SYNOPSIS

This thesis is brought out by undertaking investigations in the laboratory of the Chemistry Department of the University of Gauhati, during the period 1970-1974. Syntheses of O-mercaptoazo compounds and studies on their reactions date back only to 1950 and A. Burawoy credited to himself the honour of being the first initiator of this task in the University of Manchester. Comparatively only a few O-mercaptoazo compounds have so far been synthesised and their reactions studied as far as possible in detail. With a view to extend this work, a series of new sulphenyl derivatives of O-mercaptoazo compounds have been synthesised and their reactions studied to correlate their differences or similarities, if any, with other sulphenyl derivatives of O-mercaptoazo compounds wherever possible.

The work incorporated in the thesis has been divided into three main sections — Historical Part, Theoretical Part and Experimental Part.

The historical part relates to various difficulties encountered at the initial stages of undertaking this task of preparing the O-mercaptoazo compounds as well as the methods leading to successful syntheses of many of them. Discussions
on the preparation and properties pertaining to the similarities or differences of various other sulphenyl halides with these compounds are also incorporated in this section.

The theoretical part includes the description of the syntheses and the reactions of the O-mercaptoazo compounds newly synthesised in this laboratory and an attempt has been made to see the similarities or differences in behaviour of these compounds with other O-mercaptoazo compounds where possible. Electronic absorption spectra of the sulphenyl derivatives in the U.V.–Visible region have also been incorporated.

The third section is devoted to the description of the experimental details of the sulphenyl derivatives of O-mercaptoazo compounds synthesised in this laboratory the brief account of which is presented as follows:

A. Preparation and debenzylation of 2-methylazobenzene-2'-benzyl sulphide.

1. 2-Methylazobenzene-2'-benzyl sulphide (I) is prepared by condensing O-nitrosotoluene with O-benzylthiocianiline in glacial acetic acid.

\[
\begin{align*}
\text{CH}_3 & \quad \text{N}^+\text{H}_2\text{N} \\
\text{S-CH}_2\text{-C}_6\text{H}_5 & \quad \rightarrow \\
\text{CH}_3 & \quad \text{N}^=\text{N} \\
\text{S-CH}_2\text{-C}_6\text{H}_5 & \quad (I)
\end{align*}
\]
2. 2-Methylaminobenzene-2'-benzyl sulphone is effected debenzylation with one mole of bromine in acetic acid to yield 2-methylaminobenzene-2'-sulphonyl bromide (II).

3. 2-Methylaminobenzene-2'-sulphonyl chloride, iodide, perchlorate, thiocyanate and cyanide (III) are prepared by double decomposition reactions of 2-methylaminobenzene-2'-sulphonyl bromide with concentrated hydrochloric acid, potassium iodide, perchloric acid, potassium thiocyanate and potassium cyanide respectively.

(where M = K, or H;
X = Cl, I, ClO₄, SCN, CN)
B. Action of 2-methylbenzene-2'-sulphenyl bromide on carbon acids.

(a) Reactions of 2-methylbenzene-2'-sulphenyl bromide with compounds containing active methylene group like acetyl acetone, acetoacetic ester, malonic ester, cyanoacetic ester and acetoacetanilide.

2-Methylbenzene-2'-sulphenyl bromide reacts with acetyl acetone, acetoacetic ester, malonic ester, cyanoacetic ester and acetoacetanilide to give the corresponding sulphenyl derivatives (I-V) at room temperature in aqueous alcohol.
(b) Reactions of 2-methylamobenzene-2'-sulphenyl bromide with methyl ketones.

2-Methylamobenzene-2'-sulphenyl bromide reacts with acetone, ethylmethyl ketone, acetophenone and methyl-2-naphthyl ketone in aqueous ethanolic medium either at room temperature or at higher temperature or both and yields the corresponding sulphides. With ethylmethyl ketone, 2-methylamobenzene-2'-sulphenyl bromide yields only a liquid which reacts with 2,4-dinitrophenyl hydrazine and gives the corresponding solid hydrazone (II).

\[
\begin{align*}
\text{[Liquid]} & \rightarrow 2,4\text{-dinitrophenylhydrazine} \\
\text{[II]} & \rightarrow \text{[II]} \\
\end{align*}
\]
(c) Reactions of 2-methylazobenzene-2'-sulphenyl bromide with active substrates.

(i) With arylamines.

2-Methylazobenzene-2'-sulphenyl bromide reacts with aniline, m-toluidine, dimethylaniline, m-phenylene diamine, diphenylamine, 1-naphthylamine and 2-naphthylamine in aqueous ethanolic medium at room temperature to yield the corresponding sulphenyl derivatives (I-VII).
(ii) With phenols.

2-Methylazobenzene-2'-sulphenyl bromide reacts with 1-naphthol, 2-naphthol, resorcinol, phloroglucinol and pyrogallol in aqueous ethanolic medium at room temperature to yield the corresponding sulphenyl derivatives (I-V).
(d) Reactions of 2-methylamobenzene-2'-sulphenyl bromide with alkalis.

1. 2-Methylamobenzene-2'-sulphenyl bromide (I) reacts with excess of sodium hydroxide resulting in the formation of di-(o-2-methylphenylazo) phenyl disulphide (II) and sodium 2-methylamobenzene-2'-sulphinate (III) through the formation of unstable intermediate blue-violet sodium 2-methylamobenzene-2'-sulphenate (IV).

\[
\begin{align*}
\text{CH}_3 & \quad \text{N=N} & \quad \text{CH}_3 \\
\text{S-Br'} & \quad \text{S-Br'} & \\
\text{Alkali} & & \text{N=N}
\end{align*}
\]

2. 2-Methylamobenzene-2'-sulphenyl bromide reacts with slightly more than one equivalent amount of alkali and results in the formation of di-(o-(2-methylphenylazo) phenyl disulphide (II), di-(o-2-methylphenylazo) phenyl disulphoxide (V) and alkali 2-methylamobenzene-2'-sulphinate (III).
The disulphoxide on long standing or on heating is converted into di-o-(2-methylphenylazo) phenyl monosulphide (VI).

3. 2-Methylanisobenzene-2'-sulphenyl bromide on refluxing with zinc dust in benzene forms di-o-(2-methylphenylazo) phenyl disulphide (II), which with alkaline sodium sulphide and benzyl chloride forms 2-methylanisobenzene-2'-benzyl sulphide.
4. 2-Methylamobenzene-2'-sulphenyl bromide also reacts exactly in the same manner with other alkalis.

C. Electronic spectra and structure of the 2-methylamobenzene-2'-sulphenyl derivatives.

The electronic spectra of 2-methylamobenzene-2'-sulphenyl bromide and its derivatives (I), \(X = \text{Br,Cl,I,ClO}_4\), SCS,CS indicate that 2-methylamobenzene-2'-sulphenyl cyanide is non-ionic in nature and exists in the non-ionic form (II) both in polar and non-polar solvents; but 2-methylamobenzene-2'-
sulphonyl bromide, chloride, iodide, perchlorate and thiocyanate exist in 2-(2'-methylphenyl) benzo-1-thia-2,3-diazolium ionic form (III) and exhibit the high intensity K-band characteristic of the conjugated chromophoric system. However, 2-methylazobenzene-2'sulphonyl iodide and perchlorate in ethanolic medium probably exist as an equilibrium mixture of the thiazodiazolium ionic form (III) and the ionic form (IV), as the prominent low intensity K-band characteristic of the freeazo-group is present. On the other hand, 2-methylazobenzene-2'-sulphenyl thiocyanate in non-polar solvent (benzene) exist either in a mixture or in equilibrium with the ionic form (III) and the non-ionic form (I) as it exhibits the high intensity K-band and a mild inflexion in the higher wavelength region.