PART I

SYNTHESIS AND SPECTRAL STUDIES OF
\(\alpha,\beta\)-ETHYLENIC SULPHONES
CHAPTER I
THE RONIN ION

The synthesis and structural studies of $\alpha, \beta$-ethylenic sulphones have gained much importance quite recently. The biological studies carried out have indicated that some of the substituted phenyl vinyl sulphones are effective fungicides.\(^1\) A number of halogen substituted ethylenic sulphones were synthesized\(^5,13\) to study their acaricidal and other physiological properties. Woody plants were desiccated by contact with aryl vinyl sulphones\(^4\) which were also found to be highly toxic to snails and potent sulphhydryl inhibitors.\(^6\)

The condensation of phenylsulphonylacetic acid with aromatic aldehydes under conditions of the Perkin reaction was reported by Tröger and Willé\(^6\) in 1905. In succeeding years Tröger reported the reactions with sulphonylacetonitriles in the presence of alkali\(^7\) or pyridine\(^8\) in alcoholic solution. In 1933 Kohler and Potter\(^9\) reported the synthesis of cis- and trans-styryl-p-tolylsulphides by the addition of p-thiocrresol to phenylacetylenes. The two isomeric sulphides were separated by fractional crystallization and oxidized to get the cis (m.p. 71°) and trans
(m.p. 121°) sulphones. Liv and Yang\textsuperscript{10} prepared the same compounds by the same method and obtained 70° of the cis-styryl-p-tolylsulphone (m.p. 74-75°). Kohler and Larson\textsuperscript{11} reported in 1935 the preparation of cis and trans forms of \( \text{PhCOCH}=\text{CH'O}_2\text{Ph} \) and in 1937 they\textsuperscript{12} reported the geometrical isomers of \( \text{PhCOCH=C(Ph)'O}_2\text{Ph} \). Chodroff and Whitmore\textsuperscript{13} attempted the condensation of aromatic aldehydes with p-toluenesulphonylacetate acid in pyridine in the presence of piperidine. Among the compounds studied, only benzaldehyde and cinnamaldehyde yielded isolable unsaturated sulphones, \( \text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}=\text{CHAr} \).

Several routes were reported\textsuperscript{14-16} for the preparation of unsaturated sulphones from the corresponding \( \beta \)-hydroxy sulphones. Dehydration of the latter over \( \text{Al}_2\text{O}_3 \) or \( \text{Ca}_3(\text{PO}_4)_2 \)\textsuperscript{17} \( \text{H}_3\text{PO}_4 \) or \( \text{HCl-EtOH} \)\textsuperscript{20} or a phosphate catalyst\textsuperscript{21} gave vinyl sulphones which were tested for herbicidal activity.\textsuperscript{21} A three stage synthesis involving \( \beta \)-hydroxylation, oxidation and dehydration of the mercaptans\textsuperscript{22} yielded compounds with a similar herbicidal activity.

Dehydrohalogenation\textsuperscript{23-25} was also used successfully for the preparation of a large number of aryl vinyl sulphones. One of the methods\textsuperscript{24} for dehydrohalogenation of 1-chloro-1-aryl-2-(arenasulphonyl)ethanes was by triethylamine in
benzene, ethyl acetate or tetrahydrofuran. Dehydro-
chlorination of $\beta$-chloroethyl sulphones in alkaline
solution$^{29}$ or by triethylamine$^{27}$ gave aryl vinyl sulphones.
Dehydrochlorination$^{28}$ of $C_6H_5CO\text{CH}_2\text{CH}_2\text{N}^{2+}$C$_6$H$_5$H$_2$O$_2$-p, led
to the formation of 1-(p-nitrophenyl)-2-(ethylsulphonyl)-
ethene. Dehydrobromination$^{19}$ of $\alpha$, $\beta$-dibromoethyl sulphones
with triethylamine or with 2M sodium hydroxide gave
exclusively $\alpha$-bromo vinyl sulphones. $\beta$-Arylsulphonyl
acrylic acids$^{30}$ have also been obtained by the dehydro-
bromination of $R^1\text{CH=CHCH}_2\text{CH}_2\text{CN}$ and by the hydrolysis of the
resultant product.

Recently Truce et al.$^{80}$ reported the preparation of
some $\alpha$, $\beta$-ethylenic sulphones. The copper-catalysed
addition of sulphonyl chlorides to styrenes followed by
elimination of hydrogen chloride from the resulting $\beta$-chloro-
sulphones afforded trans-1-aryl-2-(arenesulphonyl)ethenes
and other unsaturated sulphones.

\[
\text{RCH=CH}_2 + R'\text{CO}_2\text{Cl} \xrightarrow{\text{CuCl}_2, \text{Et}_3\text{N}, \text{HCl, CH}_3\text{CN}} \text{RCHCH}_2\text{SO}_2\text{R'}
\]
Goralski in 1972 obtained \( \text{2-}(\text{trans-}-\beta\text{-styrylsulphonyl})\text{-thiophene} \) by dehydrohalogenation of \( 2-\{(\beta\text{-chlorophenyl})\text{-sulphonyl}\}\text{-thiophene} \).

\( \alpha, \beta\text{-Ethylidene sulphones were also prepared by the addition of thiols to acetylenes followed by the oxidation of the resulting unsaturated sulphides with hydrogen peroxide. The nucleophilic addition of thiols to acetylenes has been surveyed by Truce.} \)

The addition of thiophenols to aryl-acetylenes in the presence of a base was reported to proceed in the trans fashion to yield cis compounds.

\[
\text{RSH} + \text{R'C} = \text{CH} \rightarrow \text{H} \begin{array}{c} \text{C} = \text{C} \\ \text{H} \end{array} \text{C} = \text{C} \begin{array}{c} \text{H} \\ \text{R} \text{R} \end{array}
\]

When phenylacetylene was refluxed with sodium p-tolyl-sulphide in ethanol solution, a good yield of cis-styryl-p-tolylsulphide, resulting from the trans addition of p-thiocresol was obtained. Similar results have been reported with sodium methylsulphide. Thiols as sodium salts have also been added to several other electronegatively substituted acetylenes such as chloroacetylenes, dichloroacetylenes. Similarly p-thiocresol adds to ethoxyacetylene to form cis-1-ethoxy-2-p-tolylmercaptocetylene along with a very small amount of trans isomer. The stereochemistry of thiol additions has been the subject of widespread interest.
The main contribution to this field has come from Truce and his co-workers. In case of the non-conjugated and non-activated butyne-2, the catalysed addition was shown by Truce and Simms to yield a product as shown below:

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{RN} \rightarrow \text{H} - \text{C} = \text{C} - \text{CH}_3
\]

The same result was obtained with phenylacetylene and a "trans-addition rule" was formulated by them. This rule was also shown to apply for activated triple bonds, as was found for acetylenedicarboxylic acid esters and phenylpropionic esters.

The addition of phenylthioli to phenylacetylene at \(-40^\circ\text{C}\) gave the cis adduct, whereas at \(0^\circ\text{C}\) only the trans adduct was isolated. When direct addition of thiophenol to different substituted acetylenes was conducted at room temperature, the corresponding 1:1 adducts of trans configuration were isolated. When the same reactions were carried out at \(-45^\circ\text{C}\) to \(-35^\circ\text{C}\), \(p\)-nitrophenylacetylene did not react at all and the others gave adducts of cis configuration by trans additions. All these compounds with cis configuration were stable under the reaction conditions and were transformed to trans configuration at \(>160^\circ\text{C}\).

The free radical addition of thiols to acetylenes has
also been investigated and the work has been surveyed by Oswald. The monoaddition of thiols to monosubstituted acetylenes generally follows an anti-Markownikoff rule. The stereochemical path of this reaction has been extensively studied for the thiolphenylacetylene addition. An excess of acetylene has led to a high yield of cis adducts, whereas a thiol excess favoured the formation of trans adducts. The addition of benzenethiol to a twenty fold excess of phenylacetylene yielded a mixture containing 98% of the corresponding cis monoadduct, while a twenty fold excess of the thiol led to the equilibrium mixture containing only 16% of the cis adduct. The decrease in the selectivity in the presence of excess thiol suggested that a rapid post-isomerisation of the adducts by excess thiol was occurring.

The ionic and radical addition of sulphenyl chloride to acetylenes also occurs, in general, in a trans fashion. Montanari and another Italian group investigated the stereochemistry of the addition of p-nitrophenylsulphenyl chloride to phenylacetylene.

\[
\begin{align*}
\text{C}_8\text{H}_5\text{C}=\text{C}=\text{CH} + p-\text{NO}_2\text{C}_6\text{H}_4\text{SCl} & \rightarrow \\
\text{C}_8\text{H}_5\text{C} = \text{C} = \text{Cl} + p-\text{NO}_2\text{C}_6\text{H}_4\text{SCl} - p & \rightarrow \\
p-\text{NO}_2\text{C}_6\text{H}_4\text{SCl} & \rightarrow \\
\text{C}_8\text{H}_5\text{C} = \text{C} = \text{H} + p-\text{NO}_2\text{C}_6\text{H}_4\text{SCl} - p
\end{align*}
\]
The addition was proved to be solvent-dependent. I prevailing in ethylacetate (90%) while acetic acid favoured II (90%). Substituents on the sulphur compound were shown not to influence the reaction rate severely, but donating groups in conjugation with the acetylene moiety were shown to cause a marked enhancement.

Bennati et al. showed that the addition of p-bromophenylsulphonyl bromide and p-bromophenylsulphonyl chloride to tolan resulted in the formation of trans compounds only. Similarly the addition of p-toluensulphonyl chloride to tolan gave trans-1,2-diphenyl-1-chloro-2-p-tolythic-ethylene. The mechanism of the addition of sulphonyl chloride to the triple bond of acetylenes has been recently studied. Hetero and homolytic mechanisms suggested may be operative which explain divergences of results, effect of substituents, and solvents.

Recently the synthesis of β-halovinyl sulphones by a direct one-step addition reaction of sulphonyl halides to acetylenes was reported.

$$\text{RSO}_2X + \text{HCCR}' \rightarrow \text{RCOSRCR'}$$

\(X = \text{Cl}, \text{Br}, \text{and I.}\)

The addition of sulphonyl halides to acetylenes was shown to be stereoselective and affords mainly trans addition
products by free-radical chain mechanism. The stereo-
selective free radical copper-catalysed additions of PhC\textsubscript{6}H\textsubscript{5}Cl to PhC\textsubscript{6}H\textsubscript{5}Cl was shown\textsuperscript{89} to be controlled by polar factors to
give preferentially either trans or cis addition products.
Excess chloride ions or high polar solvents promoted the
formation of trans addition products while cis addition
predominates in low polarity solvents.

A novel method for the preparation of \(\alpha,\beta\)-ethylenic
sulphones by Kornet-Witting reaction via phosphonate carbanions
was reported by Popoff and his co-workers\textsuperscript{98} in 1968. Aryl
aldehydes were treated with diethyl ethylsulphonylmethylphos-
phonate, EtSCH\textsubscript{2}P(O)(OEt)\textsubscript{2}, in the presence of sodium hydride.
The configurations of all the twelve compounds excepting one
were established by then as trans isomers by n.m.r. spectral
studies. Thakur and Alam\textsuperscript{99} reported the preparation of a
series of \(\alpha,\beta\)-unsaturated sulphones and sulphones by reacting
aryl aldehydes and ketones with dimethyl methylsulphonyl-
methylphosphonate \([\text{MeSO}_{2}H\text{CH}_{2}P(O)(\text{OEt})_{2}]\) and diethyl(n-bromo-
phenylsulphonyl)methylphosphonate \([\text{p-NC}_{6}H_{4}\text{CH}_{2}P(O)(\text{OEt})_{2}]\).
Since this Kornet-Witting reaction using sodium hydride or
methoxide at room temperature to generate the phosphonate
carbanion has been limited for the preparation of aryldene
sulphones only, a modification of this procedure was reported
by Posner and Prunelle\textsuperscript{80} in 1972. When n-butyllithium was
used to generate the phosphonate anion in tetrahydrofuran at \(-78^\circ\), this anion reacts not only with aryl aldehydes but also with aliphatic aldehydes and ketones to give alkylidene sulphones in very high yields. They proved by n.m.r. coupling constants of the vinyl protons that the trans-\(\alpha,\beta\) ethylenic sulphones were the exclusive products in the reactions with aldehydes. Pascali et al.\(^{51}\) in 1973 obtained a good number of\(\alpha,\beta\)-unsaturated phenyl sulphones by the reaction between \(\alpha,\alpha\)-dimethyl derivatives of benzyl phenyl sulphones and saturated aliphatic and aromatic aldehydes and ketones including \(\alpha,\beta\)-unsaturated carboxyl compounds.

\[
\text{(EtO)}_2\text{P}(\text{O})\text{CH}_2\text{C}=\text{O} + \text{R}_1\text{R}_2\text{C}=\text{O} \rightarrow \text{R}_1\text{R}_2\text{C}=\text{CHCH}_2\text{OSiR}_3
\]

where \(\text{R}_1 = \text{alkyl and aryl}\)
\(\text{R}_2 = \text{H and CH}_3\)
\(\text{R}_3 = \text{CH}_3\) and \(\text{p-ClC}_6\text{H}_4\).

\[
\text{Li} \quad \text{PhSO}_2\text{CH}_2\text{Ph} \quad \text{n-BuLi} \quad \rightarrow \quad \text{PhSO}_2 = \text{C} = \text{Ph} \quad \text{Li}
\]

\[
\text{PhSO}_2 \quad \text{C} \quad \text{H}^2 \quad + \quad \text{R}^3 \quad \text{C}=\text{O} \quad \rightarrow \quad \text{PhSO}_2 \quad \text{C} \quad \text{H}^1 \quad \text{R}^4
\]

\[
\text{Ph} \quad \text{C}=\text{O} \quad \text{R}^3 \quad + \quad \text{H} = \text{C} = \text{C} = \text{R}^3
\]
Balasubramanian et al. synthesized a good number of $\alpha$, $\beta$-unsaturated sulphones along with $\beta$-amino sulphones by condensing aryl- or alkyl-sulphonylacetic acid with aromatic aldehydes in the presence of ammonia in glacial acetic acid.

$$\text{R}_2\text{CH}_2\text{COCH} + \text{ArCHO} \xrightarrow{\text{R}^+\text{NH}_3} \text{R}_2\text{CH}==\text{CH}\text{Ar} + \text{R}^+\text{O}_2\text{C}^\cdot\text{CH}_3\text{CH}==\text{Ar}$$

Fehnel and Resnick carried out similar condensations in pyridine solutions in the presence of piperidine but the yields of unsaturated sulphones were very low. Their attempts to improve the yields by variations in the nature of the solvent, nature and amount of catalyst, and duration of heating were unsuccessful.

Balish and B-dihapathirac condensed alkyl- and aryl-sulphonylacetic acids with aryl aldehydes in glacial acetic acid in the presence of benzylamine and reported excellent yields of unsaturated sulphones while reducing the formation of $\beta$-amino sulphones to negligible amounts. They have also reported that the yields were enhanced by refluxing the reaction mixtures for a longer period in the presence of catalytic amounts of benzylamine. Following the same procedure Gerstenfeld et al. reported a few chlorosubstituted unsaturated sulphones. Noves and Thompson synthesized some 1-aryl-2-(arenasulphonyl)ethanes by carrying out similar condensations in glacial acetic acid in the presence
of cyclohexylamine or ammonium acetate. They reported the formation of vanilin base hydrochloride salts along with very low yields of unsaturated sulphones. They suggested the following mechanism for the reaction:

\[
\begin{align*}
\text{ArCHO} & \quad \xrightleftharpoons{+\text{Br}_2} \quad \text{ArCH=NR} \\
\text{RMgBr} & \quad \xrightarrow{+\text{H}^+} \\
\text{Ar}^+\text{CO}_2\text{CH}_2\text{CH}_2\text{CO}_2^+ & \xrightleftharpoons{+\text{Ar}^+} \quad \text{Ar}^+\text{CO}_2\text{CH}=(\text{CO}_2\text{H})\text{CH}r\text{NR} \\
\text{(+Ar}^+\text{H}) & \quad \xrightarrow{+\text{H}^+} \\
\text{(=-CO}_2\text{H})\text{CH}r\text{NR} & \quad \xrightarrow{+\text{Ar}^+} \\
\text{acetate ion} & \quad \xrightarrow{\text{Catalyst}} \\
\text{CO}^2_2^{-} & \\
\text{Ar^+CO}_2\text{CH}_2\text{CH}_2\text{CO}_2^+ & \xrightarrow{+\text{Br}_2} \\
\text{Ar^+CO}_2\text{CH}_2\text{CH}_2\text{CO}_2^+ & \xrightarrow{+\text{H}^+} \\
\end{align*}
\]

Differences exist in the ultraviolet absorption spectra of cis and trans isomers. When bulky conjugation substituents are attached to the olefinic carbon atoms, the trans arrangement of the substituents allow coplanarity of the conjugating system facilitating the transition from the ground state to the first excited state. If the bulky substituents are cis to each other there will be steric inhibition of resonance due to deviation from coplanarity leading to considerable decrease in the molecular extinction coefficient.
In some cases such as steric effect may also cause a hypsochromic shift of the absorption maxima of the cis isomer. These effects are illustrated by the data given in Table I-1.

**TABLE I-1**

Ultraviolet Absorption Spectra of cis and trans Isomers.

(Wavelengths are in mp)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}}, \epsilon_{\text{max}})</th>
<th>(\lambda_{\text{max}}, \epsilon_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3\text{CH}_3)</td>
<td>280 13,500 295.5 27,000</td>
<td>97</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5(\text{CH}_3)\text{CH}=\text{CHCH}_3\text{CH}_3)</td>
<td>260 11,900 270 20,100</td>
<td>98</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5(\text{CH}_3)\text{CH}=\text{CHCH}_3\text{CH}_3^*)</td>
<td>235 8,200 243 12,100</td>
<td>99</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CH}_2)</td>
<td>265 14,000 260 20,300</td>
<td>90</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CHCOCOCH}_3)</td>
<td>280 13,500 295 27,000</td>
<td>70</td>
</tr>
<tr>
<td>(2,3\text{-Cl}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCOCOCH}_3)</td>
<td>269 8,900 270 16,600</td>
<td>71</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyCOCOCH}_3)</td>
<td>280 10,000 288 21,880</td>
<td>72</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyCOCOCH}_3)</td>
<td>220 10,730 222 10,470</td>
<td>73</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyCOCOCH}_3)</td>
<td>269 8,900 298 23,700</td>
<td>73</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyCOCOCH}_3)</td>
<td>247 14,400 225 12,200</td>
<td>73</td>
</tr>
<tr>
<td>(\text{p}-\text{O}_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCOCOCH}_3)</td>
<td>277.5 15,100 315 28,200</td>
<td>74</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{COCH}=\text{CHCOCOCH}_3)</td>
<td>233 17,800 265 21,400</td>
<td>75</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyNO}_2\text{CH}_3)</td>
<td>261 19,100 264 23,700</td>
<td>76</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}=\text{CyNO}_2\text{CH}_3)</td>
<td>269 13,300 277 25,000</td>
<td>77</td>
</tr>
</tbody>
</table>

* cis and trans refer to \(\text{C}_6\text{H}_5\) and \(\text{CH}_3\) (not to the two \(\text{CH}_3\))
The UV spectra of organic sulphides, \( R_2S \), and sulphones, \( R_3S\)O, have been studied quite extensively whereas the studies on unsaturated sulphides and sulphones were quite limited. The theoretical and experimental studies of \( \lambda_{\beta} \)-unsaturated sulphides and sulphones indicate that the conjugation effects are relatively weak in these compounds. The ethyl vinyl sulphone shows an absorption band at about 210 nm which was considered to be at a longer wavelength than was expected from either an isolated \(-SO_2-\) group or a vinyl group. And this absorption was ascribed to the resonance interaction between the sulphonyl and the vinyl group which must involve expansion of valence shell of sulphur. Using the method of molecular orbitals, Koch and Moffit concluded that conjugation of sulphonyl group with the neighbouring double bonds, though possible, does not affect the S-O bond. Also the \( \sigma \)-orbitals are very diffuse with only a slight overlapping which according to Jaffe implies only a weak conjugation in the system. The prerequisite of coplanarity was not fulfilled with sulphones but in view of the abundance and the possible hybridization of \( \sigma \)-orbitals, geometrical requirements need not necessarily be the factor limiting the conjugation.

Procháška and Palaček reported the spectral studies of a number of unsaturated sulphones. Truce and Simms assigned geometrical configurations for the cis and trans
styril p-tolyl sulphones by ultraviolet spectral studies. They found that the trans isomer has higher absorption maximum and extinction coefficient than the cis isomer. Similar results have been reported for β-chlorovinyl sulphones, and α,β-unsaturated sulphones.  

Although correlation between infrared spectra and geometrical configuration for a large number of unsaturated olefinic compounds was described in literature,  
similar studies with respect to unsaturated sulphur compounds are comparatively sparse. The bands most useful for distinguishing between cis and trans isomers are those arising from (a) the γυ stretching frequency (1600-1420 cm⁻¹) and (b) the γυ in-plane deformation frequency (1310-1290 cm⁻¹ and near 1405 cm⁻¹)  and out-of-plane deformation frequency (970 and 690 cm⁻¹). Some relevant data are presented in Table I-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis $ν_{γυ}$</th>
<th>$δ(ωγε)$</th>
<th>trans $ν_{γυ}$</th>
<th>$δ(ωγε)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$=CHCl</td>
<td>1640s</td>
<td>675a</td>
<td>1630s</td>
<td>930s</td>
</tr>
</tbody>
</table>

(cont'd)
<table>
<thead>
<tr>
<th>Compound</th>
<th>cis ( \nu_{\text{C=O}} )</th>
<th>( \delta(=\text{C}-\text{H}) )</th>
<th>trans ( \nu_{\text{C=O}} )</th>
<th>( \delta(=\text{C}-\text{H}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{CICH}=\text{CHCl} )</td>
<td>1625s</td>
<td>*</td>
<td>1625s</td>
<td>93s</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Cl}=\text{CHCl} )</td>
<td>1590s</td>
<td>697s</td>
<td>-</td>
<td>808s</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}=\text{CH}=\text{CF}_2 )</td>
<td>1614</td>
<td>685</td>
<td>1614</td>
<td>930s</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Br}=	ext{CF}=\text{CF}_2 )</td>
<td>1595</td>
<td>680</td>
<td>1595</td>
<td>933s</td>
</tr>
<tr>
<td>( \text{CH}_3	ext{CH}=\text{CH}_2\text{H}_5 )</td>
<td>1653s</td>
<td>760(?)s</td>
<td>1667m</td>
<td>962s</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}=\text{CH}=	ext{C}_3\text{H}_5 )</td>
<td>1645w</td>
<td>*</td>
<td>1655w</td>
<td>970s</td>
</tr>
<tr>
<td>( \text{n-C}_4\text{H}_9 \text{C}=\text{CHCOOH} )</td>
<td>1640</td>
<td>*</td>
<td>1652</td>
<td>924s</td>
</tr>
</tbody>
</table>

* Not recorded or identification uncertain

From theoretical considerations no \( \nu_{\text{C=O}} \) should appear in the infrared spectra of symmetrically substituted olefins since no appreciable change in dipole moment is involved in \( \text{C}=\text{O} \) stretching vibration. Thus ethylene and trans-dichloroethylene are both inactive in this region.\(^6\) On the other hand cis-dichloroethylene shows a strong infrared absorption at 1590 cm\(^{-1}\). Similarly in maleic acid \( \nu_{\text{C=O}} \) occurs at 1635 cm\(^{-1}\), but fumaric acid shows no outstanding band in this region.\(^9\)

Bernstein and Poulung\(^9\) studied the relative optical
densities of $c=c$ ab-sorption in trans- and cis-1,2-dichloro-
propene and their deuterio derivatives. The trans isomers
show high intensity $c=c$ ab-sorption compared to the cis
compounds. The $c=c$ str-eching frequency is lowered from
1667 to 1653 cm$^{-1}$ on passing from trans- to cis-methyl-
styrene. 77 Allan, Maskina and Whitina 73 observed small
but significant low frequency shifts of $\gamma_{c=c}$ on going from
trans to cis isomers. Their values are listed in Table I-3.

TABLE I-3

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma_{c=c}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH=CHCOCH$_3$</td>
<td>1644</td>
</tr>
<tr>
<td>CH$_3$CH=CHCOCH</td>
<td>1639</td>
</tr>
<tr>
<td>CH$_3$C=CCH=CHCOCH</td>
<td>1612</td>
</tr>
<tr>
<td>CH$_3$C=CCH=CHCOCH$_3$</td>
<td>1609</td>
</tr>
<tr>
<td>Cl$_2$CH=CHCH=CHCOCH</td>
<td>1615</td>
</tr>
<tr>
<td>Cl$_3$CH=CHCH=CHCOCH</td>
<td>1615</td>
</tr>
</tbody>
</table>

A moderate intensity band is found in many cis disubstituted
ethylenes near 1406 cm$^{-1}$. Sheppard and Simpson$^{83}$ attributed
this band to $\omega_{c=c}$ in-plane deformation. Sheppard and
Sutherland$^{87}$ assigned the range 1395-1310 cm$^{-1}$ for the above
vibration in trans disubstituted ethylene. Barwell and Hatch,\textsuperscript{94} after scrutinizing the spectra of halo-
substituted propenes, attributed the strong and sharp
\( \equiv C-H \) in-plane bending bands in the region 1290 and 1235 cm\(^{-1}\)
to the cis and trans compounds respectively. Their values
are cited in Table I-4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis (cm(^{-1}))</th>
<th>trans (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{CH}=\text{CHR} )</td>
<td>1285</td>
<td>1262</td>
</tr>
<tr>
<td>( \text{BrCH}_2\text{CH}=\text{CHR} )</td>
<td>1292</td>
<td>1242</td>
</tr>
<tr>
<td>( \text{HOCH}_2\text{CH}=\text{CHR} )</td>
<td>1287</td>
<td>1235</td>
</tr>
<tr>
<td>( \text{ClCH}_2\text{CH}=\text{CHR} )</td>
<td>1287</td>
<td>1238</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}=\text{C}\text{C}\text{Br} )</td>
<td>1307</td>
<td>1230</td>
</tr>
</tbody>
</table>

The out-of-plane deformation of the hydrogen atoms
attached to olefinic carbon atom gives rise to very strong
infrared absorption bands and they have assumed importance
in analytical applications. Kilpatrick and Fitzer\textsuperscript{85} showed
that the medium to strong bands at 990-965 cm\(^{-1}\) found in
trans ethylenic compounds are due to \( \equiv C-H \) out-of-plane
deformation. Rasmussen and Brattain\textsuperscript{54} have shown that
this absorption bands appear only with trans double bonds.
Typical cases of absorption within the 980–965 cm$^{-1}$ range are recorded and in almost all cases the frequency lies close to 965 cm$^{-1}$. But if the double bond is to the carbonyl group, a small displacement to higher frequency occurs. Crotonic, cinnamic and acrylic acids absorb in the range 932–974 cm$^{-1}$. The halogens attached to the double bond has a more pronounced effect. Haszeldine quoted values of 935 cm$^{-1}$ for the $\equiv\text{C}-\text{H}$ deformation of $-\text{CH}=$CHBr and $-\text{CH}=$CHCl and Kitson has confirmed this. Conjugation with aromatic rings as in stilbenes does not influence the position of the 965 cm$^{-1}$ band, but it is displaced to a slightly lower frequency when conjugated with acetylenic links.

Sheppard and Simpson reported a range of 728–575 cm$^{-1}$ for the $\equiv\text{C}-\text{H}$ out-of-plane deformation in cis disubstituted ethylenes. It is much more sensitive to the environment than the corresponding 965 cm$^{-1}$ trans band. Halogen atoms on one or both the alkyl substituents or at the olefinic carbon atom cause a marked shift to higher frequency. Shown Conjugation with carbonyl group has also a marked effect. Thus the group $-\text{CH}=\text{CH}-\text{COC}$ (cis) absorbs near 820 cm$^{-1}$. This absorption is usually much weaker in intensity than that of the trans compounds.

Boonstra and Rinzena studied 1-alkythio-2-alkenes,
RCCH=$\text{CHR}$ and found an absorption band near 1600 cm$^{-1}$, a strong band at 1350-1330 cm$^{-1}$ and another strong band at 975 cm$^{-1}$. They have also studied cis and trans 1,2-bis-(alkylthio)ethenes, ROCH=$\text{CHR}$, and assigned bands arising in the region 1545-1535 cm$^{-1}$ for the C=C stretching vibrations of the cis isomers. This band was absent in all the corresponding trans isomers. The assignment of the former band (1545-1535 cm$^{-1}$) towards the C=C stretching vibrations in the cis isomers was contradicted by Truce and Groten.$^{108}$

For a few trans$^\alpha$, $^\beta$-ethylenic sulphones Posner and Brunelle$^{60}$ observed bands in the region 1620, 1580 (C=C) and strong bands at 1320, 965 and 915 cm$^{-1}$. The bands arising at 966 cm$^{-1}$,$^3$ 980-982 cm$^{-1}$, and 975 cm$^{-1}$,$^7$ were used to confirm the stereochemical configuration of some of the trans $^\alpha$, $^\beta$-unsaturated sulphones.

The n.m.r. data appear to be the most reliable physical evidence for the configurational assignments which involves measurement of spin-spin coupling between the various protons on the double bond.$^{103-108}$ The spin-spin coupling constants of the ethylenic hydrogens in 1,2-disubstituted ethanes vary from 6-14 cps in the cis compounds and from 11-18 cps in the trans isomers.$^{195}$ Banwell and Sheppard$^{108}$ gave the following ranges for proton coupling constants, as determined
from a study of a large number of substituted olefins: 
\[ J_{\text{cis}} = 5-11 \text{ cps}; \ J_{\text{trans}} = 13-15 \text{ cps}; \ J_{\text{gen}} = 2 \text{ cps}. \]
It can be seen that the two ranges of spin-spin coupling constants for cis-trans pairs overlap. Hence, the assignments of configuration cannot be made, in the absence of further information, unless a pair of 1,2-disubstituted ethylenes is available. Since the correlations of \( J \) ethylenic with substituent electronegativity are so reliable\(^{10}\) that the assignments can be made even if one isomer of a 1,2-disubstituted ethylene is available provided the nature of the substituents is known.

The coupling constants for the homologous cis and trans 1-phenyl-2-(phenylsulphonyl)ethenes were found\(^{10}\) to be 12.4 and 15.7 cps. These values were in agreement with the observation that trans ethenes of this type invariably have higher coupling constants than the corresponding cis isomers. The spin-spin coupling constants for some unsaturated sulphides and sulphones are presented in Table I-5.
Vicinal Coupling Constants for Some cis and trans Unsaturated Sulphides and Sulphones

<table>
<thead>
<tr>
<th>Compound</th>
<th>J(_{\text{H-H}}) (\text{cps} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>trans</td>
<td></td>
</tr>
<tr>
<td>p-Cl(_2)_C(_6)_H(_4)_S(_2)<em>C(</em>=)_N(<em>2)C(</em>=)_O(_2)</td>
<td>9.7</td>
<td>15.4</td>
</tr>
<tr>
<td>p-Cl(_2)_C(_6)_H(_4)_S(_2)<em>C(</em>=)_N(<em>2)C(</em>=)_O(_2) 2(_H)_8</td>
<td>16.4</td>
<td>14.9</td>
</tr>
<tr>
<td>CH(_3)<em>C(</em>=)<em>C(</em>=)_N(<em>2)C(</em>=)_O(_2) 2(_H)_6</td>
<td>-</td>
<td>15.5</td>
</tr>
<tr>
<td>CH(_3)_C(_6)_H(_4)_CO(_2) 2(_H)<em>C(</em>=)<em>C(</em>=)_O(_2) 3(_H)_1=1,4</td>
<td>-</td>
<td>15.5</td>
</tr>
<tr>
<td>CH(_3)_C(_6)_H(_4)_CO(_2) 2(_H)<em>C(</em>=)<em>C(</em>=)_O(_2) 3(_H)_1=1,3,4</td>
<td>-</td>
<td>15.2</td>
</tr>
<tr>
<td>CH(_3)_C(_6)_H(_4)_CO(_2) 2(_H)<em>C(</em>=)<em>C(</em>=)_O(_2) 3(_H)_1=1,3,5</td>
<td>-</td>
<td>15.6</td>
</tr>
<tr>
<td>CH(_3)_C(_6)_H(_4)_CO(_2) 2(_H)<em>C(</em>=)<em>C(</em>=)_O(_2) 3(_H)_1=1,3,4</td>
<td>-</td>
<td>16.0</td>
</tr>
<tr>
<td>CH(_3)_C(_6)_H(_4)_CO(_2) 2(_H)<em>C(</em>=)<em>C(</em>=)_O(_2) 3(_H)_1=1,3,4</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td>p-Cl(_2)_C(_6)_H(_4)<em>C(</em>=)_N(<em>2)C(</em>=)_O(_2) 3(_H)_1=1,3,4</td>
<td>-</td>
<td>16.0</td>
</tr>
</tbody>
</table>

The \(\alpha, \beta\)-ethylenic sulphones which were prepared by different routes have been confirmed as trans isomers by n.m.r. spectral studies since the spin-spin coupling constants were found to be in the range of \(J_{\text{H-H}} = 14-16 \text{ cps}\).

The literature reviewed so far indicates that considerable interest has been evinced by a good number of
research workers on the synthesis and structural studies of \( \alpha, \beta \)-ethylenic sulphones. The aim of the present investigation was to prepare a series of new \( \alpha, \beta \)-ethylenic sulphones and to study their structural configurations by ultraviolet and infrared spectra. A collection of more data would be a valuable addition to our present knowledge of those compounds. Since the synthesis of a series of aryl cyclopropyl sulphones was contemplated by the reaction of dimethylsulphonium methylide with \( \alpha, \beta \)-ethylenic sulphones, these compounds were also prepared as starting materials. The results are discussed in the following pages.