

Cyclizations of Thiocarbohydrazide and its Mono-hydrazones

Part III*. Reactions with Carbon Disulphide in Pyridine

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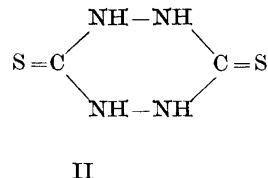
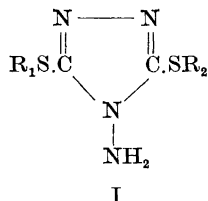
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When thiocarbohydrazide reacts with carbon disulphide in boiling pyridine, the pyridinium salts of 3,5-dimercapto-4-amino-4,1,2-triazole and 2,4-dimercapto-[4,1,2]-triazolo-[3,4-b]-[1,3,4]-thiadiazole are formed. The dimercapto-amino-triazole has been described as "dithio-*p*-urazine" by previous authors. — Under the same conditions mono-thiocarbohydrazones give 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazones.

In 1923, Arndt and Bielich¹ reported the synthesis of 3,5-dimercapto-4-amino-4,1,2-triazole (Ia) from hydrazindithiocarboxamide and hydrazine. They reported the m.p. 228° and prepared a dibenzyl derivative (Ib) with m.p. 147° and a benzylidene derivative with m.p. 136°. This synthesis has been confirmed by Hoggarth². In 1924, Guha and De^{3,4} described the preparation of "dithio-*p*-urazine" (II) in a variety of ways, one of which was by heating thiocarbohydrazide and carbon disulphide in a sealed tube. They reported the m.p. 203–204° and prepared a dibenzyl derivative with m.p. 142°, but they were unable to obtain a benzylidene derivative. In the same communication⁴ Guha and De claim to have prepared the triazole (Ia) by treatment of 1-thiocarbamoyl-thiocarbohydrazide with hydrochloric acid, but Scott and Audrieth⁵ and Beyer and Kröger⁶ have shown that the starting material of Guha and De was not 1-thiocarbamoyl-thiocarbohydrazide, which reacts quite differently with hydrochloric acid. Therefore, this statement of Guha and De is open to doubt.

Their evidence in favour of the structure (II) has recently been critically examined by Wiley⁷, who supported their conclusion. The preparation of (II) has also been reported by Beckett and Dyson⁸ and more recently by Wangel⁹, who also prepared a monobenzyl and a dicarboxymethyl derivative.

* Part II. *Acta Chem. Scand.* 14 (1960) 1939.



a, $R_1 = R_2 = H$
 b, $R_1 = R_2 = PhCH_2$
 c, $R_1 = PhCH_2, R_2 = H$

d, $R_1 = R_2 = CH_2CO_2H$
 e, $R_1 = CH_3, R_2 = H$
 f, $R_1 = R_2 = CH_3$

However, it has been known for a long time that the compound first described as the oxygen analogue of (II)¹⁰⁻¹², and several compounds first given similar structures^{11,13} are in fact 4-aminotriazoles, and there is ample reason to suspect that the alleged dithio-*p*-urazine of Guha and De is identical with the 4-amino-dithiourazole (Ia) of Arndt and Bielich.

Both preparations have now been repeated, and the products obtained gave the same melting points (222°) after several recrystallizations, and they gave identical ultraviolet and infrared spectra. The dibenzyl derivatives were also identical with m.p. 148–149°. The monobenzyl and dicarboxymethyl derivatives (Ic) and (Ie) were also prepared and were found to have melting points close to those reported by Wangel⁹.

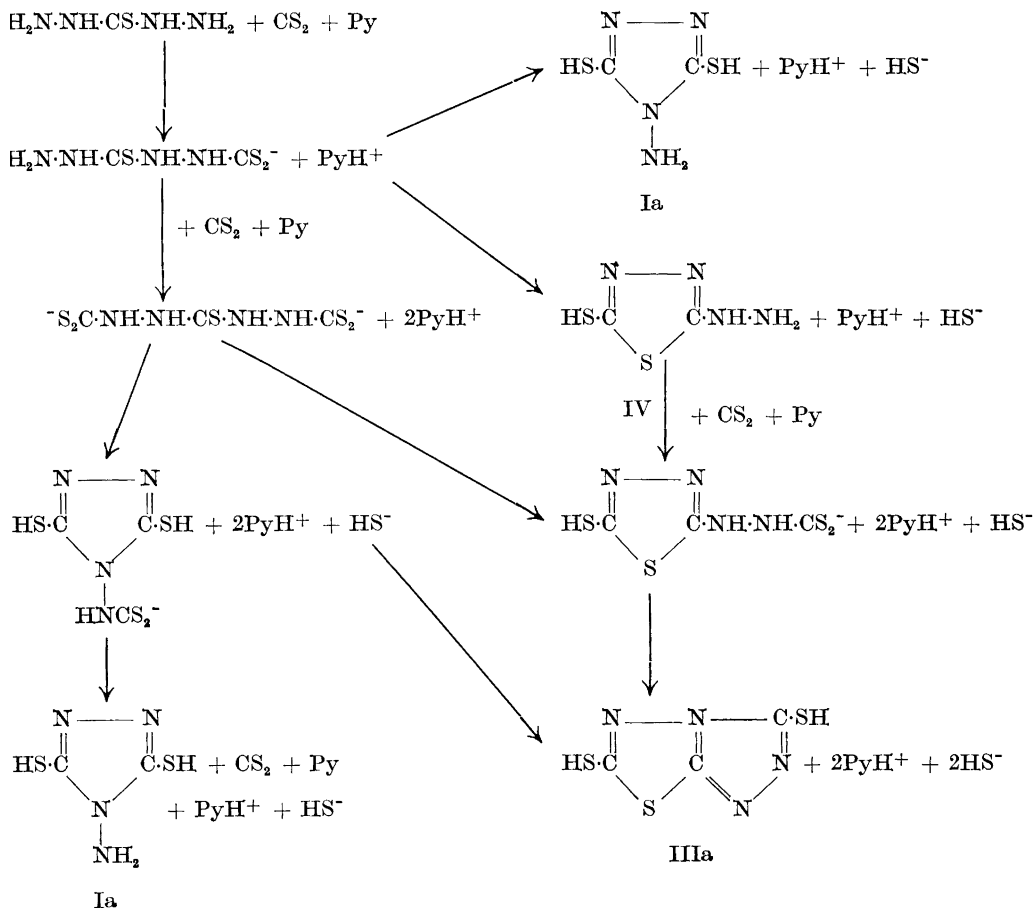
The 4-amino-triazole structure was demonstrated by deamination of the dibenzyl derivative (Ib) with nitrous acid. 3,5-Dibenzylthio-1,2,4-triazole was formed, which has already been described by Arndt and Milde¹⁴ and by Fromm¹⁵. The dibenzyl derivative (Ib) also gave a Schiff base with benzaldehyde, contrary to the statement of Arndt and Bielich¹.

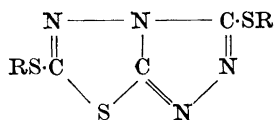
The 4-aminotriazoles (Ia-f) all show a fairly strong infrared band in the region 1 600–1 620 cm^{-1} , and a similar band is found in 3-mercapto-4-amino-4,1,2-triazole¹⁶ and in 3-mercapto-4-amino-5-methyl-4,1,2-triazole¹⁷ at 1 610 cm^{-1} . This band is missing in corresponding triazoles without 4-amino group. The band is very likely due to the scissoring vibration of the primary amino group, which is listed by Randall *et al.*¹⁸ in the region 1 560–1 640 cm^{-1} . Brown *et al.*¹⁹ have found a band at 1 590 cm^{-1} in the spectrum of 3-amino-rhodanine, which is ascribed to a N–H bending mode in the N-amino group. The N–H stretching modes are obscured by strong hydrogen bonding, and no useful information has been obtained from this region. For solubility reasons all spectra had to be recorded with the samples in potassium bromide disks.

A convenient synthesis of (Ia) was found in the reaction between thiocarbonylhydrazide and two equivalents of carbon disulphide in boiling pyridine. From the boiling solution a pyridine salt of (Ia) separates in high purity in 50 % yield. The free acid (Ia) is rapidly oxidized to the disulphide in the air, and it is therefore conveniently stored as the pyridinium salt, from which it is easily prepared by acidification of an aqueous solution with hydrochloric acid. For a spectrophotometric investigation of the structure of (Ia), the results of which will be reported in a later communication, the mono- and dimethyl thioethers (Ie) and (If) were prepared.

From the mother liquor of the pyridinium salt of (Ia) the pyridinium salt of 2,4-dimercapto-[4,1,2]-triazolo-[3,4-b]-[1,3,4]-thiadiazole (IIIa) is obtained in 40 % yield together with a small amount of the pyridinium salt of 2,5-dimercapto-1,3,4-thiadiazole. As the latter compound is formed in excellent yield when hydrazine reacts with carbon disulphide in boiling pyridine, its formation can probably be explained by a slight decomposition of the thio-carbohydrazide in the boiling pyridine with liberation of hydrazine. The thiols (Ia) and IIIa) are fairly strong acids, and the pyridinium salt of (IIIa) crystallizes unchanged from N hydrochloric acid. To obtain the free thiol, 5 N HCl had to be used to decompose the salt.

The following tentative scheme is proposed to explain the formation of (Ia) and (IIIa) in the present reaction: (Py = C₅H₅N):





III

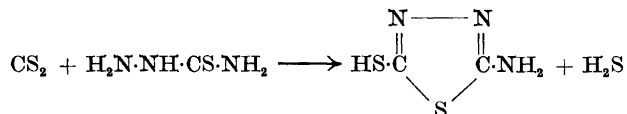
- a, R = H
 b, R = CH₃
 c, R = CH₂CO₂H
 d, R = CH₂Ph

Bicyclic compounds with the same ring system as (III) have been prepared by Kanaoka by dehydration of 4-acylamino-5-mercapto-4,1,2-triazoles with phosphorus oxychloride²⁰ and by cyclization of 1,3,4-thiadiazolyhydrazines with orthoesters and imino esters²¹.

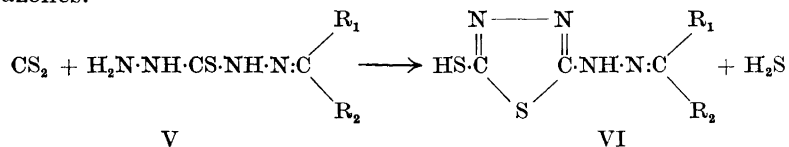
Attempts to isolate the 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazine²² (IV) by reaction between thiocarbohydrazide and carbon disulphide in the proportion 1:1 were in vain. Only unreacted thiocarbohydrazide was obtained together with (Ia) and (IIIa). However, (IV) may be an intermediate, since it reacts with carbon disulphide in pyridine to give (IIIa). On the other hand, (Ia) cannot be an intermediate, since it does not react with carbon disulphide under the conditions employed. The proportion of (IIIa) relative to (Ia) increases with the proportion of carbon disulphide relative to thiocarbohydrazide.

The thiol (IIIa) reacts readily with organic halides in alkaline solution, and the bis-thioethers (IIIb-d) have been prepared.

The course of cyclization of thiocarbohydrazide with carbon disulphide was somewhat unexpected, since thiosemicarbazide under the same conditions gave a high yield of 2-amino-5-mercapto-1,3,4-thiadiazole:



When mono-thiocarbohydrazones react with carbon disulphide in boiling pyridine, the directing influence of the azomethine group, discussed in Ref.²³, comes into play, and the main products are 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazones:



- a, R₁ = R₂ = CH₃
 b, R₁R₂ = (CH₂)₆
 c, R₁ = H, R₂ = Ph

However, with acetone and *cyclohexanone* monothiocarbohydrazones 14 % and 3 %, respectively, of (Ia) are formed. This by-product may have its origin in thiocarbohydrazide, formed by disproportionation of (V) to thiocarbohydrazide and bithiocarbohydrazone, but it may also have been formed by direct cyclization of (V) to the Schiff base of (Ia), followed by reaction with a

further mole of (V) to give (Ia) and bis-thiocarbohydrazone. To prove the structure of the thiadiazolyhydrazones (VI) they were also prepared from 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazine (IV), prepared according to Stollé and Fehrenbach²², and the appropriate carbonyl compounds, and the respective products were found to be identical. Methylation of (VIa) and (VIc) gave the corresponding methylthio-thiadiazolyhydrazones, described in Part II of this series.

As has been shown in numerous cases, cyclic thioamides, capable of thione-thiol tautomerism, preferentially exist in the thione form. Spinner²⁴ has proposed that these compounds for convenience should be referred to as thiols, even in cases where the thione structure is proved. This convention may be questionable, but it has been applied in the present work. The fine structure of (Ia) and (IIIa) will be discussed in a forthcoming communication.

EXPERIMENTAL

Reaction between thiocarbonylhydrazide and carbon disulphide

Thiocarbonylhydrazide (10.6 g) and carbon disulphide (14.4 g) were refluxed in pyridine (100 ml) for one hour. From the boiling solution a precipitate was formed, and after cooling pale yellow prisms (11.1 g, 50 % yield) were obtained, m.p. 200°, which crystallized from water as long, pale yellow rods of unchanged m.p. The product was the pyridinium salt of (Ia). (Found: C 36.9; H 4.11; N 31.0; S 28.1. Calc. for $C_7H_9N_5S_2$ (227.31): C 37.0; H 3.99; N 30.8; S 28.2).

This salt (4.6 g) was dissolved in hot water (20 ml), and conc. HCl (3 ml) was added. Colourless rods separated (2.8 g, 92 % yield), m.p. 216–217° (decomp.). The product was recrystallized three times from N HCl, and the m.p. rose to 222° (decomp.). The product, which was considerably more soluble in water than in strong dilute acids, was 3,5-dimercapto-4-amino-4,1,2-triazole (Ia). (Found: C 16.4; H 2.84; N 37.9; S 43.0. Calc. for $C_2H_4N_4S_2$ (148.20): C 16.2; H 2.72; N 37.8; S 43.3). λ_{\max} 2 600 Å with ϵ 23 400.

The pyridine mother liquor from the pyridinium salt of (Ia) was evaporated to dryness *in vacuo*. The residue was ground with water (15 ml) to remove the pyridinium salt of 2,5-dimercapto-1,3,4-thiadiazole. The undissolved material (9.0 g, 33 % yield) crystallized from water as pale yellow needles, m.p. 212° (decomp.), consisting of the pyridinium salt of (IIIa). (Found: C 35.7; H 2.60; N 26.0; S 35.4. Calc. for $C_8H_7N_5S_3$ (269.36): C 35.7; H 2.62; N 26.0; S 35.7).

This salt (2.7 g) was dissolved in boiling water (25 ml), and conc. HCl (25 ml) was added. A colourless precipitate was formed, which still contained some pyridine, but after a second precipitation colourless rods were formed (1.2 g, 63 % yield), m.p. 193–193.2° (decomp.), consisting of pure 2,4-dimercapto-[4,1,2]-triazolo-[3,4-b]-[1,3,4]-thiadiazole (IIIa). (Found: C 19.0; H 1.19; N 29.4; S 50.4. Calc. for $C_3H_2N_4S_3$ (190.27): C 18.9; H 1.06; N 29.5; S 50.6). λ_{\max} 3 035 Å with ϵ 16 700, and 2 705 Å with ϵ 12 500.

The aqueous extract of the pyridinium salt of (IIIa) was added to a solution of benzyl chloride (1 g) in ethanol (30 ml) and N NaOH (10 ml). A colourless precipitate was formed (0.65 g) which crystallized from ethanol as colourless plates, m.p. 86–87°, and which did not depress the m.p. of authentic 2,5-bis-benzylthio-1,3,4-thiadiazole²⁵. (Found: C 58.2; H 4.30; N 8.58; S 29.3. Calc. for $C_{18}H_{14}N_2S_3$ (330.47): C 58.2; H 4.27; N 8.48; S 29.1).

When the experiment was repeated as above but with 21.6 g of carbon disulphide instead of 14.4 g, the yield of the pyridinium salt of (Ia) decreased to 33 % and that of the pyridinium salt of (IIIa) rose to 48 %. When 7.2 g of carbon disulphide was employed, a 45 % yield of the salt of (Ia) was obtained. The mother liquor was distilled *in vacuo* to remove the pyridine, and the residue was ground and stirred over night with N HCl (100 ml). The undissolved material (4.9 g, 18 % yield) was identified by its m.p. and by formation of the dimethyl derivative (IIb) described below as the pyridinium salt of (IIIa). The hydrochloric acid extract was added to a solution of benzaldehyde (5 g) in

ethanol (100 ml). A flocculent precipitate (6.2 g, 22 % yield) of dibenzaldehyde thiocarbonylhydrazone¹⁶ was obtained, m.p. and mixed m.p. 193–194° (decomp.). (Found: C 63.6; H 4.94. Calc. for $C_{15}H_{14}N_4S$ (282.35): C 63.8; H 5.00).

Reaction between thiosemicarbazide and carbon disulphide

Thiosemicarbazide (9.3 g) and carbon disulphide (12 g) were refluxed with pyridine (75 ml) for 2 h. Then the pyridine was removed *in vacuo*, and the residue was crystallized from water (400 ml) as long, pale yellow rods (10.8 g, 82 % yield), m.p. 233.8–234.0° (decomp.) of 2-amino-5-mercapto-1,3,4-thiadiazole²⁶. (Found: C 18.3; H 2.35; N 31.7; S 48.2. Calc. for $C_2H_3N_3S_2$ (133.18): C 18.0; H 2.27; N 31.6; S 48.2).

Reaction between hydrazine and carbon disulphide

Hydrazine hydrate (100 %, 5.0 ml) and carbon disulphide (18 g) were refluxed in pyridine (50 ml) for one hour. The clear, yellow solution was evaporated in a stream of air to about half of the original volume, when spontaneous crystallization occurred. The product (22.0 g, 96 % yield), crystallized from a small volume of water as pale yellow rods, m.p. 176–177°, consisting of the pyridinium salt of 2,5-dimercapto-1,3,4-thiadiazole. (Found: C 36.6; H 3.12; N 18.3; S 41.7. Calc. for $C_7H_7N_3S_3$ (229.23): C 36.7; H 3.08; N 18.3; S 41.9).

This salt (2.3 g) was dissolved in water (25 ml), and conc. HCl (5 ml) was added. Colourless rods were obtained (1.36 g, 90 % yield), m.p. 169–169.5°, consisting of 2,5-dimercapto-1,3,4-thiadiazole²⁵. (Found: C 15.8; H 1.38; N 18.6; S 63.5; equiv. wt. 152. Calc. for $C_2H_2N_2S_3$ (150.24): C 16.0; H 1.34; N 18.7; S 64.0; equiv. wt. 150).

3-Alkylthio-4-amino-5-mercapto-4,1,2-triazoles

The mono-alkylthioethers of (Ia) were prepared by dissolving the pyridinium salt of (Ia) in water and adding one equivalent of the appropriate organic halide in sufficient ethanol to give a homogeneous solution. Crystallization soon started, and the products were found to be pure after one recrystallization.

3-Benzylthio-4-amino-5-mercapto-4,1,2-triazole (Ic) was obtained in 85 % yield and crystallized from toluene as colourless, irregular prisms, m.p. 158–158.5°. Wangel⁹ reports m.p. 155.5–158.2°. (Found: C 45.5; H 4.41; N 23.7; S 27.0. Calc. for $C_9H_{10}N_4S_2$ (238.33): C 45.4; H 4.23; N 23.5; S 26.9).

3-Methylthio-4-amino-5-mercapto-4,1,2-triazole (Ie) was obtained in 80 % yield and crystallized from water as colourless hairs, m.p. 182–182.5°. (Found: C 22.4; H 3.63; N 34.5; S 39.7. Calc. for $C_3H_5N_4S_2$ (162.24): C 22.2; H 3.73; N 34.5; S 39.5). λ_{\max} 2580 Å with ϵ 15400.

3,5-Dialkylthio-4-amino-4,1,2-triazoles

The pyridinium salt of (Ia, 2.3 g) was dissolved in N NaOH (20 ml), and a solution of monochloroacetic acid (2.5 g) in N NaOH (26.0 ml) was added. On the following day the mixture was acidified with 5N HCl (10 ml), and after scratching crystallization began. The product (2.45 g, 92 % yield) was recrystallized twice from water to give colourless rods of 3,5-dicarboxymethylthio-4-amino-4,1,2-triazole (Id), m.p. 180–180.6° (decomp.). Wangel⁹ reports m.p. 183.5–184°. (Found: C 27.3; H 3.07; N 21.0; S 24.3; equiv. w: 134.8. Calc. for $C_6H_8N_4O_4S_2$ (264.28): C 27.3; H 3.05; N 21.2; S 24.3; equiv. w: 132.1).

The pyridinium salt of (Ia, 2.3 g) was dissolved in N NaOH (20 ml), and methyl iodide (3 g) in ethanol (20 ml) was added. After 24 h the clear solution was evaporated to about one third of the original volume, and colourless rods then separated (1.35 g, 77 % yield), which were recrystallized twice from *n*-butanol to give colourless plates, m.p. 148–148.6°, of 3,5-dimethylthio-4-amino-4,1,2-triazole (If). (Found: C 27.6; H 4.65; N 31.9; S 36.3. Calc. for $C_4H_8N_4S_2$ (176.26): C 27.3; H 4.57; N 31.8; S 36.4). λ_{\max} 2250 Å with ϵ 8660.

The pyridinium salt of (Ia, 2.3 g) was dissolved in N NaOH (20 ml), and benzyl chloride (2.7 g) in ethanol (40 ml) was added. Crystallization started almost at once, and the product (3.0 g, 90 % yield) crystallized from ethanol as colourless plates, m.p. 148–149°, of *3,5-dibenzylthio-4-amino-4,1,2-triazole* (Ib). (Found: C 58.6; H 4.86; N 17.1; S 19.6. Calc. for $C_{16}H_{16}N_4S_2$ (328.44): C 58.5; H 4.91; N 17.1; S 19.5).

This aminotriazole (0.66 g) was ground with glacial acetic acid (5 ml), and a solution of sodium nitrite (0.4 g) in water (3 ml) was added dropwise. When the evolution of gas had ceased, the undissolved material was collected (0.55 g, 95 % yield). It crystallized from toluene as colourless, irregular prisms, m.p. 116–117°, consisting of *3,5-dibenzylthio-1,2,4-triazole*. (Found: C 61.3; H 4.92; N 13.5; S 20.2. Calc. for $C_{16}H_{15}N_3S_2$ (313.43): C 61.3; H 4.82; N 13.4; S 20.5). For this triazole the m.p. has previously been reported as 111°¹⁴ and 112°¹⁵.

The aminotriazole (Ib, 0.66 g) was dissolved in ethanol (5 ml), and benzaldehyde (0.25 g) and one drop of 5 N HCl were added. After some hours crystallization began, and the product (0.74 g, 89 % yield) crystallized from ethanol as colourless rods of *3,5-dibenzylthio-4-benzylidenamino-4,1,2-triazole*, m.p. 146–147°, strongly depressed by the starting material. (Found: C 66.2; H 4.89; N 13.6; S 15.2. Calc. for $C_{22}H_{20}N_4S_2$ (416.55): C 66.3; H 4.84; N 13.5; S 15.4). λ_{\max} 2 820 Å with ϵ 13 500.

2,4-Dialkylthio-[4,1,2]-triazolo-[3,4-b]-[1,3,4]-thiadiazoles

These compounds were prepared from the pyridinium salt of (IIIa) in the same way as the corresponding 4-aminotriazoles (I). The dimethyl derivative (IIIb) was obtained in 75 % yield and crystallized from absolute ethanol as colourless rods, m.p. 168–169°. (Found: C 27.7; H 2.90; N 25.8; S 44.3. Mol. weight 230 (Rast). Calc. for $C_5H_6N_4S_2$ (218.31): C 27.5; H 2.77; N 25.7; S 44.1). λ_{\max} 2 620 Å with ϵ 12 900.

The dicarboxymethyl derivative (IIIc) was obtained from the aqueous solution in 70 % yield and crystallized from absolute ethanol in colourless plates as the monohydrate, m.p. 174–174.5° (decomp.). (Found: C 26.0; H 2.52; N 17.2; S 29.5; equiv. wt. 163. Calc. for $C_7H_6O_4N_4S_2 \cdot H_2O$ (324.35): C 25.9; H 2.49; N 17.3; S 29.7; equiv. wt. 162).

The dibenzyl derivative (IIId) was obtained in 95 % yield and crystallized from absolute ethanol as colourless plates, m.p. 131–132°. (Found: C 55.1; H 3.88; N 15.1; S 26.2. Calc. for $C_{17}H_{14}N_4S_2$ (370.50): C 55.1; H 3.81; N 15.1; S 26.0). λ_{\max} 2 660 Å with ϵ 13 200.

Reaction between 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazine (IV) and carbon disulphide

Mercapto-thiadiazolyhydrazine hydrochloride²² (0.37 g) and carbon disulphide (0.3 ml) were refluxed for one hour in pyridine (5 ml). The solution was evaporated to dryness *in vacuo*, and the residue was dissolved in N NaOH (6 ml). Methyl iodide (0.5 ml) in ethanol (5 ml) was added, and crystallization soon set in. The product (0.33 g, 76 % yield) crystallized from absolute ethanol as colourless rods, m.p. 168–169°, which did not depress the m.p. of the 2,4-dimethylthio-triazolo-thiadiazole (IIIb) described above. (Found: N 25.7; S 44.2. Calc. for $C_5H_6N_4S_3$ (218.31): N 25.7; S 44.1).

Reactions between mono-thiocarbohydrazones (V) and carbon disulphide

Monoacetone thiocarbonylhydrazone²³ (Va, 4.5 g) and carbon disulphide (3.6 g) were refluxed in pyridine (40 ml) for 6 h. A pale yellow precipitate was formed (1.0 g, 15 % yield), which was identified as the pyridinium salt of (Ia) by its m.p. and by formation of the dibenzyl derivative (Ib). The filtrate was evaporated to about half of the original volume, and the residue was poured into water (50 ml). A crystalline product was obtained (1.9 g, 32 % yield), which crystallized from ethanol as colourless rods, m.p. 216–217°, identified by its infrared spectrum with the *acetone 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazone* (VIa) described in Part II, p. 1942. Reaction with methyl iodide in alkaline solution gave the acetone methylthio-thiadiazolyhydrazone described in the same place.

When monocyclohexanone thiocarbohydrazone²³ (Vb) and carbon disulphide reacted as in the preceding experiment, a 3 % yield of the pyridinium salt of (Ia) was obtained, and when the filtrate was poured into water, *cyclohexanone 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazone* (VIb) separated in 60 % yield. It was purified by dissolution in N sodium bicarbonate solution followed by precipitation with acetic acid and it was then recrystallized from *n*-butanol to give colourless rods, m.p. 216–219° (decomp.). (Found: C 42.1; H 5.37; N 24.7; S 27.9. Calc. for C₈H₁₂N₄S₂ (228.25): C 42.1; H 5.30; N 24.5; S 28.1).

When monobenzaldehyde thiocarbohydrazone (Vc) reacted as above, no pyridinium salt of (Ia) was obtained, but *benzaldehyde 5-mercapto-1,3,4-thiadiazol-2-yl-hydrazone*²² (VIc) separated in 85 % yield when the reaction mixture was poured into water. The product was dissolved in N sodium carbonate solution and precipitated with acetic acid and finally recrystallized from methanol to give long, colourless plates with m.p. 246–246.5° (decomp.). (Found: C 45.9; H 3.50; N 23.5; S 27.0. Calc. for C₇H₅N₄S₂ (236.30): C 45.8; H 3.41; N 23.7; S 27.1).

Reaction with methyl iodide in alkaline solution gave the benzaldehyde methylthiothiadiazolyhydrazone described in Part II, p. 1943.

The mercapto-thiadiazolyhydrazones (VIa–VIc) have also been prepared by reaction between mercaptothiadiazolyhydrazine hydrochloride²² and the appropriate carbonyl compounds in 50 % aqueous ethanol. The products were obtained in good yields and were recrystallized as above, and the identities of the products were confirmed with infrared spectra.

UV-Spectra were recorded with a Beckman DU spectrophotometer in absolute ethanol solution.

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