CHAPTER I

OXIDATION OF CARBANIONS WITH MOLECULAR OXYGEN

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PART I

1.1 - Oxidation of Fluorene in Basic Solutions in the Presence of Catalysts

The autoxidation of carbanion compounds possessing considerable ionic character has received extensive investigation.

Sprinzak oxidized 9-phenyl-, 9-methyl-, 9-ethyl- and 9-benzylfluorene in pyridine solution containing benzyl trimethyl ammonium hydroxide (Triton B) at 0°C with the formation of the hydroperoxide. At 40°C, the reaction gave alcohol as the main product. In this way, he could obtain the varying yields of hydroperoxide and alcohol, for example, 9-methyl fluorene (Eq. 1).

\[
\text{CH}_3\text{H} \xrightarrow{\text{Base}} \text{CH}_3\text{OOH} + \text{CH}_3\text{OH}
\]

In these cases no cleavage of a carbon-carbon bond alpha to the reacting centre occurs. Russell and coworkers\(^2,3\) studied this reaction further using a variety of acidic hydrocarbons as substrates. They proposed a scheme, as illustrated in the following equations, for a hydrocarbon RH₂.
Scheme I.1

\[
\begin{align*}
\text{RH}_2 & \xrightarrow{\text{Base}} \text{RH}^- & \xrightarrow{\text{Base}} (R^\cdot) \\
\text{RH}^- + O_2 & \rightarrow \text{RH}^\cdot + O_2^- \\
\text{RH}^- + O_2^- & \rightarrow \text{RH}^\cdot + O_2^- \\
\text{RH}^- + \text{II} \text{ (Catalyst)} & \rightarrow \text{RH}^\cdot + \text{II}^\cdot \\
\text{RH}^\cdot + O_2 & \rightarrow \text{RHOO}^\cdot \\
\text{RHOO}^\cdot + O_2^- & \rightarrow \text{RHOO}^- + \text{RH}^\cdot \\
\text{RHOOH} + \text{OH}^- & \rightarrow \text{R} = 0 + \text{H}_2\text{O}
\end{align*}
\]

The rate determining step can be shifted from (3) to (4) depending upon the substrate in a particular basic media or on the solvent at a particular concentration of base. Russell proposed that the oxidations of fluorene and triphenyl methane differed in that, in the former case the rate of ionization was far faster than the electron transfer step and the reverse was the case in the oxidation of fluorene. Russell has also pointed out that in the case of hydrocarbons such as triphenyl methane, relative acidities can be deduced from a comparison of their rates of autoxidation, in the region of basicity, where the observed rate is dependent of oxygen concentration.
Bethell and coworkers have suggested in a study that the slow electron transfer step for fluorenyl anions can be avoided by the use of singlet molecular oxygen with which they react very rapidly.

Russell has used the nitroaromatic compounds as the catalyst to enhance the rate of oxidation of the hydrocarbon as depicted in Scheme 1.2.

\[
\begin{align*}
\text{Ar}_2\text{CH}_2 & \rightleftharpoons \text{Ar}_2\text{CH}^- \\
\text{Ar}_2\text{CH}^- + \text{II} & \rightarrow \text{Ar}_2\text{CH}^+ + \text{II}^2 \\
\text{Ar}_2\text{CH}^+ + \text{O}_2 & \rightarrow \text{Ar}_2\text{CHO}^+ \\
\text{Ar}_2\text{CHO}^+ + \text{Ar}_2\text{CH}^- & \rightarrow \text{Ar}_2\text{CHO}^- + \text{Ar}_2\text{CH}^+ \\
\text{II}^2 + \text{O}_2 & \rightarrow \text{II} + \text{O}_2^2 \\
\text{Ar}_2\text{CHO}^+ + \text{O}_2^2 & \rightarrow \text{Ar}_2\text{CHO}^- + \text{O}_2
\end{align*}
\]

Allara has reported that a marked acceleration in the rate is observed for the oxidation of fluorene, when catalytic amounts of cuprous chloride or carboxylate salts and aliphatic polyamines are present in pyridine-methanol solutions.

Russell et al. report that fluorene gives significant amount of the ketyl when it is treated with potassium t-butoxide
base in the presence of deficient amount of oxygen in DMSO (80%)-t-butyl alcohol (20%). It is believed that at first ketone is formed which is later reduced to ketyl\(^3\) (Eq. 16).

\[
FL = 0 + FL^H \quad \longrightarrow \quad FL^2 = 0 + FL^H
\]

(16)

Supporting evidence was obtained when it was conclusively found out that in the reaction of fluorenone with fluorenyl carbanion, fluorenyl ketyl is indeed formed\(^7\).

The author describes a series of studies aimed at investigating as to how the pattern of carbanions reactivity and the product distribution as a result of oxidation of carbanions, are influenced by the following factors, namely:

1. **Effect of variation of the nature of base.**
2. **Effect of the addition of some novel catalysts, particularly fluorenone azine, hitherto not reported.**
3. **Effect of the base-solvent system especially KOH in DMSO (80%)-MeOH (20%).**

To our knowledge, no report exists of this base-solvent system and it is believed that this is as good a reagent as t-BuOK in generating carbanions from a number of weak organic acids.

The main objective of the present work is to analyse the overall kinetic behaviour and the mechanism of oxidation...
of carbanions in the presence and absence of catalysts.

Having found that fluorenone azine is a good electron acceptor which on reduction yields radical anions of appreciable stability (see Chapter II), a natural consequence was to capitalize on its utility as electron-transfer catalyst in effecting autoxidations of a number of carbanions. In the opinion of the author fluorenone azine is a better catalyst as compared to nitroaromatics, in that no adducts are formed and the rate of oxidation of carbanions is quicker. It is believed that the reactions utilizing such a catalyst will be more revealing and may be identified as of synthetic value in the near future.

Results and Discussion

The autoxidation of fluorene in solvent mixture comprising varying proportions of DMSO and alcohol was studied in the presence of (a) \( \text{t-BuOK} \), (b) KOH and (c) sodium dimesyl.

The significance of the results described here is two-fold. First, the results provide sufficient evidence that fluorenone azine \( \text{(Fl=N-N=Fl)} \) acts as an efficient catalyst in autoxidation of several carbanions. Further observations, relevant to the use of this catalyst, will be reported in later sections. Second, KOH in (80\%) DMSO-(20\%) MeOH acts as a strong base compared to \( \text{t-BuOK} \). KOH/DMSO-MeOH appears
to be a novel reagent which, besides its electron donor attributes, has sufficient basic strength to generate carbanions from a host of weak carbon acids.

An inspection of Fig. 1.1 reveals some interesting features of the autoxidation reactions. Tables 1.3-1.4 give the kinetic data of oxygen absorption at different intervals of time. The rates of oxidation are measured by observing the volume of oxygen absorbed per unit of time.

The absorption of oxygen volume has been converted into moles of oxygen absorbed and the graph (Fig. 1.1) has been plotted between mmoles of oxygen absorbed per mmoles of fluorene and time in minutes. No attempts were made to determine the rate constants but the graph serves as an index to indicate the efficiency of oxygen absorption in different base-solvent systems and in situations where catalysts have been used.

The autoxidation of fluorene in DMSO (80%)–MeOH (20%) as solvent and in the presence of KOH, a strong base, involves the reaction of the fluorenide carbanion (FLH⁻) with molecular oxygen. Indirect evidence of the generation of FLH⁻ in the set system, comes from the colour (orange) that is developed immediately upon adding the base. A similar situation occurs when the base is t-BuOK or sodium dimethyl.
Oxidation of 2 m moles fluorene in the presence of 20 ml (0.72 M) potassium tert-butoxide and 0.02 m moles of catalyst at 22°C, 640 mm Saturation oxygen pressure: in DMSO-ButOH (2:8, v/v) solvent system
(1) without catalyst (2) ferrocene (3) (FIN)$_2^+$; in DMSO-ButOH (8:2, v/v) (4) without catalyst (5) ferrocene (6) (FIN)$_2^+$; (7) KOH in DMSO-MeOH (8:2, v/v) with (FIN)$_2^+$.
medium the more of the reaction with molecular oxygen can now be considered.

Comparison of the electron affinity of oxygen in its ground state (0.43 eV) with the redox potentials of carbon ions \(^8,9,10\) (Table I.1) indicates that many carbon ions should be readily oxidized by molecular oxygen to give the corresponding radical and superoxide ion. Triplet-singlet mixing and collapse of the intermediate then yields the hydroperoxide (Eq. 17), and hydroperoxides thus formed eliminates water under the basic reaction conditions to give a carbonyl compound.

\[
R^- + O_2 \rightleftharpoons \overset{R^*O_2}{\rightarrow} \rightarrow \rightarrow NO_2^- \quad (17)
\]

Taking into account the generality of the oxidation sequence formulated by Russell \textit{et al.} \(^5\), the author proposes the mechanism of autoxidation in the absence of catalyst as in Scheme I.3.

![Scheme I.3](image)

In the case of secondary carbon acids, such as fluorene having comparatively high acidic character, mechanistic logic
would suggest that hydroperoxides will undergo base-catalyzed elimination as depicted in Eq. 18-19.

\[ \text{B} + \text{Fl} \xrightarrow{\text{OH}^-} \text{Fl} = 0 + \text{OH}^- \quad (18) \]

\[ \text{Fl} = 0 + \text{CH}_3\text{SOCH}_3 \xrightarrow{\text{Fl(OH)CH}_2\text{SOCH}_3} \quad (19) \]

fluorenone adduct

Table I.3 which gives product proportions shows that fluorenone (in some cases, the adduct) is the principal product. Its yield ca. 72% is highest in DMSO (80%)-BuOH (20%) solvent mixtures utilizing 2-BuOK as the base. When the solvent proportions are changed, for example, in the case of DMSO (20%)-BuOH (80%), the yield of fluorenone is reduced (~66%) and the reaction is very slow.

When KOH is used in MeOH only, practically no reaction occurs. Addition of DMSO to the system brings a dramatic change, and the reaction becomes analogous to 2-BuOK induced reaction as to the rate and the yield of products. The appropriate solvent combination for KOH to act as an efficient base was found to be DMSO (80%)-MeOH (20%).

Very interesting consequence of the work seems to be in the scope of reactions which exists where KOH in DMSO-MeOH can be used as a reagent. The enhanced activity of the hydroxide ion (OH⁻) may be visualised in terms of DMSO being able to
weaken any solvate shell (hydroxylic or alcoholic solvent) surrounding KOH by forming hydrogen bonds.\(^{11}\) The other significance of the observations is that the presence of the catalyst viz., fluorenone azine (Fl=N=N=Fl) dramatically enhanced the reaction rate (Fig. 1.1) and the yield of the product (Fl=O) is improved to Ca. 80% yield in DMSO (80%)-MeOH (20%), when KOH is used as a base, and to a Ca. 60% yield while using t-BuOK as base. The reaction is complete in 3 to 4 minutes in each of these basic media. With Fl=N=N=Fl as catalyst the reaction is marked by an instantaneous formation of a violet colour which disappears during the course of oxygenation. The appearance of the violet colour is suggestive of the radical anion (Fl=N=\overset{2}{\text{\textbullet}}\text{\textbullet} formation. The author has accumulated convincing evidence that these violet colour species are indeed the azine radical anions. ESR and related studies concerning these are discussed in Chapter II. The sequence of reactions thought to be involved are formulated in Scheme 1.4.

Scheme 1.4

\[
\begin{align*}
\text{Fl}_{11}^+ + (\text{Fl=N=\overset{2}{\text{\textbullet}}\text{\textbullet}}) & \rightarrow (\text{Fl=N=\overset{2}{\text{\textbullet}}\text{\textbullet}}^+ + \text{Fl}_1^-) \\
(1) & \hspace{1cm} (2) & \hspace{1cm} (3) & \hspace{1cm} (4) \\
(\text{Fl=N=\overset{2}{\text{\textbullet}}\text{\textbullet}}^+ + O_2 & \rightarrow (\text{Fl=N=\overset{3}{\text{\textbullet}}\text{\textbullet}}^+ + O_2) \\
(5)
\end{align*}
\]
\[
\begin{align*}
\text{Fl}_\cdot + O_2 & \rightarrow \text{FlO}_\cdot \cdot \\
\text{Fl}_0 + \cdot O_2 & \rightarrow \text{Fl}_0 + O_2 \\
\text{Fl}_0 + \cdot O_2 & \rightarrow \text{Fl}_0 + \cdot O_2 \\
\text{Fl}_0 + \cdot O_2 & \rightarrow \text{Fl}_0 + \cdot O_2 \\
\text{Fl}_0 + O_2 & \rightarrow \text{Fl}_0 + OH^- \\
\text{Fl}_0 + O_2 & \rightarrow \text{Fl}_0 + OH^- \\
\end{align*}
\]

The most compelling evidence for this mechanism which is analogous to that proposed by Russell et al. is the presence of nitroaromatics, is the appearance of EPR of active violet coloured species attributable to the azine radical anions. The above mechanism thus involves a free radical chain character wherein a variety of radical intermediates are implicated. Besides the azine radical anions (3), a blend of radical species such as superoxide anion (5), fluorenol (4) and peroxide radicals (6) should emerge as reactive intermediates. The generation
and the fate of superoxide ion ($\text{O}_2^-$) has been thoroughly studied\textsuperscript{12}. The usual fate of fluorenyl radical (4) is their reaction with either $\text{O}_2$ to yield the peroxyl radical (5) or with superoxide ion (5) to form the peroxo anion. Another route of the consumption (4) is their dimerisation which is however less favourable. The fact that bifluorenyl was obtained in traces along with the major product, fluorenone, lends support to this view.

Another catalyst, namely, ferrocene used in the present study also acted to increase the oxygenation rate. Since we do not have a convincing evidence as to whether or not electron transfer takes place, the studies are therefore at a very preliminary level.

In conclusion, our studies indicate that the autoxidation in the presence of ($\text{Fl}^{12} \text{Fe}$) catalyst provides an efficient method of oxygenation involving radical chain character. The regenerated catalyst does not decompose and is easily isolable in work-up procedures due to its low solubility in most of organic solvents. Further observations, relevant to the use of this catalyst, will be reported in the proceeding sections. Another important consequence of the work lies in having demonstrated the ability of the reagent KOH-DMSC-MEOH to act as a strong base and a precursor to carbanions from a host of weak carbon acids.
### Table I.1

**Half-wave reduction potential of radicals**

<table>
<thead>
<tr>
<th>Carbanion formed</th>
<th>$\text{H}_2\text{SO}_4$</th>
<th>$-\text{S}_{\text{HMPA}}$</th>
<th>MeCN</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ph}_3\text{C}^-$</td>
<td>1.11</td>
<td>0.83</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>$\text{PhF}^-\text{I}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhDiphenylcyclopropane" /></td>
<td>1.20</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhAnthracene" /></td>
<td>1.23</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$(\text{p-}\text{MeOCH}_2\text{C}_6\text{H}_4)_2\text{C}^-$</td>
<td>1.21</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2 = \text{CHCH}_2^-$</td>
<td>-</td>
<td>-</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>$\text{PhCH}_2^-\text{I}$</td>
<td>-</td>
<td>-</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>$\text{Me}_2\text{C}^-\text{I}$</td>
<td>-</td>
<td>-</td>
<td>2.56</td>
<td></td>
</tr>
</tbody>
</table>
### Table L.2

**Oxidation of Fluorene<sup>a</sup> in Basic Solution<sup>g</sup>**

<table>
<thead>
<tr>
<th>Base system&lt;sup&gt;b, d&lt;/sup&gt; V/V</th>
<th>Solvent system&lt;sup&gt;b&lt;/sup&gt; V/V</th>
<th>Catalysts 0.02 moles</th>
<th>% yield of the product (fluorenone)</th>
<th>Bifluorenyle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bu&lt;sub&gt;4&lt;/sub&gt;OK/MeSO-&lt;br&gt;MeOH (2:8)</td>
<td>MeSO-Bu&lt;sub&gt;4&lt;/sub&gt;OH (2:8)</td>
<td>Nil</td>
<td>65</td>
<td>f</td>
</tr>
<tr>
<td>2. -do-</td>
<td>-do-</td>
<td>fluorenoneazaine</td>
<td>73</td>
<td>f</td>
</tr>
<tr>
<td>3. -do-</td>
<td>-do-</td>
<td>ferrocene</td>
<td>70</td>
<td>f</td>
</tr>
<tr>
<td>4. Bu&lt;sub&gt;4&lt;/sub&gt;OK/MeSO-&lt;br&gt;MeOH (8:2)</td>
<td>MeSO-Bu&lt;sub&gt;4&lt;/sub&gt;OH (8:2)</td>
<td>Nil</td>
<td>72&lt;sup&gt;c&lt;/sup&gt;</td>
<td>f</td>
</tr>
<tr>
<td>5. -do-</td>
<td>-do-</td>
<td>fluorenoneazaine</td>
<td>86&lt;sup&gt;c&lt;/sup&gt;</td>
<td>f</td>
</tr>
<tr>
<td>6. -do-</td>
<td>-do-</td>
<td>ferrocene</td>
<td>78&lt;sup&gt;c&lt;/sup&gt;</td>
<td>f</td>
</tr>
<tr>
<td>7. KOH/MeSO-MeOH&lt;br&gt;(8:2)</td>
<td>MeSO-MeOH (8:2)</td>
<td>fluorenoneazaine</td>
<td>80&lt;sup&gt;c&lt;/sup&gt;</td>
<td>f</td>
</tr>
<tr>
<td>8. -do-</td>
<td>MeSO-MeOH (2:8)</td>
<td>Nil</td>
<td>60</td>
<td>e</td>
</tr>
<tr>
<td>9. Sodium dimethyl</td>
<td>MeSO-Bu&lt;sub&gt;4&lt;/sub&gt;OH (2:8)</td>
<td>Nil</td>
<td>64</td>
<td>e</td>
</tr>
</tbody>
</table>

---

<sup>a</sup> - 2 moles of fluorene (initial concentration)  
<sup>b</sup> - MeSO - dimethyl sulfoxide; Bu<sub>4</sub>OH - tert-butyl alcohol; MeOH - methanol;  
V/V - volume ratio; Bu<sub>4</sub>OK - potassium tert-butoxide  
<sup>c</sup> - fluorenone-adduct  
<sup>d</sup> - 20 ml of (0.72 M) base  
<sup>e</sup> - not determined  
<sup>f</sup> - in trace amount  
<sup>g</sup> - at 22<sup>o</sup>, 640 mm saturation oxygen pressure
TABLE I-3

Oxidation of fluorene\textsuperscript{a} in basic solution\textsuperscript{c, d, e}

<table>
<thead>
<tr>
<th>Time (t)</th>
<th>mmoles of oxygen absorbed (at time t)</th>
<th>mmoles of fluorene (at time t)</th>
<th>mmoles of oxygen absorbed per mmoles of fluorene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minutes</td>
<td>with- FLINHF\textsuperscript{b} with KOH</td>
<td>with- FLINHF\textsuperscript{b} with KOH</td>
<td>with- FLINHF\textsuperscript{b} with KOH</td>
</tr>
<tr>
<td></td>
<td>out ferro- (base) catalyst</td>
<td>ferro- (base) catalyst</td>
<td>ferro- (base) catalyst</td>
</tr>
<tr>
<td>1</td>
<td>- 0.667 0.506 0.643</td>
<td>- 1.333 1.494 1.257</td>
<td>- 0.500 0.440 0.474</td>
</tr>
<tr>
<td>2</td>
<td>- 1.102 0.289 1.037</td>
<td>- 0.898 1.111 0.963</td>
<td>- 1.227 0.900 1.077</td>
</tr>
<tr>
<td>3</td>
<td>- 1.365 1.036 1.200</td>
<td>- 0.645 0.964 0.800</td>
<td>- 2.100 1.076 1.500</td>
</tr>
<tr>
<td>4</td>
<td>- 1.339 1.108 1.303</td>
<td>- 0.611 0.292 0.607</td>
<td>- 2.273 1.242 1.369</td>
</tr>
<tr>
<td>5</td>
<td>0.547 1.403 1.231 1.348</td>
<td>1.453 0.597 0.759 0.652</td>
<td>0.376 2.350 1.600 2.057</td>
</tr>
<tr>
<td>6</td>
<td>0.865 - 1.347 -</td>
<td>1.145 - 0.663 -</td>
<td>0.747 - 2.032 -</td>
</tr>
<tr>
<td>10</td>
<td>1.016 - - -</td>
<td>0.924 - - -</td>
<td>1.033 - - -</td>
</tr>
<tr>
<td>15</td>
<td>1.150 - - -</td>
<td>0.850 - - -</td>
<td>1.253 - - -</td>
</tr>
<tr>
<td>20</td>
<td>1.245 - - -</td>
<td>0.755 - - -</td>
<td>1.649 - - -</td>
</tr>
<tr>
<td>30</td>
<td>1.236 - - -</td>
<td>0.734 - - -</td>
<td>1.725 - - -</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 3 mmoles of fluorene (initial concentration) in DMSO-MeOH or DMSO-Bu\textsuperscript{4}OH (8:2) solvent system

\textsuperscript{b} 20 ml (\textasciitilde{}0.72 M) of KOH (base); DMSO-MeOH (8:2, V/V) solvent mixture

\textsuperscript{c} 20 ml (\textasciitilde{}0.72 M) of Bu\textsuperscript{4}OK (base); DMSO-Bu\textsuperscript{4}OH (8:2, V/V) solvent mixture

\textsuperscript{d} at 22\degree C, 640 mm saturation oxygen pressure

\textsuperscript{e} 0.02 mmoles of catalyst in DMSO
### TABLE I.4

**Oxidation of fluorene**\(^a\) in basic solution\(^{b,c,d}\)

<table>
<thead>
<tr>
<th>Time (t) Minutes</th>
<th>mmoles of oxygen absorbed (at time t)</th>
<th>mmoles of fluorene (at time t)</th>
<th>mmoles of oxygen absorbed per mmoles of fluorene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without catalyst</td>
<td>with <strong>FL</strong>NFl</td>
<td>with ferrocene</td>
</tr>
<tr>
<td>5</td>
<td>0.411</td>
<td>0.609</td>
<td>0.595</td>
</tr>
<tr>
<td>10</td>
<td>0.592</td>
<td>0.972</td>
<td>0.951</td>
</tr>
<tr>
<td>15</td>
<td>0.757</td>
<td>1.184</td>
<td>1.160</td>
</tr>
<tr>
<td>20</td>
<td>0.896</td>
<td>1.310</td>
<td>1.245</td>
</tr>
<tr>
<td>25</td>
<td>1.047</td>
<td>1.348</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>1.061</td>
<td>1.348</td>
<td>1.317</td>
</tr>
</tbody>
</table>

\(^a\) - 2 mmoles of fluorene (initial concentration) in DMSO-Bu\(^+\)OH (2:8, V/V) solvent mixture

\(^b\) - 20 ml (0.72 M) of Bu\(^+\)OH (base); DMSO-Bu\(^+\)OH (2:8, V/V) solvent mixture

\(^c\) - at 22\(^\circ\), 640 mm saturation oxygen pressure

\(^d\) - 0.02 mmoles of catalyst in DMSO
PART II

1.3(A) - Oxidation of 9-Substituted Fluorenes in Basic Solution

9-Substituted fluorenes such as 9-phenyl, 9-methyl, ethyl, t-butyl, phenoxy and thiophenoxy ethers which are partially ionized in Bu\textsuperscript{t}OH are reported to follow the fluorene pattern of behaviour\textsuperscript{13}.

Reaction of oxygen with 9-substituted 9-fluorenyl carbanions, where the substituent is a strongly acidifying groups, e.g., CN, CO\textsubscript{2}Me, SO\textsubscript{2}Me etc., exhibit a variable pattern of behaviour.

The pK\textsubscript{a} values of a few substituted fluorenes are tabulated (Table I.5).

**Table I.5\textsuperscript{13}**

<table>
<thead>
<tr>
<th>9-substituted</th>
<th>pK\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>11.98</td>
</tr>
<tr>
<td>SO\textsubscript{2}Me</td>
<td>13.69</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>15.36</td>
</tr>
<tr>
<td>SO\textsubscript{2}Ph</td>
<td>14.96</td>
</tr>
</tbody>
</table>

\textit{a - pK\textsubscript{a} values in 22.5-48% Bu\textsuperscript{t}OH solvent}
While studying 9-substituted fluorenes, Guthrie et al. examined carbanions which lacked a leaving group at the 9-position. In the presence of aromatic nitrocompounds, these gave para substitution with the nitroaromatics as shown in Eq. 20.

\[
\begin{align*}
\text{H} & \quad \text{Me} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

The other major product type obtained from carbanions and aromatic nitrocompounds, was shown to be acenaphthene. These were believed to arise from nitrosobenzene radical anions by the mechanism suggested by Russell. The investigations reported in this Section had the object of studying the oxidation of 9-methoxy fluorene, 9-bromofluorene and 9-hydroxy fluorene, emphasis having been made on the use of KOH-DMSO reagent as carbanion producer and on the utility of fluorenoneazine catalyst in effecting electron transfer (as acceptor) free of complications as encountered in nitroaromatics.
In the case of 9-methoxy and 9-bromo fluorenes, only a single study, i.e., product analysis was carried out under both anaerobic conditions and in oxygen atmosphere (Table 1.6).

**Table 1.6**

Products of oxidation of 9-methoxy and 9-bromo fluorenes

<table>
<thead>
<tr>
<th>Substrate (4 mmoles)</th>
<th>Solvent system</th>
<th>Base 12 mmoles</th>
<th>Atmosphere</th>
<th>Catalyst 0.04 mmoles</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-methoxy fluorene</td>
<td>DMSO(80%) - MeOH(20%)</td>
<td>KOH</td>
<td>O₂ (F=H→2)</td>
<td>fluoresnone&lt;sup&gt;a&lt;/sup&gt; (8%)</td>
<td>9,9'-dimethoxy 9,9'-bifluorene (traces)</td>
</tr>
<tr>
<td>9-methoxy fluorene</td>
<td>DMSO(80%) - Bu&lt;sub&gt;6&lt;/sub&gt;OK</td>
<td>O₂ (F=H→2)</td>
<td>fluoresnone&lt;sup&gt;a&lt;/sup&gt; 8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-methoxy fluorene</td>
<td>DMSO(80%) - MeOH(20%)</td>
<td>KOH</td>
<td>N₂ (F=H→2)</td>
<td>9,9'-dimethoxy 9,9'-bifluorene (8%)</td>
<td></td>
</tr>
<tr>
<td>9-methoxy fluorene</td>
<td>DMSO(80%) - MeOH(20%)</td>
<td>KOH</td>
<td>N₂</td>
<td>No catalyst</td>
<td>9,9'-dimethoxy 9,9'-bifluorene (present, but not determined quantitatively), bifluorenylidene, ~20%</td>
</tr>
<tr>
<td>9-bromo fluorene</td>
<td>DMSO(80%) - MeOH(20%)</td>
<td>KOH</td>
<td>O₂</td>
<td>No catalyst</td>
<td>bifluorenylidene 88%, fluoresnone&lt;sup&gt;a&lt;/sup&gt; 8%</td>
</tr>
<tr>
<td>9-bromo fluorene</td>
<td>DMSO(80%) - MeOH(20%)</td>
<td>KOH</td>
<td>N₂</td>
<td>No catalyst</td>
<td>bifluorenylidene ~98%</td>
</tr>
</tbody>
</table>

<sup>a</sup> - fluoresnone adduct formed m.p. 163-165°C
The results summarized in Table 1.6 provide a valuable clue towards reaction mechanism.

Bifluorenylidene appears as the principal product in the case of 9-bromofluorene. The presence or absence of oxygen and also of the catalyst has no marked effect on the course of the reaction. Elimination of oxygen improves the yield of the olefin by a few per cent. It is therefore certain that no oxygenation takes place. Whether in oxygen or in nitrogen atmosphere, an instantaneous reaction was seen to take place when solutions of KOH or Bu<sup>4</sup>OK in DMSO-alcohol solvent were added to 9-bromofluorene. An immediate formation of red colour followed by the precipitation of a scarlet compound on work up completes the reaction.

Under the reaction conditions employed, it is possible to discern a straightforward course of the reaction which neither involves oxygenation nor electron transfer radical mechanism of any kind.

The reaction presumably involves a carbene route as formulated in Scheme 1.5. Subsequent to initial carbocation formation, it is the fluorenyl carbene (9) generated upon expulsion of Br<sup>-</sup> from the carbocation (2) that either dimerizes via route (A) to yield the olefin or adds to the initial carbocation (3) to form the intermediate (10) via route (B) that in turn yields the product, olefin (11) after expulsion of Br<sup>-</sup>.
The mechanism is reminiscent of olefin formation from benzhydryl chloride that has been reported to involve carbene-carbanion reaction in dimethylsulphoxide. For 9-methoxy fluorene, it is possible to contemplate two general courses for the oxidation.
Unlike that in the 9-bromofluorene, there exists a contrast in product forming steps in the oxidation of 9-
methoxy fluorene in oxygen atmosphere and under nitrogen in the presence of the azine catalyst.

In oxygen atmosphere, oxygenation indeed takes place and fluorenone (14) is isolated in almost quantitative yield (Table 1.6). In the absence of oxygen, and in the presence of the catalyst, the main product was identified as 9,9'-dimethoxy-9,9'-bifluorene (16) whereas in the absence of the catalyst, bifluorenylidene (16) was product along with the dimer (Table 1.6).

A radical chain mechanism involving electron transfer reactions appears to present the best rationalization for the product, fluorenone being formed in oxygenation reaction (Scheme 1.6). For the reaction carried out under nitrogen atmosphere and in the presence of the catalyst, the product 9,9'-dimethoxy-9,9'-bifluorene (16) that is formed as a principal product, may be thought to arise from the coupling of 9-methoxy-fluorene radical (13). These radicals are the natural consequence of an electron-transfer step between the carbonion (12) and the catalyst that acts as an electron-acceptor. In fact the dimer (16) has previously been shown to be the major product of the free radical oxidation of 9-methoxy fluorene by nitroaromatics in basic methanol17.
Scheme 1.2

I,2(3) - Oxidation of 9-Fluorenol in Basic Solution

Fluorenol and xanthanol are reported to react with t-BuOK and oxygen to give mainly ketones."
In the case of fluorenone in DMSO solution, the DMSO-fluorenone adduct is found. Russell and coworkers have reported that the oxidation involves methyl radical anions as intermediates, which, in the presence of excess oxygen, yield superoxide ions. The stoichiometry of the reaction in DMSO solvent employed was found to be complicated by the stabilisation of potassium superoxide by precipitation in the form of an ill-defined complex with BuOK. The mechanism of autoxidation of fluorenone or xanthanenol suggested by these authors is described in the following equations (Eq. 21-25):

\[
\begin{align*}
R_2\text{CHOH} & \xrightarrow{\text{B}^-} R_2\text{CHO}^- \xrightarrow{\text{B}^-} R_2\text{CO}^- \quad (21) \\
R_2\text{CO}^- \cdot O_2 & \rightarrow R_2\text{COO}^- + O_2^- \quad (22) \\
R_2\text{COO}^- \cdot O_2 & \rightarrow R_2\text{CO}^- + O_2^- \quad (23) \\
R_2\text{CO}^- \cdot O_2 & \rightarrow R_2\text{COO}^- + O_2^- \quad (24) \\
R_2\text{COO}^- \cdot O_2 & \rightarrow R_2\text{CO}^- + O_2^- \quad (25)
\end{align*}
\]

Results and Discussion

By choosing solvent and base, it should be possible to switch from one mechanism to another for a given substrate. Although the studies performed by the author with 9-fluorenone, present no conspicuous departures from those reported earlier by Russell et al., it is felt that the new system which has
been utilized in the present study, is much more convenient. The products are straightforward with no adduct formation and no complex formation is believed to occur especially when the base used is potassium hydroxide.

The system consists of KOH in hexamethyl phosphoramide (HMPA). For solubility consideration, methanol was added to the system. Thus, KOH in HMPA (80%)-MeOH (20%), provided reasonable good results. The work was carried out by contacting the carbinol (2 mmoles) at 27°C with molecular oxygen (saturation oxygen pressure = 640 mm) in the presence of 17 mmoles of KOH in HMPA-MeOH solvent system using fluorenoneazine as the catalyst (Table I.7). Rates of absorption were monitored by observing the mmoles of oxygen absorption per m mole of fluorenone (Fig. I.2). In all the runs, the major product was fluorenone ranging in yield from 80-90%.

The oxygenation process basically involves ionization of the α-hydrogen atom of the fluorenone to give either a carbanion or dianion. Consistent with the mechanism proposed by Russell et al., it is the radical-chain mechanism involving electron-transfer reactions that should operate (Scheme I.7).
FIGURE I.2 Oxidation of 2 mmoles 9-fluorenol in HMPA (80%) - MeOH (20%) containing 20 ml of (0.85 M) KOH (base) at 27°, 640 mm saturation oxygen pressure: (1) without catalyst; (2) with fluorenone azine.
Scheme 1.7

(17) \[ \text{F}1\text{H}^+ \xrightarrow{\text{e}^-} \text{F}1\text{H}^0 \xrightarrow{\text{e}^-} \text{F}1\text{O}^- \] (26)

(18) \[ \text{F}1\text{O}^- \xrightarrow{\text{e}^-} \text{F}1\text{N}^- \xrightarrow{\text{e}^-} \text{F}1\text{N} \] (19)

(20) \[ \text{F}1\text{O}^- + \text{F}1\text{N} = \text{F}1 \xrightarrow{\text{e}^-} \text{F}1\text{N}^\text{−} \xrightarrow{\text{e}^-} \text{F}1\text{N} \] (22)

(21) \[ \text{F}1\text{O}^- \] (23)

(22) \[ \text{F}1\text{O}^- + \text{O}_2 \xrightarrow{\text{e}^-} \text{F}1\text{O} + \text{O}_2 \] (24)

(23) \[ \text{F}1\text{N}^\text{−} \] (25)

(24) \[ \text{F}1\text{N}^\text{−} \] (26)

(25) \[ \text{F}1\text{N}^\text{−} + \text{O}_2 \xrightarrow{\text{e}^-} \text{F}1\text{N} \xrightarrow{\text{e}^-} \text{F}1\text{N} + \text{O}_2 \] (29)
<table>
<thead>
<tr>
<th>Time (t) Minutes</th>
<th>moles of oxygen absorbed (at time t)</th>
<th>moles of fluorenol (at time t)</th>
<th>moles of oxygen absorbed per moles of fluorenol</th>
<th>catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without FLNNFl</td>
<td>without FLNNFl</td>
<td>without FLNNFl</td>
<td>with FLNNFl</td>
</tr>
<tr>
<td>5</td>
<td>0.393</td>
<td>1.607</td>
<td>0.245</td>
<td>0.439</td>
</tr>
<tr>
<td>10</td>
<td>0.523</td>
<td>1.477</td>
<td>0.354</td>
<td>0.807</td>
</tr>
<tr>
<td>15</td>
<td>0.599</td>
<td>1.401</td>
<td>0.428</td>
<td>0.968</td>
</tr>
<tr>
<td>20</td>
<td>0.753</td>
<td>1.247</td>
<td>0.604</td>
<td>1.068</td>
</tr>
<tr>
<td>25</td>
<td>0.780</td>
<td>1.220</td>
<td>0.639</td>
<td>1.174</td>
</tr>
<tr>
<td>30</td>
<td>0.878</td>
<td>1.124</td>
<td>0.779</td>
<td>1.210</td>
</tr>
</tbody>
</table>

---

a - 2 moles of 9-fluorenol (initial concentration) in HMPA-MeOH (8:2, V/V) solvent system  
b - 20 ml of (0.65 M) KOH (base); HMPA-MeOH (8:2, V/V) solvent system  
c - at 27°, 640 mm saturation oxygen pressure  
d - 0.02 moles of catalyst in DM30  
HMPA = Hexamethyl phosphoramid
PART III

1.3 - Oxidation of tris-(p-nitrophenyl) methane in basic solution

The ease of oxidation of ionizable organic compound (RH) in basic solutions should depend not only on the degree of conversion to the carbanions but also on the relative stabilities of the carbanions and the corresponding radicals, factors which influence the ease of electron-transfer.

\[ R^- + X \rightarrow R^+ + X^- \]  (30)

\( X = O_2, ROO^-, RO^-, OH^-, \) or a substance not containing unpaired electrons\(^{18}\).

Substitution of groups such as nitro, CN, -CO, etc. in \( R \) would increase the degree of ionization of RH but decrease the ease of oxidation of \( R^- \). Russell et al.\(^{19}\) have observed this decreased trend of oxidation in each instance, wherein a series of substituted compounds having considerable ionization under t-butyl alcohol, with excess of t-BuOK, the rates of oxidation studied, were in the order of:

1. \( p \)-nitrotoluene > \( 2,4 \)-dinitrotoluene > \( 2,4,6 \)-trinitrotoluene;
2. \( p \)-nitrotriphenyl methane > tris-(\( p \)-nitrophenyl) methane.

Russell et al.\(^{20}\) have reported that the tris-(\( p \)-nitrophenyl) methane is converted to a mixture of hydroperoxide
and alcohol by a reaction with oxygen in basic solution\textsuperscript{21} by a process that shows many characteristics of a branched chain reactions, initiated by electron transfer\textsuperscript{5}.

Howthorne\textsuperscript{21} and coworkers have also studied the hydrocarbon (23) in detail. They generated its carbanion (26), in alcoholic alkali at room temperature. They have reported that the carbanion (26) reacts easily with the oxygen to give a 89\% yield of tris-(p-nitrophenyl) methyl peroxide.

\[
\begin{align*}
\text{tris-(p-nitrophenyl) methane} & \quad \leftrightarrow \quad -H^+ \\
\text{tris-(p-nitrophenyl) methide ion}
\end{align*}
\]

Results and Discussion

The present study is merely an extension of the use of fluorocene azine as catalyst in effecting oxidation via electron transfers of resonance stabilized anions such as tris-(p-nitrophenyl) methane.
TABLE I-2

Oxidation of Tris-(p-nitrophenyl) methane a in basic solution b,c,d

<table>
<thead>
<tr>
<th>Time (t) Minutes</th>
<th>mmoles of oxygen absorbed (at time t) without catalyst</th>
<th>with catalyst (Fl=N=2)</th>
<th>mmoles of tris-(p-nitrophenyl) methane (at time t) without catalyst</th>
<th>with catalyst (Fl=N=2)</th>
<th>mmoles of oxygen absorbed per mmoles of tris-(p-nitrophenyl) methane without catalyst</th>
<th>with catalyst (Fl=N=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-</td>
<td>0.444</td>
<td>-</td>
<td>1.626</td>
<td>-</td>
<td>0.263</td>
</tr>
<tr>
<td>10</td>
<td>0.226</td>
<td>0.718</td>
<td>1.904</td>
<td>1.412</td>
<td>0.119</td>
<td>0.508</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>0.952</td>
<td>-</td>
<td>1.172</td>
<td>-</td>
<td>0.817</td>
</tr>
<tr>
<td>20</td>
<td>0.444</td>
<td>1.026</td>
<td>1.686</td>
<td>1.104</td>
<td>0.263</td>
<td>0.929</td>
</tr>
<tr>
<td>30</td>
<td>0.718</td>
<td>1.300</td>
<td>1.412</td>
<td>0.830</td>
<td>0.508</td>
<td>1.625</td>
</tr>
<tr>
<td>40</td>
<td>0.736</td>
<td>1.348</td>
<td>1.394</td>
<td>0.762</td>
<td>0.525</td>
<td>1.724</td>
</tr>
<tr>
<td>50</td>
<td>0.802</td>
<td>1.348</td>
<td>1.330</td>
<td>0.762</td>
<td>0.603</td>
<td>1.724</td>
</tr>
<tr>
<td>60</td>
<td>0.855</td>
<td>-</td>
<td>1.275</td>
<td>-</td>
<td>0.671</td>
<td>-</td>
</tr>
</tbody>
</table>

a = 2.13 mmoles of tris-(p-nitrophenyl) methane (initial concentration) in DMSO-BuOH (8:2, v/v) solvent system
b = 2.5 ml of (0.85 M) Bu^+OH (base) in DMSO (60%) - Bu^+OH (20%) solvent system
c = at 27°C, 640 mm saturation oxygen pressure
d = 0.02 mmoles of catalyst in DMSO
The products analysed in a reaction of 2.13 mmoles of the hydrocarbon with 2.12 mmoles of t-BuOK and with 2.50 mmoles of KOH are given in Table I.9.

**Table I.9**

**Products of oxidation of tris-(p-nitrophenyl) methane in basic medium**

<table>
<thead>
<tr>
<th>Base</th>
<th>Catalyst</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOK (2.12 mmoles)</td>
<td>No catalyst</td>
<td>hydroperoxide(^b), carbinol - 20%</td>
</tr>
<tr>
<td>t-BuOK (2.12 mmoles)</td>
<td>FINNFl</td>
<td>hydroperoxide - 40%, carbinol - 20%</td>
</tr>
<tr>
<td>KOH (2.5 mmoles)</td>
<td>FINNFl</td>
<td>hydroperoxide - 30%, carbinol(^b)</td>
</tr>
</tbody>
</table>

\(^a\) - concentration of the hydrocarbon = 2.13 mmoles  
\(^b\) - not determined quantitatively  
\(^c\) - 0.02 mmoles

Fig. I.3 shows that there is a marked effect on the rate of oxygen absorption when the catalyst is used. In the absence of the catalyst, the oxygenation is very slow (Table I.9).

The product distribution as listed in Table I.9 is quite in accord with that found by Russell et al.\(^20\).

Accepting the generality of the mechanism proposed by Russell et al., for the autoxidation of triphenylmethanes in
FIG. I.3  Oxidation of 2.13 m moles tris-(p-nitrophenyl) methane in the presence of 2.5 ml of (0.85M) Bu₄OK (base) in DMSO(80%)-Bu₂OH(20%) solvent system at 27°. 640 mm saturation oxygen pressure: (1) without catalyst (2) with fluorenol azine catalyst (0.02 m moles in DMSO)
basic medium, it appears that the initial reaction product is the hydroperoxide which is formed via a sequence of steps involving the radical chain mechanism (Scheme 1.8).

**Scheme 1.8**

\[
\begin{align*}
R_2CH & \xrightarrow{R^{-}} R_2C^- \\
R_2C^- + FLMNF1 & \longrightarrow R_2C^* + (FLMN FL)^5 \\
R_2C^* + O_2 & \longrightarrow R_2COO^* \\
R_2COO^* & \xrightarrow{H} R_2COOH \\
(FLMN FL)^5 + O_2 & \longrightarrow FLMNF1 + O_2^* \\
R_2COO^* + (FLMN FL)^5 & \longrightarrow R_2COO^- + FLMNF1 \\
R_2C^* + O_2^* & \longrightarrow R_2COO^- \\
R_2C^- + R_3COOH & \longrightarrow R_2C^* + R_3CO^* + OH^- \\
R_2COO^- & \xrightarrow{H} R_2COH
\end{align*}
\]

There are two pathways by which the hydroperoxide can be considered to get decomposed. One is evidently that depicted in Eq. 37, which is essentially an electron-transfer redox reaction between the hydroperoxide and the carbonion yielding the radical products such as tris-(p-nitrophenyl) methyl and the tris (p-nitrophenyl) methoxy radicals.
It is presumably the hydrogen abstraction by the latter that the carbinol is formed. The other route to decomposition the hydroperoxide is its reaction with the base employed. Our studies indicate that this reaction is very slow. A negligible improvement in the yield of the carbinol occurs at the expense of the hydroperoxide on prolonged standing of the reaction mixture. This conclusively proves that the carbinol is the product of hydrogen abstraction reaction of the alkoxyl radical that is generated as outlined in Eq. 37 of the Scheme I.B.
PART IV

OXIDATION OF DIHYDROAROMATIC AND RELATED COMPOUNDS

I.4(a) - Oxidation of 9,10-dihydroanthracene in basic solution

It was not accepted until recently, that a methylene hydrogen of 9,10-dihydroanthracene, could dissociate in certain solvents in the presence of a base to form a carbanion, which, in the presence of molecular oxygen would yield oxidation products of dihydroanthracene.

Russell and coworkers have pointed out that in the case of the dianion of 9,10-dihydroanthracene as the donor the anthracene radical anion \( (\text{A}^-) \) was not stable in DMSO-\( t \)-butyl alcohol, the solvent system used and only the \( (\text{A}^-) \) radical anion was observed.

\[
\begin{align*}
\text{DHg} & \rightleftharpoons \text{DH}^- \rightleftharpoons \text{D}^-^2 \\
\text{D}^-^2 + \text{A} & \rightleftharpoons \text{A}^- + \text{D}^- 
\end{align*}
\]

The anthracene radical-anion has been formed in high-yield from anthracene and 9-10-dihydroanthracene in pure DMSO containing \( t \)-BuOK. Oxidation of 9,10-dihydroanthracene under these conditions also yields the anthracene radical anion. However, oxidation in DMSO (80\%)-\( t \)-butyl alcohol (20\%)
yields only 9,10-anthraquinone \(^7\).

Tutsuo and Okhatsu \(^{28}\) have noted that when 9,10-dihydroanthracene reacts electrochemically in the presence of oxygen, the mechanism is classified to be base catalyzed autoxidation, which is initiated by hydrogen abstraction from the compound, with the formation of the superoxide ion.

**Results and Discussion**

The present work has been undertaken with an aim to probe the mechanistic aspects of the oxygenation process of 9,10-dihydroanthracene in homogeneous basic conditions and in the presence of fluorenone azine catalyst. Upon addition of the DMSO solution of 9,10-dihydroanthracene to KOH in DMSO (80\%) - MeOH (20\%) or to t-BuOK in DMSO (80\%) - t-BuOH (20\%), a blood red colour presumably of the monocarbonion was immediately formed.

Fig. 1.4 presents a plot of moles of oxygen absorbed per moles of the hydrocarbon versus time (minutes). Addition of the catalyst, (Fe=Fe\(^+\)) to the system drastically increases the oxygenation rate (Table 1.10). The results are reminiscent of the electron-transfer radical chain mechanism as proposed for fluorene oxidation in Part I. The superoxide ion is indeed a key intermediate that is expected to be formed in the reaction chain. The sole products that could be easily identified and estimated are, anthraquinone adduct and anthracene.
Figure I.4 Oxidation of 1.4 mmoles 9,10-dihydroanthracene in DMSO-t-butyl alcohol (8:2, v/v) containing 21.2 ml of (0.66 M) BuOOK and 0.02 m moles of fluorenone azine catalyst at 27°, 640 mm saturation oxygen pressure: (1) without catalyst; (2) with (Fl=N₂)
In a typical exercise, starting with 1.4 mmoles of 9,10-dihydroanthracene, using 0.02 mmoles of fluorenone azine (catalyst) and in the base $\text{t-BuOK}$ (14.0 mmoles) in DMSO (80%)-$\text{t-BuOK}$ (20%), the following products were obtained:

Anthracene - (in ~75% yield)

Anthraquinone-DMSO adduct (in ~15% yield).

The compound anthraquinone-DMSO adduct showed strong IR absorption at 1060 (sulphoxide), 1603, 1683 (aryldione), and 3100 cm$^{-1}$ (OH).

To our knowledge, no electron-transfer catalyst has been used in the autoxidation of this substrate. Barton$^5$ and Russell$^5$ have performed the oxidation of dihydroanthracene using $\text{t-BuOK}$ as base. Both of these workers have proposed reaction mechanism which implicates hydroperoxide formation and its subsequent conversion to anthraquinone via anthrone formation.

The present study which the author has made utilizing the electron-transfer catalyst, namely, fluorenone azine, however rules out the possibility of anthrone being formed as a precursor to anthraquinone. To prove this, the midway oxidation products of dihydroanthracene were quenched before the reaction had gone to completion and then anthrone was searched for by an examination of the products by TLC. No indication of anthrone could be obtained except that anthraquinone, anthracene and the unreacted dihydroanthracene were
detected. It is therefore, pertinent to consider a reaction mechanism that explains the formation of anthraquinone and anthracene without occurrence of anthrone as the intermediate.

Since in the present study an electron-transfer catalyst, namely fluorenone azine, has been used, it is apparent that an one electron-transfer from the initially generated monocarbanion to yield the azine radical anion which in turn is consumed by molecular oxygen to produce the superoxide ion. More than the superoxide ion, the role of monocarbanion derived radicals (29) is important in that they react directly with oxygen to begin the propagation of the radical chains in forming peroxy radicals (30). A tentative mechanism is outlined in Scheme I.9.

**Scheme I.9**

\[
\text{(27)} \underset{\text{Base}}{\overset{\text{Base}}{\leftrightarrow}} \text{(28)} \quad \text{(41)}
\]

\[
\text{(29)} + \text{(Fl}=\text{N}=\text{N})_2 \rightarrow \text{(30)} + \text{(Fl}=\text{N}^\cdot_2) \quad \text{(42)}
\]

\[
\text{(Fl}=\text{N}^\cdot_2) + \text{O}_2 \rightarrow \text{(Fl}=\text{N}=\text{N})_2 + \text{O}_2^\cdot \quad \text{(43)}
\]
(29) + O₂ → HOO⁻ + (30) H H

(30) → HOO⁻ + (31) H

(31) → O₂ → HOO⁻ + (32) H

(32) + (33) → HOO⁻ + (31) H

(31) + (34) → HOO⁻ + (32) (33)
The peroxy radical (30) could then effect intramolecular attack on the 10-carbon-hydrogen to form the hydroperoxide radical (31). This draws support from a related study in which intermolecular attack has been demonstrated in a aliphatic system where two reactive hydrogen atoms are located in 1,4 positions.

A subsequent reaction of (31) with oxygen is expected to yield hydroperoxide-peroxy radical (32). This radical then reacts with (27) to give the dihydroperoxide (33) and the radical (28) which propagates the chain. The mechanism suggestive of the fact that anthracene is mainly formed by the decomposition of the hydroperoxide radical (31) with the carbanion (28) via the anthracene diradical (34) which in turn decays to form anthracene with termination of the chain. The route to anthraquinone formation is apparently the decomposition of the hydroperoxide (33) with the base.
TABLE I.10

Oxidation of 9,10-dihydroanthracene\(^a\) in basic solution\(^b,c\)

<table>
<thead>
<tr>
<th>Time (t) Minutes</th>
<th>moles of oxygen absorbed (at time t) without catalyst</th>
<th>moles of 9,10-dihydroanthracene (at time t) without catalyst</th>
<th>moles of oxygen absorbed per moles of 9,10-dihydroanthracene without catalyst</th>
<th>moles of oxygen absorbed (at time t) with (Fl=5) catalyst(^d)</th>
<th>moles of 9,10-dihydroanthracene (at time t) with (Fl=5) catalyst(^d)</th>
<th>moles of oxygen absorbed per moles of 9,10-dihydroanthracene with (Fl=5) catalyst(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.366</td>
<td>0.616</td>
<td>1.044</td>
<td>0.784</td>
<td>0.341</td>
<td>0.736</td>
</tr>
<tr>
<td>4</td>
<td>0.534</td>
<td>0.893</td>
<td>0.866</td>
<td>0.507</td>
<td>0.617</td>
<td>1.781</td>
</tr>
<tr>
<td>6</td>
<td>0.671</td>
<td>0.982</td>
<td>0.729</td>
<td>0.415</td>
<td>0.920</td>
<td>2.349</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>1.033</td>
<td>-</td>
<td>0.362</td>
<td>-</td>
<td>2.315</td>
</tr>
<tr>
<td>10</td>
<td>0.876</td>
<td>1.040</td>
<td>0.524</td>
<td>0.360</td>
<td>1.672</td>
<td>2.229</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>1.040</td>
<td>-</td>
<td>0.360</td>
<td>-</td>
<td>2.229</td>
</tr>
<tr>
<td>14</td>
<td>0.988</td>
<td>-</td>
<td>0.442</td>
<td>-</td>
<td>2.167</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>0.982</td>
<td>-</td>
<td>0.418</td>
<td>-</td>
<td>2.349</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>1.001</td>
<td>-</td>
<td>0.399</td>
<td>-</td>
<td>2.509</td>
<td>-</td>
</tr>
</tbody>
</table>

\(a\) - 1.4 mmoles 9,10-dihydroanthracene (initial concentration) in DMSO-Bu\(^{t}\)OH (8:2)

\(b\) - 21.2 ml of (0.66 M) Bu\(^{t}\)OK (base) in DMSO-Bu\(^{t}\)OH (8:2, v/v) solvent mixture

\(c\) - at 27\(^\circ\), 640 mm saturation oxygen pressure

\(d\) - 0.02 mmoles of fluorenone azine (catalyst) in DMSO
I.4(3) - Oxidation of anthrone in basic solution

As a natural consequence of the work, it was thought of interest to study autoxidation of anthrone, a compound related to dihydroanthracene. Russell and coworkers have made preliminary studies on its autoxidation\(^5\). The products of the reaction are reported to be anthraquinone and anthraquinone-DMSO adduct. Russell et al. have not suggested any mechanism for the reaction and to our knowledge no report exists about its mechanism by any other worker.

The sole objective of the present study was to suggest a mechanism of the reaction which is in some respect parallel to that proposed for 9,10-dihydroanthracene.

The compound was oxidised under the presence of base-solvent system, namely KOH in DMSO (80\%)-MeOH (20\%) (Table I.11). No catalytic effect was found by adding the catalyst, fluorenone azine. Fig. I.5 is a specimen plot between oxygen absorbed (mole) versus time (minutes). The products obtained were: anthraquinone (in 43\% yield) and anthraquinone-DMSO adduct (\(\sim\)3\%).

A convenient procedure proposed by Barton et al. was adopted for the separation and identification of anthraquinone-DMSO adduct. The mechanism of the reaction that implicates a blend of radical intermediates as postulated in some of the oxygenation steps of 9,10-dihydroanthracene is outlined in Scheme I.10.
FIGURE 1.5 Oxidation of 2 mmol of anthrone in DMSO-MeOH (8:2, v/v) containing 25 ml of (0.66 M) KOH/DMSO-MeOH at 27°C, 640 mm saturation oxygen pressure.
<table>
<thead>
<tr>
<th>Time (t) Minutes</th>
<th>mmoles of oxygen absorbed (at time t)</th>
<th>mmoles of anthrone (at time t)</th>
<th>mmoles of oxygen absorbed per mmoles of anthrone</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.356</td>
<td>1.644</td>
<td>0.217</td>
</tr>
<tr>
<td>10</td>
<td>0.623</td>
<td>1.377</td>
<td>0.452</td>
</tr>
<tr>
<td>15</td>
<td>0.836</td>
<td>1.166</td>
<td>0.717</td>
</tr>
<tr>
<td>20</td>
<td>0.996</td>
<td>1.004</td>
<td>0.992</td>
</tr>
<tr>
<td>25</td>
<td>1.091</td>
<td>0.909</td>
<td>1.200</td>
</tr>
<tr>
<td>30</td>
<td>1.122</td>
<td>0.873</td>
<td>1.278</td>
</tr>
<tr>
<td>35</td>
<td>1.139</td>
<td>0.861</td>
<td>1.323</td>
</tr>
<tr>
<td>40</td>
<td>1.150</td>
<td>0.850</td>
<td>1.363</td>
</tr>
</tbody>
</table>

a - 2 mmoles of anthrone (initial concentration) in DMSO-MeOH (8:2, V/V) solvent mixture
b - 25 ml of (0.06 M) KOH (base) in DMSO-MeOH solvent system
c - at 27°, 640 mm saturation oxygen pressure
Scheme I.10

\[ (35) \xrightarrow{\text{Base}} (36) + H^+ \]

\[ (36) + O_2 \rightarrow (37) + O_2^- \]

\[ (37) + O_2 \rightarrow (38) \]

\[ (38) + (36) \rightarrow (39) + (37) \]

\[ (22) \xrightarrow{\text{decomposed by base}} (40) \]
The anthrone carbanion may transfer one electron to the oxygen molecule to form superoxide and free radical of anthrone (Eq. 52). The anthrone free radical reacts with oxygen to form peroxy radical (Eq. 53). The peroxy radical of anthrone may abstract (H⁺) from the molecule of anthrone thereby forming the hydroperoxide (Eq. 54) and free radical to propagate the chain. The hydroperoxide may be decomposed by the base to give anthraquinone (Eq. 55) which reacts with DMSO to form anthraquinone-DMSO adduct.

I.4(C) - Study of autoxidation of tetraphenyl cyclopentadiene-ol in HMFA in the presence of KOH

Sprinzak¹ during his study has pointed out that all hydrocarbons of the cyclopentadiene series in which at least one hydrogen atom of the active methylene group is present, appears to behave in a similar fashion in carbanion formation in the presence of strong bases. Fluorene, xanthene, thioxanthene, tetraphenyl cyclopentadiene and phenalene all belong to cyclopentadiene series.
The Present Study

No report exists in the literature about the oxidation of tetraphenyl cyclopentadien-ol in basic solution. A preliminary report on the oxidation of tetraphenyl cyclopentadiene in a basic system comprising 1-BuOK-DMSO-BuOH describes that the oxygenation with deficient oxygen involves significant amounts of the ketyl.

A study that has been made by the author on the autoxidation of tetraphenyl cyclopentadien-ol merits a description. The reaction was found to be straightforward when the base used was KOH in HMPA. The catalyst as usual was fluorenone azine.

Immediately upon mixing HMPA solution of the carbinol (1 mmole) and KOH in HMPA (80%)-MeOH (20%) (5 mmoles), the solution assumed a dark red colour which during the course of oxygen absorption changed to violet and then to black. On working up the reaction for products, a single spot on the tlc plate was obtained which matched very well with an authentic sample of tetraphenyl cyclopentadienone. This product was isolated (see experimental) and its m.p. determined. The compound was unequivocally confirmed to be tetraphenyl cyclopentadienone in Ca. 75% yield.

A parallel experiment in which the base used was 1-BuOK in DMSO (80%)-BuOH (20%) also gave an initial red colour which
upon oxygenation, however, turned to light orange. On work up for the products, only trace amount of the ketone was found to be present. The other products were the unreacted carbinal and an unidentified substance.

While the author has no explanation for this reaction, the oxidation in the HMPA medium seems to be a straightforward example of a free radical chain oxidation.

The ease of initiation and propagation of the reaction presumably results from the ease of the dianion formation in HMPA but not in other solvents. If this assumption is true, then an electron transfer from the dianion to the acceptor (azine) should give radical anions as indicated in Scheme I.11.

**Scheme I.11**

![Diagram](image)
The above mechanism points to the involvement of ketyl radical anions (44), azine radical anions (45) and the superoxide (48) as intermediates.

While being definite about (45), the author, in the absence of EPR measurements, can not provide a convincing evidence of the existence of the ketyl radical anion (44). The existence of $\text{O}_2^-$ (48) can easily be visualised and it is expected that potassium superoxide (K02) should be precipitated along with the products, the work up of which was however not attempted due to difficulties involved in the laid down procedure for example that of Seyb and coworkers. 23
EXPERIMENTAL

Starting Materials

The following chemicals were used as such: Fluorenone (Fluka, Swiss); Sodium hydride (Fluka, Swiss); 9-Bromofluorene (Fluka); Anthrone (Loba-Chemic Indoaustralnai Co. India); 9-10-Dihydroanthracene (Fluka); Ferrocene (Sigma Chemical Company, U.S.A.); Lithium aluminium hydride (Metallgesellschaft, Frankfurt); Potassium metal (Riedel, Hannour), Pectracyclone (Fluka); Potassium hydroxide (Chemapol, Praha Czechoslovakia); Pyrogallol (Analer, London); Sodium dithionite (B.D.H., England) and Triphenyl methane (Fluka).

Method of Purification and Preparation

Fluorene (B.D.H., England) was twice recrystallized from ethanol, m.p. 116° (lit. 116°).

Tert-butyl Alcohol

T-Butyl alcohol (J.T. Baker Chemical Co., Phillipsburg, N.J.) 1-2 litres was refluxed with 30 g of freshly drawn sodium wire at about 82°-83°C. for about 6 hours and then distilling off the T-butyl alcohol. This procedure was repeated to obtain the pure alcohol (m.p. 25.5°C). T-Butyl alcohol was used as the major solvent for kinetic measurements and other experiments. The purified T-butyl alcohol was stored over calcium hydride.
1-Butyl alcohol is far more basic than ethanol or methanol. Bu^tOH with a dielectric constant of 10.9 (at 25°C) compared with a value of 73.5 for water, is far less nucleophilic than either methanol or ethanol.

Hexamethylphosphoramide (HMPA) obtained from Riedel was distilled twice and stored over calcium hydride.

Dimethyl Sulfoxide (DMSO) obtained from J.T. Baker was distilled under vacuum at 60-70°C from calcium hydride and stored over calcium hydride.

Pure DMSO can not be employed as a solvent because it may react readily with oxygen in the presence of potassium 1-butoxide, presumably due to the presence of the methyl sulfinyl carbanion (CH₃SOCH₂⁻)\(^{22,33}\). DMSO is a superior solvent for promoting the basicity of the 1-butoxide ion. It is believed that Bu^tOK is appreciably dissociated in DMSO (80%)-Bu^tOH (20%). Other solvents were purified by the method of Guthrie and coworkers\(^{34}\).

2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

To a stirred solution of tetracyclone (2.0 g, 5 mmoles) in dry ether (100 ml), was added aluminium chloride (1.330 g, 10 mmoles); followed by lithium aluminium hydride (0.2 g, 5 mmoles). After refluxing for 4 hours, excess hydride was decomposed by the addition of dilute hydrochloric acid. Dried
(MgSO₄) ether solution was evaporated under reduced pressure, which left a residue of white crystalline nature. The white solid reddened rapidly and lost its brilliant white fluorescence in air. The solid gave dark red colour in concentrated H₂SO₄. The solid was stable at room temperature.

Yield ~70%; m.p. 138° (lit. 32 138-140°)

**Fluoren-9-ol**

Fluorenone (5 g) was dissolved in 200 ml of dry diethyl ether. Lithium aluminium hydride (5 g) dissolved in 200 ml of dry ether was added to solution which was then stirred at 0°-10°C for 90 minutes. Ether layer was dried with anhydrous sodium sulphate, filtered and the volume of the ether was reduced to one-fourth then dry petroluem ether (40°-60°) was added. The white shining crystals of fluoren-9-ol were obtained, which were recrystallized (twice) with pet. ether in colourless needles:

m.p. 156° (lit. 31 154-156°)

**Tris-(p-nitrophenyl) Methane**

Triphenyl methane (10 g) was slowly added to a constantly stirred mixture of 78 g of concentrated HNO₃ (d 1.50) and 120 g of concentrated H₂SO₄ (d 1.85) at freezing mixture (0° to -5°). The temperature of the whole solution had been allowed to rise
slowly to $\sim 16^\circ$, then the whole solution was poured into much cold water. The precipitated trinitro triphenyl methane was collected by suction filtration, washed several times with water and dried. The solid was boiled with (75%) acetic acid-(25%) water (V/V) and the precipitate was obtained by suction filtration, dried and recrystallized from chloroform-ether gave light yellow crystals:

m.p. 210-211°C (Lit. 212.5°C), 60% yield of the product was found.

**9-Methoxy Fluorene**

9-Bromo fluorene (5 g) and silver nitrate (3.4 g) were dissolved in dry methyl alcohol (100 ml). The solution was refluxed for 60 minutes. The filtered solution was poured into water; the oil which separated solidified in ice and crystallized from pet. ether (40-60) in white needles:

m.p. 42°C (Lit. 31 42⁰-43⁰), 85% yield.

**Fluorenone Azine**

Fluorenone azine was prepared by the known method.

**Preparation of Authentic Samples**

**Fluorenone Adduct**

Fluorenone (3.6 g, 20 mmol) was dissolved in 25 ml of dimethyl sulfoxide-$t$-butyl alcohol (8:2 V/V). 40 ml of (0.72 M)
potassium tert-butoxide in dimethyl sulfoxide-2-buty alcohol (8:2 V/V) solvent mixture was added to fluorenone solution, which was then stirred at 22°C for 60 minutes. The mixture was poured into water (acidified with acetic acid). The yellowish precipitate was filtered and the filtrate was extracted with ether. The extract was dried (MgSO₄), and concentrated to obtain traces of fluorenone adduct which had remained in solution.

The precipitate was recrystallized from aqueous/ethanol, the melting point was 155°C (lit. 155.5-156.5); 90% yield of 9-hydroxy-9-(methyl sulfinyl methyl) fluorene was obtained:

\[
\text{HO} \quad \text{CH₂SOCH₃}
\]

**anthraquinone-**adduct

The adduct could be synthesized from anthraquinone.

Anthraquinone (282 mg) was dissolved in 20 ml of DMSO-2-BuOH (8:2 V/V) solvent system and the solution of 25 ml (0.66%) of Bu₄OK in DMSO-2-BuOH (8:2 V/V) solvent mixture was added which was then stirred at 25°C for 90 minutes. The solution was diluted with water acidified with hydrochloric acid and extracted into chloroform. The extract was dried (MgSO₄), evaporated and
crystallized from chloroform-petroleum ether (40-60) as needles, m.p. 170° (Lit. 170-171°).

The product was obtained in 90% yield.

The compound showed strong infra red absorption at 1060 (sulphoxide), 1603, 1663 (aryl ketone), and 3100 cm⁻¹ (OH).

**Bifluorenylidene**

9-Bromofluorene (5 g) was dissolved in t-butyl alcohol (100 ml). 30 ml of (0.72 M) Bu₄OK solution in Bu₄OH was added to the solution which was then stirred for 3 hours. The deep red solution was poured into 250 ml water acidified with acetic acid, and the solution was extracted with ether until colourless extracts were obtained. The extracts were washed with water to remove any t-butanol. Solvent removal gave a red solid (4 g) which was crystallized from benzene-pet. ether (40-60), m.p. 191° (Lit. 189-190°).

**Preparation of Potassium Tert-Butoxide**

Weighed amount of potassium metal (Riedel), freshly cut and washed in (40/60) petroleum ether, was washed in two successive batches of purified t-butyl alcohol and then dissolved in a further sample of known volume of t-butyl alcohol under reflux with the exclusion of carbon dioxide and water. Solutions were used for kinetic and other experimental observations only for a period of five days, after which they began to decrease in basicity.
An aliquot of the resulting solution was titrated with standardized hydrochloric acid. Solutions of base prepared in this manner contained less hydroxide ion than those made by dissolving commercial potassium tert-butoxide in t-butyl alcohol.

1.6 - Oxidation Procedure

The rates of oxidation were measured by observing the volume of oxygen absorbed per unit of time. The volumes were corrected to standard temperature and pressure and converted to moles.

The oxidations were performed at 640 mm in a 250 ml flask, equipped with a magnetic stirrer. One side opening of the flask was connected (through three way stopcock) to a two-way 100 ml graduated burette by means of a rubber tubing, with a calcium chloride drying tube and a closed end mercury manometer as a part of the line. The lower end of the burette was connected to a 500 ml bulb filled with nearly saturated sodium chloride solution. Dry oxygen from a cylinder (after passing through two bubbling flasks containing sulfuric acid), was introduced into the burette.

After introduction of the substance to be oxidised and the solvent system e.g. dimethyl sulfoxide (80%) - t-butyl alcohol (20%), the flask was flushed several times with oxygen, which was introduced through the centre tube which extended below the surface of the solution. The oxygen was allowed to escape through
mercury trap connected to the flask via a stop cock. The solution of potassium tert-butoxide was introduced into the solution by pressure equalizing dropping funnel. The apparatus was brought to atmospheric pressure and stirring was started. The pressure in the system was equalized from time to time by means of bulb.

Oxygen absorption was recorded as a function of reaction time. When oxygen absorption had ceased, the contents of the flask were poured into water, the flask rinsed with water and the solution combined. In most of the cases dilute hydrochloric acid or dilute acetic acid was added. Water insoluble products were filtered from the aqueous solution and soluble products separated by extraction with suitable organic solvent.

General Procedure

All thin layer chromatographic (TLC) determinations were made using tlc silica gel (E. Merck) and the systems: petroleum ether, benzene-petroleum ether (8:2 V/V) and benzene. Spots were visualized by a jet spray of iodine vapours. Silica-gel (NCL) was used for column chromatography. Compounds were characterized by comparison of their IR spectra with those of the authentic samples, mixed melting points and TLC comparisons. IR spectra were recorded on Perkin-Elmer model 700. All the melting points were recorded on a Toshniwal melting point apparatus and are uncorrected.

1.6 - Autoxidation of Fluorene in the Presence of Potassium Tert-Butoxide (BuO\textsuperscript{t}OK) in Dimethyl Sulfoxide (20\%) - Tert-Butyl Alcohol (80\%) Solvent System

Fluorene 0.332 g (2 mmoles) was dissolved in 20 ml of solvent mixture of DMSO (20\%) - BuO\textsuperscript{t}OH (80\%). The fluorene solution was transferred into oxygenation flask which had three openings, one side opening was connected to mercury trap via a stop cock, while the other opening was connected to pressure equalizing separating funnel, however, oxygen gas was introduced through the central opening of the flask (Fig. 1.6). The oxygenation flask was equipped with teflon coated stirring bar and was maintained at 22°C. After introduction of the substance in solvent mixture to be oxidised was flushed several times with oxygen. The oxygen was allowed to escape through mercury trap connected to the flask via a stop cock. After completing the flushing of the flask with oxygen, 20 ml of (0.72 M) potassium T-butoxide in DMSO:BuO\textsuperscript{t}OH (2:3 V/V) solvent mixture was added to the magnetically stirring solution of fluorene. Light orange colour of fluorenyl carbanion was developed immediately after
FIGURE I.6 General Oxidative Technique employed in the oxidation of hydrocarbons in basic solution.
addition of Bu\textsuperscript{t}OK solution. Orange colour changed to very light yellow colour after 3 minutes of oxygen supply to the oxygenation flask. After 20 minutes the solution attained deep yellow colour. The experiment was conducted at 640 mm of saturation oxygen pressure and at 22°C. The contents of the flask were poured into 150 ml water acidified with 10 N acetic acid, after the absorption of oxygen had ceased. The portion, insoluble in water, was filtered and the product was extracted with diethyl ether. The extracts were dried with MgSO\textsubscript{4} and evaporated and the residue on column chromatography coupled with tlc monitoring of the eluted fractions, the fluorenone was isolated. The yellow solid on recrystallization with ethanol gave the product having m.p. 85°C (lit. 85°-86°). The product showed complete taly on tlc plate with the authentic sample of fluorenone. The compound showed no depression in m.p. on mixing with an authentic sample. The IR spectra of the compound agreed with that of pure fluorenone, which has a carbonyl band at 1720 cm\textsuperscript{-1}.

**Product Distribution**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (based on the amount of fluorene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorenone</td>
<td>[ \frac{\sim 65%}{\text{yield}} ]</td>
</tr>
<tr>
<td>Bifluorenyl</td>
<td>Trace amount</td>
</tr>
</tbody>
</table>

1.7 - Oxidation of Fluorene with Bu\textsuperscript{t}OK in DMSO (80%)-Bu\textsuperscript{t}OH (80%) (V/V) Solvent Mixture in the Presence of (a) Fluorenone Azine (b) Ferrocene, As a Catalyst

(a) Fluorene 0.332 g (2 mmoles) was dissolved in 20 ml of solvent
mixture of DMSO-Bu^tOH (2:3 V/V) and the solution was kept in the oxygenation flask. 7 x 10^{-3} g (0.02 mmoles) of fluorenone azine was dissolved in 5 ml of DMSO and this solution was introduced into the oxygenation flask. 20 ml of (0.72 M) Bu^tOK was introduced into the oxygenation flask through the pressure equalizing dropping funnel. The orange colour of (PhiH^-), changed to violet and then deep yellow colour after 10 minutes. After completion of the reaction the contents were poured into water acidified with acetic acid and the reaction mixture was worked up for the products as described in experimental Section 1.6.

(b) On carrying out the reaction analogously as described in Section 1.6-1.7 (a), but in the presence of ferrocene, the following products were obtained:

<table>
<thead>
<tr>
<th>Products distribution in the presence of</th>
<th>Fluorenone azine catalyst</th>
<th>Ferrocene catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorenone 0.242 g, (≈73%)yield</td>
<td>Fluorenone 0.236 g, (≈70%)yield</td>
<td></td>
</tr>
<tr>
<td>Bifluorenyl - trace amount</td>
<td>Bifluorenyl - trace amount</td>
<td></td>
</tr>
</tbody>
</table>
1.8 - Oxidation of Fluorene with Bu\textsuperscript{+}OK in the Solvent Mixture DMSO-Bu\textsuperscript{+}OH (8:2 V/V)

The reaction was carried out under identical conditions as described in 1.6. The solvent mixture used this time was DMSO-Bu\textsuperscript{+}OH (8:2 V/V).

Products of the reaction were:

- Fluorenone adduct - m.p. \(154^\circ\text{C}\) (Lit. \(155.5^\circ\text{C}-166.5^\circ\text{C}\)); yield of the product 72%
- Bifluorenyl - Trace amount

1.9 - Oxidation of Fluorene with Bu\textsuperscript{+}OK in the Solvent System DMSO-Bu\textsuperscript{+}OH (8:2 V/V) in the Presence of (a) Fluorenone Azine and (b) Ferrocene, as Catalysts

On carrying out the reaction analogously as detailed in Sections 1.6-1.7, but in DMSO-Bu\textsuperscript{+}OH (8:2 V/V) solvent system and in the presence of 0.02 mmoles of (a) fluorenone azine catalyst, the reaction was found to complete within 2-3 minutes, while in the presence of (b) ferrocene, the reaction took about 8-10 minutes to reach the completion.

The product analysis was made that showed the products consist of fluorenone, bifluorenyl and unreacted fluorenone azine or ferrocene that recovered unreacted.
% yield of the products in the presence of:

<table>
<thead>
<tr>
<th>Fluorenone azine</th>
<th>Ferrocene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorenone adduct - 0.286 g (\sim 86.2%); m.p. 153°C (lit. 155.5-156.5)</td>
<td>Fluorenone adduct - 0.249 g (\sim 76%)</td>
</tr>
<tr>
<td>Bifluorenyl - Trace amount</td>
<td>Bifluorenyl - Trace amount</td>
</tr>
</tbody>
</table>

Preparation of 0.72 M KOH (Base) in DMSO-MeOH

4.2 g of KOH was dissolved in 100 ml of solvent mixture of MeOH (20\%)-DMSO (80\%). The basicity of the solution was determined by the same procedure as described for potassium t-butoxide.

1.10 - Oxidation in the Presence of KOH in DMSO (80\%)-MeOH (20\%) in the Solvent Mixture DMSO (20\%)-MeOH (80\%)

0.332 g (2 moles) of fluorene was dissolved in 20 ml of the DMSO (20\%)-MeOH (80\%) solvents mixture. 20 ml of (0.72 M) KOH (base) in DMSO-MeOH was then added to the above solution through the dropping funnel and the oxygen gas was passed for the specific period of time. After the usual work up the following products were obtained:

- Fluorenone - 60\% yield m.p. 85°C
- Bifluorenyl - Not determined
1.11 - Oxidation of Fluorene with KOH in DMSO-MeOH (8:2 V/V) Solvent Mixture, in the Presence of 0.02 moles of Fluorenone Azine as Catalyst

This reaction was carried out under identical conditions as described in Section 1.7, but in DMSO-MeOH (8:2 V/V) solvent mixture and in the presence of KOH (in DMSO-MeOH solvent system) as base, in this base solvent system the reaction was found to reach the completion within 4-5 minutes.

On usual work up, product analysis showed:

Fluorenone adduct - (80%) yield, m.p. 154°C
Bifluorenyl - Traces

1.12 - Oxidation in the Presence of Sodium Dimethyl Anion in BuOH-DMSO (8:2 V/V) Solvent Mixture

1.8 g of sodium hydride was dissolved in 100 ml of DMSO. Brisk effervescence of hydrogen gas were evolved by the addition of NaH to DMSO. Basicity of the solution was determined by the same procedure as was followed in the case of BuOH.

2 moles of fluorene was dissolved in 30 ml of solvent mixture of DMSO-BuOH (2:8 V/V). 20 ml of (~0.72 M) the base (NaH/DMSO) was then added to the fluorene solution through dropping funnel and the oxygen was passed for the specific period of time. After the usual work up the following product was obtained:
Fluorenone - 64% yield, m.p. 88°C
Bifluorenylidene - Not determined

1.13 - Oxidation of 9-Bromofluorene with KOH in DMSO-MeOH (8:2 V/V) (Under Oxygen Atmosphere)

A solution of 1.0 g (4 moles) of 9-bromofluorene in 20 ml of solvent mixture of DMSO-MeOH (8:2 V/V) was treated with 20 ml of (0.6 M) KOH in DMSO-MeOH (8:2 V/V) solvent system. Addition of KOH base caused the solution to become red followed by the precipitation of a scarlet compound. Oxygen was admitted in the solution immediately after addition of the base. After stirring the reaction mixture for 1 to 2 hours, the solution was quenched by the addition of water containing acetic acid (6 N), and the mixture was extracted with diethyl ether. After the usual work up, scarlet red coloured product was obtained, which showed two spots on the tlc plate which matched with authentic samples of bifluorenylidene and fluorenone adduct.

Chromatography of the resulting material gave the following compounds:

Bifluorenylidene - (~25%) yield (based on 9-bromo fluorene), m.p. 188°C (Lit. 189-190°C)
Fluorenone adduct - (~2%) yield, m.p. 155°C
I.14 - Reaction of 9-Bromofluorene with KOH in DMSO (80%) - MeOH (20%) (Under Nitrogen Atmosphere)

On carrying out the reaction analogously as described in Section I.13, but in nitrogen atmosphere, a similar colour sequence appeared in nitrogen atmosphere.

The procedure is typified by the following experiment:

The solution of 9-bromofluorene was kept in a three-necked 250 ml R.B. flask mounted over a magnetic stirring base and fitted with a pressure equalizing dropping funnel. A gas passing adapter and a mercury trap was also fitted. The contents of the solution were flushed with pure dry nitrogen gas (purified by passing through the traps containing pyrogallol, fiezer and conc. H_2SO_4 solutions) for 30 minutes. The contents of the solution were kept at room temperature 25°C. After addition of KOH/DMSO-MeOH base, nitrogen was admitted in the solution immediately and continued its supply for 90 minutes, whereby the mixture was poured into 100 ml water acidified with acetic acid and extracted with ether. After usual work up, the scarlet red product showed a single spot which matched with authentic sample of bifluorenylidene.

Chromatography of the scarlet red material gave a red solid which was recrystallised from benzene-pet. ether (1:1 V/V).

Bifluorenylidene - (~95%) yield; m.p. 180°C
**I.15 - Oxidation of 9-Methoxy Fluorene with KOH in DMSO (80%) - MeOH (20%) Solvent Mixture, in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)**

A solution of 0.784 g (4 mmoles) 9-methoxy fluorene in 20 ml DMSO (80%) - MeOH (20%) solvent mixture, was treated with 20 ml of (0.60 M) KOH in DMSO-MeOH solvent system. Addition of KOH base generated red colour which instantaneously changed into violet by the addition of fluorenone azine (0.04 mmoles) in 5 ml DMSO. The violet colour of the reaction mixture underwent a fast colour change from violet through red to yellow by passing oxygen into the reaction flask. After stirring the reaction mixture for 90 minutes, the reaction mixture was quenched by addition of water containing acetic acid, and the mixture was extracted with ether as usual. The product thus obtained showed two spots on the tlc plate. The spot of highest intensity matched with authentic sample of fluorenone adduct.

Chromatography of the resulting material gave the following compounds:

- Fluorenone adduct: \( \sim (86\%) \) yield (based on the amount of 9-methoxy fluorene)
- \(9,9'-\text{dimethoxy}-9,9'-\text{bifluorene}\): Traces

**I.16 - Oxidation of 9-Methoxy Fluorene with KOH in the Solvent Mixture of DMSO (80%) - MeOH (20%) in the Presence of Fluorenone Azine Catalyst (Under Nitrogen Atmosphere)**

On carrying out the reaction under identical conditions as described in Section I.15, but in nitrogen atmosphere similar
colour sequence were observed. Experimental details are given in Section I.14.

White crystalline material which was recrystallized from benzene gave the following product:

\[
9,9'-\text{dimethoxy-9,9'}-\text{bifluorene} \quad \xrightarrow{65\% \text{ yield (based on 9-methoxy fluorene)}} \quad \text{m.p. } 274^\circ\text{C} \quad \text{(Lit.} \quad 274-276^\circ\text{C}) \]

I.17 - Oxidation with KOH in DMSO (80%)–MeOH (20%) in the Absence of Catalyst but in Nitrogen Atmosphere

The reaction was carried out analogously as described in Section I.15, but in nitrogen atmosphere and in the absence of catalyst. reddish-brown mass showed two spots on the tlc plate.

Chromatography of the resulting material gave the following products:

- Bifluorenylidene \( \sim 20\% \) yield; m.p. 190°C
- \(9,9'-\text{dimethoxy-9,9'}-\text{bifluorene}\) Not determined quantitatively

I.18 - Oxidation of 9-Methoxy Fluorene with Potassium t-Butoxide in DMSO (80%)–BuOH (20%) Solvent

Mixture in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)

The reaction was carried out under identical conditions as described in Section I.15, but in DMSO (80%)–BuOH (20%)
solvent mixture and in the presence of Bu₂OK base. A similar colour sequence appeared in the presence of Bu₂OK base in DMSO (80%)-Bu₂OH (20%) solvent mixture. On column chromatography coupled with TLC monitoring of the eluted fraction, the following product was isolated:

Fluorenone adduct - (92%) yield; m.p. 154°C

Preparation of KOH Base in HMPA (80%)-MeOH (20%)

4.85 g of KOH was dissolved in 100 ml of solvent mixture of HMPA (80%)-MeOH (20%). The basicity of the solution was determined by the same procedure as described for Bu₂OK.

1.12 - Oxidation of Fluorenol with KOH in HMPA (80%)-MeOH (20%) Solvent System (Under Oxygen Atmosphere)

0.384 g (2 mmoles) of fluorenol was dissolved in 20 ml of HMPA (80%)-MeOH (20%) solvent system. The intense red colour was developed immediately after adding 20 ml (0.85 M) solution of KOH in HMPA-MeOH (3:2 V/V). The intensity of the red colour decreased with the absorption of oxygen in the reaction vessel. The red colour at first changed into light red and then to orange and finally the solution assumed yellow colour with indication of precipitation. The contents of the reaction flask were poured into water acidified with acetic acid. After the usual work, the resultant product was recrystallized with ethanol and characterized as fluorenone: m.p. 84°C; yield
of the product 79.8% (based on the original concentration of fluorenol).

The compound showed no depression in m.p. when mixed with the authentic sample of fluorenone.

I.20 - Oxidation of Fluorenol with KOH in HMPA (80%)-MeOH (20%) Solvent Mixture in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)

The reaction was carried out under identical conditions as described in Section I.19, but in the presence of fluorenone azine (0.02 moles) in 5 ml DMSO, the following sequence of colour changes were observed: intense red to violet and then to orange and finally the solution attained the yellow colour. On the usual work up, the following product was obtained:

Fluorenone – 90% yield; m.p. 85°C

I.21 - Oxidation of Tris-(p-Nitrophenyl) Methane with Bu4OK in DMSO (80%)-Bu4OH (20%) Solvent Mixture (Under Oxygen Atmosphere)

0.81 g (2.13 moles) of tris-(p-nitrophenyl) methane was dissolved in 20 ml DMSO (80%)-Bu4OH (20%) solvent mixture. 2.5 ml of (0.86 M) Bu4OK was then added to the above solution through the dropping funnel. Addition of the Bu4OK base caused the solution to become deep violet-blue. Oxygen was admitted in the solution immediately after addition of the base. Deep violet-blue solution changed to greenish-blue with the passage of oxygen.
The amount of oxygen absorbed by the system was noted by the gas burette. The resultant solution was poured into water containing acetic acid, the bluish-green colour immediately discharged and yellow colour persisted. The reaction product was extracted with ether. After drying (MgSO₄) the extracts were evaporated and the residue was chromatographed over silica-gel column using benzene and chloroform as eluants. The following products were obtained:

**Tris-(p-nitrophenyl) carbinol** - (25%) yield (based on the concentration of the hydrocarbon)

Two recrystallizations of the product from ethanol-water gave short white needles melting at 190°C (Lit. m.p. 190-191°C).

**Tris-(p-nitrophenyl) hydroperoxide** : It was not determined quantitatively, the product after two recrystallizations gave white leaflets from ethanol-water (1:1 V/V), m.p. 187°C (Lit. m.p. 186.5-187.5°C).

I.22 - Oxidation of **Tris-(p-Nitrophenyl) Methane with Bu₄OK in the solvent mixture of DMSO (80%)-BuOH (20%) in the presence of Fluorenone Azine Catalyst (Under Oxygen atmosphere)**

On carrying out the reaction analogously as described in Section I.21, but in the presence of fluorenone azine

Authentic samples of carbinol and hydroperoxide were obtained by the courtesy of Dr. K.L. Handoo (Supervisor).
(0.02 mmoles) in 5 ml DMSO, a similar colour sequence was observed in the presence of fluorenone azine catalyst. The following products were obtained after the usual work up.

\[
\begin{align*}
\text{Tris-}(p\text{-nitrophenyl}) & - (28\%) \text{ yield; m.p. } 190^\circ C \\
\text{carbinol} \\
\text{Tris-}(p\text{-nitrophenyl}) & - (40\%) \text{ yield; m.p. } 187^\circ C \\
\text{hydroperoxide}
\end{align*}
\]

I.23 - Oxidation of Tris-(p-Nitrophenyl) Methane with KOH in DMSO (80\%)-
HeOH (20\%) solvent mixture in the Presence of Fluorenone Azine Catalyst
(Under Oxygen Atmosphere)

The reaction was performed under identical conditions as detailed in Section I.21, but in the presence of 3 ml (0.38 M) of KOH base in DMSO:MeOH (8:2 V/V) solvent mixture and fluorenone azine catalyst, a similar colour sequence appeared. After the usual work up, the following products were isolated:

\[
\begin{align*}
\text{Tris-}(p\text{-nitrophenyl}) & - \text{ Not determined quantitatively} \\
\text{carbinol} \\
\text{Tris-}(p\text{-nitrophenyl}) & - (38\%) \text{ yield} \\
\text{hydroperoxide}
\end{align*}
\]

I.24 - Oxidation of 9,10-Dihydroanthracene with t-BuOK in DMSO (80\%)-Bu\text{OH} (20\%) (Under Oxygen Atmosphere)

0.252 g (1.4 mmole) of 9,10-dihydroanthracene was dissolved in 20 ml solvent mixture of DMSO (80\%)-Bu\text{OH} (20\%). 21.8 ml of (0.66 M) t-BuOK was added to the oxygenation flask through the
pressure equalizing dropping funnel. The deep red colour was
developed immediately after addition of 4-BuOK base. Oxygen
was admitted in the solution just after addition of the base.
After completion of the reaction, the resultant solution was
diluted with water acidified with hydrochloric acid (6 N). The
deep red solution changed to light yellow. The solution was
filtered and the white residue was washed with water and recrys-
tallized from benzene and it was found to be anthracene:

64% yield; m.p. 216°C (Lit. 216-217°C)

The identity of the compound was confirmed by the mixed
melting point and tlc analysis, which showed complete tally
with an authentic sample of anthracene.

The filtrate was extracted with chloroform and was dried
with anhydrous sodium sulphate which gave an oil like liquid,
that after keeping for 24 hours in vacuum sealed reaction
vessel provided the following product:

Residue after two recrystallization from chloroform-
petroleum ether (40-60) gave crystalline compound, m.p. 170°C
(Lit. 170-171°C) which showed no depression of m.p. on mixing
with an authentic sample.

anthraquinone adduct — (10%) yield (based on the amount
of 9,10-dihydroanthracene)

IR spectra of anthraquinone adduct showed strong infra
red absorption at 1050 (sulphoxide), 1603, 1663 (aryl ketone),
and 3100 cm⁻¹ (OH).
I.25 - Oxidation of 9,10-Dihydroanthracene with t-BuOK in DMSO (80%)-BuOH (20%) in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)

The reaction was carried out under identical conditions as outlined in Section I.24, but in the presence of 0.02 mmole fluorenone azine catalyst in 5 ml DMSO, the following colour sequence was observed: the deep red colour changed to deep violet, the intensity of violet colour did not decrease by the admittance of oxygen.

After the usual work up, the following products were obtained:

- Anthracene - (~75%) yield; m.p. 216°C
- Anthraquinone aduct - (~18%) yield; m.p. 170°C

I.25(a) - Intermediate Product Study of Reaction of Section I.25

The mid-way oxidation products of dihydroanthracene were quenched in water and extracted with CHCl₃ following the procedure as detailed in Section I.24. The tlc analysis depicted the presence of anthracene, anthraquinone aduct and the unreacted dihydroanthracene.

I.26 - Oxidation of 9,10-Dihydroanthracene with KOH in DMSO (80%)-MeOH (20%), in Oxygen Atmosphere

The reaction was performed analogously as described in Section I.24. The base used this time was KOH in DMSO-MeOH
(8:2 V/V) solvent mixture. Similar color sequence was noticed as observed in Section 1.24.

After usual work up, the following products were isolated:

Anthracene - (≈ 62%) yield, m.p. 216°C

Anthraquinone - Not determined quantitatively

Adduct

1.27 - Oxidation of anthrone with KOH in DMSO (80%)-MeOH (20%)
(Under Oxygen Atmosphere)

0.338 g (2 mmoles) of anthrone was dissolved in 20 ml solvent mixture of DMSO (80%)-MeOH (20%). To the anthrone solution kept in the oxygenation flask, 25 ml of (0.66 M) KOH/DMSO-MeOH base was added. Supply of oxygen was started immediately after the addition of the base. The reaction product was diluted with water and acidified with acetic acid, after the completion of the reaction. The reddish color immediately discharged and the solution assumed yellow color and fine yellow crystals settled down. Yellow crystals thus separated were washed with water and crystallized from chloroform-petroleum ether (40/60) gave the following product:

Anthraquinone - (43%) yield based on the amount of anthrone; m.p. 265°C (Lit. 263-266°C)

The compound showed no depression in m.p., when mixed with an authentic sample of anthraquinone.

Anthraquinone adduct was isolated with the same procedure
as described in Section I.24.

anthraquinone adduct - (~8%) yield; m.p. 169°C

I.28 - Autoxidation of Tetraphenyl Cyclopentadien-ol with KOH in HMPA (80%)-MeOH (20%) in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)

0.386 g (1 mmole) of tetraphenyl cyclopentadienol was dissolved in 20 ml solvent mixture of HMPA (80%)-MeOH (20%). 10 ml of (0.5 M) KOH base in HMPA-MeOH solvent system, was added to the reaction mixture through the dropping funnel. Addition of the KOH base caused the solution to become dark red. On adding (Fl=NO₂) (0.01 mmole in 5 ml DMSO), the deep red colour instantaneously changed into violet. Oxygen was admitted into the reaction mixture immediately after addition of the KOH base, the solution underwent colour change from violet through dark red to black. After stirring the reaction mixture for 10 hours, water was added and the mixture was extracted with diethyl ether. After drying with (MgSO₄) the extracts were evaporated and the shiny black crystals were obtained. The product showed a single spot on the tic plate which matched with an authentic sample of tetraphenyl cyclopentadienone. Recrystallization from chloroform-petroleum ether (40/60) gave material, m.p. 213°C (Lit. 29 m.p. 218-220°C); percentage yield of tetraphenyl cyclopentadienone (~ 75%) (based on the amount of cyclopentadien-ol).
The compound showed no depression of m.p. on mixing with the authentic sample.

**1.22 - Oxidation of Tetraphenyl Cyclopentadien-ol with t-BuOK in DMSO (80%)-t-BuOH (20%) in the Presence of Fluorenone Azine Catalyst (Under Oxygen Atmosphere)**

The reaction was carried out under similar conditions as detailed in Section 1.28. This time the base used was t-BuOK in DMSO (80%)-t-BuOH (20%) solvent mixture. The following colour sequence appeared during reaction: deep red to violet and finally it attained light orange by the passage of O₂.

After the usual work up, the product showed three spots on the tlc plate.

Chromatography of the resulting material gave the following compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphenyl cyclopentadienone</td>
<td>Trace amount</td>
</tr>
<tr>
<td>Unreacted tetraphenyl cyclopentadien-ol</td>
<td>40%</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>-</td>
</tr>
</tbody>
</table>
REFERENCES


30. See ref. 22, p. 2653.


