CHAPTER IV

REACTION OF 2-ARYLAZONAPHTHALENE-1-SULPHENYL BROMIDES

WITH UNSYMMETRICAL KETONE AND ACTIVE METHYLENE COMPOUND
CHAPTER-IV

REACTION OF 2-ARYLAZO NAPHTHALENE-1-SULPHENYL BROMIDE
WITH UNSYMMETRICAL KETONE AND ACTIVE METHYLENE COMPOUNDS:

REVIEW:

The sulphur atom in sulphenyl halides offers a nucleophilic site to undergo nucleophilic displacements by methyl ketones. It was reported by Zincke\textsuperscript{81} that aryl sulphenyl chloride when reacted with methyl ketones formed $\beta$-keto thioethers.

$$\text{Ar.SX} + \text{CH}_3\text{.CO.CH}_2\text{R} \rightarrow \text{ArS.CH}_2\text{CO.CH}_2\text{R} + \text{HX}$$

Further study in this regard was carried out by Kharasch et al\textsuperscript{(52,53)}, Langford et al\textsuperscript{54} and Morgan et al\textsuperscript{55} with a number of methyl ketones in inert solvents. They observed that in unsymmetrical methyl ketones $\text{CH}_3\text{.CO.CH}_2\text{R}$, the methyl group was preferentially sulphenylated. The product $\beta$-keto thioethers could be converted to their phenyl hydrazones and oximes and thus behaved like normal ketones.

$\beta$-ketothioethers could also be prepared using arene sulphenyl thiocyanate\textsuperscript{56}.

$$\text{Ar.SS.CN} + \text{CH}_3\text{COR} \rightarrow \text{ArS.CH}_2\text{COR} + \text{HSCN}$$
In systems sensitive to bromination, reactions with sulphenyl bromides could follow a different path than their corresponding sulphenyl chlorides. Kharasch et al.\textsuperscript{97} noted the effect in the reaction of 2,4-dinitrobenzene sulphenyl bromide with acetone. Similar type of sulphenylation reactions involving nucleophilic substitution at the sulphur atom of the sulphur-halogen bond of azobenzene-2'-sulphenyl halides with acetone and acetophenone in aqueous and ethanolic solutions were studied at room temperatures\textsuperscript{48}. In all the above reactions, the methyl sulphenylated product was invariably formed. The resulting β-ketothio ethers (60) were found to be unstable at elevated temperature in solvents like benzene, ethanol and underwent cleavage at the azo group to give a molecule of aryl amine (61), a molecule of benzthiazolylmethyl ketone (62a) and benzthiazolyl-phenyl ketone (62b).
The rate of conversion of β-keto thioethers into benzthiazolyl ketone could be accelerated by the addition of a few drops of hydrochloric acid to the boiling solution of β-keto thioethers in ethanol or benzene.

Nucleophiles stronger than the methyl ketone were also used in substituting halogen from sulphur-halogen bonds of orthomercaptoazo compounds. Burawoy et al[48] and Chaudhuri et al[13] studied the sulphenylation reaction of malonic acid with azobenzene-2'-sulphenyl bromides. The resulting 2-(arylazo phenylthio) acetic acid (63) could not be isolated because even at room temperature cleavage of these acids to benzthiazole-2-carboxylic acid (64) and anilines appeared to be faster than primary condensation.

On the other hand, 2-nitro and 2-(orthobenzylthio) phenylazo phenylthio acetic acids were found to be sufficiently stable and could be isolated from the reaction mixture.
Burawoy et al. also reported that 2-phenylazo naphthalene-1-sulphenyl bromide (65) failed to react with acetone, actophenone and malonic acid probably due to steric hindrance.

![Chemical Structure](image)

But it was reported recently that both 2-phenylazo naphthalene-1-sulphenyl bromide and its 4-methyl derivative reacted smoothly with active methylene compounds and acetone in polar solvent ethanol at room temperature resulting in naphthothiazole derivatives (66).

![Chemical Structure](image)

**RESULTS AND DISCUSSION:**

The reactivity of the S-Br bond in the dicoordinated organic sulphur compound of the type R-SBr is greatly influenced by the nature of the R-group and also by the inductive influence of the more distant
atom. The S-Br bond and its physical and chemical properties are effected in a significant manner by unshared electron pairs and vacant d-orbitals on each atom. Therefore, molecules containing this bond may show dichotomy in their properties by way of acting as electrophile or nucleophile depending on circumstances. Since the sulphur atom and not the bromine atom is capable of using 3d-orbitals to accept electronegativity, it is quite evident that the electrophilic properties of sulphenyl bromides will be reflected by it. We have studied 2-arylazonaphthalene-1-sulphenyl bromides (35,c-d) as the source of electrophilic sulphur in the sulphenylation reaction with methyl ketones like butanone and active methylene compounds like acetylacetone.

Because of the initiation of the nucleophilic displacement by the enol form of the ketone at the biligated sulphur of the sulphenyl compounds, the methylene sulphenylation is expected in preference to the
methyl sulphenylation in the above reactions. But we have observed that both the sulphenyl bromides (35,c-d) under study react with the ambident nucleophile butanone in an inert polar solvent dichloromethane at room temperature unaided by any basic catalyst to give a mixture of isomeric $\beta$-keto thioethers (67) and (68) along with a small amount of $\alpha,\beta$-unsaturated ketonyl sulphide (69).

However, it has been observed that the chloro compound (35c) produces a good amount of disulphide (52) along with the above products. The formation of $\beta$-keto thioethers may be attributed to the condensation of sulphenyl bromide (35,c-d) with butanone with the initial formation of hydrobromic acid. The latter may catalyze an aldol condensation of butanone resulting in the formation of an $\alpha,\beta$-unsaturated ketone (70) which may further react with unreacted sulphenyl...
bromide to give the $\alpha,\beta$-unsaturated ketonyl sulphide (69). This is corroborated by the fact that the active hydrogen is available from the methylene group and not from the methyl group of the methyl ketone in undergoing aldolization catalysed by an acid.

The $\beta$-ketothioethers (67) can be cyclized to naphthothiazoles (71) under more stringent conditions of refluxing in protic polar solvent ethanol in presence of catalytic amount of mineral acid. However, we have observed that while the 2-nitro-4-methyl compound (35d) undergoes cyclization to naphthothiazole (71) under the above conditions, the 2-nitro-4-chloro compound (35c) undergoes a wasteful reaction giving the corresponding disulphide (52c) in an appreciably high quantity.

![Chemical structure](image)

The active methylene compounds of the type $Z$-$\text{CH}_2$-$Z$ where $Z$ is an electron withdrawing group, should provide a more nucleophilic site at the methylene carbon than the ketone. It is expected, therefore, that the sulphenylation of these compounds
with the sulphenyl bromides (35,c-d) would be faster than the ketones as they are more reactive than the ketones. We have studied the sulphenylation reactions of an active methylene compound, acetylacetone, with the sulphenyl bromides (35,c-d). It has been observed that the electron deficient sulphur atom of both the sulphenyl bromides suffer a nucleophilic attack from acetylacetone. The sulphenylation reactions proceed smoothly unaided by any basic catalyst.

Unlike 2-phenylazo and 2-p-tolylazo naphthalene-1-sulphenyl bromides which react with active methylene compounds of the type Z-CH\textsubscript{2}-Z at room temperature in ethanol medium giving the precipitate of naphtho-2':1':4:5-thiazolyl compounds (72) directly in excellent yield, we have observed that 2-(2'-nitro-4'-methyl phenylazo) naphthalene-1-sulphenyl bromide (35d) and 2-(2'-nitro-4'-chloro-phenylazo) naphthalene-1-sulphenyl bromide (35c) react with acetylacetone but do not give the thiazole compound directly. Instead, both the compounds yield stable monosulphenylated compounds (73) which are isolated. However, we have observed that
2-(2'-nitro-4'-chloro phenylazo) naphthalene-1-sulphenyl bromide (35c) produces a good amount of diaryl disulphide (52c) along with the monosulphenylated compound (73). 2-(2'-nitro-4'-methyl phenylazo) naphthalene-1-sulphenyl bromide (35d), on the other hand, produces a small amount of naphtho 2':1':4:5:-thiazolyl-2-methyl ketone (72) along with the monosulphenylated compound (73).

The expected methylene mono sulphenylated compound (73) in case of 2-phenylazo naphthalene-1-sulphenyl bromide (X=H,Y=H) and 2-p-tolylazo naphthalene-1-sulphenyl bromide (X=H,Y=CH₃) are not obtained as they undergo spontaneous cyclization to form the heterocycles with simultaneous loss of the corresponding arylamine molecule (74). It is reported that the cyclization reaction is enhanced to form the
thiazole compound (72) if a few drops of concentrated hydrochloric acid is added to the reaction mixture.

The monosulphenylated compounds (73) obtained from the reaction of sulphenyl bromides (35,c-d) with acetylacetone undergo cyclization when refluxed in ethanol medium in presence of mineral acids resulting in the heterocycle (72) with simultaneous loss of aryl amine molecule (74). With excess of sulphenyl bromide (35,c-d) the disulphenylated products (75) are also found to be formed along with the monosulphenylated compounds (73).

\[
\begin{align*}
\text{ArS} & \quad \text{CO}_2\text{CH}_3 \\
\text{C} \quad \text{SAr} & \quad \text{CO}_2\text{CH}_3 \\
(75) & \quad \text{Ar} = \quad \text{N} = \text{N} \\
& \quad \text{X} \\
& \quad \text{c, X} = \text{NO}_2, \text{Y} = \text{Cl} \\
& \quad \text{d, X} = \text{NO}_2, \text{Y} = \text{CH}_3
\end{align*}
\]

However, we have observed that the monosulphenylated compound (73c) obtained from 2-(2'-nitro-4'-chloro - phenylazo) - naphthalene-1-sulphenyl bromide (35c) produces a good amount of diaryl disulphide (52c) along with the naphthothiazole (72c) when refluxed in ethanol medium in presence of mineral acid.

The formation of naphthothiazoles from the monosulphenylated compounds under the catalytic
influence of mineral acids may be rationalized as per the following scheme:

\[
\begin{align*}
\text{Uv-vis, ir and pmr spectra of the compounds obtained from} \\
\text{butanone and acetyl acetone:} \\
(A) \text{Uv-visible spectra:}
\end{align*}
\]

The uv-vis spectra of the compounds obtained from butanone and acetyl acetone comprise of two bands. The \( n \rightarrow n^* \) band due to azo group is observed at 425-430nm for the compounds (67c-69c, 73c and 75c)
and 402-420nm in case of the compounds (67d-69d, 73d and 75d). The $n \rightarrow n^*$ band due to conjugated arylazo chromophore is observed at 350-360nm for the compounds (67c-69c, 73c and 75c) and 325-330nm in case of the compounds (67d-69d, 73d and 75d).

We have observed that naphtho-$2':1':4:5$: thiazoles (76) like benzothiazoles retain the vibrational structure of the benzene ring chromophore but suffer a moderate bathochromic shift and appear as three peaks at 330nm, 324nm and 318nm. The second band appears at 300nm as a shoulder of the third short wavelength band at 288nm. The intensities of the second and the third band are higher than the first. We have seen that the substitution at 2-position of the naphthothiazoles by electron withdrawing groups like -COR (where R=CH$_3$CH$_2$ or CH$_3$ in compounds 71 and 72 respectively), the longer wavelength band undergoes a bathochromic shift of 25-30nm. This shift may be attributed to the conjugation between...
the C=O of the substituent and C=N of the hetero ring. It has also been observed that the substitution of the thiazole ring results in a clear separation of the second and the third band. The second band appears at slightly longer wavelength at 315-318nm in case of 2-substituted naphtho 2':1':4:5-thiazole (71,72). The third band at 288nm appears to have been not affected by the nature and position of the substituents. The uv-vis spectra of the compounds obtained from the reaction of sulphenyl bromides (35,c-d) with butanone and acetylacetone are summarized in Table-VII.

(B) Ir-spectra :

The ir-spectra of the compounds (67,c-d) and (68,c-d) show a strong band at 1710 cm\(^{-1}\) which is due to C=O stretch. Besides this band, the two twin peaks at 1540 cm\(^{-1}\) and 1390 cm\(^{-1}\) are due to the presence of -NO\(_2\) group. The compounds (69,c-d) show two bands at 1670 cm\(^{-1}\) and 1640 cm\(^{-1}\). The former band indicates the presence of \(\alpha,\beta\)-unsaturation in the molecule while the latter band may be assigned to the \(\alpha,\beta\)-unsaturated olefinic double bond.
Besides a strong band at 1710 cm\(^{-1}\) due to C=O stretch, the ir-spectra of the naphthothiazole derivatives (71,72) are characterized by two medium intensity bands at 1470 cm\(^{-1}\) and 1430 cm\(^{-1}\). It has been observed that the 2-substituents (COR, R=CH\(_2\)CH\(_3\) or CH\(_3\)) which are capable of conjugating with the hetero ring have no effect on the nature and position of these two bands.

The monosulphenylated (73) and the disulphenylated (75) products obtained from acetyl acetone show a strong band between 1690 cm\(^{-1}\) to 1710 cm\(^{-1}\) which is due to C=O stretch.

The ir-spectra of the compounds obtained from the reaction of sulphenyl bromides (35,c-d) with butanone and acetylacetone are summarized in Table-VIII.

(C) Pmr-spectra:

The pmr-spectra of the compounds obtained from the reaction of 2-(2'-nitro-4'-chloro-phenylazo) naphthalene-1-sulphenyl bromide (35c) with butanone is studied. The pmr-spectra of the two \(\beta\)-ketothioethers (67c) and (68c) are quite
distinguishable from their chemical shift at the higher field strength in the region of 1.0 δ evidencing their isomeric structures. The methyl suphenylated β-ketothioether (67c) shows a triplet at 0.9 δ. But the methylene sulphenylated β-ketothioether (68c) shows a doublet at 1.0 δ. The pmr-spectra of the compound (67c) shows a singlet for ArS-CH₂- at 4.0 δ and a quartlet for -CO-CH₃-CH₃ at 2.0 δ. The isomeric β-ketothio ether (68c), on the other hand, shows a singlet at 2.3 δ for (CH₃-CO) and a distorted quartlet at 4.2 δ for (ArS-CH-). The downfield signals are due to aromatic protons. The pmr-spectra of the α,β-unsaturated ketonyl sulphide corresponds well in conformity with its assumed structure (69c). The compound shows twin signals at 1.9 δ representing allyl methyl chemical shifts. In the downfield region, the compound gives a singlet at 3.9 δ which is due to (ArS-CH₂-CO) protons. The multiplet signals in the highfield region of 1.0 δ may be attributed to (CH₂-CH₃) protons.
### TABLE-VII

Uv-visible spectra of the compounds obtained from 2-arylazo naphthalene-1-sulphenyl bromides (35.c-d) with unsymmetrical ketone and active methylene compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$n\rightarrow n^*$ band</th>
<th>$n\rightarrow n^*$ band</th>
<th>$n^1$ band</th>
<th>$n^8$ band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$</td>
<td>$\varepsilon$</td>
<td>$\lambda_{\text{max}}$</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>67c, x=NO$_2$, y=Cl</td>
<td>425 1200</td>
<td>352 9000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d, x=NO$_2$, y=CH$_3$</td>
<td>405 1150</td>
<td>325 12000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>68c, x=NO$_2$, y=Cl</td>
<td>425 1250</td>
<td>355 10000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d, x=NO$_2$, y=CH$_3$</td>
<td>403 1100</td>
<td>327 12500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>69c, x=NO$_2$, y=Cl</td>
<td>430 1250</td>
<td>360 11000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d, x=NO$_2$, y=CH$_3$</td>
<td>410 1300</td>
<td>330 13000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>73c, x=NO$_2$, y=Cl</td>
<td>428 1200</td>
<td>358 12000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d, x=NO$_2$, y=CH$_3$</td>
<td>408 1050</td>
<td>328 13500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>75c, x=NO$_2$, y=Cl</td>
<td>430 1250</td>
<td>355 13000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d, x=NO$_2$, y=CH$_3$</td>
<td>415 1300</td>
<td>330 14000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>76, R=H</td>
<td>-</td>
<td>-</td>
<td>330 1700</td>
<td>300 3500</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>324 900</td>
<td></td>
</tr>
<tr>
<td>71, R=CH$_2$ CH$_3$</td>
<td>-</td>
<td>-</td>
<td>360 7000</td>
<td>318 9500</td>
</tr>
<tr>
<td>72, R=CH$_3$</td>
<td>-</td>
<td>-</td>
<td>355 6500</td>
<td>315 8700</td>
</tr>
</tbody>
</table>
**TABLE-VIII**

*Ir spectra of the compounds obtained from the reaction of 2-aryazonaphthalene-1-sulphenyl bromide (35,c-d) with unsymmetrical ketone and active methylene compound*

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Vibrational bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67 c, X=NO₂, Y=Cl</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch)</td>
</tr>
<tr>
<td>67 d, X=NO₂, Y=CH₃</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 3030 (w, methyl), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>68 c, X=NO₂, Y=Cl</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1700 (s, C=O stretch).</td>
</tr>
<tr>
<td>68 d, X=NO₂, Y=CH₃</td>
<td>3030 (w, methyl), 1540 and 1400 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>69 c, X=NO₂, Y=Cl</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch). 1670 and 1640 (m, olefinic double bond).</td>
</tr>
<tr>
<td>69 d, X=NO₂, Y=CH₃</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch). 1670 and 1640 (m, olefinic double bond).</td>
</tr>
<tr>
<td>73 c, X=NO₂, Y=Cl</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>73 d, X=NO₂, Y=CH₃</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>75 c, X=NO₂, Y=Cl</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>75 d, X=NO₂, Y=CH₃</td>
<td>1540 and 1390 (m, NO₂), 1590 (w, N=N), 1710 (s, C=O stretch).</td>
</tr>
<tr>
<td>71. R=CH₂CH₃</td>
<td>1710 (s, C=O stretch), 1430 and 1470 (m, thiazole ring).</td>
</tr>
<tr>
<td>72. R=CH₃</td>
<td>1710 (s, C=O stretch), 1430 and 1470 (m, thiazole ring).</td>
</tr>
</tbody>
</table>
UV-VISIBLE SPECTRA OF:

Monosulphenylated (73,c-d) and disulphenylated (75,c-d)
Acetyl Acetone

β-Ketothioethers (67,c-d) and α,β-unsaturated ketonyl sulphones (69,c-d)

Naphthothiazoles

76 x-x
71 o-o
72 o-o
IR Spectra of β-ketothioether (67c)

IR Spectra of α,β-unsaturated ketonyl sulphide.

IR Spectra of monosulphenylated acetylacetone.

IR Spectra of disulphenylated acetylacetone.


(WAVE NUMBER (cm⁻¹))
PMR spectra of \( \beta \)-ketothioether (67a)

PMR spectra of isomeric \( \beta \)-ketothioether (68b)

PMR spectra of \( \alpha \beta \)-unsaturated ketonyl sulphide (69c)
EXPERIMENTAL:

(1) Reaction of 2-arylazo naphthalene-1-sulphenyl bromide (8, a-b) with unsymmetrical ketone (butanone):

(A) Reaction of 2-(2'-nitro-4'-chloro-phenylazo)naphthalene-1-sulphenyl bromide (35c) with butanone:

\[
\text{ArSBr} + \text{CH}_3\text{CO.CH}_2\text{CH}_3 \rightarrow \text{ArS.CH}_2\text{CO.CH}_2\text{CH}_3 + \\
\text{CH}_3\text{CO.CH(SAr).CH}_3 + \\
\text{ArS.CH}_2\text{CO.C=C.CH}_2\text{CH}_3
\]

\[\text{(A)} \quad \text{X = NO}_2, \text{Y = Cl} \]
\[\text{(d) X = NO}_2, \text{Y = CH}_3 \]

2-(2'-nitro-4'-chloro-phenylazo)naphthalene-1-sulphenyl bromide (1g) was dissolved in dichloromethane (100ml) and to it added a solution of butanone (0.2g) in dichloromethane (10ml). The solution was shaken well and kept at room temperature. After the completion of the reaction (7 days), the solvent was evaporated. The residue was dissolved in minimum volume of chloroform and poured on a column of alumina for chromatography. The column was eluted successively with
light petrol (40-60°C), benzene and chloroform. Separation of four major zones was obtained. The zones were collected and the following compounds were identified.

(I) Pale yellow crystals of β-ketothioether (67c).

Yield - 0.32 g. M.P. 130-131°C.

Analysis: C20H16N3O2SCl

Requires: C, 58.0% ; H, 3.9% ; N, 10.2%

Found: C, 58.1% ; H, 3.8% ; N, 10.1%

Uv and visible spectra:

\[ \lambda_{\text{max}} \]

425(\epsilon, 1200, \pi\rightarrow\pi^*) , 352 (\epsilon, 9000, \pi\rightarrow\pi^*)

Ir spectra:

\[ \gamma \]

(KBr) 1590(w, N=N), 1540 and 1390(m, NO2), 1710(s, C=O stretch)

(II) Yellow crystals of isomeric β-ketothioether (68c)

Yield - 0.12 g. M.P. 122-123°C.

Analysis: C20H16N3O2SCl

Requires: C, 58.0% ; H, 3.9% ; N, 10.2%

Found: C, 58.1% ; H, 3.7% ; N, 10.3%

Uv and visible spectra:

\[ \lambda_{\text{max}} \]

425(\epsilon, 1250, N\rightarrow\pi^*), 355 (\epsilon, 10000, \pi\rightarrow\pi^*)
Ir spectra:

\( \gamma (\text{KBr}) \, 1590 (w, \text{N=N}), 1540 \text{ and } 1390 (m, \text{NO}_2), 1710 (s, \text{C=O stretch}) \)

(III) Yellow crystals of \( \alpha, \beta \)-unsaturated ketonyl sulphide (69c).

Yield - 0.17 g  M.P. 211-212°C.

Analysis: \( \text{C}_2\text{H}_2\text{N}_3\text{O}_3\text{S} \)

Requires: C, 61.6% ; H, 4.7% ; N, 9.0%

Found: C, 61.5% ; H, 4.6% ; N, 9.1%

Uv and visible spectra:

\( \lambda_{\text{max}} \, 430, (\varepsilon, 1250, \text{n---->n*}), 360 (\varepsilon, 11000, \text{n---->n*}) \)

Ir spectra:

\( \gamma (\text{KBr}) \, 1540 \text{ and } 1390 (m, \text{NO}_2), 1590 (w, \text{N=N}), 1710 (s, \text{C=O stretch}), 1670 \text{ and } 1640 (m, \text{olefinic double bond}) \).

(IV) Red crystals of diaryl disulphide (52c).

Yield - 0.25 g  M.P. and mixed m.p. 197-198°C.

Analysis: \( \text{C}_3\text{H}_8\text{N}_6\text{O}_4\text{S}_2\text{Cl}_2 \)

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

Found: C, 56.2% ; H, 2.4% ; N, 12.4%
Reaction of 2-(2'-nitro-4'-methyl-phenylazo) naphthalene-1-sulphenyl bromide (35d) with butanone:

The sulphenyl bromide (1g) was dissolved in dichloromethane (100ml) and to it added a solution of butanone (0.2g) in dichloromethane (10ml). The solution was shaken well and kept at room temperature. After the completion of the reaction (6 days), the solvent was evaporated. The residue was dissolved in minimum volume of chloroform and then poured in a column of alumina for chromatography. The column was eluted successively with light petrol (40-60°C), benzene and chloroform. Separation of three major zones were obtained and the following compounds were identified:

(I) Light yellow crystals of β-ketothioether (67d)

Yield - 0.35 g    M.P. 124-125 °C.

Analysis: C_{21}H_{15}N_{3}O_{3}S

Requires: C, 64.1% ; H, 4.8% ; N, 10.7%

Found: C, 64.2% ; H, 4.7% ; N, 10.6%

Uv and visible spectra:

\[ \lambda_{\text{max}} \quad 405 \ (\varepsilon, 1150, n\rightarrow n^*) , \ 325 \ (\varepsilon, 12000, n\rightarrow n^*) \]

Ir spectra:

\[ \gamma_{\text{KBr}} \quad 3030 \ (w, \text{methyl}), \ 1540 \ \text{and} \ 1390 \ (m, \text{NO}_2) , \ 1590 \ (w, \text{N=N}), \ 1710 \ (s, \text{C=O stretch}) . \]
(II) Yellow crystals of isomeric $\beta$-ketothioether (68d)

Yield - 0.20 g M.P. 111-112°C.

Analysis : $C_{21}H_{19}N_3O_3S$

Requires : $C$, 64.1% ; $H$, 4.8% ; $N$, 10.7%

Found : $C$, 64.2% ; $H$, 4.7% ; $N$, 10.6%

**Uv and visible spectra :**

$\lambda_{\text{max}}$ (nm)

403 ($\epsilon$, 11000, $n \rightarrow n^*$), 327 ($\epsilon$, 12500, $n \rightarrow n^*$).

**Ir spectra :**

$\nu$ (KBr cm$^{-1}$)

1540 and 1390 (m, NO$_2$), 1590 (w, N=N), 1710 (s, C=O stretch), 3030 (w, methyl).

(III) Brown crystals of $\alpha,\beta$-unsaturated ketonyl sulphide (69d).

Yield - 0.12 g M.P. 203-204°C

Analysis : $C_{23}H_{29}N_3O_3S$

Requires : $C$, 67.1% ; $H$, 5.6% ; $N$, 9.4%

Found : $C$, 67.2% ; $H$, 5.5% ; $N$, 9.4%

**Uv and visible spectra :**

$\lambda_{\text{max}}$ (nm)

410 ($\epsilon$, 1300, $n \rightarrow n^*$), 330 ($\epsilon$, 13000, $n \rightarrow n^*$)

**Ir spectra :**

$\nu$ (cm$^{-1}$)

3030 (w, methyl), 1540 and 1390 (m, NO$_2$), 1590 (w, N=N), 1710 (s, C=O stretch), 1670 and 1640 (m, olefinic double bond).
(2) **Synthesis of 2-substituted naphthothiazoles:**

(A) **Synthesis of** naphtho-2'1':4:5-thiazolyl-2-ethyl ketone (71) **from β-ketothioether (67c):**

![Chemical structure](image)

0.2 g of β-ketothioether was dissolved in 100 ml of ethyl alcohol and one drop of conc. hydrochloric acid was added. The mixture was refluxed for one hour and then cooled at room temperature. A yellow precipitate was obtained which was filtered off, washed with alcohol and dried.

**Yield - 0.095 g**

Recrystallization from ethanol gave light yellow crystals of naphtho-2'1':4:5-thiazolyl-2-ethylketone (71).

**M.P. 192-193°C.**

**Analysis:** C₁₄H₁₁NSO

**Requires:** C, 69.7%; H, 4.6%; N, 5.8%

**Found:** C, 69.5%; H, 4.7%; N, 5.6%

**Uv and visible spectra:**

\[\lambda_{\text{max}} \quad 360 \ (\varepsilon, 7000, \pi \rightarrow \pi^*) , \ 318 \ (\varepsilon, 9500, \pi^1 \\pi^* \text{ band}) , \]
\[287 \ (\varepsilon, 8500, \pi^8 \text{ band}).\]
Ir spectra:
\[ \gamma_{\text{KBr}} \] 1710 (s, C=O stretch), 1430 and 1470 (m, thiazole ring)

The solvent was evaporated from the filtrate. Red crystals of diaryl disulphide (52) was obtained. Yield - 0.036 g.

It was recrystallised from benzene : ethanol mixture.

M.P. and mixed m.p. 197-198°C.

(B) Synthesis of naptho-2':1':4:5:-thiazolyl-2-ethyl ketone (71) from β-ketothioether (67d):

0.2 g of β-ketothioether (67d) was dissolved in 100ml of ethyl alcohol and one drop of conc. hydrochloric acid was added. The mixture was refluxed for one hour and then cooled at room temperature. A yellow precipitate was obtained which was filtered off, washed with alcohol and dried. Recrystallisation from ethanol gave light yellow crystals of naptho-2':1':4:5-thiazolyl-2-ethyl ketone (71).

Yield - 0.081 g M.P. and mixed m.p. 192-193°C.
(3) Reaction of 2-arylazonaphthalene-1-sulphenyl bromide (35,c-d) with compound containing active methylene group:

(A) Reaction of 2-(2'-nitro-4'-chloro-phenylazo)naphthalene-1-sulphenyl bromide (35c) with equimolar quantity of acetylacetone:

\[
\text{Ar.SBr} + (\text{CH}_3\text{CO})_2\text{CH} \rightarrow (\text{CH}_3\text{CO})_2\text{CH} + \text{Ar-S-S-Ar} \\
\text{S.Ar}
\]

(52)

(73)

The sulphenyl bromide (1g) was dissolved in 200ml of dichloromethane and to it added a solution of acetylacetone (0.24 g) in 10ml of dichloromethane. The solution was shaken well and kept at room temperature. After the completion of the reaction (1 hour), the solvent was evaporated. The residue was then dissolved in minimum volume of chloroform and poured on a column of alumina for chromatography. On successive elution with light petrol (40-60°C), benzene and chloroform two zones were collected and the following compounds were identified.

(I) Red crystals of monosulphenylated acetylacetone (73c)

Yield - 0.42 g M.P. 207-208°C.
Analysis: C<sub>2</sub>H<sub>1</sub>N<sub>3</sub>O<sub>4</sub>S

Requires: C, 57.1%; H, 3.6%; N, 9.5%

Found: C, 57.2%; H, 3.8%; N, 9.6%

Uv and visible spectra:

\[ \lambda_{\text{max}} = 428 (\varepsilon, 1200, \pi\rightarrow\pi^*) \]
\[ \lambda_{\text{max}} = 358 (\varepsilon, 12000, \pi\rightarrow\pi^*) \]

IR spectra:

\[ \text{cm}^{-1}K\text{Br} \]
\[ 1540 \text{ and } 1390 \text{ (m. NO}_2\text{), } 1600 \text{ (w, N=N), } 1710 \text{ (s, C=O stretch).} \]

(II) Red crystals of diaryl disulphide (52c)

Yield - 0.21 g M.P. and mixed m.p. 197-198°C.

(B) Reaction of 2-(2'-nitro-4'-methyl-phenylazo)naphthalene-1-sulphenyl bromide (35d) with equimolar quantity of acetylacetone:

\[ \text{Ar.SBr} + (\text{CH}_3\text{CO})_2\text{CH} \rightarrow (\text{CH}_3\text{CO})_2\text{CH} \]

The sulphenyl bromide (1g) was dissolved in dichloromethane (200ml) and a solution of acetylacetone (0.24g) in dichloromethane (10ml) was added to it. The mixture was shaken well and kept at room
temperature. After the completion of reaction (30 minutes), the solution was filtered and the residue was recrystallized from ethanol.

Light yellow crystals of naphtho-2':1':4:5-thiazolyl-2-methyl ketone (72).

Yield - 0.156 g M.P. 179-180°C.

Analysis : C$_{13}$H$_9$NSO

Requires : C, 68.7% ; H, 3.9% ; N, 6.2%

Found : C, 68.5% ; H, 3.8% ; N, 5.9%

Uv and visible spectra :

$\lambda_{max}$ 355 ($\varepsilon$,6500, $n\rightarrow n^*$), 315 ($\varepsilon$,8700, $n^2$), 287 ($\varepsilon$, 6000, $n^3$).

Ir spectra :

$\nu$ KBr 1710 (s, C=O stretch), 1430 and 1470 (m,thiazole ring).

The filtrate was concentrated by evaporation to a minimum volume and the concentrated mass was poured over a column of alumina for chromatography. The column was eluted first with light petrol (40-60°C) and then with benzene. The major zones were collected and the following compounds were identified.
(I) Light yellow crystals of naphtho-2':1':4:5-thiazolyl-2-methyl ketone (72)

Yield - 0.021 g. M.P. and mixed m.p. 179-180°C.

(II) Red crystals of monosulphenylated acetylacetone (73d).

Yield - 0.39 g M.P. 210-211°C.

Analysis : C_{22}H_{19}N_{3}O_{4}S

Requires : C, 62.7% ; H, 4.5% ; N, 9.9%

Found : C, 62.2% ; H, 4.6% ; N, 10.1%

Uv and visible spectra :

\[ \lambda_{\text{max}} \quad 408 (\varepsilon,1050,\pi\rightarrow\pi^*) , \quad 328 (\varepsilon,13500,\pi\rightarrow\pi^*) \].

Ir spectra :

\[ \nu_{\text{KBr}} \quad 3030 (w,\text{methyl}), \quad 1540 \text{ and } 1390 (m, \text{NO}_2, \quad 1600 \\
(w,\text{N=N}), \quad 1710 (s, \text{C=O stretch}) \].

(III) Reddish yellow needles of 3-nitro-4-amino toluene (74).

Yield - 0.025 g M.P. 114-115°C

(IV) Red crystals of diaryl disulphide (52d)

Yield - 0.053 g m.p. - 191-193°C

Analysis : C_{34}H_{24}N_{6}S_{2}O_{4}

Requires : C, 63.3% ; H, 3.7% ; N, 13.0%

Found : C, 63.1% ; H, 3.8% ; N, 13.2%
(C) Reaction of excess of 2-(2'-nitro-4'-chloro-phenylazo) naphthalene -1- sulphenyl bromide (35c) with acetyl acetone:

\[
\text{Ar.SBr} + (\text{CH}_2\text{CO})_2\text{CH} \rightarrow (\text{CH}_2\text{CO})_2\text{CH} + \text{Ar.S.S.Ar}
\]

The sulphenyl bromide (1g) was dissolved in 200 ml of dichloromethane and a solution of acetyl acetone (0.1 g) in 5 ml of dichloromethane was added to it. The solution was shaken well and kept at room temperature. After the completion of the reaction (1 hour), the solvent was evaporated. The residue was dissolved in minimum volume of chloroform and poured on a column of alumina for chromatography. The column was eluted successively with light petrol (40-60°C), benzene and chloroform. The major zones were collected and the following compounds were identified.

(1) Red crystals of monosulphenylated acetylacetone (73c)

Yield - 0.075 g. M.P. and mixed m.p. 207-208°C

(2) Light red crystals of disulphenylated acetylacetone (75c).
Yield - 0.49 g  M.P.  157-158°C

Analysis :  C\textsubscript{37}H\textsubscript{24}N\textsubscript{6}O\textsubscript{6}S\textsubscript{2}Cl\textsubscript{2}

Requires :  C, 56.7% ; H, 3.1% ; N, 10.7%

Found :  C, 56.6% ; H, 3.2% ; N, 10.6%

Uv and visible spectra :
\[
\text{nm} \quad \lambda_{\text{max}} \quad 430 (\varepsilon, 1250, n\rightarrow n^*) , 355 (\varepsilon, 13000, n\rightarrow n^*).
\]

Ir spectra :
\[
\text{cm}^{-1} \quad \text{KBr} \quad 1540 \text{ and } 1390 (m, \text{NO}_2) , 1590 (w, \text{N=N}) , 1710 (s, \text{C=O} \text{ stretch}).
\]

Red crystals of diaryl disulphide (52c)

Yield - 0.19 g.  M.P. and mixed m.p.  197-198°C

D Reaction of excess quantity of 2-(2'-nitro-4'-methyl-phenylazo) naphthalene-1-sulphenyl bromide (35d) with acetylacetone :

\[
\text{Ar.SBr + (CH}_3\text{CO)}_2\text{CH} \rightarrow (\text{CH}_3\text{CO)}_2\text{CH} + \text{Ar.SS.Ar (73d)}
\]

\[
\text{S} \quad \text{C.O.CH}_3
\]

(72)

\[
\text{CH}_3
\]

NH\textsubscript{2}  (74)

The sulphenyl bromide (1g) was dissolved in 200 ml dichloromethane and the solution
containing 0.1g of acetylacetone in 5ml dichloromethane was added to it. The solution was shaken well and kept at room temperature. After the completion of the reaction (1 hour), the solvent was evaporated and the residue was dissolved in a minimum volume of chloroform which was then poured on a column of alumina for chromatography. The column was first eluted with light petrol (40-60°C) and then successively with benzene and chloroform. The major eluting zones were collected and the following products were identified.

(1) Red crystals of monosulphenylated acetylacetone (73d)

Yield : 0.167 g  M.P. and mixed m.p. 210-211°C

(2) Reddish yellow crystals of disulphenylated acetylacetone (75d)

Yield - 0.143 g  m.p. - 145-146°C

Analysis : C_{39}H_{30}N_{6}O_{6}S_{2}

Requires : C, 63.1% ; H, 4.0% ; N, 11.3%

Found : C, 62.9% ; H, 4.2% ; N, 11.1%

Uv and visible spectra:

\[ \lambda_{max} \] 415 (\epsilon, 1300, \pi\rightarrow\pi^*) , 330 (\epsilon, 14000, \pi\rightarrow\pi^*).

Ir spectra:

\[ \nu \] cm\(^{-1}\)

\[ \nu \] KBr  1540 and 1390 (m, NO\(_2\)) , 1590 (w, N=N), 1710 (s, C=O stretch)
(3) Reddish yellow needles of 3-nitro-4-amino toluene (74d)

Yield - 0.061 g  M.P. 114-115°C

(4) Light yellow crystals of naphtho-2':1':4:5-thiazolyl-2-methyl ketone (72)

Yield - 0.035 g.  M.P. and mixed m.p. 179-180°C

(5) Red crystals of diaryl disulphide (52d)

Yield - 0.056 g.  M.P. and mixed m.p. 191-193°C

(4) (A) Synthesis of naphtho-2':1':4:5-thiazolyl-2-methyl ketone(72) from monosulphenylated acetylacetone (73c):

\[
\begin{align*}
\text{CH}_3\text{CO.COOCH}_3 \quad &\xrightarrow{\text{HCl}} \quad \text{S} \quad \text{N} \quad \text{C.O.CH}_3 \\
(\text{73c}) \quad &\text{Ar} \quad \text{S.S.} \text{Ar} \\
(\text{72})
\end{align*}
\]

0.2 g of monosulphenylated acetylacetone (73c) was dissolved in 100 ml of ethanol and 2-3 drops of conc. hydrochloric was added to it. The mixture was refluxed for one hour and then cooled to room temperature. Light yellow precipitate of naphtho-2':1:4:5-thiazolyl-2-methyl ketone (72) was formed. The precipitate was filtered off, washed with alcohol and
dried. Recrystallization from ethanol gave light yellow crystals.
Yield - 0.043 g. M.P. and mixed m.p. 179-180°C

The solvent was removed from the filtrate by evaporation. Red crystals of diaryl disulphide (52c) was obtained. It was recrystallised from benzene:ethanol mixture.
Yield - 0.085 g. M.P. and mixed m.p. 197-198°C

(B) Synthesis of naphtho-2':1':4:5-thiazolyl-2-methyl ketone (72) from monosulphenylated acetylacetone (73d) :

0.2 g of monosulphenylated acetylacetone (73d) was dissolved in 100 ml of ethanol and 2-3 drops of conc. hydrochloric acid was added to it. The mixture was refluxed for one hour and then cooled to room temperature. Light yellow precipitate of naphtho-2':1':4:5-thiazolyl-2-methyl ketone (72) was formed. The precipitate was filtered, washed with ethanol and dried. Recrystallization from ethanol gave light yellow crystals.
Yield - 0.12 g. M.P. and mixed m.p. 179-180°C