results are in complete agreement with the ring current model. The theory predicts that the degree of deshielding inside or above the ring of a 4n system will be greater than the degree of shielding outside the ring.[77]

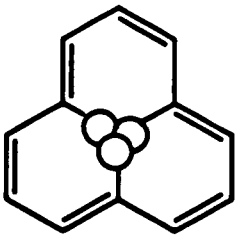
B. 12 π Annulenes

The examples in Figure 1.2-2 clearly establish the presence of a paramagnetic ring current in unbridged 4n systems. Considerable effort was expended to obtain smaller 4n annulenes, especially with n=3.



16

The parent annulene with n=3 is [12] annulene **16**, elegantly synthesized and studied by Oth and coworkers.[78] This compound has been found to be exceptionally labile, undergoing a series of photolytic and thermal electrocyclic transannular ring closures at approximately -60 °C. Its ^{1}H-NMR at -170 °C exhibits two signals at δ 7.83 (3H) and δ 5.88 (9H). The signal at lower field is due to the three internal protons which experience a modest paratropic shift. This molecule has been shown to experience considerable deformation from planarity because of the Van der Waal's repulsion of these three internal protons which cause a torsional strain angle of 50-60° for this molecule and thus its diminished paramagnetic ring current. Structure. **16'** illustrates this non-bonded interaction.



16'

The molecule is found to undergo a rapid isodynamical[79] bond shift which makes the protons on the trans double bonds isochronous as are the protons on the cis double bonds, i.e., at -80°C there are two sets of ^{1}H-NMR signals each of six protons. One set is the protons on the trans double bonds, while the other set is the protons on the cis double bonds. The diminished paramagnetic ring current in [12]annulene **16** becomes readily apparent on comparison with [16]annulene **13**. As stated before, the four internal protons in **13** resonate at δ 10.32. Thus the perimeter in the larger **13** is more planar in comparison with the smaller **16**.

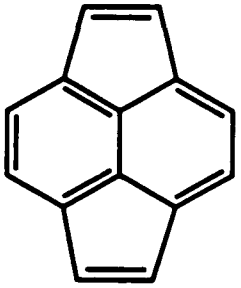
In extreme contrast to the very unstable [12]annulene **16** the [12]annulene dianion,[80] formally a diamagnetic 14 π-electron system is thermally stable up to 60°C. At -90 °C, six outer protons resonate at δ 6.98; the other three outer protons resonate at δ 6.23; and the three internal protons now resonate at δ -4.60, a typical position for internal protons in a diatropic molecule with charges.

Interestingly, despite the steric interactions which prevent achievement of planarity in **16**, the resonance stabilization associated with the 14 π-electrons in the dianion of [12]annulene **16** is at least 8 kcal/mol greater than the resonance stabilization in

the isoelectronic species, the neutral [14]annulene **6**. Simple HMO calculations indicate that the delocalization energy in the dianion of [12]annulene **16** is approximately one β unit larger than in [14]annulene **6**.

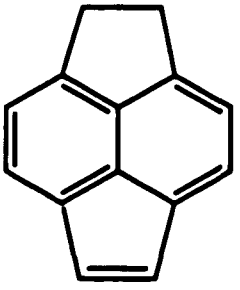
Since the parent [12]annulene **16** exhibits extreme lability, making its study quite difficult, the [12]annulene perimeter must be made more rigid. One way of achieving this is by introducing various bridges eliminating the steric overcrowding and preventing transannular reactions.

The use of bridging groups has been most profitably investigated by Vogel and his group in the [10]annulene field.[81] As previously discussed [10]annulene[82] was found to behave as a reactive polyolefin. In contrast to this, introduction of a bridging methylene group among the 1,6 C-atoms produces a stable molecule, 1,6-methano[10]annulene **8**,[83,84,85,86] that shows a strong diamagnetic ring current and thus it can be classified as aromatic. Therefore bridging groups have also been used in the [12]annulenes studies.[87]

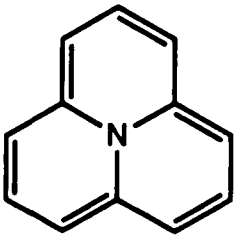


17

Pyracylene **17**, synthesized by Trost and co-workers,[88] formally possesses an ethylene bridge. Models indicate a moderate deformation from a planar geometry for this molecule. In addition this molecule is predicted to contain a strain energy of 48 kcal/mol. The ring protons resonate at δ 6.25 (for the protons on the six membered rings) and δ 6.01 (for the protons on the five membered rings). The 5,6-dihydro compound **17a** shows a downfield shift of about 1 ppm for the ring vinylic protons. This indicates a weak paramagnetic ring current exists for **17**, or the shift may be due to less strain in the dihydro compound **17a.**



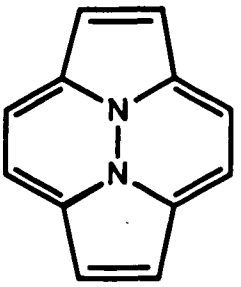
17a



18

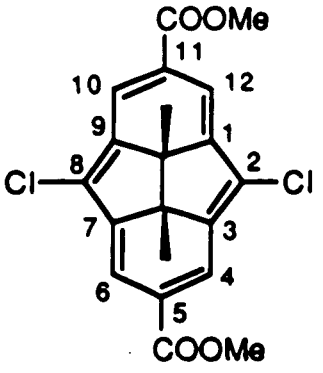
A bridged [12]annulene which shows an appreciable paramagnetic ring current is cycl[3.3.3]azine **18**.[89] This molecule has a nitrogen atom as the formal bridging group. The vinylic protons around the ring resonate at the exceptionally high upfield positions of δ 2.07 (d, 6H) and 3.65 (t, 3H). This molecule must therefore possess a significant paramagnetic ring current. Unfortunately, in the cavity of the molecule, there is no internal protons but a hetero atom, which might disturb 12-π electron system. An accurate assessment of this behavior is difficult to judge. One way to assess

the influence of the N-atom would be ^{15}N-NMR study of **18** and of its fully and partially hydrogenated derivatives.

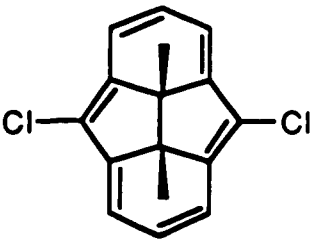


19

Another interesting molecule, similar to Trost's pyracylene is 8b,8c-diazacyclopent[*fg*]acenaphthylene **19** where the bridging group is formally a hydrazino moiety.[90] This molecule shows a modest paramagnetic ring current effect. The vinylic protons resonate at δ 5.13 (4H) and 5.22 (4H). Comparing these values with the shift positions from cycl[3.3.3]azine **18** it is apparent that the protons in **18** are considerably more shielded than in **19.** Again it is difficult to judge the effect of the hetero atoms on the paramagnetic ring current in **19.** Also **19** does not possess internal protons and may be somewhat strained.

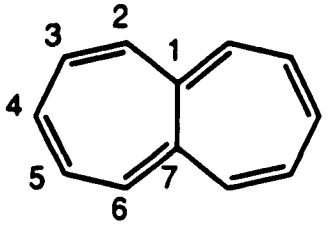


19a



19b

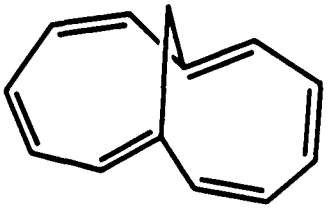
A carbocyclic bridged [12]annulene system, **19a** and **19b**, was synthezed resently by Müllen and his coworker.[91] The bridging methyl groups allow us to detect the paramagnetic ring current effect. The ^1H NMR showed δ = 2.51 for bridging methyl and 5.95 for ring protons in **19a**, while 2.58 for bridging methyl and 5.1-5.5 for ring protons in **19b**. The prsence of (alkoxycarbonyl and chloro) substituents is important since they contribute to stabilization of the 4n π annulene, but they reduce the paratropism.



20

Heptalene **20**, a [12]annulene with a carbon-carbon sigma bond as the formal bridging group, is a very unstable molecule first studied by Dauben and Bertelli.[92] In its ground state this molecule is probably non-planar as shown by low temperature ^{13}C-NMR. There is

a C_2 axis at -167°C. The molecule shows π-bond fixation, but also undergoes an extremely fast π-bond shift.[93],[94] The ^{1}H-NMR signals appear at (-80°C) δ 5.02 (H_2, H_6), 5.75 (H_4), and 5.80 (H3, H5). These chemical shifts indicate a moderate paramagnetic ring current. The molecule can be reduced with lithium to the 14 π-dianion. This species, in contrast with heptalene **20** is thermally very stable. The dianion has ^{1}H-NMR signals (-80 °C) δ 5.74 (H3, H5), 6.25(H4), and 7.65 (H2, H6). This indicates that the net upfield shift associated with the introduction of two negative charges is more than made up for by the induced diamagnetic ring current in going from the 12 π-system to the 14 π-system. Similar results were observed with the ^{13}C-NMR signals of the parent **20** and the dianion.[93] The large observed diamagnetic ring current points to a delocalization of the π-bonds through the dianion. These results probably mean that the dianion of heptalene **20** is planar; that is, the delocalization energy in the 14 π-system is great enough to overcome the strain energy associated with a planar geometry.

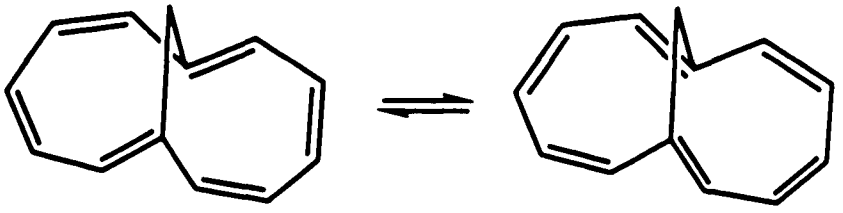


21

1,7-Methano[12]annulene **21**[95] can be considered the 12 π-analog of 1, 6-methano[10]annulene **6**.[96],[97] Models indicate that **21** is only slightly puckered about the ring. In this compound the formal

bridging group is a sp^3-hybridized methylene C-atom which "sits" over the face of the molecule. Therefore, this group should be a sensitive marker in determining the paratropic behavior of 1,7-methano[12]annulene **21**.

The ^{1}H-NMR spectrum of **21** shows a temperature dependence indicating a rapid dynamic process is occurring. This process is the valence tautomerism between **21a** and **21b**,[95](eq 3).



(eq 3.)

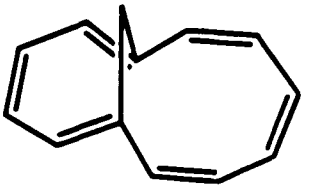
21a **21b**

The resonances appear at δ 6.06 (bridge CH_2) and 5.1-5.8 (ring protons). This is a complete reversal of the proton positions in 1,6-methano[10]annulene **6** where the bridge protons appear at δ -0.5 and the ring protons appear at δ 6.8-7.5. On lowering the temperature the signal from the bridge protons in **21** remains unchanged, while the signals from the ring protons broaden and change shape.[98]

The room temperature ^{13}C-NMR spectrum of **21** shows four signals for the ring carbons, indicating a rapid π-bond shift around the ring. As the temperature is lowered between -40°C and -120°C, magnetic equivalence is lost between C2 and C6, and between C3 and C5. Magnetic equivalence is not lost between C4 and C10 over this temperature range. Thus at -120°C the ^{13}C-NMR spectrum shows six

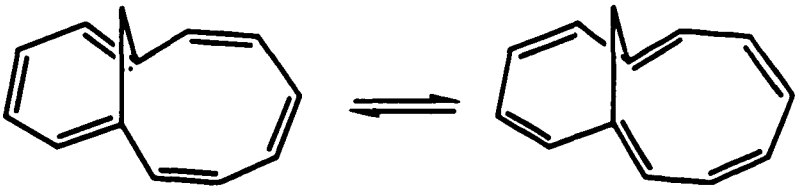
signals which means that the π-bond shift has essentially been frozen out.

The dianion of 1,7-methano[12]annulene **21** can be prepared with lithium or potassium in THF-d8.[99] The dianion shows a temperature independent ^{1}H-NMR spectrum which indicates a reorganization of the bond orders around the perimeter. This can be accounted for by a delocalization of the 14 π-electrons in the 12 Pz orbitals. There is also the lesser possibility of a very rapid valence bond tautomerism. The production of an aromatic diamagnetic ring current is manifested in the position of the ^{1}H-NMR signals. The bridge protons now appear at δ -6.44 and the ring protons appear at δ 6.41-7.16. The dianion prepared at -80°C is thermally stable.



22

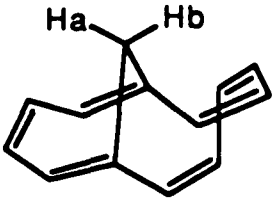
A compound related to **21** is 1,6-methano[12]annulene **22** which can exist in two forms, **22a** and **22b**.[100] These two forms can be in equilibrium or one form may not appear at all. The process leading from one to the other is a non-isodynamical[101] valence bond tautomerism, (eq 4). Models indicate that **22a** should be more favored energetically than **22b**.



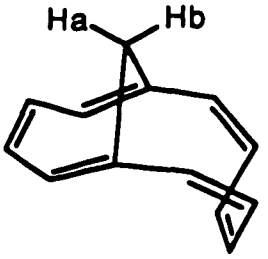
(eq 4)

22a **22b**

Valence tautomer **22a** possesses the relatively rigid conformation **22a'** or **22a"**.



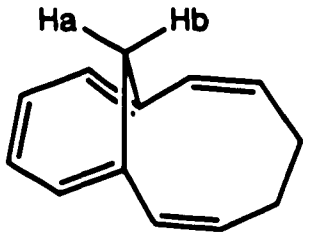
22a'



22a"

These conformations show considerable deviation from a planar ring geometry. The ^1H NMR spectrum of **22** shows no significant temperature dependence. The signals are located at δ 6.17 (H3, H4) and 5.73 (H2, H5) as an AA'BB' system, 5.5 (H7 to H12), and an AB system at 2.29 and (H13a) and 7.0 (H13b) with a coupling constant of -11.5 Hz. The AA'BB' system is consistent with a partial cycloheptatriene structure which indicates the valence tautomer **22a** must be the predominant, if not exclusive form. The remarkable splitting of the bridge protons must indicate that the preferred conformation is **22a'** which puts H_{13b} much closer to the paramagnetic ring current and consequently deshields this proton much more than H_{13a}. Although there is moderately strong deviation

from planarity, the authors conclude the compound possesses a moderate paramagnetic ring current. This is apparent on comparison with 9,10-dihydro-1,6-methano[12]annulene **23.**

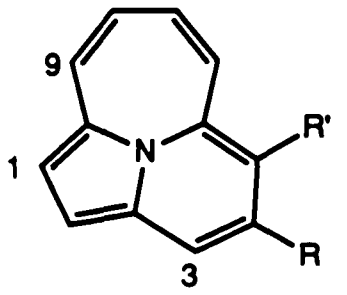


23

On going from **23** to **22** the signals from the AA'BB' system are shifted 0.5 ppm upfield, while the doublets of H13a and H13b are shifted about 0.72 and 3.87 ppm, respectively, downfield.

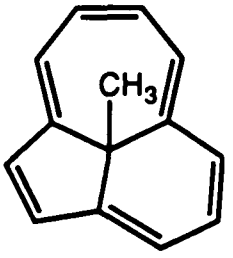
The dianion of 1.6-methano[12]annulene **22** can be prepared in a similar fashion to the 1,7-isomer.[102] The annulene protons experience a 1-2 ppm downfield shift in going to the dianion and the bridge protons experience a upfield shift, appearing at δ -5.52 and -6.08. This is completely consistent with a diatropic 14 π-electron Hückeloid system. The fact that the bridge protons now appear in almost identical shift positions is compelling evidence that the previously distorted [12]annulene perimeter has flattened due to the increase in resonance stabilization which can compensate for the ring strain in a planar species. The ^{1}H-NMR spectrum is essentially temperature independent, indicating that the molecule in the dianion form is now delocalized. The dianion is thermally stable.

A molecule related to cycl[3.3.3]azine **18** is cyclo[4.3.2]azine **24** (9b-azabenz[cd]azulene, R=R'=H).

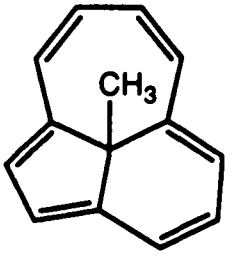


24

This molecule also possesses a 12 π-electron perimeter, but here the rings are annulated in a non-symmetric fashion. The synthesis of **24** has been attempted, but the derivative of **24** with R=R'=COOEt was obtained and could not be transformed further to **24.**[103] The ^{1}H-NMR of **24** (P=R'=COOEt) shows resonances at δ 4.92 (H1), 5.02 (H2), 6.0 (H3), 3.97 (H6), 3.65 (H7), 3.36 (H8), and 4.06 (H9). With no internal protons in this molecule it is difficult to judge the degree and magnitude of the paratropism of this molecule.



25

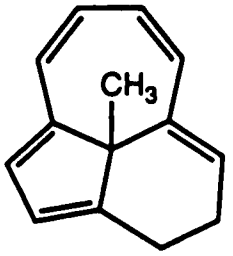


26

The carbocyclic analogs of cycl[4.3.2]azine **24** (R=R'=H) are the 9b-methy1-9b-hydro-1,2a,4,5a,7,9-benz[cd]azulene **25** and 9b-

methy1-9b-hydro-2,3,5,6,8,9a-benz[cd]azulene **26**. These valence tautomers possess a methyl group in the internal π-cavity of the molecule, which would be good probes in analyzing the paratropism. Model considerations indicate that **25** and **26** show considerable deviation from planarity because of the dissymmetric ring annulation.

25 is stable in solution up to 80°C.[104] The solid rapidly transforms into yellow high molecular products, even at -30°C. Its ^1H NMR spectrum provides interesting insights into the bonding structure of this [12]annulene, which according to model considerations has a rigid planar structure.

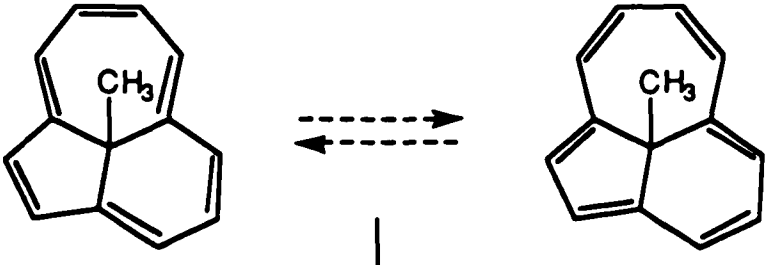


27

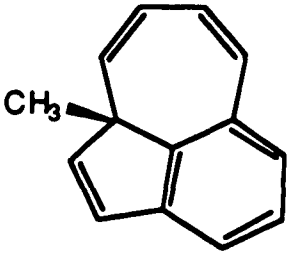
In comparison of **25** to the spectrum of the dihydro derivative **27**, in the spectrum of **25** the signals of the central methyl group and of the peripheral ring protons appear in the opposite sequence. The signals of the perimeter protons exhibit a strong upfield shift of about 2 ppm in the range δ = 3.88-4.69, whereas the methyl group singlet experiences a substantial down-field shift of about 4 ppm to δ = 4.75. The extremely high-field resonances of the ring protons of **25** compared to the ^1H NMR shifts of the perimeter protons of

[12]annulene (δ = 5.91), 1,7-methano-[12]annulene (δ = 5.1-5.8) and 1,6-methano[12]annulene (δ = 5.50-6.17) are consistent with a pronounced paramagnetic ring current in the 12 π-perimeter of **2-21.**

The electronic spectrum of **25,** like those of the mono- and bicyclic [12]annulenes and the dehydro[12]annulenes,[105] shows a strong absorption in the region of 260 nm and, in contrast to this, an additional long-wave absorption at 567 nm. The absorption corresponds to the singlet-electron transitions calculated by Lindner[106] for the localized 12π-electron system **25.**



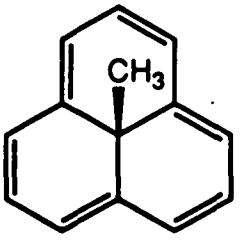
25 **26**



28

According to π-SCF force field calculations,[107] the standard enthalpies of formation of **25** and **26** should be about the same, and the activation enthalpies for the π-bond shift should be more than

25 kcal/mol. However, contrary to expectations based on these calculations, isomer **26** was not detected. Hence, the equilibrium may lie further to the side of **25** than predicted by the calculations, or a higher barrier between **25** and **26** is involved. At elevated temperatures, a presumably sigmatropic, methyl-group shift takes place in **25** and **26**, the 9a-methyl-9aH-benz[cd]azulene **28** (yellow oil) having a benzenoid partial structure is formed at 80°C (in DMSO), and proceeds quantitatively within 15 minutes in boiling xylene.

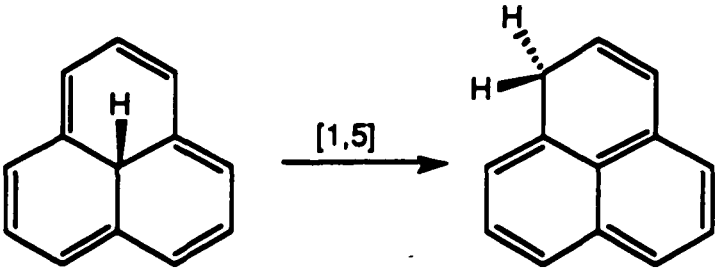


29

13-methylphenalene **29**[108] is expected to be the best example of a bridged [12]annulene. This molecule has long been sought (see section 1.2-C). It has an sp^3-hybridized C-atom as the bridging group with a methyl group attached to this bridging carbon. Formally this represents a replacement of the three internal protons of [12]annulene **16** by sigma bonds to carbon. An examination of a Dreiding model indicates that introduction of the sp^3-hybridized carbon causes very little deviation from planarity about the annulus. The internal bridging carbon "sits" at an angle of 15-20° above a mean plane formed by the ring carbons. The internal methyl group should act as a sensitive marker in studying any paratropic behavior

this molecule is expected to exhibit when it is placed in an external magnetic field.

The internal methyl group in 13-methylphenalene **29** is also expected to increase the stability of the molecule relative to the hydrogen substituted analog and to prevent any thermally allowed [1,5]-sigmatropic migration, which may be a facile process when a proton is substituted for the methyl group. This is illustrated in following equation.



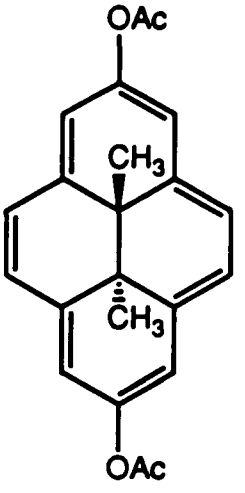
phenalene

Thus as the previous discussion has shown, there are few [12]annulenes known that combine stability, rigidity, planarity of structure containing both inner and outer protons, and unambiguous structural features that makes determination of the presence of a paramagnetic ring current easy, and not subject to extraneous effects, such as those due to a heteroatom(s), or an extra π-system in the cavity of the ring. Furthermore the above factors should result in a minimum Jahn-Tellar distortion, thus result a maximum paramagnetic ring current for **29** compared to **25** which certainly has Jahn-Tellar distortion in terms of deformation from planarity. This should make 13-methylphenalene **29** the ideal example of a bridged [12]annulene and consequently its synthesis and

investigation should considerably advance our understanding of paratropism in 4n systems.

C. Previous Approaches To 13-Methylphenalene And Related Systems

Bridged [14]annulenes which bear a striking resemblance to 13-methylphenalene **29** are the trans and cis-15,16-dimethyl-dihydropyrenes **10** and **10a** respectively, elegantly synthesized by V. Boekelheide and coworkers.[109,110] The perimeter of the trans isomer is essentially planar. In fact X-ray crystallographic examination of 2,7-diacetoxy-15,16-dimethyl pyrene **10b** has shown that no C-atom deviates more than 0.027 Å from a mean plane.[111] In addition the bond distances in this molecule vary between 1.386 Å and 1.401 Å, in excellent agreement with the standard benzene bond distance of 1.397 Å.[112] This molecule (**10b**) has a high diamagnetic susceptibility.



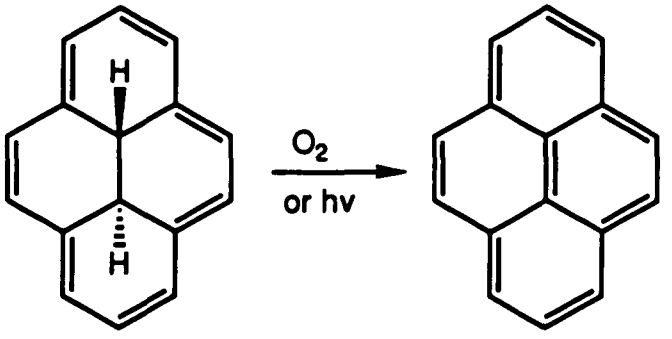
10b

Trans-15,16-dimethyldihydropyrene **10** also behaves as an aromatic molecule in that it readily undergoes electrophilic substitution

reactions. In fact it is slightly more reactive than benzene. The ^{1}H-NMR signals for this molecule, (Figure 1.2-3), appear at typically upfield positions for the internal methyls (δ -4.25) and typically downfield for the ring protons (δ 7.98-8.67). This molecule is by all criteria diatropic and aromatic.

The dianion of trans-15,16-dimethyldihydropyrene **10** can be prepared with lithium or potassium in THF-d_8. The dianion is now a 16 π-electron paramagnetic species and experiences a complete reversal of the signals in the ^{1}H-NMR. The internal methyl groups now appear at δ 21.0. This is a shift of over 25 ppm from the neutral molecule![113] The ring protons in the dianion appear at δ -3.19 to -3.96.

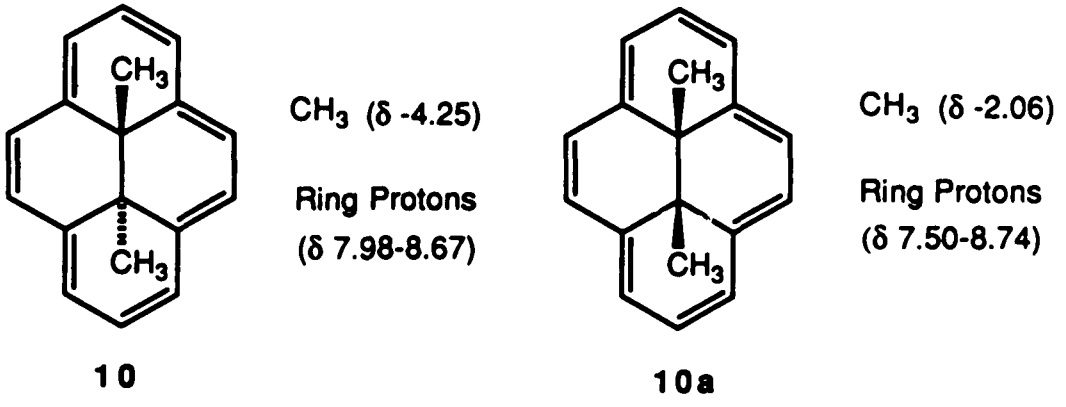
Substitution of the internal methyl groups in **10** with hydrogen leads to facile oxidation to pyrene, (eq. 6). This last reaction illustrates the use of the internal methyl groups as stabilizers, preventing certain side reactions from occurring.



eq 6.

Cis-15,16-dimethyldihydropyrene **10a** (Figure 1.2-3), shows analogous results except that the internal methyls sit further away from the source of the diamagnetic ring current, since this molecule is more saucer shaped than the trans isomer. Consequently, these

methyl protons resonate at δ -2.06.[114] This is about 2 ppm downfield from the position the internal protons in the trans isomer,[115] (Figure 1.2-3).



10 **10a**

Figure 1.2-3. ^{1}H NMR data of 15,16-dimethyldihydropyrene isomes

The first attempts at the synthesis of 13-methylphenalene **29** involved attempted trapping of the phenalenyl anion **30**,[116,117] or the phenalenyl cation **31**[118,119,120] with suitable electrophilic or nucleophilic reagents. (Figure 1.2-4.)

The phenalenyl anion **30** has been prepared by Boekelheide and Larrabee[121] by treatment of phenalene **32** with phenyllithium. They trapped the anion with methyl iodide, but they did not isolate **29**. Instead the products isolated were 4-methyl-phenalene **33** and 9-methylphenalene **34**, (Figure 1.2-4). Significantly, no 2-methylphenalene was observed.

The anion of phenalene **30** [122] shows ^{1}H-NMR signals at δ 5.17 (d, 6H) and 5.91 (t, 3H). As predicted from molecular orbital calculations the phenalenyl anion **30**, the phenalenium cation **31** and the phenalenyl radical are stable. [123] A stable phenalenium salt has

been prepared by Pettit[124] and a more general method to prepare phenalenium cation has been developed by Reid and coworkers.[125] (Figure 1.2-4.) It has also been obtained using fluorosulfonic acid and antimony pentafluoride.[126] Attempts at trapping the cation **31** with reagents like methyl lithium did not result in the formation of 13-methylphenalene, but instead yield ring methylated products.[127] (Figure 1.2-4.)

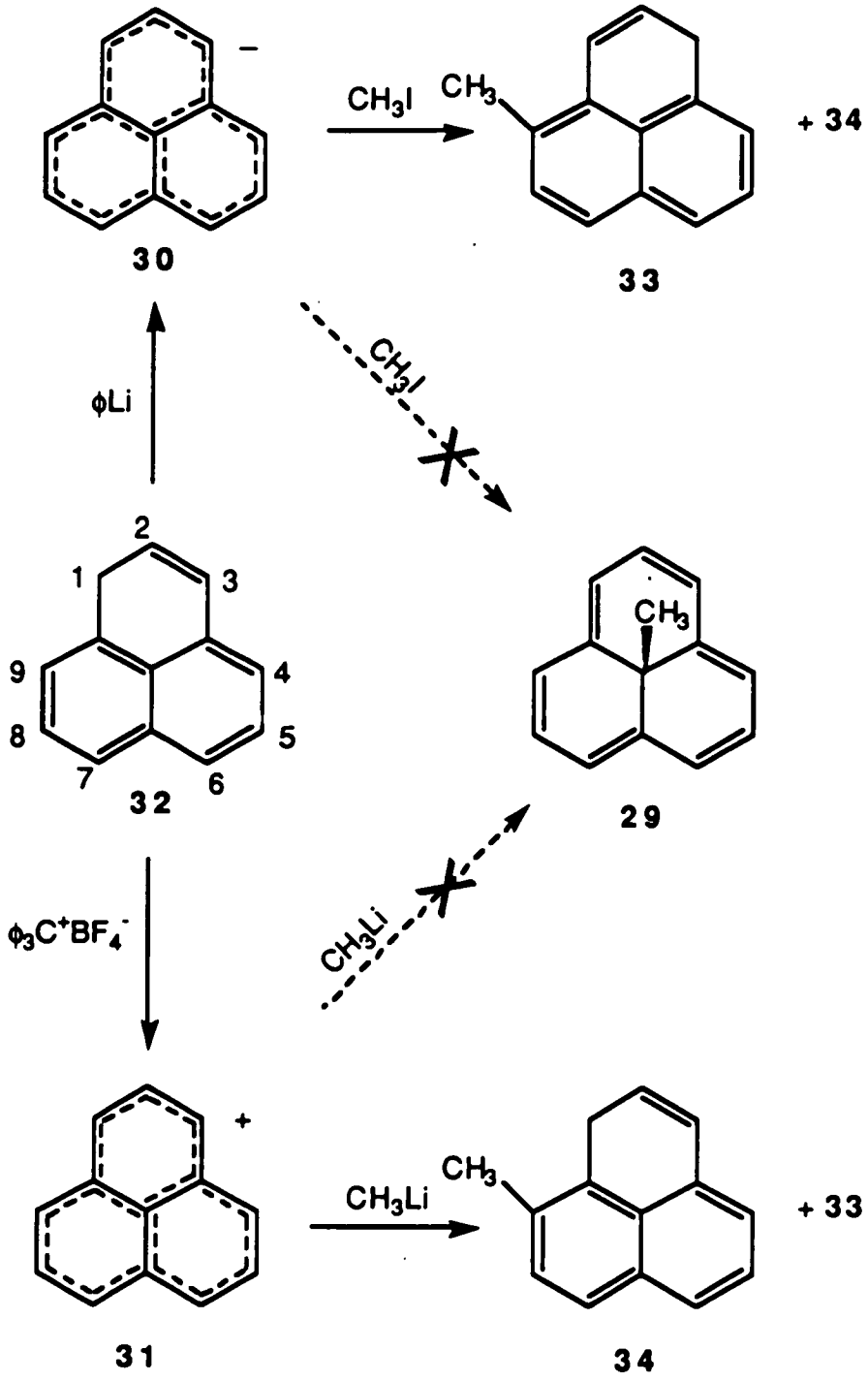
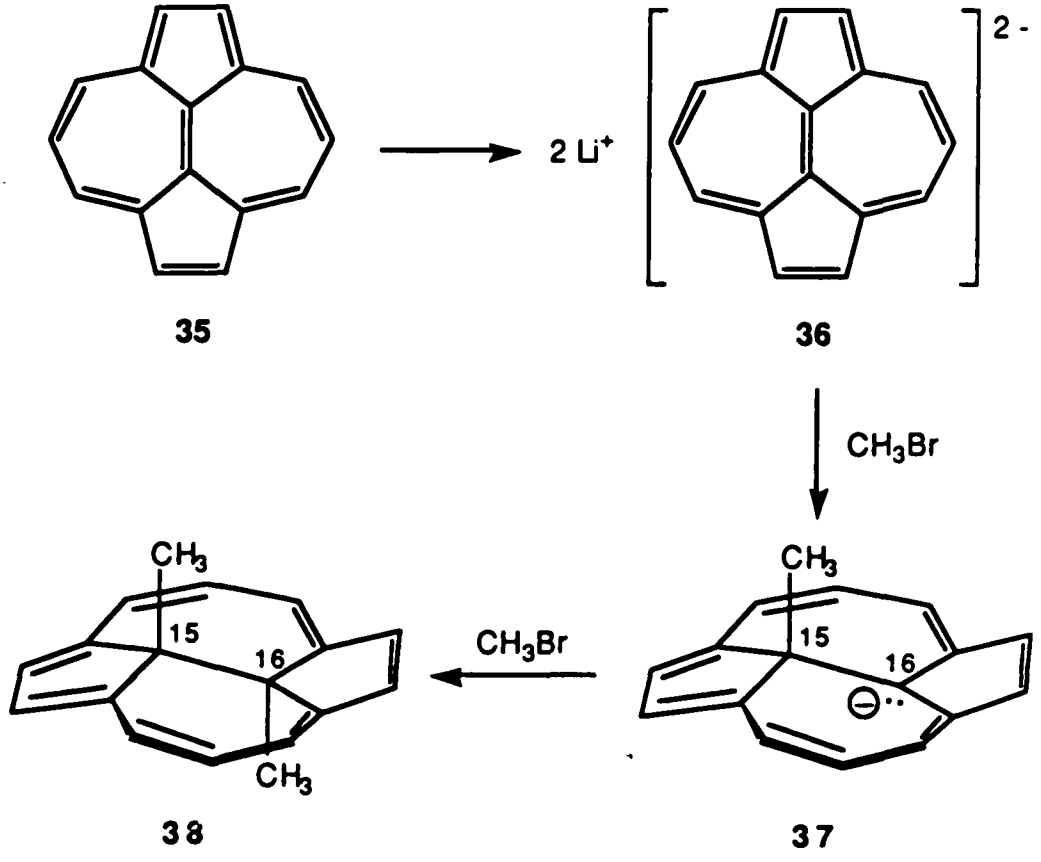


Figure 1.2-4. Some Reactions of Phenalene **32**

Contrary to the behavior of phenalenyl anion, the substitution of dicyclopenta[*ef,kl*]heptalenyl dianion **36** at a central carbon (C-15) (See Figure 1.2-5) with electrophile gives a monoanion **37** whose negative charge locates at another central carbon (C-16).[128,129,130,131,132] The resonance of C-16 at δ=103.0 (sp^3-hybridized C-atom with strong charge-induced shielding) indicates the existence of the highest π-charge density in this position,[133] therefore the second substitution undergoes at the central carbon again. (Figure 1.2-5)



35 **36** **38** **37**

Figure 1.2-5. The formation of 15,16-dimethyldicyclopenta[*ef,kl*]heptalene **38**

The reason that the phenalenium cation **31** or anion **30** do not give 13-methylphenalene **29** can be clearly understood when one analyzes the positions of the electronic charge distribution around the ring based on HMO calculation[134]. Figure 1.2-6 shows that the calculated charge is zero at the central carbon and at C2, C5, and C8 thus making it impossible for an electrophilic or nucleophilic reaction to occur at these positions. With this limitation in mind the use of phenalene **32** as a starting material for the synthesis of 13-methylphenalene **29** becomes rather unlikely.

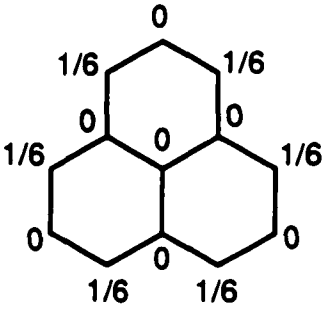
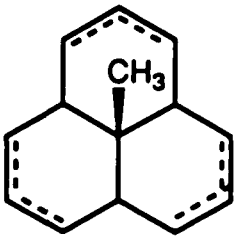


Figure 1.2-6. Electronic Charge Distribution in Phenalenyl Anion **30** And Cation **31** (HMO)

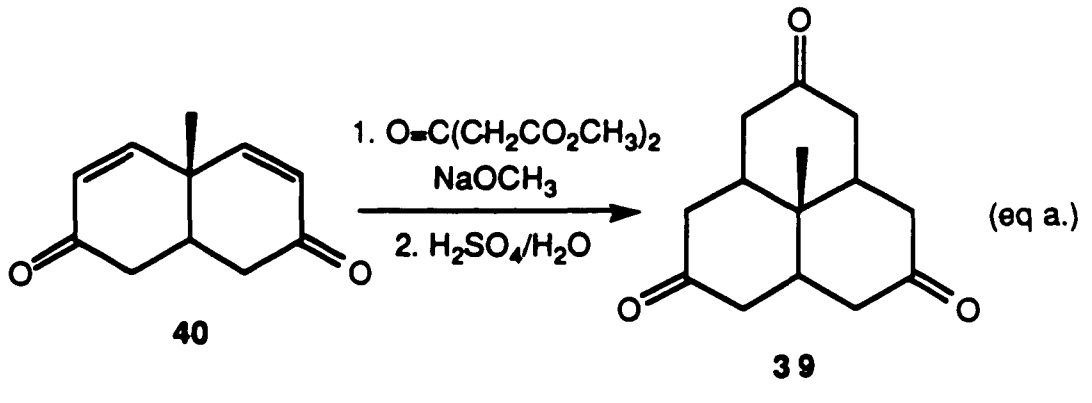
Earlier works in this group by Grohmann and Hermoso used an approach to 13-methylphenalene **29** which offered much promise, but did not lead to the final compound.[135] The known, but not so readily available tricyclic trione **39** was used (eq a.).[136] This compound is available through the bis-Michael reaction of dimethyl acetone dicarboxylate on the bis-enone **40**.[137] The intermediate diester is hydrolyzed and decarboxylated to give the desired tricyclic trione **39**, the stereochemistry of which was unknown at

that time (eq a.). This compound has the central methyl group in place and has three potential double bonds through suitable elaboration of the keto groups.

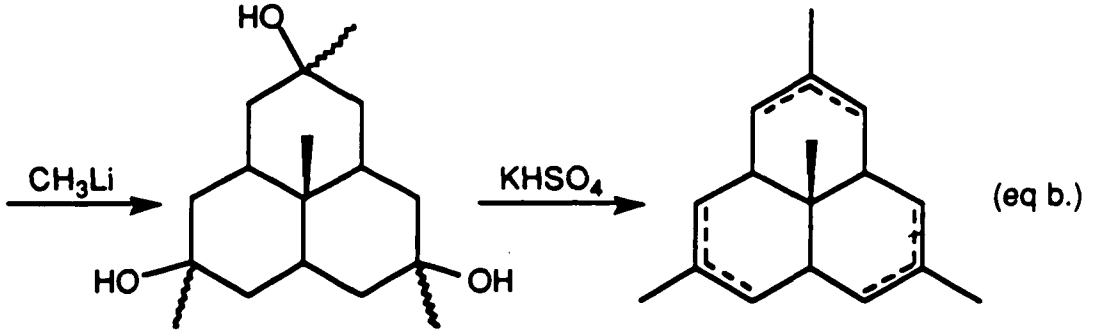


41

The tris-tosylhydrazone of **39** was made in situ and treated with excess methyllithium. A seven component mixture was isolated. The fifth peak in the GC/MS gave a molecular ion at m/e 186 in agreement with the proposed structure **41**. The ^{1}H NMR indicated a mixture of isomers for **41**. The entire seven component mixture was allowed to react with molecular bromine. The crude bromides were dehydrobrominated with potassium tert-butoxide. After work up an orange oil was isolated which could not be purified for detailed analysis. The compound(s) may have decomposed on attempted chromatographic purification.



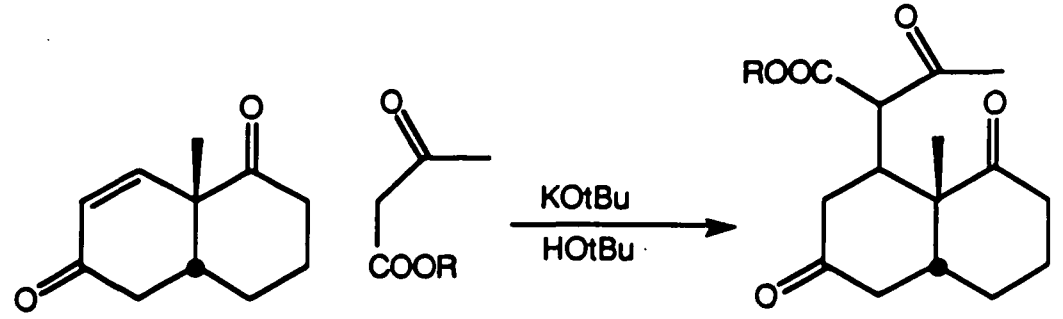
40 39 (eq a.)



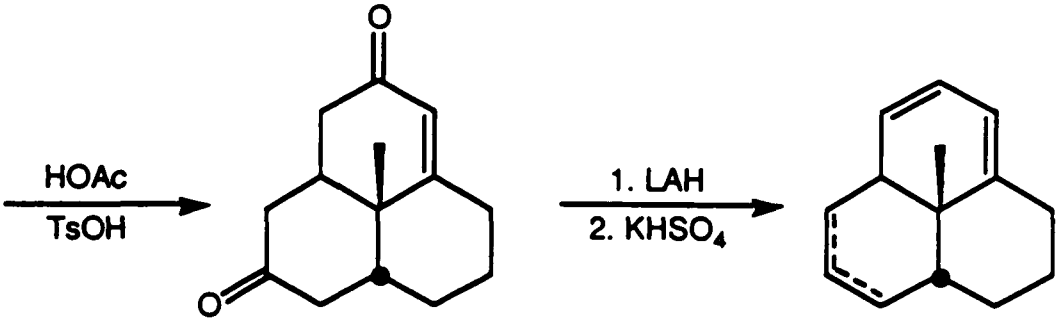
42 43 (eq b.)

Grohmann, M. Moore and P. Noire have tried two other approaches.[138] The first one starts again with the tricyclic trione **39**. This compound was treated with excess methyllithium. After work up by continuous extraction a high yield of the tertiary triol **42** was obtained, (eq b.). This compound was subjected to dehydration with potassium bisulfate. A compound was distilled whose mass spectrum was consistent with the desired tricyclic triene **43**. (eq b.). No further work has been done along these lines owing to the difficulties in obtaining bis-enone **40**. The second approach starts from cis-Δ'-3,8-octalindione **44**. (eq c.) The key intermediate enedione **45** already possessing the tricyclic skeleton and the central methyl group was synthesized from cis-octalindione

by a Michael reaction followed by ester cleavage and aldol condensation. The enedione **45** was then converted to the triene precursor **46** by reduction and dehydration. The triene **46** was isolated by a preparative TLC and the structure of its isomeric mixture was not definite.



44



45 **46**

(eq c.)

Grohmann and M. Moore repeated Grohmann and Hermoso's work. Dehydrobromination with potassium tert-butoxide in THF at 0 °C gave a strongly yellow-colored product. This product was not

conclusively characterized. Its ^1H NMR spectrum showed a sharp singlet at δ 37, a doublet at δ 2.2 and a triplet at δ 2.7. The GC indicated six components, one of which had an GC/MS of m/e = 180, consistent with 13-methylphenalene **29.**[139] When we reviewed this ^1H NMR spectrum recently, we found that these peaks may not be true signals of the compound and may be the reference frequency folding back.[140] The GC/MS of m/e = 180 could be for the known perinaphthenone, according to our present work. (See section 2.10.)

CHAPTER TWO. SYNTHESES

2.1. Strategies and General Schemes

To approach the final compounds, 13-methylphenalene and its derivatives, the key intermediates should have the following structural elements:

a. the tricyclic skeleton is already present;

b. the central methyl group is in the correct position, and it is introduced as early as possible (see section 1.2 C).

c. Double bonds and other equivalent functional groups are in well defined positions. The formation of double bond isomers is more or less excluded to a minimum.

The general Schemes I (Figure 2.1-1) and II (Figure 2.1-2) shows some of the intermediates **I-VI** and their synthetic routes.

Their syntheses involve various well-known and interesting cyclization reactions. The difficulties would be caused by the extra methyl group, which is important for the final product, and by the stereochemistry of the tricyclic system.

Route **2.2** involves a series of aldol condensations and Michael additions (or Robinson cyclizations).

Route **2.3** comprises Wittig reaction followed an electrocyclization, or a Wittig reaction followed by an intramolecular Michael addiction in one pot. (See step **a.**) As we can see there is a cross between two paths at the compound **VII**, a triene. Finally both paths may lead to two attractive key intermediates **II**

and **III** which have five double bond equivalences: one carbonyl and four double bonds.

The key step in route **2.4** is a spiro oxy-Cope rearrangement. The formation of spiro methyl ethynyl carbinol has two possible paths: (i.) including five steps and (ii.) only two facile steps.

Route **2.5** concerns a ring expansion of 10-methyltriquinacene.

The intermediate, trione **VI** in Route **2.6** is a known compound, but its stereochemistry was unknown. The overall yield was quite low and needed to be improved. Its advantage is having three carbonyl groups which may lead to various trisubstituted 13-methylphenalenes even though the stereoisomers may be obtained. The original approach (see section 1.2 C) was optimized, and the key intermediates were identified and characterized.

The general scheme III (Figure 2.1-3) shows the approaches to 13-methylphenalene and its derivatives from the trione **VI**.

In Route **2.7**, three double bonds may be introduced by silylation and palladium catalyzed dehydrosilylation. The other three required double bonds appeared easy to be introduced by elimination reactions.

In Route **2.8** and **2.9**, trisubstituted triene may be formed by metalorganic nucleophilic additions followed by dehydrations.

In Route **2.10**, formation of tritosylhydrazone followed by Shapiro reaction gives triene mixture.

The last three routes will encounter the same problem, to introduce the last three double bonds to furnish the unknown 12 π system directly, or forming dianions, the more stable 14 π system, then being oxidized. These reactions will be the most difficult steps

due to lability of the highly unsaturated molecules and their transformation into an antiaromatic system.

The results and detailed discussion for each route will be given in the subsequent sections which have the corresponding numbers.

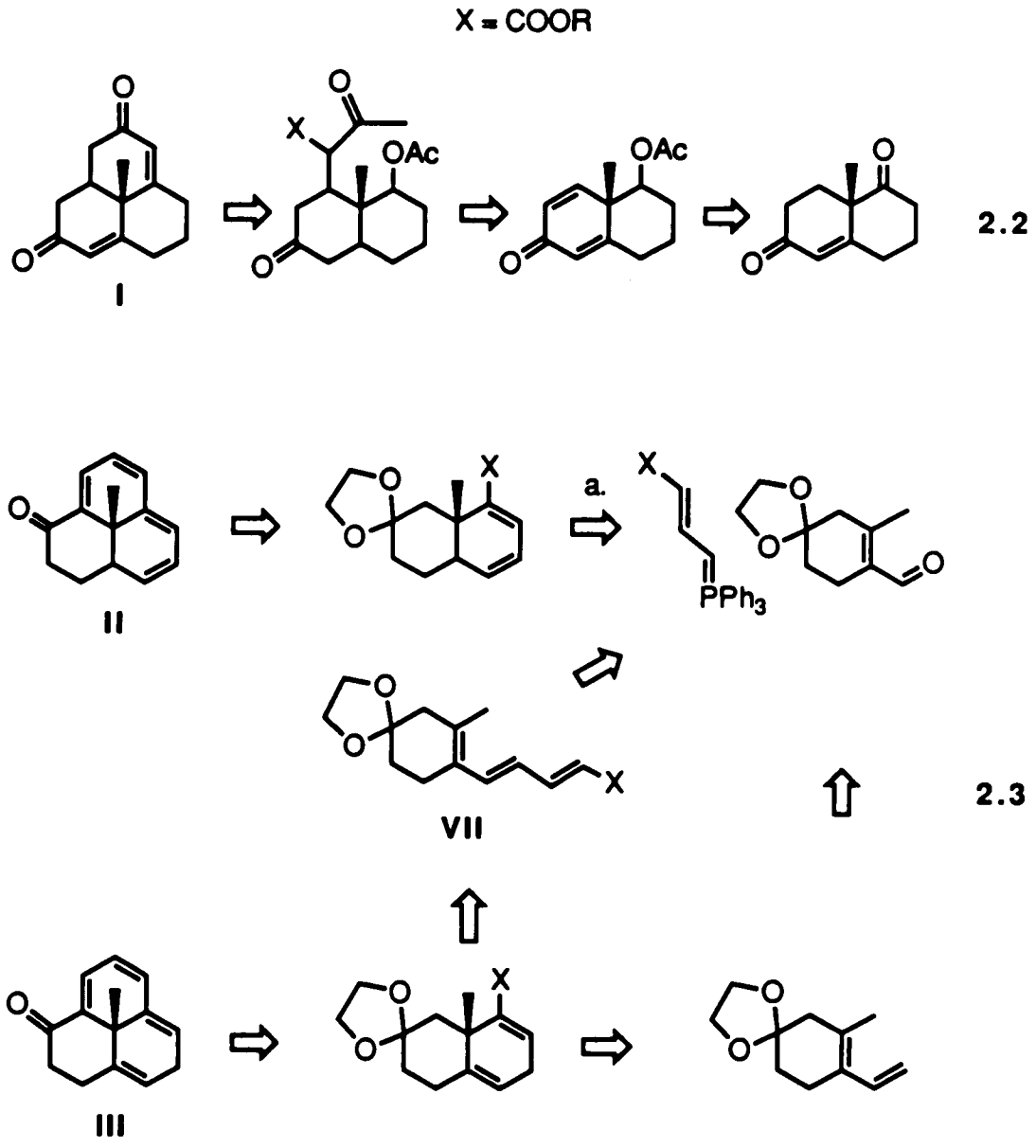


Figure 2.1-1. The general scheme I

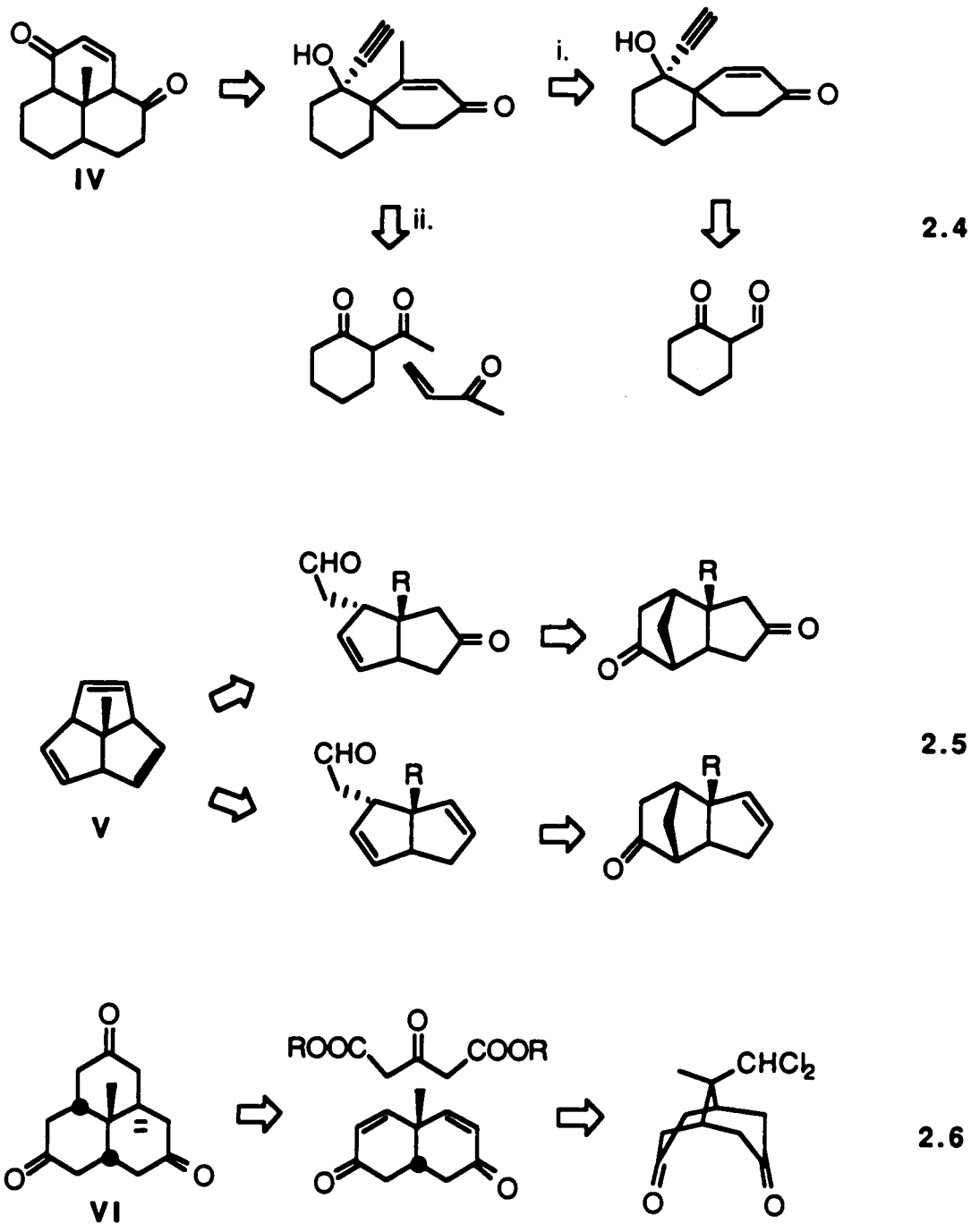


Figure 2.1-2. The general scheme II

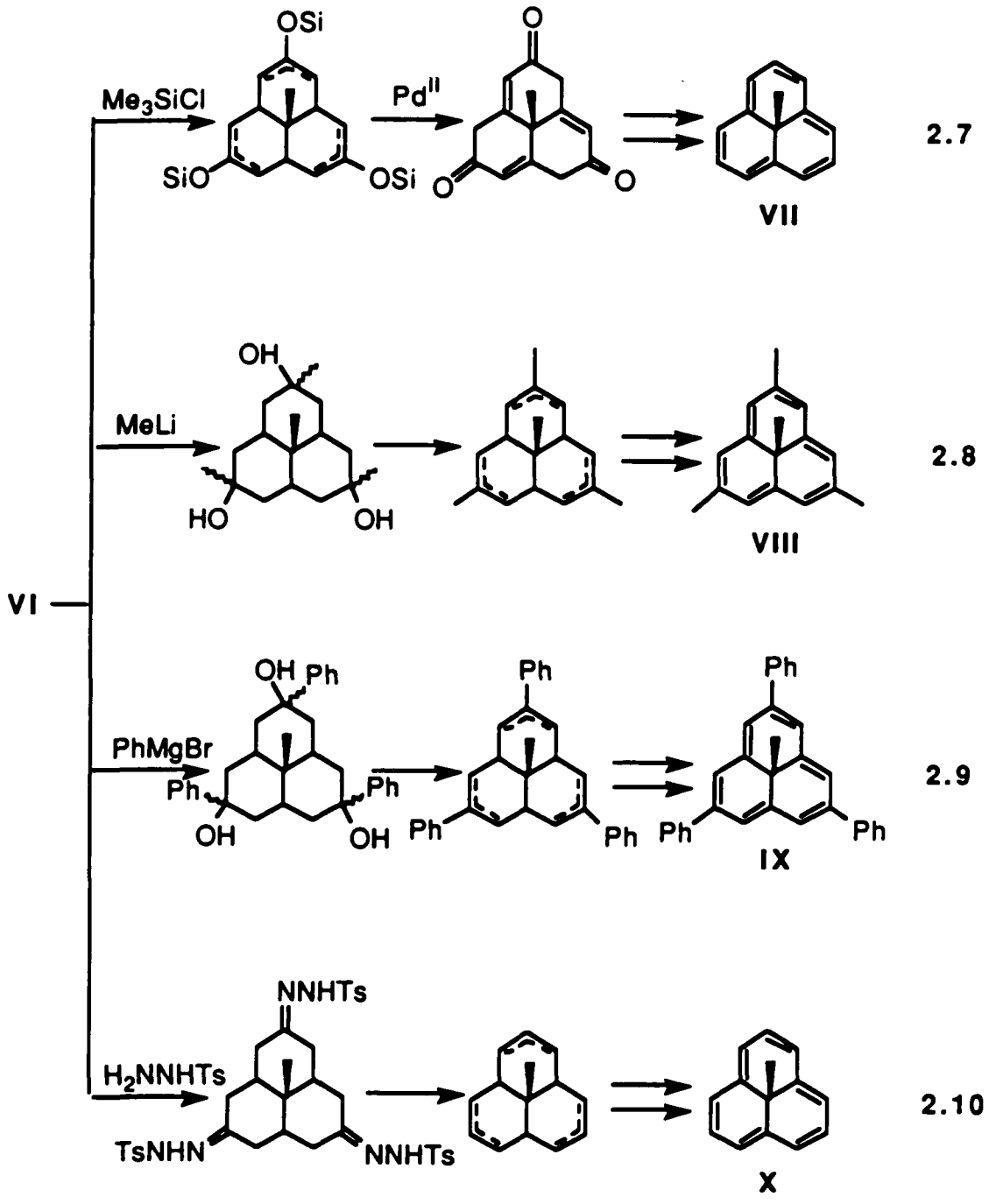


Figure 2.1-3. The general scheme III

2.2. Attempted Synthesis of Dienedione I Via Aldol Condensation

This approach starts from known 4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2,5(3H)-dione[141]. Reduction with sodium borohydride[142] gave alcohol **2-1** at 80% yield. In the strategy attempting to introduce another double bound on ring B starting with the C-5-carbonyl, several reactions have been tried (see Figure 2.2-1) and discontinued due to low yield: Dehydration with $KHSO_4$ gave only dienone **2-3** at 20% yield; Mesylation followed by elimination with Al_2O_2 gave only 18% (65% x 28%). Functionalizing ring A in 5β-acetoxy-10β-methyl-Δ-2-octalone **2-4** could be achieved with DDQ, yielding the acetoxy dienone **2-5** at 37%. However we were unable to carry out a Michael addition of tert-butyl acetoacetate to this acetoxy dienone **2-5** at converting it into the tricyclic dienedione **I**.

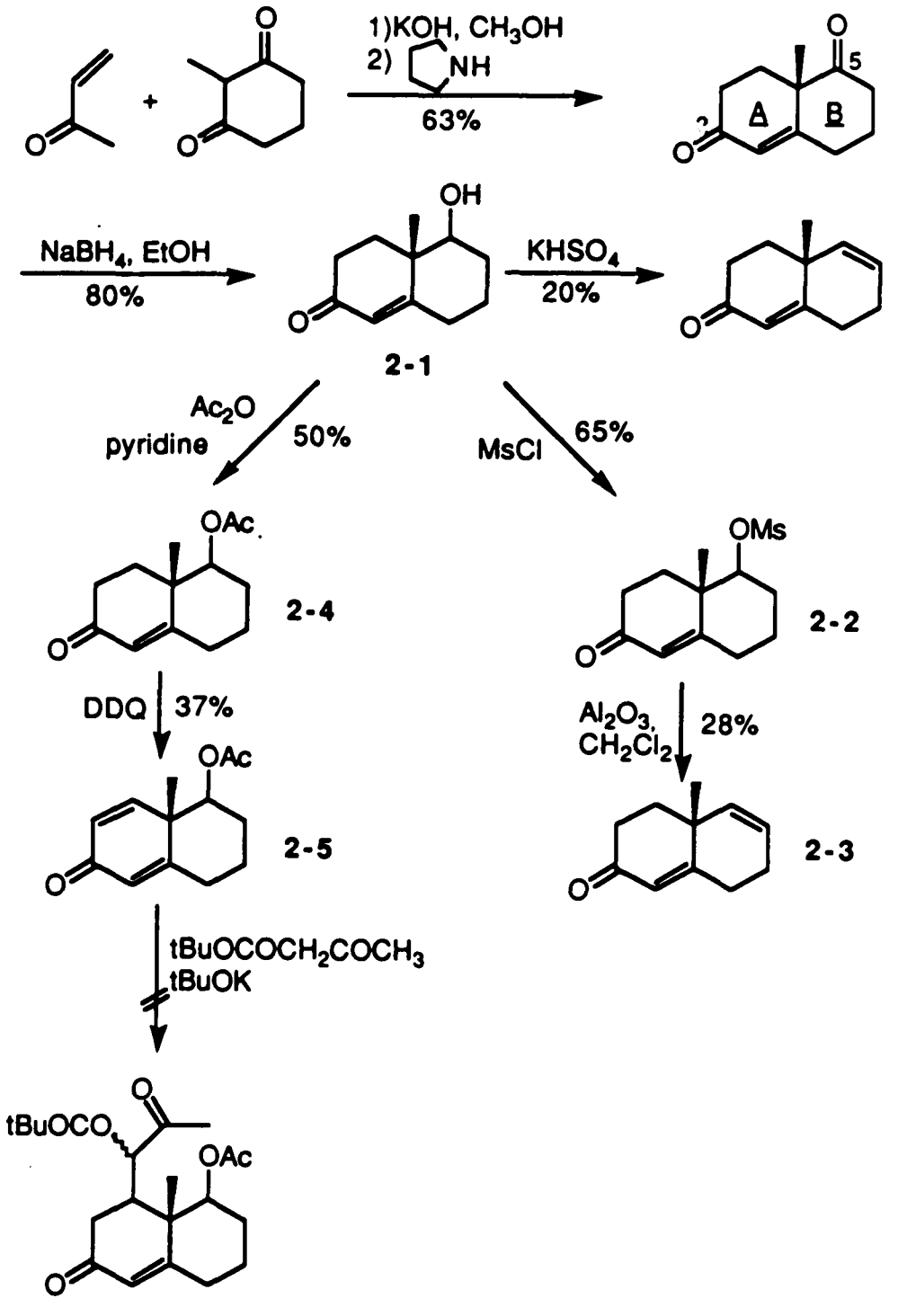
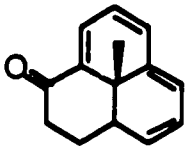


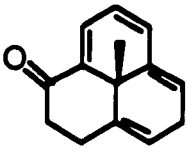
Figure 2.2-1 Functionalization of 4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2,5(3H)-dione

2.3 Attempted Synthesis of Tetraeneone II and III From Hagemann's Ester

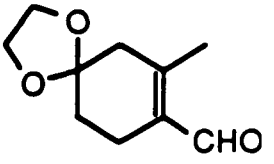
The two isomers, tetraeneones **II** and **III**, were proposed as suitable intermediates of 13-methylphenalene **X**, and both would be synthesized from aldehyde **3-1**[143]. (See figure 1.2-1)



II

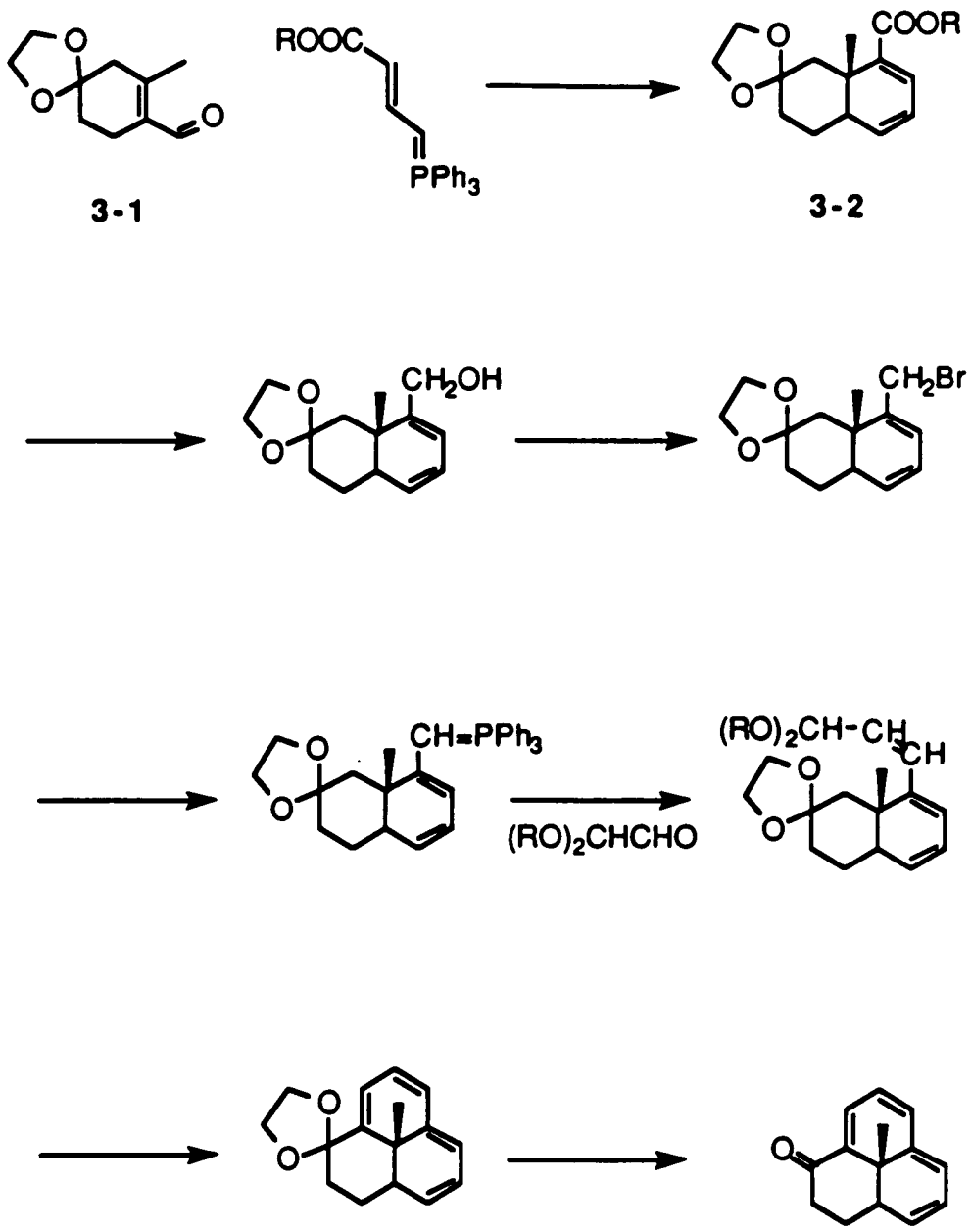


III



3-1

The proposed synthetic scheme of the first route is shown in Figure 2.3-1.

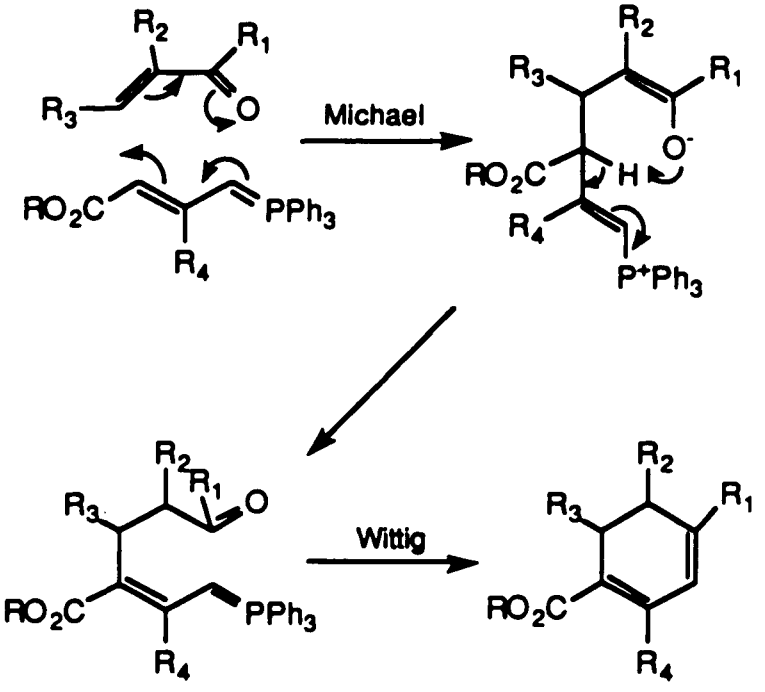


3-1 3-2

Figure 2.3-1. The synthetic scheme to tetraeneones II

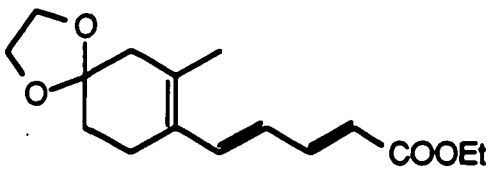
The key step, in which bicyclic **3-2** would form, is based on the formation of cyclohexadiene **3-3.**[144] The proposed mechanism follows.

The Michael addition of α,β-unsaturated aldhydes and α,β-unsaturated ylides followed by an intramolecular Wittig reaction yields a cyclohexadiene.

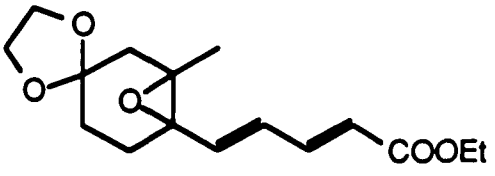


3-3

In a model reaction using crotonaldehyde (R_1 = R_2 = H, R_3 = CH_3) and the ylide derived from γ-Br-crotonic ester, (ref.) a yield of 93% for **3-3** was obtained after 14 hours at room temperature, but the reaction with aldehyde **3-1** gave only a normal Wittig product, the triene **VII**, instead of cyclohexadiene. The extra β-alkyl might be account for this, as the Michael reactions encounter difficulty with β-disubstituted α,β-unsaturated aldehydes.

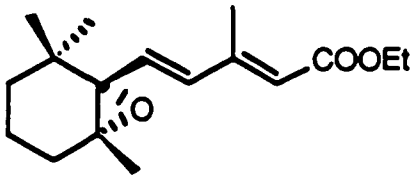


VII



3-4

^{1}H NMR (400 MHz) spectrum (Figure 2.3-2) supports that the double bonds on the chain are both trans (J = 15 Hz). Interestingly, triene **VII** crystals (m.p. 64.0-65.0 °C, Rf=0.54, 50% ethyl acetate-hexane) convert to epoxide **3-4** (m.p. 68.0-69.0 °C; Rf=0.48, 50% ethyl acetate-hexane) in an unusual way, just open to air in solid form for 24 hours in 80 % yield, while the triene **VII** kept unchanged when it stored in a refrigerator as crystals or heated at reflux in ethanol for the same period. The additional oxygen is supported by mass spectroscopy (m/e 284 M+). UV (95% EtOH): λ_{max} 265 nm. ^{1}H NMR and ^{13}C NMR. (See Figure 2.3-3 and 2.3-4) In the ^{1}H NMR spectrum of **3-4**, the peaks of the methylenes in the ketal and the cyclohexene ring are split (J = 15 Hz) that indicates the cyclohexene ring is rigid, while that of **VII** is flexible. A similar epoxide **3-4'** was synthesized by Acemoglu and Eugster.[145] The long synthetic scheme[147,146] included epoxidation with t-butylperoxid. Its UV is identical with epoxide **3-4**. Its ^{1}H NMR spectrum showed no clear coupling constant for the protons in the ring.



3-4'

Figure 2.3-2. The ^{1}H NMR spectrum of the triene VII

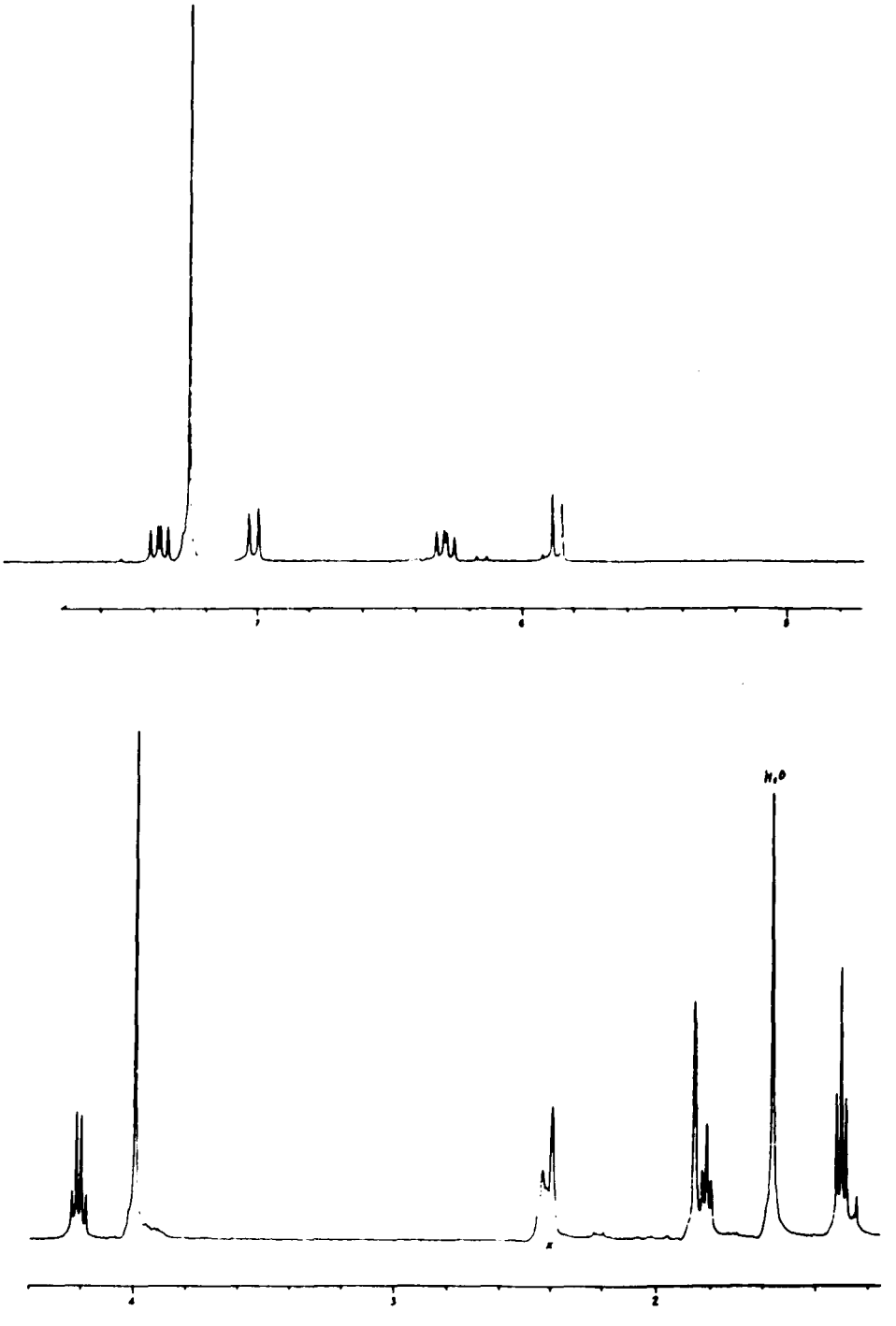


Figure 2.3-3 The ^1H NMR spectrum of the epoxide 3-4

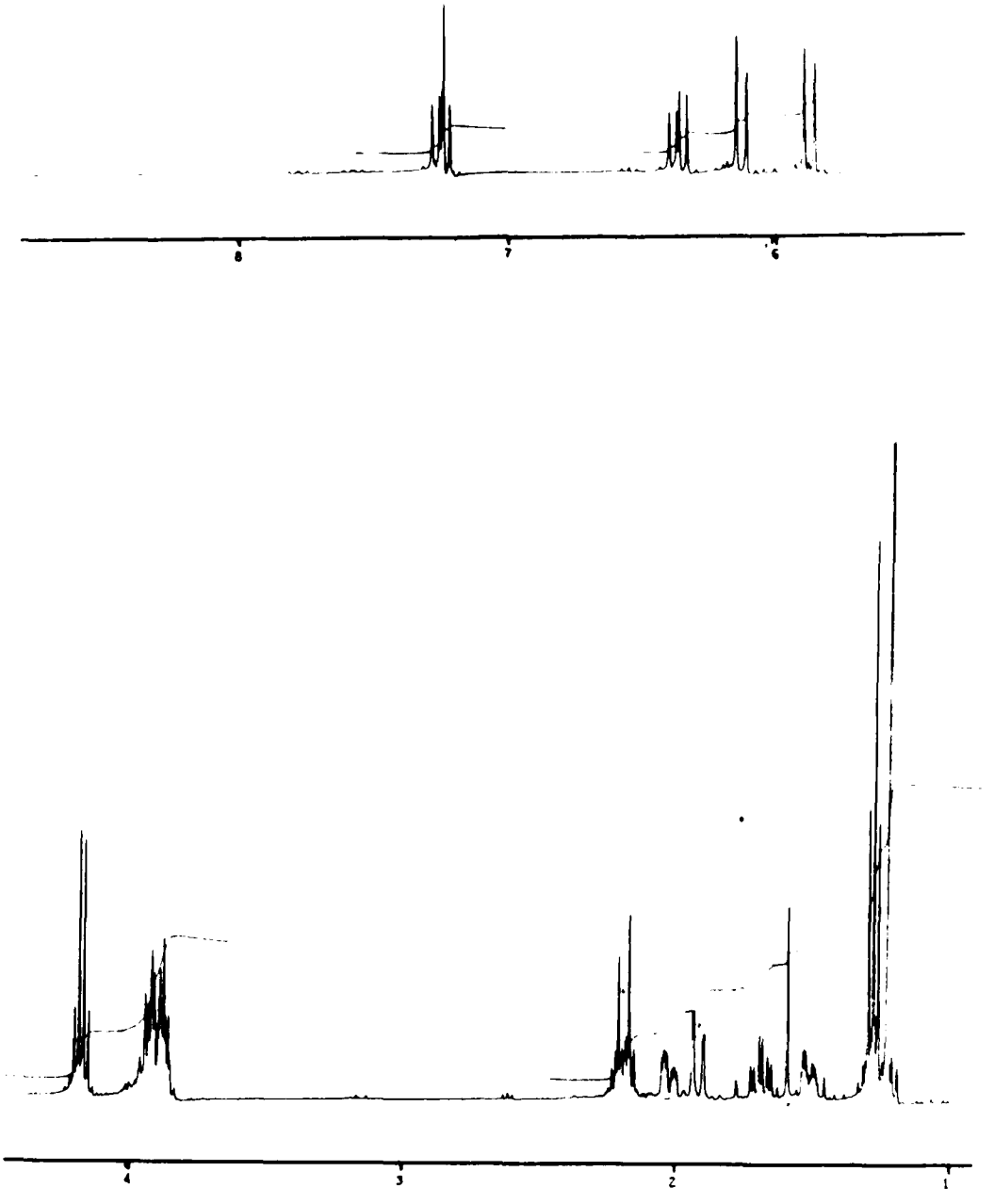
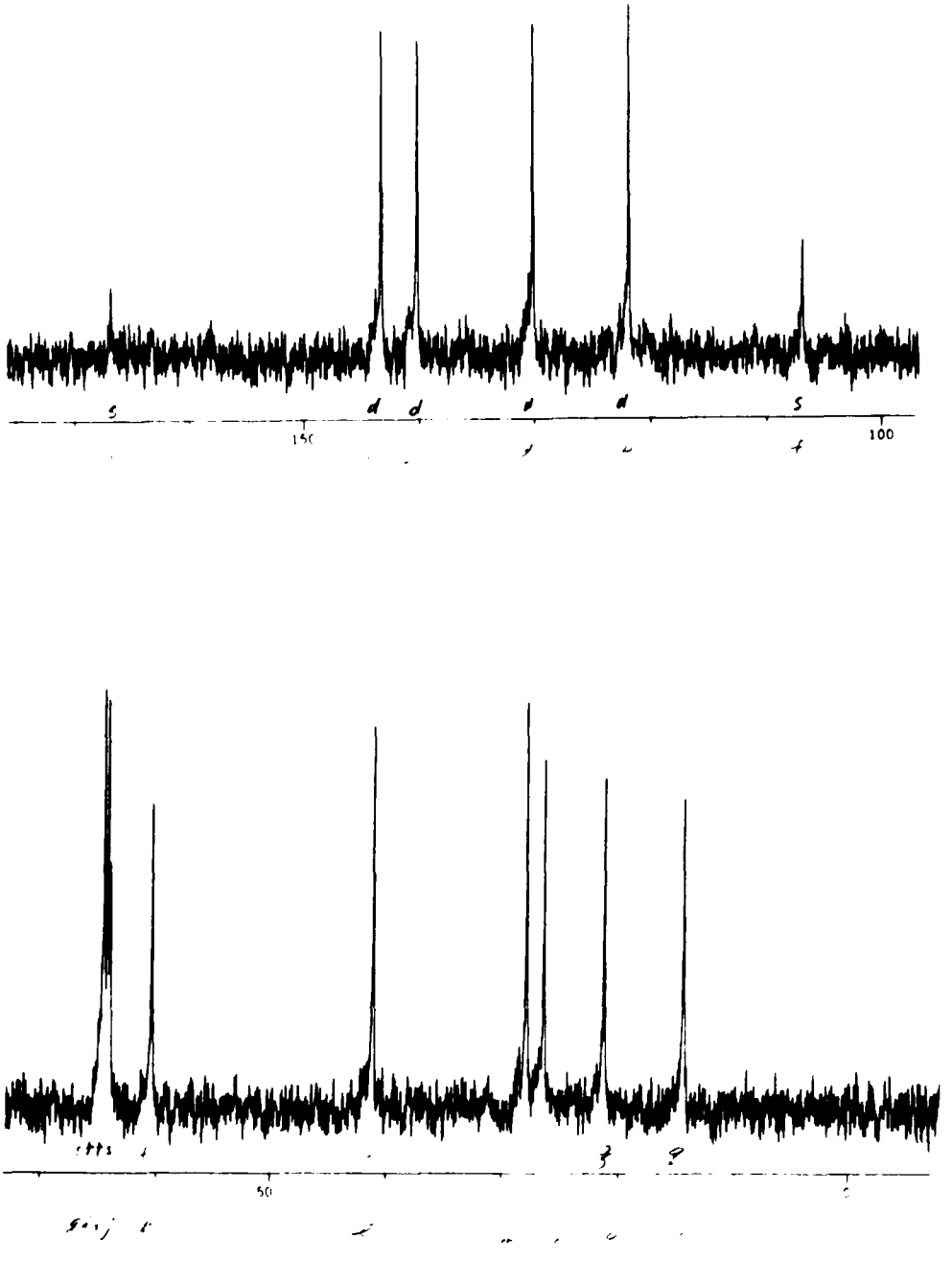


Figure 2.3-4. The ^{13}C NMR spectrum of the epoxide 3-4



Since trienes may undergo electrocyclolization at high temperature in a sealed tube as shown in the following example,[147,148] (Figure 2.3-5) the similar procedure was applied to the triene **VII**. Unfortunately most of the starting triene was recovered. The presence of of β-methyl group may lower the energy of the all-cis-double bound transition state. For the same reason, the reported the trienedione **3-5**, when heated in xylene, failed to cyclize to the bicyclic compound, and instead isomerized quantitatively to the *E,E*-trienedione **3-6**.[149] (Figure 2.3-6.)

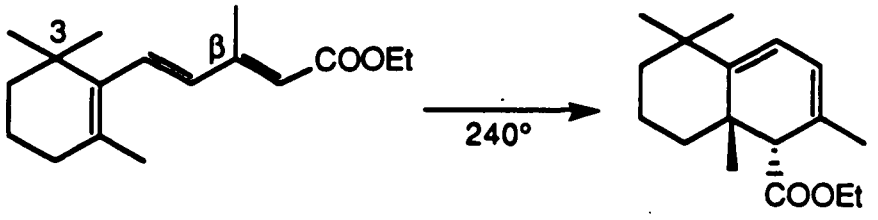
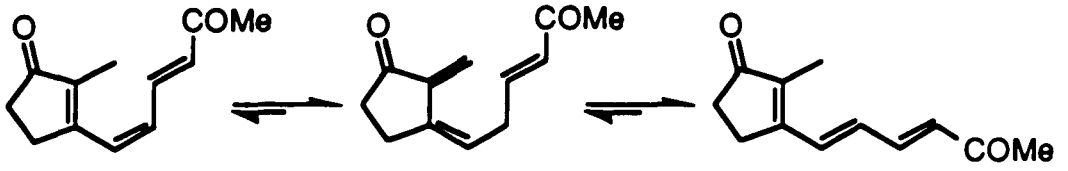


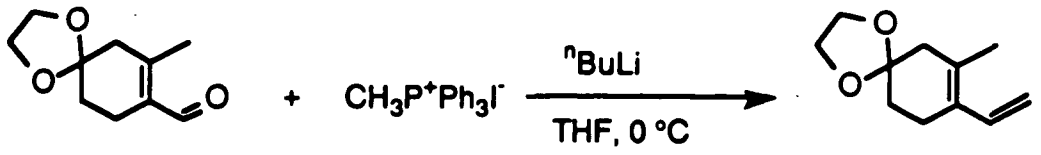
Figure 2.3-5. A reported example of an electrocyclolization of hexatrienes to cyclohexadienes



3-5 **3-6**

Figure 2.3-6. An example of failed electrocyclolization

The second route is based on the Diels-Alder reaction. The diene **3-7** was obtained in 96% yield using modified Wittig reaction[150].

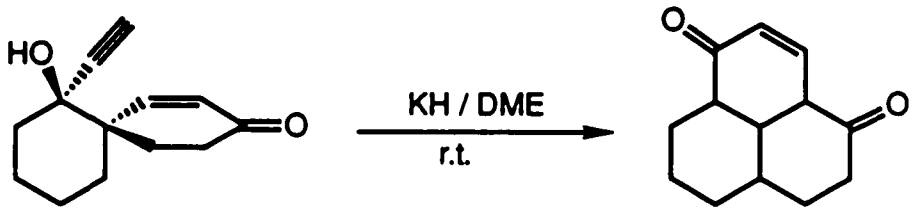


3-1 **3-7**

In a model reaction, dimethyl acetylenedicarboxylate was heated with diene **3-7** in xylene at 138 °C under nitrogen for 3 days yielding Diels-Alder product in about 40%, while neat at 110 °C the yield was about 30%[151]. The best conditions have yet to be developed.

2.4 Approach To 13-Methylphenalene Via Oxy-Cope Rearrangement

An interesting anionic oxy-Cope rearrangement in acetylenic spiro system had reported for formation of tricyclic diketone **4-2** by Indian worker Swaminathan et. al. as following.[152]



4-1 **4-2**

It appeared feasible to apply this sequence to the synthesis of 13-methylphenalene.

The formation of compound **4-2** can be rationalized as Figure 2.4-1.

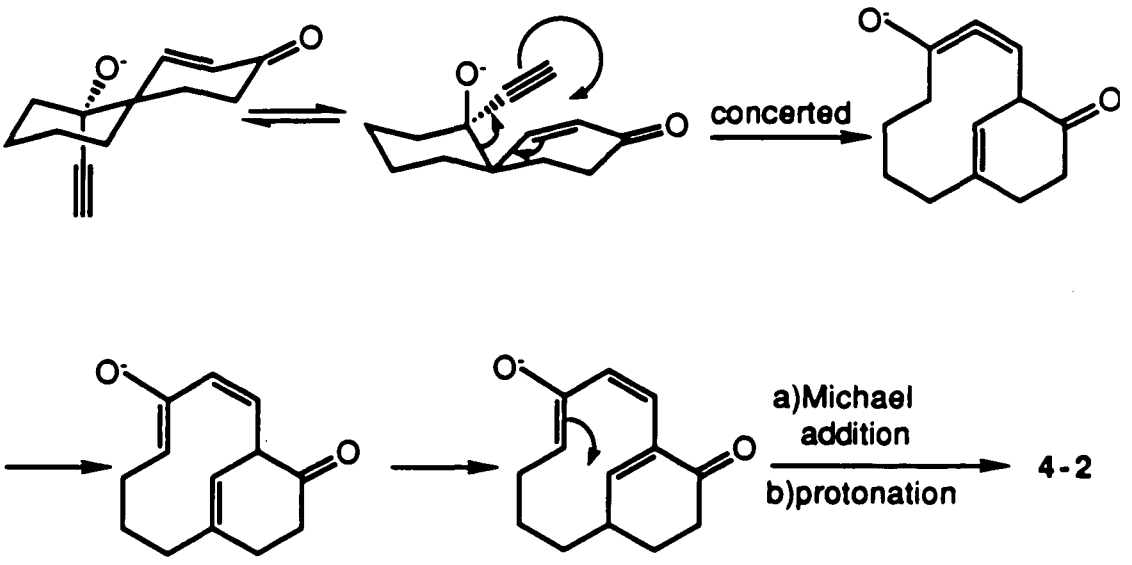


Figure 2.4-1. The formation of tricyclic diketone **4-2**

Since the experimental procedure for this reaction was not reported, our first task was to repeat and to test all reactions from the beginning as shown in Figure 2.4-2.[153,154,155]

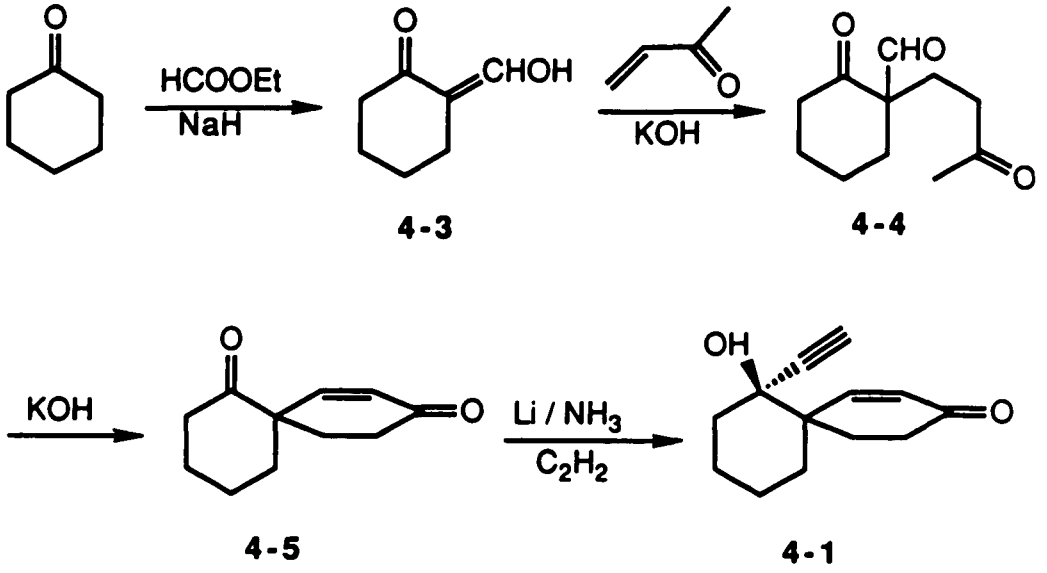
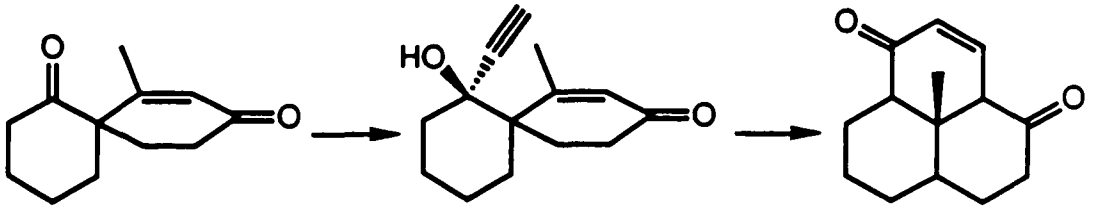


Figure 2.4-2. The scheme for synthesis of acetylenic spiro **4-1**

Cyclohexanone and ethyl formate with NaH in dry ether were stirred overnight, then hydrolyzed, offering 2-hydroxymethylene cyclohexaneone **4-3** at 74% yield.

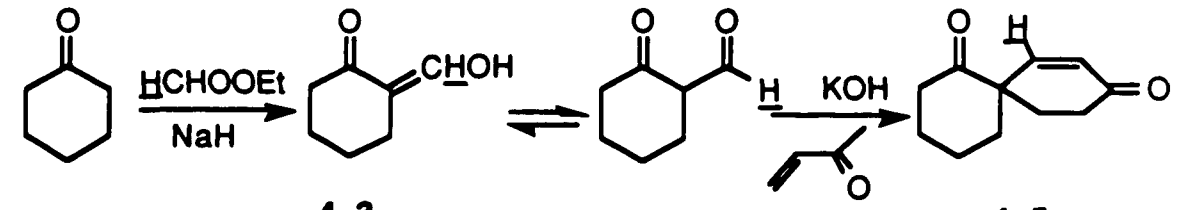
We combined next the two steps[156] into one pot. The yield of spirodione **4-5** has been improved to 57% (lit.[158]: 72% x 21% = 15%). After removal of methyl vinyl ketone, the crude dione aldehyde **4-4** with excess KOH was heated at 120 °C for 48 hr, followed by slow distillation under high vacuum. The ethynylation of spirodione **4-5** was carried out in liquid ammonia. The colorless crystalline ethynyl carbinol **4-1** (30%, m.p. 125-126 °C, lit.[155] 124-125 °C) was obtained.

Our synthetic scheme required the intermediate spiro methyl diketone **4-5m** to introduce a central methyl in the tricyclic system **4-2m**.

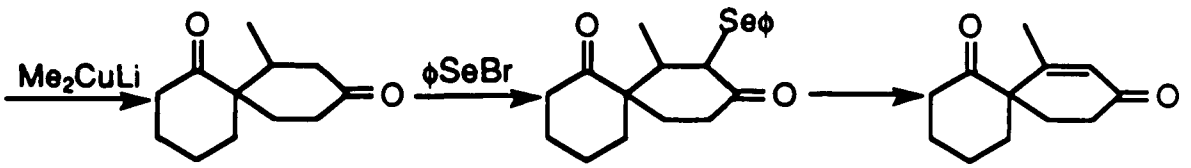


4-5m **4-1m** **4-2m**

The proposal to **4-4m** involved the following 5 steps:

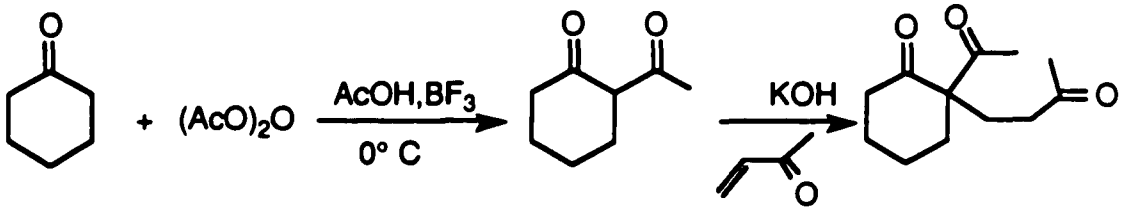


4-3 **4-5**

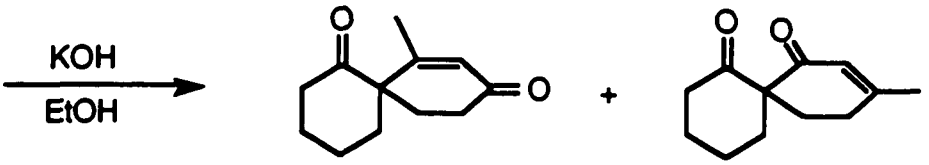


4-6 **4-5m**

However if H's in the above scheme were substituted by CH_3, the desired spiro diketone **4-5m** could have been achieved in just two facile steps. We therefore examined the following two reactions:



4-3m **4-7**



4-5m **4-5m'**

A mixture of cyclohexanone and acetic anhydride was added to a cold acetic acid saturated with boron trifluoride, stirred for 30 min. in an ice bath, allowed to stand for 4 hr, then refluxed with AcONa for 0.5 to 1 hr. The yield 84% of methyl dione **4-3m** was offered.[157]

Condensation of trione **4-7** by refluxing in EtOH for 40 hr surprisingly gave only single isomer **4-5m** or **4-5m'** at 60% based on dione **4-3m**. The ^{1}H NMR and ^{13}C NMR (see Experimental section) could not differentiate between the two isomers.

Finally, a X-ray analysis (See Figure 2.4-3.) showed clearly that oxygen O_3 bonds to carbon C_3 with distance 1.221 A; carbon C1 with carbon C_2 have a double bond (1.315 A); and methyl group C_{12} neighbors to carbon C_1. These results imply that isomer **4-5m'** is the structure of the product.

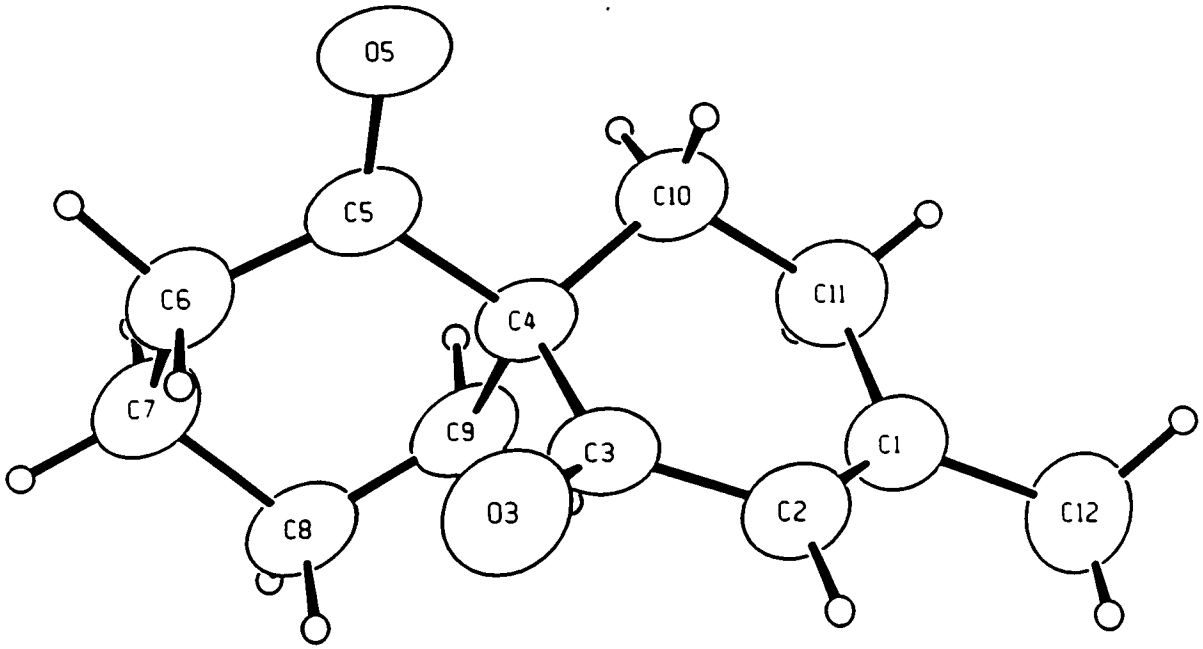
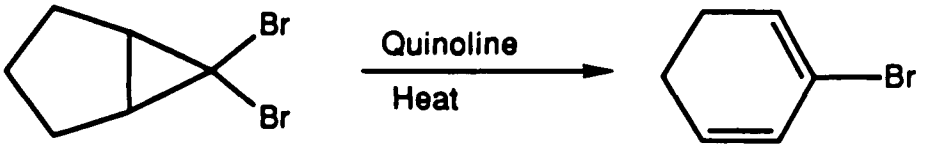


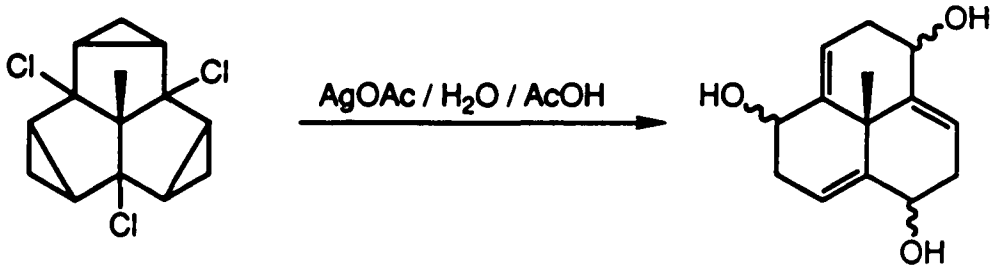
Figure 2.4-3. The x ray results of spiro diketone **4-5m'**

2.5 Attempted Synthesis of 10-Methyl-Triquinacene

This approach is based upon the known ring enlargement of 6,6-dibromobicyclo [3,1,0] hexane into 2-bromo-1,3-cyclohexadiene.[158,159] This reaction is the early work by Winstein and has been used for triquinacene.

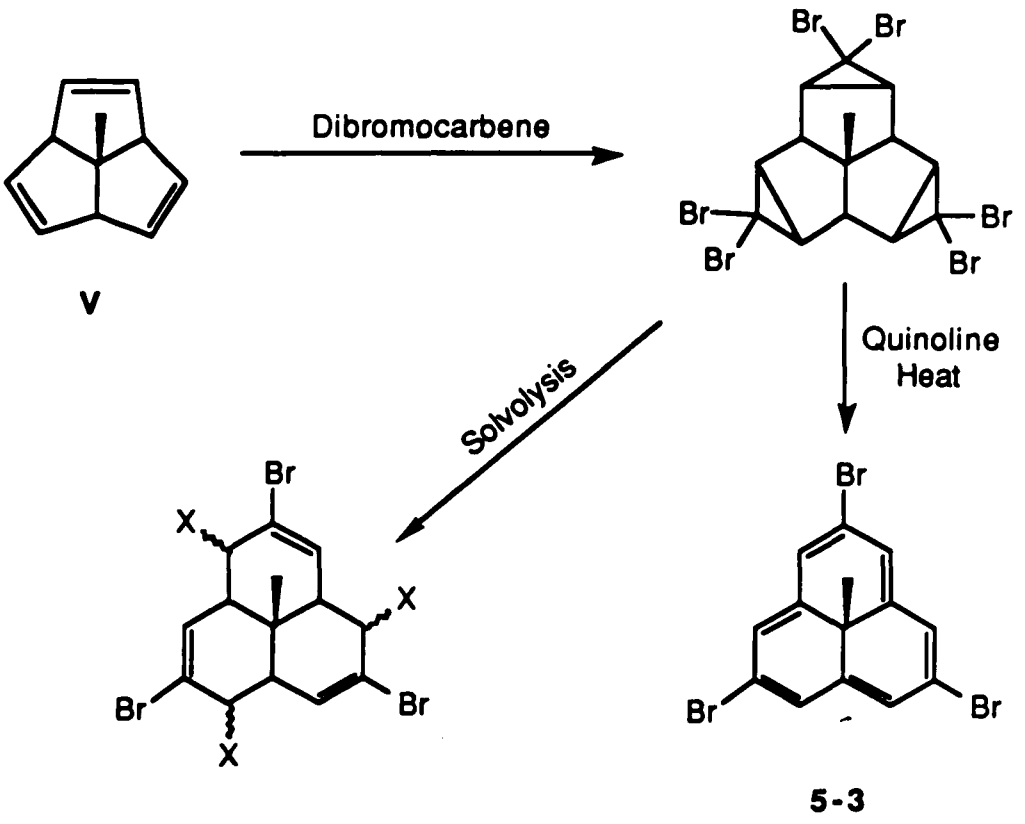


Also, the solvolytic cyclopropylcarbinyl homoallyl rearrangement of trichlorotrishomotriquinacene **5-1** has also been reported to yield the hexahydrophenalene derivative **5-2**.[160,161]



5-1 **5-2**

Starting with the yet unknown 10-methyltriquinacene **V**, these transformations are expected to yield 13-methylphenalene **X** or its sym-tribromo derivative **5-3** rather directly.



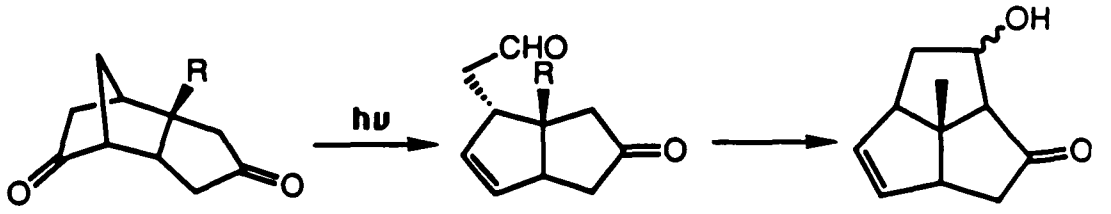
Compound **5-3** has additional advantages: not only will the three bromine substituents increase the overall stability of the system,[162] but also they enable us to introduce different substituents in those positions.

Klaus Grohmann in a joint research project with A. DeMeijere has obtained 10-methyltriquinacene **V** in a low overall yield.

Outline of the Proposed Synthetic Schemes

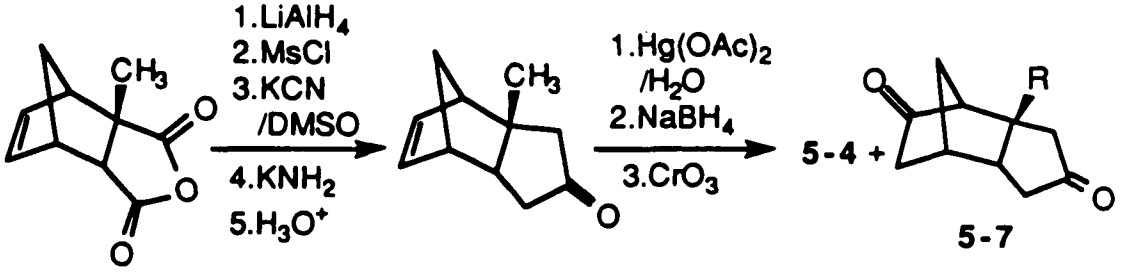
The key step in the Deslongchamp synthesis of triquinacene is the photolysis of the diketone **5-4** followed by an intramolecular aldol cyclization to the triquinacene system.[163]

For the synthesis of the required methyl substituted derivative of **5-4** (R = CH_3), the following two routes are proposed:



5-4

The readily available Diels Alder adduct **5-5** can be converted into the endo-ketone **5-6** and subsequently into **5-4** (R = CH_3).[164]



5-5 **5-6** **5-7**

One disadvantage of this scheme is the formation of isomeric diketone **5-7**. To overcome this we considered choosing the reagent $BF_3/LiBH_4$ or B_2H_6 instead of $Hg(OAc)_2/NaBH_4$.

The following scheme (Figure 2.5-1) is the summary of this route.

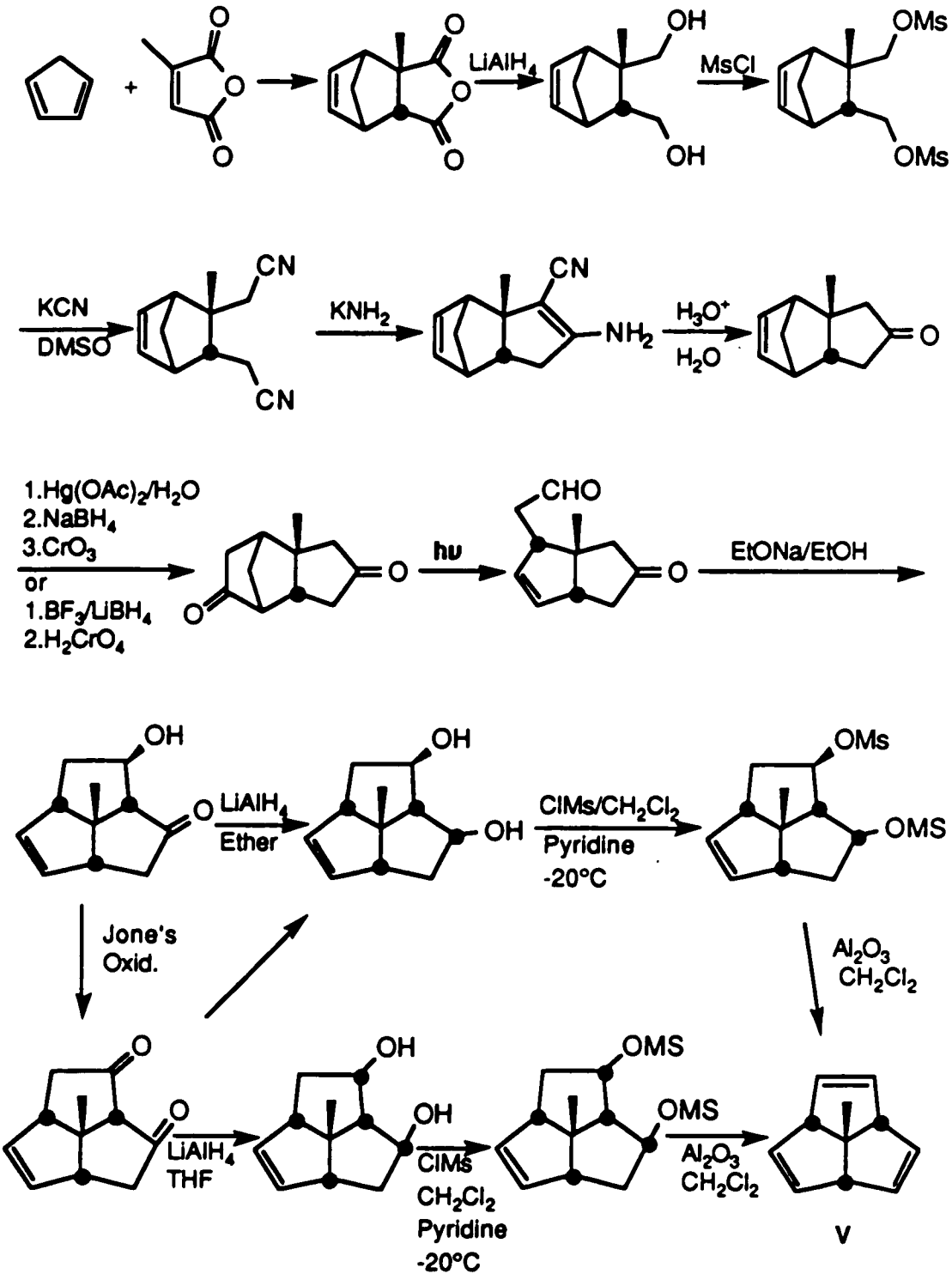
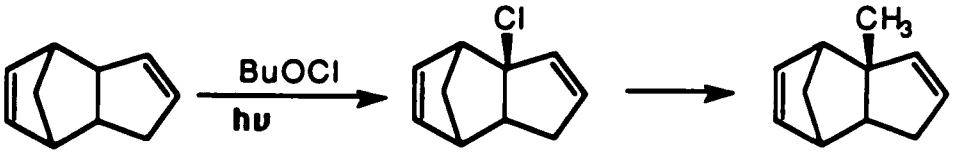


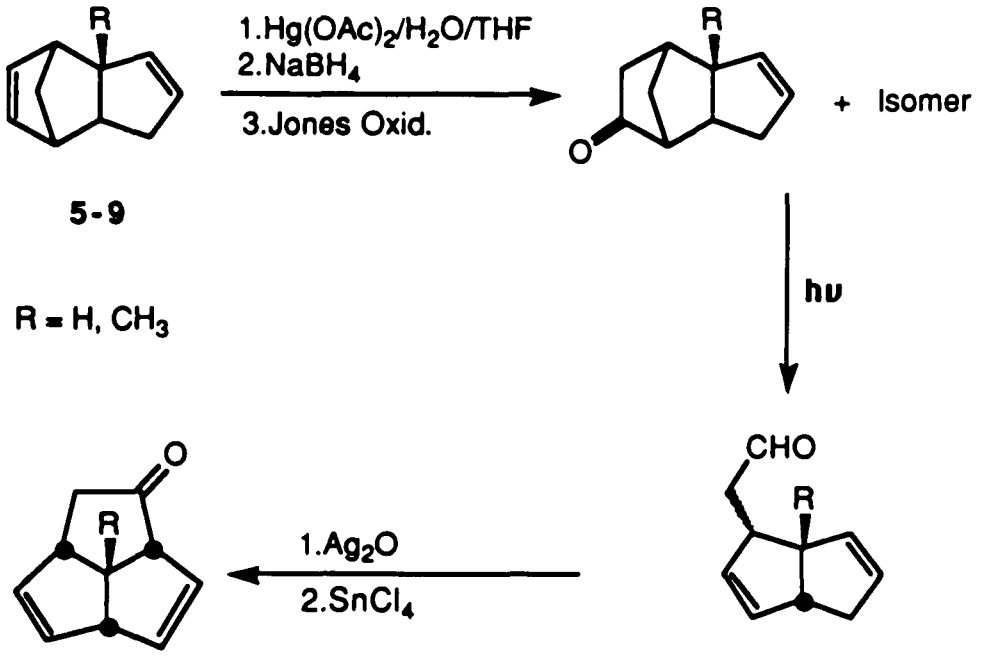
Figure 2.5-1. The scheme of the first route to 10-meyhyltriquinacene V

The second route to V is based upon unpublished observations concerning the functionalization of dicyclopentadiene.[165] According to DeMeijere and Bosse, the photochlorination of dicyclopentadiene with t-butyl hypochlorite give predominantly the 2-chlorodicyclopentadiene **5-8**. The reaction of **5-8** with trimethylaluminum or dimethyl zinc[166] is expected to yield the 2-methyldicyclopentadiene **5-9a**.

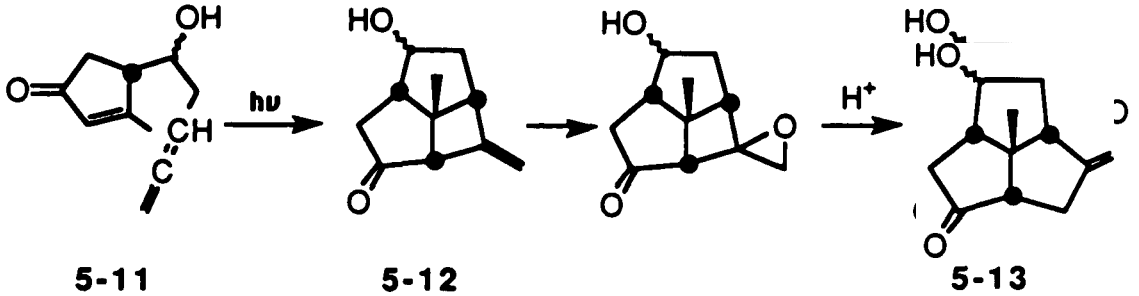


5-8 **5-9a**

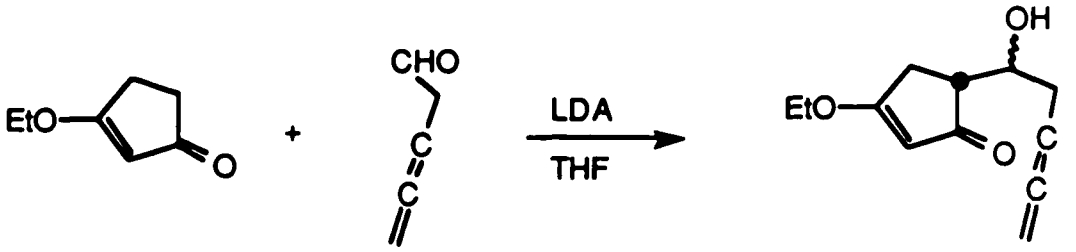
5-9a can be converted into the 10-methyltriquinacene V by the following sequence. (Preliminary experiments obtained in this lab. have resulted in the synthesis of the ketone **5-10** (R = H) from dicyclopentadiene.)[167]



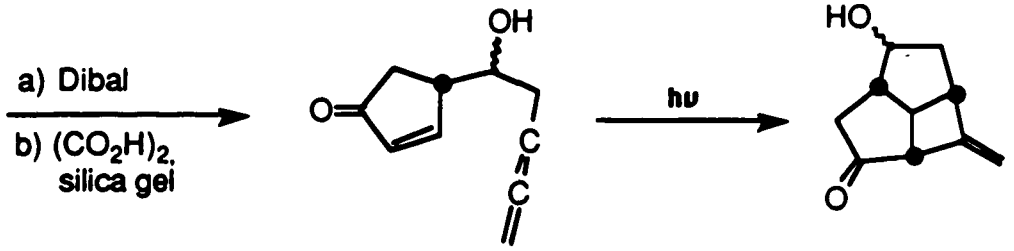
The third and the most interesting route to **V** is the intramolecular [2+2] photocycloaddition of 4-(3,4-pentadienyl)-2-cyclopenten-1-ones (**5-11**), followed by ring expansion to the triquinane (**5-13**)[168,169].



The compound **5-16** is similar to **5-12** except without methyl group. This **5-16** has been synthesezed by Dauben and coworkers as shown in the following scheme.[170]

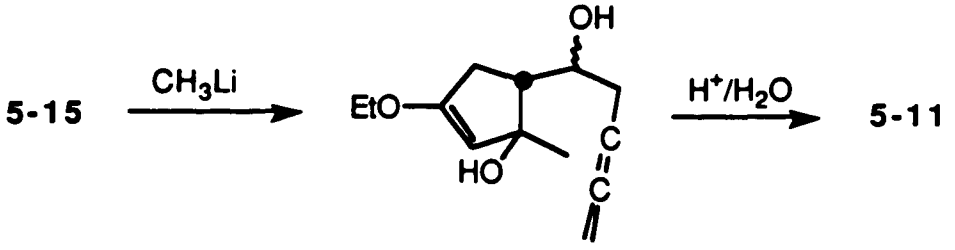


5-14 **5-15**

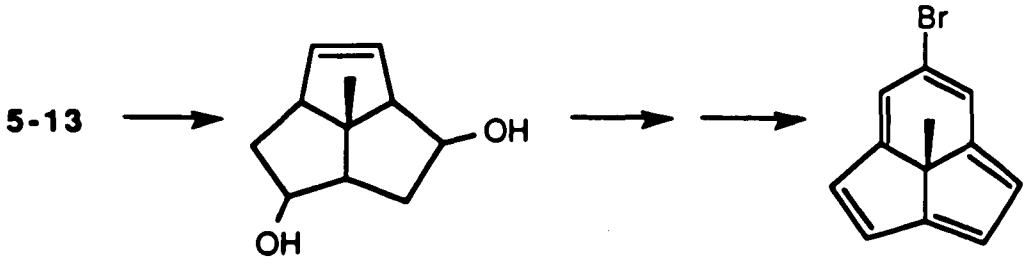


5-16

5-11 could possibly be obtained by following reactions:



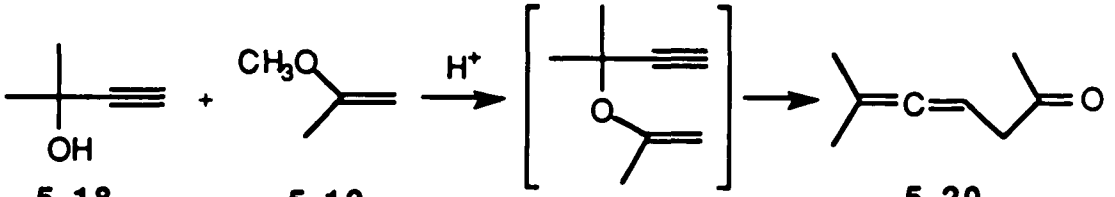
Intermediate **5-13** can also be used to synthesize the 10 π electron system compound **5-17** which has been reported by Rees.[171]



5-17

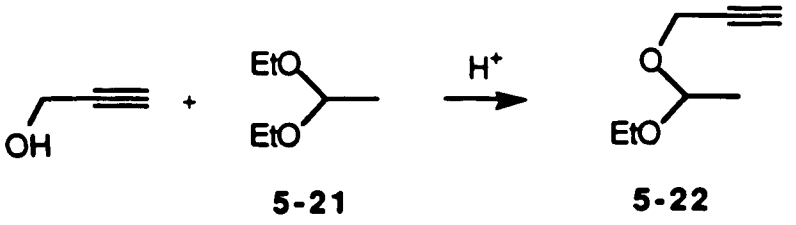
To obtain the β-allenic aldehyde **5-14**, the following reactions were investigated.

It had been reported by Saucy and Marbet that the reaction of 2-methyl-3-butyn-2-ol **5-18** with isopropenyl-methyl ether **5-19** at presence of p-toluenesulfonic acid via Claisen rearrangement gave 2-methyl-2,3-diene-hepta-2-one **5-20**,[172] (Figure 2.5-2.) we proposed that the reaction of 2-propynol with acetal **5-21** should give β-allenic aldehyde **5-14**. Unfortunately this reaction gave only the intermediate ether **5-22**. (Figure 2.5-3.) Its ^{1}H NMR (60 MHz) shows δ 4.55, (q, $OC\underline{H}CH_3O$), 3.90 (d, $HCCC\underline{H}_2O$), 3.40 (m, $OC\underline{H}_2CH_3$), 2.30(d, HCC), 1.28 (d, $OCHC\underline{H}_3O$), 1.19 (t, $OCH_2C\underline{H}_3$).



5-18 **5-19** **5-20**

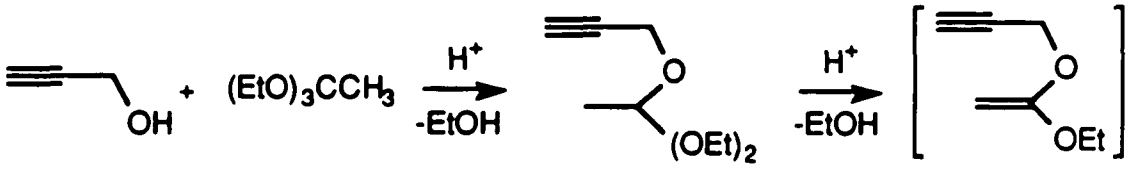
Figure 2.5-2. The formation of **5-20**

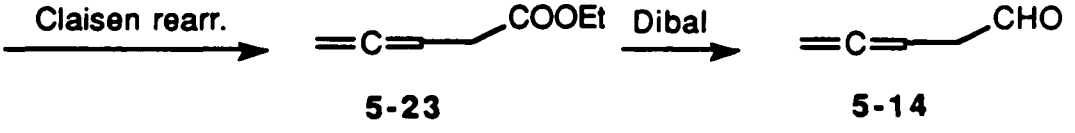


5-21 5-22

Figure 2.5-3. The formation of ether **5-22**

2-propynol reacting with triethyl orthoacetate[173] followed by reduction with Dibal[174] might furnish aldehyde **5-14**. (Figure 2.5-4.) In our experiment, the former reaction with catalyst amount of propionic acid gave reasonable yield (28 %) after ethanol was collected quantitatively. The latter reaction was tried once and did give reasonable yield before we turned to next approach.





5-23 5-14

Figure 2.5-4. The formation of β-allenic aldehyde **5-14**

Since the previous approaches gave low initial yields and needed more detailed investigations, we returned to the synthesis of the tricyclic trione **VI** as the key intermediate for the approach to the 13-methylphenalene.

2.6 The Improved Synthesis And The Investigation of Trione VI

The known trione **VI** was obtained by Wenkert and et al. in 5 steps from 4-methyl 4-dichloromethyl 2,5-cyclohexadienone **6-1** as outlined in Figure 2.6-1. [175 ,176]

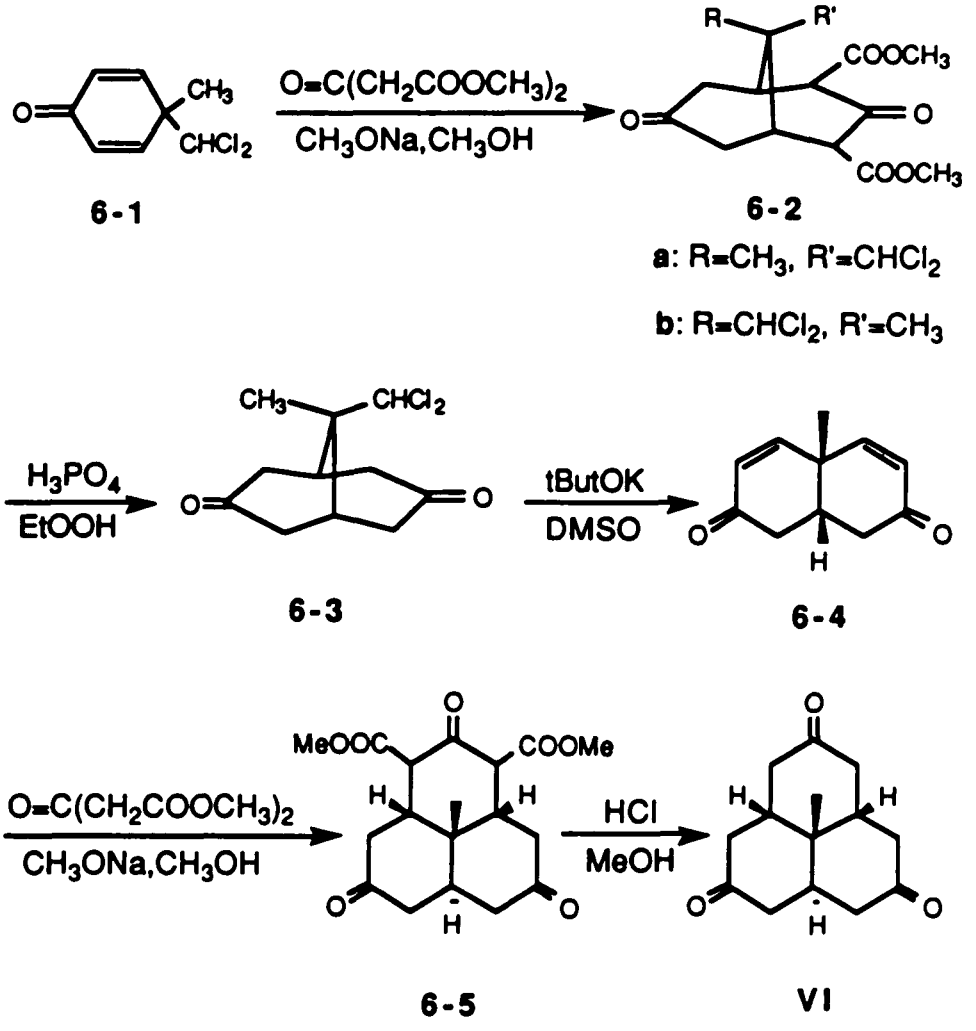


Figure 2.6-1. The scheme of synthesis of trione **VI**

When cyclohexadienone **6-1** is condensed with dimethyl acetonedicarboxylate in sodium methoxide methanol solution, it gave ester **6-2a** and **6-2b** (29:1) at 77% (lit. 72%)[179] which could be separated by recrystalization from methanol/water, **6-2a**: m.p. 190-196°C (lit.195-197 °C)[179] ^{1}H NMR: 12.34 (s, 1H), 6.04 (s, $CHCl_2$), 1.38 (s, CH_3); **6-2b**: m.p.181-186 °C, ^{1}H NMR: 12.30 (s, 1H), 6.44 (s, $CHCl_2$), 1.61 (s. CH_3). Dienone **6-1** (8%) were recovered.

Decarboxylation of **6-2a** and **6-2b** with 85% phosphoric acid instead of concentrated sulfuric acid improved the yield up to 91% (lit.75%)[179] and prevented the formation of the dark decomposed products, but it required a longer reflux time. After the mixture was refluxed for 14 hours, 10% of starting ester **6-2** was detected in ^{1}H NMR, 5% after 36 hours, 0% after 48 hours.

The interesting conversion of dione **6-3** into dienedione **6-4** first reported by Wenkert and et al.[180] was investigated in detail in order to optimize it.

The original yield was ca. 20%. To improve it, various conditions were examined. The results are listed in table 2.6-1. As one can see, the yield varies upon the amount of tBuOK, the method of addition, temperature, concentration and the time.

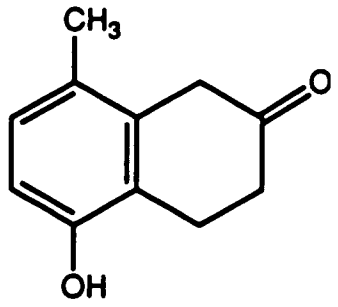
Table 2.6-1. The experimental results of formation of dienedione **6-4**

entry	TBuOK (mole)	metd*	temp (°C)	time (h.)	yield	dione	dimer	cresol	6-6	un.A	un.B
1	1.0	A	60	1.5	34%	28%					
2	1.2	B	60	3	29%		>7%				
3	1.2	A	90	1	47%	14%					
			60	1							
4	1.4	A	70	1	37%	yes	yes				
			25	0.5							
5	1.5	A	95	1.5	52%	1.5%	8.2%			3%	
6	1.6	A	95	2	47%	(see discussion)					yes
7	1.8	A	95	1.5	\			yes	yes		
8	1.9	C	60	1.5	19%			>2%	>2%		

* **method A**: solid dione **6-3** was added to tBuOK solution; **method B**: solid tBuOK was added to dione solution; **method C**: dione solution was added dropwise to a tBuOK solution.

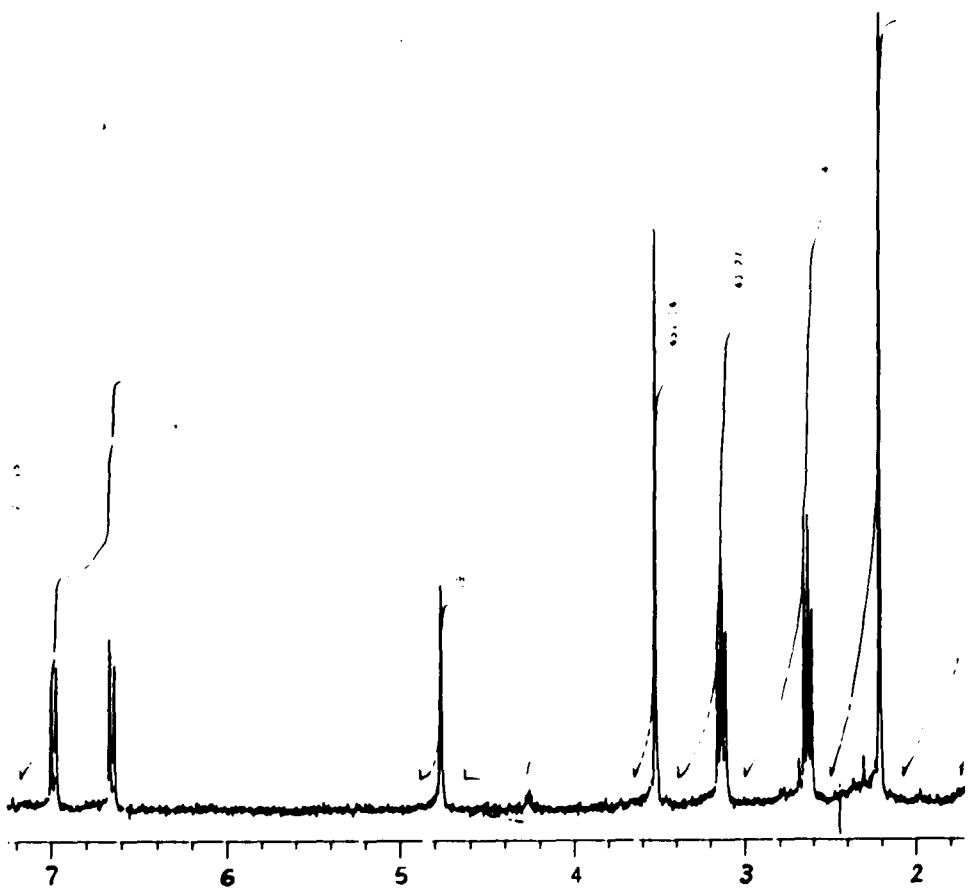
The result of entry 1 in the table 2.6-1 is identical with that in the reference[180] even though the temperature we used was 60°C instead of 25°C. Recovered dione **2-1** (28%) indicates that the yield may increase as the amount of tBuOK increases. Indeed, using 1.2 to 1.6 moles of tBuOK (entries 3,4,5,6.) improves the yield up to 52%. But when more than 1.8 (entry 7.) to 1.9 (entry 8.) moles of tBuOK were used, the yield decreased, while p-cresol and 2-oxo-5-hydroxyl-8-methyl-1,2,3,4-tetrahydronathalene (**6-6**) were formed. This was confirmed by ^{1}H NMR (see Figure 2.6-2) and IR (see Figure 2.6-3). ^{1}H NMR: 6.94 (d, J=8 Hz, 1H), 6.61 (d, J=8 Hz, 1H), 4.80 (exchangeable, 1H), 3.48 (s, 2H) 3.09 (t, J=7 Hz, 2H), 2.59 (t, J=7 Hz,

2H), 2.17 (s, 3H). IR: 3600 cm^{-1} (sharp, m), 1710 cm^{-1} (sharp, s), 1600 cm^{-1} (m), 1490 cm^{-1} (m), 790 cm^{-1}.



6 - 6

Figure 2.6-2. The ^{1}H NMR spectra of 6-6.



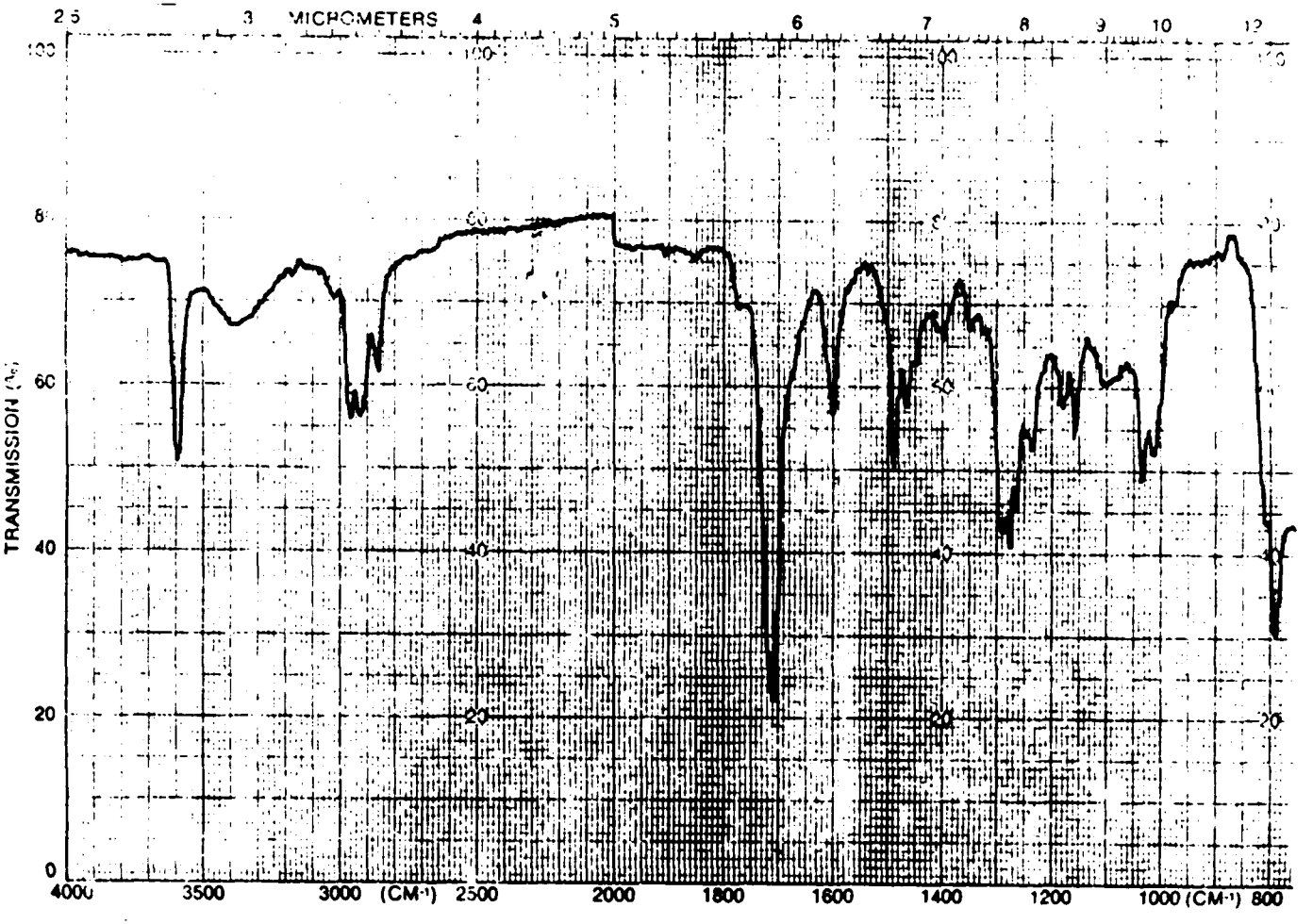
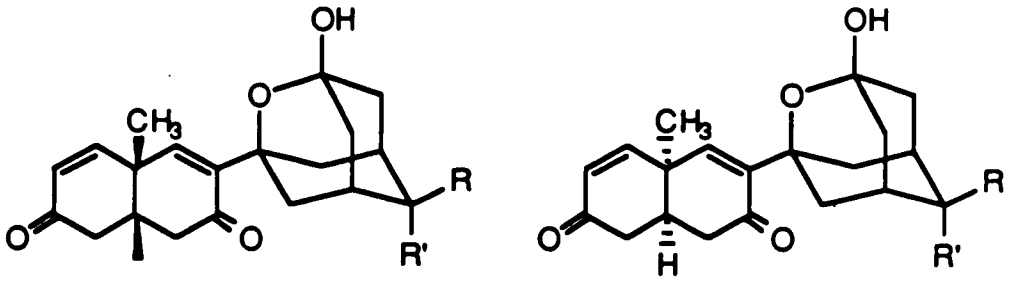


Figure 2.6-3. The IR spectra of 6-6.

A dimer **6-7** (Figure 2.6-4) was isolated and characterized by ^1H NMR (Figure 2.6-5), ^{13}C NMR (Figure 2.6-6), IR (Figure 2.6-7) and X-ray (Figure 2.6-8), and confirmed by mass spectrum and elemental analysis, when 1.2 to 1.5 mole tBuOK was added (see entry 2, 4 and 7). According to ^1H NMR data, there are diastereo isomers **6-7a** and **6-7b** (ca. 1.0:1.1). Based on X-ray analysis, **6-7a** is a racemic mixture. The other enantiomer is **6-7'a** as shown in Figure 2.6-4. All four isomers are cis to 9-CH_3 and 10-H.



6-7 **6-7'**

a: R=CH_3, R'=$CHCl_2$

b: R=$CHCl_2$, R'=CH_3

Figure 2.6-4. The structures of the racemic dimer **6-7**

Figure 2.6-5. The ^{1}H NMR spectrum of **6-7** and **6-7a**.

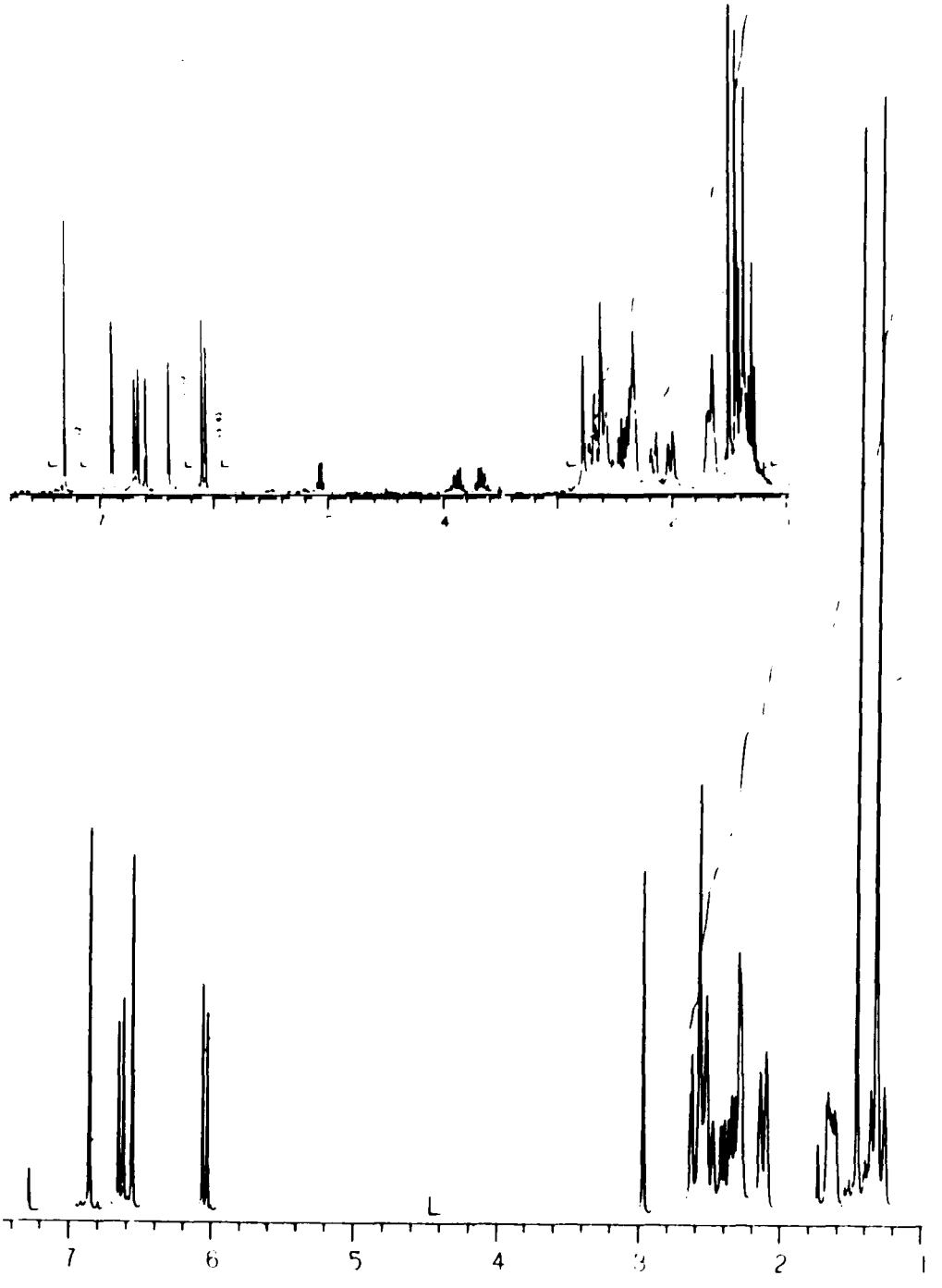
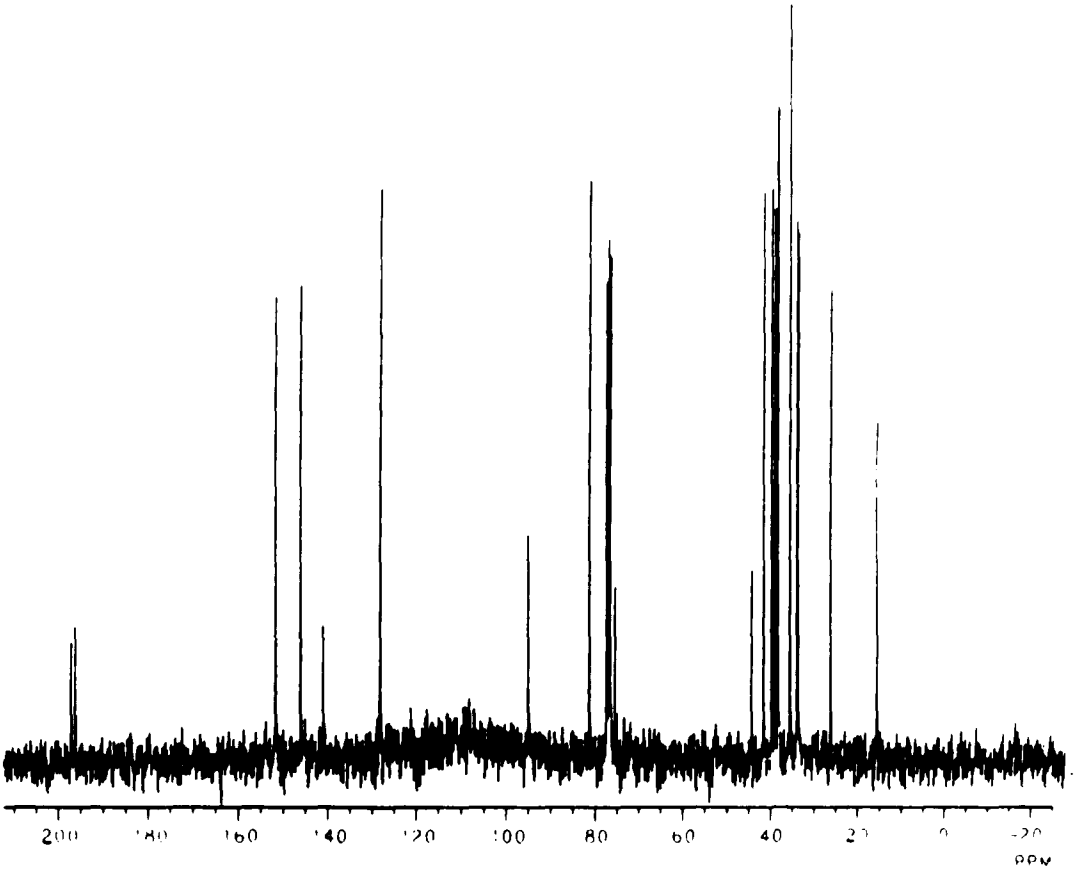


Figure 2.6-6. The ^{13}C NMR spectrum of **6-7a**.



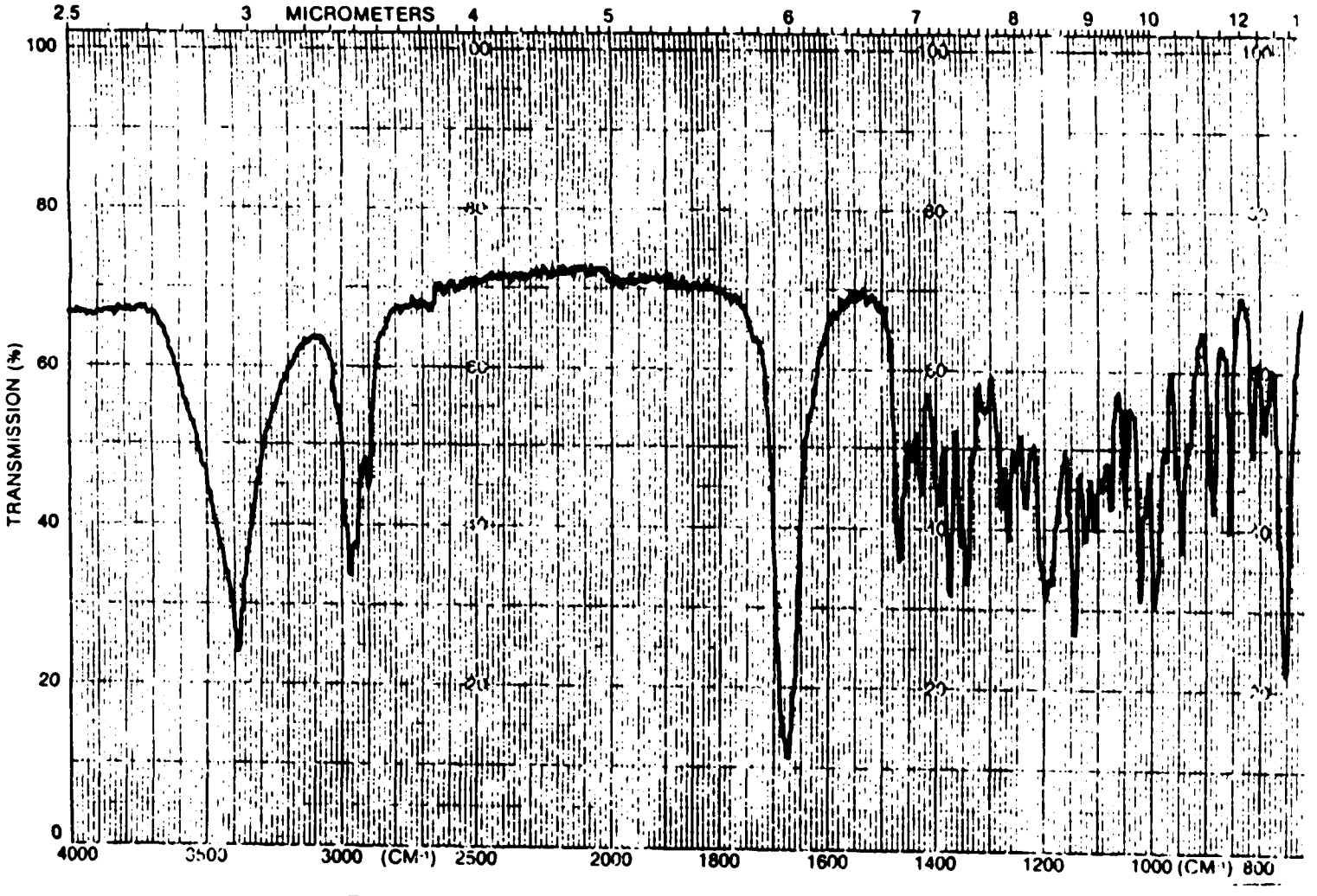


Figure 2.6-7. The IR spectrum of **6-7a**.

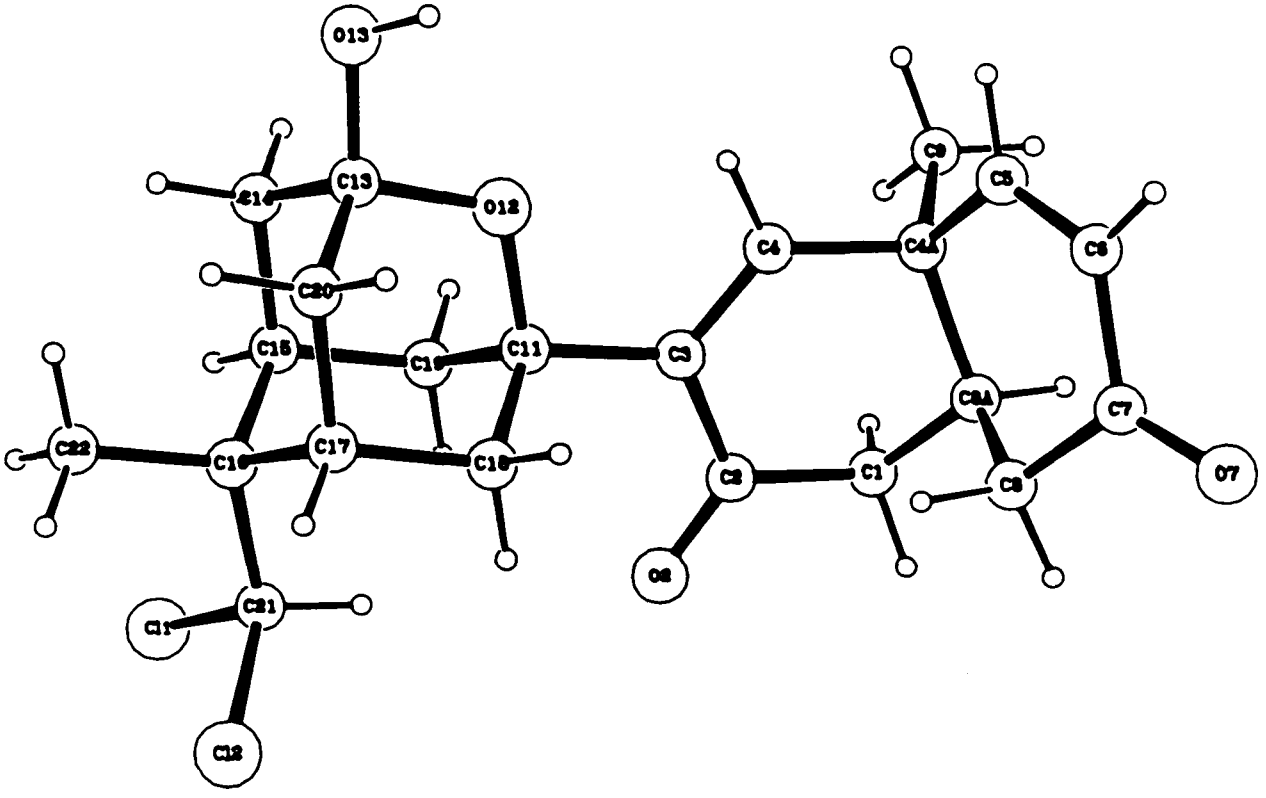


Figure 2.6-8. The X-ray result of **6-7a**.

When 1.2 moles of tBuOK were added to the dione solution, followed by heating to 60°C for 3 hours (method B, entry 2.), dimer **6-7** was obtained at 7% and no dione **6-3** was observed. This may be explained as follows: formation of one mole of dienedione **6-4** spends 2 moles of base (see later mechanism discussion); maximum 0.60 mole dienedione could be produced, the excess dione would react dienedione to furnish dimer during heating.

Interestingly, dimer appeared to be formed not only during heating with tBuOK/DMSO, but also during column chromatography of dienedione **6-4** with dione **6-3**. In entry 6, After extraction and washing, the ^1H NMR spectrum of the product mixture indicates that there is at least double the amount of dione **6-3** compared to dimers **6-7** in the mixture, but after silica gel column chromatography with ethyl acetate and hexane (instead of benzene[180]), only 1.4% of dione **6-3** were recovered while 7.8% of dimers **6-7** were seen. This means that the reaction of dione **6-3** with dienedione **6-4** or the conversion of dione **6-3** may form dimers **6-7** at the presence of silica gel.

Since dienedione **6-4** is consumed on column chromatography, other isolation methods such as crystallization and vacuum distillation were tried. Unfortunately, the former gave impure crystals, the latter gave a low yield (ca. 20-25%).

Under the conditions of entry 5, an unknown compound A at ca. 3% was found from chromatography. ^1H NMR: δ 5.97 (d, 1H), 3.42 (m, 1H), 3.37 (dd, 1H), 3.15 (ddd, 1H), 2.97 (m, 1H), 2.78 (7pk, 1H), 2.52 (dd, 1H), 2.45 (dd, 1H), 2.14 (dd, 1H), 2.10 (d, 1H), 2.04 (d, 1H), 1.89 (d, 3H). And in the condition of entry 6, another unknown compound B was found. (^1H NMR:)

Overall, entry 5 details the best conditions: dione **6-3** was added to 1.5 mole of tBuOK in DMSO (0.2 M concentration to dione) then heated at ca. 95°C for 1.5 hr. The ^1H NMR of the product mixture showed formation of at least 90% of diene dione **6-4**. After column chromatography the recover yield was 52%.

Two major mechanistic pathways for the formation of the dienedione **6-4** from dione **6-3** have been considered:[180] a stereospecific cyclobutane mechanism (**mech.1**) (Figure 2.6-9) and a regioselective retro Michael reaction mechanism (**mech.2**). (Figure 2.6-10)

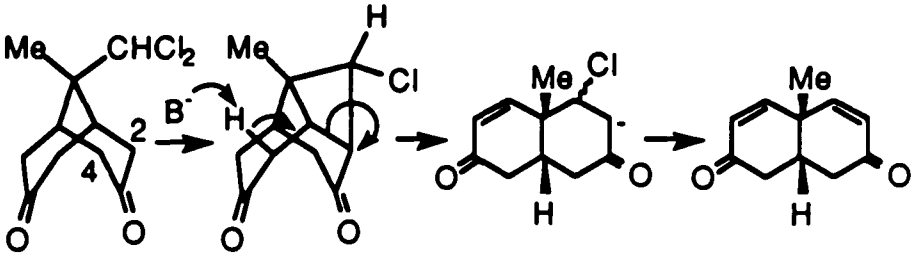


Figure 2.6-9. Stereospecific Cyclobutane Mechanism

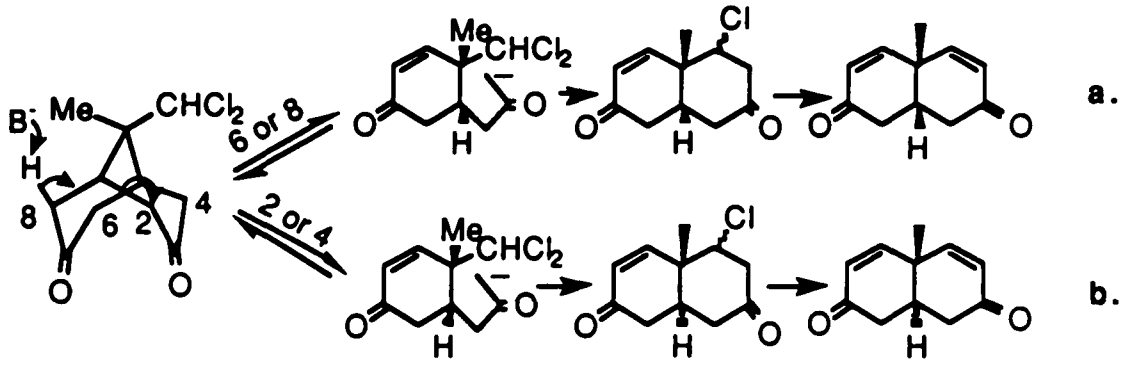


Figure 2.6-10. Regioselective Retro Michael Reaction Mechanism

First, in **mech.1** only cis dienedione is generated, while in **mech.2** cis and trans dienediones form. In our experiments, exclusively only cis products were observed. This implies that the reaction is stereospecific or that only path **a.** of **mech.2** takes place.

Second, in order to form the cis compound the 2-H or 4-H must leave first in **mech.1**, while the 6-H or 8-H must leave in **mech.2**. Considering the position near highly electronegtive chlorine, 2-H and 4-H are more acidic possibly. Therefore **mech.1** could be more preferable.

Theoretically both mechanisms show that one mole substrate consumes two moles of tBuOK, but when two moles of tBuOK were added, the formation of compound **6-6** will compete and reduce the yield.

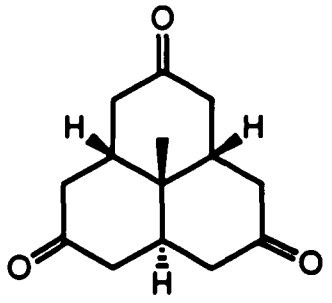
For construction of the required tricycle, the reaction of dienedione **6-4** with dimethyl acetonedicarboxylate via double Michael reaction was carried out.

Dienedione **6-4** with an equimolar dimethyl acetonedicarboxylate was refluxed in absolute methanol containing sodium methoxide for 28 hours, giving ester trione **6-5** at 84% yield. (lit.[180] 78%)

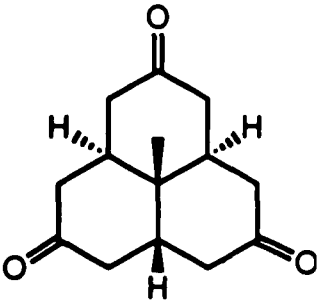
The ester trione **6-5** was converted to decarboxylated trione **VI** by refluxing with hydrochloric acid in methanol for 3 days. The reaction process was monitored by TLC. The yield of this step was 94% yield (lit.[180] 92%). Sublimation gave pure product at 86%.

So far the overall yield in the five steps from **6-1** to **VI** was (77%)(91%)(52%)(84%)(94%)=29%, compared to a previous yield of only (72%)(75%)(20%)(78%)(92%)=8%.

The stereochemistry of trione **VI** was unknown[180]. There are nine signals in ^{13}C NMR spectrum (Figure 2.6-11.) which implies that this molecule possesses Cs symmetry and has two possible structures: cis, cis, trans or cis, trans, trans as shown in Figure 2.6-12.



cis, cis, trans



cis, trans, trans

Figure 2.6-12. Two possible structures of trione **VI**

NOE (Nuclear Overhauser effect) experiments in ^1H NMR were carried out to order to decide between the two structures. When the central methyl was irradiated, there was no clear NOE result observed because too many peaks overlapped. (See Figure 2.6-13 and 2.6-14)

Eventually, this difficulty was overcome as follows. Trione **VI**, in dried THF, was treated with a solution of sodium in D_2O for 24 hours. The isolated sample had a very simple ^1H NMR spectrum (Figure 2.6-15), only three singlet signals δ 2.77 (1 H), δ 2.36 (2 H), δ 1.58 (3 H). This sample gave a beautiful NOE spectrum (Figure 2.6-16) in which only the peak δ 2.36 responded to irradiation at δ 1.58. This undoubtedly proves that the structure of trione **VI** is cis, cis, trans.

Figure 2.6-11. The ^{13}C NMR spectrum of trione VI

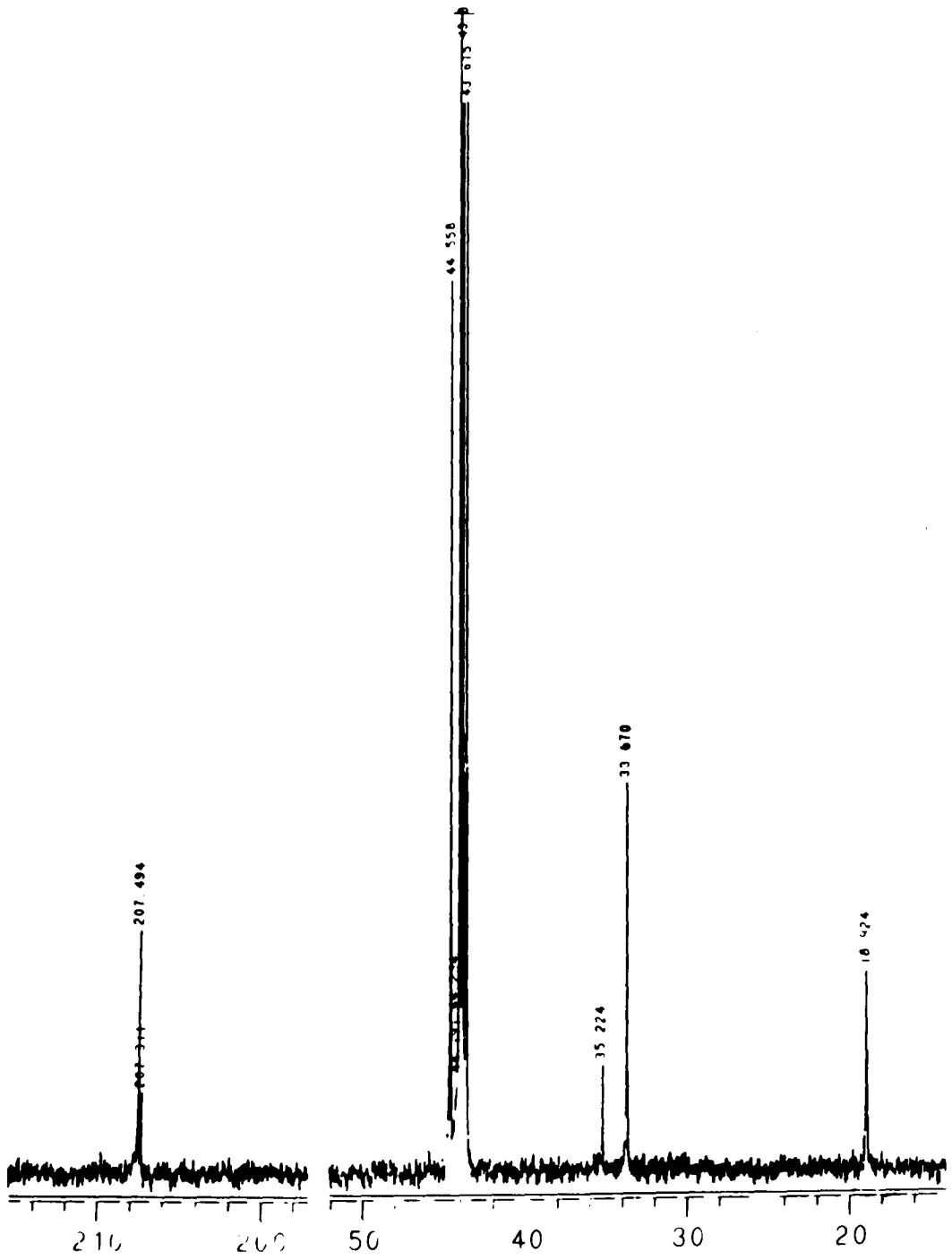


Figure 2.6-13. The ^{1}H NMR spectrum of trione VI

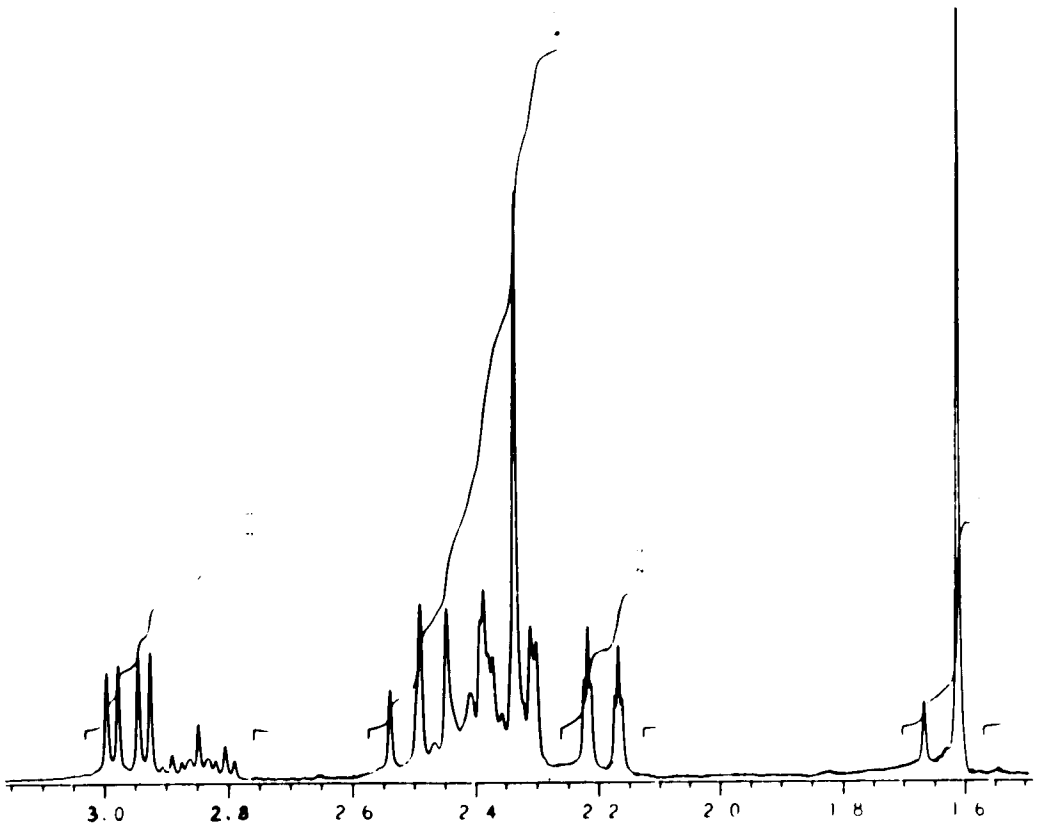


Figure 2.6-14. The unclear NOE ^{1}H NMR spectrum of trione VI

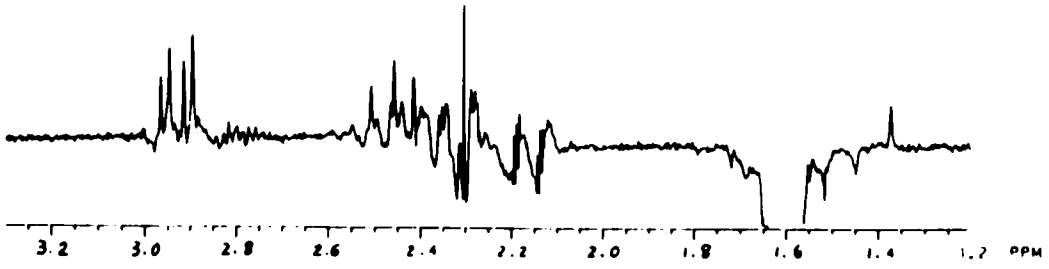


Figure 2.6-15. The ^{1}H NMR spectrum of deuterated trione VI

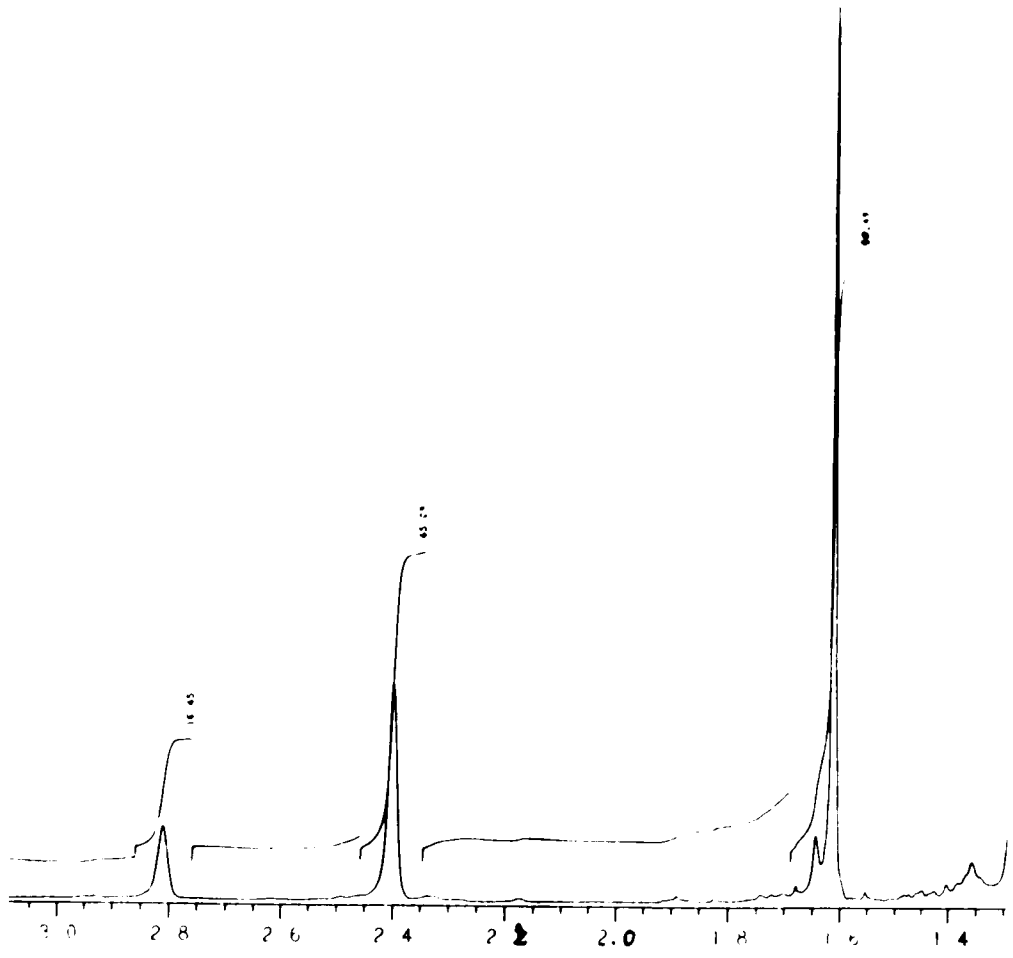
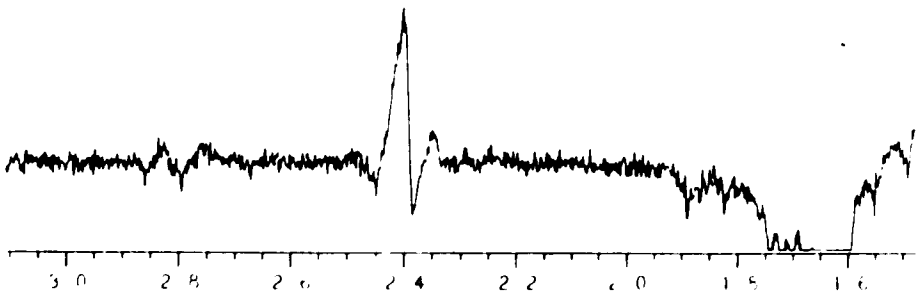
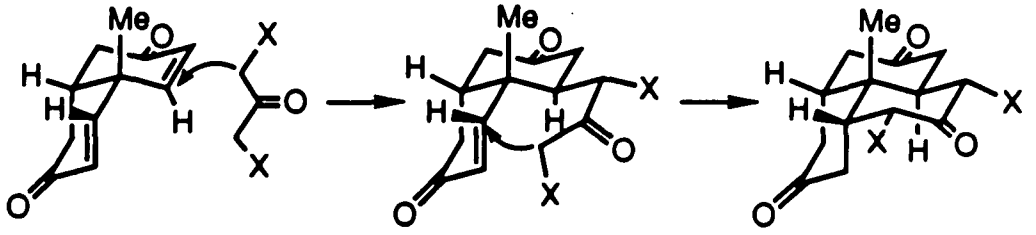


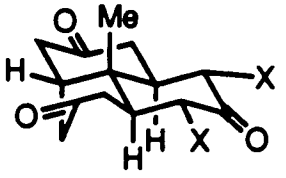
Figure 2.6-16. The NOE ^{1}H NMR spectrum of deutered trione VI



These results further provided the information about the mechanism of the double Michael reaction to form ester trione **6-5**. Since dienedione **6-4** has a cis configuration, the first attack to **6-4** should be exo, the less hindered side, and give a cis, trans intermediate. The second attack must then be endo to form the all chair form cis, cis, trans tricyclic structure, which is thermodynatically favored, compared to the cis, trans, trans structure which contains a boat form. (Figure 2.6-17)



cis, cis, trans

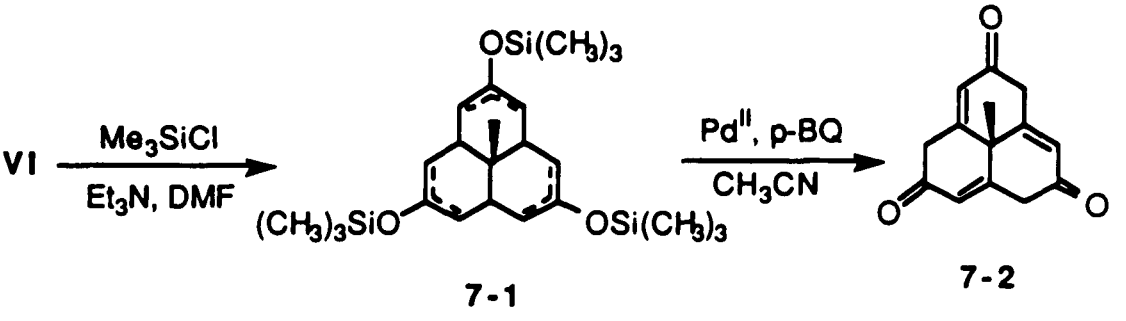


cis, trans, trans

Figure 2.6-17. The mechanism of double Michael reaction for ester trione **6-5**.

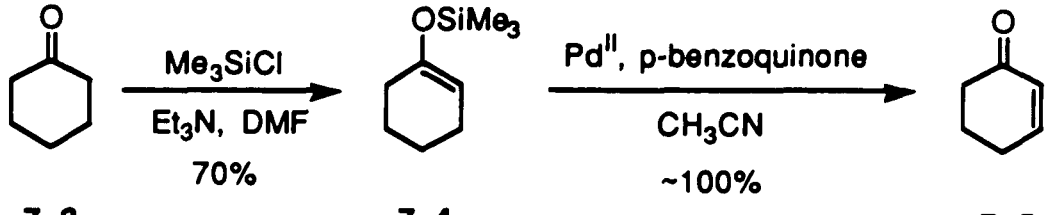
2.7 Attempted Synthesis of Trienetrione VII Via Palladium (II) Catalyzed dehydrosilylation

For functionalizing the tricyclic trione **VI** to approach 13-methylphenalene, a possible intermediate **7-2** could be considered through silylation[177] and dehydrosilylation[178].



7-1 **7-2**

The model reaction using cyclohexanone gave identical results with the literature[179] for the silylation reaction. To a solution of chlorotrimethylsilane (1.2 equimole) and triethylamine (2.4 equimole) in dimethylformamide (0.8 mL/mmol) was added cyclohexanone. The mixture was refluxed for 4.5 hours. After extracting with pentane, a 70% yield of **7-4** was obtained.



7-3 **7-4** **7-5**

For the Pd^{II} catalyzed dehydrosilylation[180], to a stirred solution of $Pd^{II}(OAc)_2$ (0.5 mmol) and p-benzoquinone (0.5 mmol) in acetonitrile (4 mL), silyl enol ether **7-4** (1.0 mmol) was added under

nitrogen at room temperature, and the resultant mixture was stirred for 3 h. ^{1}H NMR indicated 40% of product eneone **7-5** (at δ 4.89, t) and 60% of starting **7-4** (at δ 5.94, d). To improve the yield, a variety of conditions were investigated. The results are shown in Table 2.7-1. The best conditions were 0.75 mol of $Pd^{II}(OAc)_2$, 0.75 mol of p-benzoquinone, and 17 hours.

Table 2.7-1. The investigation results of Palladium (II) Catalyzed Desilylation

entry	$Pd^{II}(OAc)_2$	p-BQ	time	**7-5** : **7-4** *
1	0.5 mol	0.5 mol	3 h	40 : 60
2	0.5 mol	0.5 mol	18 h	67 : 33
3	0.75 mol	0.65 mol	17 h	89 : 11
4	0.75 mol	0.75 mol	17 h	100 : 0

* There was also 3-5 % of cyclohexanone **7-3**, shown by GC in each mixture.

For silylation of the trione **VI**, similar reaction conditions were be applied, except longer reflux time was needed (44 hours). After all volatile materials (DMF, NEt_3, Me_3SiCl) were evaporated with a rotatory evaporator (oil pump), the ^{1}H NMR spectrum of the crude product mixture clearly showed the desired trisilyl enol ether **7-1** in almost quantitative yield. This compound was very unstable and reconverted to the starting trione **VI** during evaporation at 55 °C

or crystallization in boiling CCl_4. It could be stored in refrigerator overnight.

For the Pd^{II} catalyzed dehydrosilylation reaction, when 2 mmol of $Pd^{II}(OAc)_2$ and 2 mmol of p-BQ (assuming the yield of silylation was 90%, 0.9 x 3 x 0.75 = 2.0 mmol) were used, the reaction time rose to 20 hours. After column chromatography the impure dehydrosilylation products were obtained in about 20% yield and showed the following ^1H NMR ($CDCl_3$): δ 6.49 (s), 6.32 (s), 0.08 (s). This result implies that one silyl had not reacted. Increasing the amount of $Pd^{II}(OAc)_2$ to 2.15 mmol, a mixture was obtained, which could not be separated by column chromatography. This mixture showed two dozen of singlet peaks in the δ 7.4-6.1 range in the ^1H NMR. The yield was low.

2.8 Attempted Synthesis of The Trimethyl 13-methyl-phenalene VIII From Trione VI

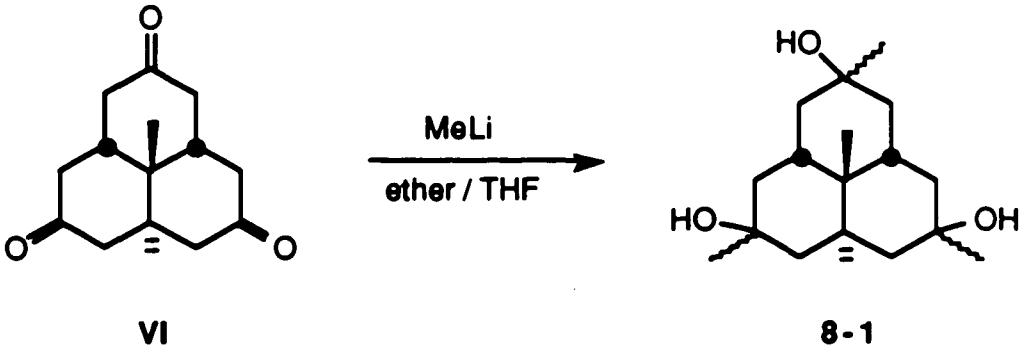
We turned our attention from 13-Methylphenalene to its derivative, 2,5,8-trimethyl 13-Methylphenalene **VIII**, based on following considerations.

1. Higher Visibility in ^1H NMR. In 13-Methylphenalene, observable signals will be a singlet for the central methyl group and a multiplet corresponding to the external vinylic protons. In 2,5,8-trimethyl 13-methylphenalene **VIII**, obviously there will be just three singlets, the central methyl group (3H), the external vinylic protons (6H), and the external methyl (9H) respectively.

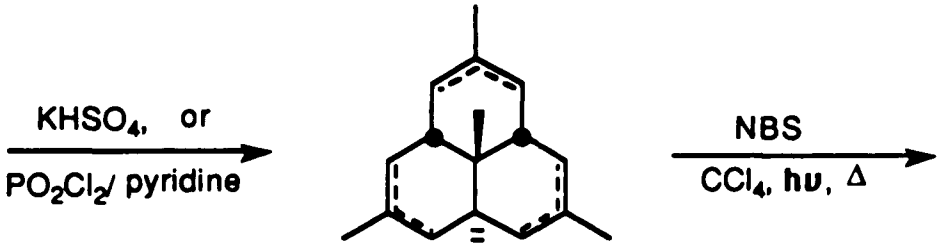
2. Higher Antiaromaticity. Three external symmetrical methyl groups should donate electron density to 12 π ring current, and in addition, could increase the planar form due to reduced the ring flapping.

3. Better Synthetic Accessibility. Dehydration of tertiary alcohols would be easier than secondary alcohols.

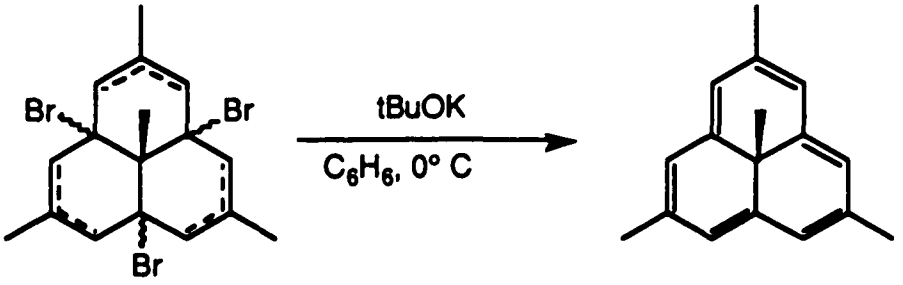
From trione **VI**, 2,5,8-trimethy1-13-methylphenalene **VIII** could be visualized in 4 steps:[181]



VI 8-1



8-2



8-3 VIII

The reaction of trione **VI** with methylithium followed by a continuous extraction with ether led to the unseparable isomeric trimethyltriols **8-1**. The mixture included an unreacted carbonyl group, as observed by IR. To obtain triene **8-2**, we have tested the following two methods:

Method 1: Heating the triols **8-1** together with pulverized potassium bisulfate caused dehydration, triene **8-2** was distilled as

soon as it was formed. The distillate mixture could be separated by a silica gel chromatography with hexane. The least polar mixture, Rf=0.40 in hexane, contained 50% of triene **8-2** were obtained in ca. 20% yield based on trione **VI**.

Method 2. To an ice-cold solution of triols **8-1** in dry pyridine, was added phosphoryl chloride dropwise over 0.5 hour. the mixture was stirred for 1 hour at 0 °C, then allowed to warm up to room temperature over 1 hour. After work-up, almost the same results as Method 1. were obtained.

GC/MS analysis shows 8 peaks:

Peak #	R.T. min.	Corr. % Max.	% of total	Molec. M/Z
1	17.78	100.00	42.30	228
2	17.86	14.96	6.33	228
3	20.46	30.43	12.87	230
4	20.57	10.06	4.26	230
5	20.65	15.85	6.70	230
6	20.86	48.53	20.53	230
7	22.04	5.69	2.41	214
8	25.19	10.90	4.61	232

Trienes (M.W. 228) were formed in 48.6 % yield and dienes (M.W. 230) were formed in 44.4% yield.

Although both methods gave low yield, the method 1 is more suitable for small scale reactions. The low yield in method 2 could

be caused by the fact that phosphoryl chloride/pyridine dehydrates axial alcohols, as discussed by Sauers.[182]

Trienes **8-2** reacted with N-bromosuccinimide in carbon tetrachloride under irradiation and refluxing. A yellow product was obtained, approximately twice the weight of starting triene mixture (F.W. of **8-2** is 222; F.W. of **8-3** is 459), and gave highly complicated peaks NMR. The dehydrobromination was carried out with potassium t-butoxide at 0 °C to room temperature, or with DBN in benzene at 80 °C.

The dehydrobromination with potassium t-butoxide was monitored by TLC. When reaction had progressed for 60 minutes or 70 minutes, TLC showed formation of a less polar compound (Rf=0.6). No significant peak downfield was found in ^{1}H NMR spectrum, but a peak at about δ 6.5 increased. This might be explained by the formation of tetraenes, pentaenes or elimination of methyl groups. In GC/MS analysis, a component having M.W. 226 has been found, which supports the formation of a tetraene.

2.9 Attempted Synthesis of Triphenyl 13-methyl-phenalene IX From Trione VI

To avoid elimination of substituents such as methyl groups, phenyl groups should be good candidates. In addition, these groups might stabilize the 12 π-electron system by resonance.

Figure 2.9-1 illustrates the scheme of our attempted synthesis of triphenyl 13-methylphenalene **IX** From Trione **VI**.

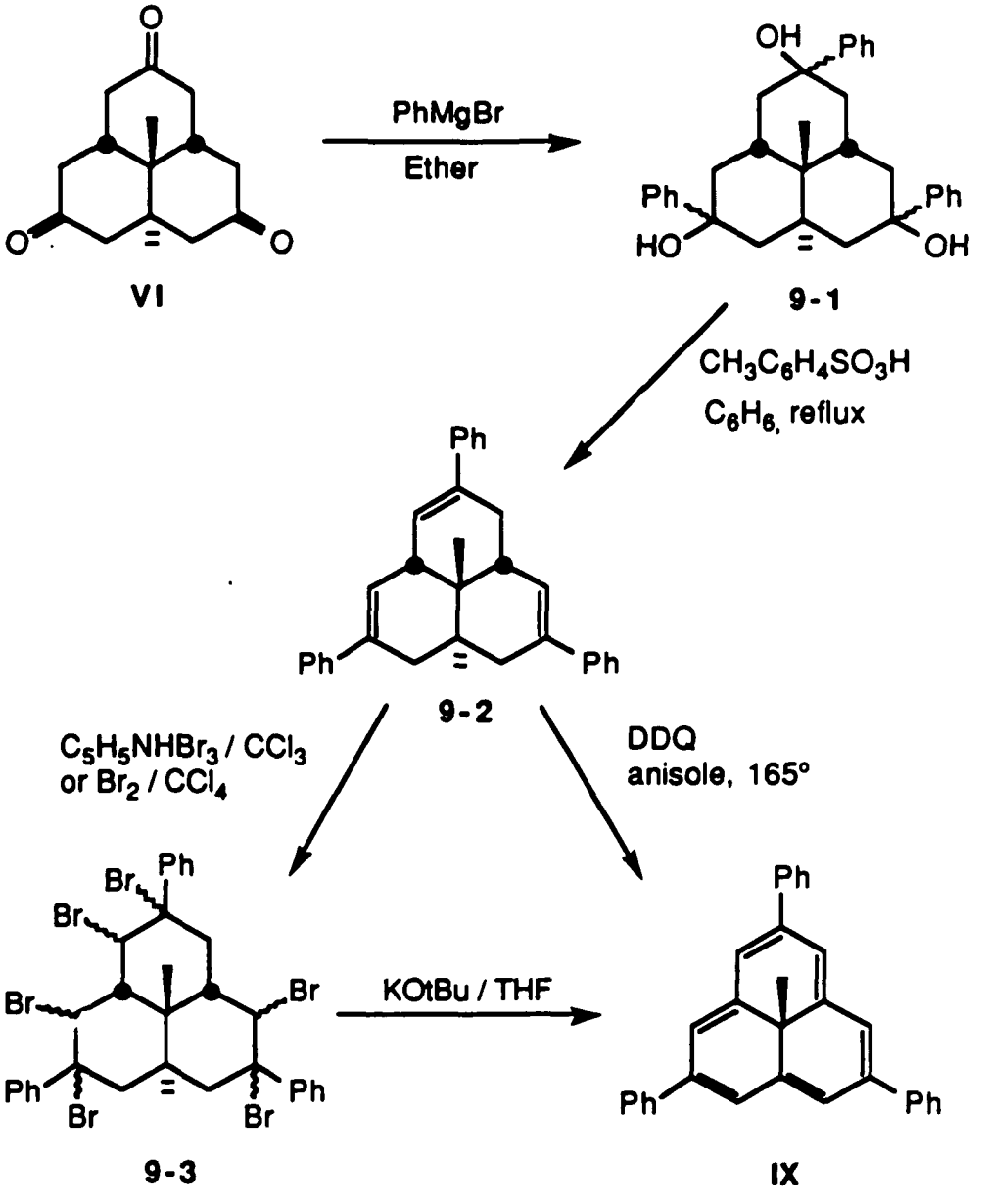
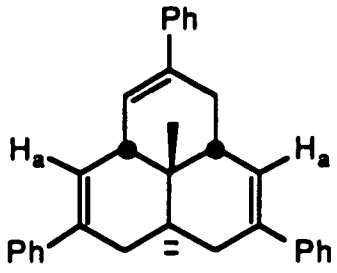


Figure 2.9-1. The Scheme of Attempted Synthesis of Triphenyl *Triene* **9-2**.

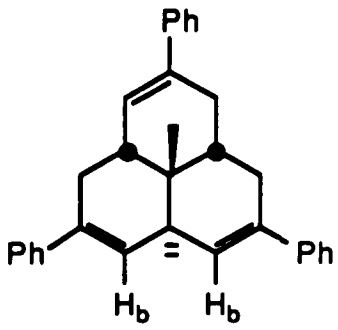
To 9 equivalents of PhMgBr in ether, the trione **VI** in THF was added, then the mixture was refluxed for 10 hours. A 90% yield of **9-1** was obtained after a silica gel column chromatography with

hexane-ethyl acetate (85:15-40:60). ^{1}H NMR spectrum of the triol **9-1**, in which there were peaks δ 1.31 (s, 3 H), δ 1.48 (s, 1 H, exchangeable), δ 1.45 (s, 2 H, exchangeable), indicated that only one isomer was formed, and that it had Cs symmetry, the same as the trione **VI**.

Triol **9-1** and p-toluene sulfonic acid (catalyst amount, 5%) in benzene was refluxed for 40 minutes in a round bottom flask with a Dean Stark apparatus. At the end of this period, TLC showed one spot with a R_f = 0.16 in hexane. A yield of 41.5% of triene **9-2** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.5-7.2 (m, 15 H), 6.41 (d, J = 6 Hz, 0.3 H), 6.17 (d, J = 5 Hz, 1 H), 5.95 (d, J = 9 Hz, 1.7 H), 3.05-2.10 (m, 9 H), 1.06 (s, 3 H). It appeared that only one isomer has been formed predominantly and it had near Cs symmetry again. Therefore it has to be one of two possible structures as following.



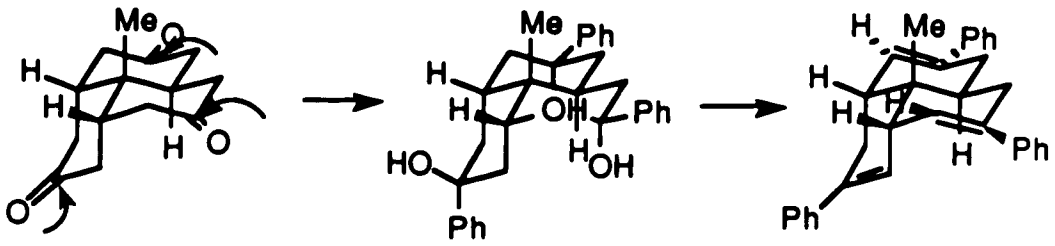
9-2a



9-2b

The major vinyl hydrogen had coupling a constant of 9 Hz, which implies that they couple to equatorial rather than to axial allyl hydrogen. Structure **9-2a** might thus be the more probable one. A possible reaction mechanism could be the following, as shown in

Figure 2.9-2. The phenyl groups attacked the less hindered side of the carbons of carbonyl groups and formed an all-axial-hydroxyl conformation which is also a good conformation for dehydration. Finally the bis-equatorial-allyl hydrogen structure **9-2a** formed.



9-2a

Figure 2.9-2. The possible mechanism of formation of triene **9-2**

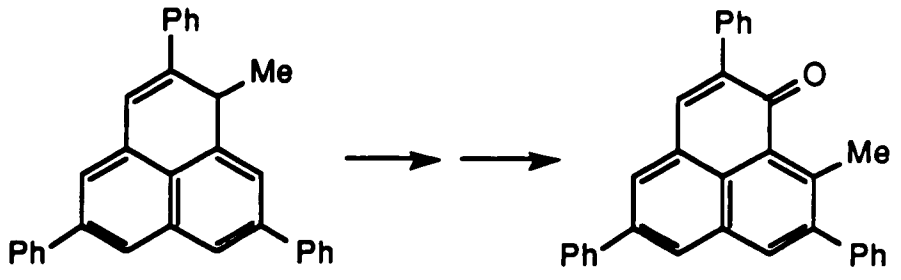
In our approach to the final triphenyl 13-methylphenalene **IX**, we investigated several reactions.

Treating triene **9-2** with DDQ in anisole at reflux for 30 minutes, followed by column chromatography (CCl_4), gave a bright yellow compound (R_f = 0.12 in hexane/benzene 2:1; R_f = 0.06 in hexane). DDQ and red compounds remained on the column. The whole process must be done under Ar, otherwise the bright yellow product converted to the red compounds. This bright yellow compound has strong fluorescence (emission at 522 nm., Max. at excitation 495 nm.); UV (CCl_4): λmax: 504.8 nm, 473.1 nm, 387.3 nm, 368.1 nm.; ^1H NMR ($CDCl_3$): singlet peaks: δ 8.88, 8.39, 8.18, 7.98, 7.86; multiplet peaks: δ 7.6-6.8.

After bromination of the triene **9-2** with Br_2 or $C_5H_5N^+HBr_3^-$ at room temperature for more than 16 hours, a crude yellow hexabromide **9-3** was obtained and was directly dissolved in 2 mL

of THF under Ar. Seven equivalents of KOtBu were added to the cold (0 °C) mixture. After the mixture was stirred for 2 hours a bright yellow compound was again collected in CCl_4 from a short column. Rf = 0.06 in hexane. UV (CCl_4): λmax: 505.6 nm, 472.3 nm, 388.1 nm, 368.1 nm. ^1H NMR ($CDCl_3$): singlet peaks: δ 8.5, 7.9; multiplet peaks: δ 7.6-6.8; doublet peek: about δ 4.

The two different approaches above gave some similar results. In the ^1H NMR spectrum, there is no significant downfield peak observed, and the peaks at δ 8.5 (s), δ 7.9 (s) are likely to be aromatic protons. λmax: 504.8 nm in UV spectrum indicates high conjugation. Considering a σ shift of 9b-methyl-9b*H*-benzo[cd]azulene **XI** (see section 1.2 B), a possible reaction of **9-3** might be the 1,5-methyl σ shift leading to compound **9-4** which is unstable. Isomerization followed by oxidation and loss of the methyl group could alternatively give a stable and red compound, triphenyl perinaphthenone. (We also considered formation of perinaphthenone, which is red too, in the approach to 13-methylphenalene (see section 2.10).)



9-4 triphenyl perinaphthenone

2.10 The Synthesis of Dihydro-13-methylphenalene and Their Reactions

We returned to a detailed study of the formation of triene **10-2** and its conversion into 13-methylphenalene (**X**) as outlined in Figure 2.10-1.

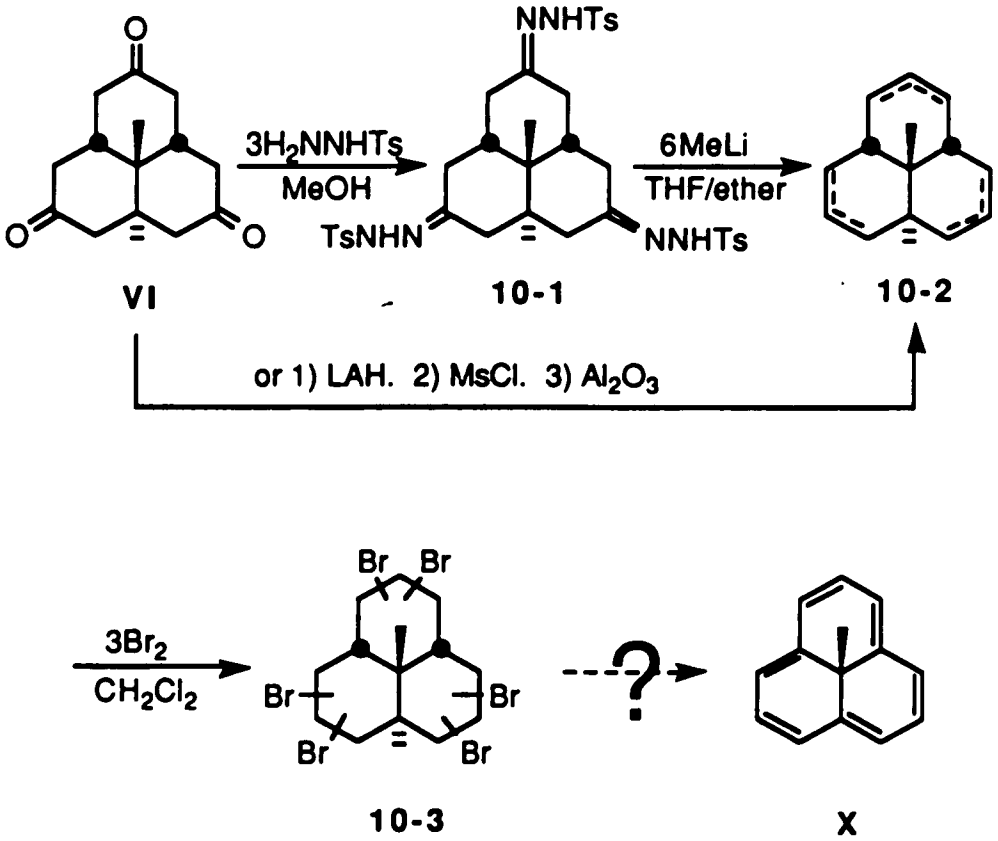
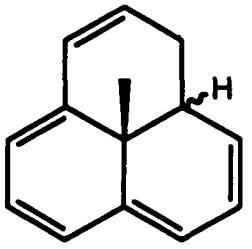


Figure 2.10-1. The outline for the synthesis of 13-methylphenalene (**X**)

After conversion of trione **VI** into triene **10-2**, bromination, and dehydrobromination gave an unexpected dihydro-13-methylphenalene (pentaene) **10-4**. Therefore the investigations and

reactions of pentaene **10-4** became the major and the most important part.

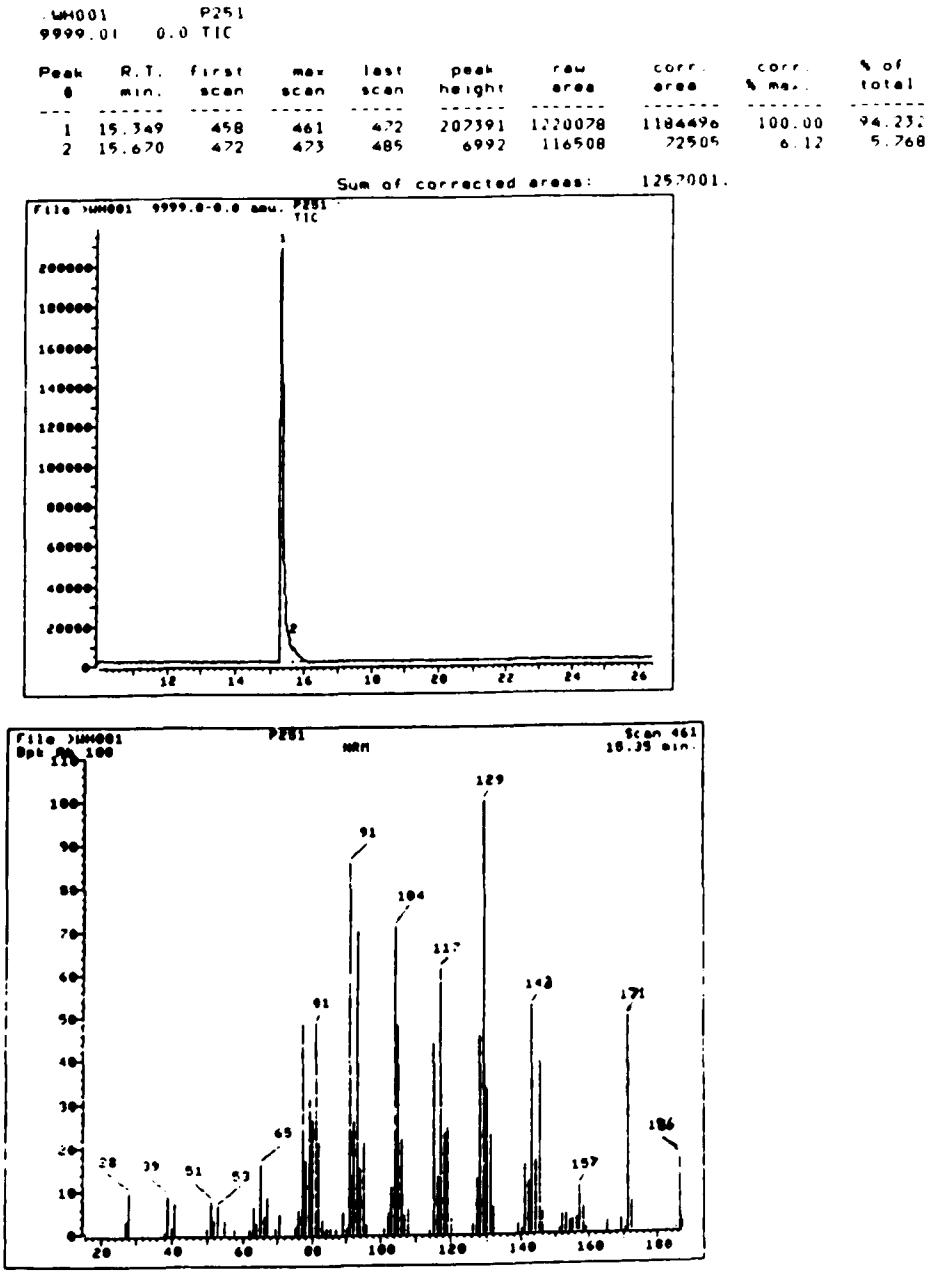


10-4

a. Formation of triene 10-2

The conversion of **VI** into triene **10-2** was accomplished via two successive steps, the formation of tritosylhydrazone and Shapiro reaction. The trione **VI** with p-toluenesulfonyl-hydrazide in methanol was refluxed for 2 hours. By distillation, methanol and water was replaced by benzene then by THF. To tris-tosylhydrazone **10-1** residue in dry fresh THF was added 6 moles of methyllithium in ether at 0 °C. The first fraction through the silica gel column was a mixture of pure trienes **10-2** in 23% overall yield. GC/Mass spectra: m/e 186 (M^+), 171 ($M\text{-}Me^+$), 157, 143, 129, 117, 104, 91, ... (Figure 2.10-2.) ^1H NMR: δ 5.3-δ 5.8 (m, 6H), δ 1.7-2.5(m, 9H), δ ca.1.0 (4 S, 3H) (Figure 2.10-3). The four singlet methyl signals imply that the triene **10-2** is a mixture of all four possible isomers as shown in Figure 2.10-4 (see section **2.8** discussion). .

Figure 2.10-2. The GC/MS spectra of triene **10-2** mixture

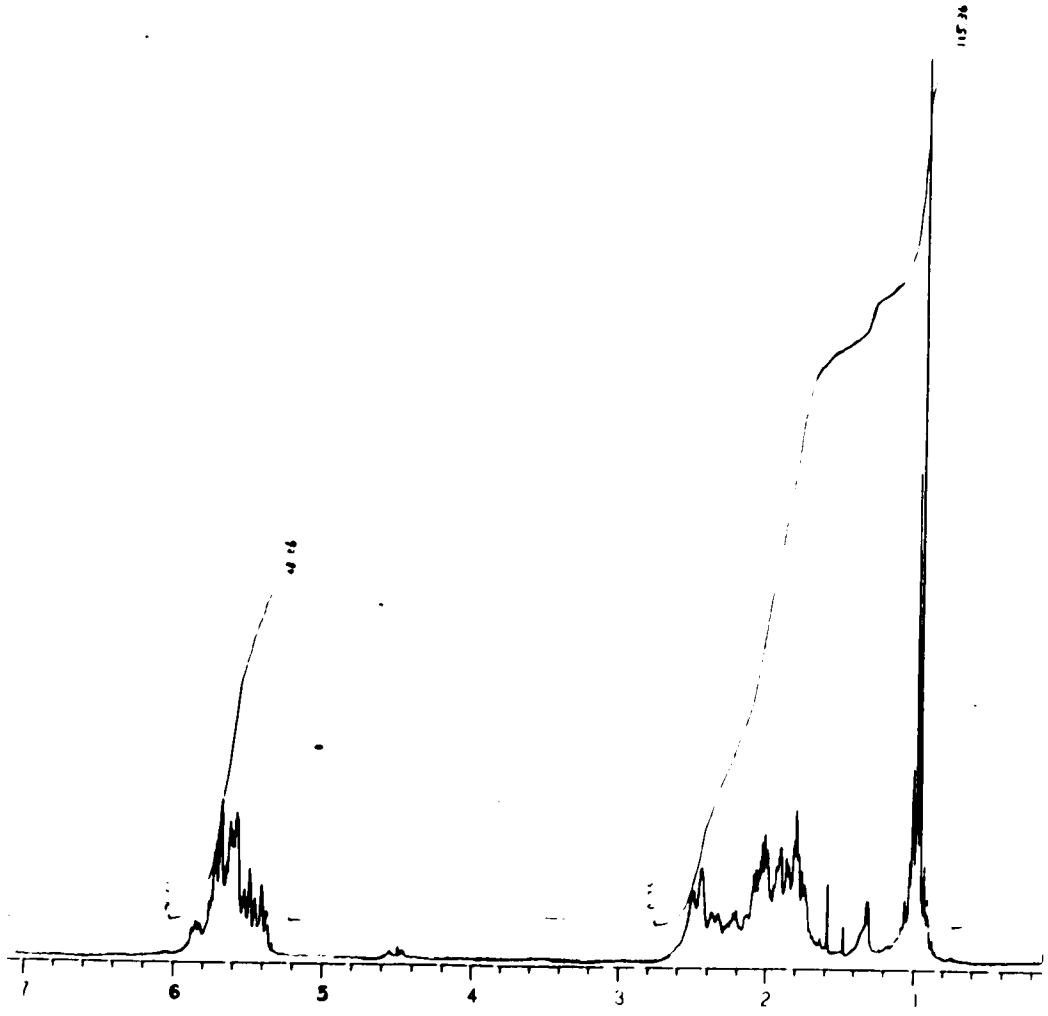


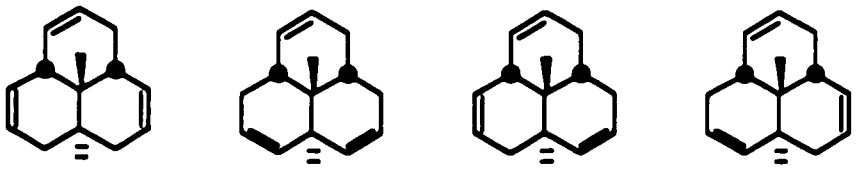
WH001 P251
9999.01 0.0 TIC

Peak #	R.T. min.	first scan	max scan	last scan	peak height	raw area	corr. area	corr. % max.	% of total
1	15.349	458	461	472	207391	1220078	1184496	100.00	94.23
2	15.670	472	473	485	6992	116508	72505	6.12	5.768

Sum of corrected areas: 1257001.

Figure 2.10-3. ^{1}H NMR spectrum of triene **10-2** mixture





1. 2. 3. 4.

note: each has anorther enantiomer.

Figure 2.10-4. The all four possible triene **10-2** isomers

Bromination of Triene 10-2

For small scale bromination, pyridinium hydrobromide perbromide ($C_5H_5N^+HBr_3^-$) may was a good reagent.[183] To 0.54 mmol of triene **10-2** in chloroform were added 1.78 mmol of perbromide salt. The mixture was stirred for 5 days. After the remained red perbromide salt was filtered, the reaction solution was concentrated and gave a pale yellow solid in 64% yield. Since the product was a mixture of bromides containing hexa and tetra bromides that could not be separated by recrystalization or column chromatography, the conversion yield was estimated by ^1H NMR. The integrations of signals δ 6.5 through δ 5.2 stand for triene **10-2** (I_{en}), that δ 5.2 through δ 4.3 for bromides (I_{Br}). Therefore the conversion yield equals $I_{Br}/(I_{Br}+I_{en})$ and the total yield will equal recover yield times conversion yield. The conversion yield of this reaction was 75%, so that the total yield was (64%)(75%)=48%.

Bromination of the triene **10-2** with distilled bromine was carried out in methylene chloride for three days, and gave a colorless solid (m.p. 66-70°C) in 90% yield. The ^1H NMR (Figure 2.10-5) indicated the conversion yield was 87% and the total yield was

79% comparable to 86% for that in a model reaction with cyclohexene. The mass spectrum analysis (Figure 2.10-6) indicated that the reaction mixture contained hexa, tetra, and di-bromides, and also some pentabromochloride. The chloride might be introduced from solvent methylene chloride.

Figure 2.10-5. The ^1H NMR spectrum of the reaction mixture for bromide **10-3**

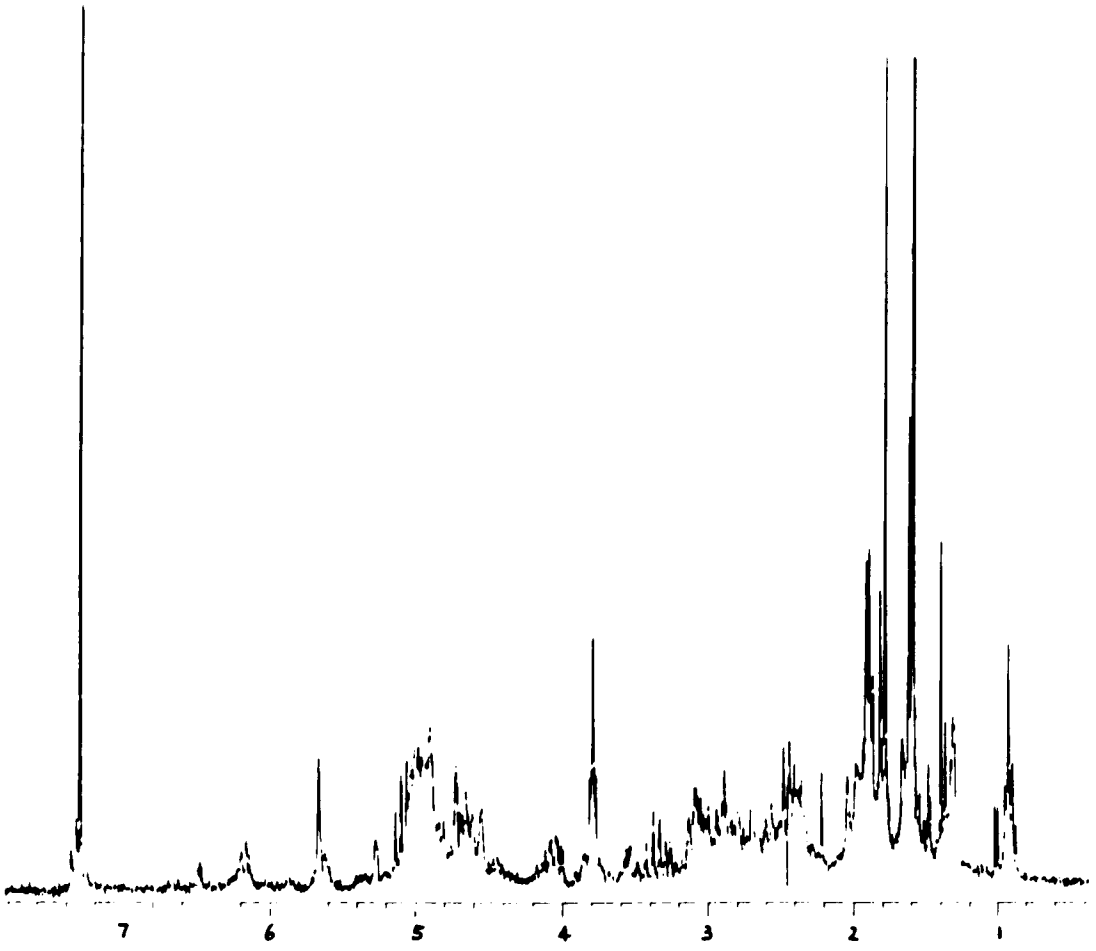
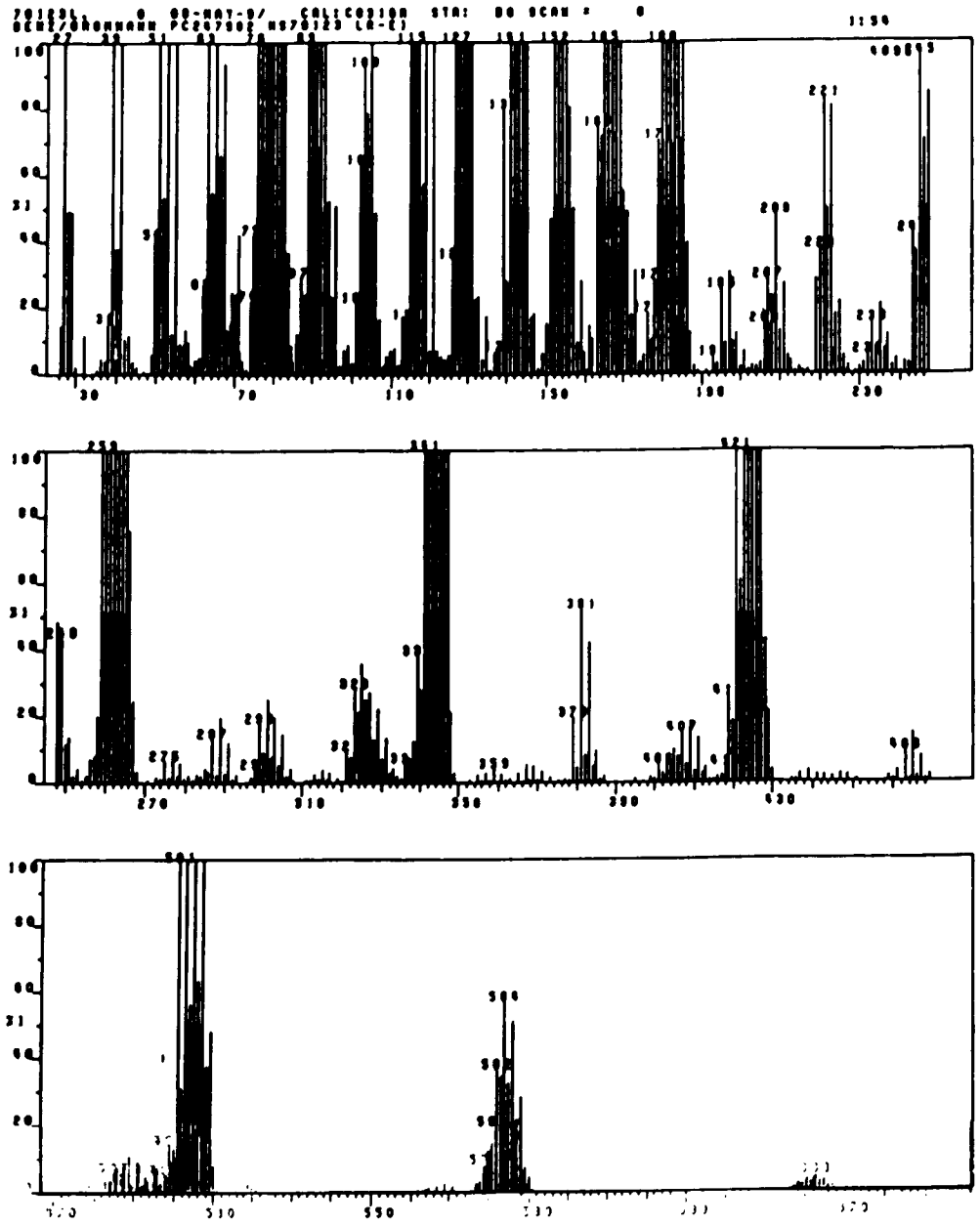


Figure 2.10-6. The mass spectra of the reaction mixture for bromide **10-3**



c. Preparation of dihydro-13-methylphenalene 10-4

Dehydrobromination of the mixture bromide **10-3** was carried out in two different ways.

(1) tBuOK (6 equivalents) was added to a solution of bromide mixture **10-3** in THF at 0 °C under Ar. After stirring for 2 hours at the same temperature, the reaction was quenched by adding saturated Na_2SO_4 solution and 10% H_2SO_4 solution. The solution was extracted with ether.

(2) DBU (12 equivalents) were added dropwise to a solution of bromide mixture **10-3** in benzene at 5-10 °C under Ar. After refluxing overnight under Ar, the reaction solution was washed with 10% H_2SO_4 then extracted with pentane. These reaction conditions were found by running model reactions with 1,2-dibromo-cyclohexane. In the model reaction, stirring at room temperature for 2 days gave 100% starting compounds, and refluxing for 1 day gave an 80% yield of cyclohexadiene, while refluxing for 2 days furnished almost 100% yield by GC determination. The reaction of bromide **10-3** did not need that long a time probably, due to a more planar transition state.

Both reactions gave almost identical results. Two very air-sensitive yellow compounds (called **A** and **B** temporarilly.) were shown to be present by TLC (Rf_A= 0.57, Rf_B= 0.49 in hexane). The TLC had to be run under inert atmosphere, otherwise compounds **A** and **B** convert to orange compounds which have Rf=0.

To isolate **A** and **B** from the reaction mixture, a long alumina column was used with distilled pentane. The first fraction, a clear yellow solution was collected. Since the compounds are very air-sensitive, to evaporate solvents the normal rotary evaporator

always gave the orange high molecular weight compounds. Handling these compounds in an inert atmosphere is necessary at all times! For this reason, a modified rotary evaporator was designed and made. It allowed us to keep the compounds an under inert atmosphere safely during the whole process. (Figure 2.10-7)

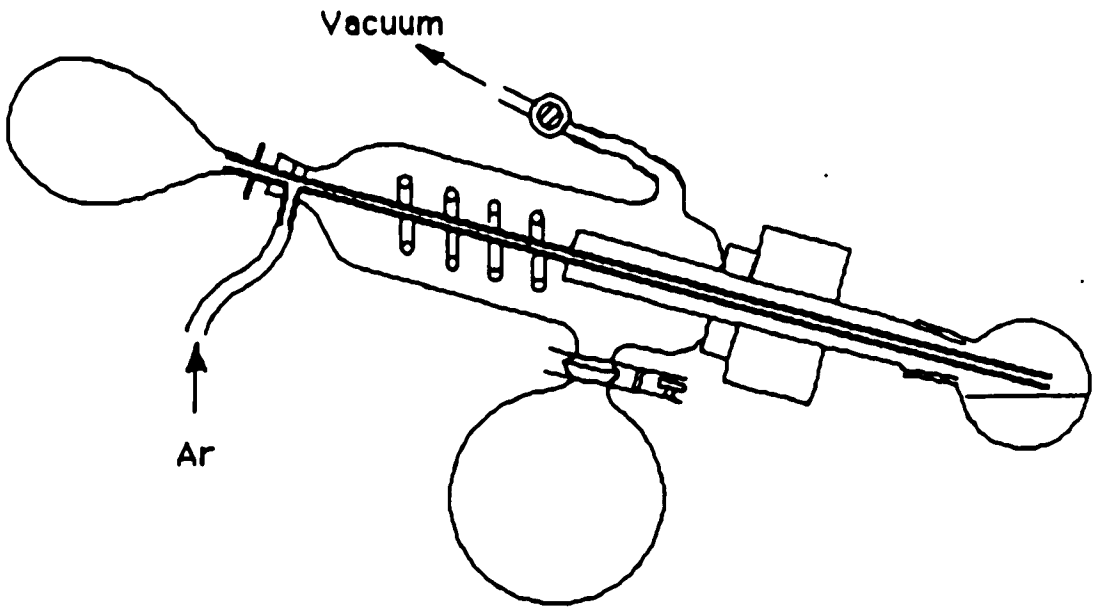
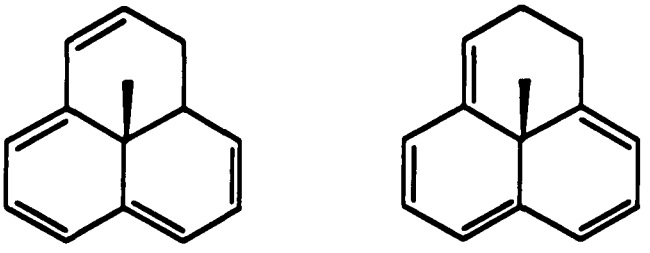


Figure 2.10-7. The modified rotatory evaporator for air sensitive compounds

A GC of the **A** and **B** mixture showed three peaks, while HPLC indicated the presence of four components. ^{1}H NMR and UV gave unclear results. Since 13-methylphenalene was expected, all trials to interpret for 13-methylphenalene failed. For solving this interesting puzzle, the GC/Mass spectrometer again showed its powerful capabilities. We thank Dr. Locke for his kind help and great patience. GC/MS told us that **A** is a mixture of two isomeric

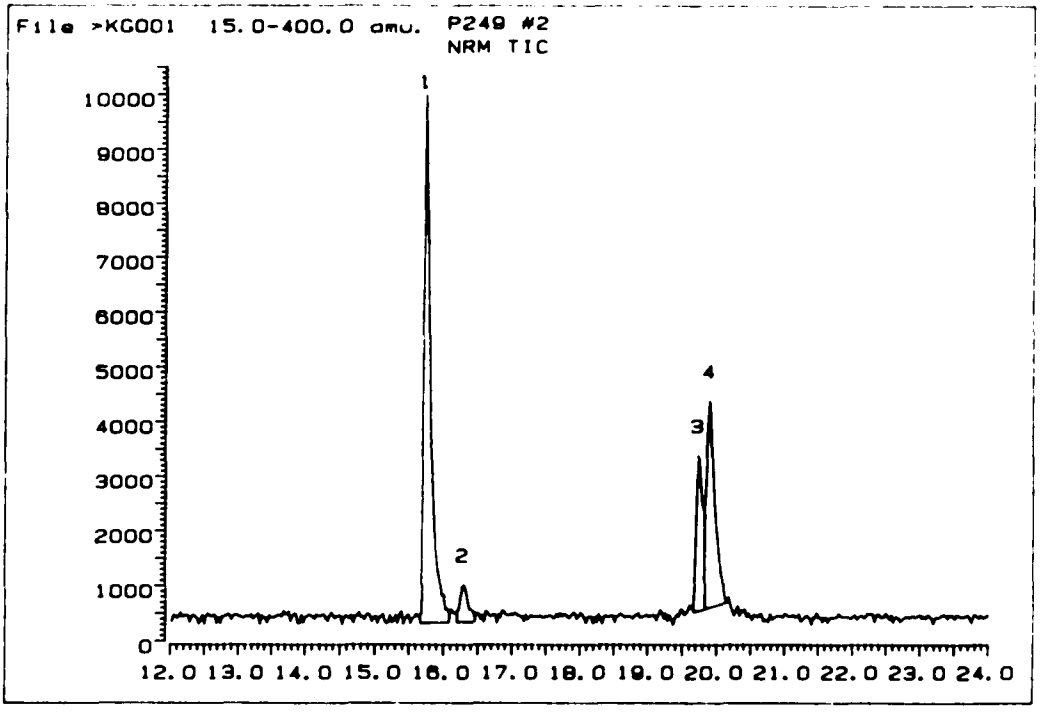
pentaenes **10-4** (54.01%) and **10-5** (4.79%); **B** is a mixture of two isomeric bromopentaene **10-6** (15.55%) and **10-7** (25.65%) and all of four compounds have significant M-CH_3 fragments. (Figure 2.10-8 through 2.10-10.) The structures of the bromopentaene are not clear yet. Considering Max: 396 nm in the UV spectrum, **10-4** should be a pentaene and has one of the two possible structures, **10-4a** and **10-4b**.



10-4a **10-4b**

The two possible structure for pentaene **10-4**

Figure 2.10-8. The GC spectra of pentaenes **10-4**, **10-5** and bromides **10-6**, **10-7** in GC/Mass spectra



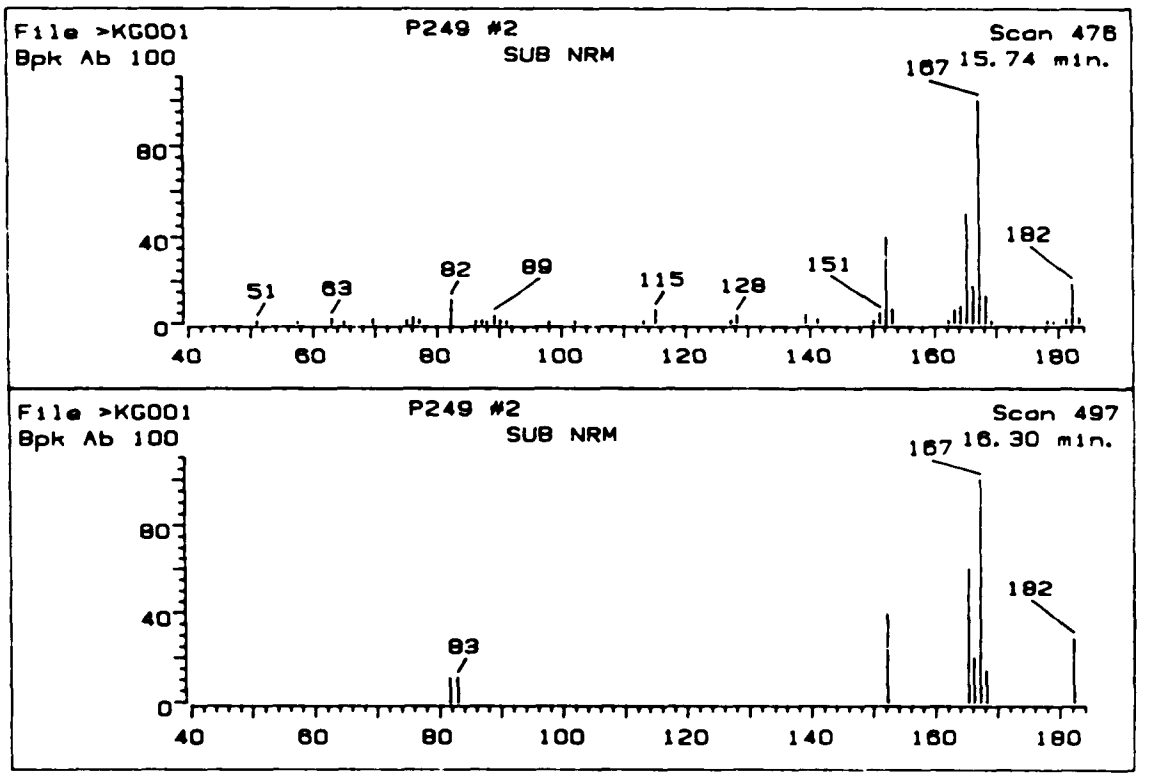


Figure 2.10-9. The mass spectra of pentaenes **10-4** and **10-5** in GC/Mass spectra

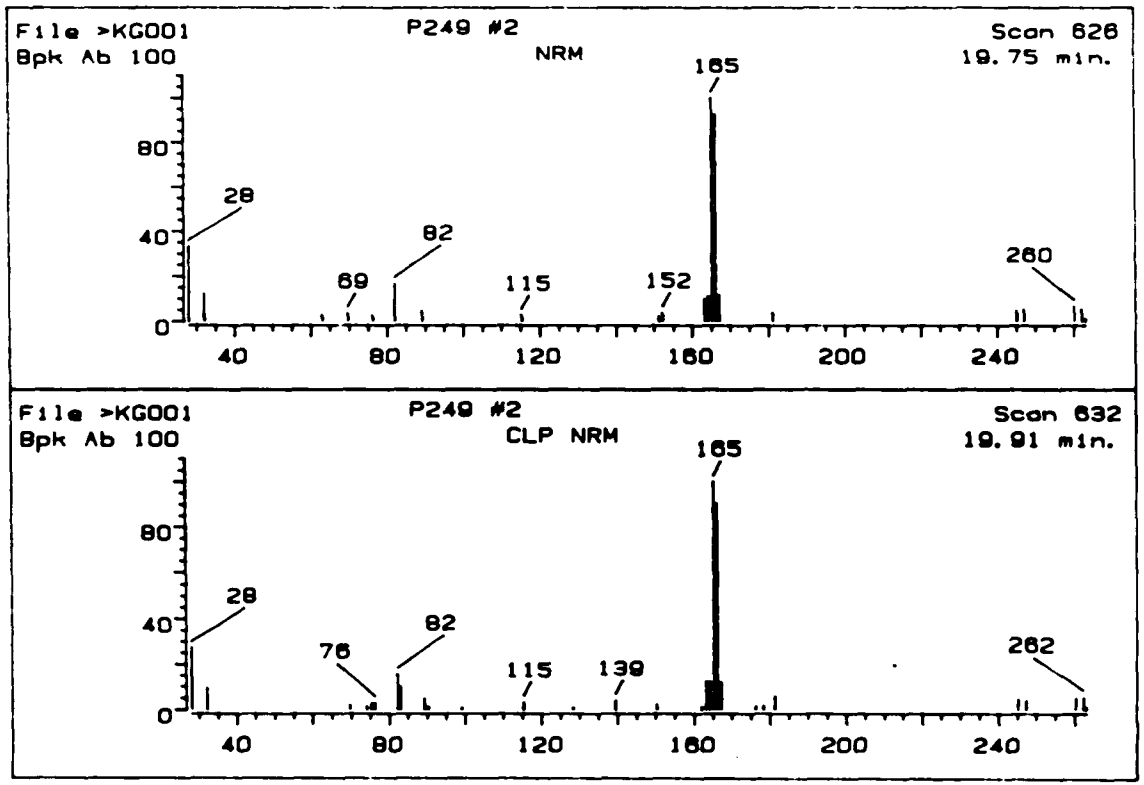


Figure 2.10-10. The mass spectra of pentaene bromide **10-6** and **10-7** in GC/Mass spectra

The bromides **10-6** and **10-7** could be converted into pentaenes through a lithium bromine exchange followed by protonation.[184] To a 2 mL THF solution containing ca. 0.037 mmol of **A** and **B** mixture was added 0.05 mL of 1.7 M t-buttylithium (0.085 mmol) at -78°. The solution was stirred for 30 minutes at the same temperature. During this period, its color turned red then green. After quenching by the addition of methanol and careful worked up under Ar, a yellow solution was obtained which showed only pentaenes **10-4** and **10-5** (10:1) in the GC and GC/Mass spectra. UV showed λ_{Max} 396 nm. The pentaenes evaporate at ca. 30 °C under ca. 15 mmHg in a rotatory evaporator. They could be stored under Ar in a refrigerator for a week when the concentration was 0.01 M, while at room temperature in an NMR tube filled with Ar, for only few hours when the concentration was 0.1 M. The pentaenes are not stable in pure form. ^{13}C NMR($CDCl_3$) shows ten sp^2 hybridized carbons: δ 137.6, 130.6, 128.0, 127.6, 126.0, 122.9, 122.2, 121.9, 118.2, 104.9. (Figure 2.10-11)

Interestingly, the ^1H NMR spectra vary in different solvents.

In chloroform, the major component (**10-4**) most likely has structure **10-4a**: eight protons in the range δ 6.65 to 5.70; three protons in the range δ 2.18 to 2.33. (Figure 2.10-12) According to decoupling experiment, (see Figure 2.10-13 through 21) proton *a* (δ 2.22, t.) couples proton *d* (δ 5.72, m.), *b* (δ 2.25, d.) and *c* (δ 2.29, dd.); *b* couples *j* (δ 6.23, m.) and *c*; *c* couples *j* and *a*. These data are suitable only to structure **10-4a** and not **10-4b**. (see Figure 2.10-22)

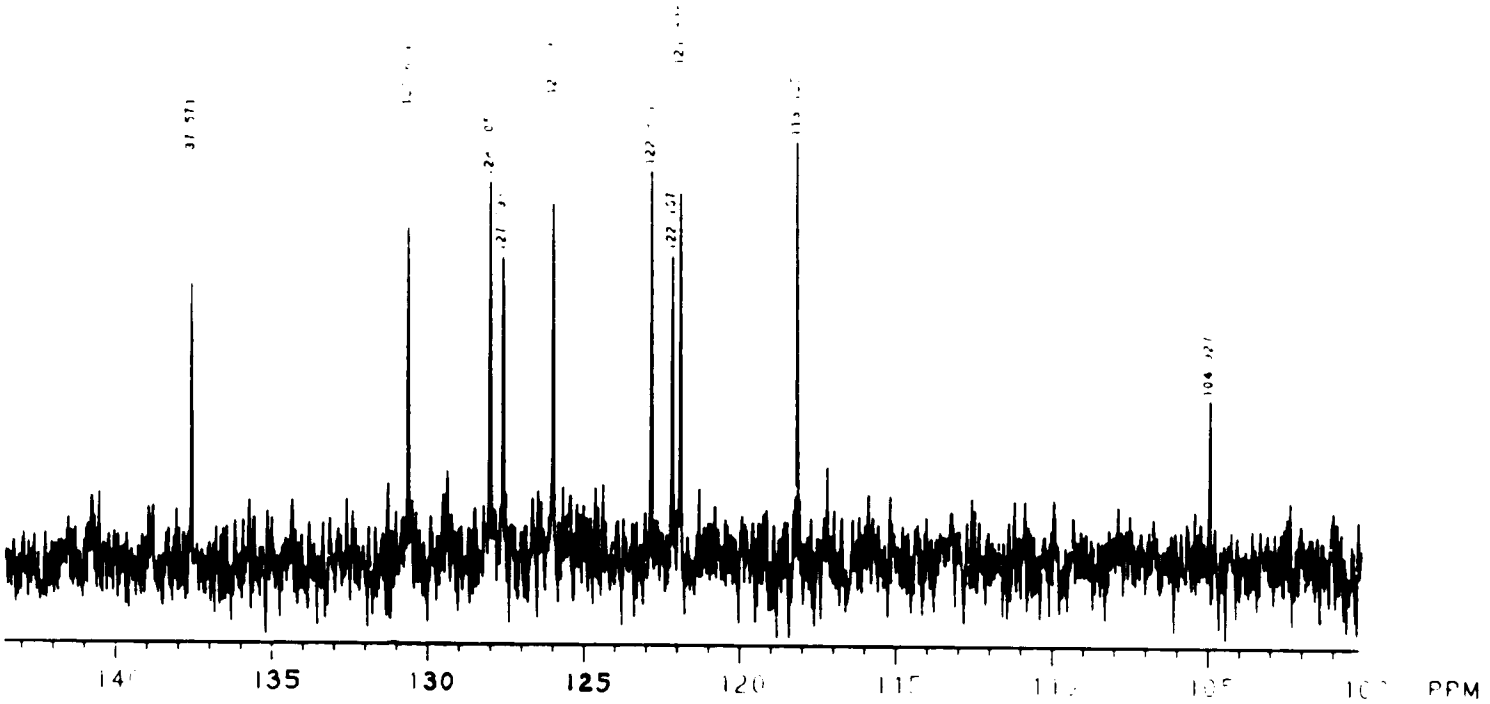


Figure 2.10-11. The ^{13}C NMR spectra of pentaene 10-4

Figure 2.10-12. ^1H NMR spectra of pentaene in $CDCl_3$

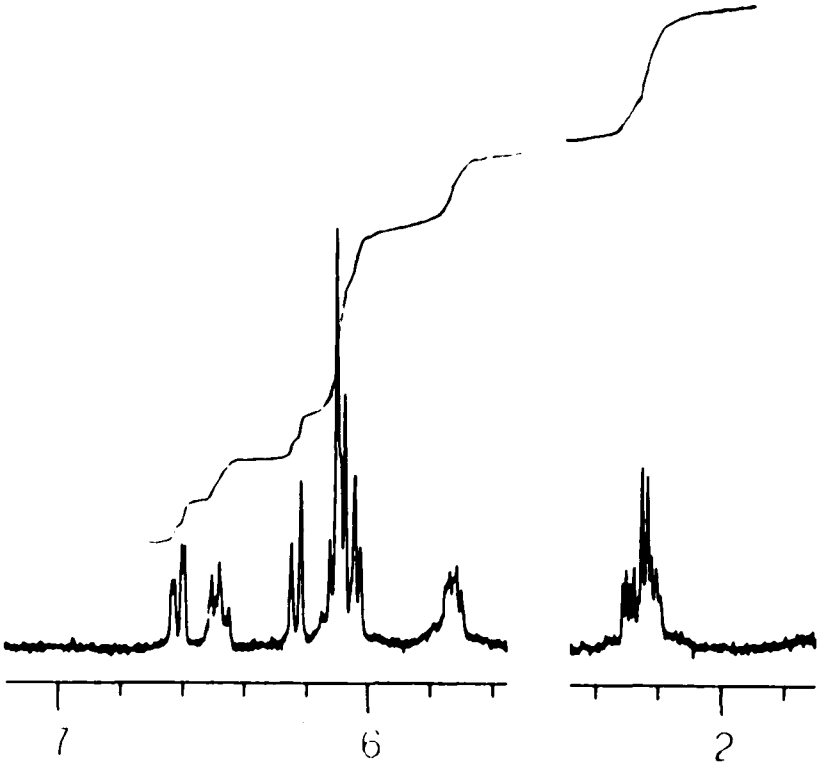


Figure 2.10-13. The decoupling experiment for proton *a* of pentaene **10-4**

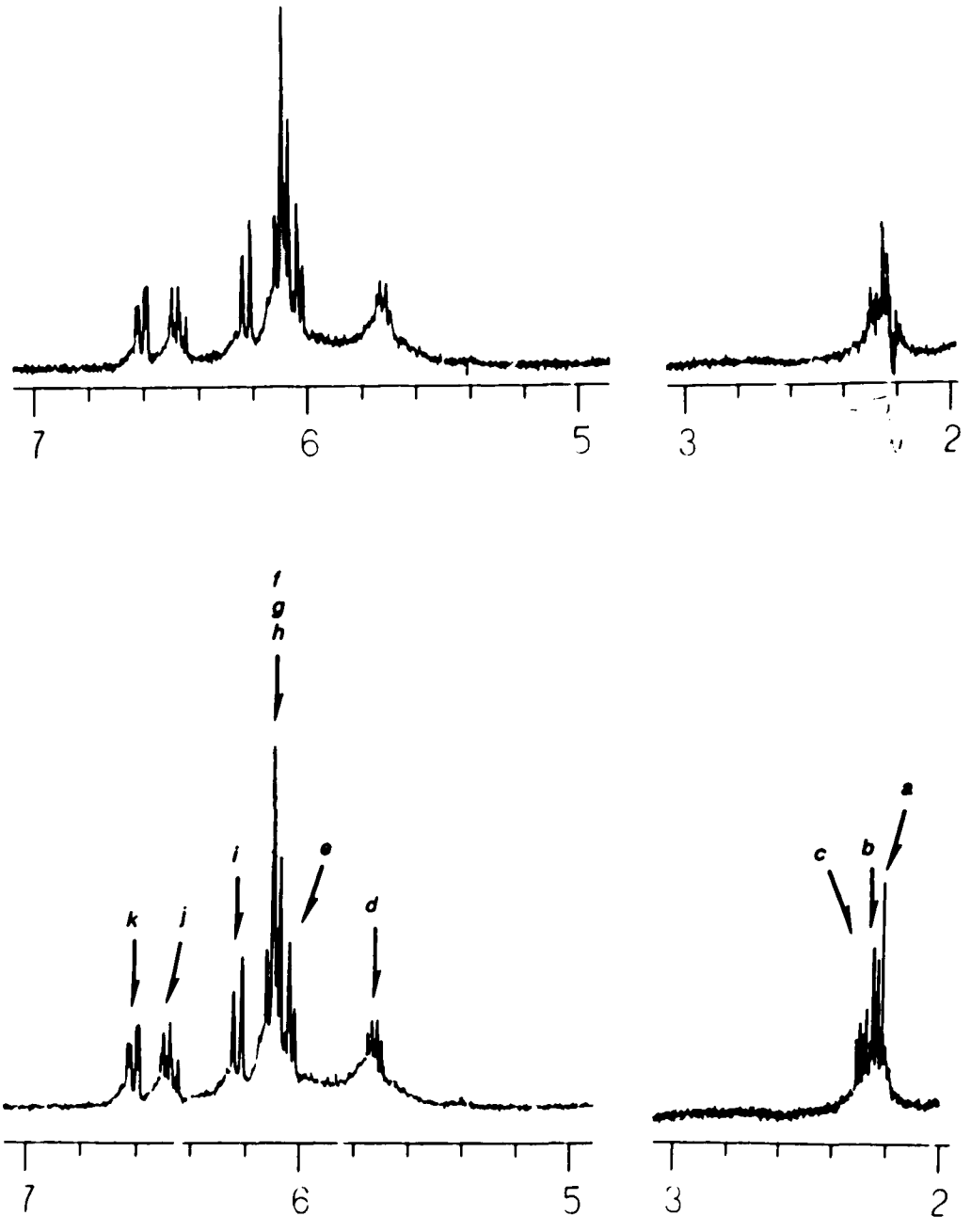


Figure 2.10-14. The decoupling experiment for proton *b* of pentaene **10-4**

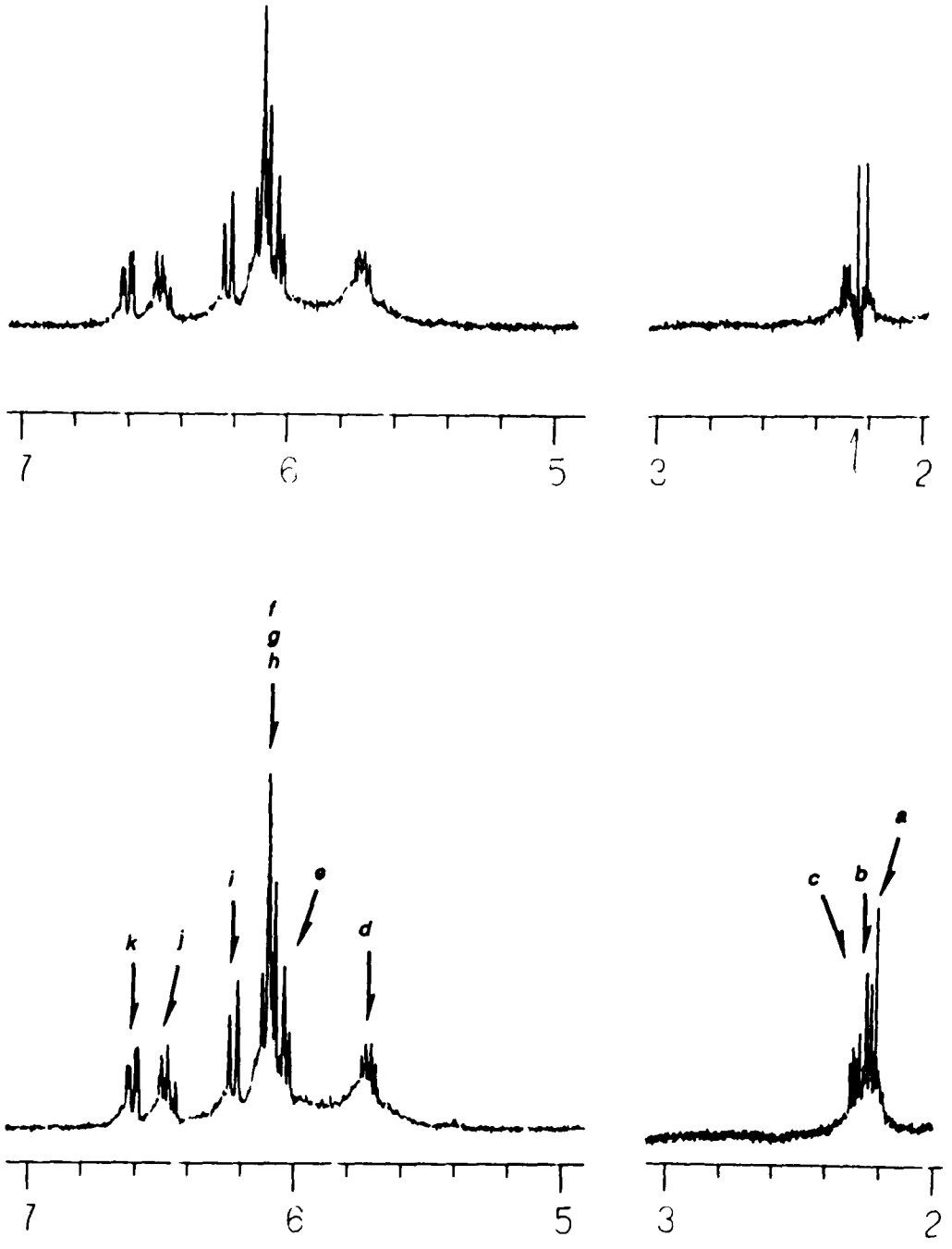


Figure 2.10-15. The decoupling experiment for proton *c* of pentaene **10-4**

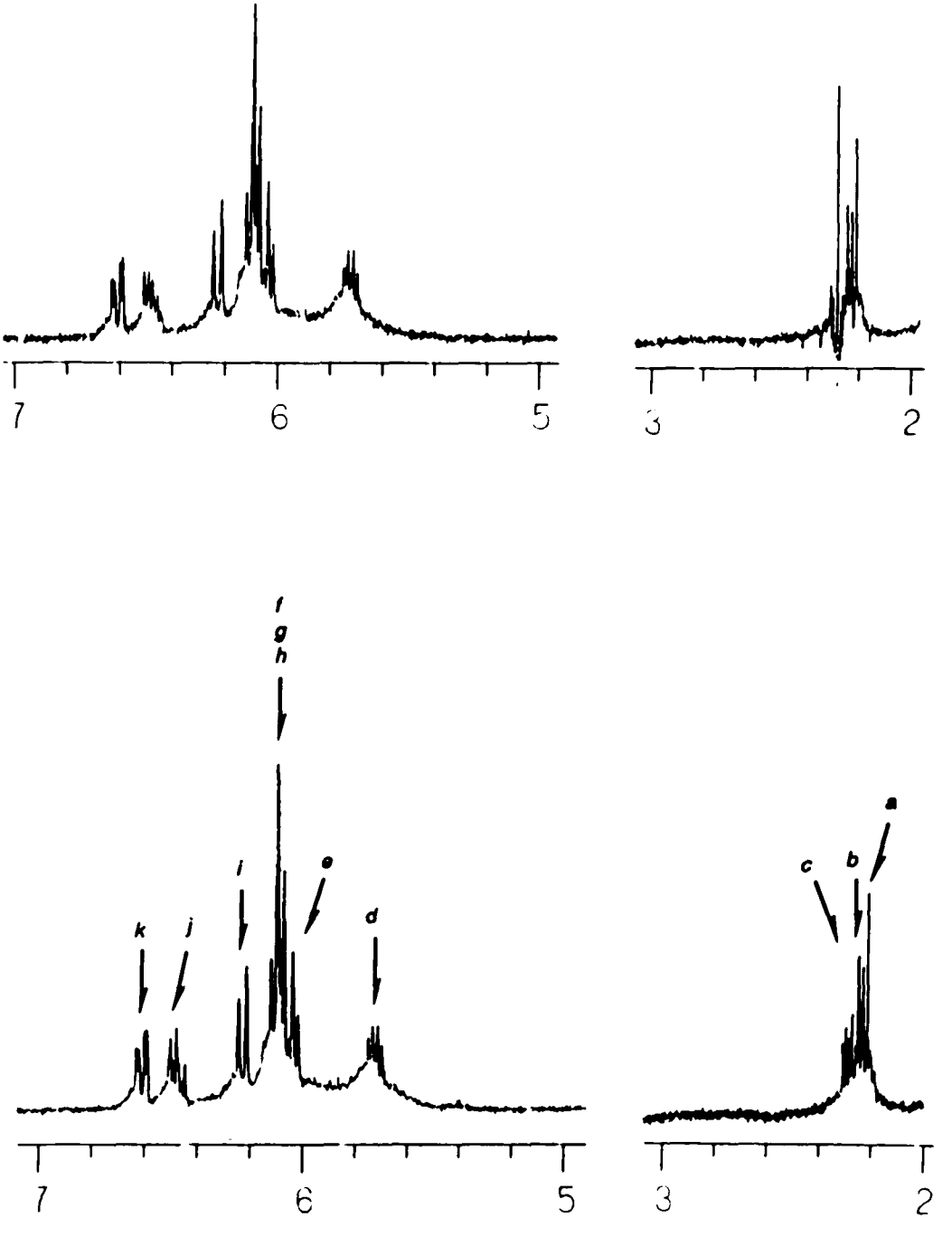


Figure 2.10-16. The decoupling experiment for proton *d* of pentaene **10-4**

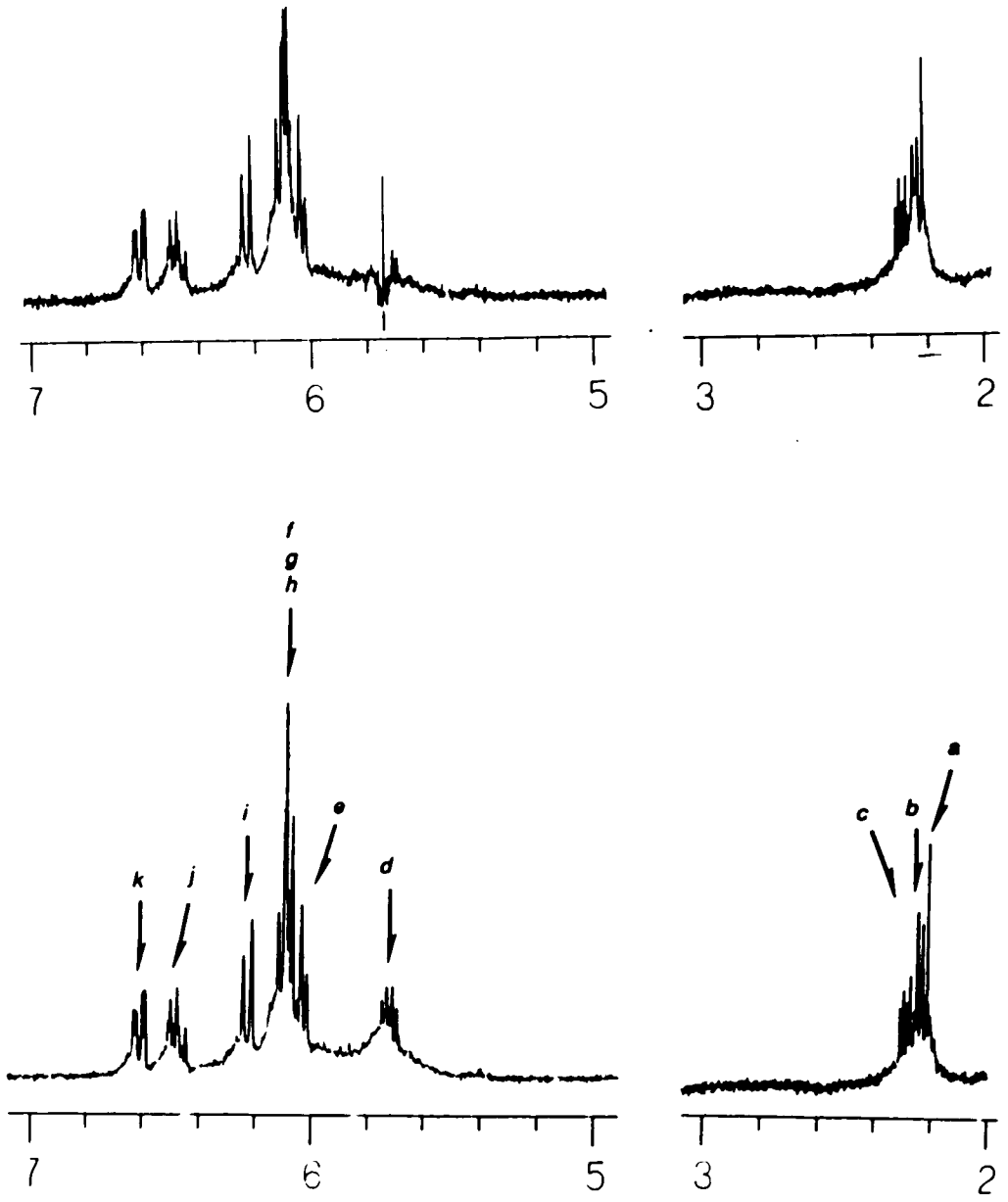


Figure 2.10-17. The decoupling experiment for proton *e* of pentaene **10-4**

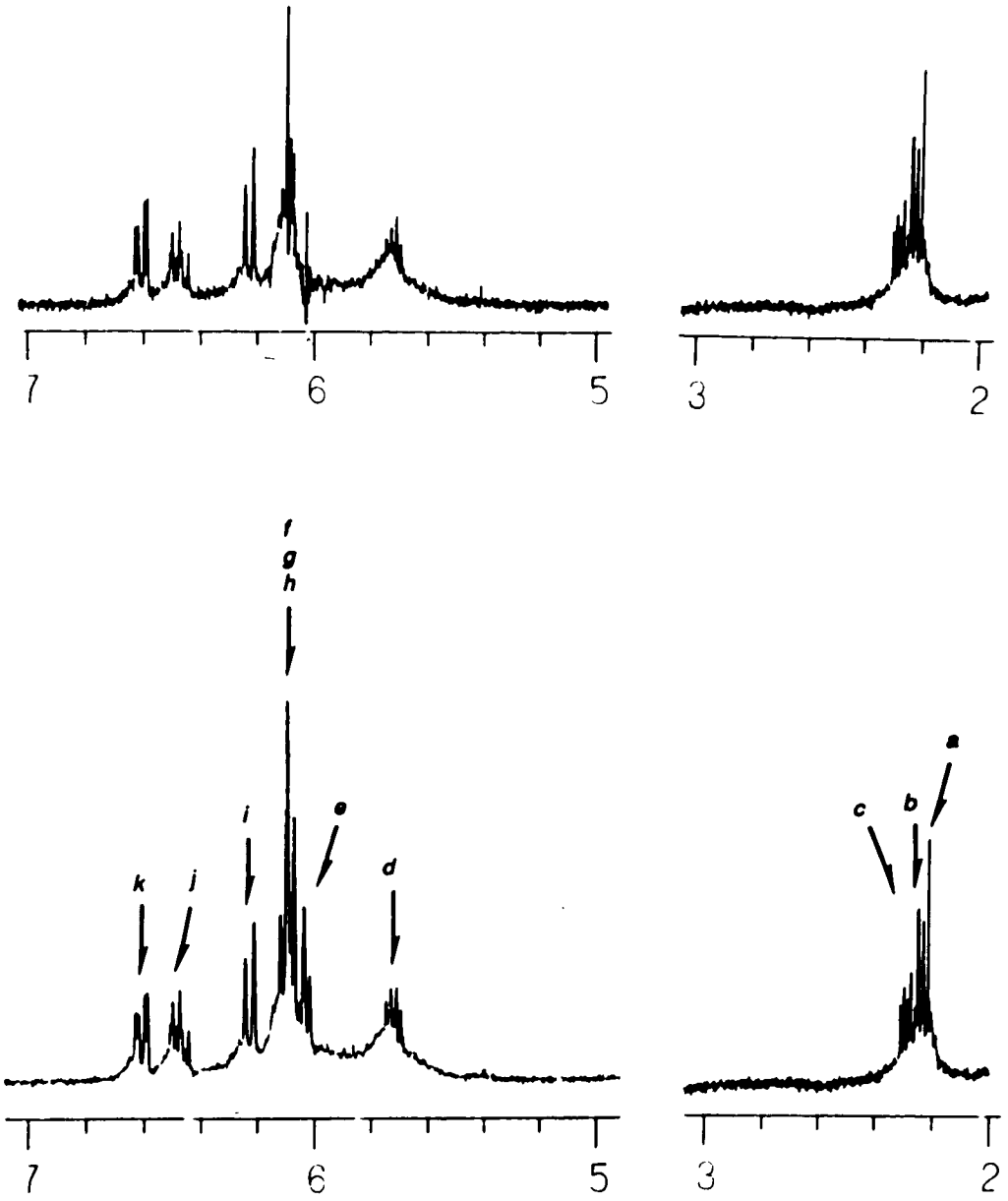


Figure 2.10-18. The decoupling experiment for proton *f,g,h* of pentaene **10-4**

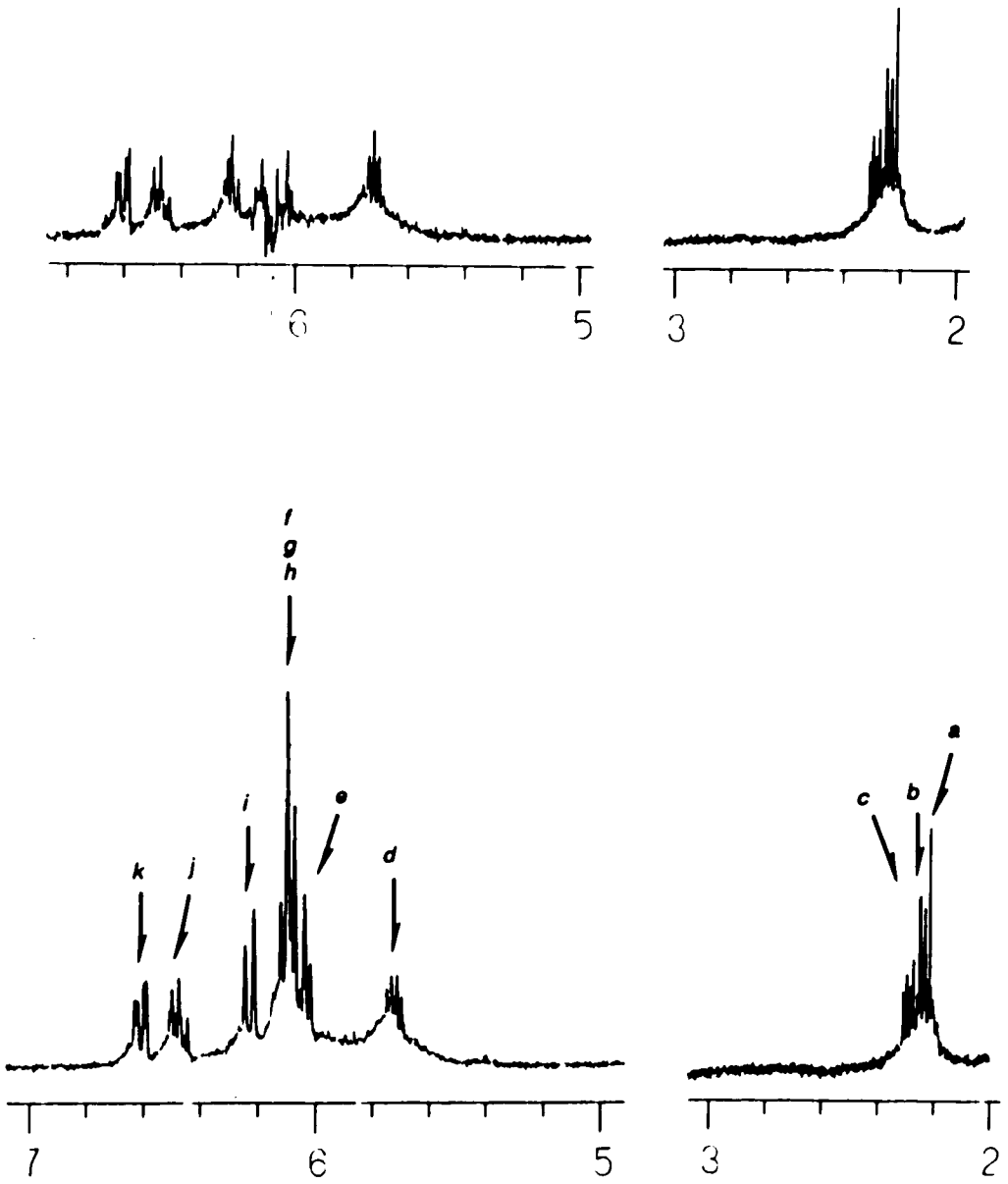


Figure 2.10-19. The decoupling experiment for proton *i* of pentaene **10-4**

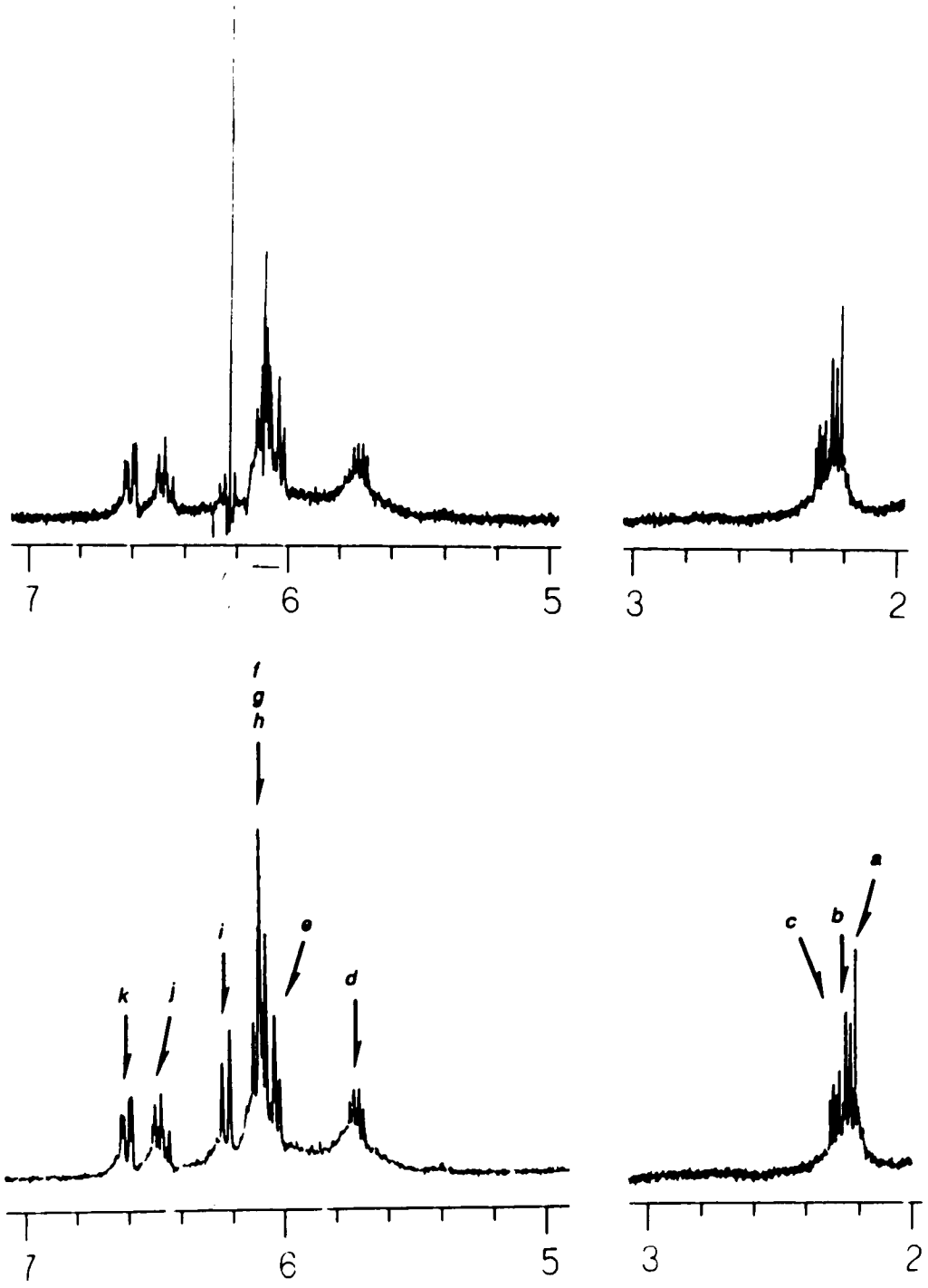


Figure 2.10-20. The decoupling experiment for proton *j* of pentaene **10-4**

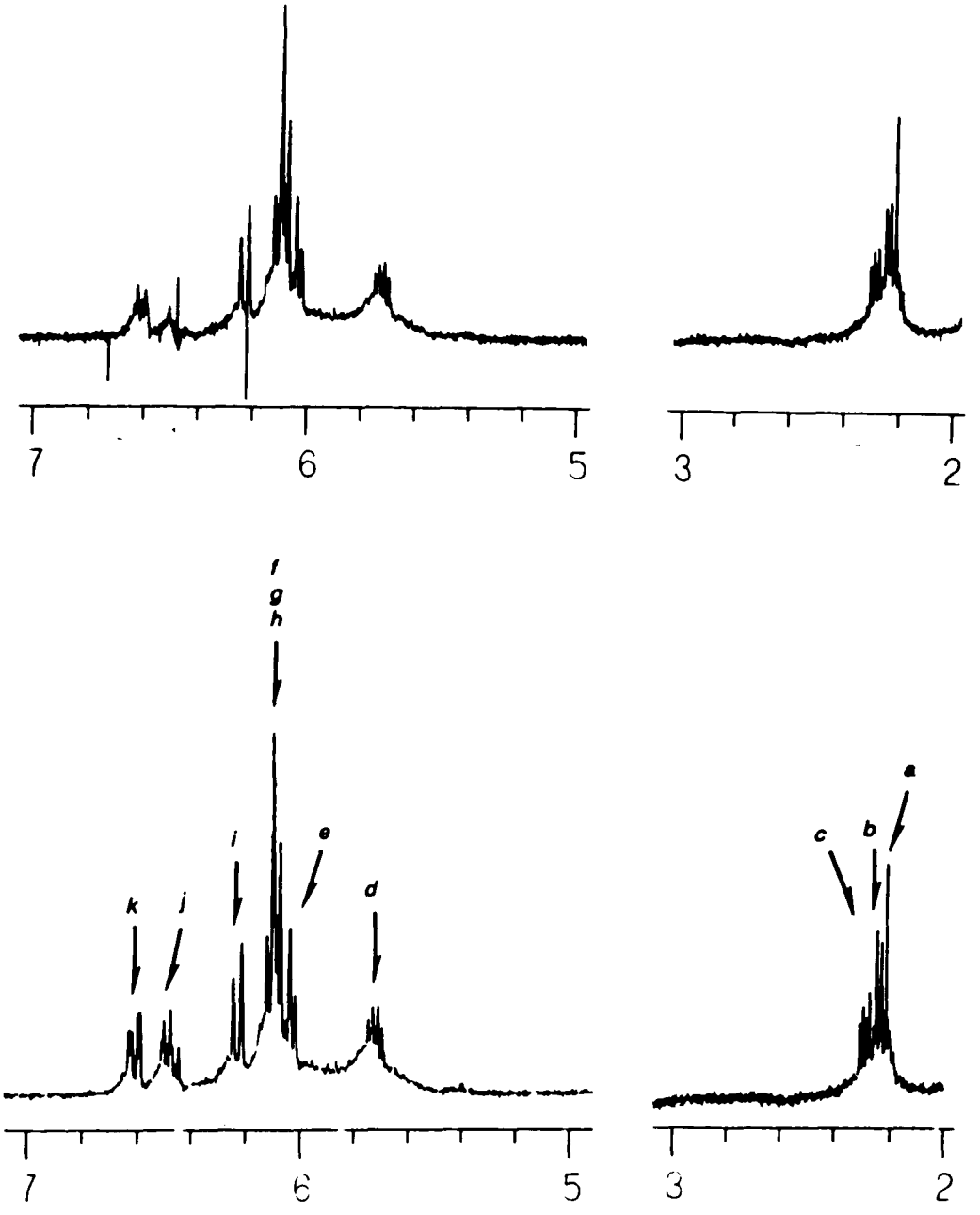
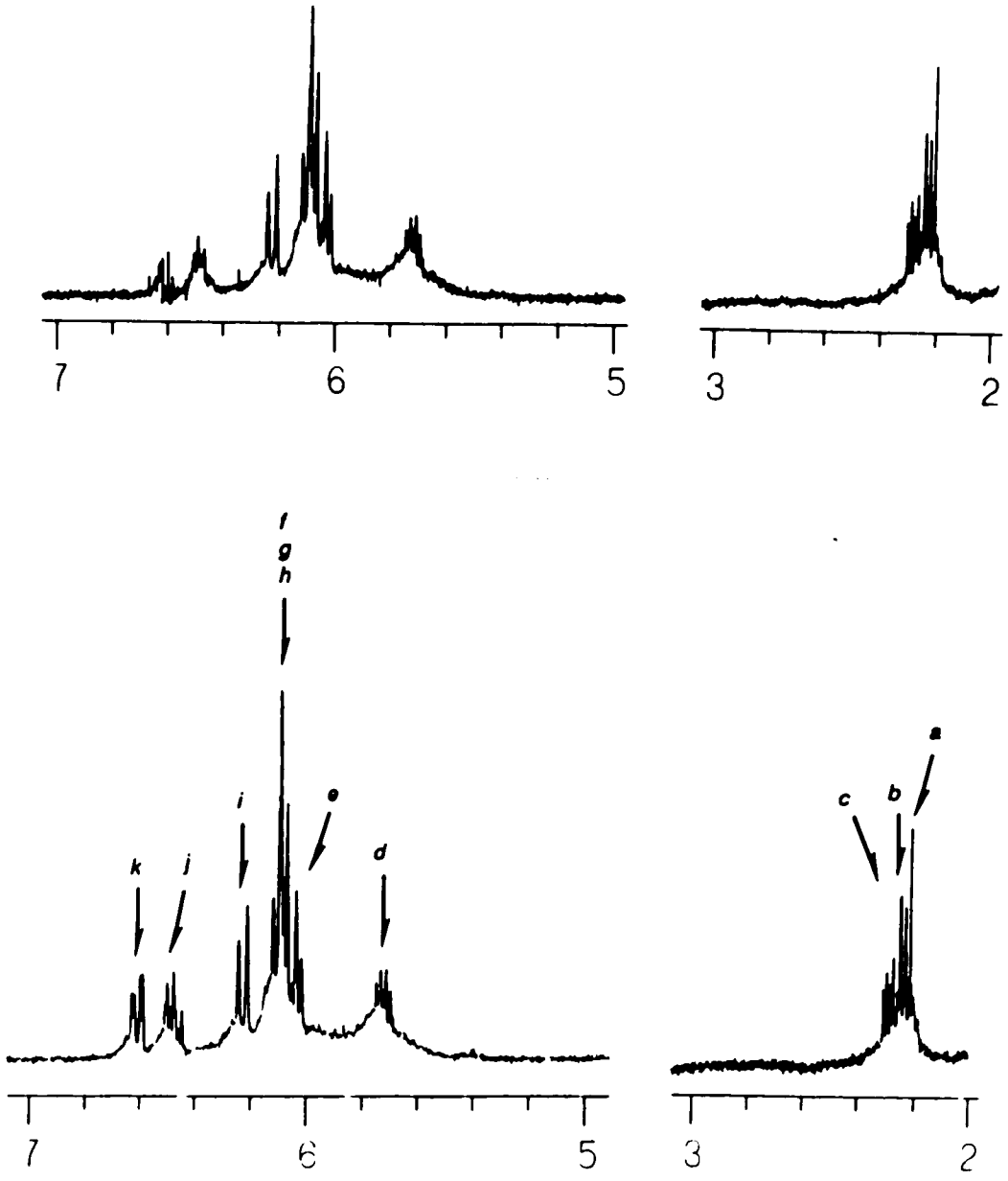
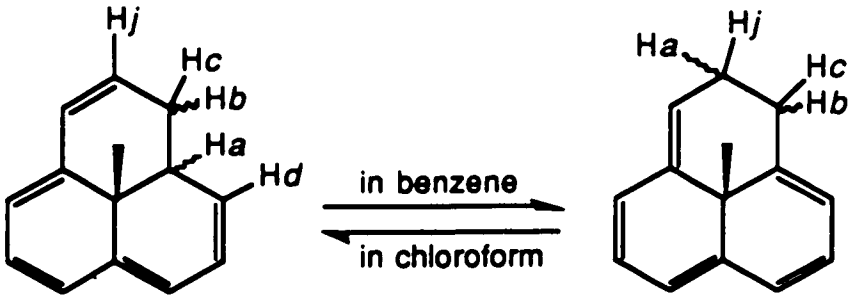


Figure 2.10-21. The decoupling experiment for proton *k* of pentaene **10-4**



Using the same sample replacing chloroform-$_d$ with benzene-d_6, the ^{1}H NMR spectrum indicated a structure more like structure **10-4b**: seven protons in the range δ 5.4 to 6.5, four protons in the range δ 1.8 to 2.1 (Figure 2.10-23)

Then using the same sample, replacing benzene-d_6 with chloroform-d, the spectrum for **10-4a** was obtained again. This suggests the following equilibrium (Figure 2.10-22), which implies a 1,11 hydrogen shift.



10-4a **10-4b**

Figure 2.10-22. The equilibrium between **10-4a** and **10-4b**

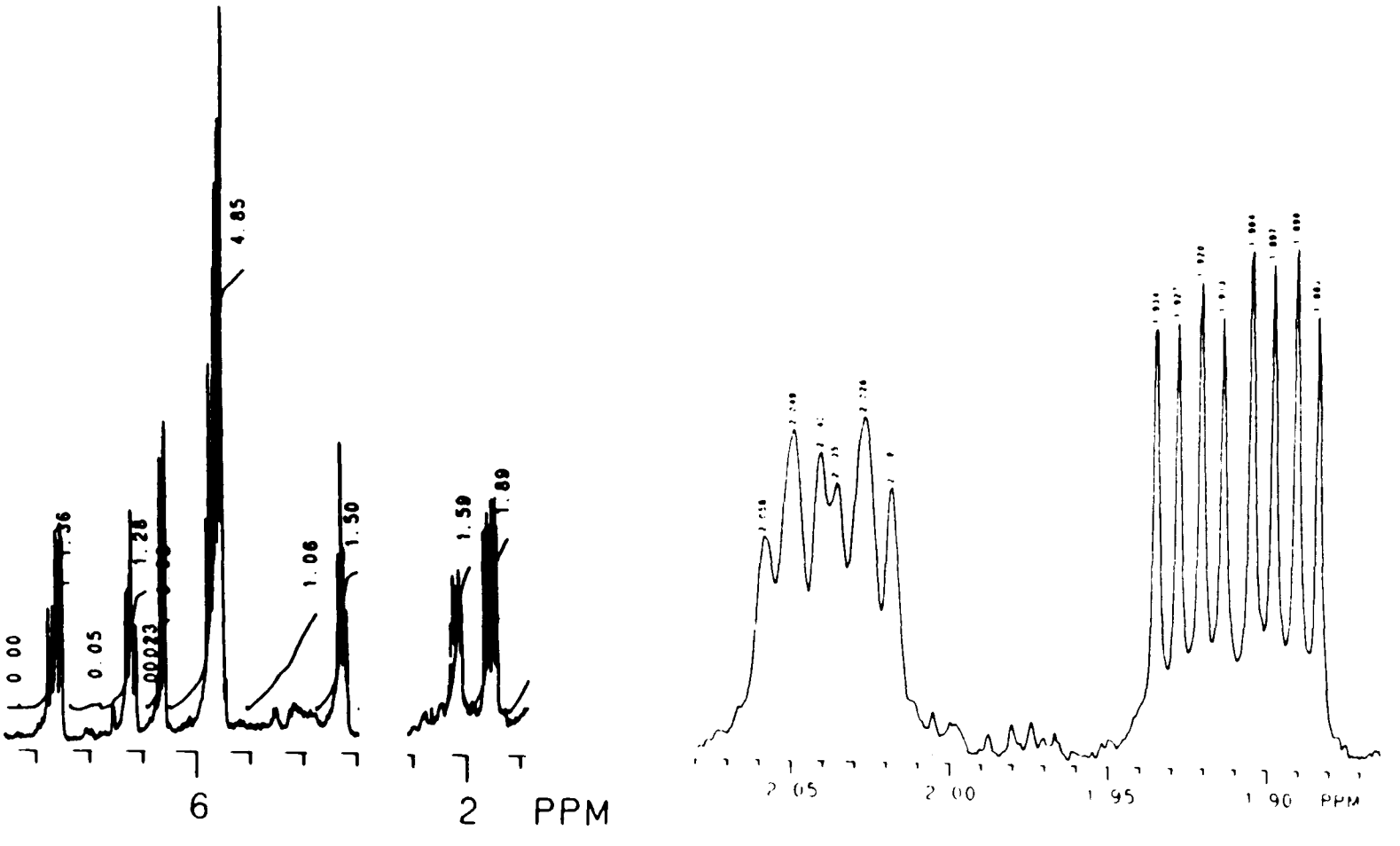
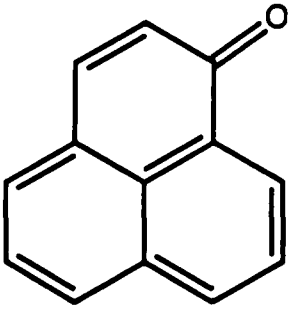


Figure 2.10-23. ^{1}H NMR spectra of pentaene **10-4b** in benzene

d. Dehydrogenation of pentaenes

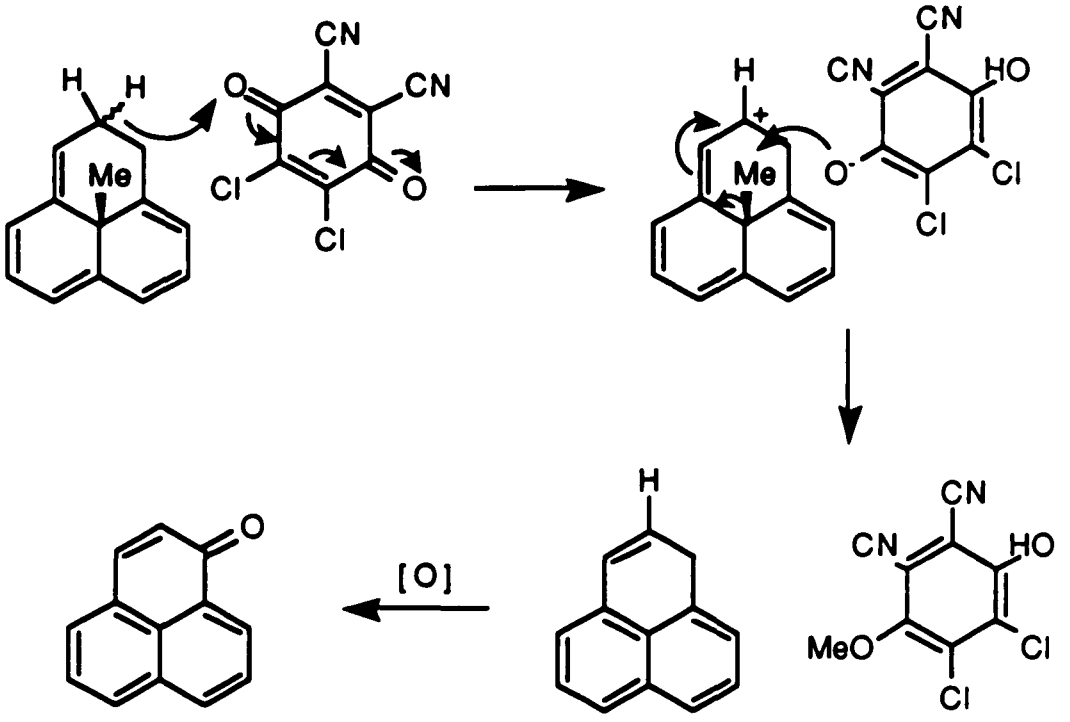
Pentaenes **10-4** and **10-5** are only one double bond short of 13-methylphenalene. For the introduction of the last double bond, dehydrogenation with DDQ[185, 186] was attempted. The pentaenes and bromopentaenes mixture (0.02 mmol) and DDQ (0.02 mmol) in 2 mL of benzene was stirred at room temperature or reflux for 2 hours. A yellow compound **10-8** was obtained. This exhibited peaks at m/z=180, 152, and 76 in the mass spectrum. The molecular weight is the same as 13-methylphenalene (180). It is surprisingly stable and could be isolated as a yellow solid. Unfortunately its ^{1}H NMR spectrum and TLC (Rf = 0.1 in hexane) was exactly the same as the known perinaphthenone. ^{1}H NMR: δ 6.72 (d, J=10 Hz, 1H), 7.58 (dd, J_1=7 Hz, J_2=8 Hz, 1H), 7.74(d, J=10, 2H), 7.76(t, J=8 Hz, 1H), 8.01 (d, J=8 Hz, 1H), 8.19 (dd, H_1=8 Hz, J_2=1 Hz, 1H), 8.62 (dd, J1=7 Hz, J2=1 Hz, 1H). That they are the same compound is confirmed by UV (in hexane): Max. (nm) 376, 354, 313, 259, 252, 246, 241.



10-8

For the dehydrogenation with DDQ, there are two possible mechanisms: **A.** cis-stereospecific[187] and **B.** stepwise sequential hydride and proton loss.[188] In the formation of perinaphthenone, the

probable mechanism could be the following: DDQ traps a hydride from a pentaene and then H-DDQ anion attacks the methyl of pentaene leading to aromatization, while H-DDQ-OMe is formed. If this is the case, it may be the first example that the group lost is not a proton in the reaction with DDQ.[189]



e. Attempted generation of dianion

As the direct formation of the antiaromatic 13-methylphenalene did not succeed, we considered first generating a 14 π electron dianion and subsequently converting it into 13-methylphenalene **X** by mild oxidation. This approach was stimulated by a recent paper by Streitwieser al et.[190] (Figure 2.10-24)

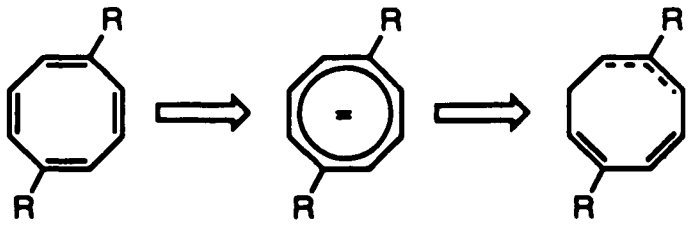


Figure 2.10-24. A strategy of approach to 4n π electron system

For the following very air-sensitive reactions, an all-in-one apparatus was designed and made as shown in Figure 2.10-25, in which a reaction container, a filter and a NMR tube are connected safely into a very tiny space. When the reactions are finished, the reaction solution will pass through the filter and be transferred to the detachable NMR tube by positive Ar pressure. With this apparatus even at high humidity, satisfactory results could be obtained.

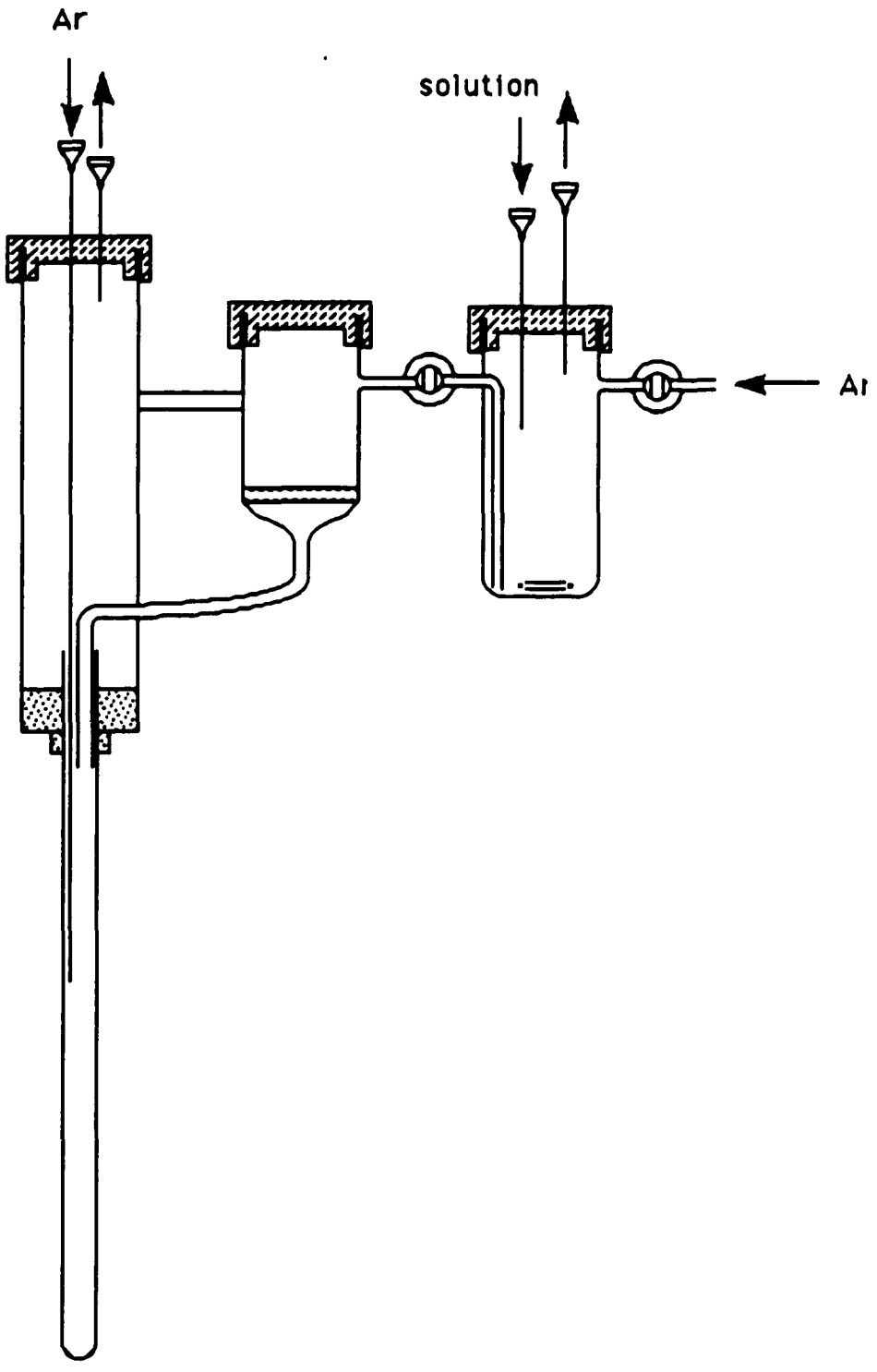


Figure 2.10-25. The all-in-one apparatus for air-sensitive reactions

For generation of the anion, according to model reactions with indene, dimsyl anion (generated with DMSO and NaH) and tBuLi were used.

(1) *The reaction of the pentaenes with Methylsulfinyl (dimsyl) Carbanion*

After the apparatus was flashed with Ar, 0.12 mmol of sodium hydride (5.1 mg, 57%) was placed in the reaction container and washed with dry pentane by a syringe (adding-withdrawing-vacuum, 4 times). 1.2 mL of DMSO-d_6 (8.3 mole %) was added. The suspension was stirred at 70-75° for 30-40 minutes. During this period hydrogen gas was evolved, and a clear pale gray solution of dimsyl anion was formed.[191,192] When it cooled to room temperature, 0.1 mmol of indene (11.6 mg, fresh distilled) was added. The solution turned to deep blue immediately and was transferred into the NMR tube through the build-in filter by positive Ar pressure. The ^1H NMR spectra in 2 hours from addition of indene (Figure 2.10-26) shows: δ 7.05 (dd, J_1= 6 Hz, J_2=3 Hz, 2H), δ 6.33 (t, J=3 Hz, 0.25H), δ 6.33 (d, J=3 Hz, 0.5H), δ 6.33 (s, 0.25H), δ 6.17 (dd, J_1=6 Hz, J_2=3 Hz, 2H), δ 5.68 (d, J=3 Hz, 2 x 0.25 + 0.50 = 1H) indicating that there is ca. 25% of indenyl anion, ca. 50% of 1d-indenyl anion and ca. 25% of 1,3-d_2-indenyl anion. The ^1H NMR spectrum after 13 hours (Figure 2.10-27) showed that the peak at δ 6.33 became a singlet and the peak at δ 5.68 completely disappeared, which indicated that 100% of 1,3-d_2-indenyl anion formed.

Figure 2.10-26. The ^{1}H NMR spectra of indenyl sodium in DMSO-d_6 after 2 hours

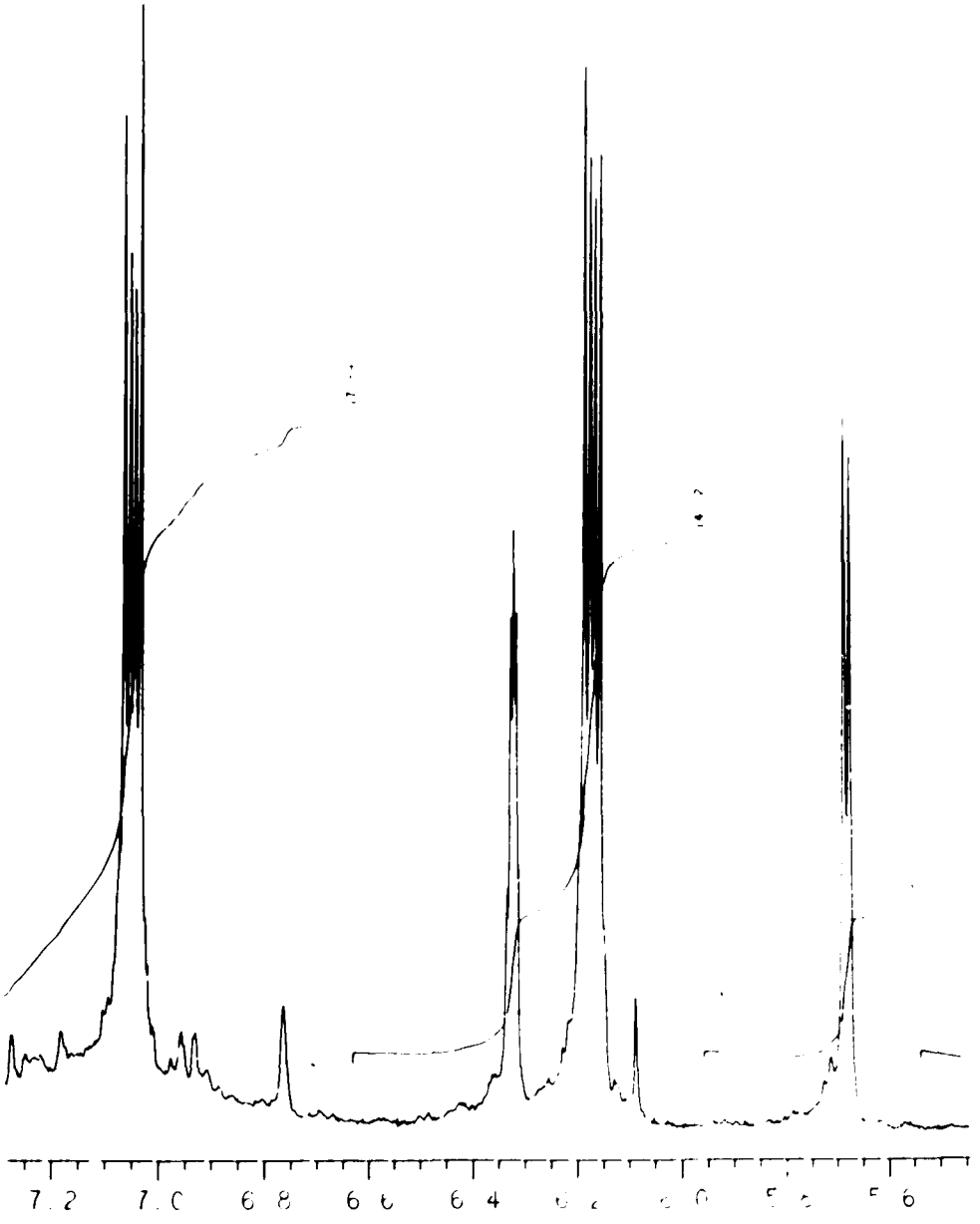
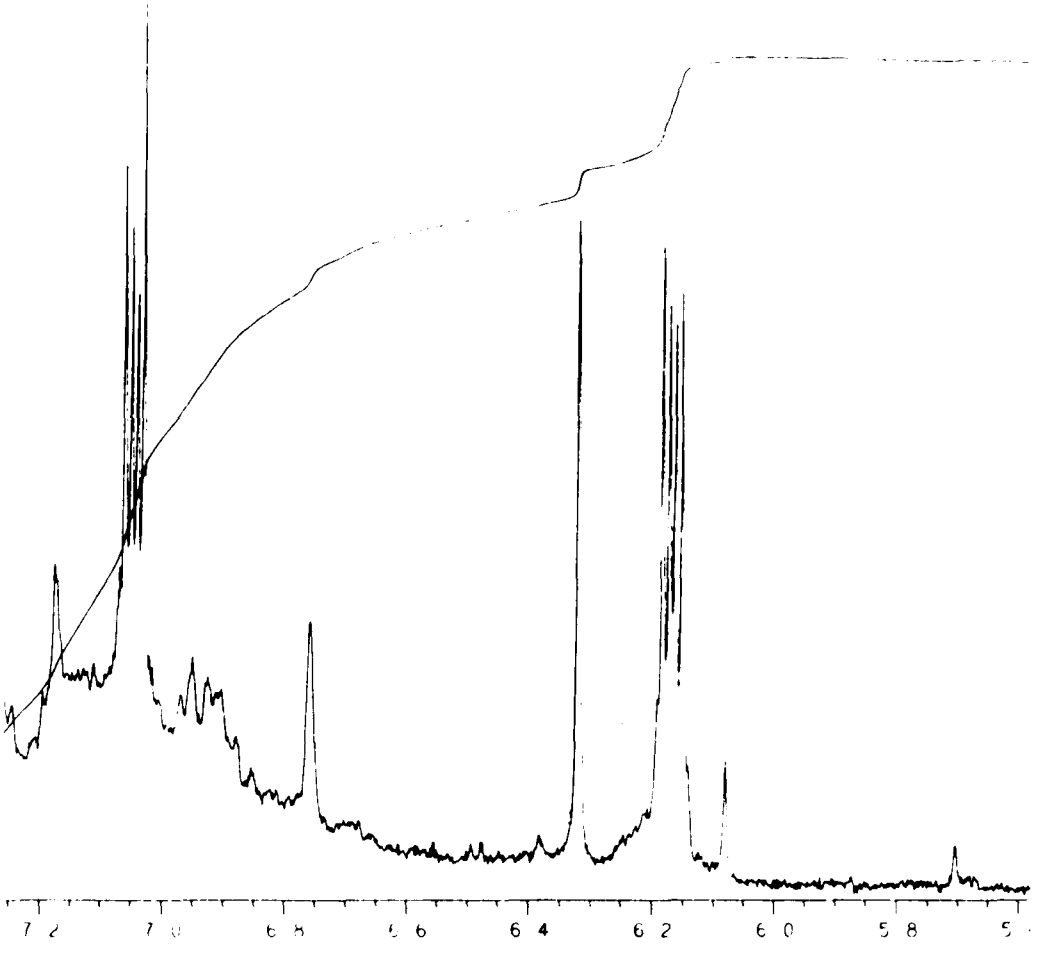


Figure 2.10-27. The ^{1}H NMR spectra of indenyl sodium in DMSO-d_6 after 13 hours



This phenomenon could be explained as shown in Figure 2.10-28. As a base, indenyl anion captures D from DMSO-d_6 at C-1, and then losts H to form 1d-indenyl anion, which repeats, to form d_2-indenyl anion. This H-D exchange is reversible. Since DMSO-d_6 is the solvent, H's at C_1 and C_3 are eventually completely replaced by D's. This is experimental evidence that C_1 and C_3 of indenyl anion have greater negative charge and indene has a quite low pKa value, 19.9,[193,194,195] while that of DMSO is 35.[196]

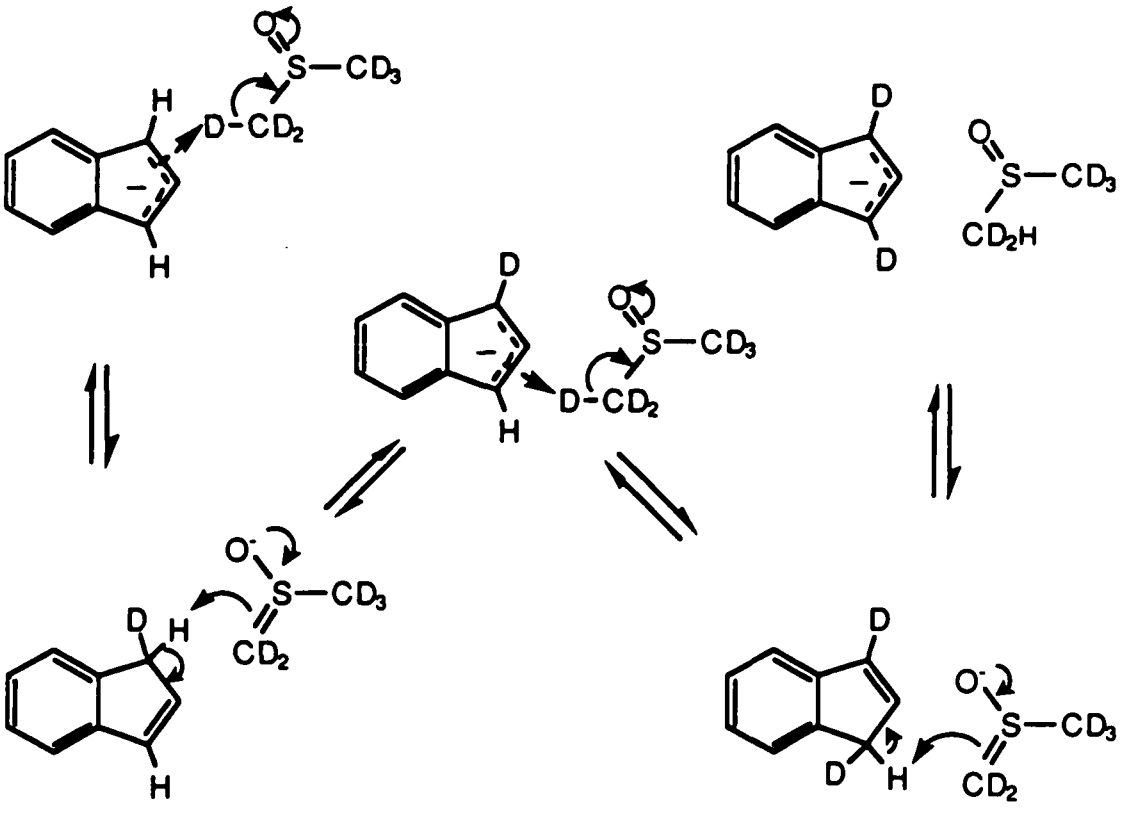
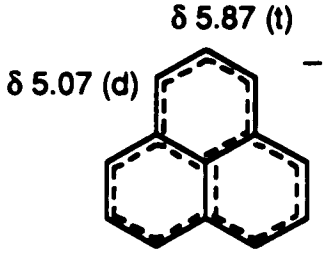


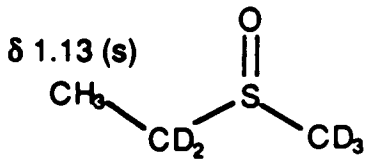
Figure 2.10-28. The reaction of indenyl anion with DMSO-d_6

Applying the above procedure to the mixture of pentaenes **10-4**, **10-5** and bromopentaene **10-5**, **10-6**, gave, surprisingly, a

known compound, phenalenyl anion.[197] This was determined as shown by the ^1H NMR spectrum, δ 5.87 (t, J=7.5 Hz, 3H), δ 5.07 (d, J=7.5 Hz, 6H), (Figure 2.10-29) (lit.[198] 60 mHz, lithium salt, δ 5.91, δ 5.17, J=7.5 Hz). This anion is a theoretically very interesting compound that is discussed in the Theories Chapter.

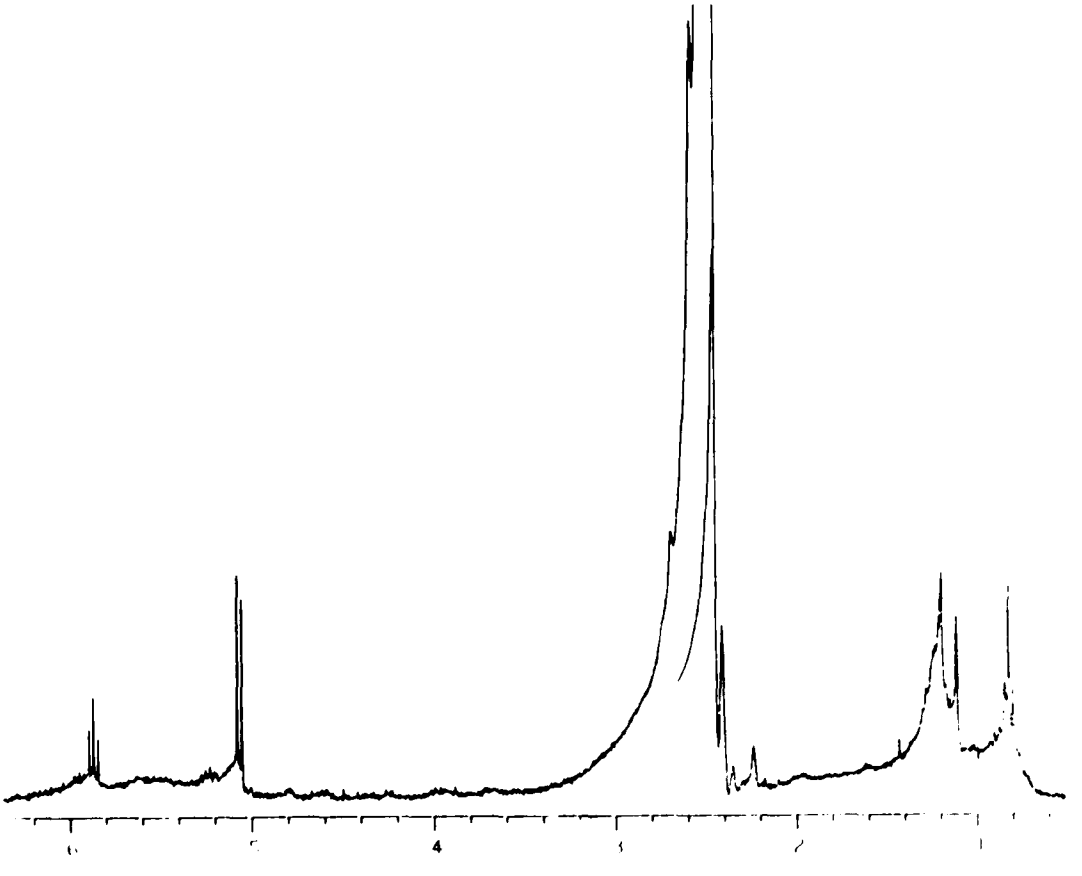


phenalenyl anion



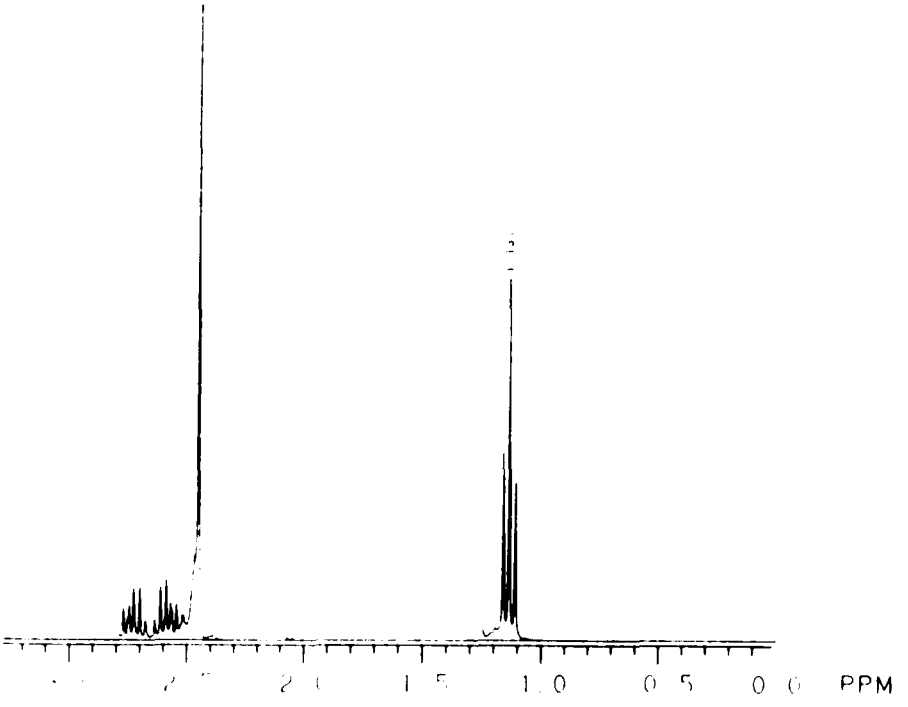
10-9

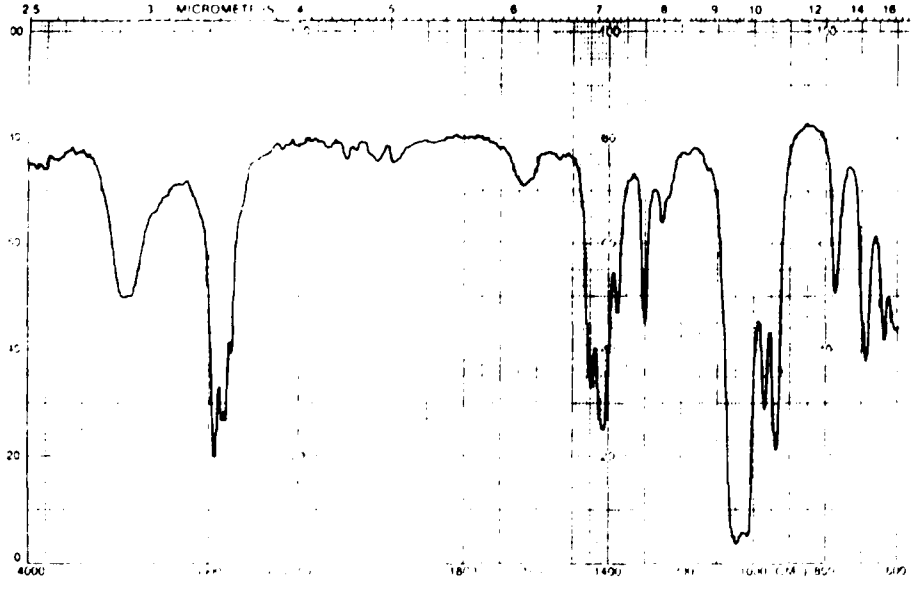
Figure 2.10-29. The ^1H NMR spectra of the products mixture in the reaction of pentaenes with dimsyl sodium in DMSO-d_6



Interestingly the methyl group was trapped by DMSO-d_5 anion to form compound **10-9** and shown as a singlet peak at δ 1.13 in ^1H NMR. This result is confirmed by ^1H NMR measurement of ethyl methyl sulfoxide, which was successively prepared by oxidation of ethyl methyl sulfite with m-chloroperbezoic acid.[199] (See Figure 2.10-30)

Figure 2.10-30. The ^1H NMR and IR spectra of ethyl methyl sulfoxide in DMSO-d_6



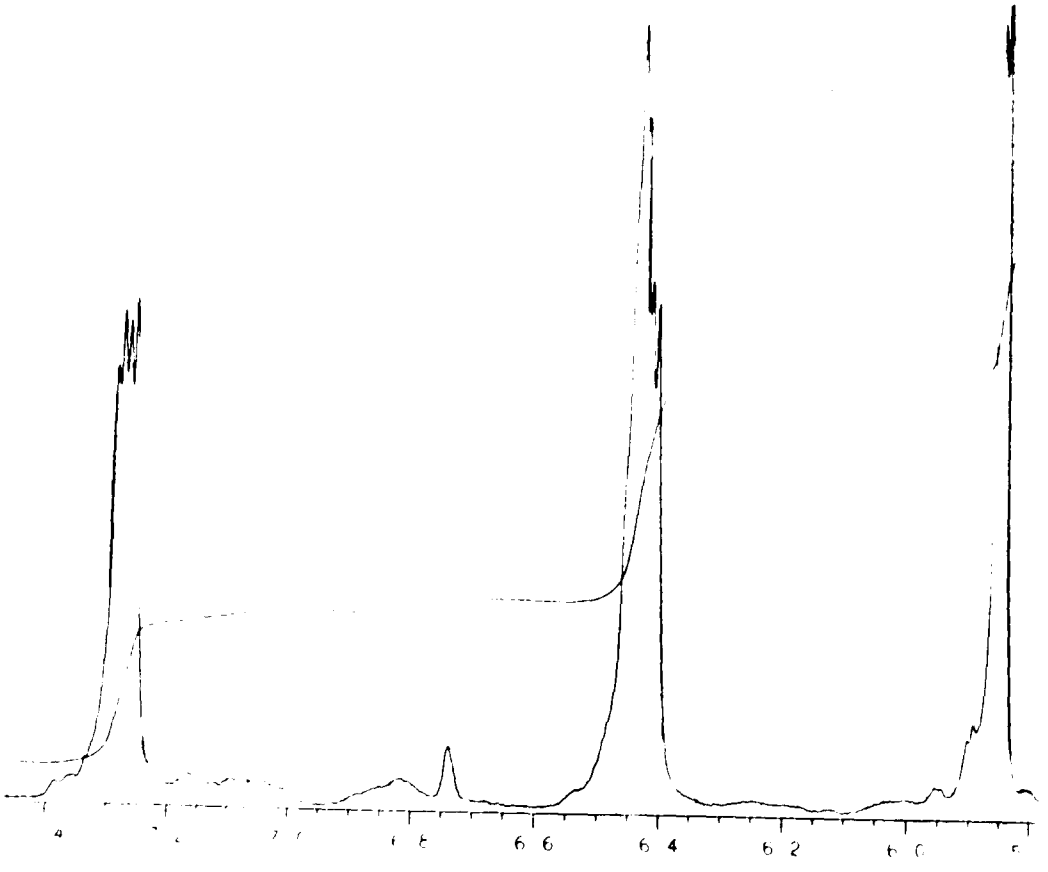


So far, the pentaenes **10-4** and **10-5** were treated with DDQ at 110 °C giving perinaphthenone **10-8**, and treated with sodium dimsyl at room temperature furnishing phenalenyl anion. In both cases the central methyl was lost, indicating that there might be a strong tendency to form a stable planar structure. As a result, the weakening of the methyl-carbon bond in 13-methylphenalene and its dianion was inferred, which was supported by AM1 calculations indicating that the methyl-carbon bond energy is very low (now-called Y-hyperconjugation) (see section 3.1 in the Theories Chapter). For these reasons, low temperature conditions were tried as following.

(2) The reaction with t-butyllithium

In an NMR tube equipped with two needles through a septum cap, one for Ar input and another for Ar exit, 0.85 mmol (0.1 mL) of indene in 0.6 mL of THF-d_8, followed by 0.85 mmol of tBuLi (1.7 M in pentane, 0.5 mL), were injected at -78°. The solution turned yellow then red brown from colorless in 10 minutes. ^{1}H NMR shown a very neat spectrum for indenyl anion (Figure 2.10-31): δ 7.279 (dd, J_1= 6.0 Hz, J_2=3.0 Hz, 2H), δ 6.443 (t, J=2.7 Hz, 1H), δ 6.429 (dd, J_1=6.0 Hz, J_2=3.0 Hz, 2H), δ 5.858 (d, J=2.7 Hz, 2H).

Figure 2.10-31. The ^{1}H NMR spectra of indenyl lithium in THF-d_8



Applying the same procedure to the pentaene mixture of **10-4** and **10-5**, a brown solution was obtained. The ^1H NMR spectrum at -78° showed peaks at δ -2.5, δ 5.4 and δ 7.2. At room temperature the peaks were shown at δ -1.2 (t), -0.2 to -0.1 (d's and s's), 4.60 (s), 5.30 (s), 6.90 (d), 6.92 (d). These peaks are still inconclusive for identification of the dianion.

To the above brown solution was added 0.2 mL of methanol for protonation. A yellow solution was obtained which showed an AA'BB' system shown at δ 7.5 to 7.7 in the ^1H NMR.

EXPERIMENTAL

General

All solvents were purified and dried by using standard procedures.

For the solutions containing air-sensitive compounds, the modified rotary evaporator (See Figure 2.10-7.) was used to evaporate solvents under an inert atmosphere.

IR spectra were obtained on a Perkin-Elmer 1310 spectrophotometer. UV-Visible spectra were run on a Beckman DU-8 Spectrophotometer in 95 % ethanol or $CDCl_3$ solution. Routine ^1H NMR and ^{13}C NMR were determined on a GE QE-300 MHz instrument in $CDCl_3$ solution using an internal TMS reference. Mass spectra were obtained at Hoffmann-La Roche. GC spectra were recorded on a Hewlett Packard 5700A Gas Chromatography instrument. GC/MS were performed by Dr Locke of Queens College of the CUNY. Melting points were determined on a Büchi (Rinco instrument Co., Inc.) melting point apparatus and were uncorrected.

Thin-layer Chromatograms were done on precoated TLC sheets of silica G. UV254, 50/4x8, 8050021 (Brinkmann Instrments Inc.), with use of 2,4-dinitrophenyl hydrazine spray, potassium permanganate spray, iodine vapor, phosphomolybdic acid spray and/or short-and-longwave ultraviolet light to visualize the spots. PLC plates were precoated TLC sheets of silica gel 60 F_{254} (E. Merck). Chromatotron (radial chromatography) plates were prepared by using Kiesegel 60 PF_{256} gipshaltig (E. Merck) and all separations using the chromatotron were done under nitrogen atmosphere.

All solvents were evaporated by a rotary evaporator with a water aspirator unless otherwise stated.

Dehydrogenation of 5-Acetoxy-4a-methy1-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one 2-4.

DDQ (4.99 g, 0.022 mol) was added to enone **2-4** (4.44 g, 0.02 mol) in 70 mL of dry benzene. After refluxing for 16 h, a gray precipitate was observed and the solution turned dark. The solution was filtered and washed with 2 x 20 mL of benzene. The combined benzene solution (100 mL) was washed with 100 mL of 10% Na_2SO_4 aqueous solution, 100 mL of water and 60 mL of saturated NaCl solution. The benzene solution was dried over Na_2SO_4 and evaporated. The residue (3.75 g of brown oil) was extracted with boiling hexane (2 x 50 mL). The extracts were decolorized with charcoal, concentrated on a steam bath and cooled. 1.65 g of (37%) of crystals **2-5** were obtained (m.p. 82.0-84.5 °C). ^1H NMR ($CDCl_3$) δ 6.9 (d, 1H), 6.2 (d, 1H), 6.15 (s, 1H), 4.5 (m, 1H), 2.1 (s, 3H), 1.3 (s, 3H), 1.5-2.6 (m, 6H).

Cyclohexadiene 3-3[200]

Lithium (0.278 g, 0.04 mol) was dissolved in 20 mL of absolute ethanol in a 200 mL round bottom flask under nitrogen. $Br^-P^+Ph_3CH_2CH{=}CHCOOEt$ (9.1, 0.02 mol) and distilled DMF (75 mL) were added at room temperature. After 5 min, 1.4 g (0.02 mol) of 2-butenal (trans) were added with a dropping funnel. The mixture was stirred for 14 h, then 50 mL of ice water were added. The aqueous solution was extracted by 3 x 100 mL of ligroin/ether (3:1). The combined organic layers were washed with 2 x 100 mL of water,

dried over $MgSO_4$ and evaporated. Vacuum distillation of the residue at 0.05 mmHg gave 3.1 g (93%) of colorless oily **3-3**. b.p. 35 °C. ^1H NMR ($CDCl_3$, 60 M Hz) δ 6.95 (dd, 1H), 5.95(m, 2H), 4.2 (q, 2H), 2.72 (m, 1H), 2.34 (m, 2H), 1.3 (t, 3H) and 0.98 (d 3H); UV (95% EtOH): λ_{max} 296 nm.

Triene VII.

Under nitrogen the ketal of Hagemann's aldehyde **3-1** (4.5 g, 0.025 mol) and $Br^-P^+Ph_3CH_2CH{=}CHCOOEt$ (11.0 g, 0.025 mol) were dissolved in 95 mL of DMF in a 500 mL two neck round bottom flask. A solution of 0.35 g (0.05 mol) of lithium in 25 mL of CH_3OH was added dropwise into the flask at room temperature. (The solution color changed from yellow to orange to tea.) After the reaction mixture was stirred for 14 h, 120 mL of ice water were added, then 200 mL of hexane/ether (1:1), and the aqueous layer was extracted with 3 x 100 mL of hexane/ether (1:1). The combined organic layers were washed with 3 x 100 mL of water, dried over $MgSO_4$ and evaporated. White crystals of **VII** (m.p. 64.0-65.0 °C) were obtained by column chromatography (silica gel, 1:3 ethyl acetate-ligrion) followed by crystallization (1:1 ethyl acetate-hexane). Rf=0.54 (50% ethyl acetate-hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, 1H, J_1=15.2 Hz, J_2=11.2 Hz), 7.01 (d, 1H, J_3=15.1 Hz), 6.29 (dd, 1H, J_2=11.2 Hz, J_3=15.1 Hz), 5.86 (d, 1H, J_1=15.2 Hz), 4.21 (q, 2H), 3.99 (s, 4H), 2.43 (t, 2H), 2.39 (s, 2H), 1.86 (s, 3H), 1.81 (t, 2H), 1.56 (t, 3H); ^{13}C NMR (400 MHz, $CDCL_3$): δ 167.11, 145.64, 138.16, 135.97, 127.30, 124.19, 119.59, 107.46, 64.35, 60.00, 42 94, 30.74, 24.49, 19.27, 14.25; UV: (95% EtOH) λ_{max} 316 nm; IR: (KBr) 1700 (s), 1610 (s), 1364 (m), 1232 (s), 1135 cm^{-1} (s).

Epoxide 3-4.

The triene **VII** (0.04 g) was dissolved ethanol (12 mL) then divided into 3 portions. Portion **A** was heated at reflux; Portion **B** was kept under sunlight (bulb); Portion **C** was kept in a refrigerator. The compponents of each of these solutions were unchanged by TLC after 24 h. Crystals of triene **VII** stored in a refrigerator for 24 h were unchanged, too. After crystals of triene **VII** (0.05 g) were kept open to air for 24 h, TLC (50% ethyl acetate-hexane) showed 2 spots (Rf=0.54 and Rf=0.48); 0.04 g of epoxide **3-4** was obtained by column chromatography (10:1-4:1, hexane-ethyl acetate). m.p. 68.0-69.0 °C; Rf=0.48, 50% ethyl acetate-hexane; ^{1}H-NMR (DCl_3, 400 MHz): δ 7.25 (dd, 1H, J_1=15.26 Hz, J_2=11.0 Hz), 6.36 (dd, 1H, J_1=15.26 Hz, J_2=11.0 Hz), 6.13 (d, 1H, J=15.25 Hz), 5.87 (d,1H, J=15.26 Hz), 4.18 (q, 2H, J=7.33 Hz), 3.96-3.85 (m, 4H, AA'BB'), 2.04-1.99 (m, 1H, J=14.65 Hz), 1.93-1.89 (m, 1H, J=15.25 Hz), 1.77-1.64 (m, 1H), 1.52-1.45 (m, 1H), 1.27 (t, 3H, J=7.33 Hz), 1.22 (s, 3H); ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 166.85 (s, C=O), 143.19 (d, H<u>C</u>=C), 140.12 (d, H<u>C</u>=C), 130.43 (d, H<u>C</u>=C), 121.84 (d, H<u>C</u>=C), 106.77 (s, O-C-O), 64.6 (s, C-O), 64.38 (t, CH_2-O), 64.07 (t, CH_2-O), 63.89 (s, C-O), 60.31 (t, COO<u>C</u>H_2), 41.00 (t, CH_2), 27.76 (t, CH_2), 26.26 (t, CH_2), 21.08 (q, CH_3), 14.23 (q, CH_2<u>C</u>H_3). UV (95% EtOH): λ_{max} 265 nm; IR: 1705 (s), 1636 (m), 1614 (m), 1365 (m), 1232 (s), 1135 cm^{-1} (s). MS: m/e 294 (M^+), 86 (<u>OCH$_2$CH$_2$OC</u>CH$_2$).

Diene 3-7

$CH_3P^+Ph_3I^-$ (6.06 g, 15 mmol) was added with stirring into 100 mL of dry THF (0.15 M) under Ar and cooled in an ice bath. ^{n}BuLi

(8.53 mL, 14.5 mmol) were injected into the flask by a syringe. The solution color changed from colorless to yellow-orange. After 3 h, a solution of 0.91 g (5 mmol) of the ketal Hagemann's aldehyde **3-1** in 5 mL of THF was added dropwise into the reaction flask. The orange solution was stirred for another 4.5 h, when TLC showed no remaining ketal Hagemann's aldehyde (1:1 hexane-ethyl acetate). Work up was as follows: 140 mL of ice water were added, and the aqueous layer was extracted by 2 x 100 mL of ether. The combined organic layers were washed with 140 mL of water, dried over $MgSO_4$, then evaporated. A colorless oil (0.86 g, 96%) was obtained after column chromatography of the residue (silica gel, 5:1 hexane-ethyl acetate). ^1H NMR ($CDCl_3$, 60 MHz): δ 6.4 (dd, 1H, J_{trans}=16 Hz, J_{cis}=10 Hz), 4.8 (d, 1H, J_{trans}=16 Hz), 4.7 (d, 1H, J_{cis}=10 Hz), 3.7 (s, 4H), 2.2 (m, 4H), 1.5-1.8 (m, 5H, CH_3 and CH_2).

2-Hydroxymethylene cyclohexanone 4-3[201]

In a 1 liter two neck round bottom flask, 30 g of NaH in oil (57%) were added to 400 mL of dry ether under nitrogen at 0 °C. A solution containing 39.2 g (42 mL, 0.40 mol) of cyclohexanone and 41.4 g (45 mL, 0.56 mol) of ethyl formate in 200 mL of dry ether was added dropwise into the flask with mechanical stirring. The reaction solution was allowed to warm up to room temperature, then stirred overnight. An orange colored precipitate was formed, and was dissolved when 1 liter of ice water was added to the mixture. The aqueous layer was separated and neutralized with 300 mL of 10% HCl, then extracted with 3 x 500 mL of ether. The combined ether layers were washed with 2 x 400 mL of NaCl solution and dried over MgSO4. After distillation with a water aspirator, 37.0 g (74%) of 2-

hydroxymethylene cyclohexanone **4-3** were obtained. ^{1}H NMR (300 MHz): δ 14.36 (s, broad, CHOH), 8.60 (s, CHOH), 2.32 (d, 4H), 1.72 (t, 4H).

Spiro dione 4-5[202]

2-hydroxymethylene ketone **4-3** (35.0 g, 0.28 mol), methyl vinyl ketone (56 mL), hydroquinone (trace) and potassium hydroxide (2.24 g) were mixed at 0 °C, the stirred at room temperature under nitrogen for 24 h. All starting ketone was converted to diketone **4-4**, as determined by ^{1}H NMR. The excess methyl vinyl ketone was evaporated (at 20 mmHg). The residue was transferred to a small flask containg 1 g of potassium hydroxide, heated at 120 °C for 48 h, then slowly distilled for 4 h, furnished 29.0 g of crude spiro-ketone **4-5**, bp 95-128 °C/0.1 mmHg, which could be purified by distillation again, bp 110-112 °C/0.1 mmHg. ^{1}H NMR (300 MHz) δ 6.95 (d, J=10.5 Hz), 6.01 (d, J=10.5 Hz).

Ethynyl carbinol 4-1[203]

Li metal (0.75 g) was added to liquid ammonia (distilled from Na metal) at -78 °C. Dry acetylene gas (passed first through two cooling towers at -78 °C to remove acetone and water.) was passed into the solution. The solution color changed from dark blue to colorless then white over 70 min. Spiro dione **4-5** (7.5 g, 0.04 mol) in dry ether (100 mL) was added dropwise during 20 min with vigorous stirring. After 1 h the mixture was quenched with solid NH_4Cl (5 g) and turned yellow. Water (20 mL) was added to the residue. The mixture was extracted with $CHCl_3$ (2 x 75 mL) after completely evaporating ammonia. The combined extracts were washed with saturated NaCl aqueous solution and dried over $MgSO_4$. Removal of the solvent and column

chromatography (silica gel,1:4 ethyl acetate- hexane) of residue (11.5 g) furnished 3.0 g (36%) of the carbinol **4-1**. m.p. 125-126 °C (lit.[204] 124-125 C). ^{13}C NMR (300 MHz): 199.88 (C9), 155.77 (C7), 129.74 (C8), 85.71 (C1), 75.21 (C13), 73.12 (C12), 43.56 (C6), 35.15, 33.74, 31.81, 25.58, 22.46, 20.65. IR (KBr): 3305 (tertiary OH), 3220(-C-CH), 1660(C=C-C=O).

Tricyclic dione 4-2

The carbinol **4-1** (0.057 g, 0.272 mmol) in dry DME (10 mL) was added to a suspension of hexane-washed KH in of dry DME (10 mL) under nitrogen at room temperature over 15 min. The mixture was stirred for 2 h, and then quenched with acetic acid and water (5 mL) until the solution turned yellow and clear. Ether (10 mL) was added. The aqueous layer was extracted with 3 x 10 mL of ether. The combined organic layer was washed with NaCl aqueous solution, dried over $MgSO_4$. Tricyclic dione **4-2** (0.01 g, ca.20%) was obtained by a chromatography (3:1 hexane-ethyl acetate). ^1H NMR (300 MHz): δ 7.11 (dd, 1H), 5.98 (d, 1H), 3.92 (dd, 1H), 2.22-2.57 (m, 3H), 1.4-2.0 (m, 10H).

Methyl dione 4-3m[205]

Acetic acid (150 mL, 86%, 2.4 mol) was placed in a three neck flask fitted with an efficient, sealed stirrer, a gas inlet tube and an outlet tube loosely closed with a cotton plug. Boron trifluoride passed in as rapidly as it was absorbed at 0 °C. Addition was continued until the contents of the flask appeared powdery solid. A dropping funnel was then substituted for the gas inlet tube, and a mixture of the ketone (40 mL, 0.4 mol) and acetic anhydride (90 mL, 0.8 mol) was

added with ice-bath cooling during 10 min. After stirring for 30 min, the ice-bath was removed. The reaction mixture was allowed to stand 4 h at room temperature, poured into a solution (500 mL) of AcONa (200 g, 2.4 mol) and then refluxed for 0.5 to 1 h. After chilling the mixture was extracted with 5 x 300 mL of hexane. The extracts were washed with $NaHCO_3$ solution and dried over $MgSO_4$. Dione **4-3m** (47.2 g, 84%) were obtained by distillation (95-99 °C/15 mmHg). ^1H NMR (300 MHz): δ 15.85 (s, 1H), 2.26 (m, 4H), 2.06 (s, 3H), 1.63 (m, 4H). ^{13}C NMR (300 MHz): δ 198.87, 181.92, 106.95, 31.07, 24.79, 24.199, 22.79, 21.62. IR: 3370, 1730, 1700, 1600 cm-l (b).

The formation and condensation of dimethyl trione 4-7

Acetyl cyclohexanone **4-3m** (8.60 g, 8.00 mL) and methyl vinyl ketone (10 mL) were dropped into a 50 mL round bottom flask with KOH (0.20 g) and hydroquinone (trace) at 0 °C under nitrogen. The mixture was stirred for 24 h at room temperature. White precipitate was formed. The excess methyl vinyl ketone was evaporated by a rotatory evaporator. Dry EthOH (100 mL) and KOH (0.2 g) were added. The mixture was refluxed for 40 h. A brown and wet solid (12 g) was gotten by removal of solvent. Pure single isomer **4-5m** or **4-5m'** (6.0 g (60%) were obtained as first fraction on chromatograghy (silica gel, 4:1 hexane-ethyl acetate). ^1H NMR (300 MHz): 5.79 (s, 1H), 2.74 (m, 1H), 2.51 (m, 2H), 2.40 (m, 1H), 2.33 (m, 2H), 1.97 (m, 1H), 1.92 (s, 3H), 1.85-1.65 (m, 4H), 1.52 (t,d, 1H). ^{13}C NMR (300 MHz): δ 210.80, 198.27, 161.01, 125.26, 58.56, 41.01, 34.98, 30.80, 27.98, 26.93, 23.90, 20.91. IR: 1700 (C=O), 1660 cm-l(C=C-C=O). x ray (For graph see Figure 2.4-3) data:

Table 2-1. The bond distances (Å) of the spiro dicyclic **4-5m'**

Atom 1	Atom 2	Distance
C1	C2	1.315
C1	C11	1.503
C1	C12	1.497
C2	H2	0.94
C7	C8	1.535
C7	C6	1.530
C7	H7"	1.03
C7	H7'	1.10
C9	C8	1.501
C9	H9	1.09
C9	H9"	1.05
C4	C3	1.530
C11	H11'	1.07
C4	C5	1.543
C11	H11"	1.00
C4	C10	1.526
C8	CH8'	1.15
C4	C9	1.550
C8	H8"	0.94
C3	O3	1.221
C6	H6"	1.05
C3	C2	1.456
C6	H6'	1.02
C5	O5	1.221
C12	H12a	0.87

C5	C6	1.482
C12	H12c	0.97
C10	C11	1.527
C12	H12b	1.07
C10	H10'	0.98
C10	H10"	0.97

Table 2-2. The bond angles (°) of the spiro dicyclic **4-5m'**

Atom 1	Atom 2	Atom 3	Angle
C11	C1	C12	115.3
C3	C2	C1	124.0
C3	C2	H2	114
C1	C2	H2	122
C8	C7	C6	109.4
C8	C7	H7"	108
C8	C7	H7'	112
C6	C7	H7"	112
C6	C7	H7'	107
H7"	C7	H7'	109
C4	C9	C8	114.0
C4	C9	H9	105
C4	C9	H9"	106
C8	C9	H9	114
C8	C9	H9"	115
H9	C9	H9"	102
C10	C11	C1	112.6
C10	C11	H11'	105

C10	C11	H11"	112
C1	C11	H11'	116
C3	C4	C5	108.7
C1	C11	H11"	110
C3	C4	C10	108.6
H11'	C11	H11"	100
C3	C4	C9	109.1
C7	C8	C9	111
C5	C4	C10	110.6
C7	C8	H8'	106
C5	C4	C9	109.3
C7	C8	H8"	104
C10	C4	C9	110.5
C9	C8	H8'	109.1
C4	C3	O3	121.5
C9	C8	H8"	112
C4	C3	C2	117
H8'	C8	H8"	114
O3	C3	C2	121.5
C5	C6	C7	114.1
C4	C5	O5	119.1
C5	C6	H6"	113
C4	C5	C6	119.5
C5	C6	H6'	104
O5	C5	C6	121.5
C7	C6	H6"	110
C4	C10	C11	112.5
C7	C6	H6"	111

C4	C10	H10'	106
H6"	C6	H6'	105
C4	C10	H10"	107
C1	C12	H12A	113
C11	C10	H10'	110
C1	C12	H12C	107
C11	C10	H10"	110
C1	C12	H12B	113
H10'	C10	H10"	112
H12A	C12	H12C	108
C2	C1	C11	121.7
H12A	C12	H12B	109

Ether 5-22

In a 100 mL round bottom flask, 2-propyn-1-ol (5.6 g, 0.1 mol), acetal **5-21** (15.0 g, 0.125 mol), hydroquinone (0.02 g) and p-toluenesulfonic acid (0.01 g) were dissolved in heptane (40 mL). The solution was stirred for 24 h at 80-85 °C, and then 0.01 g of NaOAc and 1 mL of methanol were added. After solvent was distilled at atmospheric pressure, 2.64 g of ether **5-22** (32.2%) were obtained at 45 °C by vacuum distilation (water aspirator). ^{1}H NMR (60 MHz): δ 4.55, (q, OC<u>H</u>CH$_3$O), 3.90(d, HCCC<u>H$_2$</u>O), 3.40(m, OC<u>H$_2$</u>CH$_3$), 2.30(d, HCC), 1.28(d, OCHC<u>H$_3$</u>O), 1.19(t, OCH$_2$C<u>H$_3$</u>).

β-Allenic ester 5-23

A mixture of triethyl orthoacetate (200 g, 1.23 mol, b.p. 142 °C), 2-propyn-1-ol (51 g, 0.91 mol, b.p. 110-114 °C) and propionic acid (2 mL, b.p. 140-142 °C) was heated up to 100 °C for 1 h. In this

period, 80 mL of ethanol were collected. The residue was refluxed for 4 h in a 180 °C oil bath. After cooling to room temperature, 150 mL of THF and 100 mL of 5 % HCl were added, and then stirred overnight. Addition of pentane (150 mL) caused formation of two layers. The organic layer was washed with $NaHCO_3$ and NaCl solutions, then dried over $MgSO_4$. After the solvent was removed by simple distillation, 32.19 g (28 %) of β-Allenic ester **5-23** (43-53 °C fraction) were obtained by vacuum distilation (water aspirator). ^1H NMR (60 MHz): δ 5.20 (m, C=C=CH), 4.70 (dd, H_2C=C=C), 4.12 (q, $OC\underline{H}_2CH_3$), 3.06 (m, C=C=CCH_2CO), 1.25 (t, $OCH_2C\underline{H}_3$).

4-Dichloromethyl-4-methlcyclohexa-2,5-dienone (6-1)[206]

In a 3 liter three-necked round bottom flask, equipped with a mechanical stirrer, an adding funnel and a reflux condenser, 270 g of NaOH were dissolved in 1800 mL of water (15%), and 162 g of p-cresol (1.5 mol) were added. The mixture was heated at 65°C with a water bath. Over 2 h, 240 mL (3.3 mol) of chloroform were added dropwise with vigorous stirring. Stirring was maintained at the same temperature for another 30 min. After cooling, the mixture was extracted with 3 x 1 liter of chloroform. The extracts were washed with brine, dried over MgS04 and concentrated. The dark and viscous residue was distilled under oil pump. Dienone **6-1** (71.0 g, 24.5%, lit.[206] 20%, b.p. 70-72 °C/0.05 mmHg) were obtained. The pure compound **6-1** (m.p. 55.1-55.8 °C, lit.[206] 55 °C) was furnished by recystallization from hexane. ^1H NMR: δ 6.84 (d, J=10 Hz, 2H), 6.39(d, J=10 Hz, 2H), 5.73 (s, 1H), 1.49(s, 3H).

9-methyl-9-dichloromethyl-bicyclo-(3,3,1)-nonane-2,4-dimethyl dicarboxylate-3,7-dione (6-2a and 6-2b)[207]

In a 2 liter three-necked round bottom flask, equipped with a mechanical stirrer, a reflux condenser, and maintained under nitrogen, sodium (10.5 g) were dissolved in absolute methanol (230 mL). A solution of 150 g (0.78 mol) of dienone **6-1** in 100 mL of absolute methanol and 136 g (0.78 mol) of acetone dimethyldicarboxylate were added successively. The mixture was refluxed for 2.5 days, and 400 mL of methanol were distilled. The solution was exactly neutralized with 2N sulfuric acid, and then kept at 0 °C for several hours to initiate crystallization. After washed with cold water and methanol, the isomer **6-2a** (205 g, m.p.189-196 °C, lit.[208] 195-197 °C) as first fraction was obtained. ^{1}H NMR (300 MHz): δ 12.31 (s, COCHCO), 6.44 (s, $CHCl_2$), 3.81 (s, OCH_3), 3.78 (s, OCH_3), 3.77 (?, 1H), 3.14 (q, 1H), 2.86 (q, 1H), 2.55-2.28 (m, 4H), 1.37 (s, CH_3); the second fraction was **6-2b** with trace **6-2a** (7.3 g, m.p. 181-186°C). ^{1}H NMR (300 MHz): δ 12.34 (s, 1H), 6.037 (s, $CHCl_2$), 3.80 (s, OCH_3), 3.78 (s, OCH_3), 3.72 (d, 1H), 3.23 (m, 1H), 2.84 (m, 1H), 2.67 (ddd, 2H), 2.49 (d,t, 1H), 2.30 (dd, 1H), 1.61 (s, 3H). The starting dieneone **6-1** (12.22 g, 8%) was recovered from the filtrate.

9-methyl-9-dichloromethyl-bicyclo(3.3.1)-nonan-3,7-dione (6-3)

The diester **6-2** (209 g) was heated at reflux for 48 h in a mixture of acetic acid (2.1 l.) and 85% phosphoric acid (330 mL). After cooling to 50°C, most of the acetic acid was distilled with a water aspirator, then 2.4 liters of cold water was added. After

cooling for 12 h at 0 °C, the solid products were filtered and washed with cold water rapidly until mother liquid became neutral. To remove the water completely, chloroform was added and then distilled until distillate reached 61 °C. Norite was added. After filtration, the filtrat was concentrated to about 2 liters, then 800 mL of hot hexane were added. After cooling at 0 °C for 2 h, 126.6 g (90.5 %) of the dione **6-3** crystals were obtained in three fractions. ^{1}H NMR: δ 6.48 (s, $CHCl_2$), 2.89-2.68 (m, 6H), 2.39-2.33 (dd, 4H), 1.63 (s, CH_3).

Dienedione 6-4

Method A (entry 5.)

Dione **6-3** (4.42 g, 17.8 mmol) was added to a pale yellow dimethyl sulfoxide (DMSO) solution (90 mL) of potassium t-butoxide (95%, 3.6 g, 27.0 mmol) under Ar atmosphere. It was heated on a ca. 95 °C preheated oil bath for 1.5 h. In this period reaction solution turned red. After cooling to room temperature, it was poured into ice water (1 L). The mixture was extracted with three 400 mL portions of chloroform. The extracts were washed with three 400 mL portions of water, dried over $MgSO_4$, and concentrated. The residue (2.60 g) showed in ^{1}H NMR (Figure 2.6-9) to contain at least 90% of diene dione **6-4**, ca. 5% of dione **6-3**, and ca. 2% of dimer **6-7**, which could be separated by column chromatography on aluminium (grade III) or silica gel (6:1 to 4:1 hexane-ethyl acetate). dienedione **6-4:** 1.62 g (52%) ^{1}H NMR (300 MHz): δ 6.61 (d, J=10 Hz, 1H), 6.06 (d, J=10 Hz, 1H), 2.60 (m, 3H), 2.38 (q, J=9 Hz, 2H), 1.48 (s, 3H); IR (melt): 3050, 2975, 2905, 1680, 1625, 1406, 1377 cm^{-1}. dimer **6-7:** 0.30 g (8.2%), a mixture of **6-7a** and **6-7b** (1.0 : 1.1), which can be

separated by careful crystallization from ethyl acetate. **6-7a:** Calcd for $C_{22}H_{26}Cl_2O_4$: C, 61.94; H, 6.13; Cl, 16.67. Found: C, 62.12; H, 6.16; Cl, 16.67. ^1H NMR: δ 6.87 (s, CH=C), 6.65 (d, J=10 Hz, O=C-CH=C<u>H</u>), 6.05 (d, J=10 Hz, O=C-C<u>H</u>=CH), 6.56 (s, $CHCl_2$), 1.46 (s, CH_3), 1.32 (s, $C\underline{H}_3$-C-$CHCl_2$), 1.98 (d, J=13 Hz, $2CH_2$); ^{13}C NMR (TAP): δ 197.2 (C=O), 196.5 (C=O), 151.5 (<u>C</u>H=C), 145.8 (<u>C</u>H=C), 141.0 (<u>C</u>=C), 128.2 (<u>C</u>H-C), 95.0 (O-C-OH), 81.3 (CH), 75.6 (C), ? (C), ? (C), 41.7 (CH2), 39.8 (CH2), 39.0 (CH), 38.6 (CH2), 38.5 (CH2), 34.7 (CH), 34.1 (CH2), 33.8 (CH2), 26.2 (CH3), 15.7 (CH3). IR: 3385 (O-H), 3010, 2970, 2940, 2900, 1670, 1625,1470, 1375, 755 (C-Cl). X-ray (See Figure 2.6-8.): racemic.

Table 2-3. The bond distances (Å) of the dimer **6-7a**

Atom 1	Atom 2	Distance
C11	C21	1.791
C12	C21	1.792
O2	C2	1.215
O7	C7	1.223
O12	C11	1.445
O12	C13	1.441
O13	C13	1.399
C1	C2	1.512
C1	C8A	1.530
C2	C3	1.486
c3	C4	1.377
C3	C11	1.520
C4	C4A	1.515

C4A	C5	1.510
C4A	C8A	1.540
C4A	C9	1.547
C5	C6	1.331
C6	C7	1.456
C7	C8	1.500
C8	C8A	1.526
C11	C18	1.533
C11	C19	1.539
C13	C14	1.514
C13	C20	1.520
C14	C15	1.534
C15	C16	1.560
C15	C19	1.537
C16	C17	1.556
C16	C21	1.542
C16	C22	1.537
C17	C18	1.533
C17	C20	1.542

Table 2-4. The bond angles (°) of the dimer **6-7a**

Atom 1	Atom 2	Atom 3	Angle
C11	C12	C13	113.8
C2	C1	C8A	113.1
O2	C2	C1	120.3
O2	C2	C3	123
C1	C2	C3	116.7

C2	C3	C4	119.7
C2	C3	C11	118.7
C4	C3	C11	121.5
C3	C4	C4A	126
C4	C4A	C5	107
C4	C4A	C8A	111.4
C4	C4A	C9	108.3
C5	C4A	C8A	111.2
C5	C4A	C9	108.2
C8A	C4A	C9	110.7
C4A	C5	C6	124.9
C5	C6	C7	121.7
O7	C7	C6	122
O7	C7	C8	122.2
C6	C7	C8	115.8
C7	C8	C8A	111
C1	C8A	C4A	110.5
C1	C8A	C8	110.5
C4A	C8A	C8	112.2
O12	C11	C3	106
O12	C11	C18	108.6
O12	C11	C19	107.8
C3	C11	C18	110.7
C3	C11	C19	113
C18	C11	C19	110.5
O12	C13	O13	105.3
O12	C13	C14	110
O12	C13	C20	108.9

O13	C13	C14	109.3
O13	C13	C20	112.8
C14	C13	C20	110.5
C13	C14	C15	109.1
C14	C15	C16	110.3
C14	C15	C19	106.3
C16	C15	C19	111.7
C15	C16	C17	106.9
C15	C16	C21	108.67
C15	C16	C22	111.5
C17	C16	C21	108.9
C17	C16	C22	111.4
C21	C16	C22	109.4
C16	C17	C18	111.1
C16	C17	C20	110.7
C18	C17	C20	106.6
C11	C18	C17	109.5
C11	C19	C15	109.3
C13	C20	C17	108.8
C11	C21	C12	107.6
C11	C21	C16	112.3
C11	C21	C16	112.9

6-7b: ^1H NMR: δ 6.87 (s, CH=C), 6.65 (d, J=10 Hz, O=C-CH=C<u>H</u>), 6.05 (d, J=10 Hz, O=C-C<u>H</u>=CH), 6.38 (s, $CHCl_2$), 1.46 (s, CH_3), 1.39 (s, $CHCl_2CC\underline{H}_3$), 2.11 (d, J=13 Hz, $2CH_2$); dione **6-3:** 0.06 g (1.5%)

Method B (entry 2.)

Dione **6-3** (5.80 g, 23.4 mmol) were dissolved in DMSO (120 mL) at 60 °C under Ar atmosphere. tBuOK (95%, 3.8 g, 29.5 mmol)) was added. The solution turned dark red and was heated to 60 °C for 3 h. It was worked up in the same way as described for method A, giving 1.20 g of dienedione **6-4** and 0.28 g of dimer **6-7** (7%) which was crystallized from ethyl acetate (1 mL/10 mg).

Method C (entry 9.)

tBuOK (1.5 g (11.7 mmol) were dissolved in DMSO (30 mL) at 60 °C in a three-neck round bottom flask. Dione **6-3** (1.5 g, 6.05 mmol) in DMSO (30 mL) was added through a dropping funnel. The mixture was stirred at 60 °C for 1.5 h, worked up in the same way as described for method A. It gave 0.20 g (19%) of dienedione **6-4**, 0.02 g of p-cresol, and 0.02 g of compound **6-6** ^{1}H NMR: δ 6.94 (d, J=8 Hz, 1H), 6.61 (d, J=8 Hz, 1H), 4.80 (exchangeable, 1H), 3.48 (s, 2H) 3.09 (t, J=7 Hz, 2H), 2.59 (t, J=7 Hz, 2H), 2.17 (s, 3H). IR: 3600 (sharp,m), 1710 (sharp,s), 1600 (m), 1490 cm^{-1} (m).

Tricyclic trione diester 6-5

A solution of dienedione **6-4** (4.12 g), dimethyl acetonedicarboxylate (4.2 g), and sodium methoxide (from 0.45 g of sodium) in 20 mL of absolute methanol was refluxed for 28 h. The cooled mixture was acidified with 10% sulfuric acid and filtered. The precipitate was washed with cold water, dried, and crystallized from methanol-ether, yielding colorless needles of trione diester **6-5** (6.78 g, 84%). ^{1}H NMR: δ 12.35 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.23 (d, J=10 Hz, 2H), 3.00-2.83 (m, 4H), 2.78-2.70 (d,t, 2H), 2.48-2.17 (m, 6H), 1.28 (s, 3H).

Tricyclic trione VI

A mixture of diester **6-5** (6.75 g) and 10 N HCl (135 mL) in methanol (135 mL) were refluxed for 24 h, then 10 mL of additional 10 N HCl were added. Refluxing was continued until no starting diester appeared on the monitoring TLC plate (1:1 hexane-ethyl acetate) (about two days). After cooling, the reaction solution was poured into a 2 liter beaker with 600 mL cold water and exactly neutralized with saturated sodium bicarbonate solution (ca. 270 mL). The mixture was extracted with five 600 mL portions of chloroform. The extracts were washed with 5% sodium bicarbonate solution, water and brine successively, dried over $MgSO_4$, and concentrated. The pale yellow trione **VI** (4.14 g, 94%) was obtained. It could be purified by sublimation (190 °C) and gave a white solid (3.77 g, 86%). ^1H NMR: δ 2.93 (dd, J_1=15 Hz, J_2=6 Hz, 2H), 2.8 (m, 1H), 2.51-2.28 (m, 10 H), 2.19 (t, J=2 Hz, 1H), 2.14 (t, J=2 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR: δ 18.92, 33.67, 35.22, 43.62, 43.84, 44.02, 44.56, 207.31, 207.59.

Base-catalyzed hydrogen-deuterium exchange of trione VI

A mixture of 20 mg of trione **VI** in 25 mL of dry THF and 20 mg of sodium in 25 mL of D_2O was stirred at room temperature under Ar for 20 h. The resultant solution was extracted with CCl_4. The organic layers were dried over $MgSO_4$ and concentrated. The colorless deuterated trione **VI** was dissolved in $CDCl_3$. ^1H NMR: δ 2.77 (s, 1H), 2.36 (s, 2H), 1.58 (s, 3H). NOE experiment (Also see Figure 2.6-18.): (decoupler: 1.58 ppm; power: 2900/3000) only the peak at δ 2.36 responded.

Silylation of cyclohexanone 7-3 into silyl enol ether 7-4

To a solution of chlorotrimethylsilane (8.0 g, 9.5 mL, 36 mmol) and triethylamine (14.6 g, 20 mL, 72 mmole) in of dimethylformamide (24 mL) was added cyclohexanone (6.0 g, 6.4 mL, 30 mmol). The pale yellow precipitate was formed (presumably triethylamine hydrochloride). After reflux for 4.5 h, the mixture was cooled, diluted with 48 mL of pentane, and washed with 3 x 75 mL of cold aqueous sodium bicarbonate. The aqueous layer was extracted with 2 x 60 mL of pentane. The combined organic layers were washed rapidly with cold 1.5 M HCl solution, cold sodium bicarbonate solution, dried, and concentrated. Distillation with a water aspirator gave 3.50 g (70%) of silyl enol ether **7-4** (b.p. 63-65 °C / 15 mmHg). ^{1}H NMR ($CDCl_3$): δ 4.89 (t, 1H), 2.04 (m, 4H), 1.68 (m, 2H), 1.54 (m, 2H), 0.22 (s, 9H).

Palladium (II) Catalyzed Dehydrosilylation of silyl enol ether 7-4 to cyclohexenone 7-5

To a stirring solution of $Pd^{II}(OAc)_2$ (170 mg, 0.75 mmol) and p-benzoquinone (81 mg, 0.75 mmol) (sublimed at 60 °C with an aspirator.) in acetonitrile (6 mL) (distiled from P_2O_5 then CaH_2), silyl enol ether **7-4** (170 mg, 1.0 mmol) was added under nitrogen at room temperature. The mixture was stirred for 17 h, filtered through selite with CCl_4, and then concentrated. ^{1}H NMR ($CDCl_3$): **7-5:** δ 6.95 (dt, 1H), 5.94 (d, 1H), 2.38 (t, 2H), 2.30 (m, 2H), 1.96 (m, 2H). p-BQ: 6.73 (s).

Silylation of trione VI to trisilyl enol ether 7-1

To a solution of chlorotrimethylsilane (1.5 mL, 5.6 mmole) and triethylamine (2.5 mL, 9 mmole) in dimethylformamide (2.5 mL), was added trione **VI** (229 mg, 1.0 mmole). The pale yellow precipitate was formed (presumably triethylamine hydrochloride). The mixture was refluxed at 120 °C bath for 44 h and then cooled. All volatile materials (DMF, NEt_3, Me_2SiCl) were evaporated with a rotatory evaporator and an oil pump. A white solid trisilyl enol ether **7-1** was obtained. This compound was vary unstable and reconverted to the starting trione **VI** during evaporating at 55° or crystallization in boiling CCl_4, while it could be stored in a refrigerator overnight. ^1H NMR ($CDCl_3$): δ 4.79 (d, J=5.4 Hz,1H), 4.57 (d, J=14.1, 2H), 2.60-1.66 (m, 9H), 0.9 (s, 3H), 0.20 (s, 9 H), 0.18 (s, 9H), 0.15 (s, 9H).

Palladium (II) Catalyzed Dehydrosilylation of trisilyl enol ether 7-1

To a stirring solution of $Pd^{II}(OAc)_2$ (450 mg, 2.0 mmol) and p-benzoquinone (216 mg, 2.0 mmol) (sublimed at 60 °C with an aspirator.) in acetonitrile (25 mL) (distiled from P_2O_5 then CaH_2.), trisilyl enol ether **7-1** (the product from the last reaction, 1.0 mmol) was added under nitrogen at room temperature. The resultant mixture was stirred for 20 h. After column chromatography (silica gel, 100:1 CH_2Cl_2-CH_3OH) an yellow oil was obtained. ^1H NMR ($CDCl_3$) showed the peaks δ 6.49 (s), 6.32 (s), 0.08 (s).

Trimethyl triols 8-1

In a Schlenk tube flushed with nitrogen, 7.5 mL of 1.5 M of methyllithium were mixed with 25 mL of dry ether. A solution of trione **VI** (0.50 g) in dry THF (40 mL) in a dropping funnel was added

to the Schlenk tube at 0 °C. The clear solution was warmed up to room temperature over 4 h, then stirred for 2 days. The excess methyl lithium was destroyed at 0 °C by cautious addition of a saturated sodium sulfate solution until the methane evolution had stopped. After addition of 25 mL of water, the reaction mixture was extracted continuously with ether for 3 days. The organic layers were dried over $MgSO_4$ and concentrated to give a colorless solid, trimethyl triols **8-1** (0.5 g). ^1H NMR: δ 3.54 (t, J=14 Hz, 2H), 2.80 (m, 1H), 2.10 (d, J=4 Hz, 1H), 2.05 (d, J=4 Hz, 1H), 1.90 (m, 4H), 1.56 (s, 2H), 1.43 (m, 7H), 1.24 (s, 9H), 1.20 (t, 1H), 1.00 (s, broad, 20H), 0.98 (s, broad, 10H), 0.96 (s, 3H). IR: 3450 (broad, s, OH), 1705 cm^{-1} (s).

Triene 8-2

To an ice-cold solution of triols **8-1** (140 mg (0.5 mmole) in dry pyridine (1.7 mL), was added distilled phosphoryl chloride (0.34 mL) under nitrogen over 0.5 h. The mixture was stirred for 1 h at 0 °C. A white precipitate formed. The reaction mixture was warmed up to room temperature over 1 h, then added to 10 mL of water cautiously. Hexane (10 mL) were added. The mixture was washed with a lot of cold water, dried over $MgSO_4$, and concentrated. The residue (40 mg) was obtained, which shown at TLC in hexane only 2 spots (Rf_1 = 0.40, Rf_2 = 0.01). After flush column chromatography (silica gel, hexane) 20 mg (20%) of colorless solid was furnished. ^1H NMR: δ 5.5-4.5 (m, 3H), 2.4-1.9 (m, 6H), 1.643 (s, 9H), 1.268 (m, 3H), 0.860, 0.844, 0.824 0.815 (3H). GC/MS analysis shows 8 peaks:

Peak #	R.T. min.	Corr. % Max.	% of total	Mol. ion m/z

1	17.78	100.00	42.30	228
2	17.86	14.96	6.33	228
3	20.46	30.43	12.87	230
4	20.57	10.06	4.26	230
5	20.65	15.85	6.70	230
6	20.86	48.53	20.53	230
7	22.04	5.69	2.41	214
8	25.19	10.90	4.61	232

Bromination of triene 8-2

In a round bottom flask equipped with a reflux condenser and kept under nitrogen, 20 mg (0.1 mmole) of triene **8-2** were dissolved in 50 mL of dry carbon tertrachloride, and 100 mg (4 equimoles) of N-bromosuccinimide were added. To initiate the reaction, the mixture was irradiated with a sunlight bulb and refluxed until the residual solid, succinimide, stayed in suspension at the surface about 30 min. The reaction mixture was cooled, filtered, and washed with sodium bisulfite and water. The extraction with ether yielded 40 mg of yellow oily bromide **8-3**. TLC (Rf=0.06, hexane).

Dehydrobromination of bromide 8-3

A yellow solution of bromide **8-3** (40 mg) in dry benzene (3 mL) was added dropwise into a mixture of potassium t-butoxide (120 mg) in dry benzene (3 mL) in a ice-water bath under nitrogen. After the reaction mixture was stirred for 30 min, the ice-water bath was removed. After 60 min and 70 min, a spot (Rf=0.6) shown

on monitoring TLC plate. GC/MS: The peak at 17.28 min has M.I. m/z 226 and the highest fragment m/z 107.

Triphenyl triol 9-1

1.17 g (48 mmol) of Mg were placed in a three neck round bottom flask. 7.54 g (48 mmol) of PhBr were dissolved in 30 mL of anhydrous ether in a dropping funnel. About 2 mL of PhBr solution were added into the flask with stirring and warm water bath under Ar. When the reaction started (color turned yellow-brown) in about a half min, the rest of PhBr solution was added dropwise and kept the condensing rate at 1 drop / second. The mixture was refluxed for other 15 min then cooled to room temperature. 1.26 g (5.5 mmol) of trione **VI** in 45 mL of dried THF were added, then the mixture was refluxed for 10 h. After cooling, 50 mL of ice water followed by 10 g of NH_4Cl in 30 mL water were added. The mixture was extracted with 4 x 50 mL of ether. After dried and evaporated, the residue, 3.2 g of yellow oil, were purified by column chromatography (silica gel, 60-100 mesh, 3 x 30 cm, 85:15-40:60 hexane-ethyl acetate). 2.3 g (90%) of triol **9-1** were obtained. ^1H NMR ($CDCl_3$): δ 7.60 (d, J=7.4 Hz, 2 H), 7.52 (d, J=7.4 Hz, 3H), 7.36 (t, J=7.4 Hz, 4 H), 7.26 (m, 4 H), 6.93 (t, J=7.4 Hz, 1 H), 6.83 (d, J=7.7 Hz, 1 H), 3.10 (t, J=15 Hz, 2 H), 2.98 (t, J=13 Hz, 1 H), 2.46 (dd, J_1=15 Hz, J_2=7 Hz, 2 H), 2.22 (dt, J_1=15 Hz, J_2=5 Hz, 2 H), 1.98 (t, J=13 Hz, 2 H), 1.6 (m, 6 H), 1.31 (s, 3 H), 1.48 (s, 1 H, exchangeable), 1.45 (s, 2 H, exchangeable).

Triphenyl triene 9-2

Triol **9-1** (2.66 g, 5.8 mmol) and p-toluene sulfonic acid (0.17 g, 0.87 mmol) in benzene (55 mL) were refluxed for 40 min in a round

bottom flask with a Dean Stark tube (25 mL). At the end of this period, TLC showed a spot at R_f = 0.66 in hexane. After washing with $NaHCO_3$, NaCl and H_2O respectively, the mixture was dried over $MgSO_4$, then the solvent was evaporated. Short column purification with hexane gave 0.97 g (41.5%) of triene **9-2.** ^1H NMR ($CDCl_3$): δ 7.5-7.2 (m, 15 H), 6.41 (d, J = 6 Hz, 0.3 H), 6.17 (d, J = 5 Hz,1 H), 5.95 (d, J = 9 Hz, 1.7 H), 3.05-2.10 (m, 9 H), 1.06 (s, 3 H).

Dehydrogenation of triphenyl triene 9-2 with DDQ

In a small round bottom flask filled with Ar, 40 mg (0.098 mmol) of triene **9-2** were dissolved in 2 mL of distiled anisole. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (82 mg, 0.36 mmol) was added. The mixture was refluxed for 30 min. After cooling, the reaction mixture was separated by column chromatography (silica gel, 2 x 30 cm). After anisole was removed with hexane, a bright yellow compound (R_f = 0.12 in hexane/benzene 2:1; R_f = 0.06 in hexane) was collected with CCl_4, while DDQ and the red compounds left in the column. The whole process must be under Ar, otherwise, the bright yellow compound converted to the red compounds. This bright yellow compound has fluorescence (emission at 522 nm., Max. at excitation 495 nm.) UV (CCl_4): λ_{max}: 504.8 nm, 473.1 nm, 387.3 nm, 368.1 nm. ^1H NMR ($CDCl_3$): singlet peeks: δ 8.88, 8.39, 8.18, 7.98, 7.86; multiplet peaks: δ 7.6-6.8.

Bromination of triene 9-2 with Br_2

In a small round bottom flask, 41 mg (0.1 mmol) of triene **9-2** were dissolved in 1 mL of dried CCl_4. Dried Br_2 (0.016 mL) was injected into the flask until orange-colored is steady in an ice-salt

bath under Ar. The solution was warmed up to room temperature and stirred for 2 days. The solvent was evaporated. A yellow solid (60 mg) was obtained.

Bromination of triene 9-2 with $C_5H_5N^+HBr_3^-$

Triene **9-2** (41 mg, 0.1 mmol) and $C_5H_5N^+HBr_3^-$ (96 mg, 0.3 mmol) in $CHCl_3$ (3 mL) were stirred under Ar in a salt-ice bath, and gradually warming to room temperature over 16 h. The resulted solution was washed with sodium disulfide and sodium chloride solution, and then dried over $MgSO_4$. After evaporation, 60 mg of yellow solid were obtained.

Dehydrobromination of Hexabromide 9-3

Hexabromide **9-3** (60 mg) was dissolved in dry THF (2 mL) under Ar. KOtBu (90 mg) was added in an ice bath. After stirring for 2 h, a bright yellow compound was collected in CCl_4 with short column chromatography. Rf = 0.06 in hexane. UV (CCl_4): λmax: 505.6 nm, 472.3 nm, 388.1 nm, 368.1 nm. ^1H NMR ($CDCL_3$): singlet peaks: δ 8.5, 7.9; multiplet peaks: δ 7.6-6.8; doublet peek: about δ 4.

Triene 10-2

Trione **VI** (2.7 g, 11 mmol) and p-toluenesulfonylhydrazide (8.2 g, 44 mmol) in methanol (50 mL) were refluxed for 2 h. By distillation, methanol and water were replaced by benzene then by THF. To the tris-tosylhydrazone **10-1** residue (about 14 g) in 50 mL of dry fresh THF, were added 75 mmol of methyllithium (50 mL, 1.5 M in ether) at 0 °C. After 15 min, water was added and the organic layer was extracted with ether. The ethereal solution was dried and

concentrated. The first fraction on column chromatography (silica gel, petroleum ether) was the pure triene **10-2** in 23% overall yield. GC/Mass spectra: m/e 186 (M^+), 171 ($M\text{-}Me^+$), 157, 143, 129, 117, 104, 91, ... ^1H NMR: δ 5.3-5.8 (m, 6H), 1.7-2.5(m, 9H), ca.1.0 (4 s, 3H).

Bromination of triene 10-2 with pyridinium hydrobromide perbromide

To 0.10 (0.54 mmol) of triene **10-2** in 4 mL of chloroform, was added 0.57 g (1.78 mmol) of pyridinium hydrobromide perbromide salt and stirred for 5 days, leaving some red perbromide salt in the reaction solution. After washing with $NaHSO_3$ and NaCl solution, dried over $MgSO_4$ and concentrated, 0.23 g of pale yellow solid at recover yield 64% was obtained. ^1H NMR ($CDCl_3$): δ 6.5 through δ 5.2 (m, vinyl H's, 1 part), 5.2 through 4.3 (m, bromo H, 3 parts). The conversion yield 75% and the total yield was 48% for hexabromide **10-3**.

Bromination of triene 10-2 with Br_2

To a solution of triene **10-2** (0.63 g, 3.39 mmol) in methylene chloride (42 mL), were added 2.35 g of distilled bromine in an ice bath under Ar. The yellow solution was stirred for 3 days at room temperature, and then 30 mL of methylene chloride and 30 mL of sodium disulfide were added. The organic layer was washed with 2 x 30 mL of brine and water each, dried over $MgSO_4$ and concentrated. A colorless solid (1.94 g, 90%, m.p. 66-70°) was obtained. ^1H NMR ($CDCl_3$): δ 6.5 through δ 5.2 (m, vinyl H's, 6 part), δ 5.2 through δ 4.3 (m, bromo H, 39 parts). The conversion yield 87% and the total yield

was 79% for hexabromide **10-3**. MS: m/z=186, 171, 157, 143, 129, 117, 104, 91, 81.

Dehydrobromination of 10-3 with tBuOK

tBuOK (0.42 g, 3.2 mmol) was added to a solution of bromide mixture **10-3** (0.21 g, 0.54 mmol) in THF at 0 °C under Ar. After stirring for 2 h at the same temperature, the reaction was quenched by addition of saturated Na_2SO_4 solution and 10% H_2SO_4 solution. The mixture was extracted with ether. The extrats were dried and concentrated. A yellow solution was obtained after a column chromatography (silica gel, hexane). TLC showed two spots: R_{fA} = 0.57 (shown under UV and I_2), R_{fB}= 0.49 (shown under I_2 only) in hexane. All solvents and solutions used were saturated with Ar.

Dehydrobromination of 10-3 with DBU

DBU (1.82 mL, 12 mmol) was added dropwise to a solution of bromide mixture **10-3** (0.666 g, 1 mmol) in benzene (30 mL) at 5-10 °C under Ar. After refluxing overnight under Ar, the reaction solution was washed with 10% H_2SO_4 solution then extracted with 2 x 100 mL of heptane. (Using heptane instead of pentane is for evaporating benzene later on.) The organic layers were washed with brine, dried over $MgSO_4$, and concentrated with the modified rotatory evaporator under Ar. After column chromatography (Al_3O_2, pentane), An yellow solution (50 mL, **A** and **B** in petane) was collected. To determine the yield, 10 mL of the yellow solution were concentrated under Ar with the modified rotatory evaporator and 19 mg of yellow solid were obtained. The yield was 52.2%.

Conversion of the bromopentaenes 10-6 and 10-7 into pentaenes 10-4 and 10-5

To about 0.037 mmol of **A** and **B** mixture (freshly concentrated from 10 mL of 0.0075 M in petane) in 2 mL of dried THF, was added 0.05 mL of 1.7 M t-buttyllithium (0.085 mmol) at -78° under Ar. The solution was stirred for 30 min at the same temperature. During this period, its color turned red then green. After quenching with methanol and careful work up under Ar, a yellow solution was obtained, which showed only pentaene **10-4** and **10-5** (ca. 10:1) in the GC and GC/MS. The UV spectrum showed Max: 396 nm, They could concentrated at ca. 30 °C under ca. 15 mmHg in the modified rotatory evaporator under Ar. It can be stored in a refrigerator under Ar for a week when the concentration was 0.01 M, while it was kept at room temperature in a NMR tube filled with Ar for only few h when the concentration was 0.1 M, but it was not stable at pure form. ^{13}C NMR ($CDCl_3$) shows the ten sp^2 hybridized carbons: δ 137.6, 130.6, 128.0, 127.6, 126.0, 122.9, 122.2, 121.9, 118.2, 104.9. for ^{1}H NMR see discussion section.

Dehydrogenation of the pentaenes 10-4, 10-5 and bromopentaenes 10-6, 10-7 with DDQ

Pentaenes and bromopentaenes mixture (0.02 mmol) and DDQ (0.02 mmol) in of benzene (2 mL) were stirred at room temperature (or reflux) for 2 h. The reaction solution was washed with sodium sulfite, sodium hydroxide and brine solutions, dried over $MgSO_4$ and concentrated. A yellow compound was obtained. In GC/Mass spectra, it yields the peaks at m/z 180, 152, and 76. It is surprised stable so that can be isolated to be yellow solid. Its ^{1}H NMR spectrum and TLC

(R_f = 0.1 in hexane) were exactly the same as known perinaphthenone. ^1H NMR: δ 6.72 (d, J=10 Hz, 1H), 7.58 (dd, J_1=7 Hz, J_2=8 Hz, 1H), 7.74(d, J=10, 2H), 7.76(t, J=8 Hz, 1H), 8.01 (d, J=8 Hz, 1H), 8.19 (dd, H_1=8 Hz, J_2=1 Hz, 1H), 8.62 (dd, J1=7 Hz, J2=1 Hz, 1H). That they are the same compound is confirmed by UV (in hexane): Max.(nm) 376, 354, 313, 259, 252, 246, 241.

Formation of Indenyl anion with Methylsulfinyl (dimsyl) Carbanion

After the all-in-one-piese apparatus (See section 2.10) was flashed with Ar, 0.12 mmol of sodium hydride (5.1 mg, 57%) was placed in the reaction container and washed with dry pentane by a syringe (adding-withrowing-vacumn, 4 times). DMSO-d_6 (1.2 mL, 8.3 mol %) were added. The suspension was stirred at 70-75° for 30-40 min. During this period hydrogen gas was evolved, and a almost clear pale gray solution of dimsyl anion was formed.[192,208] When it cooled to room temperature, 0.1 mmol of indene (11.6 mg, fresh distiled) was added. The solution turned to deep blue immediately and was transfered into the NMR tube through the build-in filter by positive Ar pressure. ^1H NMR (Figure 2.10-26): δ 7.05 (dd, J_1= 6 Hz, J_2=3 Hz, 2H), 6.33 (t, J=3 Hz, 0.25H), 6.33 (d, J=3 Hz, 0.5H), 6.33 (s, 0.25H), 6.17 (dd, J_1=6 Hz, J_2=3 Hz, 2H), 5.68 (d, J=3 Hz, 2 x 0.25 + 0.50 = 1H) indicating that there is 25% of indenyl anion, 50% of 1-d-indenyl anion and 25% of 1,3-d_2-indenyl anion. The ^1H NMR spectrum after 13 h (Figure 2.10-27) showed that the peak at δ 6.33 became singlet and the peak at δ 5.68 completely disappeared, which indicated that 100% of 1,3-d_2-indenyl anion formed.

The reaction of the pentaenes 10-4, 10-5 and bromopentaenes 10-5, 10-6 with Methylsulfinyl (dimsyl) Carbanion

After the all-in-one-piese apparatus (See section 2.10) was flashed with Ar, 0.20 mmol of sodium hydride (10 mg, 57%) was placed in the reaction container and washed with dry pentane by a syringe (adding-withrowing-vacumn, 4 times). DMSO-d_6 (0.5 mL) was added. The suspension was stirred at 70-75° for 40 min. During this period hydrogen gas was evolved, and a almost clear pale gray solution of dimsyl anion was formed.[192,211] When it cooled to room temperature, a solution of ca. 0.05 mmol of pentaenes **10-4, 10-5** and bromopentaene **10-5, 10-6** in DMSO-d_6 (0.5 mL) was injected. The reaction solution turned to deep blue immediately and was transfered into the NMR tube through the build-in filter by positive Ar pressure. ^{1}H NMR: δ 5.87 (t, J=7.5 Hz, 3H), δ 5.07 (d, J=7.5 Hz, 6H), (Figure 2.10-30) for phenalenyl anion (lit.[209] 60 mHz, lithium salt, δ 5.91, δ 5.17, J=7.5 Hz); δ 1.13 (s, 3H) for $CH_3D_2SOD_3$ which confirmed by following reaction.

Ethyl methyl sulfoxide

A solution of m-chloroperbezoic acid (6.9 g, 36 mmol) in methylene chloride (600 mL) was added dropwise to a solution of ethyl methyl sulfide (3.65 mL, 40 mmol) in methylene chloride (350 mL) at 0 °C. The mixture was stirred for 5.5 h at same temperature, and then washed with 3 x 200 mL of saturated sodium bicarbonate solution. The aqueous layer was extracted with 3 x 200 mL of methylene chloride. The combined organic layers were dried over $MgSO_4$ and evaporated with a rotatory evaporator. Pure ethyl methyl

sulfoxide (1.8 g) was obtained by distillation with an oil pump (b.p. 26 °C / 0.03 mmHg) and with ice water for condensing distillat. ^{1}H NMR (DMSO-d_6): δ 2.72 (m, 1H), 2.58 (m, 1H), 2.45 (s, 3H), 1.13 (t, J = 7.5 Hz). IR (neat): 1055 cm^{-1} (RR'S=O).

Formation of indenyl anion with t-butyllithium

In a NMR tube equipped two needles with a septum, one for Ar input and another for Ar exit, 0.85 mmol (0.1 mL) of indene in 0.6 mL of THF-d_8 followed by 0.85 mmol of tBuLi (1.7 M in pentane, 0.5 mL) was injected at -78°. The solution turned yellow then red brown from colorless in 10 minutes. ^{1}H NMR shown a very neat spectrum for indenyl anion (Figure 2.10-32): δ 7.279 (dd, J_1 = 6.0 Hz, J_2=3.0 Hz, 2H), δ 6.443 (t, J=2.7 Hz, 1H), δ 6.429 (dd, J_1=6.0 Hz, J_2=3.0 Hz, 2H), δ 5.858 (d, J=2.7 Hz, 2H).

The reaction of pentaenes of 10-4 and 10-5 with t-butyllithium followed by protonatation

In a NMR tube equipped two needles with a septum cap, one for Ar input and another for Ar exit, pentaenes **10-4** and **10-5** (0.1 mmol, concentrated to ca. 0.2 mL in pentane) in THF-d_8 (0.6 mL) and tBuLi (0.85 mmol, 1.7 M in pentane, 0.5 mL) was injected at -78°. The solution turned yellow then red brown from colorless in 10 min. ^{1}H NMR spectra were various. The peaks δ -2.5, 5.4 and 7.2 showed at -78°; the peaks δ -1.2 (t), -0.2 to -0.1 (d's and s's), 4.60 (s), 5.30 (s), 6.90 (d), 6.92 (d) et al. showed at room temperature.

To above brown solution, was added 0.2 mL of methanol for protonatation. A yellow solution was given and the AA'BB' system shown at δ 7.5 to δ 7.7 in the ^{1}H NMR.

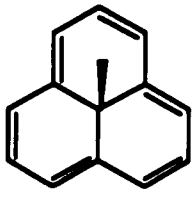
CHAPTER THREE. THEORIES

3.1. An Unusually Weak Carbon-Carbon Bond

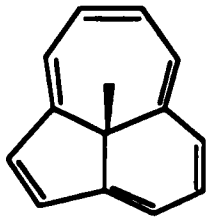
The pentaenes **10-4** and **10-5** were treated with DDQ at 80 °C giving perinaphthenone **10-8**, and treated with sodium dimsyl at room temperature furnishing phenalenyl anion. (See section 2.10.) In both cases, the stable planar highly conjugated structure, the dramatic phenalene system,[210] was formed. As a result, the central methyl was lost via either radical or nucleophilic substitution mechanisms.[211,192] In addition, syntheses of trimethyl and triphyl derivatives have not been achieved, after years of effort. Therefore the following question was raised out of curiosity to me.

How weak is carbon-carbon bond of the methyl in 13-methylphenalene?

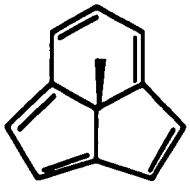
To answer this question, AM1 calculation for 13-methyl-phenalene **X**, 9b-methyl-9b*H*-benzo[cd]azulene **XI**, 7b-methyl-7b*H*-cyclopent[cd]indene **XII** and their radical without methyl (**Xr**, **XIr** and **XIIr**) have been done.



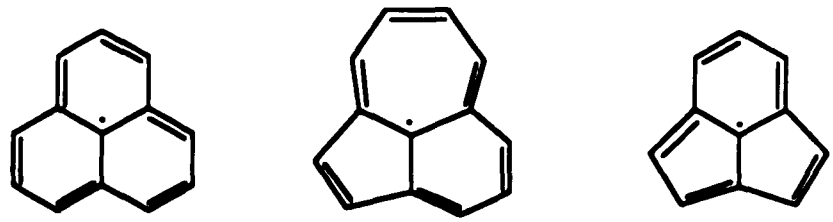
X



XI



XII



Xr XIr XIIr

Bond Dissociation Energies

As listed on Table 3.1-1, the bond dissociation energy of **X** is as low as 8.71 kcal per mole, which implies an unusually weak bond energy. On the contrary, that of **XI** is 29.57, **XII** is 52.02, and the average C-C bond is 81[212].

Table 3.1-1. Bond Dissociation Energy of tricyclic **X**, **XI** and **XII**

	Hf	Hf_r	Bond Dissociation Energy (Kcal/mol)
X	92.56	70.02	8.71
XI	102.37	100.69	29.57
XII	116.25	137.02	52.02

Hf is the heat of formation for the compounds; Hfr is the heat of formation for the corresponding radical.

The heat of formation of methyl radical (Hf_{rme}) is 31.25 kcal/mol.

Bond Dissociation Energies equal (Hf_r + Hf_{rme}) - Hf.

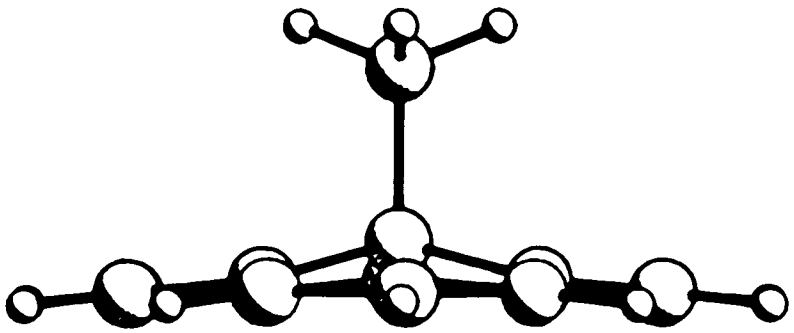
Geometry and Bond Length

The unusually weak bond for **X** also was shown in the long bond length, 1.575 Angstrom, to be contrasted with 1.531 for **XI** and 1.513 for **XII**. In addition the small bond angle, 103.4 °, compared to 108.2 ° for **XI** and 112.3 ° for **XII**. (See Table 3.1-2.) The small bond angle implies that the hybridization of central carbon is closer to sp^2 and the peripheral of the compound has a greater tendency to be planar, as shown in Figure 3.1-1.

Table 3.1-2. The bond length and bond angle of **X**, **XI** and **XII**

	Me-C bond length (Angstroms)	Me-C-C bond angle (Degrees)
X	1.575	103.4
XI	1.531	108.2
XII	1.513	112.3

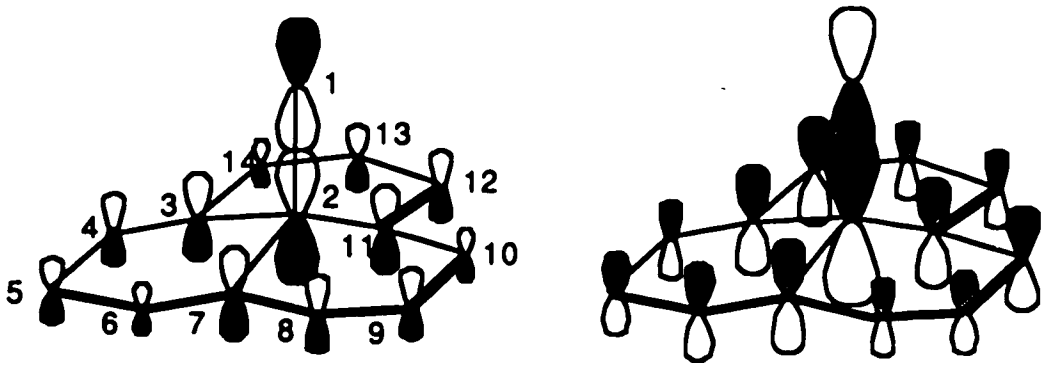
Figure 3.1-1 The nearly planer geometry for the periphery of **X**



Y-Hyperconjugation

The following data showed the lowest occupied π orbitals of **X**, and a very interesting picture was displayed. Conjugation was found to include not only the periphery of the ring, but also the central Me-C σ bond. (Figure 3.1-2)

Atom No.	Orbital 19 E = -14.61 (kcal/mol)	Orbital 20 E = -14.50 (kcal/mol)
1	+.218	-.254
2	-.233	+.298
3	-.130	+.163
4	-.096	+.094
5	-.085	+.113
6	-.063	+.156
7	-.125	+.177
8	-.092	+.100
9	-.078	+.112
10	-.055	+.151
11	-.111	+.169
12	-.089	+.095
13	-.081	+.109
14	-.065	+.147



Orbital 19 Orbital 20

Figure 3.1-2. The Y-hyperconjugation in 13-methylphenalene **X**

The hyperconjugation between the σ C-C bond and the π double bond in the allyl structure shown in Figure 3.1-3, occurs in three allyl structures instead of one, Y shaped ones as in orbitals 19 and 20. This is now called *Y-hyperconjugation*.

Since hyperconjugation may help bonds dissociate, this *Y-hyperconjugation* could help the methyl group dissociate even more strongly.

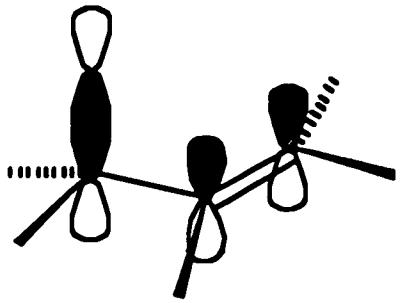


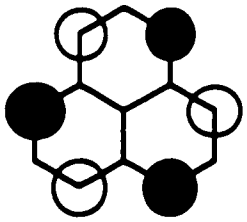
Figure 3.1-3. The hyperconjugation in the allyl structures

The Heat of Formation of The Radicals

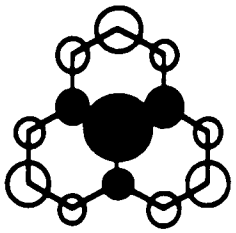
Table 3.1-1 also shows a surprisingly low energy, 70.02 kcal, for **Xr**, but 100.69 kcal for **XIr** and 137.02 kcal for **XIIr**.

The calculation results showed perfect planer geometry for all three cases. The low energy for **Xr** is due to D_{3h} symmetry. (See section 3.2) The π occupied molecular orbitals showed a very interesting Y-conjugation as in Figure 3.1-4.

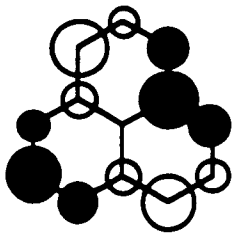
This low heat of formation of **Xr** could be the thermodynamic reason causing the break of C-CH_3 bond in compound **X**.



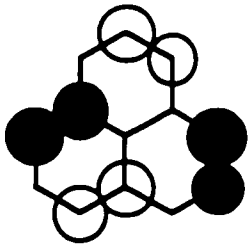
$E\psi_7$ = -4.43 kcal



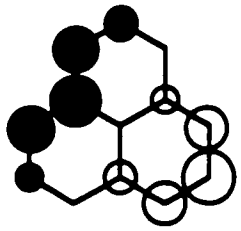
$E\psi_4$ = -9.56 kcal



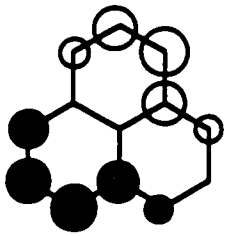
$E\psi_5$ = -9.53 kcal



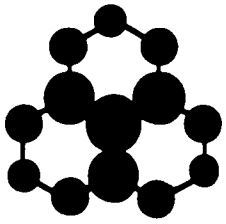
$E\psi_6$ = -9.52 kcal



$E\psi_2$ = -12.25 kcal



$E\psi_3$ = -12.25 kcal

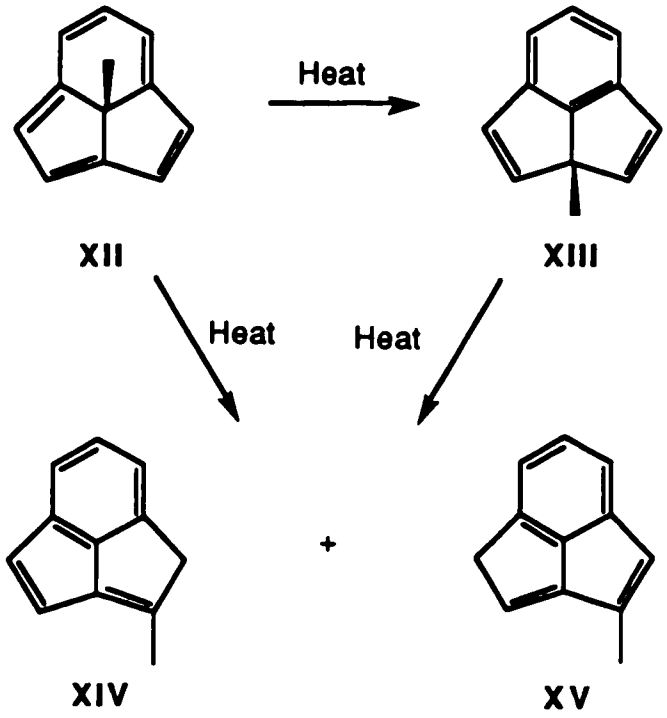


$E\psi_1$ = -14.65 kcal

Figure 3.1-4. The π OMO of Radical **Xr**

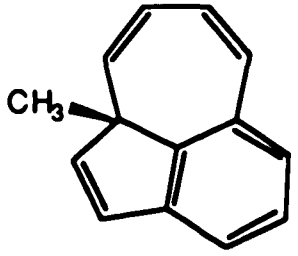
σ Shift of Methyl Group

In the case of 7b-meyhyl-7b*H*-cyclopent[cd]indene **XII**,[213] the methyl-group shift was achieved in best yield (78%) by flash-vacuum pyrolysis at 400 °C (or 673 K)/0.3 mmHg. The 2a*H*-isomer **XIII** is an oil. When the flash-vacuum pyrolysis was carried out at high temperatures (700 °C), further rearrangement occurred to give a 2:1 mixture of the 1*H*-isomer **XIV** and **XV**.



XII **XIII** **XIV** **XV**

In the case of 9b-methyl-9b*H*-benzo[cd]azulene **XI**[214], a presumably sigmatropic, methyl-group shift takes place, (see section 1.2 B.) and 9a-methyl-9a*H*-benz[cd]azulene **2-24** (yellow oil) having a benzenoid partial structure is formed at 80 °C (in DMSO), quantitatively within 15 minutes in boiling xylene (139 ° or 412 K).



2-24

Since $-\Delta G = RT\ln Keq$

So $T_1/T_2 = \Delta G_1/\Delta G_2$ (1)

Or $T_1 = T_2\Delta G_1/\Delta G_2$ (2)

Adapt $T_{XII} = 673$ K, $T_{XI} = 412$ K

$\Delta G_{XII} = 52.02$ kcal, $\Delta G_{XI} = 29.57$ kcal

(See Table 3.1-1)

Test $T_{XII} / T_{XI} = 673$ K / 412 K = 1.63

$\Delta G_{XII} / \Delta G_{XI} = 52.02$ kcal / 29.57 kcal = 1.76

Error = 1.76 - 1.63 / 1.63 = 8.0%

Considering $T_{XII} = 673$ K is at 0.3 mmHg

So equations (1) and (2) are quite good for this case.

Now use equation (2) to predict

$$T_X = T_{XI}\,\Delta G_X/\Delta G_{XI} = 412\text{ K} \times 8.71\text{ kcal} / 29.57\text{ kcal}$$
$$= 121\text{ K}$$

because Error = 8.0%

therefore T_X should be 121 K(100% ± 8.0%) = 111-131 K

or -162 to -111 °C

Presumably in the case of **X**, a sigmatropic methyl-group shift would take place at temperatures above -111 °C. The assumed product of a 1,5-σ shift, 9-methylphenalene **XVI**, has not been observed, because **XVI** is favorable for isomerization to the 1-(or 6-)-methylphenalene **XVII**[215] as shown in Figure 3.1-5.

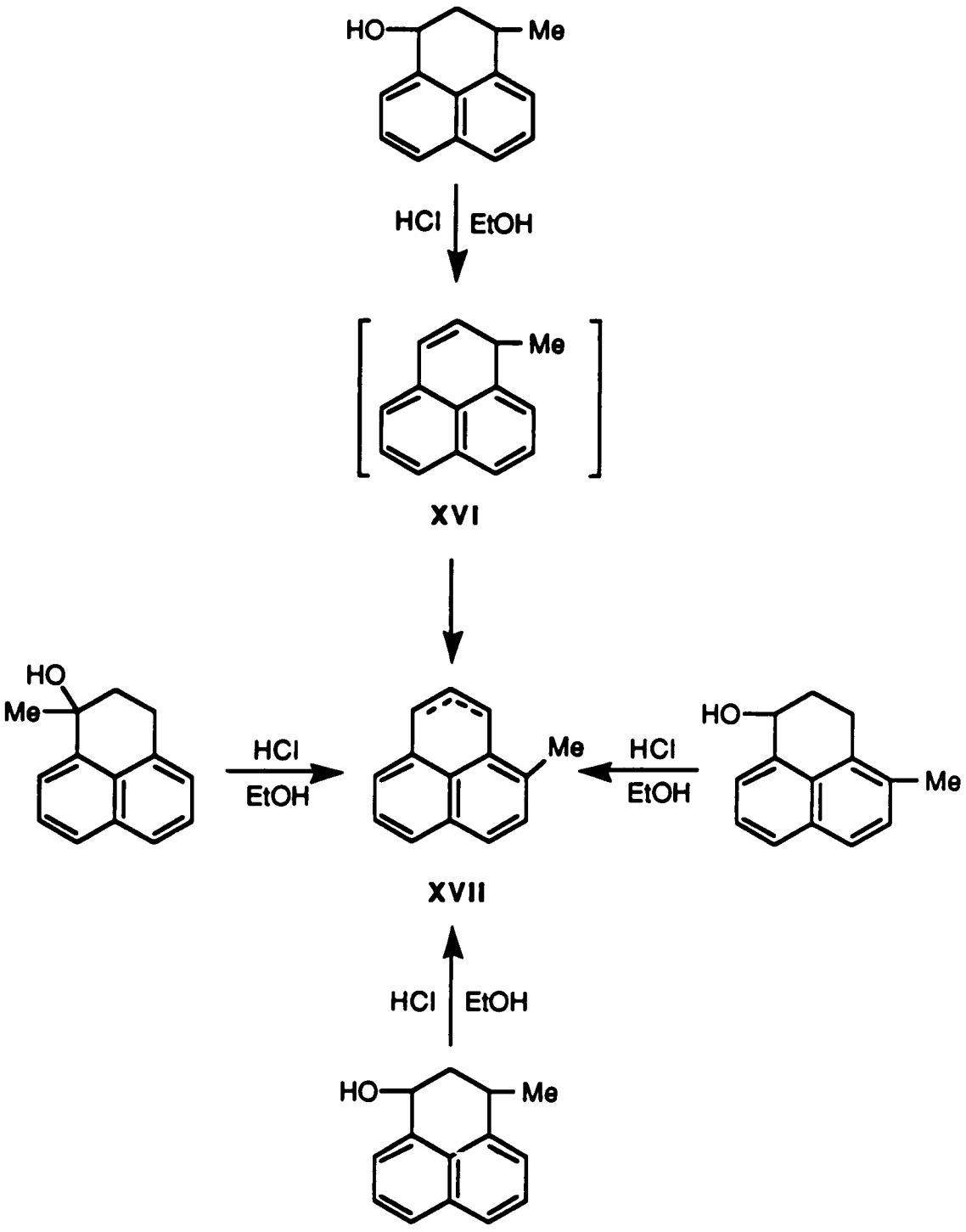


Figure 3.1-5. The unfavorable 9-methylphenalene **XVI** and the formation of 1- (or 6-)-methylphenalene **XVII**

3.2 A NEW AROMATIC SYSTEM: D_{3h} SYMMETRY, 6N π ELECTRONS

Introduction

As soon as phenalene and some its derivatives including phenalenyl anion were synthesized by Boekeheide and Larrabee in 1950, they cleverly predicted: "The symmetry of the perinaphthenyl (or phenalenyl) ion or radical makes possible a considerable amount of resonance stabilization of these entities."[216] Unfortunately, this prediction was proved with our experiment in a different way. Therefore further study of the phenalene system and its related systems become helpful.

In 1956, a yellow microcrystalline solid of phenalenyl cation **XVIII**$^+$ was prepared first by R. Pettit.[217] It was the second stable hydrocarbon ion, prepared after tropylium salts.[218] Its *pKa* should be somewhat less than that for tropylium and benztropylium cations.[219] About this unusually stable 12 π electron system a number of theoretical and experimental studies have been reported.[220]

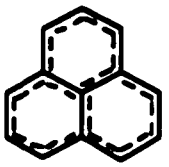
There is another unusually stable 12 π electron system, acepentalenyl dianion **XIX**$^{2-}$. It was predicted, by Butenschon and Meijere, with MNDO calculation in 1985[221] that it should be a closed-shell system with trigonal planar geometry. Within one year, this dianion dipotassium salt was quite simply prepared from triquinacene.[222]

In the last two decades, the notion of Y-aromaticity was introduced. In this trimethylenemethane dianion (TMM^{2-}) **XX**$^{2-}$ plays a major role. In 1969, Finnegan quoted a value of 26 kcal/mol for its resonance energy, ca. 11 kcal/mol more than that of the

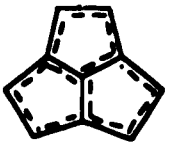
corresponding monoanion (based presumably on Hückel calculations).[223] Its dilithium derivative was prepared and characterized by Klein and Medlik in 1973.[224] XX^{2-} adapts a planar symmetrical delocalized geometry of D_{3h} symmetry. Application of the Hess and Schaad method to XX^{2-} gave a value of 0.069ß as its resonance energy per atom (REPA)[225] which is comparable to that of benzene (0.065ß). Mills found that the ^1H NMR chemical shift of XX^{2-} (δ 0.23) has a linear relationship with aromatic ions in chemical shift-charge density correlations.[226] All of above criteria and some other theoretical studies[227] support XX^{2-} having aromatic character.

To my knowledge, there has been no reported suggestion of aromaticity for $XVIII^{+}$ and XIX^{2-}.

In this section, I will try to explore the relationship between aromaticity and $XVIII^{+}$, XIX^{2-} and XX^{2-}.



XVIII



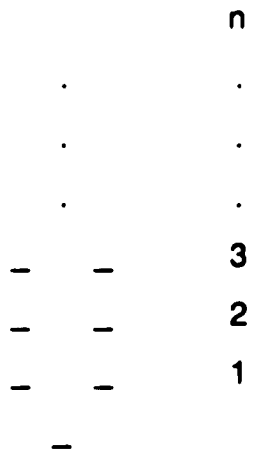
XIX

XX

Figure 3.2-1. The parent members of the new aromatic syst em

Application of Group Theory

Since Hückel applied his approximation to monocyclic polyenes, the (4n+2) rule seems to be an inviolable criterium for aromatic compounds, due to the configurations of their molecular orbitals, always being 1,2,2,2,...as follows.



Obvioursly, (a) (4n+2) electrons are needed to fill up the closed shell π-orbitals as HOMO; (b) 4n electrons for the opened shell degenerate π-orbitals.

This phenomenon can be explained with the help of group theory. Monocyclic (all cis-double bonds) hydrocarbon[228] molecules possess symmetry group D_{nh} and their P_z' orbitals possess group C_{nv} in which irreducible representations A_1 + nE + ... are obtained for π molecular orbitals. Here A_1 is a one-dimensional representation having all symmetry elements which this group has, namely a non-node non-degenerate molecular orbital, while E is a two-dimensional representation having the partial symmetry elements which this group has, namely two degenerate molecular orbitals with nodes. Therefore (4n+2) π electrons are required to form the stable closed shell electron configuration to gain stability (aromaticity).

Group theory is applied to **XVIII**, **XIX** and **XX.** They all possess symmetry group D_{3h} and their P_z' orbitals possess group C_{3v} in which irreducible representations n(A + E) + ... are obtained for π-molecular orbitals.[229] The configuration of the π-molecular orbitals should be 1,2,1,2,1,2,... as follows.

Therefore, (a) 6n electrons are needed to fill up the closed shell degenerate π-orbitals as HOMO; (b) (6n+2) electrons for the closed shell non-degenerated π-orbitals; and (c) (6n-2) electrons for the opened shell degenerate π-orbitals.

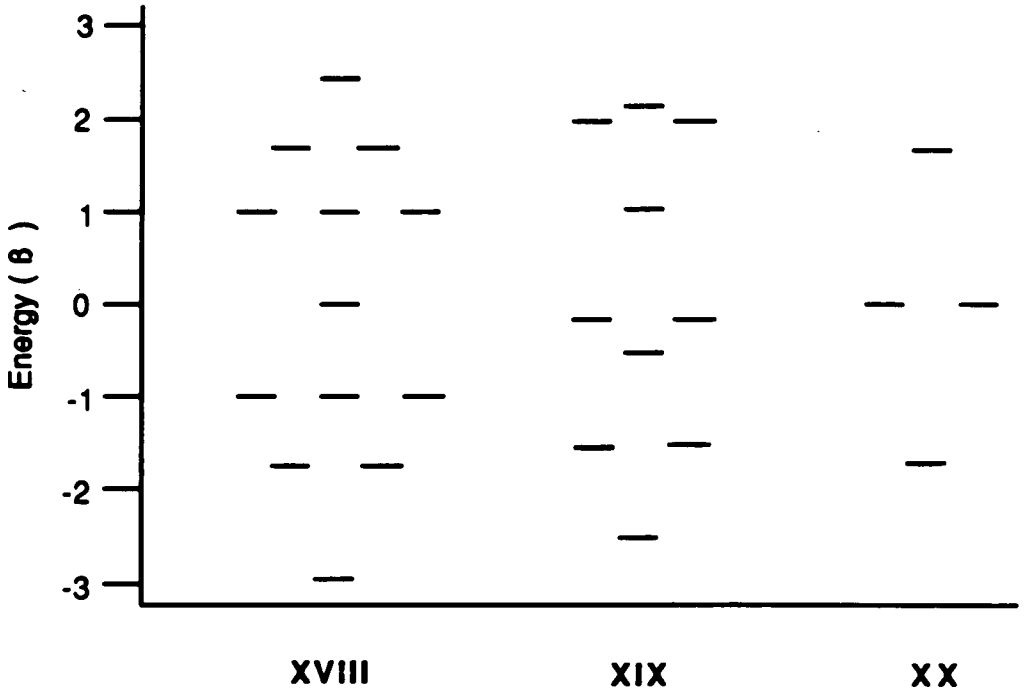


Figure 3.2-2. The π molecular orbital energy diagram of the new aromatic system by Hückel calculations

Hückel calculation shows (Figure 3.2-2.) that **XIX** and **XX** have regular configurations (1,2,1,2,...) while **XVIII** has an irregular configuration (1,2,3,1, ...) due to higher symmetry (C_{6v} for the set with C_1, C_3, C_4, C_6, C_7 and C_9) causing further degeneration.[230] However it still follows a 6n rule.

MO Calculations and Discussion

Application of Hückel calculation and the Hess-Schaad method (See section 1.1 C a.) to the ions of the above compounds gave the resonance energies per atom (REPA) in Table 3.2-1, which were computed by using

$$REPA = (E_{\pi b} - E_{ref})/n$$

where n is the number of atoms, $E_{\pi b}$ is the Hückel π binding energy and E_{ref} is the π binding energy of the localized reference structure.

All species with 6n electrons have high values of REPA (>0.065 that benzene has.) indicating strong aromaticity. The species with (6n+2) electrons have variously positive REPA values indicating some aromaticity. The species with (6n-2) electrons have significantly negative REPA values, indicating antiaromaticity.

Table 3.2-1. The results of REPA (-ß) calculations[a),b)] of **XVIII**, **XIX** and **XX**

	electrons		$E_{\pi b}$	E_{ref}	REPA
XX^{2-}	6	(6n)	3.4641	3.1900	0.069
XX^{2+}	2	(6n+2)	3.4641	3.1900	0.069
XIX^{2-}	12	(6n)	13.6869	12.5338	0.116
XIX	10	(6n-2)	12.9952	13.6104	-0.062
XIX^{2+}	8	(6n+2)	12.6006	12.5338	0.007
$XVIII^{-}$	14	(6n+2)	17.8272	16.8702	0.074
$XVIII^{+}$	12	(6n)	17.8272	16.8702	0.074

AM1 calculations give some interesting information about the molecular orbitals, geometry and charge distribution in π orbitals.

In compound XX^{2-}, the central carbon has charge +0.22 in the

π orbitals, and each peripheral carbon has -0.74 in the π orbitals. (See Figure 3.2-3) The bond orders between the central carbon and peripheral carbons are 1.287 while those between two peripheral's are 0.075, contrary to the negative overlap population from CNDO by Klein et al.[231] However our calculations again support the lack of ring current along the peripheral carbons.

XX^{2+} possesses D_{3h} as well. Its central carbon has charge -0.22 and peripheral's +0.74 indicating most charge density is condensed at the central carbon.

XIX^{2-} adapts nearly planar geometry of C_{3v} symmetry. (See Figure 3.2-3.) These geometry results are similar to those of the MNDO calculations by Butenschon and Meijere.[232] The negative charge is spread over all the carbons. The central carbon has charge of -0.18; The three peripheral carbons of the Y structure have charge of -0.24, while the six outer carbons have charge of -0.21. This implies no independent Y conjugation in this system, contrary to Y conjugation reported in MNDO calculations.[239]

XIX^{2+} possesses C_{2v} symmetry geometry with alternating bonds. (See Figure 3.2-3.)

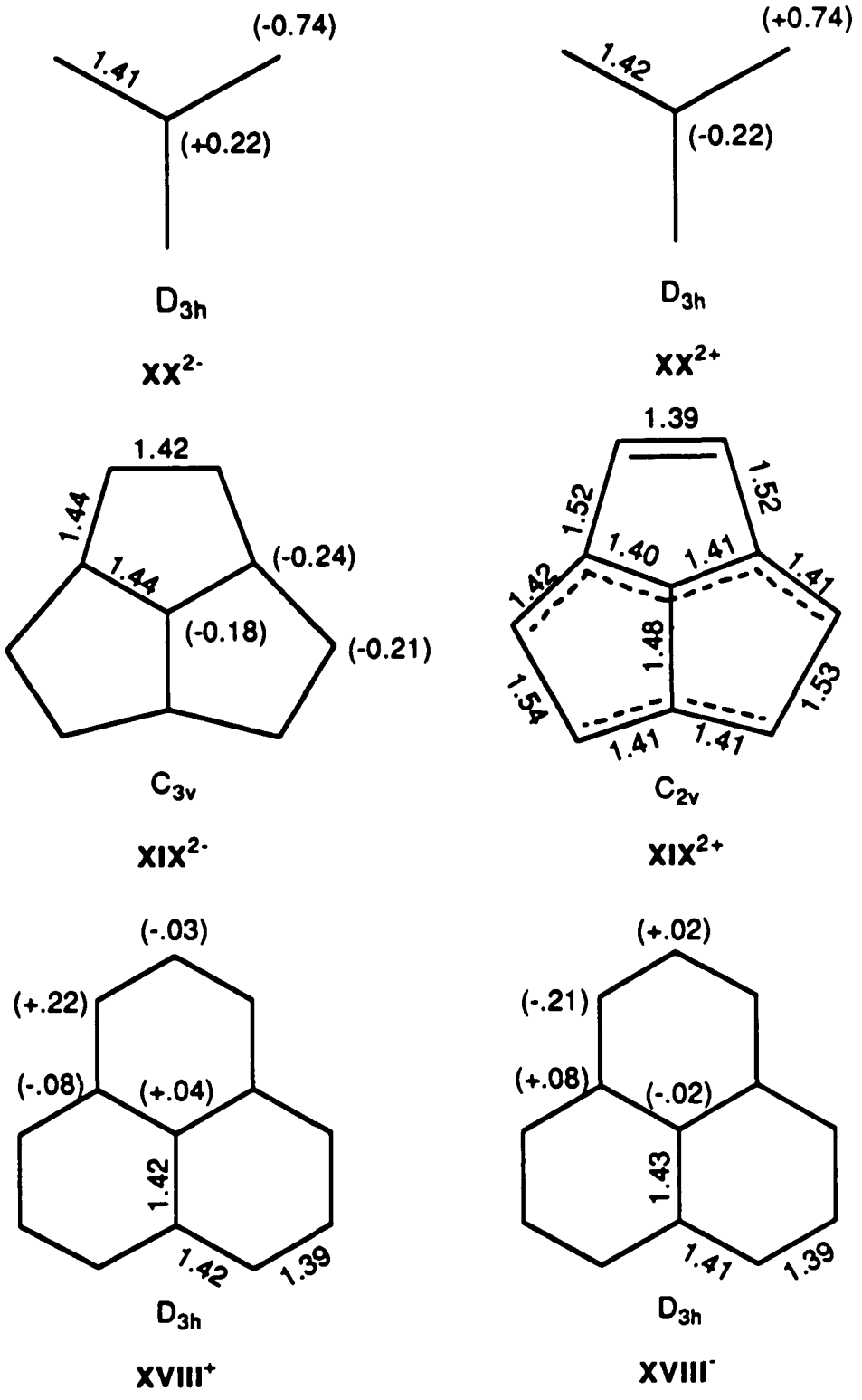


Figure 3.2-3. The Geometry And Charge distribution

XVIII$^+$ possesses perfect D_{3h} geometry. (Figure 3.2-3.) The charge is distributed almost all on C_1, C_3, C_4, C_6, C_7 and C_9, each +0.22 in π orbitals. (Figure 3.2-3.) Again there is only entire π conjugation instead of independent Y-conjugation, which includes only 4 π electrons.

XVIII$^-$ has a geometry and charge distribution similar to **XVIII**$^+$, but its bond lengths are slightly less equal. (Figure 3.2-3.) It is stable in solution.[233] (See section 2.10.)

As a result of the electron shielding effect, the HOMO-LUMO gap (a criterion for aromaticity, See section 1.1 C.) of **XVIII**$^+$ (7.214 kcal/mol) is greater than that of **XVIII**$^-$ (6.845 kcal/mol), while the SOMO-LUMO gap of **XVIII** is 4.694 kcal/mol. (Figure 3.2-4.)

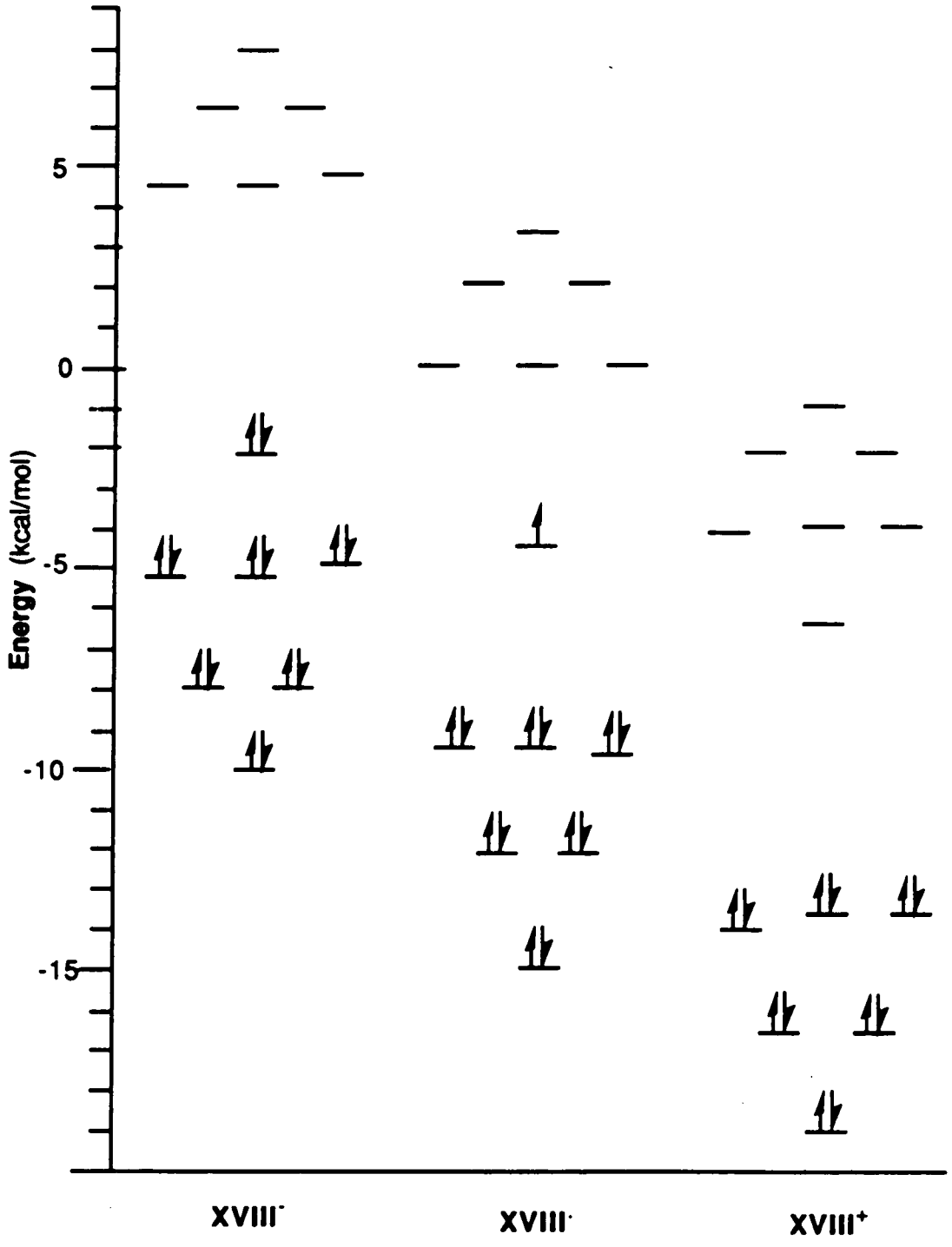


Figure 3.2-4. The π molecular orbital energy diagram for **XVIII** by AM1 calculation

NMR Study

Table 3.2-2. lists ^1H NMR chemical shifts and charges of the carbon that the hydrogen binds to.

Table 3.2-2. The charge density and ^1H NMR chemical shift of **XVIII, XIX** and **XX**.

compound	hydrogen	charge density[a]		chem. shift[b]	
XX^{2-}		-0.74	(-0.67)	δ 0.23	(7.00)
XIX^{2-}		-0.21	(-0.19)	δ 6.16[234]	(1.07)
XVIII^{+}	C_1	+0.22	(+0.17)	δ 9.44[235]	(-2.12)
	C_2	-0.03	(0.00)	δ 8.59[235]	(-1.36)
XVIII^{-}	C_1	-0.21	(-0.17)	δ 5.17[236]	(2.06)
	C_2	+0.02	(0.00)	δ 5.91[236]	(1.32)

[a] They are in π orbitals, from AM1 calculation. Those in brackets are calculated by the Hückel method. [b] Those in brackets are from benzene.

These data are put into the coordinates of Mills.[226] (The charge densities are calculated by the Hückel method.) (Figure 3.2-5.) A very interesting straight line appears, which lies on the point of 6n π electron system. It crosses the line of (4n+2) π electron (monocyclic aromatic) system at the point of TMM^{2-}, while it crosses the line of π electron densities = 0.0 at δ-0.9. This implies that (a) a 6n π electron system has different and even stronger aromaticity than a (4n+2) π electron system. (b) TMM^{2-} seems to be ambiguous; it may coordinate its π orbital configuration (1,2,...), but

it more likely belongs to the 6n system when the symmetry and π orbital behavior are considered.

The points corresponding to **XVIII**$^-$ having (6n+2) π electrons escape from both 6n and (4n+2) π electron system lines and locate below the delocalized anion lines. This might indicate that (6n+2) π electron compounds have weak aromaticity.

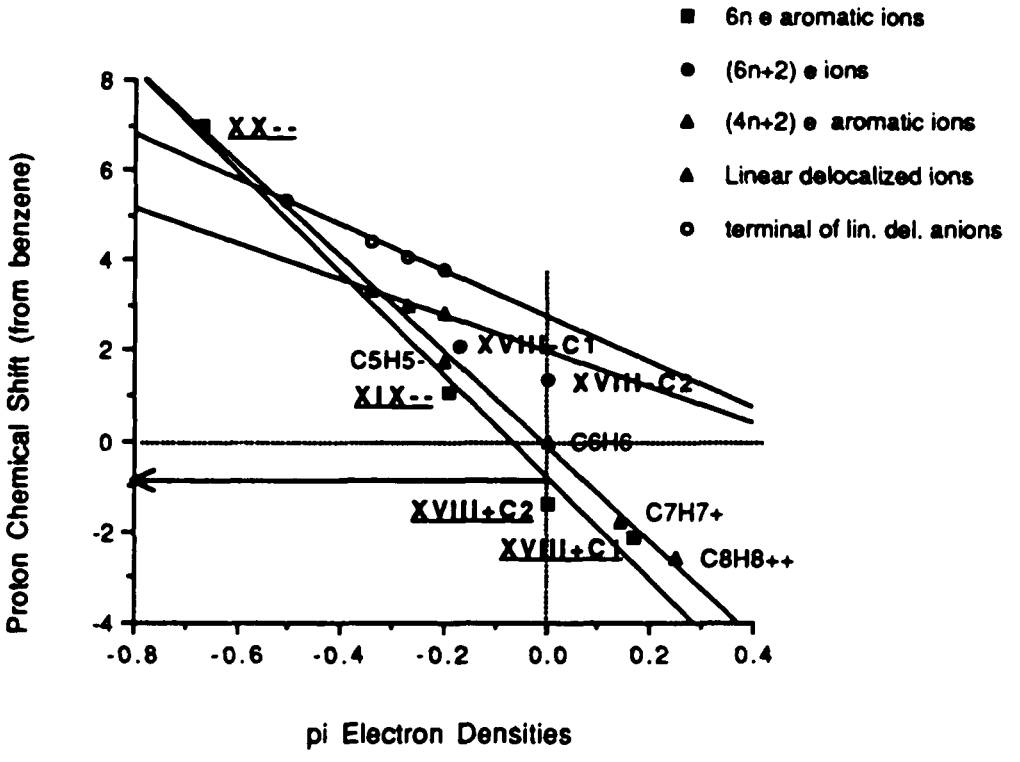


Figure 3.2-5. The chemical shift - charge density coordinate of different π electron delocalized systems

Conclusion

A new aromatic system is defined including $\mathbf{XX}^{2-}$, $\mathbf{XIX}^{2-}$ and $\mathbf{XVIII}^{+}$ as parent members which adapt symmetry D_{3h} and possess 6n π electrons instead of (4n+2). They do not necessarily have a *ring* current, but they do have a current that causes a strong diamagnetic field[237] detected by NMR. They have even stronger resonance energy than that of the (4n+2) π electron system by comparison of REPA. The π conjugate system contains a Y-structure, which however is not independent and joins the entire π system to form the even lower energy degenerated molecular orbitals. TMM^{2-} is one example of this system. Some other examples are shown in Figure 3.2-6.

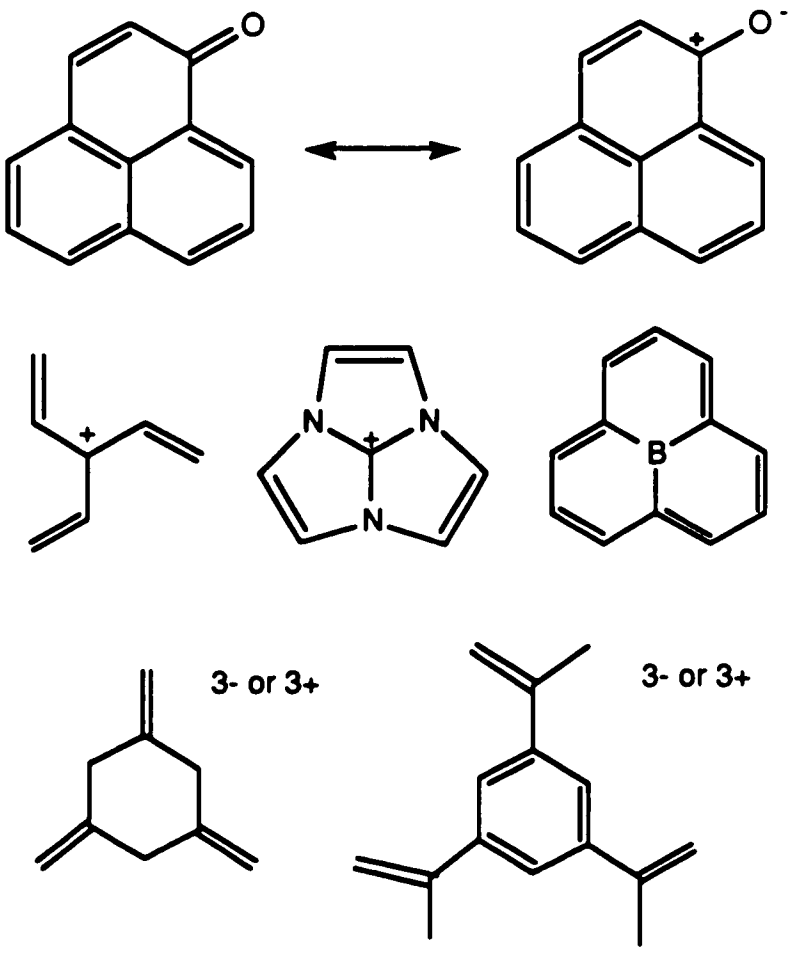


Figure 3.2-6. Some other samples of 6n π electron system

Aromaticity may be generally described by the follows. A parent conjugated system (here mainly π conjugated) possessing symmetry of at least C_{3v} will have degenerate molecular orbitals. When the degenerate orbitals are occupied, the electron shielding effect will cause the HOMO-LUMO energy gap to increase and the conjugated system will gain extra stabilization energy. When the HOMO is degenerate, the above effects will be more pronounced. Since there is high electron density in low energy delocalized

orbitals, an electronic current will be induced, and all "aromatic" properties will be exhibited.

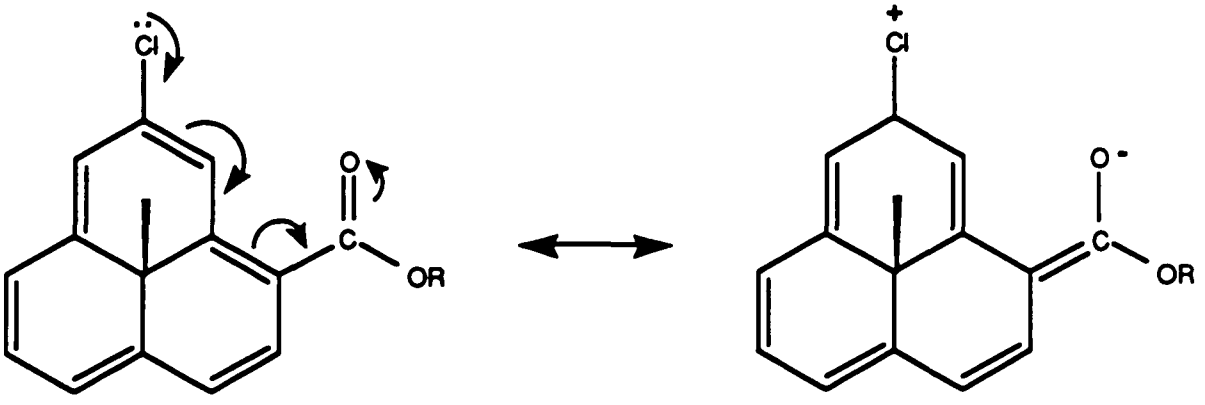
CONCLUSION AND SUGGESTION

A important precursor to the long sought 13-methylphenalene system, dihydro-13-methylphenalene (pentaene) **10-4**, has been synthesized. All approaches to 13-methylphenalene systems have not been successful because its highly symmetrical (C_{3v}) antiaromatic system causes high potential energy to loss methyl group and to convert to another even more highly symmetrical (D_{3h}) but aromatic system. The latter is an example of the new aromatic system possessing D_{3h} symmetry and 6n electrons.

To avoid loss of methyl group, I suggest follows.

1. At extreme low temperature (e.g. -160 °C or lower), synthesize 13-methylphenalene from dihydro-13-methylphenalene **10-4**;

2. Introduce some substituents to reduce the symmetry and to low the potential energy (of course, and low the antiaromaticity) as a following example.



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