

## Thin layer chromatography of aliphatic nitramines

Availability of numerous cyclic and linear nitramines resulting from recent acetolysis and nitrolysis studies<sup>1</sup> in these laboratories encouraged an investigation of their thin layer chromatographic behaviour. The results, which extend studies of HARTHON<sup>2</sup>, HANSSON<sup>3</sup>, and FAUTH AND ROECKER<sup>4</sup>, have been applied to the separation of many complex reaction mixtures.

### *Experimental*

*Materials.* Most of the nitramines examined were prepared by published methods (references are given in Table I) although some compounds were obtained from our departmental collection. Purity of samples was established by measuring melting points and infrared spectra.

Analar-grade solvents were used; solvent mixtures containing nitromethane (redistilled) were kept overnight over molecular sieve 4A before use.

*Method.* Thin layers (0.3 mm) of Silica gel G on glass plates (10 × 20 cm) were dried in air overnight, then activated at 110° for 30 min and stored in Camag drying racks over calcium chloride. Nitramines were applied in acetone (5 μl of 1% solution), then the thin layer chromatograms were developed with one of the following solvent systems:

- A Benzene–nitromethane (2:1)
- B Chloroform–nitromethane (10:1)
- C Light petroleum (b.p. 40–60°)–acetone (2:1.2)
- D Ether–acetone (10:1).

One or more spots of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) were placed on each plate to check operating conditions. Development took place in filter paper-lined chambers previously saturated with solvent vapour for 1 h. After solvents had travelled 10 cm up the plates, the chromatograms were dried in a current of warm air. Chromatograms developed with solvent mixtures A, B, or C were replaced in the appropriate chamber and subjected to a second development.

The dried plates were sprayed with diphenylamine in ethanol (1% solution) and irradiated with U.V. light<sup>5</sup>.

### *Results and discussion*

The spray reagent varied in sensitivity towards the compounds listed in Table I. After being irradiated for 30 min most of the nitramines gave purple-grey spots on a tan-coloured background. Compounds containing the nitroxy group (*e.g.* compounds nos. 14, 24 and 26) gave distinctive blue colours which developed rapidly under U.V. light. Only poorly-defined spots accompanied by considerable streaking were obtained with 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (compound no. 36) and it was difficult to identify this compound in mixtures. Difficulty was also experienced in detecting the presence of dinitropentamethylenetetramine (compound no. 47); the compound appeared as a colourless spot on a brown background after prolonged irradiation. Nitrosamines gave a characteristic yellow-brown colour which developed rapidly.

Use of light petroleum–acetone (solvent C) was previously recommended by HARTHON<sup>2</sup> for separating aliphatic nitramines on Silica gel G plates. The present

TABLE I  
THIN LAYER CHROMATOGRAPHY OF ALIPHATIC NITRIMINES

Nitramine Formula	Distance of travel (mm)						Alumina G				
	No. n	R	R'	Trivial name	Ref. to preparation	A*	B	C	D	A	B
$\begin{array}{c} \text{NO}_2 \\   \\ \text{N} \\ / \quad \backslash \\ (\text{H}_2\text{C})_n \quad \text{CH}_2 \\ \backslash \quad / \\ \text{N} \\   \\ \text{NO}_2 \end{array}$	1				6	70	69				
	2				1	71	73				
	3				1	69	71				
	4										
$\begin{array}{c} \text{NO}_2 \\   \\ \text{N}-\text{CH}_2 \\ / \quad \backslash \\ (\text{H}_2\text{C})_n \quad \text{N}-\text{R} \\ \backslash \quad / \\ \text{N}-\text{CH}_2 \\   \\ \text{NO}_2 \end{array}$	4	NO <sub>2</sub>		RDX	7	67	48	44	41	67	49
	5	NO			1, 8	67	48	41	39		
	6	COCH <sub>3</sub>		TAX	9, 10	32	15	31			
	7	NO <sub>2</sub>		Homo-RDX	11	63	43				
	8	NO			1	65	54	49			
	9	COCH <sub>3</sub>			1, 11	25	12				
	10	NO <sub>2</sub>			1, 12	57	27				
	11	NO			1	49	25	20			14
	12	COCH <sub>3</sub>			1	17	5				
	13	H		MEDNA	13	37 (c)**	16 (c)				
	14	CH <sub>2</sub> ONO <sub>2</sub>		COX	14	79	78				
	15	CH <sub>2</sub> OCOCH <sub>3</sub>		TEX	15, 16	59	65				
16	CH <sub>2</sub> OCH <sub>3</sub>			17	62	69					
17	H		EDNA	18	24 (c)	6 (c)					
18	CH <sub>2</sub> OCOCH <sub>3</sub>			11	49	47					
19	CH <sub>2</sub> OCH <sub>3</sub>			15	56	58					
20	H			15	32 (c)	8 (c)					
21	H			15	25 (c)	6 (c)					
22	CH <sub>3</sub>	H		19	54	40					
23	n-C <sub>4</sub> H <sub>9</sub>	H		20	69	65					
24	CH <sub>2</sub> ONO <sub>2</sub>	CH <sub>2</sub> ONO <sub>2</sub>		21	81	82					
25	CH <sub>2</sub> OCOCH <sub>3</sub>	CH <sub>2</sub> OCOCH <sub>3</sub>		9	62	72					
26	ONO <sub>2</sub>	ONO <sub>2</sub>		9	77	70					
27	OCOCH <sub>3</sub>	OCOCH <sub>3</sub>		22, 23	56	58		55	82	71	78
28	OCH <sub>3</sub>	OCH <sub>3</sub>		9	60	66					
29	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>		9	73	77					
30	OCOCH <sub>3</sub>	OCOCH <sub>3</sub>		1	57	60					
31	OCOCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>		9	64	70					
			ATX	9	77	70					
			BSX	22, 23	56	58					
			"104"	9	60	66					
			"107"	9	73	77					
				1	57	60					
				9	64	70					

NOTES

Structure	32	3	H	ONO <sub>2</sub>	NSX	24, 25	71	68
$R(CH_2N)_nCH_2R'$	32	3	H	ONO <sub>2</sub>	NSX	24, 25	71	68
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	33	3	H	OCOCH <sub>3</sub>	MSX	24, 25	61	63
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	34	3	H	OCH <sub>3</sub>		24, 25	61	65
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	35	3	H	OC <sub>2</sub> H <sub>5</sub>	"106"	26	69	72
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	36	4	ONO <sub>2</sub>	ONO <sub>2</sub>		27	75 (c)	0
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	37	4	OCOCH <sub>3</sub>	OCOCH <sub>3</sub>	AcAn	27	46	42
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	38	4	OCH <sub>3</sub>	OCH <sub>3</sub>		27	57	56
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	39	4	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>		27	68	70
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	40	4	OCOCH <sub>3</sub>	OCH <sub>3</sub>		1	50	46
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	41	4	OCOCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>		1	59	55
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	42		NO <sub>2</sub>	NO <sub>2</sub>	HMX	23	48	9
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	43		NO <sub>2</sub>	NO	MNX	28	46	10
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	44		NO <sub>2</sub>	COCH <sub>3</sub>	SEX	28, 29	19	3
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	45		NO	NO		1	40	7
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	46		NO	COCH <sub>3</sub>	QNX	28	14	2
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	47		NO <sub>2</sub>		DPT	21, 23	43	
$\begin{matrix} NO_2 \\   \\ H_2C-N-CH_2 \\   \quad   \\ R \cdot N \quad N \cdot R' \end{matrix}$	48		NO		Dinitroso-PT	28	17	28
$(H_2C)_n \begin{matrix} NO_2 \\   \\ NCH_2OCOCH_3 \\   \\ (NCH_2)_2OCOCH_3 \\   \\ NO_2 \end{matrix}$	49				Homo-BSX	11	45	39
$\begin{matrix} NO_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ O \end{matrix}$	50				Cyclonite oxide	17, 30	71	72
$\begin{matrix} NO_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ N-NO \end{matrix}$	51 <sup>***</sup>					28	64	54
$\begin{matrix} NO_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ N-CH_2 \\   \\ N \end{matrix}$								50

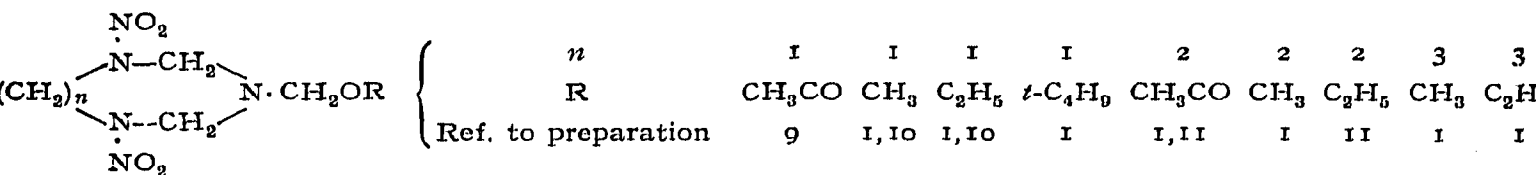
\* The letters refer to the solvent systems and development methods used (p. 253).  
 \*\* Spots accompanied by comet formation are indicated by (c).  
 \*\*\* This compound is included for comparison purposes.

work, whilst confirming HARTON's results, shows that the solvent mixture is not satisfactory for separating mixtures containing 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (compound no. 37); even when applied to the plate as a single compound this diacetate gave a poor spot with extensive comet formation. The compound showed better chromatographic behaviour on plates developed with benzene-nitromethane (solvent A) and this solvent mixture was suitable for most of the compounds in Table I.

Chloroform-nitromethane (solvent B) and ether-acetone (solvent D) were examined as alternative solvent systems for some separations. The former was particularly useful for separating mixtures of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane (compound no. 42) and 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (compound no. 37), compounds not separated by benzene-nitromethane. Cyclic nitramines containing nitrosamine groups were best separated by ether-acetone (solvent D); well-defined spots were obtained and only one development was necessary.

Examination of the results shows that rates of movement of linear nitramines on chromatograms developed with solvents A and B are related to chain length and the nature of the end groups. For a given chain length, distances of travel, when solvent A is used, follow the order: nitroxy- > ethoxy- > methoxy- > acetoxy-terminated chains; with solvent B, the order is: ethoxy- > nitroxy- > methoxy- > acetoxy-terminated chains. Shorter chain compounds travel more rapidly in both solvents, but the effect of chain-length is more marked with solvent B. The exceptional behaviour of 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (compound no. 36) with solvent B may be due to a solubility effect.

Unsuccessful attempts were made to determine distances of travel for compounds of the general formula:



These nitramines and the related eight-membered ring compound, 1-acetoxy-methyl-3,5,7-trinitro-1,3,5,7-tetrazacyclo-octane (PHX)<sup>31</sup>, failed to give detectable spots on plates developed with solvents A or B. The method was also unsuitable for detecting 3,5-dinitro-1,3,5-triazacyclohexane nitrate (PCX)<sup>32</sup>; the compound, or its decomposition products, gave a coloured spot at the origin of the developed chromatogram.

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## Preparation of a firm polyamide adsorbent for thin-layer chromatography

A thin-layer chromatographic procedure which accomplishes the separation of isomeric flavanones has been reported<sup>1</sup>. The adsorbent employed is Polyamide Woelm\* applied to glass plates as a slurry of 1 part polyamide in 7.5 parts benzene-methanol (2:3, v/v). However, due to the fragility of this adsorbent layer, the handling of the plate, removal of areas by scraping, marking and application of sample must be performed with extreme care. Furthermore, the flakiness of this adsorbent layer seriously reduces its use in autoradiography. This flakiness also increases the probability of instrument contamination when using a radiochromatogram scanner for locating radioactive areas.

The purpose of this investigation was to find a method which would give a firm polyamide layer and retain the polyamide's resolving power. Such a procedure has been found and studied with various flavonoids and under conditions necessary for the detection of radioactive areas.

\* Use of a company and/or product name by the department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.