CCXXVIII.—*Aminopropyl*-1 : 2 : 4-*triazoles*.

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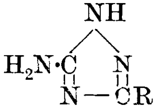
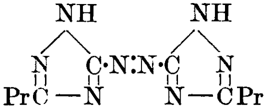
DIAZONIUM chloroaurates and *iso*diazo-hydroxides were obtained from the aminotriazole and the aminomethyltriazole of Thiele and Manchot (*Annalen*, 1898, **303**, 41) by Morgan and Reilly (J., 1916, **109**, 155) by diazotisation in presence of an oxy-acid. That work directed attention to an important heterocyclic system which from the point of view of the constitution of diazonium salts had been little investigated. The much greater stability of diazotised aminodimethylpyrazole in comparison with the corresponding unalkylated compound (Reilly and Madden, J., 1925, **127**, 2936), the indication of the greater stability of diazotised aminomethyltriazole in comparison with diazotised aminotriazole, and other considerations led the authors to an investigation of the higher aminoalkyltriazoles.

Thiele and Heidenreich (*Ber.*, 1893, **26**, 2598), by heating aminoguanidine nitrate, glacial acetic acid, and a trace of nitric acid at 100°, obtained an acetylaminoguanidine nitrate from which the ring compound was formed on removal of the nitrate radical by sodium carbonate. The corresponding ethyl and higher alkyl triazoles do not appear to have been prepared. In our experiments, aminoguanidine nitrate was heated with *n*- and with *iso*-butyric acid over a flame, with the result that no intermediate *n*- or *iso*-butyryl derivative was isolated, but after several hours' heating ring formation took place and 5-amino-3-*n*-propyl-1 : 2 : 4-

triazole (I) and 5-amino-3-*iso*propyl-1 : 2 : 4-triazole (II) were obtained directly, and they were isolated as the nitrates. The use of a higher temperature than Thiele and Heidenreich's, and the fact that weaker acids of greater molecular weight were employed probably account for the direct ring formation.



(I ; R = Pr^{α})
(II ; R = Pr^{β})



(III.)

The aminopropyltriazoles exhibit both basic and acid properties, as is shown by the formation of hydrochlorides, nitrates, and picrates on the one hand and of silver salts on the other.

Aminoalkyltriazoles are fairly stable towards oxidising agents; (I), on treatment with potassium permanganate in alkaline solution by Thiele and Heidenreich's method (*loc. cit.*), gave a propylazotriazole (III). Reduction of this produced the corresponding hydrazo-compound, which easily reverted to the azo-compound on oxidation. Reduction of 3-*n*-propyl-1 : 2 : 4-triazole-5-diazonium chloride led to a hydrazine, which was isolated as its benzaldehyde hydrazone.

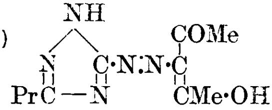
The reactivity of the amino-group in these triazoles is indicated by the great ease with which the bases give condensation products with aldehydes (*e.g.*, cinnam- and salicyl-aldehyde). In the latter case the condensation gives the salicylidene derivative in the usual way, but in the formation of the cinnamylidene compound the intermediate hydrate $C_5N_3H_8\cdot NH\cdot CH(OH)\cdot CH{:}CHPh$ appears to be formed. Further work will be necessary definitely to settle the constitution of this substance.

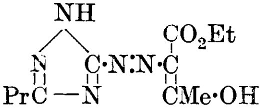
The addition of sodium nitrite and nitric acid to the aminoalkyltriazoles in solution leads to the formation of comparatively stable solutions of the diazonium nitrates, especially in presence of excess of acid. After heating for 1 hour at 55°, about 60% of the diazo-nitrogen is evolved (6 mols. of nitric acid present) and some colour develops in the solution. Under similar conditions of heating, about 80% of the diazo-nitrogen was obtained from the diazonium chloride in presence of an excess of hydrochloric acid, and gas was still being slowly evolved. Compared with the benzenediazonium salts, the diazonium nitrates and chlorides from these aminoalkyltriazoles show pronounced stability, which is, however, considerably less than that of the diazotised aminoalkylpyrazole salts. The comparative stabilities of the various diazotised aminoalkyltriazoles are being further investigated.

3-*n*-Propyl-1 : 2 : 4-triazole-5-diazonium chloride and the corresponding *iso*propyl compound, on decomposition, give 5-chloro-3-*n*-propyl-1 : 2 : 4-triazole and 5-chloro-3-*iso*propyl-1 : 2 : 4-triazole, respectively, in each of which the chlorine is firmly held.

Replacement of the mineral acid in a solution of a diazotised aminopropyltriazole by an organic acid such as acetic acid leads, as in the case of aminotriazole and aminomethyltriazole, to the formation of an *iso*diazo-compound, which does not couple with alcoholic β-naphthol. When dissolved in strong nitric or sulphuric acid, it reverts to the diazonium salt, and this, after dilution, readily couples with alcoholic β-naphthol. From the diazonium nitrates the corresponding 5-diazo-3-*n*-propyl-1 : 2 : 4-triazole chloroaurate and 5-diazo-3-*iso*propyl-1 : 2 : 4-triazole chloroaurate have been obtained, and these salts retain their coupling power on keeping. The diazonium nitrates readily yield azo-dyes with β-naphthol, β-naphthylamine and other related aromatic substances. They also couple with acetylacetone to give substances which may be either azo-compounds (IV) or hydrazones. In support of the azo-constitution is the fact that the compounds yield sodium derivatives, which give red colorations with ferric chloride and olive-green copper derivatives.

(IV.)





(V.)

Ethyl 3-propyl-1 : 2 : 4-triazole-5-azoacetoacetate (V) is formed in a similar manner from the diazonium nitrate and ethyl acetoacetate, and again the evidence favours the azo-structure rather than the ketonic constitution of the product. Thus, apparently for the first time, azo-condensation products of β-diketones with diazotised amino- or aminoalkyl-1 : 2 : 4-triazoles have been isolated. They are of interest in connexion with the relation between colour and constitution, as they represent azo-structures in which no aromatic residue is present.

EXPERIMENTAL.

*5-Amino-*3-iso*propyl- and -*3-n-*propyl-*1 : 2 : 4-*triazoles.*—Aminoguanidine nitrate (28 g.) was gently heated under reflux with 25 g. of *iso*butyric acid (b. p. 155°) for 6 hours. The product, which solidified on cooling, was dissolved in water, the solution rendered very faintly alkaline and evaporated to dryness, and the residue repeatedly extracted with dry ethyl acetate. Addition of not too much nitric acid to the extracts precipitated almost pure 5-*amino*-

3-iso*propyl*-1 : 2 : 4-*triazole nitrate* (24 g.); a further quantity was obtained from the mother-liquor. The nitrate is readily soluble in hot ethyl alcohol and in hot water, considerably less so in the cold solvents. It crystallises from water in oblong laminæ, m. p. 176° (Found: N, 37·1. $C_5H_{10}N_4,HNO_3$ requires N, 37·0%).

5-*Amino*-3-iso*propyl*-1 : 2 : 4-*triazole* was obtained by rendering an aqueous solution of the nitrate faintly alkaline with potassium carbonate, evaporating it to dryness, and repeatedly extracting the residue with ethyl acetate or boiling toluene; the base separated from the ethyl acetate extract in radiating clusters, m. p. 112°. It is very soluble in acetone, ethyl alcohol, or water, fairly easily soluble in ethyl acetate, less soluble in toluene (from which it separates in silky plates) or benzene, and almost insoluble in ether (Found: N, 44·3. $C_5H_{10}N_4$ requires N, 44·4%).

In the reaction between aminoguanidine nitrate and *n*-butyric acid, heating was continued for 10 hours, but the same method of isolation was employed. The first crop of crystals obtained on addition of nitric acid to the ethyl acetate solution of the triazole consisted of 18 g. of almost pure 5-*amino*-3-n-*propyl*-1 : 2 : 4-*triazole nitrate*. This separated from ethyl acetate in glistening plates, m. p. 153° (Found: N, 37·0%.) It is generally more soluble in solvents than the isomeric *iso*propyl compound.

5-*Amino*-3-n-*propyl*-1 : 2 : 4-*triazole* separates from ethyl acetate in tufts of long, slender, pointed crystals, m. p. 143° (Found: N, 44·4%).

The *hydrochloride* of the amino*iso*propyltriazole was hygroscopic and was dried for analysis over sulphuric acid in a vacuum (Found: Cl, 21·5. $C_5H_{10}N_4,HCl$ requires Cl, 21·8%). The isomeric *hydrochloride* also was hygroscopic (Found: Cl, 21·6%).

The *picrate* of the amino*iso*propyltriazole and of the amino-*n*-propyltriazole, prepared from the base and picric acid in aqueous ethyl alcohol, crystallised from aqueous alcohol (50%) in yellow, glistening plates, m. p. 193—194° (Found: $C_6H_3O_7N_3$, 64·8%), and in golden needles, m. p. 152° (Found: $C_6H_3O_7N_3$, 64·8. $C_5H_{10}N_4,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 64·5%), respectively.

The *silver* salt of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole, obtained from the base and silver nitrate in aqueous solution, is sparingly soluble in water but dissolves readily in nitric acid. It is stable at the ordinary temperature, but darkens slightly on warming (Found: Ag, 46·1. $C_5H_9N_4Ag$ requires Ag, 46·3%). The *silver* salt of the *n*-propyl compound also was prepared (Found: Ag, 46·2%).

5-*Acetylamino*-3-iso*propyl*-1 : 2 : 4-*triazole*, prepared by means of acetic anhydride, crystallised from water, in which it was sparingly soluble in the cold, as a white, indefinitely crystalline mass, m. p. 205° (Found: N, 33·1. $C_7H_{12}ON_4$ requires N, 33·3%). The *n*-propyl derivative was very similar.

Condensation of the Aminopropyltriazoles with Aldehydes.—An absolute ethyl-alcoholic solution containing equal molecular quantities of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole and cinnamaldehyde (purified by steam distillation) and 0·3 c.c. of piperidine was kept over-night and then warmed on the water-bath. On addition of water, a white precipitate formed, which was washed with water and further purified by dissolution in benzene and precipitation with light petroleum (b. p. 60—80°). The resulting cinnamaldehyde derivative softened at about 100° and melted at about 120°. It was very soluble in ethyl alcohol, ether, benzene, or acetone, and insoluble in light petroleum (b. p. 60—80°) (Found: N, 21·7; loss at 100°, 6·6. $C_{14}H_{18}ON_4$ requires N, 21·7; H_2O, 6·9%). Evidence for the presence of water of constitution was the change of the originally white substance at 100° to a yellow, crystalline solid which softened at 125° and melted at 130°; addition of water and re-drying at the ordinary temperature affected neither the yellow colour nor the m. p., and solution in aqueous ethyl alcohol and evaporation at a low temperature again gave the yellow compound. Cinnamaldehyde was readily split off on heating the substance with dilute acids.

The *salicylidene* derivative of 5-amino-3-*n*-propyl-1 : 2 : 4-triazole was prepared similarly. It crystallised from aqueous ethyl alcohol in clusters of pointed plates, m. p. 173°, and was very soluble in ether or ethyl alcohol and almost insoluble in water (Found: N, 24·4. $C_{12}H_{14}ON_4$ requires N, 24·3%). On being heated with dilute acids, it readily hydrolysed with liberation of salicylaldehyde.

3 : 3′-*Di*-n-*propyl*-5 : 5′-*azo*-1 : 2 : 4-*triazole* (III).—A solution of 2 g. of 5-amino-3-*n*-propyl-1 : 2 : 4-triazole and 3 g. of sodium hydroxide in about 20 c.c. of water was treated at 0° with finely powdered potassium permanganate. When the slight effervescence produced, accompanied by evolution of ammonia gas, had subsided, the whole was warmed on a water-bath and more potassium permanganate added until a permanent green colour was obtained. The filtered solution was just acidified with hydrochloric acid, and the precipitate produced was washed with water, dried, dissolved in concentrated aqueous ammonia and reprecipitated with acetic acid, the n-*propylazotriazole* being thus obtained as a pale yellow, crystalline solid. On heating, it decomposed without melting (Found: N, 45·6. $C_{10}H_{16}N_8$ requires N, 45·2%). It was easily dissolved by alkali and reprecipitated by weak acids such as acetic acid or even carbonic acid. On warming with ammoniacal silver

nitrate solution, a brownish-red silver salt separated, insoluble in nitric acid, soluble in ammonia. The azo-compound dissolved in concentrated sulphuric acid, giving a yellow solution, and was reprecipitated by water. Reduction with stannous chloride in acid solution gave a colourless solution, which on addition of ferric chloride again gave the yellow azotriazole.

3-n-*Propyl*-1 : 2 : 4-*triazolyl*-5-*hydrazine*.—Reduction of the diazotised triazole with stannous chloride was carried out by Thiele and Manchot's method (*loc. cit.*). The tin salts were removed by sodium carbonate and the filtered solution was acidified with hydrochloric acid and shaken for 12 hours with the calculated quantity of benzaldehyde; *benzaldehyde*-3-n-*propyl*-1 : 2 : 4-*triazolyl*-5-*hydrazone* was thus obtained in bushy, lustrous needles (yield about 10%). The mother-liquor, on being made alkaline, gave a precipitate of 5-chloro-3-*n*-propyltriazole (m. p. 90°). The hydrazone crystallised from aqueous ethyl alcohol in long plates, m. p. 239° (Found: N, 30·8. $C_{12}H_{15}N_5$ requires N, 30·6%). It is fairly easily soluble in ethyl alcohol and insoluble in ether or water. On being warmed with hydrochloric acid, it readily loses benzaldehyde, and the residual free hydrazine reduces Fehling's solution in the cold.

Action of Nitrous Acid on Salts of 5-*Amino*-3-iso*propyl*-1 : 2 : 4-*triazole*.—An aqueous solution of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole nitrate (1 mol.) and nitric acid (2 mols.) at 5° was treated with sodium nitrite solution (1 mol.). The pale yellow solution of the diazonium nitrate thus obtained gave an orange precipitate with monomethylaniline, a reddish-orange, soluble dye with β-naphthylamine-6 : 8-disulphonic acid, a dark blood-red solution with γ-acid, a dark bronze dye with α-naphthylamine, and, with potassium cyanide, a white precipitate which rapidly decomposed.

The diazonium chloride, obtained in a similar way, gave, on addition of silver oxide, a solution which no longer coupled with β-naphthylamine.

Reaction between the aminoisopropyltriazole nitrate (or the *n*-propyl isomeride) (1 mol.), nitric acid (2 mols.), and ethyl nitrite in alcoholic solution led ultimately to the iso*diazo-hydroxide*, which was more readily obtained as follows: to the finely divided nitrate obtained by adding 1 c.c. of nitric acid (*d* 1·42) to a solution of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole nitrate (2 g.) in 20 c.c. of water at 0°, an excess (10%) of sodium nitrite solution (6·9 g. in 100 c.c.) was slowly added, followed, after the slightly yellow solution of the diazonium nitrate had been kept for ½ hour at laboratory temperature, by an excess of solid sodium acetate. The yellow, flocculent precipitate produced was washed with water and dried over solid potassium hydroxide in a vacuum (Found : N, 44·6. $C_5H_9ON_5$ requires N, 45·1%). On heating, it became red at 90°, intumesced at about 150°, and finally shrank without melting. It was very soluble in alcohol, almost insoluble in water, and insoluble in ether. It dissolved in acids to a yellow, and in alkalis to an orange solution. It did not couple with aromatic phenols, but treatment with concentrated nitric or sulphuric acid restored this power.

3-n-*Propyl*-1 : 2 : 4-*triazole*-5-iso*diazohydroxide* separated from the sodium acetate solution more slowly than the *iso*propyl compound. It was obtained as a brownish-yellow, partly crystalline powder which intumesced at 145° and then decomposed without melting. It was very soluble in ethyl alcohol, but was reprecipitated by water. The percentage of nitrogen found in several samples made under different conditions varied from 42·4 to 42·8 ($C_5H_9ON_5,\frac{1}{2}H_2O$ requires N, 42·7%).

5-*Diazo*-3-iso*propyl*-1 : 2 : 4-*triazole Chloroaurate*.—5-Amino-3-*iso*-propyl-1 : 2 : 4-triazole nitrate was diazotised with sodium nitrite (1 mol.) and nitric acid (2 mols.), and the resulting solution treated with a concentrated solution of chloroauric acid (1 mol.); the *diazo*iso*propyltriazole chloroaurate* then separated, in good yield, as a yellow, flocculent precipitate, which was stable at the ordinary temperature. It exploded violently on heating and decomposed in warm alcoholic solution. For analysis, therefore, the weighed salt was warmed for some time with alcohol, when nitrogen was evolved, the resulting solution was evaporated to dryness, and the residue ignited (Found : Au, 45·0. $C_5H_7N_5,AuCl_3$ requires Au, 44·7%).

After remaining for a week in contact with water, this salt became redder, but it still readily coupled with alcoholic β-naphthol to give a red azo-dye.

5-*Diazo*-3-n-*propyl*-1 : 2 : 4-*triazole chloroaurate* darkened on heating and melted at 135° (decomp.) [Found : Au, 43·6. $(C_5H_7N_5,AuCl_3)_2,H_2O$ requires Au, 43·9%].

From platinic chloride and diazotised aminopropyltriazole in nitric acid, a yellow precipitate was obtained, apparently with some decomposition; the solution, after a day, still coupled with alcoholic β-naphthol.

5-*Chloro*-3-iso*propyl*-1 : 2 : 4-*triazole*.—A solution of 3·2 g. of amino*iso*propyltriazole in 50 c.c. of hydrochloric acid (*d* 1·16) was diazotised at 0° with a slight excess of sodium nitrite and then warmed to 70°. After 12 hours, it was made alkaline with sodium bicarbonate. The bulky, white precipitate obtained was isolated by means of chloroform and crystallised from water in well-defined, colourless, elongated plates, often exceeding ½ inch in length; m. p. 133° (Found: Cl, 24·7. $C_5H_8N_3Cl$ requires Cl, 24·5%). This *chloropropyltriazole* is very soluble in ethyl alcohol or chloroform, less so in benzene or water. It gave with silver nitrate a white precipitate soluble in nitric acid.

5-*Chloro*-3-n-*propyl*-1 : 2 : 4-*triazole* slowly separated, on addition of light petroleum (b. p. 60—80°) to a chloroform solution, in long, flat plates, m. p. 90°, which sublimed readily (Found: Cl, 24·4%).

The chlorine in these two compounds was not removed by heating with 20% sodium hydroxide solution or by treatment with sodium and ethyl alcohol (compare Stepanow, *Ber.*, 1906, **39**, 4056).

3-iso*Propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine*.—On mixing solutions of diazotised amino*iso*propyltriazole nitrate (1 mol.) (excess of nitrous acid having been destroyed by carbamide) and alcoholic β-naphthylamine (1 mol.), a dark reddish-blue substance separated; addition of ammonia changed this to a bulky, brick-red precipitate. Crystallised from aqueous ethyl alcohol and from ethyl acetate, it was obtained in red, radiating needles, m. p. 254—255° (decomp.) (Found: N, 30·0. $C_{15}H_{16}N_6$ requires N, 30·0%). The azo-compound was readily soluble in ethyl alcohol, acetone, or acetic acid, sparingly soluble in toluene, and almost insoluble in water. With concentrated sulphuric acid, it gave an olive-coloured solution which became pink on dilution and yellow when made alkaline.

3-n-*Propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine* was obtained in long, shining, red plates, m. p. 267° (decomp.) (Found: N, 30·1%).

3-iso*Propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthol*.—This was similarly obtained from β-naphthol. The dark red product, crystallised from aqueous ethyl alcohol and twice from ethyl acetate, formed orange needles, m. p. 186° (decomp.), easily soluble in ethyl alcohol (Found: N, 24·7. $C_{15}H_{15}ON_5$ requires N, 24·9%). With concentrated sulphuric acid, it gave a purple coloration, destroyed on dilution with water, and with aqueous potassium hydroxide a reddish-orange solution.

3-iso*Propyl*-1 : 2 : 4-*triazole*-5-*azoacetylacetone*.—This was obtained in a similar way from acetylacetone. The yellow solution, on addition of sodium acetate, gave a bulky, yellow precipitate, which was washed with water and recrystallised from aqueous ethyl alcohol and aqueous acetic acid. The acetylacetone derivative, m. p. 200—202°, was very soluble in ethyl alcohol, acetone, or acetic acid, but insoluble in benzene (Found: N, 29·3. $C_{10}H_{15}O_2N_5$ requires N, 29·5%). It formed a fairly easily soluble, orange *sodium* salt, from which it was regenerated by acids.

3-n-*Propyl*-1 : 2 : 4-*triazole*-5-*azoacetylacetone*, crystallised from aqueous ethyl alcohol, melted at 172—173° (Found : N, 29·2%).

Ethyl 3-iso*Propyl*-1 : 2 : 4-*triazole*-5-*azoacetoacetate*.—This was prepared from ethyl acetoacetate and precipitated on addition of sodium acetate. Crystallised from aqueous ethyl alcohol, it was obtained as a faintly yellow compound, m. p. 168—170°, very soluble in glacial acetic acid, acetone, or ethyl alcohol, almost insoluble in water or ether (Found : N, 26·3. $C_{11}H_{17}O_3N_5$ requires N, 26·2%). It gave with dilute aqueous sodium hydroxide a lemon-yellow colour which was discharged on addition of acid. The corresponding n-*propyl* compound, m. p. 156°, was very similar.

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