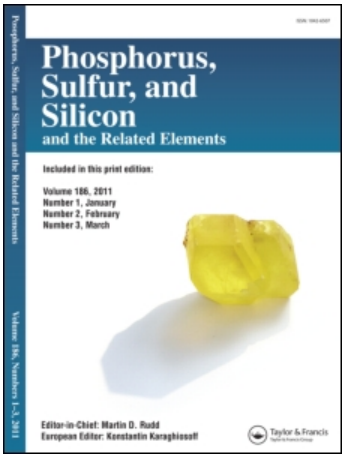

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SULFONYL CHALCONES

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SULFONYL CHALCONES

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The chalcones (1–10) have been reacted with chlorosulfonic acid to give the corresponding sulfonyl chlorides (1a–10a) (Table I). 3-Methoxychalcone (3) also gave the disulfonyl chloride. The sulfonyl chlorides were reacted with amines and hydrazine to give 44 derivatives for biocidal screening. The orientation of sulfonation is discussed in relation to the stereoelectronic factors and confirmed by formal NMR spectral analysis. Attempts to convert the hydrazinosulfonylpyrazolines (11a, 11b, 12, 13) (Table II) into the acetone and *p*-nitrobenzaldehyde hydrazines failed to give pure products.

Key words: Chalcones; chlorosulfonation; sulfonyl chlorides; disulfonyl chloride; hydrazinosulfonyl pyrazolines; sulfonyl chalcones.

TABLE I

Physical data for the chalconesulfonyl derivatives

Compd. No.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (calc) %			MS (M^+)
				C	H	N	
1a	90	134–135	$C_{16}H_{13}ClO_4S$				336
1c	61	154–156	$C_{18}H_{19}NO_4S$	66.8 (67.1)	4.8 (4.9)	3.9 (3.6)	345
1d	55	101–102	$C_{20}H_{23}NO_4S$	64.1 (64.3)	6.2 (6.2)	3.8 (3.75)	373
1h	67	152–153	$C_{22}H_{19}NO_4S$	66.9 (67.1)	4.8 (4.9)	3.8 (3.6)	393
1j	67	122	$C_{23}H_{21}NO_5S$	65.0 (65.2)	4.9 (5.0)	3.0 (3.3)	423
1l	53	133–135	$C_{23}H_{21}NO_4S$	67.8 (67.8)	5.2 (5.2)	3.6 (3.4)	407
2a	60	80	$C_{16}H_{13}ClO_4S$				336
2c	63	124	$C_{18}H_{19}NO_4S$	67.5 (67.1)	5.1 (4.9)	3.9 (3.6)	345
2d	73	96–97	$C_{20}H_{23}NO_4S$	64.4 (64.3)	6.3 (6.2)	4.0 (3.75)	373

TABLE I (*Continued*)

Compd. No.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (calc) %				MS (M^+)
				C		H	N	
2h	62	177-179	$C_{22}H_{19}NO_4S$	67.0	(67.1)	5.0 (4.9)	3.9 (3.6)	393
2j	46	164-165	$C_{23}H_{21}NO_5S$	65.3	(65.2)	5.2 (5.0)	3.1 (3.3)	423
2l	81	164-166	$C_{23}H_{21}NO_4S$	68.0	(67.8)	5.4 (5.2)	3.7 (3.4)	407
2a*	88	122-125	$C_{16}H_{12}Cl_2O_6S_2$					436
2c*	65	160-165	$C_{20}H_{24}N_2O_6S_2$	53.4	(53.1)	5.1 (5.3)	6.0 (6.2)	452
2f*	50	98-100	$C_{24}H_{28}N_2O_8S_2$	54.1	(53.7)	5.0 (5.2)	5.3 (5.2)	536
3a	65	136-138	(lit[8] 135-136)					
3d	48	144-145	$C_{20}H_{23}NO_4S$	64.4	(64.3)	6.1 (6.2)	3.8 (3.75)	373
3h	47	204-205	$C_{22}H_{19}NO_4S$	67.4	(67.1)	5.0 (4.9)	3.6 (3.6)	393
3j	47	149-150	$C_{23}H_{21}NO_5S$	65.4	(65.2)	5.0 (5.0)	3.3 (3.3)	423
3l	56	185-186	$C_{23}H_{21}NO_4S$	68.1	(67.8)	5.2 (5.2)	3.4 (3.4)	407
4a	94	115	$C_{17}H_{15}ClO_5S$					366
4c	42	170-172	$C_{19}H_{20}NO_5S$	60.4	(60.8)	5.2 (5.6)	3.8 (3.7)	375
5a	85	115	$C_{21}H_{15}ClO_3S$					382
5b	25	233-235	$C_{21}H_{17}NO_3S$	69.2	(69.4)	5.0 (4.7)	4.0 (3.8)	363
5c	45	126	$C_{23}H_{21}NO_3S$	69.0	(70.5)	5.2 (5.4)	3.6 (3.6)	391
5d	30	90-92	$C_{25}H_{25}NO_3S$	71.3	(71.6)	5.7 (6.0)	3.6 (3.3)	419
5e	33	185-186	$C_{27}H_{27}NO_3S$	73.1	(72.8)	5.9 (6.1)	2.8 (3.1)	445
5f	42	212-213	$C_{25}H_{23}NO_4S$	69.1	(69.3)	5.5 (5.3)	3.0 (3.2)	433
5g	25	156-157	$C_{27}H_{27}NO_4S$	70.1	(70.3)	6.0 (5.8)	2.9 (3.0)	461
5i	43	205	$C_{27}H_{20}ClNO_3S$	68.4	(68.4)	4.2 (4.2)	2.8 (3.0)	473
5j	15	154-155	$C_{28}H_{23}NO_4S$	71.4	(71.6)	5.2 (4.9)	3.1 (3.0)	469
5k	78	200-201	$C_{27}H_{20}FNO_3S$	70.5	(70.9)	4.8 (4.4)	3.4 (3.1)	457
5m	27	208-209	$C_{28}H_{23}NO_3S$	74.0	(74.2)	4.8 (5.1)	2.9 (3.1)	453
6a	55	125-126	$C_{13}H_9ClO_3S_2$					312

TABLE I (*Continued*)

Compd. No.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (calc) %			MS (M^+)
				C	H	N	
6d	50	94-95	$C_{17}H_{19}NO_3S_2$	58.9 (58.5)	5.4 (5.4)	4.2 (4.9)	349
6g	60	71-74	$C_{19}H_{19}NO_4S_2$	58.3 (58.3)	5.3 (5.4)	3.7 (3.6)	391
6k	90	155-156	$C_{19}H_{14}FNO_3S_2$	58.5 (58.9)	3.8 (3.6)	3.3 (3.6)	387
7a	55	120	$C_{14}H_{11}ClO_4S_2$				344
7d	62	110	$C_{18}H_{21}NO_4S_2$	56.6 (57.0)	5.4 (5.5)	3.5 (3.7)	379
8a	74	131-132	$C_{17}H_{13}ClO_3S$	60.9 (61.4)	3.5 (3.9)		332
8b	20	178	$C_{17}H_{15}NO_3S$	65.1 (65.2)	4.5 (4.8)	4.4 (4.5)	313
8c	56	132	$C_{19}H_{19}NO_3S$	66.8 (66.8)	5.4 (5.6)	4.0 (4.1)	341
8d	65	111-112	$C_{21}H_{23}NO_3S$	68.6 (69.0)	6.4 (6.2)	3.8 (3.8)	369
8f	60	175-176	$C_{21}H_{21}NO_4S$	65.7 (65.8)	5.4 (5.5)	3.6 (3.7)	383
8g	35	159-161	$C_{23}H_{25}NO_4S$	66.9 (67.1)	6.3 (6.1)	3.3 (3.4)	411
8k	25	172-173	$C_{23}H_{18}FNO_3S$	67.4 (67.8)	4.7 (4.4)	3.4 (3.7)	407
8m	29	146-148	$C_{24}H_{21}NO_3S$	71.7 (71.5)	5.3 (5.2)	3.4 (3.5)	403
8n	30	170-171	$C_{23}H_{17}Cl_2NO_3S$	60.0 (60.3)	3.9 (3.7)	2.8 (3.1)	458
8o	55	147-148	$C_{22}H_{23}NO_3S$	69.4 (69.3)	5.9 (6.0)	3.5 (3.7)	381
9a	90	140	$C_{18}H_{15}ClO_4S$				362
9c	62	205-206	$C_{20}H_{21}NO_4S$	65.0 (64.7)	5.9 (5.7)	3.5 (3.3)	371
9d	77	178	$C_{22}H_{25}NO_4S$	66.1 (66.2)	6.2 (6.3)	3.3 (3.5)	399
10c	38	168-169	$C_{20}H_{21}NO_3S$	67.4 (67.6)	6.1 (5.9)	4.0 (3.9)	355
10d	42	103-104	$C_{22}H_{25}NO_3S$	68.5 (68.9)	6.7 (6.5)	3.9 (3.6)	383

Y

a) SO_2Cl; b) SO_2NH_2; c) SO_2NMe_2; d) SO_2NEt_2; e) $SO_2NHC_6H_{11}$; f) sulfonyl morpholino; g) sulfonyl 2,6-dimethylmorpholino; h) SO_2NHPh; i) $SO_2NHC_6H_4Cl$-*p*; j) $SO_2NHC_6H_4OMe$-*p*; k) $SO_2NHC_6H_4F$-*p*; l) $SO_2NHC_6H_4Me$-*p*; m) SO_2NHCH_2Ph; n) $SO_2NHC_6H_3Cl_2$-3,4; o) sulfonyl pyrrolidino.

TABLE II

Physical data for the hydrazinosulfonylpyrazolines

Compd. No.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (calc) %			MS (M^+)
				C	H	N	
11a	62	158 dec.	$C_{16}H_{18}N_4O_3S \cdot 1H_2O$	52.9 (52.9)	5.1 (5.5)	15.3 (15.4)	-
11b	60	125 dec.	$C_{17}H_{20}N_3O_3S$	54.2 (5.43)	5.6 (5.3)	15.1 (14.8)	-
12	84	126 dec.	$C_{13}H_{14}N_4O_2S$	48.4 (48.4)	4.4 (4.3)	17.2 (17.4)	322
13	62	128 dec.	$C_{17}H_{18}N_4O_2S$	59.5 (59.5)	5.4 (5.3)	16.3 (16.4)	-

INTRODUCTION

The work described in this paper forms part of our general programme on the chemistry and biological activity of arylsulfonyl derivatives.[1-3] It extends previous studies[4-7] of the reaction of chlorosulfonic acid with various types of benzylidene derivatives, including chalcone, *p*-methoxychalcone[8] and α-naphthylchalcone.[9] We have demonstrated that the optimum conditions for the chlorosulfonation of chalcone (75% yield) were by reaction with reagent (6 mol equivalents) for 3 weeks at room temperature.[8] The more reactive *p*-methoxy- and α-naphthyl-chalcones, reacted faster under similar conditions (63% yield in 1 week,[8] or 75% yield in 24 hours respectively).[9]

Chalconesulfonyl derivatives are potential biocides and several naturally-occurring antibiotics probably owe their biological activity to the presence of the αβ-unsaturated carbonyl moiety.[10]

DISCUSSION

The present work involves the chlorosulfonation of the chalcones (1 – 10) (Chart 1):

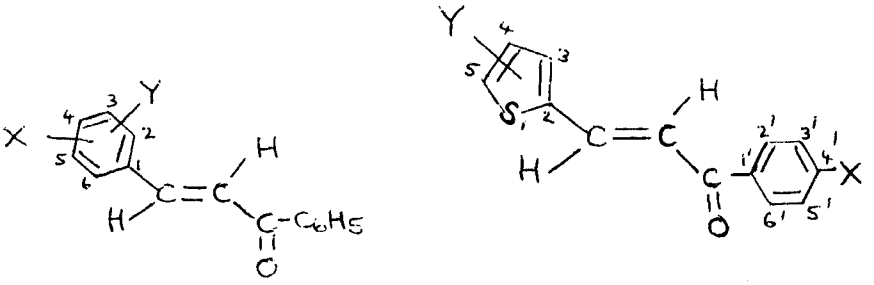
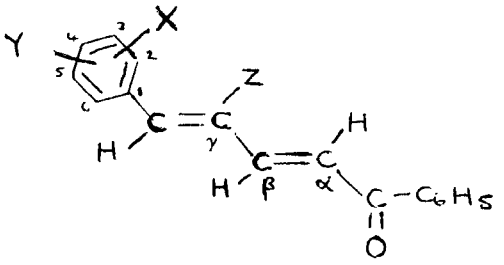


CHART 1

No.	X	Y	Position of sulfonation	No.	X	Y	Position of sulfonation
(1)	2-OMe	H	5	(6)	H	H	5
(2)	3-OMe	H	6 (or 4,6)	(7)	OMe	H	5
(3)	4-OMe	H	3				
(4)	$3,4(OMe)_2$	H	6				
(5)	$4\text{-}C_6H_5$	H	4′				



	X	Y	Z	Position of sulfonation
(8)	H	H	H	4
(9)	OMe	H	H	5
(10)	H	H	Me	4

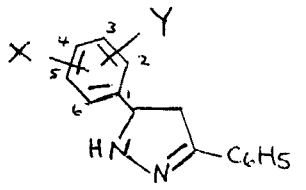
CHART 1 (*Continued*)

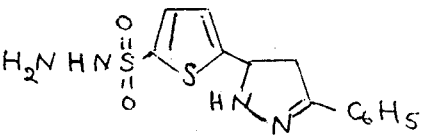
2-, 3- and 4-Methoxy (1, 2, 3), 3,4-dimethoxy (4) and 4-phenyl (5) chalcones were prepared, together with the analogues from thiophen-2-carboxaldehyde with acetophenone (6) and *p*-methoxyacetophenone (7) and those from cinnamaldehyde (8), the 2-methoxy (9) and the γ-methyl (10) derivatives (Chart 1).

The chalcones were prepared by the standard procedure[11,12] involving base-catalysed condensation of the appropriate aromatic aldehyde with acetophenone or the *p*-methoxy derivative.

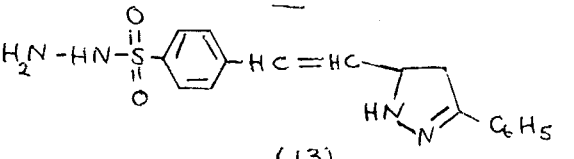
The different chalcones were reacted with excess chlorosulfonic acid, generally 6 mol equivalents or 3 mol equivalents in excess thionyl chloride at room temperature to give the corresponding sulfonyl chlorides; the orientation of sulfonation is shown in Chart 1. The sulfonyl chlorides were condensed with a range of amines to give the sulfonamides listed in Table I. These were synthesised for biological screening as pest control agents.

The chalcone sulfonyl chlorides (1a, 4a) reacted with hydrazide hydrate to give the corresponding hydrazinosulfonylpyrazolines (11a, 11b); the thienylsulfonyl chloride (6a) similarly afforded the pyrazoline (12) and the cinnamaldehyde derivative (8) gave (13). (Chart 2).





(12)



(13)

	X	Y
(11a)	2-OMe	5-SO_2NHNH_2
(11b)	3,4(OMe)$_2$	6-SO_2NHNH_2

CHART 2

In agreement with our previous results,[8] the condensation of the sulfonyl chlorides with hydrazine afforded more stable compounds than the analogous reaction with the parent chalcones (cf. Ref. 12). However, attempts to convert the hydrazinosulfonylpyrazolines (11–13) into the acetone and *p*-nitrobenzaldehyde hydrazones proved unsuccessful. The products were brownish oils, indicative of extensive decomposition (several spots on TLC).

The *m*-methoxychalcone (2) also gave disulfonyl derivatives indicated by the numbers with asterisks.

The chlorosulfonation of the *o*-, *m*- and *p*-methoxychalcones (1–3) proceeded faster than with chalcone, as would be expected due to the electron-donating properties of the methoxy group (cf. Ref. 8).

In the *o*-isomer (1), the preferred site of sulfonation is considered to be the 5-position which is *para* to the more powerful electron-donating methoxy group. 3-Sulfonation appears less likely because of increased steric hindrance by the methoxy group.

In the *m*-isomer (2), both the 4- and 6-positions are activated towards sulfonation by electron-donation from both the methoxy group and the alkenic double bond so sulfonation may occur in either the 4- or 6-position. However, the NMR spectrum of the dimethylamide (2c) showed that the resonances for the Ha alkenic proton (δ8.52, 8.44) appeared downfield as compared with the corresponding resonances (δ8.14, 8.06 and 7.79, 7.72) for the Ha proton in the *o*- and *p*-methoxy derivatives (1c, 3c). The deshielding effect shown for the Ha proton in 2c is ascribed to interaction with the sulfamoyl group and this effect clearly implies 6- rather than 4-sulfonation. The argument is supported by previous studies[13] on the NMR spectra of chalcones which demonstrated that the alkenic Ha proton was the most sensitive to substituent effects.

Reaction of *m*-methoxychalcone (2) with chlorosulfonic acid (6 mol equivalents) for 3 hours at room temperature afforded the monosulfonyl chloride (2a).

On the other hand, treatment of (2) with a mixture of chlorosulfonic acid (6 mol equivalents) in excess thionyl chloride for 1 week gave the 4,6-disulfonyl chloride (2a*). The facile disulfonation of this substrate is presumably a reflection of the

powerful combined electron-donating effects of methoxy group and the alkenic double bond in enhancing the reactivity of the benzene ring with respect to electrophilic attack. With *p*-methoxychalcone (3), stereoelectronic considerations favour 3-sulfonation, *ortho* to the more strongly electron-donating methoxy group rather than 2-sulfonation. The orientation is supported by the ^{1}H NMR resonance spectrum of the dimethylsulfonamide (3c) which showed the alkenic Ha proton resonance at δ7.79, 7.72. On the other hand, 2-sulfonation, *ortho* to the alkenic double bond, should result in deshielding of the Ha proton as was observed in the sulfonation of *m*-methoxychalcone (2).

The NMR spectra of the 2-thienylidene diethylsulfonamides (6d, 7d) showed the resonances for thiophen protons as a doublet (δ7.7) with a coupling constant ($J \simeq$ 3.5 Hz). This value is consistent with coupling between the thiophen 3 and 4 protons and clearly implies 5- and not 4-sulfonation in the thiophen ring.

The assigned orientation of sulfonation agrees with our previous results[14] on the chlorosulfonation of diaryl azines.

In order to unambiguously determine the orientation of sulfonation in the methoxychalcones (1–3), the formal analysis of each of the spectral patterns resulting from the trisubstituted benzene rings in their ^{1}H NMR spectra were carried out. The respective ABC systems, were distinguished at 250 MHz and could be analysed by an interactive procedure. The optimum parameters are given in Table III.

These chemical shifts can be assigned and the substitution patterns determined on the basis of the empirical substitution parameters (Table IV).

The assigned values of the *ortho*- and *para*-dimethylsulfamoyl group are based on the literature values for the *ortho* and *para*-methoxysulphonyl group.[15] The *meta*-value was estimated by comparison of the chemical shifts of the protons of 3-methoxychalconesulphonyl chloride with those of the disulphonyl chloride (δ8.46, 7.30). The values for the PhCOCH=CH moiety were estimated from the literature

TABLE III

Compd.	δ_A	δ_B	δ_C	J_{AB}	J_{AC}	J_{BC}
1c	7.09	7.79	8.03	8.74	0.0	2.24
2c	7.00	7.28	7.94	2.75	8.82	0.0
3c	7.07	7.76	8.25	8.62	0.0	2.22

TABLE IV

Substitutent	ortho	meta	para
CH_3O	-0.48	-0.09	-0.44
$(CH_3)_2NSO_2$	0.60	0.02	0.33
PhCOCH=CH	0.28	0.13	0.12

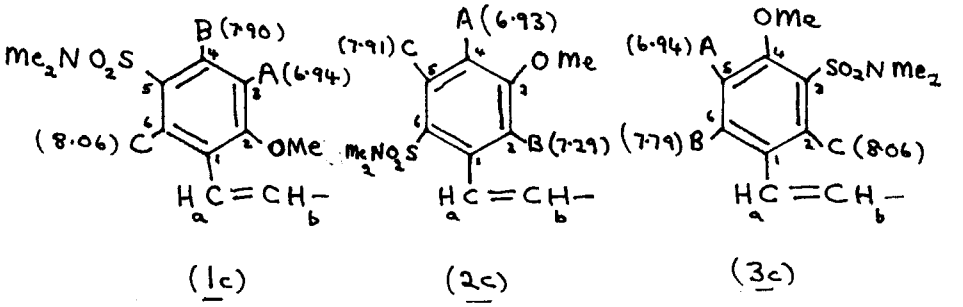


FIGURE 1

data for PhCO and CH=CH groups.[15] The results demonstrate excellent agreement between the experimental chemical shifts shown in brackets (Figure 1) and the predicted values (Table III).

The formal NMR analysis therefore supports the previously predicted orientation of sulfonation for the methoxychalcones shown in Figure 1. The electron impact mass spectra of the majority of the sulfonyl compounds showed the molecular ions (M^+) (see Table I) with the exception of the sulfonohydrazides (Table II). The latter suffered extensive fragmentation and the molecular ions were not generally observed in agreement with our previous results.[16,17]

EXPERIMENTAL

Melting points were determined with a Gallenkamp electric apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC-250 spectrometer using tetramethysilane as internal standard and DMSO-d^6 as solvent, unless otherwise stated. The resonances indicated by an asterisk were removed by D_2O treatment. MS were recorded with a VG Micromass V15 instrument and IR spectra were measured as nujol mulls using a Perkin Elmer 781 or a Unicam SP 1800 spectrophotometer. TLC was carried out on Camlab Polygram silica gel plates sensitized to UV 254 nm using cyclohexane-ethyl acetate (2:1), or for the sulfonyl chlorides petroleum ether-ethyl acetate (2:3) as eluant, unless otherwise stated.

Chlorosulfonation of the chalcones (1–10)

2-Methoxychalcone-5-sulfonyl chloride (1a). 2-Methoxychalcone (1) (5 g, 0.02 mole) was added portionwise to a mixture of chlorosulfonic acid (7.0 g, 0.06 mole) and excess thionyl chloride (20 ml) at 0°C. After 1 week at room temperature, the solution was slowly added to crushed ice (200 g). The precipitate was filtered off with suction, washed with cold water and dried (vacuum desiccator) to give 1a (6.34 g, 90%). IR ν_{max} 1610 (ArC=C), 1605 (ArC=C), 1660 (C=O), 1350, 1160 (SO_2) cm^{-1}.

3-Methoxychalcone-6-sulfonyl chloride (2a). 3-Methoxychalcone (2) (5 g, 0.02 mole) was added to chlorosulfonic acid (14 g, 0.12 mole) at 0°C. The mixture was left at room temperature for 3 hours and then carefully added to crushed ice. The precipitate was filtered off on the Buchner funnel, washed with cold water and dried (vacuum desiccator) to give 2a (4.3 g, 60%). TLC showed one spot, R_F 0.50. IR ν_{max} 1660 (C=O), 1610 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. NMR δ: 8.40-7.3 (m, 5H, ArH and CH=CH).

3-Methoxychalcone-4,6-disulfonyl chloride (2a*). 3-Methoxychalcone (5 g, 0.02 mole) was gradually added to chlorosulfonic acid (14 g, 0.12 mole) and excess thionyl chloride (20 ml) at 0°C. The solution was left 1 week at room temperature and poured onto crushed ice. The yellow precipitate was filtered off, washed with cold water and dried (vacuum desiccator) to give 2a* (8.1 g, 88%). TLC showed one spot, R_F 0.34. IR ν_{max} 1670 (C=O), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. NMR δ: 8.46-7.30, (m, 4H, ArH and CH=CH, d 8.40, 8.3 H(a), 7.31, 7.20d (H_b).

4-Methoxychalcone-3-sulfonyl chloride (3a). 4-Methoxychalcone (3) was reacted with excess chlorosulfonic acid as previously described[8] to give 3a (Table I).

3,4-Dimethoxychalcone-6-sulfonyl chloride (4a). 3,4-Dimethoxychalcone (4) (5 g) was reacted with chlorosulfonic acid-thionyl chloride as described for compound (1a) to give 4a (6.6 g, 94%). IR ν_{max} 1670 (C=O), 1600 (ArC=C), 1360, 1170 (SO_2) cm^{-1}.

4-Phenylchalcone-4'-sulfonyl chloride (5a). 4-Phenylchalcone (5) (5.7 g, 0.02 mole) was reacted with chlorosulfonic acid (14 g, 0.12 mole) for one week at room temperature. The mixture was added to ice-water to give 5a (6.5 g, 85%). TLC showed one spot, R_F 0.52. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1360, 1150 (SO_2) cm^{-1}. MS: 382 (M^+), 347 (M—Cl), 283 (M—SO_2Cl).

2-Thienylideneacetophenone-5-sulfonyl chloride (6a). 2-Thienylideneacetophenone (6) (4.3 g, 0.02 mole) was gradually added to chlorosulfonic acid (14 g, 0.12 mole) at 0°C. The solution was kept at room temperature for 24 hours and poured onto crushed ice. The resultant precipitate was washed with cold water and dried in a vacuum desiccator to give 6a (3.5 g, 56%). TLC showed one spot, R_F 0.71. IR ν_{max} 1650 (C=O), 1600 (ArC=C), 1370, 1170 (SO_2) cm^{-1}. MS: 312 (M^+), 277 (M—Cl), 213 (M—SO_2Cl).

2-Thienylidene-4'-methoxyacetophenone-5-sulfonyl choride (7a). 2-Thienylidene-4'-methoxyacetophenone (7) (4.8 g, 0.02 mole) was reacted with chlorosulfonic acid as described for compound (6a) to give 7a (3.7 g, 55%). TLC showed one spot, R_F 0.61. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1360, 1150 (SO_2) cm^{-1}.

Cinnamylideneacetophenone-4-sulfonyl chloride (8a). Cinnamylideneacetophenone (8) (4.7 g, 0.02 mole) was reacted with chlorosulfonic acid, as described for compound 5a, to give 8a (4.9 g, 74%). IR ν_{max} 1660 (C=O), 1590 (ArC=C), 1380, 1170 (SO_2) cm^{-1}. MS: 332 (M^+), 233 (M—SO_2Cl).

2-Methoxycinnamylideneacetophenone-4-sulfonyl chloride (9a). 2-Methoxycinnamylideneacetophenone (9) (5.3 g, 0.02 mole) was reacted with chlorosulfonic acid-thionyl chloride as described for compound (1a) to give 9a (6.6 g, 90%). TLC showed one spot, R_F 0.56. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. MS: 362 (M^+) 327 (M—Cl), 263 (M—SO_2Cl).

γ-Methylcinnamylideneacetophenone-4-sulfonyl chloride (10a). γ-Methylcinnamylideneacetophenone (10) was reacted with chlorosulfonic acid (6 mol equivalents) for 1 week to give the sulfonyl chloride (10a) as a gum. This was characterized by reaction with excess dimethylamine and diethylamine to give the sulfonamides (10c, 10d) respectively (Table I). For compound (10c), TLC showed one spot, R_F 0.71, and for 10d, one spot, R_f 0.70.

Reaction of chalconesulfonyl chlorides (1a, 4a, 6a, 8a) *with hydrazine.* The appropriate chalcone sulfonyl chloride (0.02 mole) was reacted with hydrazine hydrate (0.10 mole) in methanol (100 ml) at room temperature (6 hours). The mixture was diluted with ice-water (100 ml) to give the corresponding hydrazinosulfonylpyrazoline (Table II).

Compound 11a. TLC showed one spot, R_F 0.16. IR ν_{max} 3300, 3180 (NH), 1610 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. MS did not show the molecular ion (M^+, 346), but gave a fragment ion at 251 (M—SO_2 $NHNH_2$).

Compound 11b. TLC showed one spot, R_F 0.62. IR ν_{max} 3250, 3150 (NH), 1600 (ArC=C), 1360, 1140 (SO_2) cm^{-1}. MS did not give the molecular ion (M^+, 376) but gave a fragment ion at 281 (M—SO_2NHNH_2).

Compound 12. TLC showed one spot, R_F 0.24. IR ν_{max} 3380, 3340 (NH), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. MS: 322 (M^+), 306 (M—NH_2), 291 (M—$NHNH_2$), 227 (M—SO_2NHNH_2).

Compound 13. TLC showed one spot, R_F 0.35. IR ν_{max} 3310 (NH), 1595 (ArC=C), 1330, 1160 (SO_2) cm^{-1}. MS did not show the molecular ion (M^+, 342) but gave fragment ions at 280, 278, 248 (M—SO_2NHNH_2), 221, 205. NMR δ: 8.0* (2H, s, NH_2), 7.6-7.0 (11H, m, ArH, CH=CH), 4.5* (2H, s, NH), 2.6 (2H, t, CH_2).

General procedure for the reaction of the sulfonyl chlorides (1a–10a) *with amines.* The sulfonyl chloride (0.01 mole) in methanol (15 ml) was treated with the appropriate amine (0.03 moles) with stirring for 3 hours at room temperature. The mixture was poured onto crushed ice and acidified by addition of

dilute hydrochloric acid. The precipitate was filtered off under suction on a Buchner funnel, washed with water and recrystallised from methanol to give the sulfonamides (Table I).

The aromatic sulfonamides (1j, 1l, 2h, 2j, 2l, 3h, 3j, 3l, 5i, 5j, 5k, 6k, 8k, 8m, 8n) were obtained by reaction of the sulfonyl chloride (0.01 mole) with the arylamine (0.01 mole) and triethylamine (0.02 mole) in acetonitrile (15 ml) at room temperature (12 hours).

Compound (1c). TLC showed one spot, R_F 0.60. IR ν_{max} 1640 (C=O), 1600 (ArC=C), 1350, 1140 (SO_2) cm^{-1}. MS: 345 (M^+), 300 (M—NMe_2), 236 (M—SO_2NMe_2). NMR ($CDCl_3$): δ 8.2-7.0 (m, 10H, ArH) and alkenic Hs, d 8.14, 8.06, d (H_a), 7.70, 7.62 d(H_b), 3.9 (3H, s, OMe), 2.7 (6H, s, NMe_2).

Compound (1h). NMR ($CDCl_3$) δ: 9.5 (1H, s, $\overset{*}{N}H$), 8.1-7.1 (m, 15H, ArH, alkenic Hs), 3.9 (3H, s, OMe).

Compound (1j). NMR ($CDCl_3$): δ 9.8 (1H, s, $\overset{*}{N}H$), 8.1-7.06 (m, 14H, ArH, 7.06, 7.02, 6.79, 6.75, 4ArH, q, AA'BB' pattern, alkenic Hs), 3.90 (3H, s, OMe), 3.71 (3H, s, OMe).

Compound (2c). TLC showed one spot, R_F 0.68. NMR ($CDCl_3$): δ 8.52-7.03 (m, 10H, ArH and alkenic Hs, 8.52, 8.44 (H_a), 7.32, 7.24 (H_b), 3.93 (s, 3H, OMe), 2.72 (s, 6H, NMe_2).

Compound (2d). NMR ($CDCl_3$): δ 8.45-6.95 (m, 10H, ArH and alkenic Hs, 8.45, 8.37 (H_a), 7.33, 7.25 (H_b)), 3.92 (s, 3H, OMe), 3.23 (q, 4H, N—$\underline{CH_2}CH_3$), 1.06 (t, $NCH_2\underline{CH_3}$).

Compound (2c*). TLC showed one spot, R_F 0.30. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$): δ 8.5-7.2 (m, 9ArH and alkenic Hs), 4.1 (s, 3H, OMe), 2.9, 2.7 (2 × s, 12H, NMe_2).

Compound (2f*). TLC showed one spot, R_F 0.19. IR ν_{max} 1650 (C=O), 1610 (ArC=C), 1360, 1150 (SO_2) cm^{-1}.

Compound (3c). NMR ($CDCl_3$): δ8.30-7.03 (m, 10H, ArH and alkenic Hs 7.79, 7.72 (H_a), 7.53, 7.49 (H_b), 3.97 (s, 3H, OMe), 2.86 (s, 6H, NMe_2).

Compound (3j). NMR ($CDCl_3$) δ: 9.25* (s, 1H, NH), 8.07-6.70 (m, 14H, ArH and alkenic Hs 7.70, 7.63 (H_a), 7.45, 7.37 (H_b), 7.05-6.70, m, AA'BB' pattern, 4ArH, *p*-substitution, 4.11 (s, 3H, OMe), 3.69 (s, 3H, OMe).

Compound (4c). TLC showed one spot, R_F 0.57. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1350, 1150 (SO_2) cm^{-1}. MS: 375 (M^+), 266 (M^+—SO_2NMe_2), 234 (M—SO_2NMe_2, —OMe).

Compound (5c). TLC showed one spot, R_F 0.66. MS: 391 (M^+), 347 (M—NMe_2), 313 (M—SO_2NMe_2). NMR δ: 8.40-7.10 (m, 16H, ArH and alkenic Hs), 2.75 (s, 6H, NMe_2).

Compound (5d). TLC showed one spot, R_F 0.32. IR ν_{max} 1650 (C=O), 1610 (ArC=C), 1360, 1150 (SO_2) cm^{-1}. MS: 419 (M^+), 404 (M—Me), 347 (M—NEt_2), 283 (M—SO_2NEt_2).

Compound (5k). TLC showed one spot, R_F 0.68. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1350, 1140 (SO_2) cm^{-1}. NMR δ: 10.5* (s, 1H, NH), 8.2-7.0 (m, 19H, ArH and alkenic Hs. MS: 457 (M^+), 283 M—$SO_2NH \cdot C_6H_4F$).

Compound (6d). TLC showed one spot, R_F 0.78. IR ν_{max} 1650 (C=O), 1610 (ArC=C), 1365, 1150 (SO_2) cm^{-1}. MS: 349 (M^+), 277 (M—NEt_2), 213 (M—SO_2NEt_2). NMR [$(CD_3)_2CO$] δ: 8.4-7.5 (9H, m, ArH, alkenic Hs). 7.7 (d, 2H, thiophen-3,4 H, $J_{3,4}$ 3.5 Hz), 3.4-3.2 (q, 4H, $N\underline{CH_2}CH_3$), 1.3-1.15 (t, 6H, $NCH_2\underline{CH_3}$).

Compound (6g). TLC showed one spot R_F = 0.86. IR ν_{max} 1650 (C=O), 1590 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. MS: 391 (M^+), 216 (M—$SO_2NC_6H_9O$).

Compound (6k). TLC showed one spot, R_F 0.70. IR ν_{max} 1660 (C=O), 1590 (ArC=C), 1340, 1150 (SO_2) cm^{-1}.

Compound (7d). TLC showed one spot, R_F 0.34. IR ν_{max} 1650 (C=O), 1600 (ArC=C), 1360, 1140 (SO_2) cm^{-1}. MS: 379 (M^+), 243 (M—SO_2NEt_2). NMR ($CDCl_3$) δ: 8.1-6.9 (m, 8H, ArH and alkenic Hs, 8.7 (q, AABB' pattern, 4H, benzenoid Hs), 7.7 (d, 2H, thiophen-3,4 H, $J_{3,4}$ 3.7 Hz), 3.8 (s, 3H, OMe), 3.4-3.2 (q, 4H, $N\underline{CH_2}CH_3$), 1.3-1.1 (t, 6H, $NCH_2\underline{CH_3}$).

Compound (8c). IR ν_{max} 1670 (C=O), 1590 (ArC=C), 1360, 1160 (SO_2) cm^{-1}. MS: 341 (M^+), 233 (M—SO_2NMe_2), 157 (M—$C_6H_4SO_2NMe_2$). NMR ($CDCl_3$) δ: 8.10-7.0 (m, 13H, ArH and alkenic Hs), 2.7 (s, 6H, NMe_2).

Compound (8d). TLC showed one spot, R_F 0.56. IR ν_{max} 1650 (C=O), 1590 (ArC=C), 1340, 1150 (SO_2) cm^{-1}. MS: 369 (M^+), 354 (M—Me), 297 (M—NEt_2), 233 (M—SO_2NEt_2). NMR ($CDCl_3$) δ: 8.10-7.0 (m, 13H, ArH and alkenic Hs), 3.4-3.2 (q, 4H, $N\underline{CH_2}CH_3$), 1.15 (t, 6H, $NCH_2\underline{CH_3}$).

Compound (9c). TLC showed one spot, R_F 0.30. IR ν_{max} 1670 (C=O), 1610 (ArC=C), 1360, 1170 (SO_2) cm^{-1}. MS: 371 (M^+), 356 (M—Me), 341 (M—Me_2), 327 (M—NMe_2), 263 (M—SO_2NMe_2). NMR ($CDCl_3$) δ: 8.1-6.95 (m, 12H, ArH and alkenic Hs), 3.8 (s, 3H, OMe), 2.75 (s, 6H, NMe_2).

Compound (9d). TLC showed one spot, R_F 0.62. IR ν_{max} 1660 (C=O), 1600 (ArC=C), 1350, 1170 (SO_2) cm^{-1}. MS: 399 (M^+), 327 (M—NEt_2), 263 (M—SO_2NEt_2).

Compound (10c). TLC showed one spot R_F, 0.80. IR ν_{max} 1670 (C=O), 1590 (ArC=C), 1360, 1140 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.2-7.1 (m, 12H, ArH and alkenic Hs), 2.8 (s, 6H, NMe), 2.1 (s, 3H, Me).

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