CHAPTER III

OXIDATION OF CARBANIONS WITH ANIONIC OXIDANTS

SECTION III.1: OXIDATION OF FLUORENE BY ALKALINE HYPOBROMITE

SECTION III.2: OXIDATION OF FLUORENE BY PERMANGANATE, HEXACYANOFERRATE AND PERSULPHATE ANIONS
III.1 - Oxidation of Fluorene by Alkaline Hypochlorite in Dimethyl Sulphoxide-t-Butyl Alcohol Solvent System

Introduction

Oxidation of methyl ketones by means of alkaline hypochlorite solution was first reported by Lieben in 1890. Since then the process has been known as the haloform reaction, and the subject having been reviewed in 1939 by Fuson and Bull\textsuperscript{1}. Most of the recent work with hypochlorite involves direct oxidation of the organic compounds by alkaline hypochlorite for preparative purposes. Some of these reactions were documented by Fieser and Fieser\textsuperscript{2} in 1967 and 1969.

The oxidation of methylene groups to carbonyl systems by hypochlorite was first reported by Schiesaler and Eldred\textsuperscript{3} who obtained 9-oxofluorene-2-carboxylic acid as an "anomalous" oxidation product from 2-acetyl fluorene. The role of the acetyl group in activating the methyl or methylene group becomes evident from the fact that ethyl benzene or fluorene is unreactive under the exact conditions used to oxidize p-ethylacetophenone or acetyl fluorene\textsuperscript{4}. By oxidising m-methyl acetophenone to isophthalic acid where activation is limited to the inductive effect, it has been established\textsuperscript{4} that both the resonance and inductive effect of the acetyl group are conducive to the oxidation of the alkyl side chain.

Chakrabarty and Krebschoer\textsuperscript{5} have recently shown that
any electronegative group (e.g., nitro, cyano, carboxy, alkoxy, amino, thioalkoxy, or a heterocyclic ring) present in a structure makes the compound susceptible to hypohalite oxidation.

The compounds bearing an active methylene group are oxidized by hypohalite to give dimeric olefinic derivatives in alkaline solutions with some exceptions such as haloform reaction. The mechanism of the haloform reaction plays a very important role in the evaluation of the potential of a hypohalite oxidant. Benzyl cyanides react with hypohalite to give α,β'-dicyanostilbenes. A number of workers have studied these reactions and suggested mechanism involving an initial formation of carbanion, which is halogenated and then condensed to dimeric products (Eq. 1).

\[
\begin{align*}
\text{CH} & \rightarrow \text{RO}^- \\
\text{CH} & \rightarrow \text{ROH} \\
\text{CH} & \rightarrow \text{CHX} \\
\text{C} & \rightarrow \text{C} \\
\end{align*}
\]

9-Halofluorene reacts also with alkali to give bifluorenylidene, but 2-acetyl fluorene is oxidized by potassium hypochlorite to fluorenone-2-carboxylic acid, but not the expected dimer.

**The Present Study**

Being interested in oxidation of carbanions particularly anions derived from fluorene, it was desired to investigate the oxidation of fluorene with t-buty1 hypobromite in DMSO-3-BuOH
solvent system. As a part of the general procedure employed by the author, the solvent system DMSO-\(\text{t}-\text{BuOH}\) was chosen. The hypohalite : \(\text{t}-\text{butyl hypobromite}\) was deliberately made use of since under the conditions employed, it was found to be quite stable. As far as the author knows, oxidation of fluorene and the mechanism involved with \(\text{t}-\text{butyl hypobromite}\) has not yet been studied. The study has some attractive features in that the oxidation involves both carbocations and carbanions which act as precursors to products, fluorenolone and bifluorenylidine, respectively observed in the reaction.

**Results and Discussion**

On adding \(\text{t}-\text{butyl hypobromite}\) 20 ml of (0.1 M) solution to fluorene (6.4 mmoles) in DMSO (80\%) - \(\text{Bu}^+\text{OH}\) (20\%), at first the solution formed orange colour which later changed to greenish yellow colour, but in course of time the colour changed to reddish-orange. The solution was stirred for five hours, during which the reaction reached completion, an aqueous \(\text{Na}_2\text{SO}_3\) was poured into the reaction mixture to remove excess hypobromite and extracted with benzene. On column chromatography coupled with tlc monitoring of the eluted fractions, two main products were isolated. These are fluorenolone-DMSO adduct in Ca. 72% yield and bifluorenylidine in Ca. 15% yield (Table III.1).
TABLE III.1

Product distribution in the oxidation of fluorene with alkaline hypobromite at 25°C

<table>
<thead>
<tr>
<th>Oxidant/solvent system</th>
<th>Products (%)</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>fluorenone</td>
<td>bifluorenylidine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Fl=0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Bu₄OBr</td>
<td>72a</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>DMSO(80%)–Bu₄OH(20%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Bu₄OBr</td>
<td>81</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>DMSO(20%)–Bu₄OH(80%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. NaOBr</td>
<td>65a</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>DMSO(80%)–Bu₄OH(20%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a - fluorenone adduct;
Bu₄OBr - tert-butyl hypobromite;
NaOBr - sodium hypobromite

In view of the analogous studies on the reactions of 6,8,14,16 other carbonanes with hypothalites and based on the product studies, it is suggested that the reaction proceeds via three important stages.

The initial stage is that of carbanion formation, then the attack of hypobromite on the carbanion occurs giving 9-bromofluorene which yields the products via two distinct pathways, one involving carbocation formation by elimination of Br⁻ and the other involving carbanion that is generated by
abstraction of the remaining 9-proton (Scheme III.1).

Scheme III.1

\[
\text{Base} 
\begin{array}{c}
\text{Bu}^+\text{OBr} \\
\text{Bu}^-\text{O}^-
\end{array} 
\]

\[
\text{Path A} 
\begin{array}{c}
\text{Path B} \\
\text{Base}
\end{array} 
\]

\[
\text{Scheme III.1}
\]

\[
\text{Base} 
\begin{array}{c}
\text{Bu}^+\text{OBr} \\
\text{Bu}^-\text{O}^-
\end{array} 
\]

\[
\text{Path A} 
\begin{array}{c}
\text{Path B} \\
\text{Base}
\end{array} 
\]

\[
\text{Scheme III.1}
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\text{Base} 
\begin{array}{c}
\text{Bu}^+\text{OBr} \\
\text{Bu}^-\text{O}^-
\end{array} 
\]

\[
\text{Path A} 
\begin{array}{c}
\text{Path B} \\
\text{Base}
\end{array} 
\]

\[
\text{Scheme III.1}
\]

\[
\text{Base} 
\begin{array}{c}
\text{Bu}^+\text{OBr} \\
\text{Bu}^-\text{O}^-
\end{array} 
\]

\[
\text{Path A} 
\begin{array}{c}
\text{Path B} \\
\text{Base}
\end{array} 
\]

\[
\text{Scheme III.1}
\]
The initial carbanion formation is presumably the rate determining as has been suggested earlier on the oxidative coupling of benzyl cyanides with alkaline hypohalites. A mechanism that involves a rate-determining α-proton abstraction from benzyl cyanide followed by a rapid hypohalite attack to give α-halobenzyl cyanide has thus been formulated. Precisely this should happen with the present reaction as well. A fast interaction of the generated carbanion (1) with hypobromite is expected to give 9-bromofluorene (2). The products of the reactions namely fluorenone and bifluorenylidene and their proportions are suggestive of the fact that two pathways operate through which the intermediate, 9-bromofluorene reacts further. The fact that fluorenone is produced as a major product reflects that a pathway (A) indicated in Scheme III.1, may be operating. This involves formation of carbonium ion (3) as a result of the elimination of Br⁻ and its follow-up attack (presumably in a slow step) by hypobromite to yield fluorenone (5).
The other pathway which is an unequivocal route to bifluorenylidene entails straightforward generation of 9-bromofluorenyl carbanion (6) and a subsequent expulsion of Br\(^{-}\) to yield the carbene (7) which in turn dimerises to produce bifluorenylidene (8) (Path B). A confirmation that 9-bromo-fluorene in a strongly basic medium should yield bifluorenylidene was indeed obtained in Chapter I, when it was treated with a base such as \(\text{t-BuOK}\) or KOH in DMSO-alcohol solvent mixtures whereby bifluorenylidene appears in a quantitative yield.

III.2 - Oxidation of Fluorene by Permanganate, Hexacyanoferrate and Persulphate ions

The vigour of permanganate ion as an oxidizing agent assures it an important role as a reagent. Its reactions are the more interesting because of the several oxidation states to which it can be reduced. The mechanism of these reactions is determined both by reaction conditions and by the characteristics of the particular substrate with which it reacts. Manganese's +2, +4 and +7 oxidation states are only ones which are stable over wide ranges of acidity. Manganese VI and manganese V, particularly the latter, undergo disproportion to manganese VII and manganese IV in all but strongly basic solutions. In basic solutions, manganate ion VI MnO₄⁻₂ slowly disproportionates to permanganate and manganese dioxide\(^{17}\) (Eq. 2).
\[ 3 \text{MnO}_4^- + 2 \text{H}_2\text{O} \rightarrow 2 \text{MnO}_4^- + \text{MnO}_4^- + 4 \text{OH}^- \] (3)

Oxidation of aryl alcohols to ketones\textsuperscript{19} and diarylmethanes to tetra aryl ethanes\textsuperscript{19} can be brought about by manganese dioxide in organic solvents. Radical formation through hydrogen abstraction by the oxidant appears to be the reaction mechanism in the second case (Eq. 3, 4).

\[ \text{Ar}_2\text{CH}_2 + \text{MnO}_4^- \rightarrow \text{Ar}_2\text{CH}^\bullet \stackrel{\text{-H}^\bullet}{\rightarrow} \text{Ar}_2\text{CH}^\bullet \] (3)

\[ 2 \text{Ar}_2\text{CH}^\bullet \rightarrow \text{Ar}_2\text{CH}_2\text{CHAr}_2 \] (4)

The permanganate oxidation of dihydro-o-terpineol in basic solution converts the tertiary hydrogen to hydroxyl with retention of configuration.

This reaction, studied by Eastmann and Quinn, was conducted in two-phase system\textsuperscript{20}. They have noted that the presence of a hydroxyl group in the organic substrate greatly facilitates the oxidation.

Alkyl groups attached to the aromatic rings are oxidized
more readily than the ring in the most cases. Complete oxidation to the carboxylic acid usually occurs, but some compounds containing a tertiary hydrogen can be oxidized to the corresponding tertiary alcohol in excellent yield.\(^{21}\)

![Chemical structure](image1)

\[
\text{CH}_3\text{CH} \quad \text{CH}_2\text{CH}_3 \\
\text{CO}_2\text{H} \quad \text{aq. MnO}_4^- \quad \text{pH 13, 60°C,} \\
\text{30 minutes} \quad \text{CH}_3\cdot\text{C} \cdot \text{CH}_2\cdot\text{CH}_3 \\
\text{CO}_2\text{H}
\]

(6)

It is reported that Mn\(\text{VII}\) can bring about radical coupling reactions.\(^{21}\)

\[
\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\text{CH}_3 \quad \text{Mn}^{\text{VII}} \quad \text{CH}_3\cdot\text{CH}_2\cdot\text{CH} \cdot \text{CH}_2\text{CH}_3 \\
\text{C}_6\text{H}_5
\]

(7)

Aromatic compounds with electron donating groups in the ring are subject to ring rupture by permanganate. Benzene is degraded slowly by boiling alkaline permanganate.\(^{22}\) The stabilizing effect of an electron-withdrawing group such as nitro is illustrated by the pattern of oxidation of 1-nitronaphthalene.\(^{21}\)

![Chemical structure](image2)

\[
\text{NO}_2 \\
\text{MnO}_4^- \quad \text{H}_2\text{O} \quad \text{NO}_2 \\
\text{COOH} \quad \text{COOH}
\]

(8)
The destabilizing effect of an amino or hydroxyl group is illustrated by the oxidation of 1-naphthylamine \(^{21}\).

\[
\begin{align*}
\text{NH}_2 & \quad \text{MnO}_4^- \\
\text{H}_2\text{O} & \quad \rightarrow \\
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H}
\end{align*}
\] (9)

Polynuclear hydrocarbons, such as pyrene and naphthalene, are degraded by alkaline \(\text{MnO}_4^-\) to various carboxylic acids. Triphenylene forms mellitic acid \(^{22}\).

\[
\begin{align*}
\text{MnO}_4^- & \quad \text{aq. OH}^- \\
\rightarrow \\
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H}
\end{align*}
\] (10)

In neutral and mildly acidic solution, alcohols are much more stable to \(\text{MnO}_4^-\) than in basic solution \(^{23,24}\). The base catalysis, however, is due to the ionization of the alcohol \(^{25,26}\) (Eq. 11, 12).

\[
\begin{align*}
\text{R}_2\text{CHOH} + \text{OH}^- & \quad \text{R}_2\text{CHO}^- + \text{H}_2\text{O} \\
\text{R}_2\text{CHO}^- & \quad \text{Mn}^{\text{VII}} \quad \rightarrow \quad \text{R}_2\text{C} = \text{O}
\end{align*}
\] (11) (12)

The mechanism of the alcohol-permanganate reaction has
been shown by Stewart et al. \(25-27\) to involve hydrogen abstraction, either as hydride or as a hydrogen atom, by the permanganate ion from the anion of the alcohol.

\[
\begin{align*}
\text{R}_2\text{CHO}^- + \text{MnO}_4^- & \quad \text{---}\quad \text{R}_2\text{CO}^- + \text{HMnO}_4^2- \\
& \quad \text{---}\quad \text{R}_2\text{C} - \text{O}^- + \text{HMnO}_4^- \\
\end{align*}
\]

The rate controlling step is clearly between the alkoide ion and the permanganate ion.

The course of the permanganate oxidation of aromatic aldehydes has been studied by Tronov\(^28\), by Tompkins\(^29\) and by Wiberg and Stewart\(^30\).

The oxidation in alkaline solution is strongly accelerated by electron withdrawing group as revealed by the Hammett rho value\(^21\) of +1.83 for the reaction at pH 13.6.

\[
\begin{align*}
\text{ArCHO}^- + 2\text{MnO}_4^- + 3\text{OH}^- & \quad \text{---}\quad \text{ArCO}_2^- + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \\
\end{align*}
\]

Although the reaction of most-aromatic aldehydes is base catalyzed, the reaction shows only a fractional dependence on the hydroxyl ion concentration. It is thought that the anion of the hydrate of the aldehyde (A) or the corresponding radical (B) is involved in the oxidation\(^28-30\).
Wiberg and Fox found that hydrocarbons could be oxidised by potassium permanganate and proposed the mechanism. As the first step of the reaction, which must necessarily involve the abstraction of the tertiary hydrogen, the latter may be removed as a hydride ion or a hydrogen atom.

\[ R_3CH + MnO_4^- \rightarrow R_3C^+ + Mn^V \]  \hspace{1cm} (15)

\[ R_3CH + MnO_4^- \rightarrow R_3C^+ + Mn^{VI} \]  \hspace{1cm} (16)

They suggested that the abstraction of a hydride ion would lead to a carbonium ion. The carbonium ion could be formed either by an electron transfer reaction between the initially formed radical and Mn(VI) or by ionization of the manganese ester formed via the combination reaction. They assumed the latter being more feasible. The net process is given below:

\[ R_3CH + MnO_4^- \rightarrow \bigcup_{R_3C^+MnO_4^-H} \rightarrow \]

\[ R_3C - O - MnO_3H \xrightarrow{\text{hydrolysis}} R_3C - OH \]

\[ \downarrow \text{Ionization and reaction with solvent} \]

\[ R_3COH \]  \hspace{1cm} (18)
As a general rule anions are oxidised more readily by permanganate ion than are neutral molecule. Further, dianions are oxidised more readily than monoanions i.e., in general

\[ \text{Z}^{2-} \quad \text{H}^{+} \quad \text{H}_2\text{Z} \quad \text{H}_3\text{Z}^+ \]

4-butyl alcohol is fairly inert to the permanganate's oxidizing action. Stewart\[21\] has reported that many permanganate oxidations in basic solution proceed via reactions between permanganate ion and the anions of the substrate. Hypomanganate can be detected as an intermediate in the oxidation of hydrogen peroxide by strongly alkaline permanganate. The colour of the solution changes from purple \((\text{MnO}_4^-)\) to green \((\text{manganate}, \text{MnO}_4^2-)\), to deep green \((\text{hypomanganate MnO}_4^{3-} + \text{MnO}_2 \text{ brown})\) and to a brown turbidity \((\text{MnO}_2)\).

Andrews and Latimer\[32,33\], in their separate studies have reported that \(\text{Mn}^{\text{VII}} - \text{Mn}^{\text{IV}}\) couple has the values which are measurable only in basic solution, involving manganate and manganese dioxide.

\[ \text{Zn} + \text{MnO}_4^{2-} + 2\text{H}_2\text{O} \quad \longrightarrow \quad \text{MnO}_2 + 4\text{OH}^- + \text{e}^- = +0.60 \text{ volts} \]

(19)

The formation of dimer product has been reported by Symons\[34\] and Jezowska\[35\]. These workers have shown the presence of radicals and the coupling reactions during their study in
alkaline permanganate oxidations.

The Present Study

A preliminary study has been made concerning the oxidation of fluorene by alkaline permanganate. In order to obtain additional information concerning the mechanism of reactions by anionic oxidants, other oxidants such as hexacyanoferrate and persulphate salts were used. The reactions were carried out invariably under nitrogen atmosphere.

Results and Discussion

A solution of KMnO₄ (0.101 g, 0.64 mmoles) in 20 ml MeCN (80%)—water (20%), was added to a stirred solution of fluorene (0.108 g, 0.64 mmoles) in 20 ml MeCN at 25°C. Then a solution 10 ml of (0.1 N) t-BuOK in EtOH was rapidly added to the mixture under nitrogen atmosphere. During the first few minutes of the reaction, the purple colour of KMnO₄ was gradually discharged and the solution assumed a green colour which changed to brown. On allowing the reaction to proceed for a period of two hours during which time the colour intensified, a dark brown precipitate settled and the reaction took to completion.

On working up the reaction mixture for products, the following compounds could be isolated:
With potassium ferricyanide (2.11 g, 6.4 mmole) in 50 ml Bu₄OH-water mixture (2:1 V/V), the oxidation of fluorene (1.05 g, 6.4 mmole) in 30 ml Bu₄OH in the presence of 20 ml of (0.1 N) KOH in DMSO (80%)–Bu₄OH (20%), was marked by a colour sequence that involved transformation of the initially formed orange colour to dark brown and finally to reddish yellow which persisted. No change of colour was observed even after four hours, the reaction being carried out in nitrogen atmosphere. No attempts were made to investigate the reaction under oxygen atmosphere.

The contents of the reaction were acidified, the mixture filtered and an orange mass thus isolated was worked up by column chromatography coupled with TLC monitoring of the eluted fractions. The main products were:

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield</th>
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<tbody>
<tr>
<td>Fluorenol</td>
<td>15.5%</td>
</tr>
<tr>
<td>Fluorenone</td>
<td>48.8%</td>
</tr>
<tr>
<td>Bifluorenylidene</td>
<td>(in trace amounts)</td>
</tr>
<tr>
<td>Manganese dioxide</td>
<td>(not determined quantitatively)</td>
</tr>
</tbody>
</table>

Under identical conditions but with potassium peroxysulphate as oxidant (3.45 g, 12.6 mmole) in 50 ml mixture of Bu₄OH (50%)–water (50%), the reaction culminated in the
precipitation of a brown solid. Two hours after having carried out the reaction in nitrogen, the products of the reaction were found to be:

Fluorenone – 27%
Bifluorenyl – 55%

Based on the pattern of products obtained in the above oxidations and on the characteristics of the anionic oxidants used in the present study, it is presumed that when the oxidant is permanganate, the initial step of the reaction with fluorene is a non electron-transfer type. The most likely reaction is that which involves hydrogen abstraction in a cyclic process as shown in Eq. 20. The process affects oxygen insertion to yield the intermediate (2) which is susceptible to hydrolysis to form 9-fluorenol. This assumption draws support from a parallel study made by Wiberg and coworkers on the oxidation of tertiary hydrogens 31.

The fact that 9-fluorenol is obtained as a product is in conformity with this view. Fluorenol (10) thus formed has to be considered as an intermediate since the base present in the system is bound to abstract the hydroxyl proton to form the anion of the alcohol.
From this anion, hydride ion abstraction by the permanganate should take place (eq. 23) to yield the ketone (13) directly.

\[
\textbf{F1H} - \text{O} - \text{MnO}_3\text{H} \xrightarrow{\text{Hydroylse}} \textbf{F1HOH} \tag{21}
\]

\[
\text{F1H} - \text{O} - \text{MnO}_3\text{H} \xrightarrow{\text{Base}} \text{F1HO}^- \tag{11}
\]

\[
\text{F1HO}^- + \text{MnO}_4^- \rightarrow \text{F1} = 0 + \text{HMnO}_4^- \tag{12}
\]

\[
\begin{align*}
\text{F1} = 0 \xrightarrow{\text{Mn VII}} \text{F1} = 0 \tag{12}
\end{align*}
\]

Hydrogen atom abstraction from the anion (11) is also possible so that radical anions (13) may also be produced which would in turn get oxidised to the product fluorenone (13). Which one of the two pathways as outlined in Eq. 23 is more probable,
is difficult to visualize, but it may possibly be assuring that in generality, the mechanism outlined in Eqs. 20-24, is the most likely one although the author has no evidence other than the product analysis to establish it. One thing convincing about the sequence of reactions formulated in Eqs. 23-24 is an identical reaction concerning the permanganate oxidation of benzhydrol reported by Stewart et al., who claim that it is the hydrogen abstraction, either as hydride ion or as a hydrogen atom, by the permanganate ion from the anion of benzhydrol that results in the formation of benzophenone.

The results that were obtained in the oxidations by ferricyanide and peroxyc disulphate ions, are suggestive of the fact that these reactions are initiated by anion formation followed by one-electron transfer. The product bifluorenyl is to be considered arising out as a result of oxidative dimerization of the hydrocarbon (Scheme III.2).

\[ \text{Scheme III.2} \]

\[ \text{F1H}_2 \xrightarrow{\text{Base}} \text{F1H}^- \]

\[ \text{(14)} \]

\[ \text{F1H}^- \quad \text{Fe(CN)}_6^{3-} \quad \text{or S}_2\text{O}_8^{2-} \]

\[ \xrightarrow{\text{OH}^-} \text{F1}^+ \xrightarrow{\text{H}^+} \text{F1H}^+ \]

\[ \text{(15)} \quad \text{(16)} \]

\[ \text{(17)} \]
It is suggested that oxidation of fluorene with anionic oxidants such as Fe(CN)$_6^{3-}$ or S$_2$O$_8^{2-}$ proceeds through transfer of one electron from the initially formed carbanion (14) and involves fluorenyl radicals (15) as intermediates. In the absence of oxygen, the most discernible pathway is the one that involves dimerization of fluorenyl radicals. The appearance of the dimer, bifluorenyl (16) as product of the reaction is a straightforward confirmation to this assumption. Similar postulates have been made to account for the dimer formation in the chemical and electrochemical oxidation of alkane-nitronates.

The other product, i.e., fluorenone, that is formed being more favored in the oxidation with Fe(CN)$_6^{3-}$, is suggestive of the fact that fluorenyl radicals (15) are being trapped by the base (OH$^-$) present in the system to generate 9-fluorenol radical anions (17). The follow-up reaction, leading to the formation
of fluorescein (19) via a sequence of steps involving oxidation of radical anions (17), action of base and that of the oxidant, is being considered to be analogous to the oxidation with permanganate as formulated in Eqs. 17 and 18.

There are instances where it has been clearly demonstrated that radicals can add to anions to generate radical anions. In many cases this may constitute important coupling reactions in recently recognized S$_{E1}$ mechanisms. The reactions of 2-nitropropanate anion with radicals derived from substrates such as those shown in Eq. 25 are illustrative:

\[ \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2X \rightarrow X^- + \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2^+ \]  \hspace{1cm} (25)

\[ X = -\text{Cl}, -\text{SMe}^+, -\text{O}_2\text{C} \text{C}_6\text{Cl}_5, -\text{NMe}_3 \]

\[ \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2^+ + \text{Me}_2\text{C}^- = \text{NO}_2^- \rightarrow \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2^+ \]  \hspace{1cm} (26)

\[ \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2^- \rightarrow \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2X \rightarrow \text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2X \]  \hspace{1cm} (27)
EXPERIMENTAL

Starting Materials

Fluorenone (Fluka, Swiss), Fluorene (B.D.H., England), Potassium peroxido-disulfate ($\text{K}_2\text{S}_2\text{O}_8$) (K. Merck, Germany), Hexacyanoferrate (B.D.H.) and Potassium permanganate (B.D.H.) were used as such.

Acetonitrile, DMSO (Dimethyl sulfoxide), $\text{t}-\text{butyl}$ alcohol and other solvents were purified and the authentic samples of fluoren-9-ol, fluorenone-adduct, and bifluorenylidene were obtained, according to the procedure laid down in the preceding Chapters.

Inorganic materials of commercial guaranteed grade were used.

Method of Preparation of (a) Tert-Butyl Hypobromite and (b) Sodium Hypobromite

**t-Butyl hypobromite**: The solution of $t$-butyl hypobromite (0.1 M) was prepared by addition of aqueous NaOH (Analar, London) $2 \text{ g in } 60 \text{ ml}$ to Br$_2$ (~16 g). With cooling in a salt-ice bath and then diluted to 100 ml with $t$-butyl alcohol in a measuring flask. The content of hypobromite was analysed iodometrically$^{39}$. The concentration of base was determined by acidimetry with HCl.
Sodium hypobromite (0.1 M) was prepared by addition of aqueous NaOH (8.0 g in Ca. 60 ml) to Br₂ (∼16.0 g) with cooling in a salt-ice bath and then diluted to 100 ml in a measuring flask. The content of hypobromite was analysed iodometrically before use.

The solution of t-buty hypobromite or sodium hypobromite can be stored in a refrigerator for 2 months.

III.3 - Oxidation of Fluorene by t-Buty Hypobromite in DMSO:BuOH (8:2 V/V)

Fluorene 1.06 g (6.4 mmol) was dissolved in 20 ml of DMSO:BuOH (8:2 V/V) solvent system. 20 ml of (0.1 M) t-buty hypobromite was added to the fluorene solution. At first the solution formed orange colour which later changed to greenish-yellow, but in course of time the colour changed to reddish-orange. The solution stirred at 25° for 5 hours, during which time the reaction reached completion. Aqueous Na₂SO₄ was poured into the mixture to remove hypobromite and extracted with benzene.

Following products were isolated with silica gel column chromatography coupled with tlc monitoring of the eluted fractions:

Fluorenone-DMSO adduct - Ca. 72% yield; m.p. 189°C (Lit. 185.5-186.5°C)

Bifluorenylidene - Ca. 15% yield; m.p. 188°C (Lit. 189-190°C)
Compounds showed no depression of m.p. on mixing with an authentic sample.

**III.4 - Oxidation of Fluorene by Bu⁺OBr in DMSO (80%) - Bu⁺OH (20%)**

The reaction was carried under identical conditions as described in Section III.3, but in DMSO:Bu⁺OH (2:8 v/v) solvent mixture.

The following products were obtained:

- **Fluorenone** - (81%) yield (based on fluorene); m.p. 84°C

The compound was confirmed by mixture m.p. and IR with the authentic sample.

- **Bifluorenyleine** - Trace amount

**III.5 - Oxidation of Fluorene in the Presence of Sodium Hypobromite in Solvent Mixture of DMSO:Bu⁺OH (8:2 v/v)**

Fluorene 1.06 g (6.4 mmoles) was dissolved in 20 ml of DMSO:Bu⁺OH (8:2 v/v) solvent system. Water (5 ml), aqueous NaOH (0.1 M, 10 ml), and aqueous NaO Br (0.1 M, 20 ml) were added to the fluorene solution which was then stirred at 25°C for 5 hours. Similar colour sequence observed as was noticed with Bu⁺OBr as described in Section III.3.

The following compounds were isolated:
Fluorenone-adduct - (66%) yield; m.p. 154°C
Bisfluorenylidene - (13%) yield, m.p. 136°C

III.6 - Oxidation of Fluorene by Potassium Permanganate in Acetonitrile Under Nitrogen Atmosphere

A solution containing 0.108 g (0.64 mmoles) of fluorene, dissolved in 20 ml MeCN was placed in a 250 ml three necked flask containing a teflon covered magnetic bar and connected to (a) a source of deoxygenated, anhydrous nitrogen, (b) a gas exit tube with a mercury trap and (c) a pressure equalising funnel. A solution of KMnO₄ (0.101 g, 0.64 mmoles) in 20 ml MeCN-water (8:2 V/V) was added to a stirred solution of fluorene. Then fluorene solution was purged with nitrogen gas for 15 minutes while the stirring continued. 10 ml solution of (0.1 N) t-BuOK in Bu₃SOH was rapidly added to the reaction-mixture. During the first few minutes of the reaction, the purple colour of KMnO₄ was gradually discharged and the solution assumed a green colour which changed to brown. The reaction was allowed to proceed for a period of two hours during which time the colour intensified and dark brown precipitate settled and the reaction took to completion. The reaction vessel was exposed to atmosphere. The precipitate thus formed was filtered, washed with water, then with ethanol and the residue was extracted with ether as usual.

Chromatography of the resulting material gave the following compounds:
Fluoren-9-ol - (18.6%) yield (based on fluorene); m.p. 154°C (Lit. 154-156°C)

Fluorenone - 48.8% yield (based on fluorene); m.p. 84°C

Bifluorenylidene - Trace amount

Manganese dioxide - Not determined quantitatively

III.7 - Oxidation of Fluorene by Hexacyanoferrate in BuOH Solvent Under Nitrogen Atmosphere

A solution of 1.06 g (6.4 mmoles) of fluorene in 30 ml BuOH was placed in three necked flask (the reaction was carried out under the similar experimental conditions as explained in Section III.6). A solution of potassium ferricyanide (2.11 g, 6.4 mmoles) in 50 ml BuOH-water mixture (2:1 V/V) was added to a stirred solution. 20 ml of (0.1 N) KOH base in DMSO-BuOH (8:2 V/V) solvent mixture was added through funnel under nitrogen atmosphere. The reaction was marked by a colour sequence that involved transformation of the initially formed orange colour to dark brown and finally to reddish yellow, which persisted. The reaction was allowed to proceed for a period of 4 hours in nitrogen atmosphere by which time the colour intensified and precipitate settled and the reaction took to completion.

The contents of the reaction were acidified, the mixture filtered and an orange mass thus isolated was worked up by column chromatography coupled with tlc monitoring of the eluted fractions. The main products isolated were:
Fluorenone - (43%) yield (based on fluorene); m.p. 83-84°
Bifluorenyl - (23%) yield; m.p. 245-246°

III.3 - Oxidation of Fluorene by Potassium Peroxy Disulphate in BuOH Under Nitrogen Atmosphere

The reaction was carried out under identical reaction conditions as described in Section III.7, but with potassium peroxy disulphate (K₂S₂O₈) as oxidant (3.45 g, 12.8 mmoles) in 50 ml mixture of BuOH-water (1:1, V/V). The reaction was carried out for a period of 2 hours (under nitrogen atmosphere) by which time the colour intensified and brown precipitate settled.

Products of the reaction were:

Fluorenone - (27%) yield
Bifluorenyl - (65%) yield
REFERENCES


37. These oxidation reactions are similar to the Kolbe Synthesis of alkenes by electrolysis of salts of carboxylic acids\(^{37(a)}\) and the formation of diethyl tetramethyl succinate by reaction of persulfates with ethyl isobutyrate or alkaline solutions of ethyl dimethyl malonate\(^{37(b)}\).


