CHAPTER I

PREPARATION OF 2-ARYLAZONAPHTHALENE-1-SULPHENYL BROMIDE
CHAPTER-I

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REVIEW :

The initiation of the synthesis of orthomercaptoazo compounds came from A.Burawoy who first reported the successful synthesis of the compounds in 1950.\(^{(1-6)}\) Subsequent groups of authors led by Mrs.A.Chaudhuri et al and S.K.Bhattacharjee et al extended the work further and reported the synthesis of some more orthomercaptoazo compounds and studied their reactions.\(^{(7-18)}\)

Sulphenyl derivatives of orthomercaptoazo compounds constitute a class of biligated organic sulphur compounds with some unique properties. It was observed that the presence of electron withdrawing substituents in the aromatic ring add to the stability of this class of compounds.\(^{19}\) Thus unlike sulphenyl halides and thiocyanates, all azobenzene sulphenyl bromides are exceptionally stable and yet retain their characteristic reaction properties of corresponding sulphenyl compounds.\(^{(5,19-21)}\)
In an attempt to introduce orthoazoaryl groups in the synthesis of ortho-mercaptoazo compounds, it was observed that diazotised orthoaminothiophenols could not be diazocoupled with active substrates like corresponding ortho-aminophenols. This was due to the formation of benz-1-thia-2,3-diazole (1) undergoing intramolecular condensation. The synthesis of ortho-mercaptoazo compounds were, therefore, attempted via different route.

Diazocoupling reactions:

Tetrazotization of 2,2'-diamino-diphenyl disulphide (2) could be successfully carried out in conc. sulphuric acid with nitrosyl chloride. The tetrazonium salt (3) was then coupled with 2-naphthol to form di-o-(2-hydroxynaphthalene-1-azo)diphenyl disulphide (4). The disulphide bridge of (4) could be cleavaged with sodium sulphide to give the expected 1-(orthomercaptophenylazo)-2-naphthol (5) which underwent oxidation to form the anhydride (6).
The product of this diazocoupling reaction was observed to be vastly dependent on the nature and strength of the condensing bases. Thus in presence of sodium carbonate, the final products were a mixture of benz-1-thia-2,3-diazole (1) and ortho-(2-hydroxy-1-naphthylazo) phenyl sulphenic acid (7). The latter further coupled with 2-naphthol to form ortho-(2-hydroxy-1-naphthyl sulphide) (8) as the final product. When the reaction was carried out in presence of sodium acetate or pyridine, the disulphide compound (4) was formed predominantly, whereas, in presence of strong alkali (sodium hydroxide), the sulphinate (9) and the disulphide compound (4) were the final products.
In an alternative route of diazocoupling reaction, 1-thiocyanato-2-naphthylamine was diazotised and the resulting 1-thiocyanato-naphthalene-2-diazonium salt (10) was condensed with 2-naphthol to give the corresponding azo compound (11). The azo compound on treatment with aqueous alkali formed the disulphide (4). The disulphide bridge on cleavage with ethanolic sodium sulphide and subsequent acidification gave a mercaptan which was converted to the thioether (12) by S-methylation with dimethyl sulphate.\(^{(2,3)}\)
But it was observed that the mercaptan showed tendency to revert to the disulphide by aerial oxidation. Partial conversion of the amine to 2-aminonaphtho-2':1':4:5-1,3-thiazole (13) was also observed prior to diazotisation in conc. sulphuric acid.\(^{2,3}\)

Attempts were, therefore, made to diazotise 1-nitro-2-naphthylamine and subsequent replacement of the nitro group with thiocyanate group by
reacting with sodium thiocyanate. The resulting 1-thiocyanato-naphthalene-2-diazonium salt (10) was condensed with 2-naphthol to give the corresponding azo compound (11). Although, the method gave a way to prevent conversion of the amine to thiazole (13) but partial exchange of diazonium group with thiocyanato group posed another problem.

The above methods for the preparation of orthomercaptoazo compounds were found to be less fruitful in so far as the inherent problems associated with the preparations concerned.

**Preparation and debenzylation of benzylthioethers:**

The diazonium salts of ortho-benzylthio naphthylamine were prepared with nitrosyl chloride in sulphuric acid.\(^4\) These diazonium salts when coupled with 2-naphthol in an alkaline medium formed 1-benzylthio-2-arylazo-2-naphthol (14).
Debenzylation of these thioethers could be achieved almost quantitatively with aluminium bromide in benzene with the formation of corresponding orthomercaptoazo compounds (5).\textsuperscript{29}

\[
\text{SH} \quad \text{--} \quad \text{K} \quad . . 
\]

But it was found that debenzylation of (14) was not possible with hydrobromic acid. Similar attempt of debenzylation with bromine also failed resulting in nuclear bromination.

Bhattacharjee and Dasgupta\textsuperscript{7} diazotised 2-benzylthioaniline and 1-benzylthio-2-naphthylamine with nitrous acid in ethanol. The resulting diazonium salts, though unstable, could be successfully converted to their corresponding thioethers by coupling with active substrates like phenol, p-cresol, 2-naphthol and dimethylaniline. But debenzylation was successful only with the thioether obtained from the coupling with dimethylaniline while others resulted in corresponding disulphides.
A. Bayer observed that azobenzene could be prepared by condensation of nitrosobenzene with aniline in glacial acetic acid medium. But the reaction of ortho-nitroaniline with nitrosobenzene yielded 4-nitroso-2'-nitro-diphenylamine (15) instead of corresponding azobenzene.

![Chemical structure of 4-nitroso-2'-nitro-diphenylamine](image)

Gharrier and Baretta observed that the condensation was hindered by the presence of ortho-nitros substituent due to the steric hindrance of the latter. But condensation reactions of ortho-benzylthioanilines was not hindered by o-benzylthio group.

Burawoy et al tried a number of nitroso compounds to condense with o-benzylthioaniline and 1-benzylthio-2-naphthylamine and successfully obtained the corresponding azo compounds (16) and (17).

![Reactions of nitroso compounds with benzylthioanilines](image)
Debenzylation of 1-(orthobenzylthio-phenylazo)-2-naphthol with aluminium bromide in benzene gave the corresponding mercaptan (18). But ortho-benzylthioazobenzene (16) on debenzylation with aluminium bromide in benzene did not produce the corresponding mercaptan instead gave the corresponding sulphenyl bromide (19) in low yield.

Debenzylation of ortho-benzylthio azobenzene (16) was also tried with hydrobromic acid in acetic acid which resulted in the formation of equimolecular amount of sulphenyl bromide (19) along with a rearranged benzidine product (20).
Debenzylation of 2-nitro and 4-nitro derivatives of orthobenzylthio azobenzene also yielded the corresponding sulphenyl bromide in good yield without the formation of any rearranged product.

Burawoy et al. tried other compounds like bromine in hot acetic acid for debenzylation. It was observed that orthobenzylthioazobenzene (16) and orthobenzylthioazonaphthalene (17) on debenzylation with bromine in hot acetic acid almost quantitatively yielded corresponding sulphenyl bromides. But 1-benzylthio-2-p-tolylazonaphthalene failed to give a quantitative yield.

Bhattacharjee et al. observed that 4'-dimethylamino-2-benzylthioazobenzene (21) could be benzylated only with bromine in carbon tetrachloride at 40°C to the corresponding sulphenyl bromide (22).

Debenzylation of S-benzyl group was attempted by Siffered and Du Vigneaud with sodium and...
liquid ammonia. They successfully debenzylated 1-benzylthio-2-phenylazonaphthalene and 2,2'-dibenzylthio azobenzene to their corresponding disulphides and polysulphides. But with excess of sodium in liquid ammonia corresponding sodium mercaptides (23) and (24) were formed.

However, the method failed to debenzylate orthobenzylthioazobenzene.

Burawoy et al\(^{(20,21,29)}\) attempted brominolysis of benzylthio group of 2-benzylthio derivatives in boiling acetic acid and could successfully prepare a number of sulphenyl bromides of orthomercaptoazo compounds. But excess of bromine in the reaction resulted in corresponding tribromides (25).
DISCUSSION:

After the initiation of synthesis of sulphenyl compounds by Burawoy et al\(^1-6\), a good number of azobenzene sulphenyl compounds have been synthesized and their reactions in detail studied. But only a few arylazonaphthalene sulphenyl compounds are known at present in comparison with the corresponding azobenzene series. Attempts have been made, therefore, to synthesize a substituted aryazonaphthalene sulphenyl bromide and to study some of the reactions of the compound vis a vis its structure.

It is observed that the unstable 1-benzylthionaphthyl-2-diazonium compound (27) obtained from diazotisation of 1-benzylthio-2-naphthylamine (26) with nitrous acid in ethanol medium can be diazocoupled with active aromatic substrates like dimethylaniline, 2-naphthol, p-cresol under alkaline conditions below \(0\, ^\circ\)C to give the corresponding azo compounds (28).

![Chemical Structures](image-url)
But debenzylation of the above thioether (28) by brominolysis to yield the corresponding azonaphthalene sulphenyl bromide is not successful resulting in a disulphide product (29).

\[
\begin{align*}
\text{[Diagram of structure (29)]}
\end{align*}
\]

In an alternative route to prepare the azo compound, we have tried condensation of 1-benzylthio-2-naphthylamine (26) with 2-nitro-4-chloro nitrosobenzene (30) in warm acetic acid. A fairly good yield of the corresponding azo compound (31) has been obtained.

\[
\begin{align*}
\text{[Diagram of structure (38) and (31)]}
\end{align*}
\]

Debenzylation of the thioether (31) has been successful. The debenzylation reaction is carried out by brominolysis in hot acetic acid. The resulting 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide (32) is precipitated on cooling the brominolysed reaction mixture.
The reaction proceeds smoothly and no nuclear bromination is observed. The yield is found to be quite satisfactory.

The concentration of bromine in the reaction mixture is found to be the determining factor in the debenzylation step to give the sulphenyl bromide. Best result can be expected if equimolar quantity of bromine with the azo compound is used. If the concentration of bromine is more then the reaction proceeds with the formation of tetracovalent sulphur tribromide (33).

The tribromide is unstable and cannot be recrystallized without its partial decomposition to the corresponding sulphenyl bromide and bromine. But
when refluxed in a polar solvent like ethanol, the tribromide splits off a molecule of bromine to form the sulphenyl bromide.

The mechanism of brominolysis is uncertain but it may, perhaps, proceed through an electrophilic attack on sulphur in the arylthioether linkage as shown below:

\[
\text{If excess of bromine (two or more moles) is used, further attack on sulphenyl sulphur is expected resulting in the formation of sulphenyl tribromide as envisaged below:}
\]

We have also attempted debenzylation
of the thioether (31) by brominolysis in carbon tetrachloride at room temperature and also at elevated temperature in presence of iodine as catalyst. But the yield of sulphenyl bromide is found to be very low.

Attempted debenzylation of the thioether (31) with hot hydrobromic acid fails to give the sulphphenyl bromide in good yield.
EXPERIMENTAL

(I) Synthesis of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide :

(IA) Preparation of 1-benzylthio-2-naphthylamine :

1-benzylthio-2-naphthylamine was prepared as per the method suggested by Burawoy et al\(^{(29)}\) as follows:

\[
\text{NH}_2 + \text{NH}_4\text{SCN} \xrightarrow{\text{acetic acid}} \text{SCN} \text{NH}_2 + \text{NH}_4\text{SCN} \xrightarrow{\text{acetic acid}} \text{SCN} \text{NH}_2
\]

71 g of \(\beta\)-naphthylamine was dissolved in 450 ml of glacial acetic acid and 160 g of ammonium thiocyanate dissolved in 1200 ml acetic acid was mixed with it, shaken well and placed in an ice bath. To this solution 25 ml of bromine prepared in 350 ml of acetic acid was added slowly in about 45 minutes stirring continuously during addition while the temperature was kept below 5°C. Shining flakes of 1-thiocyanato-2-napthylamine (A) was formed. The product was filtered through a buchner funnel and the residue was washed with 10% sodium hydroxide and finally with water. Pure (A) was obtained. Yield - 82.5 g.
The compound A (82 g) was mixed properly with 300 g of potassium hydroxide and then fused in a porcelain basin at 200 - 220°C. The fused mass was extracted with 1.5 l of water and filtered through glass wool. The filtrate was subjected to aerial oxidation for 24 hours and the product was filtered. The residue was collected and washed with water to get dinaphthyl disulphide (B). Yield - 98.7 g.

Dry B (98.7 g) was acetylated under reflux with a mixture of 40 ml acetic acid and 40ml acetic anhydride. The reaction mixture was then poured in cold water and filtered. The residue was recrystallized from acetic acid when yellow flakes of nitrogen acetylated product (C) was obtained. M.P. 223-224°C. Yield - 102.4 g.
70 g of the acetylated compound (C) was dissolved in 2 L of ethyl alcohol and refluxed for 30 minutes. Sodium sulphide (120 g in 600 ml water) was then added to the mixture and the mixture was refluxed for 15 minutes more. 90 ml benzyl chloride was slowly poured to the reaction mixture and the reaction was allowed to continue under reflux for another 15 minutes. The reaction mixture was then cooled and 2 L of water was slowly added with constant stirring. A white precipitate was obtained which was filtered and the residue was washed with water. The residue was collected and recrystallized from a mixture of ethanol and water (9:1). Colourless crystals of S-benzyl compound (D) was obtained. M.P. 100-101°C. Yield - 40.2 g.

40 g of the s-benzylated compound
(D) was dissolved in 1.5 l of ethyl alcohol and refluxed for 15 minutes. 20 ml of 30% sodium hydroxide was then added to the mixture and the reflux was continued for another 3 hours. The reaction mixture was then cooled and diluted with 2 l of water. It was then kept overnight. A precipitate was obtained which was filtered and the residue was collected. The residue was recrystallized from light petrol (40-60°C) to obtain 1-benzylthio-2-naphthylamine (26). M.P. 65°C. Yield - 28.6 g.

(IB) Preparation of 2-nitro-4-chloro-nitrosobenzene(30):

\[
\text{\begin{array}{c}
\text{NH}_2 \\
\text{NO}_2 \\
\text{Cl}
\end{array}} \xrightarrow{\text{H}_2\text{SO}_4} \begin{array}{c}
\text{NO} \\
\text{NO}_2 \\
\text{Cl}
\end{array}
\]

A clean solution of Caro's acid was prepared by slowly adding 145 g of ammonium persulphate to 54 ml of concentrated sulphuric acid, allowing the mixture to stand for 1 hour and pouring it on to 355 g of crushed ice. This solution was added to a suspension of 40 g of 2-nitro-4-chloro aniline in 60 ml of ice cold sulphuric acid and 10 ml of water. The mixture was then mechanically stirred for 17 hours. The yellow solid thus
obtained was collected on a buchner funnel and finally recrystallized from dry acetone to get the pure 2-nitro-4-chloro-nitrosobenzene (30). M.P. 125°C. Yield - 28 g.

(IC) Preparation of 2-(2'-nitro-4'-chloro-phenylazo) naphthalene-1-benzyl sulphide (31):

25 g of 1-benzylthio-2-naphthylamine (26) was dissolved in 60 ml glacial acetic acid and 17 g of 2-nitro-4-chloro-nitrosobenzene(30) was dissolved in 70 ml of acetic acid. Both the solutions were warmed separately at 70°C in an water bath and then mixed together. The mixture was stirred thoroughly for 30 minutes maintaining a temperature of 55-60°C and then allowed to stand for 2 hours with occasional shaking. Red crystals of 2-(2'-nitro-4'-chlorophenylazo) naphthalene - 1-benzyl sulphide thus obtained was filtered off. The residue was washed, dried and recrystallized from petroleum ether (80-100°C).
M.P. 123°C. Yield - 32.8 g.
Analysis : C₂₃H₁₆N₃O₂SBr

Requires : C, 63.7% ; H, 3.7% ; N, 9.7%

Found : C, 63.8% ; H, 3.6% ; N, 9.8%

(ID) Preparation of 2-(2'-nitro-4-chlorophenylazo)-naphthalene-1-sulphenyl bromide :

\[
\begin{align*}
& \text{SCH}_2\text{Ph} \quad \text{NO}_2 \quad -\text{Cl} \quad \text{Br}_2 \\
\rightarrow & \quad \text{SBr} \quad \text{NO}_2 \quad -\text{Cl} \\
& \quad \text{Ph} \cdot \text{CH}_2\text{Br}
\end{align*}
\]

3 ml (9.2 g) bromine in 20 ml acetic acid was added to a solution of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-benzyl sulphide (25 g) in 70 ml of acetic acid. 2-3 crystals of iodine was added to the mixture and was shaken well. The reaction mixture was then warmed in a water bath for half an hour at 65-70°C with occasional shaking. Shining yellow crystals of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide was obtained and was filtered off. It was then recrystallized from acetic acid.

M.P. 230-231°C. Yield - 21.6 g
Analysis: $C_{16}H_9N_3O_2SCIBr$

Requires: C, 45.4% ; H, 2.1% ; N, 9.9%

$C_{16}H_9N_3O_2SCIBr, 1\text{ H}_2\text{O}$

Found: C, 43.7% ; H, 2.4% ; N, 9.4%

5.05126 g of 2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide when heated for 8 hours at 110°C was found to lose an weight of 0.20994 g and the colour of the compound was changed from yellow to red.

Uv and visible spectra:

\[
\begin{align*}
\lambda_{\text{max}} & \\
\text{(Water)} & 442 (\varepsilon, 1300, n\rightarrow\pi^*) ; 362 (\varepsilon, 14200, n\rightarrow\pi^*) \\
\text{(Ethanol)} & 440 (\varepsilon, 1100, n\rightarrow\pi^*) ; 360 (\varepsilon, 11800, n\rightarrow\pi^*) \\
\text{(Chloroform)} & 450 (\varepsilon, 900, n\rightarrow\pi^*) ; 366 (\varepsilon, 12600, n\rightarrow\pi^*) \\
\text{(Benzene)} & 514 (\varepsilon, 600, n\rightarrow\pi^*) ; 358 (\varepsilon, 14500, n\rightarrow\pi^*)
\end{align*}
\]

Ir spectra:

\[
\begin{align*}
\nu & \text{cm}^{-1} \\
\text{KBr} & 1590 (w, N=N) ; 1540 and 1390 (m, NO_2)
\end{align*}
\]

Mass spectra:

Molecular ion could not be detected.

m/z - (396, 237, 205, 191, 154, 126, 111, 110, 75, 74).
(IE) **Attempted preparation of sulphenyl bromide in carbon tetrachloride medium using iodine as catalyst:**

2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-benzyl sulphide (1.0 g) was dissolved in carbon tetrachloride (25 ml) and a few crystals of iodine was added. The mixture was warmed gently. 0.5 ml of bromine in 5 ml of carbon tetrachloride was slowly added to the mixture. The mixture was stirred well and heated gently for 5 minutes in an water bath. Shining yellow crystals of 2-(2'-nitro-4'-'chlorophenylazo)-naphthalene-1-sulphenyl bromide was observed but the yield of the compound was found to be very low (0.056 g).

(IF) **Preparation of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl tribromide:**

![Chemical Structure](image)

To a solution of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-benzyl sulphide (0.5 g) in 20 ml acetic acid was added a solution of bromine(0.5 ml)
in 5 ml acetic acid. 2-3 crystals of iodine was added to the reaction mixture and shaken well. The reaction mixture was then warmed in an water bath for half an hour at 65-70°C with occasional shaking. A dark brown precipitate of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl tribromide was formed. The precipitate was filtered and the residue was washed with acetic acid. The compound could not be recrystallized as it was gradually decomposed to sulphenyl bromide. Melting point of the compound could not be determined as the compound was decomposed before its melting point could be reached.