A New Sensitive and Specific Test for the Detection of Aldehydes: Formation of 6-Mercapto-3-substituted-*s*-triazolo[4,3-*b*]-*s*-tetrazines

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Summary The ready reaction of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole with aldehydes to form coloured derivatives of *s*-triazolo[4,3-*b*]-*s*-tetrazine is described.

THE classical qualitative tests with 2,4-dinitrophenylhydrazine, Fehling's solution, and Tollen's and Schiff's reagents for the detection of aldehydes are non-specific. In addition, the colour test with Schiff's reagent is unsatisfactory because its chemistry is obscure and the composition of the reagent imprecise. We describe the chemistry of a new test which is remarkably sensitive and specific for aldehydes.

4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole (I), the test reagent, can be readily prepared by the reaction of hydrazine hydrate with any one of a large range of open-chain and cyclic thioureido-compounds.[1] Under the conditions of the test,† the triazole (I) condenses with the

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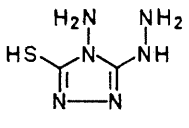
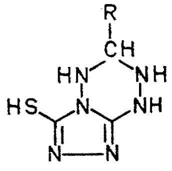
† One drop of the aldehyde is added to the triazole (*ca.* 100—200 mg) dissolved in 1N-NaOH (*ca.* 2 ml). Aeration of the reactants produces the intense colours described within 1 min.

formyl group of the aldehyde to form *inter alia* an unstable, oxygen labile, intermediate, 1,2,3,4-tetrahydro-6-mercapto-3-substituted-*s*-triazolo[4,3-*b*]-*s*-tetrazine (II). At the liquid–air interface, the intermediate (II) is rapidly oxidized ($<$ 1 min) by aerial oxygen to a purple 6-mercapto-3-substituted-*s*-triazolo[4,3-*b*]-*s*-tetrazine (III). Dependent on the nature of the 3-substituent group derived from the aldehyde moiety, the colours produced range from magenta (R = aliphatic) to purple (R = aromatic) and purple-brown (R = aliphatic and aromatic substituents with additional functional groups). Spectrometric examination of all positive test solutions showed each had an absorption band in the visible region 520—555 nm, which though reminiscent of the absorption common to all monocyclic, *aromatic* tetrazines,[2] in this instance, clearly involves a longer conjugated pathway extending throughout the fused bicyclic system. The pronounced bathochromic shift of the absorption towards blue and purple observed in alkaline solution, suggests the participation of the anion in the resonance (IV) → (V). The test, which proved highly specific for aldehydes at concentrations as low as 10^{-4}M did not yield purple condensation products with ketones, esters, amides, hydrazines, hydroxylamines, quinones, aminophenols, uric acid, or formic acid, known to interfere with some or all of the classical tests referred to above.


(I)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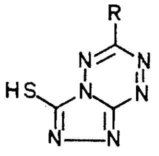
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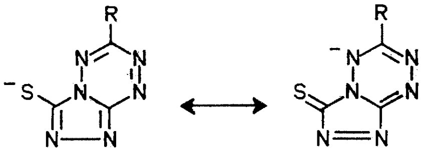
(IV) (V)

Condensation of the triazole (I) with isobutyraldehyde and benzaldehyde on a preparative scale, enabled the respective magenta and purple products to be isolated as crystalline solids. The analytical, u.v., and n.m.r. spectroscopic data of each were compatible with their being the 3-isopropyl and 3-phenyl derivatives of 6-mercapto-*s*-triazolo[4,3-*b*]-*s*-tetrazine, respectively; (III; R = Pr^{i}); m.p. 146—147° (decomp); λ_{max} (water pH 10) 268, 535 nm (ϵ 17,400, 1800); δ (Me_2SO) 1·49 (d, 6H, *J* 6 Hz) and (III; R = Ph); m.p. 192—193° (decomp); λ_{max} (water pH 10) 242, 313, 552 nm (ϵ 24,000, 11,850, 1600); δ (CF_3CO_2H) 7·45—7·96 (m, 5H).

(*Received, October* 19*th*, 1970; *Com.* 1799.)

‡ C. S. R. commercial glacial acetic acid known to contain 0·05% acetaldehyde gave a positive test with the reagent.

[1] R. G. Dickinson and N. W. Jacobsen, *Analyt. Chem.*, **1969**, **41**, 1324.

[2] J. Koenigsberger and K. Vogt, *Phys. Z.*, 1913, **14**, 1269; E. Muller and L. Herrdegen, *J. prakt. Chem.*, 1921, **102**, 113; A. Maccoll, *J. Chem. Soc.*, 1946, 670; S. F. Mason, *ibid.*, 1959, 1263.