78. Amidines. Part IV. Preparation of Amidines from Cyanides and Ammonium Thiocyanate or Substituted Ammonium Thiocyanates.

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Amidines and *N*-substituted amidines may be prepared by heating cyanides with ammonium or alkylammonium thiocyanates at *ca.* 180°. The yields are sometimes higher than those obtained with ammonium sulphonates.

The preparation of amidines from cyanides and ammonium or substituted ammonium sulphonates was described by Oxley and Short (*J.*, 1946, 147) and we now find that some amidines can be obtained in better yield by heating a cyanide with the more readily available ammonium thiocyanate. The scope of the method is illustrated by the examples given in the table, and attention is directed to a few matters of general interest arising from them. Systematic experiments on the preparation of p-*amidinophenyl methyl sulphone*, recorded in the experimental section, show that the yield of amidine (*a*) increases with increase in the ratio of ammonium thiocyanate to cyanide, the optimum quantity of thiocyanate for preparative purposes being *ca.* 4 mols., and (*b*) is considerably decreased by relatively small variations from the temperature and time of reaction found to give the best results. Part of the ammonium thiocyanate is converted into thiourea, and we find that the *thiocyanate* of *p*-amidinophenyl methyl sulphone is decomposed into *p*-cyanophenyl methyl sulphone to the extent of 47% in 5 minutes at 225°, so that the composition of the reaction product is determined by a number of concurrent reactions. The amidine is also obtained by heating the cyanide with thiourea and, since the yields are considerably lower than those obtained under identical conditions with an equivalent quantity of ammonium thiocyanate, it seems that isomerisation of thiourea to ammonium thiocyanate must precede the production of amidine. Reynolds and Werner (*J.*, 1903, **83**, 1) and Atkins and Werner (*J.*, 1912, **99**, 1172) showed that equilibrium between ammonium thiocyanate and thiourea is reached somewhat slowly at 170—180° and the indication is that in this case formation of the amidinium thiocyanate is a more rapid reaction. The low yield of *N*-benzyl-*p*-amidinophenyl methyl sulphone (No. 20) is doubtless due to the rapid and almost complete conversion of benzylammonium thiocyanate into *N*-benzylthiourea (Dixon, *J.*, 1891, **59**, 555). Anilinium thiocyanate is rapidly and almost completely converted into *N*-phenylthiourea above 85° (Krall and Gupta, *J. Indian Chem. Soc.*, 1935, **12**, 629) and only a small yield of N-*phenyl*-p-*amidinophenyl methyl sulphone* is obtained by heating *p*-cyanophenyl methyl sulphone with *N*-phenylthiourea. Moreover, since ammonium thiocyanate and aniline are formed by the decomposition of *N*-phenylthiourea (de Clermont, *Bull. Soc. chim.*, 1876, **25**, 243), it is possible that the *N*-phenylamidine is not produced from the cyanide and the anilinium thiocyanate produced from the *N*-phenylthiourea, but by the interaction of salts of aniline and *p*-amidinophenyl methyl sulphone, produced from ammonium thiocyanate and the cyanide.

p-Methoxyphenyl cyanide affords a 21% yield of *p*-methoxybenzamidine in 4 hours at 180° (No. 4) and if heating is prolonged to 16 hours, *p*-hydroxybenzamidine is obtained in 44% yield. This demethylation is reminiscent of the production of 3-hydroxy-4-methoxyphthalide and methyl cyanide from meconine and potassium cyanide at 180° (Rodinov, Kanevskaja, and Davankov, *Ber.*, **1933**, **66**, 1623; *Bull. Soc. chim.*, 1934, **1**, 677). The production of *p*-carbamidobenzamidine from *p*-cyanobenzoic acid and ammonium thiocyanate (No. 5) is not surprising since Kekule (*Ber.*, 1873, **6**, 113) obtained benzamide from benzoic acid and ammonium thiocyanate at 150—170°. The method fails with 2 : 4-dichlorophenyl cyanide and *o*-cyanophenyl methyl sulphone, so that *o*-substituted amidines are evidently not readily formed by heating an aryl cyanide with ammonium thiocyanate.

The mechanism of the thiocyanate method, which is probably different from that of the ammonium sulphonate method (Part I, *loc. cit.*), is conveniently discussed in a subsequent communication dealing with the action of other ammonium salts and nitrogen compounds upon cyanides.

Experimental.*

The ammonium thiocyanate employed was a commercial sample which was dried at 100° for 1—2 hours before use. The following general description is supplemented by detailed descriptions in those cases where special features are involved. The cyanide and ammonium thiocyanate or substituted ammonium thiocyanate were heated under the conditions specified in the table. If the reactants were immiscible, the mixture was stirred vigorously and heating was continued for *ca.* 1 hour after the two layers had coalesced. The amidine was liberated from an aqueous solution of the product with 5N-sodium

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* See also Boots Pure Drug Co. Ltd., Partridge & Short, B.P. Appln. 17,732/11.7.1945.

hydroxide or, in the case of weakly basic amidines, with ammonia, and was separated from unchanged cyanide by solution in hydrochloric acid. The amidine was reprecipitated, washed with ice-water and dissolved in an equivalent of hydrochloric acid. The amidinium chlorides were isolated by concentrating the solutions by distillation under diminished pressure, and the other salts were prepared by double decomposition with sodium picrate, etc.

p-*Carbamidobenzamidine.*—*p*-Cyanobenzoic acid (6 g.) and ammonium thiocyanate (12·2 g.) formed a homogeneous mixture when heated at 180° for 4 mins. with occasional stirring. After 20 mins. a brown solid separated and ammonia was evolved. Heating was continued for a total of 45 mins., and the cold, red melt was boiled with water (30 c.c.) and sufficient hydrochloric acid to give an acid reaction to Congo-red. The solid was extracted with hot water until the extract no longer gave the reaction described by Fuller (*Nature*, 1944, **154**, 773), and the united extracts were warmed to 60° and filtered from *ca.* 2 g. of insoluble material. The filtrate was mixed with excess of saturated aqueous ammonium Reineckate, cooled rapidly, and the Reineckate collected and crystallised from 20% aqueous acetone. The pink needles (7·8 g.) had m. p. 186—188° (decomp.) and afforded the analytical results recorded in the table. The Reineckate (1 g.) was suspended in water (2 c.c.), brought into solution by adding acetone, acidified with a few drops of dilute hydrochloric acid, and shaken with ether (10 c.c.) and acetone (2 drops) until the red colour was removed from the aqueous layer. When excess of saturated aqueous sodium picrate was added to the aqueous solution, *p*-carbamidobenzamidinium picrate, m. p. 274—276°, was precipitated (0·6 g. or 75%) and crystallisation from water produced yellow prismatic needles, m. p. 284—286°. A similar method was used for the conversion of the Reineckate into the hydrochloride (see table).

p-*Amidinophenyl Methyl Sulphone.*—(1) *p*-Cyanophenyl methyl sulphone (9 g.) and ammonium thiocyanate were heated under the conditions shown in the table below. The cold melt was boiled with water (20 c.c.), and the solution poured into a mixture of 10N-sodium hydroxide (15 c.c.) and ice (20 g.), and after being kept at 0° for an hour, the solid was collected, washed with ice-water, and the amidine was extracted from unchanged cyanide (by making an aqueous suspension just acid to brilliant-yellow) with N-hydrochloric acid. The amidine was reprecipitated with 10N-sodium hydroxide (5 c.c.), washed, with ice-water, and determined by titration with standard hydrochloric acid. The amidinium chloride, isolated by concentrating the solution by distillation under diminished pressure, had m. p. 294° in agreement with Fuller *et al.* (*loc. cit.*). The reaction was slightly exothermic and in the experiments at 260° there was vigorous effervescence and evolution of pungent vapours.

NH$_4$SCN, mols.	Reaction: Temp.	Reaction: Time, mins.	Yield of amidinium chloride, %.
1	260°	30	0·025
1	260	5	28 (*a*)
1	150	120	3·4 (*b*)
4	225	4	64
4	200	30	41
4	180°	60	62
4	180	45	70
4	180	30	64
4	180	20	37
4	170	30	9

(*a*) Recovery of cyanide, 45%. (*b*) Recovery of cyanide, 82%.

(2) A mixture of the cyanide (4·6 g.), ammonium thiocyanate (7·6 g.), and glycerol (20 g.) was heated at 180° for 30 mins. and then boiled with water. The hot filtered solution afforded the amidinium picrate, m. p. 235° (4·7 g.) with alcoholic picric acid. Recrystallisation from alcohol afforded the pure *picrate*, m. p. 262° (Found: N, 16·6. $C_{14}H_{13}O_9N_5S$ requires N, 16·4%). Yield, 3·3 g. (30%). After only 20 minutes at 180° the yield of pure picrate was 2·4 g. (22%).

(3) A mixture of *p*-cyanophenyl methyl sulphone (3·62 g.) and thiourea (6·08 g.; 4 mols.) was heated at 180° for various times with occasional stirring, and an aqueous solution of the resulting yellow gum was decomposed with 5N-sodium hydroxide at 0°. Unchanged cyanide and amidine were separated by extraction with hydrochloric acid, and the amidinium picrate, m. p. and mixed m. p. 263°, was precipitated from the solution with alcoholic picric acid. The yields of amidinium picrate were 22, 51, and 53% after 30, 45, and 60 mins., respectively, at 180°; the corresponding figures when ammonium thiocyanate was used in place of thiourea were 64, 70, and 62%, respectively.

Decomposition of p-*Methylsulphonylbenzamidinium Thiocyanate.*—A hot solution of the amidinium chloride (20 g.) in water (50 c.c.) was mixed with ammonium thiocyanate (6·5 g.; 1 mol.) in water (30 c.c.), shaken with charcoal, filtered, and cooled. The *thiocyanate* (19 g., 88%) separated on cooling in prisms, m. p. 212° (Found: N, 16·4; SCN, 22·5. $C_9H_{11}O_2N_3S_2$ requires N, 16·3; SCN, 22·6%). When the thiocyanate was heated at 225° for 5 mins. the neutral portion of the product consisted of *p*-cyanophenyl methyl sulphone, m. p. and mixed m. p. 142·5° (1·3 g.). The recovered amidinium chloride had m. p. 293° and the amount, determined by titration, was equivalent to 53% of the thiocyanate.

β-Naphthamidine.—(*a*) *β*-Naphthyl cyanide (5 g.) and ammonium thiocyanate (10 g.) were vigorously stirred for an hour at 180° and the cold melt was boiled with water (20 c.c.) and charcoal (0·2 g.) and filtered. The filtrate, mixed with 5N-sodium hydroxide (5 c.c.), was kept at 0° for 30 mins. and the solid was then collected, washed with ice-water, suspended in water (5 c.c.), and rendered acid to Congo-red with hydrochloric acid. Addition of alcoholic picric acid to the solution afforded a picrate, which was collected, washed with a little water and alcohol, and recrystallised from methanol. The *β*-naphthamidinium picrate so obtained (0·25 g., 2·2%) had m. p. and mixed m. p. 247°.

(*b*) Repetition of the experiment with thiourea (10 g.) in place of ammonium thiocyanate afforded 0·05 g. (0·4%) of *β*-naphthamidinium picrate, m. p. and mixed m. p. 247°.

4 : 4′-*Diamidino-αγ-diphenoxypropane.*—The 4 : 4′-dicyano-*αγ*-diphenoxypropane required for the preparation of this amidine was obtained as follows. *p*-Nitrophenol, alcoholic sodium hydroxide (1 mol.), and trimethylene bromide (0·5 mol.) afforded a 74% yield of 4 : 4′-*dinitro-αγ-diphenoxypropane*, which crystallised from benzene in needles, m. p. 131° (Found: N, 8·9. $C_{15}H_{14}O_6N_2$ requires N, 8·8%).

Amidine.	NH_4SCN or RNH_3SCN, mols.	Reaction.		Yield, %.	Amidine salt isolated.				
		Temp.	Time, mins.			M. p.*	Formula.	Found, N, %.	Required, N, %.
(1) Benzamidine	4	180°	240	50	Picrate	239—240°*	$C_{13}H_{11}O_7N_5$	20·2	20·1
(2) *p*-Bromobenzamidine	4	180	150	63	Picrate	269 *	$C_{13}H_{10}O_7N_5Br$	16·3	16·3
(3) p-*Hydroxybenzamidine*	4	180	120	86	*Hydrochloride*	223—224	$C_7H_9ON_2Cl$	16·3	16·2
(4) *p*-Methoxybenzamidine	4	180	240	21	Picrate	212—213	—	—	—
(5) *p*-Carbamidobenzamidine	4	180	45	39	*Reineckate*	186—188 *	$C_{12}H_{16}ON_9S_4Cr,0{\cdot}5H_2O$	25·5 25·4	25·5
(6) *p*-Sulphamidobenzamidine	4	220	4	39	Hydrochloride	246	—	—	—
(7) p-*Amidinophenyl methyl sulphone*	4	180	45	70	Hydrochloride	293	—	—	—
(8) *m*-Amidinophenyl methyl sulphone	4	180	120	84	*Thiocyanate*	184—185	$C_9H_{11}O_2N_3S$	16·2	16·3
(9) *β*-Naphthamidine	4	180	60	2·2	Picrate	247	—	—	—
(10) 4 : 4′-Diamidino-*αγ*-diphenoxypropane	8	180—195	180	61	Hydrochloride	294	$C_{17}H_{22}O_2N_4Cl_2$	14·3	14·5
(11) 4 : 4′-Diamidinodiphenyl ether	7·9	180	360	67	Hydrochloride	305—306	$C_{14}H_{16}ON_4Cl_2,2H_2O$	15·5	15·4
(12) 2-Amidinopyridine	4	180	60	59	Picrate	209	$C_{12}H_{10}O_7N_6$	23·8	24·0
(13) 4 : 4′-Diamidinostilbene	10	180—185	720	70	Hydrochloride	355—360 *	$C_{16}H_{18}N_4Cl_2,2H_2O$	14·9	15·0
(14) *α*-Amidinoheptane	4	180	600	3·5	*Picrate*	170—171	$C_{14}H_{21}O_7N_5$	18·7	18·9
(15) Phenylacetamidine	4	180	360	44	*Picrate*	227—228	$C_{14}H_{13}O_7N_5$	19·1	19·3
(16) *NN*-Dimethylbenzamidine	1	180	150	9·5	*Reineckate*	156—157 *	$C_{13}H_{19}N_8S_4Cr,1{\cdot}5H_2O$	22·7	22·7
(17) NN-*Pentamethylenebenzamidine*	1	180	180	3·4	*Picrate*	173—174	$C_{18}H_{19}O_7N_5$	16·9	16·8
(18) *N*-Methyl-*p*-amidinophenyl methyl sulphone	1	180	120	45	*Benzenesulphonate*	230—231	$C_{15}H_{18}O_5N_2S_2$	7·7	7·6
(19) *NN*-Dimethyl-*p*-amidinophenyl methyl sulphone	1	180	120	57	Hydrochloride	275 *	$C_{10}H_{16}O_2N_2ClS$	10·45	10·65
(20) *N*-Benzyl-*p*-amidinophenyl methyl sulphone	1	180	120	16	*Reineckate*	192—194 *	$C_{19}H_{23}O_2N_8S_5Cr$	18·6	18·5

* Compounds having m. p.'s marked with an asterisk decompose on melting.

Notes.—Except where otherwise indicated, the experiments were conducted with 0·02—0·05 g.-mol. of cyanide. A thorough examination of the experimental conditions was not made in all cases, so that the yields recorded are not necessarily the highest obtainable.

(1) There was no depression in m. p. on admixture with a specimen of benzamidinium picrate, m. p. 238—239°, prepared as described in Part I (*loc. cit.*).

(2) p-*Bromobenzamidinium thiocyanate* had m. p. 218—219° (Found : N, 16·3; SCN, 22·4. $C_8H_8N_3BrS$ requires N, 16·3; SCN, 22·5%).

(3) *p*-Hydroxybenzamidine was also obtained in 44·5% yield by heating *p*-methoxyphenyl cyanide and ammonium thiocyanate (4 mols.) at 180° for 16·5 hours. It was precipitated from aqueous solutions of its salts by ammonia and separated from water in needles, m. p. 233—234° (decomp.), consisting of a dihydrate after drying over potassium hydroxide in a vacuum (Found : N, 16·4, 16·3; *M*, by titration, 172·5. $C_7H_8ON_2,2H_2O$ requires N, 16·3%; *M*, 172). This phenol is insoluble in aqueous sodium hydroxide and precipitation from its salts with this reagent afforded a substance, m. p. 238—239° (decomp.), shown by analysis to consist of a mixture of amidine and amide. The crude amidine first isolated from the reaction product was sometimes contaminated with guanidine produced from the ammonium thiocyanate. This adsorbed guanidine remained in solution when the mixture of bases was neutralised with benzenesulphonic acid and the solution was cooled at 0° and filtered from *p*-hydroxybenzamidinium benzenesulphonate. Addition of sodium picrate solution to the filtrate afforded guanidine picrate, m. p. 309—310° (decomp.) (Found : N, 29·2. Calc. for $C_7H_8O_7N_6$: N, 29·2%). p-*Hydroxybenzamidinium picrate* crystallised in yellow needles, m. p. 230—231° (decomp.) (Found in material dried at 90° : N, 19·2. $C_{13}H_{11}O_8N_5$ requires N, 19·2%). The *benzenesulphonate* separated from water in needles, m. p. 187° (Found in material dried at 90° for 2 hours : N, 9·7, 9·5. $C_{13}H_{14}O_4N_2S$ requires N, 9·5%). The *sulphate* consisted of prismatic needles, m. p. 290—292° (decomp.) (Found in material dried over sulphuric acid in a vacuum : N, 15·2. $C_7H_8ON_2,\frac{1}{2}H_2SO_4$ requires N, 15·1%); and the *nitrate* crystallised from water in needles, m. p. 265—267° (decomp.) (Found in material dried at 90° for 1 hour : N, 21·1. $C_7H_9O_4N_3$ requires N, 21·1%).

(4) Unchanged *p*-methoxyphenyl cyanide amounted to 61%. The picrate and benzenesulphonate of the amidine did not depress the m. p.'s of authentic specimens prepared as described in Part I (*loc. cit.*).

(5) This compound was obtained from *p*-cyanobenzoic acid. The Reineckate contained SCN, 47·7 ($C_{12}H_{16}ON_9S_4Cr,0{\cdot}5H_2O$ requires SCN, 47·1%). The *picrate* crystallised from water in prismatic needles, m. p. 283—285° (Found in material dried at 105° for 1 hour : N, 21·4. $C_{14}H_{12}O_8N_6$ requires N, 21·4%). The hydrochloride had m. p. 304—305° (decomp.) (Found in material dried at 90° for 1 hour : N, 20·7. Calc. for $C_8H_9O_3N,HCl$: N, 21·0%); Andrewes, King, and Walker (*Proc. Roy. Soc.*, 1946, *B*, **133**, 20) state that the monohydrate has m. p. 302—303°.

(6) The m. p. was undepressed on admixture with an authentic specimen of *p*-sulphamidobenzamidinium chloride prepared as described in Part I (*loc. cit.*).

(7) See below for additional data.

(8) Fuller, Tonkin, and Walker (*J.*, 1945, 633) prepared this amidine by the Pinner method and state that the hydrochloride has m. p. 216°.

(9) The amidine was also prepared from *β*-naphthyl cyanide and thiourea (see below), and the picrate from the base did not depress the m. p. of authentic *β*-naphthamidinium picrate.

(10) After 1 hour at 190—195°, heating was continued for 2 hours at 180°. The amidinium chloride sintered at *ca.* 135° before melting at 294°; it was dried at 100° for 2 hours in a vacuum before analysis. The free base had m. p. 190—191° (decomp.). May and Baker, Ashley, Barber, Ewins, Newbery and Self (B.P. 507,565; see *J.*, 1942, 110) state that the free base and hydrochloride monohydrate have m. p. 193—194° (decomp.) and 292°, respectively.

(11) Preparation by Dr. A. Koebner (Found in the hydrochloride : Cl, 19·5. H_2O, 10·2. Calc. : Cl, 19·6; H_2O, 9·9%). This amidine was prepared from 0·1 g.-mol. of 4 : 4′-dicyanodiphenyl ether. The free base had m. p. 215—216° in agreement with May and Baker, Ashley *et al.* (*loc. cit.*).

(12) The picrate did not depress the m. p. of a sample prepared as described in Part I (*loc. cit.*).

(13) Preparation by Mr. S. W. Stroud using 0·22 g.-mol. of crude 4 : 4′-dicyanostilbene [Found in the dihydrochloride dihydrate : Cl, 18·85; H_2O (at 100°), 9·4. Calc. : Cl, 19·0; H_2O, 9·65%]. May and Baker, Ashley *et al.* (B.P. 510,097; and *J.*, 1942, 110) state that the dihydrochloride dihydrate has m. p. 300°.

(14) Found in the picrate : C, 45·3; H, 5·3. $C_{14}H_{21}O_7N_5$ requires C, 45·5; H, 5·7%.

(15) Phenylacetamidine has been described by Bernthsen (*Annalen*, 1877, **184**, 321, 340) and by Luckenbach (*Ber.*, 1884, **17**, 1423).

(16) Found in the Reineckate : SCN, 47·1, 46·8. $C_{13}H_{19}N_8S_4Cr,1{\cdot}5H_2O$, requires SCN, 47·0%. Phenyl cyanide (79%) was recovered.

(17) The recovery of phenyl cyanide was 90%. The isolation of this amidine is described in the experimental section.

(18) The amidinium chloride has been prepared by the Pinner method (Fuller, Tonkin, and Walker, *loc. cit.*).

(19) The m. p. of the hydrochloride agrees with that recorded by Fuller *et al.* (*loc. cit.*). The *picrate* crystallised from methanol in short needles, m. p. 189·5° (Found : N, 15·4. $C_{16}H_{17}O_9N_5S$ requires N, 15·4%).

(20) The benzenesulphonate was obtained as an oil.

Reduction of the dinitro-compound with aqueous sodium sulphide gave an 88% yield of 4 : *4′-diamino-αγ-diphenoxypropane*, m. p. 108—109° (Found : N, 10·8. $C_{15}H_{18}O_2N_2$ requires N, 10·85%), and the portion of the product insoluble in dilute hydrochloric acid consisted essentially of 4-*nitro*-4′-*amino-αγ-diphenoxypropane*, which crystallised from aqueous alcohol in yellow leaflets, m. p. 124—125° (Found : N, 9·7. $C_{15}H_{16}O_4N_2$ requires N, 9·7%). The yield of nitroamine was 11%, and 0·6% of the dinitro-compound was recovered. A 54% yield of 4 : 4′-dicyano-αγ-diphenoxypropane, m. p. 182—184°, was obtained by the Sandmeyer reaction, and recrystallisation from ethyl acetate raised the m. p. to 186—187°. Ashley *et al.* (*loc. cit.*, p. 114) record m. p. 188°.

A mixture of the dicyanide (5·6 g.) and ammonium thiocyanate (12·2 g.) was heated and stirred under the conditions specified in the table and the amidine was isolated from the melt in the usual way.

NN-*Pentamethylenebenzamidine*.—Phenyl cyanide (5·2 g.) and piperidinium thiocyanate (7·2 g.; Gebhardt, *Ber.*, 1884, **17**, 3041; Hofmann and Gabriel, *Ber.*, 1892, **25**, 339) afforded a homogeneous brown melt when heated at 180° for 3 hours with occasional stirring. The product was stirred with 5N-sodium hydroxide (20 c.c.) and extracted with chloroform (5 × 50 c.c.). The amidine was extracted from the concentrated chloroform solution with dilute hydrochloric acid, and phenyl cyanide, b. p. 185—190° (4·7 g.), was recovered after removal of the solvent. The aqueous solution was made alkaline with 10N-sodium hydroxide and extracted with chloroform. The solvent was removed from the dried solution, and distillation of the residue afforded NN-*pentamethylenebenzamidine*, b. p. 104°/0·6 mm. (Found : N, 14·9. $C_{12}H_{16}N_2$ requires N, 14·9%). The picrate was prepared by adding aqueous sodium picrate to a solution of the amidinium chloride (see table).

N-*Methyl*-p-*amidinophenyl Methyl Sulphone*.—Hot solutions of methylammonium chloride (67·5 g.) in 95% alcohol (300 c.c.) and ammonium thiocyanate (76 g.; 1 mol.) in 95% alcohol (200 c.c.) were mixed, cooled rapidly, and filtered from ammonium chloride. The filtrate was evaporated below 40°, and the residue dried over sulphuric acid in a vacuum and extracted with hot absolute alcohol (200 c.c.), leaving ammonium chloride undissolved. When the filtrate was cooled to 0° part of the thiocyanate was deposited and the rest was obtained by concentrating the filtrate below 40°. After drying in a vacuum over sulphuric acid the *methylammonium thiocyanate* (85 g.) was obtained in deliquescent crystals, m. p. 73—74° (Found : N, 30·7; SCN, 64·5. $C_2H_6N_2S$ requires N, 31·1; SCN, 64·5%). *p*-Cyanophenyl methyl sulphone (9 g.) and methylammonium thiocyanate (4·5 g.) were heated under the conditions specified in the table and a suspension of the product in water (15 c.c.) was poured into 10N-sodium hydroxide (25 c.c.) and ice (25 g.). The solid was collected after 2 hours at 0° and the filtrate (A) was kept. When the solid was extracted with dilute hydrochloric acid, unchanged cyanide, m. p. 140—141° (4·24 g.), remained undissolved, and the base, precipitated from the aqueous solution by adding alkali, was collected and the filtrate added to the solution A. The solid was suspended in water, neutralised to brilliant-yellow with aqueous benzenesulphonic acid, and evaporated to dryness, giving 6·2 g. of the benzenesulphonate, m. p. 230—231°. Amidine remaining in the alkaline aqueous solutions (A) was recovered by extraction with chloroform and converted into the benzenesulphonate, m. p. 229—230° (2·1 g.). Recrystallisation from water afforded prisms of the pure benzenesulphonate, m. p. 230—231° (see table).

N-*Phenyl*-p-*amidinophenyl Methyl Sulphone*.—*p*-Amidinophenyl methyl sulphone (9 g.) and *N*-phenylthiourea (7·6 g.; 1 mol.) were heated at 155° with stirring for 30 hours. The product was extracted with boiling acetone (100 c.c.), and the solution concentrated to 20 c.c., mixed with 5N-sodium hydroxide (20 c.c.) and repeatedly extracted with chloroform (280 c.c. in all). The solvent was removed and the residue extracted with warm dilute hydrochloric acid, leaving a resin undissolved. The acid solution was mixed with ammonia (*d* 0·88; 20 c.c.), cooled to 0°, and filtered. Addition of 5N-sodium hydroxide (5 c.c.) to the filtrate afforded p-*amidinophenyl methyl sulphone* (0·07 g.), m. p. 200—202° (decomp.) (Found : N, 13·9. $C_8H_{10}O_2N_2S$ requires N, 14·1%). The first precipitate afforded a gummy benzenesulphonate (2·8 g.) when its solution in an equivalent of aqueous benzenesulphonic acid was evaporated to dryness. The gum was dissolved in water, the solution made alkaline with ammonia, and the solid collected and recrystallised from alcohol (charcoal), giving *N*-phenyl-*p*-amidinophenyl methyl sulphone (0·4 g.), m. p. and mixed m. p. 230—231°.

We are indebted to Mr. P. Oxley for an authentic specimen of N-*phenyl*-p-*amidinophenyl methyl sulphone*, which crystallised from methanol in needles, m. p. 231° (Found : N, 10·4, 10·4. $C_{14}H_{14}O_2N_2S$ requires N, 10·2%). By heating a mixture of *p*-cyanophenyl methyl sulphone (9·05 g.) and anilinium benzenesulphonate (12·55 g.; 1·0 mol.) at 175—180° for 3 hours, he obtained an 86·5% yield of N-*phenyl*-p-*methylsulphonylbenzamidinium benzenesulphonate*, m. p. 222° (Found : N, 6·6. $C_{20}H_{20}O_5N_2S_2$ requires N, 6·5%).

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