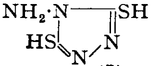
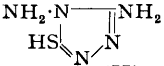
939. *The Reaction between* NN'-*Dithiocarbamylhydrazine and Hydrazine.*

By Eric Hoggarth.

Four triazoles are formed when *NN'*-dithiocarbamylhydrazine is heated with hydrazine. The separation of these compounds is described and evidence of structure given.

It is known that, when *NN'*-dithiocarbamylhydrazine $(NH_2\cdot CS\cdot NH\cdot)_2$ is heated under reflux with dilute aqueous hydrazine, three products may be isolated, *viz.*, (A) $C_2H_5N_5S$, (B) $C_2H_4N_4S_2$, and (C) ? $C_2H_5N_5S$. Compound (B) was proved to be 4-amino-3 : 5-dimercapto-4 : 1 : 2-triazole (I) (Arndt and Bielich, *Ber.*, 1923, **56**, 809), but formulæ (II), (III), and (IV) have been variously assigned to (A) and (C) on inconclusive evidence (*idem, loc. cit.*; Fromm and Layer, *Annalen*, 1923, **433**, 10; Fromm and Wetternick, *ibid.*, 1926, **447**, 300). We now provide additional evidence, confirming Fromm and Wetternick's view that (A) is (II) and (C) is (IV).


(I)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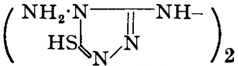
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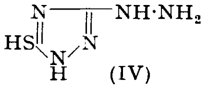
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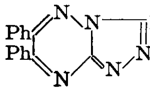
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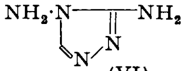
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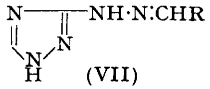
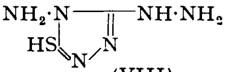
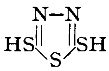
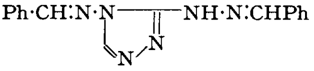

(VII)


(VIII)

(IX)



(X)

In our hands the reaction gave (A) and (C) as the two principal products. These gave almost identical analytical results and with a number of aldehydes gave distinct series of monobenzylidene derivatives. As noted by Arndt and Bielich (*loc. cit.*) methylation of the parent compounds gave water-soluble products but, by extraction of the methylation liquid with ether, isomeric *S*-methyl derivatives were isolated. This eliminates structure (III) for either compound. Further, the methyl derivative from (A) condensed very readily with a number of aldehydes, giving well-defined dibenzylidene derivatives, and with benzil gave the penta-azaindene derivative (V; R = SMe), reactions which are found to occur with other 3 : 4-diamino-4 : 1 : 2-triazoles (Hoggarth, *J.*, 1950, 614). Under similar conditions the methyl derivative from (C) reacted with only one molecule of benzaldehyde.

Presence of a thiol grouping in both (A) and (C) was proved by desulphurisations with Raney nickel. Compound (A) readily gave 3 : 4-diamino-4 : 1 : 2-triazole (VI). Although with benzil this readily gave a penta-azaindene derivative (V; R = H), it condensed under the usual conditions with one molecule only of a number of aldehydes. Raney nickel decomposed (C), but the arylidene derivatives readily gave 3-arylidenehydrazino-1 : 2 : 3-triazoles (VII).

If, after the original condensation, the 3 : 4-diamino-5-mercapto-4 : 1 : 2-triazole (II) was precipitated by cautious acidification, the sulphur content of the crude precipitate showed it to contain little 4-amino-3 : 5-dimercapto-4 : 1 : 2-triazole (I). A precipitate much richer in the dithiol was precipitated when an excess of acid was used, and the dithiol was then isolated as described by Arndt and Bielich. The 3-hydrazino-5-mercapto-1 : 2 : 4-triazole fraction was then found to contain appreciable amounts of a fourth triazole: this was separated by fractional precipitation of an acid solution with alkali and proved to be identical with 4-amino-3-hydrazino-5-mercapto-4 : 1 : 2-triazole (VIII) (Stollé and Bowles, *Ber.*, 1908, **41**, 1101). We have confirmed the somewhat doubtful structure of (VIII): the compound afforded a dibenzylidene derivative which with Raney nickel gave 4-benzylideneamino-3-benzylidenehydrazino-4 : 1 : 2-triazole (X).

EXPERIMENTAL

Reaction of NN′-*Dithiocarbamylhydrazine with Hydrazine*.—The diamide (45·0 g.) and hydrazine hydrate (63%; 70·0 c.c.) were heated in water (240 c.c.), with stirring, on the steam-bath for 2 hours, cooled, and filtered (charcoal), and the clear solution made *just* acid to Congo-red with concentrated hydrochloric acid (*ca.* 80·0 c.c.). After cooling, the crude 3 : 5-diamino-3-mercapto-4 : 1 : 2-triazole (II) was collected (6·6 g.) (Found: S, 26·0%), and dissolved in boiling aqueous ammonium carbonate (18·0 g. in 150 c.c.). After filtration, the solution was boiled (water being added to maintain constant volume) until ammonia ceased to be expelled, filtered hot, and allowed to crystallise, giving colourless needles (3·9 g.), of the diamino-triazole, which recrystallised from water (Found: C, 18·2; H, 3·8; S, 24·2. Calc. for $C_2H_5N_5S$: C, 18·3; H, 3·8; S, 24·4%). Placed in a bath at 190° and heated slowly it showed m. p. 204—206° (decomp.), but if placed in a bath at 200° and heated more quickly it gave m. p. 210—212° (decomp). Arndt and Bielich (*loc. cit.*) state that the m. p. of their compound varied between 207° and 225° depending upon the batch. Fromm and Layer (*loc. cit.*) quote m. p. 217°, and Fromm and Wetternick (*loc. cit.*) m. p. 198—199° (after many crystallisations). The ammonium carbonate liquor from the initial crystallisation was concentrated to small bulk and cooled and a further amount of (II) (1·1 g.) was removed. Acidification of the mother-liquor gave only a small precipitate.

The original filtrates from (II) were stirred in an ice-bath for 1 hour with a further 25 c.c. of concentrated hydrochloric acid, and the precipitate (9·9 g.) (Found: S, 37·7%) was collected and washed with a little water. This precipitate which contained most of the 4-amino-3 : 5-dimercapto-4 : 1 : 2-triazole was dissolved in boiling aqueous ammonium carbonate (18·0 g. in 100 c.c.), the solution was filtered, and excess of ammonia boiled off, the volume being kept constant by addition of water. The cloudy solution was filtered hot and allowed to crystallise, giving 3 : 4-diamino-5-mercapto-4 : 1 : 2-triazole (2·5 g.). The filtrates were concentrated to 50 c.c., filtered hot, and on cooling deposited a further 2·4 g. of (II). Next morning the filtrates were treated with charcoal and on treatment with concentrated hydrochloric acid gave 4-amino-3 : 5-dimercapto-4 : 1 : 2-triazole (I) (3·8 g.), which crystallised from water as colourless clumps of needles, m. p. 216—218° (decomp.) (Arndt and Bielich give m. p. 228°) (Found: C, 16·2; H, 2·6; N, 37·7; S, 42·6. Calc. for $C_2H_4N_4S_2$: C, 16·2; H, 2·7; N, 37·8; S, 43·3%).

The original, strongly acid filtrates from the crude dithiol were neutralised with solid potassium hydrogen carbonate, and the precipitate (15·0 g.) (Found: S, 14·4%) was collected and washed with a little water. This precipitate contained some inorganic material and was dissolved in N-sodium hydroxide (150 c.c.), filtered, and stirred whilst 10% acetic acid was added very slowly. At pH 9·3, again at pH 9·0, at pH 8·4, and finally at neutrality, the precipitate was collected. The first fraction (0·6 g.), consisting solely of small colourless needles, crystallised from water (300—400 c.c.) as very long, colourless, glistening needles of 4-amino-3-hydrazino-5-mercapto-4 : 1 : 2-triazole (VIII), m. p. 232° (decomp). (Found : C, 16·7; H, 4·1; N, 57·0; S, 22·3. Calc. for $C_2H_6N_6S$: C, 16·4; H, 4·1; N, 57·5; S, 21·9%) (see below). This compound (1·0 g.) with benzaldehyde (2·0 c.c.) in hot N-hydrochloric acid (50 c.c.) and alcohol (5·0 c.c.) gave the *dibenzylidene* derivative, pale yellow plates (from propyl alcohol) (0·8 g.), m. p. 245—246° (decomp.) (Found : C, 60·0; H, 4·6; S, 9·9. $C_{16}H_{14}N_6S$ requires C, 59·6; H, 4·4; S, 9·9%). The second fraction (0·4 g.) was clearly a mixture. But the third and fourth fractions (2·8 and 2·2 g., respectively) consisted almost entirely of colourless leaflets and were combined and crystallised from water, giving colourless leaflets, m. p. 237° (decomp.), of 3-hydrazino-5-mercapto-1 : 2 : 4-triazole (IV) (Found : C, 18·5; H, 4·3; N, 52·8; S, 24·0. Calc. for $C_2H_5N_5S$: C, 18·3; H, 3·8; N, 53·4; S, 24·4%). Arndt and Bielich give m. p. 240—242° (decomp.), and Fromm and Wetternick m. p. 248°. Purification by way of the sparingly soluble nitrate, and crystallisation from water, gave plates, m. p. 240—241° (decomp.) (Found : C, 18·2; H, 3·8%).

The following arylidene derivatives of 3 : 4-diamino-5-mercapto-4 : 2 : 1-triazole were obtained in good yield by shaking a solution of the triazole (2·6 g.) in hot water (150 c.c.) containing concentrated hydrochloric acid (0·1 c.c.) for 0·5 hour with the aldehyde (3·0 g.) in alcohol (10 c.c.), and crystallising the precipitate from aqueous alcohol or alcohol : 4(3)-benzylideneamino-, pale yellow leaflets, m. p. 215—216° (Found : C, 49·3; H, 4·2. Calc. for $C_9H_9N_5S$: C, 49·3; H, 4·1%) (Arndt and Bielich, *loc. cit.*, give m. p. 215°), 4(3)-p-*methoxybenzylideneamino-*, pale yellow needles, m. p. 222—224° (Found : C, 48·5; H, 4·8; S, 12·8. $C_{10}H_{11}ON_5S$ requires C, 48·2; H, 4·4; S, 12·85%), and 4(3)-p-*chlorobenzylidene-*, small colourless needles, m. p. 260—261° (decomp.) (Found : C, 42·6; H, 3·1; S, 13·1. $C_9H_8N_5ClS$ requires C, 42·6; H, 3·2; S, 12·6%).

The following substantially colourless arylidene derivatives of 3-hydrazino-3-mercapto-1 : 2 : 4-triazole were obtained similarly : benzylidene-, plates, m. p. 268—269° (decomp.) (Found : C, 49·1; H, 3·9; S, 14·9. Calc. for $C_9H_9N_5S$: C, 49·3; H, 4·1; S, 14·6%) (Arndt and Bielich give m. p. 274°), p-*methoxybenzylidene-*, plates, m. p. 264—265° (decomp.) (Found : C, 48·3; H, 4·6; S, 12·7. $C_{10}H_{11}ON_5S$ requires C, 48·5; H, 4·8; S, 12·8%), and p-*chlorobenzylidene-*, prisms, m. p. 276° (decomp.) (Found : C, 42·8; H, 3·3. $C_9H_8N_5ClS$ requires C, 42·6; H, 3·2%).

3 : 4-*Diamino*-5-*methylthio*-4 : 1 : 2-*triazole*.—The triazole (II) (26·0 g.) in N-sodium hydroxide (210 c.c.) was shaken with methyl iodide (16·0 c.c.) and alcohol (40 c.c.) for 1 hour, and the mixture neutralised with acetic acid, cooled in ice, and seeded. After 24—36 hours the crystals (17·6 g.) were crystallised from a small volume of water, giving the *methylthio*-compound as colourless flat needles (13·5 g.), m. p. 184—186° [Found : C, 24·9; H, 4·8; S, 22·1%; *M* (cryoscopic in water), 158, 160. $C_3H_7N_5S$ requires C, 24·8; H, 4·8; S, 22·1%; *M*, 145]. In the initial experiment nothing separated from the methylation liquid and the methylthio-compound was isolated by ether-extraction.

3-*Hydrazino*-5-*methylthio*-1 : 2 : 4-*triazole*.—The hydrazinotriazole (26·0) g. was methylated as described above. Nothing separated on neutralisation, even after seeding and storage overnight, and the clear liquid was extracted with ether in an automatic apparatus for 24 hours. The residue left after evaporation was allowed to harden, sucked free from syrupy impurities, and crystallised from ethyl acetate–alcohol, giving the *methylthio*-compound as colourless plates (6·0 g.), m. p. 154—156°, which become rust-coloured when kept [Found : C, 25·1; H, 4·7; S, 21·8; *M* (cryoscopic in water), 154, 153].

The following (all yellow needles) were prepared by heating 3 : 4-diamino-5-methylthio-4 : 1 : 2-triazole under reflux for 1 hour in alcohol with 5 mols. of aldehyde and a catalytic amount of potassium hydroxide, dilution with water, and crystallisation from alcohol : 3 : 4-*Dibenzylideneamino-*, m. p. 181—182° (Found : C, 63·6; H, 4·9; S, 10·3. $C_{17}H_{15}O_2N_5S$ requires C, 63·5; H, 4·7; S, 10·0%), 3 : 4-*di*-p-*methoxybenzylideneamino-*, m. p. 156—158° (Found : C, 59·7; H, 4·9; S, 8·3. $C_{19}H_{19}O_2N_5S$ requires C, 59·9; H, 5·0; S, 8·4%), and 3 : 4-*di*-p-*chlorobenzylideneamino*-5-*methylthio*-4 : 1 : 2-*triazole*, m. p. 212—214° (Found : C, 52·3; H, 3·2; S, 8·5. $C_{17}H_{13}N_5Cl_2S$ requires C, 52·3; H, 3·3; S, 8·2%).

The following colourless derivatives (needles) of 3-hydrazino-5-methylthio-1 : 2 : 4-triazole were obtained under similar conditions : *benzylidene-*, m. p. 255—257° (Found : C, 51·4;

H, 4·6; S, 13·5. $C_{10}H_{11}N_5S$ requires C, 51·5; H, 4·7; S, 13·7%), 3-p-*methoxybenzylidene-*, m. p. 260—262° (Found: C, 49·9; H, 4·8; S, 12·2. $C_{11}H_{13}ON_5S$ requires C, 50·2; H, 4·9; S, 12·2%), and 3-p-*chlorobenzylidene-*, m. p. 290—292° (from 2-ethoxyethanol) (Found: C, 44·6; H, 3·5; S, 11·9. $C_{10}H_{10}N_5Cl_2S$ requires C, 44·9; H, 3·7; S, 11·9%).

3-*Methylthio*-5 : 6-*diphenyl*-1 : 2 : 4 : 7 : 9-*penta-azaindene* (V; R = SMe).—3 : 4-Diamino-5-methylthio-4 : 1 : 2-triazole (1·5 g.), benzil (2·1 g.), and alcohol (50 c.c.) were refluxed. There was no obvious change after 1 hour. Potassium hydroxide (0·1 g.) was added, whereupon immediately the solution became deeply coloured and golden-yellow crystals began to separate (cf. *J.*, 1950, 614). After 1 hour the *aza-indene* was collected and crystallised from alcohol–2-ethoxyethanol, giving golden-yellow, flat needles (1·8 g.), m. p. 201—202° (Found: C, 64·2; H, 4·1; N, 22·2; S, 10·1. $C_{17}H_{13}N_5S$ requires C, 63·9; H, 4·1; N, 22·0; S, 10·0%).

3 : 4-*Diamino*-4 : 1 : 2-*triazole* (VI).—3 : 4-Diamino-5-mercapto-4 : 1 : 2-triazole (4·0 g.) in alcohol (100 c.c.) was stirred under reflux with Raney nickel (*ca.* 20 g.) for 1 hour. The hot filtered solution was evaporated and the residue crystallised from alcohol, giving large colourless plates (1·0 g.) of the *triazole* (VI), m. p. 216—218° (Found: C, 24·5; H, 5·2; N, 71·0. $C_2H_5N_5$ requires C, 24·3; H, 5·0; N, 70·7%). It gave a *benzylidene-*, almost colourless plates, m. p. 241—242° (Found: C, 58·0; H, 4·9. $C_9H_9N_5$ requires C, 57·8; H, 4·8%), p-*methoxybenzylidene-*, long deep yellow needles, m.p. 214—215° (Found: C, 55·4; H, 5·4. $C_{10}H_{11}ON_5$ requires C, 55·3; H, 5·1%), and p-*chlorobenzylidene*-derivative, small colourless needles, m. p. 223—225° (Found: C, 48·8; H, 3·7. $C_9H_8N_5Cl$ requires C, 48·8; H, 3·6%).

5 : 6-*Diphenyl*-1 : 2 : 4 : 7 : 9-*penta-azaindene* (V; R = H).—This *compound*, obtained from 3 : 4-diamino-4 : 1 : 2-triazole (1·0 g.) as described for the 3-methylthio-derivative, crystallised from alcohol in flat orange-red needles (1·6 g.), m. p. 182—183° (Found: C, 70·2; H, 4·1; N, 25·6. $C_{16}H_{11}N_5$ requires C, 70·3; H, 4·0; N, 25·7%).

3-*Benzylidenehydrazino*-1 : 2 : 4-*triazole* (VII; R = Ph).—3-Benzylidenehydrazino-5-mercapto-1 : 2 : 4-triazole (5·0 g.), alcohol (200 c.c.), and Raney nickel (*ca.* 20 g.) were refluxed with stirring for 1 hour and the hot filtered solution evaporated under reduced pressure. The residual *base* was crystallised several times from aqueous alcohol, giving colourless felted needles (2·0 g.), m. p. 226—228° (Found: C, 57·5; H, 4·8; N, 36·8. $C_9H_9N_5$ requires C, 57·8; H, 4·8; N, 37·4%).

3-p-*Methoxybenzylidenehydrazino-*, colourless needles, m. p. 211—212° (from alcohol) (Found: C, 54·6; H, 5·2; N, 32·3. $C_{10}H_{10}ON_5$ requires C, 55·3; H, 5·1; N, 32·2%), and p-*chlorobenzylidenehydrazino*-1 : 2 : 4-*triazole*, pale yellow felted needles, m. p. 249—251° (from aqueous alcohol) (Found: C, 48·5; H, 3·8; N, 31·0. $C_9H_8N_5Cl$ requires C, 48·7; H, 3·6; N, 31·6%), were prepared similarly.

4-*Amino*-3-*hydrazino*-5-*mercapto*-4 : 1 : 2-*triazole* (VIII).—This compound, obtained by Stollé and Bowles's method (*loc. cit.*) from 2 : 5-dimercapto-1 : 3 : 4-thiadiazole (IX) (Busch, *Ber.*, 1894, **27**, 2507), crystallised from water, in which it was very sparingly soluble, in long colourless needles, m. p. 230—231° (not depressed by the compound isolated as above) (Found: C, 16·6; H, 4·2%). 4-Benzylideneamino-3-benzylidenehydrazino-5-mercapto-4 : 2 : 1-triazole, prepared as previously, formed pale yellow plates, m. p. 245—246° also undepressed by the compound prepared as above (Found: C, 59·3; H, 4·6%).

4-*Benzylideneamino*-3-*benzylidenehydrazino*-4 : 1 : 2-*triazole*.—The mercaptotriazole (3·5 g.) was stirred vigorously under reflux in alcohol (350 c.c.) with Raney nickel (about 20 g.) for 1 hour. The clear filtrate was evaporated under reduced pressure and the residual *base* crystallised several times from alcohol, giving pale yellow needles (0·8 g.), m. p. 211—213° (decomp.) (Found: C, 65·9; H, 5·1; N, 29·2. $C_{16}H_{14}N_6$ requires C, 66·2; H, 4·8; N, 29·0%).

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