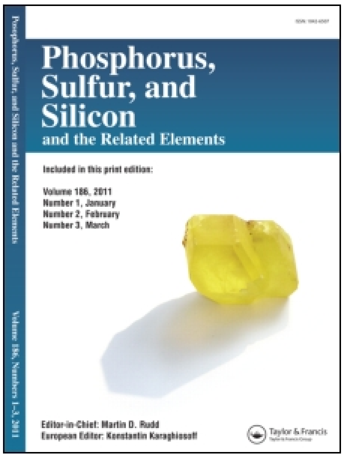

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ELECTRON IMPACT INDUCED ELIMINATIONS. III. ELIMINATION OF SO_2 *vs.* REMOTE GROUP INTERACTIONS IN ARYL ALLYL SULFONES, 1,4-BIS(ARYLSULFONYL)-2-BUTENES, 1-ARYLOXY-4-ARYLSULFONYL-2-BUTENES, AND 4-[(PHENYLSULFONYL)METHYL]-2H-1-BENZOPYRANS

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ELECTRON IMPACT INDUCED ELIMINATIONS. III. ELIMINATION OF SO_2 *vs.* REMOTE GROUP INTERACTIONS IN ARYL ALLYL SULFONES, 1,4-BIS(ARYLSULFONYL)-2-BUTENES, 1-ARYLOXY-4-ARYLSULFONYL-2-BUTENES, AND 4-[(PHENYLSULFONYL)METHYL]-2H-1-BENZOPYRANS

by

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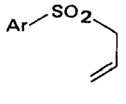
Received March 19, 1974

ABSTRACT

Aryl allyl sulfones, analogous to propynyl sulfones, undergo facile SO_2 elimination under electron impact. However, the 2-butenyl-1,4-diaryl sulfones, analogous to the 2-butynyl-1,4-diaryl sulfones exhibit propensities of remote group interaction and extrusion of the C_4H_6 moiety separating the sulfone functions. Where such remote group interaction is structurally prevented, as in the 4-[(phenylsulfonyl)methyl]-2H-1-benzopyrans, SO_2 extrusion is a major fragmentation pathway.

In recent publications[1,2] we have reported on the divergent behavior under electron impact of aryl propynyl sulfones, **1**, and 2-butynyl-1,4-diaryl sulfones, **2**. Whereas **1** readily extruded SO_2, **2** eliminates C_4H_4 moiety by a remote-group interaction. Such contrasting behavior stimulated our interest in related systems. We chose four groups of molecules, **3**, **4**, **5**, and **6** to pursue such a study. We hoped to answer the following questions: (1) What is the effect of the geometry of the unsaturation center separating the sulfones? (2) Is the remote group interaction observed in **2** a general phenomenon? (3) What is the relative efficiency of remote group interaction *vs.* SO_2 extrusion if the olefinic linkage is part of a heteroring as in **5**?



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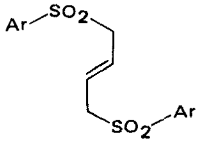

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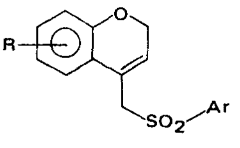

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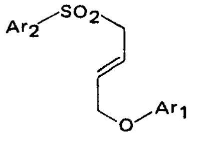


6

Facile extrusion of SO_2 from aryl *vinyl* sulfones has been reported[3,4] as has the loss of SO_2 from aryl-β-hydroxyethyl sulfones.[5] However, to date there have been no reports on aryl *allyl* sulfones.

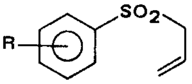
The aryl allyl sulfones and 2-butenyl-1,4-diaryl sulfones were prepared either by reaction of the appropriate alkyl chloride with potassium arylthiolate followed by oxidation or, more successfully, by reaction of the appropriate alkyl chloride with sodium aryl sulfinate (commercially available or generated *in situ* from commercially available aryl sulfinic acids and sodium hydroxide) in DMSO solution. Sulfones **5** and **6** were synthesized using our procedure published earlier.[2,6]

Aryl Allyl Sulfones

Three principal modes of fragmentation are observable in these spectra, (a) carbon–sulfur bond rupture, (b) sulfone-sulfinate rearrangement,[7] and (c) extrusion of SO_2. Table I summarizes the percentage of the total ion current carried by fragments from these modes of cleavage. In addition, hydrogen abstraction from the allylic methylene is also

TABLE I

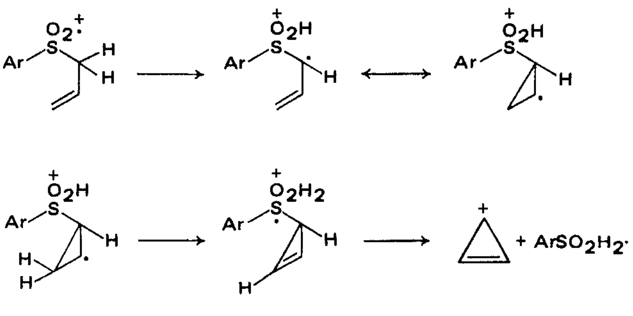
Aryl Allyl Sulfones



	$\%\Sigma_{38}$											
	$[P-SO_2]^{+\cdot}$		$[P-SO_2H]^{+\cdot}$		$ArSO_2^+$		$C_3H_5^+$		$C_3H_3^+$ (cyclopropenium)		$C_3H_5SO_2^+$	
	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
1 *p*-CH_3	7.61	13.17	2.17	5.21	15.21	27.57	7.45	5.21	4.97	0.20	0.62	0.61
2 *p*-Cl	3.56	8.00	2.08	4.16	8.02	13.55	29.70	30.79	9.06	1.08	0.00	0.00
3 *p*-NH_2	4.29	9.51	0.41	0.66	20.25	32.79	5.11	1.31	6.54	0.11	0.00	0.00
4 *m*-CH_3	4.27	11.29	4.56	11.29	9.26	1.66	11.11	10.93	6.13	0.35	0.43	0.71
5 *p*-$NHCOCH_3$	5.42	13.58	0.00	0.00	13.55	26.11	6.10	1.83	4.20	0.09	0.41	0.00
6 H	6.43	11.95	7.11	12.59	9.82	16.97	18.28	20.28	5.87	0.32	0.00	0.00
7 O–CH_3	3.19	7.97	3.70	8.86	5.56	2.30	8.61	7.79	5.56	0.17	0.51	0.53

observed. Smakman[8] has commented ". . . the number of hydrogen atoms transferred prior to the loss of the hydrocarbon chain may vary from 0 to 2 dependent upon the *size* of the alkyl part." Thus, while dimethyl sulfone gives only $MeSO_2^+$, dibutyl sulfone and higher sulfones generate almost exclusively $RSO_2H_2^+$ species. In comparing aryl propynyl sulfones,[1] **1**, and aryl allyl sulfones, **3**, we find that the former shows practically no hydrogen migration, whereas the latter shows greater abundance of $ArSO_2H_2^+$ and $ArSO_2H^+$ along with SO_2H^+ in every instance.

It is aesthetically satisfying to speculate the following sequence of changes in order to account for this pronounced hydrogen abstracting tendency by the sulfone function in the case of the aryl *allyl* sulfones.



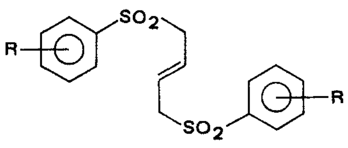
Aryl allyl sulfones parallel the behavior of aryl propynyl sulfones in their facile extrusion of SO_2, with the added feature of hydrogen migration to the sulfone moiety. Metastable peaks present in the spectra also correlate the transition from the parent peak (P) to (P-64) peaks.

2-Butenyl-1,4-diaryl Sulfones

The predominant mode of fragmentation for these sulfones appears to be the formation of the $ArSO_2^+$ moiety by cleavage of the carbon-sulfur bond. A similar mode of rupture follows a sulfone-sulfinate rearrangement (See Table II). One striking feature in these sulfones–in contrast to the spectra of simple aryl allyl sulfones–is the *total absence of SO_2 loss from the parent ion.* There is no (parent–SO_2) peak observed in any of the 2-butenyl-1,4-diaryl sulfones. Instead, one notices a (P-54) fragment and a fragment corresponding to *m*/*e* 54 very clearly. This may arise from the remote-group interaction of the two sulfone groups, paralleling the behavior of 2-butynyl-1,4-diarylsulfones.[2] The geometry of the unsaturated function separating the SO_2 groups alters very little the behavior of these sulfones in their propensity to lose C_4H_4 and C_4H_6 units from the parent molecules. However, after the initial cleavage of the bis-sulfones to form the $ArSO_2^+$, the $ArSO_2CH_2CH{=}CHCH_2^+$ ion readily loses SO_2 affording the cation corresponding to $ArC_4H_6^+$, corroborating observations made in an earlier study. Thus, when only one SO_2 group is attached to the allylic or propynylic carbon, SO_2 loss is facile; but, with symmetrical allylic or propynylic substitution as in **2** or **4**, alternative modes of fragmentation so predominate that SO_2 loss does not occur. This conclusion derives added support in the observations on the mass spectral behavior of compounds of the type **5** where such remote group interaction is prohibited by the incorporation of the allylic double bond as part of a heteroring (*vide infra*).

TABLE II

1,4-bis(Arylsulfonyl)-2-butenes



		%Σ_{38}									
		$ArSO_2^+$		$ArSO_2C_4H_6^+$		$ArC_4H_6^+$		$C_4H_6^{+\cdot}$		$P-SO_2^{+\cdot}$	
	R	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
1	*p*-Cl	18.65	23.42	7.55	21.32	1.31	4.80	3.73	1.29	0.00	0.00
2	*p*-Br	10.60	14.97	5.59	16.46	0.19	0.51	5.97	1.07	0.00	0.00
3	H	21.85	18.60	12.14	62.00	1.52	3.22	3.03	0.62	0.00	0.00
4	*p*-CH_3	26.45	37.66	4.58	16.01	0.86	0.00	2.86	0.94	0.00	0.00

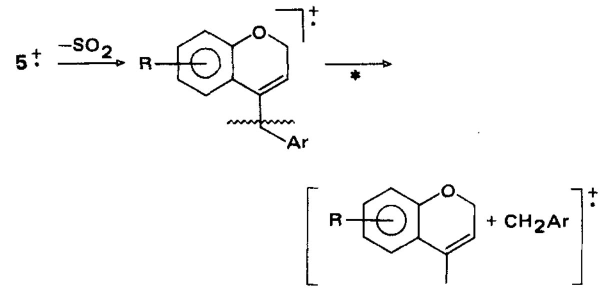
1-Aryloxy-2-butenyl-4-arylsulfones

The mass spectral behavior of these sulfones parallels that observed in the 1,4-bis(arylsulfonyl)-2-butenes discussed in the preceding section. The following modes of fragmentation, in addition to others, are prominent and pertinent to the question of SO_2 extrusion *vs.* C_4H_6 elimination: (a) Cleavage of the aryloxy-carbon bond to give $ArSO_2C_4H_6^+$. (b) Cleavage of the carbon sulfur bond to form $ArSO_2^+$, and (c) loss of C_4H_6 from the parent to give $ArSO_2OAr^+$ ion[2] (See Table III).

Again, one can see that there is *no loss of SO_2 from the molecular ion*. However, there is significant loss of SO_2 from the $ArSO_2C_4H_6^+$ ion. The parent ion shows only a loss corresponding to the elimination of C_4H_6.[2] These facts underscore the inference made above that remote group interaction and elimination of C_4H_6 override the extrusion of SO_2 from the molecular ion if the allylic double bond is shared by more than one readily ionizable group capable of bonding by remote interaction. Once such a group is removed, as in the case of the ion $ArSO_2C_4H_6^+$, then facile loss of SO_2 occurs. These conclusions are supported by deuterium labeling of the methylene *alpha* to the sulfone group. The ion corresponding to C_4H_6 now becomes $C_4H_4D_2$[2] and other ions appropriately marked $ArSO_2C_4H_4D_2^+$ and $ArC_4H_4D_2^+$ (See Table IV).

4-[(Arylsulfonyl)methyl]-2H-1-benzopyrans

These sulfones exhibit the following features: (a) Hydrogen abstraction occurs from the methylene *alpha* to the sulfone function; the base peak in every example is the loss of $ArSO_2H$ (See Table V). (b) All benzopyran derivatives **6** show a prominent loss of SO_2 from the parent ion (See Table V). A metastable peak correlating the P → P-64 transition is observed. After loss of SO_2, cleavage occurs as shown in Scheme 1.

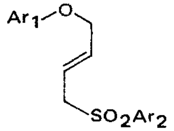


SCHEME I

Clearly restriction of the rotational freedom for interaction by the remote groups is a factor responsible for the divergent behavior of the cyclic compounds. Thus, in their ability to eject SO_2 from the molecular ion, sulfones like aryl propynyl sulfones and aryl allyl sulfones are emulated by 4-[(arylsulfonyl)-methyl]-2H-1-benzopyrans owing to the inability of the oxygen and SO_2 function to interact. On the other hand, 1,4-bis(arylsulfonyl)-2-butenes 1,4-bis(arylsulfonyl)-2-butynes, 1-aryloxy-2-butenyl-4-arylsulfones, and 1-aryloxy-2-butynyl-4-arylsulfones form a class which eliminate the C4 fragment appropriate to each class.

TABLE III

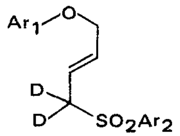
1-Aryloxy-2-butenyl-4-arylsulfones



			%Σ_{38}											
			$C_4H_6^{+\cdot}$		$Ar_2SO_2^+$		$Ar_2SO_2C_4H_6^+$		$Ar_2C_4H_6^+$		$Ar_1OC_4H_6^+$		[Parent-SO_2]$^{+\cdot}$	
	Ar_1	Ar_2	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
1	Phenyl	*β*-Naphthyl	1.82	0.64	15.76	3.09	3.33	10.80	1.21	2.51	3.88	13.50	0.00	0.00
2	Phenyl	*p*-tert butylphenyl	1.53	0.38	16.07	25.57	4.50	11.51	0.05	0.10	3.54	9.72	0.00	0.00
3	*p*-Tolyl	*p*-Chlorophenyl	2.32	0.38	12.07	10.66	3.10	6.22	0.93	2.03	4.64	11.17	0.00	0.00
4	*p*-Tolyl	*p*-Bromophenyl	4.03	0.39	5.67	6.00	1.56	3.60	0.08	0.30	4.02	12.74	0.00	0.00

TABLE IV

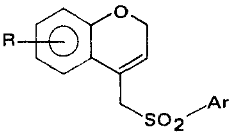
1-Aryloxy-2-butenyl-4,4-d_2-4-arylsulfones

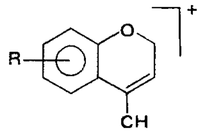


			%Σ_{38}											
			$C_4H_4D_2^{+\cdot}$		$Ar_2SO_2^+$		$Ar_2{-}SO_2C_4H_4D_2^+$		$Ar_2C_4H_4D_2^+$		$Ar_1OC_4H_4D_2^+$		[Parent-SO_2]$^{+\cdot}$	
	Ar_1	Ar_2	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
1	Phenyl	*β*-Naphthyl	2.16	1.38	8.43	13.81	0.25	0.83	0.82	2.35	3.29	12.15	0.00	0.00
2	Phenyl	*p*-tert butylphenyl	1.23	0.82	20.45	27.64	5.11	9.67	0.16	0.11	4.09	8.84	0.00	0.00
3	*p*-Tolyl	*p*-Chlorophenyl	1.64	0.27	12.65	11.96	2.40	5.10	0.63	1.76	1.90	8.35	0.00	0.00
4	*p*-Tolyl	*p*-Bromophenyl	2.92	0.33	6.42	7.13	1.69	3.79	0.12	0.45	3.50	10.24	0.00	0.00

TABLE V

4-[(Phenylsulfonyl)methyl]-2H-1-benzopyrans



			%Σ_{38}							
			Parent^{+}		[Parent-SO$_2$]$^{+}$				ArSO$_2$H^{+}	
	R	Ar	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
1	*p*-Cl	*p*-Methyoxyphenyl	2.56	7.06	2.02	5.33	9.84	13.32	0.64	1.07
2	*p*-Cl	*p*-Bromophenyl	3.23	6.37	0.36	0.50	17.07	23.73	0.15	0.18
3	H	*p*-Chlorophenyl	3.60	9.69	0.62	3.12	16.53	32.85	0.04	0.06
4	*p*-Cl	*p*-tert butylphenyl	4.69	12.06	0.84	1.76	16.75	25.13	0.17	0.25
5	*p*-Cl	*p*-Tolyl	8.35	13.25	0.76	1.20	16.87	24.10	0.08	0.07
6	*o*-CH$_3$	β-Naphthyl	5.36	12.22	2.23	3.98	17.86	26.56	0.18	0.40
7	*p*-Cl	Phenyl	7.33	12.47	0.27	0.49	17.83	24.44	0.10	0.09

Experimental Section

Low resolution mass spectra were secured on a Hitachi Perkin-Elmer RMU-6E instrument at 20 and 70 ev. It was found that variation of the sample heater temperature had very little effect on the spectra. Other spectral data was collected as follows: (a) ir; Perkin-Elmer 621, (1) = KBr pellets (2) = CCl$_4$ solution (3) = neat liquid (crystallized melt for solids) on NaCl plates; (b) nmr; Varian A-60 CDCl$_3$ unless otherwise indicated, TMS = 0.0δ. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalyses were performed in the microanalysis laboratory of this department; all compounds gave C, H, (*N*) analysis within ±0.3%.

The preparation of 1-aryloxy-4-arylsulfonyl-2-butenes,[2] 4-[(arylsulfonyl)-methyl]-2H-1-benzopyrans,[6] and 1,1-d$_2$-1-arylsulfonyl-4-aryloxy-2-butenes[2] have been reported previously by us. *o*-Tolyl allyl sulfone and *m*-tolyl sulfone were prepared according to a previously published procedure.[9]

Preparation of Aryl Allyl Sulfones

(A) Via sodium aryl sulfinates

0.1 mole of the sodium arylsulfinate in 100 ml DMSO was heated to 60-70°C and allyl chloride (15.5 gm, 0.2 mol) was added dropwise. Stirring was continued 30 min at 60-70°C, then for 2 hr at 25°C. *Ca.* 1 liter water was added and the cloudy solution decanted from the oil that separated. The aqueous solution was extracted with ether (3 x 100 ml) and the combined organic material washed with water, dried (Na$_2$SO$_4$), and evaporated. The resulting oil was then purified by distillation or crystallization.

(B) Via Aryl Sulfinic Acids

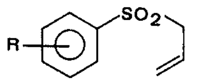
In a typical procedure 10 gm (0.05 mol) 4-acetamidophenylsulfinic acid, 2.8 gm (0.05 mol) KOH, and 55 ml DMSO were heated to 60-70°C. After stirring at this temperature 30 min, allyl chloride (15.5 gm, 0.2 mol) was added dropwise. Stirring at 60-70° was continued for 12 hr. The cooled solution was worked up as described above (using dichloromethane for extraction) to give 7.3 gm (61.0%) of an orange solid. Repeated crystallization from THF/hexane gave analytically pure 4-acetamidophenyl allyl sulfone as a pale yellow solid.

Preparation of 4-Aminophenylallyl Sulfone

3.0 gm (12.5 mmol) 4-acetoamidophenyl allyl sulfone was mixed with 10 ml conc HCl and 34 ml water and refluxed for 2 hr. Upon neutralization of the cooled solution with 28% ammonium hydroxide a crystalline precipitate formed. This was collected, washed with water, air dried, and recrystallized from ethanol to give 2.2 gm (89.4%) 4-aminophenyl allyl sulfone. Analytical data for allyl sulfones prepared in this study is given in Table VI.

TABLE VI

Aryl Allyl Sulfones



R	IR (cm^{-1}) νSO_2	$\nu CH{=}CH_2$	MP or BP (°C)	% Yield
o-CH_3	1140, 1300	935 (3)	89/0.07 mm[a]	–
p-Cl	1148, 1318	936 (3)	42.5–43[b]	61.8
p-CH_3	1140, 1320	930 (2)	51.5–52.5[c]	79.5
m-CH_3	1143, 1323	936 (3)	104–108/0.03 mm	–
H	1140, 1320	930 (2)	127–128.5/0.9 mm[d]	75.0
p-NH_2	1100, 1296	908 (3)	104–106	see text
p-$NHCOCH_3$	1140, 1320	935 (3)	124–125	61.0
m-$NHCOCH_3$	1120, 1304	935 (3)	145–148	45.7
p-OCH_3				

[a] reported bp 173–175°C/7 mm (9a).

[b] reported mp 42°; *Chem. Abstr.*, **51**, 1656 (1957).

[c] reported mp 50.5–51°C (9a).

[d] reported bp 110–113°C/0.5 mm (11).

Preparation of 1,4-Bis(arylsulfonyl)-2-Butenes

(A) From Sodium Arylsulfinate and 1,4-Dichloro-2-butene in DMSO

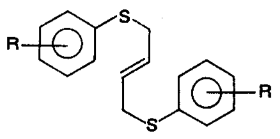
To a preheated solution of 0.1 mol sodium arylsulfinate in 50 ml DMSO was added 12.5 gm (0.1 mol) commercial grade *trans*-1,4-dichloro-2-butene in one portion. The mixture was stirred 2 to 2½ hr at 70°C, at which time the solution was poured into 400 ml ice water. Addition of ether (300 ml) induced formation of a voluminous precipitate which was filtered, air dried, and recrystallized from ethanol. Analytical samples were prepared by additional recrystallization from ethanol.

(B) From Oxidation of 1,4-Bis(arylthio)-2-butenes Derived from Arylthiol and 1,4-Dichloro-2-butene

To a stirred solution of 0.1 mol arylthiol in 100 ml ethanol, under a positive pressure of N_2, was added over 30 min, a solution of 5.6 gm (0.1 mol) KOH in 100 ml 80% ethanol. After stirring an additional 2 hr, 6.25 gm (0.05 mol) *trans*-1,4-dichloro-2-butene in 100 ml ethanol was added over 20–30 min. Stirring, under N_2, was continued 10 hr more at which time the solution was filtered. The solid was water washed free from KCl, air dried, and recrystallized from ethanol to give the *trans*-1,4-bis(arylthio)-2-butenes. Additional recrystallization from ethanol gave analytical samples (Table VII). The sulfides were converted to the corresponding sulfones using the method of Truce.[10] Analytical samples were prepared by recrystallization from ethanol (Table VIII).

TABLE VII

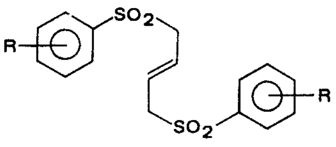
1,4-bis(Arylthio)-2-butenes



R	MP (°C)	% Yield
p-Br	85–86	73.0
p-Cl	67–68	83.8

TABLE VIII

1,4-bis(Arylsulfonyl)-2-butenes



R	MP (°C)	% Yield
H	165–167	59.5
p-CH_3	198–200	71.5
p-Br	262–263	81.0*
p-Cl	231	83.3*

* From the sulfide.

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