117. *Compounds related to Thiosemicarbazide. Part V.* 4 : 5-*Diamino*-3-*phenyl*-4 : 1 : 2-*triazole.*

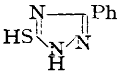
By Eric Hoggarth.

1 : 4-Dibenzoylthiosemicarbazide reacts with hydrazine to give 3-phenyl-1 : 2 : 4-triazole-5-thiol, benzhydrazide, and a compound $C_8H_9N_5$, whose reactions indicate that it is 4 : 5-*diamino*-3-*phenyl*-4 : 1 : 2-*triazole*.

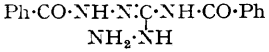
The work recorded here arose out of the observation mentioned in an earlier report (Part I, *J.*, 1949, 1160) that the hydrazine salt of 1 : 4-dibenzoylthiosemicarbazide (I) was rapidly decomposed in boiling alcohol with evolution of hydrogen sulphide. It was to be expected that hydrazine, in view of its basic nature, would cause a cyclisation of the dibenzoyl compound corresponding to that observed with 1-benzoylthiosemicarbazides (Part II, *J.*, 1949, 1163) and it was confirmed that with a solution of sodium in alcohol the expected cyclisation of (I) to 3-phenyl-1 : 2 : 4-triazole-5-thiol (II) (and benzoic acid) occurred. However the evolution of hydrogen sulphide with use of hydrazine indicated that, at least in part, interaction with elimination of the (potential) thiol grouping was taking place. When 1 : 4-dibenzoylthiosemicarbazide was refluxed with hydrazine and alcohol, a white crystalline sublimate formed. This sublimate was very unstable but a little of it, washed out with water, gave tests for hydrazine and the sulphide ion; it was probably a salt of hydrazine and hydrogen sulphide. In a stream of nitrogen no sublimate formed and absorption in acidified lead acetate solution showed that less than 50% of the theoretical amount of hydrogen sulphide (supposing complete elimination) was actually evolved. The residual solution was shown to contain the triazole-thiol (II), benzhydrazide, and a *compound* $C_8H_9N_5$, the formula of which is obtained by replacement of the thiol group by hydrazine and elimination of the elements of benzoic acid. It was shown that the triazolethiol was completely inert towards hydrazine under the reaction conditions and it seemed therefore that this new compound arose by a cyclisation of the (hypothetical) dibenzoyldiaminoguanidine (III). Of the three possible structures which must be considered (IV, V, and VI) the first two may be eliminated.

Ph·CO·NH·NH·CS·NH·CO·Ph

(I.)

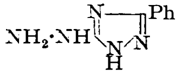


(II.)

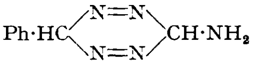


$\mathrm{Ph{\cdot}CO{\cdot}NH{\cdot}N{:}\underset{NH_2{\cdot}NH}{C}{\cdot}NH{\cdot}CO{\cdot}Ph}$

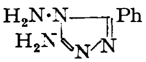
(III.)



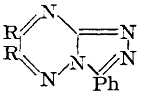
(IV.)



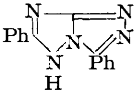
(V.)



(VI.)



(VII.)



(VIII.)

5-Hydrazino-3-phenyl-1 : 2 : 4-triazole (IV) was prepared (but not isolated) by Manchot (*Ber.*, 1910, **43**, 1312) and shown to form a well-defined monobenzylidene and related derivatives. The compound $C_8H_9N_5$ reacted with benzaldehyde or *p*-methoxybenzaldehyde in the presence of a little sodium hydroxide (but not in its absence) to give *dibenzylidene* and *di*-p-*methoxybenzylidene* derivatives having melting points quite different from those of the benzylidene derivatives described by Manchot. Further evidence for the 4 : 5-diamino-4 : 1 : 2-triazole structure was found in the ready condensation with α-diketones (benzil, diacetyl) to give 1 : 2 : 4 : 7 : 9-*penta-azaindenes* (VII; R = Ph or Me). Although these reactions seem conclusive in favour of structure (VI) it is known that dihydro-1 : 2 : 4 : 5-tetrazines are readily isomerised to *N*-aminotriazole derivatives. Thus Curtius, Darapsky, and Müller (*Ber.*, 1907, **40**, 815) found that dihydro-1 : 2 : 4 : 5-tetrazine itself gave 4-amino-4 : 1 : 2-triazole on fusion. It was possible therefore, that the compound $C_8H_9N_5$ had the dihydrotetrazine structure (V) and was giving derivatives of (VI) under the influence of alkaline catalysts. This possibility was disproved by showing that the compound was unchanged by fusion and recovered from the dibenzylidene compounds, mentioned above, by hydrolysis. Dihydrotetrazines in general are very readily oxidised to the corresponding tetrazines, many of which have an intense purple colour. The compound $C_8H_9N_5$ did not develop such a colour with oxidising agents but when first isolated was purple, the intensity varying from experiment to experiment. This colour, which may be ascribed to the oxidation of a trace of dihydrotetrazine contaminant, was lost on crystallisation.

Under mild conditions, 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole gave a *monobenzoyl* compound from which, by acid hydrolysis, the parent diamine could be recovered. By further reaction of the monobenzoyl derivative, or of the diamine with excess of benzoyl chloride, a *substance* $C_{22}H_{15}ON_5$ was obtained, corresponding to a dibenzoyl compound less the elements of water. On hydrolysis of this a *compound* $C_{15}H_{11}N_5$ was obtained which probably has the triazolotriazole structure (VIII).

EXPERIMENTAL.

Reaction of 1 : 4-*Dibenzoylthiosemicarbazide with Sodium Ethoxide Solution.*—The dibenzoyl compound (3·8 g.) was refluxed with a solution of sodium (1·2 g.) in alcohol (50 c.c.) until the copious yellow precipitate (the sodium salt of the dibenzoyl compound) had disappeared (*ca.* 16 hours). After cooling, the precipitated sodium benzoate (1·8 g.) was collected and dissolved in water, and the benzoic acid precipitated with acid (1·2 g.; m. p. 119—120°). The initial filtrate was evaporated under reduced pressure, and the residue dissolved in water (30 c.c.), filtered (charcoal), and precipitated with hydrochloric acid.

The 3-phenyl-1 : 2 : 4-triazole-5-thiol (2·0 g.; m. p. 255—256°) was crystallised from water, giving colourless needles (1·6 g.), m. p. and mixed m. p. 256—257° (Part I, *loc. cit.*) (Found: C, 54·3; H, 4·0. Calc. for $C_8H_7N_3S$: C, 54·2; H, 4·0%).

Reaction of 1 : 4-*Dibenzoylthiosemicarbazide with Hydrazine.*—A mixture of the dibenzoyl compound (6·0 g.), alcohol (50 c.c.), and hydrazine hydrate (8·0 c.c. of 50%) was refluxed in a stream of nitrogen until evolution of hydrogen sulphide ceased (8—9 hours). The effluent gas was washed in acidified lead acetate solution, and the lead sulphide collected in a Gooch crucible and dried at 110° (2·2 g.). The residual solution was evaporated under reduced pressure, the residue dissolved in water (50 c.c.), and hydrochloric acid was added, with good cooling, until the mixture was just acid to Congo-red paper. The precipitate (2·1 g.; m. p. 235—240°) was crystallised twice from water, giving colourless needles (0·7 g.) of 3-phenyl-1 : 2 : 4-triazole-5-thiol, m. p. 256—257° (Found: C, 54·5; H, 4·3%). The acid filtrates were evaporated under reduced pressure, the residue was cooled strongly, and 40% potassium hydroxide solution (10 c.c.) was added. The pink-tinged solid was collected (0·4 g.), washed with a little ice-water, and crystallised from water or alcohol, giving large colourless plates of 4 : 5-*diamino*-3-*phenyl*-4 : 1 : 2-*triazole* (0·25 g.), m. p. 224° (Found: C, 55·1; H, 5·3; N, 39·6. $C_8H_9N_5$ requires C, 54·9; H, 5·1; N, 40·0%). The alkaline filtrates were cooled, made just acid with 10% acetic acid, and evaporated under reduced pressure. The dry residue was extracted with chloroform, and the extracts were dried and evaporated, giving benzhydrazide (2·6 g.) which crystallised from benzene as colourless plates, m. p. and mixed m. p. 113° (Found: C, 61·9; H, 5·9. Calc. for $C_7H_8ON_2$: C, 61·8; H, 5·9%).

The diamine (0·5 g.) was melted in an oil-bath at 230° for 15 minutes, cooled, and crystallised from water, giving colourless plates (0·3 g.), m. p. 224°, not depressed by the original substance.

Attempt to cause 3-*Phenyl*-1 : 2 : 4-*triazole*-5-*thiol to react with Hydrazine.*—The thiol (1·8 g.), hydrazine hydrate (5·0 c.c. of 50%), and alcohol (50 c.c.) were refluxed for 36 hours. No hydrogen sulphide was evolved. The solvents were removed under reduced pressure, and water (25 c.c.) was added, followed by hydrochloric acid until the mixture was acid to Congo-red. The precipitate (1·5 g.; m. p. 258°) crystallised from water as colourless plates (1·0 g.), m. p. 258°, not depressed by the original thiol.

4 : 5-*Bisbenzylideneamino*-3-*phenyl*-1 : 2 : 4-*triazole.*—The diamino-compound (1·0 g.), freshly distilled benzaldehyde (1·0 c.c.), alcohol (20 c.c.), and potassium hydroxide (0·1 g.) were refluxed together for 0·5 hours, filtered quickly, and allowed to crystallise. The pale yellow crystals of *bisbenzylideneamino*-compound (1·0 g.) were collected and recrystallised from alcohol, giving yellow needles (0·6 g.), m. p. 202—203° (Found: C, 75·1; H, 5·0; N, 20·3. $C_{22}H_{17}N_5$ requires C, 75·2; H, 4·8; N, 20·0%). There was no precipitate when the same mixture but without the potassium hydroxide was boiled for 24 hours. This compound (0·3 g.) was boiled for 1 minute with concentrated hydrochloric acid (5 c.c.), and excess of acid evaporated in a dish. N-Hydrochloric acid (5 c.c.) was added, the oily drops of benzaldehyde were removed with ether, and the residual aqueous solution was clarified (charcoal) and treated with 40% potassium hydroxide solution. The pearly leaflets precipitated were collected, washed with ice-water, and crystallised from water, giving colourless plates (0·1 g.), m. p. 225°, not depressed by admixture with the diamine (Found: C, 54·5; H, 5·1%).

By use of *p*-methoxybenzaldehyde in place of benzaldehyde, the corresponding 4 : 5-*bis*-p-*methoxybenzylideneamino-triazole* was obtained as yellow clumps of needles (1·0 g.), m. p. 165° (from alcohol) (Found: C, 69·9; H, 4·6; N, 17·1. $C_{24}H_{21}O_2N_5$ requires C, 70·1; H, 5·1; N, 17·0%). Hydrolysis of this compound with acid gave *p*-methoxybenzaldehyde and the original diamine, m. p. and mixed m. p. 225°.

3 : 5 : 6-*Triphenyl*-1 : 2 : 4 : 7 : 9-*penta-azaindene* (VII; R = Ph).—The diamine (1·0 g.), benzil (1·2 g.), and alcohol (30 c.c.) were refluxed for 12 hours and cooled, whereupon benzil (1·0 g.) (only) separated. The original mixture, but with the addition of sodium hydroxide (0·05 g.), became intensely yellow on heating, and crystals separated. After 1 hour, the mixture was cooled, and the solid collected and crystallised from 2-ethoxyethanol giving the *penta-azaindene* as square, deep-yellow plates (1·0 g.), m. p. 250° (Found: C, 75·5; H, 4·5; N, 20·1. $C_{22}H_{15}N_5$ requires C, 75·6; H, 4·3; N, 20·1%).

3-*Phenyl*-5 : 6-*dimethyl*-1 : 2 : 4 : 7 : 9-*penta-azaindene* (VII; R = Me).—The above experiment was repeated with diacetyl (1·0 c.c.) in place of benzil, giving a yellow *product* which crystallised from aqueous diethylformamide in long deep-yellow needles (0·6 g.), m. p. 203° (Found: C, 64·2; H, 4·8; N, 31·1. $C_{12}H_{11}N_5$ requires C, 64·0; H, 4·9; N, 31·1%).

Action of Benzoyl Chloride on 4 : 5-*Diamino*-3-*phenyl*-4 : 1 : 2-*triazole.*—The diamine (1·8 g.) was dissolved in dry pyridine (75 c.c.) at 80° and a solution of benzoyl chloride (1·5 g.) in dry pyridine (10 c.c.) added with shaking. After 10 minutes, the pyridine was evaporated under reduced pressure, the residue treated with water (100 c.c.), and the solid collected, washed with water, and dried at 100° (3·0 g.; m. p. 258°). From alcohol, in which it is not very soluble, this *benzoyl* derivative crystallised in colourless leaflets, m. p. 264—266° (Found: C, 64·1; H, 4·9; N, 25·2. $C_{15}H_{13}ON_5$ requires C, 64·5; H, 4·7; N, 25·1%). The same compound was obtained by rubbing the diamine (0·5 g.) with benzoyl chloride (0·5 g.), whereupon a vigorous reaction took place. Pyridine (1 c.c.) was added, the mixture cautiously warmed to effect dissolution, and ice and water (20 g.) were added. The solid was collected and crystallised as above, giving colourless leaflets (0·4 g.), m. p. 266°. This compound (0·75 g.) was refluxed with 2-ethoxyethanol (15 c.c.) and concentrated hydrochloric acid (2·5 c.c.) for 0·5 hour and the solvent removed under reduced pressure. The residue was treated with N-sodium hydroxide (5 c.c.), and the solid collected and crystallised from water, giving colourless plates (0·25 g.), m. p. 224°, not depressed on admixture with the diamine. The benzoyl compound was stable to boiling N-sodium hydroxide, giving, on cooling, a crystalline sodium salt from which the original benzoyl compound was recovered by dissolution in N-hydrochloric acid and neutralisation with potassium hydrogen carbonate.

The above benzoyl compound (0·5 g.), benzoyl chloride (1 c.c.), and dry pyridine (10 c.c.) were refluxed for 12 hours. Water (15 c.c.) was added (too much water precipitated a tar), and the solid collected and washed, until nearly colourless, with alcohol. From alcohol the *substance* crystallised in colourless needles (0·4 g.), m. p. 196° (Found: C, 72·2; H, 4·0. $C_{22}H_{15}ON_5$ requires C, 72·3; H, 4·1%). The same substance was obtained from the original diamine (0·5 g.), benzoyl chloride (1·0 c.c.), and pyridine (10 c.c.), and crystallised from alcohol in colourless needles (0·45 g.), m. p. 196—198° (Found:

C, 72·4; H, 4·2%). This substance (2·8 g.), concentrated hydrochloric acid (5·0 c.c.), and 2-ethoxyethanol (50 c.c.) were refluxed for 3 hours. The solvent was removed under reduced pressure, and the residue dissolved in water (100 c.c.) and neutralised with potassium hydrogen carbonate. The solid was collected (2·0 g.; m. p. 230—235°) and crystallised from alcohol, giving (?) 5 : 5′-*diphenyl*-2 : 3-*dihydro*-4′ : 1′ : 2′-*triazolo*(4′ : 3′-2 : 3)-1 : 2 : 4-*triazole* (VIII) as colourless felted needles (1·5 g.), m. p. 257° (Found: C, 68·6; H, 4·5; N, 27·1. $C_{15}H_{11}N_5$ requires C, 69·0; H, 4·2; N, 26·8%).

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