PREFACE
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Chloroxylenols, like 4-chloro-3,5-xylenol (PCMX) and 2,4-dichloro-3,5-xylenol (DCMX) are well-known active ingredients used in the manufacture of antiseptic and disinfectant formulations. The source of primary xylenols for the manufacture of these agents is usually the tars obtained in the coal carbonisation industry. The Regional Research Laboratory, Hyderabad, where the present work has been carried out is operating an experimental prototype low temperature carbonisation (l.t.c.) plant (25 tonne/day) of the Lurgi Spuelgas type with the following broad ends in view:

(a) to help establishment of l.t.c. industry in the country to meet the basic demand of smokeless fuel from otherwise low grade coals;

(b) to carry out experiments in by-product recovery, processing and utilisation since the economics of larger plants is closely linked with utilisation of various by-products of coke production.

The present work is a part of the overall programme of utilisation of the tar acid fractions from the l.t.c. tars. L.t.c. of Singareni coals (high ash, low grade, non-caking, meta-ligniteous coals) yields tars which contain about 30% of tar acids, of which about 2.5% consist of cresols and about 3% of xylenols. One obvious outlet for utilisation of tar acid fractions is the isolation of pure xylenols and their conversion into useful, known and new chloro-compounds.
of high disinfectant activity. Chlorination of xylenol-rich fractions of tar acids by industrially feasible methods, can also yield commercially useful products. A study of available literature brought out the fact that chlorination of xylenols has not been adequately reported except its mention in patent literature. As a prelude to industrial utilisation of xylenols or xylenol-rich fractions of the tar acids, a systematic study of chlorination of xylenols is necessary and this was undertaken as the major objective for the present work. The investigation was expected to fulfil the following objectives:

(a) to arrive at industrially feasible methods of preparation of some chloro-xylenols;

(b) to know the behaviour of xylenols to various chlorinating agents;

(c) to study and compare the spectral data (UV, IR & NMR) of the chloroxylenols. It may be mentioned that this aspect is not at all covered in the available literature though, chloroxylenols have been known for quite some time.

(d) To establish analytical chromatographic separation techniques of the various products;

(e) to test the bactericidal activity of the chloroxylenols and of chlorinated tar acid fractions rich in xylenols, and attempt to find out structural relationships to disinfectant activity.
For this study, four commercially available xylenols viz. 2,5-, 2,3-, 3,5- and 3,4-xylenols and definite cuts of the tar acid fractions obtained in the l.t.c. plant mentioned earlier, formed the raw materials. The following three chlorinating agents were chosen:

(a) **gaseous chlorine** - it is a cheap and industrially available chlorinating agent;

(b) **sulphuryl chloride** - it is a widely used and industrially available chlorinating agent,

(c) **ter-butylhypochlorite** - it is described as principally an ortho-chlorinating agent in contrast to gaseous chlorine and sulphuryl chloride.

For convenience, presentation and discussion of the results have been divided into several chapters.

The first chapter begins with a discussion on chlorinating agents in use for benzenoid compounds, use of catalysts or carriers and mode of action of these agents. This is followed by a summary of orientation effects of the various substituents in an aromatic ring on the course of chlorination. Also included, is a critical review giving the present state of knowledge on chlorophenols as a class. The chapter is concluded by a statement in detail of the problem chosen for the dissertation.

The second chapter presents the results obtained in chlorination of the four xylenols with three different chlorinating agents. The progress of reactions was followed by the TLC technique and the
products characterised by chemical and physical methods. Convenient preparative routes are described to obtain 4-chloro-2,5-xylenol and 4-chloro-2,3-xylenol in good yields. 4,6-Dichloro-2,3-xylenol has been obtained now for the first time and its structure verified by UV, IR and NMR. The behaviour of 3,4-xylenol towards these chlorinating agents stimulated considerable interest. Here, besides the expected chloroxylenols, non-phenolic oxidation products are also formed. The latter have been separated chromatographically and identified by chemical and spectral means. A theoretical explanation involving chlorinium ion (Cl+) as the reactive entity is advanced to explain these results.

One of the most useful and widely employed modern tools in research is chromatography in its various forms, particularly paper, column, thin-layer and gas-liquid. However, except a few reports on paper chromatography of some chlorocresols, chromatography has not so far been applied to study of chlorocresols and chloroxylenols. Considerable attention was paid to application of chromatographic procedures to study these compounds and the results are presented in the third chapter. Particular mention may be made of the development of a quantitative TLC procedure and standardisation of conditions designed to achieve the best results. For paper chromatography, formamide-impregnated papers, xylene-saturated with formamide as solvent system and the descending technique were found to give a good combination. Spots were well-defined. Rf values were sensitive to experimental conditions and rigid adherence to experimental conditions
was found necessary to obtain reproducible results. Plotting \( R_m \) values against number of carbon or chlorine atoms indicated that the partition phenomenon was responsible for chromatographic separation with polar solvent systems. With non-polar solvents, influence of adsorption phenomenon becomes noticeable in these separations.

The fourth chapter contains spectroscopic data of the chlorocresols and chloroxylenols. Ultraviolet, IR and NMR spectral data are presented and discussed. In the UV-study, an attempt has been made to correlate structure of these chlorophenols in terms of bathochromic or hypsochromic effects in the absorption bands. From a study of the infrared spectra of different chloroxylenols, it has been possible to assign characteristic CH deformation and C-Cl stretching absorption bands in the 650–900 cm\(^{-1}\) region. This may be of use in their identification. The hydroxyl absorption bands in the 3615–3530 cm\(^{-1}\) region reveal differences in the types of free and intramolecular bonds in the various compounds examined. These differences may be utilised in fixing the position of chlorine in the aromatic nucleus. The NMR spectra of most of the chlorocresols and chloroxylenols have been obtained and spectral absorption assignments made; convincing proof of structure of the compounds is provided.

The last chapter discusses the results obtained for the bactericidal activity of chloroxylenols against \( S\)-typhi, both as active ingredients and as formulations. It depicts the broad correlation between chemical structures and bactericidal values and brings out
the potentiality of the hitherto unknown 4,6-dichloro-2,3-xylenols as an active bactericidal agent of commerce.

The results obtained with chlorinated tar acid mixtures indicate that these possess sufficient bactericidal activity. Since these would be cheaper to produce, the products would have great economic potentiality.