CHAPTER III

SOLVOLYSIS AND ALKALINE HYDROLYSIS OF 2-ARYLAZO-

NAPHTHALENE-1-SULPHENYL BROMIDES
The relative ease of fission of sulphur-halogen bond in the aryl sulphenyl halides has led to many reactions in which sulphenyl chlorides and bromides react with fair rapidity. This is evident from the hydrolysis reactions in which halide ion is expelled and sulphur remains divalent in sulphenic acid derivatives. It is also observed that the oxidation takes place to S(IV) or even to S(VI) compounds in the above reactions.

Zincke and Farr found that 2-nitrobenzene sulphenyl chloride (38) was hydrolysed by cold water to sulphenic anhydride (40) via the unstable sulphenic acid (39). On treatment with conc. hydrochloric acid, the anhydride regenerated the sulphenyl chloride.
The same sulphenyl chloride reacted with methanol and ethanol in cold condition to give the corresponding disulphide (41) and thiol sulphonate (42).

\[
\begin{align*}
\text{(38)} & \xrightarrow{\text{ROH, Cold}} \text{(41)} + \text{(42)} \\
\text{(38)} & \xrightarrow{\text{MeOH, Hot}} \text{(41)} + \text{(42)} + \text{(44)} + \text{(45)} + \text{(43)}
\end{align*}
\]

At elevated temperature, the disulphide and sulphinic acid (43) were obtained by disproportionation of the sulphenic anhydride (40) formed as an intermediate.

With hot aqueous methanol corresponding sulphenic acid (43), sulphonic acid (44), disulphide (41), thiol sulphonate (42) and 2-aminobenzene sulphonic acid (45) were formed. The mechanism of this reaction was, however, not explained.
Sulphenates R-\text{SO}-R which are the sulphur analogues of the peroxides, were reported to be stable enough to be used as the derivatives of alcohol.\(^{44-48}\) They were conveniently prepared by the reaction of sulphenyl halides in an inert solvent dichloromethane with alcohol in presence of an organic tertiary base\(^{48-44}\). The reaction was found to be faster than the formation of the corresponding disulphide as a by product.

It was reported that the hydrolysis of sulphenyl halides with water did not yield sulphenic acid but gave the corresponding disulphide and sulphinic acid\(^{48}\) or sulphonic and sulphenic anhydride\(^47\). The instability of sulphenic acids (R-SOH) may be viewed from the fact that they are actually bivalent sulphur compounds of thiohydroperoxides.

2-nitrobenzene sulphenyl chloride on alkaline hydrolysis with one mole of cold aqueous sodium hydroxide resulted in unstable sodium sulphenate with a transient blue colour.\(^48\) The salt quickly disproportionated to give the corresponding
disulphide (41) and thiol sulphonate (42). With excess of sodium hydroxide, the thiol sulphonate (42) was converted to disulphide (41) and sodium sulphinate (46).

\[
\text{Hydrolysis of 2,4-dinitrobenzene sulphenyl chloride with sodium carbonate gave a mixture of products including the disulphide, sulphonic acid, sulphinic acid and sulphenic anhydride.}^{47}
\]

Burawoy and Chaudhuri\(^\text{48}\) while studying the action of alkali on azobenzene-2-sulphenyl bromide and its derivatives proposed the course of the reaction in the following stages:

(I) With excess of alkali, the sulphenic acid remained in equilibrium with alkali sulphenate.

\[
\text{Ar.SBr} \quad \rightarrow \quad \text{Ar.SOH} \quad \leftrightarrow \quad \text{Ar.SO}^-\text{Na}^+
\]

(II) The sulphenic acid disproportionated to the disulphide and the thiol sulphonate.

\[
\text{Ar.SOH} \quad \rightarrow \quad \text{Ar.SO}_2\text{SAr} \quad + \quad \text{Ar.S.S.Ar}
\]
(III) Thiolsulphonate cleaved into the alkali sulphinate and sulphenic acid and the latter re-entered the reaction cycle.

\[ \text{Ar.SO}_2\text{SAr} \xrightarrow{\text{Ar.SO}_2\text{-Na}^+ + \text{Ar.SOH}} \]

The reaction of 2-phenylazo naphthalene-1-sulphenyl bromide and its 2-nitro and 4-nitro derivatives with equimolar quantity of aqueous alkali resulted in corresponding diaryl thioethers because the thiolsulphonates formed in the reactions being unstable split off sulphur dioxide to give the thioethers. However, with excess alkali, the thiolsulphonate gave the salt of sulphinic acid and the disulphide. In the latter case, the rate of reaction of thiolsulphonate with alkali was faster than its rate of dissociation into thioether and sulphur dioxide.

Chaudhuri and Bhattacharjee observed that even in the presence of excess of alkali 2-p-tolylazonaphthalene-1-sulphenyl bromide resulted in a mixture of corresponding disulphide, alkali sulphinate along with a little diaryl thioether and 2-p-tolylazo naphthalene-1-sulphenyl sulphite. They observed that in
the above reaction, the dissociation of thiolsulphonate competed with the reaction with alkali. An attempt to synthesize thiol sulphonate from the sulphenyl bromide and sodium sulphinate resulted in an unstable compound which spontaneously dissociated to the corresponding thioether.

Fries and Schurmann\(^{(48-50)}\) reported that ethanolic sodium hydroxide reacted with anthraquinone-1-sulphenyl chloride to give the corresponding disulphide and sulphinic acid. Ethanolic sodium hydroxide when reacted with 2-nitrobenzene sulphenyl chloride gave sodium sulphenate with the characteristic blue colour which then slowly disproportionated to give the disulphide and the thiol sulphonate. But with sodium hydroxide or phenoxide in chloroform or ether, the products were alkyl or aryl esters which were found to be stable and could well be converted to sulphenyl chloride with conc. hydrochloric acid.
RESULTS AND DISCUSSION:

Due to easy fission of the S-halogen bond, it is observed that the sulphenyl halides specially the chlorides and bromides are fairly reactive compounds. We have studied solvolysis and alkaline hydrolysis of sulphenyl bromides (35,a-c).

![Diagram of sulphenyl halides]

It has been observed that in aqueous solution azobenzene sulphenyl halides react with silver nitrate to give a precipitate of silver halide but do not undergo solvolysis and can be recrystallized unchanged from water and ethanol. This may be the implication of orthoazo group being tied to the sulphenyl sulphur in the preferred ground state conformation.

Out of the three azonaphthalene sulphenyl bromides (35,a-c) that we have studied, the 2-phenylazo (35a) and 2-p-tolylazo (35b) naphthalene-1-sulphenyl bromides are found to be stable in solvents
like water and ethanol even at their boiling points. They can be recrystallized unchanged from boiling water. But 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide (35c) suffers slow solvolysis with these solvents and gives red precipitate of the disulphide (52c). The aqueous solution of the compound (35c) when kept at room temperature for several days also produce disulphide. The low stability of the ortho nitrat ed compound may be attributed to the partial destruction of the co-planarity of the atoms involved in forming (azo-N)-S bonding by steric repulsion of the ortho-nitro substituent resulting in involvement of lesser amount of energy while going to the transition state of the nucleophilic substitution at the sulphur atom by the solvent nucleophiles. The solvolysis of the compound (35c) in boiling ethanol is found to be faster than that in boiling water.

The action of aqueous sodium hydroxide on sulphenyl bromides (35,a-c) both in equimolar and in excess proportions have been studied. It is observed that an aqueous solution of azobenzene sulphenyl bromide (Ar.Sbr) when reacted with equimolar
quantity of sodium hydroxide resulted in a mixture of corresponding disulphides (47) and thiolsulphonates (48).

All the thiolsulphonates can be obtained from direct synthesis of their corresponding sulphenyl bromides and sodium sulphinates.

\[
\text{Ar.SBr} + \text{Ar.SO}_2^-\text{Na}^+ \rightleftharpoons \text{Ar.S} \cdot \text{SO}_2 \text{Ar} + \text{NaBr}.
\]

With excess of aqueous sodium hydroxide, the azobenzene sulphenyl bromides first form soluble blue violet sodium sulphinates (49) which can not be isolated but their formation can be established by the fact that they rapidly form 2-arylazophenylmethyl sulphoxides (50) on treatment with dimethyl sulphate.
The blue colour of the reaction mixture disappears slowly and the sulphenates are replaced by the corresponding disulphides (47) and sodium sulphinates (51).

\[
\text{SO}_2\text{Na}^+ \quad X
\]

(51)

We have observed that all the three 2-arylanaphthalene-1-sulphenyl bromides (35,a-c) react with equimolar quantities of sodium hydroxide producing a mixture of corresponding disulphide (52), monosulphide (53), sulphenyl sulphite (54) and alkali sulphonate (55). The latter on acidification gives corresponding sulphinic acid (56).
But no thiolsulphonate (57) can be isolated from the reaction mixture.

The thiosulphonates (57) obtained from 2-arylazonaphthalene-1-sulphenyl bromides are unstable in polar solvents and decompose spontaneously to monosulphide (53) liberating sulphur dioxide which reacts with any unreacted 2-aryazoaryl sulphenyl bromide to give the corresponding sulphenyl sulphite (54). Therefore, all attempts to isolate the thiol sulphonates have resulted in the formation of monosulphide (53) only. The sulphenyl sulphites (54) are identified by directly synthesizing them from the corresponding sulphenyl bromides and sodium sulphites in aqueous solution.

The separation of the mixture containing disulphide (52), monosulphide (53) and sulphenyl sulphite (54) is carried out first by dissolving the disulphide and monosulphide in benzene. Sulphenyl sulphite is insoluble and is filtered out. The
filtrate containing the disulphide and monosulphide is evaporated to remove the solvent. The residue obtained is then refluxed with an aqueous ethanolic suspension of sodium sulphide for a few minutes. The disulphide is converted to water soluble mercaptide. The insoluble monosulphide (53) is filtered out. The disulphide is again regenerated by acidification.

We have studied the reaction of 2-aryazonaphthalene-1-sulphenyl bromides (35,a-c) with excess quantity of aqueous sodium hydroxide. The reaction is found to be analogous with that of corresponding azobenzene series. The thiolsulphonate (57) initially formed is converted to corresponding insoluble disulphide (52) and the water soluble sulphinate (55).

\[
\begin{align*}
\text{SO}_2\text{Na}^+ & \quad X \quad Y \\
\text{(55)} & \\
\text{a, } X = H, Y = H & \quad \text{b, } X = H, Y = \text{CH}_3 \\
& \quad \text{c, } X = \text{NO}_2, Y = \text{Cl}
\end{align*}
\]

The cleavage of the thiolsulphonate (57) by alkali is faster than its decomposition to monosulphide (53) and sulphur dioxide. But the
thiolsulphonates of 2-aryazonaphthalene-1-sulphenyl bromides are very unstable and as such their decomposition to the monosulphides (53) compete with their alkali cleavage to disulphides (52) and sulphinates (55). It has been observed, therefore, that a small amount of monosulphide is also obtained along with the disulphide in the reaction of sulphenyl bromides with excess alkali.

The removal of insoluble disulphide from the reaction mixture by filtration leaves the sulphinate (55) in the mother liquor from which sulphinic acid (56) is precipitated by acidification.

**Uv-visible and ir spectra of hydrolysis products of 2-arylazonaphthalene-1-sulphenyl bromides (35,a-c):**

The uv and visible spectra of different hydrolysis products of 2-arylazonaphthalene-1-sulphenyl bromides are in table-V.

The spectra of disulphides (52) and monosulphides (53) are dominated by three bands. The low intensity azo n→n* transition band is observed in the region of 400-430 nm. The characteristic high intensity
The spectral pattern of 2-aryazonaphthalene-1-sulphenyl sulphites (54) shows two bands. The first low intensity $\pi\rightarrow\pi^*$ band in the region of 400-430 nm is due to the azo group. The second high intensity $\pi\rightarrow\pi^*$ in the shorter wavelength region of 330-360 nm is due to the arylazo chromophore. This band shows marked solvatochromism with the change of solvent polarity like that of corresponding sulphenyl bromides indicating that sulphenyl sulphites are also highly polarised like sulphenyl bromides.

The 2-aryazonaphthalene-1-sulphinic acids (56) are recrystallized from benzene and light petrol as colourless plates. These acids do not display characteristic azo $\pi\rightarrow\pi^*$ band in these solvents. This implies that these sulphinic acids exist as a cyclic tautomer (58 or 59) in non polar solvents.
In polar solvents like ethanol or chloroform, however, they tautomerise to the true azo form (56) which is confirmed by the display of the azo $n\rightarrow n^*$ band at 400-430 nm by these compounds in ethanol or chloroform.

The ir-bands of different hydrolysis products of 2-arylazonaphthalene-1-sulphenyl bromides in KBr pellets are summarised in Table-VI.

\[ \text{In polar solvents like ethanol or chloroform, however, they tautomerise to the true azo form (56) which is confirmed by the display of the azo } n\rightarrow n^* \text{ band at 400-430 nm by these compounds in ethanol or chloroform.}

\text{The ir-bands of different hydrolysis products of 2-arylazonaphthalene-1-sulphenyl bromides in KBr pellets are summarised in Table-VI.} \]
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \pi\rightarrow\pi^* ) Band</th>
<th>( \sigma\rightarrow\sigma^* ) Band</th>
<th>( n^1\pi^* ) Band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max}} )</td>
<td>( \epsilon )</td>
<td>( \lambda_{\text{max}} )</td>
</tr>
<tr>
<td>a, X=Y=H</td>
<td>420</td>
<td>1100</td>
<td>335</td>
</tr>
<tr>
<td>52. b, X=H, Y=CH₃</td>
<td>410</td>
<td>900</td>
<td>340</td>
</tr>
<tr>
<td>c, X=NO₂, Y=Cl</td>
<td>425</td>
<td>950</td>
<td>360</td>
</tr>
<tr>
<td>a, X=Y=H</td>
<td>418</td>
<td>1200</td>
<td>336</td>
</tr>
<tr>
<td>53. b, X=H, Y=CH₃</td>
<td>408</td>
<td>1100</td>
<td>340</td>
</tr>
<tr>
<td>c, X=NO₂, Y=Cl</td>
<td>420</td>
<td>950</td>
<td>355</td>
</tr>
<tr>
<td>a, X=Y=H</td>
<td>420</td>
<td>1100</td>
<td>336</td>
</tr>
<tr>
<td>54. b, X=H, Y=CH₃</td>
<td>412</td>
<td>900</td>
<td>336</td>
</tr>
<tr>
<td>c, X=NO₂, Y=Cl</td>
<td>422</td>
<td>850</td>
<td>352</td>
</tr>
<tr>
<td>a, X=Y=H</td>
<td>415</td>
<td>1000</td>
<td>338</td>
</tr>
<tr>
<td>56. b, X=H, Y=CH₃</td>
<td>410</td>
<td>950</td>
<td>340</td>
</tr>
<tr>
<td>c, X=NO₂, Y=Cl</td>
<td>425</td>
<td>900</td>
<td>356</td>
</tr>
</tbody>
</table>
UV AND VISIBLE SPECTRA OF

- 2-phenylazonaphthalene-1-sulphenyl sulphite
- 2-p-tolylazonaphthalene-1-sulphenyl sulphite
- 2-(2'-nitro-4'-chlorophenylazo)naphthalene-1-sulphenyl sulphite
TABLE-VI

**Ir-spectra of hydrolysis products of 2-arylazo naphthalene-1-sulphenyl bromides (in KBr)**:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band (in Cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a,X=H,Y=H</td>
<td>1590 (w,N=N stretch)</td>
</tr>
<tr>
<td>b,X=H,Y=CH₃</td>
<td>1585 (w,N=N stretch)</td>
</tr>
<tr>
<td>c,X=NO₂,Y=Cl</td>
<td>1590 (w,N=N stretch), 1540 and 1390 (m,NO₂ group).</td>
</tr>
<tr>
<td>a,X=Y=H</td>
<td>1585 (w,azo group)</td>
</tr>
<tr>
<td>b,X=H,Y=CH₃</td>
<td>1585 (w,azo group)</td>
</tr>
<tr>
<td>c,X=NO₂,Y=Cl</td>
<td>1585 (w,azo group), 1540 and 1400 (m,NO₂ group)</td>
</tr>
<tr>
<td>a,X=H,Y=H</td>
<td>1590 (w,azo group), 1130 (s,S=O stretch)</td>
</tr>
<tr>
<td>b,X=H,Y=CH₃</td>
<td>1590 (w,azo group), 1120 (s,S=O stretch)</td>
</tr>
<tr>
<td>c,X=NO₂,Y=Cl</td>
<td>1585 (w,azo group), 1540 and 1400 (m,NO₂ group), 1140 (s, S=O stretch)</td>
</tr>
<tr>
<td>a,X=H,Y=H</td>
<td>3200 (b,may be OH), 1100 (s, S=O stretch)</td>
</tr>
<tr>
<td>b,X=H,Y=CH₃</td>
<td>3230 (b,may be OH), 1110 (s, S=O stretch)</td>
</tr>
<tr>
<td>c,X=NO₂,Y=Cl</td>
<td>3200 (b,may be OH), 1540 and 1390 (m,NO₂ group), 1100 (s, S=O stretch).</td>
</tr>
</tbody>
</table>
EXPERIMENTAL :

(I) Reaction of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide with water at room temperature:

To 0.5 g of the sulphenyl bromide 100 ml of water was added. The mixture was shaken well till the sulphenyl bromide was dissolved completely. The solution was allowed to stand at room temperature. After 5 days a dull red precipitate was obtained. The precipitate was filtered, washed with water and dried. Red crystals of diaryl disulphide (52c) was obtained.

Yield - 0.38 g. M.P. 197- 198°C.

The compound was recrystallized from benzene:ethanol mixture.

Analysis : C_{52}H_{48}N_{8}O_{4}S_{2}Cl_{2}

Requires : C, 56.1% ; H, 2.6% ; N, 12.3%

Found : C, 56.0% ; H, 2.7% ; N, 12.1%

Uv and visible spectra :

\( \lambda_{\text{max}} \) 425 (\( \varepsilon \), 950, n\( \rightarrow \pi^* \)) ; 360 (\( \varepsilon \), 12000, n\( \rightarrow \pi^* \))

312 (\( \varepsilon \), 12500, n\(^1\pi\))

Ir spectra :

\( \gamma \) cm\(^{-1}\)

(KBr) 1590 (w, N=N stretch), 1540 and 1390 (m, NO\(_2\)).
(II) Reaction of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide with boiling water:

To 0.5 g of the sulphenyl bromide, 100 ml of water was added. The mixture was shaken well till the sulphenyl bromide was dissolved completely. The solution was then heated slowly till boiling and allowed to stand. A dull red precipitate was formed which was filtered, washed with water and dried. Red crystals of disulphide (52c) was obtained.

Yield - 0.36 g. M.P. and mixed m.p. 197-198°C.

It was recrystallized from benzene:ethanol mixture.

(III) Reaction of 2-(2'-nitro-4'-chlorophenylazo)-naphthalene-1-sulphenyl bromide with ethanol at boiling condition:

To 0.5 g of the sulphenyl bromide, 100 ml of ethanol was added. The mixture was shaken well till the sulphenyl bromide was dissolved completely. The solution was then heated slowly till boiling and was allowed to stand. A dull red precipitate was formed immediately which was filtered, washed with ethanol and
dried. Red crystals of disulphide (52c) was obtained.

Yield - 0.42 g M.P. and mixed m.p. 197-198°C.

It was recrystallized from benzene:ethanol mixture.

(IV) Reaction of 2-(2'-nitro-4'-chloro phenylazo) naphthalene-1-sulphenyl bromide with equimolar quantity of sodium hydroxide:

\[
\begin{align*}
\text{NaOH} & \quad \text{Ar.SBr} \quad \rightarrow \quad \text{Ar.S.SO}_2\text{Ar} \quad + \quad \text{Ar.S.S.Ar} \\
\text{NaOH}/\text{HCl} \quad (52c) & \quad | \quad \text{Ar.S.Ar} \quad \rightarrow \quad \text{Ar.SO}_2\text{H} \\
\text{SO}_2 \quad (53c) & \quad | \quad \text{Ar.SBr} \quad \rightarrow \quad \text{Ar.SSO}_2\text{S.Ar} \\
\text{H}_2\text{O} \quad (54c) & \quad | \quad [\text{Ar} = \begin{array}{c}
\text{Ar} = \begin{array}{c}
\text{N} \quad \text{N} \\
\text{Cl} \quad \text{Cl}
\end{array}
\end{array}]
\end{align*}
\]

An aqueous alcoholic solution of 2-(2'-nitro-4'-chloro phenylazo)-naphthalene-1-sulphenyl bromide (0.5 g in 150 ml) was prepared and to this was added 1% sodium hydroxide solution (5 ml). A blue violet colour was formed which immediately disappeared resulting in a dull red precipitate consisting of disulphide (52c), monosulphide (53c) and sulphenyl sulphite (54c). The residue was filtered, washed with water and dried. A dull red precipitate was obtained. Yield - 0.35 g.

The dull red precipitate containing
disulphide (52c), monosulphide (53c) and sulphenyl sulphone (54c) was dissolved in benzene. The insoluble residue of sulphenyl sulphone (54c) was filtered off. It was then washed with benzene and dried.

Yield - 0.092 g.

Recrystallization in hot ethanol yielded red needle shaped crystals. M.P. 192-193°C.

Analysis: C\(_{33}\)H\(_{18}\)N\(_8\)O\(_7\)S\(_3\)Cl\(_2\)

Requires: C, 50.2%; H, 2.4%; N, 10.9%

Found: C, 49.8%; H, 2.1%; N, 10.1%

Uv and visible spectra:

\[ \lambda_{max} \] 422 (\( \varepsilon, 850, n\rightarrow\pi^* \)) ; 352 (\( \varepsilon, 12000, n\rightarrow\pi^* \))

Ir spectra:

\( \nu (\text{KBr}) \) 1585 (w, azo group), 1540 and 1400 (m, NO\(_2\) group)

1140 (s, S=O stretch).

The filtrate was evaporated and the residue left after evaporation was dissolved in aqueous ethanol (100 ml) and refluxed. To the refluxing solution was added an aqueous solution of sodium sulphone (0.5 g in 10 ml) followed by an aqueous solution of sodium hydroxide (0.5 g in 10 ml) and the reflux was continued.
for 15 minutes. The resulting violet coloured solution
was cooled and diluted with water (100 ml). The residue
containing monosulphide (53c) was filtered and washed
with aqueous ethanol and dried. Yield - 0.11 g.
Recrystallization from petroleum ether (60-80°C) gave red
crystals. M.P. 243-45°C.
Analysis : C₃₉H₁₈N₆O₄SCl₂
Requires : C, 55.8% ; H, 2.8% ; N, 12.9%
Found : C, 57.9% ; H, 2.6% ; N, 12.3%
Uv and visible spectra :
\[ \lambda_{\text{max}} 420 (\varepsilon, 950, n\rightarrow n^*) \],
355 (\varepsilon, 11000, n\rightarrow n^*),
316 (\varepsilon, 11500, n^2).
Ir spectra :
\[ \text{cm}^{-1} \]
\[ \gamma \text{(KBr)} 1585 \text{ (w, azo group), 1540 and 1400 (m, NO}_2 \text{)} \]
The filtrate was acidified with
dilute hydrochloric acid and extracted with benzene.
After evaporation of the solvent, red crystals of
disulphide (52c) was obtained. Yield - 0.12 g.
It was recrystallized from benzene-ethanol mixture.
M.P. and mixed m.p. 197-198°C.
The original filtrate was acidified with dilute hydrochloric acid. A deep red precipitate of 2-(2'-nitro-4'-chloro phenylazo) naphthalene-1-sulphinic acid (56c) was obtained which was filtered, washed with water and dried. Yield - 0.128 g.

Recrystallization from rectified spirit gave pale yellow crystals. M.P. 144-145°C.

Analysis : C₁₆H₁₀N₃O₄SCl

Requires : C, 51.1% ; H, 2.7% ; N, 11.2%

Found : C, 51.4% ; H, 2.2% ; N, 10.9%

Uv and visible spectra :

\[ \lambda_{\text{max}} 425 (\varepsilon, 900, n \rightarrow n^*) , 356 (\varepsilon, 12000, n \rightarrow n^*) \].

Ir spectra :

\[ \gamma \text{ (KBr) } 3200 (s, \text{ may be } \text{OH}), 1540 \text{ and } 1390 (m, \text{NO}_2) \]

1100 (s, S=O stretch)

Similar reactions of sodium hydroxide with equimolar quantities of 2-phenylazonaphthalene-1-sulphenyl bromide (35a) and 2-p-tolylazonaphthalene-1-sulphenyl bromide (35b) were carried out. The following
products were obtained:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>M.P</th>
</tr>
</thead>
<tbody>
<tr>
<td>52(a). Di-(2-phenylazo naphthyl-1-) disulphide</td>
<td>0.18 g</td>
<td>204-205°C</td>
</tr>
<tr>
<td>53(a). Di-(2-phenylazo naphthyl-1-) sulphide</td>
<td>0.085 g</td>
<td>197-198°C</td>
</tr>
<tr>
<td>54(a). Di-(2-phenylazo naphthyl-1-) sulphenyl sulphite</td>
<td>0.085 g</td>
<td>182-183°C</td>
</tr>
<tr>
<td>55(a). 2-phenylazonaphthalene-1-sulphinic acid</td>
<td>0.122 g</td>
<td>146-148°C</td>
</tr>
<tr>
<td>52(b). Di-(2-p-tolylazo naphthyl-1-) disulphide</td>
<td>0.160 g</td>
<td>193-195°C</td>
</tr>
<tr>
<td>53(b). Di-(2-p-tolylazo naphthyl-1-) sulphide</td>
<td>0.110 g</td>
<td>233-235°C</td>
</tr>
<tr>
<td>54(b). Di-(2-p-tolylazo naphthyl-1-) sulphenyl sulphite</td>
<td>0.086 g</td>
<td>187-188°C</td>
</tr>
<tr>
<td>55(b). 2-p-tolylazonaphthalene-1-sulphinic acid</td>
<td>0.125 g</td>
<td>153-155°C</td>
</tr>
</tbody>
</table>

(II) Reaction of 2-(2'-nitro-4'-chloro phenylazo)naphthalene-1-sulphenyl bromide with excess of sodium hydroxide:

\[
\begin{align*}
\text{Ar}_2\text{Br} + \text{NaOH} & \rightarrow \text{Ar}_2\text{SO}_2\text{Ar} + \text{NaBr} \\
\text{Ar}_2\text{SO}_2\text{Ar} & \rightarrow \text{Ar}_2\text{SAr} + \text{H}_2\text{O}
\end{align*}
\]

2-(2'-nitro-4'-chloro phenylazo)naphthalene-1-sulphenyl bromide (0.5 g) was dissolved in
aqueous alcohol (150 ml) and an aqueous 2% solution of sodium hydroxide (25 ml) was added to it. A dull red precipitate was obtained. The precipitate containing di-2-(2'-nitro-4'-chlorophenylazo)-naphtalene-1-disulphide (52c) and di-2-(2'-nitro-4'-chloro-phenylazo)-naphtalene-1-sulphenyl sulphide (53c) was filtered, washed with water and dried. Yield - 0.29 g.

The precipitate was refluxed in aqueous ethanol (100 ml) and to the refluxing solution aqueous sodium sulphide (0.75 g in 25 ml) was added followed by an aqueous solution of sodium hydroxide (0.75 g in 10 ml). The reflux was continued for 15 minutes more. The resulting violet coloured solution was diluted with 100 ml water. A red coloured precipitate of the monosulphide (53c) was obtained which was filtered, washed with aqueous ethanol and dried. Yield - 0.087 g. The precipitate on recrystallisation from petroleum ether (60-80°C) gave red crystals.

M.P. and mixed m.p. 197 - 198°C.

The filtrate was acidified with dilute hydrochloric acid and was extracted with benzene. After evaporation of the solvent red crystals of
disulphide (52c) was obtained. Yield - 0.15 g  
The disulphide was recrystallized from benzene-ethanol mixture. M.P. and mixed m.p. 197-198°C.

The original filtrate was acidified with dilute hydrochloric acid. A deep red precipitate of 2-(2'-nitro-4'-chloro phenylazo) naphthalene-1-sulphinic acid (56c). The precipitate was filtered, washed with water and dried. Yield - 0.105 g.

Recrystallization of the precipitate from rectified spirit gave pale yellow crystals. M.P. and mixed m.p. 144-145°C.

Similarly, reactions of sodium hydroxide in excess quantity were carried out with 2-phenylazo naphthalene-1-sulphenyl bromide (35a) and 2-p-tolylazo naphthalene-1-sulphenyl bromide (35b). The following products were obtained:
disulphide (52c) was obtained. Yield - 0.15 g

The disulphide was recrystallized from benzene-ethanol mixture. M.P. and mixed m.p. 197-198°C.

The original filtrate was acidified with dilute hydrochloric acid. A deep red precipitate of 2- (2'-nitro-4'-chloro phenylazo)-naphthalene-1-sulphinic acid (56c). The precipitate was filtered, washed with water and dried. Yield - 0.105 g.

Recrystallization of the precipitate from rectified spirit gave pale yellow crystals. M.P. and mixed m.p. 144-145°C.

Similarly, reactions of sodium hydroxide in excess quantity were carried out with 2-phenylazo- naphthalene-1-sulphenyl bromide (35a) and 2-p-tolylazo - naphthalene-1-sulphenyl bromide (35b). The following products were obtained:
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Yield</th>
<th>M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(52a). Di-(2-phenylazo naphthyl-1-) disulphide</td>
<td>0.16 g</td>
<td>204-205°C</td>
</tr>
<tr>
<td>(53a). Di-(2-phenylazo naphthyl-1-) sulphide</td>
<td>0.05 g</td>
<td>197-198°C</td>
</tr>
<tr>
<td>(56a). 2-phenylazo naphthalene-1- sulphinic acid (Na=H)</td>
<td>0.09 g</td>
<td>146-148°C</td>
</tr>
<tr>
<td>(52b). Di-(2-p-tolylazo naphthyl-1-) disulphide</td>
<td>0.14 g</td>
<td>193-195°C</td>
</tr>
<tr>
<td>(53b). Di-(2-p-tolylazo naphthyl-1-) sulphide</td>
<td>0.072 g</td>
<td>233-235°C</td>
</tr>
<tr>
<td>(56b). 2-p-tolylazo naphthalene-1- sulphinic acid (Na=H)</td>
<td>0.13 g</td>
<td>153-155°C</td>
</tr>
</tbody>
</table>