

LI.—3-*Aminoquinoline and the Colour of its Salts.*

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OF the seven possible amino-derivatives of quinoline, six have already been described. The hitherto unknown 3-derivative seemed to merit investigation from more than one point of view.

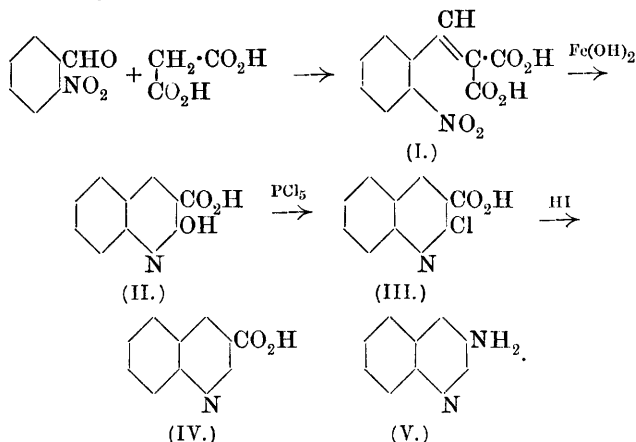
The four aminoquinolines in which the amino-group is attached to the benzene ring are diazotisable. Moreover, they form coloured salts, and the metallic salts of the corresponding hydroxy-compounds (with the possible exception of the 5-derivative) also show colour or fluorescence.

On the other hand, of the two already known aminoquinolines in which the amino-group is attached to the pyridine nucleus, the 4-derivative does not give rise to diazonium salts (Claus and Frobenius, *J. pr. Chem.*, 1897, [ii], 56, 191; Wenzel, *Monatsh.*, 1894, 15, 458), and although the behaviour of the 2-derivative towards nitrous acid does not appear to have been investigated, the same is almost certainly true of it on account of the close analogy in other respects of the 2- and 4-derivatives of quinoline to one another and to the

corresponding derivatives of pyridine. Moreover, the salts of these two substances are also colourless, and this is likewise the case with those of the corresponding hydroxy-compounds.

It appeared, therefore, of interest to determine in what manner 3-aminoquinoline, in which the amino-group, although attached to the pyridine nucleus, would yet be less directly under the influence of the ring nitrogen, would behave towards nitrous acid, and, secondly, in connexion with the origin of the colour of the salts of amino- and hydroxy-quinolines, whether or not the salts of these unknown 3-derivatives would be coloured.

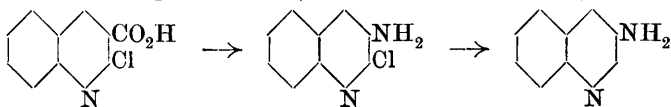
On reviewing the possible methods of obtaining this base, it appeared that it would probably be most readily prepared from quinoline-3-carboxylic acid by the replacement of the carboxyl by the amino-group, provided that some convenient method could be discovered for the preparation of this acid, since hitherto it has been a somewhat difficultly accessible compound.



We found that it could be satisfactorily prepared by the reduction by means of hydriodic acid and phosphorus of 2-chloroquinoline-3-carboxylic acid (III). This may be obtained by the action of phosphorus pentachloride (Friedländer and Göhring, *Ber.*, 1884, **17**, 460) on carbostyrylcarboxylic acid (II), and this in turn is easily prepared by the reduction of the condensation product (I) of *o*-nitrobenzaldehyde and malonic acid (Stuart, *Trans.*, 1885, **47**, 155; 1888, **53**, 143; H. Meyer, *Monatsh.*, 1908, **28**, 47). The final step in the synthesis of the base, namely, the replacement of the carboxyl in the acid (IV) by the amino-group, can be brought about without difficulty in the usual manner by treating the corresponding amide with sodium hypobromite.

The alternative course of replacing the carboxyl by the amino-

group before elimination of the chlorine was also tried, but was found to be less advantageous, since (as was to be anticipated) the chlorine



atom was less readily removable from the amino- than from the carboxyl derivative (compare Mills and Widdows, *Trans.*, 1908, **93**, 1376).

The new base exists in two modifications. As first obtained, crystallised from toluene, it melted at 84° . Suddenly in the course of our experiments the melting point rose to 94° , and for some time the form melting at the lower temperature was never again obtained. It was, however, at length discovered that after the modification melting at 94° has been fused in a melting-point tube, the resolidified substance melts sharply at 84° , and that when a minute fragment of the original solid is allowed to fall into the resulting liquid at a slightly higher temperature, it resolidifies and then melts at 94° . This observation, which was repeated on a larger scale, suggested that the production of the 94° modification was due to inoculation by particles present in the laboratory dust, and that this is actually the case was proved by the fact that, when such inoculation is guarded against, the base crystallises constantly from toluene in the form melting at 84° . An interesting confirmation of this is that after the summer vacation it was found to crystallise from toluene in this form when no precautions were taken, and it did so invariably in another laboratory which had not become infected.

The crystals which separate from aqueous or aqueous-alcoholic solutions, however, appear always to melt at 94° , even when crystallisation takes place under sterile conditions. It is probably through recrystallisation of a sample in this manner that infection of the laboratory was originally brought about.

These observations are of interest in connexion with the experiments of Biilmann (*Ber.*, 1909, **42**, 182, 1444) and Liebermann (*Ber.*, 1909, **42**, 1027, 4659) on the modifications of *allocinnamic acid*.*

3-Aminoquinoline is readily diazotised. The resulting diazonium salt couples in the normal manner with β -naphthol in alkaline solution, forming quinoline-3-azo- β -naphthol. The solution of the diazonium sulphate when heated evolves nitrogen, and on cooling deposits crystals of the sulphate of 3-hydroxyquinoline.

The salts which 3-aminoquinoline forms with one equivalent of acid

* References to the effects of inoculation have also been made by Miers and Isaac (*Proc. Roy. Soc.*, 1907, **79**, A, 328; *Min. Mag.*, 1908, **15**, 39) and by Baxter and Tilley (*Amer. Chem. J.*, 1909, **31**, 201).

are intensely yellow, both in the solid state and in solution. They also show strong, blue fluorescence in dilute solution. However, the salts of the 2-chloro-base are, on the other hand, quite colourless. Moreover, 3-aminoquinaldine has recently been described by Stark (*Ber.*, 1907, **40**, 3428), but it does not appear from his description that solutions of its salts are coloured, although he emphasises their intense fluorescence.

The base, therefore, shows fairly complete agreement in properties with the *Bz*-aminoquinolines, and the exceptional character of aminoquinolines with the amino-group in the pyridine ring seems to be confined, analogously to the derivatives of pyridine itself, to the 2- and 4-derivatives.

The closer study of the colour of the salts of the base has led to interesting results. If the effect of gradually adding acid to the solution of a fixed quantity of base is examined colorimetrically, and coefficients of extinction are plotted as ordinates against the equivalent proportions of hydrochloric acid present as abscissæ, remarkable curves are obtained, from which it appears that the intensity of the colour of the solutions is at a maximum at a point just beyond that at which the amount of hydrochloric acid corresponds with the composition $(C_9H_8N_2)_2.HCl$. Further addition of acid brings about a rapid diminution of colour, a minimum occurring when the composition of the normal salt, $(C_9H_8N_2)_2.HCl$, has been reached, the colour intensity then being only about 50 per cent. of that of the half-neutralised base. The explanation of this phenomenon that first suggests itself is that it is due primarily to the formation of complex salts in the solution of the type $(C_9H_8N_2)_2.HCl$. Since it was possible to obtain unmistakable evidence that such salts actually exist, we conclude that this explanation is the correct one.

We are not aware that the formation of complexes of this nature has been previously observed in the case of organic bases, although it is well known that hydroxylamine forms compounds of the kind, for example, $(NH_2OH)_2.HCl$ (Lossen, *Annalen*, 1871, **160**, 242), $(NH_2OH)_3.HI$ (Dunstan and Goulding, *Trans.*, 1896, **69**, 1839).

A somewhat similar phenomenon was observed by Baly and Miss Marsden in the case of alcoholic solutions of amino-aldehydes and -ketones of the aromatic series (*Trans.*, 1908, **93**, 2108).

EXPERIMENTAL.

Quinoline-3-carboxylic Acid.

The chloroquinolinecarboxylic acid, which may be regarded as forming the starting point in this investigation, was prepared in the manner indicated in the introduction.*

It was converted into quinoline-3-carboxylic acid by boiling it in quantities of 10 grams for two hours with hydriodic acid, D 1.7 (25 c.c.), red phosphorus (3 grams), and potassium iodide (3 grams). On cooling, an abundant crystallisation of the yellow hydriodide of the acid took place. This was collected and the filtrate concentrated, when a further crop of crystals was obtained. The hydriodide was decomposed by warming with an excess of aqueous potassium hydroxide, and the quinolinecarboxylic acid precipitated by acidifying with acetic acid. Some elimination of the carboxyl group apparently takes place during the reduction, since the filtrate always contains a little quinoline. The acid was purified by dissolving in hot dilute sulphuric acid, filtering from a little insoluble substance, which appears to be hydroxy-acid, and re-precipitating. The yield is about 75 per cent. of the theoretical. After recrystallising from alcohol, it formed a white solid, melting at 275°, and otherwise corresponding with the description given by previous investigators.

Quinoline-3-carboxamide.

On mixing the dry acid (10 parts) with phosphorus pentachloride (12 parts), both finely powdered, a considerable rise of temperature occurred, but no hydrogen chloride was evolved. After heating on the water-bath for an hour, the product was cooled and added in small quantities at a time to an ice-cold and nearly saturated solution of ammonia, when the amide separated as a white solid. After remaining an hour at the ordinary temperature, it was collected and recrystallised from hot water. The yield is about 80 per cent. of the theoretical.

The pure amide forms slender needles melting at 198—199°, and is fairly soluble in alcohol. It is readily hydrolysed on warming with sodium hydroxide to ammonia and quinoline-3-carboxylic acid :

0.1348 gave 19.6 c.c. N_2 (moist) at 20° and 755 mm. $N = 16.53$.

$C_{10}H_8ON_2$ requires $N = 16.28$ per cent.

* Friedländer and Göhring (*loc. cit.*) state that this compound melts at 200°. On account of the readiness with which it decomposes with carbon dioxide and chloroquinoline, it has no sharp melting point. Heated in the usual manner, it begins to soften at about 204°, darkens, and does not completely liquefy until nearly 240°.

3-Aminoquinoline.

A hypobromite solution was prepared by adding bromine (10 grams) to a cold solution of potassium hydroxide (50 grams) in water (950 c.c.). To this liquid the finely-powdered amide (11 grams) was slowly added with constant stirring. Nearly all dissolved, solution being completed by gently warming, after which the liquid was heated to 70° for a few minutes. The solution was then acidified with acetic acid, cooled, and filtered from a little dark-coloured precipitate. The filtrate was made strongly alkaline with sodium hydroxide, and extracted four times with chloroform (500 c.c.). The chloroform solution was dried with ignited sodium sulphate, evaporated, and the brown residue crystallised from toluene, when about 7.5 grams of the amine were obtained from each 11 grams of the amide. The amine was purified by distillation in a vacuum in an Anschütz flask and subsequent recrystallisation from toluene:

0.1800 gave 0.4919 CO₂ and 0.0905 H₂O. C = 74.53; H = 5.59.

0.1116 „ 18.6 c.c. N₂ at 19° and 758 mm. N = 19.55.

C₉H₈N₂ requires C = 75.00; H = 5.55; N = 19.44 per cent.

3-Aminoquinoline is a colourless, crystalline solid, slightly soluble in cold water. In hot water it is moderately soluble, and on cooling the amine separates first as an oil, but from dilute solutions it often forms slender, thread-like aggregations. It is readily soluble in ether, chloroform, or alcohol, and crystallises well from solution in aqueous alcohol or toluene.

The relationships between the two modifications of the base, melting at 94° and 84° respectively, have been described in the introduction (p. 743). To obtain the latter after the laboratory had become infected with the stable form, the flask containing the boiling toluene solution of the substance was heated up to the lip by the hot vapour and immediately closed by a cork pierced by a tube containing a long cotton-wool plug and a toluene seal, all heated to 110°. Experiments carried out less carefully occasionally failed.

The stable modification is easily obtained from solution in toluene in crystals of considerable size. The metastable form crystallises in rosettes of thin, prismatic plates. Both modifications have been examined crystallographically by Dr. G. F. Herbert Smith, of the British Museum, and the authors wish to express to him their best thanks. The following details are taken from his report.

Stable Modification.—The crystals have the form of flat plates, and belong to the sphenoidal class of the orthorhombic system. The large face was selected as the macropinakoid, and was made the pole of reference in all the measurements made:

$$a : b : c = 1.6350 : 1 : 0.9870.$$

Forms present : $a\{100\}$, $m\{110\}$, $b\{010\}$, $e\{011\}$, $d\{101\}$, $p\{111\}$, $r\{211\}$, d and r being rare.

Measurements from $a\{100\}$.

Form.	Calculated values.		Observed values.		No.	Limits of observations.	
	Azimuth.	Distance.	Azimuth.	Distance.		Azimuth.	Distance.
d (101)	90° 0'	58° 53'	*	58° 37'	1	—	—
e (011)	45 22½	90 0	*	*	5	45° 12'—45° 30'	90° 15'
p (111)	—	66 45½	—	66 43	5	—	66° 30'—67° 0'
r (211)	—	49 20	—	49 14	1	—	—
b (010)	0 0	90 0	*	*	—	—	—
m (110)	—	58 33	—	*	17	—	57 54—58 51

There is a distinct cleavage parallel to $b\{010\}$. If a cleavage plate is examined in convergent light, an interference figure of the biaxial type is seen, and the acute bisectrix is therefore at right angles to $b\{010\}$. The sign of the birefringence is negative, and the plane of the optic axes is parallel to the base $\{001\}$, the obtuse bisectrix being therefore at right angles to the large face $a\{100\}$. Refractive indices : α 1.535, β 1.873, γ 1.893, $2E = 40^\circ\text{Li}$, 45°Na , 50°Ti (observed).

Metastable Modification.—Crystalline system.—Monoclinic :

$$a : b : c = 2.2130 : 1 : 1.2889 ; \beta = 90^\circ.$$

Forms present : $\{100\}$, $\{101\}$, $\{110\}$, $\{\bar{2}03\}$.

The following approximate measurements were obtained :

100 : 101	59° 47'	(5)	
100 : 110	65 41	(3)	
102 : $\bar{2}03$	68°—70°		(68° 47') calc.

If the large face is examined in convergent light, an interference figure, which is probably that at right angles to the acute bisectrix, is seen on the edge of the field. If this direction is the acute bisectrix, the plane of the optic axes is parallel to the edge of the prism, the axial angle is very large, and the double refraction is negative in character. The bisectrix makes an apparent angle of 40° with the normal to the large face in the obtuse angle between the latter and the normal to the second prism form.

For comparison with the stable form, the axes b and c should be interchanged, giving the ratio $a : b : c = 1.7170 : 1 : 0.7759$.

3-Aminoquinoline forms colourless solutions, which exhibit a slight blue fluorescence. This becomes much more intense on the addition of an acid, even carbonic, and the solution turns yellow.

Salts of 3-Aminoquinoline.

The *monohydrochloride*, $C_9H_8N_2.HCl$, is precipitated on passing hydrogen chloride into an alcoholic solution of the base, or on dissolving the base in an equivalent of 3*N*-hydrochloric acid, adding another equivalent of strong acid, and allowing to remain. It is most

conveniently analysed by titration with *N*/10-sodium hydroxide solution, the end point being sharply indicated by the disappearance of the colour and the strong fluorescence:

0.1850 required 10.3 c.c. *N*/10-NaOH. $\text{HCl} = 20.30$.

$\text{C}_9\text{H}_8\text{N}_2, \text{HCl}$ requires $\text{HCl} = 20.20$ per cent.

The *dihydrochloride*, $\text{C}_9\text{H}_8\text{N}_2, 2\text{HCl}$, was obtained by the addition of a large excess of alcoholic hydrogen chloride to an alcoholic solution of the amine. The salt had a pale yellow colour, due probably to the presence of a little monohydrochloride, as is indicated by the analysis:

0.1968 required 17.7 c.c. *N*/10-NaOH. $\text{HCl} = 32.74$.

$\text{C}_9\text{H}_8\text{N}_2, 2\text{HCl}$ requires $\text{HCl} = 33.58$ per cent.

The *platinichloride*, $(\text{C}_9\text{H}_8\text{N}_2)_2, \text{H}_2\text{PtCl}_6$, separates as a heavy yellow precipitate when a solution of platinic chloride is added to one of the hydrochloride of the base containing an excess of hydrochloric acid. A specimen of the salt dried at the ordinary temperature did not lose weight on heating at 100° :

0.4044 gave 0.1124 Pt. $\text{Pt} = 27.79$.

$(\text{C}_9\text{H}_8\text{N}_2, \text{HCl})_2\text{PtCl}_4$ requires $\text{Pt} = 27.91$ per cent.

The *picrate*, $\text{C}_9\text{H}_8\text{N}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, is a sparingly soluble, bright yellow salt, which readily dissociates in solution. It is best obtained by dissolving the amine in aqueous alcohol and adding a slight excess of picric acid. Specimens of the picrate, dried in a vacuum, were analysed by reduction with a standard solution of titanium chloride (Knecht and Hibbert, *Ber.*, 1903, 36, 1554):

0.0508 contained 0.0312 $\text{C}_6\text{H}_3\text{O}_7\text{N}_3 = 61.38$.

$\text{C}_9\text{H}_8\text{N}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}_6\text{H}_3\text{O}_7\text{N}_3 = 61.40$ per cent.

The *chromate*, $2\text{C}_9\text{H}_8\text{N}_2, \text{H}_2\text{CrO}_4$, is obtained as a deep yellow precipitate on the addition of potassium chromate to a solution of the acetate of the base. It is slightly soluble in cold water, and undergoes some decomposition when the solution is heated:

0.4266 gave 0.1282 Cr_2O_3 . $\text{CrO}_3 = 39.53$.

$2\text{C}_9\text{H}_8\text{N}_2, \text{H}_2\text{CrO}_4$ requires $\text{CrO}_3 = 39.55$ per cent.

The Colour of Solutions of Salts of 3-Aminoquinoline.

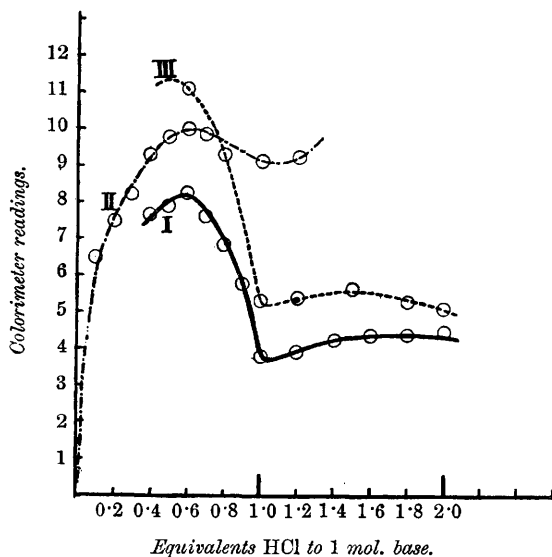
The interesting variations of colour intensity which are brought about by the gradual addition of acid to a fixed quantity of the base were studied in the following manner.

Measured quantities of a 6*N*-solution of hydrochloric acid were added to a solution of the amine containing 1.73 grams in 30 c.c. (which formed a column about 12 cm. high when placed in one of the cylindrical tubes of a colorimeter). After each addition of acid, the colour of the resulting solution was matched by adjusting the depth

of a standard solution (generally containing 3.24 grams of the amine and 0.55 gram of hydrogen chloride in 40 c.c. of water). In the accompanying diagram, the curves show the heights of the adjustable column required to give a match with the colour produced from the fixed quantity of base by the addition of different quantities of acid.

The continuous curve (I) was obtained by using an aqueous solution and matching the colour immediately after each addition of acid, the whole series of observations occupying one to two hours. It was found, however, that the colour intensity changes on standing, and

FIG. 1.



- I. Aqueous solution—initial values.
 II. Solution in aqueous alcohol—final values.
 III. Aqueous solution—final values.

that equilibrium is only reached after two or three days. Another series of observations was therefore made with an exactly similar solution, but after each addition of acid it was kept until the colour change was complete. The dotted curve (III) gives the colour values finally attained. In neither case were the observations carried beyond the point at which 2 equivalents of acid were present, as, owing to alteration of tint, matching became difficult and uncertain. It was further observed that on the ascending limb of the curve the colour deepens with time, whilst on the descending limb it diminishes. Owing to the fact that nearly 0.4 equivalent of acid is necessary to

keep the base in solution at the ordinary temperature when water is used as solvent, readings corresponding with smaller proportions of acid could not be obtained with aqueous solutions. In order to gain some idea of the form of this part of the curve, a mixture of alcohol (1 vol.) and water (3 vols.) was used as solvent, it being then possible to obtain solutions of the above concentration with only 0.1 equivalent of acid present. The dot and dash curve (II) refers to such a solution, and gives the colour values finally attained. It is by no means continuous with curve (III), the presence of alcohol diminishing the colour intensity when the quantity of acid present falls short of that corresponding with the mono-acid salt and increasing it when the acid exceeds this amount. By using a solution of the base in absolute alcohol, much lower readings are obtained for the same amounts of acid present, although the maximum at the half equivalent is still apparent.

The most striking feature of these curves is the intensity of colour at the half equivalent of acid. This suggests that a semihydrochloride is present in the solution at this point. If this is so, then the base, although very sparingly soluble in water at 0°, should readily dissolve in a dilute solution of its monohydrochloride at that temperature. This is actually the case, more than a molecular proportion of base dissolving in a 0.11*N*-solution of its hydrochloride, as will be seen from the table below. Moreover, if a compound is formed, then the freezing point of the solution should remain approximately unaltered, since no marked change in the extent of ionisation is to be anticipated. The table shows the freezing points of a solution of 0.073 gram of hydrogen chloride in 17.3 grams of water, to which 3-aminoquinoline was added in increasing amounts :

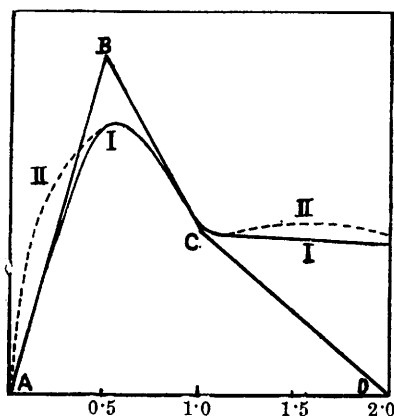
Weight (gram) of base in solution.	Equiv. of base to 1 equiv. acid.	Freezing point.
0.000	0.00	-0.437°
0.130	0.45	0.406
0.195	0.68	0.370
0.273	0.95	0.322
(Interpolated)	1.00	0.320
0.563	1.95	0.332
(Interpolated)	2.00	0.333
0.727	2.52	0.342

The depression of freezing point diminishes up to the point corresponding with the monohydrochloride, due doubtless to the smaller ionisation of this salt compared with that of hydrochloric acid. Beyond this point, although the quantities of base in solution would, if no further combination took place, produce further depressions of 0.216° and 0.337°, the actual increases in the depressions observed are only 0.010° and 0.020° respectively. The base therefore dissolves in the solution of its hydrochloride to form some compound.

This can hardly be other than the semihydrochloride, and we conclude that it is to the intensity of the colour of this salt, $(C_9H_8N_2)_2.HCl$, present in the solution that the maximum of colour near 0.5 equivalent of hydrochloric acid is due.*

On the hypothesis that the base forms a deeply coloured semihydrochloride, a paler monohydrochloride, and a colourless dihydrochloride, the colour intensities of the two former being represented by *B* and *C* (Fig. 2), the colour curve would consist of the straight lines *A B C D*, provided that no dissociation of the various compounds took place. The dissociation which occurs would result in a rounding of the angles so as to produce a curve of the type (I), the first portion of which is easily shown to be a hyperbola with asymptotes parallel to

FIG. 2.



A B and *B C*. The form of the actual curve, as indicated by the dotted line (II), differs from this mainly in two respects. In the first place, the colour produced by small amounts of acid (less than 0.25 equivalent) is much greater than can be accounted for on the above hypothesis. There are, however, strong indications of the existence of more highly basic salts than the semihydrochloride; for, from the figures given in the above table of freezing points, it will be seen that it is possible to prepare a solution containing as much as $2\frac{1}{2}$ equivalents of base to 1 of acid, and that the excess of base produces no corresponding

* It should be pointed out that these effects are not confined to the hydrochloride. An experiment carried out with the sulphate gave a colour curve reproducing the main features of that of the hydrochloride, although differing somewhat in the relative values at different points of the curve. It was also found that the base dissolved in an equivalent quantity of the *N*/10-solution of the sulphate without producing any marked effect on its freezing point.

effect on the freezing point. It may therefore well be that this large initial development of colour is due to the formation of still more complex and more highly coloured salts, such as $(C_9H_8N_2)_3HCl$. The second point to be explained is the rise in colour brought about by the addition of acid to the solution of the monohydrochloride, when a diminution might rather have been expected through the production of some of the colourless dihydrochloride. However, any diminution from this cause would be slight and easily masked, since the second basic group, as is usually the case in a di-acid base, seems to be very weak, and it requires a very large excess of acid indeed to decolorise completely a solution of the hydrochloride. The deepening of the colour on this part of the curve, we believe, may be possibly referred to the effect of the excess of hydrochloric acid in repressing the ionic dissociation of the hydrochloride. Sidgwick and Tizard (Trans., 1908, 93, 194) have shown that non-ionised or half-ionised copper acetate is more deeply coloured than the copper ion. It is possible that similar relationships hold in this case, since it was found that addition of sodium chloride to the solution of the monohydrochloride of the base produced a deepening of colour similar to that brought about by the addition of acid. Thus by the addition of two molecular proportions of sodium chloride to such a solution, the colorimeter reading was raised from 5.2 to 5.7. Moreover, the less ionised sulphate is distinctly more highly coloured than the hydrochloride on this part of the curve.

It may be pointed out that the possibility of the formation of complex salts of this nature has some practical bearing on the question of the determination of the strength of organic bases by measurement of the amount of acid set free from the normal salt by hydrolytic dissociation in dilute aqueous solutions. Such methods involve the assumption that the amount of free base present is equivalent to that of the free acid. If, however, there is a possibility that an appreciable proportion of the base set free by hydrolysis may enter into combination with the ion of the normal salt, there will be a corresponding increase in the amount of free hydrochloric acid, and the hydrolytic dissociation constant calculated on the above assumption may be considerably in excess of the actual value.

3-Acetylaminquinoline.

This derivative was readily obtained by boiling the amine for five minutes with acetic anhydride. The product was then poured into water, when a white, crystalline substance soon separated. The acetyl derivative so obtained, after recrystallising from hot water, melted at 166—167°. It was soluble in dilute acids with the formation of colourless solutions :

0.1126 gave 14.15 c.c. N_2 at 14° and 770 mm. $N = 15.22$.

$C_{11}H_{10}ON_2$ requires $N = 15.06$ per cent.

Quinoline-3-azo- β -naphthol.

A solution of 3-aminoquinoline in dilute acid appeared to behave normally when treated with sodium nitrite (see 3-hydroxyquinoline, below). In order to show that a diazonium salt had been formed, the solution was added to an alkaline solution of β -naphthol. A deep red precipitate was formed, which was collected, crystallised from glacial acetic acid, and dried in a vacuum. As thus obtained, quinoline-3-azo- β -naphthol is a dark crimson powder, melting at 185 — 186° :

0.1272 gave 15.15 c.c. N_2 at 17° and 764 mm. $N = 14.18$.

$C_{19}H_{13}ON_3$ requires $N = 14.05$ per cent.

3-Hydroxyquinoline.

3-Aminoquinoline (1 mol.) was dissolved in dilute sulphuric acid (3 equiv.), cooled in ice, and to the solution was added a cold solution of sodium nitrite until the reaction was complete. No evolution of gas occurred even when kept for some time at the ordinary temperature. When the solution was warmed to about 50° , a brisk evolution of nitrogen took place, and a slightly turbid liquid was obtained. After some time, the solution deposited tufts of brown crystals of 3-hydroxyquinoline sulphate. These were purified by dissolving in hot water, boiling with a little animal charcoal, filtering, and leaving to crystallise.

The phenol itself was obtained by dissolving the sulphate in hot water, and adding a slight excess of sodium bicarbonate, when a white precipitate was formed. This was collected, dried, and crystallised from toluene or aqueous alcohol. A specimen so prepared, after drying at 120° , melted at 198° , and gave the following results on analysis:

0.1319 gave 0.3634 CO_2 and 0.0574 H_2O . $C = 75.13$; $H = 4.85$.

0.1566 „ 13.0 c.c. N_2 at 19° and 763 mm. $N = 9.80$.

C_9H_7ON requires $C = 74.48$; $H = 4.83$; $N = 9.65$ per cent.

3-Hydroxyquinoline forms colourless crystals, melting at 198° . It is nearly insoluble in cold water, but dissolves much more readily in hot water or cold alcohol. It is not very soluble in chloroform or ether, but dissolves freely in hot benzene, toluene, or xylene, from which solvents it crystallises well. The phenol is also dissolved by aqueous solutions of alkalis and acids, and exhibits faint fluorescence in the latter solutions. Aqueous solutions of 3-hydroxyquinoline or its salts give a brownish-red colour with ferric chloride.

3-Hydroxyquinoline sulphate is obtained as an intermediate product in the preparation of the phenol or by dissolving the latter in hot dilute sulphuric acid and allowing to cool, when the sparingly soluble sulphate crystallises out. Specimens obtained by both methods were analysed, with results stated below.

The sulphate is a slightly yellow, crystalline substance, containing two molecular proportions of water of crystallisation. It melts and decomposes at 190—192°, sulphur dioxide being evolved, and a yellow sublimate, melting at 186—190° (probably 3-hydroxyquinoline), being formed :

(a) 0.1454 gave 0.0800 BaSO₄. H₂SO₄ = 23.11.

(b) 0.2428 „ 0.1332 BaSO₄. H₂SO₄ = 23.04.

(C₉H₇ON)₂.H₂SO₄.2H₂O requires H₂SO₄ = 23.11 per cent.

2-Chloroquinoline-3-carboxamide.

The product of interaction of phosphoryl chloride and carbostyryl-3 carboxylic acid when added to an ice-cold and nearly saturated solution of ammonia reacts readily. After keeping for an hour and then heating, a clear solution is obtained, from which the amide separates on cooling. By recrystallising from hot water, the product may be obtained as a white solid melting at 200—201° :

0.2916 gave 0.2024 AgCl. Cl = 17.16.

C₁₀H₇ON₂Cl requires Cl = 17.17 per cent.

2-Chloro-3-aminoquinoline.

The powdered chloroamide (1 part), obtained as above described, was added to a cold solution of hypobromite (prepared by adding 1 part of bromine to 4.2 parts of potassium hydroxide in 75 parts of water). Solution took place on stirring, and the liquid was then heated to 70°. On adding acetic acid, the base separated as a precipitate, which was collected and crystallised from aqueous alcohol. About 85 per cent. of the calculated yield was obtained. The base was obtained in colourless crystals melting at 168° by recrystallising from toluene :

0.2227 gave 0.1782 AgCl. Cl = 19.77.

C₉H₇N₂Cl requires Cl = 19.86 per cent.

2-Chloro-3-aminoquinoline is readily soluble in alcohol or chloroform, less so in ether or benzene. It appears to be but feebly basic, slowly dissolving in dilute acids on warming. On adding sodium nitrite to the cold acid solution, a product is obtained which gives a crimson dye when added to an alkaline solution of β-naphthol. The amine, therefore, seems to be normally diazotised.

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