430. *Cyclic Amidines. Part VII.* Preparation of Benziminazoles from N′-Aryl-N-hydroxyamidines.*

By M. W. Partridge and H. A. Turner.

2-Substituted benziminazoles can be prepared by treatment of an *N*′-aryl-*N*-hydroxyamidine with benzenesulphonyl chloride and a tertiary base under anhydrous conditions. A naphth[1,2]iminazole can be made in this way. In the presence of aqueous alkali, an *N*′-aryl-*N*-hydroxyamidine and benzenesulphonyl chloride afford an *NN*′-disubstituted urea.

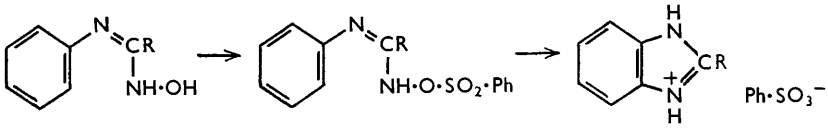
1 : 2-Disubstituted benzene derivatives in which the nitrogen atoms of the two functional groups are attached directly to the nucleus have hitherto been employed for the production of benziminazoles. Alternatively the appropriate 1 : 2-disubstituted benzene has been produced by a rearrangement of the Beckmann,[1] Curtius,[2] or Lossen [3]

* Part VI, *J.*, 1958, 614.

[1] Auwers and Meyenburg, *Ber.*, 1891, **24**, 2370.
[2] Lindemann and Schultheis, *Annalen*, 1928, **464**, 237.
[3] Scott and Wood, *J. Org. Chem.*, 1942, **7**, 508.

type. Pellizzari and Gaiter [4] have however prepared 2-cyanamido-1-cyanobenziminazole from *N*-cyano-*N*-phenylhydrazine and cyanogen bromide.

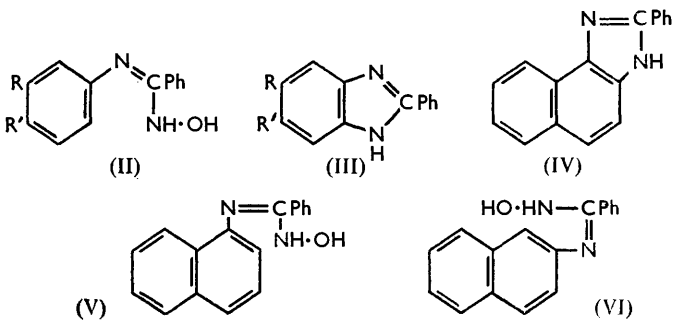
We have found that 2-substituted benziminazoles are readily produced when an *N'*-aryl-*N*-hydroxyamidine is brought into reaction under anhydrous conditions with benzenesulphonyl chloride in the presence of pyridine or triethylamine:



It is possible that the cyclisation involves the intermediate production of a strongly electrophilic imidinium cation (I), resulting from the tendency of the oxime ester to ionise, and being partially stabilised by the organic base:

(I)

Rearrangement of the oxime was not observed even when the reaction was carried out in the hot. The process recalls the cyclisation of sulphonyl esters of 4-arylbutan-2-one oximes [5] to yield products formulated as *iso*quinoline derivatives, since it was considered that the ester underwent a Beckmann transformation before cyclisation; the formation of quinolines has however been observed in analogous reactions.[6]



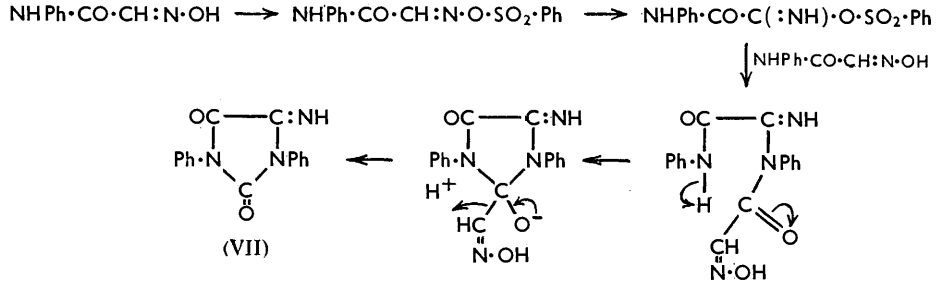
(II) (III) (IV) (V) (VI)

The orientation of the *Bz*-alkylated benziminazoles described in the Experimental section followed from the orientation of the *N'*-aryl-*N*-hydroxyamidine or was established by comparison with authentic specimens prepared from the appropriate *o*-phenylenediamine. Both *N*-hydroxy-*N'*-3-methyl- (II; R = Me, R' = H) and *N*-hydroxy-*N'*-4-methyl-phenylbenzamidine (II; R = H, R' = Me) afforded 5-methyl-2-phenylbenziminazole (III; R = Me, R' = H); and *N'*-3 : 4-dimethylphenyl-*N*-hydroxybenzamidine (II; R = R' = Me) gave 5 : 6-dimethyl-2-phenylbenziminazole (III; R = R' = Me). 2-Phenylnaphth[1,2]iminazole (IV) was obtained from both *N*-hydroxy-*N'*-1- (V) and -2-naphthylbenzamidine (VI).

α-Hydroxyiminoacetanilide, treated in the same way, furnished 4-imino-1 : 3-diphenylparabanic acid (VII) which was identified by hydrolysis to 1 : 3-diphenylparabanic acid and to diphenylurea. It is supposed that the oxime sulphonate, after rearrangement, afforded the parabanic acid by reaction with unchanged α-hydroxyiminoacetanilide

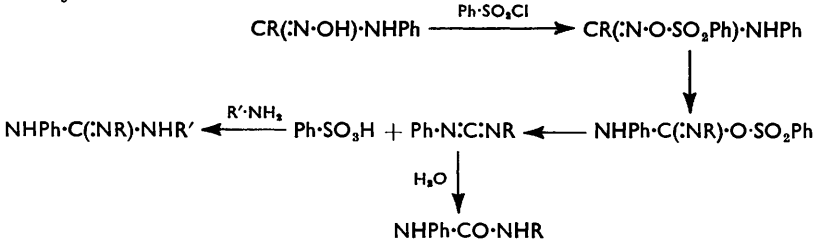
[4] Pellizzari and Gaiter, *Gazzetta*, 1918, **48**, 151.
[5] Scheuing and Walach, G.P. 576,532; 579,227/1933.
[6] Burstin, *Monatsh.*, 1913, **34**, 1443.

involving a process reminiscent of the fission of 2-2′-hydroxyiminoacylfurans to aldoximes and furoic esters, and of α-nitroso-ketones: [7]



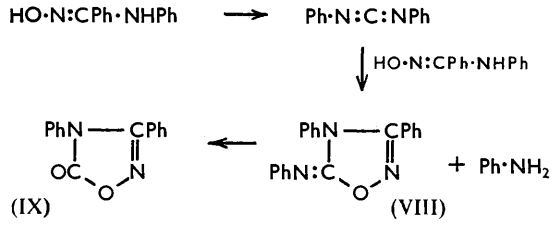
The required *N*-aryl-*N*′-hydroxyamidines, not hitherto described, were prepared by treatment with hydroxylamine of *N*-arylamidines which were themselves obtained by the sulphonate fusion [8] or aluminium chloride [9] method.

By analogy with the Tiemann reaction in which a cyanamide is produced from an amidoxime,[10] it had been expected that an *N*′-aryl-*N*-hydroxyamidine on treatment with benzenesulphonyl chloride would afford a carbodi-imide from which a urea or a guanidine could be readily obtained:



This series of reactions was effected with aqueous sodium hydroxide as acid-binding agent, and a number of ureas were thus produced. When the reaction was carried out in the presence of an amine a trisubstituted guanidine was formed.

Collateral evidence for the intermediate formation of a carbodi-imide was provided by the formation of 3 : 4-diphenyl-5-phenylimino-1 : 2 : 4-oxadiazoline (VIII) when *N*-hydroxy-*N*′-phenylbenzamidine was treated either with benzenesulphonyl chloride and

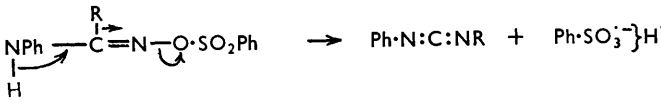


sodium ethoxide in ethanol, or with diphenylcarbodi-imide. This 5-phenylimino-oxadiazoline (VIII) was readily hydrolysed to the known, corresponding 5-oxo-oxadiazoline (IX) which was also formed, together with diphenylurea and *N*-phenylbenzamidine, when the same substituted amidoxime was treated with benzenesulphonyl chloride and potassium carbonate in acetone.

Attempts to isolate a benzenesulphonyl ester of these *N*′-aryl-*N*-hydroxyamidines were

[7] Monoya, *J. Pharm. Soc. Japan*, 1919, **447**, 357; Asahina and Murayama, *Arch. Pharm.*, 1914, **252**, 435; Woodward and Doering, *J. Amer. Chem. Soc.*, 1945, **67**, 860.
[8] Oxley and Short, *J.*, 1946, 147.
[9] Oxley, Partridge, and Short, *J.*, 1947, 1110.
[10] Tiemann, *Ber.*, 1891, **24**, 4162; Partridge and Turner, *J. Pharm. Pharmacol.*, 1953, **5**, 103.

unsuccessful, and no evidence was found of the intervention of an imidosulphonate [NHPh·C(:NR)·O·SO_2Ph] in this series of reactions. Indeed the reactions leading to the formation of ureas occurred with such facility that the elimination of the benzenesulphonate anion and a proton may be concerted with the rearrangement:



Experimental

N-2 : 3-*Dimethylphenylbenzamidine*.—Equimolecular quantities of 2 : 3-dimethylaniline, anhydrous toluene-*p*-sulphonic acid, and phenyl cyanide were heated together at 180° for 5 hr. The cooled melt was powdered, washed with ether, basified by trituration with aqueous sodium hydroxide, washed with water, and crystallised from ethanol; this *amidine* had m. p. 130° (Found: N, 12·1. $C_{15}H_{16}N_2$ requires N, 12·5%); yield 79%. Its *toluene*-p-*sulphonate*, m. p. 165°, crystallised from aqueous ethanol (Found: N, 6·9. $C_{22}H_{24}O_3N_2S$ requires N, 7·1%); the *picrate* formed prisms, m. p. 174—175°, from ethanol (Found: N, 15·3. $C_{21}H_{19}O_7N_5$ requires N, 15·5%). By the aluminium chloride method (see below), the yield was 73%.

The following amidines were prepared in a similar manner:

N-2 : 4-Dimethylphenplbenzamidine (39%), m. p. 112° (Lottermoser [11] records m. p. 107—108°) (Found: N, 12·6. Calc. for $C_{15}H_{16}N_2$: N, 12·5%). By the aluminium chloride method, the amidine was prepared in 51% yield.

N-2 : 5-*Dimethylphenylbenzamidine* (41%), m. p. 132° (Found: C, 80·2; H, 7·0. $C_{15}H_{16}N_2$ requires C, 80·3; H, 7·2%) [*picrate*, m. p. 191—192° (Found: C, 56·0; H, 3·9. $C_{21}H_{19}O_7N_5$ requires C, 55·6; H, 4·2%)].

N-3 : 4-*Dimethylphenylbenzamidine*.—Powdered aluminium chloride (27 g.) was gradually stirred into a mixture of 3 : 4-dimethylaniline (24 g., 1 mol.) and phenyl cyanide (21 g., 1 mol.) during 20 min. and the mixture was then heated at 180° for 20 min. A solution of the product in ethanol was made strongly alkaline with aqueous sodium hydroxide and extracted with chloroform. After being washed with water and dried (K_2CO_3), the chloroform solution gave the *amidine* which, after crystallisation from light petroleum, had m. p. 94° (Found: N, 12·8. $C_{15}H_{16}N_2$ requires N, 12·5%); yield 29 g.

N-m-*Tolylbenzamidine* was prepared (72%) analogously to the foregoing compound and, after crystallisation from benzene, had m. p. 105—106° (Found: N, 13·4. $C_{14}H_{14}N_2$ requires N, 13·3%).

N-*Hydroxy*-N′-p-*methoxyphenylbenzamidine*.—*N*-*p*-Methoxyphenylbenzamidine (23 g.) was added to a solution of hydroxylamine hydrochloride (10·4 g., 1·5 mols.) in water (90 ml.). The suspension was boiled for 10 min., made just alkaline to Brilliant-yellow with ammonia, and boiled for a further 10 min. The solid which separated furnished the pure *amidoxime*, as plates, m. p. 121—122°, on recrystallisation from ethanol (yield 10 g.) (Found: N, 11·6. $C_{14}H_{14}O_2N_2$ requires N, 11·6%). Its *benzoyl derivative*, prepared under Schotten–Baumann conditions, had m. p. 105° after recrystallisation from aqueous ethanol (Found: N, 8·3. $C_{21}H_{18}O_3N_2$ requires N, 8·1%).

The following amidoximes were analogously prepared from the appropriate *N*-arylamidine and hydroxylamine: N-*Hydroxy*-N′-m-*tolylbenzamidine* (60%), m. p. 138° (Found: N, 12·6. $C_{14}H_{14}ON_2$ requires N, 12·4%); N′-2 : 3-*dimethylphenyl*-N-*hydroxybenzamidine* (83%), m. p. 195—196° (Found: C, 74·9; H, 6·7; N, 11·6. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%); N′-2 : 4-*dimethylphenyl*-N-*hydroxybenzamidine* (42%), m. p. 142° (Found: N, 11·9. $C_{15}H_{16}ON_2$ requires N, 11·7%); N′-2 : 5-*dimethylphenyl*-N-*hydroxybenzamidine* (39%), m. p. 144° (Found: C, 75·3; H, 6·5; N, 11·4. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%); N′-3 : 4-*dimethylphenyl*-N-*hydroxybenzamidine* (30%), needles, m. p. 137—138°, from light petroleum (Found: N, 11·9. $C_{15}H_{16}ON_2$ requires N, 11·7%); when the foregoing compound was prepared in aqueous ethanol, the yield was 60%. N-*Hydroxy*-N′-*phenyl*-α-*phenylacetamidine* (47%), m. p. 140—141° (Found: N, 12·5. $C_{14}H_{14}ON_2$ requires N, 12·4%); N-*hydroxy*-N′-1-*naphthylbenzamidine* (79%), m. p. 183° (Found: N, 10·4. $C_{17}H_{14}ON_2$ requires N, 10·7%); this preparation was carried out in aqueous ethanol and heating was continued for 2 hr.

[11] Lottermoser, *J. prakt. Chem.*, 1896, **54**, 127.

N-*Hydroxy*-N′-2-*naphthylbenzamidine* (41%), m. p. 181—182°, depressed to about 160° by the foregoing compound (Found: N, 10·7%).

2-*Phenylbenziminazole*.—(i) *N*-Hydroxy-*N*′-phenylbenzamidine (0·025 mole), dissolved in a mixture of dry benzene (20 ml.) with dry pyridine (10 ml.) or dry triethylamine (10 ml.), was treated during 30 min. at below 10° with benzenesulphonyl chloride (0·025 mole), in dry benzene (10 ml.). After being kept at 0—5° overnight, the suspension was filtered. Solvent was removed from the filtrate under reduced pressure, and the residue triturated with aqueous sodium carbonate and crystallised from ethanol, giving 2-phenylbenziminazole (88%), m. p. and mixed m. p. 288° (Found: C, 80·0; H, 5·1; N, 14·6. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·2; N, 14·4%). The benzene-insoluble material, after being washed with water and crystallised from aqueous ethanol, afforded 2-*phenylbenziminazole benzenesulphonate* (10%), m. p. 262° (Found: C, 64·4; H, 4·5; N, 7·8. $C_{19}H_{16}O_3N_2S$ requires C, 64·8; H, 4·6; N, 8·0%) [derived *toluene*-p-*sulphonate*, m. p. 196°, from aqueous ethanol (Found: N, 7·8. $C_{20}H_{18}O_3N_2S$ requires N, 7·7%)].

(ii) When the foregoing reaction was carried out in boiling benzene during 40 min., the yield of 2-phenylbenziminazole was 58%.

The following benziminazole derivatives were prepared and purified analogously from the named *N*′-aryl-*N*-hydroxyamidine, benzenesulphonyl chloride, and pyridine or triethylamine.

4-Methyl-2-phenylbenziminazole (from *N*-hydroxy-*N*′-*o*-tolylbenzamidine [12]) (90%), m. p. 251—252°, from aqueous ethanol (Found: C, 81·1; H, 5·6; N, 13·6. Calc. for $C_{14}H_{12}N_2$: C, 80·7; H, 5·8; N, 13·5%) (Montanari and Passerini [13] record m. p. 246°) [*benzenesulphonate*, m. p. 210—212°, from aqueous ethanol (Found: C, 65·9; H, 4·7; N, 7·9. $C_{20}H_{18}O_3N_2S$ requires C, 65·6; H, 5·0; N, 7·7%); *picrate*, m. p. 237—238°, from acetic acid (Found: C, 55·2; H, 3·6; N, 16·3. $C_{20}H_{15}O_7N_5$ requires C, 54·9; H, 3·5; N, 16·0%)].

5-Methyl-2-phenylbenziminazole, (i) (from *N*-hydroxy-*N*′-p-tolylbenzamidine [14]) (63%), m. p. 246°, from benzene (Found: C, 80·9; H, 5·9. Calc. for $C_{14}H_{12}N_2$: C, 80·7; H, 5·8%) (Green and Day [15] give m. p. 249—250°) [*benzenesulphonate*, m. p. 236—237°, from ethanol (Found: N, 7·4. $C_{20}H_{18}O_3N_2S$ requires N, 7·7%); *picrate*, m. p. 265°, from aqueous acetic acid (Found: N, 16·0. $C_{20}H_{15}O_7N_5$ requires N, 16·0%)]. (ii) (From *N*-hydroxy-*N*′-*m*-tolylbenzamidine) (91%), m. p. 244°, undepressed on admixture with the foregoing specimen or with a sample obtained from the interaction of equivalent quantities of 3 : 4-diaminotoluene, phenyl cyanide, and ammonium benzenesulphonate at 200° for 4 hr.

4 : 5-*Dimethyl*-2-*phenylbenziminazole* (from *N*′-2 : 3-dimethylphenyl-*N*-hydroxybenzamidine) (62%), m. p. 204°, from benzene–light petroleum (Found: C, 81·1; H, 6·4; N, 12·3. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·4; N, 12·6%) [*benzenesulphonate*, m. p. 225—226°, from ethanol (Found: N, 7·4. $C_{21}H_{20}O_3N_2S$ requires N, 7·4%)].

4:6-Dimethyl-2-phenylbenziminazole (from *N*′-2:4-dimethylphenyl-*N*-hydroxybenzamidine) (65%), m. p. 196°, from benzene–light petroleum (Found: C, 80·9; H, 6·4; N, 12·8. Calc. for $C_{15}H_{14}N_2$: C, 81·1; H, 6·4; N, 12·6%) (Hübner [16] gives m. p. 195°) [*benzenesulphonate*, m. p. 177—178°, from aqueous ethanol (Found: N, 7·1. $C_{21}H_{20}O_3N_2S$ requires N, 7·4%); *picrate*, m. p. 258—259°, from aqueous acetic acid (Found: N, 15·2. $C_{21}H_{17}O_7N_5$ requires N, 15·5%)].

4:7-Dimethyl-2-phenylbenziminazole (from *N*′-2:5-dimethylphenyl-*N*-hydroxybenzamidine) (64%), m. p. 240°, from benzene–light petroleum (Found: C, 80·7; H, 6·5; N, 12·7. Calc. for $C_{15}H_{14}N_2$: C, 81·1; H, 6·4; N, 12·6%) (Hübner [16] records m. p. 215°) [*benzenesulphonate*, m. p. 278—279°, from ethanol (Found: C, 66·2; H, 5·6; N, 7·1. $C_{21}H_{20}O_3N_2S$ requires C, 66·3; H, 5·3; N, 7·4%); *picrate*, m. p. 254°, from ethanol (Found: C, 55·5; H, 4·0; N, 15·5. $C_{21}H_{17}O_7N_5$ requires C, 55·8; H, 3·8; N, 15·5%)].

5:6-Dimethyl-2-phenylbenziminazole (from *N*′-3:4-dimethylphenyl-*N*-hydroxybenzamidine) (36%), m. p. 254—255°, from light petroleum, undepressed by a specimen produced from the reaction between 4:5-dimethylphenylene-1:2-diamine, phenyl cyanide, and ammonium benzenesulphonate at 200° for 4 hr. (Davies, Mamalis, Petrow, and Sturgeon [17] record m. p. 251—252°) [*benzenesulphonate*, m. p. 281—282°, from ethanol (Found: C, 65·9; H, 5·2; N, 7·4.

[12] Ley, *Ber.*, 1898, **31**, 240.
[13] Montanari and Passerini, *Boll. sci. Fac. Chim. ind. Bologna*, 1953, **11**, 42.
[14] Müller, *Ber.*, 1889, **22**, 2401.
[15] Green and Day, *J. Amer. Chem. Soc.*, 1942, **64**, 1167.
[16] Hübner, *Annalen*, 1881, **208**, 278.
[17] Davis, Mamalis, Petrow, and Sturgeon, *J. Pharm. Pharmacol.*, 1951, **3**, 420.

$C_{21}H_{20}O_3N_2S$ requires C, 66·3; H, 5·3; N, 7·4%); *picrate*, m. p. 284° from acetic acid (Found: N, 15·3. $C_{21}H_{17}O_7N_5$ requires N, 15·5%)].

5-Methoxy-2-phenylbenziminazole (from *N*-hydroxy-*N*'-4-methoxyphenylbenzamidine) (69%), m. p. 147°, from benzene–light petroleum (Found: N, 12·5. Calc. for $C_{14}H_{12}ON_2$: N, 12·5%) (Poraĭ-Koshits, Efros, and Ginzburg [18] record m. p. 142°) [*picrate*, m. p. 237°, from ethanol (Found: N, 15·3. $C_{20}H_{15}O_8N_5$ requires N, 15·5%)].

5-Chloro-2-phenylbenziminazole (from *N*'-*p*-chlorophenyl-*N*-hydroxybenzamidine [12]) (90%), m. p. 210°, from benzene (Found: N, 12·3. Calc. for $C_{13}H_9N_2Cl$: N, 12·3%) (Fischer and Limmer [19] give m. p. 210°) [*benzenesulphonate*, m. p. 242°, from ethanol (Found: N, 7·0. $C_{19}H_{15}O_3N_2ClS$ requires N, 7·2%); *picrate*, m. p. 246—248°, from ethanol (Found: N, 15·4. $C_{19}H_{12}O_7N_5Cl$ requires N, 15·3%)].

2-Phenylnaphth[1,2]iminazole (i) (from *N*-hydroxy-*N*'-1-naphthylbenzamidine) (96%), m. p. 218°, from benzene (Found: N, 11·4. Calc. for $C_{17}H_{12}N_2$: N, 11·5%) (Hunter [20] gives m. p. 218°) [*picrate*, m. p. 260°, from aqueous acetic acid (Found: N, 14·8. $C_{23}H_{15}O_7N_5$ requires N, 14·8%)]; (ii) (from *N*-hydroxy-*N*'-2-naphthylbenzamidine) (75%), m. p. 217—218°, undepressed on admixture with the foregoing naphthiminazole.

2-Methylbenziminazole (from *N*-hydroxy-*N*'-phenylacetamidine [14]) (80%), m. p. 174—175°, undepressed by an authentic specimen.[21]

2-Benzylbenziminazole (from *N*-hydroxy-*N*'-phenyl-α-phenylacetamidine) (63%), m. p. 188—189°, from aqueous ethanol, undepressed by an authentic specimen [22] (Found: C, 81·2; H, 5·9. Calc. for $C_{14}H_{12}N_2$: C, 80·7; H, 5·8%).

4-*Imino*-1 : 3-*diphenylparabanic Acid*.—α-Hydroxyiminoacetanilide (4·9 g.), suspended in a mixture of dry ether (120 ml.) and triethylamine (6 g.), was treated at 5—10° with benzenesulphonyl chloride (5·3 g.). Next day, the suspension was filtered and evaporated. The parabanic acid (2·3 g.) crystallised when the gummy residue was stirred with propan-2-ol and, after crystallisation from ethanol, had m. p. 136—137° [Found: C, 68·2; H, 4·1; N, 15·5%; *M* (Rast), 251. Calc. for $C_{15}H_{11}O_2N_3$: C, 67·9; H, 4·2; N, 15·8%; *M*, 265]; Dieckmann and Kämmerer [23] record m. p. 137°. On hydrolysis with hydrochloric acid, the above compound afforded 1 : 3-diphenylparabanic acid, m. p. 204—206° (Found: C, 68·0; H, 3·8. Calc. for $C_{15}H_{10}O_3N_2$: C, 67·7; H, 3·8%); Dieckmann *et al.*[23] give m. p. 204°. Hydrolysis with aqueous alkali gave diphenylurea, m. p. and mixed m. p. 238—239°.

Diarylureas from N'-*Aryl*-N-*hydroxybenzamidines*.—To a suspension of the amidine (0·025 mole) in water (20 ml.), benzenesulphonyl chloride (0·025 mole) and 2N-sodium hydroxide (30 ml.) were gradually added with stirring and external cooling; the reaction was exothermic. Stirring was continued for 3 hr., the solid was collected, washed with water, and crystallised from ethanol.

The following ureas were thus prepared: *NN*'-Diphenyl- (69%), m. p. and mixed m. p. 237°; *N*-*p*-chlorophenyl-*N*'-phenyl- (72%), m. p. and mixed [24] m. p. 238—239°; *N*-phenyl-*N*'-*p*-tolyl- (57%), m. p. and mixed [24] m. p. 212—213°; N-2 : 3-*dimethylphenyl*-N'-*phenyl*- (83%), m. p. 189°, undepressed by a specimen prepared from phenyl *iso*cyanate and 2 : 3-dimethylaniline (Found: C, 75·1; H, 6·9; N, 11·8. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%); *N*-2 : 4-dimethylphenyl-*N*'-phenyl- (80%), m. p. 242°, undepressed by a sample prepared from phenyl *iso*cyanate and 2 : 4-dimethylaniline (Manuelli and Comanducci [25] record m. p. 242—243°); N-2 : 5-*dimethylphenyl*-N'-*phenyl*- (62%), m. p. 234° (Found: C, 74·9; H, 6·7. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7%).

NN'-*Diphenyl*-N''-o-*tolylguanidine*.—To a stirred suspension of *N*-hydroxy-*N*'-*o*-tolylbenzamidine [12] (4·5 g.) and aniline (1·9 g.) in 5N-sodium hydroxide (10 ml.), benzenesulphonyl chloride (7·1 g.) was added dropwise. After 3 hr. the suspension was filtered. The filtrate on acidification gave benzenesulphonanilide (1·9 g.), m. p. and mixed m. p. 112°. Basic material was extracted from the residue with dilute hydrochloric acid, liberated, collected in chloroform, and recovered; on crystallisation from ethanol, this afforded the guanidine (1 g.), m. p. 110°

[18] Poraĭ-Koshits, Efros, and Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*), 1949, **19**, 1545.
[19] Fischer and Limmer, *J. prakt. Chem.*, 1906, **74**, 57.
[20] Hunter, *J.*, 1945, 806.
[21] Phillips, *J.*, 1928, 172.
[22] Walther and Pulawski, *J. prakt. Chem.*, 1899, **59**, 249.
[23] Dieckmann and Kämmerer, *Ber.*, 1905, **38**, 2977.
[24] Ingold, *J.*, 1924, **125**, 87.
[25] Manuelli and Comanducci, *Gazzetta*, 1899, **29**, 143.

(Found: C, 79·7; H, 6·6; N, 14·2. Calc. for $C_{20}H_{19}N_3$: C, 79·9; H, 6·4; N, 13·9%); Marckwald [26] records m. p. 112°. Its nitrate had m. p. 174° (Marckwald [26] gives m. p. 172°). The non-basic fraction gave on repeated crystallisation from aqueous ethanol *N*-phenyl-*N'*-*o*-tolylurea (2·3 g.), m. p. and mixed m. p. 193—194°.

NN'N''-Triphenylguanidine (7%) together with *NN'*-diphenylurea (14%) were produced analogously from *N*-hydroxy-*N'*-phenylbenzamidine.

3 : 4-*Diphenyl-5-phenylimino*-1 : 2 : 4-*oxadiazoline*.—(i) *N*-Hydroxy-*N'*-phenylbenzamidine (4·2 g.) was added to a solution from sodium (0·5 g., 1·1 at.) in ethanol (30 ml.); benzenesulphonyl chloride (3·5 g., 1 mol.) in ethanol (50 ml.) was added at 10—15°. Next day the solution was boiled for 30 min. The separated solid gave the *oxadiazoline* (3 g.), m. p. 159—160°, on crystallisation from ethanol (Found: C, 76·9; H, 4·7; N, 13·4. $C_{20}H_{15}ON_3$ requires C, 76·7; H, 4·8; N, 13·4%).

(ii) A solution of *N*-hydroxy-*N'*-phenylbenzamidine (4·2 g.), diphenylcarbodi-imide (4 g., 1 mol.) and triethylamine (4 drops) in anhydrous benzene (100 ml.) was kept overnight, boiled for 30 min., concentrated, and mixed with ethanol. The precipitate (5·7 g.) gave the same oxadiazoline, m. p. and mixed m. p. 159—160°.

5-*Oxo*-3 : 4-*diphenyl*-1 : 2 : 4-*oxadiazoline*.—(i) The foregoing 5-phenylimino-1 : 2 : 4-oxadiazoline (0·5 g.) was boiled with concentrated hydrochloric acid (7 ml.) for 30 min. The precipitate gave the 5-oxo-1 : 2 : 4-oxadiazoline (0·35 g.), m. p. 167—168° (from ligroin), undepressed by a sample prepared by Müller's method [27] (Found: C, 70·7; H, 4·1; N, 11·8. Calc. for $C_{14}H_{10}O_2N_2$: C, 70·6; H, 4·2; N, 11·8%).

(ii) *N*-Hydroxy-*N'*-phenylbenzamidine (5·3 g.), benzenesulphonyl chloride (4·4 g.), and potassium carbonate (3·5 g.) were refluxed together for 2 hr. in acetone (40 ml.) which had been freed from oxidisable matter. Solvent was removed from the filtered suspension; an aqueous lactic acid extract of the tarry residue furnished on basification *N*-phenylbenzamidine (0·35 g.), m. p. and mixed m. p. 113—114°. The non-basic tar on fractional crystallisation from aqueous ethanol yielded diphenylurea (1·5 g.), m. p. and mixed m. p. 236°, and 5-oxo-3 : 4-diphenyl-1 : 2 : 4-oxadiazoline (0·25 g.), m. p. and mixed m. p. 167—168°.

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[26] Marckwald, *Annalen*, 1895, **286**, 366.
[27] Müller, *Ber.*, 1886, **19**, 1669.