STUDIES IN THE SYNTHESIS OF 4, 5- DISUBSTITUTED
PHENANTHRENES

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ABSTRACT

The work described in this thesis was initiated with the intention of exploring new routes for the synthesis of certain 4, 5-disubstituted phenanthrenes. A series of reactions have been investigated in detail and several 4, 5-disubstituted phenanthrenes have been prepared. Some of the methods employed were novel and the yields of products were comparable or even better than the existing routes.

A major observation made during the course of this work was the stability of the seven-membered ring system bridging the 4 and 5 positions of the phenanthrene nucleus. It has been found that the unbridged structures are not preferred if the compound is capable of isomerising to a bridged form. We have explained this phenomenon in terms of the stereochemistry of the 4 and 5 positions of the phenanthrene nucleus as well as the geometry of the bridge.

Low temperature NMR studies have been carried out to investigate the conformations of the benzylic hydrogens of some of the 4,5-bridged compounds. However, the results were not conclusive as more than one reason could be attributed to the observations.
INTRODUCTION
HINDERED ROTATION IN BIPHENYLS

Sterically hindered molecules are of great interest from synthetic and stereochemical points of view. Attempts to synthesise such crowded systems date back to the discovery of optically active biphenyls. In the early 1920s it was believed, following a suggestion originally made by Kaufler, (1) that biphenyl was a folded, clam-shaped molecule. The facile rearrangement of hydrazobenzene to benzidine was one of the evidences cited in favour of Kaufler's theory. But the UV spectrum of unsubstituted biphenyl exhibits a band near 250 m\(\mu\) , which is a result of a transition represented as:

\[
\begin{array}{c}
\begin{array}{c}
\text{phenyl} \\
\end{array}
\end{array}
\xrightarrow{h\gamma} 
\begin{array}{c}
\begin{array}{c}
\text{phenyl} \\
\end{array}
\end{array}
\]

Introduction of substituents into ortho positions shifts \(\lambda_{max}\) to shorter wave lengths. This observation attributes a planar configuration for unsubstituted biphenyl (2). When larger groups are substituted for hydrogen in ortho positions, the van der Waals repulsion increases and this steric hinderance forces the rings to assume non planar orientations. Actually, the biphenyl molecule is planar in the solid state, but in solution or
in the vapour phase there is an angle of approximately
45° between the planes of the two benzene rings (3).

However, from the properties of certain ortho
substituted biphenyl derivatives, it was concluded that
the two aromatic rings in these molecules are not coplanar
and there is a barrier to rotation about the single bond
joining the two rings. The explanation given by Turner (5-6)
and Lefevre in 1926 was that in the course of rotation
round the inter-nuclear bond, the ortho groups of one ring
so closely approach those of the other so as to create a
steric repulsion, which inhibits planar forms, thereby
raising the energy barriers between the enantiomeric out-
of-plane conformations. Hence, they are not likely to
undergo interconversion under ordinary conditions.

It was soon suggested by Bell and Kenyon (4) that
molecules such as I and II cannot readily exist in planar
form, because of the steric interference of the bulky

\[ \text{I} \quad \text{II} \]
ortho substituents, and any non planar form of these molecules is devoid of a plane, centre or alternating axis of symmetry.

From an energy profile of 6, 6'-dinitro diphenic acid, it is clear that (+) and (-) forms, being enantiomers, have the same free energy, whereas, the planar conformation has the maximum energy and constitutes the transition state for interconversion of the enantiomers; i.e., racemization. The molecule can be racemized in two ways, namely, by forcing a nitro group past a nitro group (transition state B) and by forcing a nitro group past a carboxyl group (transition state A). The transition state A in which groups of unequal size pass each other would be of lower energy.

When the ortho substituents tend to become larger in size, the steric interaction in the planar form also increases. Due to this steric crowding, the energy of the molecule in the planar form is comparatively larger and due to the higher energy barrier between the planar and non planar conformations, it is more difficult for the enantiomers to racemize. As the ortho substituents are less bulky, the energy barrier between the enantiomers becomes lower leading to rapid racemization. In the transition state for racemization, two pairs of bulky groups must slip past each other, which is usually difficult and hence the enantiomers once obtained are generally stable.
Energy profile for 6, 6'-dinitrodiphenic acid
Subsequent work on this type of compounds and their isomerism consisted of a detailed study of the effect of various combinations of rotation restricting groups on optical stability. In the biphenyl series, optical isomers have been separately obtained with three, two, and even one substituent ortho to the internuclear bond (5). Successful attempts have been made by Westheimer (5a) and others to calculate barrier heights from the repulsive potentials between the rotation restricting groups and atoms and the force constants of those bonds by whose stretching or bending the interatomic compressions of the planar configuration could be relieved. Some of these calculated values are in good agreement with the observed values, and some of these values are listed in the table following.

SYNTHESIS OF BRIDGED BIPHENYLS

Mislow's extensive studies on bridged biphenyils (7) reveal several interesting features of such ring systems. A number of optically active biphenyls in which both 2, 2'- and 6, 6'- positions are symmetrically bridged have been prepared with a view to study their optical activity and stability of enantiomers. Compounds I to V have been obtained in optically active form. These doubly bridged biphenyls except compound IV belong to the rare point
Arrhenius activation energies of racemization and calculated energy barriers restricting rotation around single bond in certain biphenyl derivatives (7)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>EA (obs.) kcal/mole</th>
<th>ΔE (calcd.) kcal/mole</th>
</tr>
</thead>
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<tr>
<td><img src="image1.png" alt="Compound 1" /></td>
<td>as gas or in Ph₂O</td>
<td>45.1</td>
<td>-</td>
</tr>
<tr>
<td><img src="image2.png" alt="Compound 2" /></td>
<td>in 2N aq. Na₂CO₃</td>
<td>22.6</td>
<td>-</td>
</tr>
<tr>
<td><img src="image3.png" alt="Compound 3" /></td>
<td>in 2N aq. Na₂CO₃</td>
<td>22.6</td>
<td>-</td>
</tr>
<tr>
<td><img src="image4.png" alt="Compound 4" /></td>
<td>EtOH</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td><img src="image5.png" alt="Compound 5" /></td>
<td>Na salt in H₂O</td>
<td>28.0</td>
<td>29-33</td>
</tr>
<tr>
<td><img src="image6.png" alt="Compound 6" /></td>
<td>Na salt in H₂O</td>
<td>21.6</td>
<td>21-23</td>
</tr>
<tr>
<td><img src="image7.png" alt="Compound 7" /></td>
<td>-</td>
<td>19 ± 0.5</td>
<td>18</td>
</tr>
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</table>
group $D_2$, i.e., the molecules lack reflection symmetry while possessing two mutually perpendicular twofold axes. This was the first time such compounds were obtained in optically active form.

Various problems encountered in the preparation of these compounds, made them to choose different synthetic approaches (7). The following sequence was employed for the synthesis of the racemic diketone I.
The structure of the diketone was supported by its NMR spectrum as well as by the exchange of the 7, 8-hydrogens by deuterium.

Dioxepin III was made as follows and its structure was confirmed by NMR and other physical means.
For the synthesis of Oxathiepin IV, the starting material was the diester shown below and the synthetic course followed was somewhat different from that of III.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

\[
\text{Na}_2\text{S} \quad \text{CH}_2\text{N}_2
\]

\[
\begin{align*}
\text{HO}_2\text{C} & \quad \text{CO}_2\text{H} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

\[
\text{LiAlH}_4 \\
\text{HOH}_2\text{C} \quad \text{CH}_2\text{OH}
\]

\[
\text{H}_2\text{C} = \text{C} - \text{SO}_2\text{Cl}
\]

\[
\text{O}
\]

IV

Dithiepin V, was prepared by treating the tetrabromide with sodium sulfide.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\text{Na}_2\text{S}
\]

V
An alternative method for its synthesis was from the dimethyl ester of 6, 6'-dimethyl diphenic acid.

NMR and UV spectra of all these molecules have been investigated and racemization studies also have been carried out. The optical stability of various isomers was found to be largely dependent on the structural feature of double bridging.
CONFORMATIONS OF BRIDGED BIPHENYLs

NMR spectra of the doubly bridged biphenyls were helpful in deducing their conformations. In their ground state, all these molecules are disymmetrically twisted. Calculations based on normal bond angles and distances gave values for the angle of torsion about the biphenyl 1, 1'-bond. If nonbonded interactions are ignored, these values should hold for singly bridged biphenyls, the bridged o, o'-dimethyl biphenyls and the doubly bridged biphenyls. It has been found from racemization studies, that conformation stability generally increases with increasing ground state angle of torsion. The table below shows the calculated values for angle of torsion for various singly bridged biphenyls, where the group X at the bridgehead is different. (7)

\[ X \]

<table>
<thead>
<tr>
<th>X</th>
<th>Angle of Torsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>..</td>
<td>15.3°</td>
</tr>
<tr>
<td>O</td>
<td>44.1°</td>
</tr>
<tr>
<td>NCH_3</td>
<td>45.8°</td>
</tr>
<tr>
<td>CH_2</td>
<td>50.6°</td>
</tr>
<tr>
<td>CO</td>
<td>52.4°</td>
</tr>
<tr>
<td>S</td>
<td>56.6°</td>
</tr>
</tbody>
</table>
In most of the singly bridged biphenyls, the enantiomeric conformations appeared to undergo rapid interconversion. Only in the case where sulfur is at the bridgehead, was there a possibility of stabilising the individual enantiomers at room temperature. In the twisted bridged biphenyls, two methylene protons on any of the benzylic carbon atoms are stereochemically non-equivalent and also might be expected to be magnetically nonequivalent (7). But, it has been observed that where \( X = \) single bond, \( O, \) NCH\(_3\) or C\(\cdot\)O, the methylene protons appear as sharp singlets. This indicated rapid interconversion of the conformational enantiomers, making methylene protons equivalent on the time average at room temperature. The change in the angle of torsion is also reflected in the aromatic region of the spectrum. Especially, the aromatic protons of the 9, 10- dihydrophenanthrene show up as two well separated multiplets in the ratio of 2:6. The former signal could be assigned to 4,5- protons which are each further deshielded by the opposite aromatic ring (8).

In contrast to the bridged biphenyls, the bridged \( O, O'\)-dimethylbiphenyls are conformationally more rigid and hence all of them have been obtained in optically active form (9).

The UV spectra of the bridged biphenyls are also characteristic of the angle of torsion. Mislow has compared
the UV spectra of singly bridged and doubly bridged biphenyls and it was found that the short wave length features (200-230 m\(\mu\)) were relatively insensitive to conformation, whereas, the location, intensity and shape of the conjugation bands are very much related to the magnitude of the biphenyl angle of torsion. The table on p.14 indicates some of the interesting data obtained in this connection (7).

Shape of conjugation bands depends on the dihedral angle of the interacting systems and a decrease in angle of torsion generally leads to an increase in fine structure. The UV spectrum of 9, 10- dihydro 4, 5-dimethyl phenanthrene is normal and there is no evidence for a significant distortion of the biphenyl system in this compound. Therefore, the abnormally high shielding value of the methyl protons can be due to the displacement of methyl groups out of plane as a consequence of the repulsive interactions.

Racemization studies revealed that biphenyls which are substituted in all four ortho positions by alkyl groups are conformationally stable even at higher temperatures. This generalization is not true in the case of some of the singly bridged (9) and most of the doubly bridged biphenyls. It is interesting to investigate the factors responsible for this decrease in the activation energy for racemization. If the biphenyl angle of torsion is taken to be zero in the transition state for racemization, it follows that the change in
Conjugation band characteristics of bridged biphenyls in isooctane (7)

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max}}) m(\mu)</th>
<th>(\varepsilon_{\text{max}}) x10(^{-2}) cm(^{-1})</th>
<th>(\Delta\nu) cm(^{-1})</th>
<th></th>
<th>(\lambda_{\text{max}}) m(\mu)</th>
<th>(\varepsilon_{\text{max}}) x10(^{-2}) cm(^{-1})</th>
<th>(\Delta\nu) cm(^{-1})</th>
<th></th>
<th>(\lambda_{\text{max}}) m(\mu)</th>
<th>(\varepsilon_{\text{max}}) x10(^{-2}) cm(^{-1})</th>
<th>(\Delta\nu) cm(^{-1})</th>
</tr>
</thead>
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<td>Single bond</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>280</td>
<td>176</td>
<td>4530</td>
<td>264</td>
<td>172</td>
<td>4630</td>
<td>261</td>
<td>150</td>
<td>4460</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-CH(_3)</td>
<td>256</td>
<td>144</td>
<td>4670</td>
<td>250</td>
<td>171</td>
<td>4670</td>
<td>243</td>
<td>115</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_2)</td>
<td>241</td>
<td>176</td>
<td>*</td>
<td>241.5</td>
<td>171</td>
<td>5800</td>
<td>236.5</td>
<td>136</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>252</td>
<td>142</td>
<td>4450</td>
<td>247.5</td>
<td>151</td>
<td>4790</td>
<td>240.5</td>
<td>117</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>256.5</td>
<td>122</td>
<td>4150</td>
<td>250</td>
<td>152</td>
<td>4490</td>
<td>246</td>
<td>99</td>
<td>*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Measurement was precluded by the overlap of the short wave length band.
angle of torsion will be higher if the angle of torsion at ground state is greater. This difference in the angle of torsion at ground state and transition state will reflect the extent of molecular strain. This has been qualitatively substantiated by NMR studies.

The geometry of a molecule in its ground state conformation is in principle obtainable by a minimization of the strain energy (10). This is commonly considered to be dependent on four factors: 1) valence bond stretching, 2) valence angle bending, 3) torsion about dihedral angles and 4) non bonded interaction. The geometry of the transition state is more uncertain. It is assumed that bond lengths remain invariant and the biphenyl skeleton remains collinear and undistorted. This last assumption seems to be more true in the case of doubly bridged biphenyls due to the higher degree of constitutional symmetry. The treatment of seven-membered ring bridged biphenyls are more complex. Mislow has carried out some calculations using the "buckled bridge" model in which it has been arbitrarily assumed that angle deformations and \( \pi \) delocalisation energies are chiefly responsible in determining the value of energy barrier for the doubly bridged biphenyls (11). These values were in good agreement with experimental results. However, according to Mislow, "the excellent agreement between theory and experiment is probably largely accidental and may be the result of fortuitous cancelling of errors".
NMR SPECTROSCOPY FOR CONFORMATIONAL ANALYSIS

Normally, a compound will be resolvable if the barrier to rotation is greater than about 20 kcal/mole (12). A barrier lower than this will lead to rapid racemization so that the resolution cannot be achieved under normal conditions. However, by the help of techniques like low temperature NMR spectroscopy, it has been possible to prove the existence of enantiomeric conformations in several molecules with inversion barriers lower than 10 kcal/mole. At higher temperatures, the NMR spectrum obtained for a sample is the average of the two conformations, whereas, at lower temperatures, the spectrum is the summation of the individual conformations. If two equally populated conformations are in equilibrium in a compound, at higher temperatures the resonance lines due to these conformations coalesce and when the sample is cooled down to a very low temperature the resonance lines begin to split.

An additional piece of information can also be obtained from low temperature NMR Spectra (13). If there are two conformations in equilibrium, the compound will show a low temperature spectrum which is really the separate spectra of the two conformations superimposed, and a high temperature spectrum which is a single spectrum of an averaged conformation. The transition from the low temperature to the high temperature spectrum occurs gradually, but
over a relatively small temperature interval from which it is possible to estimate a coalescence temperature. This temperature is related to the rate constant for the interconversion of the two conformations. Another method of utilising NMR Spectra in conformational analysis makes use of the magnitude of the coupling constant which varies with the dihedral angle between the coupled protons.

In systems where proton NMR Spectra are complicated by small shift differences and by coupling phenomena, the exchange processes can be studied by low temperature $^{13}C$-NMR measurements (14). The widely varying $^{13}C$ Larmor frequencies provide a wealth of information about the structure of molecules concerned and about the energetics of their interconversion. In the inversion of cis-1, 2-dimethylcyclohexane from one chair to another chair conformation of equal energy, the methyl groups change between axial and equatorial positions, causing all the carbon atoms to adopt corresponding stereoisomeric positions. This exchange process was followed from the "frozen" equilibrium at 160°K to room temperature by $^{13}C$-NMR spectroscopy. The inversion barrier for cis-1, 2, dimethylcyclohexane was found to be 9.9 kcal/mole and for the corresponding 1,4 isomer it was 9.3 kcal/mole. These values were in agreement within an experimental accuracy of ±0.5 kcal/mole with the inversion energies of cyclohexane and 1, 1- dimethylcyclohexane determined
by proton NMR (13). The fact that substituents raise the inversion barrier by only a slight amount can be explained by ring deformation or, alternatively, by a ground state of higher energy; moreover, the energy required is partly determined by the opening of the C-C angle which is affected only slightly by substituents. Identification of energetically unequal conformers and determinations of their equilibria is also facilitated by $^{13}$C-low temperature spectroscopy (14). The methyl signals of cis-4-methylcyclohexanol at 200°C gave an equilibrium containing 7.7% with axial CH$_3$.

Molecular dissymmetry in appropriately substituted vic-dialkyldenecycloalkanes was recognized at least 20 years ago (15), but it has not been quantitatively studied till now, as all the efforts to prepare an optically active sample were unsuccessful (16).

![Chemical Structure](image)

In a recent publication (17), Keifer and colleagues reported the NMR measurements of the rate of racemization
of a heterocyclic analogue of I (III below), prepared by the thermal isomerisation of the Diels-Alder adduct II of 1, 2-dimethylene - 3, 3, 4, 4-tetramethylcyclobutane and 4-phenyl -1, 2, 4-triazoline -3, 5-dione.

\[
\begin{align*}
\text{II} & \quad \xrightarrow{150^\circ} \quad \text{III} \\
\end{align*}
\]

The NMR spectrum of III at ambient temperature in carbon tetrachloride showed, in addition to phenyl absorption, methyl resonances at 1.8\(\delta\) and 1.6\(\delta\) and nonequivalent methylene proton signals at 4.6\(\delta\) and 3.76\(\delta\). The preferred conformation of the six membered ring is a half chair in which the dihedral angle between the \(\pi\) bond planes is about 50\(^\circ\); the two equatorial protons lie nearly in the nodal plane of the adjacent \(\pi\) bond and the axial protons nearly perpendicular to the plane.

The compound chosen by Keifer for NMR studies is much similar to the 4, 5-disubstituted phenanthrenes from
a stereochemical point of view. The phenanthrene ring system is even more planar than the heterocyclic system studied by Keifer. The results obtained by Keifer indicated that the energy barrier for interconversion of the conformers is 21.1 ± 0.9 kcal/mol which is comparable to the value obtained by Mislow (9) for the racemization of analogous 9, 10- dihydro -4, 5- dimethylphenanthrene (23.1 kcal/mol).

OPTICAL ACTIVITY DUE TO RESTRICTED ROTATION

Apart from the cases already cited, there are several other interesting examples of optical activity due to restricted rotation. For instance, 1- fluoro-12-methylbenz-[c]-phenanthrene owes its asymmetry to molecular distortions out of planarity, resulting in right and left handed conformations A and B as shown on page 21. This compound has been resolved by Newman (18) using an optically active complexing agent. Heptahelicene is another molecule which gave optically active crystals of high purity. Hexa and heptaheterohelicenes (19) also have been synthesized and they also exhibit similar properties. The absolute configuration of hexahelicene has also been determined by Lightner and coworkers (20).

The recent synthesis of [13]- helicene, reported by Martin and coworkers in 1969 (21) is one of the most
Enantiomeric forms of tri-o-carvacrotide
1. LiAlH₄
2. D.D.Q.

\[
\text{CO}_2\text{CH}_3 \quad \text{CO}_2\text{CH}_3 \quad \xrightarrow{h\nu, I_2} \quad \text{CO}_2\text{CH}_3 \quad \text{CO}_2\text{CH}_3
\]
\[
\text{CHO} \quad \xrightarrow{\text{C}_6\text{H}_6} \quad \text{CHO}
\]

\[
\text{2} \quad \xrightarrow{\text{C}_5\text{H}_5\text{OLi-C}_2\text{H}_5\text{OH/C}_6\text{H}_6} \quad \text{CHO}
\]

\[
\text{HELIocene}
\]
outstanding developments in this field. The product was characterised by melting point, elemental analysis and NMR and mass spectrometry. The complete synthetic scheme adopted for its preparation is outlined on page 22. Tri-c-carvacrootide (22) is reported to owe its optical activity not only to a three bladed propeller type dissymmetry, but also to helical dissymmetry. The free energy of activation of interconversion of propeller to helix (20.6 kcal/mole), helix back to propeller (20.3 kcal/mole) and helix to enantiomeric helix (17.6 kcal/mole) have been deduced from NMR studies.

Yet another example of steric inhibition of coplanarity is the diphenoquinone (23) derivative shown below. That this molecule exists as a biradical is substantiated by its paramagnetic nature; the quinonoid structure is avoided because of excessive overcrowding.

In a recent publication (24), House and coworkers reported the synthesis of several 1, 8-phenyl substituted naphthalenes.
UV, NMR and Dipole moment measurements showed that in solution these molecules exist in a conformation where the aryl rings are approximately perpendicular to the plane of the naphthalene nucleus. Derivatives with meta substituted aryl rings had an energy barrier around 16 kcal/mole for rotation of the substituted ring and hence the separation of isomers was not practical.

**4, 5- DISUBSTITUTED PHENANTHRENES**

Phenanthrene derivatives substituted at 4 and 5 positions belong to a class of compounds where dissymmetry is due to molecular overcrowding. Newman and Hussey (25) attempted to resolve the 4, 5- dimethyl substituted phenanthrene shown below, but the optical purity was very low.

From a synthetic point of view also 4, 5- substituted phenanthrenes are important. Several unsuccessful attempts were made to synthesise 4, 5-dimethyl.
phenanthrene. In 1934, Haworth (26) tried to synthesise this compound from β-(8-methyl-2-naphthoyl) propionic acid but the result was abnormal. The product they obtained was 1, 5- dimethyl anthracene and they concluded that it was impossible to introduce two methyl groups in the 4 and 5 positions of phenanthrene.

If a scale model is constructed, with the aromatic rings coplanar, the two methyl groups interfere with each other to a very great extent. Such calculations led to the predictions about the impossibility of preparation and existence of 4, 5- disubstituted phenanthrenes. However, in 1950, Badger and coworkers reported the synthesis of 4, 5- dimethylphenanthrene from pyrene (27) involving several steps. Location of the methyl groups in space in this molecule could be either bent away from each other in the same
plane of the benzene ring or they could be bent out of plane. As an alternative, the aromatic rings could be twisted in some way. But so far the optical enantiomers of 4, 5- dimethyl phenanthrene have not been isolated.

Our aim was to prepare various 4, 5- disubstituted phenanthrenes through ozonolysis of pyrene. During the course of the work we have investigated a series of reactions in order to introduce different substituents in the phenanthrene ring system. As a model compound, we have ozonised phenanthrene itself and have obtained some of the 2, 2'- disubstituted biphenyls. Some of the methods adopted for the preparation of these compounds are entirely new and the yields of products are comparable to or better than the existing methods. Spectral characteristics of these molecules are also studied in detail. Several interesting observations have been made during the course of this investigation which are discussed in detail in subsequent chapters.
EXPERIMENTAL
CALIBRATION OF THE OZONATOR

(a) **Apparatus (Ozonator)**

A Welsbach Model T.408 Laboratory Ozonator, which is designed for operation on a 115 volts, 60 cycle circuit was used for all the ozonolysis experiments. To compensate for differences in line voltage and to vary ozonator output, a variable voltage transformer has been incorporated in the primary circuit. A transformer within the cabinet increases the voltage to the relatively high voltage necessary for ozone generation. The input voltage to the high voltage transformer can be read on the panel voltmeter, which should be always set below 115 volts. The Model T-408 ozonator is capable of producing about 4% by weight of ozone if pure dry oxygen is used.

(b) **Procedure**

Ozone concentration was determined by passing a measured amount of ozonized gas through a 2% solution of neutral potassium iodide. This was done by keeping the flow meter reading constant and passing the ozonized gas for 5 mins. through the potassium iodide solution, maintaining the operating pressure and voltage constant. The resulting solution was acidified with 1M sulfuric acid and the liberated
Fig. 1  Calibration of the ozonator
Ozone production (gms. per hr.)

(85.0 volts)

(75.0 volts)

Flow rate of oxygen (Std. Lits. per min.)
iodine was titrated with 0.1 N sodium thiosulphate solution.

Ozone reacts with neutral potassium iodide solution according to the equation:

\[ \text{O}_3 + \text{H}_2\text{O} + 2 \text{KI} \rightarrow \text{O}_2 + \text{I}_2 + 2\text{KOH} \]

The curve plotted with oxygen flow rate in standard litres per minute (SLPM) against gms. of ozone generated per hour gave a fairly accurate idea about the conditions to be maintained for the production of ozone at a particular rate.

**OZONOLYSIS OF PHENANTHRENE AND PYRENE**

(a) **Preparation of biphenyl -2, 2'-dialdehyde** (28)

10.0 gms. of phenanthrene was refluxed in 200 ml of dry methanol and the solution was cooled rapidly to get a finely divided suspension. This suspension was transferred to a standard ozonolysis apparatus cooled in an acetone-dry ice mixture. Ozone was passed through the suspension at a rate of 1.0 gm per hour until all the phenanthrene has reacted; i.e. all the suspended phenanthrene has disappeared resulting in a light blue solution. Towards the end of the reaction ozone started leaking into the potassium iodide trap attached to the other end of the
ozonolysis apparatus. About 1.2 mole equivalents of ozone was consumed. To the cooled reaction mixture are added 25.0 gms. of potassium iodide and 30.0 ml of glacial acetic acid. After the addition, the reaction mixture was allowed to stand for one hour. The liberated iodine was reduced with 10% aqueous sodium thiosulphate solution after which the reaction mixture was placed under air blast immediately. As the methanol evaporated, the product separated as a yellow solid, which was extracted by ether. The ether extract was dried with anhydrous magnesium sulphate and filtered. The filtrate was concentrated and the product was recrystallised by dissolving in minimal amount of dry ether and then adding about 150.0 ml of ligroin. The recovery of pale yellow crystals m.p 61-63° was 9.1 gms. (Lit. m.p. (28) 62.5-63.5°C). I.R. spectrum showed carbonyl absorption at 1740 cm⁻¹ and two bands at 2700 and 2800 cm⁻¹ due to the C-H stretching in aldehydes. NMR spectrum showed the aromatic protons as a multiplet centred at δ7.7 as well as the low field singlet at δ8.9 due to aldehyde.

(b) Preparation of 5-formyl-4-phenanthroic acid

Standard procedure in "Organic Syntheses" Coll. Vol. IV (29) was followed for the preparation of 5-formyl-4-phenanthroic acid. The potassium hypochlorite needed
for the oxidation during the work up was prepared according to the procedure described in "Organic Syntheses" Coll. Vol. II (30). The sodium salt of the aldehydo acid was digested with 15% hydrochloric acid and the solid acid filtered and dried. The product was recrystallised from a 50/50 mixture of dimethylformamide and glacial acetic acid. From 25.0 gms. of technical pyrene a yield of 11.6 gms. of the product melting at 273-276°C was obtained (Lit. m.p. 272-276°C) (29). Infrared spectrum showed the carbonyl absorption at 1680 cm\(^{-1}\) and a broad band around 3000 cm\(^{-1}\) due to the hydroxyl group, but the band characteristic to aldehydes was not present. The NMR spectrum showed the aromatic multiplet centred at 8.0\(\delta\) and a singlet at 6.8\(\delta\) due to benzylic hydrogen. There was no low field signal due to free aldehyde but the sodium salt indicated a singlet at 10.4\(\delta\) due to free aldehyde. This is presumably due to the fact that the free aldehydo acid exists as a bridged hydroxylactone and the sodium salt has unbridged structure.

(c) Preparation of 2, 2'- (di)hydroxymethyl biphenyl

Method I: Ozonolysis of 10.0 gms. of phenanthrene was carried out in the same manner as in the preparation of 2, 2'- dialdehyde. The cold reaction mixture containing the ozonide in methanol was transferred to a conical flask
and a cold solution of 1.5 gms. of sodium borohydride in 50% aqueous ethanol was added at a slow rate with stirring from a dropping funnel. The temperature was maintained below 0°C. The mixture was stirred overnight, cooled and carefully acidified with 10% H₂SO₄. The excess acid was neutralised with Na₂CO₃ solution and the solvent was evaporated. The product was recrystallised from ethanol and the yield was 10.5 gms. and the m.p. was 112°-113°C. (Lit. m.p. (31) 112-113°C). The IR spectrum showed the band due to hydroxyl group around 3000 cm⁻¹ and there was no carbonyl absorption. NMR spectrum showed aromatic protons as a multiplet centred at 7.28 and two singlets due to methylene and hydroxyl protons at 4.36 and 3.05 respectively. Mass spectrum gave the correct molecular weight of 214.

**Method II:** 2.0 gms. of biphenyl 2, 2'-dialdehyde prepared from phenanthrene was refluxed in 25.0 ml of dry ether under nitrogen atmosphere with 0.3 gm of lithium aluminum hydride for 24 hrs. The reaction mixture was cooled and carefully acidified with 10% sulphuric acid to destroy the unreacted lithium aluminum hydride. The ether layer was separated and dried with anhydrous magnesium sulphate and filtered. The solvent was evaporated and the product crystallised from ethanol. The melting point
and spectral characteristics were identical with that of the product prepared by method I, but the yield was only 0.2 gm.

(d) **Attempted Preparation of -4, 5- (di)hydroxymethylphenanthrene**

A suspension of 5.0 gms of technical pyrene in 200.0 ml of methanol was made as in the case of phenanthrene and the ozonolysis was carried out as before. But the suspension was not stable and the pyrene precipitated blocking the ozone inlet tube. On treatment with sodium borohydride solution and further work up no useful product was isolated except pyrene.

(e) **Preparation of biphenyl -2, 2', 6, 6'-tetraldehyde (52)**

10.0 gms. of technical grade pyrene was dissolved in 100.0 ml of chloroform and the ozonolysis was carried out at 0-5°C. Ozone was passed at a rate of 1.5 gms. per hour for 3 hrs. The reaction mixture was transferred to a conical flask and 100.0 ml of dimethyl sulfide was added with stirring. The mixture was stirred for 12 hrs., maintaining the temperature below 5°C for the first 4 hrs. and filtered. The filtrate was concentrated and the oily residue was chromatographed over Florisil. The first fraction eluted with
benzene gave 2.4 gms. of yellow crystalline product which melted at 151°C on recrystallisation from chloroform (Lit. m.p. (32) 161°C). The IR spectrum showed characteristic peak for carbonyl at 1700 cm⁻¹ and two peaks at 2725 cm⁻¹ and 2800 cm⁻¹ due to aldehyde. The NMR spectrum showed the aromatic multiplet centred at 8.2δ and a low field singlet due to aldehyde proton at 9.7δ. The elemental analysis showed C = 72.17% and H = 3.81% (theoretical C = 72.18%, H = 3.76%).

REATIONS OF 5-FORMYL-4-PHENANTHROIC ACID

(a) Preparation of the cyclic ether (33)

2.5 gms. of 5-formyl-4-phenanthroic acid prepared by the ozonolysis of pyrene and 16.2 gms. of trichlorosilane in 15.0 ml of dry acetonitrile was refluxed for 2 hrs. After cooling 10.4 ml of tri-n-propyl-amine was carefully added so that the temperature did not rise above 15°C. The mixture was refluxed for 16 hrs, cooled, and was diluted to 100.0 ml by diethyl ether. The amine hydrochloride was removed by filtration. The filtrate was concentrated to remove the ether and acetonitrile and 15.0 ml of methanol was added to the residue and the solution was refluxed for 1 hour. 11.2 gms. of potassium hydroxide dissolved in a solution of 20.0 ml of methanol
and 5.0 ml of water was then added slowly and refluxed for 20 hrs. It was then diluted with 50.0 ml of water and extracted with pentane. The extract was washed with 5.0 ml of 2N hydrochloric acid, again washed with distilled water and dried. The solvent was evaporated and the product recrystallised from methanol. 1.0 gm of pale yellow crystals of the cyclic ether melting at 74-76° was obtained (Lit. m.p. (27) 76-76°C). Mass spectrum showed correct molecular weight of 220. IR spectrum indicated no carbonyl or hydroxyl absorption and the NMR spectrum showed the aromatic protons as a multiplet centred at 7.6δ as well as the singlet at 4.7δ corresponding to 4 methylene protons.

(b) Oxidation with alkaline KMnO₄

2.0 gms. of 5-formyl-4-phenanthroic acid, 3.0 gms. of potassium permanganate and 1.0 gm of sodium hydroxide were refluxed in 75.0 ml of water for 6 hours and filtered hot. The filtrate was concentrated to 20.0 ml and acidified with 10% sulfuric acid. The precipitate was filtered, washed with small amount of cold water and dried. The solid was a high melting acid and the yield was 1.9 gms. The acid was esterified with diazomethane and the NMR, IR and mass spectrum of the ester confirmed that it was the tetramethyl ester of biphenyl 2, 2', 6, 6'-tetracarboxylic acid. The ester melted at 123-125°C (lit. m.p. (34) 125-126°C).
IR spectrum showed carbonyl absorption at 1750 cm\(^{-1}\) and the mass spectrum showed showed a molecular weight of 386. NMR spectrum gave signals of aromatic multiplet centred at 8.06 and a singlet due to 4 methoxyl groups at 3.56.

(c) **Preparation of Phenanthrene-4, 5-dicarboxylic acid**

A solution of 0.85 gm. of silver nitrate in 5.0 ml of distilled water was treated with a solution of 0.22 gm. of sodium hydroxide in 2.0 ml of water. The mixture was stirred for 5 min. and the precipitated silver oxide was collected over a Buchner funnel and washed free of nitrate. The wet freshly precipitated silver oxide was transferred to a beaker and 10.0 ml of water and 1.0 gm of sodium hydroxide were added and vigorously stirred. With continued stirring 1.25 gms. of powdered 5-formyl-4-phenanthroic acid was added and the temperature was kept around 90\(^\circ\)C. After 15 min. the mixture was boiled and filtered. 10.0 ml of water was added to the precipitate, again boiled and filtered. The combined filtrates was poured into 10.0 ml of cold 20% hydrochloric acid and cooled to 5\(^\circ\)C. The precipitate was filtered and dried. The yield was 1.0 gm. The melting point of the acid was 278\(^\circ\)-282\(^\circ\)C and it was characterised after esterification with diazomethane. The methyl ester had a melting point of 129-131\(^\circ\)C and showed
spectral characteristics of the dimethyl ester of phenanthrene 4, 5-dicarboxylic acid. IR spectrum showed carbonyl absorption at 1700 cm\(^{-1}\) and the NMR signal at 3.8\(\delta\) corresponds to the methoxyl protons. The mass spectrum also indicated a molecular weight of 294.

(d) Esterification of 5-formyl-4-phenanthroic acid

1. Preparation of aldehydo methyl ester:

2.0 gms. of powdered aldehydo acid was suspended in 50.0 ml of dry acetone in a conical flask, cooled in an ice bath. 1.5 gms of N-nitrosomethylurea prepared according to "Organic Syntheses" procedure (35), was added to a round bottomed flask containing 10.0 ml of 50\% potassium hydroxide solution and 100.0 ml of dry ether. The flask was warmed to 60\(^{\circ}\) by warm water and the diazo-methane was distilled along with ether into the aldehydo acid. An additional trap containing ether cooled in ice was kept to prevent any diazomethane from escaping. When all the diazomethane was distilled into the flask containing the aldehydo acid, the arrangement was dismantled and the contents of the conical flask were stirred at room temperature for 12 hrs. The solvent was evaporated and the product crystallised from benzene-ether mixture. The yield was 1.9 gms. and the product had a melting point of 111\(^{\circ}\)-113\(^{\circ}\)C (lit. m.p. (27) 113-114\(^{\circ}\)C). IR spectrum showed character-
istics of aldehyde with absorption at 2800 and 2850 cm\(^{-1}\) and carbonyl absorption at 1750 cm\(^{-1}\). NMR spectrum indicated the aromatic multiplet, aldehydic and methoxyl protons at 8.0\(\delta\), 10.4\(\delta\) and 3.9\(\delta\) respectively. Mass spectrum was consistent with the molecular weight of 264.

2. Preparation of the Pseudo ester (Methoxylactone):

A suspension of 2.0 gms. of powdered aldehydo acid was made in 50.0 ml of a 1:1 mixture of dry ether and methanol. Diazomethane was distilled along with ether into the suspension exactly in the same way as in the preparation of the ester and the reaction mixture stirred for 12 hrs. at room temperature. After evaporating the solvent the product was crystallised from methanol. The yield was 1.95 gms. and the melting point was 176\(^o\)C-177\(^o\)C (lit. m.p. (27) 176-177\(^o\)C). IR spectrum showed carbonyl absorption at 1750 cm\(^{-1}\) but the bands due to aldehyde were missing. NMR spectrum also showed the aromatic and methoxyl protons at 8.0\(\delta\) and 3.8\(\delta\) respectively, but the CH proton of the methoxy lactone was at a much higher field of 6.2\(\delta\) than the free aldehyde. Mass spectrum showed the correct molecular weight of 264.

(e) Attempted Wolff-Kishner reduction

1.0 gm. of aldehydo acid, 1.5 gms. of potassium
hydroxide and 1.2 ml of 95% hydrazine were refluxed in 25.0 ml of triethylene glycol for 1½ hrs. Low boiling material was distilled out and the refluxing was continued for 4 hrs. The reaction mixture was poured over crushed ice and the organic layer was extracted with ether. The organic material was dark coloured and some insoluble lumps were also present. The ether extract was dried with anhydrous magnesium sulphate, filtered and concentrated. The residue was a dark oily liquid and no useful material could be isolated after column chromatography.

**REACTIONS OF PHENANTHRENE -4, 5- DICARBOXYLIC ACID**

(a) Hunsdiecker Reaction

**Method I:** 1.0 gm. of the diacid, 2.5 gms. of mercuric oxide (red) and 3.0 gms. of iodine were refluxed in 50 ml of carbon tetrachloride in dark for 6 hrs. The mixture was filtered and the solvent evaporated. The residual solid was redissolved in carbon tetrachloride and stirred with finely ground sodium thiosulphate and filtered and again concentrated. The residue was crystallised from benzene. The yellow solid obtained melted at 140-145°C and the yield was 0.12gm. NMR spectrum showed only aromatic protons centred at 8.0δ and the IR spectrum indicated the presence of carbonyl group at 1680 cm⁻¹. Mass spectrum
showed a much higher than expected molecular weight of 502; no iodine was present in the molecule.

**Method II:** 1.0 gm. of the diacid was dissolved in one equivalent of 1% sodium hydroxide solution and 10% more of theoretical amount of silver nitrate solution and stirred for 10 mins. The precipitate of silver salt was filtered and first washed with distilled water and then with acetone and dried under vacuum. The dry silver salt was refluxed with 3.0 gms. of iodine in 50.0 ml of carbon tetrachloride as in the case of the previous experiment for 6 hrs. The work up was exactly similar to the earlier experiment. The product obtained was lighter in colour but showed same spectral characteristics and molecular weight. Melting point was 142°-146° and the yield was 0.11 gm.

(b) **Attempted Synthesis of 4, 5- dimethyl phenanthrene** (33)

1.5 gms. of the diacid was refluxed with 6.0 ml of trichlorosilane in 10.0 ml of dry acetonitrile for one hour. After cooling 5.2 ml of tri-n-propylamine was added carefully. Rest of the experiment was carried out exactly in the same manner as in the case of the reaction of trichlorosilane with 5-formyl-4-phenanthroic acid. The product obtained was crystallised from ethanol and was found
identical with the cyclic ether obtained in the case of similar reaction with aldehyde acid. The yield of the cyclic ether was 0.44 gm.

**REDUCTION OF THE METHYL ESTER OF 5-FORMYL-4-PHENANTHROIC ACID WITH SODIUM BOROHYDRIDE**

0.5 gm. of the ester was dissolved in 10 ml of glyme and a solution of 0.15 gm. of sodium borohydride in glyme was added at a slow rate at room temperature with stirring. The mixture was stirred for 16 hrs. and the excess borohydride was destroyed by acidifying with 10% hydrochloric acid at 0°C. The excess acid was neutralised with sodium carbonate and the solvent evaporated. The product was recrystallised from methanol and the yield was 0.31 gm. m.p. 128-129°C. The NMR spectrum indicated the aromatic multiplet centred at 7.7 δ and singlets at 6.2 δ, 5.3 δ and 3.8 δ. IR spectrum showed carbonyl absorption at 1700 cm⁻¹ but there were no peaks corresponding to aldehyde or hydroxyl groups. Mass spectrum showed a molecular weight of 264 and also a prominent peak at 234. From all these evidences it was concluded that the product is a mixture of the lactone and methoxylactone.
ATTEMPTED OXIDATION OF PYRENE WITH KMnO₄

2.0 gm of technical pyrene was dissolved in 25.0 ml of acetone and refluxed with 1.0 gm of sodium hydroxide and 2.5 gm of potassium permanganate for 10 hrs. On filtration followed by acidification no oxidized product was obtained. The oxidation was not successful with neutral permanganate also.

REACTION OF 2,2'-6,6'-TETRA CARBOXYLIC ACID WITH TRICHLOROSILANE (33)

1.0 gm of the tetra acid was refluxed with 10 ml of trichlorosilane in 10.0 ml of acetonitrile for one hour. After cooling, 9.0 ml of tri-n-propylamine was added very carefully and refluxed for 18 hrs. The work up was exactly similar to that of the reaction of trichlorosilane with the aldehydo acid. The product obtained was a dark yellow oil and several attempts to recrystallise it failed. Thin layer chromatography showed that it was a mixture of several components and so further purification was not attempted.

CLEAVAGE OF THE CYCLIC ETHER WITH LITHIUM ALUMINUM HYDRIDE AND ALUMINUM CHLORIDE

A slurry of 0.35 gm of aluminum chloride was made in 10.0 ml of dry benzene to which 0.1 gm of lithium
aluminum hydride was added under nitrogen. A solution of 0.45 gm of the cyclic ether in 5.0 ml of dry benzene was added and refluxed under nitrogen atmosphere for 30 hrs. The reaction mixture was cooled and poured over a mixture of 5.0 gms of ice and 10.0 ml of 1N sulphuric acid. The mixture was extracted with ether three times and the combined extract was dried with anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the oily concentrate was chromatographed over Florisil. The chromatographed sample was still oily and could not be crystallised. The NMR spectrum of the oil was distinctly different from that of the starting material with three peaks at 2.6, 3.0 and 3.7 $\delta$ indicating that the ether bridge was cleaved. The peak at 4.7 $\delta$ in the starting material had completely disappeared.

GRIGNARD REACTION OF THE LACTONES

(a) Reaction of the lactone of 5-hydroxymethyl-4-phenanthroic acid

0.6 gm of magnesium turnings were stirred with 20.0 ml of dry ether in a 100 ml three necked flask for 10 mins. under nitrogen atmosphere. A solution of 1.4 ml of methyl iodide in 15.0 ml dry ether was added through a separatory funnel at a very slow rate with stirring. When all the magnesium had reacted, a solution of 0.5 gm of the lactone
in 20.0 ml of dry tetrahydrofuran was added drop wise with stirring. Once the addition was complete, the whole reaction mixture was refluxed for 2 hrs. After cooling, the excess Grignard was destroyed by adding 10% aqueous sulphuric acid. After addition of more water the organic layer was extracted with chloroform. The chloroform layer was washed thrice with water, dried with anhydrous magnesium sulfate and filtered. On concentration of the filtrate an oily gum was obtained which failed to crystallise. NMR spectrum of the crude product revealed that methyl groups are present, evidenced by signals at high field (between 1.0 and 2.0 $\delta$) and probably some olefinic material is also present. Thin layer chromatography showed two spots very close to each other.

(b) **Reaction of the methoxylactone**

0.5 gm of the methoxylactone was reacted with excess of methylmagnesium iodide exactly in the same manner as the lactone. The product was extracted with chloroform and on concentration an oily material was obtained. This was chromatographed on Florisil and the fraction eluted with 50/50 mixture of benzene and naphtha was collected. The material on concentration gave a gum, and the NMR spectrum showed a singlet at 1.2 $\delta$ and a doublet at 2.0 $\delta$. The IR spectrum showed the absence of carbonyl or hydroxyl absorption. The mass spectrum showed the parent peak at 262.
INSTRUMENTATION AND TECHNIQUES

1. **Infrared Spectra**

   Compounds were mixed with potassium bromide and compressed into pellets and the spectra were recorded from a "Perkin Elmer-Model 237B" Grating Infrared Spectrophotometer.

2. **Mass Spectra**

   The AEI-MS-30 Model Mass Spectrometer was used for the mass spectra. The gas chromatograph attached to the instrument was also used whenever the compound was impure.

3. **NMR Spectra**

   The spectra were recorded on a "Varian-A-60" Nuclear Magnetic Resonance Spectrometer. For routine analysis spectra were taken at room temperature, but in certain cases low temperature spectra were also taken.

4. **Melting Point**

   All the melting points were measured on "Gallenkamp" melting point apparatus.

5. **Gas Chromatography**

   An "Aerograph A90-P3" Gas Chromatograph was used for gas chromatography.
6. **Thin Layer Chromatography**  
   This was done on aluminum foils coated with silica gel, supplied by E. Merck, Germany.

7. **Column Chromatography**  
   All the columns were packed with Florisil (60-100 mesh) and distilled solvents were used for elution.

8. **Purification of Solvents**  
   Solvents were purified according to procedures given in "Practical Organic Chemistry" by Vogel. For experiments not requiring very pure solvents, they were used after simple distillation.
RESULTS AND DISCUSSION
**OZONOLYSIS AND RELATED REACTIONS**

Due to their comparatively large $\pi$-electron density, the 9, 10- bond in phenanthrene and the 1, 2 and 6, 7- bonds in pyrene could be selectively cleaved by electrophilic reagents like ozone. Ozonolysis of phenanthrene (28) and pyrene (29) to produce 2, 2'-diformyl biphenyl and 5-formyl-4-phenanthroic acid respectively are reported in the literature. The products have been identified by routine elemental analysis, melting points and preparation of derivatives. However, no spectral data are available to prove these structures conclusively. Our aim was to carry out the ozonolysis of these hydrocarbons and to use the products as intermediates for the preparation of certain 2, 2'-disubstituted biphenyls and 4, 5-disubstituted phenanthrenes. The products we obtained have properties identical to those reported in the literature and we have additional spectral data to prove their structures.

Badger and coworkers (27) suggested that the product of the ozonolysis of pyrene exists in the form of a cyclic hydroxylactone I, rather than as the aldehydo acid II. Badger’s reason for proposing a cyclic structure lay in the compound’s failure to form the usual carbonyl derivatives (e.g. phenylhydrazone, semicarbazone).
We prepared the 5-formyl-4-phenanthroic acid by a similar procedure (29) and the NMR spectrum of the compound gave valuable information regarding the cyclic structure. The NMR spectrum of the sodium salt of 5-formyl-4-phenanthroic acid displayed an aldehydic proton at low field; the spectrum of the acid itself showed no such proton, a result again consistent with a cyclic structure.

The reduction of aldehydes to alcohols using lithium aluminum hydride is a widely used procedure. However, due to the high sensitivity of this reagent to moisture, extreme care should be taken to get an anhydrous atmosphere. Usually, this is achieved by using dry solvents and running the reaction under a nitrogen blanket. In spite of all these precautions, the yield of the diol obtained by the reduction of biphenyl-2, 2'-dialdehyde was much lower than expected.
We tried to modify this procedure by using a different reagent which is easy to handle and the conditions to be maintained not so rigorous. Sodium borohydride has been successfully used by many workers (36-38) for reducing carbonyl groups. Apart from being more selective in its reaction, borohydride could be easily handled and used in aqueous solutions or in hydroxylic solvents. Sousa and Bluhm (39) ozonised cyclohexene in chloroform and dissolved the resinous ozonide in ethanol which was subsequently treated with a solution of sodium borohydride in 50% aqueous ethanol. The reduction product (diol) was obtained in about 63% yield.

Considering the success of this reaction, as well as the low yield and other difficulties associated with lithium aluminum hydride reduction, we thought that sodium borohydride may work as a better reagent for the reduction of phenanthrene ozonide. The result was very encouraging and the yield of the diol was nearly 87%.

\[
\begin{align*}
\text{(1) } & O_3 \text{ in Me OH at } -30^\circ C \\
\text{(2) } & \text{NaBH}_4 \text{ in 50% EtOH at } 0^\circ C
\end{align*}
\]
Fig. 2  NMR spectrum of 2, 2'- (di) hydroxymethyl biphenyl
Since it is not necessary to isolate the ozonide, this is a "one-pot" reaction, and the diol is a convenient intermediate for the syntheses of several 2, 2'-disubstituted biphenyls. This new method for the preparation of the diol is less complicated and higher yielding than the earlier method for its preparation as follows:(31)
The success of this reductive work up of phenanthrene ozonide, prompted us to extend the same procedure as a method for the preparation of 4, 5-di(hydroxymethyl) phenanthrene. Unfortunately, the result was not encouraging, because it was not possible to dissolve pyrene in methanol or ethanol at low temperatures and it was not even possible to get a fine suspension. The granular solid particles in the system blocked the inlet tube of the ozonator building up pressure within the ozonator and so we had to discontinue the reaction. Even the use of solvents like chloroform was not helpful, because several by products were formed in the reaction, the main difficulty arising primarily from the cleavage of the 9, 10-double bond in pyrene.

However, we could utilise this particular reaction with slight modifications for the synthesis of biphenyl-2, 2', 6, 6'-tetraldehyde. Pyrene was ozonised in chloroform and the solution of the ozonide was mixed with excess of dimethyl sulfide at 0°C and stirred overnight. The mixture on filtration and concentration of the filtrate afforded an oily gum which on chromatography gave yellow crystals of the tetraldehyde in about 13% yield.

\[
\begin{align*}
(1) & \quad O_3 \text{ in CHCl}_3 \\
(2) & \quad (\text{CH}_2)_2\text{S} \\
\end{align*}
\]
Fig. 3  NMR spectrum of biphenyl-2, 2', 6, 6'-tetraldehyde
Initially we thought that the tetraldehyde was a new compound, but later on we found out that Fieser (32) had reported it in 1940. However, a $10^\circ$ discrepancy in melting points between the compounds prepared by Fieser and us, and an apparent difference in water solubility (Fieser reports recrystallising his compound from boiling water; ours is water-insoluble) lead us to believe that the compounds are not identical. Due to these contradictory observations, we are inclined to believe that the two compounds are not essentially the same. Fieser did not have any spectral data to prove his structure, but had the correct elemental analysis. In our case we have the infrared spectrum corresponding to the aldehyde and also the NMR spectrum which gave the correct ratio of four aldehyde protons to six aromatic protons. The mass spectrum which showed the molecular ion at 266 was also in agreement with the structure of tetraldehyde. Although, the starting material used by Fieser and us was pyrene, the procedures employed were quite different. Our procedure was much simpler, than the hydrogenation technique employed by Fieser and the yields are comparable.

5-Formyl-4-phenanthroic acid obtained by the ozonolysis of pyrene appeared to be a good intermediate for the preparation of various 4, 5- disubstituted phenanthrenes. To introduce substitutents in 4, and 5 positions of phenanthrene is
almost impossible due to steric reasons. Here, as we already have a system where these positions are substituted, it should be relatively easier to modify these substituents to get the desired compounds, by treatment with suitable reagents.

**REDUCTIVE Silylation**

The work of Benkeser (33, 40, 41) was of particular interest to us in this regard. In 1970, he reported that aromatic carboxylic acids could be reduced to corresponding hydrocarbons by trichlorosilane in a tertiary amine (33). The reagent essentially consisted of trichlorosilane in the presence of tripropylamine in a polar solvent like acetonitrile. In one of his earlier publications (40), he had indicated that aldehydes and ketones are also reduced to the corresponding hydrocarbons in a single step by making use of the same reagent. He was successful in reducing simple aldehydes like benzaldehyde and substituted benzaldehydes as well as benzoic acid and similar acids. However, he never attempted the reduction of more complicated aromatic acids or aldehydes containing more than two fused rings.

As the 5-formyl-4-phenanthroic acid contains an aldehyde and a carboxylic group directly linked to an aromatic ring system, we thought it would be worthwhile to try the "reductive silylation technique" to prepare the
4, 5- dimethyl phenanthrene in a single vessel. If this reduction is successful, it could lead to a new method for the preparation of the dimethyl phenanthrene, superior to the existing methods all of which involve several low yielding and complicated steps. The reaction was carried out under conditions similar to those employed by Benkeser, using 5-formyl-4-phenanthroic acid as the starting material and dry acetonitrile as the solvent. The product formed was a cyclic ether in about 37% yield along with trace amounts of a substance which on the basis of mass spectral evidence is suspected to be 4, 5-dihydro-4-chloropyrene. It was surprising that the expected 4,5- dimethyl phenanthrene was not formed even in trace amounts. In order to find an explanation for this unusual observation we had to review Benkeser's work again and we found that when he carried out the reductive silylation of benzaldehyde he got compound I as intermediate and when he did similar reaction with benzoic acid, the intermediate was compound II and both

![Chemical Structures](image-url)
Fig. 4  NMR spectrum of the cyclic ether
of them got ultimately reduced to toluene. By analogy to this, we concluded that we probably might have got compound III as an intermediate in our reaction and proposed the following mechanism for the formation of the major product. Unfortunately, we were not successful in isolating the silylated intermediate.

\[
\begin{align*}
\text{O} & \quad \text{HSiCl}_3 \\
\text{CH} & \quad \text{Cl} \\
\text{O} & \quad \text{CH}_2\text{-SiCl}_3
\end{align*}
\]

III

\[
\begin{align*}
\text{OH}^\ominus & \quad \text{CH}_2\text{-SiCl}_3 \\
\text{OH} & \quad \text{CH}_2\text{-SiCl}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{H}^+ \\
\text{H}_2\text{O} & \quad \text{H}^+
\end{align*}
\]
Our next aim was to oxidise the 5-formyl-4-phenanthroic acid to the 4,5-dicarboxylic acid, which on subsequent reductive silylation could plausibly yield the dimethyl derivative. But, our initial attempts to oxidise the aldehyde group by alkaline potassium permanganate were unsuccessful, because the strong oxidising agent cleaved the 9, 10-double bond resulting in the formation of the biphenyl 2, 2', 6, 6'-tetracarboxylic acid.

However, in the light of a recent publication (53), this observation is not very surprising. MacPhee and Stewart found that the permanganate oxidation in basic medium of phthalaldehyde is inhibited by the carboxylate group in the ortho position. In our system, the distance between the aldehyde and the carboxylate could be even closer leading to a much more pronounced inhibiting effect. This could in effect, favour the competing oxidation of the 9, 10-double bond. Once this double bond is oxidised, probably due to
the non-planarity of the molecule, the carboxylate group is not in a favourable position to inhibit the oxidation of the aldehyde and hence the tetracarboxylate is formed. Our attempts to cleave the double bonds of pyrene itself to prepare the tetra acid were unsuccessful.

Ultimately, we were able to solve the problem of the cleavage of the carbon-carbon double bond in the aldehydo acid, by making use of a milder oxidising agent which selectively oxidised the aldehyde to the carboxylic acid, leaving the carbon-carbon double bond intact. A freshly precipitated sample of silver oxide, could oxidise the sodium salt of the 5-formyl-4-phenanthroic acid to the 4, 5-dicarboxylic acid in about 80% yield. The structure of the diacid was confirmed by preparing its dimethyl ester and taking the NMR and mass spectra. Incidentally, the dimethyl ester of phenanathrene-4, 5-dicarboxylic acid has not been reported so far, even though several other isomeric dicarboxylic acid esters are known for a long time. Although, the 4, 5-dicarboxylic acid has been separated as a byproduct in the ozonolysis of pyrene, a satisfactory method for its preparation in fairly good yield is not available. Oxidation of 5-formyl-4-phenanthroic acid by silver oxide appears to be the most satisfactory method for the preparation of the diacid.

When the phenanathrene-4, 5-dicarboxylic acid was
Fig. 5   NMR spectrum of the dimethyl ester of phenanthrene-4, 5-dicarboxylic acid
subjected to the reductive silylation as in the case of the aldehydo acid, again the product obtained was the cyclic ether and the expected dimethyl derivative was not formed even in trace amounts. The failure to achieve complete

reduction by the silylation technique could probably be due to the stereochemical problems associated with 4, 5- disubstituted phenanthrene ring system, which will be discussed in the later part of this chapter.

Even though we were not able to prepare the dimethyl phenanthrene, the one step synthesis of the cyclic ether from the aldehydo acid appears to be much better than the earlier method for its preparation involving several steps as shown below. (27).
WOLFF-KISHNER REDUCTION OF 5-FORMYL-4-PHENANTHROIC ACID

Due to the insolubility of the 5-formyl-4-phenanthroic acid in common organic solvents, it was almost impossible to get it in a homogenous medium to carry out further reactions. Obviously, this is one of the major reasons for the low yield of products in most of the reactions of this compound. In order to reduce the aldehyde to a methyl group, the aldehyde acid was subjected to the Huang-Minlon (42) modification of Wolff-Kishner reduction, using 95% hydrazine and triethylene glycol as the solvent. The product obtained after acidification was a resinous material which could not be crystallised even after chromatography.
ESTERIFICATION AND REACTIONS OF THE ESTERS

The two esters of the 5-formyl-4-phenanthroic acid, namely the aldehydo ester and the isomeric methoxylactone have been made earlier by Badger (27). Because of the higher solubility of the esters compared to the free aldehydo acid, we thought it would be better to prepare the esters and use them for further reactions rather than using the acid as such.

When Badger esterified the aldehydo acid (27) using methanol and hydrochloric acid as the reagent, the product was the bridged methoxylactone, and when he used diazomethane, the product was the unbridged aldehydo ester. Our observation was that it is not the reagent alone which determines the product, but the solvent as well. When we used dry acetone as the solvent and the ethereal diazomethane was distilled into the reaction flask, the product formed was the unbridged ester. But when methanol was used as the solvent and the ethereal diazomethane was distilled into the system, the bridged methoxylactone was obtained as the product. We also found that the unbridged ester I readily rearranged to the bridged methoxylactone, in the presence of a protic solvent like methanol. Badger identifies compounds I and II by the large difference in their melting points and also from the fact that no carbonyl derivatives could be prepared from
compound II. We could get the NMR spectra of the two esters and compound I showed the low field singlet due to the aldehydic proton which was missing in compound II. The IR spectrum of compound I also indicated the free aldehyde which was absent in compound II.

We also attempted the reduction of compound I with sodium borohydride, but it resulted in the rearrangement of I to II when a hydroxylic solvent was used. In fact, the 4-hydroxymethyl-5-methyl ester has not been reported so far, but the corresponding ethyl ester has been prepared by Fieser (32) by hydrogenating the 5-formyl-4-phenanthroic
Fig. 6  NMR spectrum of the ester of 5-formyl-4-phenanthroic acid
Fig. 7  NMR spectrum of the pseudo ester 
(methoxylactone)
acid in absolute ethanol using copper chromite as the catalyst at 130°C under 1400 lbs. pressure.

However, when we carried out the borohydride reduction of the ester in glyme, the product isolated appeared to be a mixture of the lactone of 1-hydroxy-4-phenanthroic acid and the methoxylactone. The product melted at 128–129°C whereas the lactone prepared (54) by the borohydride reduction of the aldehydo acid in basic solution has a melting point of 173–175°C. The NMR spectrum indicated the aromatic protons as well as a singlet at 5.3δ due to the benzylic protons of the lactone and singlets at 6.2δ and 3.7δ characteristic of the hydrogen and methoxyl of the methoxylactone. The mass spectrum also showed peaks at 264 and 232 corresponding to the molecular ions of the methoxylactone and the lactone respectively, but there was no peak at 266 corresponding to the reduced hydroxymethyl derivative. All this evidence suggests that the aldehydo ester under the
Fig. 8  NMR spectrum of the product of borohydride reduction of the aldehyde ester
Fig. 9 NMR spectrum of the lactone of 5-hydroxymethyl-4-phenanthroic acid
reducing conditions is partly rearranged to the methoxy-
lactone and partly reduced and the product is probably
converted to the lactone by eliminating methanol on
acidification.

GRIGNARD REACTION OF THE ESTER

Grignard reagents are known to react with esters
(43, 44) to produce alcohols with alkyl or aryl groups
added to the carbonyl carbon. In certain cases dehydration
of the carbonyl is also possible leading to the formation of
olefins.

\[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{MgI} \\
\text{R - C - OCH}_3 & \quad \rightarrow \quad \text{R - CH}_2\text{OH} \quad \rightarrow \quad \text{R - CH}_2\text{CH}_3
\end{align*}
\]

With a view to introduce methyl groups on the seven
membered ring, the methoxylactone was treated with methyl
magnesium iodide. As the methoxylactone was not very soluble
in ether, the Grignard reagent was prepared in ether and a
solution of the methoxylactone in tetrahydrofuran was added
at a slow rate under nitrogen atmosphere. As the product
turned out to be a dark coloured gum which was not crystal-
\text{lisable, it was chromatographed on Florisil. The NMR spectrum}
of the first fraction eluted with a 50/50 mixture of benzene
and naphtha showed the aromatic protons and a singlet at
1.2 δ and a doublet at 2.0 δ. There were no olefinic protons and no indication of the starting material being present. The IR spectrum showed no carbonyl or hydroxyl absorption. These evidences do not conclusively prove the presence of any particular compound, but it gives clear indication of the presence of methyl groups in the product.

The parent peak at 262 in the mass spectrum also gave strong indication for the presence of the following compound:

![Chemical Structure]

However, we did not attempt further purification of this material as the material started decomposing on storage.

Similar reaction with the lactone itself yielded an oil containing a mixture of two components which was difficult to separate. The NMR spectrum of the crude material indicated that the starting material had reacted completely and also the presence of methyl groups and olefinic protons. Further purification was not attempted.
HUNSDIECKER REACTION OF PHENANTHRENE

-4, 5-DICARBOXYLIC ACID

When the silver salt of a carboxylic acid is treated with bromine or iodine in an inert solvent like carbon tetrachloride in the absence of light, decarboxylation occurs and alkyl or aryl halide is produced. An improved procedure (45) for the Hunsdiecker reaction, using

\[ \text{I}_2 + \text{RCOO}^-\text{Ag}^+ \xrightarrow{\text{CCl}_4} \text{R} - \text{I} + \text{AgI} + \text{CO}_2 \]

iodine (or bromine) and mercuric oxide with the carboxylic acid in an inert solvent is also known. The mercuric salt initially formed reacts with the iodine to form a hypoiodite which undergoes thermal decomposition, presumably by a radical mechanism. After decarboxylation, radical coupling occurs resulting in the formation of an alkyl or aryl iodide.

\[ 2\text{R-COOH} \xrightarrow{\text{HgO}} (\text{RCOO})_2\text{Hg} \xrightarrow{\text{I}_2} [2\text{RCOO}] \]

\[ 2\text{R}^- + \text{CO}_2 + 2\text{I}^- \rightarrow 2\text{RI} \]

As the 4,5-diiodophenanthrene has not been reported so far, and we already have a satisfactory method for the preparation of phenanthrene-4, 5-dicarboxylic acid, it occurred to us that it would be worthwhile to try Hunsdiecker
reaction on the dicarboxylic acid. The reaction was performed in the classical way using the silver salt and also a separate experiment was carried out using the free acid and mercuric oxide. In both cases, the reaction was very slow and even after refluxing for 6 hrs., about 80% of the diacid remained unreacted. The product isolated was not the diiodo derivative as expected. The NMR spectrum showed only the aromatic protons and the IR spectrum indicated the presence of carbonyl function. Mass spectrum showed the absence of iodine, mercury or silver, but the highest molecular weight shown was 502. When the product was subjected to gas chromatography, it was found to be a mixture of four components. As there was no high molecular weight impurity in the starting material, it was definite that some unusual reaction had taken place. As the yield was very low and the required product was not formed, the separation and identification of the components was not attempted.

**CLEAVAGE OF THE CYCLIC ETHER BY MIXED HYDRIDE**

Reductive cleavage of acetals and ketalts was investigated in detail by Elieel and coworkers (46) and they found that the reduction by a mixed hydride reagent in ether is a general reaction. Best yields were obtained when the ratio of LiAlH$_4$ to AlCl$_3$ was 1:4 and the reagent was taken
in 100% excess. The cleavage of an ether (tetrahydrofuran) by this reagent has already been reported by Bailey (47). Later on, Mislow (48) was able to prepare compound II shown below by the reductive cleavage of compound I in about 80% yield.

If the cyclic ether prepared by the reductive silylation of 5-formyl-4-phenanthroic acid could be cleaved by the mixed hydride reagent, it would be possible to synthesise the 4-methyl-5-hydroxymethyl phenanthrene which has not been reported yet. From Bailey's work we found that tetrahydrofuran could not be used as a solvent as it gets cleaved by the reagent. So the reaction was initially carried out
Fig. 10  NMR spectrum of the product of mixed hydride reduction of the cyclic ether
in ether and apparently no reaction took place as the NMR spectrum of the product looked identical to that of the starting material. Therefore, in order to achieve a higher temperature, the solvent was changed to dry benzene and the reaction was prolonged for 30 hrs. The excess hydride was destroyed by careful addition of dilute sulfuric acid and the organic layer was extracted and dried. On concentration of the extract a dark oily material was obtained which was further chromatographed to get a yellow oil which failed to crystallise. NMR spectrum of the yellow oil showed that the singlet due to the methylene protons in the cyclic ether at 4.75 δ has completely disappeared and instead three new peaks appeared at 2.6, 3.0 and 3.7 δ which clearly indicated that the ether linkage had been cleaved. However, we were not able to purify the mixture further because even after repeated chromatography, the product was not crystallisable and the NMR spectrum showed no change.

**STABILITY OF SEVEN MEMBERED RINGS**

One of the interesting observations we have made during the course of this investigation is the unusual stability of the seven membered rings bridged at 4 and 5 positions of the phenanthrene nucleus. The structures I to III shown below are typical examples to cite. Structure I is preferred over the unbridged 5-formyl-4-carboxylate and
structure II is preferred over the unbridged aldehydo ester. Only the sodium salt of compound I exists in the unbridged form and the unbridged ester readily rearranges to the isomeric bridged methoxylactone II in the presence of a protic solvent. Compound III was obtained as the major product when attempts were made to prepare the 4, 5-dimethyl phenanthrene. The borohydride reduction of the aldehydo ester is an additional evidence in favour of the preference for the seven membered ring system. Both the products formed in this reaction have bridged seven membered ring structure and the unbridged hydroxymethyl derivative was not isolated;
the seven-membered lactone, rather than the hydroxy acid is also obtained from the reduction of the sodium salt of 5-formyl-4-phenanthroic acid (54).

All these observations prompted us to conclude that the seven-membered cyclic structure is thermodynamically more stable than the unbridged 4, 5- disubstituted phenanthrenes. It is quite probable that in the unbridged 4, 5- disubstituted compounds, as the bulk of the substituents increases, due to their close proximity, the Van der Waals radius of one group tend to overlap with that of the other. If a chemical bond is not formed between these groups, large repulsive interactions arise, which are likely to force the phenanthrene ring system to assume nonplanar conformations. In order to have minimum interaction of the substituents, the aromatic rings would remain in a twisted conformation with concomitant loss of aromaticity keeping the maximum possible distance between the substituents. But, in a bridged seven-membered ring, the interaction can be minimised by flipping of one or two of the carbon atoms directly linked to the 4 and 5 positions. The oxygen forming the ether linkage in structure III also can assume two conformations. In other words, the seven-membered ring can assume conformations, where the repulsive interaction is minimum, without altering the planarity of the phenanthrene ring system. As the phenanthrene nucleus prefers
not to lose its aromatic character, it assumes a planar conformation insofar as possible. In the 4, 5-bridged molecules, it is more likely that the phenanthrene ring system is planar. This could be the probable reason for the bridged seven membered ring being preferred over an unbridged 4, 5-di-substituted structure.

LOW-TEMPERATURE NMR STUDIES

NMR Spectroscopy is one of the major physical techniques used to study hindered internal rotations and conformational analysis. If the NMR spectra of various conformations of a compound differ, its spectrum will be temperature dependent and when the rate of interconversion is rapid, the spectrum is a time-averaged spectrum of the mixture of conformations. On the other hand, if the spectrum is independent of temperature changes over a reasonable range, either the energy difference between conformations is so small that temperature changes do not alter appreciably the relative populations or the energy difference is so large that essentially only one conformational isomer is present.

The chair to chair inversion of cyclohexane has been extensively investigated by low temperature NMR Spectroscopy (49). At room temperature, the proton signal of cyclohexane appears as a sharp singlet and at -70°C it
separates into two clear peaks, each of which shows a fine structure. The peak at low field is assigned to the equatorial protons and that at high field to the axial protons. This separation into two bands is clear evidence for the fact that chair to chair interconversion is slowed down at low temperature. The axial peak is broader because, axial–axial coupling is greater than equatorial–axial or equatorial–equatorial coupling. Conformations of several molecules have been assigned using low temperature NMR Spectroscopy and the energy barrier resisting interconversion also has been determined (50-52).

From the experience of earlier workers, we presumed that if some of our 4, 5-bridged phenanthrenes are subjected to low temperature NMR Spectroscopy, the splitting of the signal due to different conformations could be observed. To start with, we tried the cyclic ether in deuterated chloroform. NMR spectra in toluene were recorded at various temperatures between -50 and -70°C. Though we were not able to observe any splitting of the signal due to methylene protons, as the temperature was lowered the signal started broadening. Unfortunately, we were not able to lower the temperature further down, because the compound was insoluble at very low temperatures. Although, the two hydrogens attached to any one of the benzylic carbon atoms are stereo-chemically and magnetically nonequivalent, the two types of
protons were not distinguishable even at very low temperatures of the order of -100°C. It is not possible to make any positive conclusions from the NMR data. Either the energy barrier for the interconversion of the two conformers could be very low or their chemical shift difference is negligible, leading to accidental coincidence of the signals. A combination of the two effects is also possible. Or it could be even possible that the temperature is not low enough to split the signals.

Low temperature spectra were recorded for the methoxylactone also at different temperatures and in different solvents, but while broadening of the signal at low temperatures was observed, here also, as in the above case, no positive conclusions could be drawn. In this particular case, because of the more rigid framework, it may even be possible that actually only a single conformation is energetically feasible as the rotation is highly hindered.
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