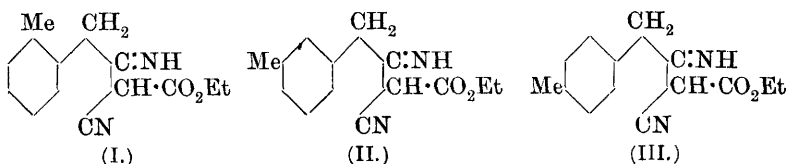


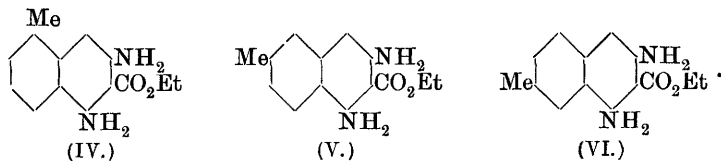
XXXIII.—*The Formation and Reactions of Imino-compounds. Part VIII. The Formation of Methyl Derivatives of 2-Phenyl-1:3-naphthylenediamine from the Three Tolylacetonitriles.*

By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

In a former communication (Trans., 1907, 91, 1687) dealing with the behaviour of ethyl β -imino- α -cyano- γ -*o*-tolylbutyrate (I), ethyl β -imino- α -cyano- γ -*m*-tolylbutyrate (II), and ethyl β -imino- α -cyano- γ -*p*-tolylbutyrate (III) towards cold concentrated sulphuric acid, it was shown



that the position of the methyl group exerted a remarkable effect on their transformation into ethyl 1-methyl-5:7-naphthylenediamine-6-carboxylate (IV), ethyl 2-methyl-5:7-naphthylenediamine-6-carboxylate (V), and ethyl 2-methyl-6:8-naphthylenediamine-7-carboxylate (VI) respectively.



Thus from the *ortho*- (I) and *para*- (II) derivatives only a small yield of the corresponding naphthalene derivatives was obtained, whereas the transformation of the *meta*-compound (III) was almost

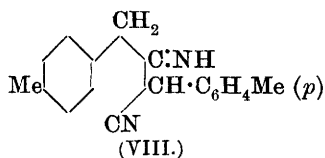
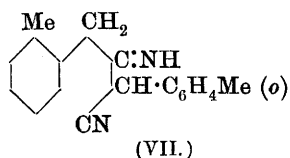
quantitative. It was suggested at the time (*loc. cit.*, p. 1695) that, as regards the ortho- and para-imino-nitriles, it was evidently the meta-position of the methyl group, with respect to the carbon atom at which ring formation was bound to ensue, which exerted a hindering effect on the formation of the naphthalene ring; because in the case of the meta-derivative, in which ring formation was proved to take place at the carbon atom in the para-position with respect to the methyl group, no hindrance was apparent. In order to gain further evidence on this point, we have therefore studied the intramolecular condensation of the three tolylacetonitriles (compare *Trans.*, 1907, 91, 1282), and have obtained β -imino- α -cyano- $\alpha\gamma$ -di-*o*-tolylpropane (VII), β -imino- α -cyano- $\alpha\gamma$ -di-*m*-tolylpropane (VIII), and β -imino- α -cyano- $\alpha\gamma$ -di-*p*-tolylpropane (XI).

During the preparation of these compounds it was at once apparent that the presence of the methyl group in the three tolylacetonitriles also exerted a marked effect on the formation of the imino-nitriles.

The same influence had been noticed in the condensation of the three tolylacetonitriles with ethyl cyanoacetate (*Trans.*, 1907, 91, 1687), for in these cases it was found that, whereas the *o*- and *p*-tolylacetonitriles gave a yield of about 40 per cent. of the condensation products, *p*-tolylacetonitrile gave as much as 60—65 per cent. of the theoretical amount.

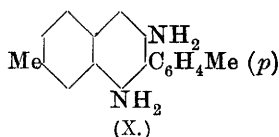
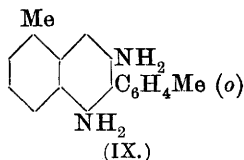
In just the same way *p*-tolylacetonitrile undergoes almost complete intramolecular condensation, and scarcely any unchanged nitrile can be recovered from the product, whilst under the most favourable conditions the imino-nitriles from *o*- and *m*-tolylacetonitrile cannot be obtained in yields greater than 35—40 per cent. of the theoretical quantity.

The hindering influence of the position of the methyl group on the formation of the naphthalene ring when this group is in the meta-position with respect to the carbon atom at which ring formation must ensue is again clearly indicated by the behaviour of the three β -imino- α -cyano- $\alpha\gamma$ -ditolylpropanes towards concentrated sulphuric acid; thus, β -imino- α -cyano- $\alpha\gamma$ -di-*o*-tolylpropane (VII) and β -imino- α -cyano- $\alpha\gamma$ -di-*p*-tolylpropane (VIII), compounds in which ring formation

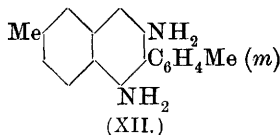
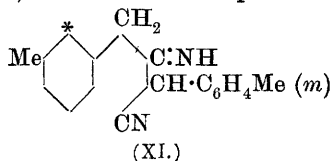


has to take place in the meta-position with respect to the methyl group, yield, on treatment with sulphuric acid, scarcely 10 per cent. of the theoretical quantity of 6-*o*-tolyl-1-methyl-5:7-naphthylene-

diamine (IX) and 7-*p*-tolyl-2-methyl-6:8-naphthylenediamine (X) respectively.

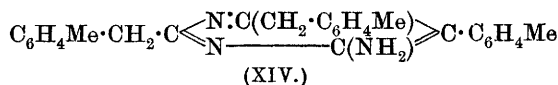
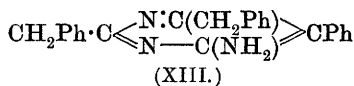


On the other hand, β -imino- α -cyano- γ -di-*m*-tolylpropane (XI) gives as much as 80 per cent. of 6-*m*-tolyl-2-methyl-5:7-naphthylenediamine (XII) under the same experimental conditions.



The ring formation in this case is represented as taking place in the para-position with respect to the methyl group in the benzene ring, although it is, of course, possible that it might ensue in the ortho-position to this group, marked in the above formula by an asterisk. The point was dealt with in a former paper (Trans., 1907, **91**, 1692) regarding the transformation of ethyl β -imino- α -cyano- γ -*m*-tolylbutyrate into ethyl 2-methyl-5:7-naphthalenediamine-6-carboxylate, and the position of the methyl group was proved by the oxidation of the naphthalene derivative to 4-methylphthalic acid by means of chromic acid. The formation of the same acid from the base derived from β -imino- α -cyano- γ -di-*m*-tolylpropane under the same experimental conditions clearly showed the correctness of the formula given above.

During the course of this investigation considerable quantities of the methyl derivatives of pyrimidine, analogous to cyanbenzylidine, have been isolated. Cyanbenzylidine (6-amino-5-phenyl-2:4-dibenzylpyrimidine) (XIII) is formed when phenylacetonitrile is treated either in alcoholic solution with sodium ethoxide or in xylene solution with metallic sodium (compare Trans., 1906, **89**, 1931; 1907, **91**, 1287), and in the same way the three 6-amino-5-tolyl-2:4-dimethylbenzylpyrimidines of the general formula (XIV) have been isolated.



The intramolecular condensations of the three nitriles were carried

out both in xylene solution by means of "molecular" sodium and in alcohol solution in the presence of sodium ethoxide, but in the former case a small quantity of alcohol was added to the xylene, since it had been found (Trans., 1908, 93, 176) that the presence of traces of sodium ethoxide materially increases the quantities of imino-nitrile formed.

The pyrimidine derivative is produced to a very much greater extent in the alcohol experiment than in xylene, and is usually separated in a crystalline condition from the solution on cooling. On the other hand, the xylene experiment yields the larger quantity of imino-nitrile, but scarcely any of the pyrimidine derivative.

It is worthy of note that, whereas the pyrimidine derivatives are formed in considerable quantities from *o*- and *p*-tolylacetoneitrile, *m*-tolylacetoneitrile yields only a very small quantity of this substance.

EXPERIMENTAL.

The Intramolecular Condensation of the Three Tollylacetoneitriles.

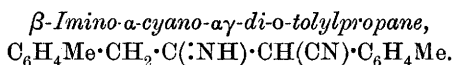
The imino-nitriles from the three tolylacetoneitriles can be prepared either by the action of "molecular" sodium on a xylene solution of the tolylacetoneitrile containing a trace of alcohol, or by the action of sodium ethoxide on an alcoholic solution of the nitrile. Since the methods adopted were the same in the case of the three nitriles, it will be sufficient to describe the details of the processes once only.

In Xylene Solution.—5.7 Grams of sodium were melted under a little xylene contained in a small flask, and brought to a fine state of division by shaking. The xylene was then poured off, the finely-divided sodium washed with dried xylene, and finally mixed with 75 c.c. of the hydrocarbon containing 1 c.c. of ethyl alcohol. Sixty-five grams of the tolylacetoneitrile were then added, and the mixture was heated on the water-bath until all sodium had passed into solution. Water was then added, and, after having been acidified by means of acetic acid, the whole was distilled in a current of steam until all xylene and unchanged tolylacetoneitrile had passed over. The residue was extracted with ether, the ethereal solution vigorously shaken with dilute hydrochloric acid to remove the pyrimidine derivative, then with dilute sodium carbonate solution, and finally dried and evaporated. The imino-nitrile was further purified by distillation under diminished pressure.

In Alcohol Solution.—5.7 Grams of sodium were dissolved in 70 grams of alcohol, and the solution mixed with 65 grams of the tolylacetoneitrile, the mixture being heated on the water-bath for two hours. In spite of the fact, already mentioned, that the three tolylacetoneitriles condense with themselves with varying degrees of

readiness, it was not found possible to increase the yield by prolonging the above reaction, since in all three cases further heating merely led to the "alcoholysis" of the unchanged nitrile with the formation of ethylamine. The alcoholic solution, after being heated for the above length of time, deposited in all three cases a quantity of the crystalline pyrimidine derivative on cooling. This was collected by filtration, and the alcoholic solution, after being mixed with water and acidified with acetic acid, was distilled in a current of steam until all unchanged tolylacetonitrile had passed over. The residue was then extracted with ether, the ethereal solution washed with dilute hydrochloric acid to remove any remaining pyrimidine derivative, and then with dilute sodium carbonate, being finally dried and distilled free from ether. The imino-nitrile was purified by distillation under diminished pressure.

Of the two methods, that carried out in xylene solution is to be recommended if the imino-nitrile is the product desired, since less of the pyrimidine derivative is formed under these conditions, and the end-point of the reaction is easily ascertained by the fact that all sodium has passed into solution; moreover, there is little or no tendency for the unchanged nitrile to "alcoholyse" under the conditions of the experiment. If, however, the pyrimidine derivative is desired, the method involving the use of alcoholic sodium ethoxide is the most suitable.



The crude imino-nitrile, prepared by either of the above processes, is a viscid liquid which, on rapid distillation, yields a fraction boiling at 270—280°/18 mm. :

0.1922 gave 0.5793 CO₂ and 0.1211 H₂O. C = 82.20 ; H = 7.0.

C₁₈H₁₈N₂ requires C = 82.4 ; H = 6.9 per cent.

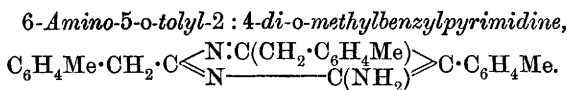
The compound is a thick syrup which shows no signs of solidifying. Its constitution was proved by the following experiment : Five grams of the imino-nitrile were added to an alcoholic solution of one and a-half times the calculated quantity of potassium hydroxide, and the solution boiled on the water-bath until the odour of ammonia was no longer apparent. Water was then added and the alcohol evaporated, when the solution, on being acidified, gave a crystalline precipitate which, when recrystallised from water, yielded long needles melting at 88° :

0.1876 gave 0.4937 CO₂ and 0.1167 H₂O. C = 71.78 ; H = 6.91.

C₉H₁₀O₂ requires C = 72.00 ; H = 6.7 per cent.

The compound is therefore *o*-tolylacetic acid, C₆H₄Me·CH₂·CO₂H.

The yield of the pure imino-nitrile represented 40 per cent. of the theory. It was thought that the low-boiling fraction, which distilled fairly constantly at 235—240°/18 mm., might contain the ketone corresponding with the imino-nitrile. This substance might be expected to have been formed during the process of the condensation, since in the analogous experiment with phenylacetoneitrile under similar conditions considerable quantities of α -cyanodibenzyl ketone were isolated. No crystalline product, however, could be obtained from the low-boiling fraction, and the amount of substance at our disposal was too small for an extended investigation.



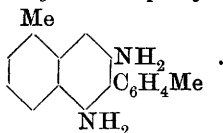
This substance is precipitated in a crystalline condition during the process of the condensation of *o*-tolylacetoneitrile by means of alcoholic sodium ethoxide, and can be obtained by filtering the solution before distilling in steam. It is, moreover, recovered in the xylene experiment on washing an ethereal solution of the product, after steam distillation, with dilute hydrochloric acid. During this process the hydrochloride of the pyrimidine derivative, which is insoluble in dilute hydrochloric acid, forms a third layer in the separating funnel midway between the ethereal solution and the aqueous layer. It can, therefore, be readily separated and converted into the free base by warming on the water-bath with dilute sodium carbonate solution. The pyrimidine derivative obtained in this way separates from alcohol in small, colourless needles melting at 140—141°:

0.1835 gave 0.5540 CO_2 and 0.1144 H_2O . $\text{C} = 82.35$; $\text{H} = 6.92$.

$\text{C}_{27}\text{H}_{27}\text{N}_3$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The base is similar in its properties to cyanbenzylamine, and when treated with concentrated hydrochloric acid forms a gummy hydrochloride which could not be obtained crystalline.

6-o-Tolyl-1-methyl-5:7-naphthylenediamine,



In order to prepare this substance, five grams of β -imino- α -cyano- α -di-*o*-tolylpropane were mixed with 30 grams of cold concentrated sulphuric acid, and the dark red solution was kept at the ordinary temperature for five minutes. On pouring the strongly acid solution

on ice, a small quantity of a bulky precipitate separated, which was filtered and the clear filtrate rendered alkaline with ammonia. The oil which separated set to a resin on cooling, and when crystallised from methyl alcohol yielded colourless plates melting at 136° :

0.1845 gave 0.5569 CO_2 and 0.1184 H_2O . $\text{C} = 82.3$; $\text{H} = 7.1$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The base is readily soluble in ethyl and methyl alcohol, benzene or chloroform, and sparingly so in light petroleum (b. p. $60\text{--}70^{\circ}$), from which solvent it can, however, be crystallised. It rapidly becomes coloured red on exposure to the air, and is obtained in yields amounting to about 10 per cent. of the theory. The other products of the reaction are the bulky precipitate already mentioned, due evidently to the presence of some α -cyano-di-*o*-methyldibenzyl ketone in the imino-compound used, and a phenolic base, which is precipitated with the naphthalene derivative, but is insoluble in methyl alcohol.

This compound is evidently analogous to the similar compounds obtained in the transformation of ethyl β -imino- α -cyano- γ -*o*-tolylbutyrate and ethyl β -imino- α -cyano- γ -*p*-tolylbutyrate into the corresponding naphthalene derivatives (compare Trans., 1907, 91, 1694); their constitutions have not yet been determined.

The *dihydrochloride*, $\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$, is precipitated on adding concentrated hydrochloric acid to a cold solution of the base in alcohol. It forms colourless plates from concentrated hydrochloric acid:

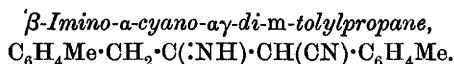
0.2178 gave 0.1849 AgCl . $\text{Cl} = 21.00$.

$\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 21.19$ per cent.

The *diacetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{N}_2(\text{Ac})_2$, is prepared by the action of acetyl chloride on the base. One gram was boiled with acetyl chloride on the water-bath until all had passed into solution, when excess of chloride was removed by evaporation. The diacetyl derivative remained as a colourless, gummy mass, which became solid on rubbing with alcohol. On recrystallisation from alcohol, it formed microscopic needles melting at 245° :

0.1901 gave 0.5303 CO_2 and 0.1095 H_2O . $\text{C} = 76.07$; $\text{H} = 6.4$.

$\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{C} = 76.3$; $\text{H} = 6.3$ per cent.



When prepared by either of the methods given on page 264, this imino-nitrile is a viscid oil, which, when rapidly distilled, gives a principal fraction boiling at $275\text{--}280^{\circ}/18\text{ mm.}$:

0.1762 gave 0.5309 CO_2 and 0.1115 H_2O . $\text{C} = 82.17$; $\text{H} = 7.03$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

As in the case of its isomeride, this substance is a viscid, colourless oil which could not be obtained crystalline. In order to prove its constitution, 5 grams were dissolved in alcohol and added to an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, the mixture being heated on the water-bath until the odour of ammonia ceased to be apparent. The solution was then freed from alcohol by evaporation, and acidified by means of hydrochloric acid. The resulting white precipitate yielded colourless needles melting at 61° when recrystallised from water:

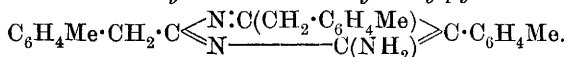
0.2011 gave 0.5294 CO_2 and 0.1229 H_2O . $\text{C} = 71.82$; $\text{H} = 6.79$.

$\text{C}_9\text{H}_{10}\text{O}_2$ requires $\text{C} = 72.00$; $\text{H} = 6.7$ per cent.

The compound is therefore *m*-tolylacetic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

The yield of the imino-nitrile is about the same as in the case of the ortho-derivative, being about 38 per cent. of the theory. Only a small quantity of low-boiling fraction was obtained, from which, however, no definite product could be isolated.

6-Amino-5-m-tolyl-2 : 4-di-m-methylbenzylpyrimidine,



This compound is formed with very much less readiness than either the ortho- or para-derivative. A small quantity is precipitated in a crystalline condition during the intramolecular condensation of *m*-tolylacetoneitrile in the presence of sodium ethoxide, and a further quantity can be obtained on washing the product from the "xylene" experiment with dilute hydrochloric acid. The base derived from the latter experiment was, however, always obtained as a viscid oil which showed no tendency to crystallise, and it was only after some crystals had been obtained in the "alcohol" experiment, which started crystallisation when added to the oil, that it could be induced to solidify. The compound crystallises from alcohol in small needles melting at 147° , but it will only separate in the crystalline form when a crystal is present; in fact, the compound exhibits very little tendency to crystallise:

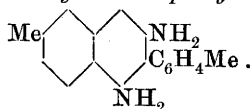
0.1834 gave 0.5549 CO_2 and 0.1136 H_2O . $\text{C} = 82.52$; $\text{H} = 6.88$.

$\text{C}_{27}\text{H}_{27}\text{N}_3$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The base shows the characteristic property of these compounds, namely, when mixed with concentrated hydrochloric acid it at once becomes gummy.

The *hydrochloride*, $\text{C}_{27}\text{H}_{27}\text{N}_3\cdot\text{HCl}$, can be obtained in a crystalline condition by adding concentrated hydrochloric acid to a cold solution of the base in alcohol, when it separates after some time in colourless needles.

6-m-Tolyl-2-methyl-5 : 7-naphthylenediamine,



This base, which is formed in larger yields than either the ortho- or para-derivatives, is best prepared in the following way: Five grams were added to well-cooled concentrated sulphuric acid, and the dark-coloured solution was allowed to remain at the ordinary temperature for ten minutes. At the end of this time, it was poured on ice, and the solution freed from a small quantity of insoluble matter by filtration. The clear solution on being rendered alkaline with ammonia, deposited an oil which set to a resin on cooling. Although readily soluble in methyl alcohol, the compound could not be separated in a crystalline condition, and it was only after the solution had remained for some weeks that crystals were ultimately obtained. The base forms slightly coloured, small plates melting at 143° :

0.1853 gave 0.5577 CO_2 and 0.1172 H_2O . $\text{C} = 82.07$; $\text{H} = 7.02$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The compound rapidly becomes coloured red on exposure, and is obtained in yields of about 80 per cent. It is the most difficult to obtain crystalline of all the bases of this type yet investigated; 2-phenyl-1 : 3-naphthylenediamine itself, as well as the methyl derivatives described in this communication, are all precipitated in a resinous condition, but, excepting the meta-compound mentioned above, they can all easily be obtained in a crystalline form. For working with these compounds it is not, however, necessary to use the crystalline substance, since the resins are quite pure if they are obtained by adding water to a clear alcoholic solution of the base.

The resin when set can be ground to a powder and dried in just the same way as a crystalline solid. The following analysis of the resin derived from the meta-compound in this way illustrates the above point:

0.1747 gave 0.5262 CO_2 and 0.1107 H_2O . $\text{C} = 82.13$; $\text{H} = 7.04$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The *dihydrochloride*, $\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$, can be obtained in white, microscopic needles on dissolving the base in concentrated hydrochloric acid and keeping the solution for some time:

0.2135 gave 0.1811 AgCl . $\text{Cl} = 20.99$.

$\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 21.19$ per cent.

The *diacetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{N}_2(\text{Ac})_2$, can be prepared by boiling the base with acetyl chloride until all has dissolved, and then

evaporating the excess of chloride on the water-bath. The diacetyl derivative remains as a colourless gum, which, when dissolved in alcohol and the solution diluted with water, yields colourless needles melting at 235° :

0.1861 gave 0.5195 CO_2 and 0.1876 H_2O . $\text{C} = 76.14$; $\text{H} = 6.40$.

$\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{C} = 76.3$; $\text{H} = 6.3$ per cent.

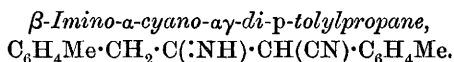
Oxidation of 6-m-tolyl-2-methyl-5 : 7-naphthylenediamine to 4-Methylphthalic Acid.—This oxidation was carried out in order to establish the constitution of this naphthalene derivative, since, although it was very probable that ring formation would ensue in the para-position with respect to the methyl group in the same way as in the case of ethyl β -imino- α -cyano- γ -m-tolylbutyrate (Trans., 1907, **91**, 1705), yet it was possible that in the present case ring formation might take place in the ortho-position with respect to the methyl group with the formation of 7-m-tolyl-1-methyl-6 : 8-naphthylenediamine. The oxidation was effected in the same way as described in the case of ethyl β -imino- α -cyano- γ -m-tolylbutyrate. Ten grams of the base were dissolved in excess of dilute sulphuric acid and the solution heated to boiling. Twenty-five grams of potassium dichromate were then dissolved in water and the two hot solutions mixed, the whole being finally heated for a few minutes on the sand-bath. The dark-coloured precipitate was then filtered and dried on a porous plate, after which it was extracted thoroughly with ether.

The substance insoluble in ether was then boiled with sodium carbonate solution and filtered, when the alkaline solution, on acidifying, deposited a solid acid which crystallised from water in colourless prisms melting at 152° :

0.1992 gave 0.5243 CO_2 and 0.1216 H_2O . $\text{C} = 71.78$; $\text{H} = 6.78$.

$\text{C}_9\text{H}_{10}\text{O}_2$ requires $\text{C} = 72.0$; $\text{H} = 6.7$ per cent.

The acid is therefore 4-methylphthalic acid (compare Niementowski, *Monatsh.*, 1891, **12**, 624, and Young, *Ber.*, 1892, **25**, 2108). The acid was further characterised by converting it by means of acetyl chloride into its anhydride melting at 92° .



p-Tolylacetonitrile undergoes intramolecular condensation much more readily than either its ortho- or meta-isomeride, and when either of the methods described on p. 264 are employed, scarcely any unchanged nitrile is recovered from the product. When the condensation is carried out in alcohol solution, about one-third of the product consists of the pyrimidine derivative, and the reaction is characterised by the fact that when the nitrile is added to the

solution of sodium ethoxide, an intense purple colour is produced, which, however, disappears on heating. When xylene is the solvent used, scarcely any of the pyrimidine derivative is formed, and the imino-nitrile is obtained in yields representing 85 per cent. of the theoretical. When prepared by either method the imino-nitrile is a viscid oil, which distils without appreciable decomposition at 280—283°/18 mm. as a colourless syrup showing no tendency to crystallise:

0·1850 gave 0·5562 CO₂ and 0·1169 H₂O. C = 81·98; H = 7·02.

C₁₈H₁₈N₂ requires C = 82·4; H = 6·9 per cent.

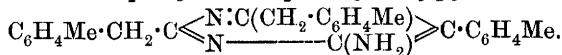
The constitution of the compound was proved, as in the previous cases, by alkaline hydrolysis, but much greater difficulty was met with in this instance in bringing about the fission of the chain than in any of the other cases recorded. The complete hydrolysis was, however, ultimately effected in the following way: Five grams were added to an alcoholic solution containing three times the calculated quantity of potassium hydroxide contained in a reflux apparatus, and the mixture was heated on the water-bath for twenty-four hours. At the end of this time, water was added, and the solution further heated on the sand-bath until the odour of ammonia was no longer apparent, when dilute hydrochloric acid was added, and the oily mass which separated was extracted with ether. The ethereal extract was then shaken with sodium carbonate solution, and the alkaline extract acidified. In this way a white solid was obtained which, when recrystallised from water, yielded colourless needles melting at 91°:

0·1916 gave 0·5039 CO₂ and 0·1173 H₂O. C = 71·72; H = 6·80.

C₉H₁₀O₂ requires C = 72·0; H = 6·7 per cent.

The acid is therefore *p*-tolylacetic acid, C₆H₄Me·CH₂·CO₂H.

6-Amino-5-p-tolyl-2:4-di-p-methylbenzylpyrimidine,



This compound is not precipitated during the condensation of *p*-tolylacetoneitrile in alcoholic solution, as is the case with the ortho- and meta-derivatives, and has to be extracted from the ethereal solution of the condensation product, after distillation with steam, by means of hydrochloric acid (see p. 266). The hydrochloric acid washings yield the pyrimidine base, on treatment with sodium carbonate solution, as a white, crystalline precipitate, which, when recrystallised from either methyl alcohol or light petroleum (b. p. 70—80°), yields colourless, concentric needles melting at 117—120°. The melting point is not sharp, but repeated recrystallisation from light petroleum fails to alter it:

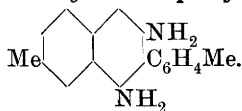
0.1888 gave 0.5705 CO_2 and 0.1165 H_2O . $\text{C} = 82.40$; $\text{H} = 6.85$.

$\text{C}_{27}\text{H}_{27}\text{N}_3$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

When added to concentrated hydrochloric acid the crystalline base at once forms an insoluble gum.

The *hydrochloride*, $\text{C}_{27}\text{H}_{27}\text{N}_3\text{HCl}$, can be obtained in a crystalline condition by adding a little concentrated hydrochloric acid to a solution of the base in alcohol, and allowing the solution to stand. It forms white needles.

7-p-Tolyl-2-methyl-6 : 8-naphthylenediamine,



The yield of this base from the imino-nitrile is scarcely more than 9 per cent. of the theory, the method found most convenient for its formation being as follows: Ten grams of β -imino- α -cyano- α - γ -di-*p*-tolylpropane were added to 60 grams of well-cooled concentrated sulphuric acid, and the dark red solution, after being kept at the ordinary temperature for fifteen minutes, was poured on ice. The aqueous solution was then filtered from a small quantity of insoluble matter, and the filtrate rendered alkaline with ammonia, when a large quantity of resinous matter was precipitated. On treatment with hot methyl alcohol, only a small portion of this dissolved, and the solution on filtering and cooling deposited the base in colourless, glistening plates melting at 160° :

0.1828 gave 0.5542 CO_2 and 0.1080 H_2O . $\text{C} = 82.67$; $\text{H} = 6.5$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 82.4$; $\text{H} = 6.9$ per cent.

The base becomes coloured red on exposure to the air, and is appreciably less soluble in solvents than the ortho- or meta-derivatives. The compound insoluble in methyl alcohol mentioned above, which is the chief product of the reaction, evidently belongs to the same series as those prepared under similar conditions from compounds in which the formation of the naphthalene ring is also hindered. Their nature has not as yet been determined.

The *dihydrochloride*, $\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$, is prepared by dissolving the base in concentrated hydrochloric acid and allowing the solution to stand. It forms colourless plates:

0.2284 gave 0.1940 AgCl . $\text{Cl} = 21.01$.

$\text{C}_{18}\text{H}_{18}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 21.19$ per cent.

The *diacetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{N}_2(\text{Ac})_2$, is best prepared by the action of acetyl chloride. The base was boiled with this substance until all had passed into solution, when the diacetyl derivative

remained as a viscid gum on evaporating the excess of chloride on the water-bath. It separates slowly from dilute alcohol in clusters of microscopic needles, melting at 176° :

0.1768 gave 0.4941 CO_2 and 0.1027 H_2O . $\text{C} = 76.21$; $\text{H} = 6.45$.

$\text{C}_{18}\text{H}_{18}\text{N}_2$ requires $\text{C} = 76.3$; $\text{H} = 6.4$ per cent.

Much of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

THE UNIVERSITY,
MANCHESTER.
