

**953.** *Purines, Pyrimidines, and Imidazoles. Part XVI.*<sup>1</sup> *Some 1-Aminoimidazoles and Derived 9-Aminopurines.*

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Hydrazine, phenylhydrazine, 1,1-dimethylhydrazine, and 2-methylsemicarbazide with ethyl *N*-(carbamoylcyanomethyl)formimidate, acetimidate, or benzimidate, and ethyl *N*-(cyano-*N*-methylcarbamoylmethyl)acetimidate gave 1-aminoimidazole-4-carboxyamides (or -*N*-methylcarboxyamides), which may be cyclised to 9-aminopurines and 9-amino-2-azapurines. 1,5-Diaminoimidazole was similarly obtained from hydrazine and ethyl *N*-(cyanomethyl)formimidate.

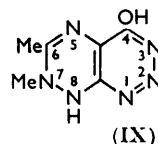
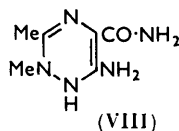
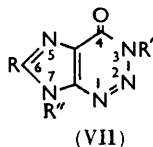
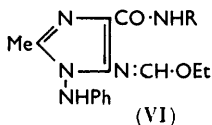
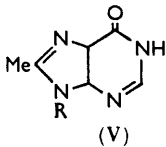
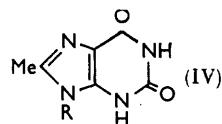
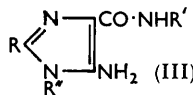
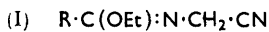
PART XIII<sup>2</sup> of this series recorded the preparation of the linear imidates (I; R = H or Me) and (II; R = H, R' = Me, and *vice versa*) and their reactions with ammonia and primary amines to give 5-aminoimidazoles and 5-aminoimidazole-4-carboxyamides (or -*N*-methylcarboxyamides), which may be cyclised to purine derivatives by conventional methods.

Similar reaction of the imidates (I) and (II) with hydrazines could lead to 1-aminoimidazoles or the analogous 1,2,4-triazines. Completion of a pyrimidine or triazine (with nitrous acid) ring in these compounds would yield, from the imidazoles, derivatives of 9-aminopurine, and, from the triazines, derivatives of a triazinopyrimidine or triazinotriazine; the last compounds may be regarded as "dihydroazapteridines." These groups

<sup>1</sup> Part XV, Dewar and Shaw, *J.*, 1961, 3254. Previously "glyoxalines" was used in the series title in place of "imidazoles."

<sup>2</sup> Shaw, Warrener, Butler, and Ralph, *J.*, 1959, 1648.

of compounds are of interest as possible growth inhibitors, and a few such compounds have been prepared recently by cyclisation of some hydrazinopyrimidines.<sup>3</sup>



Reaction of the imidate (II;  $R = Me$ ,  $R' = H$ ) with hydrazine gave the crystalline 1-aminoimidazole (III;  $R = Me$ ,  $R' = H$ ,  $R'' = NH_2$ ). The structure of this compound was confirmed as follows: (1) Infrared spectra showed the absence of cyanide bands. (2) The compound could be diazotised and coupled with an alkaline solution of  $\beta$ -naphthol to give a red dye. (3) The compound gave a diazotisable benzylidene derivative (III;  $R = Me$ ,  $R' = H$ ,  $R'' = N:CHPh$ ). (4) Fusion of the compound with urea gave 9-amino-8-methylxanthine (IV;  $R = NH_2$ ) which was deaminated by nitrous acid to the known 8-methylxanthine<sup>4</sup> (IV;  $R = H$ ). (5) The imidazole with formic acid and acetic anhydride gave a diformyl derivative, and with ethyl orthoformate and acetic anhydride gave the ethoxymethylene derivative (V;  $R = N:CH \cdot OEt$ ); hydrolysis of this with hydrochloric acid afforded 9-amino-8-methylhypoxanthine (V;  $R = NH_2$ ) which with nitrous acid gave 8-methylhypoxanthine (V;  $R = H$ ). The last compound was also formed directly from the ethoxymethylene derivative (V;  $R = N:CH \cdot OEt$ ) and nitrous acid.

In a similar manner several other 1-aminoimidazoles have been prepared from the imidates (II;  $R = H$ , Me, or Ph,  $R' = H$  or Me) by reaction with hydrazine, phenylhydrazine, 1,1-dimethylhydrazine and 2-methylsemicarbazide in water or alcohol. The parent 1,5-diaminoimidazole was also similarly prepared by reaction of hydrazine with ethyl *N*-(cyanomethyl)formimidate (I;  $R = H$ ), being isolated as a picrate. The imidazole structure of this compound is assumed by analogy with that of the carboxyamides.

The imidazoles (III;  $R = Me$ ,  $R' = H$  or Me,  $R'' = Ph \cdot NH$ ), when heated with ethyl orthoformate, gave ethoxymethylene derivatives (VI;  $R = H$  or Me) (cf. Part XIV<sup>5</sup>). The derivative (VI;  $R = H$ ) with acetic anhydride then gave the hypoxanthine (V;  $R = NHPH$ ). Several 9-amino-2-azapurines (VII;  $R = H$ , Me, or Ph,  $R' = H$  or Me,  $R'' = NH_2$ ,  $NMe_2$ ,  $NHPH$ , or  $NMe \cdot CO \cdot NH_2$ ) have also been prepared from the corresponding aminoimidazolecarboxyamides and nitrous acid.

Reaction of the imidate (II;  $R = Me$ ,  $R' = H$ ) with methylhydrazine readily gave a crystalline diazotisable amine which may be formulated as either the imidazole (III;  $R = Me$ ,  $R' = H$ ,  $R'' = NHMe$ ) or the 1,2,4-triazine (VIII), and in view of the well-known enhanced reactivity of the secondary amino-group in methylhydrazine, the latter structure is preferred. This compound with nitrous acid readily gave the triazinotriazine (IX) which may be regarded as a "dihydrodiazapteridine."

#### EXPERIMENTAL

**1,5-Diaminoimidazole.**—A solution of ethyl *N*-(cyanomethyl)formimidate<sup>2</sup> (0.71 g.) in methanol (5 ml.) was heated on a water bath with hydrazine hydrate (0.32 ml.) for 5 min.

<sup>3</sup> Pfeiderer, *Annalen*, 1958, **615**, 42; Montgomery and Temple, *J. Amer. Chem. Soc.*, 1960, **82**, 4592.

<sup>4</sup> Traube, *Ber.*, 1900, **33**, 1382.

<sup>5</sup> Shaw and Butler, *J.*, 1959, 4040.

The cooled solution with saturated methanolic picric acid (5 ml.) gave a crystalline precipitate which was collected and washed with ethanol and ether. The *imidazole picrate* (0.97 g.) recrystallised from water as yellow plates m. p. 150° (decomp.) (Found: C, 33.0; H, 2.5; N, 30.0.  $C_9H_9N_7O_7$  requires C, 32.9; H, 2.8; N, 29.3%).

*Ethyl N-(Carbamoylcyanomethyl)benzimidate.*—When a suspension of ethyl benzimidate hydrochloride (17.5 g.) and  $\alpha$ -amino- $\alpha$ -cyanoacetamide (5 g.) in water (10 ml.) was shaken for 20 min. with warming, a clear solution was obtained. This was cooled, giving a crystalline precipitate. The *benzimidate* (7.6 g.) recrystallised from ethyl acetate as plates, m. p. 109–110° (Found: C, 62.45; H, 5.5; N, 17.95.  $C_{12}H_{13}N_3O_2$  requires C, 62.3; H, 5.65; N, 18.15%).

*Preparation of 1,5-Diaminoimidazole-4-carboxyamides.*—The imidazoles could all be diazotised and coupled with an alkaline solution of  $\beta$ -naphthol to give red or magenta dyes.

*1,5-Diaminoimidazole-4-carboxyamide.* A mixture of ethyl *N*-(carbamoylcyanomethyl)-formimidate<sup>2</sup> (0.35 g.) and hydrazine hydrate (0.12 ml.) in ethanol (1 ml.) was heated on a water bath for 5 min., then cooled to give a crystalline precipitate. The *imidazole* separated from methanol as needles, m. p. 222–224° (decomp.) (Found: C, 34.25; H, 5.1; N, 50.3.  $C_4H_7N_5O$  requires C, 34.05; H, 5.0; N, 49.65%),  $\lambda_{max}$  270 m $\mu$  ( $\epsilon$  12,100) in  $H_2O$ , and 241 ( $\epsilon$  8000) and 270 m $\mu$  ( $\epsilon$  11,400) in  $N/20-HCl$ .

*5-Amino-1-anilinoimidazole-4-carboxyamide.* A solution of phenylhydrazine (0.27 g.) and the last formimidate (0.35 g.) in ethanol was heated on a water bath for 5 min. The *imidazole* (0.06 g.) separated from the cooled solution and recrystallised from ethanol as needles, m. p. 245–247° (decomp.) (Found: C, 55.1; H, 5.25; N, 32.55.  $C_{10}H_{11}N_5O$  requires C, 55.3; H, 5.1; N, 32.25%).

*1,5-Diamino-2-methylimidazole-4-carboxyamide.* Ethyl *N*-(carbamoylcyanomethyl)acetimidate<sup>2</sup> (0.85 g.), ethanol (2 ml.), and hydrazine hydrate (0.25 ml.) were warmed together for 5 min. and a crystalline precipitate was collected and washed with ethanol and ether. The *imidazole* (0.53 g.) separated from ethanol as needles, m. p. 270° (decomp.) (Found: C, 38.9; H, 5.7; N, 45.15.  $C_5H_9N_5O$  requires C, 38.7; H, 5.85; N, 45.15%),  $\lambda_{max}$  270 m $\mu$  ( $\epsilon$  13,800) in  $H_2O$ . An alcoholic solution of the base with dry hydrogen chloride gave the *hydrochloride* which separated from ethanol as needles, m. p. 240–242° (Found: C, 31.4; H, 4.65; N, 36.8.  $C_5H_9N_5O.HCl$  requires C, 31.3; H, 4.7; N, 36.6%).

*5-Amino-1-benzylideneamino-2-methylimidazole-4-carboxyamide.* A solution of the last-mentioned base (1 g.) and benzaldehyde (0.7 g.) in ethanol (250 ml.) was boiled under reflux for 2 hr. Evaporation of the solution then gave the *benzylidene derivative* (1.1 g.) which separated from ethanol as pale yellow prisms, m. p. 246–249° (Found: C, 59.25; H, 5.25; N, 28.45.  $C_{12}H_{13}N_5O$  requires C, 59.1; H, 5.35; N, 28.8%).

*5-Amino-1-anilino-2-methylimidazole-4-carboxyamide.* The last-mentioned acetimidate (0.85 g.), ethanol (2 ml.), and phenylhydrazine (0.54 g.) were warmed together, a vigorous exothermic reaction soon occurring. The cooled red solution gave a crystalline precipitate which was washed with ethanol and ether. The *imidazole* (0.63 g.) separated from ethanol as needles, m. p. 300° (decomp.) (Found: C, 57.4; H, 5.55; N, 30.0.  $C_{11}H_{13}N_5O$  requires C, 57.15; H, 5.65; N, 30.3%),  $\lambda_{max}$  231 ( $\epsilon$  16,000) and 271 m $\mu$  ( $\epsilon$  16,800) in EtOH.

*5-Amino-1-dimethylamino-2-methylimidazole-4-carboxyamide.* A suspension of the foregoing acetimidate (1.7 g.) in ethanol (4 ml.) was warmed with 1,1-dimethylhydrazine (0.63 ml.) to give a clear pale yellow solution. This was boiled for a few min., then cooled to precipitate the *imidazole* (0.96 g.) which recrystallised from ethanol as prisms, m. p. 211° (decomp.) (Found: C, 45.9; H, 7.05; N, 37.7.  $C_7H_{13}N_5O$  requires C, 45.9; H, 7.1; N, 38.25%).

*1,5-Diamino-2-methylimidazole-4-N-methylcarboxyamide.* A solution containing ethyl *N*-(cyano-*N*-methylcarbamoylmethyl)acetimidate<sup>2</sup> (0.5 g.) and hydrazine hydrate (0.15 ml.) in ethanol was boiled under reflux for 30 min. The solvent was removed *in vacuo*, to give a syrup which crystallised when stirred with ether. The *imidazole* (0.36 g.) separated from ethyl acetate or methanol as needles, m. p. 182° (Found: C, 42.85; H, 6.4; N, 41.15.  $C_6H_{11}N_5O$  requires C, 42.6; H, 6.55; N, 41.4%).

*5-Amino-1-anilino-2-methylimidazole-4-N-methylcarboxyamide.* A solution of the foregoing acetimidate (0.5 g.) in ethanol (3 ml.) was heated on a water bath for 15 min. with phenylhydrazine (0.3 ml.). The cooled solution precipitated the *imidazole* (0.28 g.) which separated from aqueous ethanol as needles, m. p. 272° (Found: C, 55.9; H, 6.2; N, 27.4.  $C_{12}H_{15}N_5O \cdot \frac{3}{2}H_2O$  requires C, 55.75; H, 6.4; N, 27.1%). A further quantity (0.41 g.) of the base was obtained from the mother liquors.

**1,5-Diamino-2-phenylimidazole-4-carboxyamide.** A solution containing hydrazine hydrate (1.1 g.) and ethyl *N*-(carbamoylecyanomethyl)benzimidate (5 g.) in ethanol (250 ml.) was boiled under reflux for 4 hr. After 5 min. a small quantity (0.32 g.) of orange crystals had separated; these were collected. The substance was insoluble in water, hydrochloric acid, sodium hydroxide solution, and common organic solvents, and failed to melt below 380° (Found: C, 61.9; H, 4.1; N, 24.75.  $C_{20}H_{15}N_7O_2$  requires C, 62.4; H, 3.9; N, 25.2%). The ethanolic solution was evaporated *in vacuo* to a low volume and saturated with hydrogen chloride to precipitate a solid. The *imidazole hydrochloride* (4.2 g.) separated from aqueous ethanol as needles, m. p. 210° (Found: C, 47.5; H, 4.6; N, 27.6.  $C_{10}H_{11}N_5O \cdot HCl$  requires C, 47.5; H, 4.75; N, 27.6%).

**5-Amino-1-anilino-2-phenylimidazole-4-carboxyamide.** A mixture of phenylhydrazine (2.34 g.) and the foregoing benzimidate (5 g.) in ethanol 250 ml. was boiled under reflux for 4 hr. The solution was evaporated to a small volume and cooled to precipitate the *imidazole* (5.3 g.) which recrystallised from ethanol as needles, m. p. 234–235° (Found: C, 65.4; H, 4.95; N, 23.75.  $C_{16}H_{15}N_5O$  requires C, 65.5; H, 5.15; N, 23.9%),  $\lambda_{max}$ . 231 ( $\epsilon$  17,200) and 271  $m\mu$  ( $\epsilon$  15,000) in EtOH.

**5-Amino-1-(*N*-carbamoyle-*N*-methylamino)-2-methylimidazole-4-carboxyamide.** A suspension of ethyl *N*-(carbamoylecyanomethyl)acetimidate (1.74 g.) and 2-methylsemicarbazide<sup>6</sup> (0.94 g.) in dry ethanol (3.5 ml.) was shaken for 30 min. at room temperature, then heated on a water bath for 15 min. The cooled solution precipitated the *imidazole* (0.88 g.) which recrystallised from ethanol as prisms, m. p. 164° (decomp.) (Found: C, 36.25; H, 6.35; N, 36.4.  $C_7H_{12}N_6O \cdot H_2O$  requires C, 36.5; H, 6.1; N, 36.5%). A further quantity (0.18 g.) was recovered from the mother liquors.

**9-Amino-8-methylxanthine.**—A finely ground mixture of 1,5-diamino-2-methylimidazole-4-carboxyamide (2 g.) and urea (2 g.) was heated at 185° (bath) for 2 hr.; ammonia was evolved. The dark melt was cooled to about 40° and dissolved in hot *n*-sodium hydroxide (15 ml.). The filtered solution, when cooled, gave a crystalline precipitate. The *sodium salt* of 9-amino-8-methylxanthine (0.95 g.) separated from water as a *monohydrate*, m. p. >360° (Found: C, 32.6; H, 4.05; N, 32.0.  $C_6H_8N_5NaO_2 \cdot H_2O$  requires C, 32.6; H, 3.6; N, 31.7%). The salt (0.95 g.) in hot water was acidified with acetic acid to precipitate 9-amino-8-methylxanthine (0.7 g.) which was obtained as needles by dissolution in sodium hydroxide solution and precipitation with acetic acid; it had m. p. >350° (Found: C, 39.6; H, 3.85; N, 36.65.  $C_6H_7N_5O_2$  requires C, 39.8; H, 3.9; N, 38.65%),  $\lambda_{max}$ . 237 ( $\epsilon$  9100) and 266  $m\mu$  ( $\epsilon$  11,150) in  $H_2O$ .

**8-Methylxanthine.**—Sodium nitrite (0.2 g.) was added portionwise to a stirred cold solution of 9-amino-8-methylxanthine (0.5 g.) in water (20 ml.) and *n*-hydrochloric acid (3 ml.). The solution was evaporated to dryness *in vacuo* and the residue extracted with ethanol. Evaporation of the extract gave 8-methylxanthine (0.25 g.) which separated from aqueous ethanol as needles, m. p. >360° (Found: C, 42.95; H, 3.55; N, 33.4. Calc. for  $C_6H_8N_4O_2$ : C, 43.35; H, 3.65; N, 33.75%),  $\lambda_{max}$ . 283–284  $m\mu$  ( $\epsilon$  6600) in 0.05*N*-NaOH. The compound was identical with a sample prepared from 5,6-diamino-2,4-dihydropyrimidine and acetamide.<sup>4</sup>

**9-Amino-8-methylhypoxanthine.**—A solution of 1,5-diamino-2-methylimidazole-4-carboxyamide (3 g.) in ethyl orthoformate (20 ml.) and acetic anhydride (20 ml.) was boiled under reflux for 2 hr., then evaporated *in vacuo* to a solid from which traces of solvent were removed by evaporation with ethanol *in vacuo*. The solid, 9-ethoxymethyleneamino-8-methylhypoxanthine (2.4 g.) separated from ethanol as needles, m. p. 260–262° (Found: C, 48.65; H, 4.7; N, 31.45.  $C_9H_{11}N_5O_2$  requires C, 48.85; H, 5.0; N, 31.65%). A solution of the compound (2 g.) in *n*-hydrochloric acid (20 ml.) was boiled under reflux for 1 hr. Evaporation then gave 9-amino-8-methylhypoxanthine (1.5 g.) which separated from aqueous ethanol as needles, m. p. 335° (decomp.) (Found: C, 43.5; H, 4.3; N, 42.2.  $C_6H_7N_5O$  requires C, 43.65; H, 4.25; N, 42.4%),  $\lambda_{max}$ . 252  $m\mu$  ( $\epsilon$  10,800) in  $H_2O$ .

**8-Methylhypoxanthine.**—9-Amino-8-methylhypoxanthine (1 g.) in water (10 ml.) and *n*-hydrochloric acid (6 ml.) with sodium nitrite (0.4 g.) gave a solid precipitate. 8-Methylhypoxanthine (0.7 g.) crystallised from aqueous ethanol as needles, m. p. >360° (Found: C, 47.9; H, 3.9; N, 37.15. Calc. for  $C_6H_8N_4O$ : C, 48.0; H, 4.05; N, 37.3%),  $\lambda_{max}$ . 247  $m\mu$  ( $\epsilon$  12,500) in  $H_2O$ . The same compound was obtained by the reaction of nitrous acid with 9-ethoxymethyleneamino-8-methylhypoxanthine.

**1,5-Diformamido-2-methylimidazole-4-carboxyamide.**—1,5-Diamino-2-methylimidazole-4-carboxyamide (3 g.) in formic acid (20 ml.) and acetic anhydride (20 ml.) was boiled under

<sup>6</sup> von Brunig, *Annalen*, 1889, 253, 11.

reflux for 2 hr. Evaporation *in vacuo* gave the *imidazole* (2.9 g.) which separated from ethanol as needles, m. p.  $>360^\circ$  (Found: C, 40.25; H, 3.95; N, 33.45.  $C_7H_5N_5O_3$  requires C, 39.8; H, 4.3; N, 33.2%).

*9-Anilino-8-methylhypoxanthine*.—(a) A mixture of 5-amino-1-anilino-2-methylimidazole-4-carboxyamide (3 g.) in ethyl orthoformate (20 ml.) and acetic anhydride (20 ml.) was boiled under reflux for 1 hr., then evaporated *in vacuo* to a solid. The *hypoxanthine* (2.6 g.) separated from ethanol as needles, m. p.  $>360^\circ$  (Found: C, 59.6; H, 4.6; N, 29.2.  $C_{12}H_{11}N_5O$  requires C, 59.7; H, 4.45; N, 29.0%). (b) The foregoing imidazole (2 g.) was boiled under reflux with ethyl orthoformate (20 ml.) for 1 hr.; evaporation *in vacuo* gave 1-anilino-5-ethoxymethylene-amino-2-methylimidazole-4-carboxyamide (1.6 g.) which separated from ethanol as needles, m. p.  $>360^\circ$  (Found: C, 58.55; H, 5.4; N, 24.45.  $C_{14}H_{17}N_5O_2$  requires C, 58.5; H, 5.95; N, 24.2%). This compound gave the hypoxanthine described under (a) when heated with acetic anhydride.

*1-Anilino-5-ethoxymethyleneamino-2-methylimidazole-4-N-methylcarboxyamide*.—5-Amino-1-anilino-2-methylimidazole-4-N-methylcarboxyamide (0.25 g.) was boiled under reflux with ethyl orthoformate (5 ml.) for 30 min., then evaporated *in vacuo* to a gum which solidified when rubbed with ether. The *product* (0.07 g.) crystallised from aqueous ethanol as needles, m. p.  $131\text{--}132^\circ$  (Found: C, 59.75; H, 6.05; N, 23.15.  $C_{15}H_{19}N_5O_2$  requires C, 59.8; H, 6.35; N, 23.25%).

*7-Amino-4-hydroxy-6-methyl-7H-imidazo[4,5-d]-v-triazine*.—A solution of 1,5-diamino-2-methylimidazole-4-carboxyamide (1 g.) in 2N-hydrochloric acid (3.25 ml.) and water (12 ml.) was added slowly to one of sodium nitrite (0.45 g.) in water (10 ml.) with cooling. Dark-brown crystals were soon obtained. The *imidazotriazine* (0.87 g.) separated from aqueous acetic acid as dark brown plates, m. p.  $>360^\circ$  (Found: C, 36.15; H, 3.35; N, 50.25.  $C_5H_6N_6O$  requires C, 36.15; H, 3.65; N, 50.6%).

*7-Anilino-4-hydroxy-6-methyl-7H-imidazo[4,5-d]-v-triazine*.—To a cold solution of 5-amino-1-anilino-2-methylimidazole-4-carboxyamide (0.55 g.) in N-hydrochloric acid (2.4 ml.) and water (12 ml.) was added dropwise sodium nitrite (0.164 g.) in water (3 ml.), giving a yellow precipitate. The *imidazotriazine* (0.33 g.) separated from ethanol as pale yellow plates, m. p.  $190^\circ$  (decomp.) (Found: C, 54.6; H, 4.0; N, 34.45.  $C_{11}H_{10}N_6O$  requires C, 54.55; H, 4.15; N, 34.7%).

*7-Dimethylamino-4-hydroxy-6-methyl-7H-imidazo[4,5-d]-v-triazine*.—A solution of 5-amino-1-dimethylamino-2-methylimidazole-4-carboxyamide (0.44 g.) in N-hydrochloric acid (6 ml.) and water (4 ml.) was added to sodium nitrite (0.2 g.) in water (2 ml.) during 10 min. with cooling. The solution was set aside overnight, then evaporated *in vacuo* to a small volume; crystals separated. The *triazine* (0.1 g.) recrystallised from water as prisms, m. p.  $161^\circ$  (decomp.) (Found: C, 43.35; H, 5.15; N, 43.75.  $C_7H_{10}N_6O$  requires C, 43.3; H, 5.2; N, 43.3%).

*7-Amino-3,4-dihydro-3,6-dimethyl-4-oxo-7H-imidazo[4,5-d]-v-triazine*.—1,5-Diamino-2-methylimidazole-4-N-methylcarboxyamide (0.105 g.) in 10N-hydrochloric acid (0.065 ml.) and water (2 ml.) with sodium nitrite (0.045 g.) in water (1 ml.) gave a yellow precipitate. The *imidazotriazine* (0.1 g.) crystallised from aqueous ethanol as pale yellow needles, m. p.  $139^\circ$  (Found: C, 39.95; H, 4.3; N, 45.5.  $C_6H_8N_6O$  requires C, 40.0; H, 4.5; N, 46.65%).

*7-Anilino-3,4-dihydro-3,6-dimethyl-4-oxo-7H-imidazo[4,5-d]-v-triazine*.—5-Amino-1-anilino-2-methylimidazole-4-N-methylcarboxyamide (0.29 g.) in 10N-hydrochloric acid (0.2 ml.) and water (5 ml.) was slowly added to sodium nitrite (0.082 g.) in water (2 ml.) to precipitate the *imidazotriazine* (0.25 g.) which separated from aqueous ethanol as pale yellow needles, m. p.  $108\text{--}109^\circ$  (Found: C, 55.6; H, 4.45; N, 31.8.  $C_{12}H_{12}N_6O$  requires C, 56.25; H, 4.7 N, 32.8%).

*6-Amino-2,3-dimethyl-1,2,4-triazine-5-carboxyamide* (?).—A suspension of ethyl N-(carbamoylcyanomethyl)acetimidate (4.25 g.) in a solution of methylhydrazine sulphate (4 g.) in N-sodium hydroxide (11.1 ml.) and water (2 ml.) was shaken and gently warmed to give a clear solution which when cooled gave a crystalline precipitate. The *triazine* (1.43 g.) recrystallised from water as diamond-shaped plates, m. p.  $254^\circ$  (decomp.) (Found: C, 42.5; H, 6.55; N, 41.4.  $C_8H_{11}N_5O$  requires C, 42.6; H, 6.5; N, 41.4%),  $\lambda_{\text{max}}$  271 m $\mu$  ( $\epsilon$  13,500). The triazine was diazotised and coupled with an alkaline solution of  $\beta$ -naphthol to give an intense magenta colour.

*4-Hydroxy-6,7-dimethyl-[1,2,4]-triazino[6,5-d]-v-triazine* (?).—The foregoing triazine (0.34 g.) in N-hydrochloric acid (2 ml.) and water (5 ml.) was slowly added to a solution of sodium nitrite (0.14 g.) in water (1 ml.) with cooling. A yellow precipitate appeared after 5 min., was

collected after 45 min., and was washed with water, ethanol, and ether. The *triazine* (0.32 g.) formed pale yellow prisms, m. p. 194° (decomp.) (Found: C, 40.05; H, 4.75; N, 46.3.  $C_6H_8N_6O$  requires C, 40.0; H, 4.45; N, 46.65%).

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