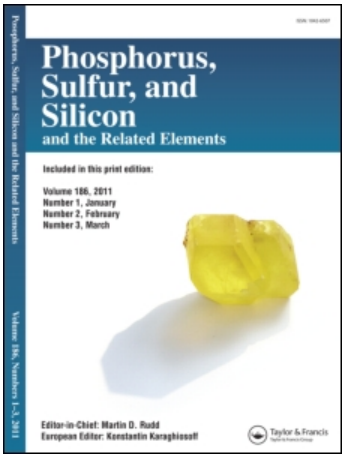

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SULFENAMIDES AND SULFINAMIDES VIII) THE CHROMATOGRAPHY OF ARYL SULFENAMIDES

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SULFENAMIDES AND SULFINAMIDES VIII.† THE CHROMATOGRAPHY OF ARYL SULFENAMIDES

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Substituent effects with respect to position and extent of substitution in a series of *N*-aryl benzenesulfenamides (ArSNHAr') have been examined over several chromatographic systems. In normal phase TLC, although methyl substitution in either ring leads to higher $R\phi$ values (*Rf* relative to that of the parent compound, *N*-(phenyl)benzenesulfenamide, **1**) a dominant influence is shown by substitution at the 2-position on the amine side—$R\phi$ value greater than that of the isomeric 4-methyl derivative. In contrast, substitution at the 4-position on the sulfenyl side gives a higher $R\phi$ value.

The respective contributions to $R\phi$ values are maintained in di-substituted derivatives so that the highest is given by the mixed derivative-2-position on the amine side plus 4-position on the sulfenyl side. Similar relative effects, but with a greater spread of $R\phi$ values, are given by chloro and methoxyl derivatives.

In reversed phase TLC (on paraffined silica gel) all the methyl and chloro derivatives have $R\phi$ values <1 but values for the chloro derivatives were lower than expected on the basis of polarity. Similarly, in reversed phase HPLC (on μBondapak C_{18} porasil) all methyl and chloro derivatives had tr values (retention time/retention time of **1**) >1 and values for the chloro derivatives were greater than expected on the basis of polarity. GC on non-polar methyl silicone, OV-1, and on mildly polar methyl phenyl silicone, OV-17 gives retention times largely consistent with molecular weight viz. **1** < monomethyl < dimethyl < monochloro < dichloro. Solubility and polar features are discussed.

Key words: Sulfenamides; chromatography.

INTRODUCTION

Few references to the chromatography of sulfenamides have appeared in the literature and the majority of these refer to compounds found in the vulcanization of rubber.[1–5] As a service to other studies on their properties and reactivities,[6] often involving separation from mixtures of reaction products,[7] a variety of chromatographic procedures has been developed for a series of aryl sulfenamides extending previous methods based on direct and reversed phase paper chromatography.[1]

RESULTS AND DISCUSSION

The almost three-fold range of $R\phi$ values (distance travelled or retention time of compound/distance travelled or retention time of *N*-(phenyl)benzenesulfenamide; **1**) in normal phase TLC shown in Table II indicates strong substituent influence.

†Part VII. *Phosphorus, Sulfur and Silicon*, **56**, 237 (1991).

TABLE I

Elemental analyses and melting points of aryl sulfenamides (Ar-S-NH-Ar')

Sulfenamide (Ar-S-NH-Ar')		mp	Lit. mp	% Found			% Calculated		
Ar	Ar'	°C	°C	C	H	N	C	H	N
C_6H_5	C_6H_5	56-56.5	54-55[10]	71.67	5.24	7.17	71.64	5.47	6.97
4-CH_3-C_6H_4	C_6H_5	76-77	77-78[10]	72.48	5.83	6.69	72.51	6.09	6.51
C_6H_5	4-CH_3-C_6H_4	50-51	51-52[10]	72.33	6.10	6.42	72.51	6.09	6.51
2-CH_3-C_6H_4	C_6H_5	77-78		72.59	5.88	6.72	72.51	6.09	6.51
C_6H_5	2-CH_3-C_6H_4	77-78		72.48	5.86	6.67	72.51	6.09	6.51
4-CH_3-C_6H_4	4-CH_3-C_6H_4	65-65.5	65[10]	73.27	6.27	6.07	73.36	6.55	6.11
2-CH_3-C_6H_4	2-CH_3-C_6H_4	66.5-67		73.24	6.79	5.84	73.36	6.55	6.11
4-CH_3-C_6H_4	2-CH_3-C_6H_4	67-68		73.30	6.34	6.05	73.36	6.55	6.11
2-CH_3-C_6H_4	4-CH_3-C_6H_4	65-66		73.36	6.32	6.38	73.36	6.55	6.11
4-Cl-C_6H_4	C_6H_5	81-82	84[11] 81-82[10]	61.05	4.31	5.80	61.15	4.25	5.95
C_6H_5	4-Cl-C_6H_4	78.5-79.5	83[12] 79-80[10]	61.12	4.25	6.06	61.15	4.25	5.95
2-Cl-C_6H_4	C_6H_5	58-59		60.94	4.26	6.08	61.15	4.25	5.95
C_6H_5	2-Cl-C_6H_4	52-53		61.02	3.96	5.90	61.15	4.25	5.95
4-Cl-C_6H_4	4-Cl-C_6H_4	75-75.5	74[12]	53.62	3.30	5.20	53.33	3.33	5.19
2-Cl-C_6H_4	2-Cl-C_6H_4	71-72		53.66	3.36	5.17	53.33	3.33	5.19
C_6H_5	4-CH_3O-C_6H_4	66.5-67.5	67[11]	67.71	5.47	6.28	67.53	5.63	6.06
C_6H_5	2-CH_3O-C_6H_4	38-39		67.53	5.51	6.18	67.53	5.63	6.06

On the basis that the nitrogen centre is the main area for interaction with the adsorbent, the high $R\phi$ values for the 2-chloro and 2-methyl substituents on the amine side apparently preclude strong adsorption. The effect is steric rather than polar since the substituents are approximately equal in size but would produce opposite polar effects. It must be noted that similar effects appear in the reaction of aryl sulfenamides with the stable diphenylpicrylhydrazyl free radical where reaction was completely inhibited by substituents in this position.[8]

This interpretation is supported by the opposite effects of further substitution on the sulfenyl side. A second chloro substitution reduced the $R\phi$ value slightly whereas methyl substitution in this position led to a higher $R\phi$ value in accordance with expectation.

Irrespective of their position, all methyl substituted derivatives had higher $R\phi$ values than the unsubstituted parent. The greatest contrast however appears with 4-chloro substitution on the amine side leading to the lowest $R\phi$ values to be contrasted with the lesser effects of substitution on the sulfenyl side.

A feature of the change to reversed phase TLC is the narrowing of the range of $R\phi$ values and the consequent narrowing of scope for good separations (Table III). With the removal of solute/adsorbent interaction, $R\phi$ values are more closely related to molecular size and solvent effects. Thus, the parent sulfenamide, devoid of retarding substituent influence, had the highest $R\phi$ values.

In general accordance with these principles, the $R\phi$ values for the methyl substituted derivatives fall into two areas with values over the ranges 1.0–0.92 for the

TABLE II

Normal phase thin-layer chromatography of sulfenamides (Ar-S-NH-Ar') stationary phase: Kieselgel; mobile phase: light petroleum-ethyl acetate (19:1)

Distance travelled cm	Relative Rφ *	-CH_3 substituted compounds Ar	Ar'	-Cl substituted compounds Ar	Ar'	-OCH_3 substituted compounds Ar	Ar'
11.41	1.63			C_6H_5	2-Cl-C_6H_4		
10.71	1.53			2-Cl-C_6H_4	2-Cl-C_6H_4		
8.82	1.26	4-CH_3-C_6H_4	2-CH_3-C_6H_4				
8.75	1.25	2-CH_3-C_6H_4	2-CH_3-C_6H_4				
8.40	1.20	C_6H_5	2-CH_3-C_6H_4				
7.98	1.14	4-CH_3-C_6H_4	4-CH_3-C_6H_4				
7.91	1.13	2-CH_3-C_6H_4	4-CH_3-C_6H_4				
7.70	1.10					C_6H_5	2-CH_3O-C_6H_4
7.63	1.09	C_6H_5	4-CH_3-C_6H_4				
7.35	1.05	4-CH_3-C_6H_4	C_6H_5				
7.35	1.05	2-CH_3-C_6H_4	C_6H_5				
7.00	1.00	C_6H_5	C_6H_5				
6.58	0.94			4-Cl-C_6H_4	C_6H_5		
5.81	0.83			2-Cl-C_6H_4	C_6H_5		
5.67	0.81			C_6H_5	4-Cl-C_6H_4		
5.04	0.72			4-Cl-C_6H_4	4-Cl-C_6H_4		
4.34	0.62					C_6H_5	4-CH_3O-C_6H_4

* Rφ distance travelled by compound/distance travelled by N-(phenyl) benzenesulfenamide

monomethyl derivatives, which does not allow for marked changes according to the position of the substitution. $R\phi$ values for the disubstituted derivatives were in the range 0.84–0.72 in which materials with 4-substitution on the amine side had the lower values. In a similar manner $R\phi$ values for the chloro substituted materials fell into two ranges: 0.93–0.81 for the monochloro compounds and 0.78–0.68 for the dichloro derivatives. Again 2-substitution led to lower values within each class.

Comparison of results according to the degree of substitution shows that the $R\phi$ values for the methyl derivatives were higher than those of the chloro derivatives.

The structure/$R\phi$ relationship of reversed phase TLC extended to reversed phase HPLC. Again the unsubstituted parent compound was very mobile with a relative retention time slightly greater than that of the 4-methoxylated derivative (Table IV). The values of the methyl and chloro derivatives fall into areas equivalent to those of the reversed phase TLC according to the type and extent of substitution.

TABLE III

Reversed phase thin layer chromatography of sulfenamides (Ar-S-NH-Ar') stationary phase: paraffined Kieselgel; mobile phase: methanol-water (85:15)

Distance travelled cm	Relative Rφ *	-CH_3 substituted compounds		-Cl substituted compounds		-OCH_3 substituted compounds	
		Ar	Ar'	Ar	Ar'	Ar	Ar'
9.05	1.07					C_6H_5	4-CH_3O-C_6H_4
8.54	1.00	C_6H_5	C_6H_5				
8.54	1.00	4-CH_3-C_6H_4	C_6H_5				
8.11	0.95	C_6H_5	2-CH_3-C_6H_4				
8.02	0.94	2-CH_3-C_6H_4	C_6H_5				
7.94	0.93			2-Cl-C_6H_4	C_6H_5		
7.86	0.92	C_6H_5	4-CH_3-C_6H_4				
7.52	0.88			4-Cl-C_6H_4	C_6H_5		
7.52	0.88			C_6H_5	4-Cl-C_6H_4		
7.43	0.87					C_6H_5	2-CH_3O-C_6H_4
7.17	0.84	2-CH_3-C_6H_4	4-CH_3-C_6H_4				
7.09	0.83	4-CH_3-C_6H_4	4-CH_3-C_6H_4				
6.92	0.81			C_6H_5	2-Cl-C_6H_4		
6.83	0.80	4-CH_3-C_6H_4	2-CH_3-C_6H_4				
6.75	0.79	2-CH_3-C_6H_4	2-CH_3-C_6H_4				
6.66	0.78			4-Cl-C_6H_4	4-Cl-C_6H_4		
5.81	0.68			2-Cl-C_6H_4	2-Cl-C_6H_4		

* Rφ distance travelled by compound/distance travelled by N-(phenyl) benzenesulfenamide.

By contrast however, better separations occurred over a greater range of relative retention times. Separation of a mixture of twelve sulfenamides is shown in Figure 1.

Gas chromatography has been examined using two stationary phases of differing polarity—the non-polar methyl silicone OV-1 (Table V) and the mildly polar OV-17 consisting of 50% methyl and phenylsilicone (Table VI) with the intention of testing degrees of influence of polar properties of sulfenamides on retention times. This difference in makeup of the two phases permitted use of a slightly higher temperature (185°C), for the OV-17 column vs 160°C with the OV-1 column.

With the removal of highly polar features in the stationary phases, it was anticipated that separations would be largely dependent on molecular weight. This expectation was realized with both columns where the general pattern of retention times viz. unsubstituted parent < monomethyl < dimethyl < monochloro < di-

TABLE IV

Reversed phase high performance liquid chromatography of sulfenamides (Ar-S-NH-Ar') stationary phase: μBondapak C_{18} porasil; mobile phase: methanol-water (60:40) isocratic

Retention time min	Relative tr *	-CH_3 substituted compounds		-Cl substituted compounds		-OCH_3 substituted compounds	
		Ar	Ar'	Ar	Ar'	Ar	Ar'
7.50	0.90					C_6H_5	4-CH_3O-C_6H_4
8.33	1.00	C_6H_5	C_6H_5				
12.00	1.44	C_6H_5	2-CH_3-C_6H_4				
12.41	1.49	2-CH_3-C_6H_4	C_6H_5				
13.08	1.57	4-CH_3-C_6H_4	C_6H_5				
13.41	1.61					C_6H_5	2-CH_3O-C_6H_4
13.50	1.62	C_6H_5	4-CH_3-C_6H_4	2-Cl-C_6H_4	C_6H_5		
16.00	1.92			4-Cl-C_6H_4	C_6H_5		
17.08	2.05			C_6H_5	2-Cl-C_6H_4		
17.16	2.06			C_6H_5	4-Cl-C_6H_4		
18.49	2.22	2-CH_3-C_6H_4	2-CH_3-C_6H_4				
20.00	2.40	4-CH_3-C_6H_4	2-CH_3-C_6H_4				
20.49	2.46	2-CH_3-C_6H_4	4-CH_3-C_6H_4				
21.32	2.56	4-CH_3-C_6H_4	4-CH_3-C_6H_4				
28.40	3.41			2-Cl-C_6H_4	2-Cl-C_6H_4		
32.40	3.89			4-Cl-C_6H_4	4-Cl-C_6H_4		

* tr retention time of compound/retention time of N-(phenyl) benzenesulfenamide

chloro derivative, resembled the order shown in reverse phase TLC and HPLC viz. unsubstituted parent < monomethyl < monochloro < dimethyl < dichloro derivative. Other differences in performance were noted although resolution of the methyl substituted derivatives was poor on both columns. First, the higher temperature used with the OV-17 column was probably responsible for the shorter retention times; 9.35 min versus 14.39 min for the parent compound and 51.78 min versus 78.74 min for the slowest moving di-4-chloro derivative. It may be noted that 2-substituted derivatives had shorter retention times and that sharper peaks were obtained at the higher temperature.

Separations of mixtures achieved with these columns are shown in Figures 2 and 3. Sharper peaks were given by the earlier emerging materials with both columns.

EXPERIMENTAL

Materials. Sulfenamides were prepared by a standard method, condensation of a sulfenyl chloride with an amine,[9] as follows.

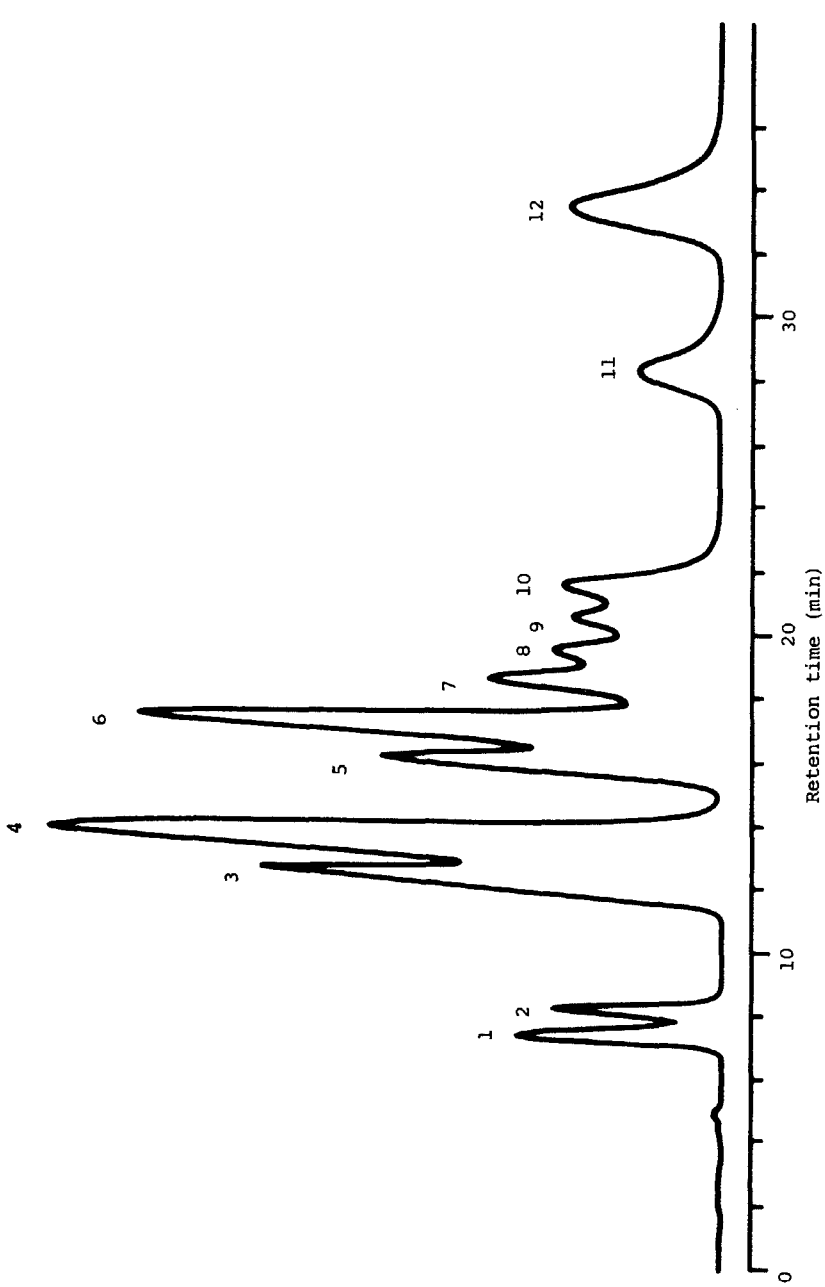

FIGURE 1 Isocratic separation of aryl sulfenamides by reversed phase HPLC on μBondapak C_{18} porasil (column 3.9 mm × 30 cm; 10 μ); solvent:methanol-water (60:40); flow rate 2 mL/min. **1**. Ph-S-NH-C_6H_4-OCH_3(4); **2**. Ph-S-NH-Ph; **3**. (2)CH_3-C_6H_4-S-NH-Ph; **4**. (4)CH_3-C_6H_4-S-NH-Ph + Ph-S-NH-C_6H_4-OCH_3(2) + Ph-S-NH-C_6H_4-CH_3(4) + (2)Cl-C_6H_4-S-NH-Ph; **5**. (4)Cl-C_6H_4-S-NH-Ph; **6**. Ph-S-NH-C_6H_4-Cl(2); **7**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2); **8**. (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2); **9**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4); **10**. (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4); **11**. (2)Cl-C_6H_4-S-NH-C_6H_4-Cl(2); **12**. (4)Cl-C_6H_4-S-NH-C_6H_4-Cl(4).

TABLE V

Gas chromatography of sulfenamides (Ar-S-NH-Ar') stationary phase: OV-1 (10% on Chromosorb W HP) at 160°C

Retention time min	Relative tr *	-CH_3 substituted compounds Ar	-CH_3 substituted compounds Ar'	-Cl substituted compounds Ar	-Cl substituted compounds Ar'	-OCH_3 substituted compounds Ar	-OCH_3 substituted compounds Ar'
14.39	1.00	C_6H_5	C_6H_5				
18.89	1.31	C_6H_5	2-CH_3-C_6H_4				
20.65	1.44			C_6H_5	2-Cl-C_6H_4		
21.65	1.50	2-CH_3-C_6H_4	C_6H_5				
21.90	1.52	C_6H_5	4-CH_3-C_6H_4				
22.24	1.55	4-CH_3-C_6H_4	C_6H_5				
28.17	1.96	2-CH_3-C_6H_4	2-CH_3-C_6H_4				
28.40	1.97					C_6H_5	2-CH_3O-C_6H_4
28.84	2.00	4-CH_3-C_6H_4	2-CH_3-C_6H_4				
30.64	2.13			2-Cl-C_6H_4	C_6H_5		
31.64	2.20			4-Cl-C_6H_4	C_6H_5		
32.78	2.28	2-CH_3-C_6H_4	4-CH_3-C_6H_4				
33.90	2.36	4-CH_3-C_6H_4	4-CH_3-C_6H_4				
34.68	2.41			C_6H_5	4-Cl-C_6H_4		
39.78	2.76					C_6H_5	4-CH_3O-C_6H_4
44.27	3.08			2-Cl-C_6H_4	2-Cl-C_6H_4		
78.74	5.47			4-Cl-C_6H_4	4-Cl-C_6H_4		

* tr retention time of compound/retention time of N-(phenyl) benzenesulfenamide

Preparation of sulfenyl chloride. Through a solution of the appropriate thiol (0.1 mol) or disulfide (0.05 mol) in carbon tetrachloride (200 mL) was passed dry chlorine gas at room temperature until the solution became deep red and further passage of chlorine did not produce any additional darkening in color. Solvent was removed *in vacuo*, the residue redissolved in carbon tetrachloride (50 mL) and the solvent again removed. The product was dissolved in diethyl ether (250 mL) and was used immediately without further purification.

Condensation with amine. To a vigorously stirred solution of the amine (0.2 mol) in dry diethyl ether (250 mL) was added dropwise the sulfenyl chloride (0.1 mol prepared as above) at room temperature. After the addition was complete, the solution was stirred for a further 10 min and the precipitated amine hydrochloride filtered off. The filtrate was removed *in vacuo* and the crude product recrystallized from light petroleum (bp 40–60°C). Products which were substantially colored were treated with activated charcoal before recrystallization. Sulfenamides prepared by this method are listed in Table I.

Normal phase TLC was performed on precoated Kieselgel 60 plates (E. Merck) with ethyl acetate-light petroleum (b.p. 40–60°C) (5:95) as developing solvent. The sulfenamides were split between two plates with compound **1** as a standard reference material on each plate. Compounds with $R\phi \geq 1.13$ were placed on one plate and those with $R\phi \leq 1.10$ on another. $R\phi$ values in this system have a reproducibility of ± 0.03. Reversed phase TLC was performed on paraffin-impregnated Kieselgel 60

TABLE VI

Gas chromatography of sulfenamides (Ar-S-NH-Ar') stationary phase: OV-17 (3% on Chromosorb W HP) at 185°C

Retention time min	Relative tr *	-CH_3 substituted compounds		-Cl substituted compounds		-OCH_3 substituted compounds	
		Ar	Ar'	Ar	Ar'	Ar	Ar'
9.35	1.00	C_6H_5	C_6H_5				
11.13	1.19			C_6H_5	2-Cl-C_6H_4		
11.18	1.20	C_6H_5	2-CH_3-C_6H_4				
11.31	1.21	2-CH_3-C_6H_4	C_6H_5				
13.44	1.44	C_6H_5	4-CH_3-C_6H_4				
13.55	1.45	4-CH_3-C_6H_4	C_6H_5				
15.66	1.67	2-CH_3-C_6H_4	2-CH_3-C_6H_4				
16.13	1.73	4-CH_3-C_6H_4	2-CH_3-C_6H_4				
17.16	1.84					C_6H_5	2-CH_3O-C_6H_4
19.13	2.05	2-CH_3-C_6H_4	4-CH_3-C_6H_4				
19.58	2.09	4-CH_3-C_6H_4	4-CH_3-C_6H_4				
19.98	2.14			4-Cl-C_6H_4	C_6H_5		
20.66	2.21			2-Cl-C_6H_4	C_6H_5		
22.80	2.44			C_6H_5	4-Cl-C_6H_4		
24.65	2.64			2-Cl-C_6H_4	2-Cl-C_6H_4		
28.00	2.99					C_6H_5	4-CH_3O-C_6H_4
51.78	5.54			4-Cl-C_6H_4	4-Cl-C_6H_4		

* tr retention time of compound/retention time of N-(phenyl) benzenesulfenamide

plates prepared by drawing through a solution (3% v/v) of liquid paraffin in light petroleum, allowing excess solution to drain off and solvent to evaporate in air from the suspended plates. Methanol-water (85:15) was used as developing solvent. Again the sulfenamides were divided between two plates with compound **1** as standard reference material on each plate. Compounds with $R\phi \geq 0.87$ were placed on one plate and those with $R\phi \leq 0.84$ on another. $R\phi$ values in this system have a reproducibility of ± 0.04. Spots were detected under short wavelength UV light.

HPLC employed a Waters Associates instrument equipped with two 6000 A pumps, U6K injector, 440 UV detector (254 nm), 730 data module and 720 system controller and separations were performed isocratically on a μBondapak C_{18} porasil column (3.9 nm × 30 cm; 10 μ particle size; Waters Associates) using methanol-water (60:40) as developing solvent at a flow rate of 2 mL/min. Peaks in Figure 1 were identified by comparison of the retention times with those of standard substances which had been injected one at a time.

GC employed a Hewlett Packard 5840A instrument equipped with flame ionization detector and separations were performed isothermally either at 160°C on OV-1 (10% on Chromosorb W HP (80–100 mesh; Johns-Manville); column 1.8 m × 3.2 mm; nitrogen flow rate 30 mL/min; injection temperature 250°C) or at 185°C on OV-17 (3% on Chromosorb W HP (80–100 mesh); column 1.8 m × 3.2 mm; nitrogen flow rate 30 mL/min; injection temperature 250°C). Peaks in Figures 2 and 3 were identified by comparison of the retention times with those of standard substances which had been injected one at a time.

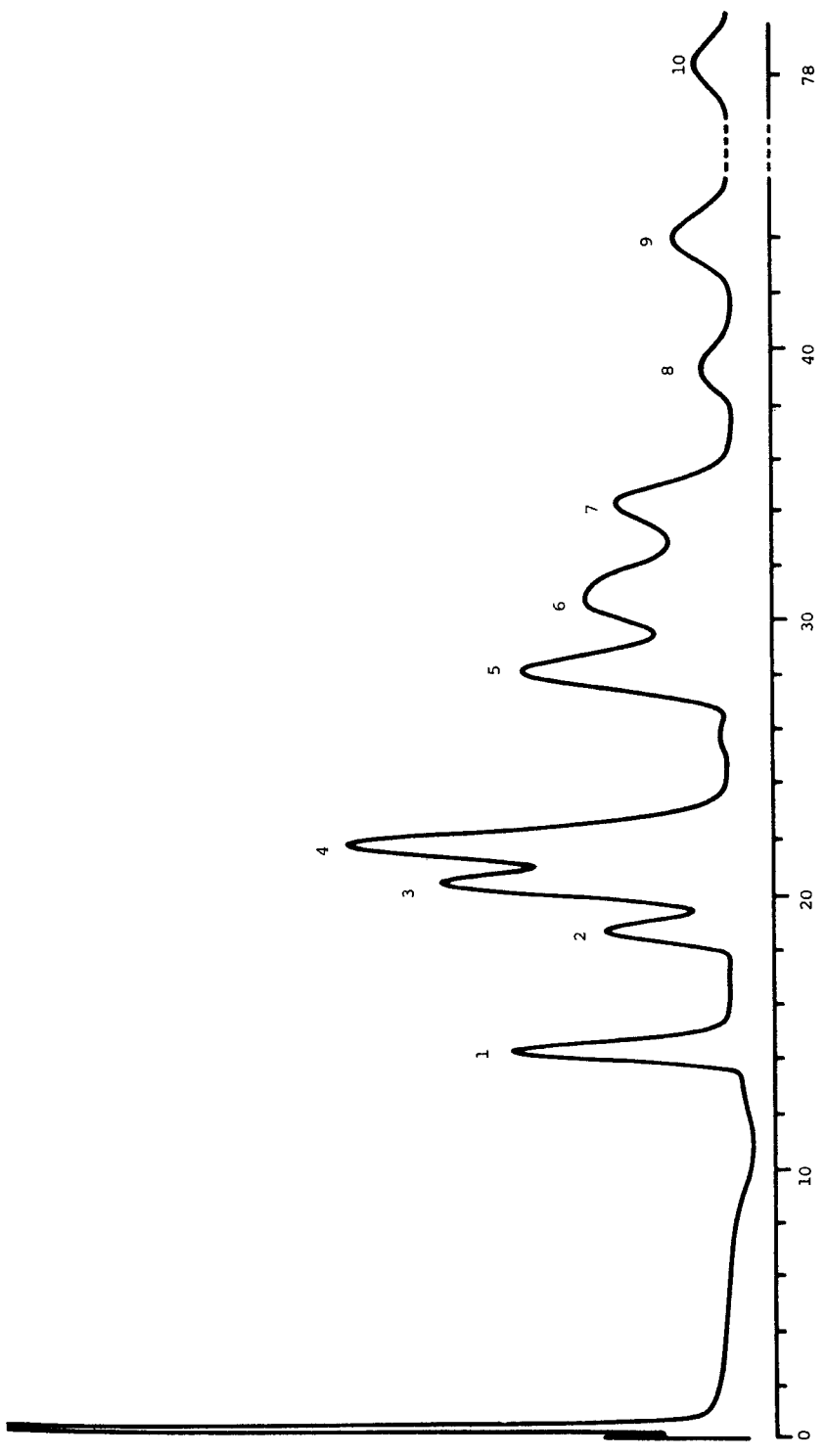

FIGURE 2 Separation of aryl sulfenamides by GLC on OV-1 (10% on Chromosorb W HP; column 6′ × 1/8″); oven 160°C isothermal; carrier gas nitrogen; flow rate 30 mL/min. **1**. Ph-S-NH-Ph; **2**. Ph-S-NH-C_6H_4-Cl(2); **3**. Ph-S-NH-C_6H_4-CH_3(2); **4**. (2)CH_3-C_6H_4-S-NH-Ph + Ph-S-NH-C_6H_4-CH_3(4) + (4)CH_3-C_6H_4-S-NH-Ph; **5**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2) + (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2) + Ph-S-NH-C_6H_4-OCH_3(2); **6**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4) + (2)Cl-C_6H_4-S-NH-Ph + (4)Cl-C_6H_4-S-NH-Ph; **7**. (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4) + Ph-S-NH-C_6H_4-Cl(4); **8**. Ph-S-NH-C_6H_4-OCH_3(4); **9**. (2)Cl-C_6H_4-S-NH-C_6H_4-Cl(2); **10**. (4)Cl-C_6H_4-S-NH-C_6H_4-Cl(4).

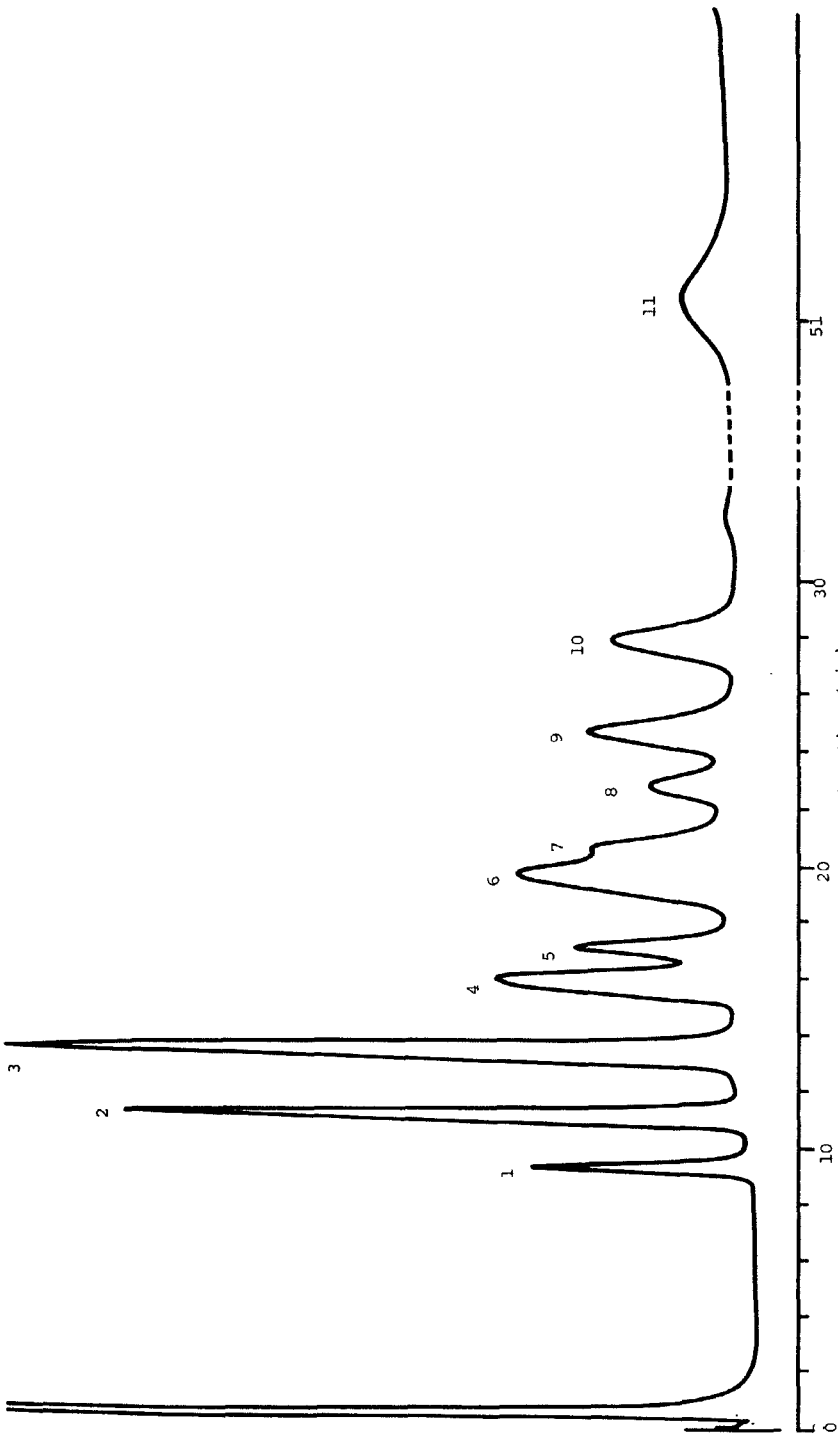

FIGURE 3 Separation of aryl sulfenamides by GLC on OV-17 (3% on Chromosorb W HP (column 6′ × 1/8″); oven 185°C isothermal; carrier gas nitrogen; flow rate 30 mL/min. **1**. Ph-S-NH-Ph; **2**. Ph-S-NH-C_6H_4-CH_3(2) + (2)CH_3-C_6H_4-S-NH-Ph + Ph-S-NH-C_6H_4-Cl(2); **3**. Ph-S-NH-C_6H_4-CH_3(4) + (4)CH_3-C_6H_4-S-NH-Ph; **4**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2) + (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(2); **5**. Ph-S-NH-C_6H_4-OCH_3(2); **6**. (2)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4) + (4)CH_3-C_6H_4-S-NH-C_6H_4-CH_3(4); **7**. (4)Cl-C_6H_4-S-NH-Ph + (2)Cl-C_6H_4-S-NH-Ph **8**. Ph-S-NH-C_6H_4-Cl(4); **9**. (2)Cl-C_6H_4-S-NH-C_6H_4-Cl(2); **10**. Ph-S-NH-C_6H_4-OCH_3(4); **11**. (4)Cl-C_6H_4-S-NH-C_6H_4-Cl(4).

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