SECTION V

INTRODUCTION AND DISCUSSION TO STUDIES ON FRIES MIGRATION WITH OPTICALLY ACTIVE PHENOLIC ESTERS
INTRODUCTION

There are several convenient methods available for preparing phenolic ketones like Nencki, Hoesch, Grignard and Friedel-Crafts reactions. Fries and Finck\textsuperscript{196-199} with an attempt to avoid difficulties encountered in Friedel-Crafts reaction, while preparing certain phenolic ketones, suggested that the phenolic ester on treatment with anhydrous aluminium chloride undergoes migration of the acyl group in the \textit{o}- and \textit{p}- position and gives phenolic ketones.

\[ \text{OH} \quad \text{CCCH}_2\text{Cl} \quad \text{AOCH}_2\text{Cl} \]

Similarly \textit{p}-cresyl chloroacetate on heating with aluminium chloride gave only the \textit{o}-hydroxy ketone.

This modification of the Friedel-Crafts reaction was found to be valuable because it did not only give better yields of \textit{o}- and \textit{p}-hydroxy ketones, but also the by-products
and the tarry matter were found in negligible quantities. This reaction was applied for the migration of a large number of phenolic esters.\textsuperscript{200-202}

Doebner\textsuperscript{203} even earlier had used almost the same principle for preparing hydroxy benzophenone. We are indebted to Rosenmund and Schnür\textsuperscript{204,205} as regards the development of the technique of this reaction.

The reaction has been studied by a number of workers and experimental conditions developed to give better yields. It has been found that certain factors have a potential effect upon the ease of the reaction and the nature of the products\textsuperscript{206} which are described as below:

(a) The structure of phenol,
(b) The temperature,
(c) The solvent,
(d) The ratio of ester to reagent,
(e) The Reagents, and
(f) The structure of the acyl group.

(a) The Structure of Phenol

The structure of phenol is one of the most important factor in determining the ease of the reaction and the nature of the products of migration. As a rule the presence of electronegative groups hinders the reaction e.g., the ester of nitrophenol were reported not to undergo
the reaction; nor was the migration of acyloxy benzoic acid successful. Recently both these types of compounds have been rearranged but the experimental conditions are somewhat different from the normal Fries reaction. However, the presence of electronegative groups generally activates the ring, but it introduces steric hindrance as well.

Ortho and para halogen substituted phenolic esters were studied by Klarmann and esters of meta halophenols, para ethyl phenyl and methyl phenyl esters were studied by Sen and Tiwari.

The alkyl group has a specific effect upon the position of the migrating groups. Thus p-cresyl esters always give o-hydroxy ketone, meta alkyl groups preferentially direct the migrating group to the ortho position, while ortho alkyl derivatives favour migration to the para position. However, except in the case of p-alkyl derivatives, the directive influence of the alkyl groups in meta or ortho position can be overshadowed by other factors like temperature and the structure of the acyl groups etc.

The esters of the dialkyl monohydric phenols like, 2:5 dimethoxy phenol, 2-methyl 1:5 ethyl phenol, 2-methyl-6-ethyl phenol, 2:6 xylyl propionates; thymol and 3-methyl-5-ethyl phenol; 3:5 dimethyl phenol; carvacrol; 2:6 dimethyl and 2:6 dichloro phenols have been studied.
The esters of dihydroxy phenols e.g., catechol, resorcinol and hydroquinone, have been migrated. Catechol esters mainly furnished 4-acyl derivatives along with some 3-acyl derivatives. Resorcinol esters mainly give 4-acyl resorcinol in the 4:6 diacyl resorcinol. Esters of hydroquinone have been successfully migrated by Shah and co-workers. Desai and Mavani also studied the Fries migration of the esters of the resorcinol, orcinol and hydroquinone. The Fries migration of guiacol acetate is interesting as m-hydroxy ketone is also obtained along with ortho and para isomers. Coulthard, Marshall and Miller have supported the rearrangement of the guicol esters. Mauthner has shown that dimethylation also took place during the rearrangement.

The Fries migration of poly hydroxy phenols like phloroglucinol, pyrogallol and hydroxy dimethoxy benzene has been studied.

The Fries rearrangement of α-naphthyl esters and β-naphthyl esters have been studied by many workers.

In the diphenyl series the usual o- and p-products are obtained, but in the case of 4-hydroxy diphenyl esters, the acyl group not only migrates to give 3-acyl derivatives but 4-acyl derivatives also.

The esters of hydroxy coumarins and chromones have also been successfully migrated.
(b) The Temperature

Another important factor which affects the rate of the reaction and nature of the products is the temperature. A striking example has been reported by Rosenmund and Schnurr (loc. cit.) who found that at 25° only the p-hydroxy ketone (85%) was obtained from m-cresyl acetate, while at 165° only the ortho-hydroxy ketone (95%) was formed. Similar observations were made in the rearrangement of m-cresyl benzoate. The higher aliphatic esters of m-cresol gave o-hydroxy ketones at low temperature and esters of o-cresol gave p-hydroxy ketones as principle products even at high temperature.

(c) The Solvent

The Fries reaction carried out in the presence of the solvents usually give better yields and requires lower temperature. The two effects of the solvents are well known: (i) they bring homogeneity and (ii) the energy of activation of the complex is considerably lowered and the reaction proceeds at a useful rate at much lower temperature. Nitrobenzene is the most commonly employed solvent. Other solvents used are tetrachloroethane, chlorobenzene, carbon disulphide, dichloroethane, anhydrous ether etc. There is little information at present concerning the effect of different solvents on the ratio in which the isomers are produced.
(d) **The Ratio of Ester to Reagent**

The effect of the quantity of aluminium chloride has been recently studied by a number of workers. They have come to the conclusion that the quantity of aluminium chloride is very important especially in the ease of esters in which the migration are hindered sterically or otherwise. The migration of guiacol acetate\(^\text{284}\) requires 2 moles of monohydric phenol esters and 4.5 moles\(^\text{285-286}\) of anhydrous aluminium chloride. In the Fries migration of phenyl caprylate\(^\text{287}\), if we increase the amount of the reagent from 1 mole to 2 moles, the yield of p-isomer increases from 45 to 63%.

(e) **The Reagents**

Although aluminium chloride is the most effective catalyst for the reaction, other analogous compounds such as anhydrous ferric chloride, fused zinc chloride, and stannic chloride\(^\text{283-291}\) were also found satisfactory. The action of the reagents like fused zinc chloride\(^\text{292,293}\), ferric chloride\(^\text{294}\), stannic chloride, hydrofluoric acid\(^\text{295,296}\) have been studied and boron trifluoride\(^\text{297,298}\) has been used successfully for the low temperature reactions leading to p-hydroxy ketones. Phosphorous pentoxide has also been employed by Schonberg and Miss Mustafa\(^\text{299}\) who were successful to isolate the product.
(f) The Structure of the Acyl Group

The structure of the acyl group plays an important part in the Fries migration. The effect of the weight of the acyl group is most remarkably shown by m-cresyl ester of acetic acid, and its homologous. Driver\textsuperscript{300} and Ralston\textsuperscript{301} have studied the migration of esters of aliphatic acids like stearic and palmitic acids. The esters of chloroacetic acid, alky1 aromatic acids, alkoxy aromatic acids, halogeno substituted aromatic acids (loc. cit.) esters of aliphatic unsaturated acids\textsuperscript{302,303} phenylcaprylate\textsuperscript{304,305} and cinnamic acid esters\textsuperscript{306} have been found to rearrange.

Reynold, Fuson, Scott and Speck\textsuperscript{307} studied the rearrangement of the esters of hindered acids and showed that p-tolyl 2:6 xylate and p-tolyl 2:6 mesitioate gave usual o-derivatives. The two methyl groups, ortho to the carboxy group had no hindering effect on rearrangement. Cocker\textsuperscript{308,309} carried out the rearrangement of 2:3 xyyl succinate and 2:4 xyyl succinate and obtained o-hydroxy ketones. Amstuz and Fehnel\textsuperscript{310} studied the Fries rearrangement of o-chloro methoxy phenyl iso-butyrates and isolated the p-hydroxy ketones. Saharia\textsuperscript{311} has reported the successful rearrangement of the phenyl esters of the α-naphthoic acid and β-naphthoic acid. Phenyl esters of carbamic acid\textsuperscript{312} rearranged to anilides of hydroxy carboxy acid.
The unusual meta migration has been reported by Ballio and co-workers\textsuperscript{313,314} in the case of the rearrangement of 3:4 disubstituted phenyl acetates.

Saharia and co-workers\textsuperscript{315-322} have carried out the Fries migration of o- and m-anisic acid esters, p-anisic acid esters, phenyl and isomeric o-cresyl esters, phenolic esters of 1- and 2-naphthoic acids, phenyl and isomeric cresyl esters and naphthyl esters of m-chloro benzoic acids, phenolic esters of o- and m-nitro benzoic acids and some thiophenyl esters. Wilhelm Treibs and co-workers\textsuperscript{323} carried out the Fries migration of dicarboxylic acid esters. Setalvad, Amin and Shah\textsuperscript{324} studied the Fries migration of acyl esters of methyl 2:6 dihydroxy benzoates and 3:5 dihydroxy benzoic acid. Bhatt and Shah\textsuperscript{325} studied the migration of acyl esters of o- and p-hydroxy acetophenones and p-hydroxy benzophenone. The Fries migration of a number of negatively substituted phenolic esters has been investigated in recent years by Brown\textsuperscript{326}, Shah and co-workers\textsuperscript{327} and Amin\textsuperscript{328-330}. The reversal of the Fries migration has been observed by Rosenmund and Schnurr (loc.cit.) in the case of p-hydroxy ketones which were converted to phenol esters. The reversal is effected by heating with sulphuric acid and camphor sulphonic acid or phosphoric acid. Christian and Amin\textsuperscript{331,332} carried out the Fries migration of phenyl cinnamate and recently the Fries migration of esters of 2-nitroresorcinol\textsuperscript{333}, 4-nitro-
resorcinol, m-halogen phenyl acetate, o-carboxy \( \beta \)-substituted phenol esters etc. have been carried out.

W. Baker and co-workers in a pioneering work on the localisation of the double bonds in the derivatives of resorcinol, studied the Fries migration of the acyl esters of rassacetophenone and other 4-substituted resorcinols having electron donating groups and found that the unusual \( \tau \)-position underwent substitution simultaneously with the \( \beta \)-substitution.

**MECHANISM**

There are different views regarding the mechanism of Fries reaction according to which it is considered as intermolecular or intramolecular. Three different mechanisms have been put forward for discussion and supported by several workers.

**First Mechanism**

This has been suggested by Skraup and Pollar (loc.cit.) and later supported by Cox (loc.cit.). They have assumed that the ester reacts with aluminium chloride to give a phenoxy aluminium chloride (a complex) and a free acid chloride (step A) followed by nuclear acylation of the former by latter (step B).
Step B should be considered to take path (2), as hydrochloric acid is evolved during reaction.

**Second Mechanism**

Rosenmund and Schnürr (loc.cit.) proposed the reaction to be intermolecular and bimolecular of the type in which 1 mole of the phenyl ester serves to acylate the second molecule. This mechanism has been supported by Ralston and co-workers (loc.cit.), Tarbell and Fanata (loc.cit.), Desai and Mavani (loc.cit.), Mustafa and Schonberg (loc.cit.).
The view that the Fries reaction is a true intramolecular rearrangement without the intervention of normal valency compounds as intermediates has been put forward by Fries and Wilt\textsuperscript{342} and supported principally by Auwers and Mauss\textsuperscript{343,344}. The acyl group is considered to shift directly from oxygen atom to the carbon atom of the ring.

![Chemical Structure](image_url)

Recently a new mechanism has been advocated and supported by Saharia and co-workers (Sharma, M.Sc. Thesis, Punjab Uni. 1954). It is based on the fundamental fact that aluminium chloride behaves as an acid because the aluminium atom in the molecule has got an incomplete octet. Its tendency to complete the octet is so great that even in the gaseous state it exists as a dimer. Aluminium chloride being an acid catalyst forms a complex with nucleophilic position in the case of simple esters at the phenoxyloxygen atom, which subsequently provides the reactive oxocarbonium ions and phenolate anions. These fragments further react to give the final products. That
the reaction is intermolecular and bimolecular has been recently shown by Desai and co-workers (loc.cit.) and also by Baltzly and Phillips\textsuperscript{345}, it has been shown that in the reaction, the formation of acid chloride is not necessary though it may be formed in abnormal cases.
The present investigation has been undertaken to prepare the hydroxy ketones from esters, particularly the optically active esters like: (+) phenyl-(2-methyl) valerate, (+) o-, m- and p-cresyl-(2-methyl) valerate and (+) o-, m- and p-chlorophenyl-(2-methyl) valerate so as to ascertain the mode of reaction mechanism. If the mechanism of reaction is followed by intramolecular, the hydroxy ketones obtained by the use of optically active starting material should result into optically active compounds. The optically active esters were obtained by condensation of different phenols like: phenol, o-, m- and p-cresols and o-, m- and p-chlorophenols with optically active (+) 2-methyl valeryl chloride $[\alpha]_D^{30} + 2.95$ (1,1), (Sec. III), and they were further subjected to Fries migration with anhydrous aluminium chloride under suitable experimental conditions.

\[
\begin{align*}
\text{R} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{CO.CH}_2\text{CH.CH}_2\text{CH}_3
\end{align*}
\]

and/or

\[
\begin{align*}
\text{R} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{CO.CH}_2\text{CH.CH}_2\text{CH}_3
\end{align*}
\]
The retention of optical activity confirms the bimolecular mechanism as well as intramolecular postulation.

None of the workers so far studied this mechanism by taking the use of optically active compounds and hence with the use of optically active esters, the above mechanism has been confirmed.

The experimental conditions, i.e., the reaction temperature and the reaction period was selected in such a way that only the desired product was obtained in good yields and with less impurities of any isomeric compounds.

The optical rotations of these ketones have been recorded in Table I and it was found in the following order:

In the case of ketones obtained from cresylic esters, the optical rotation of (+) 2-hydroxy 5-methyl ω : ω methyl ethyl propiophenone > (+) 2-hydroxy 4-methyl ω : ω methyl ethyl propiophenone > (+) 2-hydroxy 3-methyl ω : ω methyl ethyl propiophenone whereas in the case of ketones obtained from chloro phenolic esters, the optical rotation of (+) 2-hydroxy 5-chloro ω : ω methyl ethyl propiophenone > (+) 2-hydroxy 4-chloro ω : ω methyl ethyl propiophenone > (+) 2-hydroxy 3-chloro ω : ω methyl ethyl propiophenone. The optical rotation of (+) 4-hydroxy ω : ω methyl ethyl propiophenone was found to $[\alpha]_D^{32} + 2.61 (1,1)$. 
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of the Ketone</th>
<th>b.p. (°C/15-20 mm.)</th>
<th>Yield (%)</th>
<th>Density (g/cm³)</th>
<th>Refractive Index (nD)</th>
<th>Specific Rotation [α]D (1,1)</th>
<th>Molecular Rotation [β]D (1,1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4-Hydroxy ω : ω methyl ethyl propiophenone</td>
<td>160-165</td>
<td>58.6</td>
<td>0.9885</td>
<td>1.473</td>
<td>+ 2.61</td>
<td>+ 5.01</td>
</tr>
<tr>
<td>2.</td>
<td>2-Hydroxy 3-methyl ω : ω methyl ethyl propiophenone</td>
<td>195-200</td>
<td>45.3</td>
<td>0.9765</td>
<td>1.469</td>
<td>+ 2.03</td>
<td>+ 4.18</td>
</tr>
<tr>
<td>3.</td>
<td>2-Hydroxy 4-methyl ω : ω methyl ethyl propiophenone</td>
<td>180-185</td>
<td>72.8</td>
<td>0.9816</td>
<td>1.475</td>
<td>+ 2.46</td>
<td>+ 5.06</td>
</tr>
<tr>
<td>4.</td>
<td>2-Hydroxy 5-methyl ω : ω methyl ethyl propiophenone</td>
<td>220-225</td>
<td>61.1</td>
<td>0.9802</td>
<td>1.478</td>
<td>+ 2.78</td>
<td>+ 5.72</td>
</tr>
<tr>
<td>5.</td>
<td>2-Hydroxy 3-chloro ω : ω methyl ethyl propiophenone</td>
<td>200-205</td>
<td>53.2</td>
<td>0.9912</td>
<td>1.466</td>
<td>+ 1.95</td>
<td>+ 4.42</td>
</tr>
<tr>
<td>6.</td>
<td>2-Hydroxy 4-chloro ω : ω methyl ethyl propiophenone</td>
<td>208-212</td>
<td>58.6</td>
<td>0.9932</td>
<td>1.471</td>
<td>+ 2.66</td>
<td>+ 6.03</td>
</tr>
<tr>
<td>7.</td>
<td>3-Hydroxy 5-chloro ω : ω methyl ethyl propiophenone</td>
<td>215-220</td>
<td>64.0</td>
<td>0.9932</td>
<td>1.478</td>
<td>+ 2.91</td>
<td>+ 6.59</td>
</tr>
</tbody>
</table>
REACTIONS

(1) \( R = -\text{H (Phenol)} \)

(+ 4-Hydroxy \( \omega : \omega \) methyl ethyl propiophenone)
(2) \( R = \text{CH}_3 \) (o-Cresol)

\[
\begin{align*}
\text{CO.CH}_2.\text{CH.CH}.\text{CH}_3 \\
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\end{align*}
\]

(+) 2-Hydroxy 3-methyl \( \omega : \omega \) methyl ethyl propiophenone

(3) \( R = \text{CH}_3 \) (m-Cresol)

\[
\begin{align*}
\text{CO.CH}_2.\text{CH.CH}_2.\text{CH}_3 \\
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\end{align*}
\]

(+) 2-Hydroxy 4-methyl \( \omega : \omega \) methyl ethyl propiophenone

(4) \( R = \text{CH}_3 \) (p-Cresol)

\[
\begin{align*}
\text{CO.CH}_2.\text{CH.CH}.\text{CH}_2.\text{CH}_3 \\
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\end{align*}
\]

(+) 2-Hydroxy 5-methyl \( \omega : \omega \) methyl ethyl propiophenone
(5) \( R = -\text{Cl} \) (o-Chloro phenol)

\[
\begin{align*}
\text{CO.CH}_2\text{.CH.CH}_2\text{.CH}_3 \\
\text{OH CH}_3 \\
\text{Cl}
\end{align*}
\]

(+) 2-Hydroxy 3-chloro \( \omega : \omega \) methyl ethyl propiophenone

(6) \( R = -\text{Cl} \) (m-Chloro phenol)

\[
\begin{align*}
\text{CO.CH}_2\text{.CH.CH}_2\text{.CH}_3 \\
\text{OH CH}_3 \\
\text{Cl}
\end{align*}
\]

(+) 2-Hydroxy 4-chloro \( \omega : \omega \) methyl ethyl propiophenone

(7) \( R = -\text{Cl} \) (p-Chloro phenol)

\[
\begin{align*}
\text{CO.CH}_2\text{.CH.CH}_2\text{.CH}_3 \\
\text{OH CH}_3 \\
\text{Cl}
\end{align*}
\]

(+) 2-Hydroxy 5-chloro \( \omega : \omega \) methyl ethyl propiophenone.
EXPERIMENTAL
(1) (+) 4-Hydroxy \omega : \omega Methyl Ethyl Propiophenone

Into a 500 cc. round bottomed flask were placed anhydrous aluminium chloride (79.95 gm., 0.6 M) and nitrobenzene (100 cc.) and (+) phenyl (2-methyl) valerate \([\{\alpha\}^D_{20} + 2.95 (1,1) (57.6 gm., 0.3 M)]\) was added slowly during half hour at a temperature below 50°. The contents of the flask were heated on water bath at 70° for 6 hours. Next day the reaction mixture was decomposed by ice-cold hydrochloric acid (6 N) and extracted with ether. The ether extract was shaken with sodium hydroxide solution (3 N) and the aqueous layer was then acidified with the concentrated hydrochloric acid. The crude (+) 4-hydroxy \omega : \omega methyl ethyl propiophenone thus obtained was extracted with ether, dried (sodium sulphate) and the ether was removed by distillation. The residual ketone was purified by distillation under reduced pressure, b.p. 160-165°/15 mm., yield 58.6 %, \([\alpha]_{D}^{32} + 2.61 (1,1),
\)  \(d_{4}^{32} 0.9335, \ n_{30}^{20} 1.473.\)

Found : C, 72.31 %; H, 8.08 %

\(C_{12}H_{16}O_2\) required : C, 73.26 %; H, 8.33 %
(2) (+) 2-Hydroxy 3-Methyl \omega : \omega\text{ Methyl Ethyl Propiophenone}

Into a 250 cc. round bottomed flask was placed anhydrous aluminium chloride (120.15 gm., 0.9 M) and (+) o-cresyl (2-methyl) valerate \([\alpha]^3_{D} + 2.26 (\perp,1), 61.8\text{ gm., 0.3 M} \] was added slowly during half hour at a temperature below 50°. The reaction mixture was refluxed at 160-180° for half hour on oil bath and was completed as before to get (+) 2-hydroxy 3-methyl \omega : \omega\text{ methyl ethyl propiophenone, b.p. 195-200°/15 mm., yield 45.8 %,} \([\alpha]^3_{D} + 2.03 (\perp,1), \delta^4 0.9765, n^3 1.469.\]

Found : C, 75.21 %; H, 8.49 %
C_{13}H_{18}O_{2} required : C, 75.71 %; H, 8.738 %

(3) (+) 2-Hydroxy 4-Methyl \omega : \omega\text{ Methyl Ethyl Propiophenone}

The reaction was carried out as above by using anhydrous aluminium chloride (120.15 gm., 0.9 M) and (+) m-cresyl (2-methyl) valerate \([\alpha]^3_{D} + 2.84 (\perp,1), 61.8\text{ gm., 0.3 M} \] at a temperature 120-140° for one hour. The (+) 2-hydroxy 4-methyl \omega : \omega\text{ methyl ethyl propiophenone had b.p. 180-185°/15 mm., yield 72.8 %,} \([\alpha]^3_{D} + 2.46 (\perp,1), \delta^4 0.9816, n^3 1.475.\]

Found : C, 75.58 %; H, 8.56 %
C_{13}H_{18}O_{2} required : C, 75.71 %; H, 8.738 %
(4) (+) 2-Hydroxy 5-Methyl \(\omega:\omega\) Methyl Ethyl Propiophenone

Into a 250 cc. round bottomed flask containing anhydrous aluminium chloride (120.15 gm., 0.9 M) was added (+) p-Cresyl (2-methyl) valerate \([\alpha]_D^{30} + 3.02 (1,1),\) 61.8 gm., 0.3 M slowly during half hour at a temperature below 50° and the contents were heated on oil bath at 120° for half hour. The reaction was completed as above to get (+) 2-hydroxy 5-methyl \(\omega:\omega\) methyl ethyl propiophenone, b.p. 220-225°/15 mm., yield 61.1 %, \([\alpha]_D^{32} + 2.35 (1,1),\) \(d_4^{32}\) 0.9802, \(n_2^{32}\) 1.478.

Found: C, 75.53 %; H, 8.65 %

\(C_{13}H_{18}O_2\) required: C, 75.71 %; H, 8.738 %

(5) (+) 2-Hydroxy 3-Chloro \(\omega:\omega\) Methyl Ethyl Propiophenone

Into a 250 cc. round bottomed flask was placed anhydrous aluminium chloride (120.15 gm., 0.9 M). To this (+) o-Chloro phenyl (2-methyl) valerate \([\alpha]_D^{30} + 2.19 (1,1),\) 67.95 gm., 0.3 M was added slowly during half hour at room temperature. The reaction mixture was heated on an oil bath at 160-170° for two hours and was completed as above to get (+) 2-hydroxy 3-chloro \(\omega:\omega\) methyl ethyl propiophenone, b.p. 200-205°/15 mm., yield 53.2 %, \([\alpha]_D^{32} + 1.95 (1,1),\) \(d_4^{32}\) 0.9912, \(n_2^{32}\) 1.466.

Found: C, 63.12 %; H, 6.40 %

\(C_{12}H_{15}O_2Cl\) required: C, 63.54 %; H, 6.62 %
(6) (+) 2-Hydroxy 4-Chloro \( \omega : \omega \) Methyl Ethyl Propiophenone

The reaction was carried out as above by using anhydrous aluminium chloride (120.15 gm., 0.9 M) and (+) m-chloro phenyl (2-methyl) valerate \([\alpha]_D^{20} + 2.95 \, (1,1)\), 67.95 gm., 0.3 M \] at 120-130\(^\circ\) for two hours. The product then treated as before to get (+) 2-hydroxy 4-chloro : methyl ethyl propiophenone, b.p. 208-212\(^\circ\)/15 mm., yield 58.6 \%, \([\alpha]_D^{32} + 2.66 \, (1,1)\), \(d_4^{32} 0.9923\), \(n_32 1.471\).

Found : C, 63.05 %; H, 6.48 %

\(\text{C}_{12}\text{H}_{15}\text{O}_2\text{Cl}\) required : C, 63.54 %; H, 6.62 %

(7) (+) 2-Hydroxy 5-Chloro \( \omega : \omega \) Methyl Ethyl Propiophenone

Into a 250 cc. round bottomed flask containing anhydrous aluminium chloride (120.95 gm., 0.9 M) was added (+) p-chloro phenyl (2-methyl) valerate \([\alpha]_D^{30} + 3.27 \, (1,1)\), 67.95 gm., 0.3 M \] slowly during half hour at room temperature. The reaction mixture was heated on oil bath at 130\(^\circ\) for one hour and was completed as before to get (+) 2-hydroxy 5-chloro \( \omega : \omega \) methyl ethyl propiophenone, b.p. 215-220\(^\circ\)/15 mm., yield 64.0 \%, \([\alpha]_D^{32} + 2.91 \, (1,1)\), \(d_4^{32} 0.9932\), \(n_32 1.478\).

Found : C, 63.23 %; H, 6.51 %

\(\text{C}_{12}\text{H}_{15}\text{O}_2\text{Cl}\) required : C, 63.54 %; H, 6.62 %.