Heterocyclic Compounds from Urea Derivatives. Part XI.[1] Synthesis of 1,2,4-Triazoles from 1,2-Diamino-3-phenylguanidine

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1,2-Diamino-3-phenylguanidine, synthesised by successive *S*-methylation and hydrazinolysis of 4-phenyl-3-thiosemicarbazide, reacts with an excess of diphenylcarbodi-imide yielding 3,5-dianilino-4-phenyl-1,2,4-triazole. Its interaction with aryl isothiocyanates produces 3-hydrazino-5-mercapto- and (mainly) 3-arylamino-5-mercapto-4-aryl-1,2,4-triazoles. Action of the appropriate quantities of phenyl isocyanate yields non-cyclic stable mono- or di-addition compounds. The results are correlated with the comparable behaviour of the parent, *NN'*-diaminoguanidine.

THE interaction of *NN'*-diaminoguanidine and carbodi-imides or iso(thio)cyanate esters is a useful general route to 1,2,4-triazole derivatives.[1-4] The initial addition of these reactive unsaturated systems to both amino-[5,6] and *NN'*-diaminoguanidine occurs preferentially at their hydrazino groups,[1,2,4,5b,c] but is directed to their central imino group[1-3,5a,6] when the hydrazine-groups are blocked. The present Paper briefly reports selected examples of this general synthesis employing an *NN'*-diaminoguanidine bearing a substituent at its central imino group: 1,2-diamino-3-phenylguanidine (I), chosen for this purpose, has given results that supplement those recorded for the parent compound, and are interpreted in terms of the general reaction mechanism previously employed.[1-4]

The action of diphenylcarbodi-imide on 1,2-diamino-3-phenylguanidine (I) in dimethylformamide afforded 3,5-dianilino-4-phenyl-1,2,4-triazole (VI) as the main product. Since 2 mol. of triazole arise from 1 mol. of guanidine (I) under the influence of excess of carbodi-imide, both hydrazino groups of (I) participate in the triazole formation. The general mechanism,[2] involving an intermediate adduct such as (V), accounts satisfactorily for the observations. On fission and cyclisation, this intermediate (V), incorporating 3 mol. of carbodi-imide, is visualised to yield 2 mol. of the triazole (VI) and 1 mol. of aniline. The latter competes for carbodi-imide and is converted by a fourth molecule of this reagent into *s*-triphenylguanidine (VII). In agreement with this interpretation, the use of 4 mol. of carbodi-imide does indeed give maximum yields of the two products (VI) (85%) and (VII) (55%); a larger excess

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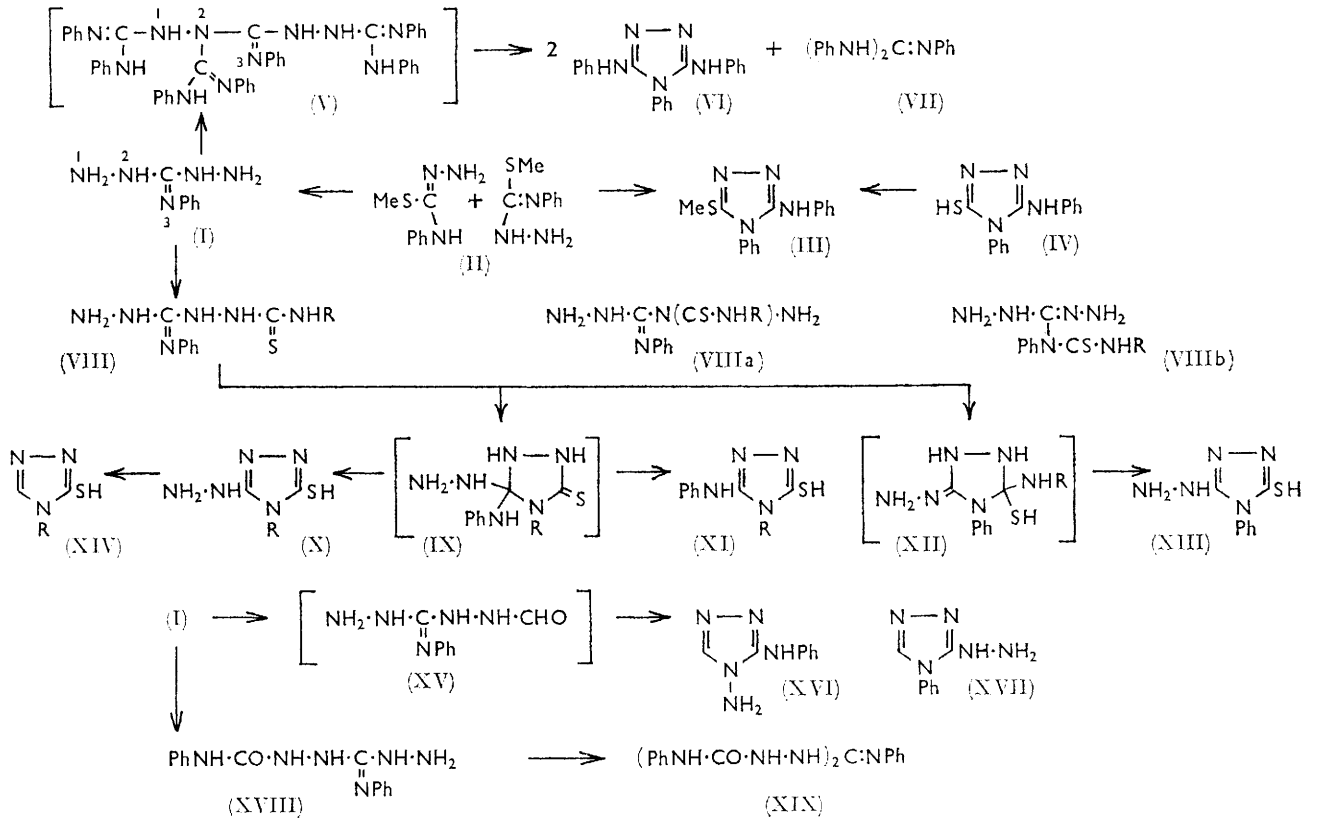
[3] F. Kurzer and K. Douraghi-Zadeh, *J. Chem. Soc.*, 1965, 4448.
[4] F. Kurzer and K. Douraghi-Zadeh, *J. Chem. Soc.* (*C*), 1966, 1.
[5] L. E. A. Godfrey and F. Kurzer, *J. Chem. Soc.*, (*a*) 1960, 3437; (*b*) 1961, 5137; (*c*) 1962, 3561.
[6] F. Kurzer and K. Douraghi-Zadeh, *J. Chem. Soc.*, 1965, 932.

is not advantageous, because it leads to the formation of carbanilide as additional by-product which is not readily separated from the mixture.

Equimolar proportions of phenyl isothiocyanate and 1,2-diamino-3-phenylguanidine (I) in dimethylformamide at 100° gave 3-hydrazino-5-mercapto-4-phenyl- (XIII) (18%) and 3-anilino-5-mercapto-4-phenyl-1,2,4-triazole (XI; R = Ph) (46%), which were identified by comparison with authentic samples.[3,5c] *p*-Methoxyphenyl isothiocyanate similarly yielded 3-anilino-5-mercapto-4-*p*-methoxyphenyl-1,2,4-triazole (XI; R = *p* MeO·C_6H_4) (52%), together with some 3-hydrazino-5-mercapto-4-phenyl- (XIII) (12%) and 3-mercapto-4-*p*-methoxyphenyl-1,2,4-triazole (XIV; R = *p*-MeO·C_6H_4) (8%). The formulation of the latter is based on its alternative synthesis by alkaline degradation of authentic 3-hydrazino-5-mercapto-4-*p*-methoxyphenyl-1,2,4-triazole [4] (X; R = *p*-MeO·C_6H_4), *i.e.*, by the path (X) ⟶ (XIV) by which it probably arises in the present reaction. The structure of the remaining product (XI; R = *p*-MeO·C_6H_4) is assigned by analogy with the confirmed formulations. Under the prevailing conditions, cyclisation with loss of hydrogen sulphide does therefore not occur. In yielding 3-mercapto-1,2,4-triazole derivatives throughout, the reaction thus follows closely that of the parent, *NN'*-diaminoguanidine.[3]

The action of isothiocyanates is interpreted in terms of the usual mechanism involving the formation and ring-closure of primary adducts (VIII), possibly by way of cyclic intermediates (IX) and (XII) arising by intramolecular nucleophilic attack of the RNH (or PhNH) group of (VIII) on the remote carbon atom of the guanidino chain, followed by elimination of the appropriate fragments (cf. reaction scheme). In this reaction sequence, two distinct cyclic intermediates, (IX) and (XII), are considered, since the first (IX) cannot alone account for the observed formation of 3-hydrazino-5-mercapto-4-phenyl-1,2,4-triazole (XIII) from *p*-methoxyphenyl isothiocyanate and the guanidine (I). The scheme further shows that the aryl group of the isothiocyanate ester reappears in the 4-position of the resulting 1,2,4-triazole; its retention in the 3(or 5)-position would necessitate the loss of the elements of hydrogen sulphide in the cyclisation.



The observations provide sufficient evidence to disprove the possible primary formation of alternative adducts (VIIIa, b) by the attack of the isothiocyanate at N(2) or N(3) of the guanidine compound (I). Adduct (VIIIa) would yield 4-aminotriazoles [*e.g.*, the 3-mercapto-derivative of (XVI), by loss of arylamine]; adduct (VIIIb) may act as precursor of (XIII), but not of (XI) or (XIV), which are in fact all obtained.

The adducts of diaminophenylguanidine (I) and phenyl isocyanate differed from their analogues incorporating isothiocyanates and carbodi-imide [*i.e.*, (VIII) and

(V)] in the expected manner [1,5b] in lacking their tendency to cyclise spontaneously under the experimental conditions. Thus, action of 2 mol. of phenyl isocyanate on 1,2-diamino-3-phenylguanidine (I) gave 60—75% yields of a diaddition-product, which is formulated, in agreement with comparable examples,[1,5b] as the open-chain adduct (XIX). The compound was a monoacid base, giving a picrate; it was isolated as the free base more readily than its parent, *NN'*-di-(ω-phenylureido)-guanidine.[1] The mono-adduct (XVIII) was similarly formed from appropriate proportions of the reactants. Since it retained a free hydrazine group, it readily gave derivatives with ketonic reagents (*e.g.*, benzaldehyde, acetylacetone); these were particularly useful for isolation purposes, since the adduct itself was difficult to purify.

In conclusion, the condensation of 1,2-diamino-3-phenylguanidine (I) and formic acid has been examined. It proceeded with loss of 2 mol. of water, and thus gave rise to either 4-amino-3-anilino- (XVI) or 3-hydrazino-4-phenyl-1,2,4-triazole (XVII) (possible tetrazine formation being discounted). The product, obtained in moderate yield as the picrate, did not give a pyrazolyl derivative on treatment with acetylacetone and is therefore formulated as (XVI). This interpretation brings the reaction into line with that of *NN'*-diaminoguanidine, which is converted into 3,4-diamino-1,2,4-triazole by formic acid.[7]

1,2-Diamino-3-phenylguanidine (I) required in this work was readily prepared by a modification of a synthesis of the parent compound.[8] Successive *S*-methylation and hydrazinolysis of 4-phenyl-3-thiosemicarbazide gave the desired product as the hydriodide in 75—85% yield. Small quantities (4—7%) of 3-anilino-5-methylthio-4-phenyl-1,2,4-triazole (III) arose as by-product, presumably by the condensation of 2 mol. of the *S*-methyl intermediate (II), with elimination of hydrazine and methanethiol (see also ref. 9). The structure of this by-product was confirmed by its identity with authentic material [10] obtained by *S*-methylation of 3-anilino-5-mercapto-4-phenyl-1,2,4-triazole (IV). 1,2-Diamino-3-phenylguanidine is a monoacid base, giving a monopicrate and a mononitrate, but it reacted with 2 mol. of ketonic reagents (*e.g.*, acetone, benzaldehyde) as expected. It is recalled that *NN'*-diaminoguanidine, the parent base, behaves analogously.[2,11]

EXPERIMENTAL

Light petroleum had b. p. 60—80°. Dimethylformamide was redistilled before use, and the water-containing forerun rejected. Ultraviolet absorption measurements were made with a Unicam S.P. 500 spectrophotometer on 0·00005M-ethanolic solutions.

1,2-*Diamino*-3-*phenylguanidine*.—A solution of 4-phenyl-3-thiosemicarbazide (16·7 g., 0·1 mole) in methanol (200 ml.)–methyl iodide (56·8 g., 0·4 mole) was refluxed for 30 min., and distilled under reduced pressure to approximately one-quarter bulk. The liquid was diluted with methanol (120 ml.)–water (120 ml.), treated dropwise at room temperature, while being stirred, with 10% aqueous hydrazine hydrate (50 ml., 0·1 mole) during 1 hr., and stirring continued for 24 hr. Methanethiol was evolved, and a fine precipitate (A) appeared and was filtered off. The pink filtrate was evaporated to small volume (*ca.* 25 ml.) in a vacuum; dilution of the residual liquid with ethanol (10 ml.) and storage at 0° gave prisms (22—25 g., 75—85%) of 1,2-*diamino*-3-*phenylguanidine hydriodide*, m. p. 157—158° (Found: C, 28·3; H, 4·7; I, 42·6; N, 23·6. $C_7H_{11}N_5$,HI requires C, 28·7; H, 4·1; I, 43·3; N, 23·9%). (Material for analysis and m. p. determination was recrystallised from 80% ethanol and kept for successive 30 min. periods at 70, 80, 90, and 110°.)

Precipitate A gave, on crystallisation from ethanol (70 ml. per g.), felted needles (total, 0·56—1·0 g., 4—7%) of 3-anilino-5-methylthio-4-phenyl-1,2,4-triazole, m. p. and mixed m. p.[10] 229—231° (Found: N, 19·65, S, 11·1. Calc. for $C_{15}H_{14}N_4S$: N, 19·9; S, 11·35%).

1,2-*Diamino*-3-*phenylguanidine picrate*, prepared from the hydriodide in ethanol, formed large spikes (from 80% ethanol), m. p. 157—159° (decomp.) (80%) (Found: C, 39·6; H, 3·6. $C_7H_{11}N_5$,$C_6H_3N_3O_7$ requires C, 39·6; H, 3·55%).

A stirred solution of the hydriodide (14·65 g., 0·05 mole) in warm water (25 ml.) was treated dropwise with silver nitrate (8·5 g., 0·05 mole) dissolved in water (20 ml.). The precipitated silver iodide (rapidly turning black) was filtered off at the pump, washed with boiling water (5 × 10 ml.), and the combined filtrate and washing liquid were distilled in a vacuum to very small volume (*ca.* 8—10 ml.). The liquid was diluted with hot ethanol (20 ml.), filtered if necessary, again distilled down, and slowly diluted with half its volume of ether. Crystallisation of the resulting solid (9·8 g., 80%) from ethanol–ether (1 : 1) gave prismatic needles of the *hydrated nitrate*, m. p. 108—110° (Found: C, 34·2; H, 5·6; N, 34·6. $C_7H_{11}N_5$,HNO_3,H_2O requires C, 34·15; H, 5·7; N, 34·15%).

Derivatives. To the suspension obtained by addition of sodium (0·23 g., 0·01 g.-atom) to acetone (40 ml.), 1,2-diamino-3-phenylguanidine hydriodide (2·93 g., 0·01 mole) was added. The stirred liquid was refluxed for 30 min., distilled to one-third of its volume, and stirred into ice–water. The collected precipitate was extracted with cold methanol (5 ml.), and the resulting white solid (m. p. 92—93°; 1·75 g., 72%) crystallised from a little ethanol–acetone (3 : 1), yielding prismatic needles of 1,2-*di*(*isopropylideneamino*)-3-*phenylguanidine*, m. p. 94—95° (Found: C, 63·7; H, 7·8; N, 28·8. $C_{13}H_{19}N_5$ requires C, 63·7; H, 7·75; N, 28·6%).

A solution of 1,2-diamino-3-phenylguanidine hydriodide (1·46 g., 0·005 mole) in 0·5N-sodium hydroxide (10 ml., 0·005 mole) was treated, with shaking, with benzaldehyde (1·06 g., 0·01 mole) dissolved in ethanol (5 ml.) during 15 min., and shaking was continued for 30 min. The suspension was diluted with water (10 ml.), and the solid col-

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[11] L. F. Audrieth and G. C. Hale, U.S.P. 2,929,698/1960 *Chem. Abs.*, 1960, **54**, 12,588).

lected at 0°. Crystallisation from ethanol (12 ml. per g.) gave ivory-white felted needles (1·4 g., 82%) of 1,2-*di*-(*benzylideneamino*)-3-*phenylguanidine*, m. p. 140—141° (Found: C, 73·5; H, 5·6; N, 20·85. $C_{21}H_{19}N_5$ requires C, 73·9; H, 5·6; N, 20·5%).

1,2-*Diamino*-3-*phenylguanidine*.—(a) *Action of diphenylcarbodi-imide*. A solution of 1,2-diamino-3-phenylguanidine hydriodide (1·47 g., 0·005 mole) in dimethylformamide (5 ml.) was treated dropwise with diphenylcarbodi-imide (3·9 g., 0·02 mole), kept at 100° for 2 hr., cooled, and stirred into ice–water (60 ml.). The solidified resinous precipitate was digested with cold methanol (2 × 10 ml.), and the white solid filtered off (filtrate M). Crystallisation from ethanol gave lustrous platelets (2·78 g., 85%) of 3,5-dianilino-4-phenyl-1,2,4-triazole, m. p. and mixed m. p.[2,5c] 232—234°, further identified by its ultraviolet spectrum.[2] Filtrate M was decanted from a small amount of separated gum and treated with picric acid (1·4 g., 0·006 mole) in ethanol (20 ml.); the liquid deposited *s*-triphenylguanidine picrate, m. p. and mixed m. p.[12] 180—181° (1·42 g., 55%) (from 80% ethanol). In an experiment employing 3 mol. of carbodi-imide, the yields of the two products were reduced to 75 and 18%, respectively. The use of 2 mol. of carbodi-imide gave the triazole in 45% yield (based on the carbodi-imide).

(b) *Action of phenyl isothiocyanate*. A solution of 1,2-diamino-3-phenylguanidine hydriodide (2·93 g., 0·01 mole) in hot dimethylformamide (5 ml.) was treated dropwise with phenyl isothiocyanate (1·35 g., 0·01 mole), and the liquid kept at 100° for 18 hr. The separated solid was collected at room temperature and rinsed with a little ethanol; it was 3-hydrazino-5-mercapto-4-phenyl-1,2,4-triazole, m. p. and mixed m. p.[4] 244—245° (decomp.) (0·37 g., 18%). The filtrate therefrom was evaporated (to *ca.* 8 ml.) in a vacuum, and the liquid stirred into ice–water. The supernatant aqueous liquid (L) was decanted from the semi-solid reddish gum, which was stirred with cold methanol (5 ml.). The resulting purple solid gave, on crystallisation from methanol (carbon), needles of 3-anilino-5-mercapto-4-phenyl-1,2,4-triazole, m. p. and mixed m. p.[5c] 204—206° (1·23 g., 46%) (Found: C, 61·9; H, 4·8; N, 20·9. Calc. for $C_{14}H_{12}N_4S$: C, 62·7; H, 4·5; N, 20·9%).

The aqueous liquid L was acidified with hydrochloric acid and treated with 0·05M-picric acid (0·005 mole); the separated product, collected after partial spontaneous evaporation, and crystallised from water (10 ml.) was hydrazine picrate hemihydrate, m. p. and mixed m. p.[13] 195—196° (decomp.) (lit.,[13] 201·3) (0·97 g., 36%).

(c) *Action of* p-*methoxyphenyl isothiocyanate*. Interaction of the reactants (0·01 mole each) (as described immediately above) during 36 hr. at 100° slowly deposited crystalline 3-hydrazino-5-mercapto-4-phenyl-1,2,4-triazole, m. p. and mixed m. p.[4] 244—245° (0·25 g., 12%). Addition of the filtrate therefrom to ice–water gave a gum, which solidified on storage, and was collected at 0° (filtrate L). It was digested with cold methanol (2 × 10 ml.) and crystallised from methanol (50 ml. per g., recovery 60%), yielding solvated 3-*anilino*-5-*mercapto*-4-p-*methoxyphenyl*-1,2,4-*triazole* as glass-like large prisms, m. p. 227—229° (total, 1·7 g., 52%) (Found: C, 59·2; H, 4·7; N, 16·8; S, 10·2. $C_{15}H_{14}N_4OS,CH_3OH$ requires C, 58·2; H, 5·45; N, 17·0; S, 9·7%).

The aqueous filtrate L was extracted with ether (4 × 20 ml.). Removal of the solvent and crystallisation of the small residue from methanol gave white felted needles of 3-mercapto-4-*p*-methoxyphenyl-1,2,4-triazole, m. p. and mixed m. p. (see immediately below) 196—198° (0·17 g., 8%) (Found: C, 52·1; H, 4·4; N, 19·9; S, 15·0. Calc. for $C_9H_9N_3OS$: C, 52·2; H, 4·35; N, 20·3; S, 15·5%). The aqueous layer from the ether extracts gave, on addition of picric acid, a mixture of picrates (*ca.* 1 g.) which were not completely separable by fractional crystallisation.

3-*Mercapto*-4-p-*methoxyphenyl*-1,2,4-*triazole*.—A solution of 3-hydrazino-5-mercapto-4-*p*-methoxyphenyl-1,2,4-triazole (0·59 g., 0·0025 mole) in 3N-sodium hydroxide (3·33 ml., 0·01 mole) was kept at 100° for 24 hr. (slight gas evolution). The cooled purple liquid was acidified (to pH 3) with 3N-hydrochloric acid and evaporated, with addition of ethanol and benzene, to dryness in a vacuum. The residue was 3-*mercapto*-4-p-*methoxyphenyl*-1,2,4-*triazole*, m. p. 196—198°, forming prismatic needles (0·35 g., 68%) (from ethanol) (Found: C, 52·2; H, 4·3. $C_9H_9N_3OS$ requires C, 52·2; H, 4·35%).

Action of Phenyl Isocyanate on 1,2-*Diamino*-3-*phenylguanidine*.—(a) 1-*Benzylideneamino*-2-*phenyl*-3-(ω-*phenylureido*)*guanidine*. A solution of 1,2-diamino-3-phenylguanidine hydriodide (1·76 g., 0·006 mole) in dimethylformamide (12 ml.), treated with phenyl isocyanate (0·6 g., 0·005 mole), was kept on a steam-bath for 1·5 hr. It was diluted with ethanol (20 ml.), treated with benzaldehyde (1 ml.) and concentrated hydrochloric acid (0·5 ml.), and refluxed for a further 1 hr. Dilution of the liquid with ice–water (100 ml.), and basification with 3N-ammonium hydroxide gave a soft resinous precipitate. This was dissolved in boiling ethanol (50 ml.), and a trace of insoluble material filtered off. Partial evaporation of the filtrate and storage gave white felted needles (1·12 g., 60%) of 1-*benzylideneamino*-2-*phenyl*-3-(ω-*phenylureido*)*guanidine*, m. p. 174—176° (Found: C, 67·1; H, 5·1; N, 22·5. $C_{21}H_{20}N_6O$ requires: C, 67·7; H, 5·4; N, 22·6%). Evaporation of the filtrates therefrom and crystallisation of the residue from very little ethanol gave silky needles (0·41 g., 20%) of 1,2-di(benzylideneamino)-3-phenylguanidine, m. p. and mixed m. p. (see above), 140—141°.

Interaction of the above reactants (30 min., 1 or 2 mol. of phenyl isocyanate) in boiling dimethylformamide gave merely *s*-diphenylurea (70%).

(b) 3,5-*Dimethyl*-1-(N-*phenyl*-N′-ω-*phenylureido*)*amidinopyrazole*. Interaction of the reactants as in (a) above, but with addition of acetylacetone (5 ml.) in place of benzaldehyde, gave a liquid that deposited a crystalline precipitate early during the final period of refluxing (1 hr.). It was collected at 0° (m. p. 232—235°; 0·65—0·82 g., 35—45%) (filtrate F), and consisted, after being boiled with ethanol (20 ml.), of minute lustrous prisms of hydrated 3,5-*dimethyl*-1-(N-*phenyl*-N′-ω-*phenylureido*)*amidinopyrazole*, m. p. 235—238° (Found: C, 62·2;, H 5·2; N, 22·2. $C_{19}H_{20}N_6O,H_2O$ requires C, 62·3; H, 6·0; N, 22·95%). It had a steep $\lambda_{max.}$ 240 mμ (log ε 4·67). (It is noted that the composition of this product also agrees with its being a simple hydrazone of the reactants, and this has not been disproved.)

Filtrate F was diluted with water (150 ml.), and basified with 3N-ammonium hydroxide. The resulting precipitate was collected after prolonged storage, and gave, on crystallisation from a large volume of acetone–ethanol (1 : 1) (partial evaporation necessary), felted needles of 1,2-di-(ω-phenylureido)-3-phenylguanidine, m. p. and mixed

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[13] E. C. Gilbert, *J. Phys. Chem.*, 1929, **33**, 1236.

m. p. (see below) 204—206° (0·2—0·3 g., 20—30%) (Found: C, 62·6; H, 5·3; N, 25·1%).

(c) 1,2-*Di*-(ω-*phenylureido*)-3-*phenylguanidine*. A cold solution of 1,2-diamino-3-phenylguanidine hydriodide (2·93 g., 0·01 mole) in dimethylformamide (20 ml.) was treated dropwise with phenyl isocyanate (2·62 g., 0·022 mole), and the resulting hot liquid kept on a steam-bath for 2 hr. It was stirred into ice–water (150 ml.), the clear solution decanted from a little oily deposit (T), and basified with 3N-ammonia. The resulting white precipitate was collected, washed with water (m. p. 198—200°; 2·0—2·4 g., 50—60%), and gave, on crystallisation from a large volume of ethanol (2 l. per g.), minute needles (of faintly purple tinge) of 1,2-*di*-(ω-*phenylureido*)-3-*phenylguanidine*, m. p. 204—206° (Found: C, 62·6; H, 5·0; N, 24·4. $C_{21}H_{21}N_7O_2$ requires C, 62·5; H, 5·2; N, 24·3%). The product was almost insoluble in the usual organic solvents. It dissolved in ethanol with addition of 3N-hydrochloric acid, and was reprecipitated therefrom by ammonia or sodium hydroxide.

The solidified resin T was dissolved in acetone (25 ml.), the whole allowed to evaporate spontaneously, and the residue digested with cold methanol (2 × 5 ml.); the undissolved white powder was 1,2-di-(ω-phenylureido)-3-phenylguanidine, m. p. 202—204° (0·4—0·6 g., 10—15%).

The foregoing substituted guanidine (0·4 g., 0·001 mole) in hot ethanol (10 ml.)–3N-hydrochloric acid (1 ml.) gave, on treatment with 10% ethanolic picric acid (0·46 g., 0·002 mole), the *monopicrate* nearly quantitatively. It formed felted microneedles, m. p. 197—199° (decomp.) (from a large volume of 75% ethanol) [Found (for a specimen dried at 120°): C, 51·6; H, 4·0; N, 22·2. $C_{21}H_{21}N_7O_2,C_6H_3N_3O_7$ requires C, 51·3; H, 3·8; N, 22·15%].

4-*Amino*-3-*anilino*-1,2,4-*triazole*.—1,2-Diamino-3-phenylguanidine (2·93 g., 0·01 mole) and formic acid (98%; 0·56 g., 0·012 mole) were kept on a steam-bath for 8 hr. (temporary solidification of reaction mixture during first 2 hr.). The reddish liquid was diluted with methanol (10 ml.) and treated with picric acid (2·3 g., 0·01 mole) dissolved in methanol (10 ml.). On partial evaporation, the liquid deposited successive non-homogenous crops (2·9 and 0·9 g.), which gave, after two crystallisations from 80% ethanol (4 ml. per g.), prisms (1·54 g., 38%) of 4-*amino*-3-*anilino*-1,2,4-*triazole picrate*, m. p. 178—180° (decomp., after sintering from 170°) (Found: C, 42·2; H, 3·4; N, 27·2. $C_8H_9N_5,C_6H_3N_3O_7$ requires C, 41·6; H, 3·0; N, 27·7%. This picrate (0·001 mole) was recovered (85%) after its ethanolic solution containing acetylacetone (0·0015 mole) had been kept at 100° for 3 hr.

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