SYNTHESIS OF 1,2,4-TRISUBSTITUTED
-2-IMIDAZOLIN-5-ONES

P.A. Mohamed Basheer “Synthesis of some imidazole derivatives and
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CHAPTER I
SYNTHESIS OF 1,2,4-TRISUBSTITUTED
-2-IMIDAZOLIN-5-ONES

Imidazolinones are found to have several pharmacological activities\textsuperscript{56-59}. The benzylidene imidazolinone chemistry with its diverse biological properties like central nervous system depressant\textsuperscript{60}, anticonvulsant\textsuperscript{61}, and monoamine oxidase inhibitor\textsuperscript{57} has received importance in recent years. Amino acids are the precursors of various macro molecules in the biological system and they play a prominent role in the pathophysiology of inflammation\textsuperscript{62-63}. With a view to extend the scope and validity of these observations, it is worthwhile to synthesise and characterise new imidazolinones containing both these moities. In this chapter the synthesis of 1,2,4-trisubstituted-2-imidazolin-5-ones containing both these moieties is presented.

A. Synthesis of 2-aryl-4-arylidene-1- (carbethoxymethyl)
-2-imidazolin-5-ones

Results and discussion

4-Arylidene-2-phenyl-2-oxazolin-5-ones (azalactones) undergo ring opening at C-5 by the interaction with amines to yield $\alpha$-benzoylamino
cinnamic acid amides. These amides under suitable conditions undergo cyclisation to give 2-aryl-4-arylidene-2-imidazolin-5-ones.

The reaction can be depicted as follows.

\[
\begin{align*}
\text{Heat} & \quad -\text{H}_2\text{O} \\
\text{Oxazolinone} & \quad \text{Glycine Ethyl Ester} \\
\end{align*}
\]

In this work azlactones were heated with glycine ethyl ester and the amides formed were converted into imidazolinones by heating in vacuum for 2 hours.

In the general procedure the oxazolinone and glycine ethyl ester in equimolar amounts were heated under reflux in ethanol for 2 hours. Within a few minutes of boiling the solid compound dissolved to give a practically colourless solution. After 2 hours of refluxing, it was poured into cold water and the amide precipitated was filtered, washed and dried. The dried amide on heating in vacuum for 2 hours yielded 2-aryl-4-arylidene-1-(carbethoxymethyl)-2-imidazolin-5-ones. The compounds thus prepared are given in Table-1.1
Table 1.1

2-Aryl-4-arylidene-1-(carbethoxymethyl)-2-imidazolin-5-ones

<table>
<thead>
<tr>
<th>No.</th>
<th>R¹</th>
<th>R²</th>
<th>M.P</th>
<th>Yield</th>
<th>λₘₐₓ</th>
<th>Molecular Formula</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>phenyl</td>
<td>Phenyl</td>
<td>108</td>
<td>71</td>
<td>409</td>
<td>C₂₀H₁₈N₂O₃</td>
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<tr>
<td>2.</td>
<td>p-chlorophenyl</td>
<td>Phenyl</td>
<td>105</td>
<td>70</td>
<td>404</td>
<td>C₂₀H₁₇N₂O₃Cl</td>
</tr>
<tr>
<td>3.</td>
<td>o-chlorophenyl</td>
<td>Phenyl</td>
<td>93</td>
<td>65</td>
<td>408</td>
<td>C₂₀H₁₇N₂O₃Cl</td>
</tr>
<tr>
<td>4.</td>
<td>p-methoxyphenyl</td>
<td>Phenyl</td>
<td>125</td>
<td>74</td>
<td>414</td>
<td>C₂₁H₂₀N₂O₄</td>
</tr>
<tr>
<td>5.</td>
<td>o-hydroxyphenyl</td>
<td>Phenyl</td>
<td>165</td>
<td>65</td>
<td>414</td>
<td>C₂₀H₁₈N₂O₄</td>
</tr>
<tr>
<td>6.</td>
<td>p-dimethylamino phenyl</td>
<td>Phenyl</td>
<td>130</td>
<td>62</td>
<td>513</td>
<td>C₂₂H₂₃N₃O₃</td>
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<tr>
<td>7.</td>
<td>furfuryl</td>
<td>Phenyl</td>
<td>117</td>
<td>50</td>
<td>416</td>
<td>C₁₈H₁₆N₂O₄</td>
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<tr>
<td>8.</td>
<td>p-tolyl</td>
<td>p-chlorophenyl</td>
<td>150</td>
<td>64</td>
<td>408</td>
<td>C₂₁H₁₉N₂O₃Cl</td>
</tr>
<tr>
<td>9.</td>
<td>p-methoxyphenyl</td>
<td>o-chlorophenyl</td>
<td>143</td>
<td>61</td>
<td>396</td>
<td>C₂₁H₁₉N₂O₄Cl</td>
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<tr>
<td>10.</td>
<td>p-tolyl</td>
<td>o-chlorophenyl</td>
<td>115</td>
<td>64</td>
<td>404</td>
<td>C₂₁H₁₉N₂O₃Cl</td>
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<tr>
<td>11.</td>
<td>phenyl</td>
<td>methyl</td>
<td>228</td>
<td>69</td>
<td>407</td>
<td>C₁₅H₁₆N₂O₃</td>
</tr>
</tbody>
</table>
The identity of all the compounds were confirmed by elemental analysis. The mass spectrum and $^1$H nmr spectrum of one of the compounds, 4-Benzylidene-1-(carbethoxymethyl)-2-phenyl-2-imidazolin-5-one was recorded. The structure was arrived at as follows.

The mass spectrum has M$^+$ peak at 334 corresponding to the proposed structure. The even mass justified the presence of two nitrogen atoms. Other important peaks in the mass spectrum were at m/z = 305, 261, 233, 204, 247, 130, 117, 105 and 77 which further supported the proposed structure.

The fragment at m/z = 305 is formed by the elimination of an ethyl radical.

An ion with m/z = 289 is due to the removal of ethoxy group.
The ion with m/z = 261 correspond to the radical ion formed by the elimination of the radical \( \cdot \text{COOC}_2\text{H}_5 \) which further eliminates one CO molecule giving the fragment with m/z = 233.

An alternate fragmentation pathway give rise to the peak at m/z = 247. It is due to the removal of \( \cdot \text{CH}_2\text{COOC}_2\text{H}_5 \) from the molecular ion.

The highly intense peak at m/z = 130 is formed by the following fragmentation of the molecular ion. In this fragmentation both the
fragments can be formed either as a neutral molecule or as a radical ion. The high intensity of the ion at m/z 130 proves its higher stability than the one at m/z 204.

![Chemical structure](image)

Intense peaks at m/z = 117, 105 and 89 are due to the fragments given below.

![Chemical structure](image)
The $^1$H nmr spectrum also supported this structure. The CH$_2$ proton (methylene group attached to nitrogen) absorbed at a highfield of $\delta = 4.49$ (Singlet). This is reasonable as CH$_2$ group is flanked by the carbonyl group of the ester on one side and nitrogen on the other. It also showed absorptions due to ten aromatic protons and the -CH= proton in the region 7.25- 7.72. The -CH$_2$-group in the ethoxy moiety absorbed at $\delta = 4.16$ (quartet). A triplet at $\delta = 1.19$ is due to CH$_3$ group of the ethoxy moiety.

The UV-visible spectra of these compounds had an absorption maximum in the range of 396-513 nm. Comparison of these values with those of 4-arylidene-2-phenyl-2-imidazolin-5-ones$^{134}$ showed that introduction of carbethoxymethyl group at position-1 of the imidazolinone ring has very little influence on the absorption maximum of these compounds. This can be justified on the basis that the absorption is due to the $n-\pi^*$ transition of the carbonyl group perturbed by the intramolecular charge transfer from arylidene residue to the polarised carbonyl group$^{128}$. The lone pair electron on the adjacent nitrogen can influence the electronic environment of the carbonyl group. The availability of the electron pair on the nitrogen at position-1 of the imidazolinone ring for conjugation with the C=O bond can be practically the same in the unsubstituted and substituted imidazolinones.

Once the structure of the compound was established the following mechanism could be proposed for its formation.
EI-MS of 4-Benzylidene-1-(carbethoxymethyl)-2-phenyl-2-imidazolin-5-one.
$^1$H nmr spectrum of 4-Benzylidene-1-(carboxethylmethyl)-2-phenyl-2-imidazolin-5-one.
Mechanism
B. Hydrolysis of the ester group in 2-Aryl-4-arylidene-1-(carbethoxymethyl)-2-imidazolin-5-one

Results and Discussion

In an attempt to synthesise and characterise new imidazolinones the ester group in 2-aryl-4-arylidene-1-(carbethoxymethyl)-2-imidazolin-5-one was hydrolysed using strong alkali and dilute mineral acids. In both cases the reaction mixture turned red and we could not separate any solid product probably due to breaking of the imidazolinone ring. In the presence of strong bases the enolate formation also is possible as the methylene group is flanked by the ester carbonyl on one side and nitrogen on the other. However the esters could be hydrolysed using sodium- or potassium carbonate solution.

In every case 2g of the imidazolinone was dissolved in ethanol (10 mL) and refluxed with saturated sodium carbonate solution (15 mL) for one hour. After refluxing, the reaction mixture was cooled and acidified with dilute hydrochloric acid. The solidified product was filtered, washed with water and dried. The compounds thus prepared are given in Table I.2.
All the acid synthesised above gave satisfactory analytical result for nitrogen. The mass spectrum of l-(carboxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one was recorded. It had M⁺ peak at m/z = 336 (76%) in accordance with the structure proposed. Other peaks present were 305, 291, 277, 162, 146, 134, 117, 105 and 77 which further supported its structure.

The 'H nmr spectrum also supported this structure. The methoxy protons absorbed at δ=3.8. The methylene group protons attached to nitrogen absorbed at δ=4.49. It also showed absorptions due to nine aromatic protons and the -CH= proton in the region 6.9 - 8.2.
EI-MS of 1-(Carboxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one.
$^1$H nmr spectrum of 1-(Carboxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imida zolin - 5-one.
The UV-visible absorption maxima of these acids are very close to their ester precursors (Table I.1) showing a negligible influence on esterification.

**Mechanism of Hydrolysis**

\[
\begin{align*}
\text{slow} & \quad \text{Fast} \\
\text{OH}^- & \quad \text{OH} \\
\text{C}_6\text{H}_5\text{C}_\text{H}_2\text{C}-\text{OC}_2\text{H}_5 & \quad \text{C}_6\text{H}_5\text{N-N-CH}_2\text{C-OC}_2\text{H}_5 \\
\text{C}_6\text{H}_5\text{C}_\text{HY} & \quad \text{C}_6\text{H}_5\text{N-N-CH}_2\text{COOH} \\
+ \text{OEt}^- & \quad + \text{EtOH} \\
\end{align*}
\]
EXPERIMENTAL

Melting points recorded on Toshniwal capillary melting point apparatus are uncorrected. The mass spectrum was recorded on Finnigan MAT 8200 spectrometer. The $^1$H nmr spectrum were recorded on Unity plus 300 Varian spectrometer using TMS as internal standard. UV - visible spectra were recorded in ethanol on a Shimadzu 1601- UV - visible spectrometer.

SYNTHESIS OF STARTING MATERIALS

N-Acetylglucose

N-Acetylglucose (Aceturic acid) is prepared by known method$^6$. Glycine (75g) was dissolved in 300 mL of water and stirred while 95% acetic anhydride (215g) was added in one portion. The mixture became warm and stirred for further 15-20 minutes. The crystallisation that has begun is completed by external cooling. The product was collected next day. Washed with cold water and dried at 100-110°. It melted at (207 - 208°C)$^6$.

Benzoyl glycine

Benzoyl glycine was prepared by benzyolating glycine. Glycine (25g, 0.33 mole) was dissolved in 250mL of 10% sodium hydroxide solution contained in a conical flask. Added 45mL (0.385 mole) of benzoylchloride in five portions to this solution, stoppered the vessel and shook vigorously
after each addition until all the chloride has reacted. Transferred the solution to a beaker and rinsed the conical flask with a little water. A few grams of crushed ice was put in the solution and added con. HCl slowly and with stirring until the mixture was acidic to congo red. The crystals formed were filtered on a buchner funnel and air dried. The melting point was found to be 188°C. The reported m.p. is 187°C.

**p-Chlorobenzoylglycine**

Dry powdered p-chlorobenzoic acid (38.4g, 0.246 mole) was placed in a 250 -mL round bottomed flask fitted with a condenser. Thionyl chloride (22mL. 0.306 mole) was added and heated the flask on a boiling water bath for one hour until the evolution of HCl stopped. The contents were left to cool and transferred into a separatory funnel. Ice-cold water (50mL) and solvent ether (100mL) were added into the funnel and shaken well. The ether layer was separated and dried using anhydrous sodium sulphate. Ether was removed by distillation and the crude product again distilled to get pure p-chlorobenzoylchloride.69

Glycine (12g, 6.16 mole) was dissolved in 150 mL of 10% sodium hydroxide solution contained in a conical flask, added the p-chlorobenzooyl chloride prepared in five portions to this solution, stoppered the vessel and shook vigorously after each addition until all the chloride had reacted. Transferred the solution to a beaker and rinsed the conical flask with a little water. A few grams of crushed ice was put in the solution and added
conc. HCl slowly and with stirring until the mixture was acidic to congo red. The crystals formed were filtered on a buchner funnel and air dried. The melting point was found to be 142°C. The reported melting point is 143°C.

Azlactones

Azlactones were prepared following the known method. Aromatic aldehyde and benzoylglycine were taken in a dry 250 mL conical flask in equimolar proportions (0.04 mole). Twelve mL of acetic anhydride and 3.5g of anhydrous sodium acetate were also added and the mixture heated over a flame with shaking. When the mixture liquified it was transferred over to a boiling water bath and heated. After one hour, 20 mL of alcohol was added to the flask and allowed the mixture to stand for one and half hours. The crystalline product formed was filtered, washed with 5mL portions of cold alcohol, small portions of boiling water and dried at 100°C. The different azactones thus prepared are given in table 1.3

For the preparation of azlactone of aceturic acid, warmed a mixture of 29g (0.25 mole) of acetylglycine, 39.5g (37.5 mL, 0.37 mole) of redistilled benzaldehyde, 15 g (0.183 mole) anhydrous sodium acetate and 63.5 g (59 mL) acetic anhydride in a 500 mL flask with a reflux condenser on a water bath with occasional stirring until the solution is complete (10 - 20 minutes). Boiled the resulting solution for one hour. Cooled and left in a fridge over night. Stired the solid mass of yellow crystals with 60 mL cold water. Filtered washed with cold water and dried. It was recrystallised from ethylacetate.
Table 1.3

<table>
<thead>
<tr>
<th>Name</th>
<th>MP(°C)</th>
<th>Yield(%)</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 4-Benzylidene-2-phenyl-2-oxazolin-5-one</td>
<td>169</td>
<td>56</td>
<td>5.5 5.6</td>
</tr>
<tr>
<td>2. 4-(p-Methylbenzylidene)-2-phenyl-2-oxazolin-5-one</td>
<td>203</td>
<td>46</td>
<td>5.1 5.3</td>
</tr>
<tr>
<td>3. 4-(o-Chlorobenzylidene)-2-phenyl-2-oxazolin-5-one</td>
<td>195</td>
<td>52</td>
<td>4.7 4.94</td>
</tr>
<tr>
<td>4. 4-(p-Chlorobenzylidene)-2-phenyl-2-oxazolin-5-one</td>
<td>145</td>
<td>49</td>
<td>4.81 4.94</td>
</tr>
<tr>
<td>5. 4-(p-Methoxybenzylidene)-2-phenyl-2-oxazolin-5-one</td>
<td>164</td>
<td>48</td>
<td>5.0 5.03</td>
</tr>
<tr>
<td>6. 4-Benzylidene-2-(p-chlorophenyl)-2-oxazolin-5-one</td>
<td>163</td>
<td>45</td>
<td>4.9 4.94</td>
</tr>
<tr>
<td>7. 4-(p-Methylbenzylidene)-2-(p-Chlorophenyl)-2-oxazolin-5-one</td>
<td>133</td>
<td>48</td>
<td>4.6 4.71</td>
</tr>
<tr>
<td>8. 4-(p-Chlorobenzylidene)-2-(p-chlorophenyl)-2-oxazolin-5-one</td>
<td>199</td>
<td>47</td>
<td>4.4 4.41</td>
</tr>
<tr>
<td>9. 4-(o-Chlorobenzylidene)-2-(p-chlorophenyl)-2-oxazolin-5-one</td>
<td>202</td>
<td>49</td>
<td>4.3 4.41</td>
</tr>
<tr>
<td>10. 4-(p-Methoxybenzylidene)-2-(p-chlorophenyl)-2-oxazolin-5-one</td>
<td>117</td>
<td>41</td>
<td>4.5 4.47</td>
</tr>
<tr>
<td>11. 4-Benzylidene-2-methyl-2-oxazolin-5-one.</td>
<td>149</td>
<td>60</td>
<td>7.4 7.5</td>
</tr>
</tbody>
</table>
Glycine ethyl ester hydrochloride

Glycine ethyl ester hydrochloride was prepared according to the method developed by Curtius and Goebel\textsuperscript{72} and improved by others\textsuperscript{42,73,74}.

In a 2 litre round bottomed flask with ground glass joint was placed a mixture of glycine (75g, 1 mole) and absolute ethanol (750 mL) and the flask was fitted with a rubber cork carrying an inlet tube and a calcium chloride guard tube. Hydrogen chloride gas dried by bubbling through concentrated sulphuric acid was passed into the mixture till 100g (2.7 mole) of the gas was absorbed. The flask was fitted with a reflux condenser carrying a calcium chloride guard tube and the mixture was heated under reflux. The glycine completely went into solution within about 30 minutes. After a total refluxing of two hours the flask was allowed to cool and the solution was transferred into a 1000 mL conical flask for the sake of convenience. The solution was seeded to induce crystallisation, when a lot of glycine ethyl ester hydrochloride crystals separated. The flask was tightly stoppered and placed in the refrigerator overnight to effect complete crystallisation of the product. The crystals were quickly filtered on a large Buchner funnel, washed with two 50 mL portions of ice cold absolute ethanol and dried in the oven at 80°C for one hour. The colourless glycine ethyl ester hydrochloride weighed 118 g (84%) and melted at 144 - 146°C. Kidwai and Devasia\textsuperscript{42} reported m.p. 144 - 145°C for this compound.
Glycine ethyl ester

Glycine ethyl ester hydrochloride was converted to glycine ethyl ester according to the method developed by Fischer$^{75-76}$ and improved by Kidwai and Devasia$^{42}$. 

A saturated solution of glycine ethyl ester hydrochloride (25g, 0.18 mole) in 30mL of water was placed in a 500 mL conical flask. To this solution was added ether (100 mL) and the mixture was cooled in icebath and neutralised with 20 mL of ice cold sodium hydroxide solution (40%). The aqueous layer was saturated with potassium carbonate by keeping the flask in icebath. The contents of the flask was transferred into a separatory funnel, shaken well and the ether layer was collected in a 500 mL conical flask. The aqueous layer was extracted twice more with 50 mL portions of ether. To dry the combined ether extracts anhydrous potassium carbonate was added, the flask was stoppered and placed in refrigerator for 6 hours. The ether solution of glycine ester was filtered through a fluted filter paper by decantation and the residue was washed with dry ether. The ether was evaporated under reduced pressure from a cold water bath. The yield of colourless glycine ethyl ester thus obtained was 16.1 g (87%)
Synthesis of 1,2,4-trisubstituted-2-imidazolin-5-ones

4-Benzylidene-1-(carbethoxymethyl)-2-phenyl-2-imidazolin-5-one

4-Benzylidene-2-phenyl-2-oxazolin-5-one (4g 0.016 mole), glycine ethyl ester (1.65g, 0.016 mole) and ethanol (15mL) were taken in a round bottomed flask and heated under reflux on a water bath. Within few minutes the yellow solution turned colourless. After a refluxing of 2 hours, it was added to cold water. The white solid formed was filtered, washed with water and dried. The dried amide was then heated at 170°C in vacuum for 2 hours in an oil bath. It was then cooled and dissolved in benzene and Petroleum ether added. The pale yellow solid formed was filtered, washed and dried. The yellow product weighed 3.8g. (71%) which melted at 107°C. The reported melting point is 108 - 110°C64.

The unsaturated 2-imidazolin-5-one was recrystallised from ethanol. The yellow crystals melted at 108°C.

Analysis

\[
\begin{align*}
\text{N\%} & \\
\text{Found} & : 8.3 \\
\text{Calculated} & : 8.4 \\
\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3 & \\
\text{UV - Visible} & : \lambda_{\text{max}} = 409 \text{ nm}
\end{align*}
\]
1-(Carbethoxymethyl)-4-(p-chlorobenzylidene)-2-phenyl-2-imidazolin-5-one

4-(p-chlorobenzylidene)-2-phenyl-2-oxazolin-5-one (2g, 0.007 mole), glycine ethyl ester (0.7g, 0.007 mole) and ethanol (15 mL) were taken in a round bottomed flask and heated under reflux for two hours. It was cooled and added to cold water. The white residue formed was filtered, washed with water and dried. The dried amide was then heated at 180°C in vacuum for 2 hours in an oil bath. It was then cooled and dissolved in benzene and petroleum ether added. The pale yellow solid formed was filtered, washed and dried. The yellow product weighed 1.81g (70%) which melts at 105°C.

The unsaturated 2-imidazolin-5-one was recrystallised from ethanol. The yellow crystals melted at 105°C.

**Analysis**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N%</td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>7.48</td>
</tr>
<tr>
<td>Calculated</td>
<td>7.6</td>
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</table>

C_{20}H_{17}N_{2}O_{3}Cl

UV-Visible $\lambda_{\text{max}} = 404$ nm
1-(Carbethoxymethyl)-4-(o-chlorobenzylidene)-2-phenyl
-2-imidazolin-5-one

4-(o-chlorobenzylidene)-2-phenyl-2-oxazolin-5-one (2g 0.007 mole),
glycine ethyl ester (0.7g 0.007 mole) and alcohol (15 mL) were heated under
reflux in a water bath for 2 hours. It was then cooled and added to water.
The white residue formed was filtered, washed with water and dried. The
dried product was then heated at 180 °C in vacuum for 2 hours. It was then
cooled and dissolved in benzene. Petroleum ether was added and the yellow
solid formed was filtered, washed and dried. The yellow product weighed
1.5g (65%) which melted at 91°C.

The unsaturated 2-imidazolin-5-one was recrystallised from
ethanol. The yellow crystals melted at 93°C.

Analysis

N%  

Found : 7.5

Calculated : 7.6

C_{20}H_{17}N_{2}O_{3}Cl

UV-Visible \( \lambda_{\text{max}} = 408 \text{ nm} \)
1-(Carbethoxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one

4-(p-methoxybenzylidene)-2-phenyl-2-oxazolin-5-one (3g 0.01 mole), glycine ethyl ester (1.1g. 0.01mole) and alcohol (15 mL) were heated under reflux in a waterbath. After a total refluxing of 2 hours, it was cooled and added to cold water. The white residue formed was filtered, washed with water and dried. The dried product was heated at 180°C in vacuum for 2 hours. It was then cooled and dissolved in benzene and petroleum ether was added and the yellow crystalline product formed was filtered, washed and dried. The yellow product weighed 2.9g (74%) and melted at 124°C.

The unsaturated imidazolinone was recrystallised from ethanol. The yellow crystals melted at 125°C.

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>N%</th>
</tr>
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<tbody>
<tr>
<td>Found</td>
<td>7.8</td>
</tr>
<tr>
<td>Calculated</td>
<td>7.7</td>
</tr>
<tr>
<td>( C_{21}H_{20}O_4N_2 )</td>
<td></td>
</tr>
<tr>
<td>UV-Visible</td>
<td>( \lambda_{\text{max}} = 414 \text{ nm} )</td>
</tr>
</tbody>
</table>
1-(Carbethoxymethyl)-2-(p-chlorophenyl)-4-(p-methylbenzylidene)-2-imidazolin-5-one

2-(p-chlorophenyl)-4-(p-methylbenzylidene)-2-oxazolin-5-one (3g 0.01 mole), glycine ethyl ester (1g 0.01 mole) and ethanol (15mL) were heated under reflux in a water bath for 2 hours. It was then cooled and added to water. The white residue of the amide formed was filtered, washed with water and dried. The dried product was then heated at 180°C in vacuum for 2 hours in an oil bath. It was dissolved in benzene and petroleum ether was then added. The yellow solid formed was filtered, washed and dried. The yellow product weighed 2.5g (64%) and melted at 149°C.

The unsaturated imidazolinone was recrystallised from ethanol. The yellow crystals melted at 150°C.

**Analysis**

<p>| | |</p>
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<tbody>
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</tr>
<tr>
<td>Calculated</td>
<td>7.3</td>
</tr>
<tr>
<td>$C_{21}H_{19}O_3N_2Cl$</td>
<td></td>
</tr>
<tr>
<td><strong>UV-Visible</strong></td>
<td>$\lambda_{\text{max}} = 408$ nm</td>
</tr>
</tbody>
</table>
(1-Carbethoxymethyl)-2-(o-chlorophenyl)-4-(p-methoxybenzylidene)-2-imidazolin-5-one

2-(o-chlorophenyl)-4-(p-methoxybenzylidene)-2-oxazolin-5-one (2g, 0.006 mole), glycine ethyl ester (0.65g, 0.006 mole) and ethanol (15mL) were heated under reflux in a water bath for 2 hours. It was then cooled and added to cold water. The white residue formed was filtered, washed with cold water and dried. The dried product was then heated at 180°C in vacuum for 2 hours. It was then cooled and dissolved in benzene. Petroleum ether was added and the yellow solid formed was filtered, washed and dried. The yellow product weighed 1.6g (61%) which melted at 140°C.

The unsaturated imidazolinone was recrystallised from ethanol. The yellow crystals melted at 143°C.

**Analysis**

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Found</td>
<td>7.15</td>
</tr>
<tr>
<td>Calculated</td>
<td>7</td>
</tr>
<tr>
<td>$C_{21}H_{19}N_2O_4Cl$</td>
<td></td>
</tr>
<tr>
<td>UV-Visible</td>
<td>$\lambda_{max} = 396$ nm</td>
</tr>
</tbody>
</table>
1-(Carbethoxymethyl)-4-(furfurylidene)-2-phenyl-2-imidazolin-5-one

4-Furfurylidene-2-phenyl-2-oxazolin-5-one (3g, 0.01 mole), glycine ethyl ester (1.3g, 0.01 mole) and alcohol (15 mL) were heated under reflux in a water bath for 2 hours. It was then cooled and added to cold water. The white residue formed was filtered, washed with water and dried. The dried product was heated at 180°C in vacuum for 2 hours. It was then cooled, dissolved in benzene and petroleum ether was added. The yellow solid separated was filtered, washed and dried. The yellow product weighed 2g. (50%) and melted at 116°C.

The unsaturated imidazolinone was recrystallised from ethanol. The yellow crystals melted at 117°C.

**Analysis**

N(%)  
Found : 8.4  
Calculated : 8.6  

C_{18}H_{16}N_{2}O_{4}  

UV-vis. \( \lambda_{\text{max}} = 416 \) nm
4-Benzylidene-1-(carbethoxymethyl)-2-methyl-2-imidazolin-5-one

4-Benzylidene-2-methyl-2-oxazolin-5-one (2g, 0.01 mole), glycine ethyl ester (1.1g, 0.01 mole) and alcohol (15 mL.) were heated under reflux in a water bath. After a total refluxing of 2 hours it was cooled and added to cold water. The white residue formed was filtered, washed with water and dried. The dried product was heated at 180°C in vacuum for 2 hours in an oil bath. It was cooled and dissolved in benzene. Petroleum ether was added and the yellow solid formed was filtered and dried. The yellow product of the imidazolinone weighed 2g (69%) which melted at 226°C.

The unsaturated imidazolinone was recrystallised from ethanol and the yellow crystals melted at 228°C.

**Analysis**

<table>
<thead>
<tr>
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<th>N(%)</th>
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<tbody>
<tr>
<td>Found</td>
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<td>Calculated</td>
<td>10.3</td>
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</tbody>
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C_{15}H_{16}N_{2}O_{5}

UV-vis. $\lambda_{\text{max}} = 407$ nm
1-(carbethoxymethyl)-4-(o-hydroxybenzylidene)-2-phenyl-2-imidazolin-5-one

4-(o-hydroxybenzylidene)-2-phenyl-2-oxazolin-5-one (2g, 0.0075 mole), glycine ethyl ester (0.8g, 0.0075 mole), and ethanol (15 mL) were heated under reflux for 2 hours. It was added to cold water and the white residue formed was filtered washed with water and dried. The dried product was heated at 180° C in vacuum for 2 hours in an oil bath. It was then dissolved in benzene and petroleum ether added. The yellow solid formed weiged 1.7g (65%) which melted at 164° C.

The unsaturated imidazolinone was recrystallised from ethanol. It melted at 165° C.

Analysis

N(%)  

<table>
<thead>
<tr>
<th>Found</th>
<th>7.8</th>
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</thead>
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<tr>
<td>Calculated</td>
<td>8</td>
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</tbody>
</table>

C_{20}H_{18}N_2O_4

UV-vis. $\lambda_{max} = 414$ nm
1-(carbethoxymethyl)-4-(p-dimethylaminobenzylidene)-2-phenyl-2-imidazolin-5-one

4-(p-Dimethylaminobenzylidene)-2-phenyl-2-oxazolin-5-one (1g, 0.0034 mole), glycine ethyl ester (0.35g 0.0034 mole), ethanol (15 mL) were heated under reflux for 2 hours. It was then cooled and added to cold water. The amide formed was filtered, washed with water and dried. The dried product was heated at 190°C in vacuum for 2 hours. It was then cooled and dissolved in benzene. Petroleum ether was added and the brown solid formed was filtered, washed and dried. The reddish brown solid of the imidazolinone weighed 0.8g (62%) which melted at 128°C.

The unsaturated imidazolinone was recrystallised from etharol and melted at 130°C.

**Analysis**

N(%)  

*Found* : 11  

*Calculated* : 11.1  

*Chemical formula* : C_{22}H_{23}N_{3}O_{3}  

*UV-vis.* $\lambda_{\text{max}} = 513$ nm
1-(carboxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one

1-(carbethoxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one (2g, 0.005 mole) was dissolved in 10mL alcohol and refluxed with saturated sodium carbonate solution (15 mL) for 1 hour. After cooling, it was acidified with dilute hydrochloric acid. The yellow product formed was filtered, washed with warm water and dried.

The unsaturated imidazolinone was recrystallised from alcohol. The yellow crystals of 1-(carboxymethyl)-4-(p-methoxybenzylidene)-2-phenyl-2-imidazolin-5-one melted at 195°C.

Analysis

N%

Found : 8.4
Calculated : 8.3

$C_{19}H_{16}O_4N_2$

UV-vis $\lambda_{\text{max}} = 415$ nm
4-Benzyldene-1-(carboxymethyl)-2-phenyl-2-imidazolin-5-one

4-Benzylidene-1-(carbethoxymethyl)-2-phenyl-2-imidazolin-5-one (2g, 0.006 mole) was dissolved in 10 mL. alcohol and refluxed with saturated sodium carbonate solution (15 mL). After a refluxing of 1 hour, it was cooled and acidified with dilute hydrochloric acid. The orange red product formed was filtered, washed with hot water and dried.

The unsaturated imidazolinone was recrystallised from ethanol. The orange red crystals melted at 198°C.

**Analysis**

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<tbody>
<tr>
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<tr>
<td>Calculated</td>
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</tbody>
</table>

\[ \text{Formula: } \text{C}_{18}\text{H}_{14}\text{O}_{3}\text{N}_{2} \]

\[ \text{UV-vis. } \lambda_{\text{max}} = 412 \text{ nm} \]

All the other 2-aryl-4-arylidene-1-carboxymethyl-2-imidazolin-5-ones were prepared according to the above method.