52. *Preparation of* N-*Substituted Amidines.*

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N-Monosubstituted amidines can be prepared in good yield by heating equimolecular quantities of a nitrile and a primary amine with an equivalent of sodium or sodamide. Acetonitrile and benzonitrile on treatment with aniline under the conditions of the Hoesch reaction afford the corresponding *N*-phenylamidines.

N-ARYLAMIDINES have recently been observed to exhibit high, selective activity *in vitro* against *Mycobacterium tuberculosis* (Partridge, *J.*, 1949, 2683, 3043; 1950, 2901; *J. Pharm. Pharmacol.*, 1952, **4**, 533; Cooper and Partridge, *J.*, 1950, 459; Charlton, Maliphant, Oxley, and Peak, *J.*, 1951, 485). Since relatively few methods are available for the preparation of these compounds in good yield and free from *NN'*-diarylamidines, we examined the reaction of arylamines with nitriles in the presence of sodium (Lottermoser, *J. pr. Chem.*, 1896, **54**, 113; von Walther and Grossmann, *ibid.*, 1908, **78**, 478).

Lottermoser (*loc. cit.*) concluded that this reaction may be represented by the equation

$$2\mathrm{R{\cdot}CN} + \mathrm{Ar{\cdot}NH_2} + 2\mathrm{Na} \longrightarrow \mathrm{R{\cdot}C({:}NAr){\cdot}NH^-\}Na^+} + \mathrm{RH} + \mathrm{NaCN}$$

although no evidence was presented for the formation of the hydrocarbon, RH. We have confirmed these observations, and from *p*-tolunitrile have demonstrated the formation of toluene (characterised as benzoic acid). By analogy with the reaction of sodamide and a nitrile which affords an unsubstituted amidine (Cornell, *J. Amer. Chem. Soc.*, 1928, **50**, 3313; Ziegler, Rohm, and Haas, U.S.P. 2,049,582; Ziegler and Ohlinger, *Annalen*, 1932, **495**, 84; Kirsanov and Polyakova, *Bull. Soc. chim.*, 1936, **3**, 1600; Ewins, Barber, Newbery, Ashley, and Self, B.P. 538,463; Ewins and Ashley, B.P. 545,708; Newbery and Webster, *J.*, 1947, 738), it appeared likely that the production of the sodio-*N*-arylamidine involved the intermediate formation of a sodioarylamine :

$$\mathrm{Ar{\cdot}NH_2} + \mathrm{Na} \longrightarrow \mathrm{Ar{\cdot}NH^-\}Na^+} + \mathrm{H} \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{R{\cdot}CN} + \mathrm{Ar{\cdot}NH^-\}Na^+} \longrightarrow \mathrm{R{\cdot}C({:}NAr){\cdot}NH^-\}Na^+} \quad . \quad . \quad . \quad . \quad (2)$$

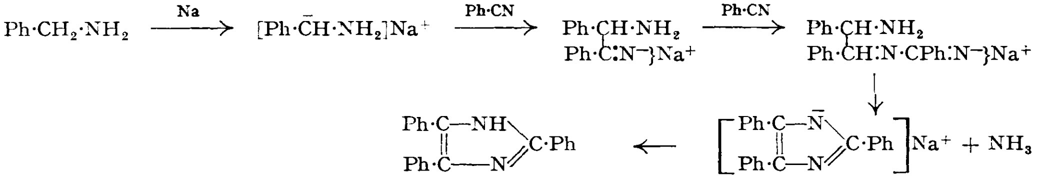
and that the hydrocarbon and sodium cyanide resulted from the reduction of the nitrile by hydrogen liberated in stage (1). In support of this it was found that sodioaniline, produced by heating aniline and sodamide in boiling benzene, afforded *N*-phenylbenzamidine in 64% yield on subsequent treatment with benzonitrile. When equimolecular quantities of sodium, benzonitrile, and aniline were brought into reaction in benzene, *N*-phenylbenzamidine was formed in 77% yield; in addition, small quantities of ionisable cyanide, benzylamine, and benzaldehyde were found but no permanent gas was evolved and neither 1 : 2-dihydro-2 : 2 : 4 : 6-tetraphenyl-1 : 3 : 5-triazine nor kyaphenin was detected (cf. Anker and Cook, *J.*, 1941, 323; Swamer, Reynolds, and Hauser, *J. Org. Chem.*, 1951, **16**, 43). Benzylamine and benzaldehyde may have arisen by reduction of either the nitrile or the amidine (Bamberger and Lodter, *Ber.*, 1887, **20**, 1703; Paal and Gerum, *Ber.*, 1909, **42**, 1553; Kirsanov and Ivastchenko, *Bull. Soc. chim.*, 1935, **2**, 1944). Introduction of naphthalene into the reaction mixture as an acceptor of nascent hydrogen (Bamberger and Lodter, *Annalen*, 1895, **288**, 74) led to only a slight increase in the yield.

Sodioaniline has hitherto been prepared from sodium and aniline at temperatures above 140°, usually in the presence of a catalyst (Belart, D.R.-P. 207,981; Deutsche Gold- und Silber-Scheide-Anstalt, D.R.-P. 215,339; Victoria, *Mem. Acad. Cienc. Artes Barcelona*, 1928, **21**, 227); in refluxing benzene the yield of sodioaniline (characterised as 2 : 4 : 6-tribromoaniline) was only 2%. Cessation of the reaction may be attributed to the formation of a protective coating on the powdered sodium in the absence of benzonitrile. The quantities of ionisable cyanide and amidine formed when equimolecular quantities of aniline, benzonitrile, and sodium were boiled in benzene excluded the possibility of the formation of sodioaniline by a mechanism similar to that postulated by Anker and Cook (*loc. cit.*) in the preparation of 1 : 2-dihydro-2 : 2 : 4 : 6-tetraphenyl-1 : 3 : 5-triazine from sodium and benzonitrile :

$$\mathrm{R{\cdot}CN + 2Na \longrightarrow RNa + NaCN}$$
$$\mathrm{RNa + Ar{\cdot}NH_2 \longrightarrow Ar{\cdot}NH^{-}\}Na^{+} + RH}$$

Two other mechanisms for the main course of the reaction cannot be sustained. *N*-Arylamidine formation could be a consequence of the displacement of an equilibrium, set up between a nitrile, an arylamine, and an *N*-arylamidine, by conversion of the *N*-arylamidine into its insoluble sodio-derivative (cf. a similar equilibrium in the preparation of amidines and *N*-alkylamidines; Oxley, Partridge, and Short, *J.*, 1948, 303). *N*-Phenylbenzamidine does indeed react readily with powdered sodium in benzene to form its insoluble sodio-derivative, together with some benzylamine and aniline, but without the evolution of any permanent gas. However, no trace of *N*-phenylbenzamidine could be detected when aniline and benzonitrile were boiled together in benzene, and only a trace of *NN'*-diphenylbenzamidine was formed when these reagents were boiled together without solvent (cf. Oxley, Partridge, and Short, *loc. cit.*; Bernthsen, *Annalen*, 1877, **184**, 341; 1878, **192**, 4). The production of kyaphenin when benzonitrile is brought into reaction with sodium in boiling benzene (Hofmann, *Ber.*, 1868, **1**, 198; Lottermoser, *loc. cit.*) led us to examine the possibility of aminolysis of kyaphenin by aniline in the presence of sodium, but no amidine was detected.

The scope of the reaction when equimolecular quantities of a nitrile, an amine, and sodium or sodamide are employed, and its extension to the preparation of a benziminazole derivative, are illustrated by the examples described in the Experimental section. No amidine was obtained from *m*-nitrobenzonitrile, *p*-acetoxybenzonitrile, or *p*-nitroaniline. Some dehalogenation was observed in the preparation of *N*-*p*-chlorophenylbenzamidine. The formation of 2 : 4 : 5-triphenylglyoxaline as a by-product in the preparation of *N*-benzylbenzamidine may be accounted for as follows :



An alternative mechanism involving an addition of benzonitrile to sodio-*N*-benzylbenzamidine and subsequent cyclisation of the resultant sodio-diamidide by loss of ammonia is rendered unlikely by the observation that no 2 : 4 : 5-triphenylglyoxaline could be isolated when sodio-*N*-benzylbenzamidine and benzonitrile were heated together. The formation of *p*-*sec.*-butoxy- (63%) and of *p*-benzyloxy-*N*-phenylbenzamidine (83%) is noteworthy, since these compounds could not be prepared by fusion of the appropriate nitriles with anilinium benzenesulphonate; by the fusion method, dealkylation occurred (cf. Sprung and Wallis, *J. Amer. Chem. Soc.*, 1934, **56**, 1715; Short and Stewart, *J.*, 1929, 553) and *p*-hydroxy-*N*-phenylbenzamidine was isolated in each case.

NN-Diaryl- and *N*-alkyl-*N*-aryl-amidines could not be prepared by this method. This may be related to a difference in stability of the carbazylate anions (Franklin, "The Nitrogen System of Compounds," New York, 1935); thus the anion derived from an *N*-arylamidine has a mesomeric structure, $R{\cdot}C({:}NH){\cdot}\bar{N}Ar \longleftrightarrow R{\cdot}C({\cdot}NH^-){:}NAr$, analogous to that of a carboxylate anion, whereas for the anion of an *NN*-disubstituted amidine only one similar structure can be written, $R{\cdot}C({:}N^-){\cdot}NR'R''$. Stabilisation of the carbazylate anions of *N*-arylamidines may also provide an explanation of the failure of sodio-*N*-phenylbenzamidine to react with benzonitrile to form a diamidide or with bromobenzene to form *NN*- or *NN'*-diphenylbenzamidine.

An *N*-arylamidine is postulated by Hao-Tsing (*J. Amer. Chem. Soc.*, 1944, **66**, 1421) as an intermediate in the preparation of *p*-aminobenzaldehyde and *p*-aminoacetophenone by heating at 250—300° the product of interaction of aniline and hydrogen cyanide or acetonitrile respectively in the presence of hydrogen chloride. Spoerri and Du Bois ("Organic Reactions," New York, 1949, Vol. V, p. 396), however, consider these to be examples of the Hoesch reaction. We find that interaction of acetonitrile, aniline, and hydrogen chloride in dry ether at room temperature for a month affords *N*-phenylacetamidine in 90% yield; *N*-phenylbenzamidine (23%) was similarly prepared from benzonitrile. The thermal rearrangement of the *N*-arylamidinium chloride involved in the mechanism put forward by Hao-Tsing is analogous to the isomerisation of *N*-acylanilines to amino-ketones (Dippy and Wood, *J.*, 1949, 2719).

EXPERIMENTAL

Interaction of Aniline, p-*Tolunitrile, and Sodium.*—Aniline (10·1 g.), *p*-tolunitrile (25·4 g., 2 mols.), and powdered sodium (5 g., 2 atoms) were boiled together in dry, toluene-free benzene (100 c.c.) under reflux for 3 days. The mixture, when worked up essentially as described by Lottermoser (*loc. cit.*), afforded *N*-phenyl-*p*-toluamidine (0·95 mol.) and ionisable cyanide equivalent to 0·88 mol. of *p*-tolunitrile; in addition, toluene was characterised as benzoic acid (3·85 g., 0·15 mol.) by oxidation with potassium permanganate. In an oxidation of a similar artificial mixture containing toluene, benzoic acid was obtained in 49% yield.

N-*Phenylbenzamidine.*—(i) Aniline, benzonitrile (2 mols.), and sodium (2 atoms), on reaction as described above, gave *N*-phenylbenzamidine (0·96 mol.), ionisable cyanide equivalent to 0·88 mol. of benzonitrile, and kyaphenin (0·005 mol.).

(ii) Finely powdered sodamide (3·9 g.) and aniline (9·3 g., 1 mol.) were refluxed in benzene (100 c.c.) until most of the ammonia had been evolved (about 75 min.); benzonitrile (10·3 g., 1 mol.) was added, and the mixture boiled for a further 135 min. Basic material was extracted with hydrochloric acid and liberated by ammonia, whereby *N*-phenylbenzamidine (12·6 g., 64%), m. p. and mixed m. p. 114—115°, was obtained. With granular sodamide, the yield was 57%, and with dimethylaniline as solvent it was 23%.

(iii) A mixture of aniline (9·3 g.), benzonitrile (10·3 g., 1 mol.), and powdered sodium (2·3 g., 1 atom) in dry benzene (100 c.c.) was refluxed for 27 hours whilst connected to a gas burette; no permanent gas was evolved. After addition of ethanol (10 c.c.), ionisable cyanide was extracted with dilute sodium hydroxide and recovered as silver cyanide (0·73 g., 5·5%). Basic material was then collected in dilute hydrochloric acid, and *N*-phenylbenzamidine, m. p. and mixed m. p. 114—115°, was precipitated by sodium hydroxide. The alkaline filtrate was extracted with chloroform and from this, after concentration, an acetate-buffer extract (pH 4·5) afforded, on addition of sodium picrate, benzylammonium picrate (0·25 g.), m. p. 195—197°, not depressed on admixture with an authentic specimen (Found: N, 16·7. Calc. for $C_{13}H_{12}O_7N_4$: N, 16·65%). Benzaldehyde was isolated from the benzene liquors as its 2 : 4-dinitrophenylhydrazone (0·15 g.), m. p. and mixed m. p. 237—238°. With periods of heating of 6, 7, 15, and 23 hours, the yields of amidine were 68, 70, 69, and 76%, respectively; with ether as solvent and 6 hours' heating, the yield was 32%. Addition of naphthalene (1 mol.) raised the yield to 81% but no 1 : 4-dihydronaphthalene could be isolated as its mercuric acetate complex.

Reaction between Aniline and Sodium.—When powdered sodium (2·3 g.) and aniline (9·3 g., 1 mol.) were refluxed in dry benzene (100 c.c.), the metal apparently underwent no change. The suspension was filtered. The residue was thoroughly washed with benzene and dissolved in ethanol and hydrochloric acid; after evaporation of the ethanol, addition of bromine afforded 2 : 4 : 6-tribromoaniline (0·7 g., 2%).

Reaction between N-*Phenylbenzamidine and Sodium.*—A suspension of sodium (1·15 g.) in a solution of *N*-phenylbenzamidine (9·8 g., 1 mol.) in dry benzene (150 c.c.) was refluxed in an apparatus connected to a gas burette until all the sodium had reacted (12 hours); no permanent gas was evolved. The suspended solid immediately dissolved on addition of hydrochloric acid; from the acid solution, *N*-phenylbenzamidine (7·75 g., 79%), benzylammonium picrate (1·4 g., 8%), and 2 : 4 : 6-tribromoaniline (2·05 g., 12%) were obtained as indicated above.

Interaction of Aniline and Benzonitrile.—(i) A mixture of aniline (18·6 g.) and benzonitrile (20·6 g., 1 mol.) was boiled for 8 hours, and material volatile at 100°/10 mm. distilled off. A lactic acid extract of the residue afforded with sodium picrate, *NN'*-diphenylbenzamidinium picrate (0·2 g.), m. p. and mixed m. p. 216° (Found : N, 14·0. Calc. for $C_{25}H_{19}O_7N_5$: N, 13·95%). (ii) Repetition of the foregoing experiment but with benzene as solvent and 3 days' heating yielded no material not volatile at 100°/10 mm. giving a water-insoluble base or picrate. (iii) *N*-Phenylbenzamidine when heated at 183° for 24 hours yielded aniline (24%) (characterised as 2 : 4 : 6-tribromoaniline), benzonitrile (20%) (characterised as *m*-nitrobenzonitrile), and *NN'*-diphenylbenzamidine (19%); no unchanged *N*-phenylbenzamidine was detected.

Attempted Aminolysis of Kyaphenin.—From the mixture obtained after refluxing kyaphenin (10·3 g.), sodium (2·3 g., 3 atoms), and aniline (9·3 g., 3 mols.) in dry benzene (100 c.c.) for 29 hours, kyaphenin (9·3 g., 90%) was recovered unchanged.

General Methods.—The results of experiments involving two general methods (A and B) for the preparation of *N*-substituted amidines are summarised in the Table. Further details are given below of cases which involved special features.

A. Powdered sodium (2·3 g.), the amine (0·1 mol.), and the nitrile (0·1 mol.) were refluxed in dry benzene (100 c.c.) with a soda–lime guard-tube for 20—30 hours. Ethanol (15 c.c.) was added to dissolve any unchanged sodium and to decompose the sodioamidine. The base was collected in aqueous lactic acid; after charcoal treatment, it was recovered by addition of ammonia and crystallised, usually from light petroleum (b. p. 100—120°).

B. Granular sodamide (4·3 g.), the amine (0·1 mol.), and the nitrile (0·1 mol.) were used in a procedure which was otherwise identical with method A.

N-p-*Chlorophenylbenzamidine.*—Interaction of benzonitrile, *p*-chloroaniline, and sodium for 2 days by method A afforded crude basic material (12·7 g.), m. p. 83—91°. This on treatment with hydrochloric acid yielded N-p-*chlorophenylbenzamidinium chloride dihydrate* (12·8 g., 42%), which crystallised as needles, m. p. 103—106° (efferv.), from water (Found : loss at 50°/2 mm., 11·65. Found, on dried material : N, 10·75. $C_{13}H_{12}N_2Cl_2,2H_2O$ requires H_2O, 11·9%. $C_{13}H_{12}N_2Cl_2$ requires N, 10·5%); von Walther (*J. pr. Chem.*, 1903, **67**, 450) records m. p. 103—108° (decomp.) but no analyses. The *acetate* crystallised as needles, m. p. 131—132°, from benzene (Found : N, 10·0. $C_{15}H_{15}O_2N_2Cl$ requires N, 9·65%). The base had m. p. 114—115°, depressed to below 100° by *N*-phenylbenzamidine (Found : N, 12·4. Calc. for $C_{13}H_{11}N_2Cl$: N, 12·15%), and the picrate had m. p. 180—181°; Oxley and Short (*J.*, 1949, 453) state that the amidine and its picrate have m. p. 117° and 183°, respectively. The mother-liquor from the crystallisation of the chloride was basified, and the precipitate afforded on crystallisation from light petroleum (b. p. 100—120°) *N*-phenylbenzamidine (0·4 g.), m. p. and mixed m. p. 114—116°, depressed to 83—93° by *N*-*p*-chlorophenylbenzamidine.

N-*Benzylbenzamidine.*—The base, obtained after interaction of benzylamine, benzonitrile, and sodium by method A, on treatment with hydrochloric acid yielded *N*-benzylbenzamidinium chloride (7·6 g., 31%), m. p. and mixed m. p. 226—228° after crystallisation from *iso*propanol. The free base had m. p. 77·5—78·5°; Pyman (*J.*, 1923, **123**, 3373) records m. p. 77—78°. The solid (2·3 g., m. p. 276—278°) which separated during extraction of the base was crystallised from ethanol and afforded 2 : 4 : 5-triphenylglyoxaline (1·55 g.), m. p. 280—281°, undepressed on admixture with an authentic specimen.

When equimolecular quantities of *N*-benzylbenzamidine, benzonitrile, and sodium were boiled together in benzene for 24 hours no 2 : 4 : 5-triphenylglyoxaline could be detected amongst the products; *N*-benzylbenzamidine (89%) and a trace of kyaphenin were recovered.

N-2-*Hydroxyethylbenzamidine.*—Ethanolamine, benzonitrile, and sodium, brought into reaction by method A, afforded kyaphenin (0·55 g.) and a mixture of bases which was converted into the mixed picrates (4·4 g.); by fractional crystallisation from ethanol, these were separated into benzamidinium picrate (1·25 g., 4%), m. p. and mixed m. p. 237—238°, and N-2-*hydroxyethylbenzamidinium picrate* (2·15 g., 6%) which crystallised as prisms, m. p. 140—142°, with resolidification and melting again at 180—215° (decomp.) (Found : C, 46·0; H, 3·95; N, 17·6. $C_{15}H_{15}O_8N_5$ requires C, 45·8; H, 3·85; N, 17·8%).

No.	Compound	Method	Yield, %	M. p.	Formula	Found : N, %	Reqd. : N, %
1	*N*-Phenyl-*p*-toluamidine	A	65	151—152°	—	—	—
2	*N*-Phenyl-*p*-anisamidine	A	51	147—148	—	—	—
3	p-*Chloro*-N-*phenylbenzamidine*	A	64	140—141	$C_{13}H_{11}N_2Cl$	12·3	12·15
4	p-sec.-*Butoxy*-N-*phenylbenzamidine*	A	63	116—116·5	$C_{17}H_{20}ON_2$	10·5	10·45
5	*N*-*o*-Tolylbenzamidine	A	61	109—110	$C_{14}H_{14}N_2$	13·3	13·3
6	*N*-*p*-Methoxyphenylbenzamidine ...	A	73	115·5—116·5	$C_{14}H_{14}ON_2$	12·3	12·4
7	N-2-*Naphthylbenzamidine*	A	39	128·5—129·5	$C_{17}H_{14}N_2$	11·2	11·4
		B	54	—	—	11·4	—
8	*N*-2-Pyridylbenzamidine	A	65	98·5—99·5	$C_{12}H_{11}N_3$	21·0	21·3
9	*N*-*cyclo*Hexylbenzamidine	A	43	115—116	$C_{13}H_{18}N_2$	14·1	13·85
10	*N*-Phenyl-*o*-toluamidine	B	47	122—123	$C_{14}H_{14}N_2$	13·4	13·3
11	p-*Benzyloxy*-N-*phenylbenzamidine*...	B	83	183·5—184·5	$C_{20}H_{18}ON_2$	9·45	9·25
12	N-2-*Thiazolylbenzamidine*	B	6	90—91	$C_{10}H_9N_3S$	20·9	20·65
13	*N*-Phenylphenylacetamidine	B	64	140—141	$C_{14}H_{14}N_2$	13·3	13·3
14	*N*-Phenylacetamidine	B	36	—	—	—	—
15	2-Phenylbenziminazole	B	72	299—301	$C_{13}H_{10}N_2$	14·4	14·45

Picrate of No.	M. p.	Formula	Found : N, %	Reqd. : N, %
1	152—153°	—	—	—
2	129—130	$C_{20}H_{17}O_8N_5$	15·2	15·4
3	175—176	$C_{19}H_{14}O_7N_5Cl$	15·5	15·25
4	138—140	$C_{23}H_{23}O_8N_5$	14·3	14·1
5	152—153	$C_{20}H_{17}O_7N_5$	15·5	15·95
6	171—173	—	—	—
7	216·5—218	$C_{23}H_{17}O_7N_5$	14·9	14·75
8	206—207	—	—	—
9	142—143	$C_{19}H_{21}O_7N_5$	16·5	16·25
10	175—176	$C_{20}H_{17}O_7N_5$	15·9	15·95
11	145—146	$C_{26}H_{21}O_8N_5$	13·3	13·2
12	162—163	$C_{16}H_{12}O_7N_6S$	18·9	19·45
13	109—110	$C_{20}H_{17}O_7N_5$	15·8	15·95
14	190—191	$C_{14}H_{13}O_7N_5$	19·05	19·25
15	275—276 (decomp.)	$C_{19}H_{13}O_7N_5$	16·8	16·55

Notes.—1 and 2, Admixture with authentic specimens (Oxley and Short, *J.*, 1949, 453; Hullin, Miller, and Short, *J.*, 1947, 394) caused no depression of the m. p. of these bases. Oxley and Short (*loc. cit.*) record m. p. 153° for *N*-phenyl-*p*-toluamidinium picrate. 4, The reaction was exothermic and was initiated without heating. 5, Lottermoser (*loc. cit.*) records m. p. 105—108° for this amidine. 6, The base and picrate exhibited no depression of m. p. on admixture with authentic specimens (Oxley and Short, *loc. cit.*). 7, The period of heating in method B was 80 hours. The base crystallised from light petroleum (b. p. 100—120°) as colourless rods, m. p. 128·5—129·5°, whereas from aqueous ethanol, it afforded pale yellow plates, m. p. 122—123°; neither of the two forms was solvated and they were readily interconverted by crystallisation from the appropriate solvent. This compound was also prepared in 75% yield by interaction in the usual way (Oxley, Partridge, and Short, *J.*, 1947, 1110) of equimolecular quantities of benzonitrile, *β*-naphthylamine, and aluminium chloride at 180—190° for 30 minutes; its *hydrochloride* crystallised as prisms, m. p. 250·5—251°, from dilute hydrochloric acid (Found: N, 10·1. $C_{17}H_{15}N_2Cl$ requires N, 9·9%). 8, Authentic specimens (Oxley, Partridge, and Short, *J.*, 1947, 1115) did not depress the m. p.s of the base and its picrate. 9, The period of heating was 2 days; Oxley and Short (*loc. cit.*) record m. p. 116—116·5° for the base and m. p. 143° for the picrate. 10, Lottermoser (*loc. cit.*) records m. p. 121—123° for this base. 12, The m. p. of the base was depressed to below 80° on addition of 2-aminothiazole (Found, for the picrate: C, 44·6; H, 3·2. Reqd.: C, 44·45; H, 2·8%). 13, Before the addition of the phenylacetonitrile, the aniline and sodamide were refluxed in the benzene for 30 minutes. 14, The reaction was conducted as described for example 13, but the second period of heating was reduced to 7 hours and the product was isolated as the picrate. 15, Heating was for 6 hours.

p-sec.-*Butoxybenzonitrile*, prepared in 53% yield from *sec.*-butyl bromide, *p*-cyanophenol, and sodium ethoxide (Partridge, *J.*, 1949, 3043), had b. p. 109—111°/1·3 mm., n_D^{20} 1·5256 (Found : N, 8·0. $C_{11}H_{13}ON$ requires N, 8·0%).

p-sec.-*Butoxybenzonitrile and Anilinium Benzenesulphonate.*—There was considerable effervescence when this nitrile (16·4 g.) and the salt (23·5 g., 1 mol.) were heated at 210° for

75 minutes. A solution of the product in hot water, on cooling, deposited *p*-hydroxy-*N*-phenylbenzamidinium benzenesulphonate (21·7 g., 63%), m. p. 180—182°, not depressed on admixture with an authentic specimen. The mother-liquors afforded no alkali-insoluble base on the addition of sodium hydroxide. p-*Hydroxy*-N-*phenylbenzamidinium picrate* crystallised from aqueous *iso*propanol as prisms, m. p. 82—84° (Found : loss at 60°/1 mm., 7·1. Found, on dried material: N, 16·05. $C_{19}H_{15}O_8N_5,2H_2O$ requires H_2O, 7·55%. $C_{19}H_{15}O_8N_5$ requires N, 15·85%). The *base*, liberated by sodium hydrogen carbonate, crystallised from *iso*propanol as clusters of small needles, m. p. 182·5—183° (Found : N, 13·0. $C_{13}H_{12}ON_2$ requires N, 13·2%).

p-*Benzyloxybenzonitrile and Anilinium Benzenesulphonate.*—Equimolecular quantities of these reagents reacted exothermally when heated at 210° for 90 minutes; from the melt only *p*-hydroxy-*N*-phenylbenzamidine could be isolated as its picrate (3·4 g., 12%).

p-*Acetoxybenzonitrile and Anilinium Benzenesulphonate.*—The basic fraction of an aqueous extract of the melt obtained by heating the nitrile (8·05 g.) and the aniline salt (12·6 g., 1 mol.) at 210° for 1 hour consisted of *NN'*-diphenylacetamidine (1·2 g.) and *N*-phenylacetamidine [picrate (1·35 g.), m. p. and mixed m. p. 188—189°]. Since all the substances used in this experiment were dry, it is possible that *N*-phenylacetamidine was formed from the *p*-acetoxybenzonitrile :

$$3Ph{\cdot}NH_3^+ + 2CH_3{\cdot}CO_2{\cdot}C_6H_4{\cdot}CN + Ph{\cdot}SO_3^- \longrightarrow CH_3{\cdot}C(\!:\!NHPh^+){\cdot}NHPh + CH_3{\cdot}C(\!:\!NH_2^+){\cdot}NHPh + HO{\cdot}C_6H_4{\cdot}CN + HO{\cdot}C_6H_4{\cdot}CO_2H + Ph{\cdot}SO_3H$$

In agreement with this, phenyl acetate and anilinium benzenesulphonate, brought into reaction under the same conditions, afforded as basic product only *NN'*-diphenylacetamidine (3%).

Interaction of Nitriles, Aniline, and Hydrogen Chloride.—(i) A solution of aniline (9·3 g.) in dry ether (50 c.c.) was saturated with dry hydrogen chloride, acetonitrile (8·2 g.; 2 mols.) added, and the mixture kept at room temperature for a month; the anilinium chloride slowly dissolved and a viscous oil separated. The solvent was evaporated, and the residue dissolved in water and diluted to 250 c.c. *N*-Phenylacetamidinium picrate (3·2 g., 9%), m. p. and mixed m. p. 191—192°, was precipitated from an aliquot (25 c.c.). The base was liberated from the remainder, collected in chloroform, dried (K_2CO_3), and recovered (yield 11 g., 82%, m. p. 55—63°). On recrystallisation from light petroleum (b. p. 60—80°), it crystallised as needles, m. p. 70—71° (Found : N, 21·0. Calc. for $C_8H_{10}N_2$: N, 20·9%). Bernthsen (*Annalen*, 1877, **184**, 358) describes this compound as an oil.

(ii) Benzonitrile under the same conditions afforded *N*-phenylbenzamidine in 23% yield.

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