PART I

SECTION - A
Synthesis of 1-(2-hydroxy-3,4-benzo-phenyl)-3-styryl-propan-1,3-diones

SECTION - B
Synthesis of 2-bromo/iodo-1-(2-hydroxy-3,4-benzo-phenyl)-3-styryl-propan-1,3-diones

SECTION - C
Synthesis of 2-styryl-7,8-benzophenyl chromones and 3-bromo/iodo-2-styryl-7,8-benzophenyl chromones

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Chapter IV: Experimental and Discussion of the Results ... 34-80
Propane-1,3-diones:

Diketones are characterised by presence of two oxo groups. Diketones are classified as \( \alpha \) or 1,2, (1), \( \beta \) or 1,3 (2), or \( \gamma \) or 1,4 (3) diketones as per the position of oxo groups.

\[
\begin{align*}
R - C - C - R' & \quad R - C - CH_2 - C - R' & \quad R - C - CH_2CH_2 - C - R' \\
\| & \| & \| \\
O & O & O \\
\end{align*}
\]

(1) (2) (3)

R & R' = alkyl or aryl or acyclic

\( \beta \)-Diketones exists in two forms, keto and enol form.

\[
\begin{align*}
R - C - CH_2 - C - R' & \quad R - C = CH - C - R' \\
\| & \| \\
O & OH & O \\
\end{align*}
\]

Keto Enol

\( \beta \)-Diketones or 1,3-propanediones are also known as diacetylmethane derivatives.

\[
\begin{align*}
\text{O} & \quad \text{C} - \text{CH}_2 - \text{C} - \text{O} \\
\| & \| \\
\end{align*}
\]

1,3-diphenyl propan-1,3-dione
or
dibenzoylmethane

Curcumine\(^1\) (4) an orange red pigment occurs in roots and shoots of curcuma tictoria and it is extracted with alcohol and precipitated as lead salt.

---

Seed oil of Pongamia globra contains a crystalline compound, Pongomal which is 5-benzoyl-acetyl-4-methoxy benzofuran$^2$.

$\beta$-Diketones are starting compounds of flavonoids, pyrazoles, isoxazoles etc. Formation of B and C depends on pH of reaction mixture, below $pH = 5.0$ compound C is formed while above $pH = 8.0$ compound B is formed.

Synthesis of propane-1,3-diones:

Various methods are available to synthesise 1,3-diones. Usually 1,3-diones are synthesised by Claisen condensation of ketone and ester in presence of alkali like sodamide$^3$, alcohol free sodium ethoxide, sodium in xylene$^4$, sodium triphenyl methane$^5$.

Hauser\(^6\) employed a modified Claisen condensation to prepare 1-(2-hydroxy phenyl)-3-phenyl-propane-1,3-dione by using o-hydroxy acetophenone and ethyl benzoate in liquid NH\(_3\) with KNH\(_2\).

\[
\begin{align*}
\text{OH} & \quad \text{CH}_3 \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{CH}_3 \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\text{O} & \quad \text{CH}_3\text{C} - \text{C} \\
\end{align*}
\]

Acetophenone condenses with acetic anhydride to form benzoyl acetone in presence of BF\(_3\).\(^7\)

\[
\begin{align*}
\text{O} & \quad \text{H}_3\text{C} - \text{C} \\
\text{O} & \quad \text{H}_3\text{C} - \text{C} \\
\text{O} & \quad \text{H}_3\text{C} - \text{C} \\
\text{O} & \quad \text{H}_3\text{C} - \text{C} \\
\end{align*}
\]

This reaction depends on the rate of mixing of reactant and temperature.\(^8\) A more convenient method of synthesis of propandione is Baker-Venkataraman transformation\(^9\-10\) of o-aroyloxy-acetophenone in the presence of base like K\(_2\)CO\(_3\) in benzene,\(^9\) NaOEt\(^11\), K\(_2\)CO\(_3\) in pyridine,\(^12\) KOH in pyridine,\(^13\) sodium triphenyl methane.\(^14\)

6. Robley, J. Light and Charles, R. Hauser, 
7. Adams, J.T. and Hauser, C.R., 
8. Hauser, C.R., Swamer, F.W. Adams, J.T., 
9. Baker, W., 
10. Mahal, H.S. and Vankataraman, K., 
11. Baker, W., Ollis, W.D., Poole, V.D., 
12. Doyles, B.G., Gogan, F., Gawan, J.E., Keane, J. and Wheeler, T.S., 
13. Ollis, W.D. and Weight, D., 
14. Wadodkar, K.N.,

Wheeler and coworkers\textsuperscript{12} found that pyridine with KOH gives better yield. Wadodkar\textsuperscript{14} used aprotic solvent like dimethyl formamide (DMF) and KOH for B.V.T.

Nair\textsuperscript{15} synthesised 1-(2-furyl)-3-(2'-hydroxy phenyl)-propane-1,3-dione from furoyl ester of 2-hydroxy acetophenone using pulvarised KOH in pyridine.

\[ \text{BVT} \rightarrow \text{Py/KOH} \]

Paranjape\textsuperscript{16} has synthesised 2-hydroxy-(3,4-benzo) dibenzoyl methane from 2-benzoyloxy-3,4-benzo acetophenone using pulvarised KOH in pyridine medium.

\[ \text{BVT} \rightarrow \text{Py/KOH} \]

Gaggad\textsuperscript{17} has synthesised 1-(2-hydroxy phenyl)-5-phenyl-4-pentene-1,3-dione from o-cinnamoyloxy acetophenone using pulvarised KOH in DMF.

\[ \text{BVT} \rightarrow \text{KOH/DMF} \]

\begin{itemize}
  \item \textsuperscript{15} Nair, S.D. and Wadodkar, K.N., \textit{Indian J. Chem.}, \textbf{21B} (1982), 573.
  \item \textsuperscript{16} Paranjape, M.V., "\textit{a-Naphthyl analogous of flavonoids in the synthesis of oxygen and nitrogen heterocycles}". Ph.D. Thesis, Amravati University, (1986).
  \item \textsuperscript{17} Gaggad, H.L., Wadodkar, K.N. and Ghiya, B.J., \textit{Indian J. Chem.}, \textbf{24B} (1985), 1244.
\end{itemize}
Rajput\textsuperscript{18} has synthesised 1-(2-hydroxy-3-chloro-5-methyl phenyl)-3-(4'-methoxy phenyl)-1,3-propaniones by BVT in pyridine medium.

\begin{center}
\begin{tikzpicture}
\node at (-1.5,0) {\text{OH}};
\node at (-1,1) {\text{Cl}};
\node at (0,0) {\text{H}_3\text{C} \quad \text{OCH}_3};
\node at (1,0) {\text{O}};
\end{tikzpicture}
\end{center}

A.K. Ahluwalia et al\textsuperscript{19} has synthesised 3-(2',4'-dimethoxy-3'-methyl phenyl)-1-methyl propan-1,3-dione (A) and 3-(2',4'-dimethoxy-6'-methyl phenyl)-1-methyl-propan-1,3-dione (B) by Claisen condensation of 2,4-dimethoxy-3-methyl acetophenone and 2,4-dimethoxy-6-methyl acetophenone respectively with ethyl acetate in presence of pulvarised sodium metal.

\begin{center}
\begin{tikzpicture}
\node at (-1.5,0) {\text{H}_3\text{CO}};
\node at (-1,0) {\text{R}_1 \text{OCH}_3};
\node at (0,0) {\text{O}};
\node at (1,0) {\text{CH}_3};
\end{tikzpicture}
\end{center}

A : \( R_1 = \text{CH}_3 \)
\begin{align*}
R_2 &= \text{H} \\
B : \ R_1 &= \text{H} \\
R_2 &= \text{CH}_3
\end{align*}

Sharma et al\textsuperscript{20} reported the formation of 1-methyl-3-(2-naphthyl)-propan-1,3-dione.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{O}};
\node at (1,0) {\text{O}};
\node at (0,1) {\text{C} - \text{CH}_2 - \text{C} - \text{CH}_3};
\end{tikzpicture}
\end{center}

Sonare\textsuperscript{21} reported the formation of 1-(2-hydroxy-4-methoxy phenyl)-3-(4-methoxy phenyl)-1,3-propandione.

Bhadange et al\textsuperscript{22} has synthesised 2-hydroxy-3-bromo-5-chloro-4'-nitro dibenzoyl methane.

Thakare\textsuperscript{23} synthesised 1-coumaryl-3-aryl-propan-1,3-dione in pyridine medium by BVT.

Prabha Solanki\textsuperscript{24} reported the formation of 1-(2-hydroxy-5-methyl phenyl)-3-methyl-1,3-propanedione from 2-hydroxy-5-methyl acetophenone in presence of Na metal and ethyl acetate.

\begin{itemize}
\item \textsuperscript{22} Bhadange, R.E., Doshi, A.G. and Raut, A.W., \textit{Asian J. Chem.}, 13(3) (2001) 1153.
\end{itemize}
SECTION - B

Bromination and Iodination of propan-1,3-diones:

Bromination of organic compounds has received significant interest in recent years, because of increasing commercial importance of bromoorganics in the synthesis of large number of natural products as well as in manufacture of pharmaceuticals, intermediates for agrochemicals and other special chemicals.

Protection and deprotection of double bond via bromination - debromination increasing application in organic synthesis.

Bromination reactions are carried out with bromine dissolved in suitable solvent. Various solvents were used like water, conc. sulphuric acid, acetic acid, CCl₄, carbontetramide, chloroform, carbondisulphide, ethyl acetate, ether formic acid, dioxane, DMF, DMSO etc. When bromination proceeds with difficulty then catalyst or halogen carriers are used to facilitate the reaction.

In Halogenation ferric chloride, ferric bromide, aluminium chloride, aluminium bromide, iron, iodine, sulphur, sulphuric acid, zinc chloride have been employed and ferric chloride has been found to most satisfactory.

(b) Christophersen, C.,
27. Ranu, B.C., Guchhait, S.K. and Sarkar, A.
28. Schenfelen,
Tri bromophenol bromine can be used as brominating agent.\textsuperscript{29} NBS in carbon tetrachloride and pyridine bromine complex\textsuperscript{30} is used for nuclear bromination of o-hydroxy ketone.

Elizember et al\textsuperscript{31} have reported the bromination of ketone in presence of AlCl\textsubscript{3} in 1,2-dichloroethane giving metabrominated product.

Using Cu(II) halide, halogenation of ketone has been carried out to produce ω-halo ketone in aliphatic and aromatic ketones.\textsuperscript{32,33}

N-Bromo succinamide and other N-bromoiiodides are used for allylic bromination.\textsuperscript{34-36} The reaction proceeds by free radical mechanism.

Yanovskaya and coworkers\textsuperscript{37} have used dioxane-dibromide as brominating agent.

Lorette et al\textsuperscript{38} has employed pyridine bromine complex to brominate some natural flavanones which on treatment with alcoholic alkali gave flavones.

Schneider and Mills\textsuperscript{39} have reported the use of dioxane-dibromine monochloride complex as brominating agent. This complex is found better and powerful brominating agent.

\begin{footnotesize}
\begin{itemize}
  \item Edinger and Goldberg, \textit{Ber.}, 33 (1900) 2884.
\end{itemize}
\end{footnotesize}
Kaushik et al\textsuperscript{40} has synthesised N-octylquinolinium tribromide a new efficient brominating agent. N-octylquinolinium act as solvent source of bromine for complete bromination of phenols, aromatic amines, alkenes and alkynes.

\[
\begin{align*}
\text{[C}_8\text{Qui}^{+}]\text{Br}_3^- & \quad \text{Br} \quad \text{XH} \\
\text{[C}_8\text{Qui}^{+}]\text{Br}_3^- & \quad \text{Br} \quad \text{XH} \\
\text{[C}_8\text{Qui}^{+}]\text{Br}_3^- & \quad \text{Br} \quad \text{XH}
\end{align*}
\]

\[X = \text{OH, NH}\]

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

Bromination of 1,3-diones:

The first reported example of bromination of dibenzoyl methane is bromine in acetic acid or in suitable solvent for obtaining \(\alpha\)-bromo or \(\alpha\)-\(\alpha'\)-dibromo derivatives.\textsuperscript{41-42}

Bromine atom of \(\alpha\)-bromo diketone is reactive and labile in nature\textsuperscript{43} and it liberates iodine from acidified KI solution and regenerating the original diketone\textsuperscript{44}.

\begin{itemize}
\item 41. Nenfeville, R.D. and Peclimann, H.V., \textit{Ber.}, \textbf{23} (1890) 3375.
\item 44. Conant, J.B. et al., \textit{J. Am. Chem. Soc.}, \textbf{46} (1924) 232.
\end{itemize}
When acetylacetone or 1-phenyl-1,3-butadione on bromination gave two isomeric products (A,B),

\[
\begin{align*}
\text{R} - &\text{C} - \text{CH}_2 - \text{C} - \text{CH}_3 \\
\text{O} &\text{O} \\
\downarrow &\text{Br}_2 \\
\text{R} - &\text{C} - \text{CH} - \text{C} - \text{CH}_3 \\
\text{O} &\text{Br} &\text{O} \\
\end{align*}
\]

\[+\]

\[
\begin{align*}
\text{R} - &\text{C} - \text{CH}_2 - \text{C} - \text{CH}_2\text{Br} \\
\text{O} &\text{O} \\
\end{align*}
\]

(A) \hspace{1cm} (B)

It is essential to remove HBr product in reaction mixture, otherwise HBr converts A into B.

Cu and Na salts of 1,3-diones yields exclusively monobromo-methylene substituted products.\(^{45-46}\)

Doifode\(^{47}\) brominated 1-(2-hydroxyphenyl)-3-phenyl-1,3-diones by three different methods as given below.

i) Bromination of 1-(2-hydroxyphenyl)-3-phenyl-1,3-dione with bromine in acetic acid gave two products - bromo flavone (a) and flavone (b).

ii) Bromination of Cu complex of 1,3-dione in CCl\(_4\) medium also results in the formation of same (a) and (b) products.

iii) Bromination of 1,3-dione in acetic acid and sodium acetate buffer afforded α-bromo product (c).

---

Wadodkar\textsuperscript{48} obtained 3-bromo flavones from dibenzoylmethane using dioxane-dibromide complex as brominating agent. By using same reagent in presence of DMF yield \( \alpha \)-bromo-2-hydroxy dibenzoyl methane, here DMF acts as an HBr scavenger.

Gaggad\textsuperscript{49} has employed dioxane dibromide for bromination of 1-(2-hydroxyphenyl)-5-phenyl-4-pentene-1,3-dione and obtained 3-bromo-2-styryl chromone. By using dioxane dibromide in presence of DMF, 2-bromo-1-(2-hydroxyphenyl)-5-phenyl-4-pentene-1,3-dione is obtained.

Binda Saraf\textsuperscript{50} has prepared 2-bromo-1-(2-hydroxyphenyl)-5-aryl-4-pentene-1,3-diones by using bromine in acetic acid in presence of sodium acetate-acetic acid buffer.

\[
\begin{align*}
\text{R} & \quad \text{CH} = \text{CH} \quad \text{OCH}_3 \\
\text{O} & \quad \text{O} & \quad \text{Br}_2 \text{acetic acid} \\
\text{Sodium acetate} & \\
\end{align*}
\]

Same 1,3-diones have also been brominated by N-bromo succinimide in carbontetrachloride to get 3-bromo-2-styryl chromones.

\[
\begin{align*}
\text{R} & \quad \text{CH} = \text{CH} \quad \text{OCH}_3 \\
\text{O} & \quad \text{O} & \quad \text{NBS} \text{CCl}_4 \\
\end{align*}
\]

Kluiber\textsuperscript{51} has used N-bromosuccinimide for bromination of metal chelate.

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{M} < \\
\text{NBS} & \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{Br} \quad \text{O} \\
\text{O} & \quad \text{M} < \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{O} & \quad \text{M} < \\
\end{align*}
\]

\textsuperscript{50} Binda Saraf, "Reactivity of 1-(2-hydroxyphenyl)-6-phenyl-4-pentene-1,3-dione", Ph.D. Thesis (1988).

1,3-Diaryl-2-bromo-1,3-propanediones were prepared from 1,3-diaryl-1,3-propanediones on treatment with liquid Br₂ in dioxane-DMSO mixture.⁵²

Joshi et al.⁵³ reported the formation of ω-iodo-2-aryloxy acetophenone with iodine monochloride in acetic acid.

3-Iodoflavanones⁵⁴ are obtained from 2-hydroxy-4-methoxy chalcones and ICl in acetic acid.

Heda⁵⁵ has prepared ω-iodo-1,3-dione by using ICl in dioxane.

⁵² Gudadhe, S.K.,
⁵³ Joshi, M.G. and Wadodkar, K.N.,
⁵⁴ Joshi, M.G. and Wadodkar, K.N.,


SECTION - C

Synthesis of 2-aryl chromones:

Chromones are substituted heterocyclic $\alpha,\beta$-unsaturated ketones.
Chromones are benzoderivatives of $\gamma$ pyrones.

The numbering is illustrated in following formula (I).

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{O} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7} \\
\text{8}
\end{array}
\]

(1)

2-Aryl chromones are known as flavones (II). Fundamental structural unit is $\gamma$-pyrone\textsuperscript{56} ring.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{C}
\end{array}
\]

Flavone (II)

Eugin and Eugenetin\textsuperscript{57} are naturally occurring chromones which were extracted from Eugenia carphyllata.

Various methods are available for the synthesis of chromones.

Claisen condensation\textsuperscript{58} is most common method for the preparation of chromones. $o$-alkoxyphenyl or alkyl ketone on treatment with carboxylic ester in presence of strong base like sodium metal to give $o$-alkoxybenzo acylmethane (III) which then cyclises to chromone (IV).


\textsuperscript{58} Bloch and Kostanecki, Ber., 33 (1900) 471.
The Kostanecki-Robinson reaction is a reliable method for the preparation of chromones and 3-acyl chromones only from aromatic anhydrides and corresponding Na salts. Cinnamic acid derivatives give 2-styryl chromones. 59

\[
\begin{align*}
\text{OCH}_3 & \text{Na} \\
\text{OCH}_3 & \text{HI}
\end{align*}
\]

(III) (IV)

O-Cresyl acetate 60 on heating with sodium metal, o-cresol, 2,8-dimethyl chromone and 3,5-dimethyl-1-hydroxy xanthone mixture was obtained.

1-(2-Hydroxy-4-methoxy-5-methyl) buta-1,3-dione on cyclisation with ethanolic \( \text{H}_2\text{SO}_4 \) gave 2,6-dimethyl-7-methoxy chromone 61.

Sarbaggya et al\textsuperscript{62} synthesised furyl chromones by oxidative ring closing of chalcone with SeO\textsubscript{2}.

Photocyclisation\textsuperscript{63} of enolacetate of o-acetoxyacetophenone by irradiation in benzene using medium pressure Hg-lamp gave chromone.

Some aldosereductose inhibitor chromone derivatives\textsuperscript{64} were prepared from 2,4-hydroxy (NO\textsubscript{2}) \textsubscript{2}C\textsubscript{6}H\textsubscript{3}COCH\textsubscript{2}COOEt and drops of HCl/AcOH.

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\textsuperscript{64} Santen Pharm. Co. Ltd. \textit{Jpn. Tokkyo Koho}, \textbf{80}, 14, 9279.
An unusually facile reaction occurred\(^{65}\) when resacetophenone and cinnamoyl chloride were heated at 100°C in toluene for 8 hr to obtain 4-o-cinnamoyl resacetophenol in 17% yield in addition to 7-cinnamoyloxy-2-styryl chromone.

\[
\text{HO-CH=CH-O} + \text{Ph-CH=CH-COCl} \xrightarrow{100^\circ C} \text{15\%} \rightarrow \text{HO-CH=CH-O} + \text{Ph-CH=CH-COCl} \xrightarrow{100^\circ C} \text{15\%} \rightarrow 
\]

Nair\(^{66}\) has reported 2-(2'-furyl) chromone from 1-(2'-furyl)-3-(2-hydroxyphenyl)-propanedione with acetic acid and \(H_2SO_4\) and also by oxidation of acrylophenones with SeO\(_2\) in amyl alcohol.

Kostanecki\(^{67}\) synthesised flavone by action of ethanolic alkali with 2-hydroxy chalcone dibromide.


2-Hydroxy chalcone on refluxing with DMSO in presence of a crystal of iodine gave flavone.\(^6^8\)

Flavones on treatment with NBS in methanol and NBS in ethanol gives 2-methoxy-3-bromo flvanone and 2-ethoxy-3-bromo flvanone respectively.\(^6^9\)

---

These 2-methoxy-3-bromo flavanone and 2-ethoxy-3-bromo flavanone on treatment with alcoholic KOH at room temperature gave 3-bromo flavone.

\[
\text{OCH}_3\quad \text{Br} \\
\text{O}_2\text{N}\quad \text{R} \\
\text{nC}_2\text{H}_5\text{O} \\
\text{KOH} \\
\text{C}_2\text{H}_5\text{OH}
\]

These 3-bromo flavones were found physiologically active.  

3-Bromoflavone has been synthesised from flavone by using bromine in acetic acid in presence of mercuric acetate.

\[
\text{Hg(OAc)}\text{AcOH} \\
\text{Dioxane} \\
\text{Br}_2\text{/AcOH}
\]

70. Ankhiwala, M.B.,  
71. Ankhiwala, M.B.,  
72. Sonare, S.S. and Doshi, A.G.,  

3-iodo and 3-bromo flavones were prepared from 1-(2-hydroxy-3-substituted-5-chloro-phenyl)-3-(4'-substituted phenyl)-1,3-propanediones.\(^\text{73}\)

\[
\begin{align*}
\text{ICl / DMF} & \quad \text{Br}_2 / \text{DMF} \\
\begin{array}{c}
\text{Cl} \\
\text{OH}
\end{array} & \quad \begin{array}{c}
\text{Cl} \\
\text{O}
\end{array}
\end{align*}
\]

where, \(R = \text{NO}_2, \text{Cl}, \text{NH}_2\)
\(R_1 = \text{Br}, \text{NO}_2\)

Joshi et al\(^\text{74}\) obtained 95% EtOH extract of the leaves of Baccharis halimifolia by chromatographic separation, the trilerpene oleonolic acid\(^\text{75}\), the flavonoids, hipidulin (dinatin,5,7,4'-trihydroxy-6-methyl flavone)\(^\text{76-77}\) and cirsimaritin (scrophulein 5,4'-dihydroxy-6,7-dimethoxy flavone).\(^\text{78}\)

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73. Bhadange, R.E.,
74. Joshi, Balawant S., Syed, Imtiaz Haider, S. William Pelletier,
75. Karrer, W.,
76. (i) Mues, R., Trimmerman, B.N., Ohnon and Mobry, T.J.,
     (ii) Herr, W. and Sumi, Y.,
     (iii) Bharawaj, D.K., Nelkantha, K., Seshadri, T.R.
77. Kapchan, S.M., Sirol, C.W., Hemingway R.J., Knox J.R., Udayamurthy M.S.
78. i) Brieskon C.G. & Biechelew
     ii) Wallace J.W. & Bohm B.A.


*Phytochemistry,* 18 (1979) 1379.


*Phytochemistry,* 10 (1970) 452.
Novel flavonoid compounds 5,2'-dihydroxy-7,8,4'-trimethoxy flavone\(^79\) were isolated from the benzene extract of the arial parts and roots of the same plant.

\[ \text{where, (I) } R = H \]
\[ \text{(II) } R = CH_3 \]

Novel bio-active flavone glycoside (6,4'-dihydroxy-3'-phenyl-3,7,5'-tetramethoxy flavone-6-o-\(\alpha\)-Lrhamnopyranoside was isolated from seeds of Bauhinia parpurea commonly known as Kaniar in Hindi\(^80\).

2-Hydroxy-\(\omega\)-cinnamylidene acetophenone on oxidative cyclisation with I\(_2\)/DMSO gives 2-styryl chromones in high yeild.\(^81\)

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79. Mukherjee K.S., Brahmachari G., Manna T.K. & Mukherjee P.  
80. Yadava R.N. & Sheetal Sodhi  
81. Gupta S.S., Yadav N.S. & Dhawan S.N.
3-Allylchromones (A)\textsuperscript{82} on refluxing with N,N-diethylaniline yield corresponding Claisen rearranged product 3-hydroxy-2-(proplenyl) chromone.

\[
\begin{array}{c}
\text{R} & \text{O} & \text{OH} \\
\text{Br} & \text{K}_2\text{CO}_3/ >=O \\
\end{array}
\]

Jayprakash Rao et al\textsuperscript{83} were synthesised 7-hydroxy-6/8-allylchromones (A) and 2'-methyl-2',3'-dihydrofuranochromes (B) by Claisen rearrangement.

Chauhan et al\textsuperscript{84} isolated 5-acetoxy-3,3'-4',5'-tetramethoxy flavone from acetone and Quercetin from methanolic extract of dry leaves of Quercum semicarpifolia.

\begin{itemize}
\end{itemize}
The petrol extract of aerial part of roots of Limnophila indica (Scrophulariaceae) yielded a new flavone 5,8-dihydroxy-6,7,4'-trimethoxy flavone.  

Makrand et al. selectively chlorinated and brominated 1-(2-hydroxy phenyl)-3-phenyl-propane-1,3-diones using ammonium chloride and ammonium bromide with hydrogen peroxide in biphasic medium using tetra-n-butyl ammonium hydrogen sulphate as PTC.


Chapter - II

PROBLEM

Diketones are 1,3-dicarbonyl/1,3-diones containing a reactive methylene group between two carbonly groups and it exhibits keto-enol tautomerism.

1,3-Diones are precurser of heterocyclic compounds like pyrazoles, isoxazoles, flavones, flavanones etc.

1,3-Diones and heterocycles show promising chemical, biological activity and have medicinal applications.

Literature survey showed that the 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones have not yet been synthesised and therefore, we thought of interest to synthesise such propan-1,3-diones. Propan-1,3-diones have three reactive centres : Reactive methylene group, An olefinic bond and Phenyl ring having –OH group.

The present work presented in three sections.

Section-A :

This section deals with the synthesis of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c).

Section-B :

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones has three reactive centers as mention above and to study the reactivity of an olefinic bond we have decided for bromination and iodination studies of propan-1,3-diones.

Present work deals with bromination and iodination at α-position using bromine in acetic acid and iodine monochloride in acetic acid reagents
in presence of sodium acetate as buffer which acts as HBr/HI scavenger to obtain 2-bromo/2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-1,3-propaniones (3a-3f).

Section-C :

Various chromones have been synthesised at various research centers and tested for CNS and diuretic, biological, medicinal activities.

Keeping this view in mind, we thought it better to synthesise chromones from 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones.

The present work of this section deals with synthesis of 2-styryl chromones (4a-4c) from 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones using acetic acid, dilute sulphuric acid.

3-Bromo/Iodo-2-styryl chromones (5a-5f) were prepared by using 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones.
Scheme - I

[Diagram of chemical reactions]

where, \( R = \text{H, 4-OC}H_3, 3-\text{NO}_2 \)
\( R_1 = \text{Br, I} \)
Chapter - III

SUMMARY OF THE WORK

SECTION - A

Synthesis of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl propan-1,3-diones (2a-2c):

Synthesis of 2-acetyl-1-naphthol:

2-Acetyl-1-naphthol was synthesised by modified Nenchi method in which hot glacial acetic acid and fused ZnCl₂ were mixed and refluxed till ZnCl₂ dissolved in acetic acid and then to it powdered 1-naphthol was added. This mixture was refluxed for 8 hrs. and the reaction mixture was cooled and poured in acidulated water. The solid was filtered and crystallised from rectified spirit to get 2-acetyl-1-naphthol, m.p. 98°C, yield 75%.

Synthesis of 3,4-benzophenyl-2-cinnamoyloxy acetophenones (1a-1c):

Esterification of 2-acetyl-1-naphthol was carried out with cinnamic acid/p-methoxy cinnamic acid/m-nitro cinnamic acid using phosphorous oxichloride in pyridine medium. Thus the following 3,4-benzophenyl-2-cinnamoyloxy acetophenones (1a-1c) were synthesised.

1) 3,4-Benzophenyl-2-cinnamoyloxy acetophenone (1a)

![Chemical structure of 1a]

- m.p. 80-80°C
- Yield 70%

2) 3,4-Benzophenyl-2-(4-methoxy cinnamoyloxy) acetophenone (1b)

![Chemical structure of 1b]

- m.p. 150-152°C
- Yield 75%
3,4-Benzophenyl-2-(3-nitro cinnamoyloxy) acetophenone (1c)

\[
\begin{align*}
\text{O} & \quad \text{C} - \text{CH} = \text{CH} & \text{NO}_2 \\
\text{O} & \quad \text{O} & \text{CH}_3
\end{align*}
\]

m.p. 156-158°C  
Yield 70%

**Synthesis of 1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c):**

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) were obtained by Baker-Venkataraman transformation of 3,4-benzophenyl-2-cinnamoyloxyacetophenones (1a-1c) using pulvarised KOH in DMF medium.

Thus the following 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones were prepared.

1] 1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a)  
\[
\begin{align*}
\text{O} & \quad \text{O} & \text{OH} & \quad \text{CH} = \text{CH} & \text{CH} = \text{CH} & \text{O} \\
\text{CH} & \quad \text{CH} & \text{CH} & \quad \text{O} & \text{O} & \text{CH} = \text{CH}
\end{align*}
\]

m.p. 152°C  
Yield 75%

2] 1-(2-Hydroxy-3,4-benzophenyl)-3-(4-methoxyphenyl styryl)-propan-1,3-dione (2b)  
\[
\begin{align*}
\text{O} & \quad \text{O} & \text{OH} & \quad \text{CH} = \text{CH} & \text{CH} = \text{CH} & \text{CH} = \text{CH} & \text{O} \\
\text{CH} & \quad \text{CH} & \text{CH} & \quad \text{O} & \text{CH}_3
\end{align*}
\]

m.p. 182°C  
Yield 75%

3] 1-(2-Hydroxy-3,4-benzophenyl)-3-(3-nitrophenyl styryl)-propan-1,3-dione (2c)  
\[
\begin{align*}
\text{O} & \quad \text{O} & \text{OH} & \quad \text{CH} = \text{CH} & \text{CH} = \text{CH} & \text{CH} = \text{CH} & \text{O} \\
\text{CH} & \quad \text{CH} & \text{CH} & \quad \text{O} & \text{O} & \text{NO}_2
\end{align*}
\]

m.p. 210-212°C  
Yield 70%
SECTION-B

2-Bromo/2-Iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (3a-3f):

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) were brominated and iodinated by bromine in acetic acid + sodium acetate buffer and iodine in acetic acid + sodium acetate as buffer respectively to obtain 2-bromo/2-iodo propan-1,3-diones (3a-3f).

Thus the following 2-bromo/2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones were obtained.

1] 2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (3a)

\[
\begin{align*}
\text{m.p.} & \quad 120-122^\circ C \\
\text{Yield} & \quad 40\%
\end{align*}
\]

2] 2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxyphenyl styryl)-propan-1,3-dione (3b)

\[
\begin{align*}
\text{m.p.} & \quad 122-125^\circ C \\
\text{Yield} & \quad 48\%
\end{align*}
\]

3] 2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitrophynyl styryl)-propan-1,3-dione (3c)

\[
\begin{align*}
\text{m.p.} & \quad 122^\circ C \\
\text{Yield} & \quad 48\%
\end{align*}
\]
4] 2-Iodo-l-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (3d)

\[ \text{m.p. 140°C} \quad \text{Yield 48%} \]

5] 2-Iodo-l-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxyphenyl styryl)-propan-1,3-dione (3e)

\[ \text{m.p. 170°C} \quad \text{Yield 45%} \]

6] 2-Iodo-l-(2-hydroxy-3,4-benzophenyl)-3-(3-nitrophenyl styryl)-propan-1,3-dione (3f)

\[ \text{m.p. 198°C} \quad \text{Yield 45%} \]

**SECTION - C**

**Synthesis of 2-styryl-7,8-benzophenyl chromones (4a-4c) & 3-bromo/iodo-2-styryl-7,8-benzophenyl chromones (5a-5f):**

This section deals with the preparation of 2-styryl chromones (4a-4c) from 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) and 3-bromo/iodo-2-styryl chromones (5a-5f) from 2Br/I-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (3a-3f).

Thus the following chromones were synthesised.
1] (4a)  m.p. 137°C  Yield 80%

2] (4b)  m.p. 192°C  Yield 82%

3] (4c)  m.p. 224°C  Yield 80%

4] (5a)  m.p. 160°C  Yield 60%

5] (5b)  m.p. 186°C  Yield 60%

6] (5c)  m.p. 202°C  Yield 60%
Part - 1

7) (5d)

\[
\begin{align*}
\text{m.p. } 265^\circ\text{C} \\
\text{Yield 60%}
\end{align*}
\]

8) (5e)

\[
\begin{align*}
\text{m.p. } 220^\circ\text{C} \\
\text{Yield 65%}
\end{align*}
\]

9) (5f)

\[
\begin{align*}
\text{m.p. } 252^\circ\text{C} \\
\text{Yield 60%}
\end{align*}
\]
Chapter - IV

EXPERIMENTAL AND DISCUSSION OF RESULTS

SECTION - A

Synthesis of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones

This part of thesis deals with the synthesis of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) from 2-cinnamoyloxyacetophenones (1a-1c) in DMF medium.

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones have been characterised on the basis of chemical properties, elemental analysis and spectral analysis.

The melting points were recorded on precision melting point apparatus and were uncorrected.

The infra red spectra were recorded on 'Perkin Elmer 577' spectrophotometer. The PMR spectra were recorded on 'Brucker AC300' spectrophotometer in CDCl₃. The elemental analysis and spectral analysis were carried out at RSIC Chandigarh.

The chemicals used were of laboratory reagent grade and purity of the compounds was tested by TLC.

Preparation of Starting Materials:

The preparation of starting materials involves following steps.

i) The preparation of 2-acetyl-1-naphthol

ii) The preparation of 2-cinnamoyloxyacetophenones (1a-1c)

iii) The preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c).
Experiment No. 1:

Synthesis of 2-acetyl-1-naphthol (Fries Migration):

1-Naphthol acetate (0.1 mole, 18.6 g) was mixed with anhydrous AlCl₃ (0.2 mole, 25.9 g) and heated at 100°C for about 2 hrs and then at 120°C for 2 hrs. in an oil bath. The reaction mixture was cooled and decomposed with cold water containing a little HCl to get ketone containing a mixture of ortho and para isomers. These two isomers were separated by steam distillation. The ortho isomer distills over and a para isomer remains in the flask. The yellow solid thus separated was recrystallised from rectified spirit. m.p. 98°C, yield 52%.

Experiment No. 2:

Synthesis of 2-acetyl-1-naphthol (Friedel-Craft Method):

Fused ZnCl₂ (0.15 mole, 20.4 g) was dissolved in glacial acetic acid (20 ml) and 1-naphthol (0.1 mole, 14.4 g) was added and mixture was refluxed for about 15 to 20 minutes. The cooled reaction mixture was treated with acidified water. The solid obtained was subjected to steam distillation to get product which was crystallised from rectified spirit to obtain yellow needles. m.p. 98°C, yield 60%.
Experiment No. 3 :

Synthesis of 2-acetyl-1-naphthol (Modified Nenchi's Method) :

In hot glacial acetic acid (80 ml), fused ZnCl₂ (0.36 mole, 50 g) was added. The reaction mixture was refluxed till ZnCl₂ dissolved, then powdered 1-naphthol (0.20 mole, 30 g) was added. The reaction mixture was refluxed for about 8 hrs. and then it was cooled and poured in acidified water. The solid was filtered, washed with water and crystallised from rectified spirit to obtain the product, m.p. 98°C, yield 70%.

\[
\begin{align*}
\text{ZnCl}_2 & \quad \text{CH}_3\text{COOH} \\
\Delta, 8 \text{ hrs} & \quad \rightarrow \\
\text{OH} & \quad \text{OH} \quad \text{CH}_3
\end{align*}
\]

Synthesis of 3,4-benzophenyl-2-cinnamoyloxyacetophenones (1a-1c) :

Esterification of 2-acetyl-1-naphthol was carried out with

(i) Cinnamic acid

(ii) p-OCH₃-cinnamic acid

(iii) m-Nitro cinnamic acid

Various methods are available for esterification of phenol and alcohol with organic acids.¹⁻²

Wadodkar et al.³ carried out esterification of o-hydroxy acetophenone with aromatic acids using POCl₃ in pyridine medium gave o-cinnamoyloxy acetophenone in 80% yield. This method has been used for esterification.

Experiment No. 4 to 6:

General Procedure:

2-Acetyl-1-naphthol (0.04 mole, 7.12 g) and cinnamic acid (0.05 mole) were dissolved in dry pyridine (30 ml) in 250 ml beaker. Reaction mixture was treated with ice cold POCl₃ (3 ml) dropwise with cooling and constant stirring. During addition of POCl₃, temperature was maintained below 40°C. The reaction mixture was slowly thickened. After 6 hours it was treated with ice cold HCl (50%). The granular product obtained was washed with cold water and then with NaHCO₃ (10%) to remove any unreacted organic acids. The product was further washed with NaOH (1%) to remove unreacted ketone. The product was finally washed with water and crystallised from ethanol, yield 80%.

Mechanism of Esterification:

Wadodkar and Marathey³ has proposed probable path, which involves the formation of intermediate with phenol and POCl₃, with this intermediate organic acid will react to give corresponding ester. The HCl and H₃PO₄ formed in the reaction mixture were taken up by pyridine. Stepwise reaction is given below.
i)

\[
3 \text{PhOH} + \text{POCl}_3 + 3 \text{C}_2\text{H}_5\text{N} \rightarrow \text{Ph-O-PO} + 3 \text{C}_2\text{H}_5\text{N} \cdot \text{HCl}
\]

ii)

\[
\text{3PhO} + 3 \text{HO-CH=CH-} \rightarrow \text{3PhO-CH=CH-} + \text{H}_3\text{PO}_4
\]

where, \( R = \text{H, 4-OCH}_3, \text{3-NO}_2 \)

At higher temperature \( \text{POCl}_3 \) and phenol gives dihalophate.

\[
\text{POCl}_3 + \text{ArOH} \rightarrow \text{Ar-POCl}_2 + \text{HCl}
\]

This reaction is possible only at reflux temperature.⁴

The experimental condition used in the work ruled out this possibility.

---

Experiment No. 4 :

Preparation of 3,4-benzophenyl-2-cinnamoyloxy acetophenone (1a) :

2-Acetyl-1-naphthol (0.04 mole, 7.12 g) and cinnamic acid (0.05 mole, 7.40 g) were dissolved in pyridine (30 ml). POC\textsubscript{3} (3 ml) was added dropwise with constant stirring. The reaction mixture was processed as per general procedure to obtain 3,4-benzophenyl-2-cinnamoyloxy acetophenone (1a), m.p. 82°C, yield 80%.

\[
\begin{align*}
\text{O} & \quad \text{POCl}_3 \\
\text{Pyridine} & \\
\end{align*}
\]

Properties and Constitution of the Compound (1a) :

1] The compound is greenish white crystalline solid, m.p. 82°C.

2] Alcoholic solution of (1a) did not give green or blue colouration with neutral FeCl\textsubscript{3} solution. This showed absence of phenolic –OH group.

3] TLC :

Solvent (Benzene) height : 4.4 cm
solute height : 2.3 cm
R\textsubscript{f} value : 0.52

4] The IR spectrum of compound (1a) (Spectrum No. 1) recorded in Nujol showed following absorption bands.
<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3066.1</td>
<td>m</td>
<td>CH = CH stretching</td>
</tr>
<tr>
<td>2823.6</td>
<td>m</td>
<td>C – CH(_3) stretching</td>
</tr>
<tr>
<td>1721.3</td>
<td>s</td>
<td>C – C = stretching</td>
</tr>
<tr>
<td>1679.3</td>
<td>s</td>
<td>C – CH(_3) stretching</td>
</tr>
<tr>
<td>1629.3</td>
<td>s</td>
<td>C – CH = CH stretching</td>
</tr>
<tr>
<td>1597.3</td>
<td>m</td>
<td>C=C Ar stretching</td>
</tr>
<tr>
<td>1494.3</td>
<td>m</td>
<td>C=C Ar stretching</td>
</tr>
<tr>
<td>1425.7</td>
<td>m</td>
<td>C=C Ar stretching</td>
</tr>
<tr>
<td>1358.7</td>
<td>s</td>
<td>C–O–C stretching</td>
</tr>
<tr>
<td>1203.5</td>
<td>m</td>
<td>C–O–C Asy. stretching</td>
</tr>
<tr>
<td>1129.6</td>
<td>s</td>
<td>C–O–C stretching</td>
</tr>
<tr>
<td>989.0</td>
<td>m</td>
<td>trans CH=CH</td>
</tr>
</tbody>
</table>

[5] The PMR spectrum of compound (1a) (Spectrum No. 2) was recorded in CDCl\(_3\) with TMS as an internal standard. The observed chemical shifts can be correlated as follows.

<table>
<thead>
<tr>
<th>Chemical shift ((\delta)) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>s</td>
<td>3H</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C–CH(_3)</td>
</tr>
<tr>
<td>7.7</td>
<td>d</td>
<td>1(H_b)</td>
<td>CH=CH(_b)=Ph</td>
</tr>
<tr>
<td>6.8</td>
<td>d</td>
<td>1(H_a)</td>
<td>O</td>
</tr>
<tr>
<td>6.9-8.4</td>
<td>m</td>
<td>11H</td>
<td>C–CH(_a)=CH–Ph</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ar–H</td>
</tr>
</tbody>
</table>
SPECTRUM NO. 1

06/05/05 11:05 AH, CODE-I-1
X: 4 scans, 4.0cm⁻¹, flat, smooth, zbin

SHIF NO.-147
On the basis of spectral analysis, analytical results and chemical properties, the compound (1a) was assigned the structure as,

\[
\text{3,4-Benzophenyl-2-cinnamoyloxy acetophenone}
\]

Experiment No. 5:

**Preparation of 3,4-benzophenyl-2-(4-methoxy)-cinnamoyloxy acetophenone (1b):**

2-Acetyl-1-naphthol (0.04 mole, 7.12 g) and 4-methoxy cinnamic acid (0.05 mole, 9 g) were dissolved in dry pyridine (30 ml). Reaction mixture was treated with ice cold POCl₃ (3 ml) dropwise with constant stirring. The reaction mixture was kept for 6 hours and processed as per general procedure to obtain ester (1b), m.p. 151°C, yield 78%.

**Properties and Constitution of the Compound (1b):**

1) All chemical properties of compound (1b) were found similar to those of compound (1a).
2] TLC:

Solvent (Benzene) height : 4.4 cm
solute height : 1.6 cm
Rf value : 0.39

On the basis of chemical properties and analytical results, the compound (1b) was assigned the structure as,

![Chemical structure of 3,4-Benzophenyl-2-(4-methoxy)-cinnamoyloxy acetophenone]

3,4-Benzophenyl-2-(4-methoxy)-cinnamoyloxy acetophenone

Experiment No. 6:

Preparation of 3,4-benzophenyl-2-(3-nitro)-cinnamoyloxy acetophenone (1c):

2-Acetyl-1-naphthol (0.04 mole, 7.12 g) and 3-nitro cinnamic acid (0.05 mole, 9 g) were dissolved in dry pyridine (30 ml). Reaction mixture was treated with ice cold POCl3 (3 ml) dropwise with constant stirring. The reaction mixture was kept for 6 hours and processed as per general procedure to obtain ester (1c), m.p. 158°C, yield 75%.

![Chemical reaction of preparation of 3,4-benzophenyl-2-(3-nitro)-cinnamoyloxy acetophenone (1c)]
Properties and Constitution of the Compound (1c):

1] All chemical properties of compound (1c) were found similar to those of compound (1a).

2] TLC:
   - Solvent (Benzene) height : 4.4 cm
   - Solute height : 1.3 cm
   - R_f value : 0.29

3] Elemental Analysis:
   - N% Found - 3.58 Calculated - 3.84

   The analytical results of the compound (1c) agreed with the molecular formula C_{21}H_{15}O_{5}N.

   On the basis of chemical properties and analytical results, the compound (1c) was assigned the structure as,

   ![structure]

   3,4-Benzophenyl-2-(3-nitro)-cinnamoyloxy acetophenone

Experiment No. 7-9:

General Procedure:

Preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) from 3,4-benzophenyl-2-cinnamoyloxy acetophenones (1a-1c):

   3,4-Benzophenyl-2-cinnamoyloxy acetophenones (1a-1c) (0.01 mole) was suspended in DMF (10 ml) and pulvarised KOH (0.03 mole, 3 g) was added with stirring. The reaction mixture was slowly warmed up to 50°C. After 2 hours, it was decomposed with ice cold HCl (50%). The crude mass
was washed with NaHCO₃ (10%) solution to remove mineral acid. The product was crystallised from acetic acid and ethanol mixture (1:1), yield 70-75%.

\[
\begin{align*}
&\text{O} \\
&\text{O} \quad \text{CH} = \text{CH} \quad \text{CH} = \text{CH} \quad \text{O} \\
&\text{B.V.T} \\
&\text{KOH, DMF}
\end{align*}
\]

\(1a-1c\)  2a : R = H  
2b : R = 4-OCH₃  
2c : R = 3-NO₂

**Mechanism:**

Wheeler and coworkers⁵ have shown that Baker-Venkataraman Transformation (B.V.T.) is a base catalysed intramolecular Claisen condensation between ether and methyl ketone.

Proof for intramolecular nature of the reaction was given by Gowan and Wheeler⁵ and Schmidth et al⁵. A mixture of two o-aryloxy acetophenone subjected to B.V.T. yield no cross products.

The formation of benzoyl cinnamoyl methanes confirmed from IR, NMR, C¹³ data. It was shown that the presence of bulkier group cinnamoloxyl group (–C=CH–Ph) did not hindered the migration.

---

Experiment No. 7:

Preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a):

3,4-Benzophenyl-2-cinnamoyloxy acetophenone (1a) (0.01 mole, 3 g) was suspended in DMF (10 ml). Pulvarised KOH (0.03 mole, 3 g) was added in proportion with constant stirring. After complete addition, reaction mixture was processed as per general procedure to obtain 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a), m.p. 153°C, yield 70%.
Properties and Constitution of the Compound (2a):

1] It is brick red coloured crystalline solid, m.p. 153°C.

2] Alcoholic solution of (2a) gave deep violet colouration with neutral FeCl₃ solution indicating the presence of phenolic –OH group.

3] It decolourised bromine water indicating presence of unsaturation.

4] TLC:
   Solvent (Benzene) height : 4.8 cm
   solute height : 4.1 cm
   Rf value : 0.85

5] The IR spectrum of compound (2a) (Spectrum No. 3) recorded in Nujol showed following absorption bands.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3433.6</td>
<td>s</td>
<td>–O–H stretching</td>
</tr>
<tr>
<td>2827.6</td>
<td>m</td>
<td>CH₂ symm stretching</td>
</tr>
<tr>
<td>1627.5</td>
<td>s</td>
<td>C – C – C</td>
</tr>
<tr>
<td>1585.5</td>
<td>s</td>
<td>O – – – H – – O</td>
</tr>
<tr>
<td>1469.3</td>
<td>s</td>
<td>&gt;CH₂ stretching</td>
</tr>
<tr>
<td>1353.6</td>
<td>s</td>
<td>Ph–O–H stretching</td>
</tr>
<tr>
<td>1266.9</td>
<td>s</td>
<td>&gt;C–O stretching</td>
</tr>
<tr>
<td>961.0</td>
<td>s</td>
<td>–CH=CH– trans stretching</td>
</tr>
</tbody>
</table>
6] The PMR spectrum of compound (2a) (Spectrum No. 4) was recorded in CDCl₃ with TMS as an internal standard. The observed chemical shifts can be correlated as follows.

<table>
<thead>
<tr>
<th>Chemical shift (δ) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.8</td>
<td>s</td>
<td>1H</td>
<td>O–H</td>
</tr>
<tr>
<td>14.65</td>
<td>s</td>
<td>1H</td>
<td>enolic –OH</td>
</tr>
<tr>
<td>7.7</td>
<td>d</td>
<td>1H</td>
<td>Ph–CH₃=CH</td>
</tr>
<tr>
<td>6.6</td>
<td>d</td>
<td>1H</td>
<td>Ph–CH=CH₃</td>
</tr>
<tr>
<td>6.3</td>
<td>s</td>
<td>1H</td>
<td>C–H</td>
</tr>
<tr>
<td>7.2–7.6</td>
<td>m</td>
<td>11H</td>
<td>Ar–H</td>
</tr>
</tbody>
</table>

7] C¹³-NMR spectrum of compound (2a) (Spectrum No.5) showed following peaks.

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>δ ppm</th>
<th>Carbon atom</th>
<th>δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>194.86</td>
<td>C₁₁</td>
<td>123.46</td>
</tr>
<tr>
<td>C₂</td>
<td>97.12</td>
<td>C₁₂</td>
<td>126.93</td>
</tr>
<tr>
<td>C₃</td>
<td>173.48</td>
<td>C₁₃</td>
<td>121.86</td>
</tr>
<tr>
<td>C₄</td>
<td>138.96</td>
<td>C₁₄</td>
<td>122.99</td>
</tr>
<tr>
<td>C₅</td>
<td>136.51</td>
<td>C₁₅</td>
<td>129.41</td>
</tr>
<tr>
<td>C₆</td>
<td>134.38</td>
<td>C₁₆</td>
<td>118.11</td>
</tr>
<tr>
<td>C₇</td>
<td>125.42</td>
<td>C₁₇</td>
<td>111.75</td>
</tr>
<tr>
<td>C₈</td>
<td>127.51</td>
<td>C₁₈</td>
<td>124.71</td>
</tr>
<tr>
<td>C₉</td>
<td>128.49</td>
<td>C₁₉</td>
<td>129.60</td>
</tr>
<tr>
<td>C₁₀</td>
<td>161.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
On the basis of spectral analysis, analytical results and chemical properties, the compound (2a) was assigned the structure as,

![Chemical structure of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione]

1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione

Experiment No. 8:

Preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (2b):

3,4-Benzophenyl-2-(4-methoxy)-cinnamoyloxy acetophenone (1b) (0.01 mole, 3 g) was suspended in DMF (10 ml) and pulvarised KOH (0.03 mole, 3 g) was added in portion with constant stirring. Reaction mixture was processed as per general procedure to obtain 1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy)-styryl-propan-1,3-dione (2b), m.p. 181°C, yield 75%.

![Chemical structures of 1b and 2b]

Properties and Constitution of the Compound (2b):

1] All chemical properties of compound (2b) were found similar to those of compound (2a).
TLC:
Solvent (Benzene) height : 4.8 cm
solute height : 3.8 cm
R<sub>f</sub> value : 0.79

On the basis of chemical properties and analytical results, the compound (2b) was assigned the structure as,

![Chemical Structure](image)

1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy-styryl)-propan-1,3-dione

Experiment No. 9:
Preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (2c):

3,4-Benzophenyl-2-(3-nitro)-cinnamoyloxy acetophenone (1c) (0.01 mole, 3 g) was suspended in DMF (10 ml) and pulvarised KOH (0.03 mole, 3 g) was added in portion with constant stirring. Reaction mixture was processed as per general procedure to obtain 1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro-styryl)-propan-1,3-dione (2c), m.p. 210°C, yield 70%.
Properties and Constitution of the Compound (2c):

1] All chemical properties of compound (2c) were found similar to those of compound (2a).

2] TLC:
   - Solvent (Benzene) height: 4.8 cm
   - Solute height: 3.5 cm
   - Rf value: 0.73

3] Elemental Analysis:
   - N% Found: 3.75
   - Calculated: 3.86

The analytical results of the compound (2c) agreed the molecular formula C$_{21}$H$_{15}$O$_5$N.

On the basis of chemical properties and analytical results, the compound (2c) was assigned the structure as,

![Structural formula of compound (2c)](image)

1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro-styryl)-propan-1,3-dione
SECTION - B
Synthesis of 2-bromo/iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones

This section deals with the bromination and iodination of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) by using bromine in acetic acid and iodine monochloride in acetic acid with sodium acetate as HBr/HI scavenger.

Doifode\textsuperscript{1} reported the formation of 2-bromo-1-(2-hydroxy phenyl)-3-phenyl-1,3-dione by buffered bromination of 1-(2-hydroxy phenyl)-3-phenyl-1,3-dione. Sodium acetate acts as HBr scavanger.

Wadodkar and Gaggad\textsuperscript{2} carried out bromination in DMF.

It was reported that if HBr produced in reaction mixture was not removed then it brought about the cyclisation of 2-bromo-1,3-dione to 3-bromo flavone.

Here isolation of 2-bromo/2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (3a-3f) was possible only when sodium acetate was used as HBr and HI scavanger.

Experiment No. 10-15:

Bromination and Iodination of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (3a-3f):

General Procedure:

1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) (0.01 mole, 3 g) was suspended in acetic acid (20 ml) and sodium acetate


Ghiya, B.J.
solution (10%, 10 ml). Solution of bromine or iodine monochloride in acetic acid (6.5 ml w/v) was added dropwise with constant stirring. After one hour the reaction mixture was diluted with water to get dark yellow product. The crude product was washed with water and crystallised from ethanol.

\[
\text{BryCl} \quad \text{Acetic Acid}
\]

**Experiment No. 10:**

**Preparation of 2-bromo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (3a):**

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a) (0.01 mole, 3 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this bromine in acetic acid (6.4 ml 25 w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3a), m.p. 122°C, yield 40%.
Properties and Constitution of the Compound (3a):

1] The compound (3a) is dark yellow solid, m.p. 122°C.

2] Alcoholic solution of (3a) gave deep green colouration with neutral FeCl₃ solution, indicates presence of phenolic –OH group.

3] It decolourised bromine water indicating presence of unsaturation.

4] TLC:

Solvent (Benzene) height : 5.0 cm
solute height : 3.4 cm
Rₚ value : 0.68

5] The IR spectrum of compound (3a) (Spectrum No. 6) recorded in Nujol showed following absorption bands.
<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3055.0</td>
<td>v</td>
<td>O - H stretching</td>
</tr>
<tr>
<td>1627.8</td>
<td>s</td>
<td>C—C =C—O</td>
</tr>
<tr>
<td>1577.7</td>
<td>s</td>
<td>O——H ——O</td>
</tr>
<tr>
<td>1332.7</td>
<td>m</td>
<td>Phenolic O–H stretching</td>
</tr>
<tr>
<td>1269.1</td>
<td>m</td>
<td>Phenolic C–O stretching</td>
</tr>
<tr>
<td>964.3</td>
<td>s</td>
<td>trans CH=CH</td>
</tr>
<tr>
<td>542.0</td>
<td>m</td>
<td>C–Br stretching</td>
</tr>
</tbody>
</table>

6] The PMR spectrum of compound (3a) (Spectrum No. 7) was recorded in CDCl₃ with TMS as an internal standard. The observed chemical shifts can be correlated as follows.

<table>
<thead>
<tr>
<th>Chemical shift (δ) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.66</td>
<td>s</td>
<td>1H</td>
<td>Enolic –OH</td>
</tr>
<tr>
<td>13.89</td>
<td>s</td>
<td>1H</td>
<td>–OH</td>
</tr>
<tr>
<td>7.76</td>
<td>d</td>
<td>1H</td>
<td>CHₐ=CH</td>
</tr>
<tr>
<td>7.25</td>
<td>d</td>
<td>1H</td>
<td>CHₖ</td>
</tr>
<tr>
<td>6.0-8.4</td>
<td>m</td>
<td>11H</td>
<td>Ar–H</td>
</tr>
</tbody>
</table>

On the basis of spectral analysis, analytical results and chemical properties, the compound (3a) was assigned the structure as,

![Structure diagram](image)

2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione
Mechanism of Bromination:

$\text{(HBr + CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COOH + NaBr)}$
Experiment No. 11:

Preparation of 2-bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (3b):

1-(2-Hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-diones (2b) (0.01 mole, 3.4 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this bromine in acetic acid (6.4 ml 25 w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3b), m.p. 125°C, yield 45%.

Properties and Constitution of the Compound (3b):

1] All the chemical properties of compound (3b) were found similar to those of compound (3a).

2] TLC:

<table>
<thead>
<tr>
<th>Solvent (Benzene) height</th>
<th>5.0 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute height</td>
<td>3.2 cm</td>
</tr>
<tr>
<td>R_f value</td>
<td>0.64</td>
</tr>
</tbody>
</table>

On the basis of analytical results and chemical properties, the compound (3b) was assigned the structure as,
Part I

D, OCH, CH = CH

2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione

Experiment No. 12:

Preparation of 2-bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitrostyryl)-propan-1,3-dione (3c):

1-(2-Hydroxy-3,4-benzophenyl)-3-(3-nitrostyryl)-propan-1,3-diones (2c) (0.01 mole, 3.4 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this bromine in acetic acid (6.4 ml 25 w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3c), m.p. 130°C, yield 40%.

Properties and Constitution of the Compound (3c):

1] All the chemical properties of compound (3c) were found similar to those of compound (3a).
2] TLC:

Solvent (Benzene) height : 5.3 cm
solute height : 2.6 cm
Rf value : 0.49

3] Elemental Analysis:

N% Found - 3.09 Calculated - 3.16

The analytical results of the compound (3c) agreed the molecular formula C_{21}H_{14}O_5NBr.

On the basis of chemical properties and analytical results, the compound (3c) was assigned the structure as,

![Structure of 2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione](image)

2-Bromo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione

Experiment No. 13:

Preparation of 2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (3d):

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a) (0.01 mole, 3 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this iodine monochloride in acetic acid (6.4 ml 25% w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3d), m.p. 140°C, yield 50%.
Properties and Constitution of the Compound (3d):

1] The compound (3d) is dark yellow solid, m.p. 140°C.

2] All the chemical properties of compound (3d) were found similar to those of compound (3a).

3] TLC:
   - Solvent (Benzene) height: 4.7 cm
   - Solute height: 4.2 cm
   - R_f value: 0.89

4] The IR spectrum of compound (3d) (Spectrum No. 8) recorded in Nujol showed following absorption bands.

<table>
<thead>
<tr>
<th>Frequency (cm^{-1})</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3055.0</td>
<td>v</td>
<td>O-H stretching</td>
</tr>
</tbody>
</table>
| 1627.8              | s         | C —— C —— C  
|                     |           | O —— H —— O  |
| 1577.7              | s         | Phenolic O—H stretching |
| 1332.7              | m         | Phenolic C—O stretching |
| 1263.3              | m         | trans CH=CH |
| 962.4               | s         | C—I stretching  |
| 489.9               | m         |             |
The PMR spectrum of compound (3d) (Spectrum No. 9) was recorded in CDCl₃ with TMS as an internal standard. The observed chemical shifts can be correlated as follows.

<table>
<thead>
<tr>
<th>Chemical shift (δ) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.6</td>
<td>s</td>
<td>1H</td>
<td>Enolic −OH</td>
</tr>
<tr>
<td>13.88</td>
<td>s</td>
<td>1H</td>
<td>−OH</td>
</tr>
<tr>
<td>7.7</td>
<td>d</td>
<td>1H</td>
<td>CHₐ=CH</td>
</tr>
<tr>
<td>7.29</td>
<td>d</td>
<td>1H</td>
<td>CHₐ</td>
</tr>
<tr>
<td>6.0-8.4</td>
<td>m</td>
<td>11H</td>
<td>Ar−H</td>
</tr>
</tbody>
</table>

On the basis of spectral analysis, analytical results and chemical properties, the compound (3d) was assigned the structure as,

![Chemical Structure](image)

2-Iodo-1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione

**Experiment No. 14**:  
**Preparation of 2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (3e)**:

1-(2-Hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (2b) (0.01 mole, 3.4 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this iodine monochloride in acetic acid (6.4 ml 25% w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3e), m.p. 170°C, yield 45%.
Properties and Constitution of the Compound (3e):

1] All the chemical properties of compound (3e) were found similar to those of compound (3a).

2] TLC:

Solvent (Benzene) height : 5.0 cm
solute height : 3.4 cm
R_f value : 0.68

On the basis of analytical results and chemical properties, the compound (3e) was assigned the structure as,

2-Iodo-1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione
Experiment No. 15 :

Preparation of 2-iodo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (3f) :

1-(2-Hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (2c) (0.01 mole, 3.4 g) was suspended in acetic acid (20 ml) and sodium acetate solution (10%, 10 ml). To this iodine monochloride in acetic acid (6.4 ml 25 w/v) was added dropwise with constant stirring. After one hour the reaction mixture was worked up as per general procedure to obtain compound (3f), m.p. 198°C, yield 45%.

Properties and Constitution of the Compound (3f) :

1] All the chemical properties of compound (3f) were found similar to those of compound (3a).

2] TLC :

\begin{align*}
\text{Solvent (Benzene) height} & : 5.0 \text{ cm} \\
\text{solute height} & : 3.8 \text{ cm} \\
R_f \text{ value} & : 0.76
\end{align*}

3] Elemental Analysis :

\begin{align*}
\text{N\% Found} & : 2.78 \\
\text{Calculated} & : 2.86
\end{align*}
The analytical results of the compound (3f) agreed the molecular formula $C_{21}H_{14}O_5NI$.

On the basis of chemical properties and analytical results, the compound (3f) was assigned the structure as,

![Chemical structure diagram](image)

2-lodo-1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitrostyryl)-propan-1,3-dione
SECTION - C

Synthesis of 2-styryl-7,8-benzophenyl chromones and
3-bromo/iodo-2-styryl-7,8-benzophenyl chromones

This section deals with the synthesis of 2-styryl-(7,8-benzophenyl)-chromones (4a-4c) and 3-bromo/iodo-2-styryl-(7,8-benzophenyl)-chromones (5a-5f) from 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c). Synthesised compounds have been characterised by chemical properties, elemental analysis and spectral data. Purity of these compounds was tested by TLC.

Preparation of Starting Materials:

The procedure for the preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) has been described in Section-A of Part-I, of this Thesis Experiment No. 7-9.

Thus the following 1,3-diones were used for the synthesis of chromones (4a-4c) and (5a-5f).

(2a) 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones
(2b) 1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-diones
(2c) 1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-diones

Experiment No. 16-18:
Preparation of 2-styryl-(7,8-benzophenyl)-chromones (4a-4c):

General Procedure:

1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (2a-2c) (0.01 mole) was refluxed in acetic acid (30 ml) containing H₂SO₄.
Part - 1

(5 ml, 2%) for about 1 hour. The reaction mixture was cooled and poured into water. White wooly product was separated. It was filtered and washed with water and crystallised from ethanol (70%) to get shiny white wooly compound (4a-4c), yield 70-80%.

where

\[
R = H, 4-\text{OCH}_3, 3-\text{NO}_2
\]

Experiment No. 16:

Preparation of 2-styryl-(7,8-benzophenyl)-chromone (4a):

1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a) (0.01 mole, 3 g) was refluxed in acetic acid (30 ml) containing \( \text{H}_2\text{SO}_4 \) (5 ml, 2%) for about 1 hour. Then reaction mixture was processed as per general procedure to obtain the compound (4a), m.p. 137°C, yield 80%.
Properties and Constitution of the Compound (4a):

1] The compound (4a) is white wooly solid, m.p. 137°C.
2] Alcoholic solution of (4a) did not give any colouration with neutral FeCl₃ solution, indicates absence of phenolic –OH group.
3] It was found insoluble in dil. NaOH.
4] It decolourised bromine water indicates presence of unsaturation.
5] TLC:
   Solvent (Ethyl acetate) height : 4.8 cm
   solute height : 3.9 cm
   Rf value : 0.81
6] The IR spectrum of compound (4a) (Spectrum No.10) recorded in Nujol showed following absorption bands.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3020.0</td>
<td>m</td>
<td>CH = CH stretching</td>
</tr>
<tr>
<td>3058.9</td>
<td>m</td>
<td>Ar CH = CH stretching</td>
</tr>
<tr>
<td>1639.4</td>
<td>s</td>
<td>Ar–C=O stretching</td>
</tr>
<tr>
<td>1392.5</td>
<td>s</td>
<td>γ-pyron ring</td>
</tr>
<tr>
<td>1199.0</td>
<td>s</td>
<td>C – C – C stretching</td>
</tr>
<tr>
<td>1085.8</td>
<td>s</td>
<td>C–O–C Assy. stretching</td>
</tr>
<tr>
<td>962.4</td>
<td>m</td>
<td>trans CH=CH</td>
</tr>
</tbody>
</table>

7] The PMR spectrum of compound (4a) (Spectrum No.11) was recorded in CDCl₃ with TMS as an internal standard. The observed chemical shifts can be correlated as follows.
Part - I

<table>
<thead>
<tr>
<th>Chemical shift (δ) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.14</td>
<td>d</td>
<td>1H</td>
<td>CH_A=CH_B</td>
</tr>
<tr>
<td>6.88</td>
<td>d</td>
<td>1H</td>
<td>CH_B=CH_A</td>
</tr>
<tr>
<td>6.4</td>
<td>s</td>
<td>1H</td>
<td>&gt;C-H_C</td>
</tr>
<tr>
<td>6.0-8.6</td>
<td>m</td>
<td>11H</td>
<td>Ar-H</td>
</tr>
</tbody>
</table>

8] C\textsuperscript{13}-NMR spectrum of compound (4a) (Spectrum No. 12) showed following peaks.

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>δ ppm</th>
<th>Carbon atom</th>
<th>δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{1}</td>
<td>153.10</td>
<td>C\textsubscript{11}</td>
<td>129.89</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>136.49</td>
<td>C\textsubscript{12}</td>
<td>134.94</td>
</tr>
<tr>
<td>C\textsubscript{3}</td>
<td>178.20</td>
<td>C\textsubscript{13}</td>
<td>160.89</td>
</tr>
<tr>
<td>C\textsubscript{4}</td>
<td>111.71</td>
<td>C\textsubscript{14}</td>
<td>128.19</td>
</tr>
<tr>
<td>C\textsubscript{5}</td>
<td>129.02</td>
<td>C\textsubscript{15}</td>
<td>125.07</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>129.18</td>
<td>C\textsubscript{16}</td>
<td>135.98</td>
</tr>
<tr>
<td>C\textsubscript{7}</td>
<td>123.95</td>
<td>C\textsubscript{17}</td>
<td>127.04</td>
</tr>
<tr>
<td>C\textsubscript{8}</td>
<td>122.23</td>
<td>C\textsubscript{18}</td>
<td>127.70</td>
</tr>
<tr>
<td>C\textsubscript{9}</td>
<td>122.23</td>
<td>C\textsubscript{19}</td>
<td>120.75</td>
</tr>
<tr>
<td>C\textsubscript{10}</td>
<td>120.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the basis of spectral analysis, analytical results and chemical properties, the compound (4a) was assigned the structure as,

2-styryl-(7,8-benzophenyl)-chromone
BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

Current Data Parameters
NAME Feb21-2007
EXPMO 189
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070221
Time 19.13
INSTRUM spect
PROBND 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 823.585 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
ZW 60.400 usec
DE 6.00 usec
TE 294.9 K
D1 1.00000000 sec
TDO 1

---------- CHANNEL f1 ----------
NUC1 1H
P1 10.90 usec
PL1 -3.00 dB
SF01 400.1324710 MHz

F2 - Processing parameters
CI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
FC 1.00

SPECTRUM NO. II

avtar_saifpu@yahoo.co.in
Experiment No. 17:

Preparation of 2-(4-methoxy styryl)-(7,8-benzophenyl)-chromone (4b):

1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (2b) (0.01 mole, 3.2 g) was refluxed in acetic acid (30 ml) containing H₂SO₄ (5 ml, 2%) for about 1 hour. Then reaction mixture was processed as per general procedure to obtain the compound (4b), m.p. 192°C, yield 80%.

Properties and Constitution of the Compound (4b):

1] All the chemical properties of compound (4b) were found similar to those of compound (4a).

2] TLC:
   Solvent (Ethyl acetate) height : 5.0 cm
   Solute height : 3.6 cm
   R_f value : 0.72

On the basis of chemical properties and analytical results, the compound (4c) was assigned the structure as,

2-(4-methoxy styryl)-(7,8-benzophenyl)-chromone
Experiment No. 18:

Preparation of 2-(3-nitro styryl)-(7,8-benzophenyl)-chromone (4c):

1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (2c) (0.01 mole, 3.4 g) was refluxed in acetic acid (30 ml) containing H$_2$SO$_4$ (5 ml, 2%) for about 1 hour. Then reaction mixture was processed as per general procedure to obtain the compound (4c), m.p. 224°C, yield 80%.

![Chemical structure](image)

Properties and Constitution of the Compound (4c):

1] All the chemical properties of compound (4c) were found similar to those of compound (4a).

2] TLC:
- Solvent (Ethyl acetate) height : 5.0 cm
- solute height : 3.6 cm
- $R_f$ value : 0.72

3] Elemental Analysis:
- N% Found - 3.90
- Calculated - 4.08

The analytical results of the compound (4c) agreed the molecular formula $C_{21}H_{13}O_4N$. 

... 69
On the basis of chemical properties and analytical results, the compound (4c) was assigned the structure as,

![Structure of (4c)](attachment://structure.png)

2-(3-nitro styryl)-(7,8-benzophenyl)-chromone

Experiment No. 19-21:

Preparation 3-bromo/Iodo-2-styryl-(7,8-benzophenyl) chromones (5a-5f):

**General Procedure:**

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-styrylpropan-1,3-diones (2a-2c) (0.01 mole) in acetic acid (30 ml), bromine in acetic acid/ICl in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was poured in water. Solid obtained was filtered, washed with water. It was recrystallised from ethanol to obtain compounds (5a-5c), yield 60-70%.

![General Procedure](attachment://general_procedure.png)

where,

\[ R = H, 4-OCH_3, 3-NO_2 \]

\[ R_1 = Br, I \]
Experiment No. 19:

Preparation 3-bromo-2-styryl-(7,8-benzophenyl) chromone (5a):

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-dione (2a) (0.01 mole, 3 g) in acetic acid (30 ml), bromine in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5a), m.p. 160°C, yield 65%.

![Chemical structure of compounds (2a) and (5a) with chemical reactions](image)

Properties and Constitution of the Compound (5a):

1] Compound (5a) is dark yellow solid, m.p. 160°C.

2] Alcoholic solution of compound (5a) showed no colouration with neutral FeCl₃ solution indicated absence of phenolic –OH group.

3] It decolourised bromine water showed presence of unsaturation.

4] TLC:

<table>
<thead>
<tr>
<th>Solvent (Ethyl acetate) height</th>
<th>4.6 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute height</td>
<td>3.6 cm</td>
</tr>
<tr>
<td>Rₜ value</td>
<td>0.78</td>
</tr>
</tbody>
</table>
On the basis of chemical properties and analytical results, the compound (5a) was assigned the structure as,

\[
\text{CH} = \text{CH}^3\text{-bromo-2-styryl-(7,8-benzophenyl) chromone}
\]

**Mechanism:**

Propan-1,3-dione exhibit keto-enol tautamerism and exist in equilibrium.

In general, in 1,3-dione the enol content is more. The stability of enol form is due to (i) conjugation of carbon-carbon double bond with the second carbonyl group, and (ii) the chelation i.e. by formation of an intramolecular hydrogen bond between enolic hydroxyl group and second carbonyl group.
Experiment No. 20:

Preparation 3-bromo-2-(4-methoxy styryl)-(7,8-benzophenyl) chromone (5b):

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (2b) (0.01 mole, 3.4 g) in acetic acid (30 ml), bromine in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5b), m.p. 186°C, yield 60%.

\[
\begin{align*}
\text{OH} & \quad \text{CH} = \text{CH} & \text{OCH}_3 \\
\text{O} & \quad \text{CH} \quad \text{CH} & \text{O} \\
\text{O} & \quad \text{CH} \quad \text{CH} & \text{OCH}_3 \\
\text{O} & \quad \text{CH} \quad \text{CH} & \text{OCH}_3 \\
\end{align*}
\]

Properties and Constitution of the Compound (5b):

1) All the chemical properties of compound (5b) were found similar to those of compound (5a).

2) TLC:

- Solvent (Ethyl acetate) height : 4.6 cm
- Solute height : 4.0 cm
- R_f value : 0.86

3) The IR spectrum of compound (5b) (Spectrum No.13) recorded in Nujol showed following absorption bands.
<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3060.8</td>
<td>m</td>
<td>CH = CH stretching</td>
</tr>
<tr>
<td>1693.4</td>
<td>m</td>
<td>&gt;C=O stretching conjugation</td>
</tr>
<tr>
<td>1629.7</td>
<td>s</td>
<td>C=C stretching conjugation</td>
</tr>
<tr>
<td>1388.7</td>
<td>m</td>
<td>(\gamma)-pyron ring</td>
</tr>
<tr>
<td>1205.4</td>
<td>m</td>
<td>O</td>
</tr>
<tr>
<td>1178.4</td>
<td></td>
<td>(\parallel) C – C – C stretching</td>
</tr>
<tr>
<td>1089.7</td>
<td>m</td>
<td>C – O – C Assy. stretching</td>
</tr>
<tr>
<td>966.3</td>
<td>s</td>
<td>trans CH=CH</td>
</tr>
<tr>
<td>565.1</td>
<td>m</td>
<td>C–Br stretching</td>
</tr>
</tbody>
</table>

4] The PMR spectrum of compound (5b) (Spectrum No. 14) was recorded in CDCl\(_3\) with TMS as an internal standard. The observed chemical shifts can be correlated as follows.

<table>
<thead>
<tr>
<th>Chemical shift ((\delta)) ppm</th>
<th>Multiplicity</th>
<th>No. of Proton</th>
<th>Types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>s</td>
<td>3H</td>
<td>–OCH(_3)</td>
</tr>
<tr>
<td>8.17</td>
<td>d</td>
<td>1H</td>
<td>CH(_A)</td>
</tr>
<tr>
<td>7.94</td>
<td>d</td>
<td>1H</td>
<td>CH(_B)</td>
</tr>
<tr>
<td>6.0-8.0</td>
<td>m</td>
<td>10H</td>
<td>Ar–H</td>
</tr>
</tbody>
</table>

On the basis of spectral analysis, analytical results and chemical properties, the compound (5b) was assigned the structure as,

\[
\begin{align*}
\text{CH}_A & = \text{CH}_B = \text{CH}\_3 \\
\text{3-bromo-2-(4-methoxy styryl)-(7,8-benzophenyl) chromone}
\end{align*}
\]
BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

Current Data Parameters
NAME: Feb21-2007
EXPNO: 190
PROCNO: 1

P2 - Acquisition Parameters
Date: 20070221
Time: 19.21
INSTRUM: spect
PROBHD: 5 mm PABBO BB-
PULPROG: zg30
TD: 65536
SOLVENT: CDC13
NS: 16
DS: 2
SWH: 8223.685 Hz
FIDRES: 0.125483 Hz
AQ: 3.9846387 sec
RG: 512
DW: 60.800 usec
DE: 6.000 usec
TE: 294.9 K
D1: 1.00000000 sec
TDD: 1

--------------- CHANNEL 1 --------------
NUC1: 1H
F1: 10.90 usec
PL1: -3.00 dB
FSP1: 400.1324710 MHz

F2 - Processing parameters
SI: 32768
SF: 400.1300080 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

SPECTRUM NO. 14

avtar_saifpu@yahoo.co.in
Experiment No. 21:

Preparation 3-bromo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone (5c):

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (2c) (0.01 mole, 3.4 g) in acetic acid (30 ml), bromine in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5c), m.p. 202°C, yield 60%.

Properties and Constitution of the Compound (5c):

1] All the chemical properties of compound (5c) were found similar to those of compound (5a).

2] TLC:

Solvent (Ethyl acetate) height : 4.6 cm
solute height : 4.1 cm
Rf value : 0.89

3] Elemental Analysis:

N% Found - 3.29       Calculated - 3.32

The analytical results of the compound (5c) agreed the molecular formula C_{21}H_{12}O_{4}N.
On the basis of chemical properties and analytical results, the compound (5c) was assigned the structure as,

![Structure of 3-bromo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone](attachment:image)

3-bromo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone

Experiment No. 22:

Preparation 3-iodo-2-styryl-(7,8-benzophenyl) chromone (5d):

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-styrylpropan-1,3-dione (2a) (0.01 mole, 3 g) in acetic acid (30 ml), iodine monochloride in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5d), m.p. 265°C, yield 65%.

![Reaction of (2a) with ICl in CH₃COOH](attachment:image)

Properties and Constitution of the Compound (5d):

1] All the chemical properties of compound (5d) were found similar to those of compound (5a).
2] TLC:

Solvent (Ethyl acetate) height : 4.8 cm
solute height : 3.9 cm
R_f value : 0.81

On the basis of chemical properties and analytical results, the compound (5d) was assigned the structure as,

![Structure of 3-iodo-2-styryl-(7,8-benzophenyl) chromone](image)

3-iodo-2-styryl-(7,8-benzophenyl) chromone

Experiment No. 23:

**Preparation 3-iodo-2-(4-methoxy styryl)-(7,8-benzophenyl) chromone (5e):**

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-(4-methoxy styryl)-propan-1,3-dione (2b) (0.01 mole, 3.2 g) in acetic acid (30 ml), iodine monochloride in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5e), m.p. 220°C, yield 60%.

![Conversion of 2b to 5e](image)
Properties and Constitution of the Compound (5e):

1] All the chemical properties of compound (5e) were found similar to those of compound (5a).

2] TLC:
Solvent (Ethyl acetate) height : 4.8 cm
solute height : 3.4 cm
Rf value : 0.70

On the basis of chemical properties and analytical results, the compound (5e) was assigned the structure as,

\[
\begin{align*}
\text{CH} & = \text{CH} \\
\text{O} & \\
\text{O} & \\
\text{I} & \\
\end{align*}
\]

3-iodo-2-(4-methoxy styryl)-(7,8-benzophenyl) chromone

Experiment No. 24:

Preparation 3-iodo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone (5f):

To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-(3-nitro styryl)-propan-1,3-dione (2c) (0.01 mole, 3.4 g) in acetic acid (30 ml), iodine monochloride in acetic acid (25% w/v) (6.4 ml) was added dropwise with constant stirring. After one hour reaction mixture was processed as per general procedure to obtain compound (5f), m.p. 252°C, yield 60%.
Properties and Constitution of the Compound (5f):

1] All the chemical properties of compound (5f) were found similar to those of compound (5a).

2] TLC:
   - Solvent (Ethyl acetate) height : 4.8 cm
   - Solute height : 3.3 cm
   - R_f value : 0.68

3] Elemental Analysis:
   - N% Found - 2.86
   - Calculated - 2.98

The analytical results of the compound (5f) agreed the molecular formula C_{21}H_{12}O_{4}N.

On the basis of chemical properties and analytical results, the compound (5f) was assigned the structure as,

![Structural formula of 3-iodo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone]

3-iodo-2-(3-nitro styryl)-(7,8-benzophenyl) chromone