CXLIX.—*The Methylation of Benziminazoles.*

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Between 1910 and 1925, Pyman and his co-workers studied the methylation of glyoxalines and, using methyl sulphate as methylating agent, showed that in every case the more basic of the two possible isomerides predominated in the product. Using methyl sulphate and alkali, they often obtained the weaker base in greater amount.

Pyman's more important results are given in Table I.

TABLE I.

Methylation of Glyoxalines.

Glyoxaline.	Ratio of 1 : 5- to 1 : 4-isomeride. With Me_2SO_4.	With Me_2SO_4 and alkali.	References.
4(or 5)-Methyl-	1 : 2·2	—	Pyman, J., 1922, **121**, 2616.
4(or 5)-Bromo-	34 : 1	—	Hazeldine, Pyman, and Winchester, J., 1924, **125**, 1431.
4(or 5)-Nitro-	350 : 1	1 : 10	Forsyth and Pyman, J., 1925, **127**, 573.
4(or 5)-Phenyl-	1 : 5	insoluble in alkali	,, ,,
4(or 5)-Bromo-5(or 4)-methyl-	∞ *	3 : 2	Forsyth and Pyman, J., 1925, **127**, 573, and Pyman, J., 1910, **97**, 1814.
2 : 4(or 2 : 5)-Dibromo-5(or 4)-methyl- ...	45 : 1	1 : 1	Forsyth and Pyman, J., 1925, **127**, 573.
4(or 5)-Nitro-5(or 4)-methyl-	233 : 1	—	Pyman, J., 1922, **121**, 2616.

* ∞ indicates that no isomeride could be detected.

In general, Pyman's conclusion was that substituents of positive polarity favour the formation of 1 : 5- rather than of 1 : 4-derivatives when methyl sulphate is the methylating agent.*

A study of the methylation of various 5(or 6)-methyl-, bromo-, and nitro-benziminazoles has now led to the same general conclusion, namely, that positive substituents in the benzene ring favour the formation of the 1 : 6-isomeride (which corresponds to the 1 : 5-glyoxaline derivative) rather than the 1 : 5 (corresponding to the 1 : 4-glyoxaline derivative) when methyl sulphate is the methylating agent. In the presence of aqueous alkali, the proportion of 1 : 6-isomeride (as found by Pyman for the corresponding glyoxalines) is reduced. In the benziminazole series, also, the effect of the nitro-group is more powerful than that of the bromine atom; since 5(or 6)-nitro-2-methylbenziminazole is much more readily soluble than the corresponding bromo-compound in dilute aqueous caustic alkalis, it seems that relative basicity is the factor determining the ratio of 1 : 6- to 1 : 5-isomeride produced, as in the case of the glyoxalines.

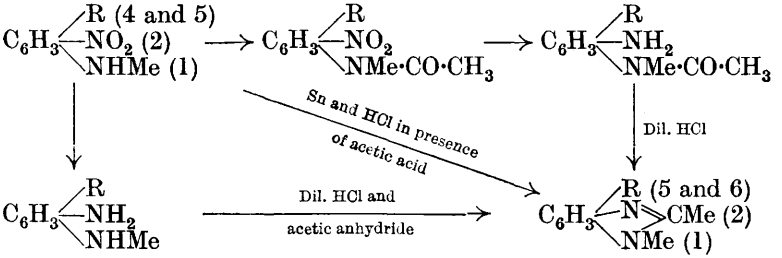
The methylation of 5(or 6)-methyl- and of 2 : 5(or 2 : 6)-dimethylbenziminazoles presents some curious features, for, whereas the former with methyl iodide at 120° gives a good yield of 1 : 6-dimethylbenziminazole, the latter under the same conditions gives a mixture of unchanged material, quaternary methiodide, and 1 : 2 : 5-

* Brady and Reynolds (J., 1930, 2667) have indicated a similar analogy in the methylation of nitrobenztriazoles.

trimethylbenziminazole (Bamberger and Lorenzen, *Annalen*, 1893, **273**, 283). In view of the positive nature of the benzene nucleus it is probable that the former result, although not paralleled in the glyoxaline series, is consistent with the polarity hypothesis, in which case the methylation of 2 : 5(or 2 : 6)-dimethylbenziminazole must be considered anomalous, since no difference in the relative basicity of 5(or 6)-methyl- and 2 : 5(or 2 : 6)-dimethyl-benziminazole was observed. The anomalous case of Pyman's 4(or 5)-phenyl-glyoxaline (see Table I) is recalled by this apparent discrepancy; in the absence of other evidence, a hypothesis similar to that advanced by Pyman is tentatively adopted, namely, that in this case molecular structure and not basicity determines the relative proportions of the methylated isomerides. Both 5(or 6)-methyl- and 2 : 5(or 2 : 6)-dimethyl-benziminazole are, like benziminazole and 2-methylbenziminazole, almost insoluble in dilute caustic alkali solutions.

Bamberger and Lorenzen obtained 1 : 2 : 5-trimethylbenziminazole by the action of methyl iodide on the silver salt of 2 : 5(or 2 : 6)-dimethylbenziminazole; this recalls the same anomaly, since all other silver salts examined gave the 1 : 6-isomeride under these conditions.

The synthesis of the 1 : 5- and 1 : 6-isomerides corresponding to 5(or 6)-nitro-2-methyl- and 5(or 6)-bromo-2-methyl-benziminazoles has been accomplished for purposes of identification, by the following rational methods :—



(R = Me,* NO_2, or Br.)

Separation of the isomerides formed in the methylation of 2-methylbenziminazole-5(or 6)-arsonic acid was difficult : the product obtained in the larger amount by methylation with methyl sulphate was designated the 1 : 6-derivative on account of the positive nature of the arsonic acid group. Table II shows the results obtained on methylation of various benziminazole derivatives.

* 1 : 5-Dimethylbenziminazole, Fischer, *Ber.*, 1889, **22**, 195; 1 : 2 : 5-trimethylbenziminazole, Niementowski, *Ber.*, 1887, **20**, 1878; 1 : 2 : 6-trimethylbenziminazole, Fischer and Rigaud, *Ber.*, 1902, **35**, 1260.

TABLE II.

Methylation of Benziminazoles.

Benziminazole.	Solubility of initial material in 2*N*-NaOH.	Ratio of 1 : 6- to 1 : 5-isomeride. MeCl.	MeI.	Me_2SO_4.	Me_2SO_4 and alkali.
5(or 6)-Methyl-	Slightly soluble	No methylation at 160°	∞	10 : 1	1 : 1
2 : 5(or 2 : 6)-Dimethyl-	,,	,,	0	10 : 1	1 : 1
5(or 6)-Bromo-2-methyl-	Soluble in excess		∞	50 : 1	2 : 1
5(or 6)-Nitro-2-methyl-	Readily soluble	∞	—	100 : 1	5 : 1
2-Methyl-5(or 6)-arsonic acid	,,		—	∞	10 : 1

In the cases of 4- and 5-nitro-1-methylglyoxalines, 4- and 5-bromo-1-methylglyoxalines and 4- and 5-phenyl-1-methylglyoxalines, Pyman and his collaborators found that the quaternary methiodide from each pair of isomerides existed in one form only. The same result was obtained for the quaternary methiodide from 1 : 2 : 5- and 1 : 2 : 6-trimethylbenziminazoles by Fischer (*J. pr. Chem.*, 1907, **75**, 88) and has now been shown to be true for the pairs of isomerides derived from the first four benziminazoles in Table II (first column). As these methiodides are soluble in water (compare Hübner, *Annalen*, 1881, **210**, 328) and contain ionisable iodine removable by bases, they are represented by formula (II) rather than (I), since the former shows their symmetrical character and also their ready convertibility into the ψ-bases (III) and the insoluble carbinols or benziminazoles (IV). It seems unnecessary to postulate " labile "

(I.) $C_6H_3R\langle^{NMe}_{N(MeI)}\rangle CR'$ $\left[C_6H_3R\langle^{NMe}_{NMe}\rangle CR'\right]^+\cdots I^-$ (II.)

(III.) $\left[C_6H_3R\langle^{NMe}_{NMe}\rangle CR'\right]^+\cdots OH^-$ $C_6H_3R\langle^{NMe}_{NMe}\rangle CR'\cdot OH$ (IV.)

intermediate methiodides as suggested by Fischer (*loc. cit.*), because the ionised form (II) can easily be produced directly from each isomeride, (5 or 6)R·$C_6H_3\langle^{NMe}_{\quad N}\rangle CR'$.

The action of moist silver oxide on 1 : 5(or 1 : 6)-dimethylbenziminazole methiodide (Fischer and Rigaud, *Ber.*, 1902, **35**, 1258) gives the ψ-base (III), which is rapidly transformed by caustic alkali into the un-ionised carbinol (IV) : from the other methiodides, only the carbinols were obtained. The strongly positive nitro- and bromo-radicals have the effect of increasing the solubility

in water of the quaternary methiodides (II), the nitro-compound being more soluble than the bromo-; the 5(or 6)-methyl compounds are only sparingly soluble in cold water. This may indicate that positive groups cause increased ionisation.

The distillation of the methiodides could not be accomplished owing to their non-volatility.

A study of the rates of fission by alkali of the carbinols (IV) corresponding to the benziminazoles of Table II has shown that the nitro- and the bromo-derivative break down most easily and that the 5(or 6)-methyl derivative is relatively stable. The fission products, *NN'*-dimethyl-*o*-phenylenediamines, give the corresponding carbinols in good yield when treated with a boiling dilute mineral acid and acetic (or formic) acid (compare Phillips, J., 1929, 2826).

$$C_6H_3R\langle^{NMe}_{NMe}\rangle CR\cdot OH \underset{\text{HCl and fatty acid}}{\overset{\text{Alk.}}{\rightleftharpoons}} C_6H_3R\langle^{NHMe}_{NHMe}$$

Experimental.

Silver salts of the following benziminazoles (compare Bamberger and Lorenzen, *loc. cit.*) were made in 90% yield by dissolving the base in boiling water and adding the calculated amount of 10% silver nitrate solution: benziminazole (Ag found, 48·0; calc., 48·0%); 2-methylbenziminazole (Ag found, 45·0; calc., 45·2%); 2 : 5(or 2 : 6)-dimethylbenziminazole (Bamberger and Lorenzen, *loc. cit.*) (Ag found, 43·2; calc., 42·7%); 5(or 6)-bromo-2-methylbenziminazole (Ag found, 33·7; calc., 34·0%); 5(or 6)-nitro-2-methylbenziminazole (Ag found, 38·3%; calc., 38·0%). The salts, dried at 90°, were refluxed for 5 hours with methyl alcohol and methyl iodide (5 parts of each); filtration and evaporation of the filtrates gave the 1-methyl derivatives.

5(or 6)-*Methylbenziminazole.*—This substance, obtained from 3 : 4-tolylenediamine, formic and hydrochloric acids (compare J., 1928, 2395, etc.), crystallised from water in colourless prisms, m. p. 114° (compare Bistrzycki and Przeworski, *Ber.*, 1912, **45**, 3483).

Methylation. (a) *With methyl iodide.* Since methyl-alcoholic hydrogen chloride at 160° gave only the methochloride of the unmethylated compound, a mixture of the base (3 g.) with methyl iodide (1 mol.) and absolute methyl alcohol (7·5 c.c.) was heated at 140° for 3 hours. Basification of the product and extraction with chloroform gave an oil, b. p. 280°, probably 1 : 6-dimethylbenziminazole (compare Fischer, *Ber.*, 1893, **22**, 644). The hydrochloride formed colourless prisms [Found: N (in base), 19·0; Cl (in hydrochloride), 19·25. Calc.: N, 19·2; Cl, 19·4%].

(b) *With methyl sulphate.* The base (5 g.) was warmed with methyl sulphate (1 g.-mol.) for 10 minutes on the water-bath, a vigorous reaction occurring; the mixture was then made alkaline with 2*N*-sodium hydroxide and extracted with chloroform. The dried extract was evaporated, and the gummy residue converted into picrates, which were fractionated from dilute alcohol. The approximate ratio of 1 : 6- to 1 : 5-picrate was 10 : 1; the base from the 1 : 5-picrate melted at 96° (compare Fischer, *Ber.*, 1893, **22**, 195).

(c) *With methyl sulphate and alkali.* To the base (5 g.), suspended in excess of boiling 5*N*-sodium hydroxide, methyl sulphate was added until alkalinity to phenolphthalein was removed. After addition of further alkali and methyl sulphate, the solution was treated as in (b). The approximate ratio of 1 : 6- to 1 : 5-picrate was 1 : 1.

2 : 5(or 2 : 6)-*Dimethylbenziminazole.*—3-Amino-4-acetamidotoluene, which formed colourless hexagonal plates, m. p. 132°, from water, was obtained in 77% yield by reduction of 3-nitro-4-acetamidotoluene with iron powder and boiling 5% acetic acid. The melting point agrees with that given by Boessneck (*Ber.*, 1886, **19**, 1757) and there was no evidence that the true melting point is 110—112° or that the higher melting point is due to partial ring formation as suggested by Morgan and Micklethwait (J., 1913, **103**, 1397) (Found, in two experiments: N, 17·1, 17·3. Calc. for $C_9H_{12}ON_2$: N, 17·1. Calc. for $C_9H_{10}N_2$: N, 19·2%). Acetylation of this compound with acetic anhydride gave a 92% yield of 3 : 4-diacetamidotoluene, which formed white needles, m. p. 210°, from alcohol (Found: N, 13·5. Calc.: N, 13·6%). That the 3-amino-4-acetamidotoluene, m. p. 132°, described above contained no ring compound was clearly shown by the fact that treatment with nitrous acid gave 1-acetyl-4-methyl-1 : 2 : 3-benztriazole (Morgan and Micklethwait's 4-acetyl-3 : 4-diazoimide), m. p. 130°, in quantitative yield.

2 : 5(or 2 : 6)-Dimethylbenziminazole * was obtained as colourless rectangular plates, m. p. 202°, from 50% alcohol (Found: N, 19·3. Calc.: N, 19·2%). It was prepared from 3 : 4-tolylenediamine and acetic and hydrochloric acids or from 3-amino-4-acetamido- or

* Morgan and Micklethwait obtained this compound by reduction of 3-nitro-4-acetamidotoluene with iron and a small amount of dilute acetic acid. Repetition of the similar reduction of *o*-nitroacetanilide (compare Phillips, J., 1928, 174) gave, in a small amount of solvent, a mixture of 2-methylbenziminazole and *o*-aminoacetanilide; when the larger amount stated in that paper was used, *o*-aminoacetanilide only was obtained. No modification of the process, however, was successful in producing *o*-aminoformanilide from the corresponding nitro-derivative (compare Phillips, J., 1928, 2396).

3 : 4-diacetamido-toluene and hydrochloric acid by the general method described in previous papers (compare Hobrecker, *Ber.*, 1872, **5**, 920; Ladenburg, *Ber.*, 1875, **8**, 677).

Methylation. (a) Methyl-alcoholic hydrogen chloride at 160° gave unmethylated material. Treatment with methyl iodide as described for the lower homologue gave 1 : 2 : 5-trimethylbenziminazole, m. p. 142°, in 50% yield (Found: N, 17·5. Calc.: N, 17·5%), in addition to some quaternary compound and its periodide. No trace was found of the 1 : 2 : 6-isomeride or of unchanged material (compare Bamberger and Lorenzen, *loc. cit.*).

(b) Methylation with methyl sulphate as described under 5(or 6)-methylbenziminazole (b) gave a similar mixture of bases on removal of chloroform. These were separated by the greater solubility of the 6-isomeride in alcohol; the approximate ratio of 6- to 5-isomeride was 10 : 1. 1 : 2 : 6-Trimethylbenziminazole (Found: N, 17·4%) melted at 121°.

(c) Methylation with methyl sulphate and alkali gave a mixture of 1 : 2 : 5- and 1 : 2 : 6-trimethylbenziminazoles in equal quantities, which were separated from unchanged material (*ca.* 30%) by means of the silver salt of the latter.

4-Bromo-2-nitroacetanilide, obtained by acetylation of 4-bromo-2-nitroaniline (Phillips, J., 1930, 2401), gave, on reduction with iron and boiling dilute acetic acid, an 80% yield of 4-*bromo*-2-*aminoacetanilide*, which formed colourless needles, m. p. 154°, from 25% alcohol (Found: N, 12·1; Br, 34·6. $C_8H_9ONBr_2$ requires N, 12·2; Br, 34·9%). The *hydrochloride* (Found: Cl + Br, 43·0. $C_8H_9ON_2Br,HCl$ requires Cl + Br, 43·5%), treated with sodium nitrite, gave 4-*bromo*-1-*acetyl*-1 : 2 : 3-*benztriazole*, m. p. 112° after crystallisation from 50% alcohol (Found: Br, 33·1. $C_8H_6ON_3Br$ requires Br, 33·3%). 4-*Bromo*-1 : 2 : 3-*benztriazole*, obtained from the acetyl derivative and cold dilute caustic alkali or from 4-bromo-*o*-phenylenediamine and nitrous acid, formed white prisms, m. p. 150° after crystallisation from 30% alcohol (Found: Br, 40·1. $C_6H_4N_3Br$ requires Br, 40·4%). 4-*Bromo*-1 : 2-*diacetamidobenzene*, obtained by addition of acetic anhydride to the filtrate in the reduction of 4-bromo-2-nitroacetanilide or by the action of acetic anhydride on 4-bromo-*o*-phenylenediamine, crystallised in colourless needles, m. p. 215°, from 50% alcohol (Found: N, 10·6; Br, 29·4. $C_{10}H_{11}O_2N_2Br$ requires N, 10·3; Br, 29·5%).

5(or 6)-Bromobenziminazole was obtained from 4-bromo-*o*-phenylenediamine and formic and hydrochloric acids by the standard method or by boiling benziminazole-5(or 6)-arsonic acid with concentrated hydrobromic acid (J., 1930, 2401). A small amount was also obtained by boiling together 3 : 4-diaminophenylarsonic, formic,

and hydrobromic acids for 30 minutes. It formed colourless needles, m. p. 137°, from 50% alcohol (compare Fischer, *Ber.*, 1905, **38**, 327).

5(or 6)-*Bromo*-2-*methylbenziminazole*.—This compound was prepared by the standard methods from 4-bromo-*o*-phenylenediamine, 4-bromo-2-aminoacetanilide, or 4-bromo-1 : 2-diacetamidobenzene, and also by the action of hydrobromic acid on 2-methylbenziminazole-5(or 6)-arsonic acid, 3-amino-4-acetamidophenylarsonic acid, or 3 : 4-diaminophenylarsonic acid, acetic anhydride being present in the last case.

The action of boiling methyl-alcoholic hydrogen chloride on 4-bromo-1 : 2-diacetamidobenzene gave a mixture of the ring compound and 4-bromo-*o*-phenylenediamine in the proportion of 3 : 1, indicating, as shown elsewhere, the independent formation of both these compounds in this case as well as in that of the corresponding nitro-compound (Phillips, J., 1930, 1401). When 4-bromo-*o*-phenylenediamine hydrochloride is treated with sodium acetate and acetic anhydride, a mixture of the ring compound and 4-bromo-1 : 2-diacetamidobenzene is formed; this recalls the parallel case of 4-nitro-*o*-phenylenediamine hydrochloride, which, under similar conditions, gives the corresponding cyclic compound and 5-nitro-2-aminoacetanilide (Phillips, *loc. cit.*, pp. 1411, 1412). On the other hand, 3 : 4-tolylenediamine hydrochloride, similarly treated, gives an excellent yield of 3 : 4-diacetamidotoluene and no ring compound. Made by any of the above methods, 5(or 6)-bromo-2-methylbenziminazole consists of colourless prisms, m. p. 215° (compare Fischer, *loc. cit.*) (Found : Br, 38·0. Calc. : Br, 37·9%).

Methylation. (a) Methylation with methyl iodide as described under the methylation of 5(or 6)-methylbenziminazole gave 6-*bromo*-1 : 2-*dimethylbenziminazole*, which formed colourless needles, m. p. 180°, from alcohol (Found : Br, 35·5. $C_9H_9N_2Br$ requires Br, 35·5%). No isomeride was detected in this case.

(b) Methylation with methyl sulphate gave the 6- and the 5-bromo-isomeride in the approximate ratio of 50 : 1; the 5-*bromo*-compound formed colourless needles, m. p. 141°, from 80% alcohol (Found : N, 12·2; Br, 35·4. $C_9H_9N_2Br$ requires N, 12·4; Br, 35·5%).

(c) Methylation with methyl sulphate and alkali gave the same two isomerides in the approximate ratio of 2 : 1.

Synthesis of 5- *and of* 6-*Bromo*-1 : 2-*dimethylbenziminazole*.—4-Bromo-2-nitromethylaniline (from 3-nitro-4-methylaminophenylarsonic acid and hydrobromic acid; Phillips, J., 1930, 2401) was reduced with tin (2 parts) and 5*N*-hydrochloric acid (12 parts), tin removed by hydrogen sulphide, and the filtrate evaporated to

dryness. The residual 4-bromo-2-aminomethylaniline hydrochloride was heated under reflux for 1 hour with 4*N*-hydrochloric acid (3 parts) and acetic anhydride (1 part), and the solution basified with ammonia; an excellent yield was obtained of 5-bromo-1 : 2-dimethylbenziminazole, m. p. 141° after crystallisation from 80% alcohol, identical with one of the products of methylation of 5(or 6)-bromo-2-methylbenziminazole (Found: Br, 35·3%).

By similar treatment, 5-bromo-2-nitromethylaniline (Phillips, *loc. cit.*) was converted into 6-bromo-1: 2-dimethylbenziminazole (yield, good), m. p. 180°, identical with the product of the methylation of 5(or 6)-bromo-2-methylbenziminazole with methyl iodide (Found: N, 12·3; Br, 35·6%).

Methylation of 5(or 6)-*Nitro*-2-*methylbenziminazole.*—(a) *With methyl-alcoholic hydrogen chloride.* No methylation occurred at 80° (under reflux); methylation at 160° for 3 hours in a sealed tube gave an 85% yield of 6-*nitro*-1 : 2-*dimethylbenziminazole*, m. p. 242°. No 5-nitro-1 : 2-dimethylbenziminazole was detected (Found: N, 21·85. $C_9H_9O_2N_3$ requires N, 22·0%).

(b) *With methyl sulphate.* The base (15 g.) and methyl sulphate (7·5 c.c.) were heated on the water-bath for 1 hour, sodium hydroxide (4*N*) was added, and the solid removed. The filtrate gave on acidification with acetic acid 1·5 g. of unchanged material. The solid, m. p. 240° after crystallisation from 90% alcohol, was 6-nitro-1 : 2-dimethylbenziminazole (Found: N, 21·9%). The mother-liquors from this and several other preparations contained mixtures of this ring compound and the 5-isomeride, m. p. 216° (Found: N, 22·1%). The estimated proportion of 6- to 5-isomeride is about 100 : 1.

(c) Methylation with methyl sulphate and alkali gave a mixture of the 6- and the 5-isomeride in the approximate ratio of 5 : 1.

Synthesis of 6-*Nitro*-1 : 2-*dimethylbenziminazole.*—2-*Chloro*-5-*nitromethylaniline*, m. p. 99° (Found: N, 15·3. $C_7H_7O_2N_2Cl$ requires N, 15·0%), obtained from 2-chloro-5-nitroaniline by methylation with methyl sulphate, gave, on treatment with aqueous ammonia (*d* 0·880) (10 parts) at 160° for several hours, a 55% yield of 5-*nitro*-2-*aminomethylaniline*, which formed yellow plates, m. p. 184°, from benzene (Found: N, 25·0. $C_7H_9O_2N_3$ requires N, 25·1%). This compound, treated with acetic and hydrochloric acids by the general method, gave 6-nitro-1 : 2-dimethylbenziminazole, which crystallised in pale yellow or colourless needles, m. p. 242°, from 50% alcohol. It was soluble in mineral acids and acetic acid (glacial), insoluble in alkalis and ether, and identical in all respects with 6-nitro-1 : 2-dimethylbenziminazole obtained by methylation of 5(or 6)-nitro-2-methylbenziminazole (Found: N, 21·8%).

5-Nitro-1 : 2-dimethylbenziminazole (Phillips, J., 1930, 1418, 1419; Fries, *Annalen*, 1927, **454**, 121) consists of pale yellow needles, m. p. 226°. It resembles its isomeride in solubility (Found : N, 21·9. Calc. : N, 22·0%).

Methylation of 2-Methylbenziminazole-5(or 6)-arsonic Acid.—The arsonic acid (5 g.) and methyl sulphate (1 equiv.) were heated on the steam-bath for 2 hours, *N*-caustic alkali was added, followed by 2*N*-hydrochloric acid until the boiling solution was faintly acid to Congo-red. The first crop of crystals consisted of unchanged material. Subsequent crops, which appeared to be identical, were assumed to be 1 : 2-*dimethylbenziminazole-6-arsonic acid* (2·2 g.); this crystallised in white rectangular plates, not molten at 300°. It was much more soluble than 2-methylbenziminazole-5(or 6)-arsonic acid in water (Found : As, 27·5; N, 10·4. $C_9H_{11}O_3N_2As$ requires As, 27·8; N, 10·3%).

Methylation in 2*N*-sodium hydroxide gave the same product mixed with a small amount of a more soluble isomeride, which was not obtained pure (Found for the mixture : As, 27·75%).

Quaternary Compounds (II) *and Carbinols* (IV).—The methiodides were obtained from the 5- or 6-isomeride at 120—130°, or from the parent compound at 120—150°, by treatment in sealed tubes with 1 mol. (in the former case) or 2 mols. (in the latter) of methyl iodide, methyl alcohol (an equal volume) being used as solvent. In the latter case, a certain amount of periodide, ($C_6H_3R<\overset{N}{\underset{NMe}{\rangle}}CMe,MeI,I_2$) was formed; it was easily separated owing to its insolubility in water. The formation of periodides from the nitro-derivatives was almost completely avoided by working at 120—130° (compare Fischer and Hess, *Ber.*, 1903, **36**, 3970).

The quaternary compound of 2 : 5(or 2 : 6)-dimethylbenziminazole was obtained by treatment of the unmethylated compound with 1 mol. only of methyl iodide at 160° : the methyl alcohol evidently took part in the methylation.

The carbinols were obtained by precipitation of aqueous solutions of the methiodides with sodium hydroxide solution. They were also obtained in excellent yield by refluxing the corresponding *NN'*-dimethyl-*o*-phenylenediamines (1 part) for 30 minutes with 4*N*-hydrochloric acid (5 parts) and formic acid or acetic anhydride (1 part) (compare Phillips, J., 1929, 2826).

The methiodides and the carbinols had the m. p.'s recorded in the literature (Fischer and Rigaud, *loc. cit.*; Niementowski, *loc. cit.*; Fischer, *Ber.*, 1905, **38**, 327), except 5(or 6)-nitro-1 : 2-dimethylbenziminazole methiodide, m. p. 280° (Fischer and Hess, *Ber.*, 1903, **36**, 3969, give m. p. 267°).

5 (or 6)-*Amino*-2-*hydroxy*-1 : 2 : 3-*trimethyl*-2 : 3-*dihydrobenziminazole*.—This was obtained by reduction of the corresponding nitro-compound with iron and boiling 5% acetic acid (compare Phillips, J., 1928, 174). After basification with ammonia, the filtered solution was evaporated to dryness, and the residue treated with excess of alcoholic hydrogen chloride (3*N*). The precipitated *dihydrochloride*, after being washed with ether and air-dried, consisted of steel-blue prisms (yield, 80%), m. p. 130°, soluble in 3 parts of cold water (Found: H_2O, 6·6. $C_{10}H_{15}ON_3,2HCl,H_2O$ requires H_2O, 6·4%. Found for material dried at 90°: N, 16·1; Cl, 26·5. $C_{10}H_{15}ON_3,2HCl$ requires N, 15·8; Cl, 26·7%). Its aqueous solution on treatment with sodium acetate gave a *monohydrochloride* in colourless prisms, m. p. 295°, soluble in 2 parts of cold water (Found: N, 18·3; Cl, 15·0. $C_{10}H_{15}ON_3,HCl$ requires N, 18·3; Cl, 15·5%). The base was not isolated crystalline owing to its great solubility in water. The dihydrochloride was converted by the Bart process into 2-*hydroxy*-1 : 2 : 3-*trimethyl*-2 : 3-*dihydrobenziminazole*-5(or 6)-*arsonic acid* (30% yield), which formed colourless needles readily soluble in cold water (Found: As, 25·0; N, 9·3. $C_{10}H_{15}O_4N_2As$ requires As, 24·8; N, 9·3%). Attempted fission of this compound with aqueous or alcoholic potash led to its complete decomposition.

Fission of the Carbinols.—That the stability of carbinols of the type $C_6H_3R\langle^{NMe}_{NMe}\rangle CMe{\cdot}OH$ is dependent upon the nature of R is shown by the following table, which records the times required for complete decomposition by 50% alcoholic potash.

R.	Time (mins.).	% Yield of $C_6H_3R(NHMe)_2$.	M. p.	References.
Me	360	45	(b. p. 260°)	Fischer and Rigaud, *loc. cit.*
H	180	45	168°	Fischer, *Ber.*, 1907, **34**, 938.
Br	90	50	78	Fischer, *Ber.*, 1905, **38**, 327.
NO_2	60	50	172	Fischer and Hess, *loc. cit.*

The first and the third diamine are also obtained from $C_6H_3R\langle^{NMe}_{NMe}\rangle CH{\cdot}OH$.

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