

CHAPTER - III

DISCUSSION

Biological studies carried out on bis (arylothio)ethylenes¹ and bis (organo-sulphonyl)ethylenes² have revealed that they can be used as effective fungicides to protect seed. They are also effective against mildew on cotton-cloth, paint and various plant foliage diseases. This activity was found to vary depending on the substituents present and also on the stereochemical configurations (*cis* and *trans*) of the substances.

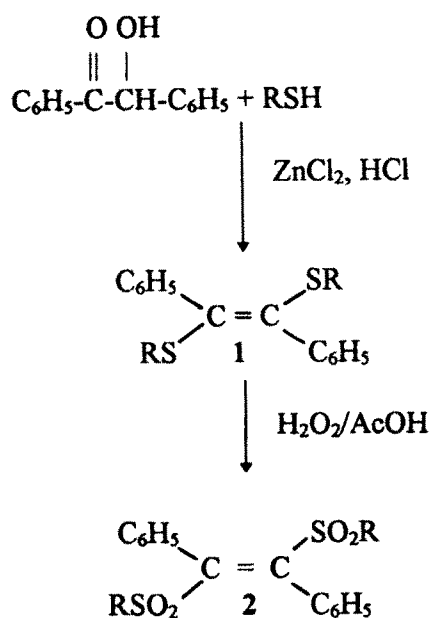
Eventhough considerable work has been reported on the synthesis and physico-chemical studies of simple *cis* and *trans* - 1,2-bis(alkylsulphonyl or arylsulphonyl)ethylenes¹⁻¹³, the work done on the synthesis and structural studies of *cis* and *trans* - 1,2-bis(alkyl-or aryl-sulphonyl)stilbenes is quite limited.

In 1949, Schönberg and Mustafa¹⁴ reported the preparation of α , β -bis(*p*-tolylthio)stilbene. They reported the preparation of this compound by the reaction between benzoin and *p*-thiocresol in presence of anhydrous zinc chloride and HCl gas. Later Benati and his co-workers¹⁵ reported the preparation of 1,2-bis(*p*-bromophenylthio)stilbene from benzoin and *p*-bromothiophenol and established its configuration as *trans* isomer through stereospecific synthesis.

Weis¹⁶ reported the preparation of a few *trans*-1,2-bis(alkyl-and aryl-thio and alkyl-and aryl-sulphonyl)-1,2-bis(*p*-chlorophenyl)ethylenes from *trans*-1,2-dichloro-1,2-bis(*p*-chlorophenyl)ethylene. Recently Peeran and his co-workers have reported the synthesis of a few *trans*-1,2-bis(alkylthio and alkylsulphonyl)-1,2-bis (*p*-bromophenyl)ethylenes¹⁷ and (*E*) and (*Z*)-1,2-bis(arylothio and aryl-sulphonyl)stilbenes¹⁸.

Benzoin is known to react with aromatic thiols^{3,14, 17}, and to result in the formation of (*E*) 1,2-bis(arylthio)stilbene. Similarly, the reaction between benzoin and aliphatic and aromatic thiols in the present investigation should also result in the formation of (*E*) -1,2-bis(alkylthio and arylthio)stilbenes.

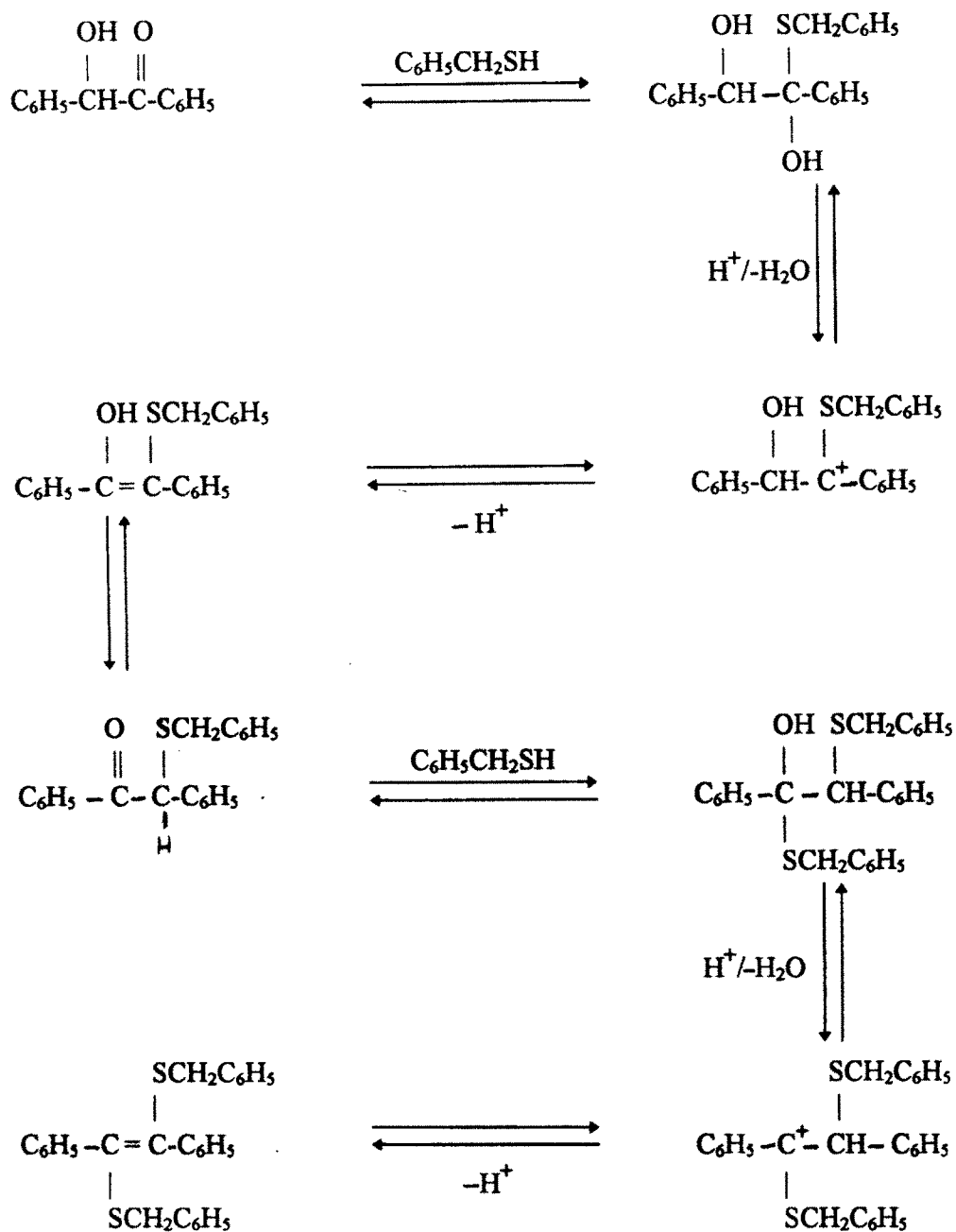
Scheme - 1



Where R = CH₃, CH₂, CH₂, (CH₃)₂CH, C₆H₅CH₂, *p*-CH₃ C₆H₄, *p*-Cl C₆H₄ and C₁₀H₇.

The (*E*)-1,2-bis(alkylthio and arylthio)stilbenes (1) on oxidation with hydrogen peroxide resulted in the formation of the corresponding (*E*)-1,2-bis(alkylsulphonyl and arylsulphonyl)stilbenes (2).

Campaigne and Leal¹⁹ while suggesting the mechanism for the reaction between desoxybenzoin and thiols giving rise to unsaturated monosulphides have extended the same mechanism to explain the abnormal reaction of benzylmercaptan with benzoin to form 1,2-dithio derivatives, the mechanism is represented as shown.



From the above mechanism it is clear that the product formed from the reaction of benzoin with thiols should possess the (*E*)-configuration. Hence the 1,2-bis-(alkylthio and arylthio)stilbenes (1) as well as 1,2-bis(alkylsulphonyl and

arylsulphonyl)stilbenes (2) prepared in the present investigation should also possess (*E*)-configuration.

Physical properties of (*E*)-1,2-bis(alkylthio and arylthio)stilbenes and (*E*)-1,2-bis(alkylsulphonyl and arylsulphonyl)stilbenes

The yields and the melting points of all the (*E*)-1,2-bis(alkylthio and arylthio)stilbenes and (*E*)-1,2-bis(alkylsulphonyl and arylsulphonyl)stilbenes prepared in the present investigation are presented in Table 1 and Table 2 respectively. From the yields of the (*E*)-1,2-bis(alkylthio and arylthio)stilbenes, it appears that the formation of (*E*)-1,2-bis(alkylthio)stilbenes is better facilitated than (*E*)-1,2-bis(arylthio)stilbenes. This may be attributed to the better nucleophilicity of the aliphaticthiols when compared to aromaticthiols.

Table - 1

Yields and melting points of (*E*)-C₆H₅ (RS) C = C (SR) C₆H₅

R	Yield %	M.P. (°C)
n-Propyl	75.43	56 - 57
Isopropyl	64.65	165 - 166
Benzyl	50.00	180 - 181
<i>p</i> -Totyl	53.30	168 - 169
<i>p</i> -Chlorophenyl	51.78	158 - 160
α -Naphthyl	51.29	114 - 115

Table - 2

Yields and melting points of (*E*)-C₆H₅ (RSO₂) C = C (SO₂R) C₆H₅

R	Yield %	M.P. (°C)
n-Propyl	62.75	239 - 240
Isopropyl	66.94	281 - 282
Benzyl	71.68	267 - 268
<i>p</i> -Totyl	65.17	288 - 289
<i>p</i> -Chlorophenyl	79.10	279 - 280
α -Naphthyl	57.57	318 - 319

Infrared Absorption Spectra

The study of infrared spectral characteristics of (*E*)-1,2-bis(alkyl - and aryl-thio)stilbenes and (*E*)-1,2-bis(alkyl- and aryl-sulphonyl)stilbenes was undertaken in order to confirm the configurations assigned to them on the basis of their mode of formation. The spectral data of the compounds prepared in the present investigation are given in the experimental section. The relation of infrared absorption to geometric configurations about ethylenic double bond has been well documented. But the literature is relatively sparse with regard to the unsaturated sulphur compounds²⁰⁻²⁹. The data can be best discussed by considering the frequencies associated with certain types of vibrations.

The characteristic bands in the infrared spectra of geometrical isomers is mainly due to three types of vibrations. They are (a) the C = C stretching vibrations, (b) the C - H in-plane and out-of-plane deformation vibrations and

(c) the = C - H out-of-plane deformation vibration and in-plane deformation vibration.

The present (*E*)-bis sulphides and (*E*)-bis sulphones present two major difficulties, when attempting to find information in the above listed regions. The first difficulty is that the present compounds being tetra substituted, do not contain any hydrogen atoms attached to the ethylenic carbon atoms and hence the absorption regions under (b) and (c) can not be studied. The second difficulty is that the aromatic rings have both C = C stretching and = C - H bending absorptions in the regions which are very close to those of the ethylenes. This is particularly troublesome when the extent of the frequency shifts of the olefinic absorption due to the pendant sulphide or sulphone groups are not well known.

C = C stretching frequency

The C = C stretching frequency for various kinds of substituted ethylenes³⁰⁻³⁴ appears between 1620 and 1660 cm⁻¹. The exact region and intensity of absorption depends upon the nature, mode and extent of substitution in the ethylenic double bond. The aromatic rings have bands at 1600, 1580, 1500 and 1460 cm⁻¹ in the C = C stretching frequency region. After assigning the aromatic bands, C = C stretching frequencies are observed for (*E*)-bis sulphides between 1648 - 1686 cm⁻¹ and for (*E*)-bis sulphones between 1651 - 1682 cm⁻¹ and are presented in the Tables - 3 and 4 respectively.

Table - 3

C = C Stretching frequency in RS (C₆H₅) C = C (C₆H₅) SR

R	(E)-(cm ⁻¹)
n-Propyl	1686
Isopropyl	1648
Benzyl	1672
<i>p</i> -Totyl	1666
<i>p</i> -Chlorophenyl	1668
α -Naphthyl	1666

Table - 4

C = C Stretching frequency in RSO₂ (C₆H₅) C = C (C₆H₅)SO₂ R

R	(E)-(cm ⁻¹)
n-Propyl	1651
Isopropyl	1656
Benzyl	1675
<i>p</i> -Totyl	1650
<i>p</i> -Chlorophenyl	1670
α -Naphthyl	1682

Trans olefins in general exhibit C = C stretching frequency around 1620 - 1660 cm⁻¹³⁰. The observed C = C stretching frequency for (E)-bis sulphides between 1648 - 1686 cm⁻¹ and 1651 - 1682 cm⁻¹ confirms that these compounds possess (E)-configuration.

Sulphonyl group frequency

The bands observed for all the (*E*)-bis sulphones in the region of 1150 and 1300 cm^{-1} are given in the Table 5.

Table - 5

**The 1150 and 1300 cm^{-1} band of
(*E*)- $\text{RSO}_2(\text{C}_6\text{H}_5)\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{SO}_2\text{R}$**

R	In the region 1150 cm^{-1}	In the region 1300 cm^{-1}
n-Propyl	1139	1315
Isopropyl	1127	1319
Benzyl	1139	1327
<i>p</i> -Totyl	1150	1325
<i>p</i> -Chlorophenyl	1152	1331
α -Naphthyl	1150	1306

It is well known^{35,36} that the $-\text{SO}_2-$ group has characteristic infrared absorption around 1340 - 1290 cm^{-1} and 1165 - 1120 cm^{-1} . These absorptions are due to the asymmetric and symmetric stretching of the $-\text{SO}_2-$ group.

The absorption bands for (*E*)-bis sulphones indicate, strong absorption around 1300 - 1150 cm^{-1} region which are characteristic of the $-\text{SO}_2-$ group.

S-alkyl and S-aryl group frequency

The alkyl-s-linkage usually shows a characteristic band near 690 cm^{-1} and aryl-s-linkage at 1090 cm^{-1} . It is thought to be an S-alkyl and aromatic ring vibration having some C-S stretching character³⁷. The relevant data for these bis sulphides and bis sulphones are given in the Tables 6 and 7 respectively.

Table - 6

S-alkyl/S-aryl stretching frequency in $RS(C_6H_5)C=C(C_6H_5)SR$

R	S-alkyl/S-aryl
n-Propyl	691
Isopropyl	628
Benzyl	638
<i>p</i> -Totyl	1072
<i>p</i> -Chlorophenyl	1092
α -Naphthyl	1069

Table 7

S-alkyl/S-aryl stretching frequency in $RSO_2(C_6H_5)C=C(C_6H_5)SO_2R$

R	S-alkyl/S-aryl
n-Propyl	627
Isopropyl	671
Benzyl	606
<i>p</i> -Totyl	1083
<i>p</i> -Chlorophenyl	1084
α -Naphthyl	1073

Mass spectrometry

Mass spectral studies of diarylsulphones containing carbon chains of various lengths and degree of unsaturation³⁸⁻⁴³ and styryl sulphones⁴⁴ have been described. The fragmentation pattern observed in these compounds include the loss of SO₂^{45,38,44, 46} as well as sulphone-sulphinat rearrangements⁴⁷. Although some mass spectral studies have been carried out on unsaturated sulphones, little work concerning the mass spectra of geometrical isomers is reported. Liu and Hong⁴⁸ reported the mass spectra of some (*E*)-1-alkylsulphonyl-2-phenylethenes. In order to study the effect of geometry of the double bond upon fragmentation pathways, Hill and his co-workers⁴⁹ have reported the mass spectral behaviour of a series of (*E*)-1-arylsulphonyl-2-arylsulphenylpropenes and (*E*)-1,2-bis(arylsulphonyl)-propenes. They have also determined the mass spectra of (*E*) and (*Z*)-1-*p*-tolylsulphonyl-2-*p*¹-tolylsulphenylstilbenes and (*E*) and (*Z*)-1,2-bis(*p*-tolylsulphonyl)stilbenes. Recently Peeran and his co-workers have reported the mass spectral rearrangements of some unsaturated bis-sulphides and bis-sulphones¹⁸ and mixed vinylsulphide-sulphones and disulphones⁵⁰. Notable fragmentation patterns observed include Smiles-type rearrangement in sulphide-sulphones and loss of SO₂ and sulphone-sulphinat rearrangement in bis-sulphones.

Although the mass spectra of some sulphides and sulphones have been reported, little work concerning the mass spectra of 1,2-bis-sulphides and 1,2-bis-sulphones have been reported. In the present investigation the electron impact mass spectral rearrangements of (*E*)-1,2-bis(alkylthio)stilbenes and (*E*)-1,2-bis(alkylsulphonyl)stilbenes have been reported.

The mass spectrum of (*E*)-1,2-bis(isopropylthio)stilbene (**1**) is presented in Fig. 1 and the data is given in the experimental section. The mass spectral features of (*E*)-1,2-bis(isopropylthio)stilbene showed strong molecular ion peak (**A**) at m/z 328. The molecular ion peak is followed by a weak $M^{\dagger} + 2$ peak at m/z 330. The fragmentation pattern is shown in Scheme 1. An interesting feature observed was the presence of a prominent peak at m/z 243 which is assumed to be due to the ion (**B**) formed from the molecular ion (**A**) involving McLafferty-type rearrangement, where migration of γ -hydrogen from isopropyl group to the ethylenic carbon, with the expulsion of propene, followed by the loss of an isopropyl radical (Scheme 2). The peak at m/z 165 (**C**) is probably observed by the loss of benzene molecule from the ion (**B**).

Another notable feature observed was the electron impact-induced Smiles-type rearrangement of (**A**) leading to the formation of diphenylacetylene ion (**D**) m/z 178 and a base peak at m/z 210 assigned to the ion (**E**). The proposed rearrangement mechanism involves (Scheme 3) initial ionisation of the bis-sulphide (**1**) which permits rotation into a *cis* geometry which is a pre-requisite for such a rearrangement and hence was observed in the (*E*)-isomer. The ion (**E**) can further undergo fragmentation giving rise to the ion (**F**) at m/z 121. The peak at m/z 211 is believed to be due to the ion (**G**) which is formed as shown in Scheme 3, the peak at m/z 43 is assigned to isopropylcation (**H**). Similar fragmentation pattern is observed in the other (*E*)-1,2-bis(alkylthio and arylthio)stilbenes under present investigation.

The mass spectrum of (*E*)-1,2-bis(isopropylsulphonyl)stilbene (**2**) is shown in Fig 2 and the spectral data is given in experimental section. The fragmentation

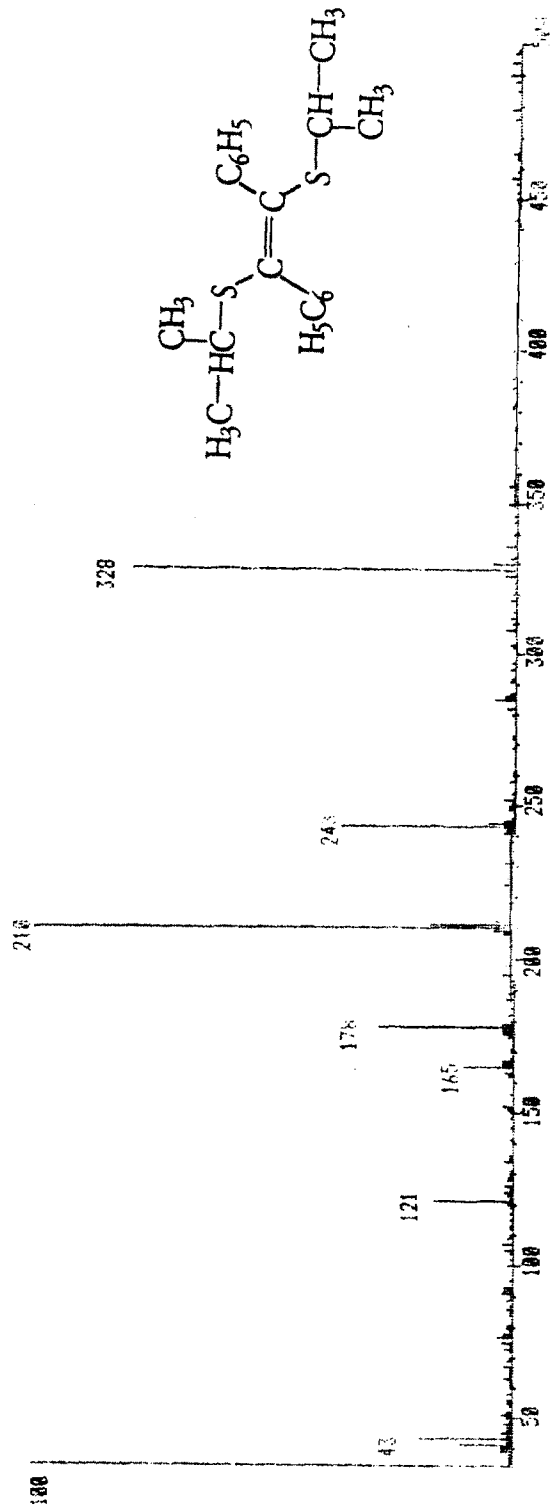


Fig 1 Mass spectrum of (E) - 1,2 - bis (isopropylthio) stilbene

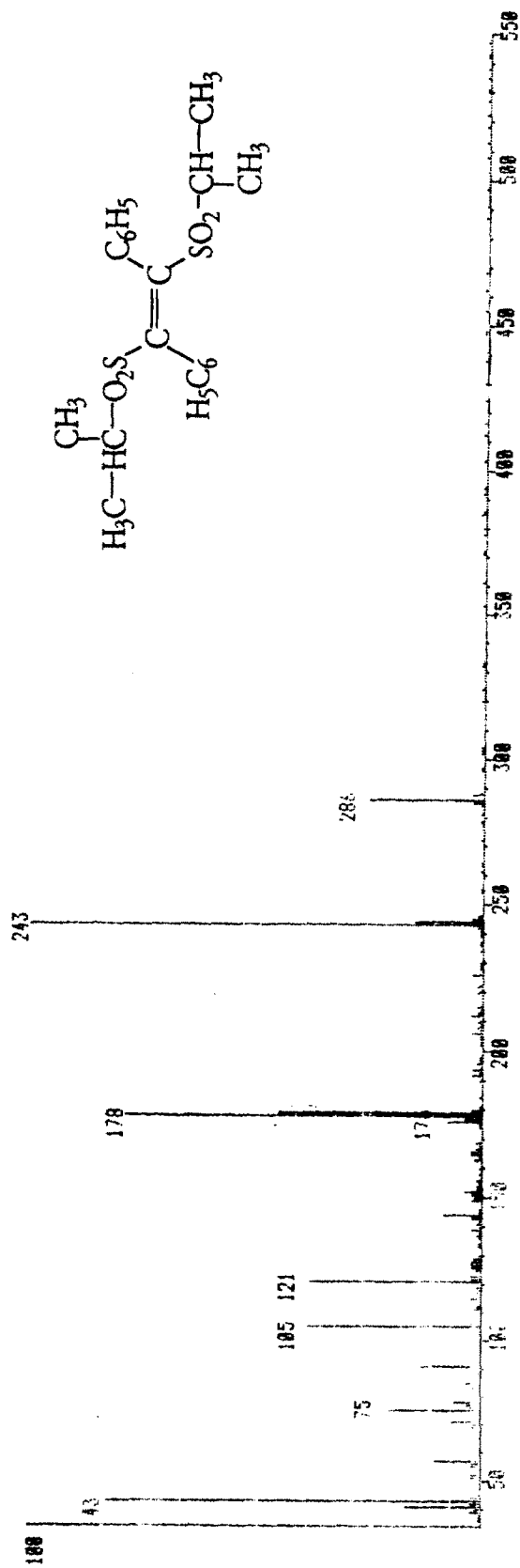
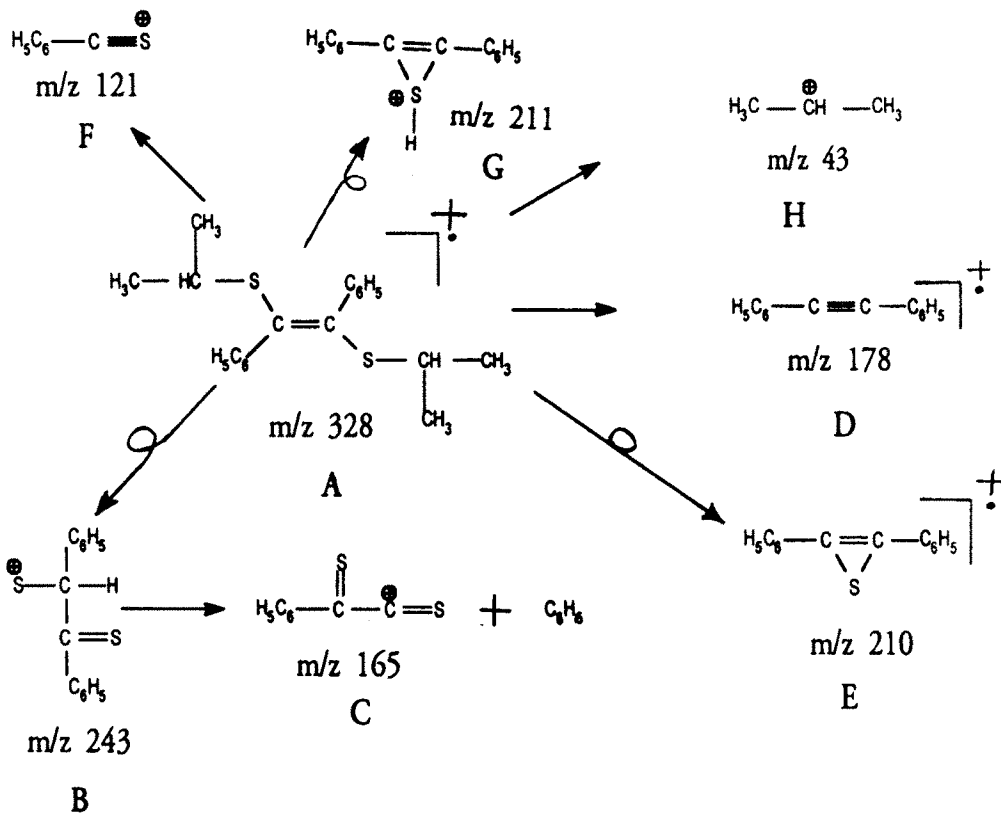
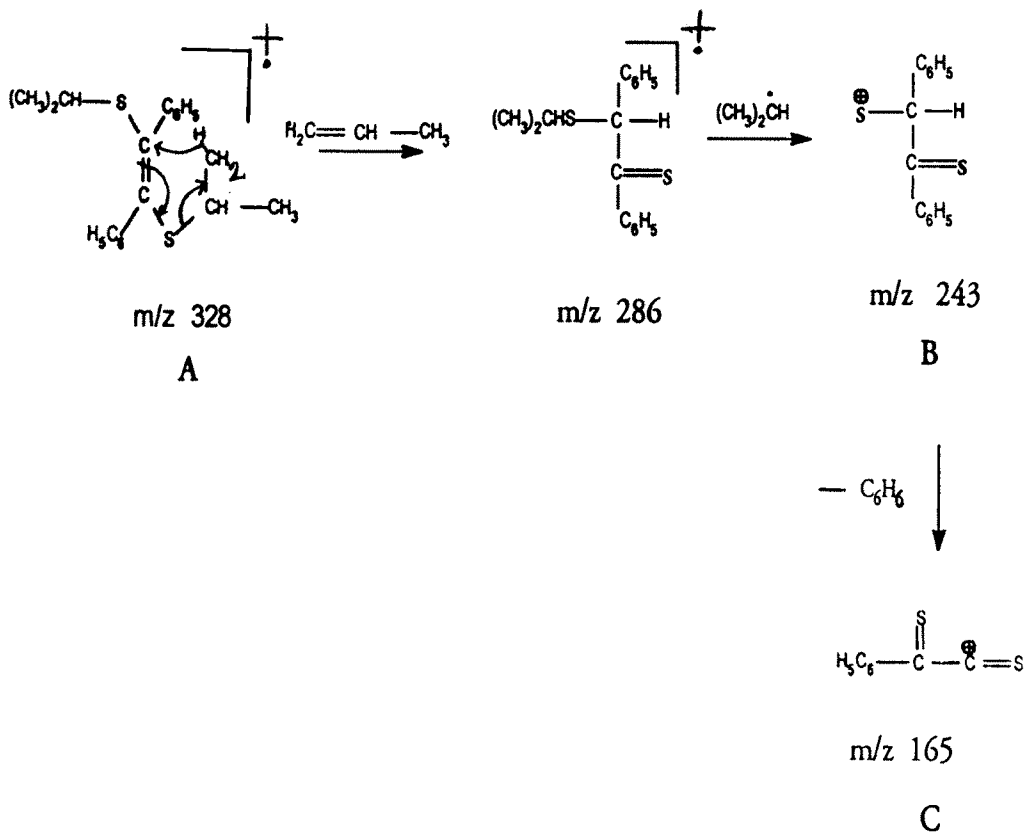


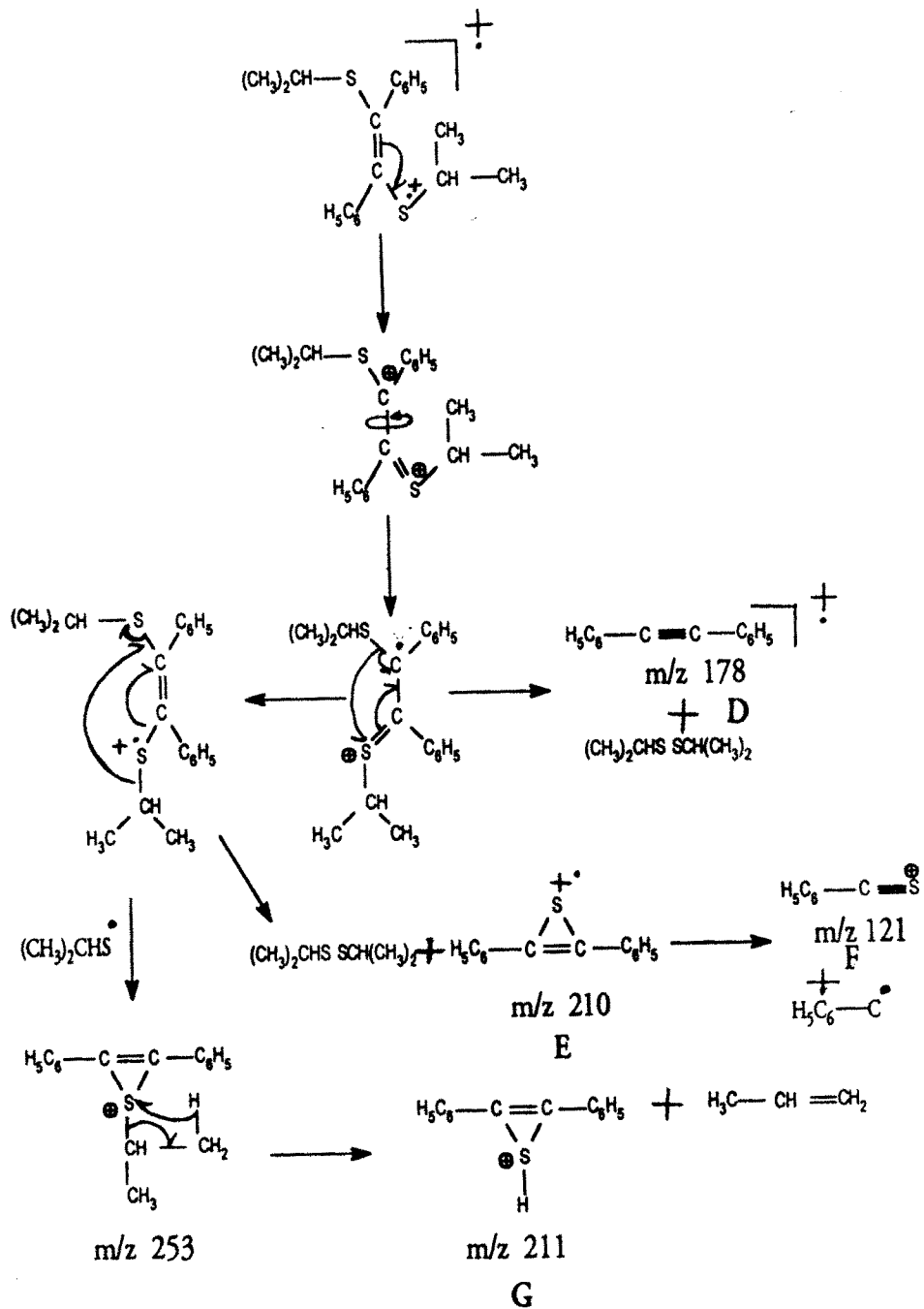
Fig 2 Mass spectrum of (E) - 1,2 - bis (isopropylsulphonyl) stilbene



Scheme 1



Scheme 2

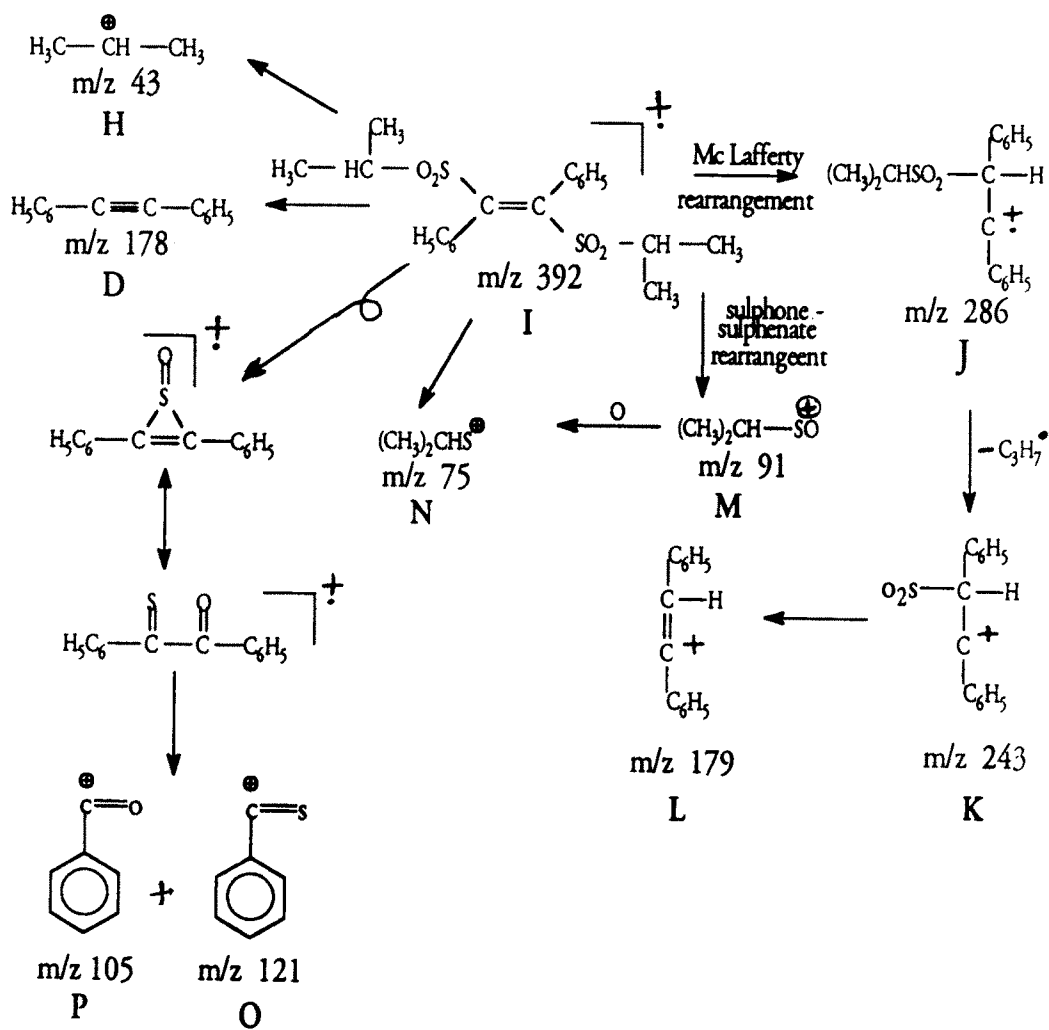


Scheme 3

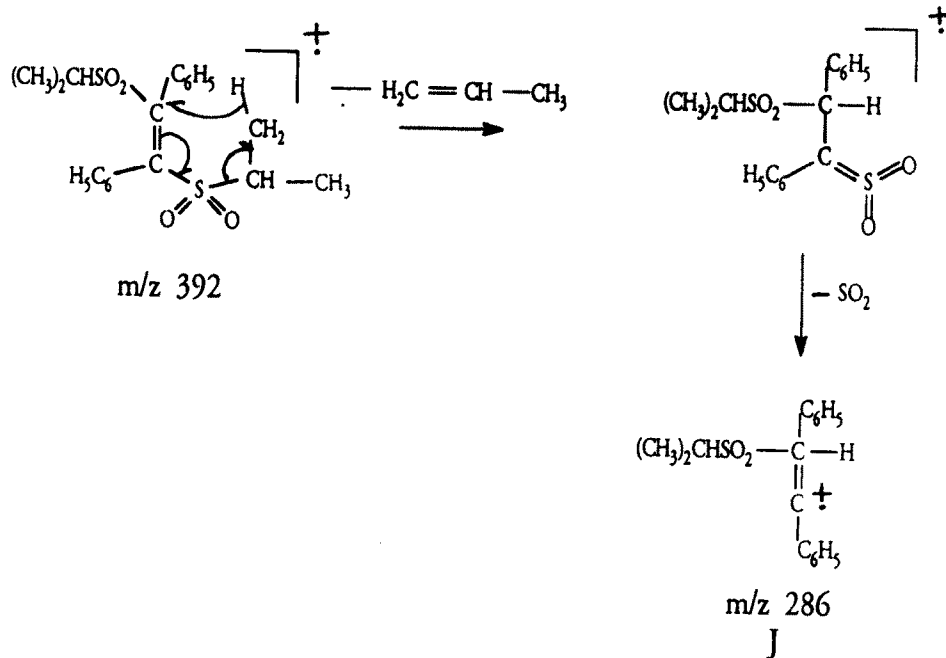
pattern of (*E*)-1,2-bis(isopropylsulphonyl)stilbene is shown in Scheme 4. Unlike the (*E*)-1,2-bis(isopropylthio)stilbene, no molecular ion peak is observed in the mass spectrum of (*E*)-1,2-bis(isopropylsulphonyl)stilbene. The absence of the molecular ion peak in the bis sulphone may be due to the thermal decomposition of the bis sulphone during sample vapourisation.

Unlike bis-sulphides¹⁸, (*E*)-1,2-bis-sulphones showed no Smiles-type rearrangement. This may be attributed to the loss of a free electron pair of the sulphur which has been oxidised to the sulphone and thus sulphur is in higher oxidation state. The change in oxidation state could manifest itself in the loss of the radical located in divalent sulphur $-S^{\ddagger}$, which is responsible for initiating the Smiles-type rearrangement after double bond isomerisation has occurred.

Like (*E*)-1,2-bis-(isopropylthio)stilbene, (*E*)-1,2-bis(isopropylsulphonyl)stilbene also undergoes McLafferty rearrangement. The peak appearing at m/z 286 may be due to the ion (**J**) formed from the molecular ion, involving McLafferty-type rearrangement; where migration of γ -hydrogen from the isopropyl group through a six membered transition state occurred. This fragmentation mechanism is depicted in scheme 5. Similar type of rearrangement was observed by Liu and Hong⁴⁸ in the mass spectra of (*E*)-1-alkylsulphonyl-2-phenylethylenes. The radical ion (**J**) may lose an isopropyl radical to give cation (**K**) with m/z 243 which constitutes the base peak in the mass spectrum of **2**. The peak at m/z 179 may be due to the ion (**L**) which can be obtained by loss of SO_2 from the cation (**K**). The intense peak observed at m/z 178 may be assigned to diphenylacetylene radical cation (**D**), however, its origin is uncertain. The diphenylacetylene radical cation (**D**) may lose a hydrogen molecule to give a peak at m/z 176.



Scheme 4



Scheme 5

The bis-sulphone **2** also undergoes the well known sulphonyl-sulphinate rearrangement with subsequent cleavage resulting in $(\text{CH}_3)_2\text{CHSO}^+$ (**M**) m/z 91. Vinyl migration is the prominent path way of the sulphonyl-sulphinate rearrangement with no evidence of $(\text{CH}_3)_2\text{CHO}^\bullet$ to indicate an alkyl migration. Similar observations were made by Hill and his co-workers⁴⁹. The ion (**N**) with m/z 75 may be obtained by the loss of an oxygen atom from the ion (**M**). The other predominant peaks of m/z 121 and 105 may be ascribed to the ions (**O**) ($\text{C}_6\text{H}_5\text{CS}^+$) and (**P**) ($\text{C}_6\text{H}_5\text{CO}^+$) respectively. A plausible mechanism for their formation is depicted in Scheme 4. The intermediate depicted is similar to the intermediate postulated by Dittmer⁵¹ and Vouros⁴⁴ in their separate studies. The intense peak (**H**) m/z 43 is attributed to the isopropyl cation.

The mass spectral characteristics of other (*E*)-1,2-bis-sulphones were almost similar to that of (*E*)-1,2-bis(isopropylsulphonyl)stilbene. (*E*)-1,2-bis(*p*-tolyl-sulphonyl)stilbene also undergoes McLafferty-type rearrangement. The base peak appearing at m/z 270 in the mass spectrum of (*E*)-1,2-bis(*p*-tolylsulphonyl)stilbene Fig 3 may be due to the ion (**R**) formed from the molecular ion (**Q**) involving McLafferty-type rearrangement, where migration of ortho-hydrogen (γ -hydrogen to olefinic double bond) from the *p*-tolyl group occurs, followed by the successive loss of two molecules of SO_2 . This fragmentation mechanism is outlined in Scheme 6. The peak at m/z 270 is absent in the mass spectrum of the isomeric compound (*E*)-1,2-bis(benzylsulphonyl)stilbene, Fig 4. This may be attributed to the absence of γ -hydrogen to the olefinic double bond in (*E*)-1,2-bis(benzylsulphonyl)stilbene, hence cannot undergo McLafferty-type rearrangement (Scheme 7).

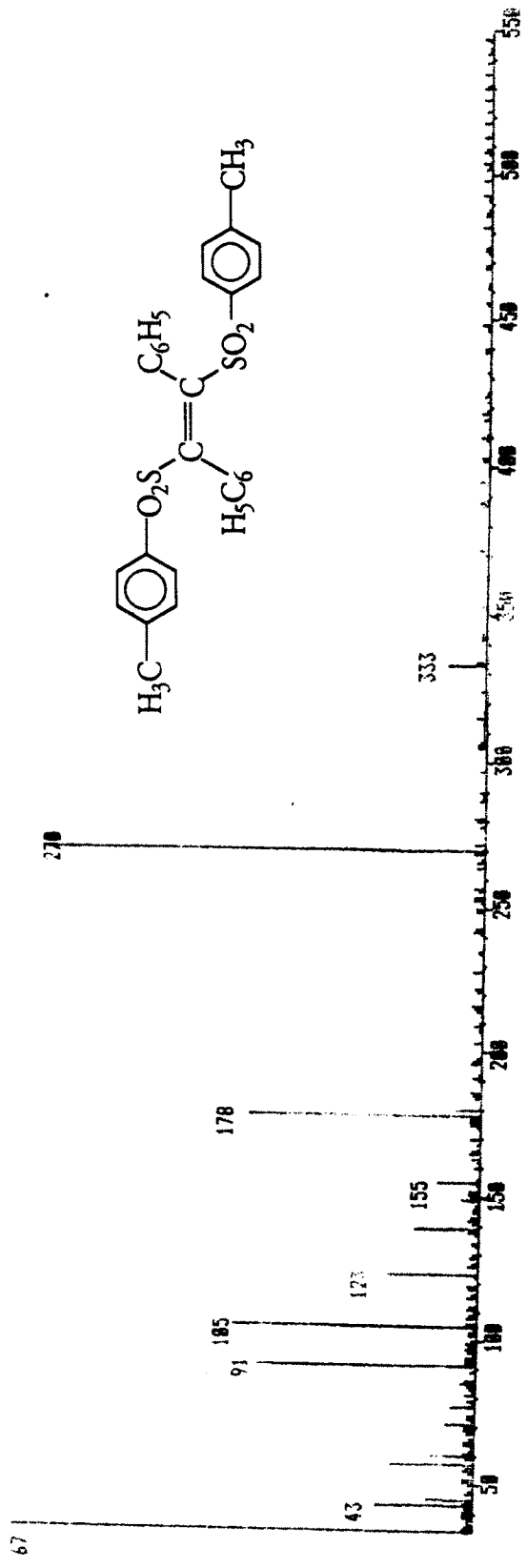


Fig 3 Mass spectrum of (E) - 1,2 - bis (p - tolylsulphonyl) stilbene

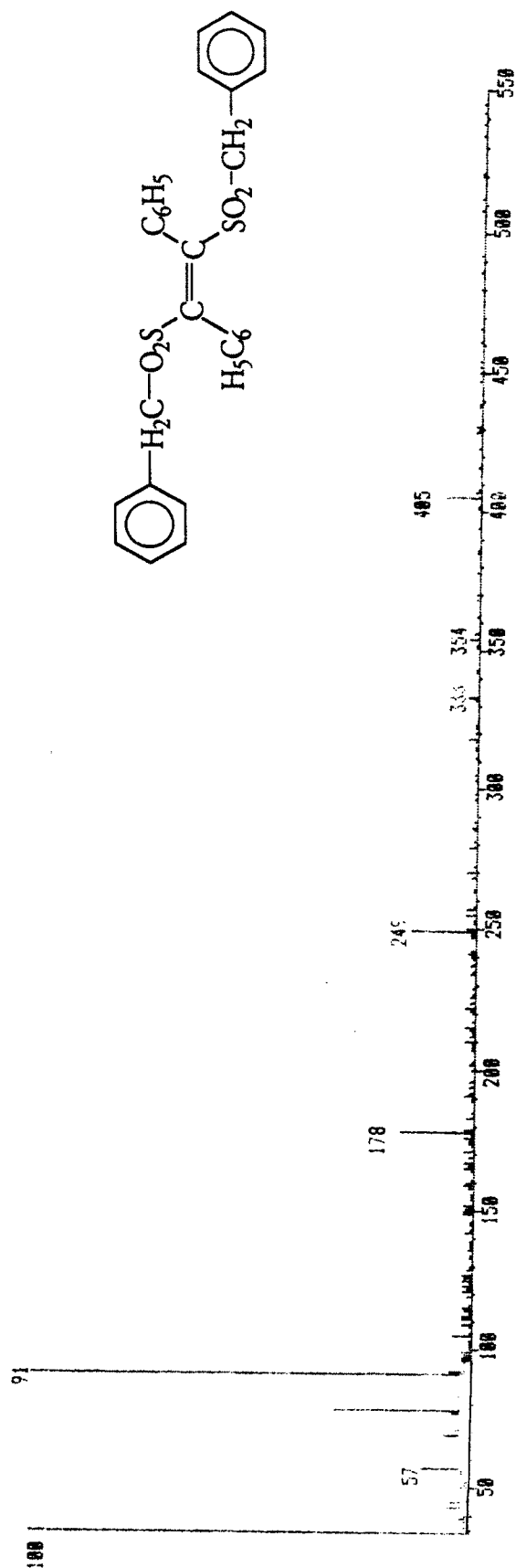
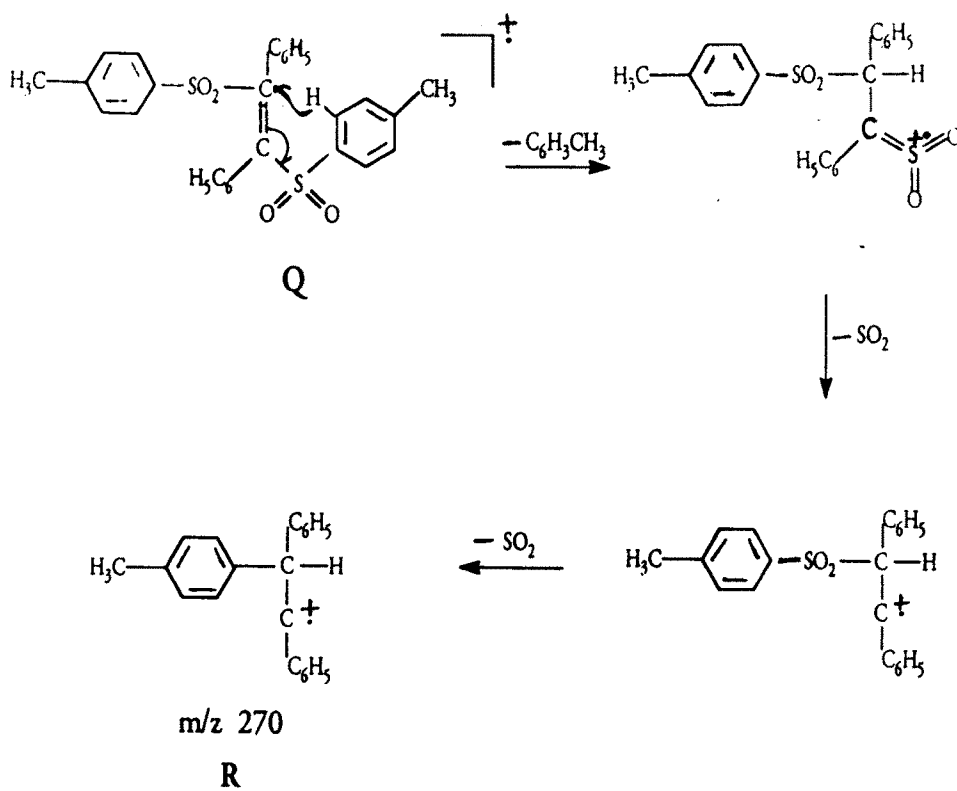
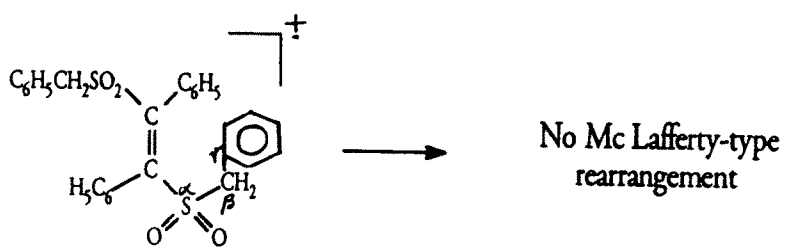


Fig 4 Mass spectrum of (E) - 1,2 - bis (p - benzy/sulphony) stilbene



Scheme 6



Scheme 7