6-Substituted *s*-Triazolo[4,3-*b*]-*s*-tetrazine-3-thiols: a Sensitive and Specific Test for Aldehydes

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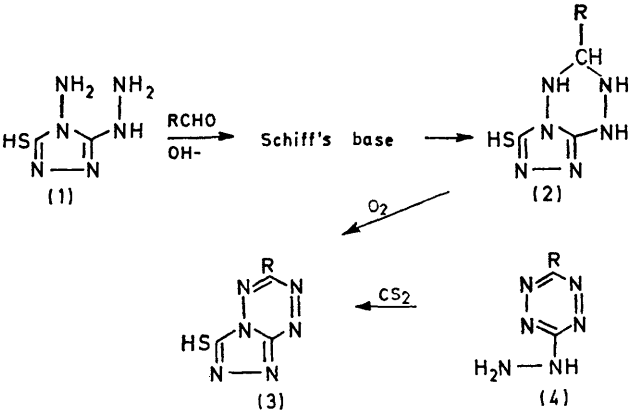
4-Amino-5-hydrazino-1,2,4-triazole-3-thiol reacts in acid solution with benzaldehyde to give the 4-benzylideneamino-derivative, and in alkaline solution, under nitrogen, to give the 5-benzylidenehydrazino-isomer. The latter cyclises to give 5,6,7,8-tetrahydro-6-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine-3-thiol, which in the presence of aerial oxygen is converted rapidly into the purple coloured 6-phenyl-*s*-triazolo-[4,3-*b*]-*s*-tetrazine-3-thiol, the chromogen of the triazolotetrazine test for aldehydes. In the absence of oxygen, the 5-benzylidenehydrazinotriazole slowly undergoes an irreversible isomerisation *via* the tetrahydrotriazolotetrazine to the 4-benzylideneamino-isomer.

4-AMINO-5-HYDRAZINO-1,2,4-TRIAZOLE-3-THIOL (1) reacts in alkaline solution with aldehydes to form *inter alia*, unstable, oxygen-labile, 6-substituted 5,6,7,8-tetrahydro-*s*-triazolo[4,3-*b*]-*s*-tetrazine-3-thiol intermediates (2). At the liquid–air interface, such intermediates are rapidly oxidised to purple- or magenta-coloured 6-substituted *s*-triazolo[4,3-*b*]-*s*-tetrazine-3-thiols (3). This reaction sequence is a very sensitive qualitative test for aldehydes [1] and one which lacks the non-specificity of the classical tests with Fehling's, Tollen's, and Schiff's reagents. Recently the method has been adapted to the quantitative assay of aliphatic aldehydes at dilutions down to 0·5 p.p.m. by weight with an accuracy of ±3%.[2] We now report the results of our investigation into the chemistry of this triazolotetrazine test for aldehydes.

Two representative derivatives of the triazolotetrazine chromogen were isolated from preparative-scale condensations of 4-amino-5-hydrazino-1,2,4-triazole-3-thiol (1) with isobutyraldehyde and with benzaldehyde. Even on the preparative scale, oxidation by aeration was superior to the use of chemical oxidising agents which invariably caused oxidation of both the aldehyde and the triazole. The 3-isopropyl- and 3-phenyl-triazolotetrazines (3; R = Pr^i or Ph) were deep magenta-coloured crystalline compounds with analytical and spectral properties compatible with the assigned structures. The bicyclic triazolotetrazine structure was confirmed by synthesis of the 3-phenyl derivative (3; R = Ph) from 3-hydrazino-6-phenyl-*s*-tetrazine [3] (4; R = Ph) and carbon disulphide. *X*-Ray diffraction studies [4] also established the triazolotetrazine skeleton of the chromogen and showed it to have a predominance of the thioamide tautomer in the crystalline state.

Identification of the Monobenzylidene Intermediate.— The reaction of the triazole (1) with benzaldehyde leading to the triazolotetrazine (3; R = Ph) was investigated in an attempt to resolve the ambiguity in the structure of the intermediate Schiff's base and to isolate and characterise the tetrahydro-intermediate (2; R = Ph).

In acidic and neutral solutions, a single mono- or di-benzylidene derivative was obtained, depending upon the proportion of benzaldehyde used, and the structure of the former was clearly ambiguous (5; $R^1 = NH_2$, R^2 = PhCH=N or *vice versa*). In alkaline solution, and



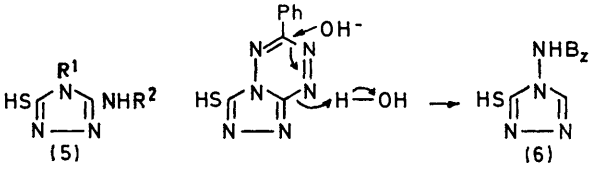
under nitrogen, a second monobenzylidene derivative was obtained. Both isomers gave the dibenzylidene derivative when treated with an excess of benzaldehyde in acid solution, but only that formed in alkaline solution was a precursor of the purple triazolotetrazine (3; R = Ph). Attempts to identify either of the monobenzylidene derivatives directly by degradation (*e.g.* oxidative removal of a hydrazino-group [5–7]) or synthesis were unsuccessful. Equally unsuccessful were attempts to prepared suitable crystals of either isomer for *X*-ray crystallography. Finally, the isomer formed in alkaline solution under nitrogen was reasoned to be the 5-benzylidenehydrazino-derivative (5; $R^1 = NH_2$, R^2 = PhCH=N) as this compound alone could be the precursor of 4-amino-5-*N'*-benzoylhydrazino-1,2,4-triazole-3-thiol (5; $R^1 = NH_2$, R^2 = PhCONH) which was also isolated, in 2% yield, from the reaction.

This monobenzoyl derivative was identical with that formed by direct benzoylation of the triazole (1) in pyridine. Of six possible structures, that of the *N'*-benzoylhydrazino-isomer was confirmed by *X*-ray crystallography.[8] Significantly, this product was not

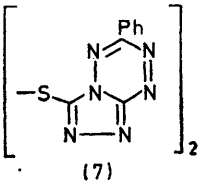
[1] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, 1719.
[2] N. W. Jacobsen and R. G. Dickinson, *Analyt. Chem.*, 1974, **46**(2), 298.
[3] V. A. Ershov and I. Ya. Postovskii, *Khim. geterotsikl. Soedinenii*, 1968, **6**, 1134.
[4] R. C. Seccombe and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 11.
[5] F. D. Chattaway, *Trans. Chem. Soc.*, 1907, **91**, 1323.
[6] A. Albert and G. Cotterall, *J. Chem. Soc.*, 1967, 1533.
[7] M. E. C. Biffin, D. J. Brown, and T. C. Lee, *Austral. J. Chem.*, 1967, **20**, 1041.
[8] R. C. Seccombe and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 4.

found to be an intermediate in the route to the purple triazolotetrazine. Its formation therefore under the conditions of the reaction was attributed to the oxidation of the triazole–benzaldehyde adduct [5; $R^1 = NH_2$, $R^2 = PhCH(O^-)\cdot N^+H_2$] either as it was formed initially or as it was regenerated through a reverse hydration of the Schiff's base. On this evidence, the latter was therefore the 5-benzylidenehydrazino-compound (5; $R^1 = NH_2$, $R^2 = Ph–CH=N$). This assignment was valid only so long as the coloured triazolo-tetrazine end-product was not the source of the monobenzoyl derivative by a pathway initiated by hydration of the 3,4-bond and followed by reduction and opening of the tetrazine ring.

Under alkaline conditions similar to those of the principal reaction, the triazolotetrazine was unchanged. At higher than ambient temperatures, or in stronger alkali, hydrolysis was accompanied by loss of nitrogen to give, in turn, 4-benzoylamino-1,2,4-triazole-3-thiol (6) and the 4-amino-compound,[9] the direction of these decompositions being determined by an initial hydroxide ion attack at C-3 as for the hydrolysis of 3,6-diphenyl-*s*-tetrazine.[10]



(5) (6)



(7)

Isomerisation of the Monobenzylidene Derivatives.—The second stage of the reaction leading to the triazolotetrazine must involve cyclisation of 4-amino-5-benzylidenehydrazino-1,2,4-triazole-3-thiol (5; $R^1 = NH_2$, $R^2 = PhCH=N$) to give the tetrahydrotriazolotetrazine (2; R = Ph). Efforts to isolate and characterise the tetrahydro-compound were unsuccessful and the absence of ^1H n.m.r. signals in the region δ 3·5—4·5 expected for ring protons of a hexahydro-*s*-tetrazine [11] strengthened the belief that the intermediate was of transitory existence only. Probably this was due to it being the common intermediate of two reaction pathways.

The first of these involved its oxidation by air to the coloured triazolotetrazine (3; R = Ph); the second, an irreversible isomerisation in the absence of oxygen to give the 4-benzylideneamino-derivative (5; $R^1 =$ PhCH=N, $R^2 = NH_2$) which was not a precursor of the triazolotetrazine. Evidence for the latter isomerisation came from the ^1H n.m.r. data. The diagnostic features in the ^1H n.m.r. spectra of all the benzylidene derivatives were the –CH=N– chemical shifts, which for the dibenzylidene derivative (5; $R^1 = R^2 =$ PhCH=N) in trifluoroacetic acid were δ 8·30 and 8·71. For the 4-benzylideneamino-compound (5; $R^1 =$ PhCH=N, $R^2 = NH_2$) the resonance occurred at δ 8·32, and in the same solvent, the oxidisable benzylidenehydrazino-derivative (5; $R^1 = NH_2$, $R^2 =$ PhCH=N) showed a principal signal at δ 8·57 with that from a minor component at δ 8·32. The proportions of these signals showed no change with time in trifluoroacetic acid, but in oxygen-free solutions of sodium deuterioxide the higher-field singlet (8·32) slowly increased in intensity at the expense of the other. This suggested that in the absence of the oxygen necessary to effect the oxidation to the triazolotetrazine (3; R = Ph), the benzylidenehydrazinotriazole was changing to its non-oxidisable isomer, presumably *via* the tetrahydrotriazolotetrazine intermediate.

A preparative scale isomerisation induced by recrystallising the oxidisable benzylidenehydrazino-derivative from alcohol enabled the product to be identified by direct comparison with the benzylideneamino-isomer (5; $R^1 =$ PhCH=N, $R^2 = NH_2$).

The Triazolotetrazine Disulphide (7).—Bis-(6-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazin-3-yl) disulphide (7) was a prominent product (7%) which originated during the work-up procedure. Oxidation of the purple triazolotetrazine to the yellow disulphide was found to occur under a variety of conditions: in aqueous neutral or acidic solutions on exposure to air; in the solid state on exposure to air (slow); and in ethanolic solution with hydrogen peroxide (rapid and quantitative). These facts, its elemental analysis, and its reconversion into the parent under reducing conditions, confirmed its structure. The S–S bond was also cleaved in dilute alkaline solution in the absence of a reducing agent. Such reactions involving heterolytic cleavage by attack of hydroxide ion have been reported for other systems.[12]

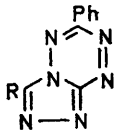
Spectroscopy.—The 6-substituted *s*-triazolo[4,3-*b*]-*s*-tetrazine-3-thiols all showed a long-wavelength absorption band in the region 520—555 nm.[1,2] Though fortuitously in the same region as that of the monocyclic tetrazines [13] this absorption is due to participation of the electrons of the thiolate anion in a resonance system extending throughout the bicyclic system. When anion participation was suppressed by reducing the pH below 10, or removed altogether through disulphide formation, then massive hypsochromic shifts of 84 and 96 nm (respectively) resulted. The spectra (see Table 1) then approximated to that of 6-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine (R = H).[3]

Oxidation of 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol.—Solutions of the triazole (1) in aqueous sodium hydroxide exposed to the air slowly (8 h) developed a purple colouration ($\lambda_{max.}$ 550 nm). During several days this colour was discharged with evolution of nitrogen,

[9] R. Stolle and P. E. Bowles, *Ber.*, 1908, **41**, 1099.
[10] A. Pinner, *Ber.*, 1894, **27**, 894.
[11] W. Skorianetz and E. Kovats, *Helv. Chim. Acta*, 1970, **53**, 251.
[12] O. Foss, 'Organic Sulphur Compounds,' Pergamon, New York, 1961, vol. 1, p. 83.
[13] E. Muller and L. Herrdegen, *J. prakt. Chem.*, 1921, **102**, 113.

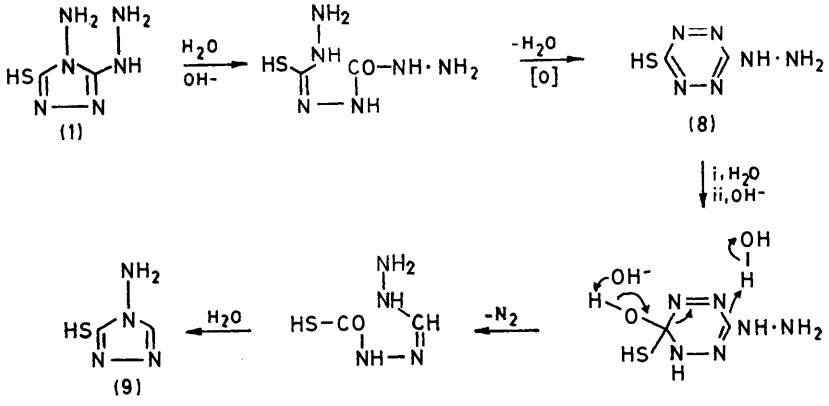
indicative of oxidative removal of hydrazine. This was confirmed by the isolation and characterisation of 4-amino-1,2,4-triazole-3-thiol (9).[9] The reaction was dependent upon the availability of oxygen and the concentration of base, and was considerably hastened by addition of ethanol. A plausible pathway leading to the

TABLE 1
U.v. data



R	$\lambda_{max.}$/nm (log ε)			
H	460 (2·64)	338 (3·65)	264 (4·32)	
SH †	466 (2·74)	344sh (3·43) ¶	306 (4·14)	243 (4·34)
–S–S– ‡	454 (2·95)	344 (3·99)	272 (4·54)	
S– §	552 (3·20)	313 (4·07)	242 (4·38)	

† pH 3·0. ‡ Acetic acid. § Ph 10. ¶ May be due to disulphide impurity.



SCHEME

removal of a hydrazino-substituent from aromatic compounds has been proposed by Chattaway.[5] Such a mechanism, in this instance, does not explain the transient purple colour (550 nm). Under the present circumstances it is tempting to attribute the latter to a *s*-tetrazine intermediate (8) (see Scheme). This susceptibility of the triazole (1) to slow decomposition in aqueous alkaline solutions not protected from oxygen makes it inadvisable to use any but freshly prepared stock solutions of the reagent [14] for the triazolotetrazine test.

EXPERIMENTAL

M.p.s were taken with an electrically-heated silicone oil bath (Büchi). U.v. spectra were recorded with a Unicam SP 800A spectrophotometer, i.r. spectra with a Perkin-Elmer 247 or Beckman IR-8 spectrophotometer for Nujol mulls, and ^{1}H n.m.r. spectra with a Varian A-60 or JEOL MH-100 spectrometer (tetramethylsilane as internal standard).

The Triazolotetrazine Test for Aldehydes.—One drop (or a few crystals) of the aldehyde was added to 4-amino-5-hydrazino-1,2,4-triazole-3-thiol (*ca.* 100—200 mg) dissolved in M-sodium hydroxide (*ca.* 2 ml). Aeration produced an intense magenta or purple colour within 1 min. Dependant on the nature of the 6-substituent group derived from the aldehyde, the colours ranged from magenta (aliphatic) to purple (aromatic) and brown-purple (aliphatic and aromatic substituents with additional functional groups). All positive test solutions had a visible absorption band at 520—555 nm (Table 2). The test was rapid, highly sensitive, and specific for aldehydes. It did not yield purple condensation products with ketones, esters, amides, hydrazines, hydroxylamines, quinones, aminophenols, uric acid, or formic acid, which are known to interfere with some of or all the classical tests.

6-Isopropyl-s-triazolo[4,3-b]-*s-tetrazine-3-thiol* (3; R = Pr^i).—Isobutyraldehyde (1·45 g) was added to 4-amino-5-hydrazino-1,2,4-triazole-3-thiol (2·9 g) dissolved in M-sodium hydroxide (24 ml). The mixture was shaken vigorously for *ca.* 4 min and then aerated for 2 h by using a microbubbler (with occasional shaking) connected to a clean source of compressed air. The magenta solution was then cooled in ice and acidified to pH 5—6 with 2M-hydrochloric acid (12·5 ml). The tarry precipitate was solidified by scratching and cooling, filtered off, washed with cold water, and dried under vacuum ($CaCl_2$). Recrystallisation from absolute ethanol gave the *triazolotetrazine* (3; R = Pr^i) as magenta needles (1·1 g, 29%), m.p. 146—147° (decomp.) (Found: C, 36·7; H, 4·3; N, 42·7; S, 16·5. $C_6H_8N_6S$ requires C, 36·7; H, 4·1; N, 42·8; S, 16·3%);

TABLE 2
Visible spectra of aldehyde test solutions

Aldehyde	Colour	$\lambda_{max.}$/nm
HCHO	Purple	549
MeCHO	Magenta	537
EtCHO		536
Pr^{n}CHO		532
Pr^{i}CHO		535
Bu^{n}CHO		536
Me[CH$_2$]$_4$CHO		536
MeCH:CH·CHO		538
MeCH:CMe·CHO	Purple	545
MeCO·CHO	Brown-purple	540
OHC·CHO	Brown-purple	527sh
PhCHO	Magenta	540
p-MeO·C$_6$H$_4$·CHO	Brown-purple	541
PhCH:CH·CHO		521sh
o-HO·C$_6$H$_4$·CHO		520sh
m-O$_2$N·C$_6$H$_4$·CHO		530
4-HO-3-MeO·C$_6$H$_3$·CHO		525

[14] R. G. Dickinson and N. W. Jacobsen, *Org. Prep. and Procedures Int.*, 1974, **6**(3), 156.

$\lambda_{max.}$ (H_2O; pH 10) 268 (ε 17,400) and 535 nm (1800); δ [$(CD_3)_2SO$] 1·49 (6H, d, *J* 6 Hz, 2 × CMe); $\nu_{max.}$ 3100 (N–H), 3020, 2820 (C–H), 1600 (C=N), 1545 (N–H), 1460 (C–H), and 1265 (C=S) cm^{-1}.

6-*Phenyl*-s-*triazolo*[4,3-b]-s-*tetrazine*-3-*thiol* (3; R = Ph). —(a) *From* 4-*amino*-5-*hydrazino*-1,2,4-*triazole*-3-*thiol* (1). Benzaldehyde (2·15 g) in ethanol (10 ml) was added to the triazole (2·9 g) dissolved in the minimum of cold 0·5M-sodium hydroxide (45 ml). The mixture was shaken vigorously for *ca.* 4 min, aerated for 2 h with frequent shaking, cooled in ice for 20 min, and filtered. The residue was discarded and 2M-hydrochloric acid (5 ml) was added with stirring to the filtrate. The mixture was cooled in ice and filtered. The residue was washed with water and then boiled in ethanol (200 ml) with activated charcoal for 10 min. The mixture was filtered and the filtrate was evaporated to *ca.* 10 ml and cooled. The solid was collected and recrystallised from water to give 4-*amino*-5-N′-*benzoylhydrazino*-1,2,4-*triazole*-3-*thiol* (5; $R^1 = NH_2$, R^2 = PhCO·NH) as plates (0·2 g, 4%), m.p. 241—242° (decomp.) (Found: C, 43·2; H, 4·0; N, 33·8; S, 13·1. $C_9H_{10}N_6OS$ requires C, 43·2; H, 4·0; N, 33·6; S, 12·9%); δ (CF_3·CO_2H) 7·55—8·05 (m, Ph); $\nu_{max.}$ 3300, 3220, 3200, 3120 (N–H), 3045 (C–H), 1680 (C=O), 1635 (C=N), 1630, 1580, 1495 (arom. C=C), 1605, 1595, and 1520 (N–H) cm^{-1}. The mother liquor was acidified to pH 5—6 with 2M-hydrochloric acid (6 ml) and cooled in ice. The tarry precipitate was collected, washed with water, and dried ($CaCl_2$). Extraction with boiling absolute ethanol (25 ml) and filtration gave a yellow residue and a magenta filtrate. The filtrate was concentrated and cooled and the solid collected. Recrystallisation from the minimum of absolute ethanol gave the *triazolotetrazine* (3; R = Ph) as magenta needles (0·9 g, 20%), m.p. 192—193° (decomp.) (Found: C, 46·75; H, 2·6; N, 36·3; S, 14·05. $C_9H_6N_6S$ requires C, 46·95; H, 2·6; N, 36·3; S, 13·9%); $\lambda_{max.}$ (water; pH 10) 242 (ε 24,000), 313 (11,800), and 552 nm (1600); δ(CF_3·CO_2H) 7·45—7·96 (m, Ph); $\nu_{max.}$ 3120 (N–H), 3060, 3025 (C–H), 1600 (C=N), 1580, 1485 (arom. C=C), 1525 (N–H), and 1260 (C=S) cm^{-1}. The yellow residue was washed twice with boiling ethanol (20 ml). Recrystallisation from absolute ethanol (3 l) gave *bis*-(6-*phenyl*-s-*triazolo*[4,3-b]-s-*tetrazin*-3-*yl*) *disulphide* (7) as yellow needles (0·3 g, 7%), m.p. 254·5—255·5° (decomp.) (Found: C, 46·8; H, 2·4; N, 36·5; S, 14·1. $C_{18}H_{10}N_{12}S_2$ requires C, 47·1; H, 2·2; N, 36·3; S, 14·0%); $\lambda_{max.}$ (>250 nm; glacial AcOH) 272 (ε 35,000), 344 (9800), and 454sh nm (900); δ (CF_3·CO_2H) 7·65—7·85 and 8·35—8·55 (m, 2 × Ph); $\nu_{max.}$ 3060 (C–H), 1617, 1585 (arom. C=C), 1600, and 1605 (C=N) cm^{-1}.

(b) *From* 3-*hydrazino*-6-*phenyl*-s-*tetrazine* (4; R = Ph). 3-Hydrazino-6-phenyl-*s*-tetrazine [3] (0·1 g) was refluxed in carbon disulphide (5 ml) and sodium ethoxide [from sodium (0·012 g) in ethanol (2 ml)] for 30 min. The blue solution was evaporated to dryness, water (5 ml) was added, and the mixture neutralised with 0·1M-hydrochloric acid (5 ml) and chilled. The solid was collected and twice recrystallised from absolute ethanol to give magenta needles (0·025 g, 22%), identical (mixed m.p., i.r., and ^1H n.m.r.) with the triazolotetrazine from (a).

Synthesis of 4-*Amino*-5-N′-*benzoylhydrazino*-1,2,4-*triazole*-3-*thiol* (5; $R^1 = NH_2$, R^2 = PhCO·NH).—The powdered triazole (1) (1·45 g) was added to a mixture of benzoyl chloride (1·4 g) and dry pyridine (1·6 g). The thick suspension was stirred and gently refluxed for 12 h. The resultant tar was then stirred with cold water (20 ml) until an even suspension was obtained, and this was then filtered. The residue was boiled in ethanol (250 ml) for 10 min and filtered from unchanged triazole (1). The filtrate was evaporated to *ca.* 30 ml, cooled, and filtered. Recrystallisation of the residue from ethanol gave 4-amino-5-*N*′-benzoylhydrazino-1,2,4-triazole-3-thiol (5; $R^1 = NH_2$, R^2 = PhCO·NH) as needles (0·7 g, 28%), identical (mixed m.p., i.r., ^1H n.m.r.) with previous samples.

Oxidation of 6-*Phenyl*-s-*triazolo*[4,3-b]-s-*tetrazine*-3-*thiol* (3; R = Ph).—The tetrazine (3; R = Ph) (0·23 g) was dissolved in warm ethanol (10 ml). Hydrogen peroxide (100 vol.; 1 ml) was added and the warm solution was set aside for 10 min. The magenta colour was discharged simultaneously with precipitation of fine yellow needles, which were collected, washed with hot ethanol, and dried. The product (0·22 g, 96%) was identical (mixed m.p. and i.r.) with disulphide (7).

Scission of the Disulphide Linkage of Compound (7).—The disulphide (7) (0·46 g) was stirred with water (3 ml) to give a homogeneous slurry which was then cooled in ice. 2M-Sodium hydroxide (5 ml) was added and the mixture vigorously stirred for 3 min. The yellow suspension effervesced giving a blue-brown solution which precipitated the magenta sodium salt of the parent thiol. The mixture was neutralised with 2M-hydrochloric acid (5 ml) and cooled in ice. The solid was collected, vacuum-dried ($CaCl_2$), boiled with absolute ethanol (5 ml), and filtered from unchanged disulphide (0·14 g, 30%). The solid which precipitated from the magenta filtrate on cooling was recrystallised from the minimum of absolute ethanol to yield magenta needles (0·12 g, 52%), identical (mixed m.p. and i.r.) with the tetrazine (3; R = Ph).

Decomposition of the Tetrazine (3; R = Ph) *in Alkali;* 4-*Benzoylamino*-1,2,4-*triazole*-3-*thiol* (6).—The tetrazine (3; R = Ph) (0·23 g) was dissolved in 2M-sodium hydroxide (10 ml) and the intense purple solution warmed for 10 min. The purple colour was discharged simultaneously with liberation of nitrogen. The solution was acidified to pH 4—5 with 10M-hydrochloric acid and cooled in ice. The precipitate was collected, washed with water, and recrystallised from water to afford 4-benzoylamino-1,2,4-triazole-3-thiol (6) as fine needles (0·2 g, 91%), m.p. 272—273° (Found: C, 48·95; H, 3·8; N, 24·9; S, 14·7. $C_9H_8N_4OS$ requires C, 49·1; H, 3·6; N, 25·4; S, 14·6%); δ (CF_3·CO_2H) 7·48—8·04 (5H, m, Ph) and 8·55 (1H, s, CH=N); $\nu_{max.}$ 3170, 3110 (N–H), 3070, 3010sh (C–H), 1668 (C=O), 1655sh (C=N), 1600, 1580 (arom. C=C), 1553, and 1515 (N–H) cm^{-1}.

Hydrolysis of 4-*Benzoylamino*-1,2,4-*triazole*-3-*thiol* (6).—The triazole (6) (0·44 g) was refluxed in 2M-sodium hydroxide (10 ml) for 12 h. The solution was then acidified to pH 5—6 with 10M-hydrochloric acid, cooled in ice, and filtered from unchanged (6) (0·05 g, 11%). The mother liquor was further acidified to pH 2—3 to give benzoic acid (0·08 g, 75%), m.p. and mixed m.p. 121—122° (from water). Cooling the mother liquor in ice for several hours gave 4-amino-1,2,4-triazole-3-thiol as needles (from propan-1-ol) (0·12 g, 52%), m.p. and mixed m.p.[9] 170—171°.

Monobenzylidene Derivatives of 4-*Amino*-5-*hydrazino*-1,2,4-*triazole*-3-*thiol* (1).—The triazole (1) (2·9 g) was dissolved in M-sodium hydroxide (24 ml) in a two-necked flask equipped with condenser and a gas inlet. Nitrogen gas was continuously flushed through the system. The solution was boiled for 2 min to remove dissolved oxygen and cooled to room temperature. Benzaldehyde (2·1 g) in

ethanol (10 ml) was added down the condenser and the mixture was stirred for 20 min, then cooled and acidified (with stirring) with 2M-hydrochloric acid (13 ml). The copious cream precipitate was collected, washed with water, and vacuum dried ($CaCl_2$). The crude solid (4·5 g) was readily oxidised to the purple triazolotetrazine by alkaline aeration. The ^1H n.m.r. spectrum indicated the presence of a mixture of the benzylideneamino- and benzylidene-hydrazino-derivatives [δ ($CF_3 \cdot CO_2H$) 7·40—7·95 (m, Ph), 8·32 (s, CH=N), and 8·57 (s, CH=N)]. The crude product was quickly extracted with boiling absolute ethanol (2 × 2 l) and the extracts were immediately chilled. The insoluble residue was unchanged triazole (1) (0·22 g, 7%). The precipitate from the ethanolic extracts was recrystallised from absolute ethanol to give 4-*benzylideneamino*-5-*hydrazino*-1,2,4-*triazole*-3-*thiol* (5; R^1 = PhCH=N, R^2 = NH_2) as small cream plates (3·4 g, 72%), m.p. 245—246° (decomp.) (Found: C, 46·25; H, 4·45; N, 36·0; S, 14·0. $C_9H_{10}N_6S$ requires C, 46·15; H, 4·3; N, 35·9; S, 13·7%); δ ($CF_3 \cdot CO_2H$) 7·40—7·85 (5H, m, Ph) and 8·32 (1H, s, CH=N); $\nu_{max.}$ 3255, 3200sh, 3160, 3115sh (N–H), 3085, 3010sh (C–H), 1633sh, 1620 (C=N), 1608, 1576sh (arom. C=C), 1583, and 1510 (N–H) cm^{-1}, which was not converted into a purple substance on alkaline aeration.

4-*Benzylideneamino*-5-*hydrazino*-1,2,4-*triazole*-3-*thiol* (5; R^1 = PhCH=N, R^2 = NH_2).—The triazole (1) (1·45 g) was dissolved in hot 1M-hydrochloric acid (75 ml). Benzaldehyde (1·05 g) in ethanol (10 ml) was added with stirring over 10 min, and the mixture was stirred a further 10 min and then cooled. The precipitate was washed with water and recrystallised from ethanol to give the imine (5; R^1 = PhCH=N, R^2 = NH_2) as small cream plates (1·9 g, 82%), identical (mixed m.p. and i.r.) with the sample obtained above.

4-*Benzylideneamino*-5-*benzylidenehydrazino*-1,2,4-*triazole*-3-*thiol* (5; R^1 = R^2 = PhCH=N).—The monobenzylidene derivative (5; R^1 = PhCH=N, R^2 = NH_2) (0·5 g) was suspended in M-hydrochloric acid (20 ml). Benzaldehyde (0·5 g) in ethanol (5 ml) was added and the mixture refluxed with stirring for 20 min. The product was collected and washed with water and ethanol. Recrystallisation from ethanol gave the dibenzylidene derivative as pale yellow plates (0·58 g, 84%), m.p. 244—246° (decomp.), identical (mixed m.p. and i.r.) with an authentic specimen [15] prepared directly from the triazole (1).

Decomposition of 4-*Amino*-5-*hydrazino*-1,2,4-*triazole*-3-*thiol* (1); 4-*Amino*-1,2,4-*triazole*-3-*thiol* (9).—The triazole (1) dissolved in M-sodium hydroxide (50 ml) was set aside open to the atmosphere. Evolution of nitrogen commenced after *ca.* 8 h, simultaneously with production of an intense purple colouration. After 5 days, evolution of nitrogen had ceased and the purple colour had been discharged. The pale yellow solution was acidified to pH 3—4 with 10M-hydrochloric acid and the mixture cooled in ice. The precipitate was collected, washed with ice–water, and vacuum dried ($CaCl_2$). Recrystallisation from propan-1-ol gave 4-amino-1,2,4-triazole-3-thiol (9) as needles (1·8 g, 78%), m.p. 170—171°, identical (mixed m.p. and i.r.) with an authentic specimen.[9]

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[15] E. Hoggarth, *J. Chem. Soc.*, 1952, 4817.