CLXXXIII.—*The Hydrolysis of Diacetyl-o-diamines.*

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THE view that *o*-diamines are produced as intermediates in the formation of benziminazoles by the hydrolysis of diacetyl-*o*-diamines (J., 1928, 2393) has now been shown to be only partly correct. The acid hydrolysis of 4-nitro-1 : 2-diacetamidobenzene and of 5-*nitro*-1 : 2 : 4-*triacetamidobenzene* proceeds in two directions with the formation of the benziminazole and, to a less extent, of 4-nitro-1 : 2-diaminobenzene and 5-*nitro*-1 : 2 : 4-*triaminobenzene* respectively.

If the reaction is stopped when the acetyl compound is largely unchanged, a considerable quantity of the benziminazole, mixed with some diamine (or triamine) can be isolated; at the completion of the hydrolysis, the proportion of ring compound to amine is unchanged, although the amounts are greater. When the reaction is continued, the amount of amine decreases at a rate independent of the concentration of the mineral acid and corresponding with the rate of reaction between the *o*-diamine and acetic acid in the presence of mineral acid; a corresponding increase in the amount of cyclic compound occurs.

Although the rate of hydrolysis in the first stage depends on the concentration of mineral acid, the proportion of *o*-diamine to the ring compound is independent of this. It is possible that the first stage involves hydrolysis to the monoacetyl derivative, especially as it has been shown (Phillips, J., 1928, 172) that *o*-aminoacetanilide is formed together with 2-methylbenziminazole by acid hydrolysis of diacetyl-*o*-phenylenediamine. Although no monoacetyl derivative was isolated in the hydrolysis of 4-nitro-1 : 2-diacetamidobenzene, owing possibly to its lability, it was found that 4-*nitro*- and 5-*nitro*-2-*aminoacetanilides* behave with boiling hydrochloric acid as does 4-nitro-1 : 2-diacetamidobenzene, *i.e.*, 4-nitro-1 : 2-diaminobenzene and 5-nitro-2-methylbenziminazole are both produced and the latter increases in amount at the expense of the former as the reaction proceeds.

When methyl-alcoholic hydrogen chloride is used as the hydrolysing agent, acetic acid is removed as methyl acetate as it is formed, and the cyclic compound obtained must be produced from the diacetyl derivative (possibly, however, with the transient formation of monoacetyl derivatives). It is known that the ring compounds are stable to hot concentrated hydrochloric acid, hence the diamine also is formed from the diacetyl compound. At 80°, with 4-nitro-1 : 2-diacetamidobenzene, the proportion of 4-nitro-1 : 2-diaminobenzene to the benziminazole was greater than that found in a similar hydrolysis with aqueous hydrochloric acid, and was unchanged after several hours; at 160°, the yield of the diamine was 96%. Analogous results were obtained with 5-nitro-1 : 2 : 4-triacetamidobenzene.

The use of methyl alcohol and the formation of methyl acetate would account for the formation of amino-ketones from diacyldiaminoethylenes (Windaus, Dorries, and Jensen, *Ber.*, 1921, **54**, 2754); in the absence of the alcohol, it is probable that a glyoxaline would be formed.

With diacetyl-*o*-phenylenediamine and hot hydrochloric acid, the reaction proceeds rapidly to give the benziminazole, no diamine

being found even with limited hydrolysis. However, by the use of methyl-alcoholic hydrogen chloride at 160°, *NN'*-dimethyl-*o*-phenylenediamine was obtained, no ring compound being detected.

Taking into consideration all these facts, it is probable that the hydrolysis of diacetyl-*o*-diamines follows the course

$$R{\cdot}C_6H_3(NH{\cdot}CO{\cdot}CH_3)_2 \longrightarrow R{\cdot}C_6H_3(NH_2){\cdot}NH{\cdot}CO{\cdot}CH_3 \xrightarrow{HOAc} R{\cdot}C_6H_3\langle\begin{smallmatrix}N\\NH\end{smallmatrix}\rangle CMe \quad \text{or} \quad R{\cdot}C_6H_3(NH_2)_2$$

The action of caustic alkali on the nitrodiacetyl-*o*-diamines proceeds in the same way, except that the proportion of nitrodiamine to cyclic compound is independent of the time of heating, since 4-nitro-1 : 2-diaminobenzene is unchanged by sodium acetate and sodium hydroxide at 100°. With diacetyl-*o*-phenylenediamine and 25% caustic alkali solution, the ring compound only was detected.

The reduction of 2 : 4-dinitroacetanilide, giving 4-nitro-2-aminoacetanilide, was accompanied by the formation of 5-nitro-2-methylbenziminazole; monoacetylation of 4-nitro-1 : 2-diaminobenzene yielded, in addition to 5-nitro-2-aminoacetanilide, the same cyclic compound. Since the solution was alkaline (ammonia) in the former case and acid (acetic acid only) in the latter, it seems that the ring compound in both cases is formed directly from the initial material.

In the 1-methylbenziminazole series, similar principles probably apply. Treatment of 4-nitro-2-acetamidomethylaniline with methyl-alcoholic hydrogen chloride gave a mixture of 5-nitro-1 : 2-dimethylbenziminazole and 4-nitro-2-aminomethylaniline; as before, both compounds must have been formed independently from the initial material. With hot aqueous hydrochloric acid, no estimation of the rate of disappearance of the methylaniline derivative was recorded; the time after which the *pure* cyclic compound was obtained, however, corresponded with the time after which the *pure* cyclic compound was formed from the methylaniline derivative and acetic acid in the presence of a mineral acid. Shorter periods of heating gave a mixture of the cyclic compound and 4-nitro-2-aminomethylaniline.

The nitration of 5(or 6)-acetamido-2-methylbenziminazole gives 6(or 5)-*nitro*-5(or 6)-*acetamido*-2-*methylbenziminazole*, which was oriented by deamination of the corresponding *amino*-compound, 5(or 6)-nitro-2-methylbenziminazole being formed in good yield. 1 : 2 : 4-Triacetamidobenzene on nitration gives the 5-nitro-derivative, which was oriented by conversion into 6(or 5)-nitro-5(or 6)-amino-2-methylbenziminazole. The orientation of 5-nitro-1 : 2 : 4-triaminobenzene follows from this and also from its reduction to 1 : 2 : 4 : 5-tetra-aminobenzene (compare Nietzki and Hagenbach,

Ber., 1887, **20**, 329). Reduction of 5(or 6)-nitro-6(or 5)-acetamido-2-methylbenziminazole gives 5(or 6)-*amino*-6(or 5)-*acetamido*-2-*methylbenziminazole*; this compound and 5(or 6)-diacetamido-2-methylbenziminazole on treatment with boiling dilute mineral acids pass rapidly into α-2 : 2′-dimethylbenzbisiminazole (compare Nietski and Hagenbach, *loc. cit.*), which is also obtained readily from 1 : 2 : 4 : 5-tetra-aminobenzene or 5 : 6-diamino-2-methylbenziminazole (compare Kym and Ratner, *Ber.*, 1912, **45**, 3249) by treatment with acetic and hydrochloric acids. In the presence of formic and hydrochloric acids, α-2-*methylbenzbisiminazole* is obtained from 5 : 6-diamino-2-methylbenziminazole, and α-*benzbisiminazole* from the tetra-aminobenzene.

5(or 6)-*Nitro*-2-*methylbenziminazole*-6(or 5)-*arsinic acid*, prepared from 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole by the Bart reaction, gives the *amino*-derivative on reduction.

EXPERIMENTAL.

4-*Nitro*-2-*aminoacetanilide*.—2 : 4-Dinitroacetanilide (10 g.) was boiled for 15 minutes with ammonium sulphide solution (6%, 50 c.c.); on acidification to Congo-red with hydrochloric acid and addition of excess of sodium acetate to the filtered solution, 7 g. of mixed bases were obtained. By digestion with 2*N*-caustic soda solution, 5-nitro-2-methylbenziminazole (3·8 g., m. p. 221°, crystallised from alcohol. Found: N, 23·6. Calc.: N, 23·7%) was extracted; it was precipitated from the alkaline solution with acetic acid. The residue, after crystallisation from alcohol (80%), melted at 205° and was shown to be 4-*nitro*-2-*aminoacetanilide* (1·8 g.). It was completely soluble in excess of dilute mineral acids, readily soluble in alcohol or acetic acid, and insoluble in water (Found: N, 21·5. $C_8H_9O_3N_3$ requires N, 21·5%).

5-*Nitro*-2-*aminoacetanilide*.—4-Nitro-1 : 2-diaminobenzene (5·4 g.) was dissolved in 20 c.c. of water with 5 c.c. of hydrochloric acid (*d* 1·16). On addition of acetic anhydride (10 c.c.), followed rapidly by excess of solid sodium acetate (until acidity to Congo-red was removed), the nitro-diamine was reprecipitated as a red solid; this rapidly became yellow as it was acetylated. After 15 minutes, the solid was collected and digested with 2*N*-caustic soda solution; this removed 2·6 g. of 5-nitro-2-methylbenziminazole (m. p. 221° after crystallisation from alcohol. Found: N, 23·7%). The residue (1·6 g.) was crystallised from alcohol until it melted at 195°; it was shown to be 5-*nitro*-2-*aminoacetanilide* by the solubility in mineral acids (excess), insolubility in alkalis, and analysis (Found: N, 21·4%). It is sparingly soluble in cold alcohol and insoluble in water or ether, and is a much weaker base than the isomeric 4-nitro-derivative.

5(or 6)-*Nitro*-6(or 5)-*acetamido*-2-*methylbenziminazole*.—5(or 6)-Acetamido-2-methylbenziminazole (9 g.), mixed with potassium nitrate (5 g.), was added at 0—5° to sulphuric acid (60 c.c.); after 1 hour, the mixture was poured into ice-water (1 l.) and basified at 50° with 15% aqueous ammonia. The voluminous yellow mass was collected, washed with water, and crystallised from 50% alcohol (yield, 7·7 g. or 70%). No trace of isomerides was detected in the liquors. 5(or 6)-*Nitro*-6(or 5)-*acetamido*-2-*methylbenziminazole* forms orange-yellow needles, m. p. 235°, insoluble in boiling alcohol or cold water, soluble in about 10 parts of boiling 50% aqueous alcohol. It is readily soluble in caustic alkalis, mineral acids, and in dilute acetic acid, from which it is reprecipitated by bases (Found : N, 23·7. $C_{10}H_{10}O_3N_4$ requires N, 23·9%).

5(or 6)-*Amino*-6(or 5)-*acetamido*-2-*methylbenziminazole*, obtained by reduction of the above nitro-compound with iron and boiling dilute acetic acid (see J., 1928, 174), consists of white needles, m. p. above 300°, moderately easily soluble in boiling water (Found : N, 27·8. $C_{10}H_{12}ON_4$ requires N, 27·4%). The *dihydrochloride* is sparingly soluble in cold water (Found : Cl, 25·2. $C_{10}H_{12}ON_4,2HCl$ requires Cl, 25·6%), and the *triazole* (Found : N, 33·0. $C_{10}H_9ON_5$ requires N, 32·6%) forms prisms from boiling water, not molten at 300°.

5 : 6-Diacetamido-2-methylbenziminazole (compare Kym and Ratner, *loc. cit.*), obtained by the action of acetic anhydride on the above amino-compound, formed colourless needles, m. p. above 300°, from boiling water (Found : N, 22·7. Calc. : N, 22·8%).

5-*Nitro*-1 : 2 : 4-*triacetamidobenzene*.—1 : 2 : 4-Triacetamidobenzene (15 g.) was mixed with potassium nitrate (6·6 g.) and added at 5—10° to sulphuric acid (75 c.c.); after remaining for 1 hour at 10°, the mixture was poured on ice, and the *nitro*-compound collected and washed; it crystallised from glacial acetic acid in yellow prisms (9 g.), m. p. 261°. The mother-liquor on concentration gave a further 2 g. of fairly pure nitro-compound, making the total yield 65%. This compound is sparingly soluble in hot alcohol and insoluble in water (Found : N, 19·1. $C_{12}H_{14}O_5N_4$ requires N, 19·0%).

5-Nitro-1 : 2 : 4-triaminobenzene, obtained, together with 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole (see Table VI, p. 1417) by hydrolysis of the triacetyl derivative, crystallised in deep red needles, m. p. 210°, from aqueous alcohol. It is insoluble in alkalis and only slightly soluble in ether.

5(or 6)-Nitro-6(or 5)-amino-2-methylbenziminazole, obtained by hydrolysis of its acetyl derivative, by the action of hydrochloric acid (Table VI) on 5-nitro-1 : 2 : 4-triacetamidobenzene, or by the action of acetic anhydride and boiling dilute mineral acids on 5-nitro-

1 : 2 : 4-triaminobenzene, crystallised in red prisms, m. p. 292°, from alcohol. It is soluble in *excess* of caustic alkalis and readily soluble in mineral acids (compare Biedermann and Ledoux, *Ber.*, 1874, **7**, 1532; Nietzki and Hagenbach, *loc. cit.*) (Found: N, 28·8. Calc.: N, 29·2%). The *hydrochloride* consists of brown needles, sparingly soluble in water (Found: Cl, 15·3. $C_8H_8O_2N_4$,HCl requires Cl, 15·5%). The amino-group in this compound is very stable to hot concentrated aqueous alkalis.

5(or 6)-Nitro-2-methylbenziminazole (yield, 70%) was obtained from 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole by treatment of its diazo-compound with excess of boiling alcohol.

5 : 6-Diamino-2-methylbenziminazole (Kym and Ratner, *loc. cit.*) was obtained as its *dihydrochloride* (Found: Cl, 29·9; N, 23·9. $C_8H_{10}N_4$,2HCl requires Cl, 30·2; N, 23·9%) by reduction of 5(6)-nitro-6(5)-amino-2-methylbenziminazole (3 g.) with boiling 5*N*-hydrochloric acid (30 c.c.) and tin (8 g.). After removal of tin by hydrogen sulphide, the filtrate was evaporated to dryness under reduced pressure (yield, 70%). The *triazole* melted above 300° (Found: N, 40·5. $C_8H_7N_5$ requires N, 40·5%).

5(6)-*Nitro-2-methylbenziminazole*-6(5)-*arsinic Acid.*—5(6)-Nitro-6(5)-amino-2-methylbenziminazole (7·5 g.) in 30 c.c. of water and 30 g. of ice with 12 c.c. of 10*N*-hydrochloric acid was diazotised at 0° with 3 g. of sodium nitrite. The diazo-solution was added at 50° to a sodium arsenite mixture prepared from arsenious oxide (5·4 g.) and sodium hydroxide (8·0 g.) in water (15 c.c.) to which 7 c.c. of 2*N*-copper sulphate solution had been added. After remaining for 30 minutes at 60°, the reaction mixture was submitted to filtration and the filtrate was acidified to litmus, again filtered, and acidified faintly to Congo-red. The *arsinic acid*, obtained in 60% yield, formed pale yellow, hexagonal plates, not molten at 300°, from glacial acetic acid, in which it was sparingly soluble (Found: As, 24·75; N, 13·7. $C_8H_8O_5N_3As$ requires As, 24·9; N, 13·9%). The calcium and magnesium salts are amorphous but the barium salt forms fine needles. The acid can be recovered unchanged after several hours' boiling with 20% caustic alkali solution.

On reduction of the nitro-acid by freshly precipitated ferrous hydroxide at 60°, a 65% yield of 5(6)-*amino-2-methylbenziminazole*-6(5)-*arsinic acid* is obtained. The acid forms white needles, is amphoteric, and is remarkably stable towards boiling 5*N*-hydrochloric acid (Found: As, 27·8; N, 15·5. $C_8H_{10}O_3N_3As$ requires As, 27·6; N, 15·5%). The *acetyl* derivative forms colourless prisms, readily soluble in alkalis and mineral acids (Found: As, 23·7; N, 13·2. $C_{10}H_{10}O_4N_3As$ requires As, 24·0; N, 13·4%).

1 : 2 : 4 : 5-Tetra-aminobenzene tetrahydrochloride (compare

Nietzki and Hagenbach, *loc. cit.*) was obtained by reduction of 5-nitro-1 : 2 : 4-triaminobenzene with tin and boiling 5*N*-hydrochloric acid. It is sparingly soluble in cold water and on treatment of its aqueous solution with ammonia and acetic anhydride gives 1 : 2 : 4 : 5-tetra-acetamidobenzene (Found : N, 18·2. Calc. : N, 18·3%).

α-*Benzbisiminazole* was obtained as an amorphous white solid, not molten at 300°, when 1:2:4:5-tetra-aminobenzene hydrochloride was treated with formic acid (1part) and 5*N*-hydrochloric acid (5 parts) for ½ hour at the boiling point, and the solution made alkaline with ammonia (Found : N, 35·0. $C_8H_6N_4$ requires N, 35·4%).

α-2-*Methylbenzbisiminazole.*—5:6-Diamino-2-methylbenziminazole dihydrochloride (2 g.) was refluxed for 30 minutes with 6 c.c. of 5*N*-hydrochloric acid and 2 c.c. of formic acid; on basification with ammonia the cyclic *compound* was precipitated. It is an amorphous solid, not molten at 300°, readily soluble in acids but not in caustic alkali (Found : N, 32·2. $C_9H_8N_4$ requires N, 32·6%).

α-2 : 2′-Dimethylbenzbisiminazole was obtained (*a*) from 5 : 6-diamino-2-methylbenziminazole by the action of acetic and 5*N*-hydrochloric acids, (*b*) by the action of boiling 5*N*-hydrochloric acid (5 parts) on 5 : 6-diacetamido-2-methyl- or 5(6)-amino-6(5)-acetamido-2-methyl-benziminazole, and (*c*) by the action of acetic anhydride (2 parts) and boiling 5*N*-hydrochloric acid (3 parts) on 1 : 2 : 4 : 5-tetra-aminobenzene hydrochloride. It is an amorphous white solid resembling its lower homologues in solubility, and is unmelted at 300° (Found : N, 30·3. Calc. : N, 30·1%).

4-Nitro-2-aminomethylaniline was obtained in 60% yield by reduction of 2 : 4-dinitromethylaniline with aqueous ammonium sulphide solution. By the action of acetic anhydride on the dry solid or of sodium acetate on an aqueous solution of its hydrochloride, was obtained 4-*nitro*-2-*acetamidomethylaniline*, which crystallised from acetone in yellow rhombs, m.p. 185° (Found : N, 20·1. $C_9H_{11}O_3N_3$ requires N, 20·1%); no trace of 4-nitro-2-acetamidomethylacetanilide was formed even when a large excess of acetic anhydride was used. The difficulty of acetylating a methylamino-group in the *o*- or *p*-position with respect to a nitro-group is also shown in the case of 2 : 4-dinitromethylaniline, which cannot be acetylated with acetic anhydride even in the presence of fused sodium acetate.

Formation of 5-*Nitro*-2-*methylbenziminazole.*—Before the quantitative work was undertaken, it was shown that the cyclic compound was stable to 10*N*-hydrochloric acid at 160° and to boiling 50% sodium hydroxide solution, the recovery of unchanged material after many hours being almost quantitative in both cases.

General method of estimation. Aliquot portions of the reaction

mixture were withdrawn after various times, cooled rapidly, and treated with sodium acetate. The solids obtained were digested with excess of 2*N*-caustic soda, and the nitro-diamine collected. The filtrate was acidified with acetic acid, and the cyclic compound filtered off. The combined mother-liquors were evaporated to dryness, and the residual solids extracted with acetone. The substance obtained by evaporation of the acetone was redigested with caustic alkali and separated into the same two compounds.

TABLE I.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1 : 2-diaminobenzene, acetic anhydride (1 part), and hydrochloric acid (5 parts) at the boiling point.*

	2*N*-HCl.		4*N*-HCl.		10*N*-HCl.	
Time (mins.).	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
15	40	54	38	50	42	48
30	24	67	20	62	27	60
45	13	70	11	77	14	75
60	5	75	5	82	5	80
75	trace	85	trace	85	trace	86
90	nil	86	nil	85	nil	85

TABLE II.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1 : 2-diacetamidobenzene and hydrochloric acid (5 parts) at the boiling point.* The method of estimation was as before, except that in the cases marked (a) the unchanged material was removed by filtration after cooling and weighed and the estimation was performed on the filtrate. In the following tables, (a) has this significance and (b) indicates complete hydrolysis as shown by complete solution.

	2*N*-HCl.		4*N*-HCl.		10*N*-HCl.	
Time (mins.).	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
5	—	—	—	—	29 (b)	60 (b)
7	—	—	† 6 (a)	14 (a)	—	—
10	—	—	‡19 (a)	30 (a)	—	—
15	—	—	23 (b)	64 (b)	19	70
18	*11 (a)	22 (a)	—	—	—	—
30	27 (b)	67 (b)	11	80	8	80
45	20	72	6	90	4	90
60	10	80	1	92	nil	93
75	5	87	nil	94	—	—
90	nil	90	—	—	—	—

Unchanged material : *55%, †75%, ‡42%.

TABLE III.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1 : 2-diacetamidobenzene and 25% caustic alkali solution.*

Time (mins.)	5	30	60	180
% Nitro-diamine	4	5	6	4
% Ring compound	82	85	78	83

TABLE IV.—*Formation of 5-nitro-2-methylbenziminazole from 4- and 5-nitro-2-aminoacetanilide and 4N-hydrochloric acid (5 parts) at the boiling point.* Owing to the sparing solubility in cold mineral acids of these two bases, it was found possible approximately to estimate the amounts of unchanged material after limited action of the mineral acid (a) by a method analogous to that employed for the acid hydrolysis of 4-nitro-1 : 2-diacetamidobenzene.

	From 4-nitro-compound.		From 5-nitro-compound.	
Time (mins.).	% Nitro-diamine.	% Ring compound.	% Nitro-diamine.	% Ring compound.
1	*19 (a)	47 (a)	†22 (a)	50 (a)
5	32 (b)	51 (b)	30 (b)	60 (b)
15	10	84	12	72
30	—	—	4	79
60	nil	92	nil	83

Unchanged material : *24%, †20%.

TABLE V.—*Formation of 5-nitro-2-methylbenziminazole and of 4-nitro-1 : 2-diaminobenzene from 4-nitro-1 : 2-diacetamidobenzene and 20% methyl-alcoholic hydrogen chloride (5 parts).* The nitro-diamine and acetic acid do not react in the presence of methyl-alcoholic hydrogen chloride, methyl acetate being formed.

	At the boiling point (atmospheric pressure).		
Time (mins.).	% Unchanged.	% Nitro-diamine.	% Ring compound.
(a) 10	58	15	17
(b) 30	—	38	47
60	—	35	50
180	—	40	52

At 160°. 4-Nitro-1 : 2-diacetamidobenzene (2 g.) was heated in a sealed tube for 3 hours at 160° with 20% methyl-alcoholic hydrogen chloride (10 c.c.); on dilution with water (20 c.c.) and basification with dilute caustic soda solution, 1·2 g. (96%) of 4-nitro-1 : 2-diaminobenzene were obtained. No trace of the cyclic compound was found in the acidified filtrate.

TABLE VI.—*Formation of 5(6)-nitro-6(5)-amino-2-methylbenziminazole from 5-nitro-1 : 2 : 4-triacetamidobenzene and hydrochloric acid (5 parts) at the boiling point.*

	2*N*-HCl.		4*N*-HCl.		20% Methyl-alcoholic hydrogen chloride.	
Time (mins.).	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
2	—	—	*10 (a)	42 (a)	—	—
5	—	—	—	—	†12 (a)	52 (a)
6	—	—	23 (b)	67 (b)	—	—
12	20 (b)	64 (b)	—	—	—	—
15	—	—	8	83	15 (b)	80 (b)
30	8	79	trace	89	17	78
60	(nil)	87	nil	91	15	80

Unchanged material : *40%, †20%.

Formation of Benziminazole and of 2-Methylbenziminazole from o-Phenylenediamine, Formic Acid (1 part) or Acetic An-

hydride (1 *part*), *and* 4N-*Hydrochloric Acid* (5 *parts*) *at the Boiling Point.*—Aliquot portions of the reaction mixture were periodically withdrawn, rapidly cooled, and treated with sodium nitrite; the triazole corresponding to the unchanged diamine was then precipitated. The filtrate from the triazole on basification with dilute aqueous ammonia gave the cyclic compound; a further quantity was obtained by concentration of the filtrate.

TABLE VII.

	Benziminazole.		*2-Methylbenziminazole.*	
Time (mins.).	% Diamine.	% Ring compound.	% Diamine.	% Ring compound.
5	39	55	45	50
15	12	80	20	70
30	nil	95	nil	87

Formation of 2-Methylbenziminazole from Diacetyl-o-phenylenediamine and Hydrochloric Acid (5 *parts*) *or Caustic Alkali at the Boiling Point.*—When 2*N*- or 4*N*-acid had been used, examination of the solution for diamine (or *o*-aminoacetanilide) by means of nitrous acid gave, even after short periods of treatment, traces only of the triazole and more than 80% yields of the ring compound. The use of 25% caustic alkali solution gave similar results.

Formation of NN′-*Dimethyl-o-phenylenediamine.*—Diacetyl-*o*-phenylenediamine (2 g.) was heated at 160° for 3 hours in a sealed tube with 20% methyl-alcoholic hydrogen chloride (10 c.c.). The blue solution was basified; extraction with ether and removal of the solvent gave 0·4 g. of *NN*′-dimethyl-*o*-phenylenediamine, m. p. 34° after crystallisation from acetone. No cyclic compound could be isolated.

Formation of 5-Nitro-1:2-dimethylbenziminazole.—The separation of amine from ring compound recorded below was done by fractional crystallisation from alcohol.

TABLE VIII.

	Formation from 4-nitro-2-aminomethylaniline, acetic anhydride (1 *part*) *and* 4N-*hydrochloric acid at the boiling point.*		*Formation from 4-nitro-2-acetamidomethylaniline and* 4N-*hydrochloric acid at the boiling point.*	
Time (mins.).	Amine.	% Ring compound.	Amine.	% Ring compound.
5	Present, not estimated	71	—	—
15	—	—	Present, not estimated	60
30	Present, not estimated	60	,, ,,	64
45	Trace	70	Trace	78
60	Nil	85	Nil	78

Formation of 5-Nitro-1 : 2-dimethylbenziminazole from 4-Nitro-2-acetamidomethylaniline and Methyl-alcoholic Hydrogen Chloride at the Boiling Point.—4-Nitro-2-acetamidomethylaniline (5 g.) and 20% methyl-alcoholic hydrogen chloride (25 c.c.) were boiled under reflux for 1 hour and the mixture was evaporated to dryness. The residue, dissolved in water (10 c.c.) and filtered, was basified with ammonia and the bases (3·1 g.; 70%) were fractionated from 70% alcohol, giving 1·8 g. (40%) of 5-nitro-1 : 2-dimethylbenziminazole and 0·4 g. (12%) of 4-nitro-2-aminomethylaniline.

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