The Mass Spectral Rearrangements of Aryl Propenyl Sulfones. An Electron Impact Induced Smiles Type Rearrangement

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The mass spectral behavior of *trans*-1-arylsulfonyl-2-arylsulfenyl-propenes, *trans*-1-arylsulfonyl-2-arylsulfinyl-propenes and *trans*-1,2-(arylsulfonyl)-propenes was examined. A Smiles type rearrangement was present in the sulfonyl-sulfides, but was completely absent in the *trans*-1-arylsulfonyl-2-arylsulfinyl-propenes and *trans*-1,2-(arylsulfonyl)-propenes. Vinyl migration to the sulfone oxygen predominates over aryl migration in all of the compounds studied. The mass spectra of the *cis* and *trans* isomers of 1-*p*-tolylsulfenyl-2-*p*'-tolysulfonyl-propene and 1,2-(*p*-tolylsulfonyl)-propene are also described.

Mass spectral studies of alkyl sulfides, sulfoxides and sulfones,[1-3] aryl alkyl and vinyl sulfones,[2,4-6] diaryl sulfoxides and sulfones containing carbon chains of various lengths and degrees of unsaturation,[7-13] and styryl sulfoxides and sulfones[14] have been described. The fragmentation patterns observed in these compounds include the loss of SO_2[4,5,7,13,14] as well as sulfone-sulfinate and sulfoxide-sulfenate rearrangements.[15] We have previously reported electron impact induced sulfone-sulfone remote group interaction in 1,4-bis(arylsulfonyl)-2-butynes.[9] We now wish to report the results of a mass spectral study of a series of *trans*-1-arylsulfonyl-2-arylsulfenyl-propenes (**1**), *trans*-1-arylsulfonyl-2-arylsulfinyl-propenes (**2**) and *trans*-1,2-(arylsulfonyl)-propenes (**3**). We chose these compounds in order to examine the following questions: (1) What is the effect of the oxidation state of the sulfur atom on the mass spectral fragmentation? and (2) What is the effect of geometry and carbon chain length on remote group interaction between the two sulfur atoms? Especially noteworthy is our observation of a Smiles type rearrangement occurring in all of the sulfides (**1**), but absent in the sulfoxides (**2**) and sulfones (**3**). No report of this process in any similar compounds containing remote sulfur atoms has appeared.

RESULTS AND DISCUSSION

Sulfides (1)

All of the variously *para* substituted *trans*-1-arylsulfonyl-2-arylsulfenyl-propenes (**1**) which were subjected to electron impact at 20 and 70 eV gave a Smiles rearrangement to form a diarylsulfide ion-radical (*a*). The intensities of this fragment ranged from 4.34 to 10.33% $\sum$ at 20 eV and are recorded in Table 1. A proposed rearrangement mechanism (Scheme 1) involves initial ionization of the sulfide, which permits rotation into a *cis* geometry from the originally introduced *trans* isomer (**1**). A bond between the R_1-C_6H_4 group and the sulfide is formed and the aryl group rearomatizes by loss of the neutral thiirene dioxide fragment or simultaneous expulsion of SO_2 and propyne. This Smiles type rearrangement is supported by metastable peaks corresponding to the formation of $[M-104]^+$ from the molecular ion in all of the sulfonyl-sulfides studied. Formation of *m/e* 148 was also observed in all of the sulfonyl-sulfides. This fragment is believed to result from loss of $R_1C_6H_4SO_2$, followed by loss of R_2, as shown in Scheme 2. The second cleavage, involving the R_2—C_6H_4 bond, appears to be related to bond strength (see Table 1). As reported earlier,[15] some sulfones undergo sulfonyl-sulfinate rearrangement. This rearrangement was present in the sulfonyl-sulfides (**1**). The sulfonyl-sulfides (**1**) showed various simple cleavages; the intensities of the resulting fragments are given in Table 1 and a typical example of a sulfonyl-sulfide (**1**) mass spectrum is shown in Fig. 1(a).

Sulfoxides (2)

Unlike the sulfonyl-sulfides (**1**), the sulfonyl-sulfoxides (**2**) showed no rearrangement resulting in the formation of $[M-104]^+$. This may be due to the loss of a free electron pair of the sulfur which has been oxidized to the sulfoxide. This possibility will be discussed further below. The intensity of *m/e* 164, which is analogous to the *m/e* 148 fragment of the sulfonyl-sulfides (**1**), was also markedly reduced in the sulfonyl-sulfoxides (**2**) (see Table 2). This may also be due to the loss of the unshared electron pair on the sulfur by oxidation. The sulfonyl-sulfoxides (**2**) gave various

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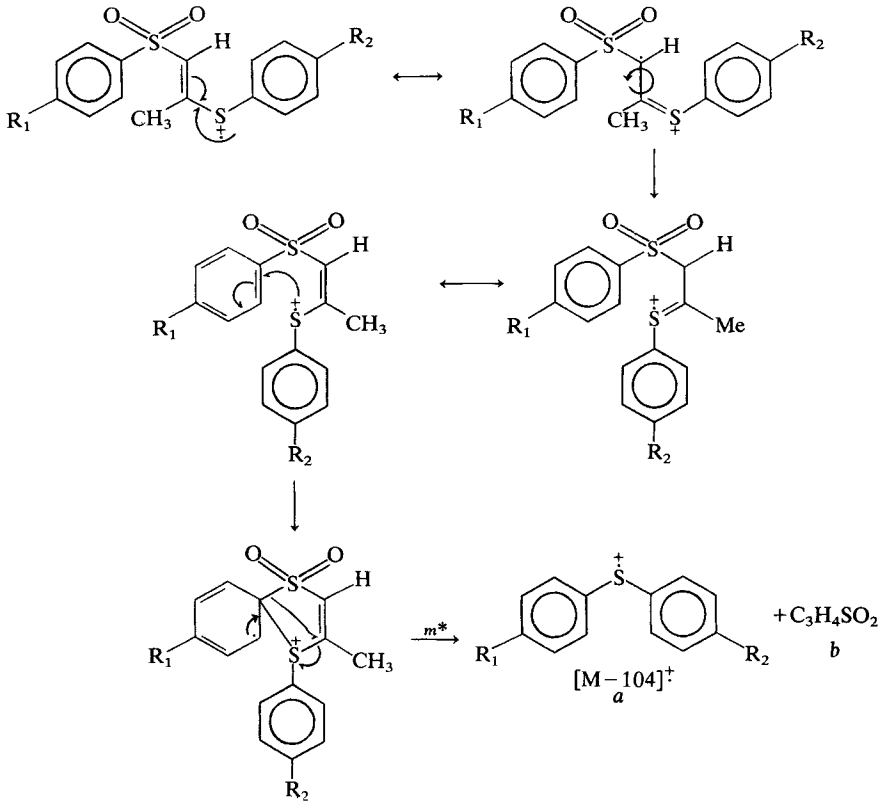
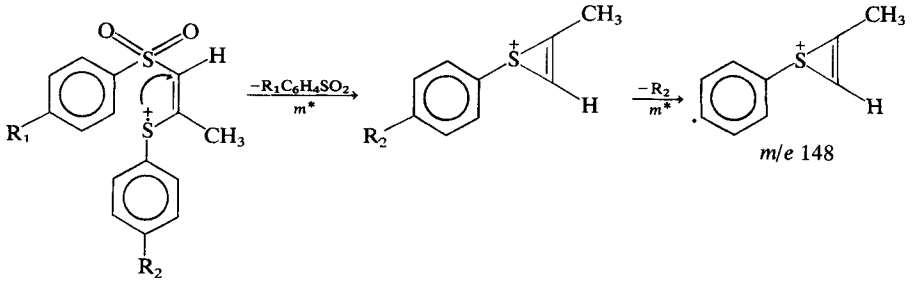
Table 1. Principal fragment ions in the 20 eV mass spectra of 1-arylsulfonyl-2-arylsulfenyl-*trans*-propenes (1)

		[M−104]		$[R_2C_6H_4SC_3H_4]$ $[M-R_1C_6H_4SO_2]$		$[C_6H_4SC_3H_4]$		$[M-R_2C_6H_4S]^+$		$[R_1C_6H_4S]^+$		$[R_1C_6H_4]^+$		$[R_2C_6H_4]^+$		$[R_1C_6H_4SO]^+$		$[R_2C_6H_4S]^+$	
R_1	R_2	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.	% Σ	r.a.
Cl	Br	2.54	11.16	2.93	12.88	22.77	100.0	0.29	1.29	0.39	1.72	3.50	15.36	—	—	0.84	3.69	1.66	7.30
Cl	OMe	4.34	17.09	10.46	41.24	0.90	3.53	4.98	19.63	2.86	29.46	1.72	6.78	—	—	0.25	0.99	25.37	100.00
Br	Br	4.56	17.65	3.89	15.10	25.82	100.00	—	—	2.10[a]	11.38[a]	2.67[a]	10.34[a]	2.67[a]	10.34[a]	0.90[a]	3.43[a]	2.94[a]	11.38[a]
Cl	Cl	4.79	38.99	9.10	74.08	12.28	100.00	—	—	5.03[a]	40.99[a]	4.92[a]	40.40[a]	4.92[a]	40.40[a]	1.31[a]	10.64[a]	5.03[a]	40.99[a]
Cl	Me	5.11	29.19	17.50	100.00	7.39	42.22	—	—	—	—	1.75	10.00	0.97	5.56	0.29	1.63	6.22	35.56
Me	Cl	8.34	85.86	7.43	76.43	9.10	93.60	0.41	4.21	3.83	39.90	9.72	100.00	—	—	3.88	39.90	2.86	29.46
Me	Me	10.33	61.41	16.82	100.00	6.79	40.40	0.23	1.38	5.37[a]	31.91[a]	5.95[a]	35.52[a]	5.95[a]	35.52[a]	1.91[a]	11.38[a]	5.37[a]	31.91[a]

[a] $R_1 = R_2$.



Scheme 1



Scheme 2

simple cleavages which were generally similar to the sulfonyl-sulfides (**1**). Sulfonyl-sulfinate and sulfinyl-sulfenate rearrangements[15] were present in the sulfonyl-sulfoxides (**2**); the intensities of the $[R_1C_6H_4SO]^+$ and $[R_2C_6H_4S]^+$ fragments are listed in Table 2. Figure 1(b) shows a typical mass spectrum of a sulfonyl-sulfoxide (**7**).

Sulfones (3)

The sulfones (**3**) showed no formation of the $[M-104]^+$ fragment ion or the *m/e* 180 fragment which would be analogous to the *m/e* 148 in the sulfonyl-sulfides (**1**) and the *m/e* 164 ion in the sulfonyl-sulfoxides (**2**). Again this can be rationalized as being

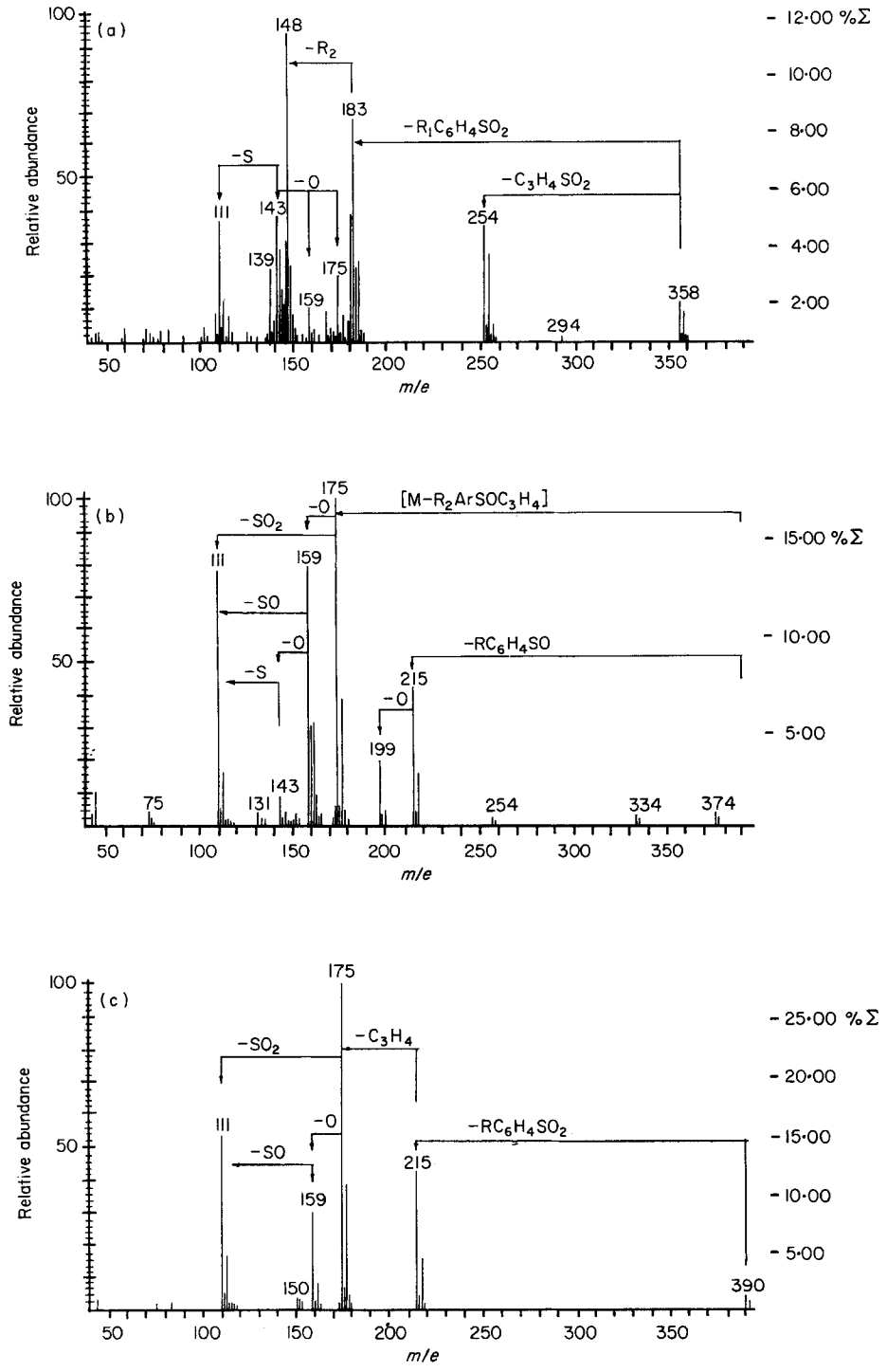


Figure 1. Mass spectra (20 eV) of (a) 1-*p*-chlorosulfonyl-2-*p*-chlorosulfenyl-*trans*-propene; (b) 1-*p*-chlorosulfonyl-2-*p*-chlorosulfinyl-*trans*-propene; (c) bis[(1,2)-*p*-chlorosulfonyl]-*trans*-propene.

Table 2. Principal fragment ions in the 20 eV mass spectra of 1-arylsulfonyl-2-arylsulfinyl-*trans*-propenes (2)

		$[R_2C_6H_4SOC_3H_4]^+$		$[C_6H_4SOC_3H_4]^+$		$[R_1C_6H_4S]^+$		$[R_2C_6H_4S]^+$		$[R_1C_6H_4SO]^+$		$[R_2C_6H_4SO]^+$		$[R_1C_6H_4SO_2]^+$		$[R_1C_6H_4]^+$		$[R_2C_6H_4]^+$	
R_1	R_2	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.
Cl,	Br	1.52	8.87	1.56	9.13	0.75	4.37	0.88	5.14	1.36	7.97	8.24	48.20	17.10	100.00	12.48	73.01	0.40	2.31
Br,	Br	2.05	19.17	1.80	16.88	1.39[a]	13.06[a]	1.39[a]	13.06[a]	8.96[a]	83.97[a]	8.96[a]	83.97[a]	10.67	100.00	5.45[a]	51.06[a]	5.45[a]	51.06[a]
Cl,	Cl	3.32	19.20	0.62	3.60	2.00[a]	11.60[a]	2.00[a]	11.60[a]	13.98[a]	80.88[a]	13.98[a]	80.88[a]	17.28	100.00	13.38[a]	77.44[a]	13.38[a]	77.44[a]
Cl,	Me	6.03	19.95	—	—	0.40	1.33	5.23	17.29	0.52	1.73	30.23	100.00	6.83	22.61	6.71	22.21	1.65	5.45
Me,	Cl	2.42	7.00	—	—	0.33	0.96	—	—	1.43	4.12	3.29	9.47	34.73	100.00	32.49	93.55	0.33	0.96

[a] $R_1 = R_2$.

Table 3. Principal fragment ions in the 20 eV mass spectra of 1,2-bis(arylsulfonyl)-*trans*-propenes (3)

		$[R_1C_6H_4SO]^+$		$[M-R_1C_6H_4SO_2]^+$		$[M-R_2C_6H_4SO_2]^+$		$[R_1C_6H_4SO_2]^+$		$[R_2C_6H_4SO_2]^+$	
R_1	R_2	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.	%Σ	r.a.
Cl	Br	2.45	10.32	—	—	61.72	14.65	23.73	100.00	3.67	15.48
Cl	OMe	—	—	2.67	13.81	—	—	18.40	95.05	—	—
Br	Br	5.24[a]	33.08[a]	6.84[a]	43.18[a]	6.84[a]	43.18[a]	15.84[a]	100.00[a]	15.84[a]	100.00[a]
Cl	Cl	8.12[a]	28.77[a]	11.98[a]	42.47[a]	11.98[a]	42.47[a]	28.22[a]	100.00[a]	28.22[a]	100.00[a]
Cl	Me	1.26	7.15	0.32	1.81	11.77	66.73	9.92	56.24	17.64	100.00
Me	Me	8.87[a]	26.76[a]	15.71[a]	47.35[a]	15.71[a]	47.35[a]	33.17[a]	100.00[a]	33.17[a]	100.00[a]

[a] $R_1 = R_2$.

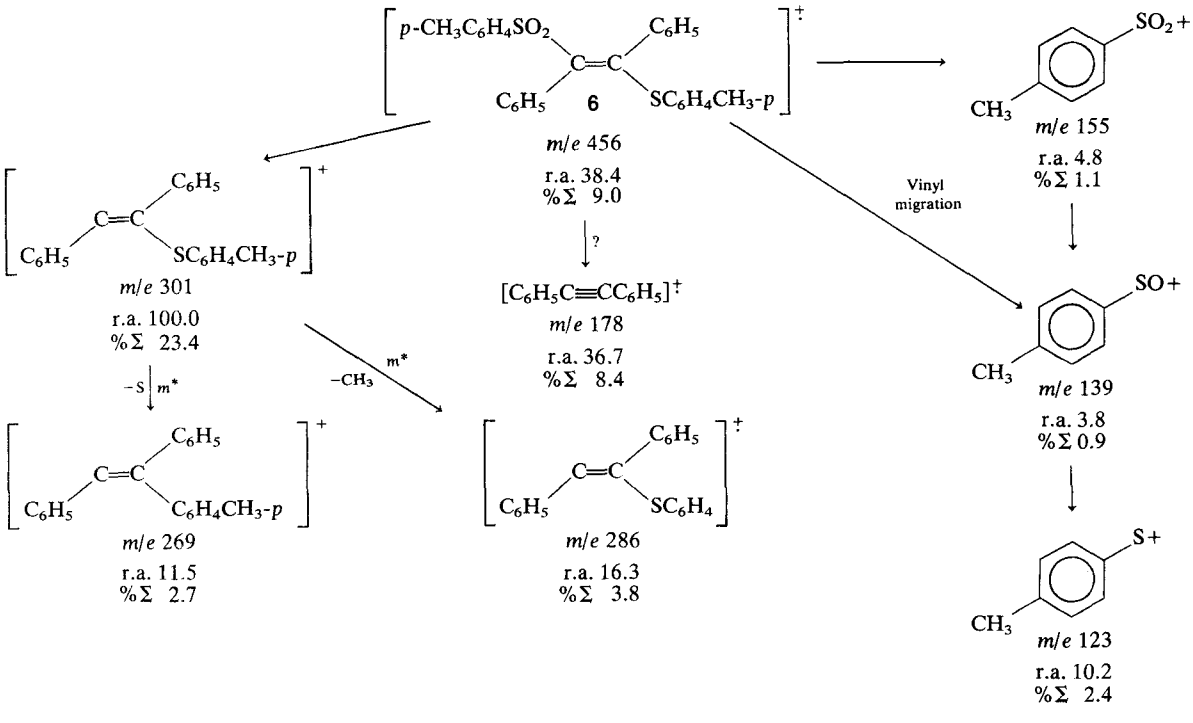
due to the absence of unpaired electrons on sulfur. The only rearrangement observed was the well-known sulfonyl-sulfinate rearrangement,[15] with subsequent cleavage resulting in $[RC_6H_4SO]^+$ and/or $[RC_6H_4S]^+$. Vinyl migration was the predominant pathway of the sulfonyl-sulfinate rearrangement in all of the compounds (**1**), (**2**) and (**3**) with no evidence of $[C_6H_4O]^+$ to indicate an aryl migration. This supports the work of Soothill and Williams[4] who also observed vinyl migration in preference to aryl migration in aryl vinyl sulfones. Fewer fragmentations were seen with the sulfones as compared with the sulfonyl-sulfides (**1**) or sulfonyl-sulfoxides (**2**). Fragmentations were basically similar to those of the other two groups of compounds (**1** and **2**). Figure 1(c) shows a typical spectrum of a bis-sulfone (**3**) and Table 3 lists the structures and intensities of the major fragments.

Effect of double bond geometry

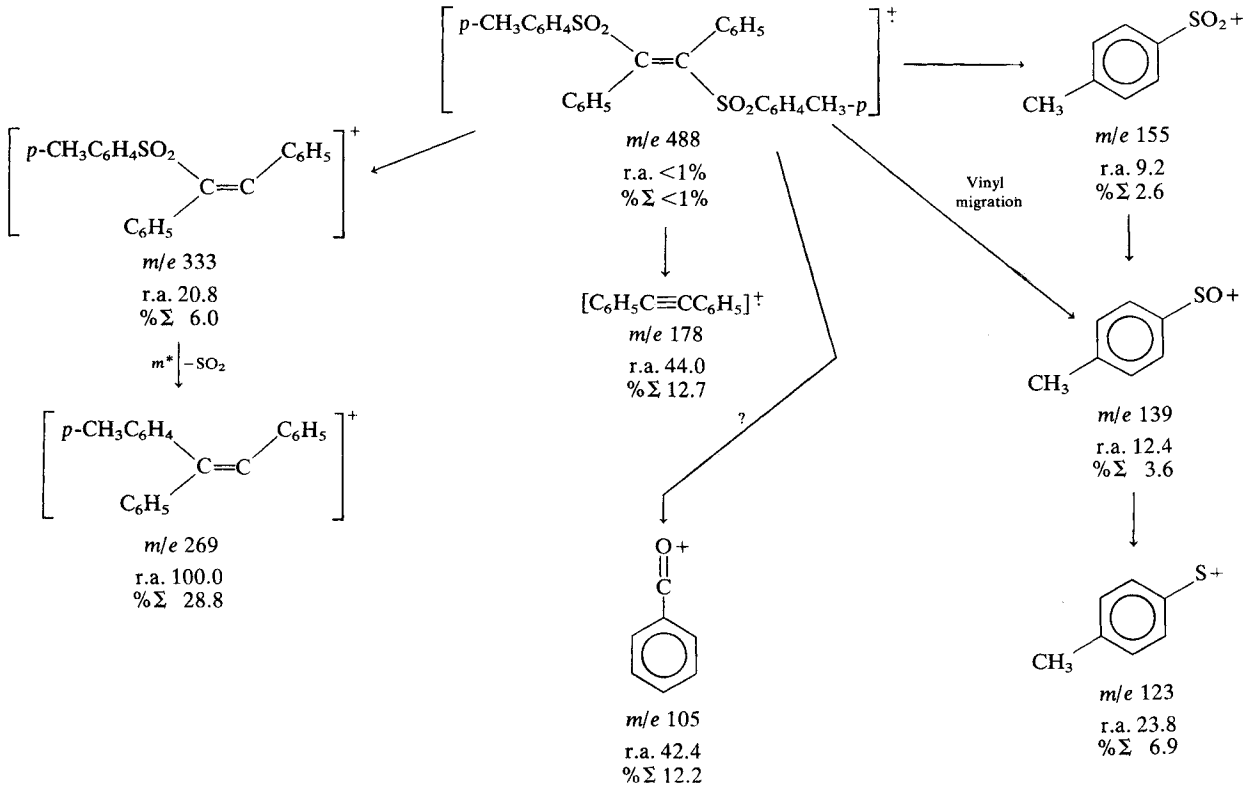
To study the effect of the geometry of the double bond upon the fragmentation pathways, the mass spectra of *cis*- and *trans*-1-*p*-tolylsulfenyl-2-*p'*-tolylsulfonyl-stilbene (**6a, 6b**) and *cis*- and *trans*-1,2-(*p*-tolysulfonyl)-stilbene (**7a, 7b**) were determined.[17] The low resolution mass spectra of **6a** and **6b** were identical as were the spectra of **7a** and **7b**. High resolution mass spectra were also obtained for **6b** and **7b**. The Smiles type rearrangement, giving *m/e* 214 was again only present in the sulfonyl-sulfides (**6**). Diphenylacetylene radical ion was a prominent fragment in **6** and **7**: however, its origin is uncertain. Vinyl migration to the oxygen of the sulfone was again the predominant pathway for the sulfonyl-sulfinate rearrangement. The major fragments of **6** and **7** are shown in Schemes 3 and 4, respectively, with relative abundance and % Σ values below the corresponding fragment.

Summary

We have compared the mass spectra of a series of sulfonyl-sulfides (**1** and **6**), sulfonyl-sulfoxides (**7**) and sulfonyl-sulfones (**3** and **7**). The most notable difference is that only the sulfonyl-sulfides (**1**) undergo a Smiles type rearrangement leading to an $[M-104]^+$ ion (Scheme 1). The rearrangement is independent of the initial carbon–carbon double bond geometry, being equally important in **6a** and **6b**, and being completely absent in **7a** and **7b**. The absence of this



Scheme 3



Scheme 4

rearrangement in the sulfoxides (**2**) and sulfones (**3** and **7**) is clearly attributable to the higher oxidation state of the sulfur atom. The change in oxidation state could manifest itself in the loss of the radical located in divalent sulfur, $-S^{\pm}$, which is responsible for initiating the Smiles type rearrangement after double bond isomerization has occurred (Scheme 1).

Synthesis of compounds

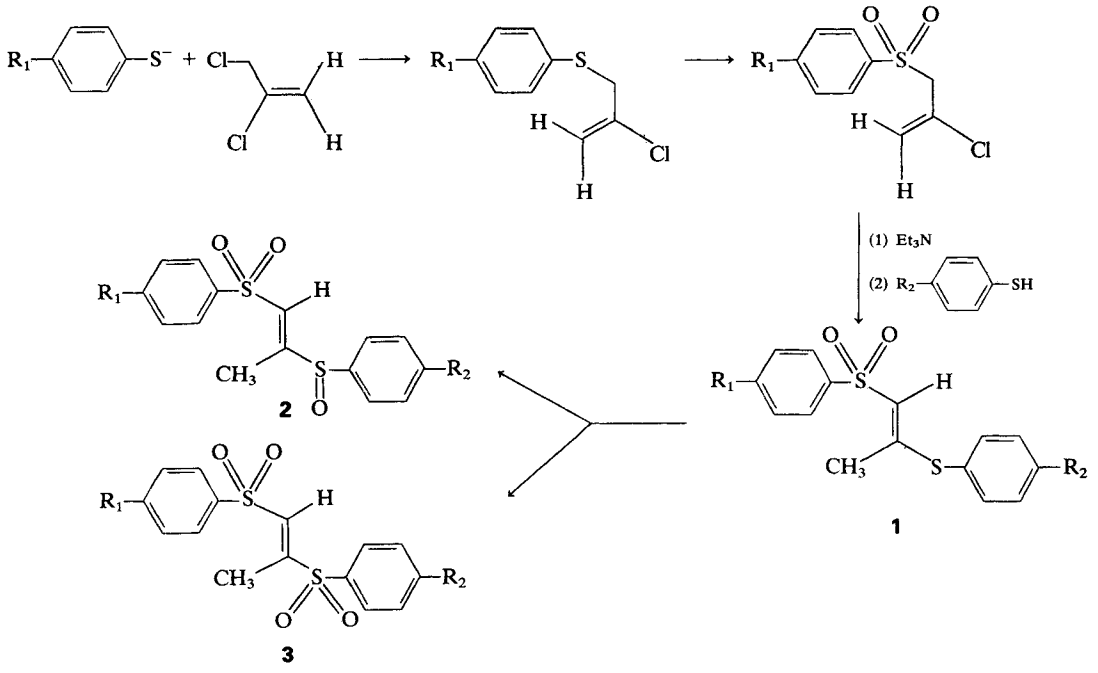
Scheme 5 shows the general procedure for the synthesis of the compounds in this study. Nucleophilic attack of a thiophenylate anion on 2,3-dichloropropene formed the desired 3-arylsulfenyl-2-chloropropene (**4**). The latter compound was then oxidized to the corresponding sulfone (**5**) using peracetic acid. The 3-arylsulfonyl-2-chloro-propene (**5**) was then refluxed in benzene with triethylamine and the desired thiophenol. Neither the 2-arylsulfenyl-3-arylsulfonyl-propene nor the isomeric *cis*-1-arylsulfenyl-2-arylsulfonyl-propene could be detected in any of the reactions studied. Formation of the *trans*-1-propenes is in accord with the earlier studies of Stirling[18] who found that of the three possible isomers the *trans*-1-propene was the most stable. The *trans*-1-arylsulfonyl-2-arylsulfenyl-propene was then oxidized to the corresponding sulfoxide and sulfone. Purity and structure were checked at each step of the synthesis by means of elemental analysis, mass spectrometry and proton magnetic resonance spectroscopy.

EXPERIMENTAL

Mass spectra were run on an Hitachi Perkin–Elmer RMU-6E spectrometer, at electron energies of 20 and 70 eV. Nuclear magnetic resonance spectra were determined in $CDCl_3$ using tetramethylsilane as an internal standard with a Varian A-60 or EM-360 instrument. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Microanalyses were performed with a Perkin–Elmer 240 elemental analyzer in this department.

General procedure for preparation of 3-arylsulfenyl-2-chloro-propenes (4)

The appropriate thiophenol (0.2 mol) was dissolved in 100 ml of 95% ethanol and the flask containing the solution was flushed with nitrogen. A solution of potassium hydroxide (11.2 g, 0.2 mol) in 200 ml of 80% ethanol was then added over a period of *c.* 20 min. The solution was stirred an additional 20–30 min and then a solution of 2,3-dichloropropene (20.0 g, 0.2 mol) in 100 ml of 95% ethanol was added over *c.* 2 h. The mixture was stirred under nitrogen for an additional 4 h. The solution was then filtered in air and the solvent was removed *in vacuo* to produce a yellow oil. The oil was taken up in 250 ml of ether, washed with 5% potassium hydroxide (2×250 ml) and with saturated NaCl (2×250 ml). The ethereal solution was dried over anhydrous $NaSO_4$, filtered, and the ether removed *in vacuo*. The residue was distilled



Scheme 5

in vacuo to produce a clear, colorless oil. The analytical and spectral properties of the samples thus obtained are listed in Table 4.

General procedure for the preparation of 3-arylsulfonyl-2-chloro-propenes (5)

The 3-arylsulfenyl-2-chloro-propene (**4**) (0.1 mol) in 90 ml of ethyl acetate was cooled in an ice bath. Peracetic acid (FMC Corp., Industrial Chemical Division, Buffalo, New York) (40.6 g, assumed to be 40%, 0.2 mol) in 80 ml of ethyl acetate was added over *c.* 2 h with stirring. The solution was allowed to warm to 25 °C and was stirred for an additional 4–5 h. The solution was then washed with 5% potassium hydroxide (2×250 ml), saturated NaCl (2×250 ml), dried over anhydrous $NaSO_4$, filtered, and the solvent was removed by rotary evaporation. The white crystals thus obtained, after recrystallization from petroleum ether (60–110 °C)/diethyl ether, had the physical and spectral properties listed in Table 5.

General procedure for the preparation of *trans*-1-arylsulfonyl-2-arylsulfenylpropenes (1)

Equimolar amounts (0.2 mol) of the appropriate 3-arylsulfonyl-2-chloro-propene, the thiophenol and triethylamine in 25 ml of benzene, under nitrogen, were heated on a steam bath for *c.* 2.5 h. The solution was then cooled and extracted with chloroform. The chloroform solution was washed with ice cold water (2×500 ml), dried over anhydrous $NaSO_4$, filtered, and the solvent was removed *in vacuo*. If crystals formed they were recrystallized from petroleum ether (60–100 °C)/diethyl ether and a small amount of THF. If the residue remained as an oil, it was passed through a basic aluminum oxide column (2.5×11 cm) eluted with benzene/petroleum ether (1:1), and then recrystallized from petroleum ether (60–100 °C)/diethyl ether and a small amount of THF. Table 6 contains the properties of the samples thus obtained.

General procedure for the preparation of *trans*-1,2-(arylsulfonyl)-propenes (3)

The *trans*-1-arylsulfonyl-2-arylsulfenyl-propenes (**1**) were oxidized using slightly more than two equivalents of peracetic acid in ethylacetate in the same manner as described for the oxidation of 3-arylsulfenyl-2-chloro-propenes (**5**). The crystals obtained were recrystallized from petroleum ether (60–100 °C)/chloroform. Table

Table 4. 3-Arylsulfenyl-2-chloro-propenes

Compound	B.p. (°C)	% Yield	Molecular formula	Anal. % Calc. C	Calc. H	Found C	Found H	^{1}H n.m.r.
R=Cl	70/0.015 mm	72	$C_9H_8Cl_2S$	49.54	3.67	49.52	3.70	3.58(2H, s); 5.16(2H, s); 7.2(4H, s)
R=Me	74/0.0001 mm	67.4	$C_{10}H_{11}ClS$	60.61	5.56	60.33	5.56	2.13(3H, s); 3.48(2H, s); 5.01(2H, s); 6.81–7.26(4H, m)
R=Br	93/0.010	76	C_9H_8BrClS	41.22	3.05	41.17	3.05	3.64(2H, s); 5.18(2H, s); 7.07(4H, m)

Table 5. 3-Arylsulfonyl-2-chloro-propenes

Compound	M.p. (°C)	% Yield	Molecular formula	Anal. % Calc. C	Calc. H	Found C	Found H	^{1}H n.m.r.
R = Cl	107–108	75	$C_9H_8Cl_2O_2S$	43.20	3.20	43.03	3.19	4.08(2H, s); 5.31(1H, d, J = 1.5); 5.43(1H, d, J = 1.5); 7.42–7.93(4H, m)
R = Me	85–86	72	$C_{10}H_{11}ClO_2S$	52.17	4.78	51.88	4.81	2.40(3H, s); 4.0(2H, s); 5.35(1H, d, J = 1.5 5.45(1H, d, J = 1.5); 7.3–7.9(4H, m);
R = Br	128–129	88	$C_9H_8BrClO_2S$	36.73	2.72	36.72	2.71	4.05(2H, s); 5.5(2H, broad s); 7.9(4H, m)

Table 6. 1-Arylsulfonyl-2-arylsulfenyl-*trans*-propenes

Compound	M.p. (°C)	% Yield	Molecular formula	Anal. % Calc. C	Calc. H	Found C	Found H	^{1}H n.m.r.
R_1 = Cl R_2 = Cl	109–110	65	$C_{15}H_{12}Cl_2O_2S_2$	50.14	3.34	49.86	3.28	2.33(3H, s);5.56(1H, s); 7.35–7.8(8H, m)
R_1 = Cl R_2 = Br	119–120	20	$C_{15}H_{12}BrClO_2S_2$	44.78	2.99	44.61	3.05	2.32(3H, s); 5.57(1H, s); 7.14–7.8(8H, m)
R_1 = Cl R_2 = Me	104–105	25	$C_{16}H_{15}ClO_2S_2$	56.80	4.44	56.86	4.29	2.3(6H, s); 5.66(1H, s); 7.23–7.8(8H, m)
R_1 = Cl R_2 = OMe	97–98	20	$C_{16}H_{15}ClO_3S_2$	54.24	4.49	54.39	4.11	2.23(3H, s); 3.78(3H, s); 5.48(1H, s); 6.75–7.85 (8H, m)
R_1 = Br R_2 = Br	122–123	20	$C_{15}H_{12}Br_2O_2S_2$	40.36	2.69	40.13	2.45	2.34(3H, s); 5.56(1H, s); 7.2–7.66(8H, m)
R_1 = Me R_2 = Me	91–92	20	$C_{17}H_{18}O_2S_2$	64.15	5.66	64.02	5.77	2.22(9H, s); 5.56(1H, s); 7.18–7.7(8H, m)
R_1 = Me R_2 = Cl	111–112	27	$C_{16}H_{15}ClO_2S_2$	56.80	4.44	56.70	4.42	2.30(3H, s); 2.32(3H, s); 5.62(1H, S); 7.12–7.78(8H, m)

Table 7. 1-Arylsulfonyl-2-arylsulfinyl-*trans*-propenes

Compound	M.p. (°C)	% Yield	Molecular formula	Anal. % Calc. C	Calc. H	Found C	Found H	^{1}H n.m.r.
R_1 = Cl R_2 = Cl	117–118	74	$C_{15}H_{12}Cl_2O_3S_2$	48.13	3.29	47.95	3.22	2.04(3H, s); 7.12–7.9(9H, m)
R_1 = Cl R_2 = Br	129–130	75	$C_{12}H_{12}BrClO_3S_2$	43.06	2.87	42.77	2.79	2.12(3H, s); 7.21–8.01(9H, m)
R_1 = Cl R_2 = Me	121–122	65	$C_{16}H_{15}ClO_3S_2$	54.24	4.24	54.07	4.19	2.1–2.11(3H, s); 2.41(3H, s); 7.2–7.92(9H, m)
R_1 = Br R_2 = Br	139–140	75	$C_{15}H_{12}Br_2O_3S_2$	38.96	2.60	38.75	2.45	2.1(3H, s); 7.19–7.81(9H, m)
R_1 = Me R_2 = Cl	110–111	62	$C_{16}H_{15}ClO_3S_2$	54.24	4.24	53.96	4.21	2.1–2.11(3H, s); 2.41(3H, s); 7.21–7.9(9H, m)

Table 8. 1,2-bis(arylsulfonyl)-*trans*-propene

Compound	M.p. (°C)	% Yield	Molecular formula	Anal. % Calc. C	Calc. H	Found C	Found H	^{1}H n.m.r.
R_1 = Cl R_2 = Cl	181–182	75	$C_{15}H_{12}Cl_2O_4S_2$	46.15	3.08	45.87	2.87	2.29(3H, s); 7.1–7.7(9H, m)
R_1 = Cl R_2 = Br	193–194	75	$C_{15}H_{12}BrClO_4S_2$	41.47	2.76	41.19	2.57	2.22(3H, s); 7.1–7.88(9H, m)
R_1 = Cl R_2 = Me	148–149	68	$C_{16}H_{15}ClO_4S_2$	51.89	4.05	51.79	4.28	2.46(6H, s); 7.2–7.92(9H, m)
R_1 = Cl R_2 = OMe	155–156	65	$C_{16}H_{15}ClO_5S_2$	49.74	3.89	49.69	4.03	2.32(3H, s); 3.90(3H, s); 6.93–8.0(9H, m)
R_1 = Br R_2 = Br	185–186	72	$C_{15}H_{12}Br_2O_4S_2$	37.66	2.51	37.64	2.43	2.27(3H, s); 6.85–7.73(9H, m)
R_1 = Me R_2 = Me	149–150	76	$C_{17}H_{18}O_4S_2$	58.29	5.14	58.10	5.14	2.40(9H, s); 7.27–7.9(9H, m)

7 lists the analytical and spectral properties of the samples thus obtained.

General procedure for the preparation of *trans*-1-arylsulfonyl-2-arylsulfinyl-propenes (2)

meta-Chloroperbenzoic acid (assumed 85%, 0.0025 mol) in 25 ml of dichloromethane was added slowly to a stirred solution of the *trans*-1-arylsulfonyl-2-arylsulfenyl-propene (**1**) (0.0025 mol) in 25 ml dichloromethane cooled to 0 °C. After the addition was complete the solution was stirred at 25 °C for an additional 3 h, at which time potassium iodide starch paper indicated completion of the reaction. The dichloromethane solution was then washed with 5% potassium carbonate (2×250 ml), and with water (2×250 ml). The organic layer was dried over anhydrous $NaSO_4$, filtered, and the solvent was evaporated to give a white solid which was recrystallized from petroleum ether (60–100 °C)/chloroform. Physical, analytical and spectral properties of the samples thus obtained are listed in Table 8.

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