CHAPTER-V

SYNTHESIS OF 5-OXO-2ARYLAMINO THIAZOL [4,5-d] PYRANS
CHAPTER - V

SYNTHESIS OF 5-OXO-2-ARYLAMINO-THIAZOL [4, 5-d] PYRANS

V.1 INTRODUCTION:

The pyranones constitute an important group of compounds. Their utility being demonstrated by the numerous references in patents. Coumarins also constitute a very important class of compounds as they are reported to possess anthelmintic, anticoagulant, growth regulators, bactericidal, hypotensive, and other properties. Some of the coumarins are used as insecticides and pesticides.

A large number of coumarins are used as fluorescent brightening agents, antioxidants, brighteners in electroplating and optical bleaching agents. Some coumarins are used in cosmetics, perfumery and photography.

Coumarins show fluorescence properties, notably, when an electron donating group is present at 7-position. N-acyl derivatives of some 7-amino coumarins serve as fluorescent markers for the detection of proteinases.

Coumarins show a tendency to absorb UV light and this results in a number of applications e.g. Umbelliferone, 7-hydroxy coumarin, has been used in sun screen lotions. 7-Diethylamino-4-methyl coumarin is used to sensitize a weak fluorescent second material in a mixture designed for use as an insitu flaw detector in metal surfaces.
\[
\text{(I) NaO}_{3}\text{SCH}_{2} \rightarrow \text{Ph-N-OH}
\]

\[
\text{(II) R}_{2}\text{N} \rightarrow \text{CH}_{2}\text{COMe}
\]

\[
\text{(IIIa) IIIB)
\]

\[
\text{(IV) OH CH}_{2}\text{COMe}
\]

\[
\text{(V) OH CH}_{2}\text{CH-COMe}
\]

\[
\text{(VI) N-OH}
\]
The absorption of UV light by coumarins is also fundamental to their use as optical brightening agents in laundry and domestic detergents and as additives to fibres and papers. The coumarins containing a substituted amino group at C-7 and derivatives such as I (R=Et or Ph) are applied to wool and nylon. The presence of a 3-phenyl group and elaboration of the basic 7-substituent gives products like II, which are suitable for application to cellulose, polyamide, polyacrylonitrile and wool or to inert polyesters by incorporation into the melt. 7-Amino coumarins IIIa and IIIb act as laser dyes as these compounds exhibit larger stockes shifts.

Many oxygen heterocycles including naturally occurring coumarins show insecticidal properties. Coumarin derivatives such as Warfarin, 4-(4-hydroxy coumarin-3-yl)-4-phenylbutan-2-one, IV and Nicoumalone, V have found uses as anticoagulants and are widely used as rodenticides.

Coumarins also show biological activities such as vasodilatators, anthelmintics and diuretics. Many compounds containing pyran and benzopyran moieties act as antibiotics and marketed as an antibacterial or antimicrobial preparations under variety of names.

Compounds possessing pyran moiety such as 5-hydroxy chromone and some of its derivatives show chelating properties and have been utilised in the determination of a number of metals. Both 3-hydroxy chromone and chroman-2,3,4-trione-3-oxine, VI show a similar ability to complex with metal ions.
As a result of these useful properties, a large number of groups are lured in synthesis of new compounds even today. The important methods for the synthesis of these pyranones are summarised in Schemes I to VI.

Based on this it appears that a simple synthesis of 5-oxo-2-arylamino thiazol [4,5-d] pyrans would be useful. Previous work carried by O. Meth-Cohn et al\textsuperscript{31} has successfully converted quinolonyl acrylic acid (VII) into a pyranoquinoline (IX) with polyphosphoric acid. The intermediate (VIII) was being selectively converted either into the Pyran (IX) with cold alkali or into cis acrylic acid (X) by acid hydrolysis. They have also reported the spontaneous cyclisation of cis acid to same pyranoquinoline (IX) on heating (Scheme VII).

We used this methodology to get 5-oxo-2-arylamino thiazol [4,5-d] pyrans (10a-f).

V.2. PRESENT WORK:

The first target for the synthesis was preparation of substituted (E)-5-(4-oxo-aryl thiazolyl) acrylic acids (8a-f) from 4-oxo-2-arylamino thiazole-5-carboxaldehydes (5a-f). These compounds (5a-f) were prepared by carrying out hydrolysis of 4-chloro-2-arylamino thiazole-5-carboxaldehydes (4a-f) using 6N HCl.

The next requirement was to prepare 5-oxo-2-arylamino thiazol [4,5-d] pyran (10a-f). These compounds were prepared from corresponding (E)-5-(4-oxo-arylamino thiazolyl) acrylic acids

\[
\begin{align*}
\text{(i) } & \text{NaOAc, Ac}_2\text{O } \\
\text{(ii) } & \text{H}_3\text{O}^+ \\
\end{align*}
\]

Scheme I


\[
\begin{align*}
\text{Me}_2\text{N} & \text{-OH } \\
\text{Me}_2\text{N} & \text{-CO-CH-R } \\
\text{Me}_2\text{N} & \text{-OH } \\
\end{align*}
\]

Scheme II


\[
\begin{align*}
\text{Ph}_3\text{P} & = \text{C} = \text{C} = \text{O} \\
\end{align*}
\]

Scheme III

\[ \text{EtOOC} \quad \xrightarrow{\text{Resorcinol}} \quad \text{HCl} \]

\[ \text{COOEt} \quad \xrightarrow{\text{HCl}} \quad \text{COOEt} \]

**Scheme IV**

5) Method due to Becker and Lingnert \(^{29}\) (1982).

\[ \text{But} \quad \xrightarrow{\text{Pyridine}} \quad \text{MeOH, \Delta} \]

**Scheme V**

6) Method due to Zagorevskii and Orlova \(^{30}\) (1982).

\[ \xrightarrow{\text{SOCl}_2} \quad \text{DMF} \quad \xrightarrow{\text{ROH}} \quad \xrightarrow{\text{RCI}} \quad \xrightarrow{-\text{CO}} \]

**Scheme VI**
Scheme VII

**VII**

\[
\text{Scheme VII}
\]
(8a-f), using the methods described by O. Muth-Cohn et al., via intermediates (9a-f). These intermediates were being selectively converted into (10a-f) with cold alkali. The strategy visualized is shown in Scheme VIII.

\[
\begin{align*}
5a-f & \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}(\text{i}) \text{ CH}_3\text{COOK}} 8a-f \\
\text{Perkin's reaction} & \\
9a-f & \xrightarrow{\text{PPA, } 2h \quad 245^\circ \text{C}} \\
& \xrightarrow{\text{Aq. NaOH}} \\
10a-f & \\
\text{a}, \text{Ar} = & \quad \text{b}, \text{Ar} = \\
& \quad \text{c}, \text{Ar} = \\
\quad \text{d}, \text{Ar} = & \quad \text{e}, \text{Ar} = \\
& \quad \text{f}, \text{Ar} =
\end{align*}
\]

Scheme VIII
V. 3. PREPARATION OF (E)-5- (4-OXO-2-ARYLAMINO THIAZOLYL) ACRYLIC ACIDS:

The compound 4-oxo-2-phenylamino thiazole-5-carboxaldehyde (5a) was heated with acetic anhydride, potassium acetate followed by steam distillation. It formed pale yellow coloured crystals (8a) in 67% yield, m.p. 201°C. Its identity as acrylic acid was established by IR spectroscopy (carbonyl band of α,β-unsaturated acid at 1680 cm⁻¹ and O-H stretching bonded at 3400 cm⁻¹).

The compound 4-oxo-2-(2-methylphenyl) aminothiazole-5-carboxaldehyde (5b) when heated with acetic anhydride, potassium acetate followed by steam distillation and work-up gave a dark brown coloured compound in 62% yield, m.p. 180°C. In IR spectrum (Fig. 1), it showed band at 1700 cm⁻¹ for carbonyl stretching of α,β-unsaturated acid and very broad band at 3200 cm⁻¹ for bonded O-H.

Similar sequence of reactions with 4-oxo-2-(4-methylphenyl) aminothiazole-5-carboxaldehyde, (5c) resulted into the formation of 8c, as a dark brown coloured compound, in 63% yield, m.p. 165°C. The compound 8c showed IR band at 1700 cm⁻¹ for carbonyl frequency of α,β-unsaturated acid. The presence of carboxylic acid group was also supported by very broad bonded O-H stretching frequency at 3300 cm⁻¹. Other significant IR peaks are observed at 1360 cm⁻¹ (C = N), 1460 cm⁻¹ (O-H deformation) and 1500 cm⁻¹ (C = C).
Fig. I-1: IR spectrum of (E)-5-[4-Oxo-2-(2-methylphenyl) amino thiazolyl] acrylic acid (8b).
The 4-oxo-2-(2-chlorophenyl) amino thiazole-5-carboxaldehyde (5d) was heated with acetic anhydride and fused potassium acetate. The resultant reaction mixture was then steam distilled until all the unchanged aldehyde was removed. The residual solution on workup yielded, 8d as a dark brown coloured compound in 57% yield, m.p. 195-200°C. The 4-oxo-2-(4-chlorophenyl) amino thiazole-5-carboxaldehyde (5e) on similar reaction sequence gave a yellowish compound 8e, in 59% yield, m.p 203°C. It showed in its IR spectrum (Fig. 12) peaks at 1700 cm\(^{-1}\) for carbonyl stretching of \(\alpha,\beta\)-unsaturated acid and 3240 cm\(^{-1}\) (broad) for bonded O-H stretching of acid. The structure 8e assigned to the compound was also supported by elemental analysis.

A mixture of 4-oxo-2-(4-methoxyphenyl) amino thiazole-5-carboxaldehyde (5f), acetic anhydride and potassium acetate was heated and the reaction mixture was then steam-distilled until all the unchanged aldehyde was removed. The residual solution on workup formed, 8f as a dark yellow compound in 65% yield, m.p. 178°C. It showed IR (Fig. 13) band at 1680 cm\(^{-1}\) for carbonyl frequency of \(\alpha,\beta\)-unsaturated acid. The presence of carboxylic acid group was also supported by a very broad bonded O-H stretching frequency at 3200 cm\(^{-1}\). The structure 8f assigned to the compound was also supported by its elemental analysis.
Fig. 1-2: IR spectrum of (E)-5-[4-oxo-2-(4-chlorophenyl) amino thiazolyl] acrylic acid (8e)
Fig. 1-3: IR spectrum of (E)-5-[4-Oxo-2-(4-methoxyphenyl) amino thiazolyl] acrylic acid (8f).
Mechanism:

The proposed mechanism for the formation of substituted (E)-5-(4-oxo-aryl thiazolyl) acrylic acids (8a-f) can be similar to that of aldol type condensation involving the carbonyl group of the aldehyde and an active methylene group of the acetic anhydride. The function of the basic catalyst i.e. acetate anion \( \text{CH}_3\text{COO}^- \) from fused potassium acetate is to form an anion by removal of a proton from the acetic anhydride followed by dehydration. Base catalysed hydrolysis yielded (8a-f) Scheme IX.

V. 4. PREPARATION OF 5-OXO-2-ARYLAMINO THIAZOL-14, 5- D) PYRANS:

The acid (E)-5-(4-oxo-2-phenylamino thiazolyl) acrylic acid, (8a) was stirred with polyphosphoric acid at 245°C for two hours in an oil bath. The reaction mixture was diluted with water and then made alkaline with aqueous NaOH, which formed a dark brown compound. The crude product was purified by sublimination to afford 10a in 70% yield, m.p. 240°C (decomp.). In IR spectrum of 10a, \( \text{O-H} \) deformation peak at 1440 cm\(^{-1}\) was found absent. Similarly very broad band in 3500-3000 cm\(^{-1}\) region for \(-\text{COOH}\) group was found absent. These frequencies were present in starting acid 8a. The IR frequency observed at 1750 cm\(^{-1}\) can be assigned to carbonyl frequency of pyran. These IR frequencies indicated the cyclization of acid in pyran. The structure 10a assigned to the compound was supported by elemental analysis.
Scheme IX
The acid (E)-5-[4-oxo-2-(2-methylphenyl) amino thiazolyl] acrylic acid, 8b was stirred with polyphosphoric acid at 245°C for two hours. The reaction mixture was diluted with water and then made alkaline with aqueous NaOH which yielded a brown compound. It was purified by sublimation to afford 10b in 55% yield, m.p. 280°C (decom.). The IR spectrum (Fig. 14) of 10b showed absence of O-H deformation peak. A very broad O-H bonded stretching frequency in 3500-3000 cm⁻¹ region was also found absent. Both of these bands were present in the starting acid 8b. The carbonyl frequency was found at 1700 cm⁻¹. These data indicated the cyclization of (E) acrylic acid, 8b to pyran. The structure 10b assigned to the compound was also confirmed by elemental analysis.

The titled acid (E)-5-[4-oxo-2-(4-methylphenyl) amino thiazolyl] acrylic acid, 8c was stirred with polyphosphoric acid at 245°C for two hours. The reaction mixture was diluted with water and then made alkaline with aqueous NaOH, which gave a dark yellow compound. It was purified by sublimation to afford 10c as a dark yellow compound in 72% yield, m.p. 256°C (decomp.).
Fig. I-4: IR spectrum of 5-Oxo-2(2-methylphenyl) amino thiazol [4,5-d] pyran (10b).
Similar reaction sequence on (E)-5-[4-oxo-2-(2-chlorophenyl) amino thiazolyl] acrylic acid, 8d formed brown coloured compound. The crude product on purification afforded 10d in 62% yield, m.p. 260°C (decomp.).

\[
\begin{align*}
\text{10} c
\end{align*}
\]

(E)-5-[4-oxo-2-(4-chlorophenyl) amino thiazolyl] acrylic acid, 8e was stirred with polyphosphoric acid at 245°C for 2 hours. The reaction mixture was diluted with water and then made alkaline with aqueous NaOH which yielded a dark brown coloured compound. The crude product was purified by sublimation to afford 10e in 67% yield, m.p. 300°C (decomp.).

\[
\begin{align*}
\text{10} d
\end{align*}
\]

Similar sequence of reactions on (E)-5-[4-oxo-2-(4-methoxyphenyl) amino thiazolyl] acrylic acid, 8f gave a dark brown compound. The crude compound on purification afforded 10f in 73% yield, m.p. 221 - 222°C (decomp.).

\[
\begin{align*}
\text{10} e \\
\text{10} f
\end{align*}
\]
EXPERIMENTAL
V.5. EXPERIMENTAL

Preparation of (E)-5-(4-oxo-2-arylamino thiazolyl) acrylic acids (8a-f).

A mixture of 4-oxo-2-arylamino thiazole-5-carboxaldehyde (5a-f) (0.02 mole), acetic anhydride (3.0 g, 0.028 mole), freshly fused and finely powdered potassium acetate (1.2 g, 0.012 mole) was taken in a dry 250 ml round bottom flask, fitted with an air condenser carrying a calcium chloride guard tube. The reaction mixture was mixed well and heated in oil bath at 160°C for 1 hour and at 170-180°C for 3 hours. Then the mixture was poured while still hot (80-100°C) into about 10 ml of water contained in a round bottom flask, which was previously been fitted for a steam distillation.
The reaction flask was rinsed with a little hot water. Then saturated aqueous solution of sodium carbonate was added with vigorous shaking until a drop of the liquid withdrawn on the end of a glass rod turned red litmus a distinct blue. Steam distillation of the solution was carried out until all the unchanged aldehyde is removed and distillate was clear. The residual solution was cooled and filtered. The filtrate was then acidified by adding conc. HCl, slowly with vigorous stirring until the evolution of CO₂ ceased.

After cooling the acid product was filtered at the pump. It was then washed with cold water and drained well. The crude product was recrystallised from hot water to afford (8a-f). The colour, yield, m.p. and significant IR frequencies are recorded in Table-I.
<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Molecular formula</th>
<th>Colour</th>
<th>Yield %</th>
<th>m.p. °C</th>
<th>Significant IR frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>C₁₂H₁₀N₂SO₉</td>
<td>Pale yellow</td>
<td>67.00</td>
<td>201</td>
<td>1680 cm⁻¹ carbonyl of α,β-unsaturated acid, 3400 cm⁻¹ broad acid O-H stretching bonded</td>
</tr>
<tr>
<td>8b</td>
<td>C₁₃H₁₂N₂SO₉</td>
<td>Dark brown</td>
<td>62.00</td>
<td>180</td>
<td>1700 cm⁻¹ carbonyl of α,β-unsaturated acid, 3200 cm⁻¹ broad acid O-H stretching bonded</td>
</tr>
<tr>
<td>8c</td>
<td>C₁₃H₁₂N₂SO₉</td>
<td>Dark brown</td>
<td>63.00</td>
<td>165</td>
<td>800 cm⁻¹, 1700 cm⁻¹, 3300 cm⁻¹</td>
</tr>
<tr>
<td>8d</td>
<td>C₁₃H₁₂N₂SO₉Cl</td>
<td>Dark brown</td>
<td>57.00</td>
<td>200</td>
<td>710 cm⁻¹, 1720 cm⁻¹, 3280 cm⁻¹</td>
</tr>
<tr>
<td>8e</td>
<td>C₁₃H₁₂N₂SO₉Cl</td>
<td>Yellowish</td>
<td>58.00</td>
<td>203</td>
<td>850 cm⁻¹, 1700 &amp; 1740 cm⁻¹, 3240 cm⁻¹</td>
</tr>
<tr>
<td>8f</td>
<td>C₁₃H₁₂N₂SO₉</td>
<td>Dark yellow</td>
<td>65.00</td>
<td>178</td>
<td>840 cm⁻¹, 1680 cm⁻¹, 3200 cm⁻¹</td>
</tr>
</tbody>
</table>
Preparation of 5-Oxo-2-arylamino thiazol [4,5-d] pyrans (10a-f).

(A) Preparation of 5-Oxo-2-phenylamino thiazol [4,5-d] pyran (10a).

\[
\begin{align*}
\text{PPA, 2h} & \quad 245^\circ C \\
\text{Aq,NaOH} & \quad 10a
\end{align*}
\]

The acid, (E)-5-(4-oxo-2-phenylanino thiazolyl) acrylic acid, (8α). (0.914 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4M), allowed to stand and then filtered. The residue was washed with water and dried. The crude product was purified by sublimation to afford 10a, as dark brown compound, 0.600 g (70%) m.p. 240°C (decomp.).

**Elemental analysis**:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>59.12%</td>
<td>3.34%</td>
<td>11.28%</td>
</tr>
<tr>
<td>Calculated for</td>
<td>59.02%</td>
<td>3.28%</td>
<td>11.48%</td>
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</table>

*We are grateful to the referee for suggesting the more attractive mechanism (α).*
(E)-5-[4-Oxo-2-(2-methylphenyl) amino thiazolyl] acrylic acid, (8b). (0.966 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4M), allowed to stand and then filtered. The residue was washed with water and dried. The crude compound was purified by sublimation to afford 10b, as brown coloured compound, 0.500 g (55%) m.p. 280°C (decomp.).

**Elemental analysis:**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
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</tr>
</thead>
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<tr>
<td>Observed</td>
<td>60.64%</td>
<td>3.68%</td>
<td>10.70%</td>
</tr>
<tr>
<td>Calculated for</td>
<td>60.47%</td>
<td>3.86%</td>
<td>10.85%</td>
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</table>
(E)-5-[4-Oxo-2-(4-methylphenyl) amino thiazolyl] acrylic acid, (8c). (0.866 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4 M), allowed to stand and then filtered. The residue was washed with water and dried. The crude product was purified by sublimation to afford 10b, as dark yellow coloured compound, 0.650 g (72%) m.p. 256°C (decomp.).

Elemental analysis:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
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</tr>
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<tbody>
<tr>
<td>Observed</td>
<td>60.35%</td>
<td>3.95%</td>
<td>10.74%</td>
</tr>
<tr>
<td>Calculated for</td>
<td>60.47%</td>
<td>3.88%</td>
<td>10.85%</td>
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</table>

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(D) Preparation of 5-Oxo-2-(2-chlorophenyl) amino thiazol (4,5-dl pyran (10d).

\[ \text{PPA, 2h at 245°C} \]

\[ \text{mechanism (a)} \]

\[ \text{PPA, 2h at 245°C} \]

\[ \text{mechanism (b)} \]

\[ \text{PPA, 2h at 245°C} \]

\[ \text{mechanism (c)} \]

\[ \text{PPA, 2h at 245°C} \]

\[ \text{mechanism (d)} \]

(E)-5-[4-Oxo-2-(2-chlorophenyl) amino thiazolyl] acrylic acid, (8d). (1.038 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4M), allowed to stand and then filtered. The residue was washed with water and dried. The crude compound was purified by sublimation to afford 10d, as brown coloured compound, 0.600 g (62%) m.p. 280°C (decomp.).

**Elemental analysis:**

<table>
<thead>
<tr>
<th></th>
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<td>Observed</td>
<td>57.90%</td>
<td>2.76%</td>
<td>9.86%</td>
</tr>
<tr>
<td>Calculated for</td>
<td>57.71%</td>
<td>2.51%</td>
<td>10.05%</td>
</tr>
</tbody>
</table>

\[ \text{C}_{12}H_{7}N_{2}SO_{3}Cl \]
Preparation of 5-Oxo-2-(4-chlorophenyl) amino thiazol [4,5-d] pyran (10e).

(E)-5-[4-Oxo-2-(4-chlorophenyl) amino thiazolyl] acrylic acid, (8e). (1.038 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4M), allowed to stand and then filtered. The residue was washed with water and dried. The crude compound was purified by sublimation to afford 10e, as dark brown coloured compound, 0.850 g (67%) m.p. 300°C (decomp.).

**Elemental analysis:**

<table>
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<td>57.80%</td>
<td>2.70%</td>
<td>9.80%</td>
</tr>
<tr>
<td>Calculated for</td>
<td>57.71%</td>
<td>2.51%</td>
<td>10.05%</td>
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C₁₂H₆N₂SO₂Cl
(E)-5-[4-oxo-2-(4-methoxyphenyl) amino thiazolyl] acrylic acid, (8f). (1.022 g, 0.0035 mole) was stirred in polyphosphoric acid (10 g) for 2 hours at 245°C. After cooling and dilution with ice water (100 ml), the clear solution was made alkaline with aqueous sodium hydroxide (4M), allowed to stand and then filtered. The residue was washed with water and dried. The crude compound was purified by sublimation to afford 10f, as dark brown coloured compound, 0.700 g (73%) m.p. 221 - 222°C (decomp.).

**Elemental analysis:**

<table>
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<td>56.82%</td>
<td>3.78%</td>
<td>10.15%</td>
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<tr>
<td>Calculated for</td>
<td>56.93%</td>
<td>3.85%</td>
<td>10.22%</td>
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REFERENCES
CHAPTER - V

REFERENCES

1. (a) H.S. Mahal, Proc. Ind. Acad. Sci., 5B, 186 (1937);


