CHAPTER TWO

RESULTS & DISCUSSION
CHAPTER II

RESULTS AND DISCUSSION

From the foregoing discussion contained in the first introductory chapter, it is obvious that if a change is to be made in the frequency of the first absorption band, it is futile to tackle the acid part in the resonance of the molecule, but at the same time it has been observed that alteration in the number of auxochromes, their position and nature in resonating part produces a marked effect on $\lambda_{\text{max}}$. It has already been described that two quinonoid forms XXVII and XXIX in the alkaline medium can represent the lactone form of phenolphthalein. Thus, if a condition could be created to accomplish radical alteration in molecule by replacing one of the hydroxyl aromatic nuclei by an alkyl or an aryl group or by a heterocyclic ring, the resonance in the phenolphthalein nucleus is rendered possible in one of the two quinonoid form mentioned above and the colour development of the substance will be expected to be much less intense than in the case of phenolphthalein. To study this effect of the above planned alterations in the upper part (non acid) of the phthalein molecule, twelve $\gamma$-keto acids (series A,B,C) were prepared and condensed with various aromatic hydroxyl compounds to get novel analogues of the phthaleins.

To see the effect of the lower acid part in the colour of the dye, four $\beta$-aroyl propionic acids (series D) were also prepared and condensed with various phenolic compound to get novel analogues of succineinds i.e. succin-as-eins. General structure of phthal-as-eins and succin-as-eins prepared are given by XLV A and B respectively.

ACIDS OF SERIES A

1. 2-(2’ 4’ dimethyl benzoyl) benzoic acid
2. 2-(3’ carbmethoxy 4’ hydroxy benzoyl) benzoic acid
3. 2-(5’ chloro 2’ chloromethyl benzoyl) benzoic acid.
4. 2-(3’ acenaphthoyl) benzoic acid

ACIDS OF SERIES B

1. 2-(2’ 4’ dimethyl benzoyl) tetrachlorobenzoic acid

-54-
2. 2-(3' carboxymethoxy 4' hydroxy benzoyl) tetrachlorobenzoic acid
3. 2-(5' chloro 2' chloromethyl benzoyl) tetrachlorobenzoic acid.
4. 2-(3' acenaphthoyl) tetrachlorobenzoic acid

**ACIDS OF SERIES C**
1. 2-(2' 4' dimethyl benzoyl)-3- nitrobenzoic acid
2. 2-(3' carboxymethoxy 4' hydroxy benzoyl)- 3- nitrobenzoic acid
3. 2-(5' chloro 2' chloromethyl benzoyl)- 3- nitrobenzoic acid.
4. 2-(3' acenaphthoyl)- 3- nitrobenzoic acid

**ACIDS OF SERIES D**
1. β-(2, 4 dimethyl benzoyl) propionic acid
2. β-(3 carboxymethoxy 4 hydroxy benzoyl) propionic acid
3. β-(5 chloro 2 chloromethyl benzoyl) propionic acid.
4. β-(3 acenaphthoyl) propionic acid

The nomenclature of these dyes has been arrived at by considering the asymmetry in the structure of the molecule. These may be regarded as mixed or unsymmetrical phthalieins XLV-A as derivatives of phthalide, and unsymmetrical succineins XLV-B. For convenience and uniformity, and owing to the asymmetric carbon (C) present in all, the more satisfactory nomenclature for XLV-A and XLV-B is adopted, and the compounds are named as follows:

Phthal-as-eins, Succin-as-eins, as representing asymmetry, ein representing the class of dyes (Phthalein or succinein).

**STRUCTURE OF PHTHAL-AS-EINS:**

On the basis of study of the chemical constitution of these XLV-A dyes
For dyes derived from series A, B, C and D:

\[ R = 2, 4 \text{ dimethyl phenyl} \quad (-C_6H_3(CH_3)_2); \quad 3 \text{ Carboxy} \quad 4-H \text{ Hydroxy} \quad \text{phenyl} \quad [-\begin{array}{c} \text{COOCH}_3 \\ \end{array}] \]

2 Chloromethyl, 5 Chlorophenyl \quad [-\begin{array}{c} \text{Cl} \\ \text{CH}_2\text{Cl} \\ \end{array}] \quad 3 - \text{acenaphthyl} \quad [-\begin{array}{c} \text{C} \\ \text{H}_7 \\ \end{array}] \\
R_1, R_2, R_3, R_4, R_5 = \text{H or OH; } R_2 = R_4 = \text{H or Br} \\
R_1 = R_3 = \text{OOC-CH}_3 \\
R_1' = R_2' = R_3' = R_4' = \text{H} \quad (\text{for dyes derived from series A}) \\
R_1' = R_2' = R_3' = R_4' = \text{Cl} \quad (\text{for dyes derived from series B}) \\
R_1' = R_2' = R_3' = \text{H; } R_4' = \text{NO}_2 \quad (\text{for dyes derived from series C})
(discussed in the preceding section) structure XLVI has been assigned to phenolphthalein.

It may be noticed that the assigned structure of phenol-phthal-as-ein XLVI is similar to dimethyl\textsuperscript{11} and diethyl\textsuperscript{12} XLVII derivative of phenolphthalein. In these derivatives, there seems the possibility of the same type of resonance to occur as exhibited by phenolphthalein itself. In the same way the resonance of phenolphthalein type will be altogether absent in XLVI.

The analogue of dimethyl derivative is orange red and the corresponding diethyl derivative is yellow even in the solid state.

\textbf{SERIES A:}

The representative dyes of this series are the following:

1. 2, 4 dimethyl phenyl phenol phthal-as-ein.
2. 3 carbmethoxy 4 hydroxy phenyl phenol phthal-as-ein.
3. 5 chloro 2 chloromethyl phenyl phenol phthal-as-ein.
4. 3 acenaphthyl phenol phthal-as-ein.

The above four dyes are brown, dark brown, brown and reddish brown respectively.

\textbf{SERIES B:}

The representative dyes of this series are the following:

1. 2, 4 dimethyl phenyl, phenol tetra chloro phthal-as-ein.
2. 3 carbmethoxy 4 hydroxyl phenyl phenol tetra chloro phthal-as-ein
3. 2 chloromethyl 5-chlorophenyl phenol tetra chloro phthal-as-ein.
4. 3-acenaphthyl phenol tetra chloro phthal-as-ein

The above four dyes are pale rosy, pinkish white, light red and rosy respectively.
SERIES C:

The representative dyes of this series are the following.

1. 2, 4 dimethyl phenyl phenol nitro phthal-as-ein.
2. 3 carbethoxy 4 hydroxyl phenyl phenol nitro phthal-as-ein.
3. 5 chloro 2 chloromethyl phenyl phenol nitro phthal-as-ein.
4. 3acenaphthyl phenol nitro phthal-as-ein.

The above four dyes are pinkish red, light pink, pinkish white and light pink respectively.

SERIES D:

The representative dyes of this series taken are as follows:

1. 2, 4 dimethyl phenyl phenol succin-as-ein.
2. 3 carbethoxy 4- hydroxyl phenyl phenol succin-as-ein.
3. 5 chloro 2 chloromethyl phenyl pbenol succin-as-ein.
4. 3acenaphthyl phenol succin-as-ein.

The above four dyes are leaf-brown, brown, gulf-red and leaf green respectively. The colour of these phenol phthal-as-ein dyes in neutral as well as alkaline medium and their $\lambda_{\text{max}}$ values, are given in tabular form at the end of this thesis.

The colour of phenol phthal-as-eins may be explained, as already discussed, and interpreted in chapter I.

The colour of phenol tetra chloro phthal-as-eins may be explained on the basis of resonance occurring among various neutral (XLVIII and XLIX) and polar (L and LI) structures of the molecules. Due to occurrence of resonance in the molecule, the presence of quononoidal conjugation becomes possible in different participating structures and at the same time the formal charge is created in the polar resonating states in the basic medium. A symmetry of
phenolphthalein is altogether absent here but possibly the charge travels through
the dotted lines (L1) and the absorption maxima is nearly the same as that of
phenolphthalein (XXVII-XXIX) in moderate basic medium. The phenol tetra
chloro phthal-as-eins studied here exhibit similar behaviour in basic medium as
phenolphthalein. The monovalent anion of phenolphthalein is colourless
derivative, while the divalent anion (XXVII and XXIX) gives pink colour but the
trivalent anion (XXX) is again colourless. In the same way the present phenol
tetra chloro phthal-as-eins described in the thesis give pink colour in moderate
basic medium and the disodium salts become almost colourless anions with
strong acids show again the enhancement of colour (L).

Similarly, the colour of phenol nitro phthal-as-eins incorporated in the
thesis may also be explained by considering the neutral (LII) and (LIII) and the
polar (LIV) and (LV) resonating structures for the molecule.

The colour of the resorcinol phthal-as-eins (LVI) may be explained in
relation to their chemical structures discussed in the preceding section on the
basis of description in the case of phenol phthal-as-eins.

Resorcinol Phthal-as-in
LVI

In resorcinol phthal-as-eins, there are two hydroxyl groups (2:4 position)
instead of one hydroxyl group (4 position) in the hydroxyl aromatic part of the
molecule (LVI). Out of the two hydroxyl groups, one acts as a chromophore to
produce conjugation, while the other hydroxyl group acts as an auxochrome.
Hence, even the neutral molecule can possible exist as a resonance hybrid of the
LVI to LVIII structures. Thus, the colour of the resorcinol phthal-as-eins is well
accounted for either in solid state (yellow, yellowish orange, yellowish brown) as well as in neutral medium (\( \lambda_{\text{max}} \) 460-485 nm). However, by the addition of the alkali, the polar forms (LVIIa, LVIIia, LVIIb and LVIIIb) of the molecule are produced resulting in increase in the number of resonating structures of the molecules. This increase is responsible for producing more crowded and depressed energy levels; consequently a bathochromic shift in \( \lambda_{\text{max}} \) takes place. Actually all these dyes have absorption bands at 460-485 nm in neutral medium while in slightly alkaline \( \lambda_{\text{max}} \) at 490-520 nm have been observed.

In most of the poly hydroxy phenol phthal-as-eins, one hydroxyl group takes part as the chromophore and rest of the hydroxyl groups present, may act as auxochromes causing a respective deepening of the colour of these dyes (appearance varies from yellow to dark brown). In some cases these dyes e.g. Hydroquinone, Catechol, Phloroglucinol and Pyrogallol phthal-as-eins have been found to decompose in alkaline medium. Due to this decomposition of dyes, reliable absorption maxima can not be determined. Hence, it is difficult to put forward a satisfactory explanation for their colour.

**COLOUR OF SUCCIN-AS-EINS AND \( \lambda_{\text{max}} \) CALCULATIONS:**

The \( \lambda_{\text{max}} \) value for various forms of succi-as-eins have been observed by some workers and it falls between 390-430 nm. In the present investigation, the succi-as-eins were prepared from four \( \beta \)-aryl propionic acids. The various aryl phenol succi-as-eins are represented by the resonating structures LIX, LX and LXI which also explain their colour and \( \lambda_{\text{max}} \) (425-440 nm) here \( R = \) substituted phenyl and structure LXI makes a real contribution in alkaline medium. The dotted line indicates the possible path of travel of the electron along the conjugated chain. In this case it is not possible for conjugation to extend beyond the chiral carbon atom present at position 6 and the pi – electron gas consist of 8 electrons for four pi bonds (i.e. \( m = 4 \)), out of which six electrons are contributed by three double bonds and two electrons by the charge free oxygen atom \( O1 \) (i.e. four pi bonds are contributed in the coulombic field). Stretching of electron gas is not at both ends, but only in one end i.e. \( \alpha = \alpha/2 \), hence from equation 8 of the first chapter.

\[
\lambda_{\text{max}} = \frac{127(m + \alpha/2)^2}{(m + 3/2)} \text{ nm}
\]

\[
= 127 \times (4 + 0.33/2)^2 / (4 + 3/2) = 400 \text{ nm}
\]

The \( \lambda_{\text{max}} \) observed is in the range of 425-440 nm. It may be noticed that
the two values are in good agreement. In the case of succi-as-eins conjugation does not extend beyond the chiral carbon atom at position 6, (like fuschone structure XXII and its $\lambda_{\text{max}}$ is 390 nm.) as shown in structure (LXI) where resonance occurs only in ring B and this ring possesses benzenoid as well as quinonoid forms where no formal charge is found in the resonating forms, as the charge present in the carboxylate is insulated.

The $\lambda_{\text{max}}$ values of various aryl resorcinol succi-as-eins fall in the range of aryl resorcinol phthal-as-eins (480 nm and in alkali 500 nm) which is explained well when the resonating structures (LXII to LXVI) are considered. These structure LXII to LXVI explain the colour of the dyes even in the solid state as due to the formation of ionic structure LXV and LXVI in alkaline medium, a bathchromic shift (500-480- = 20 nm) is observed.

In the case $\alpha$ – quinonoid structures LXIV and LXVI make more contribution than the $\beta$ – quinonoid structures LXIII and LXV. Due to auxocromic effect of the OH group situated meta to quinonoid oxygen $\lambda_{\text{max}}$ value is found in the range of the phthal-as-eins.

It may be well concluded from the foregoing discussion that no single theory of the colour of the dyes is capable of explaining and predicting the colour with a fair degree of accuracy. However, despite of this almost sweeping observation, FEMO gas model has been found a better fit than the other theories. There might arise a few mathematical complexities in the application of the two-dimensional free electron gas model. As far as rigorous assumptions are concerned, all the theories, VB, MO and FEMO require these without which it would be impossible to make any calculation even for very simple molecules.

**COLOUR (CALCULATION OF ABSOPRTION MAXIMA) OF PHTHAL-AS-EIN DYES:**

The theoretical values of absorption maxima of phenol phthal-as-eins may only be calculated by making rigorous approximation for the $\pi$- electron gas model (equation 8, chapter I). Here each dye molecule is unsymmetrical; hence two equivalent extreme structures with formal charge like phenolphthalein or fluorescein are not possible. Thus, unsymmetrical extended conjugated chains with formal charge at one end only may be present in all the resonating forms, contributing to the dye molecule. Therefore, for calculation purposes major contributing structures LI and LVIIa are considered. Here in all ten electrons are required to take part in the formation of $\pi$- electron gas, eight $\pi$ electrons of four $\pi$ bonds and two $\pi$ electrons from the charge free QI (neutral oxygen atom). The
effective conjugated chains have been depicted by dotted lines and for
simplification, the lower portion is neglected by making approximations that do
not vitiate the results. Thus, a polar five \( \pi \) electron gas is possible which is
responsible for the creation of Coulomb force along the polar molecule with
formal charge. To consider the stretching beyond the two ends of the conjugated
chain, here it is possible only at one end i.e. at Q1. The value \( \alpha = 0.33 \) has been
derived from the observed \( \lambda_{\text{max}} \) value of benzaurine dye XXV depicted in the
first chapter with oxygen end groups. Thus by applying the equation 8.

\[
\lambda_{\text{max}} = 127 \left( m + \frac{\alpha}{2} \right)^2 (m + 3/2) \text{ in nm}
\]

\[
= 127 \left( 5 + 0.33/2 \right)^2 / (5 + 3/2) \text{ nm}
\]

\[
= 127 (5.165)^2 / 6.5 \text{ nm}
\]

\[
= 520 \text{ nm}
\]

The value may be regarded as in agreement with the observed value of
phenol phthal-as-eins (530-560 nm) and resorcinol phthal-as-eins (530-560 nm).
It has not been possible to apply the free electron molecular orbital treatment in
the cases of polyhydroxy phenol phthal-as-eins due to unmanageable difficulties
presented by their structural complications to derive a simplified expression for
the calculation of their absorption maxima.

H.Kuhn\textsuperscript{3-4} has more given a refined treatment on the basis of ‘one
dimensional wave shape potential model’ which is applicable for completely
symmetrical type of dye molecules. A still better treatment on the basis of ‘two
dimensional electron gas model’ has been proposed by the same author\textsuperscript{5} and it is
claimed that this may be applied to dye molecules of any complicated shape.
However, the prospect of mathematical calculations is very discouraging. The
various phenol phthal-as-eins prepared i.e. 2, 4 dimethyl phenyl, phenol phthal-
as-ein, 3 carbomethoxy 4 hydroxy phenyl phenol phthal-as-ein, 5 chloro 2
chloromethyl phenyl phenol phthal-as-ein and 3 acenaphthyl phenol phthal-as-
ein, are orange, light brown and grey respectively in colour. The bathochromic
sift is quite significant in these phenol phthal-as-eins in the alkaline medium.
Their \( \lambda_{\text{max}} \) values in neutral and in alkaline mediums are 520-545, 510-530, 500-
520 and 520-550 nm respectively.

The colours and the \( \lambda_{\text{max}} \) values of the dyes, 2,4, di methyl phenyl phenol
tetra chloro phthal-as-ein, 3-carbomethoxy 4-hydroxy phenyl phenol tetra chloro
phthal-as-eins, 5-chloro 2-chloromethyl phenyl phenol tetra chloro phthal-as-
ein, 3-acenaphthyl phenol tetra chloro phthal-as-ein; 2,4-dimethyl phenyl phenol 
nitro phthal-as-ein, 3-carbomethoxy 4-hydroxy phenyl phenol nitro phthal-as-ein, 
5-chloro 2-chloromethyl phenyl phenol nitro phthal-as-ein, 3-acenaphthyl phenol 
nitro phthal as-ein are pink ($\lambda_{\text{max}}$ 530-535 nm), orange ($\lambda_{\text{max}}$ 
520-530 nm), light brown ($\lambda_{\text{max}}$ 530 nm), light brown ($\lambda_{\text{max}}$ 
500-530 nm), light red ($\lambda_{\text{max}}$ 520nm), pinkish ($\lambda_{\text{max}}$ 510-530 nm), 
light brown ($\lambda_{\text{max}}$ 535 nm) and light brown ($\lambda_{\text{max}}$ 
510-530 nm) respectively. These dyes are colourless in the neutral medium and 
in basic medium give violet, reddish orange with green fluorescence, light violet, 
violet, pink and pinkish red colours respectively.

The above $\lambda_{\text{max}}$ values observed are in good agreement with the $\lambda_{\text{max}}$ 
values found for analogous phenol phthal-as-eins.

1. Phenol phthal-as-eins, $\lambda_{\text{max}}$, 550 nm in alkaline medium.

2. Phenol tetra chloro phthaleins, $\lambda_{\text{max}}$, 580 nm in alkaline medium.

3. Phenol nitro phthaleins, $\lambda_{\text{max}}$, 560 nm in alkaline medium.

The higher $\lambda_{\text{max}}$ values observed in the case of some phenol tetra chloro 
phthal-as-eins and phenol nitro phthal-as-eins may be attributed to the presence 
of auxochromes in the phenyl ring. These groups may be responsible for the 
enhancement of colour. Nitro group in the acid part in phenol nitro phthaleins and 
chlorine atoms in the phenol tetra chloro phthaleins may be partly responsible for 
the enhancement of $\lambda_{\text{max}}$ values and the colour of the dyes.

In various resorcinol phthal-as-ein dyes prepared the $\lambda_{\text{max}}$ (460-480nm in 
normal and 490-520 nm in the alkaline medium) is lower than the $\lambda_{\text{max}}$ values 
observed in various phenol phthal-as-ein dyes prepared during the present 
investigations. A possible explanation for this observation may be that in 
resorcinol phthal-as-ein dyes LVI, there are two hydroxy groups at 2:4 positions 
instead of one hydroxy group at 4 position as in phenol phthal-as-ein dye 
structure XLVI. Thus, in one of the main contributing structures of the molecule, 
conjugation is blocked beyond the 2 hydroxy group LVIIa and consequently, the 
length of the conjugated chain is decreased. This shortening of the conjugated 
chain (LVIIIa) may be held responsible for the lowering of the $\lambda_{\text{max}}$ values in 
these compounds.

All the resorcinol phthal-as-eins studied have absorption maxima at 460-
480 nm in neutral medium, and 490-520 nm in moderate alkaline medium. Value of absorption maxima for these resorcinol phthal-as-ein dyes have been presented in a tabular form at the end of this thesis.

In the case of novel analogues of succineins, the \( \lambda_{\text{max}} \) values have been observed for the resorcinol dyes.

2,4 dimethyl phenyl resorcinol succin-as-ein, 3- carbmethoxy 4- hydroxy phenyl resorcinol succin-as-ein, 5-chloro 2-chloromethyl phenyl resorcinol succin-as-ein and 3- acenaphthyl resorcinol succin-as-ein were prepared. The colour of the dyes and their \( \lambda_{\text{max}} \) values are dark brown (\( \lambda_{\text{max}} \) 460-500 nm), reddish black (\( \lambda_{\text{max}} \) 455-500 nm), light brown (\( \lambda_{\text{max}} \) 455-510 nm) and brown (\( \lambda_{\text{max}} \) 470-500 nm) respectively. These \( \lambda_{\text{max}} \) values are in good agreement with the reported aryalted succin-as-eins.

1. The significant difference between the phthalein dyes (pyronine dyes) and phthal-as-ein dyes reported in the present dissertation may be observed that while considering the different charged structure to explain their respective colour or to calculate the theoretical value of, in the first case the acid part is not considered at all while in the second case the acid part is involved and is capable of producing a number of charged structures which may be held responsible for their colour.

2. Practically, there is no significant effect of different substituents in the aromatic ring of the acid part but it may be noted that the phthal-as-ein dyes derived from \( \gamma \) -keto acids having 2, 4 dimethyl phenyl, 3- carbmethoxy 4-hydroxy phenyl, 5-chloro 2-chloromethyl phenyl and 3- acenaphthyl substituted in the lactol carbon (central carbon atom) show a little more bathochromic shift. As already explained it might be due to these very substituents mentioned above.

3. The distinguishing feature of the two types of dyes (phthal-as-ein XLVa and succin-as-ein XLVb) is that the structure XLVa contains phthalide (aromatic lactone system) whereas structure LXVb contains butyro lactone system. When the quinonoid forms of the two class of dyes i.e. LI and LXI are compared, it is observed that in the case of phthal-as-ein (structure LI), the conjugation is extended between oxygen atom present in ring (B) at position 1 to 8 of the ring (C) beyond the chiral carbon atom present at position 6, which is not possible in the case of succin-as-eins (structure LXI), even then \( \lambda_{\text{max}} \) values of two classes of dyes fall within the same region. The high value for \( \lambda_{\text{max}} \) for succin-as-eins has already been explained that the ortho quinonoid form makes much more contribution than the para quinonoid form and the auxochromic effect enabled the structure to show \( \lambda_{\text{max}} \) value in the range of phthal-as-eins.
4. Though no one single theory is able to explain and predict the colour and the absorption maxima of all types of dyes, still the FEMO gas theory is the best at present to calculate and predict the colour and absorption maxima after making some assumptions which do not vitiate our problem at all. In the present work, the FEMO gas model has been successfully employed and the calculated values are in excellent agreement with the observed.

**CHEMICAL CONSTITUTION OF PHTHA-AS-FIN DYES:**

The open chain substituted or unsubstituted \( \gamma \)-keto acids possess a characteristic structural requirement due to which they are capable of existing in cyclic tautomeric form too. The formation of the ring tautomer (lactol form)\(^6\) takes place due to electrophilic ring chain tautomerism where the electrophile is the proton (hydrogen). Amount of lactol depends on the extent of prototropic change. Generally it has been observed that the \( \gamma \)-keto acids exist chiefly as lactol or equilibrium mixture of ring and chain tautomers\(^7\), \(^8\). The lactols give well-defined crystalline acetyl derivatives, still retaining their cyclic structures. Therefore, it is obvious that the cyclic tautomer is comparatively more stable form than the chain isomer\(^9\)-\(^12\). The formation of pseudoesters\(^13\) of o-benzoyl benzoic acid LXVII has been proposed on the basis of cyclisation of lactol LXVIII that can yield a pseudochloride\(^14\) LXIX. This pseudochloride on heating with appropriate alcohol yields the corresponding ester LXX.

Formation of compound LXXI from o-benzoyl benzoic acid and metaxylene catalyzed by perchloric acid has been proposed through the 3-phenyl phthalyl carbonium ion, where the precursor of this carbonium ion is definitely the cyclic isomer\(^15\),\(^16\) LXVIII of o-benzoyl benzoic acid.

The formation of lactol intermediate has also been used to explain some of the other chemical reactions of o-benzoyl benzoic acid e.g. the reductive coupling\(^17\) of the acid with phosphorous and hydroiodic acid. The cyclic structures for pseudoesters have been confirmed by IR\(^18\) and Raman\(^19\) spectra.

O-acetyl benzoic acid has been shown to yield the acetyl derivative through the formation of lactol\(^9\) intermediate as in the case of o-benzoyl benzoic acid. Peculiarly enough, o-acetyl benzoyl chloride chemically behaves abnormally. All attempts fail to convert o-acetyl benzoyl chloride into o-acetyl benzaldehyde by Rosenmund reduction or into o-diacetyl benzene\(^20\). Its conversion to amides with amines has also resulted in failure or very poor yield\(^21\). This abnormal chemical
behaviour of o-acetyl benzoyl chloride is actually to be expected, if one considers that acid chloride prepared in each case with thionyl chloride, is undoubtedly cyclic and ring tautomeric acid chlorides invariably lead to cyclic products rather than those intended in the above preparative attempts. The lactol formation has been further confirmed by IR$^{22}$ and NMR$^{23}$ spectral studies. Recently, it has been reported that the acid in liquid form exists chiefly in the lactol form$^{24}$.

The formation of pseudoesters as well as a large number of other alkyl derivatives$^{25,26}$ of phthal aldehydic acid LXXII can be explained by considering the lactol LXXXIII form of the acid. NMR spectra of phthaldehydic acid and o-acetyl benzoic acid indicate that the acids exist in cyclic forms$^{27}$. IR spectrum of phthal aldehydic acid shows bands at 3322 cm$^{-1}$, 1745 cm$^{-1}$ which support the presence of the acid chiefly in the lactol form.

Open chain $\gamma$-keto acids viz. Laevulinic acid or $\beta$-acetyl propionic acid (LXXIV, $R=CH_3$) and $\beta$-benzoyl propionic acid (LXXIV, $R=C_6H_5$) have also been reported to exist in their tautomeric lactol forms LXXV.

![Chemical structures](image)

LXXIV  | LXXV  | LXXVI

These two $\gamma$-keto acids form acetyl derivatices$^{12,13}$ LXXVI that is possible through their lactol form only. Due to this type of chemical behaviour, laevulinic acid has been shown to be mixture of ring and chain tautomeris$^{7,8}$. It has been noted that ring tautomerism$^{27}$ is further exalted by changing $R$ to larger alkyl group or aryl group and it further increases when hydrogen atoms on $\alpha$-carbon atom to the carboxylic group, are also changed to larger alkyl group $\alpha$-$\beta$-ethylenic bond$^{28}$. Invariably the cyclic isomer has been found to predominate in solution.
SPECTRAL STUDIES OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES:

Sixteen γ-keto acids listed earlier in the chapter in four different series i.e. A.B.C. and D have been used for preparation of dyes described in the presentation. IR spectral examination of these acids clearly reveals their existence as a mixture of ring and chain tautomers. There are notable peaks showing the presence of diaryl ketoic >C=O (1675-1700 cm⁻¹); and aryl ketonic group –CH₂-CO-Ar (1660-1670 cm⁻¹); carboxyl>CO=O (1695-1710 cm⁻¹); and lactonic >C=O (1735-1790 cm⁻¹); carboxylic –OH (2600-2700 cm⁻¹) and lactol –OH (3100-3500 cm⁻¹).

IR spectra of acetyl derivatives of the acids were also studied. It showed notable peaks of >C=O in acetate (new peaks 1000-1250 cm⁻¹ and 1735-1760 cm⁻¹); and lactonic >C=O (1735-1790 cm⁻¹). The peaks due to diaryl Ketonic >C=O (1675-1700 cm⁻¹); aryl ketonic >C=O (1660-1670 cm⁻¹); carboxylic >C=O (1695-1710 cm⁻¹) carboxylic – OH (2600-2700 cm⁻¹) and lactol –OH (3100-3500 cm⁻¹), which were present originally in acids found absent in the acetyl derivatives of the acids.

NMR SPECTRA OF γ-KETO ACIDS (1-16) AND THEIR ACETYL DERIVATIVES:

Chemical shifts recorded in NMR spectra of different acids (1-16) and their derivatives further confirm the presence of lactol tautomer in each case (τ=4.2-4.35) which disappears in the case of their acetyl derivatives and a new chemical shift of O-COCH₃ (τ=7.65-7.85) was observed. Thus, it is amply clear that the γ-keto acids exist in keto as well as lactol form which means it is possible to condense these acids with different phenolic compounds giving unsymmetrical phthaleins and succineins. In addition to the above characteristic chemical shifts, others were mostly of aromatic protons (τ=1.85-3.45) depending on the chemical environment in the aromatic rings. However, chemical shift of -COOH in the keto form could not be recorded as NMR spectra were recorded on Varian A-60.

Thus, from the IR and NMR spectral studies of acid and their acetyl derivatives, it is quite clear that γ-keto acids exhibit the phenomenon of ring chain tautomerism and most of their chemical reactions take place via more stable lactol (ring) form. Now it is quite certain that the cyclisation of γ-keto acids provides a hydroxyl group in the form of the corresponding lactol, which is
capable of condensing with various aromatic hydroxyl compounds resulting in the formation of the novel analogues of phthaleins, (phthal-as-eins) and succinies (succin-as-eins). It is also quite reasonable to conclude that the acetylation of γ-keto acids takes place via the ring tautomer (lactol form), and also that acetyl derivatives of the acids, phthal-as-a-eins and succin-as-eins possess cyclic structures.

Thus, the formation of acetyl derivatives, phthal-as-eins and succin-as-eins may be shown in the form depicted on the next page.

Recently, Gupta, Beg, Ali and coworkers\textsuperscript{39-48} have reported the preparation of a large number of mixed phthal-as-eins and succin-as-eins from γ-keto acids. They have also shown that the lactol form of γ-keto acids is involved in the syntheses of these compounds.
$\gamma$-keto acid \quad \Leftrightarrow \quad \text{Lactol form} \quad \xrightarrow{\text{Acetylation}} \quad \text{Acetyl derivative}

Phenolic compound

$\gamma$-keto acid \quad \Leftrightarrow \quad \text{Lactol form} \quad \xrightarrow{\text{Acetylation}} \quad \text{Acetyl derivative}

Phenolic compound

XLVb
Succin-as-cin
CHEMICAL STRUCTURE OF PHTHAL-AS- EINS AND SUCCIN-AS EINS DYES:

Here, an attempt has been made to assign suitable and satisfactory chemical structure to various novel analogues of phthaleins (phthal-as-ein and succin-as-eins) incorporated in the thesis on the basis of their chemical behaviour and the study of IR and NMR spectra of \( \gamma \)-keto acids used for the syntheses of phthal-as-eins and succin-as-eins. In order to establish the chemical structure; following sixteen representative dyes have chosen:

A.1.3 (2, 4 dimethyl phenyl) resorcinol phthal-as-ein
B.1.3 (2,4 dimethyl phenyl) resorcinol tetra chloro phtha-as-ein
C.1.3 (2,4 dimethyl phenyl) resorcinol nitro phthal-as-ein
D.1.3 (2,4 dimethyl phenyl) resorcinol succin-as-ein
A.2.3 (3- carbethoxy 4- hydroxyphenyl) resorcinol phthal-as-ein
B.2.3 (3-carbethoxy 4- hydroxy phenyl) resorcinol tetra chloro phthal-as-ein
C.2.3 (3-carbethoxy 4- hydroxyphenyl) resorcinol nitro phthal-as-ein
D.2.3 (3-carbethoxy 4- hydroxyphenyl) resorcinol succin-as-ein
A.3.3 (5- chloro 2-chloromethyl phenyl) resorcinol phthal-as-ein
B.3.3 (5- chloro 2-chloromethyl phenyl) resorcinol tetra chloro phthal-as-ein
C.3.3 (5- chloro 2-chloromethyl phenyl) resorcinol nitro phthal-as-ein
D.3.3 (5- chloro 2-chloromethyl phenyl) resorcinol succin-as-ein
A.4.3 (3-acenaphthyl) resorcinol phthal-as-ein
B.4.3 (3-acenaphthyl) resorcinol tetra chloro phthal-as-ein

-74-
(3-acenaphthyl) resorcinol nitro phthal-as-ein

(3-acenaphthyl) resorcinol succin-as-ein

For each dye a suitable molecular structure has been suggested on the basis of its elemental analysis, molecular weight determination, identification and determination of the number of the characteristic functional groups. Study of brominated product and determination of number of bromine atoms in each case has been used to find out the number of resorcinol molecules in a dye. Each dye has also been subjected to caustic potash treatment that has helped in assigning the structure of the dye on a firmer basis.

Their IR spectra and also that of their acetyl derivatives have further supported the structures of dyes chosen. Each dyes shows peak due to lactonic-C=O (1735-1790 cm⁻¹) and the phenolic hydroxyl group (3300-3500 cm⁻¹). The peak due the hydroxyl group does not appear in the IR spectra of the acetyl derivatives. New ester peaks were observed in the range of 1000-1250 cm⁻¹ and 1735-1760 cm⁻¹ in the spectra of these acetyl derivatives.

**A.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL PHTHAL-AS-EIN:**

The dye was prepared by condensing 2-(2' 4' dimethyl benzoyl) benzoic acid and resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described in a subsequent chapter. The dye 2, 4 dimethyl phenyl-resorcinol phthal-as-ein having molecular formula C₂₃H₁₈O₄ molecular weight 346 on acetylation yielded a diacetyl derivative indicating the presence of two phenolic groups. When brominated with calculated amount of bromine, the dye gave a dibromo derivative confirming the presence of a molecule of resorcinol in the dye. On caustic potash treatment the dye yielded a molecule of 2-(2' 4' dimethyl benzoyl) benzoic acid and a molecule of resorcinol. With an excess of bromine, the dye yielded a molecule of the same acid and a molecule of tribromo resorcinol. On the basis of chemical evidence, the structure LXXVIIa has been assigned to the dye.

**B.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINAOL TETRA CHLORO PHTHAL-AS-EIN**

The dye (2, 4 dimethyl phenyl) resorcinol tetra chloro phthal-as-ein was prepared by condensing resorcinol and 2-(2' 4' dimethyl benzoyl) tetra chloro benzoic in presence of concentrated sulphuric acid as described later
LXXVIIa $R'_1=R'_2=R'_3=R'_4=H$
LXXVIIb $R'_1=R'_2=R'_3=R'_4=Cl$
LXXVIIc $R'_1=R'_2=R'_3=H, R'_4=NO_2$

**CHARTA**

76
in chapter on the experimental part. The dye having the molecular formula C_{22}H_{14}Cl_{4}O_{4} molecular weight 484, on acetylation yielded a derivative and on bromination too with calculated amount of Br_{2} yielded dibromo derivative indicating the presence of two phenolic hydroxyl groups in the dye. Thus only one molecule resorcinol is present in dye molecule. Caustic potash treatment of the dye yielded a molecule of 2-(2’ 4’ dimethyl benzoyl) tetra chloro benzoic acid and a molecule of resorcinol. On treatment with an excess of bromine the dye molecule gave the same acid with a molecule of tribromo resorcinol. All these reactions can be explained by assigning the structure LXXVIIb to the dye molecule.

C.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing 2-(2’ 4’ dimethyl benzoyl)-3-nitro benzoic acid with resorcinol in presence of concentrated sulphuric acid as described later in chapter on the experimental part. The dye having the Molecular formula C_{22}H_{17}NO_{6} molecular weight 391, yielded a diacetyl derivative on acetylation and on bromination too with calculated amount bromine, gave a dibromo derivative, indicating the presence of two phenolic hydroxyl groups in the dye molecule. Thus, only one molecule of resorcinol is present in the dye molecule. Caustic potash treatment of the dye yielded a molecule of 2-(2’ 4’ dimethyl benzoyl)-3-nitro benzoic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. From the foregoing reactions the structure LXXVIIc was assigned to (2, 4 dimethyl phenyl) resorcinol nitro phthal-as-ein.

All the reactions of the dyes LXXVIIa, b and c depicted in chart A.

D.1.3 STRUCTURE OF (2, 4 DIMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:

The dye 2, 4 dimethyl phenyl-resorcinol succin-as-ein having the molecular formula C_{18}H_{18}O_{4}, molecular weight 298 was prepared by condensing β-(2,4 dimethyl benzoyl) propionic acid with resorcinol in presence of concentrated sulphuric acid as described later in chapter on the experimental part. The dye yielded a diacetyl derivative on acetylation and a dibromo derivative too on bromination with calculated amount of bromine. Caustic potash fusion of the dye gave β-(2, 4 dimethyl benzoyl) propionic acid and a molecule of resorcinol. Treatment of the dye with an excess of bromine yielded β-(2, 4 dimethyl benzoyl) propionic acid and a molecule of tribromo resorcinol. Based on the evidence cited above, the dye has been assigned the structure LXVIIid. All the reactions have been depicted in Chart B.
CHART B
The dye (3-carbmethoxy 4-hydroxy phenyl)-resorcinol-phthal-as-ein having a molecular weight of 380, molecular formula C$_2$H$_{16}$O$_7$ was prepared by condensing 2-(3’ carbmethoxy 4’ hydroxyl benzoyl) benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described later in a chapter on experimental part of the work. The dye on acetylation with acetic anhydride in presence of glacial acetic yield a triacetyl derivative and upon bromination with a calculated amount of bromine, yielded a tribromo derivative, thus indicating the presence of one resorcinol molecule in dye molecule. On caustic potash treatment, the dye gave a molecule of 2-(3’ carbmethoxy 4’ hydroxy benzoyl) benzoic acid and a molecule of resorcinol. The dye, with excess of bromine yielded a molecule of the same acid and a molecule of resorcinol. On the basis of the evidence listed above, the structure LXVIIIa was proposed for the dye.

B. 2.3 STRUCTURE OF 3 CARBMETHOXY 4- HYDDROXY PHENYL) RESORCINOL-TETRA CHLORO PHTHAL-AS EIN

The dye 3-carbmethoxy 4-hydroxyl phenyl- resorcinol-tetrachloro phthal-as-ein having molecular formula C$_2$H$_{12}$O$_7$ molecular weight 518 was prepared by condensing resorcinol and 2-(3’ carbmethoxy 4’ hydroxyl benzoyl) tetra chloro benzoic acid in presence of a little sulphuric acid as the condensing agent as described later. The dye formed the triacetyl and the tribromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3’ carbmethoxy 4’ hydroxy benzoyl) tetrachloro benzoic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. Based on the chemical evidence it could be deduced that the structure of the dye was LXXXVIIib.

C. 2.3 STRUCTURE OF (3- CARBMETHOXY 4- HYDROXY PHENYL) -RESORCINOL – NITRO-PHTHAL –AS –EIN

The dye (3-carbmethoxy 4- hydroxyl phenyl)-resorcinol-nitro-phthal-as-ein was prepared by condensing 2-(3’carbmethoxy 4’ hydroxyl benzoyl)-3-nitro benzoic acid in presence of a little concentrated sulphuric acid as the condensing agent as per details given later in the thesis. The dye molecule having the formula C$_{21}$, H$_{15}$, NO$_3$ molecular weight 425, gave triacetyl and tribromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3’
CHART C

LXXVIII a  \[ R'_1 = R'_2 = R'_3 = R'_4 = H \]
LXXVIII b  \[ R'_1 = R'_2 = R'_3 = R'_4 = \text{Cl} \]
LXXVIII c  \[ R'_1 = R'_2 = R'_3 = \text{H, } R'_4 = \text{NO}_2 \]
carbmethoxy 4’ hydroxyl benzoyl)-3-nitro benzoic acid and a molecule of resorcinol. The dye, with excess of bromine yielded a molecule of the same acid and a molecule of tribromo resorcinol. This evidence clearly established that the structure of the dye is as depicted LXXVIIIc.

The foregoing reactions of the LXXVIIIa, b and c are shown in chart C.

D. 2.3 STRUCTURE OF (3-CARB METHOXY 4-HYDROXY PHENYL) RESORCINOL-SUCCIN-AS-EIN

This dye was prepared by condensing resorcinol with β- (3-carmethoxy 4-hydroxyl benzoyl) propionic acid in presence of some drops of concentrated sulphuric acid as the condensing agent as described later. The dye (3-carbmethoxy 4-hydroxyl phenyl)-resorcinol-succin-as-ein has the molecular weight of 344 molecular formula C₁₈H₁₆O₇ on acetylation yielded triaethyl derivative and a tribromo derivative too on bromination with calculated amount of bromine, showing the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded β-β(3-carmethoxy 4-hydroxyl benzoyl) propionic acid and a molecule of resorcinol. On treatment with excess of bromine, the dye molecule yielded the same acid and a molecule of tribromo resorcinol. Based on the chemical evidence it could be deduced that the structure of the dye was LXXVIIIId.

All these reactions have been summarized in chart D.

4.3.3 STRUCTURE OF (5-CHLORO 2-CHLOROMETHYL PHENYL) RESORCINOL-PHTHAL-AS-EIN:

The dye (5- chloro 2-chloromethyl phenyl)-resorcinol-pthal-as-ein was prepared by condensing 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid with resorcinol in presence of 3-4 drops of concentrated sulphuric acid as described later in the thesis. The dye molecule having the molecular formula C₂₁H₁₄Cl₂O₄ molecular weight 401, gave diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid and a molecule of resorcinol. The dye when treated with an excess of bromine formed 2-(5-chloro 2-chloromethyl benzoyl) benzoic acid and a molecule of dibromo resorcinol. These results lead us to formulate the structure of the dye as LXXIXa.

B.3.3 STRUCTURE OF (5-CHLORO 2-CHLOROMETHYL PHENYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN:

The dye (5-chloro 2-chloromethyl phenyl) resorcinol tetra chloro phthal-as-ein was synthesized by the condensation of 2-(5-chloro 2-
chloromethyl benzoyl) tetra chloro benzoic acid with resorcinol in presence of a little concentrated sulphuric acid as per description later in the experimental part. The dye has the molecular weight of 539, molecular formula $C_{21}H_{10}Cl_{6}O_4$ on acetylation yielded diacetyl derivative and a dicromo derivative too on bromination with calculated amount of bromine, showing the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(5-chloro 2-chloromethyl benzoyl) tetra chloro benzoic acid and a molecule of resorcinol. On treatment with excess bromine, the dye yielded 2-(5-chloro 2-chloromethyl benzoyl) tetra chloro benzoic acid along with a molecule of tribromo resorcinol. The dye was thus assigned the structure LXXIXb.

**C.3.3 STRUCTURE OF (5- CHLORO 2- CHLOROMETHYL PHENYL) RESORCINOL NITRO PHTHAL-AS-EIN:**

The dye (5-chloro 2- chloromethyl phenyl) resorcinol nitro-phthal-as-ein, with the molecular weight 446, molecular formula $C_{21}H_{13}NCl_2O_6$, was obtained by condensing resorcinol with 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid in presence of a small amount of sulphuric acid as a condensing agent as per detail listed later. The dye gave diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid and a molecule of resorcinol. Treatment of the dye with excess of bromine leads to the formation of 2-(5-chloro 2-chloromethyl benzoyl)-3-nitro benzoic acid along with a molecule of tribromo resorcinol. Based on the evidence cited above, the dye molecule was assigned the structure LXXIXc.

All the chemical reactions of the dyes LXXIXa, b and c are summarized in chart E.

**C.3.3 STRUCTURE OF (5- CHLORO 2- CHLOROMETHYL PHENYL) RESORCINOL SUCCIN-AS-EIN:**

The dye having molecular formula $C_{17}H_{14}O_4Cl_2$ mol weight 353, was prepared by condensing $\beta$-(5-chloro 2-chloromethyl benzoyl) propionic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as described later in a chapter on experimental part of the work. The dye formed the diacetyl and the dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. On caustic potash treatment, the dye gave a molecule of $\beta$-(5-chloro 2-chloromethyl benzoyl) propionic acid and a molecule of resorcinol. The dye,
LXXIXa: $R'_1 = R'_3 = R'_4 = H$
LXXIXb: $R'_1 = R'_2 = R'_3 = R'_4 = Cl$
LXXIXc: $R'_1 = R'_2 = R'_3 = H, R'_4 = NO_2$

**CHART E**
with excess of bromine yielded a molecule of the same acid and a molecule of tribromo resorcinol. On the basis of the evidence listed above, the structure LXXIXd was proposed for the dye molecule.

All the reactions described above have been summarized in chart F.

\subsection*{A.4.3 (3-ACENAPHTHYL) RESORCINOL PHTHAL-AS-EIN:}

The dye (3-acenaphthyl)-resorcinol-phthal-as-ein was prepared by condensing resorcinol with 2-(3’ acenathoyl) benzoic acid using a small amount of concentrated sulphric acid as the condensing agent. The dye was found to have a molecular formula C\textsubscript{26} H\textsubscript{18} O\textsubscript{4} and molecular weight 394. The dye gave diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. Caustic potash fusion of the dye yielded 2-(3’ acenaphthoyl) benzoic acid and a molecule of resorcinol. But the dye on treatment with excess of bromine formed 2-(3’ acenaphthoyl) benzoic acid along with a molecule of tribromo resorcinol. The evidence conclusively pointed out the structure LXXXa for the dye.

\subsection*{B.4.3 STRUCTURE OF 3-ACENAPHTHYL) RESORCINOL TETRA CHLORO PHTHAL-AS-EIN:}

The dye (3’ acenaphthyl) resorcinol tetra chloro phthal-as-ein, having the molecular formula C\textsubscript{26}H\textsubscript{14}Cl\textsubscript{4}O\textsubscript{4} and molecular weight 532 was prepared by the condensation of 2-(3’acenaphthoyl) tetra chloro benzoic acid with resorcinol in presence of concentrated sulphuric acid as the condensing agent. The dye formed the diacetyl and dibromo derivatives on acetylation and bromination with calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye molecule. On caustic potash treatment, the dye yielded 2-(3’ acenaphthoyl) tetra chloro benzoic acid and a molecule of resorcinol was formed. The reaction of the dye with an excess of bromine yielded 2-(3’acenaphtoyl) tetrachloro benzoic acid and a molecule of tribromo resorcinol. The dye was assigned the structure LXXXb on the basis of the above evidence.

\subsection*{C.4.3 STRUCTURE OF (3- ACENAPHTHYL) RESORCINOL NITRO PHTHAL-AS-EIN:}

The dye (3 acenaphthyl)-resorcinol-nitro-phthal-as-ein has been prepared by condensing 2-(3’ acenaphthoyl)-3-nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as described later. The dye with molecular weight 439 and molecular formula C\textsubscript{26}H\textsubscript{17}NO\textsubscript{5} yielded on acetylation a diacetyl derivative and a dibromo derivative on bromination with a calculated amount of bromine indicating the presence of a molecule of resorcinol in the bigger dye molecule. Caustic potash
CHART F
LXXIXa $R'_1= R'_2= R'_3= R'_4= H$
LXXIXb $R'_1= R'_2= R'_3= R'_4= Cl$
LXXIXc $R'_i= R'_j= R'_3= H, R'_4= NO_2$

**CHART G**
treatment gave 2-(3' acenaphthoyl)-3-nitro benzoic acid and a molecule of resorcinol. Treatment of the dye with an excess of bromine yielded 2-(3' acenaphthoyl)-3-nitro benzoic along with a molecule of tri bromo resorcinol. On the basis of evidences deduced above the dye was assigned the structure LXXXc.

All the chemical reactions of the dyes LXXXa, b and a are summarized in chart G.

D.4.3 STRUCTURE OF (3-ACENAPHTHYL) RESORCINOL SUCCIN-AS-EIN:

The dye (3' acenaphthyl) resorcinol succin-as-ein was prepared by condensing β-(3' acenaphthoyl) propionic acid with resorcinol in presence of a little concentrated sulphuric acid as described later. It had the molecular formula C_{22} H_{18} O_{4} and molecular weight 346. It yielded on acetylation a diacetyl derivative and a dibromo derivative on bromination with a calculated amount of bromine indicating the presence of a molecule of resorcinol in the bigger dye molecule. Caustic potash treatment of the dye lead to the formation of β-(3' acenaphthoyl) propionic acid along with a molecule of tribromo resorcinol. The dye was, therefore, assigned the structure LXXXd on the basis of the evidence.

All the reaction of the dye molecule have been graphically outlined in the chart H.
CHART H
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<td>1710 1735 2665 (week) 3660</td>
<td>-</td>
<td>-</td>
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<th>Aryl ketonic -H₂C.CO.Ar</th>
<th>Carboxyl lactonic -OH</th>
<th>Carboxyl lactonic -OH</th>
<th>Ester group</th>
<th>Phenolic -OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl derivative</td>
<td>-</td>
<td>-</td>
<td>1778</td>
<td>-</td>
<td>1745, 1240, 1210,1010</td>
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</tr>
<tr>
<td>C.4 2-(3' acenaphthoyl) -3-Nitro- benzoic acid</td>
<td>1670</td>
<td>-</td>
<td>1705</td>
<td>1735</td>
<td>2620(week) 3460</td>
<td>-</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1785</td>
<td>-</td>
<td>1740, 1240, 1210,1005</td>
</tr>
<tr>
<td>D.1 β-(2-4 dimethylbenzoyl) propionic acid</td>
<td>1695</td>
<td>1665</td>
<td>1710</td>
<td>1742</td>
<td>2640(week) 3500</td>
<td>-</td>
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<tr>
<td>Acetyl derivative</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1778</td>
<td>-</td>
<td>1745, 1230, 1205,1000</td>
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<tr>
<td>D.2 β-(3' carbamethoxy 4' hydroxybenzoyl)- propionic acid</td>
<td>1680</td>
<td>1660</td>
<td>1710</td>
<td>1740</td>
<td>2660(week) 3450</td>
<td>- 3580</td>
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<td>Acetyl derivative</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1785</td>
<td>-</td>
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<td>D.3 β-(5' chloro 2' chloromethyl Benzoyl) propionic acid</td>
<td>1700</td>
<td>1668</td>
<td>1705</td>
<td>1742</td>
<td>2655(week) 3500</td>
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<td>Acetyl derivative</td>
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<td>1775</td>
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<td>D.4 β-(3- acenaphthoyl) propionic acid</td>
<td>1682</td>
<td>1670</td>
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<td>1745</td>
<td>2650</td>
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<td>Acetyl derivative</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1785</td>
<td>-</td>
<td>1750, 1250, 1220,1030</td>
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-92-
<table>
<thead>
<tr>
<th>Acids and their acetyl derivatives</th>
<th>Solvent</th>
<th>Chemical shift (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A.1 2-(2’-4’ dimethyl benzoyl)</td>
<td>DMSO</td>
<td>1.95-3.45(m; 7 unsymmetrical aromatic protons)</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td></td>
<td>7.85(s; 6 two CH₃ Protons); 4.30 (singlet, lactol-OH proton).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>1.90-3.35(m; 7 aromatic protons); 7.80 (s; 6 two CH₃ protons)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.65(Singlet 3-OCOCCH₃ protons).</td>
</tr>
<tr>
<td>A.2 2-(3’ carbethoxy 4’hydroxy</td>
<td>DCl₃</td>
<td>1.85-3.40 (m; 7 unsymmetrical aromatic protons); 4.32(br; s; Lactol</td>
</tr>
<tr>
<td>benzoyl) benzoic acid</td>
<td></td>
<td>proton); 4.78 (s; 1 phenolic –OH proton); 5.90(s; 3-OCOCH₃ protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>1.80-3.35 (m; 7 unsymmetrical aromatic protons); 7.65 (s; 3 lactol-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O,OCCH₃ Proton); 7.80 (s; phenolic 3- O,OCCH₃ protons); 5.90(s; 3-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>COOCH₃ proton)</td>
</tr>
<tr>
<td>A.3 2-(5’ chloro 2’ chloromethyl</td>
<td>DMSO</td>
<td>1.92-3.20(m; 7 unsymmetrical aromatic protons); 4.35 (br; S; lactol</td>
</tr>
<tr>
<td>benzoyl) benzoic acid</td>
<td></td>
<td>proton) 6.5 (s; 2-CH₂Cl protons)</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>DMSO</td>
<td>1.95-3.25(m, 7 unsymmetrical aromatic protons); 7.60 (S,3-O,OCCH₃ protons, 6.5 (s; 2 CH₂Cl protons)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.85-2.85 (m; 9 aromatic protons); 4.25(br; s; lactol H); 7.40 (m; 4-CH₃ - CH₂ – protons)</td>
</tr>
<tr>
<td>A.4 2-(3’ acenapthoyl)</td>
<td>DMSO</td>
<td>1.95- 2.90(m; 9 aromatic protons); 7.65(s, 3-OCOCCH₃ Protons); 7.45 (m; 4-CH₂-CH₂-protons)</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>CDCl₃</td>
<td></td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acids and their acetyl derivatives</td>
<td>Solvent</td>
<td>Chemical shift (τ)</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>---------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>B1. 2-(2’ 4’ dimethyl benzoyl), Tetrachloro benzoic acid</td>
<td>CDCl₃</td>
<td>2.30-3.25 (m; 3 symmetrical protons); 4.32(br; S; Lactol 1-OH proton; 7.90 (S; 6 two CH₃ protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.35-3.20 (m; 3 unsymmetrical aromatic protons); 7.60 (S; Lactol 3-O.OCC₃ protons); 7.82 (S; 6 Two– CH₃ Protons)</td>
</tr>
<tr>
<td>B2. 2-(3’ carbmethoxy 4’ hydroxy Benzoyl) tetrachloro benzoic Acid</td>
<td>CDCl₃</td>
<td>2.30-3.20 (m; 3 unsymmetrical aromatic protons); 4.30 (S; br; Lactol 1-OH proton); 4.78 (S; 1 phenolic OH proton); 5.90 (S; 3-COOCH₃ protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.35-3.40 (m; 3 unsymmetrical aromatic protons); 7.60 (S; Lactol 3-O.OCC₃ protons); 5.90 (S; 3-COOCH₃ protons); 7.80 (S; Phenolic 3-OOCCH₃ protons).</td>
</tr>
<tr>
<td>B3. 2-(5’ chloro 2’ chloromethyl Benzoyl ) tetrachloro benzoic Acid</td>
<td>DMSO</td>
<td>1.95-3.25 (m; 3 unsymmetrical aromatic protons); 4.30 (Br; S; Lacto –OH proton ); 6.55 ( S; 2-CH₂-Cl protons )</td>
</tr>
<tr>
<td>Acetyl acid</td>
<td>CDCl₃</td>
<td>2.05-3.40 (m; 3 unsymmetrical aromatic protons); 7.60 (S; 3-OOCCH₃); 6.5 (S; 2-CH₂-Cl protons).</td>
</tr>
<tr>
<td>B4. 2-(3’ acenaphthoxy) tetra Chlorobenzoic acid</td>
<td>DMSO</td>
<td>1.95-3.30 (m, 5 aromatic ring H ); 4.20 (S; lactol H ); 7.40 (m; 4-CH₂-OH-Protons)</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.05-3.35 (m; 5 aromatic ring protons); 7.65 (S, 3, O-OC-CH₃ protons); 7.40 (m; 4-CH₂-CH₂-Protons).</td>
</tr>
</tbody>
</table>

-94-
<table>
<thead>
<tr>
<th>Acids and their acetyl derivatives</th>
<th>Solvent</th>
<th>Chemical shift (( \tau ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.1 2-(2’ 4’ dimethyl benzoyl) 3-nitro benzoic acid</td>
<td>CDCl₃</td>
<td>2.35-3.25 (m; 6 unsymmetrical protons); 4.32 (br, S; lactol –OH proton); 7.90 (S; 6 two-CH₃ protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.05-3.15 (m; 6 unsymmetrical aromatic protons); 7.62 (S; 3-OCCH₃ Protons); 7.80 (S; 6 two –CH₃ protons)</td>
</tr>
<tr>
<td>C.2 2-(3’ Carbmethoxy 4’ Hydroxyl benzoyl) 3-nitro Benzoic acid</td>
<td>CDCl₃</td>
<td>2.05-2.95 (m, 6 unsymmetrical aromatic protons); 4.25 (S; lactol H); 4.78 (S; 1-Phenolic OH proton), 5.90 (S; 3-COOCCH₃protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.10-2.90 (m; 6 aromatic ring protons); 7.65 (S; 3 lactol –OCO CH₃ Protons); 7.80 (S; Phenolic 3-OOCCH₃ protons); 5.90 (S; 3-COOCCH₃ Protons)</td>
</tr>
<tr>
<td>C.3 2-(5’ Chloro 2’ chloro methyl benzoyl)-3-nitro Benzoic acid</td>
<td>DMSO</td>
<td>2.05-3.30 (m; 6 unsymmetrical aromatic protons); 4.30(br; S; lactol H); 6.55 (S; 2-CH₂Cl protons)</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>DMSO</td>
<td>2.10-3.30 (m; 6 unsymmetrical aromatic protons); 7.62 (S; 3-OOCCH₃ Protons); 6.52 (S; 2-CH₂-Cl protons)</td>
</tr>
<tr>
<td>C.4 2-(3’ acenaphthoyl) -3-nitro benzoic Acid</td>
<td>DMSO</td>
<td>1.90-2.85 (m; 8 unsymmetrical aromatic protons); 7.40 (m; 4-CH₂-CH₂ protons); 4.20 (S; lactol H).</td>
</tr>
</tbody>
</table>
### NMR Spectra of γ-Keto Acids and Their Acetyl Derivatives

<table>
<thead>
<tr>
<th>Acids and their acetyl derivatives</th>
<th>Solvent</th>
<th>Chemical shift (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>1.95-2.95 (m; 8 aromatic protons); 7.50 (m; 4-CH₂-CH₂ protons); 7.65 (S, 3-O-OC-CH₃ protons); 1.90-3.05 (m; 3 unsymmetrical ring protons); 4.30 (br; S; lactol proton); 7.90 (S; 6 two –CH₃ protons); 9.65 (triplet; 2-CH₂ ring protons); 8.62 (triplet; 2-CO-CH₂ ring protons).</td>
</tr>
<tr>
<td>D.1 β-(2,4 dimethyl Benzoyl) propionic Acid</td>
<td>CDCl₃</td>
<td>2.15-3.05 (m; 3 unsymmetrical aromatic protons); 7.65 (S; Lactol 3-O.OCH₃ protons); 9.62 (triplet, 2-CH₂ ring protons); 8.60 (triplete 2-COCH₂ ring protons.</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>1.95-2.85 (m; 3 aromatic ring protons); 4.35(br; S; Lactol –OH proton); 9.7 (triplet, 2 -CH₂ ring products); 8.45 (triplet; 2 –COCH₂ protons); 4.78 (S; 1 Phenolic –OH protons); 5.90 (S; 3 –COOCH₃ protons).</td>
</tr>
<tr>
<td>D.2 β-(3 carbethoxy 4 hydroxy Benzoyl) propionic Acid</td>
<td>CDCl₃</td>
<td>2.05-2.90 (m; 3 aromatic ring protons); 7.74(S; 3-OOCCH₃ protons); 9.80 (triplet, 2 –CH₂ ring protons); 8.48 (triplet, 2 –COCH₂ ring protons); 4.80 (S, 1 Phenolic –OH protons); 5.90 (S; -COOCH₃ protons).</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>2.10-3.30 (m; 3 aromatic ring protons); 4.35 (br; S; 1 Lactol proton); 9.8 (triplet, 2 -CH₂ ring protons); 8.7 (triplet, 2 -CH₂-CO- ring protons) 6.52 (S; two –CH₂-Cl protons).</td>
</tr>
</tbody>
</table>
**NMR SPECTRA OF γ-KETO ACIDS AND THEIR ACETYL DERIVATIVES**

<table>
<thead>
<tr>
<th>Acids and their acetyl derivatives</th>
<th>Solvent</th>
<th>Chemical shift (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl derivative</td>
<td>DMSO</td>
<td>2.05-3.25 (m; 3 aromatic ring protons); 7.65 (S; 3 –OOCCH₃ protons); 9.75 (triplet, 2 –CH₂ ring protons); 8.45 (triplet, 2 –CO-CH₂ ring protons); 6.55 (S; two –CH₂Cl protons).</td>
</tr>
<tr>
<td>D.4 β-(3 acenaphthoyl) Propionic acid</td>
<td>DMSO</td>
<td>1.95-2.95 (m; 8 unsymmetrical aromatic protons); 4.20 (br; S; 1 lactol proton); 9.75 (triplet, 2 –CH₂ ring protons); 8.55 (triplet, 2 –CO-CH₂ ring protons); 7.40 (m; 4 –CH₂-CH₂- ring protons)</td>
</tr>
<tr>
<td>Acetyl derivative</td>
<td>CDCl₃</td>
<td>1.95-2.95 (m; 8 unsymmetrical ring protons); 7.70 (S; 3 –OOCCH₃ protons); 9.8 (triplet, 2 –CH₂ ring protons); 8.60 (triplet, 2 –COCH₂ ring Protons); 7.40 (m, 4 –CH₂-CCH₂- ring Protons).</td>
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</tbody>
</table>
REFERENCES:

1. A. C. Green and P. King, Ber., 1907, 40, 3724.

2. R. Meyer and K. Mark, Ber., 1907, 40, 3603.


5. H. Kuhn, Chimia, 1955, 9, 237.


9. S. Gabriel., 1881, 14, 919.


17. F. Ullman, Ann. (1896), 17, 291.


23. H. Kuhn and Schretzmann, Ber., 1957, 90, 557.


-99-


During the investigations leading to this presentation four series of \(\gamma\)-keto acids were synthesized. As already described in Chapter II the labels A, B, C and D have indicated the four series. The acids of A, B, C series were condensed with various aromatic hydroxy compounds to get novel analogues of phthaleins. The members of D series acids i.e. \(\beta\)-aroyl propionic acids were condensed with different phenolic compounds to obtain novel analogues of succineins. The experimental part of the investigations has, therefore, been reported in four chapters as per the following scheme:

**Chapter III** Experimental A (for dyes obtained from A series of \(\gamma\)-keto acids)

**Chapter IV** Experimental B (for dyes obtained from B series of \(\gamma\)-keto acids)

**Chapter V** Experimental C (for dyes obtained from C series of \(\gamma\)-keto acids)

**Chapter VI** Experimental D (for dyes obtained from D series of \(\beta\)-aroyl propionic acids)