170. *Heterocyclic Compounds from Urea Derivatives. Part VI.* Synthesis and Cyclisation of* 1-*Amino*-3-(NN′-*diarylamidino*)*guanidines and Some Analogues.*

By Frederick Kurzer and K. Douraghi-Zadeh.

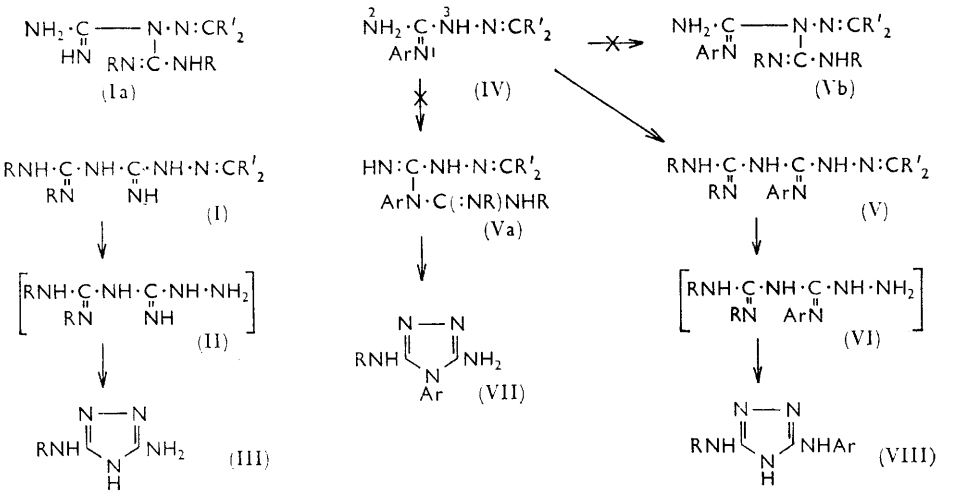
1-(*NN*′-Diarylamidino)-3-isopropylideneaminoguanidines, obtained from aminoguanidine and carbodi-imides in acetone, are cyclised to 3-amino-5-arylamino-1,2,4-triazoles in acid media. By the same sequence of reactions, 1-amino-3-phenylguanidine yields 3,5-di(arylamino)-1,2,4-triazoles.

Acetone isothiosemicarbazone fails to react with diarylcarbodi-imides, but does so after being *S*-alkylated. The resulting acetone 4-(*NN*′-diarylamidino)-*S*-benzylisothiosemicarbazones are ring-closed by mineral acids to 3-arylamino-5-benzylthiol-1,2,4-triazoles.

Analogous cyclisations of the related *S*-benzyl-*N*-isopropylideneamino-amidino-*N*′-phenylisothiourea are also described.

Previous Parts of this series described the addition of compounds containing twinned double bonds, including isothiocyanate or isocyanate esters,[1,2] and carbodi-imides[3] to aminoguanidine[4] and related compounds, and the cyclisation of the resulting products. In aminoguanidine, addition occurs preferentially at the hydrazino-group, but may be directed to the amidino-part of the molecule when the hydrazino-group is suitably blocked.[1-3] We now complete our account of this group of reactions by dealing with the addition of carbodi-imides to the amidino-group of aminoguanidine.

The interaction of diarylcarbodi-imides and aminoguanidine (converted into its isopropylidene-derivative *in situ*) in acetone gave fair yields of 1-(*NN*′-diarylamidino)-3-isopropylideneaminoguanidines (I). The possible alternative formulation of these



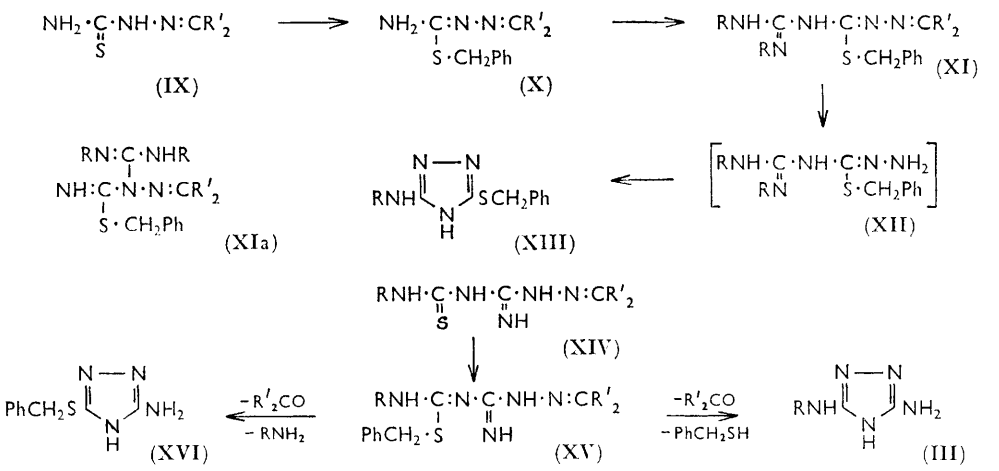
products as (Ia) is excluded by their ready cyclisation to triazoles (III) of established structure. Thus, mineral acid converted 1-(*NN*′-diphenylamidino)-3-isopropylideneaminoguanidine (I; R = Ph, R′ = Me) almost quantitatively into 3-amino-5-anilino-1,2,4-triazole (III; R = Ph); acetic anhydride similarly afforded the corresponding

* Part V, Kurzer and Sanderson, *J.*, 1963, 240.

[1] Godfrey and Kurzer, *J.*, 1960, 3437.
[2] Godfrey and Kurzer, *J.*, 1961, 5137.
[3] Godfrey and Kurzer, *J.*, 1962, 3561.
[4] Kurzer and Godfrey, *Angew. Chem.*, 1963, **75**, 1157; *Internat. Ed.*, 1963, **2**, 459.

acetyl derivative [of (III)]. Because of the rapidity of this ring-closure the intermediate free hydrazine (II; R = Ph) was not obtained. In contrast, the guanidino-derivative (I; R = Ph, R′ = Me) was very stable towards alkalis, being unaffected by boiling aqueous or ethanolic sodium hydroxide. These observations supplement our previous results on the closely related 1-substituted 3-(aminoamidino)thioureas (XIV);[1] their synthesis and cyclisation are strictly analogous, except for their additional ability to ring-close in alkaline media (to (III)), due to the presence of the thioamido-group.

Similarly, 1-(isopropylideneamino)-3-phenylguanidine (IV) reacted with diarylcarbodi-imides in acetone to yield 1-(*NN*′-diarylamidino)-2-isopropylideneamino-3-phenylguanidine (V). The addition of the carbodi-imide at N-2 of the " protected " phenylaminoguanidine (IV) is again demonstrated by the cyclisation of the resulting products (V) in acidic media, to the known 3,5-di(arylamino)-1,2,4-triazoles (VIII) in excellent yield. Of the possible alternative primary products, compound (Va) would cyclise to 3-amino-4-aryl-5-aryl-amino-1,2,4-triazoles (VII), while (Vb) could not form this five-membered ring system at all. The superior reactivity of N-2 in compound (IV) [and of the corresponding centre in 1-(isopropylideneamino)guanidine, $NH_2{\cdot}C(:NH)NH{\cdot}N{:}CR'_2$], over that of N-3 towards



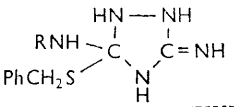
carbodi-imides is noteworthy. In contrast, diphenylcarbodi-imide is added to " unprotected " aminoguanidine [$NH_2C(:NH)NH{\cdot}NH_2$] at the ultimate and penultimate nitrogen atoms of its hydrazino-group (the latter corresponding to N-3 in IV, above), while the amidino-group remains unaffected.[3]

Thiosemicarbazide, which adds carbodi-imide readily at its hydrazino-grouping,[3] failed to react under the conditions of the present synthesis, the thioamido-group of its carbazone form (IX) being obviously not sufficiently basic to participate in the addition reaction. *S*-Alkylation, which converts thioureas into the strongly basic[5] isothiuronium compounds and facilitates the addition of isocyanate and isothiocyanate esters to the thioureido-structure,[6] was effective in promoting the present addition reaction. Thus, the interaction of acetone *S*-benzylisothiosemicarbazone (X; R′ = Me) with diarylcarbodi-imides in acetone gave good yields of acetone 4-(*NN*′-diarylamidino)-*S*-benzylisothiosemicarbazones (XI), which were rapidly ring-closed by acids to 3-aryl-amino-5-benzylthio-1,2,4-triazoles (XIII) as expected. The course of this cyclisation excludes once again the alternative formulation of the primary addition products as (XIa). Action of hydrazine [on (XI; R = Ph)] did not yield, by an initial replacement of the benzylthio-group, a hydrazino-1,2,4-triazole, but caused merely the usual cyclisation to

[5] Bernthsen and Klinger, *Ber.*, 1878, **11**, 493; Albert, Goldacre, and Phillips, *J.*, 1948, 2241; Pearson and Tucker, *J. Amer. Chem. Soc.*, 1949, **71**, 749.
[6] Kurzer, *Chem. Rev.*, 1956, **56**, 95, 160, 161.

XIII. Acetone *S*-methylisothiosemicarbazone proved unsuitable in condensation attempts with carbodi-imides under the usual conditions, because of its pronounced tendency to lose methanethiol.

The cyclisation of the structurally related *S*-benzyl-*N*-(isopropylideneaminoamidino)-*N'*-phenylisothiourea (XV; R = Ph; R' = Me), obtained from the corresponding thiourea (XIV),[1] gave analogous results. Like its parent compound (XIV), this *S*-benzyl derivative was rapidly ring-closed by acids or alkalis, to yield 3-amino-5-benzylthio- (XVI) or 3-amino-5-anilino-1,2,4-triazole (III), respectively. In this and analogous cyclisations [*e.g.*, (of XIV)] [1] the transient formation of intermediates that approach the structural type (XVII) may be considered; these would give rise to the observed products by the elimination of either aniline or toluene-ω-thiol under the influence of the appropriate reagents.



(XVII)

Experimental

Light petroleum had b. p. 60—80°. Dimethylformamide was 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, and 0·00005M-ethanolic solutions.

Reactions of Aminoguanidine.—1-(NN'-*Diphenylamidino*)-3-*isopropylideneaminoguanidine*. To the stirred orange-red suspension obtained on introducing sodium (1·38 g., 0·06 g.-atom) into acetone (150 ml.), finely powdered aminoguanidine sulphate monohydrate (9·5 g., 0·072 mole) was added. The stirred suspension was refluxed during 30 min., treated with diphenylcarbodi-imide (9·7 g., 0·05 mole), and refluxing continued during another 30 min. About two-thirds of the solvent was removed under reduced pressure, and the residue added to ice–water (100 ml.); the resulting dark greenish-brown oil became semi-solid on occasional stirring and storage at 0°. The aqueous phase (L) was decanted, the product rinsed with water, air-dried, and stirred with cold methanol (20 ml.). The resulting suspension was set aside to ensure maximum separation of the crude product, which was collected at 0° (8—10 g.) (the methanol filtrate contained only intractable oil). Crystallisation from ethanol (3 ml. per g., recovery over 80%) gave white opaque prisms (6·5—7·4 g.; 42—48%) of 1-(NN'-*diphenyl amidino*)-3-*isopropylideneaminoguanidine*, m. p. 134—136° (Found: C, 66·1; H, 5·8; N, 27·6. $C_{17}H_{20}N_6$ requires C, 66·2; H, 6·5; N, 27·3%); $\lambda_{min.}$ 236v sh mμ (log ε 4·23); $\lambda_{max.}$ 274sh (4·42). The product was insoluble in hot 3N-sodium hydroxide. It did not yield a picrate (in ethanol) or a toluene-*p*-sulphonate.

Addition of 0·05M-picric acid to the acidified aqueous phase L gave in some, but not all, experiments a precipitate (up to 1·6 g., 8%) of 3-amino-5-anilino-1,2,4-triazole picrate, m. p. and mixed m. p.[1] 230—232° (decomp.) (platelets from 90% ethanol).

Reactions of 1-(NN'-*Diphenylamidino*)-3-*isopropylideneaminoguanidine*. (*a*) *With hydrochloric acid.* A solution of the reactant (0·92 g., 0·003 mole) in 3N-hydrochloric acid (5 ml.) was refluxed for 30 min., cooled, and basified with 3N-ammonia. The precipitate, collected at 0° (m. p. 157—159°; 0·42 g., 80%) consisted of 3-amino-5-anilino-1,2,4-triazole, m. p. and mixed m. p.[1,7] 159—161° (from ethanol–light petroleum). Alternatively, the hydrolysate was basified with 3N-sodium hydroxide (10 ml.), the liquid distilled to half-bulk (to remove the aniline), acidified with 3N-hydrochloric acid, and treated with 0·05M-picric acid (0·0025 mole). The precipitate (1·1 g., 90%) was 3-amino-5-anilino-1,2,4-triazole picrate, m. p. and mixed m. p.[1] 230—232° (decomp.) (platelets from 90% ethanol).

(*b*) *With acetic anhydride.* A solution of the reactant (0·92 g., 0·003 mole) in acetic anhydride (8 ml.)—3N-acetic acid (0·5 ml.) was kept at 100° during 45 min., then stirred into water (80 ml.). The white solid (m. p. *ca.* 150°; 0·4—0·5 g.) which separated gradually gave, on crystallisation from boiling 75% acetic acid, an opaque white crystalline powder (0·29 g., 45%) of the *monoacetyl derivative* of 3-amino-5-anilino-1,2,4-triazole, m. p. 319—321° (decomp). (Found: C, 55·6; H, 5·5; N, 32·2. $C_{10}H_{11}N_5O$ requires C, 55·3; H, 5·1; N, 32·3%).

3-Amino-5-anilino-1,2,4-triazole [1] (0·35 g., 0·002 mole) was refluxed in acetic anhydride–glacial acetic acid (1 : 1, 5 ml.) during 30 min. and diluted with water. The resulting solid

[7] Fromm and Kapeller-Adler, *Annalen*, 1928, **467**, 240, 266.

consisted, after crystallisation from boiling 75% acetic acid, of the same monoacetyl derivative (0·33 g., 75%), m. p. and mixed m. p. 318—320° (decomp.).

(*c*) *With alkali.* The reactant did not dissolve in and was unaffected by boiling 3N-sodium hydroxide during 30 min. A solution of the reactant (0·77 g., 0·0025 mole) in 3N-sodium hydroxide (10 ml.)–ethanol (15 ml.) was refluxed for 1·5 hr. Dilution with water (40 ml.) and chilling resulted in a 65% recovery of the starting material.

1-(NN′-*Diphenylamidino*)-3-*diethylmethyleneaminoguanidine.* Interaction of the reagents as described for the 3-isopropylidene homologue (see above), but in diethyl ketone (150 ml.) at 60—70° gave, after removal of most of the solvent in a vacuum and addition of the residual liquid to water, a viscous orange oil. This was rinsed with water and dissolved in methanol (60 ml.). The crude product (5·4 g., 32%) that separated slowly on storage and partial evaporation gave, on crystallisation from ethanol (5 ml. per g., with addition of a drop of diethyl ketone), prisms of the 3-*diethylmethylene* derivative, m. p. 97—99° (Found: C, 67·85; H, 7·25; N, 24·5. $C_{19}H_{24}N_6$ requires C, 67·9; H, 7·1; N, 25·0%); $\lambda_{min.}$ 234sh mμ (log ε 4·25); $\lambda_{max.}$ 274sh (4·42).

1-(NN′-*Di*-p-*tolylamidino*)-3-*isopropylideneaminoguanidine.* (*a*) *Preparation.* Interaction of aminoguanidine and di-*p*-tolylcarbodi-imide (5·55 g., 0·025 mole) (as described for the phenyl-homologue; half quantities) gave a crude product solidifying on storage at 0°. It was digested with ethanol (10 ml.) and gave, on storage at 0° during 48 hr., an off-white solid (3·7 g., 45%). Crystallisation from ethanol (6 ml. per g.; 50% recovery) afforded minute prisms of the *substituted guanidine,* m. p. 111—113° (Found: C, 67·8; H, 6·9; N, 25·3. $C_{19}H_{24}N_6$ requires C, 67·85; H, 7·1; N, 25·0%); $\lambda_{min.}$ 235v sh mμ (log ε 4·27); $\lambda_{max.}$ 275sh (4·43).

(*b*) *Action of hydrochloric acid.* A solution of the reactant (0·67 g., 0·002 mole) in 3N-hydrochloric acid (5 ml.) was refluxed for 20 min., cooled, strongly basified with 3N-sodium hydroxide (12 ml.), and slowly distilled to half bulk. The distillate contained *p*-toluidine which was collected at 0° (m. p. 45°, from aqueous ethanol; 0·10 g., 48%). The residual alkaline liquid was carefully acidified with 3N-acetic acid; the precipitate, collected at 0°, and crystallised from water (carbon), was 3-amino-5-*p*-toluidino-1,2,4-triazole (0·32 g., 85%), m. p. and mixed m. p.[1] 179—180°.

1-(NN′-*Di*-p-*bromophenylamidino*)-3-*isopropylideneaminoguanidine.* Interaction of aminoguanidine and freshly prepared di-*p*-bromophenylcarbodi-imide (8·8 g., 0·025 mole) (as described for the phenyl homologue, half quantities) gave, after addition of the concentrated mixture to water, a viscous gum. This was stirred with cold methanol (50 ml.) and set aside at 0° until no more solid separated (crude: m. p. 129—132°; 3·7 g., 32%). Crystallisation from acetone–ethanol (5 ml. each, per g.), and finally ethanol (removal of a trace of sparingly soluble high-melting product, if necessary) gave clusters of prismatic needles of the *substituted guanidine,* m. p. 139—140° (Found: C, 44·0; H, 3·3; Br, 34·6; N, 17·8. $C_{17}H_{18}Br_2N_6$ requires: C, 43·8; H, 3·9; Br, 34·3; N, 18·0%). Its spectrum had a plateau at 226—240 mμ (log ε 4·32); $\lambda_{max.}$ 275sh (4·52).

1-(NN′-*Diphenylamidino*)-2-*isopropylideneamino*-3-*phenylguanidine.* (*a*) *Preparation.* To the stirred orange-brown suspension obtained on introducing sodium (0·46 g., 0·02 g.-atom) into acetone (60 ml.), finely powderd 1-amino-3-phenylguanidine nitrate [8] (5·33 g., 0·025 mole) was added, and the stirred suspension refluxed during 30 min. Diphenylcarbodi-imide (3·9 g., 0·02 mole) was next added during 5 min. (colour change to pale yellow) and refluxing continued for 1·5 hr. Most of the acetone was removed in a vacuum, and the residual oil stirred into ice–water (50 ml.). The resinous material hardened partially on storage at 0°. The supernatant aqueous layer was decanted, and the resin stirred with methanol (25 ml.). The resulting white powder (m. p. 153—156°; 3·5 g., 46%) gave, on crystallisation from acetone (15 ml. per g.), lustrous prisms of the *substituted guanidine,* m. p. 159—160° (Found: C, 72·2; H, 6·5; N, 21·45. $C_{23}H_{24}N_6$ requires C, 71·9; H, 6·25; N, 21·9%); $\lambda_{min.}$ 236sh mμ (log ε, 4·23); $\lambda_{max.}$ 277sh (4·45).

(*b*) *Action of hydrochloric acid.* A solution of the foregoing compound (0·77 g., 0·002 mole) in acetone (15 ml.)-3N-hydrochloric acid (8 ml.) was refluxed for 30 min., basified with 3N-sodium hydroxide, distilled to half bulk in a vacuum and filtered (pump) while hot. The solid which separated on cooling was collected at 0°. Crystallisation from acetone–ethanol gave felted

[8] Kirsten and Smith, *J. Amer. Chem. Soc.*, 1936, **58**, 800; Finnegan, Henry, and Lieber, *J. Org. Chem.*, 1953, **18**, 779; Kurzer, *J.*, 1961, 1617.

needles of 3,5-dianilino-1,2,4-triazole, m. p. and mixed m. p. with authentic [9] material 251—252° (total, including material from the mother-liquors, 0·38 g., 75%).

1-*Isopropylideneamino*-2-*phenyl*-3-(NN′-*di*-p-*tolylamidino*)*guanidine*. (*a*) *Preparation*. This was carried out as described above, but using di-*p*-tolylcarbodi-imide (4·44 g., 0·02 mole), and refluxing the final reaction mixture for 2 hr. The crude product, obtained after digestion with cold methanol (2 × 10 ml.) (m. p. 128—132°; 3·7 g., 45%) gave, on crystallisation from acetone (5 ml. per g.) clusters of needles of the *substituted guanidine*, m. p. 136—137° (Found: C, 72·2; H, 6·9; N, 20·8. $C_{25}H_{28}N_6$ requires C, 72·8; H, 6·8; N, 20·4%); $\lambda_{max.}$, 280sh mμ (log ε 4·52); plateau at 230—250 (4·33).

(*b*) *Action of hydrochloric acid*. Hydrolysis of this guanidine derivative (0·82 g., 0·002 mole) as described for the *NN′*-diphenylamidino-homologue (see above) gave a crude solid which afforded, on crystallisation from acetone–light petroleum, opaque white microcrystalline 3-*anilino*-5-p-*toluidino*-1,2,4-*triazole*, m. p. 222—224° (total, including material from the mother-liquors, 0·38 g., 72%) (Found: C, 67·9; H, 5·7; N, 26·4. $C_{15}H_{15}N_5$ requires C, 67·9; H, 5·7; N, 26·4%). Unless carefully purified, the product was light-sensitive, and turned pink on exposure to air.

Reactions of Thiosemicarbazide.—Acetone S-*methylisothiosemicarbazone hydriodide*. A suspension of finely ground acetone thiosemicarbazone (13·1 g., 0·1 mole) in methanol (30 ml.) was treated with methyl iodide (42·6 g., 0·3 mole) and refluxed. After 30 min., the excess of methyl iodide was boiled off and the product collected at 0° [m. p. 178—183° (decomp.); 24·6 g., 90%]. Addition of ether to the filtrate gave more salt (raising the yield to nearly quantitative). Crystallisation from 90% aqueous methanol–ether (4 and 8 ml. per g., recovery 50%) gave large needles of the *hydriodide*, m. p. 178—180° (decomp., somewhat rate-dependent) (Found: C, 22·0; H, 4·4; N, 15·8. $C_5H_{11}N_3S,HI$ requires C, 22·0; H, 4·4; N, 15·4%).

Because of the rapidity with which methanethiol was lost by the free base, this compound was less suitable than its *S*-benzyl homologue (see below) for condensation with carbodi-imides. Attempts to add diphenylcarbodi-imide to the hydriodide (dissolved in dimethylformamide at room temperature or at 100°, or in acetone) resulted in each case in intractable mixtures emitting methanethiol.

Acetone S-*benzylisothiosemicarbazone*. A suspension of finely powdered acetone thiosemicarbazone (6·55 g., 0·05 mole) in ethanol (25 ml.)–benzyl chloride (7·0 g., 0·055 mole) was treated with 3N-sodium hydroxide (18·3 ml., 0·055 mole), shaken vigorously at room temperature during 1 hr., and then added to ice–water (50 ml.). The separated oil, which solidified very slowly, was collected after 2—3 days, washed with water, and air-dried. Crystallisation from light petroleum (5 ml. per g.) gave prisms (7·7—8·85 g., 70—80%), m. p. 49—51° or 72—73°. The lower-melting changed into the higher-melting form on storage (Found (for higher-melting modification): C, 59·8; H, 6·6. Calc. for $C_{11}H_{15}N_3S$: C, 59·7; H, 6·8%) (lit.,[10] m. p. 51—52°).

Acetone 4-(NN′-*diphenylamidino*)-S-*benzylisothiosemicarbazone*. (*a*) *Preparation*. A solution of acetone *S*-benzylisothiosemicarbazone (2·21 g., 0·01 mole) in acetone (50 ml.) was treated with diphenylcarbodi-imide (1·94 g., 0·01 mole), refluxed during 45 min., distilled to one-third bulk and diluted with an equal volume of ethanol. The resulting crystalline solid, collected at 0° (total, including material from mother-liquors, 2·7—3·1 g., 65—75%; m. p. 149—151°) consisted, after crystallisation from acetone (10 ml. per g.), of needles of *acetone* 4-(NN′-*diphenylamidino*)-S-*benzylisothiosemicarbazone*, m. p. 149—151° (Found: C, 69·7; H, 6·65; N, 16·5; S, 7·7. $C_{24}H_{25}N_5S$ requires C, 69·4; H, 6·0; N, 16·9; S, 7·7%); $\lambda_{min.}$ 245 mμ (log ε 4·11); $\lambda_{max.}$ 272sh (4·38); plateau at 296—312 (4·29). The material was insoluble in 3N-sodium hydroxide, even on boiling, and did not give a positive plumbite test.

(*b*) *Action of acid*. A solution of the foregoing isothiosemicarbazone (0·83 g., 0·002 mole) in ethanol (25 ml.)—concentrated hydrochloric acid (6 ml.) was refluxed during 45 min., distilled to one-third bulk, and basified with concentrated ammonia. The precipitated white solid, collected at 0° and crystallised from ethanol (5 ml.), gave felted needles (total, 0·40 g., 70%) of 3-anilino-5-benzylthio-1,2,4-triazole, m. p. 170—171°, undepressed in admixture with a specimen obtained by the benzylation of authentic [3] 3-anilino-5-mercapto-1,2,4-triazole (lit.,[11] 168°).

(*c*) *Action of hydrazine*. A solution of the isothiosemicarbazone (0·83 g., 0·002 mole) in

[9] Underwood and Dains, *Univ. Kansas Sci. Bull.*, 1936, **24**, 5; Kurzer and Sanderson, *J.*, 1963, 1333.
[10] Wilson and Burns, *J.*, 1922, **121**, 870.
[11] Fromm, *Annalen*, 1922, **426**, 329.

ethanol (10 ml.)–hydrazine hydrate (0·25 g., 0·005 mole) was refluxed during 4 hr., then diluted with water (2 ml.). The product which crystallised out on cooling was collected at 0°. It was 3-anilino-5-benzylthio-1,2,4-triazole, m. p. and mixed m. p. 170—171° (0·48 g., 85%).

Acetone 4-(NN′-*di*-p-*tolylamidino*)-S-*benzylisothiosemicarbazone*. (*a*) *Preparation*. This was carried out as described for the diphenylamidino-homologue (see above), except for the use of di-*p*-tolylcarbodi-imide (2·22 g., 0·01 mole). Crystallisation from acetone (10 ml. per g., recovery 80%) gave the substituted *isothiosemicarbazone* as lustrous prisms, m. p. 157—158° (2·9 g., 65%) (Found: C, 69·8; H, 6·5; N, 16·0; S, 7·6. $C_{26}H_{29}N_5S$ requires C, 70·4; H, 6·5; N, 15·8; S, 7·2%); $\lambda_{min.}$ 245 mμ (log ε 4·15); $\lambda_{max.}$ 273sh (4·36); plateau at λ 296—308 (4·31).

(*b*) *Action of acid*. Acid hydrolysis of this compound as described for the diphenylamidino-homologue gave 3-benzylthio-5-*p*-toluidino-1,2,4-triazole, m. p. 174—176°, in 80% yield (Found: C, 64·55; H, 5·3. Calc. for $C_{16}H_{16}N_4S$: C, 64·9; H, 5·4%) (lit.,[12] m. p. 182°).

Reactions of N-(*Aminoamidino*)-N′-*phenylthiourea*.—S-*Benzyl*-N-(*isopropylideneamino-amidino*)-N′-*phenylisothiourea*. (*a*) *Preparation*. *N*-(Isopropylideneaminoamidino)-*N*′-phenylthiourea [1] (5·0 g., 0·02 mole) dissolved rapidly on being stirred with ethanol (40 ml.)–benzyl chloride (2·53 g., 0·02 mole)—3N-sodium hydroxide (6·7 ml., 0·02 mole). The solution, which began to deposit sodium chloride after a few minutes, was stirred at room temperature during 1 hr., diluted with water (200 ml.), and the separated solid (6—6·5 g.) collected at 0°. Crystallisation from ethanol (6 ml. per g.) gave felted needles of the S-*benzyl-derivative*, m. p. 124—127° (decomp.) (total, 4·5—5·1 g., 66—75%) (Found: C, 63·7; H, 6·1. $C_{18}H_{21}N_5S$ requires C, 63·7; H, 6·2%).

(*b*) *Action of acid*. A solution of the reactant (1·02 g., 0·003 mole) in N-hydrochloric acid (10 ml., 0·01 mole) was refluxed during 10 min., cooled, and treated with ammonia solution (to pH 6). The separated oil, which solidified on storage at 0°, was collected (filtrate: P). Crystallisation from boiling water gave platelets (0·18—0·22 g., 30—35%) of 3-amino-5-benzylthio-1,2,4-triazole, m. p. and mixed m. p.[1,7] 109—111°. The aqueous filtrate P was treated with 0·05M-aqueous picric acid (100 ml., 0·005 mole). The resulting yellow crystalline precipitate, collected after storage at 0°, and crystallised from ethanol, consisted of hydrazine dipicrate, m. p. and mixed m. p.[2] 290—292° (decomp.) (0·88 g., 60%).

(*c*) *Action of alkali*. The *S*-benzyl derivative (0·68 g., 0·002 mole) dissolved rapidly when heated to boiling with 3N-sodium hydroxide (10 ml.)–ethanol (5 ml.). The liquid was refluxed during 45 min., acidified with glacial acetic acid (2 ml.), and steam-distilled during 10 min. to remove toluene-ω-thiol and ethanol. The residual aqueous phase, on storage at 0° during 24 hr., deposited platelets (0·25 g., 70%), which consisted, after crystallisation from water (15 ml.), of lustrous flakes of 3-amino-5-anilino-1,2,4-triazole, m. p. and mixed m. p.[7] 158—160°. The aqueous filtrate, on treatment with 0·05M-picric acid (10 ml.), slowly gave the picrate (8—12%), m. p. and mixed m. p.[1] 229—231°, of the foregoing triazole.

(*d*) *Action of aniline*. A solution of the *S*-benzyl derivative (0·68 g., 0·002 mole) in aniline (6 ml.) was refluxed during 30 min. (faint odour of hydrogen sulphide), treated with water (20 ml.), and steam-distilled to remove the aniline. The residual aqueous phase (approx. 20 ml.) was decanted from a trace of sticky oil (O), and treated with 0·05M-picric acid (30 ml., 0·0015 mole). The yellow precipitate (0·58 g., 72%) was 3-amino-5-anilino-1,2,4-triazole picrate, m. p. and mixed m. p.[1] 229—231° (decomp.) (from 90% ethanol) (Found: C, 41·8; H, 3·2. Calc. for $C_8H_9N_5 \cdot C_6H_3N_3O_7$: C, 41·6; H, 3·0%). A solution of the oil O in ethanol failed to yield a picrate.

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[12] Fromm, Brück, Runkel, and Mayer, *Annalen*, 1924, **437**, 106, 113.