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Note

Separation of aromatic sulphinylamines by thin-layer chromatography. II

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The analysis of dichlorosulphinylamine isomers described here is a continuation of earlier thin-layer chromatographic (TLC) studies on arylsulphinylamines^{1,2}. Examination by thermal analysis has enabled the stability of the arylsulphinylamines to be determined³, making it possible to apply gas chromatography for their analysis^{4,5}.

The arylsulphinylamines show extremely high reactivity, owing to the sulphinyl group, Ar-N=S=O, which makes them suitable for use in certain chemical processes^{6,7}. The dipole moments and proton magnetic resonance spectra of substituted N-sulphinylanilines indicate that these compounds adopt preferentially a *cis*- or *syn*-structure (*Z*-configuration) with respect to the central N=S bond⁸⁻¹⁰. The *trans*-sulphinylation reaction was developed and its kinetics were investigated using gas chromatography¹¹.

In this paper we describe TLC investigations of isomeric dichlorosulphinylanilines.

EXPERIMENTAL

Reagents and materials

The following pure reagents were used: benzene, chloroform, amyl alcohol, carbon tetrachloride, diethyl ether and ethyl acetate (POCh, Gliwice, Poland); *n*-hexane (VEB Jenapharm-Laborchemie, Apolda, G.D.R.); and acetone (Chem. Inds., Oświęcim, Poland). The solvents were dehydrated and distilled under vacuum, and the 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 (DC-Alufolien Kieselgel, Art. 5553, Merck, Darmstadt, G.F.R.) 20 × 20 cm, layer thickness 0.25 mm, were used.

Dichlorosulphinylamines. The dichlorosulphinylamines were prepared by the Michaelis and Herz^{12,13} method, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorosulphinylaniline being investigated. The purities of the products were checked by using NMR and mass spectrometry and gas-liquid chromatography.

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

Procedure

The aromatic sulphinylamines were used as 20% solutions in benzene, and a mixed solution was prepared by mixing 1 cm³ of each benzene solution. The solutions of the samples and those of standard substances were placed on the plate 2.5 cm from the edge, and the plate was then dried for 5 min at 60–70°. 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 1–5 ml of hydrochloric acid (18%) into 10 ml of 20% sodium nitrite solution. The nitrogen dioxide liberated was collected under a 5-l cover-glass for 30 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 well rounded yellow, orange and brown spots appeared.

RESULTS

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

TABLE I
SOLVENT SYSTEMS EMPLOYED TO SEPARATE DICHLOROSULPHINYLAMINES

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

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

The dichlorosulphinylamines are very alike in their behaviour, especially 2,3- and 2,4-dichlorosulphinylaniline, which led to considerable difficulties in their separation even though the chromatograms were developed twice. The best separation was obtained with solvent systems III, VI, VII and IX, where the differences in the R_F values were sufficient to enable the mixtures to be completely separated in routine work. 2,5-, 2,6-, 3,4- and 3,5-dichlorosulphinylaniline showed considerable differences in their R_F values.

TABLE II

 $R_F \times 100$ VALUES OF DICHLOROSULPHINYLAMINESa, $R_F \times 100$ for single samples; b, $R_F \times 100$ for mixtures of dichlorosulphinyamine isomers.

Dichloro- sulphinyl- amine	Solvent system*																					
	I		II		III		IV		V		VI		VII		VIII		IX		X		XI	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
2,3-	54	54	71	68	60	61	70	71	70	71	70	68	71	70	75	75	60	60	63	60	47	48
2,4-	53	54	68	68	55	54	70	71	66	67	69	68	71	70	75	75	58	60	62	60	49	48
2,5-	63	63	72	73	60	61	75	75	74	76	77	77	75	75	80	81	65	66	70	69	60	60
2,6-	73	72	79	78	74	74	78	75	84	84	83	85	81	81	85	85	75	76	80	79	73	72
3,4-	37	33	55	52	34	34	60	60	62	63	47	43	58	55	57	53	38	39	46	46	30	30
3,5-	54	52	63	59	48	42	69	68	67	67	62	57	67	63	68	67	56	57	60	60	47	48

* Solvent systems according to Table I.

TABLE III

COLOURS OF SPOTS OF DICHLOROSULPHINYLAMINES

Dichlorosulphinyamine	Colour of spot
2,3-	Orange
2,4-	Brown
2,5-	Bright yellow
2,6-	Bright brown
3,4-	Dark red
3,5-	Red-orange

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

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