727. *Heterocyclic Compounds from Urea Derivatives. Part VII.* Addition-products of Diaminoguanidine and Carbodi-imides, and their Cyclisation*

By Frederick Kurzer and K. Douraghi-Zadeh

NN'-Di(isopropylideneamino)guanidine adds carbodi-imides at its central imino-group yielding 3-(*NN'*-diarylamidino)-1,2-di(isopropylideneamino)-guanidines. The addition products are cyclised in acid media to 3-arylamino-5-hydrazino-1,2,4-triazoles; these form hydrazones, and undergo the expected reactions with acetylacetone and ethyl acetoacetate. Their formulation is supported by the degradation of the toluene-*p*-sulphonyl derivative of 3-anilino-5-hydrazino-1,2,4-triazole to authentic 3-anilino-1,2,4-triazole.

The main products of the interaction of an excess of diarylcarbodi-imide with diaminoguanidine lacking protecting groups are 4-aryl-3,5-diarylamino- and 3-amino-4-aryl-5-arylamino-1,2,4-triazoles. Primary addition-products are not isolated, but the formation of the triazoles is accounted for by a mechanism involving the successive addition of carbodi-imide molecules to the hydrazino-groups of diaminoguanidine, followed by cyclisation. The superior reactivity, towards carbodi-imides, of the hydrazino- over the imino-group in diaminoguanidine is in agreement with analogous observations made with aminoguanidine.

Carbodi-imides, and isothiocyanate and isocyanate esters, containing reactive twinned double bonds, are readily added to aminoguanidine, at either its hydrazino- or amidino-group, depending on the conditions. This group of reactions, followed by appropriate cyclisations, provides useful routes to 1,2,4-triazole and 1,3,4-thiadiazole derivatives.[1-3]

* Part VI, F. Kurzer and K. Douraghi-Zadeh, *J.*, 1965, 932.

[1] L. E. A. Godfrey and F. Kurzer, *J.*, (*a*) 1960, 3437; (*b*) 1961, 5137; (*c*) 1962, 3561.
[2] F. Kurzer and K. Douraghi-Zadeh, *J.*, 1965, 932.
[3] F. Kurzer and L. E. A. Godfrey, *Angew. Chem.*, 1963, **75**, 1157; *Internat. Edn.*, 1963, **2**, 459.

In continuation of this work, the behaviour of diaminoguanidine in this series of reactions has been examined; this Paper describes its condensation with carbodi-imides, and the cyclisation of the resulting addition products.

Interaction of equimolar proportions of *NN'*-di(isopropylideneamino)guanidine (II) and diarylcarbodi-imides in acetone or dimethylformamide gave 3-(*NN'*-diarylamidino)-1,2-di(isopropylideneamino)guanidines (III) rapidly in good yield. In the former solvent, the diaminoguanidine (I) was converted into the dihydrazone (II) advantageously *in situ*. The results of the cyclisation (see below) of the addition products (III) exclude their alternative formulation as (IIIa); in the presence of blocking-groups on the hydrazino-moieties of diaminoguanidine, the added carbodi-imide thus reacts exclusively at the central imino-group (of II).

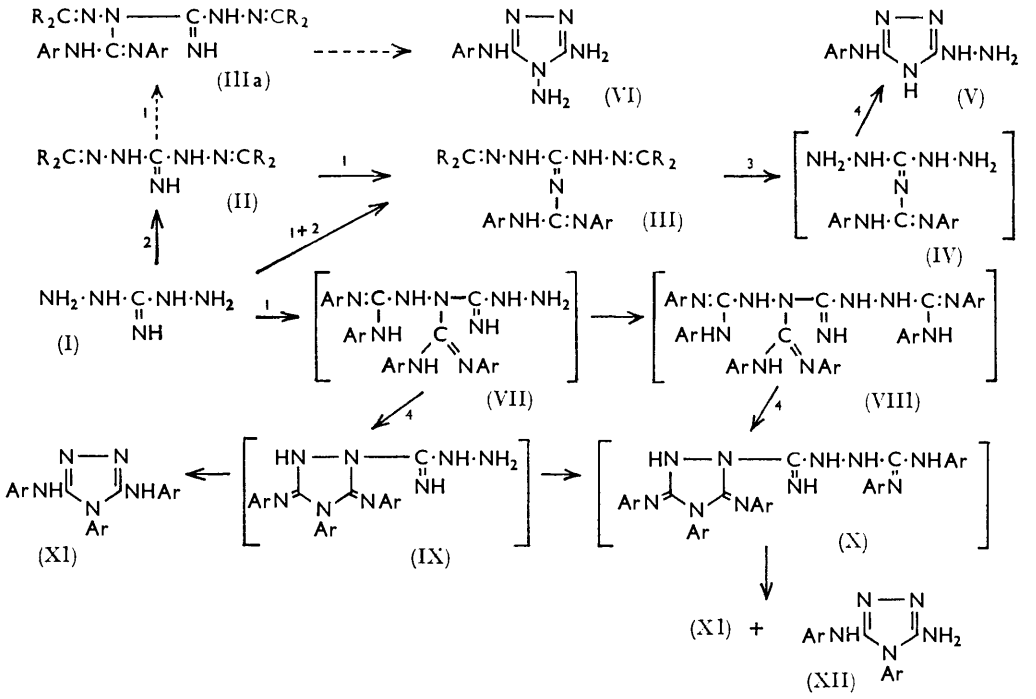
In dilute mineral acid the addition products (III) are cyclised to 3-arylamino-5-hydrazino-1,2,4-triazoles (V) in very good yield, with simultaneous elimination of arylamine and acetone: the cyclisation proceeded so rapidly that the presumed intermediate-free hydrazine derivatives (IV) were not obtained. Part of the reactant (III) was lost in a hydrolytic side-reaction, as shown by the isolation of smaller quantities (up to 24%) of hydrazine (as dipicrate). The cyclisation is thus entirely analogous to that of 1-(*NN'*-diarylamidino)-3-isopropylideneaminoguanidine [2] derived from aminoguanidine, except for the production, as expected, of 3-hydrazino- instead of the corresponding 3-amino-5-arylamino-1,2,4-triazoles.[2] Since hydrazino-1,2,4-triazoles are not readily accessible from the preformed heterocyclic system by the usual methods, *e.g.*, hydrazinolysis of the corresponding alkanethiol [4] or alkanesulphonyl compounds (see below), their production by direct cyclisation is of special preparative value. Comparable syntheses, involving generically related derivatives of diamino- [5,6] and triamino-guanidine [7] have recently been described.

The possible alternative interpretation of the above sequence of reactions (*i.e.*, as II ⟶ IIIa ⟶ VI) is rejected by confirmation of the final cyclisation products as 3-arylamino-5-hydrazino-1,2,4-triazoles (V), based on their general chemical properties, and the degradation of the 3-anilino-homologue (V; Ar = Ph). They slowly reduced ammoniacal silver nitrate and readily gave hydrazones (XIII) with ketonic compounds (*e.g.*, acetone, diethyl ketone, benzaldehyde). 3-Anilino-5-hydrazino-1,2,4-triazole (V; Ar = Ph) gave the monobenzylidene-derivative (XIII; Ar = Ph, $:CR_2 = :CHPh$) under conditions when 3,4-diamino-1,2,4-triazoles yield dibenzylidene derivatives.[8a] The hydrazones were stable towards alkalis, but were reconverted into the free hydrazines (*e.g.*, V; Ar = Ph) by acid hydrolysis. Simultaneous removal of the liberated acetone from the reaction mixtures was essential, to prevent its ready recombination with the hydrazine (V); this was done, as in the case of less stable 3-hydrazino-1,2,4-thiadiazoles,[9] by the addition of aminoguanidine, with which the ketone appears to react preferentially. More simply, because of the superior stability of 5-hydrazino-1,2,4-triazoles towards mineral acids, the acetone could be removed directly by distillation.

Being predominantly basic, the hydrazines (V) gave picrates, and were soluble in dilute mineral acids and reprecipitated by ammonia; their amphoteric nature, presumably attributable to the influence of the nucleus,[10a] was reflected by their solubility in strong alkalis. The hydrazones (XIII) showed the same properties, though to a less pronounced degree.

[4] C. F. Kröger, E. Tenor, and H. Beyer, *Annalen*, 1961, **643**, 121.
[5] H. Gehlen and G. Robisch, *Annalen*, 1963, **665**, 132; H. Gehlen and F. Lemme, *Naturwiss.*, 1963, **50**, 645.
[6] G. I. Chipen, V. Y. Grinstein, and R. P. Preiman, *Zhur. obshchei. Khim.*, 1962, **32**, 454.
[7] C. F. Kröger, G. Etzold, and H. Beyer, *Annalen*, 1963, **664**, 146.
[8] (*a*) E. Fromm and L. Wetternick, *Annalen*, 1926, **447**, 300; (*b*) E. Fromm, L. Brück, R. Runkel, and E. Meyer, *ibid.*, 1924, **437**, 112.
[9] L. E. A. Godfrey and F. Kurzer, *J.*, 1963, 4558.
[10] J. H. Boyer, in R. C. Elderfield's "Heterocyclic Compounds," vol. 7, Wiley, London, 1961, p. 384 (*a*) p. 456.

The ready conversion of 3-anilino-5-hydrazino-1,2,4-triazole into pyrazoles by the standard synthesis [11] provided further evidence for the presence of the hydrazino-group (in V). Thus, action of acetylacetone [11a] rapidly gave 3-anilino-5-(3,5-dimethylpyrazol-1-yl)-1,2,4-triazole (XIV; X = Me) almost quantitatively. Ethyl acetoacetate similarly gave a product which, on the basis of a large number of precedents,[11b,12] is



Reagents: 1, ArN:C:NAr. 2, R_2CO. 3, HCl. 4, $-ArNH_2$.

formulated as the 5-(5-hydroxy-3-methylpyrazol-1-yl) derivative (XIV; X = OH; *i.e.*, a pyrazol-5-one). Both pyrazoles are bases, giving picrates.

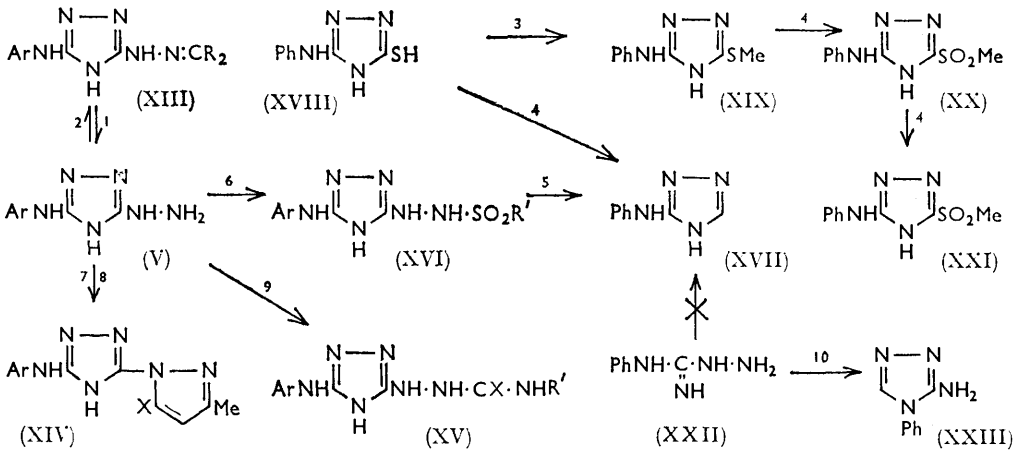
3-Anilino-5-hydrazino-1,2,4-triazole reacted additively with phenyl isothiocyanate and isocyanate; since the resulting products are no longer convertible into hydrazones, they may be formulated as substituted (thio)semicarbazides (XV; Ar = R′ = Ph, X = S or O).

Amongst methods for removing hydrazino-groups from aromatic systems, treatment of the corresponding toluene-*p*-sulphonylhydrazide with alkali has been successfully employed in the heterocyclic field.[13] Applied to the present case, the procedure converted 3-anilino-5-hydrazino-1,2,4-triazole into 3-anilino-1,2,4-triazole (V ⟶ XVI ⟶ XVII), of established structure. Provided that rearrangement does not occur, this degradation appears to provide the necessary confirmation of the structure assigned to the triazoles (V). A monotoluene-*p*-sulphonyl derivative of (VI), even if capable of eliminating the toluene-*p*-sulphonamido-group,[14] would give rise to an amino-arylamino-1,2,4-triazole.

3-Anilino-1,2,4-triazole has previously been obtained [8b] in poor yield, together with much 3-anilino-5-mercapto-1,2,4-triazole, in the alkaline decomposition of di-(3-anilino-1,2,4-triazol-5-yl) disulphide. The required authentic anilino-triazole (XVII) has now been

[11] L. Jacobs, in R. C. Elderfield's " Heterocyclic Compounds," vol. 5, Wiley, New York, 1957, p. 45; (*a*) p. 48; (*b*) p. 114.
[12] L. Knorr, *Ber.*, 1883, **16**, 2597; 1884, **17**, 546, 2032; *Annalen*, 1887, **238**, 137.
[13] R. Escales, *Ber.*, 1885, **18**, 893; M. J. S. Dewar, *J.*, 1944, 619; A. Albert, D. J. Brown, and H. Duewell, *J.*, 1948, 1284; A. Albert and R. Royer, *J.*, 1949, 1148.
[14] A. Nickon and A. S. Hill, *J. Amer. Chem. Soc.*, 1964, **86**, 1152.

produced in 56% yield by the oxidative removal [15] of the mercapto-group from the thiol (XVIII) [16] by hydrogen peroxide; more far-reaching decomposition of part of the reactant resulted in hydrazine (up to 28%). Under more restrained conditions, however, the 3-anilino-5-mercapto-1,2,4-triazole was merely oxidised to the disulphide. Another



Reagents: 1, HCl. 2, R_2CO. 3, MeI. 4, H_2O_2. 5, NaOH. 6, *p*-Me·$C_6H_4SO_2Cl$. 7, $(MeCO)_2CH_2$. 8, $MeCOCH_2COOEt$. 9, R'NCS or R'NCO. 10, H·CO_2H.

attempt to obtain 3-anilino-1,2,4-triazole by Thiele's classical synthesis [17] from *N*-amino-*N'*-phenylguanidine (XXII) and formic acid, gave instead 3-amino-4-phenyl-1,2,4-triazole (XXIII), the reaction thus resembling the production of 3-amino-4-methyl-(5-substituted)-1,2,4-triazoles [18] by this route. The preferential involvement of the anilino- rather than the imino-group in the dehydration of the presumed intermediate, *N*-formamido-*N'*-phenylguanidine, in the acid medium is noteworthy. That *N*-acylamino-*N'*-arylguanidines may be cyclised to either 3-arylamino-5-alkyl- or 3-amino-4-aryl-5-alkyl-1,2,4-triazoles under alkaline or neutral conditions, respectively, has recently been demonstrated by Gehlen and Dost.[19]

Attempts to synthesise 3-anilino-5-hydrazino-1,2,4-triazole (V; Ar = Ph) from the pre-formed heterocyclic system have so far not been successful. The corresponding methyl sulphide (XIX) was convertible in stages, by controlled oxidation with hydrogen peroxide,[20] into the sulphoxide (XX) and sulphone (XXI). The latter, unlike corresponding compounds in the 1,3,4-thiadiazole series,[21] was unaffected by hydrazine, even at 120°. The observation thus agrees with the known [16] resistance of 1,2,4-triazolyl methyl sulphides and sulphones to aminolysis.

The interaction of diarylcarbodi-imides and diaminoguanidine lacking protecting groups has also been examined. In dimethylformamide, action of an excess of the carbodi-imide (preferably >3 mole) gave mainly 4-aryl-3,5-diarylamino- (XI) together with some 3-amino-4-aryl-5-arylamino-1,2,4-triazole (XII) directly in one stage. The former compounds are thought to arise by addition of two moles of carbodi-imide to adjacent nitrogen atoms of *one* of the hydrazino-groups of diaminoguanidine, followed by cyclisation of the

[15] E. R. Buchmann, A. O. Reims, and H. Sargent, *J. Org. Chem.*, 1941, **6**, 764.
[16] E. Hoggarth, *J.*, 1949, 1160.
[17] J. Thiele, *Annalen*, 1892, **270**, 1; J. Thiele and W. Manchot, *ibid.*, 1898, **303**, 45, 54; G. Sjostedt and L. Gringas, *Org. Synth.*, Coll. Vol. III, Wiley, London, 1955, p. 95; C. F. H. Allen and A. Bell, *Org. Synth.*, 1946, **26**, 11.
[18] C. F. Kröger, G. Schoknecht, and H. Beyer, *Chem. Ber.*, 1964, **97**, 396.
[19] H. Gehlen and J. Dost, *Annalen*, 1961, **643**, 116, 118; see also Y. Makisumi and H. Kano, *Chem. pharm. Bull. (Tokyo)*, 1963, **11**, 67.
[20] J. Goerdeler and H. Rachwalski, *Chem. Ber.*, 1960, **93**, 2190.
[21] K. Fuji, H. Yoshikawa, and M. Yuasa, *J. Pharm. Soc. Japan*, 1954, **74**, 1056.

primary product (VII) with loss of arylamine (to IX), and final hydrolytic removal of the 1-aminoamidino-group (from IX). Part of the arylamine, reacting competitively with the carbodi-imide, reappeared as *s*-triarylguanidine. The reaction sequence thus resembles closely the analogous formation of (XI) from carbodi-imides and aminoguanidine, thiosemicarbazide, or semicarbazide, where an intermediate corresponding to (IX) could be isolated.[1c] 3-Amino-4-aryl-5-arylamino-1,2,4-triazoles (XII) may arise by the action of a third molecule of carbodi-imide, *e.g.*, on (VII) or (IX), and subsequent fission and cyclisation of the precursor (X) into compounds (XI) and (XII).

The ultraviolet absorption spectra of all 5-substituted 3-anilino(and *p*-toluidino)-1,2,4-triazoles now described are strikingly similar, featuring a high-intensity peak between 254 and 258 mμ (log ε 4·3—4·5). The resemblance of these spectra to that of the parent compound, 3-anilino-1,2,4-triazole ($\lambda_{max.}$ 255 mμ; log ε 4·29), shows that introduction into the 5-position of hydrazino, pyrazolyl, sulphoxide, and sulphonyl groups is virtually without effect on the resulting spectrum. In 3,5-dianilino-[22] and 3,5-dianilino-4-phenyl-1,2,4-triazoles, however, the maxima are displaced towards the longer wavelengths (261 and 270 mμ, respectively). A similar bathochromic shift resulting from the introduction of phenyl groups into the 1,2,4-triazole system has been observed.[23]

The results of both types of addition reactions now reported demonstrate the analogous behaviour of aminoguanidine [1c,2] and diaminoguanidine towards carbodi-imides. Free hydrazino-groups in both compounds preferentially add successive molecules at their ultimate and penultimate nitrogen atoms, the latter addition proceeding possibly even faster than the former.[1c] In contrast, the hydrazine group blocked by a ketone, though still containing a mobile hydrogen atom on the pentultimate nitrogen, tends to resist addition, the addendum being directed to another reactive centre in both amino-[2] and diaminoguanidine.

Experimental

Light petroleum had b. p. 60—80°. Dimethylformamide wes redistilled before use and the water-containing fore-run rejected. Acetone was dried over calcium sulphate hemihydrate.

Ultraviolet absorption measurements were made with a Unicam S.P. 500 spectrophotometer on 0·00005M-ethanolic solutions.

NN′-*Diaminoguanidine*. The hydriodide, prepared in 85—92% yield by the hydrazinolysis of *S*-methylisothiosemicarbazide [24] according to the method of Keim *et al.*[25] formed platelets, m. p. 132—134° (from 90% ethanol) (Found: N, 32·9; 32·6. Calc. for CH_7N_5,HI: N, 32·3%).

Addition to Diaminoguanidine Hydrazones

NN′-*Di*(*isopropylideneamino*)*guanidine*. To the stirred suspension obtained on introducing sodium (1·15 g., 0·05 g.-atom) into boiling acetone (150 ml.), finely powdered *NN′*-diaminoguanidine hydriodide (10·85 g., 0·05 mole) was added. The resulting clear reddish-brown liquid was refluxed during 30 min., then stirred at room temperature during ½ hr., most of the solvent removed under reduced pressure, and the residual viscid liquid treated with ice (20 g.), crystallisation setting in at once. The crude product was collected after storage at 0° for 24 hr. (m. p. 118—124°; 6·75 g., 80%). Crystallisation from ethanol–water (1 : 2; 4 ml. per g.; recovery 60%) gave ivory-white scales of NN′-*di*(*isopropylideneamino*)*guanidine*, m. p. 125—127° (Found: C, 49·95; H, 8·6. $C_7H_{15}N_5$ requires C, 49·7; H, 8·9%). The *picrate* formed platelets, m. p. 198—200° (decomp.) (from 85% ethanol) (85%) (Found: C, 39·3; H, 4·7; N, 27·95. $C_7H_{15}N_5$,$C_6H_3N_3O_7$ requires C, 39·2; H, 4·5; N, 28·1%).

The *hydriodide*, obtained nearly quantitatively when *NN′*-diaminoguanidine hydriodide (1·08 g., 0·005 mole) was dissolved in acetone containing 10% water (15 ml.), formed refractive columns (from 95% acetone), m. p. 220—222° (decomp.) (Found: C, 28·5; H, 5·4; I, 43·4. $C_7H_{15}N_5$,HI requires C, 28·3; H, 5·4; I, 42·7%).

[22] F. Kurzer and P. M. Sanderson, *J.*, 1963, 3333.
[23] M. R. Atkinson, E. A. Parkes, and J. B. Polya, *J.*, 1954, 4256.
[24] M. Freund and T. Paradies, *Ber.*, 1901, **34**, 3110.
[25] G. I. Keim, R. A. Henry, and G. B. L. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 4944.

3-(NN′-*Diphenylamidino*)-1,2-*di*(*isopropylideneamino*)*guanidine*. (*a*) To the stirred orange-brown suspension obtained on introducing sodium (0·35 g.; 0·015 g.-atom) into acetone (60 ml.), finely powdered diaminoguanidine hydriodide (4·35 g., 0·02 mole) was added, and the stirred suspension refluxed during 30 min. Diphenylcarbodi-imide (2·35 g., 0·012 mole) was added, refluxing continued for 1 hr., most of the acetone removed in a vacuum, and the residual viscid liquid stirred into ice–water (50 ml.), when partial solidification occurred on storage at 0°. The aqueous layer, L, was decanted and the resin stirred with cold methanol (15 ml.). The resulting powder (3 g.) gave, on crystallisation from acetone–ethanol (20 and 10 ml. per g.), prismatic needles of 3-(NN′-*diphenylamidino*)-1,2-*di*(*isopropylideneamino*)*guanidine*, m. p. 172—173° (total, 2·5 g., 57%) (Found: C, 66·25; H, 7·1; N, 26·4. $C_{20}H_{25}N_7$ requires C, 66·1; H, 6·9; N, 27·0%). It had $\lambda_{min.}$ 220 mμ (log ε 4·39); $\lambda_{max.}$ 240 (4·46); $\lambda_{min.}$ 252 (4·44); $\lambda_{max.}$ (principal) 272 (4·50) (all shallow). It formed a *picrate*, m. p. 177—178° (decomp.) (from acetone–ethanol) (Found: C, 52·55; H, 4·75. $C_{20}H_{25}N_7,C_6H_3N_3O_7$ requires C, 52·7; H, 4·7%).

The aqueous layer, L, was adjusted to pH 1 with concentrated hydrochloric acid and treated with 0·05M-picric acid until no further precipitate appeared. The product (0·5 g., 6%) was *NN′*-di(isopropylideneamino)guanidine picrate, m. p. and mixed m. p. 198—200° (decomp.) (from 85% ethanol).

(*b*) A solution of *NN′*-di(isopropylideneamino)guanidine (1·69 g., 0·01 mole) in dimethylformamide (5 ml.) was treated with diphenylcarbodi-imide (1·94 g., 0·01 mole) (exothermic reaction), kept on the steam-bath during 30 min., and the dark brown liquid stirred into water (50 ml.). The solidified resinous material was collected and stirred with methanol (20 ml.), and the resulting white powder (2·5—3 g.) crystallised as above, affording the substituted guanidine, m. p. and mixed m. p. 173—174° (total, 2·25 g., 62%).

Interaction of the above reactants (0·025 mole each) in boiling acetone (150 ml.) during 1 hr. gave a clear liquid which deposited the same substituted guanidine, m. p. and mixed m. p. 172—173°, on cooling (4·55 g., 50%). Vacuum evaporation of the filtrate gave more product of satisfactory quality, m. p. 171—173° (1·8—2·3 g., 20—25%).

3-(NN′-*Di*-p-*tolylamidino*)-1,2-*di*(*isopropylideneamino*)*guanidine*. (*a*) Interaction of the reactants as described for the (*NN′*-diphenylamidino)-homologue (quantities and conditions as above) except for the use of di-*p*-tolylcarbodi-imide (3·3 g., 0·015 mole) gave, after trituration of the crude oil with cold methanol, a white solid (m. p. 142—144°; 3·28 g., 56%), which consisted, after crystallisation from ethanol (10 ml. per g.; recovery 80%) or acetone (10 ml. per g.; recovery 50%), of felted needles of the substituted *guanidine*, m. p. 145—147° (Found: C, 67·3; H, 7·6; N, 25·1. $C_{22}H_{29}N_7$ requires C, 67·5; H, 7·4; N, 25·1%). It had $\lambda_{min.}$ 220 mμ (log ε 4·37); $\lambda_{max.}$ 240 (4·48); $\lambda_{min.}$ 255 (4·46); $\lambda_{max.}$ 274 (4·50) (all shallow).

(*b*) Interaction of *NN′*-(isopropylideneamino)guanidine and di-*p*-tolylcarbodi-imide (0·01 mole each) in dimethylformamide (5 ml.) at 100° during 1 hr., and addition of the resulting dark liquid to ice–water (30 ml.), gave an oil which solidified on stirring. After digestion with cold methanol, the white solid (m. p. 140—142°, 3·1 g., 80%) consisted, after crystallisation as above, of needles, m. p. 145—147°.

3-(NN′-*Di*-p-*bromophenylamidino*)-1,2-*di*(*isopropylideneamino*)*guanidine*. (*a*) The use of di-*p*-bromophenylcarbodi-imide (5·3 g., 0·015 mole) gave a white solid (5—6 g.) by procedure (*a*) (quantities and conditions as above). This was refluxed with ethanol (75 ml.), and a little insoluble material filtered off. The filtrate deposited a white crystalline powder [m. p. 160—163° (decomp.); 2·75 g., 35%], which consisted, after crystallisation from acetone (15 ml. per g., recovery 70%), of lustrous prisms of the substituted *guanidine*, m. p. 165—167° (decomp.) (Found: C, 46·4; H, 4·6; N, 19·4; Br, 31·4. $C_{20}H_{23}Br_2N_7$ requires C, 46·1; H, 4·4; N, 18·8; Br, 30·7%). It had $\lambda_{min.}$ 218 mμ (log ε 4·39); $\lambda_{max.}$ 275 (4·59), and a plateau at 235—260 mμ (4·51).

(*b*) The same compound was obtained (in 48% yield) from *NN′*-di(isopropylideneamino)-guanidine and di-*p*-bromophenylcarbodi-imide (0·01 mole each) in dimethylformamide (12 ml.) by the usual procedure.

Cyclisation to 1,2,4-*Triazoles*.—3-*Anilino*-5-*hydrazino*-1,2,4-*triazole*. (*a*) A solution of 3-(*NN′*-diphenylamidino)-1,2-di-(isopropylideneamino)guanidine (7·26 g., 0·02 mole) in 3N-hydrochloric acid (80 ml.) was refluxed during 10 min., then slowly distilled to approximately half volume during 30—35 min. so as to remove the acetone (distillate D). The residual liquid was slowly basified with ammonia solution (*d* 0·88; 25 ml.). The resulting precipitate was

collected at 0° (aqueous filtrate A), rinsed with water, and crystallised from ethanol (free from acetaldehyde) (150 ml. per g.), affording platelets (2·5—2·7 g., 65—71%) of 3-*anilino*-5-*hydrazino*-1,2,4-*triazole*, m. p. 198—200° (decomp., somewhat rate-dependent) (Found: C, 50·8; H, 5·4; N, 44·9. $C_8H_{10}N_6$ requires C, 50·5; H, 5·3; N, 44·2%). It had $\lambda_{min.}$ 230 mμ (log ε 3·80); $\lambda_{max.}$ 257 (4·30). The compound was readily soluble in both dilute mineral acids and aqueous sodium hydroxide, and was reprecipitated therefrom by ammonia or acetic acid, respectively. A little of the hydrazine, dissolved in 3N-sulphuric acid, treated with ammoniacal 0·1N-silver nitrate, and then with 3N-ammonia dropwise just short of reprecipitation, and kept at 100°, gave a finely-divided black precipitate, action being complete within about 10 min.

It was not practicable to recover further crops from the large volume of ethanolic filtrate by evaporation, but the hydrazino-compound was recoverable therefrom (70—80%) by addition of benzaldehyde (2 ml.) and slow distillation to small volume, as the 5-benzylidenehydrazino-derivative, m. p. and mixed m. p. (see below) 264—265° (decomp.).

Filtrate A was acidified with concentrated hydrochloric acid (to pH 1) and treated with 0·05M-picric acid (120 ml., 0·006 mole). The precipitate was collected at 0° (2·4 g., 24%); it formed elongated platelets of hydrazine dipicrate, m. p. and mixed m. p.[1b] 288—290° (decomp.) (from 90% ethanol) (Found: C, 30·0; H, 2·35; N, 22·7. Calc. for $N_2H_4,2C_6H_3N_3O_7$: C, 29·4; H, 2·0; N, 22·9%). Acetone in distillate D was identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 126—128°.

In one experiment, the triazole was precipitated by dropwise addition of 3N-sodium hydroxide (to pH 10; excess of alkali redissolves the product). The alkaline filtrate was treated with 40% sodium hydroxide (20 ml.) (appearance of oily droplets) and shaken with benzoyl chloride (4 and 2 ml.). The precipitated solid was benzanilide, m. p. and mixed m. p. 161—163° (from ethanol) (total, 80%).

(*b*) A solution of 3-anilino-5-isopropylidenehydrazino-1,2,4-triazole (1·15 g., 0·005 mole) and aminoguanidine sulphate hemihydrate (2·65 g., 0·02 mole) in 3N-hydrochloric acid (20 ml.) was heated on the steam-bath during 20 min. The somewhat cooled liquid was basified with ammonia solution (*d* 0·88). The precipitate consisted, after crystallisation from ethanol, of the 5-hydrazino-compound, m. p. and mixed m. p. [see (*a*) above] 198—200° (decomp.) (65%).

A solution of this triazole (0·19 g., 0·001 mole) in ethanol (12 ml.) containing 2 drops of 3N-hydrochloric acid was treated with picric acid (0·345 g., 0·0015 mole) in ethanol (3 ml.). The hot filtered liquid slowly deposited yellow granules (0·30 g., 72%) of the *picrate*, m. p. 171—173° (decomp., somewhat rate-dependent) (Found: C, 40·8; H, 3·3. $C_8H_{10}N_6,C_6H_3N_3O_7$ requires C, 40·1; H, 3·1%). Attempted crystallisation appeared to damage the salt.

3-*Anilino*-5-*isopropylidenehydrazino*-1,2,4-*triazole*. (*a*) A solution of 3-(*NN'*-diphenylamidino)-1,2-di(isopropylideneamino)guanidine (3·63 g., 0·01 mole) in 3N-hydrochloric acid (30 ml.) was refluxed during 30 min., then basified with ammonia solution. The resulting precipitate (2·3 g., m. p. between 216 and 220°), when crystallised from acetone–ethanol (1 : 3, 40 ml. per g.) and finally from ethanol (50 ml. per g.), gave felted needles of the 5-*isopropylidenehydrazino-compound*, m. p. 228—230° (decomp.) (1·5 g., 65%) (Found: C, 57·6; H, 6·0; N, 36·2. $C_{11}H_{14}N_6$ requires C, 57·4; H, 6·1; N, 36·5%). It had $\lambda_{min.}$ 220 mμ (log ε 4·07); $\lambda_{max.}$ 256 (4·48). The derivative was soluble in cold dilute mineral acids and aqueous sodium hydroxide (containing a few drops of acetone), and was reprecipitated therefrom by ammonia or acetic acid, respectively.

(*b*) The compound was also obtained nearly quantitatively when the 5-hydrazinotriazole was crystallised from acetone–ethanol.

Its *picrate* (65%), prepared in acetone–ethanol, formed minute plates, m. p. 220—224° (decomp., somewhat rate-dependent) (from 80% ethanol) (Found: C, 44·5; H, 3·6; N, 26·8. $C_{11}H_{14}N_6,C_6H_3N_3O_7$ requires C, 44·4; H, 3·7; N, 27·45%).

Analogous Derivatives.—The use of diethyl ketone in ethanol [procedure (*b*)] gave the 5-sym-*pentylidenehydrazino-compound* (50%). Crystallisation from ethanol containing a drop of diethyl ketone afforded felted needles, m. p. 219—221° (decomp.) (Found: C, 59·8; H, 6·5. $C_{13}H_{18}N_6$ requires C, 60·5; H, 7·0%).

A solution of the 5-hydrazino-compound (0·48 g., 0·0025 mole) in ethanol (80 ml.) and benzaldehyde (1 ml.) was refluxed during 30 min., then distilled to one-third bulk. The separated crystals were collected at 0° (0·7 g., 70%) and gave, on crystallisation from ethanol (400 ml. per g., recovery 70%), felted needles of the 5-*benzylidenehydrazino-compound*, m. p. 264—265° (decomp.) (Found: C, 64·2; H, 5·2; N, 30·25. $C_{15}H_{14}N_6$ requires C, 64·75; H, 5·0; N, 30·2%).

The same product resulted when the reaction was performed in boiling benzaldehyde during 1 hr.

3-*Anilino*-5-(3,5-*dimethylpyrazol*-1-*yl*)-1,2,4-*triazole*. A suspension of 3-anilino-5-hydrazino-1,2,4-triazole (0·95 g., 0·005 mole) in ethanol (30 ml.), glacial acetic acid (2 ml.), and acetylacetone (2·0 g., 0·02 mole) was placed on the steam-bath. A clear pale yellow solution was first formed, but white crystals were precipitated almost immediately. The suspension was refluxed during 15 min. and cooled; the product, collected at 0°, was rinsed with ethanol. Crystallisation from ethanol (150 ml. per g.) gave prismatic needles (1·21 g., 95%, including material from the filtrates) of 3-*anilino*-5-(3,5-*dimethylpyrazol*-1-*yl*)-1,2,4-*triazole*, m. p. 263—265° (Found: C, 61·55; H, 5·5; N, 33·2. $C_{13}H_{14}N_6$ requires C, 61·4; H, 5·5; N, 33·1%). It had $\lambda_{min.}$ 225 mμ (log ε 4·02); $\lambda_{max.}$ 256 (4·48).

A solution of the triazole (0·125 g., 0·0005 mole) in ethanol (5 ml.) containing a drop of 3N-hydrochloric acid, treated with picric acid (0·23 g., 0·001 mole) in ethanol (3 ml.), slowly deposited the *picrate*, forming orange prisms (66%), m. p. 179—181° (decomp.) (from 80% ethanol) [Found (specimen dried at 120° during 2 hr.): C, 47·2; H, 3·5; N, 26·05. $C_{13}H_{14}N_6$,$C_6H_3N_3O_7$ requires C, 47·2; H, 3·5; N, 26·1%].

3-*Anilino*-5-(5-*hydroxy*-3-*methylpyrazol*-1-*yl*)-1,2,4-*triazole*. A solution of 3-anilino-5-hydrazino-1,2,4-triazole (0·38 g., 0·002 mole) in ethanol (10 ml.) plus ethyl acetoacetate (4 ml.) was refluxed during 1 hr., then stirred into ice–water (40 ml.). The solidified oil was dissolved in ethanol (10 ml.); the solid which separated slowly (m. p. 155—156°; 0·38 g., 63%) consisted, after further crystallisation from the same solvent, of opaque granules of the solvated 1,2,4-*triazole*, m. p. 152—154° (decomp.) (Found: C, 55·4; H, 5·5; N, 28·5. $C_{12}H_{12}N_6O$,C_2H_5OH requires C, 55·6; H, 6·0; N, 27·8%). The product, when dried for successive hours at 80, 90, 100, and 110° (immediate heating at 110° caused melting) formed pink granules of the 1,2,4-*triazole*, m. p. 145—147° (decomp.) (Found: N, 32·5. $C_{12}H_{12}N_6O$ requires N, 32·8%). It had $\lambda_{min.}$ 225 mμ (log ε 4·07); $\lambda_{max.}$ 257 (4·50).

Its *picrate* formed felted yellow needles (60%), m. p. 165—167° (decomp.) (from ethanol) (Found: C, 44·75; H, 3·5. $C_{12}H_{12}N_6O$,$C_6H_3N_3O_7$ requires C, 44·5; H, 3·1%).

1-(3-*Anilino*-1,2,4-*triazol*-5-*yl*)-4-*phenylthiosemicarbazide*. A solution of 3-anilino-5-hydrazino-1,2,4-triazole (0·38 g., 0·002 mole) in dimethylformamide (5 ml.), treated with phenyl isothiocyanate (0·27 g., 0·002 mole), was kept at 100° during 30 min., then stirred into ice–water (50 ml.). The white precipitate, crystallised from ethanol (300 ml. per g.), consisted of platelets of the substituted *thiosemicarbazide*, m. p. 218—220° (decomp.) (0·49 g., 75%) (Found: C, 55·8; H, 4·55; N, 30·8; S, 9·6. $C_{15}H_{15}N_7S$ requires C, 55·4; H, 4·6; N, 30·15; S, 9·85%). The compound gave lead sulphide with boiling alkaline sodium plumbite. It crystallised unchanged from acetone (showing the absence of a free hydrazine group).

1-(3-*Anilino*-1,2,4-*triazol*-5-*yl*)-4-*phenylsemicarbazide* was similarly prepared from phenyl isocyanate (0·24 g., 0·002 mole). Crystallisation from a large volume of ethanol–acetone (3 : 1, followed by partial evaporation) gave microcrystals (0·46 g., 75%), m. p. 245—247° (decomp.) (Found: C, 57·9; H, 4·6; N, 31·3. $C_{15}H_{15}N_7O$ requires C, 58·25; H, 4·85; N, 31·7%).

3-*Anilino*-5-*toluene*-p-*sulphonylhydrazino*-1,2,4-*triazole*. 3-Anilino-5-hydrazino-1,2,4-triazole (2·85 g., 0·015 mole), suspended in anhydrous pyridine (10 ml.), was treated with toluene-*p*-sulphonyl chloride (3·4 g., 0·018 mole) during 5 min. The resulting warm yellow solution was kept on the steam-bath during 15 min., then stirred into ice–water (200 ml.). The solidified oil was collected, after storing for 72 hr. at 0°, and digested with methanol (20 ml.); the remaining white powder was crystallised from ethanol (300 ml. per g.), yielding microplatelets (total 3·2—3·6 g., 62—70%) of the *toluene*-p-*sulphonyl-derivative*, m. p. 218—220° (decomp., somewhat rate-dependent) (Found: C, 52·5; H, 4·6; N, 24·2; S, 9·2. $C_{15}H_{16}N_6O_2S$ requires C, 52·3; H, 4·65; N, 24·4; S, 9·3%). It had $\lambda_{min.}$ 217 mμ (log ε 4·24); $\lambda_{max.}$ 226 (4·28); $\lambda_{min.}$ 241 (4·09); $\lambda_{max.}$ 258 (4·33). It crystallised unchanged from acetone–ethanol (showing the absence of a free hydrazino-group).

3-*Anilino*-1,2,4-*triazole*. (*a*) A solution of the foregoing sulphonyl derivative (0·69 g., 0·002 mole) in N-sodium hydroxide (20 ml., 0·02 mole) was kept on a steam-bath during 1·5 hr., effervescence occurring during the first 15 min. The reddish-brown liquid was cooled, adjusted to pH 7—8 by addition of concentrated hydrochloric acid, and a trace of coagulated orange-brown solid filtered off. The filtrate (M) deposited, on prolonged storage at 0°, pale brown crystals (m. p. 174—176°; 0·21 g., 66%; filtrate therefrom, N) which gave, on crystallisation from 50% ethanol (12 ml. per g.), off-white aggregates of microprisms of 3-anilino-1,2,4-triazole, m. p.

and mixed m. p. with authentic material (*b*) 172—174° (Found: C, 59·9; H, 5·0; N, 35·1. Calc. for $C_8H_8N_4$: C, 60·0; H, 5·0; N, 35·0%). Its ultraviolet absorption curve coincided with that of authentic material (*b*). The yield was raised to near quantitative by the recovery, from filtrate N, of the remaining 3-anilino-1,2,4-triazole as its picrate (see below).

Alternatively, filtrate M, on being treated with picric acid (0·46 g., 0·002 mole) in hot water (15 ml.) and stored at 0°, directly gave 3-anilino-1,2,4-triazole picrate, m. p. and mixed m. p. (see below) 174—176° (decomp.) (from ethanol) in 88% yield.

(*b*) A suspension of finely powdered 3-anilino-5-mercapto-1,2,4-triazole [1c] (0·48 g., 0·0025 mole) in ethanol (8 ml.) (contained in an evaporating dish) was treated, in one portion at 50°, with 15% hydrogen peroxide (1·70 ml., 0·0075 mole) and concentrated hydrochloric acid (1 ml.). The resulting clear yellow liquid was evaporated on the steam-bath to small bulk (3 ml.), cooled, and basified (to pH 9) with ammonia solution. The collected precipitate (filtrate G) consisted, after crystallisation from ethanol (4 ml.; carbon–Kieselguhr) of microprisms of 3-anilino-1,2,4-triazole, m. p. 172—174° (total, 0·22 g., 56%). It had $\lambda_{min.}$ 224 mμ (log ε 3·55); $\lambda_{max.}$ 255 (4·29). The compound has been obtained from di-(3-anilino-1,2,4-triazol-5-yl) disulphide by Fromm *et al.*,[8] who give m. p. 180° (from water). Its *picrate*, prepared in 50% ethanol, and crystallised from ethanol, formed microplatelets, m. p. 174—176° (decomp.) [Found (sample kept at 120° for 3 hr.): C, 43·2; H, 3·0; N, 25·1. $C_8H_8N_4,C_6H_3N_3O_7$ requires C, 43·2; H, 2·8; N, 25·2%).

Filtrate G, when treated with 0·05M-picric acid (50 ml., 0·0025 mole), gave hydrazine dipicrate on cooling and storage, m. p. and mixed m. p.[1b] 289—292° (decomp. after darkening from 270°) (0·34 g., 28%).

Di-(3-anilino-1,2,4-triazol-5-yl) disulphide. A solution of 3-anilino-5-mercapto-1,2,4-triazole [1c] (0·48 g., 0·0025 mole) in boiling ethanol (20 ml.) was treated with 6% hydrogen peroxide (2·3 ml., 0·004 mole) containing 1 drop of conc. hydrochloric acid. The yellow liquid rapidly deposited pale yellow opaque crystalline disulphide, m. p. 230—232° (decomp.), which was collected at 0° (0·41 g., 85%) (lit., m. p. 225° [8,26] or 233° [27]).

3-Amino-4-phenyl-1,2,4-triazole. A mixture of 1-amino-3-phenylguanidine nitrate [28] (2·15 g., 0·01 mole) and formic acid (0·92 g., 0·02 mole) was kept at 120° during 5 hr. The dark reddish-brown liquid was diluted with ethanol (15 ml.) and treated with picric acid (2·3 g., 0·01 mole) in ethanol (15 ml.). The deep reddish-brown spikes (3 g.) gave on crystallisation from 85% ethanol (60 ml. per g. carbon) deep orange needles (2·9 g., 75%) of *3-amino-4-phenyl-1,2,4-triazole picrate*, m. p. 221—223° (decomp.) (Found: C, 42·6; H, 3·3. $C_8H_8N_4,C_6H_3N_3O_7$ requires C, 43·2; H, 2·8%).

Amberlite resin (" IRA-400 ") (40—50 ml.) was prepared by being percolated by 3N-sodium hydroxide (50 ml.), followed by deionised water (approximately 1 l.) until the filtrate was no longer alkaline (pH 7). To a solution of the foregoing picrate (0·59 g., 0·0015 mole) in 66% ethanol (150 ml.) at room temperature, about half the resin was added in small portions with stirring until it had nearly decolourised the liquid; this was then passed over the remaining resin (column) which was finally washed with 50% ethanol (3 × 20 ml.). The combined colourless eluate was distilled to very small volume (6 ml.) in a vacuum. The separated product was collected at 0° (m. p. 216—218°; 0·13 g., 56%) (filtrate F), and gave, on crystallisation from 50% ethanol, prismatic needles of 3-amino-4-phenyl-1,2,4-triazole, m. p. 216—218° (Found: C, 59·9; H, 5·4; N, 35·6. Calc. for $C_8H_8N_4$: C, 60·0; H, 5·0; N, 35·0%). Its ultraviolet absorption curve is approximately given by the points λ 220, 260 mμ (log ε 3·88, 2·94). The compound has previously been obtained [29] by cyclising *N*-phenyl-*N'*-thioureidoformamidine and had m. p. 221—223°.

The remaining triazole was recovered from filtrate F as the picrate; crystallisation of the salt from this source gave a purer specimen, forming pale yellow platelets (36%), m. p. 221—223° (decomp.) (Found: N, 24·85. Calc. for $C_8H_8N_4,C_6H_3N_3O_7$: N, 25·2%).

3-Anilino-5-methylthio-1,2,4-triazole. 3-Anilino-5-mercapto-1,2,4-triazole [1c] (9·6 g., 0·05 mole), in a solution from sodium (1·15 g., 0·05 g. atom) in methanol (200 ml.), was treated with methyl iodide (71 g., 0·5 mole). The pale yellow solution was refluxed during 1 hr., distilled

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[27] F. Arndt, *Ber.*, 1922, **55**, 15.
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[29] C. G. Raison, *J.*, 1957, 2858

to small volume (50 ml.), and the resulting crystalline suspension stirred into ice–water (150 ml.). Crystallisation of the precipitate from ethanol (10 ml. per g.) gave the triazole derivative, m. p. 187—188° (8·25—9·1 g., 80—88%). The use of dimethyl sulphate in preparing this compound has been described by Arndt [27] who also gives m. p. 187—188°.

3-*Anilino*-1,2,4-*triazol*-5-*yl methyl sulphoxide*. A suspension of 3-anilino-5-methylthio-1,2,4-triazole (1·03 g., 0·005 mole) in glacial acetic acid (7 ml.) and 30% hydrogen peroxide (1·7 ml., 0·015 mole) was stirred at 55—60° during 60 min. The reactant dissolved during the first 15 min., the liquid gradually turning dark brown; later solid again began to separate. The cooled suspension was diluted with water (12 ml.), and the white precipitate collected at 0°. Crystallisation from ethanol (50 ml. per g.) gave needles (0·87 g., 78%) of the *sulphoxide*, m. p. 240—242° (decomp., somewhat rate-dependent) (Found: C, 48·55; H, 4·45; N, 25·9. $C_9H_{10}N_4OS$ requires C, 48·65; H, 4·5; N, 25·2%). It had $\lambda_{min.}$ 224 mμ (log ε 3·58); $\lambda_{max.}$ 254 (4·33) (both steep). The compound did not give a picrate.

3-*Anilino*-1,2,4-*triazol*-5-*yl methyl sulphone*. A stirred suspension of the 5-methylthiol (2·06 g., 0·01 mole) in glacial acetic acid (20 ml.) and 30% hydrogen peroxide (11·2 ml., 0·1 mole) was kept at 60—65° (initial cooling required) during 1 hr., when solution occurred gradually. The dark liquid was treated with a further portion of 30% hydrogen peroxide (0·1 mole) and glacial acetic acid (4 ml.), and heating at 60—65° was continued for another 1 hr. Separation of the product on cooling was completed by dilution with water (25 ml.), the solid being collected at 0°. Crystallisation from ethanol (40 ml. per g.) gave opaque white needles with a slight orange tinge, of the *sulphone*, m. p. 246—248° (decomp.) (total, 1·78 g., 75%) (Found: C, 45·4; H, 4·4; N, 24·0; S, 13·8. $C_9H_{10}N_4O_2S$ requires C, 45·4; H, 4·2; N, 23·5; S, 13·4%). It had $\lambda_{min.}$ 222 mμ (log ε 3·54); $\lambda_{max.}$ 252 (4·32). The addition of the second portion of oxidising agent appears to be essential; in an experiment in which this was omitted, the product (1·85 g., m. p. 232—234°) was a mixture of the sulphoxide and sulphone (Found: C, 47·0; H, 4·4%).

At a higher temperature (95—100°; 2 hr.; 0·08 mole of oxidising agent), the reactant was destroyed and no product separated on cooling and dilution.

The sulphone, m. p. and mixed m. p. 245—247°, was similarly obtained (65%), when the sulphoxide (0·005 mole) was oxidised with perhydrol (0·06 mole) at 60° during 1·5 hr. as described above (Found: C, 45·4; H, 3·8%). *Attempted hydrazinolysis*. The sulphone (0·002 mole) was recovered (80%) (by acidification) after being refluxed in ethanol (5 ml.), hydrazine hydrate (0·5 ml., 0·01 mole), and water (0·5 ml.) during 2 hr., or after being heated with hydrazine hydrate (5 ml.) and ethanol (5 ml.) under pressure at 120° during 6 hr.

3-*Hydrazino*-5-p-*toluidino*-1,2,4-*triazole*. A solution of 3-(*NN'*-di-*p*-tolyamidino)-1,2-di-(isopropylideneamino)guanidine (1·96 g., 0·005 mole) in 1·5N-hydrochloric acid (18 ml.) and ethanol (8 ml.) was refluxed during 10 min., distilled to half volume, and basified with ammonia solution. The precipitate gave, on crystallisation from ethanol (AnalaR grade, 40 ml. per g.), lustrous platelets (0·73 g., 72%) of the *triazole derivative*, m. p. 195—197° (decomp.) (Found: C, 52·7; H, 5·85; N, 41·7. $C_9H_{12}N_6$ requires C, 52·9; H, 5·9; N, 41·2%). It had $\lambda_{min.}$ 230 mμ (log ε 3·82); $\lambda_{max.}$ 258 (4·32).

3-*Isopropylidenehydrazino*-5-p-*toluidino*-1,2,4-*triazole*. 3-(*NN'*-Di-*p*-tolylamidino)-1,2-di-(isopropylideneamino)guanidine (0·005 mole) was hydrolysed as described immediately above, but the subsequent distillation was omitted. Crystallisation of the crude product from acetone–ethanol (1 : 1, 100 ml. per g.) gave the 3-*isopropylidenehydrazino-derivative* as ivory felted needles, m. p. 254—255° (decomp.) (0·80 g., 65%) (Found: C, 59·5; H, 6·75; N, 33·8. $C_{12}H_{16}N_6$ requires C, 59·0; H, 6·6; N, 34·4%). It had $\lambda_{min.}$ 220 mμ (log ε 4·10); $\lambda_{max.}$ 257 (4·48).

The following additional derivatives were prepared as in the case of the anilino-homologue (see above): 3-*Benzylidenehydrazino*-5-p-*toluidino*-1,2,4-*triazole*; felted needles, (70%), m. p. 272—273° (decomp.) (from ethanol) (Found: C, 65·5; H, 5·55; N, 28·8. $C_{16}H_{16}N_6$ requires C, 65·75; H, 5·5; N, 28·8%); and 3-(3,5-*dimethylpyrazol*-1-*yl*)-5-p-*toluidino*-1,2,4-*triazole*, needles (62%), m. p. 220—221° (decomp.) (from glacial acetic acid–water) (Found: C, 62·9; H, 6·1; N, 31·0. $C_{14}H_{16}N_6$ requires C, 62·7; H, 6·0; N, 31·3%), which was very soluble in the usual solvents.

Addition to Diaminoguanidine

Interaction of Diaminoguanidine and Excess of Diphenylcarbodi-imide.—A solution of *NN'*-diaminoguanidine hydriodide (2·17 g., 0·01 mole) in dimethylformamide (15 ml.), treated with

diphenylcarbodi-imide (4·25 g., 0·022 mole), was kept at 100° during 1·5 hr. The reddish-brown liquid was stirred into ice–water (100 ml.), and the precipitate collected after storage at 0° during 12 hr. (filtrate F). The filter-cake was covered with methanol (10 ml.) and the solid collected (m. p. 220—225°; 1·85 g., 56%) at 0°. Crystallisation from ethanol (10 ml. per g.), gave lustrous platelets of 3,5-dianilino-4-phenyl-1,2,4-triazole, m. p. and mixed m. p. [1c] 232—234° (lit.,[30] 234°) (Found: C, 72·6; H, 5·1. Calc. for $C_{20}H_{17}N_5$: C, 73·4; H, 5·2%). It had $\lambda_{min.}$ 228 mμ (log ε 4·06); $\lambda_{max.}$ 260 (4·36).

Addition of 0·05M-picric acid (200 ml., 0·01 mole) to filtrate F precipitated a yellow solid which gave, on crystallisation from 66% ethanol, 3-amino-5-anilino-4-phenyl-1,2,4-triazole picrate, m. p. and mixed m. p. with authentic material,[1c] 268—270° (decomp., after darkening from 260°) (0·85 g., 24%) (Found: C, 50·15; H, 3·2. Calc. for $C_{14}H_{13}N_5,C_6H_3N_3O_7$: C, 50·0; H, 3·3%).

The use of 3·5 moles of diphenylcarbodi-imide raised the yield of 3,5-dianilino-4-phenyl-1,2,4-triazole to 72%; fractionation of the crude picrate (from F) from 66% ethanol gave 3-amino-5-anilino-4-phenyl-1,2,4-triazole picrate (22%), and the more soluble *s*-triphenylguanidine picrate (10%), m. p. and mixed m. p. 181—183° (Found: C, 57·8; H, 3·8; N, 16·7. Calc. for $C_{19}H_{17}N_3,C_6H_3N_3O_7$: C, 58·1; H, 3·9; N, 16·3%). The use of equimolar quantities of diphenylcarbodi-imide reduced yields of the triazole, m. p. 232—234°, to 12—15%.

*Interaction of Diaminoguanidine and Excess of Di-*p*-tolylcarbodi-imide.*—*NN'*-Diaminoguanidine hydriodide (2·17 g., 0·01 mole) in dimethylformamide (10 ml.) treated with di-*p*-tolylcarbodi-imide (4·44 g., 0·02 mole), was kept at 100° during 3 hr. and stirred into ice–water. The semi-solidified oil was collected at 0° (aqueous layer, L), and dissolved in methanol (10 ml.). Addition of ether (20 ml.) and partial spontaneous evaporation produced solid, which gave, on crystallisation from ethanol (30 ml. per g., recovery 80%), lustrous platelets (turning into a white powder on air-drying) (1·04 g., 28%) of 3,5-di-*p*-toluidino-4-*p*-tolyl-1,2,4-triazole, m. p. 227—228° (decomp.) (Found: C, 74·25; H, 6·2; N, 19·4. Calc. for $C_{23}H_{23}N_5$: C, 74·8; H, 6·2; N, 19·0%). It had $\lambda_{min.}$ 234 mμ (log ε 4·14); $\lambda_{max.}$ 263 (4·41) (lit.,[30] m. p. 223—224°). Its *picrate* formed orange spikes, m. p. 210—212° (decomp.) (from 85% ethanol) (Found: C, 58·2; H, 4·3. $C_{23}H_{23}N_5,C_6H_3N_3O_7$ requires C, 58·2; H, 4·35%).

Acidification of the aqueous layer with concentrated hydrochloric acid, and addition of 0·05M-picric acid (100 ml., 0·005 mole) gave a precipitate (1 g.) which consisted, after crystallisation from 85% ethanol, of yellow opaque prisms (0·56 g., 17%) of 3-*amino*-5-p-*toluidino*-4-p-*tolyl*-1,2,4-*triazole picrate*, m. p. 268—270° (decomp.) (Found: C, 51·4; H, 4·0; N, 22·8. $C_{16}H_{17}N_5,C_6H_3N_3O_7$ requires C, 52·0; H, 3·9; N, 22·0%).

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