CHAPTER 4
SYNTHESIS OF FLUORENONE AND FLUORENE DERIVATIVES (PART- II)
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Synthesis of Fluorenone and Fluorene Derivatives:

This chapter deals with the synthesis of some 1,4-disubstituted-2,3-(1',8'-naphtylene) fluorenone (4-VI) and fluorene derivatives (4-V). No simple method had yet been reported for preparing such compounds containing alkyl groups in which the position of the substituent is known.

It has been found that the most suitable procedure is that of Dilthey who treated acetylone (4-I, R = Ph) with maleic anhydride and finally obtained 7,10-diphenylfluoranthene-8,9-dicarboxylic anhydride. Extension and modification of this method to suitable dienophiles has led to the formation of a new series of fluorenone (4-VI) and fluorene derivatives (4-V).

Acenaphthaquinone, the starting material, was condensed with various aliphatic ketones having reactive methylene group in the α-position, on water bath in an alcoholic medium in presence of an alkaline catalyst to form the cyclopentadienones (4-I). The fluoranthene derivatives were all obtained by the Diel's-Alder cycloaddition reaction of cyclopentadienones (4-I) with the phenylpropionic esters (4-II).
The reaction was continued until the colour of the cyclo-
pentadienones disappeared. During the course of reaction
carbonmonoxide was evolved which was tested by the blacken-
ing of filter paper moistened with a 1% solution of pallad-
dium chloride when exposed to the effluent gas stream. The
aromatic structure (4-IV) was obtained as would be expected.31. No carbonyl bridged adduct was obtained even if the reaction
was carried at low temperature. The ease with which the
carbonyl bridge is lost in these endo adducts (4-III) is
noteworthy.

The fluoranthene-8-carboxylic esters (4-IV) are very
resistant to hydrolysis. But, when treated with hydriodic
acid in phenol, cyclisation to, and reduction of the ketone
(4-VI) occurred simultaneously to form the fluorene derivatives
(4-V). IR spectra of 4-V showed the absorption bands at
between 3100-2800 (C-H stretching), 790 - 650 (out-of-plane
C-H bending) and 1600-1450 cm\(^{-1}\) (C-C stretching). The esters
(4-IV) also underwent smooth cyclisation to fluorenone
(4-VI) on treatment with conc. sulphuric acid at room tempe-
rature. IR spectra of the ketones (4-VI) showed a strong
absorption in the region 1700 - 1715 cm\(^{-1}\) which indicates a
phenyl group conjugated with carbonyl group. Only one fluo-
renone (4-VII) could not be obtained as an analytically
pure sample. It was identified by the preparation of its
2,4-DNP derivative, m.p. 191° (Found: N, 8.96. C\(_{38}\)H\(_{34}\)N\(_4\)O\(_4\)
requires N, 9.17\% could also be reduced to the corresponding hydrocarbons (4-V) on heating with hydroiodic acid in phenol. This indicates that the ketone (4-VI) is an intermediate product during the conversion of the adducts (4-IV) to hydrocarbons (4-V) in the above reaction. The carbonyl ring of the ketone (4-VI) could not be opened by fusion with potassium hydroxide to give a mixture of isomeric acids and was not anticipated even though it had occurred previously in some instances\textsuperscript{190}.

Phenylpropionic acids (4-VII) were found to react with cyclopentadienones (4-I) less readily than the corresponding esters (4-II). The progress of the reaction may be qualitatively determined by noting the time taken for decolourisation of the reaction mixture. In all condensations, it was found that the colour of the cyclopentadienones (4-I) discharged readily when the esters (4-II) were used as dienophiles than the acids (4-VII). This may be attributed to the difference in electronegativities of the - CO\textsuperscript{2}Et and - CO\textsuperscript{2}H groups. During the course of reaction, carbondioxide was evolved as well as carbonmonoxide giving a mixture of 9-aryl-7,10-dialkylfluoranthenes (4-VIII) and 9-aryl-7,10-dialkylfluoranthenes-8-carboxylic acid (4-IX). Dilthey and coworkers\textsuperscript{181,182} have not reported this partial decarboxylation. Carbondioxide was found to evolve whether the reaction was carried out at low or high temperature.
After the completion of the reaction between phenyl-propionic acids (4-VII) and cyclopentadienones (4-I), the solvent was removed by steam distillation. The fluoranthene-8-carboxylic acids (4-IX) were extracted from the residue with sodium bicarbonate solution. Acidification of the alkaline solution gave 9-aryl-7,10-dialkyl-fluoranthene-8-carboxylic acids (4-IX). The hydrocarbons, 9-aryl-7,10-dialkyl-fluoranthene derivatives (4-VIII), were obtained from the residue left after treatment with sodium bicarbonate solution. The acids (4-IX) also underwent smooth cyclisation to fluorenones (4-VI) on treatment with conc. sulphuric acid.

All the reactions were carried out under mild conditions and in all cases the yields were good.

The following fluorenone and fluorene derivatives have been synthesised according to scheme 4.

**Fluorenones and Derivatives Synthesised**

1,4-Dimethyl-2,3-(1',3'-naphthylene)fluorenone (4-VIa).
1,4-Diethyl-2,3-(1',3'-naphthylene)fluorenone (4-VIb).
1,4-Di-n-propyl-2,3-(1',3'-naphthylene)fluorenone (4-VIc).
1,4-Di-n-butyl-2,3-(1',3'-naphthylene)fluorenone (4-VId).
1,4-Di-n-pentyl-2,3-(1',3'-naphthylene)fluorenone (4-VIe).
1,4,6-Trimethyl-2,3-(1',3'-naphthylene)fluorenone (4-VIf).
1,4-Diethyl-2,3-(1',3'-naphthylene)-6-methylfluorenone (4-VIg).
1,4-Di-n-propyl-2,3-(1',3'-naphthylene)-6-methylfluorenone (4-VIh).
Fluorene Derivatives Synthesized:

1,4-Dimethyl-2,3-(1',8'-naphthylene)fluorene (4-Va).
1,4-Diethyl-2,3-(1',8'-naphthylene)fluorene (4-Vb).
1,4-Di-n-propyl-2,3-(1',8'-naphthylene)fluorene (4-Vc).
1,4-Di-n-butyl-2,3-(1',8'-naphthylene)fluorene (4-Vd).
1,4-Di-n-pentyl-2,3-(1',8'-naphthylene)fluorene (4-Ve).
1,4,6-Trimethyl-2,3-(1',8'-naphthylene)fluorene (4-Vf).
1,4-Diethyl-2,3-(1',8'-naphthylene)-6-methylfluorene (4-Vg).
1,4-Di-n-propyl-2,3-(1',8'-naphthylene)-6-methylfluorene (4-Vh).
1,4-Di-n-butyl-2,3-(1',8'-naphthylene)-6-methylfluorene (4-Vi).
Scheme 4.

4-I a. \( R = \text{CH}_3 \); b. \( R = \text{C}_2\text{H}_5 \); c. \( R = \text{n-C}_3\text{H}_7 \); d. \( R = \text{n-C}_4\text{H}_9 \); e. \( R = \text{n-C}_5\text{H}_{11} \)

4-II. a. \( R_1 = \text{H} \); b. \( R_1 = \text{CH}_3 \)

4-III

4-IV. a. \( R = \text{CH}_3, R_1 = \text{H} \); b. \( R = \text{C}_2\text{H}_5, R_1 = \text{H} \); c. \( R = \text{n-C}_3\text{H}_7, R_1 = \text{H} \); d. \( R = \text{n-C}_4\text{H}_9, R_1 = \text{H} \); e. \( R = \text{n-C}_5\text{H}_{11}, R_1 = \text{H} \); f. \( R = \text{CH}_3, R_1 = \text{CH}_3 \); g. \( R = \text{C}_2\text{H}_5, R_1 = \text{CH}_3 \); h. \( R = \text{n-C}_3\text{H}_7, R_1 = \text{CH}_3 \); i. \( R = \text{n-C}_4\text{H}_9, R_1 = \text{CH}_3 \)

4-V

4-VII a. \( R_1 = \text{H} \); b. \( R_1 = \text{CH}_3 \)

4-VIII

4-IX

4-VIII
INFRARED SPECTRUM OF COMPOUND No. 4-VC (S)