SYNTHESIS AND CHARACTERIZATION OF 
HETEROCYCLIC BASED REACTIVE DYES.

This chapter deals with the synthesis and characterization of 
various reactive dyes prepared from 3-(4-amino phenyl)-5-benzylidene-
2-substituted phenyl-3, 5-dihydro-imidazol-4-one nucleus.

Series of monoazo bifunctional/monofunctional reactive dye are 
synthesized having imidazolones ring system as diazo component and 
coupled with various substituted amino napthol sulphonic acids.

Various studies have shown that imidazolone nucleus has 
considerable biological importance. Based on these characteristics of 
imidazolone group, it was proposed to prepare the various imidazolone 
based dyes which can show biological activities.
2.1 Introduction

Oxazolone is a class of small heterocycles, which are important intermediates in the synthesis of several small molecules, including amino acids, peptides [1-6] antimicrobial or antitumour compounds [7,8], heterocyclic precursors [9-12] as well as biosensors coupling and/or photosensitive composition devices for proteins [13]. Some oxazolone have shown a wide range of pharmaceutical properties [14]. The Erlenmeyer-Plochl Azlactone synthesis is a very common and most widely accepted process for the preparation of the 4-benzylidene-2-Phenyl/Methyl-5-oxazolone. The condensation of aldehydes with an acyl derivative (usually benzoyl or acetyl) of glycine in the presence of acetic anhydride and sodium acetate to give an oxazolone (azlactone) [15-17]. With benzaldehyde and acetylglycine the product is 4-benzylidene-2-methyl-5-oxazolone [18].

\[
\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CONHCH}_2\text{COOH} \rightarrow \text{N} \begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} \end{array}
\]

The reaction is a special type of Perkin reaction and is best suited for aromatic aldehydes. However, lower aliphatic aldehydes have been shown to react with 2-phenyl-5-oxazolone to give the unsaturated azlactone [19]. Bennet and Niemann [20] demonstrated that in several instances a transacylation reaction occurred during the azlactone synthesis which involved replacement of a benzoyl group by an acetyl group.

\[
\text{F-C}_6\text{H}_4\text{CHO} + \text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH} \underset{(\text{CH}_3\text{CO})_2\text{O}}{\text{CH}_3\text{CONa}} \rightarrow \text{F-C}_6\text{H}_5\text{CH} \begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{N} \end{array}
\]

\[
\text{F-C}_6\text{H}_5\text{CH} \begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{N} \end{array} \]
For example in the condensation of p-fluorobenzaldehyde with hippuric acid in the presence of acetic anhydride and sodium acetate, the product consisted of a mixture of 2-phenyl- and 2-methyl-4-(p-fluorobenzylidene)-5-oxazolones.

The azlactone are useful intermediates for the synthesis of a variety of different types of compound including \( \alpha \)-amino and \( \alpha \)-keto acids. Hydrolysis of the azlactone yields \( \alpha \)-acylaminoacrylic acids which on reduction give \( \alpha \)-amino acids. Phenyl amine has been prepared by this method in 86% yields [21].

\[
\begin{align*}
R-CH\ &=\ CH=\ C-COOH \\
&\rightarrow \ R-CH_{2}CH=\ COOH
\end{align*}
\]

Treatment of the azlactone with amines and amino acids produces amides and dipeptide derivatives. Hydrolysis with strong mineral acids or alkali leads to \( \alpha \)-keto acids. 3,4-dimethoxyphenyl acetic acid has been prepared in this manner by oxidation of the keto acid with hydrogen peroxide [22].

\[
\begin{align*}
R-CH\ &=\ CH\ =\ CO-COOH \\
&\rightarrow \ OH- \rightarrow \ R-CH_{2}CO-COOH \\
&\rightarrow \ R-CH_{2}COOH
\end{align*}
\]

Many researchers have reported the synthesis of 4-arylidene-5-oxazolones by varying the reaction conditions as reported [23-28]. Tripathy et al have reported 2-substituted-2-oxozolin-5-one, generated by cyclization of \( \alpha \)-N-acylamino acids with benzene sulphonyl chloride in the presence of triethylamine, which gives 2-substituted-4-arylmethylene-2-oxazolidin-5-ones on reaction with aromatic aldehydes to their N-phenyl imines. This reaction occurs in one pot [29]. This procedure overcomes some of the disadvantages of the earlier methods regarding the speed of the reaction and stereo chemical purity of the products. For example the Erlenmeyer azlactone synthesis employs acetic anhydride for the cyclization and it affords a mixture of (E) and (Z)-isomers of the unsaturated oxazolones which have to be separated by fractional crystallizations.
2.1.1 Synthesis, Biological Activity of Some Oxazolone-Imidazolinone Derivatives.

5-Oxazolone derivatives are known for their usefulness in preparing various heterocyclic compounds [30]. These compounds are also used as versatile reagents for the synthesis of α-keto and aryl acetic acid peptides and α-amino acids [31]. New cycloaddition reaction between 4-arylidene-2-phenyl-5-(4H)-1,3-oxazolone and benzyne give a 1,4(H)-benzoxazepine-2-ones and their phenyl derivatives [32].

\[
\begin{align*}
\text{Ar} & \quad \text{H} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{Ar} \\
\end{align*}
\]

Some 4-(4′-acetoxy benzylidene)-2-methyl-5-oxazolone were prepared which on hydrolysis gave some unexpected products [33]. Some novel bicyclic oxazolone derivatives where reported as anti-angiogenic agents [34]. Certain 2-Phenyl-4-arylidene-5-oxazolone and cyclopentadienes in the presence of Lewis acid gave cycloaddition products [35]. Some 4-ethoxy methylene-2-[1]-napthyl-5-(4H)-oxazolone are also reported. [36].

\[
\begin{align*}
\text{Ar} & \quad \text{R}_1 \\
\text{O} & \quad \text{R}_2 \\
\end{align*}
\]

where \( R_1 = R_2 = \text{H}, \text{CH}_3 \) and \( \text{Ar} = \text{Phenyl and Naphthyl} \)

Certain oxazolones under acidic conditions were transformed to furanones by Maria et al [37]. Villemin et al have reported the use of \( \text{Al}_2\text{O}_3\)-KF and acidic clay KSF in dry condensation of arylaldehyde with a variety of heterocyclic compounds under microwave irradiation [38-40]. Kidwai et al have reported the synthesis of the 4-Arylidene-5-oxazolone by using the Lewis acids. The effect of anhydrous \( \text{ZnCl}_2 \), \( \text{BF}_3 \), \( \text{EtO}_2 \), \( \text{AlCl}_3 \) and sodium acetate as catalyst in acetic anhydride has been observed [41]. The synthesis of azlactone under microwave irradiation has become well known since the last decade and has been
reported in open vessels using acetic anhydride which acts both as reagent and as the organic phase [42]. Acetic anhydride is well known toxic reagent and its use for carrying out reaction would spoil the cavity of the oven and also lead to emission of toxic vapor in the environment. So bismuth (III) acetate and calcium acetate were used as supports which are inexpensive [43].

Literature survey reveals that various imidazolinone derivatives posses a broad spectrum of pharmacological actions which are reflected by their use as anticonvulsant [44], antiparkinsonian [45] and monoamine oxidase inhibitory (MAO) [46] agents. Some novel disubstituted imidazolinones were investigated as anticonvulsant, MAO and succinate dehydrogenase (SDH) inhibitory agents [47]. Some novel imidazolinones were synthesized and their therapeutic importance has been reported [48, 49].

Patel et al have reported some 2-hydrazinobenzthiazole on condensation with different oxazolones gave Imidazolinone derivatives and the prepared compounds were evaluated for their antibacterial, antifungal and anti-tubercular activity [50].

\[
\begin{align*}
\text{[Imidazolinone structure]}
\end{align*}
\]

Certain synergistic fungicidal compounds were also reported to have imidazolinone in their backbone [51].

\[
\begin{align*}
\text{[Fungicidal compound structure]}
\end{align*}
\]

Arief et al have reported some aryl cinnamides and imidazolinone derivatives of expected biological activities [52].

\[
\begin{align*}
\text{[Imidazolinone derivative structure] where } R=N\text{-Phthimidomethyl.}
\end{align*}
\]
Banarjee et al have reported the cyclocondensation of RNHCONH$_2$ with R’COCN gave the corresponding 1,4-diaryl-5-imino-3-imidazolin-2-one [53].

![Chemical structure](image)

where R= 2-, 3-, 4-Me-C$_6$H$_4$, 4-OMe-C$_6$H$_4$, 4-EtO-C$_6$H$_4$, 4-Br-C$_6$H$_4$; R’= Ph, 4-Cl-C$_6$H$_4$, 4-NO$_2$-C$_6$H$_4$.

Some 2-amino-5-benzylidene-4($H$)-imidazolin-4-one derivatives were prepared and showed antifungal activity. The compounds were prepared by the reaction of Ph-CH=C(CO$_2$Et)-N=PPPh$_3$ with RNCO gave Ph-CH=C(CO$_2$Et)-N=CNR which on cyclization with R’H gave the desired compound [54].

![Chemical structure](image)

R=Ph, 4-Cl-C$_6$H$_4$; R’= Et$_2$N, i-Pr$_2$N, PhNMe, dihexylamino, dicyclohexylamino, piperidino, morpholino, imidazolyl.

Ding Mingwu et al have reported the preparation of 2-(4-methylthio phenoxy)-5-(2-furanylmethylene)-4-imidazolinone and 2-(1$H$-1,2,4-triazol-1-yl)-5-furanyl methylene imidazolinone derivatives as fungicidal activity against Pyricularia Oryzae and Pellicularia sasaei at 50 ppm [55, 56].

![Chemical structure](image)

R= Ph, 3-ClC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$

Vyas et al have reported certain pyrimidinedione hydrazine on condensation with oxazolones gave the corresponding imidazolinones and the compounds were screened for their antibacterial activity [57].
Joshi et al have reported some imidazolinones from hydrazine-s-triazines as potential antimicrobial agents [58].

Some imidazolinone derivatives were prepared from oxazolones and 2,6-dinitro-4-(trifluoromethyl)-N-(arylsulfonylhydrazinoethyl)-N-propylamines. The prepared compounds were scanned for the antimicrobial activity [59].

Certain trimethoxy benzamide bearing imidazolinone were synthesized and where screened for their antibacterial and antifungal activity [60].

Oza et al have reported certain important compounds by using acid hydrazides and oxazolone to give new 5-imidazolinone derivatives [61].
Some imidazolinone derivatives were prepared by the condensation of isoniazid with 5-oxazolone. The compounds prepared showed anticonvulsant activity [62].

2.1.2 Imidazole Chemistry

Imidazoles is an azapyrrole, the two nitrogen atom being separated by one carbon atom. It is an important ring system, for many substances of biological and chemical interest, both natural and synthetic. The parent substance was first obtained from glyoxal and ammonia, and for this reason it was named glyoxaline. This name still persists and does the alternative name iminazole.

The imido hydrogen atom in imidazole is tautomeric, and in practice the two nitrogen atoms are indistinguishable. 4-Methylimidazole is therefore identical with 5-Methylimidazole, and this fact is often indicated by giving the alternative numbering in parenthesis, as in 4(5)-methylimidazole, with N-substituted imidazoles, however, no tautomerism is possible, and 1,4-dimethylimidazole is not identical with 1,5-dimethylimidazole.
Imidazole is a base of moderate strength (pKa 7.16) having boiling point 2650, behave like heterocyclic aromatic compounds, is stable to chromium trioxide; but it is attacked by potassium permanganate and by hydrogen peroxide to give oxamide. The ring system is also remarkably stable to acids, and bases, and it resists catalytic hydrogenation. Furthermore, imidazoles undergo typical aromatic substitution reactions, such as halogenation, nitration and sulfonation.

The bromination of imidazoles occurs very readily under mild conditions and the tribromo derivatives are generally obtained. Similarly, imidazole reacts with iodine to give 2,4,5-triiodoimidazole. Nitration with a mixture of fuming nitric and sulfuric acids gives 4(5)-nitroimidazoles, and polynitro derivatives are not formed. Imidazole couples with phenyl diazonium chloride, the main product being 2-phenylazoimidazole; but sulfonation leads to the formation of 4(5)-imidazolesulfonic acid. Nitration and sulfonation presumably involve the free base or the imidazole cation; but the coupling reaction is evidently on the imidazole anion, as a free imido group is a necessary condition for coupling [63]

2.1.3 Synthesis of Imidazole

Perhaps the most common imidazole synthesis is the Radziszewski, which involves the condensation of a dicarbonyl compound (e.g. glyoxal, α-diketones, α-ketoaldehydes) with ammonia
and an aldehyde. The original synthesis of imidazole itself, from glyoxal and ammonia, is evidently of this type, some of the glyoxal being cleaved to formaldehyde under the influence of the ammonia.

\[
\text{CHO} + \text{NH}_3 + \text{OCHR} \rightarrow \text{Radziszewski synthesis}
\]

Several other synthesis are closely related to this. For example \(\alpha\)-diketones reacts with amines of the type \(R\text{CH}_2\text{NH}_2\) to give an intermediate which cyclizes to an imidazole [64].

Similarly, \(\alpha\)-diketones reacts with amidines. Diacetyl and benzamidine, for example, gives 4-hydroxymethyl-5-methyl-2-phenylimidazole [65].

Another synthesis involves the reaction of an amidine with an \(\alpha\)-halogeno ketone [66].

\[
\text{Chapter-2}
\]
It is also possible to obtain imidazoles from oxazoles by heating with ammonia. 2-Phenyl-4-methylimidazole, for example, is readily prepared from 2-phenyl-5-methyloxazole-4-carboxylic acid [67].

2.1.4 Biologically Important Compounds Containing Imidazole Nucleus

The imidazole series includes a number of natural and synthetic compounds which possess marked physiological activity. Imidazole, itself, has little action and is relatively nontoxic [68]. 4(5)-Methylimidazole is more toxic [69] and is reported to exert a slight hypertensive action [70]. 4,5-Dimethylimidazole, imidazole-4-aldehyde, 4-chloroimidazole, 4-aminomethyl- and N-substituted 4-aminomethylimidazoles cause vasoconstriction and increase in blood pressure [71].

Imidazoles of the type shown below are reported to have some antimalarial action [72] when R is hydrogen and R¹ is an alkyl group containing eleven to fourteen carbon atoms. 1-Decyl-2-methylimidazole is said to be a topical anesthetic [73]. N-Aryl substitution also seems to induce anesthetic activity [74]. 2-thio-4-aminomethylimidazole is said to possess some insulin-like action in diabetes [75].
2.1.5 Imidazolone Chemistry

The imidazolones are keto dihydroimidazoles. They are commonly designated as 2-, 4-, 5-imidazolones, where the number indicates the position of the ketone group. The position of the double bond in the 4-imidazolones is obvious. In the 2-imidazolones the double bond may occupy either of two positions. The better known 2-imidazolones have the double bond in 4,5 position, and the 5-imidazolones have it in 2,3 position. In the few compounds where the double bond is in the 3,4 position, the name isoimidazolone has been applied. The 4- and 5-imidazolones are identical except when there is a substituent in the 1 position.

2-isonimidazolone 2-imidazolone 4-isonimidazolone 4-imidazolone 5-isonimidazolone 5-imidazolone

2.1.6 Synthesis of 4(5H) or 5(4H) - Imidazolones

The first representative of the class of imidazoles, the compounds 2-phenyl-4(or )-benzylidene-4(5H) (or5(4H))-imidazolone, was obtained by Ruhemann and Cunnington [76] from the sodium ethoxide catalyzed reaction of ethyl phenyl propionate and benzamidine hydrochloride. A more generally applicable procedure for the synthesis of these imidazolones involves the condensation of equimolar proportions of an amidine and ester of an α-amino acid. The reaction of glycine ester with an amidine leads to the formation of a 2-monosubstituted 4(5 H) (or 5(4 H))-imidazolone, while the use of
other α-amino acids esters affords 2, 4 (or 2,5)-disubstituted 4(5 H) (or 5(4 H))-imidazolones. The reaction proceeds rapidly

\[
\begin{align*}
\text{HN} & \equiv \text{C} \equiv \text{NH}_2 + \text{NH}_2 \text{R'} \rightarrow \text{HN} \equiv \text{C} \equiv \text{NH} \equiv \text{R'} \\
\text{H-C} & \equiv \text{C} \equiv \text{H} + \text{HN} \equiv \text{C} \equiv \text{NH}_2 \rightarrow \text{HN} \equiv \text{C} \equiv \text{NH} \equiv \text{R'} \\
\text{HN} \equiv \text{C} & \equiv \text{NH} \equiv \text{R'} + \text{HN} \equiv \text{C} \equiv \text{NH} \equiv \text{R'} \rightarrow \text{HN} \equiv \text{C} \equiv \text{NH} \equiv \text{R'}
\end{align*}
\]

on mixing the components at room temperature and in some instances is so violent that cooling is necessary. The method is applicable to the preparation of a great variety of imidazolones since the groups R and R' may be aromatic or aliphatic in nature [65, 77, 78]. The condensation in the presence of a base of an α-ketoaldehyde with an amidine is an other route to 2,4 (or 2,5)-disubstituted 4(5 H) (or 5(4 H))-imidazolones. An example of this reaction is the formation of 2-phenyl-4(or 5)-methyl-4(5H) (or 5(4H))-imidazolone from methyl glyoxal and benzamidine [65,78-81]. This reaction seems to proceed through the stage of a 4,5-dihydroxy-2-imidazoline in the manner indicated below.

Closely related to this synthesis is the formation of 2-phenyl-4 (or 5) arylidene-4 (5 H) (or 5(4H))-imidazolones from the interaction of benzamidine-glyoxal with aromatic aldehyde. The addition of potassium hydroxide to a mixture of glyoxal and benzamidine hydrochloride results in the formation of a labile, basic substance which may be represented either as an open chain compound or, preferably, as a 2-phenyl-4,5-dihydroxy-2-imidazoline (bensamidine-glyoxal) [65]. This benzamidine-glyoxal addition compounds
dissociates in aqueous solution, and the addition of phenyl hydrazine leads to the formation of glyoxal phenyl osazone.

In the presence of an aromatic aldehyde and sodium or potassium hydroxide this substance is converted in good yields into a 2-phenyl-4-(or 5)-arylidene-4(5 H) (or 5(4H))-imidazolones. Using the more plausible 4,5-dihydroxy-2-imidazoline formulation for the benzamidine-glyoxal complex as the basis, this reaction may be formulated in the manner illustrated below. Under the influence of the base, the dihydroxyimidazoline is assumed to lose a molecule of water with the formation of the highly reactive 2-phenyl-4(5 H) (or 5(4H))-imidazolones, which in turn undergoes an aldol-type condensation with the aldehyde to give the final product.

The ability to undergo this type of condensation is a typical property of 4(5 H) (or 5(4 H))-imidazolones, since the proximity of the carbonyl group activates the adjacent methylene groups. Numerous 2-phenyl-4(5 H) (or 5(4 H))-imidazolones are accessible by this method [81-85].

The dehydration of α-acylamido-β-phenyl acrylic acid amides (readily available from the reaction of azlactones with ammonia) represents another route to 2-phenyl-4(5 H) (or 5(4 H))-imidazolones. The synthesis of 2-phenyl-4(5 H) (or 5(4 H))-imidazolones serves as an illustration of the method. The reaction of hippuric acid with benzaldehyde in the presence of
mixture of acetic anhydride and sodium acetate leads to the formation of benzoyl-α-cinnamic azlactone (4-benzylidene-5-oxazolone). This substance is readily converted into the amide of α-benzamido-β-phenylacrylic acid by exposure to aqueous ammonia and the amide under the influence of hot dilute sodium hydroxide loses a molecule of water with formation of 2-phenyl-4(or 5) benzylidene-4(5 H) (or 5(4 H))-imidazolones. Numerous other azlactones are converted into the corresponding imidazolones according to the reaction scheme given below. [86-89].

It is of interest to note that treatment with hot dilute sodium hydroxide converts the amide of α-benzamidoisobutyric acid into 2-phenyl-4, 4 (or 5,5) dimethyl -4(5 H) (or 5(4 H))-imidazolones, while similar treatment of the amides of benzoylglycine and benzoylalanine leads to hydrolysis of the carboxamide linkage [90,91].

Certain amides and the anilide of α-benzamido-β-phenylacrylic acid are not convertible into the respective imidazolones by treatment with hot alkali. Here, more drastic treatment such as heating in vacuum at temperature 170-200 °C is required to bring about the ring closure.
The reaction is not generally applicable as heating of the isopropylamide of α-benzamido-β-phenylacrylic acid results in the regeneration of benzoyl-β-aminocinnamic azlactone and not in the formation of the expected 1-isopropl-2-phenyl-4-benzylidene-5(4 H)-imidazolone. A similar situation prevails in the case of a number of acylated dehydrophenyl alanyl dipeptide ester. Heating in vacuum at 170°C converts benzoyldehydrophenyl alanylglycine ethyl ester into 1-carbethoxymethyl-2-phenyl-4-benzylidene-5-imidazolone. The same treatment converts such compounds as benzoyldehydrophenylalanylalanine ethyl ester or benzoyldehydrophenylalanylleucine-ethyl.

\[
\begin{align*}
\text{Ester into benzoyl-α-cinnamic azlactone and the respective amino acid ester} & \ [92, 93]. \\
\end{align*}
\]

The anilide of α-benzamido-β-(o-nitrophenyl) acrylic acid is readily converted into 1,2-diphenyl-4-(o-nitrobenzylidene)-5-imidazolone when subjected to the action of phosphorus oxychloride [94].
The reaction between huppuramide and phosphorus pentachloride leads to the formation of hippuronitrile and not to the formation of 2-phenyl-4(5 H) (or 5(4 H))-imidazolones [95,96].

4(5 H) (or 5(4 H))-Imidazolones-2-carboxylic acid results from the oxidation of diketopiperazine with alkaline hypobromite. The compound couples with diazotized aniline, is extremely unstable, and in the presence of alkali decomposes with the liberation of hydrogen cyanide [97].

2.1.7 Structural Considerations and Properties of 4(5 H) (or 5(4 H))-Imidazolones

In addition to many plausible contributions in the resonance sense, four tautomeric forms of the 4(5 H) (or 5(4 H))-imidazolones have to be considered.

These are the results of the presence of an amidine and a keto-enol system in these molecules. The available chemical evidence suggests the importance of both the imidazolones and the hydroxyimidazole forms. The dibenzoyl derivatives which results when 2-methyl-4(5 H) (or 5(4 H))-imidazolones or 2-benzyl-4(5 H) (or 5(4 H))-imidazolone are treated with benzoyl chloride in pyridine solution must arise from the enolic form and may possess either of the two structure shown below [77,78].
Similarly, the acetyl derivative of 2-phenyl-4(or 5)-methyl-4(5 H) (or 5(4 H))-imidazolone is best regarded as an o-acetyl derivative arising from the hydroxyimidazole form. The basic medium of the acetyl derivative supports this view [65].

The observations that 4(5 H) (or 5(4 H))-imidazolones possessing an unsubstituted methylene group couple with diazotized aromatic amines, and form benzylidene derivatives on treatment with benzaldehyde are best explained in terms of the keto form, the activation of the methylene group being due to the electron-attracting effect of the neighboring carbonyl group and possibly of the tertiary nitrogen atom [77,78].

The 4(5 H) (or 5(4 H))-imidazolones are amphoteric compounds having the ability to form salts with both acids and metals. 2-phenyl-4-(or 5)-methyl-4(5 H) (or 5(4 H))-imidazolone, for example forms a silver salt when treated with silver nitrate and also has the ability to give a sparingly soluble picrate [65]. The amidine part of the molecule must be responsible for the basic properties, while the acidic character may be due to the enolic hydroxyl group. The acidic character of the 2-phenyl-4(or 5)-arylidene-4(5 H) (or 5(4 H))-imidazolones is not
explicable in terms of enolization. A plausible formulation for the anions of these compounds is illustrated:

\[
\begin{array}{c}
\text{\includegraphics[width=0.5\textwidth]{structure.png}}
\end{array}
\]

The 4(or 5)-arylidene-4(5 H) (or 5(4 H))-imidazolones exhibit characteristic U.V. absorption spectra and are readily reduced either catalytically or by sodium amalgam in acetic acid solution. Both the exocyclic and the ring double bond are saturated. The conversion of 2-phenyl-4(or 5)-benzylidene-4(5 H) (or 5(4 H))-imidazolone into 2-phenyl-4-benzyl-5-imidazolidone is illustrative.

2.1.8 Biological Active Imidazolones

A large number of biological active compounds containing imidazolone moiety are reported.

Badr and Co-workers [98] have synthesized 1,2-disubstituted 4-benzylidene -2-imidazolin-5-one and their thione derivatives which shows antibacterial activity.

\[
\begin{array}{c}
\text{\includegraphics[width=0.5\textwidth]{structure.png}}
\end{array}
\]

where \(R = H, \text{p-MeO, o-MeO}; R^1 = H, \text{p-Me, o-Me, p-Br, p-MeO etc.}\)

The imidazolone derivatives [99] have been reported for potential antibacterial and antifungal activity having the following structure (II).
The imidazolone derivatives having the following general structure (III) are reported as antibacterial agents [100].

\[
\begin{align*}
\text{R}^1\text{CH}=\text{N} &\text{N} &\text{O} &\text{SO}_2\text{NH}\text{R}^2 \\
\text{R}^1 &\text{= CH}_3, \text{C}_6\text{H}_5, \text{p-O}_2\text{N}\text{C}_6\text{H}_4 \\
\text{R}^2 &\text{= H, o-OH} \\
\end{align*}
\]

where \( R = \text{H, R}^1 = 3,4\text{-MeO}\text{C}_6\text{H}_3, 4\text{-}(\text{Me}_2\text{N})\text{C}_6\text{H}_4 \)  
\( R^2 = R^3 = \text{H} \)

Mukherji et al. [101] have synthesized new 1-(2-methoxy-4-nitrophenyl)-2-phenyl-4-substituted arylidene-5-imidazolones which displayed central nervous system (CNS) depressant properties at 200 mg/kg concentration. They have also been reported for anticonvulsant activity in pentetrazole test.

\[
\begin{align*}
\text{R}^1\text{CH}=\text{N} &\text{O} &\text{Me} &\text{OMe} \\
\text{R}^2 &\text{= (un) substituted Ph, furyl, napthyl.} \\
\end{align*}
\]

Badr and Co-workers [102] have synthesized the compound (V) which shows antibacterial and antifungal activity.
where R = H, p-MeO, o-MeO
R1 = COOH, COOMe, COOEt, SO2NH2, 2-pyrimidinyl amino sulfonyl etc.

The imidazolone derivatives having the following general structure (VI) are reported as CNS active agents [103].

where R, R1 = H, MeO; R2 = H, MeO, Cl etc

Mohan et al. [104] have synthesized substituted imidazolone derivatives which shows CNS, anthelmintic and anti-inflammatory activities. Most (VII) showed anti-inflammatory activity against carrageenin induced edema.

where R = Me, Ph; R1, R2 = H, MeO

The imidazolone derivatives having the following general structure (VIII) are reported as potential antibacterial, antifungal and AchE inhibitory agents [105].
Sengupta and Co-worker [106] synthesized imidazolone derivative as antibacterial agent which were effective against Bacterium pumilis at 200 µg/0.1 ml concentration.

Imidazolone compounds [107] of the following structure (X) has been reported useful as antibacterial agents against *S.aureus* and *E.coli*.

The imidazolone derivatives [108] have been reported recently for antiparkinson activity having following structure (XI & XII)

Bousquet and Co-workers [109] have synthesized imidazolone compounds which shows analgesic and anti-inflammatory activities.
Most (XIII) showed a higher analgesic activity at 10 mg/kg and exhibited anti-inflammatory at 100 mg/kg (oral) in rat paw edema test.

![Structure XIII]

where $R = H, o$-Br

$R' = p$-NO$_2, p$-Cl

Parekh and Co-workers [110-115] have synthesized imidazoline compounds of the following structure (XIV) which exhibits anticonvulsant, antibacterial and antifungal activities.

![Structure XIV]

where $R = H, o$-Br

$R' = p$-NO$_2, p$-Cl

The most recent references of the biological active imidazolone derivatives are as follows:

1. The novel indolyl imidazolines [116] of the following structure (XV) are reported useful for antibacterial activity.

![Structure XV]

2. Imidazoline compounds [117] of the following structure (XVI) are reported useful for antibacterial and antifungal activities.
The references of the imidazolone derivatives used in azo dyes are as follows:

1. Bykova and Co-workers [118] have synthesized new imidazolone-4,5-dicarboxylic Acid derivatives which are used in synthesis of new azo dyes.

2. Matsushita and Co-workers [119] have synthesized 2-substituted imidazoles which are used as couplers for recording materials.

3. Mocckli and Co-workers [120] have synthesized Imidazolium azo dyes which are used on paper.

4. Szadowski and Co-workers [121] have synthesized reactive dyes using benzimidazolone residue.
In this line of exploration we thought that, 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one was found interesting and would serve as heterocyclic diazo component in preparation of reactive as well as acid dyes. Hence these dyes were prepared and presented in following parts.

a) Hetero-bifunctional reactive dyes from various 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one.

b) Monofunctional reactive dyes from various 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one.

c) Azo acid dyes from various 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one. (Chapter – 3)

2.2 Experimental

Various 4-benzylidene-2-Phenyl-5-oxazolones were prepared by Erlenmeyer reaction using benzoyl glycine (Hippuric acid), acetic anhydride and sodium acetate. The prepared 5-oxazolone were treated with p-phenylene diamine in basic medium to give corresponding 1-(4-amino)-2-phenyl-4-substituted benzylidene-5-imidazolone. These substituted imidazolones are further used for the synthesis of azo dyes. Melting points were taken in open capillary tubes and are uncorrected. Infrared Spectra (KBr,cm\(^{-1}\)) were recorded on a Shimadzu-8400 and Nicllet 400D FT-IR spectrometer, \(^1\)H NMR spectra on a Brucker spectrometer, 300MHz FT-NMR and Hitachi R-1500, 60MHz spectrometer, using TMS as a internal standard (chemical shift in \(\delta\), ppm) in CDCl\(_3\) and DMSOd\(_6\). All the synthesized compounds gave satisfactory C, H, N analyses on Perkin Elmer (U.S.A) 2400 Series II.

2.3 Materials

The benzoyl glycine (Hippuric acid), acetic anhydride and sodium acetate have been used for the synthesis of above compounds. Other chemicals used were of LR grade.
Chapter – 2 A

Hetero-bifunctional reactive dyes from various 3-(4-amino phenyl)-
5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one.

2A.1.1 Reaction scheme

- **1)** Diazotization
- **2)** Coupling

![Reaction scheme diagram](image-url)
where,

<table>
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<th>Dyes</th>
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<td>4-N(CH₃)₂</td>
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<td>4-Cl</td>
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</tr>
<tr>
<td>D5</td>
<td>2-OH, 3-OCH₃</td>
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<td></td>
</tr>
</tbody>
</table>

2A.1.2. Preparation of 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2).
4-Arylidene-2-phenyl-5-(4H)-oxazolones were prepared according to the reported method [122,123].

2A.1.3. General procedure for the Preparation of 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one. (3)

Equimolar amount of 4-Arylidene-2-phenyl-5-(4H)-oxazolone and p-phenylene diamine were taken in a reaction flask attached with a reflux condenser and kept under reflux for 6 hours, with dry pyridine as solvent. The reaction was monitored by thin layer chromatography, on completion of the reaction the contents were poured in ice water to give colored precipitates. T.L.C (Methanol: Toluene: 2:8), Yield 85-87 %.

Preparation of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro- imidazol-4-one) (3).

Equimolar amount of 4-methoxy benzylidene-2-phenyl-5-(4H)-oxazolones and p-phenylene diamine were taken in a reaction flask attached with a reflux condenser and kept under reflux for 6 hours with dry pyridine as solvent. The reaction was monitored by thin layer chromatography, on completion of the reaction the contents were poured in ice water to give dark colored precipitates.
**IR Data:** (cm⁻¹)
3300-3270(-NH),
3010–3100 (Aromatic C-H), 2972–2916 (C=C stretch),
1690 (C=O, Imidazolinone ring),
1251 (C-O-C Asymmetric Stretch), 1026 (C-O-C Symmetric Stretch).
(FIGURE 2.1, I.R Spectra of 3-(4-amino phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)

**¹H NMR Data:** (δ, ppm)
δ 8.04-6.60 (m, 13H, Ar-H),
δ 6.01 (s, 1H, Ph-C=CH),
δ 4.63 (br, 2H, -NH₂),
δ 3.78 (s, 3H, -OCH₃).
(FIGURE 2.2, NMR Spectra of 3-(4-amino phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)
FIGURE 2.1 Infrared Spectra of;
3-(4-amino phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)
FIGURE 2.2 NMR Spectra of;
3-(4-amino phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)
3-(4-aminophenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3).

Equimolar amount of 4-N,N-dimethylbenzylidene-2-phenyl-5-(4H)-oxazolones and p-phenylene diamine were taken in a reaction flask attached with a reflux condenser and kept under reflux for 6 hours with dry pyridine as solvent. The reaction was monitored by thin layer chromatography, on completion of the reaction the contents were poured in ice water to give red colored precipitates.

**IR Data:** (cm\(^{-1}\))

- 3270 (-NH),
- 3010–3100 (Aromatic C-H), 2972–2916 (C=C stretch),
- 1690 (C=O, Imidazolinone ring),
- 1251 (C-O-C Asymmetric Stretch), 1026(C-O-C Symmetric Stretch).

(Figure 2.3, I.R Spectra of 3-(4-amino phenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)

**\(^1\)H NMR Data:** (δ, ppm)

- δ 8.16-6.59 (m, 13H, Ar-H),
- δ 6.43 (s,1H, Ph-C=CH-),
- δ 4.59 (br, 2H, -NH\(_2\)),
- δ 3.09 (s, 6H, -N(CH\(_3\))\(_2\)).

(Figure 2.4, NMR Spectra of 3-(4-amino phenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)
FIGURE 2.3 Infrared Spectra of:
3-(4-amino phenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one)
FIGURE 2.4 NMR Spectra of;
3-(4-amino phenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro-imidazol)-4-one
2A.1.4 Preparation of 3-[4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-substituted-benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one.(4)

A solution of cyanuric chloride (9.75 g, 0.053 mole) in acetone (40 ml) was poured into a vigorously stirred mixture of crushed ice (100 gm) and water (100 ml). To this mixture a solution of 3-(4-Amino-phenyl)-5-(4-substituted-benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (3), in water (100 ml, pH 6.5) was added dropwise at 0-5°C over 30 min at pH 3.5-4.5, using Na$_2$CO$_3$ solution (10 % w/v). The solution was stirred for a further 60 min to complete the reaction.[124]

2A.1.5. Diazotization of 4-aminophenyl-$\beta$-sulfatoethyl sulfone (5) and coupling with 1-napthol-8-amino-3,6-disulphonic acid [H-Acid]. (6)

To the 25ml of water in a beaker 2.96 g (95 % 0.01 mole) of 4-aminophenyl-$\beta$-sulfatoethyl sulfone (5) was added. While stirring the suspension was cooled down to 5°C using ice. To this solution 3.67 ml (3 N, 0.011 mole) of NaNO$_2$ and 5g of ice were added. Then, 2.6 ml of conc. HCl was added to obtain a diazo component of 4-aminophenyl-$\beta$-sulfatoethyl sulfone. Completion of diazotization reaction was checked by starch iodide test. Excess HNO$_2$ was removed by adding a small amount of sulfamic acid.

The coupler solution was prepared by taking 3.9 g (82 %, 0.01 mole) of 1-napthol-8-amino-3,6-disulphonic acid (H-acid) in another beaker and 40 ml of water was added and the pH was adjusted between 9-10, using 10% Na$_2$CO$_3$. The above prepared diazo solution was transferred to dropping funnel and was added dropwise to coupler solution while keeping the temperature 0-5°C to complete the coupling reaction.[125]
2A.1.6. Preparation of 5-(4-Chloro-6-[4-[4-(4-hydroxybenzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino]-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxyethanesulfonyl)-phenylazo]-napthalene-2,7-disulfonic acid. (7)

A solution of 3-[4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-hydroxy-benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (4) (5 gm, 0.01 mole) was prepared in 100 ml water and 10ml of 10% HCl in a beaker.

To this resulting solution, an aqueous solution (200 ml, pH 6.5) of compound (6) (6.1 g, strength 93%, 0.01 mol) was added dropwise at 35 °C over 60 min with the pH maintained between 6-6.5 using sodium carbonate solution (10% w/v) and 10% HCl. The mixture was stirred for a further 60 min to complete the reaction. The product was then used as dyes. [126]

**IR Data: (cm⁻¹)**

3447 OH, 3290 N-H(S),
1707 C=O(S) Imidazolinone ring,
1596 N=N(S),
1600-1500 (C=C stretch), below 900 C-H(B),
1900-1500 C=N(s),
1221 (C-O-C Asymmetric Stretch),
1042 (C-O-C Symmetric Stretch),
1138 S=O(S),
780 C-Cl stretch(S).

(Figure 2.5, Infrared Spectra of 5-(4-Chloro-6-[4-[4-(4-hydroxybenzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino]-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxyethanesulfonyl)-phenylazo]-napthalene-2,7-disulfonic acid). (7)
$^1$H NMR Data: ($\delta$, ppm)
$\delta$ 7.52-6.74 (m, 20H, Ar-H),
$\delta$ 4.47 (m, 2H, OH),
$\delta$ 3.77 (br, 2H, NH),
$\delta$ 2.82-2.36 (s, 4H, CH$_2$O)

(FIGURE 2.6 NMR Spectra of 5-(4-Chloro-6-{4-[4-(4-hydroxybenzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxyethanesulfonyl)-phenylazo]-naphthalene-2,7-disulfonic acid.)(7)
FIGURE 2.5 Infrared Spectra of 5-(4-Chloro-6-\{4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino\} \{1,3,5\}triazin-2-ylamino\}-4-hydroxy-3-[4-(2-sulfoxy-ethanesulfonyl)-phenylazo]-napthalene-2,7-disulfonic acid.(7)
FIGURE 2.6 NMR Spectra of 5-(4-Chloro-6-{4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxy-ethanesulfonyl)-phenylazo]-napthalene-2,7-disulfonic acid.(7)
# TABLE 2.1 Physical and Elemental Data

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2A.1.7. Result and Discussion

Starting compound 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2) derivatives were prepared by Erlenmeyer condensation of benzoylglycine with different aldehydes in presence of sodium acetate and acetic anhydride.

The prepared 5-oxazolone were treated with p-phenylene diamine in basic medium to prepared 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3). The IR Spectrum of compound (a) showed the NH bands at 3300-3270 cm\(^{-1}\), and the C=O band nearly at 1690 cm\(^{-1}\).

The \(^1\)H NMR spectrum shows broad peak at 4.63ppm was due to the protons of the –NH\(_2\) group. The benzylidene proton of (Ph-C=CH) was found in downfield region at \(\delta\) 6.01 ppm. In the case of 4-OCH\(_3\), singlet is observed at \(\delta\) 3.78 ppm which corresponds to the three protons of –OCH\(_3\). Compound (4) and (6) were prepared by known reported methods. The final dye (7) was the condensation product of compounds (4) and (6). The IR Spectrum of compound (7) showed the OH bands nearly at 3447 cm\(^{-1}\), NH bands nearly at 3290 cm\(^{-1}\), the C=O band nearly at 1707 cm\(^{-1}\), N=N bands nearly at 1596 cm\(^{-1}\) and the C-Cl bands nearly at 780 cm\(^{-1}\).

The \(^1\)H NMR spectrum showed a multiplet at \(\delta\) 7.527-6.754 ppm due to aromatic protons (20 H), the benzylidene proton of (Ph-C=CH) was also found in the same region but was over lapped by multiplet of aromatic protons, the spectrum showed a peak at \(\delta\) 4.475 ppm due to –OH protons (2H), a singlet was seen at \(\delta\) 3.775 ppm due to –NH protons (2H). The position of protons of –NH and –OH groups may depend upon the intramolecular hydrogen bonding into the sample tube. A triplet was seen at \(\delta\) 2.827-2.763 ppm due to protons of –H\(_2\)C-CH\(_2\)-O-SO\(_3\)Na (2H), an another triplet was seen at \(\delta\) 2.486-2.367 ppm due to protons of –H\(_2\)C-CH\(_2\)-O-SO\(_3\)Na (2H).

2A.2.1 Reaction scheme
where,

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2A.2.2 Preparation of 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2). 
Same as 2A.1.2

2A.2.3 General procedure for the preparation of 3-(4-aminophenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (2). 
Same as 2A.1.3

Preparation of 3-(4-aminophenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3). 
Same as 2A.1.3

Preparation of 3-(4-aminophenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro- imidazol-4-one) (3). 
Same as 2A.1.3

2A.2.4. Preparation of 3-[4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-substituted-benzylidene)-2-phenyl-3,5-dihydro- imidazol-4-one.(4) 
Same as 2A.1.4

2A.2.5. Diazotization of 4-aminophenyl-β-sulfatoethyl sulfone (5) and coupling with 1-naphthol-7-amino-3-sulphonic acid (γ-Acid). (6)

To the 25ml of water in a beaker 2.96 g (95 % 0.01 mole) of 4-aminophenyl-β-sulfatoethyl sulfone (5) was added. While stirring the suspension was cooled down to 5°C using ice. To this solution 3.67 ml (3 N, 0.011 mole) of NaNO₂ and 5g of ice were added. Then, 2.6 ml of conc. HCl was added to obtain a diazo component of 4-aminophenyl-β-sulfatoethyl sulfone. Completion of diazotization
reaction was checked by starch iodide test. Excess HNO\textsubscript{2} was removed by adding a small amount of sulfamic acid.

The coupler solution was prepared by taking 3.9 g (82 %, 0.01 mole) of 1-naphthol-7-amino-3-sulphonic acid (\(\gamma\)-acid) in another beaker and 40 ml of water was added and the pH was adjusted between 9-10, using 10% Na\textsubscript{2}CO\textsubscript{3}. The above prepared diazo solution was transferred to dropping funnel and was added dropwise to coupler solution while keeping the temperature 0-5\textdegree C to complete the coupling reaction.[125]

2A.2.6. Preparation of 6-(4-Chloro-6-[4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino]-[1,3,5]triazine-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxy-ethanesulfonyl)-phenylazo]-napthalene-2-sulfonic acid. (7)

A solution of 3-[4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-hydroxy-benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (4) (5 gm, 0.01 mole) was prepared in 100 ml water and 10ml of 10 % HCl in a beaker.

To this resulting solution, an aqueous solution (200 ml, pH 6.5) of compound (6) (6.1 g, strength 93%, 0.01 mol) was added dropwise at 35\textdegree C over 60 min with the pH maintained between 6-6.5 using sodium carbonate solution (10% w/v) and 10 % HCl. The mixture was stirred for a further 60 min to complete the reaction. The product was then used as dyes. [126]
IR Data: (cm\(^{-1}\))
3435 OH,
3250 N-H(S),
1691 C=O(S) Imidazolinone ring,
1593 N=N(S),
1600-1500 (C=C stretch), below 900 C-H(B),
1900-1500 C=N(s),
1226 (C-O-C Asymmetric Stretch),
1045 (C-O-C Symmetric Stretch)
1124 S=O(S),
753 C-Cl stretch(S).

(FIGURE 2.7 Infrared Spectra of 6-(4-Chloro-6-{4-[4-(4-hydroxybenzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}]-[1,3,5]triazine-2-ylamino]-4-hydroxy-3-[4-(2-sulfoxyethanesulfonyl)-phenylazo]-napthalene-2-sulfonic acid.) (7)

\( ^1\)H NMR Data: (\( \delta \), ppm)
\( \delta \) 7.52-6.75 (m, 20H, Ar-H),
\( \delta \) 4.44 (m, 2H, OH),
\( \delta \) 3.97 (br, 2H, NH),
\( \delta \) 2.87-2.36 (s, 4H, CH\(_2\)O).

(FIGURE 2.8 NMR Spectra of 6-(4-Chloro-6-{4-[4-(4-hydroxybenzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}]-[1,3,5]triazine-2-ylamino]-4-hydroxy-3-[4-(2-sulfoxyethanesulfonyl)-phenylazo]-napthalene-2-sulfonic acid.) (7)
FIGURE 2.7 Infrared Spectra of 6-(4-Chloro-6-{4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}-[1,3,5]triazine-2-ylamino)-4-hydroxy-3-[4-(2-sulfoxy-ethanesulfonyl)-phenylazo]-napthalene-2-sulfonic acid (7)
FIGURE 2.8 NMR Spectra of:
6-(4-Chloro-6-\{4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino\}-[1,3,5]triazine-2-ylamino)-4-hydroxy-3-[4-(2-sulfoxy-ethanesulfonyl)-phenylazo]-napthalene-2-sulfonic acid (7)
## TABLES 2.2-Physical and Elemental Data

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2A.2.7. Result and Discussion

Starting compound 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2) derivatives were prepared by Erlenmeyer condensation of benzoylglycine with different aldehydes in presence of sodium acetate and acetic anhydride.

The prepared 5-oxazolone were treated with \(p\)-phenylene diamine in basic medium to prepared 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3). The IR Spectrum of compound (3) showed the NH bands at 3300-3270 cm\(^{-1}\), and the C=O band nearly at 1690 cm\(^{-1}\).

The \(^1\)H NMR spectrum shows broad peak at 4.63ppm was due to the protons of the \(-\text{NH}_2\) group. The benzylidene proton of (Ph-C=CH) was found in downfield region at \(\delta\) 6.01 ppm. In the case of 4-OCH\(_3\), singlet is observed at \(\delta\) 3.73 ppm which corresponds to the three protons of \(-\text{OCH}_3\). Compound (4) and (6) were prepared by known reported methods. The final dye (7) was the condensation product of compounds (4) and (6).The IR Spectrum of compound (7) showed the OH bands nearly at 3435cm\(^{-1}\), NH bands nearly at 3250 cm\(^{-1}\), the C=O band nearly at 1691 cm\(^{-1}\), N=N bands nearly at 1593 cm\(^{-1}\) and the C-Cl bands nearly at 753 cm\(^{-1}\).

The \(^1\)H NMR spectrum showed a multiplet at \(\delta\) 7.529-6.754 ppm due to aromatic protons(20 H), the benzylidene proton of (Ph-C=CH) was also found in the same region but was over lapped by multiplet of aromatic protons, the spectrum showed a peak at \(\delta\) 4.441 ppm due to \(-\text{OH}\) protons (2H), a singlet was seen at \(\delta\) 3.975 ppm due to \(-\text{NH}\) protons (2H). The position of protons of \(-\text{NH}\) and \(-\text{OH}\) groups may depend upon the intramolecular hydrogen bonding into the sample tube. A triplet was seen at \(\delta\) 2.875-2.762 ppm due to protons of \(-\text{H}_2\text{C-CH}_2\text{-O-SO}_3\text{Na}\) (2H), an another triplet was seen at \(\delta\) 2.465-2.363 ppm due to protons of \(-\text{H}_2\text{C-CH}_2\text{-O-SO}_3\text{Na}\) (2H).
Chapter – 2 B

Monofunctional reactive dyes from various 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one
2B.1. Synthesis of 5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-substituted-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid.

2B.1.1 Reaction scheme

where,

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2B.1.2 Preparation of 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2).
Same as 2A.1.2

2B.1.3. General procedure for the preparation of 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3)
Same as 2A.1.3

Preparation of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3).
Same as 2A.1.3

Preparation of 3-(4-aminophenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro- imidazol-4-one) (3).
Same as 2A.1.3

2B.1.4. Preparation of 4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-5-hydroxy-naphthalene-2,7-disulfonic acid (4)

Cyanuric chloride (1.9504 g, 0.0106 mole) was stirred with acetone (40 ml) and water (10 ml) for 1 h to form a fine suspension at temperature 2°C. After 1 h, a neutral solution of 1-naphthol-8-amino-3,6-disulphonic acid (H-acid) (3.16 g, 0.01 mole) in water (25 ml) was added and in such a way that the temperature did not exceed a level above 5°C. The reaction mass was stirred up to 3 hours maintaining the pH 6.9 to 7 using sodium bicarbonate solution (10% w/v). The solution was stirred for a further 60 min at room temperature to complete the reaction. [127]

2B.1.5. Preparation of 5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid (5).

To the 25 ml of water in a beaker 2.96 g (95 % 0.01 mole) of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3) was added. While stirring the suspension was cooled down to 5°C using ice. To this solution 3.67 ml (3 N, 0.011 moles) of NaNO₂ and 5 g of ice were added. Then, 2.6 ml of conc. HCl was added slowly at 5°C to obtain a diazo component of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-
Completion of diazotization reaction was checked by starch iodide test. Excess HNO$_2$ was removed by adding a small amount of sulfamic acid.

To another beaker 3.9 g (82 %, 0.01 mole) of compound (4) and 40 ml of water was added and the pH was adjusted between 9-10, using 10% Na$_2$CO$_3$. Into this aqueous solution, the above prepared diazo solution was added dropwise using dropping funnel while keeping the temperature 0-5$^\circ$C to complete the coupling reaction. [125].

**IR Data:** (cm$^{-1}$)
3363 OH, 3122 N-H(S),
1708 C=O(S) Imidazolinone ring,
1578 N=N(S), 1900-1500 C=N(s),
1600-1500 (C=C stretch),
1272 (C-O-C Asymmetric Stretch),
1113 (C-O-C Symmetric Stretch)
1141 S=O(S),
below 900 C-H(B),
787 C-Cl(s).

(FIGURE 2.9 Infrared Spectra of 5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid.) (5)

**$^1$H NMR Data:** ($\delta$, ppm)
$\delta$ 7.997-6.909(m, 16H, Ar-H),
$\delta$ 5.247 (s, 1H, -OH),
$\delta$ 4.391(s, 1H, -NH),
$\delta$ 3.603-3.591 (s, 3H, -OCH$_3$).

(FIGURE 2.10 NMR Spectra of 5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid.) (5)
FIGURE 2.9 Infrared Spectra of; 5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid (5).
FIGURE 2.10 NMR Spectra of:
5-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2,7-disulfonic acid (5).
# TABLES 2.3 –Physical and Elemental Data

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2B.1.6. Result and Discussion

Starting compound 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2) derivatives were prepared by Erlenmeyer condensation of benzoylglycine with different aldehydes in presence of sodium acetate and acetic anhydride.

The prepared 5-oxazolone were treated with p-phenylene diamine in basic medium to prepared 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3). The IR Spectrum of compound (3) showed the NH bands at 3300-3270 cm\(^{-1}\), and the C=O band nearly at 1690 cm\(^{-1}\).

The \(^1\)H NMR spectrum shows broad peak at 4.63 ppm was due to the protons of the \(-\text{NH}_2\) group. The benzylidene proton of (Ph-C=CH) was found in downfield region at \(\delta\) 6.01 ppm. In the case of 4-OCH\(_3\), singlet is observed at \(\delta\) 3.73 ppm which corresponds to the three protons of \(-\text{OCH}_3\).

The IR Spectrum of final compound (5) showed the OH bands nearly at 3363 cm\(^{-1}\), NH bands nearly at 3122 cm\(^{-1}\), the C=O band nearly at 1708 cm\(^{-1}\), N=N bands nearly at 1578 cm\(^{-1}\) and the C-Cl bands nearly at 787 cm\(^{-1}\).

The \(^1\)H NMR spectrum showed a multiplet at \(\delta\) 7.997-6.909 ppm due to aromatic protons (16H), the benzylidene proton of (Ph-C=CH) was also found in the same region but was over lapped by multiplet of aromatic protons. The spectrum showed a singlet at \(\delta\) 5.247 ppm due to the protons of \(-\text{OH}\) group. The spectrum showed a singlet at \(\delta\) 4.391 ppm due to the protons of \(-\text{NH}\) group. The position of protons of \(-\text{NH}\) and \(-\text{OH}\) groups may depend upon the intramolecular hydrogen bonding into the sample tube. In the case of 4-OCH\(_3\), singlet is observed at \(\delta\) 3.603-3.591 ppm which corresponds to the three protons of \(-\text{OCH}_3\).

2B.2.1 Reaction scheme

\[
\begin{align*}
\text{CONHCH}_2\text{COOH} & \overset{1)}{\longrightarrow} \text{RCHO} \overset{2)}{\longrightarrow} \text{Acetic Anhydride} \quad \text{Sodium Acetate} \\
\text{Reflux for 6 hours in dry Pyridine} & \\
\text{(3) + (4)} & \overset{i)}{\longrightarrow} \text{Diazotization} \quad \overset{ii)}{\longrightarrow} \text{Coupling} \\
\end{align*}
\]

where,

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2B.2.2 Preparation of 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2).
Same as 2A.1.2

2B.2.3. General procedure for the preparation of 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3)
Same as 2A.1.3

Preparation of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3).
Same as 2A.1.3

Preparation of 3-(4-aminophenyl)-5-(4-N,N-dimethylbenzylidene-2-phenyl-3,5-dihydro- imidazol-4-one) (3).
Same as 2A.1.3

2B.2.4. Preparation of 6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-naphthalene-2-sulfonic acid (4).

Cyanuric chloride (1.9504 g, 0.0106 mole) was stirred with acetone (40 ml) and water (10 ml) for 1 h to form a fine suspension at temperature 2°C. After 1h, a neutral solution of 6-Amino-4-hydroxynaphthalene-2-sulfonic acid (γ-acid) (3.16 g, 0.01 mole) in water (25 ml) was added and in such a way that the temperature did not exceed a level above 5°C. The reaction mass was stirred up to 3 hours maintaining the pH 6.9 to 7 using sodium bicarbonate solution (10% w/v). The solution was stirred for a further 60 min at room temperature to complete the reaction. [127]

2B.2.5 Preparation of 6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo]-naphthalene-2-sulfonic acid (5).

To the 25ml of water in a beaker 2.96 g (95 % 0.01 mole) of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (3) was added. While stirring the suspension was cooled down to 5°C using ice. To this solution 3.67 ml (3 N, 0.011 moles) of NaNO₂ and 5g of ice were added. Then, 2.6 ml of conc. HCl was added slowly at 5°C to obtain a diazo component of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one). Completion of diazotization reaction was checked by starch
iodide test. Excess HNO$_2$ was removed by adding a small amount of sulfamic acid.

To another beaker 3.9 g (82 %, 0.01 mole) of compound (4) and 40 ml of water was added and the pH was adjusted between 9-10, using 10% Na$_2$CO$_3$. Into this aqueous solution, the above prepared diazo solution was added dropwise using dropping funnel while keeping the temperature 0-5$^0$C to complete the coupling reaction. [125].

**IR Data**: (cm$^{-1}$)
- 3313 OH,
- 3201 N-H(S),
- 1747 C=O(S) Imidazolinone ring,
- 1560 N=N(S),
- 1900-1500 C=N(s),
- 1600-1500 (C=C stretch),
- 1224 (C-O-C Asymmetric Stretch),
- 1092 (C-O-C Symmetric Stretch)
- 1015 S=O(S),
- below 900 C-H(B),
- 782 Cl (s).

(FIGURE 2.11 Infrared Spectra of 6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2-sulfonic acid.)

**$^1$H NMR Data**: ($\delta$, ppm)
- $\delta$ 7.867-6.701 (m, 16H, Ar-H),
- $\delta$ 5.432 (s, 1H, -OH),
- $\delta$ 4.431(s, 1H, -NH),
- $\delta$ 3.521-3.511 (s, 3H, -OCH$_3$).

(FIGURE 2.12 NMR Spectra of 6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo} -naphthalene-2-sulfonic acid.)
**FIGURE 2.11** Infrared Spectra of; 6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo} - naphthalene-2-sulfonic acid.
FIGURE 2.12 NMR Spectra of:
6-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-{4-[4-(4-methoxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylazo}-naphthalene-2-sulfonic acid.
**TABLES 2.4 – Physical and Elemental Data**

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2B.2.6 Result and Discussion

Starting compound 4-Arylidene-2-phenyl-5-(4H)-oxazolones (2) derivatives were prepared by Erlenmeyer condensation of benzoylglycine with different aldehydes in presence of sodium acetate and acetic anhydride.

The prepared 5-oxazolone were treated with \( p \)-phenylene diamine in basic medium to prepared 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (3). The IR Spectrum of compound (3) showed the NH bands at 3300-3270 cm\(^{-1}\), and the C=O band nearly at 1690 cm\(^{-1}\).

The \(^1\)H NMR spectrum shows broad peak at 4.63 ppm was due to the protons of the \(-\text{NH}_2\) group. The benzylidene proton of (Ph-C=CH) was found in downfield region at \( \delta \) 6.01 ppm. In the case of 4-OCH\(_3\), singlet is observed at \( \delta \) 3.73 ppm which corresponds to the three protons of \(-\text{OCH}_3\).

The IR Spectrum of final compound (5) showed the OH bands nearly at 3313 cm\(^{-1}\), NH bands nearly at 3201 cm\(^{-1}\), the C=O band nearly at 1747 cm\(^{-1}\), N=N bands nearly at 1560 cm\(^{-1}\) and the C-Cl bands nearly at 782 cm\(^{-1}\).

The \(^1\)H NMR spectrum showed a multiplet at \( \delta \) 7.867-6.701 ppm due to aromatic protons (16H), the benzylidene proton of (Ph-C=CH) was also found in the same region but was over lapped by multiplet of aromatic protons. The spectrum showed a singlet at \( \delta \) 5.432 ppm due to the protons of \(-\text{OH}\) group. The spectrum showed a singlet at \( \delta \) 4.431 ppm due to the protons of \(-\text{NH}\) group. The position of protons of \(-\text{NH}\) and \(-\text{OH}\) groups may depend upon the intramolecular hydrogen bonding into the sample tube. In the case of 4-OCH\(_3\), singlet is observed at \( \delta \) 3.521-3.511 ppm which corresponds to the three protons of \(-\text{OCH}_3\).
REFERENCES:


[17]. The chemistry of 5-oxazolones is reviewed by E Baltazzi, Quart. Revs. (London), 1955, 9, 150.


[120]. Mocckli, Peter, (Ciba speciality Chemical Holding Inc. Switz.) *PCT Int. Appl. WO 02, 31,056 (Cl. CO9B44/16), 2000.*


