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Short Communication

2-Trichloromethylbenzimidazole, a selective chromogenic reagent for the detection of *o*-phenylenediamine on thin-layer plates

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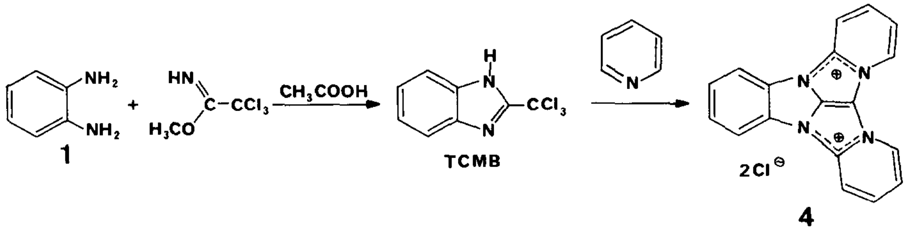
ABSTRACT

A new, selective method for the detection of *o*-phenylenediamine and some of its derivatives on thin-layer plates is described. *o*-Phenylenediamine is treated with methyl trichloromethylacetimidate and exposed to pyridine vapours. The derivatization is performed before the chromatography or *in situ* on the thin-layer chromatographic plate. The detection limit is between 80–2000 ng, depending on the procedure and the compound detected.

INTRODUCTION

In previous papers [1,2], the application of 2-trichloromethylbenzimidazole (TCMB) for the detection of the azines on thin-layer chromatographic (TLC) plates was described. TCMB was synthesized from *o*-phenylenediamine (**1**) and methyl trichloroacetimidate [3] and was then used as a spray reagent for the detection of the azines on TLC plates due to the formation of a highly coloured product (**4**):



The most probably structure of the major component of **4** seems to be 4*a*,4*c*,8*b*,12*b*-tetraazadibenzo[*a*,*f*]lindano[1,2,3-*cd*]pentalene-4*a*,4*c*-diinium dichloride dihydrate [2].

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The analogous spray reagent *o*-phenylenediamine (**1**)–trichloroacetic acid is also known [4–6], but this mixture is not a source of TCMB [3]. It appears that the reaction of **1** with methyl trichloroacetimidate is the only way to synthesize TCMB [3].

In this work, the reaction pathway shown above was applied to the selective detection of **1** and some its derivatives on TLC plates.

EXPERIMENTAL

Materials

Methyl trichloroacetimidate [7] was purified by distillation over anhydrous potassium carbonate (b.p. 150–152°C). Pre-coated silica gel 60 F_{254} plastic sheets, 0.2 mm thick (Merck, Darmstadt, Germany) were used for TLC. All tested amines were of analytical-reagent grade.

Detection of o-phenylenediamine

Procedure A. Methyl trichloroacetimidate (150 μl) was added to 1 ml of a solution of **1** (100–1000 μg) in acetic acid and the mixture was shaken once and left for 15 min. A 1-μl volume of the solution obtained was spotted directly on the TLC plates. Chromatograms were developed in acetone as eluent; the migration distance was 8 cm. The dried chromatograms were placed in pyridine vapour at room temperature. The colour appeared after 10–20 min.

Procedure B. A solution of **1** (50–1000 ng) in acetone was spotted on the TLC plate and developed with acetone. The dried chromatograms were sprayed with 10% methyl trichloroacetimidate in glacial acetic acid, allowed to stand for 15 min and placed in pyridine vapour.

Procedure C. A solution of **1** (1–10 μg) in acetone, methyl trichloromethylacetimidate (1 μl) and acetic acid (10 μl) were succesively spotted on the TLC plate. After 15 min the plates were dried, developed and detected in pyridine vapour.

RESULTS AND DISCUSSION

The results are presented in Table I. No difference was observed between procedures A and B, but procedure C seems to be less sensitive. The detection limit was less than 100 ng and depends on the procedure.

TABLE I

DETECTION LIMITS, R_FVALUES AND COLOURS OF THE AROMATIC DIAMINES EXAMINED ON TLC PLATES

1,2-Diamine	Procedure	R_F	Colour (for 1000 ng in spot)	Detection limit (ng)
o-Phenylenediamine (**1**)	A,B	0.67	Amaranth-brown	100
	C		Amaranth-brown	2000
3,4-Diaminotoluene (**2**)	A,B	0.58	Brown	100
4-Nitro-*o*-phenylenediamine (**3**)	A	0.66	Brown	80

Of the other compounds tested, 3,4-diaminotoluene (**2**) and 4-nitro-*o*-phenylenediamine (**3**) gave similar results to **1**. The following compounds gave no colour using any of the procedures: 1,2- and 2,3-naphthylenediamine and 2,3-diaminophenazine (all *ortho*-substituted) and 1,8-naphthylenediamine (*peri*-), probably for steric reasons; 1,2-ethylenediamine, 2,3-dimethyl-2,3-butylenediamine and *m*- and *p*-phenylenediamine, because the aromatic benzimidazole ring cannot be formed; *o*-aminophenol and N-methyl-*o*-phenylenediamine, which probably form a suitable benzoxazole or benzimidazole ring in the reaction with methyl trichloroacetimidate, but the heterocyclic obtained do not react subsequently with pyridine and the formation of another highly coloured product such as **4** does not occurs; and 2-amino-3-hydroxyphenazine for the same reason and also for steric reasons.

The R_F values, spot colours and detection limits of the aromatic 1,2-diamines **1**–**3** are presented in Table I.

This highly selective method for the detection of *o*-phenylenediamine and some aromatic diamines may be applied to the determination of residues, *e.g.*, *o*-phenylenediamine in the presence of *o*-nitroaniline and *m*- and *p*-phenylenediamine or in some pesticides such as carbendazim and benomyl. This will be the object of further investigations.

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