CHAPTER - VI

ADDITION REACTION
OF
2'-CHLOROAZOBENZENE - 2 - SULPHENYL BROMIDE.
REVIEW:

The dichotomous behaviour of the sulphenyl bromides may be attributed to the nature of the S-Br bond where unshared electron pairs and vacant d-orbital on each atom play a significant role. The net result is that the reaction at sulphur atom may take place either in electrophilic mode or nucleophilic mode depending on circumstances.

The electrophilic addition of sulphenyl derivative to alkenes is known for many years. The mechanism of such reactions were first proposed by Kharasch N et. al (1952); Kharasch N. and Buess C. (1949); Kharasch N. and Hogg D. (1956) in accordance with the generally held mechanistic approach to the other AdE reactions. They reported that the intermediacy of a cyclic thiiranium ion in these reactions. It was noticed that such an addition could yield both Markownikoff and anti Markownikoff orientation products (Bohme H et. al, 1957, Bohme H. and Clement M., 1951). Solvent incorporated and rearranged adducts could also form in polar media used for addition (Schmid G H. and Csimadia V M., 1972).

Burawoy A et al (1955), obtained 2-nitrophenyl-2'-bromocyclohexyl sulphide (73) with 2-nitrobenzene sulphenyl bromide (65) and cyclohexene.

\[
\begin{align*}
\text{SBr} & \quad \text{NO}_2 \\
\text{(65)} & + \\
\text{NO}_2 & \quad \text{S} \quad \text{Br} \\
\text{(73)} &
\end{align*}
\]
The expected Markownikoff products were reportedly obtained by the addition of 2,4-dinitrobenzene sulphenyl chloride with cyclohexene, styrene, allyl alcohol and ethene in acetic acid and dichloromethane medium (Kharasch N. and Orr W. L., 1953; Kharasch N. and Hogg D., 1956, Kharasch N and Buess C., 1949). The formation of 1. 1 adduct was reported from the reaction of 2-nitrobenzene sulphenyl chloride, bromide and thiocyanate, 2,4-dinitrobenzene sulphenyl chloride and 2-nitro-4-carboxybenzene sulphenyl chloride with butene (Kharasch N. and Havlik A. J. 1953, 1955). Bohme H. et. al (1951), reported the formation of normal addition product from acetyl thio sulphenyl chloride by the reaction with ethene, cyclohexene and styrene.

Normal addition products were also obtained by Mueller W. and Butler P E (1966, 1967, 1968), from the reaction of dimethyl sulphenyl chloride and 0-0'-dimethyl phosphoryl sulphenyl chloride with alkenes.

Recently, reactions are reported where allylic hydrogens are substituted in reactions of internal alkenes with sulphenyl chloride (Brodikov I. V. et. al, 1992).

The addition product of 0-0'-diethyl phosphoryl sulphenyl chloride with butadiene have been reported by Pudovik A. N. and Ishmaeva E. A. (1965).

The formation of β-chloro thioethers (74 a-d) was reported by Poointe N. et. al (1974), while studying the reaction of sulphenyl chloride with ethylene derivative (75 a-d).
\[ C_6H_5CH = CHCH_2COX \]

Where:

- \( a, X = NH C_6H_5 \)
- \( b, X = Cl \)
- \( c, X = OCH_3 \)
- \( d, X = OH \)

\[ C_6H_5CH(\text{Cl}) - CH(SR)CH_2COX \]
RESULTS AND DISCUSSION:

From a comparative study of addition reactions of different sulphenyl halides with alkenes, it has been observed that the presence of less electron withdrawing substituents on the sulphur and fewer carbonium stabilizing substituents on the double bond favour the carbonium ion path in the addition reaction.

The reactions of different sulphenyl halides with olefins have been extensively studied and reported but very few works on similar reactions are reported with respect to the sulphenyl bromide of orthomercaptoazo compounds. We have studied the nucleophilic displacement at the biligated sulphur atom of 2'-chloroazobenzene -2-sulphenyl bromide with styrene.

The external π-electrons of alkenes are sufficiently polarizable. It is, therefore, expected that alkenes, though not very electronegative, may attack the sulphenyl sulphur nucleophilically. We have studied the reaction of styrene with sulphenyl compound (19) in dichloro methane and ethanol medium at 30°C. The Markownikoff adduct β-bromo thioether was the single product in the reaction. This is indicative of an unsymmetrical thiiranium ion path followed in the reaction which may be due to the presence of 1-phenyl group. The 1-phenyl group ensures the formation of an unsymmetrical near open thiiranium ion as an intermediate. Though the Br⁻ ion is an bulky nucleophile, the adverse steric effect of the phenyl group on the orientation of addition is of lesser importance in comparison with stabilization of the cataionic intermediate by the phenyl group.
When excess of sulphenyl bromide is used in the reaction the product becomes complex, because the product contains a little of expected β -bromo thioether (77), appreciable amount of disulphide (38) and 1, 2- dibromo- 1- phenyl ethane (79). The formation of the latter compound may be explained by thiophilic attack of the of sulphenyl bromide on the S- atom of the β – bromo thioether (77) to give dithonium cataion which behaves as an excellent leaving group. This catalyze the displacement of the disulphide unit by a relatively powerful Br (−) nucleophile. This is an example of electrophile catalyzed nucleophilic displacement.
In case of the reaction of styrene with 2'-chloroazobenzene - 2'-sulphenyl bromide (19) in ethanol medium we obtain two products - one is Markownikoff adduct β-bromo thioether and other is solvent incorporated product - β-ethoxy thioether. The formation of β-ethoxy thioether may, perhaps, be due to the competition of nucleophilicity of Br⁻ and HOC₂H₅ and therefore in this case we have both the products.
Ph - CH = CH₂ + Br - S - N - N

Ph - CH - CH₂ + δ⁺

Ph - CH - (OC₂H₅) - CH₂ - S

Ph - CH*(OC₂H₅) - CH₂ - S

Cl

Br(⁻)

OC₂H₅

Ph - CH*(Br) - CH₂ - S

Cl

N = N

N = N

N = N

N = N

[76]

[77]

[78]
Uv-visible, ir and nmr spectra of the addition products of sulphenyl bromide (19).

I. Uv and visible spectra:

uv-visible spectra of the addition products (77) and (78) show two bands. The low intensity azo n → π* band appears in the region of 428-432 nm and high intensity π→π* band in the region of 334-339 nm.

II. Ir spectra:

( a ) weak band at 1585 cm⁻¹ due to N = N.

( b ) a band at 1250 cm⁻¹ due to -C-O-C stretch in ethoxy incorporated addition product.

III. Nmr spectra:

nmr spectra of β-bromothioether shows:

( a ) a doublet at δ 1.2 due to methylene proton.

( b ) a triplet at δ 3.2 due to methine proton.

( c ) a distorted multiplet at δ 7.3 due to aromatic protons

nmr spectra of β-ethoxy thioether (78):

( a ) a doublet at δ 1.2 due to methylene-proton.

( b ) a multiplet at δ 3.1 due to ethoxy protons.

( c ) a triplet at δ 4.2 due to methine.proton.

( d ) a distorted multiplet at δ 7.3 due to aromatic protons.
IR SPECTRA OF β-ETHOXY THIOETHER (78)
NMR SPECTRA OF J-BROMO THIOETHER (77)
EXPERIMENTAL:

Equimolar reaction of 2'-chloroazobenzene - 2 - sulphenyl bromide with styrene in dichloromethane medium.

\[
\text{Ar.SBr} + \text{Ph-CH=CH}_2 \rightarrow \text{Ph-CH-CH}_2\text{SAr} + \text{Ar.SS.Ar} \quad \quad (77)
\]

(38)

1 mili mole sulphenyl bromide was dissolved in dichloromethane (75 ml), to it, a solution of 1 mili mole styrene in dichloromethane (25 ml) was added. The resulting mixture was shaken vigorously under a mechanical stirrer for 12 hours and was allowed to stand in room temperature (30 oC) for 7 days. After 7 days reaction was found to be complete. Solvent was evaporated and residue subjected to column chromatography on alumina column. Two fractions were separated, the major fraction yielded red crystals of β-bromo thioether.

Yield: 0.123 g

Melting point: 149-150 oC

Analysis: C 55.61%, H 3.70%, N 6.48%

Requires C 55.61%, H 3.70%, N 6.48%

Found C 55.4%, H 3.6%, N 6.5%
Uv-visible spectra:

$$\lambda_{\text{max}}^{\text{nm}} \quad (\text{chloroform}) \quad 428-430 \ (\log \varepsilon 3.560 \ ; n\rightarrow \pi^*)$$

$$338 \ (\log \varepsilon 3.890 \ ; \pi\rightarrow \pi^*)$$

Ir spectra:

$$\nu_{\text{cm}^{-1}}^{\text{KBr}} \quad 1595 \ (w, N = N \text{ stretch}).$$

Nmr spectra:

( a ) a doublet at $\delta 1.2$ due to methylene proton.

( b ) a triplet at $\delta 3.2$ due to methine proton.

( c ) a distorted multiplet at $\delta 7.3$ due to aromatic protons.

The other minor fraction yielded reddish-orange crystals of disulphide (38).

Yield: 0.06 g.

Melting and mixed melting point: 198 - 200 $^0$C.
3.1 molar reaction of 2'-chloroazobenzene-2-sulphenyl bromide with styrene in dichloromethane medium:

\[
\text{Ar-SBr + Ph - CH = CH}_2 \rightarrow \text{Ph CH ( Br ) CH}_2 - \text{SAr} + \text{Ar-SS-Ar} + \text{Ph CH ( Br ) CH}_2 \text{ Br}
\]

(77)  (38)

2.8 mili mole sulphenyl bromide (19) was dissolved in dichloromethane (100 ml). To it 1 mili mole of styrene taken in dichloromethane (5 ml), was added. Resulting solution was stirred for 12 hours. After 4 days solvent was evaporated. Solid mass was subjected to column chromatography under alumina column. Three different fractions were separated of which major one, reddish-orange colour crystals was identified to be the 1,2-dibromo-1-phenyl ethane (79).

(i) reddish-orange crystals of 1,2 dibromo-1-phenyl ethane (79).

Yield: 0.060 g

melting point: 100-102 °C.

Analysis: C_{8}H_{8}Br_{2}.

Requires: C: 36.36 %; H: 3.03 %.

Found: C: 37.0 %; H: 3.5 %.
( ii ) Red crystals of β-bromo thioether (77)

Yield: 0.040 g.

Melting and mixed melting point: 149 - 150 °C

( iii ) Reddish-orange crystals of disulphide (38).

Yield: 0.170 g.

Melting and mixed melting point: 198 - 200 °C.
Equimolar reaction of 2'-chloroazobenzene-2-sulphenyl bromide with styrene in ethanol medium.

\[
\text{Ar.SBr} + \text{Ph-CH=CH}_2 \rightarrow \text{Ph-CH}_2\text{SAr} + \text{Ph-CH}_2\text{SAr} + \text{H}_5\text{C}_2\text{O} + \text{Br}
\]

(78) (77)

1 mili mole of sulphenyl bromide (19) was dissolved in ethanol (75 ml). 1 mili mole of styrene was taken in ethanol (25 ml) and added to the bromide solution. Reaction mixture was stirred for 12 hours. After completion of 10 days the reaction was found to be complete. Solvent was evaporated. Residue obtained was subjected to column chromatography on silica column. Two fractions were separated and identified to the following compounds.

(i) Red crystals of \( \beta \)-bromo thioether (77).

Yield: 0.120 g.

Melting and mixed melting point: 149 - 150 °C

(ii) Orange-red crystals of \( \beta \)-ethoxy thioether (78).

Yield: 0.080 g.

Melting point: 143 - 144 °C.
Analysis. C_{22}H_{21}N_{2}O_{5}S\ Cl

Requires: C: 66.58\% ; H: 5.29\% ; N: 7.06\% .

Found C: 65.0\% , H: 5.5\% , N: 7.2\% .

_Uv-visible spectra_

\[ \lambda^{n_{m}}_{\text{max}} \ (\text{chloroform}) \]

\begin{align*}
428-432 & \ (\log \varepsilon 3.980; n\rightarrow\pi^{*}) \\
338 & \ (\log \varepsilon 4.190; \pi\rightarrow\pi^{*})
\end{align*}

_Ir spectra:_

\[ \nu^{\text{cm}^{-1}}_{\text{KBr}} \]

\begin{align*}
1585 & \ (w, N = N \text{ stretch}) \\
1250 & \ (w, -C-O-C- \text{ stretch})
\end{align*}

_Nmr spectra:_

(a) a doublet at \( \delta 1.2 \) due to methylene proton

(b) a multiplet at \( \delta 3.1 \) due to ethoxy protons.

(c) a triplet at \( \delta 4.2 \) due to methine protons.

(d) a distorted multiplet at \( \delta 7.3 \) due to aromatic protons.