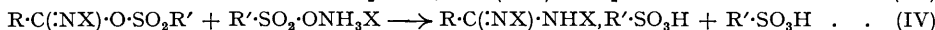
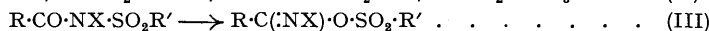
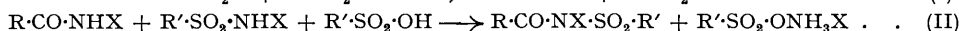
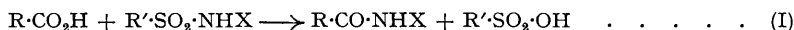


### 77. Amidines. Part III. Preparation of Substituted Amidines from Ammonium or Substituted Ammonium Salts and N-Acylbenzenesulphonalkylamides or Acylbenzenesulphonanilides.

By P. OXLEY and W. F. SHORT.

Mixed imides,  $\text{Ar}\cdot\text{SO}_2\cdot\text{NX}\cdot\text{CO}\cdot\text{R}$ , and ammonium salts,  $\text{YZNH}_2^{\oplus}\text{A}^{\ominus}$ , afford salts of amidines,  $\text{R}\cdot\text{C}(\text{NX})\cdot\text{NYZ}$ . When  $\text{Z} = \text{H}$ , the main product,  $\text{R}\cdot\text{C}(\text{NX})\cdot\text{NH}_2$ , is sometimes accompanied by  $\text{R}\cdot\text{C}(\text{NX})\cdot\text{NHX}$  and  $\text{R}\cdot\text{C}(\text{NY})\cdot\text{NH}_2$ , produced in some instances by disproportionation of the amidine salt first formed, and in others by a series of reactions involving (1) partial aminolysis of the mixed imide,  $\text{Ar}\cdot\text{SO}_2\cdot\text{NX}\cdot\text{CO}\cdot\text{R}$ , to  $\text{Ar}\cdot\text{SO}_2\cdot\text{NHX}$  and  $\text{R}\cdot\text{CO}\cdot\text{NH}_2$ , (2) formation of  $\text{Ar}\cdot\text{SO}_2\cdot\text{NY}\cdot\text{CO}\cdot\text{R}$  by elimination of  $\text{X}\cdot\text{NH}_2$  (as a salt) from the carbonamide and sulphonamide, (3) reaction of each of the mixed imides with the salts of  $\text{X}\cdot\text{NH}_2$  and of  $\text{Y}\cdot\text{NH}_2$ .

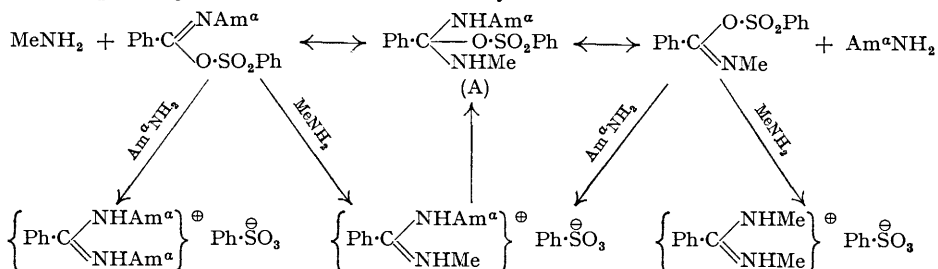
In Part II (*J.*, 1946, 763) evidence was advanced to show that the production of amidines from carboxylic acids and sulphonamides involves an exchange of functional groups between the reactants, followed by the formation of a "mixed imide",  $\text{R}'\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ , and its decomposition to a cyanide which is then converted into an amidinium sulphonate by the ammonium sulphonate produced in the second stage of the reaction. When a carboxylic acid was heated with a sulphondialkylamide a carbondialkylamide was produced, and we now find that acids and *N*-monosubstituted sulphonamides (2 mols.) afford *NN'*-disubstituted amidinium sulphonates. We suggest that the reaction takes place in stages as follows:



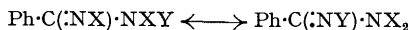
Stages I and II are analogous to reactions which were shown to occur with the unsubstituted sulphonamides. The isomerisation III, also analogous to that assumed to occur with the unsubstituted mixed imide, affords a rational explanation of the production of an amidinium salt as the final product. Stage IV, representing the aminolysis of a sulphonic ester by an ammonium sulphonate, receives support from the observation that methyl benzenesulphonate and ammonium benzenesulphonate at  $225^\circ$  afford methylammonium benzenesulphonate and, in a subsequent communication, Stages III and IV will be correlated with the Beckmann transformation. Further, it is now found that a number of substituted mixed imides,  $\text{R}'\cdot\text{SO}_2\cdot\text{NX}\cdot\text{CO}\cdot\text{R}$ , prepared from an acid chloride and an *N*-substituted sulphonamide, react with the sulphonic acid salts of ammonia and primary and secondary amines at *ca.*  $200^\circ$  to give  $\text{R}\cdot\text{C}(\text{NX})\cdot\text{NYZ}$ ,  $\text{R}'\cdot\text{SO}_3\text{H}$ . The use of sulphonic acid salts is convenient since both the amidinium salt and the free sulphonic acid produced in the reaction are stable at the temperature employed and the sulphonates are less hygroscopic and more soluble in the melt than other salts. An equivalent quantity of the hydrochloride or the sulphate of the base has been successfully used in a number of cases, and the scope of the method is illustrated by the examples given in the Table. This reaction provides a convenient method for the preparation of a number of *N*-mono- and *NN'*-di-, and tri-substituted amidines, in which the substituents may all be different if desired, some of which cannot be prepared by the Pinner reaction, the imido-chloride method, or the method described in Part I (*J.*, 1946, 147). Methylation of mono- and *NN'*-di-substituted amidines invariably gives a mixture of products, and one of the isomers is usually produced in such small quantity that it could not be prepared economically in this way (see Burtles and Pyman, *J.*, 1923, 123, 361; Pyman, *ibid.*, pp. 367, 3359); each of the isomers may be obtained with equal ease by heating a mixed imide with the appropriate amine salt.

In normal cases only a single amidine appears to be produced by the interaction of a mixed imide and an ammonium salt, since the crude amidine and/or its salt has almost the optimum melting point and complete purification involves only a small loss. In a few cases (Nos. 14—16, 23, 24) the expected amidine,  $\text{Ph}\cdot\text{C}(\text{NX})\cdot\text{NH}_2$ , is accompanied by the products of its disproportionation,  $\text{Ph}\cdot\text{C}(\text{NX})\cdot\text{NHX}$  and  $\text{Ph}\cdot\text{C}(\text{NY})\cdot\text{NH}_2$ . Insufficient examples are at present available to allow the structural factors leading to this disproportionation to be discerned, but it is already clear that a mixture of symmetrical amidines can be produced from the salt of the unsymmetrical amidine initially formed, or, when this is stable at the temperature of the reaction, three amidines may be produced by concurrent reactions which occur at an earlier stage. Thus, when *N*-methyl-*N'*-*n*-amylbenzamidinium benzenesulphonate is heated at  $200^\circ$ , *ca.* 70% is recovered unchanged

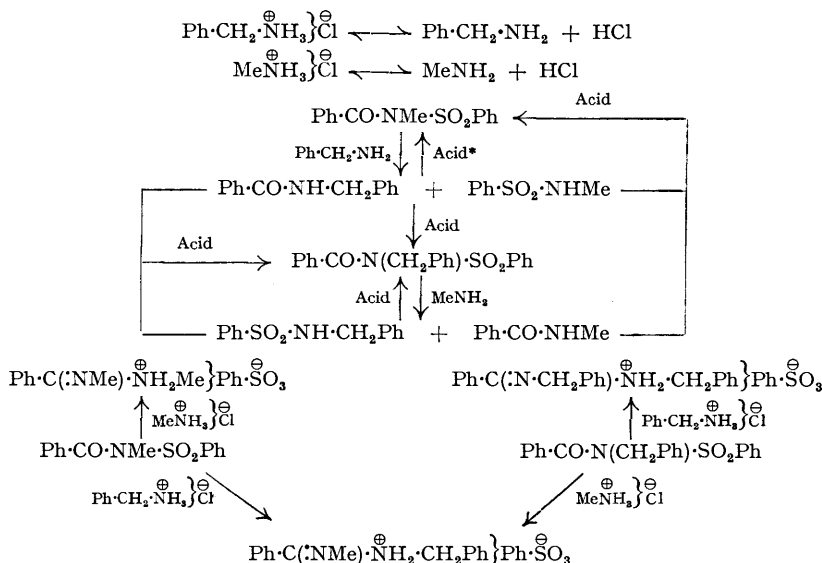
and the rest is converted into the benzenesulphonates of *NN'*-dimethylbenzamidine and *NN'*-di-*n*-amylbenzamidine. A mixture having approximately the same composition is obtained from *N*-benzoylbenzenesulphonmethylamide and *n*-amylammonium benzenesulphonate at 200° (No. 14). The mechanism of the disproportionation of the amidinium salt is uncertain, but may involve its conversion into a sulphonic ester (A) decomposing into two different imido-sulphonates and the corresponding amines, which then react to yield three amidinium salts.



So far as we are aware, the only other changes involving the migration of hydrocarbon radicals substituted in the amidino-group concern a number of pairs of isomeric triarylbenzamidines which were shown by Chapman (*J.*, 1929, 2133 and subsequent papers) to afford equilibrium mixtures when the free bases are heated at 300–334°, the rearrangement being an intramolecular process.



*N*-Benzoylbenzenesulphonmethylamide also affords a mixture of amidines with benzylammonium chloride (No. 15) and with phenylammonium toluene-*p*-sulphonate (No. 16) but this cannot be due to disproportionation of the amidinium salt initially formed since *N*-benzyl-*N'*-methylbenzamidinium hydrochloride and toluene-*p*-sulphonate and *N*-phenyl-*N'*-methylbenzamidinium benzenesulphonate remain substantially unchanged when heated at 200° for an hour. We suggest that in these cases three amidines are produced by a series of reactions which may be illustrated by reference to the first example (No. 15) as follows. The mixed imide is attacked by benzylamine, resulting from the dissociation of its hydrochloride, with formation of benzbenzylamide and benzenesulphonmethylamide, which, in presence of acid, afford either *N*-benzoylbenzenesulphonbenzylamide and a methylammonium salt or *N*-benzoylbenzenesulphonmethylamide and a benzylammonium salt. Each of these mixed imides then reacts with a methylammonium salt or a benzylammonium salt to give an amidinium salt, so that the composition of the amidine mixture is determined by the following reactions, many of which must reach equilibrium.



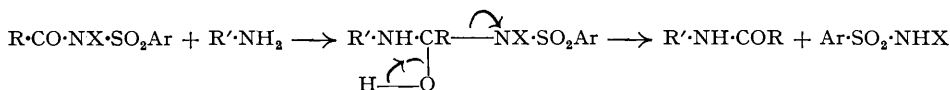
\* In each case "acid" signifies that the reaction which takes place follows the generalised equation (II).

Amide (g.).	Ammonium salt.*	Temp.	Time (mins.).	Amidime, R·C:(NX)·NYZ.						Yield (%)	Amidine picrate, m. p.
				R.	X.	Y.	Z.	M. p.	B. p.		
<i>Amidines from N-Acetylbenzenesulphonmethylamide:</i>											
(1)	21.3 NH <sub>3</sub> MeCl	170°	30	Me	Me	Me	H	38—40°	75°/10 mm.	24	132.5°
<i>Amidines from N-Acetylbenzenesulphonanilide:</i>											
(2)	11.0 Ph·SO <sub>3</sub> NH <sub>4</sub>	200	30	Me	Ph	H	H	—	—	19	188
(3)	5.5 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Ph	180	30	Me	Ph	Ph	H	132.5	—	57	171
<i>Amidines from N-Benzoylbenzenesulphonmethylamide:</i>											
(4)	2.75 Ph·SO <sub>3</sub> NH <sub>4</sub>	225	15	Ph	Me	H	H	—	—	93	130—131
(5)	6.9 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	225—230	40	Ph	Me	H	H	—	—	46	130—131
(6)	27.5 Ph·SO <sub>3</sub> NH <sub>3</sub> Me	235	30	Ph	Me	Me	H	81	127—128/11 mm.	97	172—173
(7)	13.75 Ph·SO <sub>3</sub> NH <sub>2</sub> Me <sub>2</sub>	200	15	Ph	Me	Me	Me	—	106—107/11 mm.	60.5	137.5
(8)	55.5 NH <sub>2</sub> Me <sub>2</sub> Cl	205	20	Ph	Me	Me	Me	—	83/2 mm.	62	137.5
(9)	13.75 NH <sub>2</sub> EtCl	220	30	Ph	Me	Et	H	63—64	124—126/9 mm.	86.5	168.5—169
(10)	13.75 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>2</sub> MeEt	210	45	Ph	Me	Me	Et	—	115—117/13 mm.	61	101
(11)	13.75 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Pr <sup>α</sup>	205	60	Ph	Me	Pr <sup>α</sup>	H	—	137/11 mm.	74	138
(12)	13.75 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Pr <sup>β</sup>	225	30	Ph	Me	Pr <sup>β</sup>	H	—	119/11 mm.	174	174
(13)	13.75 Ph·SO <sub>3</sub> NH <sub>2</sub> Et <sub>2</sub>	200—205	20	Ph	Me	Et	Et	—	124/15 mm.	62	150
(14)	13.75 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Am <sup>α</sup>	200	50	Ph	Me	Am <sup>α</sup>	H	—	157—159/7 mm.	60	109
(15)	13.75 NH <sub>3</sub> (CH <sub>2</sub> Ph)Cl	200	40	Ph	Me	Ph·CH <sub>2</sub>	H	—	—	19	121.5—122
(16)	13.75 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Ph	160	30	Ph	Me	Ph	H	135	—	21	169
(17)	13.75 Ph·SO <sub>3</sub> NH <sub>2</sub> <[CH <sub>2</sub> ] <sub>4</sub> >CH <sub>2</sub>	200	30	Ph	Me	Me	<[CH <sub>2</sub> ] <sub>4</sub> >CH <sub>2</sub>	—	153—155/11 mm.	54	143
<i>Amidines from N-Benzoyltoluenesulphonmethylamide:</i>											
(18)	13.0 Ph·SO <sub>3</sub> NH <sub>4</sub>	225	15	Ph	Et	H	H	—	—	82	145
(19)	15.15 Ph·SO <sub>3</sub> NH <sub>3</sub> Et	210	15	Ph	Et	Et	H	72	102—104/1 mm.	82	185
(20)	15.15 Ph·SO <sub>3</sub> NH <sub>2</sub> Me <sub>2</sub>	220—240	15	Ph	Et	Me	Me	—	130/12 mm.	54.5	120.5
(21)	15.15 Ph·SO <sub>3</sub> NH <sub>2</sub> MeEt	210	40	Ph	Et	Me	Et	—	112/11 mm.	53	103.5—104
(22)	15.15 Ph·SO <sub>3</sub> NH <sub>2</sub> Et <sub>2</sub>	225	30	Ph	Et	Et	Et	—	121/11 mm.	49	102
<i>Amidines from N-Benzoyltoluene-p-sulphonanilide:</i>											
(23)	17.55 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>4</sub>	225	30	Ph	Ph	H	H	116	—	27	—
(24)	17.55 Ph·SO <sub>3</sub> NH <sub>3</sub> Me	225	15	Ph	Ph	Me	H	135	—	38	169
(25)	17.55 C <sub>6</sub> H <sub>4</sub> Me(p)·SO <sub>3</sub> NH <sub>3</sub> Ph	190	30	Ph	Ph	Ph	H	147	—	95	221

\* 1 Mol. of ammonium salt was used except in the case of ammonium sulphate.

- (1) *NN'-Dimethylacetamidinium picrate* separated from isopropanol in long daggers, m. p. 132.5° (Found: N, 22.3.  $C_{10}H_{13}O_7N_5$  requires N, 22.2%). The *toluene-p-sulphonate* crystallised from isopropanol in short needles, m. p. 119° (Found: N, 10.8.  $C_{10}H_{13}O_3N_5S$  requires N, 10.88%). Pinner ("Die Imidoäther", p. 112) prepared the hydrochloride, m. p. 218°.
- (2) Brunner, Matzler, and Mössner (*Monatsh.*, 1927, **48**, 125) state that *N*-phenylacetamidinium picrate has m. p. 188.5°. *NN'*-Diphenylacetamidinium (7%) was obtained as by-product and had m. p. 131—132°, undepressed on admixture with an authentic specimen.
- (3) The reaction was exothermic so that the internal temperature remained at 190° for some minutes. The crude amidine (3.7 g., m. p. 115—125°) was recrystallised from ligroin (b. p. 100—120°), and the pure compound, m. p. 132.5°, did not depress the m. p. of an authentic specimen (Brunner, Matzler, and Mössner, *loc. cit.*).
- (4) Pyman (*J.*, 1923, **123**, 3371) states that the picrate has m. p. 130—132°. *N-Methylbenzamidinium benzenesulphonate* had m. p. 129° (Found: N, 9.5.  $C_{14}H_{16}O_4N_2S$  requires N, 9.6%).
- (5) *N*-Benzoylbenzenesulphonmethyamide was heated with 0.5 mol. of ammonium sulphate.
- (6) Pyman (*loc. cit.*) states that *NN'*-dimethylbenzamidinium and its picrate have m. p. 80—81° and 171—172° respectively. The *sulphonate* consisted of long prisms, m. p. 159° (decomp.) (Found: N, 17.05.  $C_9H_{13}O_3N_2S$  requires N, 16.75%).
- (7) and (8) Dimethylammonium benzenesulphonate had m. p. 116°. Norton and Westenhoff (*Amer. Chem. J.*, 1888, **10**, 130) record m. p. 110°. Pyman (*loc. cit.*) states that *NNN'*-trimethylacetamidinium picrate has m. p. 136—138°. The *benzenesulphonate* had m. p. 156.5° (Found: N, 8.7.  $C_{18}H_{20}O_3N_3S$  requires N, 8.75%).
- (9) *N-Methyl-N'-ethylbenzamidinium* was very hygroscopic and had m. p. 63—64° (Found: N, 16.9.  $C_{10}H_{14}N_3$  requires N, 17.3%). The *picrate* had m. p. 168.5—169° (Found: N, 17.9.  $C_{16}H_{17}O_7N_5$  requires N, 17.9%).
- (10) Ethylation of *NN'*-dimethylbenzamidinium afforded the same amidine thus confirming the structure. The *picrate* had m. p. 101° (Found: N, 17.2.  $C_{17}H_{19}O_7N_5$  requires N, 17.3%) and the *benzenesulphonate* m. p. 121.5—122° (Found: N, 8.4.  $C_{17}H_{22}O_3N_2S$  requires N, 8.4%). Methyllethylammonium toluene-*p*-sulphonate, m. p. 38—40°, was exceedingly hygroscopic.
- (11) *n-Propylammonium toluene-p-sulphonate* separated from isopropanol in plates, m. p. 139—139.5° (Found: N, 6.2.  $C_{10}H_{13}O_3NS$  requires N, 6.1%). *N-Methyl-N'-n-propylbenzamidinium picrate* had m. p. 138° (Found: N, 17.5.  $C_{17}H_{19}O_7N_5$  requires N, 17.3%).
- (12) *isoPropylammonium toluene-p-sulphonate* crystallised in rods, m. p. 128° (Found: N, 6.0.  $C_{10}H_{17}O_3NS$  requires N, 6.1%). *N-Methyl-N'-isopropylbenzamidinium picrate* had m. p. 174° (Found: N, 17.5.  $C_{16}H_{17}O_3NS$  requires N, 17.3%), and the *benzenesulphonate*, m. p. 161—161.5° (Found: N, 8.3.  $C_{17}H_{20}O_3N_2S$  requires N, 8.4%).
- (13) *N-Methyl-N'-diethylbenzamidinium picrate* had m. p. 150° (Found: N, 16.9.  $C_{15}H_{21}O_7N_5$  requires N, 16.7%), and the *benzenesulphonate*, m. p. 114° (Found: N, 8.0.  $C_{15}H_{24}O_3N_2S$  requires N, 8.05%).
- (14) *N-Methyl-N'-n-amylobenzamidinium picrate* had m. p. 109° (Found: N, 16.35.  $C_{19}H_{23}O_7N_5$  requires N, 16.2%). *NN'*-Dimethylbenzamidinium (17%) and *NN'*-*n*-amylobenzamidinium (12%) were also produced (see below).
- (15) *N-Benzyl-N'-methylbenzamidinium picrate* had m. p. 121.5—122° (Found: N, 15.6. Calc. for  $C_{21}H_{25}O_7N_5$ : N, 15.45%). Pyman (*J.*, 1923, **123**, 3359) records m. p. 118—122°. *NN'*-Dibenzylbenzamidinium (29%) was also formed (see below).
- (16) *NN'*-Diphenylbenzamidinium, m. p. and mixed m. p. 147°, was also produced (5.4 g. or 40%). *NN'*-Dimethylbenzamidinium would not have been detected by the method used for isolating the products.
- (17) *Piperidinium benzenesulphonate* separated from acetone in hygroscopic prisms, m. p. 88° (Found: N, 5.8.  $C_{11}H_{17}O_3NS$  requires N, 5.8%). A by-product of the amidine reaction (3.8 g.), b. p. 178—182°/11 mm., was not investigated. *N-Methyl-N'-pentamethylbenzamidinium picrate* had m. p. 143° (Found: N, 16.3.  $C_{19}H_{21}O_7N_5$  requires N, 16.2%), and the *benzenesulphonate*, m. p. 166° (Found: N, 7.7.  $C_{19}H_{24}O_3N_2S$  requires N, 7.8%).
- (18) *N-Ethylbenzamidinium picrate* had m. p. 145° (Found: N, 18.6.  $C_{15}H_{19}O_7N_5$  requires N, 18.6%), and the *benzenesulphonate*, m. p. 162.5—163° (Found: N, 9.2.  $C_{15}H_{18}O_3N_2S$  requires N, 9.15%).
- (19) Ethylammonium benzenesulphonate had m. p. 101°. Norton and Westenhoff (*loc. cit.*) record m. p. 92°. *NN'*-Diethylbenzamidinium was very hygroscopic (Found: N, 15.3.  $C_{11}H_{15}N_2$  requires N, 15.9%), the *picrate* had m. p. 185° (Found: N, 17.25.  $C_{17}H_{19}O_7N_5$  requires N, 17.3%), and benzoylation afforded *N*-benzoyl-*NN'*-diethylbenzamidinium, m. p. 91° (Found: N, 9.9. Calc. for  $C_{15}H_{19}ON_2$ : N, 10.0%). Lander (*J.*, 1903, **83**, 320) states that this benzoyl derivative has m. p. 90—91.5°.
- (20) *NN'*-Dimethyl-*N'*-ethylbenzamidinium afforded a *picrate*, m. p. 120.5° (Found: N, 17.3.  $C_{17}H_{19}O_7N_5$  requires N, 17.3%), and a *benzenesulphonate*, m. p. 138° (Found: N, 8.4.  $C_{17}H_{22}O_3N_2S$  requires N, 8.4%).
- (21) Methylation of *NN'*-diethylbenzamidinium afforded the same amidine thus confirming the structure. *N-Methyl-N'-diethylbenzamidinium picrate* had m. p. 103.5—104° (Found: N, 16.8.  $C_{18}H_{21}O_7N_5$  requires N, 16.7%).
- (22) *NNN'*-Triethylbenzamidinium afforded a *picrate*, m. p. 102° (Found: N, 16.1.  $C_{18}H_{23}O_7N_5$  requires N, 16.2%), and a *benzenesulphonate*, m. p. 104—105° (Found: N, 7.7.  $C_{18}H_{26}O_3N_2S$  requires N, 7.7%).
- (23) Brunner, Seeger, and Dittrich (*Monatsh.*, 1924, **45**, 69) state that *N*-phenylbenzamidinium has m. p. 113.5°. Oxley and Short (*J.*, 1946, 147) record m. p. 116°. *NN'*-Diphenylbenzamidinium (8.5%) was produced as by-product (see below).
- (24) Pyman (*loc. cit.*, p. 368) states that *N*-phenyl-*N'*-methylbenzamidinium has m. p. 135—136°. *NN'*-Dimethylbenzamidinium (7%) and *NN'*-diphenylbenzamidinium (22%) are produced as by-products (see below).
- (25) Busch and Falco (*Ber.*, 1910, **43**, 2559) state that *NN'*-diphenylbenzamidinium has m. p. 144°.

The fission of *N*-benzoylbenzenesulphonmethylamidé by amines postulated above has been confirmed in two cases. Thus, the mixed imide and benzylamine at 230° afford benzenesulphonmethylamide and benzbenzylamide, each in 88% yield, whilst aniline at 245° yields benzanilide (88%), benzenesulphonmethylamide (64%), and *N*-phenyl-*N'*-methylbenzamidine benzenesulphonate (4%). The presence of an additional basic centre in the molecule of the salt can also lead to fission of the mixed imide; thus *N*-benzoylbenzenesulphonmethylamide and 2-aminopyridine toluene-*p*-sulphonate afford benzenesulphonmethylamide and 2-benzamidopyridine. Similarly, whilst *N*-benzoylbenzenesulphon-2-pyridylamide is converted into *N*-2-pyridyl-*N'*-methylbenzamidine (60%) by methylammonium benzenesulphonate (1 mol.) at 200°, 2-aminopyridine toluene-*p*-sulphonate (1 mol.) produces 2-benzamidopyridine (ca. 100%) and 2-benzenesulphonamidopyridine (77%). Addition of acid, by increasing the degree of neutralisation of the basic centres in the aminopyridine, should promote the formation of amidine and hinder aminolysis of the mixed imide to a sulphonamide and a carbonamide. In agreement with this deduction, equimolecular quantities of *N*-benzoylbenzenesulphon-2-pyridylamide, 2-aminopyridine benzenesulphonate, and benzenesulphonic acid afford *NN'*-di-(2-pyridyl)benzamidine (17.5%), 2-benzamidopyridine (52%), and 2-benzenesulphonamidopyridine (46%) when heated at 200°. It is probable that fission of a mixed imide by an amine involves addition at the carbonyl group as follows:



We find that dibenzoylmethylamine and methylammonium benzenesulphonate at 210° afford *NN'*-dimethylbenzamidine benzenesulphonate (49%), and it seems probable that this reaction involves isomerisation of the diacylamine to  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{CPh}\cdot\text{NMe}$ , which then reacts with the substituted ammonium salt (cf. equations III and IV above). A diacylamine may also function as an intermediate in the production of an *NN'*-disubstituted amidine from an acid and an *N*-monosubstituted sulphonamide, but could not be involved in the formation of amidines from mixed imides except where the imide undergoes fission and a mixture of amidines results.

In view of the production of amidines from *N*-substituted mixed imides and ammonium benzenesulphonate, it seemed possible that amidines could be produced directly from imides of the type  $\text{R}'\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ , rather than by decomposition to a cyanide which then reacts with the ammonium salt (Part II). Investigation of this point in the case of *N*-*p*-methylsulphonylbenzoylbenzenesulphonamide and ammonium benzenesulphonate showed that after two hours at 190—195°, the lowest temperature required to produce a change, the main product is *p* cyanophenyl methyl sulphone, and the trace of amidine (Fuller reaction) simultaneously formed is no more than could be accounted for by the interaction of the cyanide and the ammonium salt at that temperature.

The interaction of *N*-acylbenzenesulphonalkylamides with the salts of diamines will be described in a later communication.

#### EXPERIMENTAL.\*

*NN'*-Dimethylbenzamidine.—(1) *From benzoic acid.* Benzoic acid (12.2 g.) and benzenesulphonmethylamide (36 g.; 1.2 mols.) reacted exothermally at 235°, the temperature rising to 270°. The product dissolved completely in water and required one equivalent of sodium hydroxide for neutralisation to Congo-red. The liquid was made strongly alkaline and extracted with chloroform, the extract (13.5 g.) giving the following fractions on distillation. (a) B. p. 127—128°/11 mm., m. p. 70—75°. Recrystallisation from benzene-light petroleum (1:1) afforded *NN'*-dimethylbenzamidine, m. p. and mixed m. p. 81°. Yield, 12.1 g. (82%). (b) B. p. 126—128°/2 mm. This fraction had m. p. 78—79°, undepressed by admixture with benzomethylamide. Yield, 1.2 g. It is probable that this compound was produced by hydrolysis of the amidine, rather than by functional exchange between benzoic acid and benzenesulphonmethylamide.

(2) *From benzomethylamide.* (a) A mixture of benzomethylamide (10.1 g.) and anhydrous benzenesulphonic acid (11.85 g.; 1 mol.) was heated at 225° for 30 minutes, and then cooled, diluted with water (100 c.c.), and extracted with chloroform. Benzoic acid (3.8 g. or 83%), m. p. and mixed m. p. 121°, was isolated from the chloroform solution. The aqueous solution, which contained acid equivalent to 0.7 mol. (Congo-red), was made strongly alkaline and extracted with chloroform to which it yielded *NN'*-dimethylbenzamidine, m. p. 74—77° (2.65 g. or 48%). One crystallisation raised the m. p. to 81°, undepressed on admixture with an authentic specimen.

(b) An equimolecular mixture of benzomethylamide (3.4 g.), benzenesulphonmethylamide (4.3 g.), and benzenesulphonic acid (4.0 g.), heated at 220—225° for 30 minutes, afforded crude *NN'*-dimethylbenzamidine, m. p. 75—77° (3.5 g., 94%). Recrystallisation raised the m. p. to 81°, and the

\* See also Boots Pure Drug Co., Oxley and Short, B.P. Appln., 9288/13.4.1945.

benzenesulphonate had m. p. 104°, either alone or after admixture with an authentic specimen of *NN'*-dimethylbenzamidinium benzenesulphonate. An attempt to isolate *N*-benzoylbenzenesulphonmethylamide by conducting the reaction at a lower temperature was unsuccessful.

(3) *From dibenzoylmethylamine.* Dibenzoylmethylamine (4.78 g.) and methylammonium benzenesulphonate (4 g.; 1.1 mol.) were heated at 210° for an hour and the strongly acid product was dissolved in water, made strongly alkaline, and extracted with chloroform. Evaporation of the solvent gave crude *NN'*-dimethylbenzamidinium (1.4 g., 47%) which was converted into the picrate, m. p. and mixed m. p. 172—173° (2.45 g. or 32.5%), when added to a solution of picric acid (2.5 g.) in methanol. When the mixture was heated for an hour at 225° the yields of crude amidine and picrate were 49 and 36% respectively.

*Preparation of N-Acylbenzenesulphonalkylamides and N-Acylbenzenesulphonanilides.*

*N-Acetylbenzenesulphonmethylamide.*—Addition of a solution of potassium hydroxide (35 g.; 1.05 mol.) in hot methanol (100 c.c.) to benzenesulphonmethylamide (85.5 g.) in hot isopropanol (100 c.c.) and cooling to 0° afforded the potassium salt (100 g. or 96%). A solution of acetyl chloride (39 g.; 1 mol.) in benzene (50 c.c.) was added to the potassium salt suspended in benzene (200 c.c.) and the mixture boiled for 10 minutes, cooled, washed with water and dilute sodium hydroxide, dried, and evaporated. Distillation of the residue afforded *N-acetylbenzenesulphonmethylamide* as a colourless oil, b. p. 130°/0.7 mm. (Found: C, 50.3; H, 5.2; N, 6.5.  $C_9H_{11}O_3NS$  requires C, 50.7; H, 5.2; N, 6.6%). Yield, 90.4 g. (89%).

*N-Acetylbenzenesulphonanilide.*—Acetyl chloride (14.5 g.; 1 mol.) was added dropwise to a mixture of benzenesulphonanilide (43 g.) and pyridine (30 c.c.; 2 mols.), and the semi-solid mass was heated on the steam-bath for  $\frac{1}{2}$  hour. The solid obtained after shaking with dilute hydrochloric acid was recrystallised from 80% aqueous alcohol (200 c.c.) to give elongated plates, m. p. 115.5°. Wheeler, Smith, and Warren (*Amer. Chem. J.*, 1897, **19**, 760) record m. p. 116.5°.

*N-Benzoylbenzenesulphonmethylamide.*—Benzmethylamide, benzenesulphonyl chloride, and pyridine afforded a neutral oil which slowly dissolved in water to a strongly acid solution and was probably the benzenesulphonic ester of the isoamide,  $PhSO_2 \cdot O \cdot CPh \cdot NMe$ . A mixture of benzenesulphonmethylamide (35 g.), benzoyl chloride (28.8 g.; 1 mol.), and pyridine (16 c.c.; 1 mol.) was heated on the steam-bath for 14 hours, diluted with chloroform, and shaken with water and dilute sodium hydroxide. Distillation of the chloroform solution afforded *N-benzoylbenzenesulphonmethylamide* as a colourless oil, b. p. 200°/2 mm., which quickly solidified and separated from methanol in colourless plates, m. p. 89.5° (Found: N, 5.2.  $C_{14}H_{13}O_3NS$  requires N, 5.1%). Yield, 51 g. (90%).

*N-Benzoyltoluene-p-sulphonmethylamide,* prepared in the same way from toluene-*p*-sulphonethylamide, benzoyl chloride, and pyridine, separated from methanol in colourless prisms, m. p. 51° (Found: N, 4.6.  $C_{16}H_{17}O_3NS$  requires N, 4.6%).

*N-Benzoyltoluene-p-sulphonanilide.*—Toluene-*p*-sulphonyl chloride (95 g.; 1 mol.) was added to aniline (46.5 g.) and pyridine (150 c.c.) so that the temperature remained below 60°. Subsequent addition of benzoyl chloride (70 g.; 1 mol.) to the reddish-brown mixture produced an almost colourless solution which soon solidified. After 45 minutes' heating on the steam-bath, the solid was collected and crystallised from alcohol, to give colourless prisms, m. p. 150—151°. Yield, 122 g. (69.5%). Remsen and Palmer (*Amer. Chem. J.*, 1886, **8**, 242) prepared *N-benzoyltoluene-p-sulphonanilide* from toluene-*p*-sulphonanilide and benzoyl chloride at 140° and record m. p. 149° (corr.).

*N-Benzoylbenzenesulphon-2-pyridylamide.*—The potassium salt of 2-benzenesulphonamidopyridine was obtained in 97% yield by dissolving 2-benzenesulphonamidopyridine (46.8 g.) (English, Chappell, Bell, and Roblin, *J. Amer. Chem. Soc.*, 1942, **64**, 2516) and potassium hydroxide (15 g.; 1.1 mol.) in warm methanol (50 c.c.), diluting the solution with isopropanol (100 c.c.), and collecting the colourless needles (53 g.) which separated on cooling. A suspension of the potassium salt in benzene (250 c.c.) was boiled with benzoyl chloride (28 g.) for 4 hours, and the resulting solid collected, washed with water, and dried. *N-Benzoylbenzenesulphon-2-pyridylamide* was obtained in colourless plates (54 g. or 82%), m. p. 175—176° (Found: N, 8.5.  $C_{18}H_{14}O_3N_2S$  requires N, 8.3%). Benzoyl chloride, 2-benzenesulphonamidopyridine, and pyridine afforded an unstable compound which was probably 1-benzoyl-2-benzenesulphonimido-1 : 2-dihydropyridine.

*Fission of N-Benzoylbenzenesulphonmethylamide by Amines.*—(1) *By aniline.* A mixture of *N-benzoylbenzenesulphonmethylamide* (13.75 g.) and aniline (4.65 g.; 1 mol.) was heated at 245—250° for 30 minutes. The powdered reaction product was extracted with warm water (100 c.c.); the solution deposited almost pure *N-phenyl-N'-methylbenzamidinium*, m. p. 133° (0.4 g. or 3.85%), on being made alkaline. Benzenesulphonmethylamide (5.5 g. or 64%) was extracted from the solid with dilute aqueous sodium hydroxide; the residue (10.1 g.) afforded benzanilide, m. p. and mixed m. p. 163° (8.7 g. or 88.5%), when crystallised from alcohol.

(2) *By benzylamine.* An equimolecular mixture of *N-benzoylbenzenesulphonmethylamide* (5.50 g.) and benzylamine (2.14 g.) was heated at 230—235° for an hour, and the cooled product was dissolved in benzene. The benzene solution yielded benzenesulphonmethylamide (3.0 g., 88%) to dilute sodium hydroxide solution, and removal of most of the benzene and trituration of the residue with light petroleum gave benzbenzylamide, m. p. 103—104° (3.7 g., 88%). Crystallisation from benzene-light petroleum raised the m. p. to 105.5—106°, in agreement with the value recorded by Beckmann (*Ber.*, 1890, **23**, 3334). Dilute acetic acid removed basic material (0.1 g.) from the original mother liquor, evaporation then gave unchanged benzoylbenzenesulphonmethylamide (0.5 g. or 9%), which had m. p. 89° after crystallisation from methanol.

(3) *By 2-aminopyridine toluene-p-sulphonate.* Equimolecular quantities of 2-aminopyridine and anhydrous toluene-*p*-sulphonic acid in isopropanol afforded 2-aminopyridine toluene-*p-sulphonate*, m. p. 133° (Found: N, 10.7.  $C_{15}H_{14}O_3N_2S$  requires N, 10.5%). A mixture of this salt (13.3 g.; 1 mol.) with *N-benzoylbenzenesulphonmethylamide* (13.75 g.) was heated at 230° for 30 minutes, and the cold melt dissolved in water. The solution was decolorised with charcoal, made alkaline with aqueous sodium

hydroxide, and extracted with chloroform. Distillation of the extract (9.9 g.) gave (a) 2-aminopyridine, b. p. 100—120°/11 mm. (1.2 g.; 25%), identified as picrate, m. p. and mixed m. p. 223°; (b) a fraction (7.0 g.), b. p. 143—145°/1 mm.; and (c) a small dark residue. Fraction (b) afforded colourless needles, m. p. 81.5°, on recrystallisation from light petroleum (b. p. 100—120°) and was identified as 2-benzamido-pyridine (Found : N, 14.2. Calc. for  $C_{12}H_{10}ON_2$ : N, 14.1%) by comparison with a sample prepared as described by Tschitschibabin and Bylinkin (*Ber.*, 1922, 55, 1000) who record m. p. 87°. The picrate, prepared from material obtained by either method, had m. p. 199° (Found : N, 16.5. Calc. for  $C_{18}H_{13}O_6N_5$ : N, 16.4%), whereas Tschitschibabin and Bylinkin (*loc. cit.*) record m. p. 193°. The benzenesulphonate had m. p. 130° (Found : N, 8.0.  $C_{18}H_{16}O_4N_2S$  requires N, 7.9%). The distillation residue (c) and picric acid afforded 2-benzamidopyridine picrate, m. p. and mixed m. p. 199° (1.2 g.), making the total yield of 2-benzamidopyridine 76%.

*Preparation of Amidines from N-Acylbenzenesulphonalkylamides  
and N-Acylbenzenesulphonanilides.*

The reactants were heated, preferably with stirring, under the conditions specified in the Table. The methods used for the isolation of the amidines are illustrated by reference to the following cases in which some exceptional features necessitate a detailed description of the procedure.

*N-Methyl-N'-n-amybenzamidine.*—An equimolecular mixture of *N*-benzoylbenzenesulphonmethylamide (13.75 g.) and *n*-amylammonium toluene-*p*-sulphonate (12.95 g.) was heated at 200° for 50 minutes, cooled, and dissolved in chloroform (50 c.c.). An aqueous extract (100 c.c.) of this chloroform solution afforded *NN'*-dimethylbenzamidine, m. p. and mixed m. p. 81° (1.25 g. or 17%), when made strongly alkaline and extracted with chloroform. The amidine salts in the original chloroform solution were decomposed by shaking it with 5*N*-sodium hydroxide, and the liberated amidines were separated by fractional distillation. The fraction, b. p. 155—160°/7 mm. (mainly 157—159°/7 mm.), gave *N*-methyl-*N'*-*n*-amybenzamidine (6.1 g. or 60%), which was characterised as the picrate, m. p. 109° (see Table, No. 14). The portion, b. p. 175—180°/7 mm. (mainly 176—177°/7 mm.) (1.6 g., 12%), consisted of *NN'*-*di-n*-amybenzamidine (Found : N, 10.8.  $C_{17}H_{28}N_2$  requires N, 10.8%), and was characterised as the picrate, m. p. 83° (Found : N, 14.6.  $C_{23}H_{31}O_7N_5$  requires N, 14.3%).

*N-benzyl-N'-methylbenzamidine.*—*N*-Benzoylbenzenesulphonmethylamide (13.75 g.) and benzylammonium chloride (7.2 g.; 1 mol.) were heated at 200° for 40 minutes, and the oil which separated when the product was shaken with water was collected in benzene. The aqueous solution was made alkaline and extracted with chloroform, and the gum (2.1 g. or 19%) which remained after removal of the solvent was converted into *N*-benzyl-*N'*-methylbenzamidinium picrate, m. p. 121.5—122° (see No. 15). The benzene solution afforded *NN'*-dibenzylbenzamidine (4.4 g. or 29%) which was converted into the picrate, m. p. 145° (Found : N, 13.1. Calc. for  $C_{27}H_{23}O_7N_5$ : N, 13.2%). Pyman (*J.*, 1923, 123, 3373) states that *NN'*-dibenzylbenzamidinium picrate has m. p. 146—147° (corr.).

*N-Phenyl-N'-methylbenzamidine.*—(1) The product obtained by heating an equimolecular mixture of *N*-benzoylbenzenesulphonmethylamide (13.75 g.) and aniline toluene-*p*-sulphonate (13.25 g.) at 155—160° for an hour was dissolved in benzene (50 c.c.) and the solution extracted with water (4 × 50 c.c.). The aqueous solution afforded *N*-phenyl-*N'*-methylbenzamidine, m. p. and mixed m. p. 135° (2.2 g. or 21%), further identified as the picrate, m. p. 168—169°, and benzenesulphonate, m. p. 143°, which did not depress the m. p.'s of authentic specimens. The benzene solution was shaken with 2*N*-sodium hydroxide and concentrated to give *NN'*-diphenylbenzamidine, m. p. and mixed m. p. 147° (5.4 g., 40%). (2) *N*-Benzoyltoluene-*p*-sulphonanilide (17.55 g.) and methylammonium benzenesulphonate (9.5 g.; 1 mol.) exhibited a slightly exothermic reaction when heated at 225°; after 15 minutes at this temperature, the mixture was cooled and shaken with chloroform and aqueous sodium hydroxide. Distillation of the mixed amidines afforded *NN'*-dimethylbenzamidine, b. p. 74—76°/1 mm., m. p. and mixed m. p. 80—81° (0.5 g., 7%), and the residue was neutralised with hydrochloric acid. The sparingly soluble salt which separated was decomposed with alkali giving *NN'*-diphenylbenzamidine, m. p. and mixed m. p. 147° (3 g. or 22%), and the base, precipitated by adding alkali to the mother liquors, afforded *N*-phenyl-*N'*-methylbenzamidine, m. p. and mixed m. p. 135° (4 g., 38%), after crystallisation from benzene.

*N-Phenylbenzamidine.*—*N*-Benzoyltoluene-*p*-sulphonanilide (17.55 g.) and ammonium toluene-*p*-sulphonate (9.5 g.; 1 mol.) were heated at 225° for 30 minutes and the product was shaken with chloroform and 5*N*-sodium hydroxide. The dark oil (7.6 g.) obtained from the chloroform solution was dissolved in benzene, and the solution shaken with *n*-hydrochloric acid (40 c.c.) and filtered to remove the solid. Trituration of this solid with aqueous sodium carbonate afforded *NN'*-diphenylbenzamidine, m. p. and mixed m. p. 146—147° (1.15 g., 8.5%). The aqueous portion of the filtrate gave *N*-phenylbenzamidine, m. p. 113—115° (2.65 g. or 27%), on being made alkaline with aqueous sodium carbonate; crystallisation from petroleum (b. p. 100—120°) raised the m. p. to 116°, undepressed on admixture with an authentic specimen.

*N-2-Pyridyl-N'-methylbenzamidine.*—*N*-Benzoylbenzenesulphon-2-pyridylamide (8.45 g.) was heated with methylammonium benzenesulphonate (4.73 g.; 1 mol.) at 197° for an hour. The product was dissolved in water (50 c.c.), made strongly alkaline with 5*N*-sodium hydroxide (30 c.c.), and extracted with chloroform. Distillation of the extract yielded *N*-2-pyridyl-*N'*-methylbenzamidine as a pale yellow gum, b. p. 180—182°/2.5 mm. (3.15 g., 58.5%), which separated from light petroleum (b. p. 80—100°) in colourless rhombic crystals, m. p. 101° (Found : C, 73.6; H, 6.1; N, 19.7.  $C_{13}H_{13}N_3$  requires C, 73.9; H, 6.2; N, 19.9%). The picrate separated from methanol in rectangular plates, m. p. 180° (Found : N, 19.2.  $C_{19}H_{16}O_7N_5$  requires N, 19.1%).

*NN'-Di-2-pyridylbenzamidine.*—An equimolecular mixture of *N*-benzoylbenzenesulphon-2-pyridylamide (8.45 g.), 2-aminopyridine benzenesulphonate (6.3 g.), and benzenesulphonic acid (4 g.) was heated at 200° for an hour, and the cold melt was then stirred with water, made strongly alkaline with 5*N*-sodium hydroxide, and extracted with chloroform. The aqueous solution afforded a precipitate of 2-benzenesulphonamidopyridine, m. p. and mixed m. p. 173—174° (2.7 g.; 46%), on neutralisation with

hydrochloric acid. The residue (5.1 g.) obtained by removing the chloroform was recrystallised from benzene, and gave colourless prisms (1.4 g. or 17.5%) of *NN'*-di-2-pyridylbenzamidine, m. p. 175° (Found: N, 20.3.  $C_{17}H_{11}N_4$  requires N, 20.4%). 2-Benzamidopyridine, m. p. and mixed m. p. 81.5° (2.6 g. or 52%), was obtained by evaporating the benzene mother liquors and crystallising the residue from light petroleum. Under the same conditions, *N*-benzoylbenzenesulphon-2-pyridylamide (8.45 g.) and 2-aminopyridine toluene-*p*-sulphonate (6.65 g.) afforded only 2-benzenesulphonamidopyridine (77%) and 2-benzamidopyridine (ca. 100%).

#### Action of Heat on some Amidinium Salts.

*N*-Methyl-*N'*-*n*-amylbenzamidine.—Benzmethylamide imidochloride and *n*-amylamine in ether afforded a gummy hydrochloride which was converted into *N*-methyl-*N'*-*n*-amylbenzamidinium picrate, m. p. 108° (Found: N, 16.3.  $C_{19}H_{23}O_2N_5$  requires N, 16.2%). *N*-Methyl-*N'*-*n*-amylbenzamidine crystallised in colourless needles, m. p. 40° (Found: N, 13.6.  $C_{13}H_{20}N_2$  requires N, 13.7%). The benzenesulphonate was a viscous oil which did not crystallise. The benzenesulphonate (9 g.) was heated at 200° for an hour, and a solution of the cooled melt in chloroform (25 c.c.) was extracted with water (150 c.c.). The base (0.8 g.), obtained from the aqueous solution by making alkaline and extracting with chloroform, was recrystallised from light petroleum (b. p. 60–80°) and gave colourless rectangular plates of *NN'*-dimethylbenzamidine, m. p. 80–81°, converted into its picrate, m. p. 172–173°. Admixture of these preparations with authentic specimens produced no depression in m. p. Distillation of the chloroform extract after making alkaline gave *N*-methyl-*N'*-*n*-amylbenzamidine, b. p. 92°/0.3 mm., m. p. and mixed m. p. 39–40° (3.5 g.), and the residue was converted into a mixture of picrates separated by fractional crystallisation into *N*-methyl-*N'*-*n*-amylbenzamidinium picrate, m. p. and mixed m. p. 105–107° (0.5 g.), and *NN'*-di-*n*-amylbenzamidinium picrate, m. p. 80–83° (1.1 g.), raised to 83° by recrystallisation and undepressed on admixture with an authentic specimen. That is, *N*-methyl-*N'*-*n*-amylbenzamidine, *NN'*-dimethylbenzamidine, and *NN'*-di-*n*-amylbenzamidine were isolated from the product in 74, 11, and 9% yield respectively.

*N*-Benzyl-*N'*-methylbenzamidine.—Benzmethylamide (45 g.) and phosphorus pentachloride (70 g.; 1.01 mol.) gave a 64% yield of the imidochloride when brought into reaction as described by v. Pechmann (*Ber.*, 1895, **28**, 2367), and addition of a solution of benzylamine (22.7 g.) in ether (50 c.c.) to the imidochloride (32.6 g.) in ether (50 c.c.) afforded crude *N*-benzyl-*N'*-methylbenzamidinium chloride, m. p. 160–170° (47 g. or 85%), after being washed with acetone. Traces of benzylammonium chloride were removed by liberating the base and crystallising it from light petroleum (b. p. 60–80°); it was then obtained in needles, m. p. 73°. Pyman (*J.*, 1923, **123**, 3374) states that *N*-benzyl-*N'*-methylbenzamidine has m. p. 71–73° and the picrate m. p. 118–122°, and that the hydrochloride does not crystallise. We obtained a picrate, m. p. 121.5–122°, and the hydrochloride, obtained from hydrogen chloride and a solution of the base in isopropanol, had m. p. 180.5–181° (Found: N, 10.5.  $C_{15}H_{17}N_2Cl$  requires N, 10.7%). The toluene-*p*-sulphonate had m. p. 123° (Found: N, 7.2.  $C_{22}H_{24}O_3N_2S$  requires N, 7.1%). When the hydrochloride (10 g.) was heated at 200° for an hour and then cooled and powdered, it had m. p. 180.5–181° and afforded a quantitative yield of the free base, m. p. 72–73° (8.6 g.), with alkali. The toluene-*p*-sulphonate was maintained at 200° for an hour, cooled, dissolved in chloroform, and shaken with water (30 c.c.). The chloroform solution, when shaken with alkali, dried, and evaporated, afforded 5.6 g. of unchanged amidine, m. p. and mixed m. p. 73°. The aqueous layer, which would have contained *NN'*-dimethylbenzamidine, afforded 0.05 g. of base with alkali, and, when mixed with an equivalent of picric acid in ether, afforded a picrate, m. p. 113–117°, raised to 120–122° by crystallisation from isopropanol and unchanged on admixture with *N*-benzyl-*N'*-methylbenzamidinium picrate.

*N*-Phenyl-*N'*-methylbenzamidine.—This amidine was obtained in 83% yield from benzmethylamide imidochloride and aniline (v. Pechmann, *Ber.*, 1897, **30**, 1782; Pyman, *J.*, 1923, **123**, 3366). The hydrochloride separated from isopropanol as a colourless powder, m. p. 213° (Found: N, 11.3.  $C_{14}H_{15}N_2Cl$  requires N, 11.4%), and the benzenesulphonate had m. p. 143° (Found: N, 7.8.  $C_{20}H_{20}O_3N_2S$  requires N, 7.6%). When the benzenesulphonate (7.36 g.) was heated at 200° for an hour and the product was crystallised from isopropanol (10 c.c.), the bulk of the salt (7 g.) was recovered unchanged, m. p. and mixed m. p. 143°. Addition of ether to the filtrate afforded a second crop, m. p. 142.5–143° (0.26 g.), making the total recovery 98.6%. When *N*-phenyl-*N'*-methylbenzamidinium chloride was heated at 220° for 30 minutes, the m. p. of the product was 208–210°, indicating that very little change had taken place.

*Methylammonium Benzenesulphonate*.—There was no reaction between methyl benzenesulphonate (7.8 g.) and ammonium benzenesulphonate (8.75 g.; 1.2 mols.) at 140°, but after an hour at 225° the product contained methylammonium benzenesulphonate. The product was triturated with a mixture of acetone (20 c.c.) and ether (80 c.c.), and the residual solid, m. p. 200–220° (6.5 g.), was extracted in a Soxhlet apparatus with chloroform. The undissolved solid consisted of crude ammonium benzenesulphonate, m. p. 275–280°, and the chloroform solution deposited crude methylammonium benzenesulphonate (1.9 g., 24%), which afforded the pure salt, m. p. and mixed m. p. 165°, on crystallisation from isopropanol (Found: N, 7.4. Calc. for  $C_7H_{11}O_3NS$ : N, 7.4%). Norton and Westenhoff (*Amer. Chem. J.*, 1888, **10**, 130) state that methylammonium benzenesulphonate has m. p. 147°.

Methyl toluene-*p*-sulphonate (18.6 g.) and ethylammonium chloride (8.15 g.) at 120–150° gave methyl chloride and ethylammonium toluene-*p*-sulphonate, m. p. 113–115°, which crystallised from isopropanol in needles, m. p. and mixed m. p. 118° (Norton and Otten, *Amer. Chem. J.*, 1888, **10**, 140, give m. p. 111°) (Found: N, 6.45. Calc. for  $C_9H_{15}O_3NS$ : N, 6.45%). The yield was 19.6 g. (90%).