CLXXXV.—*The Formation and Reactions of Imino-compounds. Part II. Condensation of Benzyl Cyanide Leading to the Formation of 1:3-Naphthylenediamine and its Derivatives.*

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The Condensation of Benzyl Cyanide with the Sodium Derivative of Ethyl Cyanoacetate.

IN Part I. of this series it was pointed out by Baron, Remfry, and Thorpe (Trans., 1904, 85, 1726) that ethyl cyanoacetate readily reacted with its sodium derivative, forming ethyl β -imino- α -cyano-glutarate, and that the reaction evidently proceeded according to the equation *

It was also pointed out that, on treatment with concentrated sulphuric acid, ethyl β -imino- α -cyanoglutarate (1) is quantitatively converted into ethyl glutazinecarboxylate (2).

The tendency for the straight chain compound to pass into the

* Subsequent experiments have shown that this view of the course of the condensation, which was based on the position of the sodium atom in the condensation product, is not quite correct, and that it is the reactive hydrogen atom of the sodium derivative which forms the imino-group. The course of the action is therefore best represented by the equation :

The change in the position of the sodium atom must be attributed to the more strongly acidic character of the hydrogen of the methylene group.

pyridine ring, which is indicated by this reaction, was still more strongly shown by the behaviour of ethyl hydrogen β -imino- α -cyano-glutarate (3), which was found to undergo conversion into ethyl glutazinecarboxylate (2) on being heated a few degrees above its melting point (*loc. cit.*, 1746). There seemed to be, therefore, a considerable tendency for a nitrile group in the γ -position to a carboxyl group in a compound such as ethyl hydrogen β -imino- α -cyanoglutarate to pass, by intermolecular change with that group, into a six-membered ring, and that this tendency is also shown by the corresponding β -ketonic derivatives was demonstrated by the conversion of ethyl hydrogen cyanoacetonedicarboxylate (4) into ethyl 2:4:6-trioxypyridine-3-carboxylate (5), on heating a few degrees above its melting point.

Whilst desiring to continue the investigation of the conditions of formation of these imino-compounds, we wished at the same time to ascertain whether the tendency of the nitrile group to enter into ring formation might not be applied to the formation of carbon rings as well as those containing nitrogen, and with this object in view and for other reasons which will be given later, we have investigated the condensation of benzyl cyanide with the sodium compound of ethyl cyanoacetate and also with its own sodium derivative.

It is apparent that the most probable course of the first reaction would be represented by the equation (I), and that the product on acidifying would be ethyl β -imino- α -cyano- γ -phenyl-*n*-butyrate (6).

But it is also possible that the sodium derivative of ethyl cyanoacetate might react with benzyl cyanide, forming the sodium derivative of the latter, in which case the course of the condensation would be represented by equation (II), and on acidifying ethyl β -imino- $\gamma\gamma$ -cyanophenyl-*n*-butyrate (7) would be the chief product.

Under conditions given in the experimental portion of this paper, a good yield of a well-defined crystalline compound (m. p. 125°) is formed on condensing benzyl cyanide with ethyl sodiocyanoacetate, and there can be no doubt that its constitution is represented by formula (6), although, under certain experimental conditions, there is evidence that a compound of formula (7) also occurs as an intermediate product.

In Part I. of this series (p. 1728), it was shown that β -imino-ethyl salts are decomposed on treatment with alkaline hydrolytic agents and that the products formed, which are the same as those derived by the alkaline hydrolysis of the corresponding β -keto-ethyl salts, often afford valuable evidence as to the formula of the compound hydrolysed. It is apparent, however, that this method fails when applied to two compounds of formulæ (6) and (7), since these two substances would yield the same products, namely, a mixture of malonic and phenylacetic acids, on complete hydrolysis, thus :

The compound melting at 125° is readily hydrolysed by means of an alcoholic solution of potash, and the product consists of about equal proportions of malonic and phenylacetic acids. Although by this means, therefore, it is not possible to distinguish between the two formulæ (6) and (7), yet the evidence is valuable, since, taken in conjunction with the boiling point of the compound (235°/20 mm.) and its percentage composition, it shows that it has been formed by the condensation of one molecule of benzyl cyanide with one molecule of ethyl cyanoacetate.

It was necessary, therefore, to adopt some other means of distinguishing between the two compounds of formulæ (6) and (7), and since we were unable to isolate any intermediate products during the alkaline hydrolysis, the formation of which might throw some light on the problem, we were led to study the action of concentrated sulphuric acid on the compound melting at 125°.

If the two formulæ are examined, it will be seen that the action of this reagent must give rise to different compounds.

A substance of formula (7) is closely allied to ethyl β -imino- α -cyanoglutarate (see page 1906) in constitution, and therefore should readily give phenylglutazine (8) on treatment with concentrated sulphuric acid, thus :

whereas a compound of formula (6), in which the nitrile group and the carboxyl group are united with the same carbon atom, cannot yield a derivative of glutazine under the same conditions.

The compound melting at 125° does not give phenylglutazine on treatment with concentrated sulphuric acid, and there can therefore be no doubt that it possesses a constitution represented by formula (6), a view which is confirmed by a close study of the compound which is actually formed with this reagent.

It has already been mentioned that one of our objects in investigating the interaction of benzyl cyanide and ethyl sodiocyanoacetate was to prepare a compound in which the nitrile group could by reason of its position pass into a six-membered carbon ring instead of the pyridine ring formed from the other compounds which have already been investigated.

This object will be more clearly understood when the formula of ethyl β -imino- α -cyano- γ -phenylbutyrate is written thus (9) :

It was thought possible that the nitrile group might react with the ortho-hydrogen atom of the benzene ring, forming a di-imino-compound (10), which in its amino-form would be ethyl 1-3-diaminonaphthalene-2-carboxylate (11), and that by this means an interesting synthesis of the naphthalene ring might be effected.

Since the original imino-compound (9) was formed in the presence of sodium ethoxide, we intended to attempt to obtain the di-imino-derivative (10) by treating ethyl β -imino- α -cyano- γ -phenylbutyrate with excess of this reagent. We were therefore considerably astonished to find that, on treating this ethyl salt with concentrated

sulphuric acid, in the attempt already mentioned to determine its constitution, it was quantitatively converted into the sulphate of ethyl 1:3-diaminonaphthalene-2-carboxylate (11).

This result was all the more surprising because it has been shown by Metzner (*Annalen*, 1901, 298, 386) that a similarly constituted compound, namely, ethyl phenylacetylmalonate (12), on treatment with cold, concentrated sulphuric acid, is converted with loss of alcohol into ethyl 1:3-dihydroxynaphthalene-2-carboxylate (13), the reaction taking place at the ordinary temperature,

and it was therefore to be expected that ethyl β -imino- α -cyano- γ -phenylbutyrate (9) would behave in the same way, yielding 3-amino-2-cyano-1-naphthol (14) :

The yield, however, of ethyl 1:3-diaminonaphthalene-2-carboxylate (11) from ethyl β -imino- α -cyano- γ -phenylbutyrate (9), on treatment with sulphuric acid, is quantitative, and the reaction takes place with remarkable ease. Thus it is only necessary to add a quantity of well-ground ethyl salt to three times its weight of concentrated acid and allow the mixture to stand for one minute in order to complete the change. On first adding the ethyl salt it dissolves, forming a yellow solution which rapidly changes in colour in the course of a few seconds to deep malachite-green, heat at the same time being generated.

When this green solution is poured on ice the colour is discharged and a clear yellow solution is formed from which the sulphate of ethyl 1:3-diaminonaphthalene-2-carboxylate separates on standing as a pale yellow, crystalline precipitate. The sulphate is readily soluble in water, and if the aqueous solution is rendered alkaline the base is precipitated as an intense yellow crystalline compound, which, when purified by recrystallisation from alcohol, is obtained in deep yellow plates.

There can be no doubt that this yellow compound represents the di-imino-form of ethyl 1:3-diaminonaphthalene-2-carboxylate (10). The salts, especially the hydrochloride, can be obtained in almost colourless crystals, and they are therefore probably the salts of the amino-form (11). It is interesting to note, however, that although the solutions of these salts are colourless when cold, they become intensely coloured on boiling, the colour being again discharged on cooling.

The green colour which is formed when ethyl β -imino- α -cyano- γ -phenylbutyrate is treated with concentrated sulphuric acid is difficult to explain, since ethyl 1:3-diaminonaphthalene-2-carboxylate dissolves in the concentrated acid, forming a yellow solution which does not change on warming. That this coloration is not necessary for the production of the naphthalene ring is shown by the fact that if the solution of ethyl β -imino- α -cyano- γ -phenylbutyrate in concentrated sulphuric acid is brought about at 0°, and the temperature is not allowed to rise above this point, no green colour appears, the solution remaining a light brown. Whether the green colour is formed or not, the yield of the naphthalene is not apparently affected.

The corresponding carboxylic acid (15) can be readily prepared from ethyl 1:3-diaminonaphthalene-2-carboxylate (11) on treating it with an alcoholic solution of potash. The free acid, which is colourless, is unstable at temperatures above its melting point (85°), being then transformed with evolution of carbon dioxide into 1:3-naphthylenediamine (16).

1:3-Naphthylenediamine prepared in this way is identical with the compound obtained by Urban (*Ber.*, 1887, 20, 973) by the reduction of 1:3-dinitronaphthalene, and by Friedländer (*Ber.*, 1895, 28, 1953) by the action of ammonia on 4-amino-2-naphthol.

It was pointed out in Part I. of this series that ethyl β -imino- α -cyanoglutarate (17) reacted with sodium ethoxide, forming a sodium

derivative, and that the metal entered in the position (1), that after the sodium atom in this had been replaced by an alkyl radicle, the hydrogen marked (2) could be replaced by sodium, and that finally, after this sodium had been treated with an alkyl iodide, the third hydrogen atom marked (3) could be replaced.

It is interesting to note that, although the hydrogen atom marked (2) is attached to the same carbon atom as a nitrile- and a carbethoxyl-group, yet the first hydrogen atom replaced is that marked (1), which is attached to the same carbon atom as the carbethoxyl- and the carbimino-group.

In the case of ethyl β -imino- α -cyano- γ -phenylbutyrate (18), the influence of the phenyl group is at once apparent, and we have only succeeded in introducing one alkyl group into this compound after repeatedly treating it with sodium ethoxide and the alkyl iodide. The hydrogen atom replaced is that marked (*), and apparently the hydrogen atom of the cyanoacetic residue is not replaceable under ordinary conditions.

We have carefully studied both the methyl and ethyl derivatives of ethyl β -imino- α -cyano- γ -phenylbutyrate, and have found that it is necessary to treat the ethyl salt four successive times with the calculated quantity of sodium ethoxide and excess of methyl (or ethyl) iodide in order to convert the whole of it into its mono-alkyl derivative.

The positions of the alkyl groups in the alkylated compounds can be readily shown by the products they give on complete hydrolysis with alcoholic potash. Thus the ethyl salt which is prepared by the action of sodium ethoxide and methyl iodide on ethyl β -imino- α -cyano- γ -phenylbutyrate gives phenylacetic and malonic acids under these conditions, thus:

It is therefore ethyl β -imino- α -cyano- γ -phenyl-*n*-valerate,

In the same way, the corresponding ethyl derivative gives a mixture of α -phenyl-*n*-butyric and malonic acids on complete alkaline hydrolysis. Its formula is therefore $\text{Ph}\cdot\text{CHEt}\cdot\text{C}(\text{NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$.

Both these ethyl salts behave in the same way as ethyl β -imino- α -cyano- γ phenylbutyrate on treatment with concentrated sulphuric acid. In each case a similar green to blue coloration is produced if the solution is allowed to become warm, but is not formed if the temperature is kept below 0° , and in each case, also, on pouring the mixture on ice a clear solution is obtained from which the sulphate of the base separates on standing. Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate (19) and ethyl 2:4-diamino-1-ethylnaphthalene-3-carboxylate (22) are in each case precipitated from the solutions of their sulphates on the addition of ammonia as yellow oils which on extraction by means of ether are obtained as syrups rapidly solidifying to yellow, crystalline solids.

Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate passes on hydrolysis with alcoholic potash into the corresponding carboxylic acid (20), which, like the unalkylated derivative, is a colourless, crystalline compound, decomposing with evolution of carbon dioxide on being heated above its melting point and passing into 2:4-diamino-1-methylnaphthalene (21).

In the same way, ethyl 2:4-diamino-1-ethylnaphthalene-3-carboxylate (22) yields 2:4-diamino-1-ethylnaphthalene-3-carboxylic acid (23) and 2:4-diamino-1-ethylnaphthalene (24).

The Condensation of Benzyl Cyanide with its Sodium Derivative.

The interaction of benzyl cyanide with its sodium derivative was first studied by Wache (*J. pr. Chem.*, 1889, ii, 39, 251), who investi-

gated the action of finely divided sodium on an ethereal solution of the nitrile. Although this chemist was unable to isolate the bimolecular nitrile, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, he found that, on heating the precipitate formed in the above reaction with excess of benzyl cyanide in a sealed tube at 180° for several hours, it was transformed into a white, crystalline, basic substance of the empirical formula $\text{C}_{24}\text{H}_{21}\text{N}_3$, to which he gave the name of cyanbenzylidine (6-amino-5-phenyl-2:4-dibenzylpyrimidine), and the formula $\text{CH}_2\text{Ph}\cdot\text{C} \begin{smallmatrix} \text{N}:\text{C}(\text{CH}_2\text{Ph}) \\ \text{N}-\text{C}(\text{NH}_2) \end{smallmatrix} \text{CPh}$,

on account of the similarity between its mode of formation and properties and those of cyanethine and cyanmethine, which E. v. Meyer (*J. pr. Chem.*, 1889, ii, 39, 156) had previously shown to be derivatives of pyrimidine. Wache subsequently found that the best way to prepare cyanbenzylidine was to heat a mixture of the nitrile and dry sodium ethoxide in a sealed tube at 170 – 180° for many hours.

E. v. Meyer (*J. pr. Chem.*, 1895, ii, 52, 114), in conjunction with O. Probst (*Inaug. Diss. Leipzig*, 1894), repeated the work of Wache, and found that if the precipitate which was formed by the action of finely divided sodium on an ethereal solution of benzyl cyanide was washed with light petroleum and then added to dilute acetic acid, a viscid oil was obtained which could not be distilled without undergoing decomposition, but which evidently consisted of β -imino- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, since on treatment with hydroxylamine it gave the same oxime as that derived from cyanodibenzyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Later, v. Walther and Schickler (*J. pr. Chem.*, 1897, ii, 55, 350) prepared the same compound by the action of ammonia on the cyanoketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$, but also failed to obtain it in the solid condition.

The termolecular nitrile cyanbenzylidine was thoroughly investigated by Herfeldt (*J. pr. Chem.*, 1896, ii, 53, 246), who prepared many of its derivatives, and still more recently v. Walther (*J. pr. Chem.*, 1903, ii, 67, 447) has found that it can be prepared by the action of finely divided sodium on an ethereal solution of benzyl cyanide containing dimethylaniline. Owing to the similarity in constitution between benzyl cyanide and ethyl cyanoacetate, we decided, in order to prepare β -imino- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, to investigate the interaction of benzyl cyanide with its sodium derivative in alcoholic solution, since in the case of ethyl cyanoacetate a good yield of ethyl β -iminocyanoglutarate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{CO}_2\text{Et}$, had been obtained by Baron, Remfry, and Thorpe by this means (*Trans.*, 1904, 85, 1726).

We found that the products formed in this condensation varied with the length of time during which the heating was continued at 100° . Thus, when two molecular equivalents of benzyl cyanide and one of

sodium ethoxide dissolved in alcohol were heated on the water-bath for half an hour, the product consisted of about 70 per cent. of β -imino- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, mixed with unchanged benzyl cyanide. When the heating was prolonged, an odour resembling ammonia became apparent at the mouth of the condenser and on working up the product at the end of two hours it was found to consist of about equal proportions of β -imino- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, β -keto- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$, and cyanbenzylidine, some benzyl cyanide being at the same time recovered unchanged.

On prolonging the heating until the odour resembling ammonia ceased to be perceptible, an operation which usually required twenty-four hours to accomplish, the product was found to consist entirely of β -keto- α -cyano- α -diphenylpropane and cyanbenzylidine.

Subsequently it was found by experiment that the odour resembling ammonia was not due to this substance itself, but to ethylamine, which was probably formed by the action of the alkaline alcoholic solution on β -imino- α -cyano- α -diphenylpropane, the reaction evidently proceeding according to equation (III):

It is apparent, therefore, that the first action of benzyl cyanide on its sodium derivative in alcoholic solution at 100° is to form β -imino- α -cyano- α -diphenylpropane according to equation (IV):

and that if the reaction is stopped at the end of about half an hour a good yield of this compound can be obtained. After this time, the initial product is slowly decomposed in accordance with equation (III) and β -keto- α -cyano- α -diphenylpropane is formed; at the same time, the sodium derivative of β -imino- α -cyano- α -diphenylpropane reacts with the unchanged benzyl cyanide, forming cyanbenzylidine in accordance with the observation of Wache. Like all previous investigators, we have been unable to obtain β -imino- α -cyano- α -diphenylpropane (23) in a crystalline condition, although we find that it can be distilled without decomposition under a pressure of 20 mm. if the operation is conducted rapidly and only small quantities are used. When treated with cold concentrated sulphuric acid, it behaves in just the same way as ethyl β -imino- α -cyano- γ -phenylbutyrate, being converted into 1:3-diamino-2-phenylnaphthalene (24) thus:

It is worthy of note that, whereas ethyl 1:3-diaminonaphthalene-2-carboxylate is intensely yellow in colour, 1:3-diamino-2-phenyl-naphthalene is colourless, and a comparison of the three following formulæ is of interest as showing the influence of the carbethoxyl, carboxyl, and phenyl groups respectively on the stable forms of similar compounds:

It is also of interest to note that the same phenomenon occurs in the corresponding hydroxy-compounds, thus: Metzner (*Annalen*, 1901, 298, 386) finds that ethyl 1:3-dihydroxynaphthalene-2-carboxylate (25) is yellow, whereas the corresponding acid (26) is colourless. 1:3-Dihydroxy-2-phenyl-naphthalene (27), which has been prepared by Volhard (*Annalen*, 1900, 296, 16) by the action of concentrated sulphuric acid on ethyl diphenylacetoacetate, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{Ph})\cdot\text{CO}_2\text{Et}$, is also colourless.

The salts of 1:3-diamino-2-phenyl-naphthalene are colourless, but become intensely coloured on exposure to the air. A full investigation of its properties are in progress.

EXPERIMENTAL.

Formation of Ethyl β-Imino-α-cyano-γ-phenylbutyrate, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$

This ester was produced by the condensation of the sodium derivative of ethyl cyanoacetate with benzyl cyanide in alcoholic solution. Twenty-three grams of sodium were dissolved in 275 grams of alcohol and mixed with 113 grams of ethyl cyanoacetate. To

the well-cooled solution 117 grams of benzyl cyanide were added and the whole heated on the water-bath. It was found that the yield of the condensation product varied considerably with the length of time during which the mixture was heated and that much care had to be exercised in order to obtain the above compound in yields sufficiently large for the purposes of the research. This was necessary owing to the fact that soon after being formed, the condensation product was found to pass rapidly into another compound (see below) which has not yet been identified. This difficulty will be realised when it is pointed out that after the above mixture had been heated for twelve hours at 100° only about 10 per cent. of ethyl β -imino- α -cyano- γ -phenylbutyrate could be isolated, the majority of the benzyl cyanide being recovered unchanged, whereas if the heating was prolonged at the same temperature for twenty-four hours the product, whilst containing 25 per cent. of the ester, was found to be mixed with as much as 40—45 per cent. of another compound of high molecular weight, and only a relatively small proportion of the benzyl cyanide was recovered unchanged. On heating for a still longer time the quantity of the complex substance increased and the amount of ethyl β -imino- α -cyano- γ -phenylbutyrate formed and of unchanged benzyl cyanide diminished.

After numerous experiments carried out under different conditions in which yields of the ethyl ester varying from 10—50 per cent. of the theoretical amount were obtained, the following method was ultimately adopted as being the most convenient.

The molecular mixture described above was heated on the steam-bath for fifteen hours, the flask being vigorously shaken from time to time. It was observed that the white insoluble sodium derivative of ethyl cyanoacetate gradually dissolved and that the solution became deep red in colour and very viscous. After being heated for the specified time the product was cooled, when it set to a thick jelly. Dilute hydrochloric acid was then added and the heavy oil which separated extracted by means of ether, the ether solution being washed with water and then with dilute sodium carbonate solution. During the washing with sodium carbonate a considerable quantity of acid oil was extracted, a description of which will be found below.

The ether solution, without being dried, was evaporated free from ether, and the residue subjected to distillation in a current of steam, whereby the whole of the unchanged benzyl cyanide was recovered in the distillate. The residue, which consisted of a viscid brown oil solidifying on cooling, was then separated by filtration, dried on a porous plate, and recrystallised from absolute alcohol.

Ethyl β -imino- α -cyano- γ -phenylbutyrate, purified in this way, was obtained in long, colourless needles, which melted at 125°:

0.1877 gave 0.4659 CO_2 and 0.1068 H_2O . $\text{C} = 67.69$; $\text{H} = 6.32$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.81$; $\text{H} = 6.1$ per cent.

The ethyl ester is insoluble in solutions of alkali carbonates and in aqueous caustic alkalis and is not acted on, even on prolonged boiling, by concentrated hydrochloric acid. It can be recrystallised from either methyl or ethyl alcohol or from benzene, but is almost insoluble in light petroleum.

The sodium carbonate washings from the ether solution were acidified, when a heavy oil separated, which partially solidified. This was filtered by the aid of the pump and the mixture of oil and solid washed with ether, in which solvent the solid was found to be quite insoluble. The residue was dried on a porous plate and found to consist of a light brown amorphous substance apparently insoluble in all the usual organic solvents with the exception of hot glacial acetic acid in which it was only very sparingly soluble. It was insoluble in concentrated hydrochloric acid, but dissolved in concentrated sulphuric acid apparently unchanged, since it was reprecipitated on the addition of water. It is, however, readily soluble in dilute solutions of alkali carbonates and in caustic alkalis and in the latter case on the addition of excess of the alkali a crystalline alkali salt slowly separates. This salt is, however, difficult to purify since it is dissociated by water, and therefore cannot be freed from the excess of alkali. For the purpose of analysis the compound was purified by conversion into the potassium salt, which was effected by first washing the crude product thoroughly with ether and then dissolving it in a moderately dilute solution of caustic potash. On standing a crystalline *potassium* salt slowly separated which was filtered and reconverted into the original acid by treatment with dilute hydrochloric acid. The white amorphous precipitate thus obtained was then recrystallised from a large quantity of glacial acetic acid, from which solvent it separated in colourless, microscopic needles which melted to a brown liquid at 335° : *

I. 0.3086 gave 0.8346 CO_2 and 0.1416 H_2O . $\text{C} = 73.76$; $\text{H} = 5.14$.

II. 0.2072 ,, 0.5610 CO_2 ,, 0.0940 H_2O . $\text{C} = 73.84$; $\text{H} = 5.08$.

III. 0.2508 ,, 35.0 c.c. nitrogen at 18° and 767 mm. $\text{N} = 15.95$.

$\text{C}_{21}\text{H}_{18}\text{ON}_4$ requires $\text{C} = 73.7$; $\text{H} = 5.2$; $\text{N} = 16.4$ per cent.

These figures furnish no clue as to the identity of the substance.

Considerable quantities of this compound having accumulated during the course of this research, it is our intention further to investigate its properties.

The ethereal layer which floated on the filtrate from the above

* This melting point was taken in cyanbenzylne (see p. 1932).

compound after washing it free from oil was separated in the funnel, washed with water, dried and the ether evaporated. The residue, which consisted of a viscid, dark oil readily soluble in dilute sodium carbonate solution, was, without further purification, mixed with three times its volume of absolute alcohol and an equal volume of concentrated sulphuric acid and after being allowed to stand for twelve hours, heated on the water-bath for three hours. The mixture was then poured into water, the oil which separated extracted with ether, and after any unchanged acid had been extracted by means of dilute sodium carbonate solution, the ethereal solution was dried and evaporated free from ether. The brown liquid which remained deposited a considerable quantity of crystals on standing, and these were collected and purified by recrystallisation from hot alcohol, being obtained in silky needles melting at 178° :

- I. 0.1868 gave 0.5252 CO_2 and 0.0882 H_2O . C = 76.68 ; H = 5.28.
 - II. 0.1950 „ 0.5472 CO_2 „ 0.0908 H_2O . C = 76.52 ; H = 5.17.
 - III. 0.2284 „ 24.6 c.c. nitrogen at 13° and 756 mm. N = 12.78.
 - IV. 0.2264 „ 24.6 c.c. „ „ 13° „ 752 mm. N = 12.81.
- $\text{C}_{21}\text{H}_{17}\text{ON}_3$ requires C = 77.0 ; H = 5.2 ; N = 12.9 per cent.

The compound is insoluble in alkalis and in concentrated hydrochloric acid. Its constitution has not yet been determined.

The Constitution of Ethyl β -Imino- α -cyano- γ -phenylbutyrate.

Formation of Phenylacetic and Malonic Acids by the Action of Methyl Alcoholic Potash.

The proof of the constitution of ethyl β -imino- α -cyano- γ -phenylbutyrate was derived from a study of the products which were formed when it was completely hydrolysed by means of an alcoholic solution of potash. As already mentioned in the introduction, this proof is not in itself conclusive, since ethyl β -imino- γ -cyano- γ -phenylbutyrate, $\text{CHPh}(\text{CN})\cdot\text{C}(\text{:NH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which might conceivably be formed in the same reaction would also give the same products on alkaline hydrolysis, but that, taken in conjunction with the other reactions of this ethyl salt, places its constitution beyond question.

When ethyl β -imino- α -cyano- γ -phenylbutyrate was mixed with a solution of $1\frac{1}{2}$ times the calculated quantity of potash dissolved in methyl alcohol, considerable heat was generated and much ammonia was evolved on heating the solution on the water-bath. After heating for six hours the evolution of ammonia had ceased and a clear solution was obtained on pouring the hydrolysed product into water. The excess of methyl alcohol was then evaporated and the residue acidified by means of hydrochloric acid, when a white, crystalline substance

separated. This was collected and recrystallised from dilute alcohol, being thus obtained in glistening plates melting at 76° . An analysis proved, as its appearance and odour indicated, that it was phenylacetic acid:

0.2107 gave 0.5222 CO_2 and 0.1232 H_2O . $\text{C} = 67.61$; $\text{H} = 6.49$.

$\text{C}_7\text{H}_8\text{O}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.4$ per cent.

The filtrate from the phenylacetic acid was evaporated to dryness, acidified with concentrated hydrochloric acid and again evaporated, being finally placed in a Soxhlet apparatus and extracted with ether. The ethereal solution on drying and evaporating deposited a quantity of oil which rapidly solidified and then melted at 132° with decomposition. The analysis, together with the fact that on distillation it yielded acetic acid, showed it to be malonic acid:

0.2217 gave 0.2796 CO_2 and 0.0778 H_2O . $\text{C} = 34.39$; $\text{H} = 3.89$.

$\text{C}_3\text{H}_4\text{O}_4$ requires $\text{C} = 34.6$; $\text{H} = 3.8$ per cent.

Formation of Ethyl 1:3-Diaminonaphthalene-2-carboxylate,

When dry ethyl β -imino- α -cyano- γ -phenylbutyrate ground to a fine powder is added to three times its weight of cold, concentrated sulphuric acid it dissolves rapidly forming a yellow solution. If the mixture is allowed to become warm this solution becomes deep malachite-green in colour, but it remains yellow if placed in a mixture of ice and salt. If, as soon as the ethyl salt has all dissolved, an operation which usually takes about one minute, the strong sulphuric acid solution is poured on ice, a clear yellow solution is produced from which an almost white crystalline substance separates on standing. This compound is the *sulphate*, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$, of the above base and can be obtained in almost colourless plates by recrystallisation from water:

0.1539 gave 0.2706 CO_2 and 0.0705 H_2O . $\text{C} = 47.95$; $\text{H} = 5.12$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 47.6$; $\text{H} = 4.9$.

The sulphate gradually becomes yellow on exposure to the air, and when dissolved in water forms, in the cold, an almost colourless solution, which on warming becomes bright yellow; this yellow colour is discharged on cooling.

Ethyl-1:3-diaminonaphthalene-2-carboxylate is precipitated as a yellow, crystalline solid on adding aqueous ammonia to a solution of the sulphate dissolved in water. It was collected by filtration and

recrystallised from ether, being obtained in this way in golden yellow plates melting at 108° :

0.2244 gave 0.5568 CO_2 and 0.1262 H_2O . $\text{C} = 67.65$; $\text{H} = 6.24$.

0.3238 „ 32.4 c.c. of nitrogen at 12° and 769 mm. $\text{N} = 12.13$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.1$; $\text{N} = 12.2$ per cent.

The *hydrochloride*, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$, is best prepared by dissolving the base in dilute hydrochloric acid and then adding excess of concentrated hydrochloric acid to the almost colourless solution. On standing, colourless needles of the above salt separate :

0.2911 gave 0.2734 AgCl . $\text{Cl} = 23.30$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 23.4$ per cent.

Ethyl 1 : 3-diaminonaphthalene-2-carboxylate is very readily oxidised by the mildest oxidising agents, being even slowly altered on exposure to the air. The compounds produced in these circumstances as well as the products formed by the action of nitrous acid on this ethyl salt are still under investigation,

This acid was prepared from the ethyl salt by hydrolysing it with methyl alcoholic potash. 5 grams were added to a solution of $1\frac{1}{2}$ times the calculated quantity of caustic potash dissolved in methyl alcohol and the solution warmed on the water-bath. On cooling a crystalline *potassium* salt, $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{K}$, separated, which was collected by filtration, purified by washing with a little methyl alcohol, and dried on a porous plate. It is a yellow, crystalline solid readily soluble in water :

0.2195 gave 0.0788 K_2SO_4 . $\text{K} = 16.09$.

$\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{K}$ requires $\text{K} = 16.25$ per cent.

The free acid is precipitated as a white, crystalline solid on adding dilute hydrochloric acid to a solution of the potassium salt in water. It was collected by filtration, dried on a porous plate and recrystallised from warm water. Since the acid rapidly loses carbon dioxide at 80° , it is necessary that the aqueous solution should be considerably below this temperature. Since, however, the acid is readily soluble in warm water and separates again on cooling, it can easily be recrystallised in quantities without raising the temperature of the solution above 60° . 1 : 3-Diaminonaphthalene-2-carboxylic acid can be obtained in this

way in colourless needles melting at 85° with immediate elimination of carbon dioxide:

0.2258 gave 0.5374 CO_2 and 0.1064 H_2O . $\text{C} = 64.90$; $\text{H} = 5.27$.

$\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C} = 65.3$; $\text{H} = 4.9$ per cent.

The carboxylic acid does not form salts with acids.

1 : 3-Naphthylenediamine.

This base was prepared from the above carboxylic acid by heating it at 100° until the evolution of carbon dioxide had ceased. The operation was carried out in a small flask which was placed in a bath of sulphuric acid and heated to the requisite temperature. When the evolution of gas had ceased, the product was dissolved in dilute hydrochloric acid and the deep red solution, after filtering, rendered alkaline with caustic potash. The base, which was then precipitated, was recrystallised from water and obtained in small plates, usually slightly red in colour, which melted at 96° :

0.1622 gave 0.4520 CO_2 and 0.0910 H_2O . $\text{C} = 76.00$; $\text{H} = 6.28$.

$\text{C}_{10}\text{H}_{10}\text{N}_2$ requires $\text{C} = 76.0$; $\text{H} = 6.3$ per cent.

The diacetyl derivative, $\text{C}_{10}\text{H}_8\text{N}_2(\text{CO}\cdot\text{CH}_3)_2$ was prepared by dissolving the base in acetic anhydride and heating the solution on the sand-bath for one hour. The excess of the anhydride was then evaporated by placing the solution in an evacuated desiccator over potash until solid. Recrystallised from acetic acid, it was obtained in fine needles melting at $263\text{--}265^{\circ}$ (Friedlander, *Ber.*, 1895, 28, 1953):

0.1693 gave 0.3826 CO_2 and 0.1112 H_2O . $\text{C} = 61.64$; $\text{H} = 7.29$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 61.9$; $\text{H} = 7.2$ per cent.

Formation of Ethyl β -Imino- α -cyano- γ -phenylvalerate,

As stated in the introduction, the methylation of ethyl β -imino- α -cyano- γ -phenylbutyrate by means of sodium ethoxide and methyl iodide in alcoholic solution is not easily accomplished. The difficulty is probably due to the fact that the unreactive character of the methylene hydrogen atom causes a state of equilibrium to be set up between the sodium ethoxide, the ethyl salt and its sodium derivative, in which only about one-third of the last-named is formed. Thus, by the action of methyl iodide on a cold mixture of equimolecular proportions of sodium ethoxide and ethyl β -imino- α -cyano- γ -phenylbutyrate, only about one-third of the ethyl salt is converted into its methyl derivative. Therefore, in order to complete the conversion,

the process of methylation was repeated four times in the following manner :

Ten grams of the ethyl salt were added to a solution containing 1 gram of sodium dissolved in 12 grams of alcohol, and the whole, after being well cooled, treated with 12 grams of methyl iodide. After standing for some time in the cold the mixture was heated on the water-bath until a test portion diluted with water gave a neutral reaction with litmus, when, after the excess of alcohol and unchanged methyl iodide had been distilled off as completely as possible on the water-bath, a further quantity of sodium ethoxide made by dissolving 1 gram of sodium in 12 grams of alcohol was added, and the solution treated with methyl iodide and again heated until neutral. After this process had been repeated four times, water was added and the oil, which then separated and which almost immediately solidified, was filtered by the aid of the pump and purified by recrystallisation from alcohol. *Ethyl β -imino- α -cyano- γ -phenylvalerate* is obtained in this way in large needles melting at 92° :

0.1596 gave 0.4052 CO_2 and 0.0959 H_2O . $\text{C} = 69.24$; $\text{H} = 6.72$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C} = 68.8$; $\text{H} = 6.6$ per cent.

Formation of α -Phenylpropionic Acid and Malonic Acid from Ethyl β -Imino- α -cyano- γ -phenylvalerate.

The proof of the constitution of ethyl β -imino- α -cyano- γ -phenyl- γ -methylbutyrate was derived from the study of the products formed from it on alkaline hydrolysis. The operation was carried out as follows :

Five grams of the ethyl salt were mixed with a solution containing one-and-a-half times the calculated quantity of caustic potash dissolved in methyl alcohol and heated on the water-bath until the odour of ammonia, which was apparent at the commencement of the hydrolysis, had entirely disappeared. The product was then diluted with water and evaporated on the water-bath until free from methyl alcohol, when it was acidified with concentrated hydrochloric acid and allowed to stand. Since the oil which separated on the addition of the acid showed no tendency to crystallise, the solution was extracted by means of ether and the ethereal solution, after drying, evaporated free from ether. The oil which remained was then distilled under the ordinary pressure and was found to boil constantly at $264\text{--}265^{\circ}$, at which temperature α -phenylpropionic acid, which does not appear to be a solid at the ordinary temperature, boils (Fittig and Wurster, *Annalen*, 1879, **195**, 165) :

0.2100 gave 0.5532 CO_2 and 0.1295 H_2O . $\text{C} = 71.84$; $\text{H} = 6.85$.

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

The aqueous solution after the extraction of the above acid was evaporated to dryness and extracted in a Soxhlet apparatus with ether. The ethereal solution after drying was evaporated free from ether yielding a solid residue which melted at 132° and gave acetic acid on distillation, evidently therefore consisting of malonic acid:

0.1774 gave 0.2237 CO_2 and 0.0622 H_2O . $\text{C} = 34.41$; $\text{H} = 3.90$.

$\text{C}_3\text{H}_4\text{O}_4$ requires $\text{C} = 34.6$; $\text{H} = 3.8$ per cent.

The above analysis indicates that the substance is malonic acid and not methylmalonic acid, and therefore shows that only one methyl group had entered into the molecule of ethyl β -imino- α -cyano- γ -phenylbutyrate on its being completely methylated in the manner already described.

Owing to there being only a slight difference between the percentage compositions of ethyl β -imino- α -cyano- γ -phenylbutyrate and its methyl derivative, this fact could not be definitely settled on the results of their analysis alone.

Formation of Ethyl 2:4-Diamino-1-methylnaphthalene-3-carboxylate,

The conversion of ethyl β -imino- α -cyano- γ -phenylvalerate into the above derivative of naphthalene takes place with the same ease as that already described in the case of the unmethylated derivative. Five grams of the finely-ground ethyl salt were added slowly to three times its weight of concentrated sulphuric acid cooled in ice. On each addition, the salt instantly dissolved, and in spite of the low temperature the sulphuric acid solution became deep bluish-green. When all had been added, the solution was allowed to stand for two or three minutes and then poured on ice. The deep bluish-green colour of the solution was instantly discharged on mixing with the ice, forming a clear yellow solution from which the *sulphate*, $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$, of the base slowly separated on standing as a pale yellow, crystalline precipitate:

0.1708 gave 0.3064 CO_2 and 0.0828 H_2O . $\text{C} = 48.92$; $\text{H} = 5.42$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 49.1$; $\text{H} = 5.3$ per cent.

The sulphate is readily soluble in hot water, but separates from its concentrated solutions in this solvent on cooling. An aqueous solution of the salt at 0° is nearly colourless, but becomes a deep yellow on being heated to the boiling point. On being again cooled, the colour

is discharged. The sulphate is insoluble in alcohol and this fact can be utilised in its formation, since on pouring the bluish-green sulphuric acid solution into three times its volume of well-cooled absolute alcohol, the salt is completely precipitated and can be isolated by filtration. The free base was prepared by dissolving the sulphate in water and adding ammonia until strongly alkaline. The deep yellow oil which was then precipitated did not show any signs of crystallising, and was therefore extracted by means of ether, the ethereal solution being washed with a little water, dried with calcium chloride, and evaporated. The yellow syrup which remained instantly solidified on scratching, forming a deep yellow solid, which was recrystallised from methyl alcohol and thus obtained in orange-yellow prisms melting at 75° :

0.1676 gave 0.4245 CO_2 and 0.1017 H_2O . $\text{C} = 69.08$; $\text{H} = 6.74$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C} = 68.8$; $\text{H} = 6.6$ per cent.

Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate is readily soluble in cold ether and can in this way be distinguished from the lower homologue. It is also soluble in all the usual organic solvents excepting light petroleum, and is readily oxidised, but is not altered on exposure to the air so rapidly as ethyl 1:3-diaminonaphthalene-2-carboxylate.

Formation of 2:4-Diamino-1-methylnaphthalene-3-carboxylic Acid,

This acid was prepared from the ethyl salt by the action of alcoholic potash. Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate was added to a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol and the mixture heated on the water-bath until a test portion diluted with water remained clear. Water was then added and the solution evaporated on the water-bath until free from methyl alcohol, when it was acidified, and the colourless, glistening leaflets of the acid which then separated collected by filtration. The acid, which is slowly decomposed by boiling water, was recrystallised rapidly from hot water, and obtained in this way in colourless needles which decomposed with evolution of carbon dioxide at $155\text{--}160^{\circ}$ apparently without melting:

0.1697 gave 0.4139 CO_2 and 0.0875 H_2O . $\text{C} = 66.52$; $\text{H} = 5.73$.

$\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 66.7$; $\text{H} = 5.6$ per cent.

This base was prepared from the carboxylic acid by heating it for some time at 180° . The finely-ground and purified acid was placed in a small flask and heated in a bath of sulphuric acid at the required temperature until carbonic acid ceased to be evolved, when the residue was treated with dilute hydrochloric acid, and the deep red solution thus formed boiled with animal charcoal and filtered. On adding dilute aqueous caustic soda to the filtrate, the base was precipitated as a resin, which did not crystallise on standing. It was therefore dissolved in concentrated hydrochloric acid and the solution allowed to stand, when the *hydrochloride*, $C_{11}H_{12}N_2 \cdot 2HCl$, slowly separated in white, silky needles:

0.2117 gave 0.2467 $AgCl$. $Cl = 28.91$.

$C_{11}H_{12}N_2 \cdot 2HCl$ requires $Cl = 29.0$ per cent.

The hydrochloride readily dissolved in water, and the solution on being made alkaline with caustic soda solution deposited the base as a white solid, which, when recrystallised from dilute methyl alcohol, was obtained in fine, white needles melting at 65° :

0.1912 gave 0.5358 CO_2 and 0.1245 H_2O . $C = 76.43$; $H = 7.23$.

$C_{11}H_{12}N_2$ requires $C = 76.7$; $H = 7.0$ per cent.

The base becomes slowly coloured on exposure to air and light.

The *platinichloride*, $C_{11}H_{12}N_2 \cdot H_2PtCl_6$, is precipitated as a yellow, crystalline powder on adding excess of platinic chloride to a solution of the hydrochloride of the base in water:

0.2513 gave 0.0839 Pt . $Pt = 33.38$.

$C_{11}H_{12}N_2 \cdot H_2PtCl_6$ requires $Pt = 33.5$ per cent.

Formation of Ethyl β -Imino- α -cyano- γ -phenyl-n-hexoate,
 $Ph \cdot CHEt \cdot C(NH) \cdot CH(CN) \cdot CO_2Et$.

The preparation of the ethyl derivative of ethyl β -imino- α -cyano- γ -phenylbutyrate was undertaken in order to show conclusively that only one alkyl group could be introduced into this compound by the action of sodium ethoxide and an alkyl iodide. The process adopted was the same as that already described in the case of the methyl derivative, only in the present instance even greater difficulty was experienced in introducing the alkyl group, and, after the process of ethylation

had been repeated four times, considerable quantities of unchanged ethyl salt were recovered. The actual operation was carried out as follows: 10 grams of ethyl β -imino- α -cyano- γ -phenylbutyrate were added to a solution containing 2 grams of sodium in 30 grams of alcohol, which, after being well cooled, was mixed with 24 grams of ethyl iodide and warmed on the water-bath until a test portion diluted with water showed a neutral reaction to litmus. The excess of alcohol and ethyl iodide was then distilled off as far as possible on the water-bath and the above process again repeated. When the treatment had been carried out four times, water was added, and the oil, which was then precipitated and which solidified on standing, separated by filtration. In the first place, the solid was recrystallised from dilute methyl alcohol, from which solvent it separated in needles having a melting point of $60-80^\circ$. These were then ground with cold benzene, in which a considerable quantity dissolved, leaving a residue which melted at $124-125^\circ$.

The following analysis showed this substance to be unchanged ethyl β -imino- α -cyano- γ -phenylbutyrate :

0.1554 gave 0.3888 CO_2 and 0.0903 H_2O . $\text{C} = 68.23$; $\text{H} = 6.50$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.1$ per cent.

The benzene filtrate on evaporation left a residue which melted at $60-65^\circ$, which was again ground with cold benzene yielding a further small quantity of unchanged ethyl β -imino- α -cyano- γ -phenylbutyrate.

The benzene solution from this second separation gave a product which melted at $60-61^\circ$. This was finally recrystallised from methyl alcohol, pure ethyl β -imino- α -cyano- γ -phenyl-*n*-hexoate being thus obtained in small prisms melting at 60° :

0.1564 gave 0.3990 CO_2 and 0.0996 H_2O . $\text{C} = 69.58$; $\text{H} = 7.12$.

$\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 69.8$; $\text{H} = 7.0$ per cent.

*Formation of α -Phenylbutyric Acid, $\text{Ph}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$, and Malonic Acid from Ethyl β -Imino- α -cyano- γ -phenyl-*n*-hexoate.*

The position of the ethyl group in ethyl β -imino- α -cyano- γ -phenylethylbutyrate was determined by the products formed on its complete hydrolysis with methyl alcoholic potash. Five grams of the ethyl salt were heated on the water-bath with a solution containing one-and-a-half times the calculated quantity of caustic potash dissolved in methyl alcohol until the odour of ammonia has ceased to be apparent. Water was then added and the solution evaporated on the water-bath until free from methyl alcohol, when it was acidified with hydrochloric acid and the product allowed to stand. The oil which was first pre-

precipitated on the addition of the acid became solid on standing and was isolated by filtration. Recrystallised from dilute alcohol it was obtained in crystals melting at 42° which is the correct melting point of α -phenylbutyric acid (Neure, *Annalen*, 1889, 250, 154) :

0.2001 gave 0.5358 CO_2 and 0.1333 H_2O . $\text{C} = 73.03$; $\text{H} = 7.40$.

$\text{C}_{10}\text{H}_{12}\text{O}_2$ requires $\text{C} = 73.2$; $\text{H} = 7.3$ per cent.

The aqueous filtrate after extraction with ether was evaporated to dryness on the water-bath, and the residue extracted in a Soxhlet apparatus with ether. The ether solution, after being dried with calcium chloride, was evaporated free from ether, yielding a white solid melting at 132° , which was converted on distillation into acetic acid. It was evidently, therefore, malonic acid, and its formation together with that of α -phenylbutyric acid indicates clearly that the ethyl group in ethyl β -imino- α -cyano- γ -phenyl- γ -ethylbutyrate is attached to the same carbon atom as is the benzene nucleus.

Formation of Ethyl 2:4-Diamino-1-ethylnaphthalene-3-carboxylate,

The conversion of ethyl β -imino- α -cyano- γ -phenyl- n -hexoate into the above derivative of naphthalene was accomplished in the following manner. The finely-ground ethyl salt was added gradually to three times its weight of concentrated sulphuric acid, the acid being kept well cooled in ice through the addition. When all had been added, the sulphuric acid solution, which had become deep indigo blue in colour, was allowed to stand at the ordinary temperature for about two minutes, when it was poured on to ice. On coming in contact with the ice the blue colour of the solution instantly disappeared, forming a light yellow solution from which, however, no separation of the sulphate of the base took place on standing. The clear solution was therefore made alkaline with ammonia and the yellow oil, which was then precipitated, extracted by means of ether. In order further to purify the base, this ethereal solution was extracted twice with dilute sulphuric acid, and the sulphuric acid extract made alkaline with ammonia. The yellow oil precipitated in this way, and which became solid on standing, was collected by filtration and recrystallised from dilute methyl alcohol, being obtained in small yellow prisms melting at 63° :

0.1282 gave 0.3298 CO_2 and 0.0832 H_2O . $\text{C} = 70.16$; $\text{H} = 7.21$.

$\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 69.8$; $\text{H} = 7.0$ per cent.

The *hydrochloride*, $C_{15}H_{18}O_2N_2 \cdot 2HCl$, is prepared by dissolving the base in concentrated hydrochloric acid, and allowing the solution to stand. It consists of almost colourless needles :

0.2102 gave 0.1838 AgCl. $Cl = 21.67$.

$C_{15}H_{18}O_2N_2 \cdot 2HCl$ requires $Cl = 21.5$ per cent.

Formation of 2 : 4-Diamino-1-ethylnaphthalene-3-carboxylic Acid,

In order to prepare this acid, 4 grams of the ethyl salt were mixed with a methyl alcoholic solution of one-and-a-half times the calculated quantity of potash, and heated on the water-bath until a test portion was completely soluble in water. The product was then diluted with water and evaporated on the water-bath until free from methyl alcohol, when dilute hydrochloric acid was added and the precipitate, which then separated, isolated by filtration. The acid, like those already described, is rapidly decomposed by boiling water. It was therefore crystallised by dissolving it in water at 60° and allowing the solution to cool, when the acid separated in small leaflets which melted and decomposed at about 130° , the observed melting point, however, varied from $128-133^\circ$ with the same specimen, depending on the rapidity with which the temperature was raised :

0.1729 gave 0.4281 CO_2 and 0.0969 H_2O . $C = 67.52$; $H = 6.22$.

$C_{13}H_{14}O_2N_2$ requires $C = 67.8$; $H = 6.1$ per cent.

Formation of 2 : 4-Diamino-1-ethylnaphthalene.

This base was prepared by heating the carboxylic acid a few degrees above its melting point. The acid was placed in a small flask and heated in a bath of sulphuric acid at 150° until the evolution of carbon dioxide ceased. The residue, which consisted of a viscid red gum, was dissolved in dilute hydrochloric acid and the solution, after being filtered, made alkaline with dilute aqueous caustic soda. The precipitated base, which solidified on standing, was then collected by filtration and recrystallised from dilute methyl alcohol, being obtained in glistening plates melting at 74° :

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0.1812 gave 0.5127 CO_2 and 0.1256 H_2O . $\text{C} = 77.17$; $\text{H} = 7.70$.

$\text{C}_{12}\text{H}_{14}\text{N}_2$ requires $\text{C} = 77.4$; $\text{H} = 7.5$ per cent.

The *hydrochloride*, $\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$, is precipitated as a white, crystalline powder on dissolving the base in concentrated hydrochloric acid and allowing the solution to stand for some time:

0.2207 gave 0.2429 AgCl . $\text{Cl} = 27.31$.

$\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 27.4$ per cent.

The *platinichloride*, $\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, is formed when a solution of the hydrochloride is mixed with an aqueous solution of platinic chloride. It is a yellow, crystalline powder:

0.2401 gave 0.0781 Pt . $\text{Pt} = 32.53$.

$\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 32.7$ per cent.

Condensation of Benzyl Cyanide with its Sodium Derivative.

As mentioned in the introduction, this condensation was carried out in three different ways, the nitrile being heated with its sodium derivative in alcoholic solution at 100° for (1) half an hour, (2) two hours, (3) twenty-four hours.

(1) *Formation of β -Imino- α -cyano- α -diphenylpropane,*
 $\text{CH}_2\text{Ph} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN})\text{Ph}.$

After a number of preliminary experiments it was ascertained that this substance was produced in the greatest yields in the following way. 11.5 grams of sodium were dissolved in 130 grams of alcohol and mixed with 117 grams of benzyl cyanide, the whole being heated on the water-bath for half an hour. After this time the contents of the flask, which had a slight odour resembling ammonia, were mixed with water and the oil which then separated extracted with ether. The ethereal solution after being freed from alcohol by washing with water was, without drying, evaporated free from ether, and then after being mixed with water distilled in a current of steam until all unchanged benzyl cyanide had passed over. The residue, which consisted of a viscid oil, was then extracted by means of ether, and the ethereal solution, after being dried with calcium chloride, evaporated free from ether. The oil which remained was rapidly distilled under reduced pressure and was found to boil at $274^\circ/20$ mm., passing over as a colourless syrup:

0.2016 gave 0.6070 CO_2 and 0.1111 H_2O . $\text{C} = 82.12$; $\text{H} = 6.17$.

$\text{C}_{16}\text{H}_{14}\text{N}_2$ requires $\text{C} = 82.0$; $\text{N} = 6.0$ per cent.

The identity of this compound with that prepared by E. v. Meyer was shown by the fact that with hydroxylamine it gave an oxime melting

at 107°, identical with that formed by the action of this reagent on the ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Even when carefully purified by distillation β -imino- α -cyano- α -diphenylpropane is a viscid liquid and shows no tendency to become crystalline.

(2) *Formation of β -Imino- α -cyano- α -diphenylpropane,*

β -Keto- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Cyanbenzylidine (6-Amino-5-phenyl-2:4-dibenzylpyrimidine) and Ethylamine.

In this experiment the reacting substances were mixed in the same proportions as in experiment (1) but were heated on the water-bath for two hours. The odour resembling ammonia which was apparent at the end of the first half hour, became very marked on further heating, the contents of the flask becoming at the same time dark red. At the end of the specified time a small quantity of alcohol was distilled over and collected in dilute hydrochloric acid, the solution evaporated on the water-bath to a small bulk and mixed with excess of a solution of platinic chloride. On adding a little alcohol to the mixture a yellow precipitate separated out which was collected by filtration and recrystallised from a little hot water, being thus obtained in yellow cubes. The following analysis showed it to be the platinichloride of ethylamine :

0.2713 gave 0.1054 Pt. Pt = 38.85.

$(\text{C}_2\text{H}_5\text{NH}_2)_2, \text{H}_2\text{PtCl}_6$ requires Pt = 39.0 per cent.

As soon as the small quantity of alcohol necessary for the above experiment had been distilled over, the alcohol solution without further evaporation was mixed with water, acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution after being washed with water to remove alcohol was thoroughly shaken with a solution of three volumes of concentrated hydrochloric acid to one of water.

It was found that by shaking the ethereal solution with this mixture the cyanbenzylidine could be completely extracted in the form of its hydrochloride. This hydrochloride, which is a viscid liquid under ordinary conditions, is quite insoluble in both dilute hydrochloric acid and in ether. Therefore on shaking the ethereal solution with the dilute acid three layers are formed, an upper layer consisting of ethereal solution from which the hydrochloride has been extracted, a middle layer consisting of this hydrochloride in the form of a viscid oil and a lower aqueous layer of dilute hydrochloric acid. The three layers were completely separated in the separating funnel, and it was found that on repeating the process three times the whole of the cyan-

benzylamine present was extracted from the solution. The oily hydrochloride on warming on the water-bath with excess of sodium carbonate solution yielded cyanbenzylamine as a crystalline mass which when recrystallised from absolute alcohol or from light petroleum (b. p. 90—100°) was obtained in slender needles melting at 107°:

0.2076 gave 0.6250 CO₂ and 0.1160 H₂O. C = 82.11; H = 6.25.

C₂₄H₂₁N₃ requires C = 82.0; H = 6.0 per cent.

The properties of cyanbenzylamine have already been described by the investigators mentioned in the introduction. In addition to the published data concerning this substance, we find that it can be distilled under diminished pressure without undergoing any decomposition, passing over at 307° (20 mm.) as a colourless oil which sets to a highly refractive colourless glass on cooling. On dissolving this glass in hot alcohol the solution deposits the original cyanbenzylamine on cooling.*

The *hydrochloride*, C₂₄H₂₁N₃.HCl, was obtained as a crystalline solid in the following way: cyanbenzylamine was dissolved in absolute alcohol containing a small quantity of concentrated hydrochloric acid in which mixture it is readily soluble. Water was then added until a clear solution just remained, when, on standing, the hydrochloride separated in small, colourless needles:

0.1690 gave 0.0640 AgCl. Cl = 9.39.

C₂₄H₂₁N₃.HCl requires Cl = 9.2 per cent.

Cyanbenzylamine is converted into 6-hydroxy-5-phenyl-2:4-dibenzylpyrimidine on heating it with a 10 per cent. sulphuric acid for twenty-four hours. This substance, which was originally prepared by Wache (*J. pr. Chem.*, 1889, [ii], 39, 251), crystallises from alcohol in small needles and melts at 187°:

0.1540 gave 0.4646 CO₂ and 0.0816 H₂O. C = 82.28; H = 5.93.

0.2710 ,, 18.8 c.c. nitrogen at 20° and 752 mm. N = 7.88.

C₂₄H₂₀ON₂ requires C = 81.8; H = 5.7; N = 7.9 per cent.

The ethereal solution after the extraction of cyanbenzylamine was, without drying, evaporated free from ether and the residue distilled in a current of steam until free from the small quantity of unchanged

* The stability of cyanbenzylamine is such that it can be distilled at the ordinary pressure without undergoing decomposition boiling under these conditions above 400°. When once melted, it cools to a clear glass, which does not become crystalline except on long standing. We have found this substance extremely useful for determining the melting points of compounds between 230° and 380°, for which purpose it is well adapted since it does not fume and does not become coloured unless kept near its boiling point for some considerable time.

benzyl cyanide, when it was again extracted with ether, the ethereal solution dried by means of calcium chloride and the ether evaporated. The residue, which consisted of a viscid oil, yielded two chief fractions on distillation under diminished pressure. The lower fraction which boiled at 225—230° (20 mm.) solidified on cooling and was purified by recrystallisation from a mixture of benzene and light petroleum (b. p. 70—80°) being obtained in needle clusters, melting at 86° :

0.1566 gave 0.4712 CO₂ and 0.0800 H₂O. C = 82.06 ; H = 5.71.

0.2406 „ 12 c.c. nitrogen at 20° and 756.5 mm. N = 5.70.

C₁₆H₁₃ON requires C = 81.7 ; H = 5.5 ; N = 6.0 per cent.

The analysis and melting point show this substance to be β -keto- α -cyano- α -diphenylpropane, originally prepared by v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 115), by the action of sodium ethoxide on a mixture of ethyl phenylacetate and benzyl cyanide, a view which was confirmed by its conversion into the oxime (m. p. 107°) by the action of hydroxylamine.

The higher fraction which boiled constantly at 274° (20 mm.) did not solidify on standing, but from the following analysis evidently consisted of β -imino- α -cyano- α -diphenylpropane :

0.2013 gave 0.6042 CO₂ and 0.1110 H₂O. C = 81.86 ; H = 6.12.

C₁₆H₁₄N₂ requires C = 82.0 ; H = 6.0 per cent.

(3) *Formation of β -Keto- α -cyano- α -diphenylpropane and Cyanbenzyliline.*

In this experiment the mixture of benzyl cyanide and sodium ethoxide in alcoholic solution was heated for twenty-four hours at 100°, when the odour of ethylamine was hardly apparent. The product was mixed with water and the oil, which then separated, extracted with ether. The ethereal solution, after being washed with water to remove alcohol, was thoroughly washed with a mixture of three parts of concentrated hydrochloric acid to one of water, when the hydrochloride of cyanbenzyliline separated as a middle layer in the manner already described. From this oily hydrochloride the free base was isolated by means of sodium carbonate the yield of cyanbenzyliline obtained in this way being about 60 per cent. of that theoretically possible. The ethereal solution, after being dried by means of calcium chloride, was evaporated free from ether and distilled under diminished pressure. It was found to boil constantly at 225—230° (20 mm.), and on cooling solidified to a crystalline cake which when recrystallised from a mixture of benzene and light petroleum (b. p. 70—80°) yielded β -keto- α -cyano- α -diphenylpropane, melting at 86°. There is, therefore, apparently no β -imino- α -cyano- α -diphenylpropane formed under these experimental conditions,

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the amount produced in the first instance having either condensed with unchanged benzyl cyanide to form cyanbenzylidine, or having passed into β -keto- α -cyano- α - γ -diphenylpropane through the "hydrolysis" of the imino-group.

Formation of 1:3-Diamino-2-phenylnaphthalene,

The transformation of β -imino- α -cyano- α - γ -diphenylpropane into 1:3-diamino-2-phenylnaphthalene was effected in the following manner: five grams of the liquid nitrile were added gradually to 15 grams of concentrated sulphuric acid, the solution being kept well cooled throughout the addition, since the liquid, which dissolved rapidly in the concentrated acid, caused a considerable rise in temperature. When all had dissolved, the solution, which was dark brown, was allowed to stand at the ordinary temperature for from three to four minutes and then poured into a large volume of water. The solution thus obtained, after being filtered to remove any impurities, was made alkaline with ammonia, and the base, which was then precipitated, collected by filtration and purified by recrystallisation from methyl alcohol or benzene. 1:3-Diamino-2-phenylnaphthalene crystallises in colourless, glistening plates melting at 116° :

0.1564 gave 0.4699 CO_2 and 0.0853 H_2O . $\text{C} = 81.94$; $\text{H} = 6.10$.

0.3238 „ 32.6 c.c. nitrogen at 15.8° and 758.4 mm. $\text{N} = 11.73$.

$\text{C}_{16}\text{H}_{14}\text{N}_2$ requires $\text{C} = 82.0$; $\text{H} = 6.0$; $\text{N} = 12.0$ per cent.

The base becomes slowly coloured red on exposure to the air. It is easily soluble in alcohol or benzene, sparingly so in cold ether, and insoluble in light petroleum. Its solutions exhibit a marked blue fluorescence.

The *hydrochloride* is precipitated in fine feather-like needles on dissolving the base in a little dilute hydrochloric acid, and, after adding an equal volume of concentrated hydrochloric acid, allowing the solution to stand:

0.2211 gave 0.2043 AgCl . $\text{Cl} = 22.92$.

$\text{C}_{16}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 23.1$ per cent.

The hydrochloride is rapidly coloured red on exposure to light.

The *diacetyl* derivative, $\text{C}_{16}\text{H}_{12}\text{N}_2(\text{Ac})_2$, is best prepared by boiling the base with excess of acetyl chloride until all has passed into solution. A considerable quantity of acetyl chloride is necessary for this purpose, since the acetyl derivative is only sparingly soluble in this reagent. When all had dissolved the solution was cooled and allowed

to stand, the crystalline precipitate which then separated being isolated by filtration and purified by dissolving in alcohol and diluting the solution with water. On standing, the *acetyl* derivative separated in small needles, melting at 267° :

0.1743 gave 0.4805 CO_2 and 0.0928 H_2O . $\text{C} = 75.18$; $\text{H} = 5.96$.

$\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 75.5$; $\text{H} = 5.7$ per cent.

The *acetyl acetate*, $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Ac}\cdot\text{CH}_3\cdot\text{CO}_2\text{H}$, was formed in an attempt to prepare the diacetyl derivative by the action of acetic anhydride on the base.

1:3-Diamino-2-phenylnaphthalene was boiled with excess of acetic anhydride for two hours and the solution evaporated in an evacuated desiccator over caustic potash. The gummy residue became completely solid on scratching, and when recrystallised from absolute alcohol was obtained in small prisms melting at 185° :

I. 0.1847 gave 0.4864 CO_2 and 0.0969 H_2O . $\text{C} = 71.82$; $\text{H} = 5.87$

II. 0.1872 ,, 0.4931 CO_2 ,, 0.0988 H_2O . $\text{C} = 71.84$; $\text{H} = 5.90$.

$\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{C} = 71.4$; $\text{H} = 5.9$ per cent.

Other derivatives of this base are still under investigation.

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