

CHROM. 9695

## Note

## Separation of aromatic sulphinylamines by thin-layer chromatography

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(Received May 28th, 1976)

Recently, it has been found that aromatic N-sulphinylamines (Ph-N=S=O) form interesting donor-acceptor systems<sup>1</sup>, and have been increasingly used in the

TABLE I  
SOLVENT SYSTEMS EMPLOYED TO SEPARATE DIMETHYLSULPHINYLAMINE ISOMERS

No.	Solvent system
I*	Chloroform- <i>n</i> -hexane (80:20)
II*	Benzene-amyl alcohol-carbon tetrachloride (20:10:70)
III*	Benzene- <i>n</i> -hexane-diethyl ether (60:20:20)
IV	Benzene-acetone-chloroform (40:10:50)
V*	Carbon tetrachloride- <i>n</i> -hexane-diethyl ether (50:10:40)
VI*	Carbon tetrachloride-chloroform-diethyl ether (50:10:40)
VII	Chloroform-ethyl acetate- <i>n</i> -hexane (40:40:20)
VIII	Carbon tetrachloride-amyl alcohol (75:25)
IX	Benzene- <i>n</i> -hexane-ethyl acetate (70:20:10)
X	Benzene

\* With these systems, the development of the chromatogram was carried out twice.

TABLE II  
 $R_F \times 100$  VALUES OF DIMETHYLSULPHINYLAMINES

Dimethylsulphinylamine	Solvent system*							
	I		II		III		IV	
	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$
2,6-Dimethylsulphinylaniline	52	55	69	69	43	43	50	49
2,5-Dimethylsulphinylaniline	47	48	65	64	37	36	45	44
2,3-Dimethylsulphinylaniline	44	45	60	57	32	31	42	41
2,4-Dimethylsulphinylaniline	40	41	54	47	31	31	41	41
3,5-Dimethylsulphinylaniline	42	41	58	57	30	31	41	41
3,4-Dimethylsulphinylaniline	36	33	48	50	24	23	37	36

\* Solvent systems according to Table I.

\*\*  $R_F \times 100$  for single samples.

\*\*\*  $R_F \times 100$  for mixtures of dimethylsulphinylamine isomers.

synthesis of organic chemicals<sup>2-6</sup>. The trans-sulphinylation reaction was developed and its kinetics were investigated using gas chromatography<sup>7</sup>. A thermal analytical examination carried out previously enabled us to measure the stabilities of isomeric derivatives of tolylsulphinylaniline, chlorosulphinylaniline and  $\alpha$ - and  $\beta$ -naphthylsulphinylanilines<sup>8</sup>. A gas chromatographic method for the analysis of arylsulphinylamines has been described<sup>9</sup>, but so far thin-layer chromatography (TLC) has not been used because of problems in carrying out analyses in an entirely non-aqueous medium.

In this paper, we describe TLC investigations of the isomeric dimethylsulphinylanilines.

## EXPERIMENTAL

### *Reagents and materials*

The following pure reagents were used: benzene (POCh, Gliwice, Poland); chloroform (POCh); *n*-hexane (VEB Jenapharm-Laborchemie, Apolda, G.D.R.); amyl alcohol (POCh); carbon tetrachloride (POCh); diethyl ether (POCh); acetone (Z. Chem. Oświęcim, Poland); and ethyl acetate (POCh). The solvents were dehydrated and distilled under vacuum, and amounts of moisture present were tested using the Van der Meulen reagent and by means of gas-liquid chromatography.

Silica gel on aluminium TLC sheets (20 × 20 cm), layer thickness 0.25 mm, were used (Cat. No. 5553; Merck, Darmstadt, G.F.R.).

### *Dimethylsulphinylamines*

The dimethylsulphinylamines were prepared by the Michaelis and Herz method<sup>10</sup>, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethylsulphinylaniline being investigated. The purities of the products were checked by using NMR and mass spectrometry and gas-liquid chromatography.

To protect the dimethylsulphinylamines against moisture, they were stored in sealed glass ampoules.

V		VI		VII		VIII		IX		X	
$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$	$R_F^{**}$	$R_F^{***}$
65	63	54	53	47	46	61	63	60	62	20	24
57	58	45	44	42	42	50	55	50	52	17	18
53	51	40	41	40	40	45	49	46	47	14	15
50	51	38	38	39	40	47	49	44	45	13	15
80	79	37	38	40	40	53	55	44	45	13	15
77	79	35	32	37	37	41	39	43	45	10	10

### Procedure

The aromatic sulphinylamines were used as 20% solutions in benzene, and the solution of the sample was prepared by mixing 1 cm<sup>3</sup> of each benzene solution. The solutions of the samples and those of the standard substances were placed on the plate 3 cm from the edge, and the plate was then dried for 5 min at 60°. The dried plate was inserted in a chromatographic chamber lined with filter-paper saturated with the solvent system. The migration distance of the solvent front was 15 cm.

A gaseous developing agent, nitrogen dioxide, was used, which was prepared by dropping 3–4 cm<sup>3</sup> of hydrochloric acid (1:1) into 10 cm<sup>3</sup> of 20% sodium nitrite solution. The nitrogen dioxide liberated was collected under a 5-l cover-glass for 3 min, then the plate bearing the developed and dried chromatogram was placed under the cover-glass. After 30–60 sec, the plate was removed from under the cover-glass and allowed to stand in air for 24 h until yellow, orange and red-brown, well-rounded spots appeared.

### RESULTS

To study optimal TLC conditions for the separation of the dimethylsulphinylamines, a variety of polar and non-polar solvent systems were employed (Table I). The  $R_F$  values obtained are summarized in Table II.

The spots were eluted from the plate using benzene and then identified by GLC. It was found that the spots remained stable and were not subject to hydrolysis on silica gel.

The dimethylsulphinylamines are very alike in their behaviour, especially 2,3-, 2,4- and 3,5-dimethylsulphinylaniline, which led to considerable difficulties in their separation, although the chromatograms were developed twice. The best separation was obtained with solvent systems I, II and VI, where the differences in the  $R_F$  values were sufficient to enable the mixtures to be completely separated in routine work. 2,6-, 2,5- and 3,4-dimethylsulphinylaniline showed considerable differences in their  $R_F$  values.

TABLE III  
COLOURS OF SPOTS OF DIMETHYLSULPHINYLAMINES

<i>Dimethylsulphinylamine</i>	<i>Colours of spot</i>
2,6-Dimethylsulphinylaniline	Bright yellow
2,5-Dimethylsulphinylaniline	Red-orange
2,3-Dimethylsulphinylaniline	Bright orange
2,4-Dimethylsulphinylaniline	Bright brown
3,5-Dimethylsulphinylaniline	Dark red
3,4-Dimethylsulphinylaniline	Brown

It was found that with a short developing time (30–60 sec) in the nitrogen dioxide atmosphere, the individual isomeric dimethylsulphinylamines could be identified on the chromatograms by using the specific colours of the spots (Table III).

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