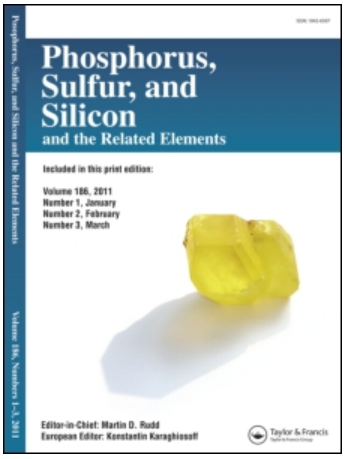

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Synthesis and Mass Spectral Studies of Some (*E*)- and (*Z*)-1-Alkylthio - and 1-Alkylsulphonyl-2-*P*-Tolylsulphonylstilbenes

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Synthesis and Mass Spectral Studies of Some (*E*)- and (*Z*)-1-Alkylthio - and 1-Alkylsulphonyl-2-*P*-Tolylsulphonylstilbenes

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A number of (E)*- and* (Z)*-1-alkylthio-2-*p*-tolylsulphonylstilbenes (**3a–i** and **5a–i**) were synthesized by the nucleophilic displacement of halogens with sodium salts of various alkanethiols on* (E)*-1-chloro-2-*p*-tolylsulphonylstilbene **(1)** and* (Z)*-1-bromo-2-*p*-tolylsulphonylstilbene **(2)** respectively. Oxidation of these* (E) *- and* (Z)*-1-alkylthio-2-*p*-tolylsulphonyl gave the corresponding* (E)*- and* (Z)*-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes (**4a–i** and **6a–i**) respectively. Mass spectral data of all the synthesized compounds were examined. Smiles-type rearrangement observed in* (E)*-and* (Z)*- sulphide-sulphones (**3a–i** and **5a–i**) was absent in* (E)*- and* (Z)*-disulphones (**4a–i** and **6a–i**). Loss of sulphur dioxide and sulphonyl-sulphinate rearrangement with vinyl migration was noticed in all the synthesized compounds. McLafferty-type rearrangement was observed only in* (E)*- sulphide-sulphones and* (E)*- disulphones but not in the corresponding* (Z)*-isomers.*

Keywords (*E*)-1-Alkylthio-2-*p*-tolylsulphonylstilbenes; (*E*)-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes; (*Z*)-1-alkylthio-2-*p*-tolylsulphonylstilbenes; (*Z*)-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes

INTRODUCTION

Biological studies carried out on vinylsulphonyl compounds[1] and bis (organosulphonyl)ethylenes[2,3] revealed that they can be used as effective fungicides to protect seeds. Although some reports[4–8] have appeared on the synthesis of *cis*- and *trans*-sulphide-sulphones and disulphones, the mass spectral data available on these compounds is scanty. In order to study the effect of geometry of double bonds

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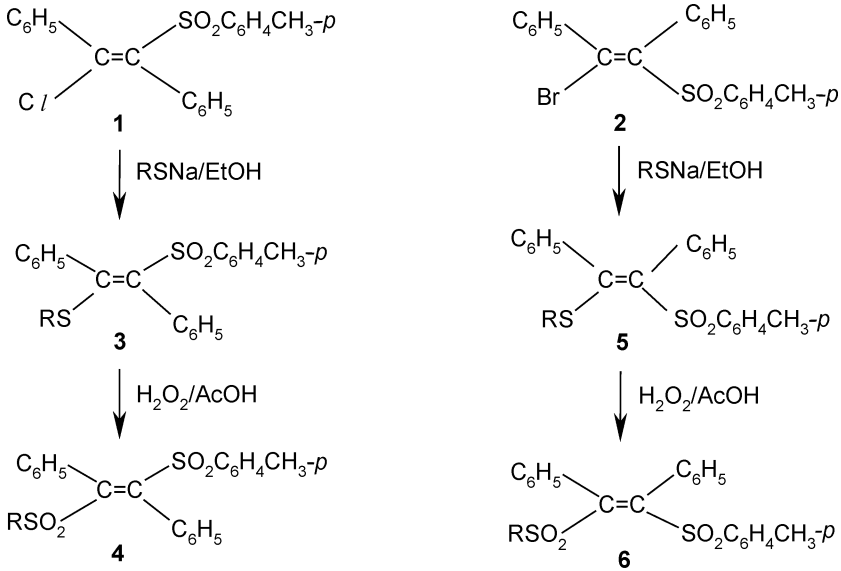
upon fragmentation path ways, we have under taken the synthesis and mass spectral studies of some (*E*)- and (*Z*)-1-alkythio - 2-*p*-tolylsulphonylstilbenes (**3a–i** and **5a–i**) and (*E*)- and (*Z*)-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes (**4a–i** and **6a–i**).

DISCUSSION

When (*E*)-1-chloro-2-*p*-tolylsulphonylstilbene (**1**) was treated with sodium salts of various alkanethiols, nucleophilic displacement of chlorine took place with retention of configuration[5,9,10] and gave (*E*)-1-alkylthio-2-*p*-tolylsulphonylstilbenes (**3a–i**) (Scheme **1**). Compounds **3a–i** on oxidation with hydrogen peroxide afforded (*E*)-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes (**4a–i**). Similarly when (*Z*)-1-bromo-2-*p*-tolylsulphonylstilbene (**2**) was treated with sodium salts of



3,4,5 and 6

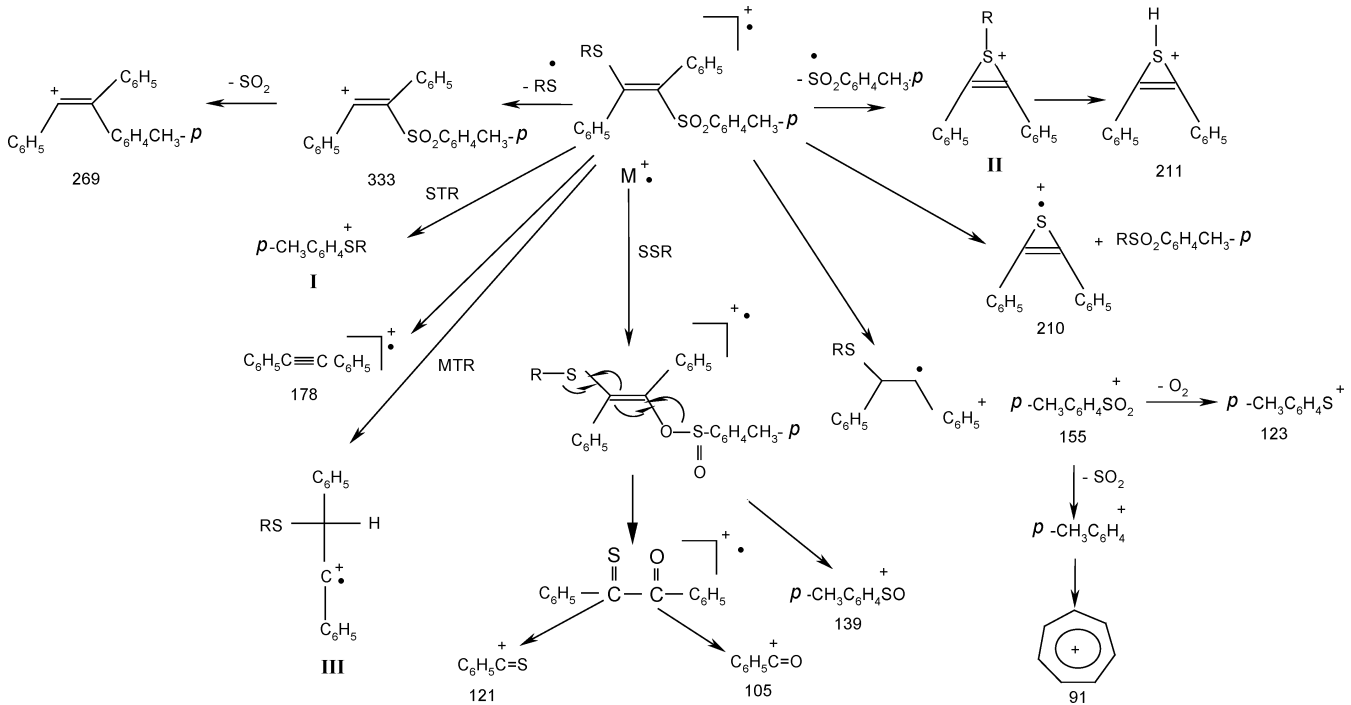
a: R= CH_3
b: R= CH_3CH_2
c: R= $CH_3(CH_2)_2$
d: R= $(CH_3)_2CH$
e: R= $CH_3(CH_2)_3$
f : R= $(CH_3)_2CHCH_2$
g: R= $(CH_3)_3C$
h: R= $CH_3(CH_2)_4$
i : R= $(CH_3)_2CH(CH_2)_2$

SCHEME 1

TABLE I The m/z Values and Intensities of the $M^{+\cdot}$ Peaks of (*E*)-and (*Z*)-*P*-$CH_3C_6H_4SO_2(C_6H_5)$ C═C (C_6H_5)SR

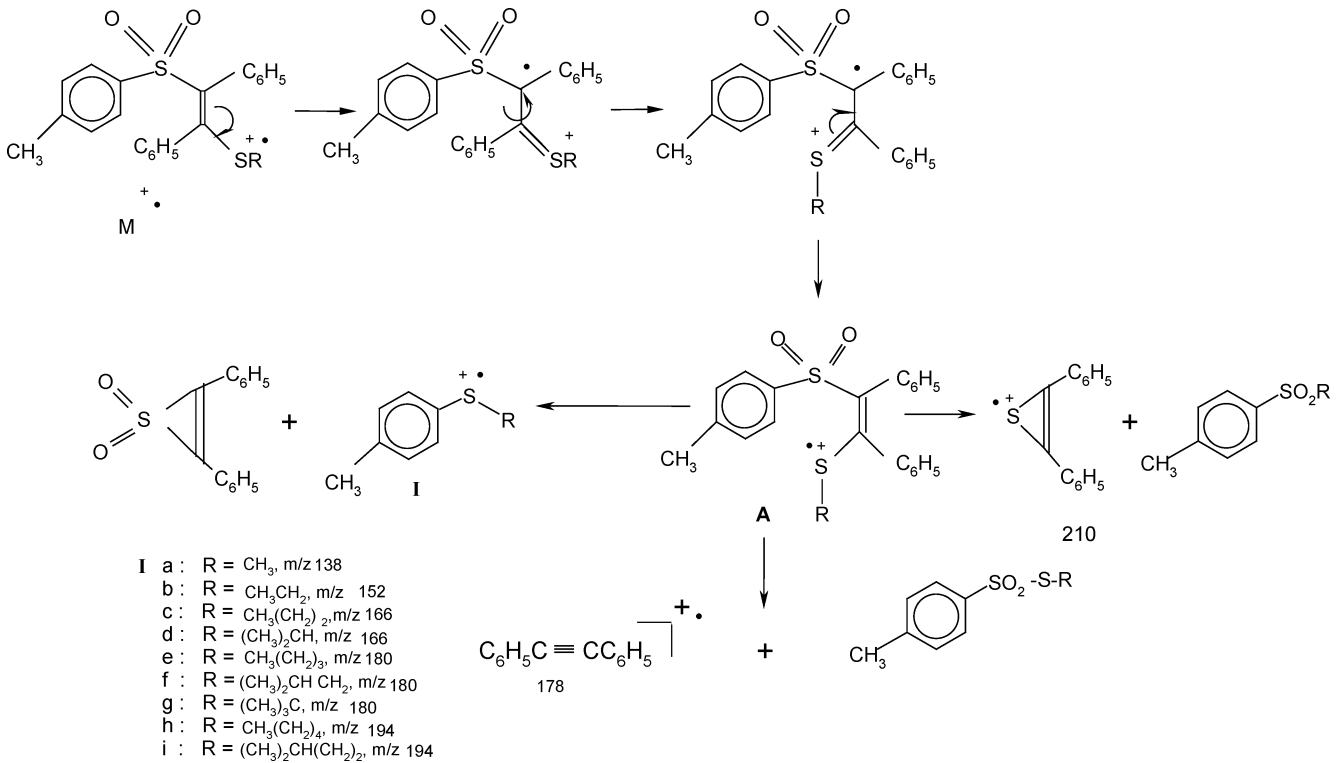
	$M^{+\cdot}$	
R	(*E*) m/z (rel. int. %)	(*Z*) m/z (rel. int. %)
CH_3	380(37)	380(29)
CH_3 CH_2	394(26)	394(20)
$CH_3(CH_2)_2$	408(38)	408(25)
$(CH_3)_2CH$	408(36)	408(18)
$CH_3(CH_2)_3$	422(32)	422(20)
$(CH_3)_2CH$ CH_2	422(28)	422(16)
$(CH_3)_3C$	422(26)	422(10)
$CH_3(CH_2)_4$	436(24)	436(14)
$(CH_3)_2CH(CH_2)_2$	436(25)	436(16)

various alkanethiols, nucleophilic displacement of bromine occured resulting in the formation of (*Z*)-1-alkylthio-2-*p*-tolylsulphonylstilbenes (**5a–i**) with retention of configuration[5,6] (Scheme 1). Oxidation of **5a–i** with hydrogen peroxide afforded (*Z*)-1-alkylsulphonyl-2-*p*-tolylsulphonylstilbenes (**6a–i**). The mass spectral features of (*E*)- and (*Z*)-1-alkylthio-2−*p*-tolylsulphonylstilbenes (**3a–i** and **5a–i)** and their corresponding disulphones (**4a–i** and **6a–i**) were examined at 70 eV. Molecular ion peaks were observed in all the (*E*)- and (*Z*)-sulphide-sulphones, however the molecular ion peaks of the (*E*) -isomers (**3a–i**) were more intense than their corresponding (*Z*)-isomers (**5a-i**), Table I. A peak at m/z value 333 was observed in the mass spectra of all the (*E*)- and (*Z*)-isomers and is believed to be produced by the loss of $RS^{\cdot}$ from the molecular ions (Scheme 2). The base peaks were observed either at m/z 178 or at m/z 210. The 178 peak is assigned to diphenylacetylene radical cation and the 210 peak to a cyclic sulphenium cation (Scheme 3). Smiles-type rearrangement leading to the formation of alkyl *p*-tolylsulphide radical cations (*p*-$CH_3C_6H_4SR^+$) **(I)** was noticed[11] in all the (*E*)- and (*Z*)-sulphide-sulphones. The proposed rearrangement mechanism (Scheme 3), involves initial ionisation of the sulphide which permits the rotation of *trans*- into *cis*-geometry, which is a prerequisite for such a rearrangement and hence was observed in (*E*)-isomers also. The molecular ions also underwent fragmentation by the loss of *p*-$CH_3C_6H_4SO_2$ forming a cation (**II**) whose proposed structure is shown in Scheme 4. An intense peak at m/z 211 was observed in all the sulphide-sulphones except in **3a** and **5a** which may be formed from the cation **II** by the loss of an olefin, where in the transfer of β-hydrogen from the alkyl group to the sulphur atom followed by cleavage of *C*—*S*

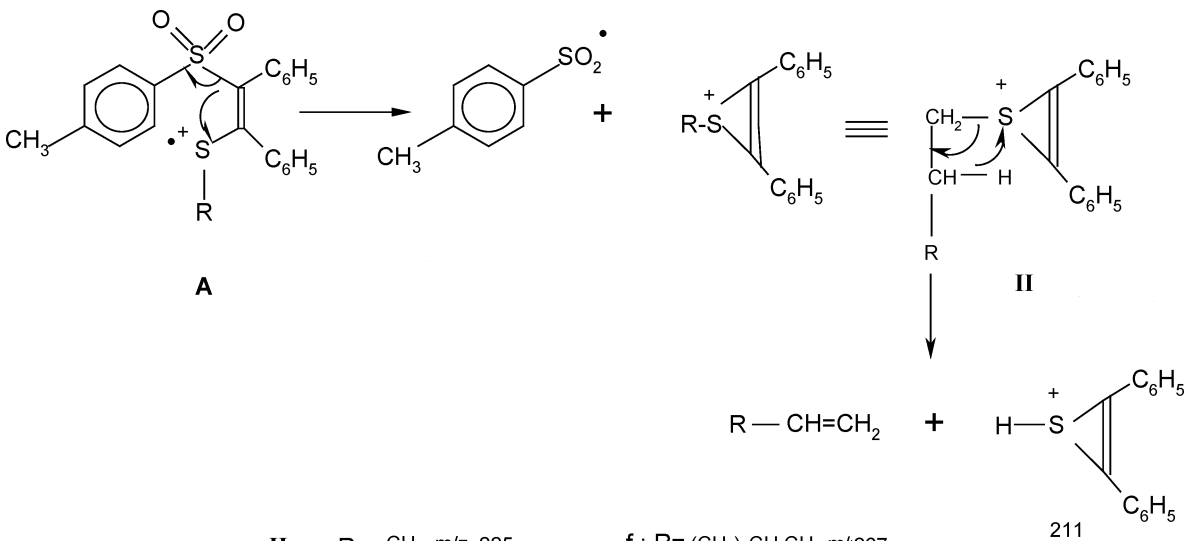


STR : Smiles - Type Rearrangement , MTR : McLafferty - Type Rearrangement , SSR : Sulphonyl - Sulphinate Rearrangement.

SCHEME 2



SCHEME 3

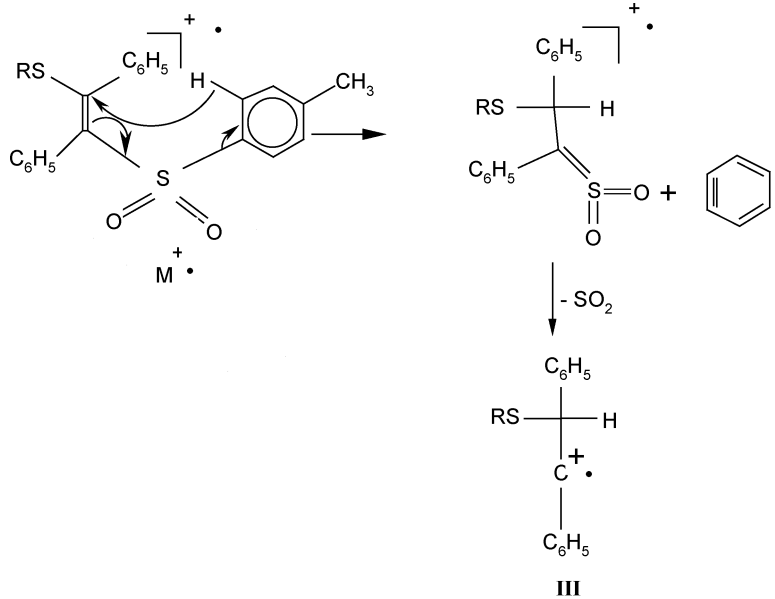


II a: R= CH_3, m/z 225
b: R= CH_3CH_2, m/z 239
c: R= $CH_3(CH_2)_2$, m/z 253
d: R= $(CH_3)_2CH$, m/z 253
e: R= $CH_3(CH_2)_3$, m/z 267
f : R= $(CH_3)_2CH\ CH_2$,m/:267
g : R= $(CH_3)_3C$, m/z, 267
h : R= $CH_3(CH_2)_4$, m/z 281
i : R= $(CH_3)_2CH(CH_2)_2$, m/z 281

SCHEME 4

bond occurs. The absence of 211 peak in **3a** and **5a** may be explained as being due to the absence of β-hydrogen in alkyl group of these compounds.

All the (*E*)- and (*Z*)-sulphide-sulphones underwent the well known sulphonyl-sulphinate rearrangement[12,13] furnishing with subsequent cleavages p-$CH_3C_6H_4SO^+$ (139), $C_6H_5\overset{+}{C}{=}S$ (121) and $C_6H_5\overset{+}{C}{=}O$ (105). The 121 and 105 peaks are assumed to be formed via thiobenzil radical cation (Scheme 2). Vinyl migration is the only predominant pathway observed in sulphonyl-sulphinate rearrangement. McLafferty-type rearrangement[14] was noticed only in (*E*)-sulphide-sulphones. In McLafferty-type rearrangement the migration of ortho hydrogen from *p*-tolylsulphonyl group to the ethylenic carbon involving a six membered cyclic transition state is taking place. The ions produced in this rearrangement by the loss of SO_2 gave the ions **(III)** (Scheme 5).



III

III	R	m/z (rel.int.%)
a:	CH_3	226(14)
b:	CH_3CH_2	240(12)
c:	$CH_3(CH_2)_2$	254(14)
d:	$(CH_3)_2CH$	254(16)
e:	$CH_3(CH_2)_3$	268(38)

III	R	m/z (rel.int.%)
f:	$(CH_3)_2CH\,CH_2$	268(40)
g:	$(CH_3)_3C$	268(8)
h:	$CH_3(CH_2)_4$	282(25)
i:	$(CH_3)_2CH(CH_2)_2$	282(15)

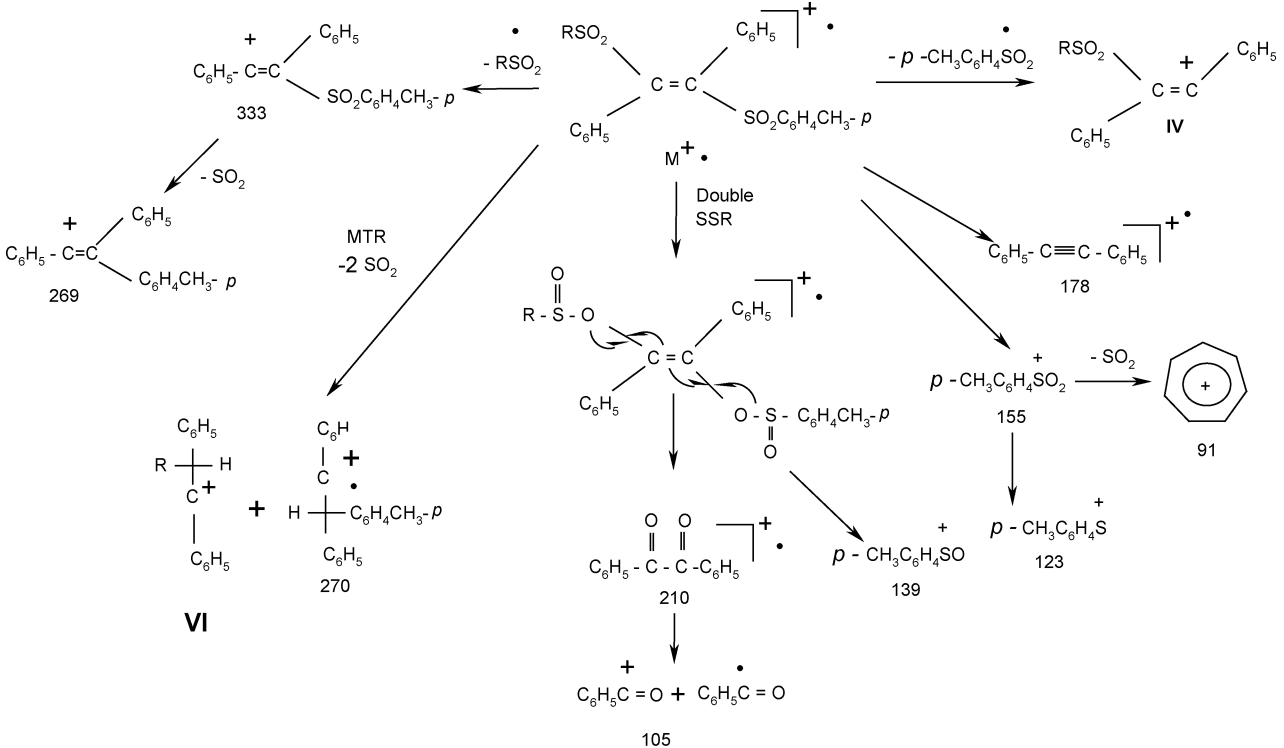
SCHEME 5

McLafferty-type rearrangement was not observed in (*Z*)-sulphide-sulphones and this may be attributed to the steric interactions present in these isomers which prevents the formation of the six membered cyclic transition state.

In the mass spectra of all the (*E*)- and (*Z*)-disulphones $\overset{+\cdot}{M}$ peaks were not observed. This may be due to the thermal decomposition of the samples during sample evaporation. The fragmentation pattern of (*E*)-disulphones is shown in Scheme 6. The base peaks in the disulphones were observed either at m/z 178 $(C_6H_5C \equiv CC_6H_5)^{+\cdot}$ or m/z 105 $(C_6H_5\overset{+}{C}{=}O)$. The peak at m/z 333 present in all the disulphones may be obtained by the loss of RSO_2 from the $\overset{+}{M}$. which can further expel SO_2 to give a peak at m/z 269. All the $\overset{+\cdot}{M}$ also undergo fragmentation by the loss of *p*-$CH_3C_6H_4SO_2$ forming a cation **(IV).** Smiles-type rearrangement was totally absent in all the (*E*)- and (*Z*)-disulphones and this may be attributed to the absence of unshaired electron pair on the sulphur atoms which are necessary for this rearrangement to occur. Double sulphonyl-sulphinate rearrangement was observed in all the (*E*)- and (*Z*)-disulphones. This rearrangement followed by subsequent cleavages formed *p*-$CH_3C_6H_4SO^+$m/z (139) and $C_6H_5C^+{=}O$ m/z (105). Benzoyl cation may be formed via benzil radical cation (Scheme 6). It is noteworthy that McLafferty-type rearrangement was observed only in (*E*)-disulphones involving both the*p*-tolylsulphonyl group, as well as alkylsulphonyl groups (having γ-hydrogen) Scheme 7. When *p*-tolylsulphonyl group is involved, migration of ortho hydrogen to the ethylenic carbon via a six membered cyclic transition state occurs and gave peaks **V** and **VI** by the successive loss of one and two molecules of SO_2. The m/z values and intensities of the peaks **V** and **VI** are shown in Table II . When alkylsulphonyl group is involved in McLafferty-type rearrangement migration of γ-hydrogen to the ethylenic carbon occurs and results in the formation of peaks at m/z 334 and 270 by the loss of one and two molecules of SO_2, respectively. The m/z 334 and 270 peaks were not observed in **4a** as it does not contain -γ hydrogen in alkylsulphonyl group. McLafferty-type rearrangement was not observed in all the (*Z*)- disulphones probably due to steric hindrance.

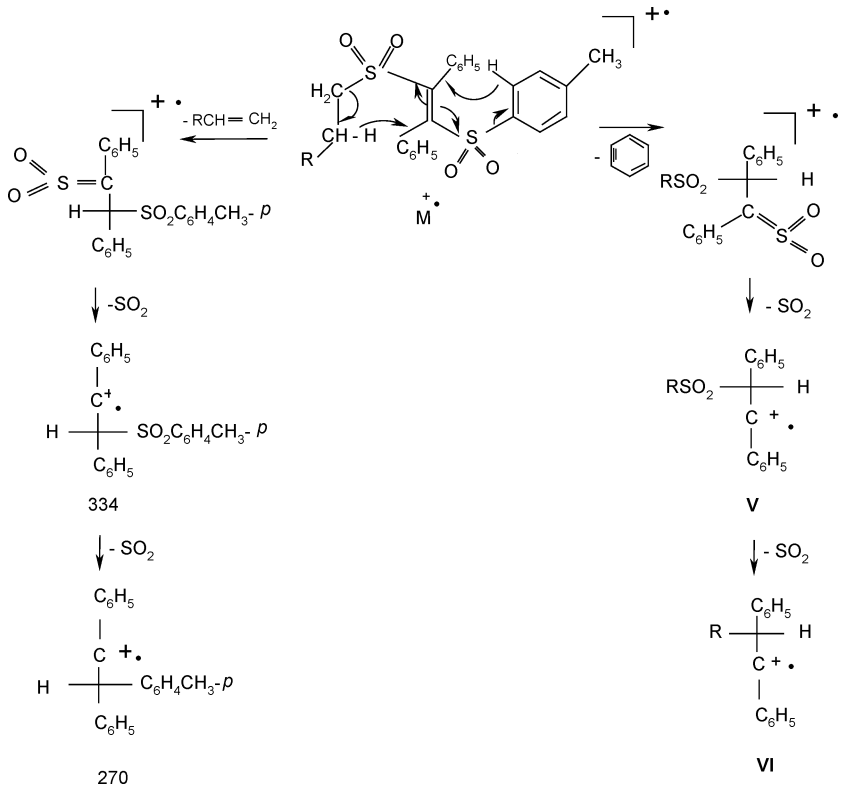
EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus and are uncorrected. Mass spectra were recorded on Auto



MTR = McLafferty - Type Rearrangement, SSR = Sulphonyl - Sulphinate Rearrangement

SCHEME 6



SCHEME 7

TABLE II The m/z Values and Intensities of V and VI Peaks Obtained from (*E*)-*p*-$CH_3C_6H_4SO_2(C_6H_5)C{=}C(C_6H_5)SO_2R$ on McLafferty-type Rearrangement.

Comp.	R	V m/z (rel.int. %)	VI m/z (rel.int. %)
4a	CH_3	258 (13)	194 (14)
4b	CH_3CH_2	272 (18)	108 (15)
4c	$CH_3(CH_2)_2$	286 (5)	222 (10)
4d	$(CH_3)_2CH$	286 (6)	222 (15)
4e	$CH_3(CH_2)_3$	300 (4)	236 (9)
4f	$(CH_3)_2CHCH_2$	300 (6)	236 (10)
4g	$(CH_3)_3C$	300 (4)	236 (8)
4h	$CH_3(CH_2)_4$	314 (5)	250 (8)
4i	$(CH_3)_2CH(CH)_2$	314 (4)	250 (7)

Spec–M Micro Mass Instrument, Manchester, U.K. (*E*)-1-Chloro-2-*p*-tolylsulphonylstilbene (**1**) and (*Z*)-1-bromo-2-*p*-tolylsulphonylstilbene (**2**) were prepared as reported earlier.[5]

(*E*)-1-Alkylthio-2-*p*-tolylsulphonylstilbenes (3a–i)—General Procedure

A solution of sodium alkanethiolate prepared by adding an appropriate alkanethiol (6 mmol) to a solution of sodium (6 mg atom) in abs. ethanol (25 ml) was added to a solution of **1** (6 m mol) dissolved in abs. ethanol (75 ml). The reaction mixture was heated under reflux. Refluxion time varied from 5 to 7 h in different cases. In many cases, the solution upon cooling deposited the sulphide-sulphones, (**3**) which were recrystallized from an appropriate solvent.

(E)-1-methylthio-2-p-tolylsulphonylstilbene (3a)

Recrystallized from aqueous ethanol as shining needles, m.p. 172–173°C, yield 91% (Found: C, 69.13; H, 5.25; S, 16.61. $C_{22}H_{20}O_2S_2$ requires C, 69.44; H, 5.30; S, 16.82%). EIMS: m/z (rel. int.%) 380(37), 333(8), 269(15), 259(12), 226(14), 225(19), 210(42), 179(15), 178(100), 176(8), 155(15), 139(5), 138(6), 126(5), 123(9), 121(22), 105(19), 91(21), and 78(11).

(E)-1-ethylthio-2-p-tolylsulphonylstilbene (3b)

It was recrystallized from methanol, m.p. 149–50°C (lit.[6] m.p. 149–50°C). EIMS: m/z (ret.int.%). 394(26), 333(8), 269(17), 257(16), 240(12), 239(10), 211(36), 210(52), 179(30), 178(100), 176(15), 155(18),152(8), 139(10), 123(15), 121(10), 105(31), 91(20), and 29(5).

(E)-1-n-propylthio-2-p-tolylsulphonylstilbene (3c)

Recrystallized from isopropanol m.p. 141–142°C (lit.[6] m.p. 140—41°C). EIMS: m/z (rel.int.%) 408(38), 333(5), 301(5), 269(16), 254(14), 253(79), 243(8), 238(15),211(52), 210(100), 179(15), 178(62), 176(8), 166(42), 165(20), 155(20), 139(21), 123(14), 121(11), 105(10), 91(25), and 43(23).

(E)-1-isopropylthio-2-p-tolylsulphonylstilbene (3d)

Recystallized from ethanol, m.p. 180–181°C (lit.[6] m.p. 180–181°C). EIMS: m/z (rel.int.%) 408(36), 333(4), 269(23), 254(16), 253(89), 211(42), 210(100), 179(20), 178(66), 176(10), 166(51), 165(21), 155(18), 139(19), 123(14), 121(11), 91(15), and 43(33).

(E)-1-n-butylthio-2-p-tolylsulphonylstilbene (3e)

It was recrystallized from isopropanol, m.p. 137–138°C (lit.[6] m.p. 136–137°C). EIMS: m/z (rel.int.%) 422(32), 333(5), 269(30), 268(38),

267(21), 257(11), 254(4), 253(50), 212(23), 211(26), 210(42), 180(59), 179(13), 178(100), 176(9), 165(25), 155(10), 139(6), 123(7), 121(5), 105(36), 91(49), and 57(22).

(E)-1-isobutylthio-2-p-tolylsulphonylstilbene (3f)

Recrystallized from methanol, m.p. 156-157°C (lit.[6] m.p. 155–156°C). EIMS: m/z (rel. int.%) 422(28), 333(6), 269(18), 268(40), 267(26), 257(15), 254(15), 253(15), 212(10), 211(25), 210(35), 180(46), 179(25), 178(100), 165(20), 155(9), 139(6), 123(7), 121(4), 105(28), 91(40), and 57(60).

(E)-1-t-butylthio-2-p-tolylsulphonylstilbene (3g)

It was recrystallized from isopropanol as colorless crystals, m.p. 161–62°C, yield 95.1% (Found: C, 71.28; H, 6.12; S, 15.04. $C_{25}H_{26}O_2S_2$requires C, 71.06; H, 6.20; S, 15.14%). EIMS: m/z (rel.int.%) 422(26), 333(8), 301(4), 269(29), 268(8), 267(30), 212(18), 211(96), 210(30), 180(70), 179(28), 178(100), 165(15), 155(14), 139(11), 123(8), 121(6), 105(18), 91(40),6 9(16), 57(49), 55(14), and 43(19).

(E)-1-n-amylthio-2-p-tolylsulphonylstilbene (3h)

Recrystallized from isopropanol, m.p. 141–142°C (lit.[6] m.p. 141–142°C). EIMS: m/z (rel.int.%). 436(24), 333(9), 282(25), 281(26), 269(30), 211(95), 210(100), 194(15), 179(20), 178(83), 165(21), 155(18), 139(20), 123(9), 121(10), 91(21), 71(80), and 43(70).

(E)-1-isoamylthio-2-p-tolylsulphonylstilbene (3i)

It was recrystallized from ethanol, m.p 152–153°C (lit[6]. m.p. 151–152°C) EIMS: m/z (rel.int.%) 436(25), 333(5), 282(15), 281(29), 269(24), 211(90), 210(100), 194(10), 179(20), 178(85), 176(8), 165(23), 155(10), 139(18), 123(7), 121(8), 91(30), 71(80), and 43(75).

(*E*)-1-Alkylsulphonyl-2-*p*-tolylsulphonylstilbenes (4a–i)—General Procedure

A solution of **3** (15 m mol) in 20 ml of glacial acetic acid was treated with 30% hydrogen peroxide, and the reaction mixture was heated under reflux for 1 h. The solid separated, **4,** on cooling, was collected by filtration and recrystallized from an appropriate solvent.

(E)-1-methylsulphonyl-2-p-tolylsulphonylstilbene (4a)

It was recrystallized from isopropanol, yield 93%, m.p. 211–212°C (Found: C, 64.29; H, 4.70; S, 15.68. $C_{22}H_{20}O_4S_2$ requires C, 64.05;

H, 4.89; S, 15.51%). EIMS: m/z (rel.int.%) 333(3), 269(70), 258(13), 257(39), (IV), 243(16), 210(7), 194 (14), 193(3), 179 (15), 178 (88), 176(12), 155(11), 153(6), 139(9), 123(21), 105(100), 93(10), 91 (64), and 89 (29).

(E)-1-ethylsulphonyl-2-p-tolylsulphonylstilbene (4b)

Recrystallized from acetic acid, m.p. 215–16°C(lit.[6] m.p 214–15°C). EIMS : m/z (rel.int.%) 334(5), 333(6), 272(18), 271(19),(IV), 270(82), 269(65), 210(5), 208 (15), 207(11), 179(25), 178(100), 176(12), 155(9), 139(15), 123(5), 105(76), 91(67) and 29(8).

(E)-1-n-propylsulphonyl-2-p-tolylsulphonylstilbene (4c)

It was recrystallized from methanol, m.p. 202–03°C (lit.[6] m.p. 202–203°C). EIMS: m/z (rel.int.%) 334(4), 333(6), 286(5), 285(14), (IV), 270(79), 269(62), 222(10), 210(5), 179(10), 178(100), 176(8), 155(8), 139(5), 123(12), 105(45), 91(60), 57(15), and 43(39).

(E)-1-isopropylsulphonyl-2-p-tolylsulphonylstilbene (4d)

Recrystallised from aqueous dioxane, m.p. 233–234°C (lit.[6] m.p. 232–233°C). EIMS: m/z (rel.int.%) 334(6), 333(4), 286(6), 285(7), (IV), 270(96), 269(55), 244(43), 222(15), 210(6), 179(19), 178(100), 176(9), 155(6), 139(4), 123(19), 105(55), 91(13), 57(22), and 43(93).

(E)-1-n-butylsulphonyl-2-p-tolylsulphonylstilbene (4e)

Recrystallized from ethanol, m.p. 203–204°C (lit.[6] m.p. 203–204°C). EIMS: m/z 334(5), 333(6), 300(4), 299(5), (IV), 270(11), 269(63), 243(6), 236(9), 235(11), 210(5), 179(15), 178(72), 176(11), 155(6), 139(8), 123(22), 105(100), 91(60), and 57(53).

(E)-1-isobutylsulphonyl-2-p-tolylsulphonylstilbene (4f)

It was recrystallized from acetic acid, m.p. 224–225°C (lit.[6] m.p. 224–225°C). EIMS : m/z (rel.int.%) 334(4), 333(4), 300(6), 299(4),(IV), 270(32), 269(60), 236(10), 235(13), 210(4), 179(5), 178(78), 176(10), 155(8), 139(5), 123(26), 105(100), 91(55), 89(19), 57(39), and 55(20).

(E)-1-t-butylsulphonyl-2-p-tolylsulphonylstilbene (4g)

It was recrystallized from ethanol, m.p. 220–221°C, yield (84%). (Found : C, 65.98; H, 5.62; S, 14.01. $C_{25}H_{26}O_4S_2$ requires C, 66.04; H, 5.76; S, 14.08%). EIMS: m/z (rel.int.%) 334(4), 333(5), 300(4), 299(4), (IV), 270(30), 269(63), 236(8), 235(15), 210(5), 179(4), 178(72), 176(9), 155(5), 139(4), 123(22), 105(100), 91(60), 89(21), 57(55), and 43(49).

(E)-1-n-amylsulphonyl-2-p-tolylsulphonylstilbene (4h)

It was recrystallized from acetic acid, m.p. 209–10°C (lit.[6] m.p. 209–210°C). EIMS:m/z (rel.int.%). 334(4), 333(6), 314(5), 313(5), (IV), 270(26), 269(33) , 250(8), 243(19), 210(6), 179(20), 178(80), 176(15), 155(8), 139(5), 123(17), 105(100), 91(43), 71(70), and 43(60).

(E)-1-isoamylsulphonyl-2-p-tolylsulphonylstilbene (4i)

It was recrystallized from isopropanol, m.p. 210–211°C (lit.[6] m.p 208–209°C). EIMS: m/z (rel.int.%) 334(6), 333(8), 314(4), 313(4), (IV), 270(18), 269(40), 250(7), 243(20), 210(4), 179(8), 178(83), 176(19), 155(4), 139(9), 123(21), 105(100), 91(50), 71(76), and 43(81).

(Z)-1-alkylthio-2-p-tolylsulphonylstilbenes (5a–i) General Method

To a solution of sodium ethoxide (5.5 mg atom of sodium dissolved in 10 ml of abs. ethanol) an appropriate alkanethiol (5.5 m mole) was added. The resulting alkanethiolate solution was mixed with a solution of **2** (5.5 m mol) in ethanol (50 ml) and refluxed. Reflux time varied from 3 to 6 h, in different cases. The solution upon cooling deposited the (*Z*)-1-alkylthio-2-*p*-tolylsulphonylstilbenes (**5**) as crystalline material, which was recrystallized from 95% ethanol or any other suitable solvent.

(Z)-1-methylthio-2-p-tolylsulphonylstilbene (5a)

It was recrystallized from 95% ethanol, yield 94%, m.p. 126–127°C (Found:C, 69.42; H, 5.21; S, 16.74. $C_{22}H_{20}O_4S_2$ requires C, 69.44; H, 5.30; S, 16.82%). EIMS:m/z (rel.int.%) 380(29), 333(6), 301(10), 269(15), 261(6), 257(15), 225(42), 210(60), 179(15), 178(100), 176(6), 139(5), 138(26), 137(11), 123(7), 121(8), 105(23), 91(15), 78(11), and 51(5).

(Z)-1-ethylthio-2-p-tolylsulphonylstilbene (5b)

Recrystallized from 95% ethanol, m.p. 161–162°C (lit.[6] m.p. 160–161°C). EIMS : m/z (rel.int.%) 394(20), 333(5), 269(15), 239(48), 211(31), 210(100), 179(11), 178(56), 176(31), 155(10), 152(15), 139(5), 123(12), 121(22), 105(41), 91(35), and 29(5).

(Z)-1-n-propylthio-2-p-tolylsulphonylstilbene (5c)

Recrystallized from 95% ethanol, m.p. 118–119°C (lit.[6] m.p. 118–119°C). EIMS:m/z (rel.int.%) 408(25), 333(6), 269(18), 253(90), 243(4), 211(40), 210(100), 179(15), 178(59), 176(12), 166(50), 155(6), 139(17), 123(10), 121(13), 91(10), and 43(30).

(Z)-1-isopropylthio-2-p-tolylsulphonylstilbene (5d)

It was recrystallized from 95% ethanol, m.p. 158–59°C (lit.[6] m.p. 158–159°C). EIMS:m/z (rel.int.%) 408(18), 333(3), 269(26), 253(80), 243(9), 211(72), 210(100), 179(20), 178(65), 176(10), 166(45), 155(10), 139(21), 123(5), 121(10), 91(14), and 43(37).

(Z)-1-n-butylthio-2-p-tolylsulphonylstilbene (5e)

It was recrystallized from aqueous ethanol, m.p. 129–130°C (lit.[6] m.p. 128–29°C) EIMS:m/z (rel.int.%) 422(20), 333(5), 269(10), 267(15), 211(20), 210(76), 180(22), 179(28), 178(100), 176(20), 155(15), 139(6), 123(5), 121(6), 105(36), 91(50), and 57(20).

(Z)-1-isobutylthio-2-p-tolylsulphonylstilbene (5f)

Recrystallized from aqueous isopropanol, m.p. 93–94°C (lit.[6] m.p. 92–93°C). EIMS:m/z (rel.int.%) 422(16), 333(4), 269(21), 267(18), 212(5), 211(15), 210(90), 180(26), 179(23), 178(100), 176(13), 167(4), 165(4), 155(19), 139(10), 123(7), 121(5), 91(54), and 57(38).

(Z)-1-t-butylthio-2-p-tolylsulphonylstilbene (5g)

Recrystallized from aqueous ethanol as shining needles, yield 89.7%., m.p, 95–96°C. Found:C, 71.02; H, 6.02; S, 14.98. $C_{25}H_{26}O_2S_2$ requires C, 71.06; H, 6.20; S, 15.14 %). EIMS:m/z (rel. int. %) 422(10), 333(4), 287(15), 269(30), 267(11), 212(10), 211(47), 210(18), 180(34), 179(23), 178(100), 176(10), 167(5), 165(8), 155(11), 139(8), 123(6), 121(10), 105(23), 98(10), 91(26), 73(29), 71(27), 69(49), 67(10), 57(9), and 43(38).

(Z)-1-amylthio-2-p-tolylsulphonylstilbene (5h)

Recrystallized from aqueous ethanol. m.p. 115–116°C (lit.[6] m.p. 115–116°C). EIMS:m/z (rel. int.%) 436(14), 333(6), 301(29), 281(32), 269(15), 211(90), 210(100), 194(18), 179(23), 178(50), 176(15), 165(19), 155(6), 139(23), 123(7), 121(5), 105(18), 91(20), 71(81), 57(5), 43(80), and 41(9).

(Z)-1-isoamylthio-2-p-tolylsulphonylstilbene (5i)

It was recrystallized from aqueous isopropanol, m.p. 130–131°C (lit.[6] m.p. 130–131°C). EIMS:m/z (rel.int.%) 436(16), 333(7), 301(4), 281(40), 269(16), 211(95), 210(100), 194(24), 179(19), 178(58), 176(10), 165(22), 155(5), 139(25), 123(5), 121(7), 105(27), 91(15), 71(97), 57(6), 43(98), and 41(11).

(Z)-1-alkylsulphonyl-2-p-tolylsulphonylstilbenes (6a–i)—General Procedure

A solution of **5** (2 m mol) in glacial acetic acid (50 ml) was mixed with an excess of 30% hydrogen peroxide (10 ml). The reaction mixture was

heated to boiling for 1 min, the solution was allowed to stay for 1 h at room temperature, and then it was poured onto crushed ice. The disulphones, **6**, separated were filtered and recrystallized from an appropriate solvent.

(Z)-1-methylsulphonyl-2-p-tolylsulphonylstilbene (6a)

Recrystallized from acetic acid m.p. 188–189°C, yield (89.6%) (Found: C, 63.81; H,5.02; S, 15.78; $C_{20}H_{22}O_4S_2$ requires C, 64.05; H, 4.89; S, 15.78%). EIMS : m/z (rel.int.%) 333(31), 269(69), 257(21), (IV), 243(23), 210(9), 179(19), 178(100), 176(7), 155(4), 139(6), 123(15), 105(34), and 91(37).

(Z)-1-ethylsulphonyl-2-p-tolylsulphonylstilbene (6b)

It was recrystallized from isopropanol, m.p. 176–177°C (lit.[6] m.p. 176–177°C). EIMS : m/z (rel. int. %) 333(35), 271(15), (IV), 269(58), 210(6), 179(11), 178(100), 176(6), 155(8), 139(7), 123(10), 91(41), and 29(5).

(Z)-1-n-propylsulphonyl-2-p-tolylsulphonylstilbene (6c)

Recrystallized from methanol, m.p 162–163°C (lit.[6] m.p. 161–162°C). EIMS: m/z (rel. int. %) 333(8), 285(10),(IV), 269(50), 210(5), 179(20), 178(100), 176(15), 155(10), 139(8), 123(23), 105(47), 91(40), and 43(25).

(Z)-1-isopropylsulphonyl-2-p-tolylsulphonylstilbene (6d)

It was recrystallized from methanol, m.p. 198–199°C (lit.[6] m.p. 198–199°C). EIMS: m/z (rel. int. %) 333(6), 285(11), (IV), 269(65), 210(6), 179(16), 178(100), 176(6), 155(12), 123(21), 105(45), 91(60), and 43(39).

(Z)-1-n-butylsulphonyl-2-p-tolylsulphonylstilbene (6e)

Recrystallized from isopropanol, m.p. 158–159°C (lit.[6] m.p. 157–158°C). EIMS: m/z (rel.int.%) 333(4), 299(4), (IV), 269(75), 243(6), 210(8), 179(10), 178(88), 176(16), 155(7), , 139(5), 123(21), 105(100), 91(61), and 57(18).

(Z)-1-isobutylsulphonyl-2-p-tolylsulphonylstilbene (6f)

It was recrystallized from isopropanol, m.p. 164–165°C (lit.[6] m.p. 164–165°C) EIMS: m/z (rel.int.%) 333(4), 299(4), (IV), 269(70) 243(7), 210(5), 179(19), 178(80), 176(14), 155(5), 139(9), 123(25), 105(100), 91(69), 57(10), and 41(20).

(Z)-1-t-butylsulphonyl-2-p-tolylsulphonylstilbene (6g)

Yield (80.5%) Recrystallized from isopropanol as colorless needles, m.p. 168–169°C (Found: C, 65.80; H, 5.52; S, 13.89, $C_{25}H_{26}O_4S_2$ requires

C, 66.06; H, 5.76; S, 14.08%) EIMS: m/z (rel. int %) 333(4), 299(5), (IV), 269(75), 235(10) 210(6), 179 (15), 178(90), 176(10), 155(8), 139(6), 123(21), 105(100), 91(64), 89(28), 57(73), and 55 (30).

(Z)-1–n-amylsulphonyl-2-p-tolylsulphonylstilbene (6h)

It was recrystallized from isopropanol, m.p.136–137°C (lit,[6] m.p.136–137°C). EIMS: m/z (rel.int%) 333(5), 313 (4), (IV), 269(51), 243(20), 210(5), 179(18), 178(100), 176(12), 155(12), 139(15), 123(18), 105(48), 91(21), 71(52), and 43(20).

(Z)-1-isoamylsulphonyl-2-p-tolylsulphonylstilbene (6i)

Recrystallized from 95%, ethanol, m.p. 125–126°C (lit.[6] m.p. 123–124°C) EIMS: 333(6), 313 (4), (IV) 269 (69), 243 (22), 210(4), 179(20), 178 (100), 176 (10), 155(8), 139 (11), 105(30), 91(31), 71(65), and 43 (71).

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