CHAPTER - I

SYNTHESIS OF
2'-CHLOROAZOBENZENE -2- SULPHENYL BROMIDE.
REVIEW:

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 (Megee P.S.). Thus, unlike sulphenyl halides and thiocyanates, all azobenzene sulphenyl bromides are stable and yet retain their characteristic chemical properties of corresponding sulphenyl compounds (Burawoy A. and Vellins C.E., 1954, Burawoy A. et. al., 1955, 1956.).

A Burawoy, initiated the synthesis of orthomercaptoazo compounds and reported the successful synthesis of the compounds in the year 1950 (Burawoy A. et. al., 1950, 1952, 1954, 1955, 1959). Subsequent group of authors led by Mrs A. Chaudhury 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 (Bhattcharjee S.K et al, 1977, 1981; Chaudhury A. et. al., 1973, 1978, 1979, 1980.).

In an attempt to introduce orthoazo-aryl group in the synthesis of orthomercaptoazo compounds, it was observed that diazotised orthoaminothiophenols could not be diazocoupled with active substrates. This was due to the formation of benz-1-thia-2,3-diazole (1) undergoing intramolecular condensation (Bernthesen A., 1889; Jacobson P., 1893). The synthesis of orthomercaptoazo compounds were, therefore, attempted via different route.
Diazo coupling reaction

Bhattacherjee S.K. and Dasgupta S.K. (1977) 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 dimethylaniline while others resulted in corresponding disulphides.

Bayer A. (1874) observed that azobenzene could be prepared by condensation of nitrosobenzene with aniline in glacial acetic acid medium. But the reaction of ortho nitro aniline with nitrobenzene yielded 4-nitroso-2'-nitro-diphenylamine (2) instead of corresponding azobenzene (Gharrier G and Beretta A. 1924)
Gharrier and Baretta (1924) observed that the condensation was hindered by the presence of ortho-nitro substituent. But the condensation reaction of ortho-benzylthioaniline was not hindered by ortho-benzylthio group (Burawoy A and Veilns C. E, 1954).

Burawoy et. al (1954), tried a number of nitroso compounds to condense with ortho-benzylthioaniline and 1-benzylthio-2-naphthylamine and successfully obtained the corresponding azo compounds (3) and (4).

Debenzylzation of 1-(orthobenzylthio-phenylazo)-2-naphthol with aluminium bromide in benzene however, gave the corresponding mercaptan (5). (Harnish D.P and Tarbell D. S, 1948)
Contrary to the above observation, ortho-benzylthioazobenzene (3) on debenzylation with aluminium bromide in benzene did not produce the corresponding mercaptans, but gave the corresponding sulphenyl bromide (6).

\[
\begin{align*}
\text{SBr} \\
\text{N} = \text{N}
\end{align*}
\]

(6)

Debenzylation of orthobenzylthioazobenzene (3) was also tried with hydrobromic acid in acetic acid which resulted in formation of equimolar amount of sulphenyl bromide (6) along with rearranged benzidine product (7).

Debenzylation of 2-nitro and 4-nitro derivative of orthobenzylthio azobenzene also yielded the corresponding sulphenyl bromide in good yield without the formation of any rearranged product.

Burawoy et. al. (1954) tried other compounds like bromine in hot acetic acid for debenzylation. It was observed that orthobenzylthioazobenzene (3) and orthobenzylthioazo-naphthalene (4), on debenzylation with bromine in hot acetic acid almost quantitatively yielded corresponding sulphenyl bromide. But 1-benzylthio-2-p-tolylazonaphthalene failed to give the quantitative yield.

Bhattacharjee et al. (1977), observed that 4'-dimethylamino-2-benzylthioazobenzene (8) could be debenzylated only with bromine in carbon tetrachloride at 40° C to the corresponding sulphenyl bromide (9).
Debenzylation of S-benzyl group was attempted (Siffered R. and Vigneaud V. Du. 1935) with sodium and liquid ammonia and successfully debenzylated 1-benzylthio-2-phenylazonaphthaline and 2,2'-dibenzylazobenzene to their corresponding disulphides and poly sulphides. But with excess of sodium in liquid ammonia, corresponding sodium mercaptides (10) and (11) were formed.

However, the method failed to debenzylate orthobenzylthioazobenzene.

Burawoy et. al. (1955, 1956), attempted brominolysis of benzthio group of 2-benzylthio derivatives in boiling acetic acid and could successfully prepare a number of sulphenyl bromides of orthomercaptoazo compounds. But excess bromine in the reaction resulted in the corresponding tribromide (12)
Discussion:  

The present development of sulphenyl compounds is mainly due to the process of synthesis initiated by Burawoy et. al (1950, 1952, 1954, 1955, 1959). A good number of azobenzene sulphenyl compound as well as a few azonaphthalene sulphenyl compounds have been reported so far.

It is observed that 1-benzylthiophenyl-2-diazonium compound (14) obtained from diazotisation of 1-benzylthioaniline (13) with nitrous acid in ethanol medium can be diazocoupled with active aromatic substrates like dimethylaniline, 2-naphthol, p-cresol under alkaline conditions below 0 °C to give corresponding azo compound (15).

![Structural formulas](13) (14) (15)

But debenzylation of above thioether (15) by brominolysis to yield the corresponding azobenzene sulphenyl bromide is not successful and results in disulphide products (16).

![Structural formula](16)
In an alternative route to prepare the azo compound, we have tried condensation of 2-benzylthio aniline (13) with 1-chloro-2-nitrosobenzene (17) in warm acetic acid. A fairly good yield of corresponding azo compound (18) has been obtained.

\[
\begin{align*}
\text{(17)} & \quad \text{(18)} \\
\end{align*}
\]

Debezylation of the thioether (18) has been successful. The debenzylation reaction is carried out by brominolysis in warm acetic acid. The resulting 2'-chloroazobenzene-2-sulphenylbromide (19) is precipitated from the brominolysed reaction mixture, on standing.

\[
\begin{align*}
\text{(19)} \\
\end{align*}
\]

The reaction proceeds smoothly and no nuclear bromination is observed. The yield is found to be 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
The concentration of bromine is more, then the reaction proceeds with the formation of tetravalent sulphur tribromide (20).

\[
\begin{align*}
\text{Cl} & \quad \text{N} = \text{N} & \quad \text{SBr}_3 \\
\end{align*}
\]

(20)

The tribromide is unstable and can not 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.

We have tried debenzylation of the thioether (18) by brominolysis in carbon tetrachloride at room temperature and also at elevated temperature in presence of iodine catalyst. But the yield of sulphenyl bromide is found to be very low. Same is the case, of debenzylation of thioether (18) in hot hydrobromic acid.
EXPERIMENTAL:

1. Preparation of 2-benzylthio aniline:

2-benzylthio aniline was prepared as per following method:

\[
\text{NO}_2 \quad \text{Cl} + \text{Na}_2\text{S} \quad \xrightarrow{\text{S-powder, EtOH, } \Delta} \quad \text{NO}_2 \quad \text{S} - \text{S} \quad \text{NO}_2
\]

Sodium sulphide (anhydrous, 60g.) was dissolved in ethanol (750ml.) in a flask by heating in a water bath. Flower of sulphur (24g.) was added to the flask. The above solution was slowly added with frequent shaking to a solution of 1-Chloronitrobenzene (157g.) in ethanol (250ml.). The mixture was boiled for two hours in the water bath. The product 2,2'-dinitro diphenyl disulphide (22) resulted, filtered through a buchner funnel. The product was recrystallised from chloroform-ethanol mixture. Pure (22) was obtained.

Yield: 95 g. (62% of theory).

Melting point: 195 °C.
2,2'-Dinitro diphenyl disulphide (90 g.) dissolved in ethanol (2200 ml) and water (500 ml.) by boiling in water bath. A solution of sodium hydroxide (30 g.) and sodium sulphide (45 g.) in ethanol (300 ml.) and water (150 ml.) was added to the above solution. The mixture was boiled for five minutes, and filtered out for unchanged mass, and allowed to be refluxed in water bath. To the refluxing solution sodium hydroxide (20 g) in water (500 ml.) was added. The mixture was allowed to boil. After 15 minutes, boiling was discontinued. When the temperature of the mixture dropped to 70 °C, benzyl chloride (50 ml.) was added. The mixture was shaken well and refluxed for 1 hour. Boiling was discontinued and mixture was kept over night. Mixture was filtered, residue, 1-thiobenzyl-2-nitrophenol (23) was washed with water and dilute alcohol and dried. Recrystallized from ethanol.

Yield : 65 g.

Melting point : 84-85 °C.

\[
\begin{align*}
\text{NO}_2 & \quad \text{SCH}_2 \text{Ph} \\
\text{Fe/CH}_3\text{COOH} & \quad \Delta \quad \text{Fe/CH}_3\text{COOH} \\
\text{NH}_2 & \quad \text{SCH}_2 \text{Ph}
\end{align*}
\]

(23) \quad (13)

Iron powder (40 g., 90 mesh BDH) and water (50 ml.) was stirred mechanically in a two necked distilling flask and heated to boiling. To it added acetic acid (3 ml.) followed by 1-thiobenzyl-2-nitrophenol (20 g) (23) dissolved in hot toluene (100 ml). The suspension was stirred well under refluxing condition for six hours. Reaction
mixture was allowed to cool and made alkaline with 10% sodium hydroxide solution. Filtered through buchner funnel and residue was washed with warm toluene. From the filtrate toluene layer was collected. Toluene was evaporated, and the residue was recrystallized from petroleum ether (b.p. 40-60°C), to give pure white flakes.

Yield: 15 g.

Melting point: 44°C.
2. Preparation of 1-chloro-2-nitrosobenzene:

\[
\text{Cl} \quad \text{NO}_2 \quad \text{Zn} / \text{NH}_4 \text{Cl} (aq) \quad \text{[H]} \quad \text{Cl} \quad \text{NH}_2 \text{OH} \quad 0^\circ \text{C} \quad \text{Na}_2 \text{Cr}_2 \text{O}_7 / \text{H}_2 \text{SO}_4 \quad \text{Cl} \quad \text{NO}
\]

(21) (24) (17)

1-chloro-2-nitrobenzene (78 g.) was added to a well stirred mixture of ammonium chloride (30 g.) in water (1000 ml.). Mixture was stirred vigorously. Zinc-dust (75 g.) was added to the mixture in installments within 5 minutes. Reaction mixture was heated to 50 °C and stirred well for one hour and thirty minutes keeping the temperature at 50 °C. The mixture was filtered out in buchner funnel. Zinc-dust was washed with hot water several times.

The filtrate was cooled to 0 °C by adding sufficient quantity of ice in regular intervals. To the reaction mixture, ice cold concentrated sulphuric acid (150ml.) was added with continuous stirring. To the mixture a ice cold solution of sodium dichromate (34 g.) in water was added. The reaction mixture assumed tea colour and after 4 minutes precipitation occurred. The mixture was filtered out at buchner funnel. Residue was taken in a distilling flask and steam distilled and green vapours evolved was collected in ice cold water to give pure 1-chloro-2-nitrosobenzene (17).

Yield : 13.5 g. Melting point : 68 °C.
3. Preparation of 2'-chloroazobenzene-2-benzylsulphide:

\[
\begin{align*}
\text{Cl} & \quad \text{NO} & \quad \text{SCH}_2\text{Ph} \\
(17) & & (13) \\
\text{Cl} & \quad \text{N= N} & \quad \text{SCH}_2\text{Ph} \\
(18)
\end{align*}
\]

1-chloro-2-nitrosobenzene (17) (12 g.) was dissolved in glacial acetic acid (25 ml.) 2-benzylthioaniline (13) (20 g.) was dissolved in glacial acetic acid (30 ml.). Both the mixtures were warmed separately to 50 °C in water bath, and mixed together and stirred well for 30 minutes maintaining a temperature range of 60-70 °C. The mixture was allowed to stand for two hours in room temperature. Mixture was kept in the refrigerator over night. Orange-red precipitate of 2'-chloroazobenzene-2-benzyl sulphide (18) thus formed was filtered off. The residue was dried and recrystallized from acetic acid, to give orange needles.

Yield : 23 g (74 % of theory)

Melting point : 142 °C

Analysis : C_{19} H_{15} N_{2} Cl

Requires : C: 74.38 %; H: 4.89 %; N: 9.13%.

Found : C: 74.28%; H: 4.81%; N: 9.1%. 
Uv-visible spectra:

\[ \lambda_{\text{nm}} \text{ max (Ethanol)} \]

(a) 324-326 \( (\log e 3.934, \pi \rightarrow \pi^*) \)

(b) 402-414 \( (\log e 3.732, n \rightarrow \pi^*) \)

(Chloroform)

(a) 325 \( (\log e 3.918, \pi \rightarrow \pi^*) \)

(b) 400-414 \( (\log e 3.720, n \rightarrow \pi^*) \)

(Benzene)

(a) 324 \( (\log e 3.899, \pi \rightarrow \pi^*) \)

(b) 402-411 \( (\log e 3.726, n \rightarrow \pi^*) \)

ir spectra:

\[ \nu_{\text{cm}^{-1}} \text{ kBr} \]

1595 \( (w, \text{N=N stretch.}) \).
4. Preparation of 2'-chloroazobenzene-2-sulphenylbromide:

3 ml bromine in 17ml acetic acid was added to a solution of 2'-chloroazobenzene-2-benzylsulphide (18 g.) in 100 ml acetic acid and was shaken well. The reaction mixture was warmed in water bath for thirty minutes at 65-70 °C, with occasional shaking. On cooling, shining golden yellow precipitate was obtained. Precipitate was filtered out and recrystalized from acetic acid.

Yield: 15.5 g (89 % of theory).

Melting point: Decomposes at 215-218 °C.

Analysis: C_{12}H_{8}N_{2}ClSBr.

Requires: C: 43.96 %; H: 2.44 %; N: 8.54 %

Found: C: 43.85 %; H: 2.48 %; N: 8.32 %

Uv-visible spectra:

\[ \lambda_{\text{nm}}^{\text{max}} \text{(Ethanol)} = 332 \text{ (log } \varepsilon 4.245, \pi \rightarrow \pi^* \text{)} \]
(Chloroform) (a) 324 (log e 4.146, \(\pi \rightarrow \pi^*\))

(Benzene) (a) 332 (log e 4.150, \(\pi \rightarrow \pi^*\))

ir - spectra

\[ \nu_{\text{Kbr}} \text{ cm}^{-1} \]

1585 (w, N=\(\equiv\)N stretch)
5. Attempted preparation of 2'-chloroazobenzene-2-sulphenylbromide in carbon tetra chloride medium using iodine as a catalyst:

2'-chloroazobenzene-2-benzylsulphide (1 g) was dissolved in carbon tetra chloride (25 ml) and a few crystals of iodine was added. The mixture was warmed gently 0.5 ml bromine in 5 ml of carbontetrachloride was slowly added to the mixture. The mixture was stirred well and heated gently in water bath for five minutes. A yellow crystals of 2'-chloroazobenzene-2-sulphenylbromide formed but the yield of the compound was found to be very low.

yield 0.042 g. (4% of theory).
IR SPECTRA OF 2'-Chloroazobenzene-2-benzyl sulphide (18)
IR SPECTRA OF 2'-Chloroazobenzene-2-sulphenyl bromide (19)