CCCLXXXII.—*The Formation of 1-Substituted Benziminazoles.*

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IN previous communications (J., 1928, 172, 2393, 3134) it was shown that 2-substituted benziminazoles are generally formed by the hydrolytic action of dilute mineral acids on mono- and di-substituted acyl-*o*-diamines and also from *o*-diamines by the action of the appropriate organic acid in the presence of the same hydrolytic agent. These reactions have now been successfully applied to the formation of 1-substituted and of 1 : 2-disubstituted benziminazoles, the *N*-substituent being methyl and phenyl. In the latter case, 4-nitro-2-aminodiphenylamine in the presence of dilute hydrochloric acid gave in good yield, with formic and acetic acid respectively, 5-nitro-1-phenyl- and 5-nitro-1-phenyl-2-methyl-benziminazole. The former had previously been obtained by the prolonged action of sulphuric acid on 4-nitro-2-formamidodiphenylamine (von Walther and Kessler, *J. pr. Chem.*, 1906, **74**, 188) and also by the action of ethyl oxalate on 4-nitro-2-aminodiphenylamine (Reissert and Goll, *Ber.*, 1905, **38**, 90); in the latter case, compare von Walther and Kessler, *J. pr. Chem.*, 1904, **69**, 40. Reduction of 5-nitro-1-phenyl-2-methylbenziminazole gave the corresponding amino-compound, also obtained from 2 : 4-diaminodiphenylamine, acetic anhydride, and dilute hydrochloric acid and by the hydrolysis of 2 : 4-diacetamidodiphenylamine. These results were repeated in the case of 2-aminodiphenylamine-4-arsinic acid, which with formic and hydrochloric acids gave 1-*phenylbenziminazole-5-arsinic acid*. By the use of acetic anhydride and lactic acid, respectively, instead of formic acid, 1-phenyl-2-methylbenziminazole-5-arsinic

acid and *1-phenyl-2-α-hydroxyethylbenziminazole-5-arsinic acid* were obtained. In addition, 1-phenylbenziminazole itself was obtained by the action of formic and hydrochloric acids on 2-aminodiphenylamine; 2-acetamidodiphenylamine and hydrochloric acid, or 2-aminodiphenylamine with acetic anhydride and hydrochloric acid, gave 1-phenyl-2-methylbenziminazole.

In the *N*-methylbenziminazole series, 1-methylbenziminazole has been obtained (Fischer, *Ber.*, 1892, **25**, 2841; 1901, **34**, 938) by methylation of benziminazole with methyl iodide at 140° or with potassium methyl sulphate (Skraup, *Annalen*, 1919, **419**, 1). 1 : 2-Dimethylbenziminazole has been obtained similarly (Fischer, *loc. cit.*).

These two compounds have now been obtained by the action of formic acid and acetic anhydride, respectively, on *o*-aminomethylaniline in the presence of hydrochloric acid. 1 : 2-Dimethylbenziminazole has also been obtained by the acid hydrolysis of *o-aminoacetomethylanilide* and of *diacetyl-o-aminomethylaniline*.

The action of methyl sulphate on 1-methylbenziminazole gives the *methosulphate*, which, like the methiodide (compare Fischer, *Ber.*, 1901, **34**, 938), gives with caustic alkali 2-hydroxy-1 : 3-dimethyl-1 : 2-dihydrobenziminazole. This compound appears to be more stable towards alkali than is indicated by Fischer; treatment for many hours with concentrated sodium hydroxide solution was required to convert it into *o*-phenylenedimethyldiamine. This compound gives with formic acid and hydrochloric acid, 2-hydroxy-1 : 3-dimethyl-1 : 2-dihydrobenziminazole; acetic anhydride in the presence of dilute hydrochloric acid causes the formation of 2-hydroxy-1 : 2 : 3-trimethyl-1 : 2-dihydrobenziminazole.

N-Substituted *o*-phenylenediamines do not appear to condense with dibasic organic acids in the presence of boiling mineral acids of various strengths; from oxalic acid and *o*-aminomethylaniline, 2-aminodiphenylamine, or 2-aminodiphenylamine-5-arsinic acid, unchanged material only was isolated (compare Phillips, J., 1928, 172, 3134).

2-Methylbenziminazole-5(6)-arsinic acid (this vol., p. 3134) has now been obtained by acid hydrolysis of *3-amino-4-acetamidophenylarsinic acid* and of *4-amino-3-acetamidophenylarsinic acid*.

The former was obtained by reduction of *3-nitro-4-acetamidophenylarsinic acid*. *4-Nitro-3-aminophenylarsinic acid* was obtained by the action of aqueous ammonia on 3-chloro-4-nitrophenylarsinic acid. Acetylation, followed by reduction, then gave 4-amino-3-acetamidophenylarsinic acid. The acetylation of the above nitro-amino-arsinic acids was not possible in alkaline solutions; acetylation by means of acetic anhydride in the presence of sulphuric

acid was resorted to, as also in the case of a stronger acid, 3 : 5-dinitro-4-aminophenylarsinic acid.

Experimental.

4-Amino-2-acetamidodiphenylamine.—The corresponding nitro-derivative (von Walther and Kessler, *loc. cit.*, p. 40) (5 g.), mixed with iron powder (10 g.), was added to a boiling solution of acetic acid (2 c.c.) in water (100 c.c.). After the reduction, the mixture was neutralised with ammonia and the isolated solids were exhaustively extracted with boiling water. The combined extract and filtrate was evaporated to dryness under reduced pressure; the residue, crystallised from 50% spirit, gave 2·3 g. of *4-amino-2-acetamidodiphenylamine* in colourless rectangular plates, m. p. 165°, readily soluble in dilute mineral acids (Found : N, 17·7. $C_{14}H_{15}ON_3$ requires N, 17·4%). On treatment with acetic anhydride, 2 : 4-diacetamidodiphenylamine was formed.

5-Nitro-1-phenylbenziminazole.—(*a*) 4-Nitro-2-aminodiphenylamine (5 g.), 4*N*-hydrochloric acid (50 c.c.), and formic acid (2 c.c.) were boiled under reflux for 30 minutes; the base separated on addition of excess of alkali (yield, 70%) (Found : N, 17·4. Calc. : N, 17·6%).

(*b*) 4-Nitro-2-formamidodiphenylamine (Reissert and Goll, *loc. cit.*) was refluxed with ten times its weight of 2*N*-hydrochloric acid for 40 minutes. A yield of 60% of the base, isolated as in (*a*), was obtained (Found : N, 17·5%).

5-Nitro-1-phenyl-2-methylbenziminazole was obtained similarly by method (*a*), acetic anhydride (2 c.c.) being used instead of formic acid. It was identical with the product obtained by the method of von Walther and Kessler (*loc. cit.*, p. 40) (Found : N, 16·4. Calc. : N, 16·6%).

5-Amino-1-phenylbenziminazole.—2 : 4-Diaminodiphenylamine (5 g.) was refluxed with formic acid (2 c.c.) and 4*N*-hydrochloric acid (50 c.c.) for 30 minutes; the mixture then gave, on addition of alkali, the above base in 66% yield. It formed colourless needles, m. p. 131°, from water and was identical with the product obtained by reduction of 5-nitro-1-phenylbenziminazole by stannous chloride and hydrochloric acid (compare Reissert and Goll, *loc. cit.*) (Found : N, 19·9. Calc. : N, 20·1%).

5-Amino-1-phenyl-2-methylbenziminazole.—(*a*) 2 : 4-Diaminodiphenylamine (10 g.) was refluxed for 20 minutes with acetic anhydride and 3*N*-hydrochloric acid (100 c.c.); on basification the product gave 6·5 g. (59%) of the above cyclic compound.

(*b*) 2 : 4-Diacetamidodiphenylamine (2 g.) or 4-amino-2-acetamidodiphenylamine (2 g.) was refluxed for 30 minutes with 10 c.c.

of 4*N*-hydrochloric acid; the mixture was then basified. In each case the yield was 1·1 g. (52%). The above base forms colourless needles, m. p. 145—146°, from water and is identical with the reduction product of 5-nitro-1-phenyl-2-methylbenziminazole by iron and hydrochloric acid (compare von Walther and Kessler, *locc. cit.*) (Found in specimens prepared by the above four methods: N, 18·6, 18·4, 18·4, 18·9. Calc.: N, 18·8%). The acetyl derivative forms white plates, m. p. 230°, from aqueous alcohol (compare von Walther and Kessler, *loc. cit.*, p. 188).

1-*Phenylbenziminazole* (compare Wolff, *Annalen*, 1912, **394**, 63; 1913, **399**, 300).—2-Aminodiphenylamine (0·5 g.), 5 c.c. of 4*N*-hydrochloric acid, and 1 c.c. of formic acid were boiled under reflux for 30 minutes; on basification, 1-phenylbenziminazole, m. p. 98° (from alcohol), was obtained (Found: N, 14·2. Calc.: N, 14·4%).

1-*Phenyl-2-methylbenziminazole*.—2-Aminodiphenylamine (0·5 g.) 5 c.c. of 4*N*-hydrochloric acid, and 1 c.c. of acetic anhydride, treated by the general method, gave 0·2 g. of the above cyclic compound, m. p. 70° after crystallisation from aqueous alcohol (Found: N, 13·1. Calc.: N, 13·4%). The same compound was obtained by gently refluxing 2-acetamidodiphenylamine with five times its weight of 4*N*-mineral acid for 30 minutes (Found: N, 13·2%) (compare Skraup, *loc. cit.*, pp. 20, 73).

2-Nitrodiphenylamine-4-arsinic acid, 2-aminodiphenylamine-4-arsinic acid, and 2-acetamidodiphenylamine-4-arsinic acid were obtained by a modification of Barber's method (this vol., p. 471).

1-*Phenylbenziminazole-5-arsinic acid* could not be obtained from 5-amino-1-phenylbenziminazole by the Bart reaction, owing, presumably, to nitrosation of the nucleus during diazotisation. It was obtained in 70% yield, however, by boiling together 2-aminodiphenylamine-4-arsinic acid (5 g.), 4*N*-hydrochloric acid (50 c.c.), and formic acid (4 c.c.) and neutralising the filtered solution. It formed buff-coloured needles, readily soluble in dilute alkalis, alkali carbonates, and mineral acids (Found: As, 23·4; N, 8·9. $C_{13}H_{11}O_3N_2As$ requires As, 23·6; N, 8·8%).

1-Phenyl-2-methylbenziminazole-5-arsinic acid was obtained similarly to its lower homologue from 2-aminodiphenylamine-4-arsinic acid, acetic anhydride, and 4*N*-hydrochloric acid. It was identical with the product obtained from 2-acetamidodiphenylamine-4-arsinic acid by Barber (*loc. cit.*) (Found: As, 22·4. Calc.: As, 22·6%).

1-*Phenyl-2-α-hydroxyethylbenziminazole-5-arsinic acid*, obtained from 2-aminodiphenylamine-4-arsinic acid, lactic acid, and 4*N*-hydrochloric acid by the general method, formed colourless plates, readily soluble in alkalis, alkali carbonates, and mineral acids (Found: As, 20·65. $C_{15}H_{15}O_4N_2As$ requires As, 20·7%).

o-Nitromethylaniline was obtained from *p*-toluenesulphon-*o*-nitroanilide by Usherwood and Whiteley's method (J., 1923, 1084) with the following modification: 48 G. of *p*-toluenesulphon-*o*-nitroanilide were suspended in 40 c.c. of 4*N*-sodium hydroxide solution, and 12 c.c. of methyl sulphate added. When the mixture was boiled gently, a moderate reaction set in; alkalinity to phenolphthalein was maintained throughout by addition as required of 10*N*-sodium hydroxide solution. A further 12 c.c. of methyl sulphate were added after the disappearance of the first instalment and the treatment was repeated. The alkaline mixture was cooled, and the solid collected and crystallised from alcohol. The yield of *p*-toluenesulphon-*o*-nitromethylanilide, m. p. 128—130°, was 44 g. (88%). The hydrolysis by sulphuric and acetic acids to *o*-nitromethylaniline followed the details of Usherwood and Whiteley (*loc. cit.*).

Since experimental details for the reduction of this compound to *o*-aminomethylaniline are not to be found in the literature, the following are given: *o*-Nitromethylaniline (10 g.) was suspended in hydrochloric acid (30 c.c., *d* 1·16), and tin (15 g.) added at 50° in portions of 3—4 g. After being kept for 15 minutes at 90°, the mixture was made alkaline to phenolphthalein with 25% sodium hydroxide solution and filtered from tin compounds. The mixed filtrate and washings were extracted with ether and the dried extract was evaporated. To the residual oil, hydrochloric acid (4 c.c., *d* 1·16) was added; on cooling, *o*-aminomethylaniline dihydrochloride separated (yield, 3 g.; m. p. 191°. Compare Fischer and Wreszinski, *Ber.*, 1892, **25**, 2711; Usherwood and Whiteley, *loc. cit.*).

o-Nitroacetomethylanilide.—*o*-Nitromethylaniline (20 g.) was suspended in acetic anhydride (40 c.c.), and 0·1 c.c. of sulphuric acid added. On warming, solution, accompanied by disappearance of the red colour, ensued. The oil which separated when the solution was poured into water (200 c.c.) crystallised very slowly. After recrystallisation from benzene (1 c.c. for every 2 g. of solid), it formed pale yellow cubes, m. p. 70°, exceedingly soluble in the common organic solvents, sparingly soluble in light petroleum (b. p. 40—60°), and insoluble in water (Found: N, 14·0. $C_9H_{10}O_3N_2$ requires N, 14·4%).

o-Aminoacetomethylanilide, which formed colourless needles, m. p. 67—68°, from 30% aqueous alcohol, was obtained by reduction of the above nitro-compound by iron and dilute acetic acid as described under 4-amino-2-acetamidodiphenylamine (Found: N, 16·8. $C_9H_{12}ON_2$ requires N, 17·1%).

Diacetyl-o-aminomethylaniline was obtained either by the action of acetic anhydride on *o*-aminoacetomethylanilide (Found: N,

13·6%) or on *o*-aminomethylaniline (Found: N, 13·9%), or by the action of acetic anhydride and sodium acetate on an aqueous solution of *o*-aminomethylaniline hydrochloride (Found: N, 13·8%). It formed white plates, m. p. 172°, from water, in which it is somewhat soluble ($C_{11}H_{14}O_2N_2$ requires N, 13·6%).

1-*Methylbenziminazole.*—*o*-Aminomethylaniline (1 g.), 4*N*-hydrochloric acid (3 g.), and formic acid (1 c.c.) were heated under reflux for 30 minutes. After addition of excess of aqueous ammonia, extraction with chloroform, and removal of the dried solvent, a gum remained which formed colourless plates, m. p. 30°, from alcohol. It was identical with the compound obtained by methylation of benziminazole with potassium methyl sulphate (Skraup, *loc. cit.*; compare also Fischer and Wreszinski, *loc. cit.*; Fischer, *Ber.*, 1901, **34**, 938) (Found: N, 21·4. Calc.: N, 21·2%). On addition of 1 g. of methyl sulphate to 1·5 g. of the above compound a vigorous reaction occurred. The solid obtained formed colourless needles, m. p. 128°, from alcohol and was shown to be 1-*methylbenziminazole methosulphate* (Found: S, 12·9. $C_8H_8N_2,Me_2SO_4$ requires S, 12·4%).

5-*Dimethylamino*-1 : 2-*dimethylbenziminazole Methosulphate.*—5-Amino-2-methylbenziminazole base was obtained by reduction of the corresponding nitro-compound by iron and boiling dilute acetic acid; the filtrate from the iron oxides was evaporated to dryness and the gummy residue treated while still warm with methyl sulphate (12 c.c. for the amino-compound formed from 10 g. of the nitro-derivative). After the reaction had moderated, the oil was dissolved in water (10 c.c.) and treated with charcoal; addition of alcohol (3 vols.) to the filtered solution precipitated, in poor yield, 5-*dimethylamino*-1 : 2-*dimethylbenziminazole methosulphate* in white plates, m. p. 255° (decomp.) (Found: S, 10·7. $C_{11}H_{13}N_3,Me_2SO_4$ requires S, 10·1%).

1 : 2-*Dimethylbenziminazole.*—(*a*) Diacetyl-*o*-aminomethylaniline (2 g.) and 4*N*-hydrochloric acid (10 c.c.) were refluxed for 30 minutes. On addition of excess of alkali, the above compound separated as an oil which rapidly crystallised (yield, 65%).

(*b*) *o*-Aminoacetomethylanilide, similarly treated, gave a yield of 67%.

(*c*) *o*-Aminoacetomethylanilide dihydrochloride (2 g.), acetic anhydride (1·5 c.c.), and 4*N*-hydrochloric acid (8 c.c.) were refluxed for 30 minutes; the cyclic base was isolated as before and consisted of a *trihydrate*, m. p. 65°, which lost its water at 50°, yielding the anhydrous compound, which crystallised in stout prisms, m. p. 112°, from benzene or absolute alcohol (compare Fischer, *Ber.*, 1892, **25**, 2838; Pinnow, *Ber.*, 1899, **32**, 1669; Pinnow and Sämann, *ibid.*,

pp. 2185, 2191) (Found in trihydrate : H_2O, 27·1. $C_9H_{12}N_2,3H_2O$ requires H_2O, 27·0%. Found in anhydrous compound : N, 19·1. Calc. : N, 19·2%).

1-*Methyl*-2-*α*-*hydroxyethylbenziminazole*, obtained from *o*-aminomethylaniline dihydrochloride, lactic acid, and 4*N*-hydrochloric acid by the general method, formed colourless hexagonal plates, m. p. 80°, from water. It is readily soluble in cold ethyl alcohol (Found : N, 16·0. $C_{10}H_{12}ON_2$ requires N, 15·9%).

o-Phenylenedimethyldiamine was obtained by prolonged hydrolysis of 1-methylbenziminazole methosulphate, 2-hydroxy-1 : 3-dimethyl-1 : 2-dihydrobenziminazole (see below), or 2-hydroxy-1 : 2 : 3-trimethyl-1 : 2-dihydrobenziminazole (see below) with alcoholic or concentrated aqueous potassium hydroxide solution.

2-Hydroxy-1 : 3-dimethyl-1 : 2-dihydrobenziminazole (compare Fischer, *Ber.*, 1901, **34**, 938) was obtained in colourless needles, m. p. 74° (hydrochloride, m. p. 245°), by the action of formic acid (1 c.c.) and 4*N*-hydrochloric acid (5 c.c.) on *o*-phenylenedimethyldiamine (1 g.) by the general method (yield, 45%) (Found : N, 17·0. Calc. : N, 17·1%), and 2-hydroxy-1 : 2 : 3-trimethyl-1 : 2-dihydrobenziminazole (Found : N, 15·4. Calc. : N, 15·7%) was obtained similarly by using acetic anhydride instead of formic acid (colourless rhombs, m. p. 162°, from 50% alcohol; compare Fischer, *loc. cit.*).

3-*Nitro*-4-*acetamidophenylarsinic Acid*.—When acetic anhydride (12 c.c.) was added to 3-nitro-4-aminophenylarsinic acid (4 g.), heat was developed and a crystalline solid formed. This was collected, washed with acetic anhydride, and crystallised from alcohol, 3-*nitro*-4-*acetamidophenylarsinic acid* (3·0 g.; 64%) being obtained in fine, pale yellow needles, not molten at 300° (Found : As, 24·9. $C_8H_9O_6N_2As$ requires As, 24·7%). The acid is readily soluble in alkalis and alkali carbonates; excess of these reagents readily hydrolyses it. The calcium and magnesium salts form microcrystalline nodules. Treatment of the parent acid or its acetyl derivative with boiling sulphuric acid (*d* 1·45) for 1 hour gives a 35% yield of *o*-nitroaniline.

3-Nitro-4-formamidophenylarsinic acid could not be obtained by the action of formic acid on 3-nitro-4-aminophenylarsinic acid; the nitration of 4-formamidophenylarsinic acid with mixed nitric–sulphuric acids at 0° gave a 70% yield of 3-nitro-4-aminophenylarsinic acid, oriented by conversion into *o*-nitroaniline as above.

On reduction of 3-nitro-4-acetamidophenylarsinic acid by ferrous sulphate and sodium hydroxide (compare Jacobs, Heidelberger, and Rolf, *J. Amer. Chem. Soc.*, 1918, **40**, 1581) at 35°, a 30% yield of 3-*amino*-4-*acetamidophenylarsinic acid*, which crystallised in

stout hexagonal tablets, m. p. 275°, from water, was obtained (Found : As, 27·5. $C_8H_{11}O_4N_2As$ requires As, 27·4%). This acid differs from the isomeric 2-amino-4-acetamidophenylarsinic acid (compare Fourneau, Navarro-Martin, and Tréfouel, *Ann. Inst. Pasteur*, 1923, **37**, 590; Haythornthwaite, this vol., p. 1013) in giving a triazole on treatment with nitrous acid; the 2-amino-acid is diazotised by such treatment and the product couples normally. The calcium salt forms colourless plates, the magnesium salt is micro-crystalline. Attempts to monoacetylate 3 : 4-diaminophenylarsinic acid by Lewis and Bent's method (*J. Amer. Chem. Soc.*, 1926, **48**, 949) and by various modifications of it failed to produce the above acid.

1-*Acetyl*-1 : 2 : 3-*benztriazole*-5-*arsinic acid*, obtained from the above acetyl derivative and nitrous acid, forms colourless diamonds or needles, not molten at 300°, from 80% acetic acid (Found : As, 26·0. $C_8H_8O_4N_3As$ requires As, 26·3%). It is readily decomposed by boiling water or alkali carbonates, giving 1 : 2 : 3-benztriazole-5(6)-arsinic acid. The magnesium salt is amorphous.

4-*Nitro*-3-*aminophenylarsinic Acid*—4-Chloro-3-nitrophenylarsinic acid (5 g.) (Balaban, J., 1928, 820) was heated in a sealed tube at 160° for 8 hours with aqueous ammonia (*d* 0·880; 50 c.c.). On acidification, filtration and purification by precipitation from its alkaline solution, 2 g. of the above *acid* were obtained. It formed rich yellow, boat-shaped crystals, not molten at 300°, which dissolved readily in alkalis but only in a large excess of hydrochloric acid (*d* 1·16) (Found : As, 28·3. $C_6H_7O_5N_2As$ requires As, 28·6%). The acid is diazotisable and the product couples normally. Concentrated caustic soda solution produces, on being heated with the acid, 4-nitro-3-hydroxyphenylarsinic acid, and reduction with ferrous hydroxide or sodium hyposulphite (compare Bertheim, *Ber.*, 1911, **44**, 3095) gives 3 : 4-diaminophenylarsinic acid. The magnesium salt forms microcrystalline nodules from neutral solution; the ammonium salt is sparingly soluble in cold water.

4-*Nitro*-3-*acetamidophenylarsinic acid*, obtained from the above acid by treatment with acetic anhydride and a trace of sulphuric acid at 80°, forms pale yellow needles from alcohol. It is readily hydrolysed by alkali (Found : As, 24·7. $C_6H_9O_6N_2As$ requires As, 24·7%).

4-*Amino*-3-*acetamidophenylarsinic acid*, obtained by reduction of the above acid with ferrous sulphate and alkali, forms colourless needles very similar to those of its isomeride described above (Found : As, 27·35. $C_8H_{11}O_4N_2As$ requires As, 27·4%). On acetylation in sodium carbonate solution, both isomerides give 3 : 4-diacetamidophenylarsinic acid (compare Phillips, J., 1928,

3136). On treatment with nitrous acid, the former gives 1-*acetyl*-1 : 2 : 3-*benztriazole*-6-*arsinic acid* (Found : As, 26·25. $C_8H_8O_4N_3As$ requires As, 26·3%); like its isomeride, this readily loses its acetyl group on treatment with boiling water.

On boiling 3-amino-4-acetamido- or 4-amino-3-acetamido-phenylarsinic acid with 5 parts of 4*N*-hydrochloric acid for 40 minutes and neutralising the mixture, a 60% yield of 2-methylbenziminazole-5(6)-arsinic acid was obtained. The cyclic acid, since it forms a monohydrate isomeric with the amino-acid from which it is formed, is most readily distinguished from the latter by the fact that it does not react with nitrous acid (compare Phillips, *loc. cit.*).

3 : 5-*Dinitro*-4-*acetamidophenylarsinic acid* was obtained by the action of boiling acetic anhydride on 3 : 5-dinitro-4-aminophenylarsinic acid in the presence of a trace of sulphuric acid. It formed pale yellow prisms not molten at 300° and was readily soluble in alkalis, which hydrolyse it with extreme ease (Found : As, 21·8. $C_8H_8O_8N_3As$ requires As, 21·5%). The magnesium salt is amorphous. Attempts to reduce this acid with sodium hyposulphite or ferrous hydroxide to the corresponding diamino-acid were unsuccessful. On boiling the dinitro-acid or its acetyl derivative under reflux for 30 minutes with sulphuric acid (*d* 1·45), 2 : 6-dinitroaniline, m. p. 135—136°, was formed; it was isolated by steam distillation (yield, 30%).

Picrates of various benziminazoles have been prepared in the course of this work; since these are not recorded in the literature, their properties are given below :—

Benziminazole.	Picrate, m. p.	Solvent.	Crystalline form.	Picric acid, %. Found.*	Calc.
Unsubstituted	220°	Water	Yellow prisms	65·6	66·0
2-Methyl-	207—208	Alcohol	Yellow rhombs	63·1	63·5
2-Ethyl-	137	Alcohol	Yellow hexagonal plates	60·8	61·1
1-Methyl-	248	Alcohol	Yellow needles	63·7	63·5
1 : 2-Dimethyl-	238	50% Alcohol	Yellow prisms	61·3	61·1
1-Methyl-2-α-hydroxyethyl-	210	Water	Yellow rhombs	56·1	56·5

* As nitron picrate.

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