CHAPTER I
CHLORINATION OF AROMATIC COMPOUNDS

Chlorination essentially consists in the introduction of one or more chlorine atoms in a molecule of an organic compound. This may take place either by addition or substitution reaction or by replacement of any functional group present in the molecule. In general, chlorination is an exothermic reaction. The heat of reaction ($\Delta H$) in substitutive chlorination is of the order of $-23000$ to $-27000$ cals. regardless of the nature of the compound.

Preparative methods of chlorination, generally fall into three main classes. In the first class, molecules of halogens or any other neutral species themselves act as electrophilic reagents. These reagents are most useful for chlorination in the aromatic nuclei which are already activated by electron donating substituents. These activating substituents direct the entering group (chlorine) almost exclusively to the ortho- and para-positions, the former predominating. The second class deals with chlorination of aromatic compounds of reactivity similar to or less than that of benzene; here, the molecular species of halogens reacts rather slowly and usually, it is convenient to employ a "carrier" or a catalyst. The third class comprises methods which involve positively charged chlorinating species. It has been recently elaborated that a positive chlorine can be supplied under non-oxidizing conditions (e.g. in concentrated $H_2SO_4$, with silver sulphate to remove any hydrogen halide liberated). The conditions are conducive to heterolytic reaction and facilitate the chlorination of otherwise quite unreactive compounds.
Chlorinating agents

Molecular chlorine is one of the most commonly used neutral chlorinating agent, especially as a solution in a reasonably polar organic solvent. In this form it rapidly attacks aromatic compounds which are more reactive than toluene. Such compounds, usually contain ortho-para-directing substituents and the product is a mixture of ortho- and para-chloro-isomers. From a preparative angle, these reactions are useful in special structural situations where only one isomer is possible, or alternatively, when the required component can readily be separated from the reaction mixture. Acetic acid is one of the most convenient and commonly used solvent, e.g. in the preparation of 3-chloro-2,6-dimethylacetanilide. Orton and Bradfield have discussed the kinetics of chlorination with molecular chlorine in solutions which are nearly anhydrous. Here, chlorine is the effective electrophilic reagent. The rate of chlorination of phenolic ethers and of anilides in 99 per cent acetic acid has been shown by these authors to be governed by:

\[ -\frac{d(C_1_2)}{dt} = K_2(\text{ArH})(C_1_2) \]

The second-order rate-coefficient $K_2$ has been shown to be little affected by the addition of hydrogen chloride. Robertson et al. studied the effect of electrolytes like perchloric acid, sulphuric acid, hydrogen chloride, sodium acetate, etc., on the rates of chlorination of naphthalene and of meta-xylene in anhydrous acetic acid and found that all of them accelerate the reaction to a small extent. The extent of catalysis is reasonably closely related to the degree of
ionization of these electrolytes. Their results perfectly agree with the view that the molecular chlorine is formed as the intermediate. The little catalytic effect of the electrolytes or increase in the rate of reaction on addition of water to the solvent, probably results from the fact that the transition state for the reaction involves polarization of molecules of both chlorine as well as of aromatic compound. The transition state is, therefore, more polar than the starting materials, and the reaction is facilitated by an increase in the ionizing power of the environment\(^3,6,7\). Kinetics of chlorination by molecular chlorine in other solvents (e.g. nitrobenzene, chloroform) has been studied by Roberts and Soper\(^8\) shown to be in the following form: \(\frac{-d(Cl_2)}{dt} = k(ArH)(Cl_2)\). No further details of the reaction have been established.

Catalysts which promote nuclear substitution in the benzene ring are generally used when the substances have lesser reactivity than toluene. These catalysts include ferric chloride, aluminium chloride, chlorides of other metals\(^9-11\), iodine\(^12\) and pyridine etc. The mode of their action differs considerably in details and is not known with certainty, except that they polarise the interhalogen bond at some intermediate stage of the reaction. Use of such catalysts minimises homolytic processes, which, otherwise, often supervene when the reaction mixture is irradiated or the aromatic compound simply contains an alkyl group. The preparation of meta-chlorobenzoyl chloride from benzoyl chloride\(^13\) illustrates the action of FeCl\(_3\) in the chlorination. Here, the substitution takes place in the meta-position due to the deactivating influence exercised by the acid
chloride group and the other two isomers are only obtained in small quantities. In the chlorination of naphthalene, the catalytic activity of antimony, iron, aluminium chlorides and alumina have been reported in the decreasing order. Iodine in combination with iron has been used as a powerful catalyst for the rapid chlorination of nitrobenzene, ortho- and para-nitrotoluenes and para-chloronitrobenzene. Chlorination can be carried out at lower temperatures with this catalyst and the reaction is so fast that external cooling is necessary. Mixtures of sulphur, antimony trichloride and lead have been mentioned as catalysts for the chlorination of benzene and naphthalene. It has also been pointed out that heat and light cause the chlorine molecule to become dissociated into chlorine atoms. Active carbon has been used in chlorination as a catalyst but its action can also be interpreted as the effect of the increased surface area.

A positive chlorine has been shown to be the reactive entity in several chlorination reactions, e.g. the electrophilic chlorinating agent is positive in the case of hypochlorous acid in presence of aqueous mineral acid. Under these or analogous conditions, the positive entity is available in situ and plays a special preparative role. Relatively unreactive compounds can be chlorinated in this way and the chlorination of p-nitrotoluene to yield 2-chloro-4-nitrotoluene can be cited as an example. Through a study of kinetics of chlorination of sodium toluene-sulphonate, benzene and toluene with hypochlorous acid in aqueous solution, it has been suggested that the reaction proceeds through one of the following mechanisms:
(a) where hypochlorous acidium ion is the active chlorinating agent.

\[ \text{ClOH} + \text{H}^+ \rightleftharpoons \text{ClOH}^+ \]
\[ \text{ClOH}^+ + \text{ArH} \rightarrow \text{products} \]

(b) where the hypochlorous acidium ion is further in equilibrium with chlorinium ion (\( \text{Cl}^+ \)) and the latter is the reactive entity.

\[ \text{ClOH}^+ \rightleftharpoons \text{Cl}^+ + \text{H}_2\text{O} \]
\[ \text{Cl}^+ + \text{ArH} \rightarrow \text{products} \]

Work with more reactive substances e.g., anisole\(^{23}\) has led to the conclusion that under the same conditions, the rate of such chlorinations is limited by the rate of fission of the hypochlorous acid or the hypochlorous acidium ion into the chlorinium ion.

\[ \text{ClOH} \rightarrow \text{Cl}^+ + \text{OH}^-; \quad \text{ClOH}^+ \rightarrow \text{Cl}^+ + \text{H}_2\text{O} \]

Evidence in favour of \( \text{Cl}^+ \) acting as an intermediate in these chlorinations was given by Swain & Ketley\(^{24}\) by measuring the rate of reaction in \( \text{D}_2\text{O} \). However, thermodynamic calculations\(^{25}\) have come in the way of universal acceptance of the hypothesis that \( \text{Cl}^+ \) is the effective intermediate in these reactions. These calculations do not favour the formation of \( \text{Cl}^+ \). It may also be pointed out that the analogies drawn while assigning the energy and entropy of solvation of these ions may not be based on very sound comparisons.

\( \text{N-chloroamides} \) or anilides have been used as source of chlorine. Orton & coworkers\(^{5,26}\) have made use of this elegant method of chlorination.
Though the reaction $R_2NC\text{I} + HCl \rightleftharpoons R_2N\text{H} + Cl_2$ is a reversible one, the forward reaction is usually rapid and the equilibrium lies so far to the right that this process can be considered to be practically irreversible. The amount of hydrochloric acid controls the amount of chlorine; the former is kept constant by regeneration in the actual chlorination of the aromatic compound. Thus, employing a catalytic amount of $HCl$, the standing concentration of both chlorine and acid can be kept to a minimum. This method has a special preparative value when highly reactive and readily oxidisable organic compounds are to be chlorinated, such as, aromatic amines, phenols and their derivatives, etc. Since aromatic chlorinating agents falling in this group can replace, not only the aromatic hydrogen but also the hydrogen of $OH$, $NH_2$ or $NHR$ groups, the corresponding classes of positively charged species also exist, e.g.,

$$ClO^+HR, ClN^+H_2R, Cl^+NHR_2, ClN^+R_3$$

these can, in principle, act as electrophilic chlorinating agents.

Hence, chlorine or hypochlorous acid in presence of hydroxylic solvent or an amine can lead to the existence of the following type of equilibrium:

$$ClOH + HOAc \rightleftharpoons ClOAc + H_2O$$

$$ClOAc + H^+ \rightleftharpoons ClOHAc^+$$

This complicates interpretation of chlorination process in mixture of acetic acid and water and there is evidence to show that the above mentioned equilibria are important in the system$^{27,28}$. The fact that
pyridine and other tertiary amines act as powerful catalysts for chlorination suggests that the ions of the type $\text{PYCl}^+$ formed by the equilibria shown in the following equation may be the effective chlorinating agent:

$$\text{Py} + \text{Cl}_2 \rightleftharpoons \text{PyCl}^+ + \text{Cl}^-$$

Brown and Sopper's work on the reaction of diethylchloramine with phenol has shown that the reactants in this case are the ions.

$$\text{R}_2\text{NHCl} + 0\text{Ar}^- \rightarrow \text{Chlorinated product}$$

*N-chlorosuccinamide* has also been used in chlorination of reactive aromatic compounds though orientation in these chlorinations is not the same as that found with other chlorinating agents.

Sulphuryl chloride either alone or in presence of a catalyst, like aluminium chloride has been used as a chlorinating agent for aromatic hydrocarbons, phenols and its derivatives, aliphatic hydrocarbon etc. Brown has discussed the versatility and potentialities of sulphuryl chloride in organic synthesis. The simplicity of the reaction, high yields and ease of control have made this reagent an important industrial raw material.

ter-Butylhypochlorite and other esters of hypochlorous acid have also been employed as chlorinating agents for many organic compounds, the nature of the species responsible for chlorination depending on the reactivity as well as the conditions of chlorination. For example, chlorination of methylene group in allylic systems, and of methyl group...
in toluene and substituted toluenes\textsuperscript{35} by \textit{ter}-butylhypochlorite has been shown to involve an attack by chlorine atoms. Olefins react with this reagent in acidic or neutral aqueous solution to form chlorohydrins\textsuperscript{36,37} and in alcoholic solution to form chlorohydrin ethers. These reactions are analogous to two-stage ionic addition of molecular chlorine in these solvents\textsuperscript{38}. The reaction of \textit{ter}-butylhypochlorite with benzenoid compounds, however, neither involves atomic nor molecular chlorine. \textit{Ortho}- and \textit{para}-chlorotoluene are obtained in the ratio of 3:2 on chlorination of toluene with molecular chlorine\textsuperscript{39} whereas the former\textsuperscript{40} alone is obtained in 93\% yield in the reaction of toluene with \textit{ter}-butylhypochlorite. Likewise, anisole and phenol\textsuperscript{41} give \textit{ortho}-chloroderivatives with \textit{ter}-butylhypochlorite in yields of 87\% and 94\%, respectively, as compared to the respective yields of 21\%\textsuperscript{42} and 50\%\textsuperscript{43} obtained in their reaction with molecular chlorine.

In these reactions, chlorinium ion is the reactive species, the formation of which has been recently explained by Norman et al.\textsuperscript{44} in hydroxylic solvents.

\[
\text{Bu}^+\text{O.Cl} \xrightleftharpoons{H^+} \text{Bu}^+\text{O}^+ \xrightarrow{H} \text{Bu}^+\text{OH} + \text{Cl}^+
\]

Homolytic processes involving halogen atoms have not proved very useful for substitution reactions in aromatic systems. Instead, addition reaction is often the preferred course. In such chlorinations of aromatic compounds having alkyl side-chains, side-chain chlorination products are often formed, unless light is rigorously excluded. Under certain conditions, either in presence of peroxides or when the reaction is carried out at elevated temperatures, the side chain chlorination is the predominant or even the exclusive process.
Chlorination of aromatic compounds can be envisaged under alkaline conditions; however, the available reagents for such processes are limited. Hypochlorous acid has acidic dissociation constant in the region of $10^{-8}$ to $10^{-9}$, and can exist in reasonable concentrations as the free molecular species under alkaline conditions. However, it has been shown to be unreactive with anisole\textsuperscript{45}. It nevertheless, halogenates phenoxide ions and tertiary amines\textsuperscript{46}.

**STRUCTURAL EFFECTS OF CHLORINATION**

Chlorination of benzene derivatives is explained satisfactorily by qualitative electronic theory. Furthermore, chlorination studies have provided a sensitive method for investigating and clarifying the nature of electronic movements which occur during these electrophilic substitutions. The data in literature are scattered and restricted in most cases to reaction under preparative conditions. Some of the more significant comparisons available for mono-substituted benzenes are given in Table I.

Available data regarding the orientation in the chlorination of disubstituted benzenes are collected in Table II. The general pattern of orientation is similar to that found in nitration and fits well with qualitative electronic theory of organic chemistry. A qualitative observation has also been recorded that when ortho-, para-directing groups are meta- to each other, electrophilic substitution often occurs between them\textsuperscript{2}. To support this observation, the example of chlorination of meta-hydroxybenzaldehyde\textsuperscript{64} and of meta-nitrophenol can
Table I - Isomers distribution in chlorination of mono-substituted benzenes with molecular chlorine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Directing substituent</th>
<th>Isomers, per cent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>OH</td>
<td>50 - 50</td>
<td>47</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>NHCOCH₃</td>
<td>30 - 70</td>
<td>5</td>
</tr>
<tr>
<td>Anisole</td>
<td>OCH₃</td>
<td>21 - 79</td>
<td>48, 42</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>C₆H₅</td>
<td>ca. 30 - ca. 50</td>
<td>49, 50, 51</td>
</tr>
<tr>
<td>Toluene</td>
<td>CH₃</td>
<td>59.8 - 39.7</td>
<td>52, 53</td>
</tr>
<tr>
<td>tert-Butylbenzene</td>
<td>(CH₃)₃-C</td>
<td>(74.7) - (23.1)</td>
<td>52, 53</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>F</td>
<td>- - ca. 90</td>
<td>54</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Cl</td>
<td>39 - 55</td>
<td>47, 54, 55</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>Br.</td>
<td>42 - 52</td>
<td>47, 54, 55</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>COOH</td>
<td>- ca. 100 -</td>
<td>55, 56</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>NO₂</td>
<td>1 - 95 - 4</td>
<td>55, 57, 58</td>
</tr>
</tbody>
</table>

1. Chlorination of bromobenzene is catalysed by metallic halides
2. Values in ( ) are for chlorinium ion (Cl⁺)
3. In most cases in which the absence of isomer is indicated, component is not sought exclusively.
Table II - Influence of directing groups of disubstituted benzenes in chlorination

<table>
<thead>
<tr>
<th>Group</th>
<th>Aromatic compound</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| (1)   | ![Aromatic Compound](image) | (3) 58, 59 | Illustrates dominance of 
\(\text{NH}_2\) and \(\text{OH}\) and derived groups over less powerfully ortho-, para-directing substituents |
<p>| A     | (X = \text{NH}_2, \text{NMe}_2, \text{NHAc}, \text{NH}_2\text{SO}_2\text{Ac}, \text{OH}, \text{OMe}, \text{OPh}) | | (R = \text{Ph, Alkyl, Halogen, or meta-directing groups}) |
| (2)   | <img src="image" alt="Aromatic Compound" /> | | |
| B     | (R = \text{Halogen, Alkyl, OMe, OH, NHAc, NH}_2, \text{NMe}_2.) | (3) 58, 61 | Illustrates that an ortho-, para-directing substituent usually takes control over meta-directing substituents |</p>
<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Methyl and Chlorine Similarity" /></td>
<td><img src="image2" alt="OEt and NHAc Comparison" /></td>
<td>Illustrates that methyl and chlorine are similar in directing power</td>
<td>60</td>
</tr>
<tr>
<td><img src="image3" alt="OEt Dominance" /></td>
<td><img src="image4" alt="Cl and NR2 Transition" /></td>
<td>Illustrates apparent dominance in directing power of OEt over NHAc contrast nitration</td>
<td>62</td>
</tr>
<tr>
<td><img src="image5" alt="Nitration Dominance" /></td>
<td><img src="image6" alt="Cl and NR2 Transition" /></td>
<td>Illustrates the dominance of NH₂ and related groups over OMe, OEt etc</td>
<td>62, 63</td>
</tr>
</tbody>
</table>

R = Me, Et, etc;
R¹ = H, Me, Et.
be cited. It has been suggested that the mesomeric effect of the electron withdrawing group favours structures as given below:

\[
\begin{align*}
\text{OH} & \\
\text{N}^+\text{O}^- & \\
\text{O}^- & 
\end{align*}
\]

This type of orientation is seldom exclusive and by no means always dominant as is apparent in the cited examples in Table II.

**CHLORINATION OF PHENOLS AND CRESOLS**

Chlorination of phenol and all the three cresols is known for a long time. Properties and methods of preparation of all possible isomeric chlorophenols and chlorocresols are well documented by Huntress. This literature is not discussed in detail here. Direct substitutive chlorination of phenol and cresols with electrophilic reagents like molecular chlorine, sulphuryl chloride etc., generally introduces chlorine at positions where electron densities are increased due to hydroxy substituents i.e. ortho- and para-positions. Thus, ortho-chloro, 2,4-dichloro and 2,4-6-trichlorophenols etc., have been prepared by direct chlorination methods. Extent of chlorination and yields of compounds are generally dependent on the nature of chlorinating agents, experimental conditions, solvents etc. The reaction of molecular chlorine with phenol with or without a solvent, gives monochloro-, and 2,4-dichlorophenol. Further chlorination leads to
2,4,6-trichlorophenol. Imamura worked out conditions of stepwise chlorination of phenol with chlorine gas employing ferric chloride, iron, aluminium chloride, antimony chloride and antimony as catalysts for preparation of mono-, di-, tri, tetra- and penta-chlorophenols. Para-chlorophenol is obtained by chlorination of phenol with sulphuryl chloride using stoichiometric quantity of the latter, whereas chlorination of phenol with tert-butylhypochlorite in hydroxylic solvent has been reported to yield ortho-chlorophenol as major component. Recently, Campbell et al. have studied the effect of solvent on mechanism of chlorination of ortho-cresol. The ratio of 4-chloro-o-cresol : 6-chloro-o-cresol produced has been correlated with the phenomenon of steric hindrance. Anomalous high yields of 4,6-dichloro-o-cresol in polar solvents at low temperatures, have been explained in terms of hydrogen bonding involving the aromatic -electron of ortho-cresol. Rosen et al. carried out a study of addition-chlorination of phenol. Normally, a benzene derivative like phenol undergoes substitution chlorination only, due to presence of strong electron-releasing group, like hydroxyl. These authors modified this property of the hydroxy group by attaching electron-withdrawing group to the oxygen atom and thus readily explained addition-chlorination to give 1, 2, 3, 4, 5, 6-hexachloro-cyclohexyl trichloroacetate (II). The structure of (II) was established as it gave 2,4,6-trichlorophenols (VI) on acid hydrolysis. The proposed sequence of reactions indicated below:
CHLORINATION OF XYLENOLS

Chlorination of xylenols has not been so far exhaustively studied. It might be due to the fact that indirect preparative methods have to be applied for synthesis of specific chloroxylenols. Lesser and Gad\textsuperscript{76} chlorinated 3,5-xylenol with sulphuryl chloride in chloroform and reported the formation of 2-chloro-3,5-xylenol in addition to 4-chloro-3,5-xylenol. They also commented that sulphuryl chloride is not a \textit{para-}chlorinating agent\textsuperscript{77} only. When chlorination was carried out further they obtained a dichloro-isomer. They surmised that phenols with negative substituent \textit{ortho-} to hydroxyl and with the \textit{para-}position blocked, do not get chlorinated with sulphuryl-chloride. According to them, the following phenols did not respond to chlorination by this reagent:

\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{VII} & \quad \text{VIII} & \quad \text{IX} \\
\text{Cl} & \quad \text{NH}_2 & \quad \text{H}_3\text{C} \\
\text{OH} & \quad \text{NO}_2 & \quad \text{CH}_3 \\
\text{Cl} & \quad \text{NO}_2 & \quad \text{Cl} \\
\text{X} & \quad \text{XI} & \quad \text{XII}
\end{align*}

Later Jones\textsuperscript{78} obtained 2,4-dichloro-3,5-xylenol (DCMX) from 4-chloro-3,5-xylenol (PCMX) by chlorination with N-chloroacetamide applying the Orton and Kings\textsuperscript{26} method and reported its melting point as 83° C., later corrected by Gamell\textsuperscript{79} as 94-95° C. The wrong reporting of melting point by Jones\textsuperscript{98} has created a confusion in the literature, and has led Huntress\textsuperscript{65} to classify the dichloro-isomer obtained by Lesser and Gad\textsuperscript{76}
to be 2,6-dichloro-3,5-xylenol. On the basis of Gamell's work, it can be taken that 2,6-dichloro-3,5-xylenol is not known. Lockemann and Kuzmann chlorinated 2,3-, 3,4-, 3,5- and 2,5-xylenols with sulphuryl chloride in acetic acid. Their results were corrected by Heicken, who also published the bactericidal action of chloroxylenols. Interesting results have been published by Mueller & Linde on the action of gaseous chlorine on 2,5- and 3,5-xylenols. Action of chlorine on 3,5-xylenol (XIII) in aqueous dispersion at 0° C. yielded 2,4,4,6-tetrachloro-3,5-dimethylcyclohexa-2,5-dien-1-one (XIV)

\[
\begin{align*}
\text{XIII} & \xrightarrow{\text{aq } 0^\circ C; \text{Cl}_2} \text{XIV} \\
\text{XIV} & \xrightarrow{\text{hot water}} \text{XVI}\end{align*}
\]

along with a small quantity of hypochlorite of 2,4,6-trichloro-3,5-xylenol (XV), which according to authors is the tautomeric form of (XIV). At higher temperatures in presence of acetic acid, the product was 2,6-dichloro-3,5-dimethyl-p-benzoquinone (XVI). In addition, a molecular compound (XVII) of the following structure containing 2-molecules of 2,4,6-trichloro-3,5-xylenol and one molecule of 2,6-dichloro-3,5-dimethyl-p-benzoquinone was also isolated.
Chlorination of 2,5-xylenol under similar conditions, instead of yielding the expected tri- or tetrachloro-derivatives, gave pentachloro-compound, 2,3,4,5,6-pentachloro-2,5-dimethyl-5-cyclohexanone-1-one (XIX) and an oil. On longer standing, the oily by-product gave a pentachloro-compound; this on reduction, yielded 4,6-dichloro-2,5-xylenol (XXI) and the pentachloro-compound was assigned a structure 2,3,4,5,6-pentachloro-2,5-dimethyl-cyclohexane-4-one-1 (XX). They concluded that in general, in phenols where ortho- and para-positions are free, as in phenol, meta-cresol and 3,5-xylenol, prolonged chlorination in aqueous acidic medium leads to 90 to 100% quinone formation. This can lead one to conclude that only the para-dichlorocyclohexadien-one compound is formed as a major intermediate. In xylenols where ortho-, and para-positions are partially or fully occupied, the chlorinated quinones are found in lower yields because the intermediate ortho-chloro compound is not hydrolysable to give a quinone (cf. 2,5-xylenol).

Indirect methods have been frequently employed to prepare
mono-, di-, and trichloro-xylenols to and these are exemplified below:

(a) from the corresponding amino-dimethylphenol via diazotisation and reaction with cuprous chloride.

(b) from dinitroxylene

(c) replacement of sulphonic group by chlorination

It has been found that when a current of chlorine gas is introduced in an aqueous solution of sulfonic acid, the sulphonic group is detached with the simultaneous production of the corresponding chloro-derivative.

(d) conversion of hydroaromatic to aromatic compounds

Chloro-dimethylidihydroresorcinol (XXIX) on reacting with
phosphorus pentachloride gives a chloroxylenol (XXXIII). The mechanism of formation of chloroxylenol is shown below:
STATEMENT OF PROBLEM - STUDIES ON CHLORINATED XYLENOLS

It would be apparent from the preceding review that chlorination of xylenols has not been adequately investigated. In particular the direct chlorination of xylenols has not received much attention and published work in this direction has been limited and scattered. Hence, a systematic study of chlorination of xylenols was undertaken as the major objective. Chlorination of four available xylenols viz., 2,5-, 2,3-, 3,5- and 3,4-xylenols was carried out with (a) gaseous chlorine, (b) sulphuryl chloride, and (c) tert-butylhypochlorite. Search for suitable methods for identification of the products of chlorination, especially when present in mixtures, led to a study and development of paper-chromatographic separation of chlorophenols, chlorocresols and chloroxylenols. These results have yielded interesting theoretical correlations based on Martin's equation. The paper-chromatographic technique, however, was found time-consuming and not suitable for studying the progress of the various chlorination procedures. A better method was found in the application of thin-layer chromatography (TLC). Since, hardly any data were available on the TLC of chlorophenols as a class, a systematic investigation of the separation of chlorophenols, chlorocresols and chloroxylenols by the TLC procedure was also included as an important aspect in this study. The work also led to development of a quick method for quantitative estimation of chloroxylenols. So far as the author is aware, quantitative TLC technique has not hitherto been applied to this class of compounds.
Apart from the HLC method, other available physical tools which are normally employed in understanding chemical structures and reactions namely UV, IR, and NMR spectroscopy, have also been utilised wherever necessary. Interesting correlations arrived at from these spectral data are discussed at appropriate places in this thesis. The behaviour of the chlorophenols in gas-liquid chromatography (GLC) was also examined but the results were not very encouraging or particularly useful in respect of these compounds. Hence only a preliminary account of the GLC work is included.

Since, chlorinated xylenols, especially 2,4-dichloro-3,5-xylenol (DCMX) is a commercial product of high disinfectant activity, a relative evaluation of disinfectant activity of various other chloroxylenols and its relation to structural features was considered interesting. The results obtained in this study prompted, further, only from a commercial angle, chlorination of mixtures of tar acids (predominant in xylenols and their evaluation for Riedel-Walker Coefficient (RWC) has also been included. For this purpose, tar acid fractions, obtained as definite cuts in the fractionation of phenolic by-products of the low-temperature carbonisation plant (l.t.c.) working at the Regional Research Laboratory, Hyderabad, (25 tonne/day) were available.
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