

Discussion

2-Trichloromethylbenzimidazole as a selective chromogenic reagent for the detection of some azoles on thin-layer plates

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In previous papers, the applications of 2-trichloromethylbenzimidazole (TCMB) for the detection of azines [1,2] and *o*-phenylenediamine [3] on TLC plates were described. TCMB was used as a chromogenic spray reagent for the detection of some azines on the basis of the formation of highly coloured polycyclic products [2]. A necessary condition was that both α -positions on the azine ring should be unsubstituted. The method was checked with six-membered heteroaromatic compounds containing one or two nitrogen atoms such as pyridine, pyridazine, pyrimidine, pyrazine and their derivatives. We have now found that the application of TCMB can be extended to five-membered heteroaromatic rings containing 1–4 nitrogen atoms.

The experimental details were the same as described previously [1]. The following 22 compounds were examined: (a) unsubstituted five-membered heterocyclic rings containing 1–4 nitrogen atoms, (b) all their N-methyl derivatives, (c) some C-methyl derivatives and (d) several compounds with nitro and thiol groups introduced on the ring. The compounds were derivatives of pyrrole (1 and 2), pyrazole (3–5), imidazole (6–10), 1,2,3-triazole (11–13), 1,2,4-triazole (14–18) and tetrazole (19–22).

We found that the following compounds were detected using TCMB as a chromogenic agent (colour, detection limit in μg): pyrrole (1) (brown, 0.1), 1-methylimidazole (7) (brown-yellow, 10), 1-ethylimidazole (8) (yellow, 5), 1,2,3-triazole (11) (brown, 0.05), 4-methyl-(4*H*)-1,2,4-triazole (16) (yellow, 1) and tetrazole (19) (khaki, 1). Other compounds examined gave no colour after spraying with TCMB solution: 1-methylpyrrole (2), pyrazole (3), 1- and 3-methylpyrazole (4 and 5), imidazole (6), 4-methyl- and 4-nitroimidazole (9 and 10), 1-methyl-(1*H*)-1,2,3-triazole (12), 2-methyl-(2*H*)-1,2,3-triazole (13), 1,2,4-triazole (14), 1-methyl- and 3-nitro-(1*H*)-1,2,4-triazole (15 and 17), (1*H*)-1,2,4-triazole-3-thiol (18), 1-methyl-(2*H*)- and 2-methyl-(2*H*)-tetrazole (20 and 21) and (1*H*)-1,2,3,4-tetrazole-5-thiol (22).

The results show that probably two different reaction mechanisms take place. For azoles without three vicinal nitrogen atoms in the heteroaromatic ring and with a weakly acid NH group, such as pyrazole, imidazole and 1,2,4-triazole, a chromogenic reaction analogous to that described for the azines [1] seems to occur. The necessary conditions for this reaction to occur are that both α -positions should be unsubstituted with respect to the basic tertiary nitrogen atom $-\text{N}=\text{}$ and that there should be substitution of the labile hydrogen atom at the weakly acid secondary nitrogen NH. The presence of the

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hydrogen in the azole molecule in this series of compounds causes the reaction with TCMB in the manner described for secondary amines [4] and the formation of other products. Quaternization of a basic nitrogen atom with TCMB and subsequent intramolecular cyclizations effect the formation of tetracyclic coloured product (the cyclization requires that both α -positions should be free) [5]. Therefore, for evident reasons, coloured products are not formed with N-methylpyrrole, pyrrole and its derivatives (2–5) and N-unsubstituted imidazoles and 1,2,4-triazoles (6, 9, 10, 14, 17 and 18). On the other hand, detection is possible with N-substituted imidazoles (7 and 8) and 4-substituted 1,2,4-triazole (16). However, the reaction is slower and the colours are not very intense, so the detection limit is higher (1–10 μg) than for pyridine and diazines (10–100 ng [1]). The relatively high volatility of compounds 7 and 8 may cause dispersion of the spot and additionally an increase in the detection level. 1-Substituted 1,2,4-triazoles, such as 1-methyl-(1*H*)-1,2,4-triazole (15), cannot be detected using this method as the chromogenic reaction does not occur. The reason is unclear; possibly the relative basicities of different nitrogen atoms in the triazole ring are of consequence.

For the compounds with a more acid hydrogen in the NH group, such as pyrrole (1), or three or more subsequent vicinal nitrogen atoms in the azole ring, as with 1,2,3-triazoles and tetrazoles, the above reaction does not take place or may be a side-reaction, but another reaction may be observed. Pyrrole (1) and 1,2,3-triazole (11) are unexpectedly detected with a low detection limit of 50–100 ng even at room temperature in spite of the unprotected NH group, whereas both 1- and 2-methyl-1,2,3-triazole (12 and 13) do not form any coloured product with TCMB. The reaction of TCMB with an excess of 11 as a solvent in the manner described previously [2] was then carried out and the formation of a

brown product and evolution of nitrogen were observed. The mass and IR spectra showed no volatile products except unreacted starting materials. Probably the decomposition of triazole and TCMB occurs with evolution of nitrogen and the formation of unidentified, probably polymeric, products. In the N-methyl-1,2,3-triazoles 12 and 13, initiation of decomposition does not occur because no secondary amine is present in the molecule and, additionally, in the 13 direct evolution of nitrogen is not possible. The reaction with the tetrazoles (19–22) seems to proceed by a similar mechanism and, as with triazoles, the N-protected compounds 20–22 are not detected.

The reaction with TCMB may be used, in spite of its moderate detection limit in some instances, for the detection of some azoles on TLC plates. In our opinion, this method of detection is important because, as distinct from azines, most azoles are not visible in the UV region at either 254 or 365 nm.

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