

**Note**

**Thin-layer chromatography of 2,4-dinitrobenzenediazonium coupling products with malononitrile and some analogues**

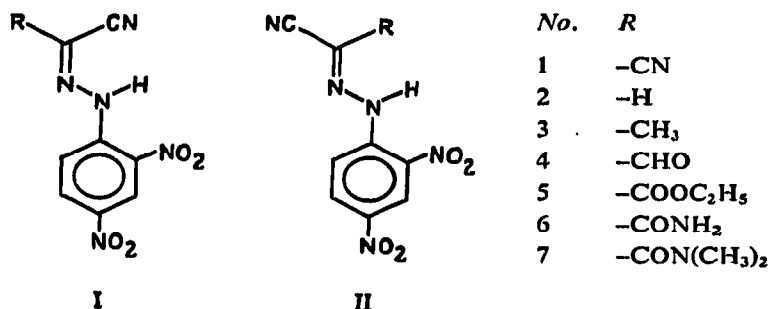
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2,4-Dinitrobenzenediazonium tetrafluoroborate<sup>1</sup> has been used for the analysis of phenols in the form of dinitrophenylazophenols<sup>2</sup>. The high coupling activity of the salt suggests its use also in the analysis of other types of compounds that undergo the coupling reaction to form 2,4-dinitrophenylhydrazones (DNPHs), e.g., activated methylene compounds. Dinitrobenzenediazonium salts also couple with ketones and aldehydes<sup>3</sup>, but at a slower rate. The strong golden yellow, orange or red colour reaction obtained from the coupling products with bases may therefore serve as a basis for a simple and sensitive spot test for activated methylene compounds in the presence of aldehydes and ketones. When combined with thin-layer chromatography (TLC), the derivatives may also be used for identification purposes. In the latter form of analysis, the possibility of *cis-trans* isomer pairs should be considered; these often appear as separate spots on the chromatograms.

The isomeric DNPHs I and II obtained from various cyanoacetic acid derivatives (Nos. 1 and 4-7) have now been isolated and examined, as part of a study of



the structure, properties and chromatographic behaviour of DNPHs. In this paper, the TLC of the compounds is described and discussed, and their structural features<sup>4</sup> and acid strengths<sup>5</sup> will be considered elsewhere. Compounds Nos. 2 and 3 were included for comparison.

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## EXPERIMENTAL

For analytical purposes, about 0.1 mg of the methylene compound, or an equivalent amount of test solution, was dissolved in 0.2 ml of acetonitrile (p.a. grade, Fluka, Buchs, Switzerland), and a slight excess (0.5 mg) of solid 2,4-dinitrobenzene-diazonium tetrafluoroborate<sup>1</sup> added. After 5 min, 2 ml of 1% sulphuric acid was added, and the coupling products were extracted into 0.5 ml of ethyl acetate. The same procedure was easily applied at one tenth of this scale, using small glass tubes.

The preparation of the pure compounds on the gram scale will be described elsewhere<sup>4</sup>.

The coupling reaction to form hydrazones Nos. 4–7 leads to the exclusive formation of the *syn*-CN isomer (I). The other isomer is formed slowly from I on standing in neutral solution at room temperature, or rapidly on irradiation in solution, or on the silica gel layer, with ultraviolet light (366 nm).

Orientating work was carried out on 26 × 76 mm slides coated with a 0.25-mm layer of Kieselgel PF<sub>254</sub> (E. Merck, Darmstadt, G.F.R.). The *R<sub>F</sub>* values (Table I) were measured on MN Polygram Sil-H/UV 254 sheets (10 × 10 cm; 8.4 cm solvent movement) at 20–25° in horizontal cabinets<sup>2</sup>. For separation on an acid layer (*cf.*, solvent S<sub>8</sub> in Table I), the sheet was dipped in 0.5% sulphuric acid in acetone and air-dried.

TABLE I

*R<sub>F</sub>* × 100 VALUES OF 2,4-DINITROPHENYLHYDRAZONES OF MESOXALONITRILE AND SOME ANALOGUES ON SILICA GEL

Solvents: S<sub>1</sub> = light petroleum (boiling range 60–80°)–ethyl acetate (1:1); S<sub>2</sub> = 1,1,1-trichloroethane; S<sub>3</sub> = 1,1,1-trichloroethane–ethyl acetate (9:1); S<sub>4</sub> = light petroleum (boiling range 60–80°)–ethyl acetate–triethylamine (2:2:0.5); S<sub>5</sub> = diisopropyl ether–1,1,1-trichloroethane–isopropyl acetate (3:1:0.5); S<sub>6</sub> = toluene; S<sub>7</sub> = toluene–ethyl acetate (9:1); S<sub>8</sub> = acid layer (see text) with solvent S<sub>1</sub>.

No.	<i>R</i> in I or II	Configuration		Colour*** with Et <sub>2</sub> NH	<i>R<sub>F</sub></i> × 100 <sup>§</sup>							
		Position of CN*	IUPAC**		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>	S <sub>8</sub>
1	CN	—	—	gy	12s <sup>§§</sup>	08s <sup>§§</sup>	15s <sup>§§</sup>	02 <sup>§§</sup>	04 <sup>§§</sup>	34 <sup>§§</sup>	54 <sup>§§</sup>	61 <sup>§§§</sup>
2	H	<i>anti</i> (II)	E	or	61	20	49	19	45	22s	64	57
		<i>syn</i> (I)	Z	or	51	48	55	35	45	40s	64	50
3	CH <sub>3</sub>	<i>anti</i> (II)	E	r	61	25	60	27	53	44s	70	57
		<i>syn</i> (I)	Z	r	55	38	63	47	53	44s	70	53
4	CHO	<i>syn</i> (I)	E	gy	24s <sup>§§</sup>	10s <sup>§§</sup>	20s <sup>§§</sup>	00 <sup>§§</sup>	16s <sup>§§</sup>	14s <sup>§§</sup>	47 <sup>§§</sup>	46 <sup>§§§</sup>
5	COOC <sub>2</sub> H <sub>5</sub>	<i>anti</i> (II)	Z	or	63	33	63	03	57	41	77	60
		<i>syn</i> (I)	E	or	56	20	53	00	49	13	64	55
6	CONH <sub>2</sub>	<i>anti</i> (II)	Z	gy	42	04	20	02	29	02	27	42
		<i>syn</i> (I)	E	or-r	09	00	03	00	04	00	03	10
7	CON(CH <sub>3</sub> ) <sub>2</sub>	<i>anti</i> (II)	Z	or	43	13	47	04	36	03	51	42
		<i>syn</i> (I)	E	or	16	03	19	00	11	00	10	17

\* *Cf.*, I and II.

\*\* Ref. 6.

\*\*\* gy = Golden yellow; or = orange; r = red.

§ s = Streaking.

§§ Moving as golden yellow spot.

§§§ Moving as faint yellow spot.

## RESULTS AND DISCUSSION

The low mobilities of Nos. 1 and 4 in most solvents, and the colour of their spots on neutral silica gel, suggest that they move in the form of anions; this is confirmed by the marked changes in  $R_F$  values and colour on pre-treating the TLC plate with sulphuric acid. The acid strengths of Nos. 1 and 4 ( $pK_a$  3.11 and 3.5, respectively<sup>5</sup>) are far below the pH of the neutral silica gel layer (7–7.5), and explain the full ionization of the compounds.

The *syn*-acyl isomers of Nos. 5–7 move the most rapidly of the isomers, as the chromatographically active NH hydrogen<sup>2</sup> is more strongly chelated than in the *syn*-CN isomer. In Nos. 2 and 3, this order is reversed: in spite of the *syn*-CN isomer apparently having the more strongly bonded NH hydrogen (to both cyano- and 2-nitro-groups), it moves more slowly than the other isomer, in which NH is bonded only to a nitro-group. This order corresponds with the relative acid strengths of the isomers<sup>5</sup>; in the absence of other hydrogen-donating groups, the chromatographic activity of the compounds depends mainly on the activity of the NH group<sup>2</sup>, and hence should be directly related to the acidity of this group, as far as the conditions on the silica gel layer and in aqueous dimethyl sulphoxide solution<sup>5</sup> can be compared. The greater acidity of the NH group of the *syn*-CN isomers of Nos. 2 and 3, relative to the other isomer, was explained<sup>5</sup> by the lack of mesomeric effects in the chelate "5½" ring.

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