LVIII.—*The Formation and Reactions of Imino-compounds. Part III. The Formation of 1:3-Naphthylenediamine and its Derivatives from o-Toluenitrile.*

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In the preceding part of this series (Trans., 1906, 89, 1906) it was demonstrated that derivatives of benzene containing a saturated side-chain of three carbon atoms substituted in the α -position by a nitrile group and in the β -position by an imino-group passed, on treatment with cold concentrated sulphuric acid, into derivatives of 1:3-naphthylenediamine, ring formation taking place between the carbon atom of the benzene ring in the o -position to the side-chain and the carbon atom of the nitrile group. It was further shown that this property was exhibited by other substituted compounds of this class,

provided that a hydrogen atom remained attached to the α - and γ -carbon atoms respectively. The general formula representing this reaction can therefore be represented as follows :

(R = hydrogen or substituting group).

In the present paper it is shown that derivatives of benzene containing a saturated side-chain of two carbon atoms substituted at the α -carbon atom by a nitrile group and at the β -carbon atom by an imino-group also pass under similar treatment into derivatives of 1:3-naphthylidenediamine provided that the ortho-position in the benzene ring in respect to the side-chain is occupied by a methyl group. In this case, therefore, ring formation takes place between the carbon atom of the methyl group and the carbon atom of the nitrile group, and can be represented by the following general formula :

(R = hydrogen or substituting group).

Following along the lines adopted in the previous research in which the truth of the first generalisation mentioned above was established, it is apparent that one of the best compounds to test the truth of the second would be ethyl β -imino- α -cyano- β -*o*-tolylpropionate.

the sodium derivatives of which (III) should be readily prepared by the condensation of *o*-toluonitrile (I) and the sodium compound of ethyl cyanoacetate (II).

There seems to be, however, very little tendency for an ortho-substituted nitrile such as *o*-toluonitrile to enter into condensation with ethyl sodiocyanoacetate to form an imino-compound. That this is due to the presence of the methyl group is shown by the fact that benzonitrile readily reacts with ethyl sodiocyanoacetate under the same conditions, forming the sodium derivatives of ethyl β -imino- α -cyano- β -phenylpropionate (IV),

and that it is the ortho-position of the methyl group which is the inhibiting factor is indicated by the fact that E. v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 113) prepared γ -imino- β -cyano- γ -*p*-tolylpropane, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{:NH})\cdot\text{CHMe}(\text{CN})$, by the action of sodium on a mixture of *p*-toluonitrile and propionitrile in dry ethereal solution.

It is possible by working under the conditions described in the experimental portion to obtain a small quantity of ethyl β -imino- α -cyano- β -*o*-tolylpropionate (I) by the interaction of *o*-toluonitrile and the sodium compound of ethyl cyanoacetate in alcoholic solution, but the yield under the most favourable conditions is scarcely 5 per cent. of the theoretical amount, and it is frequently less than this. A means was therefore sought by which this imino-compound could be prepared in larger quantities, and ultimately the following method was found to give slightly better results.

Many years ago v. Baeyer (*Ber.*, 1886, 19, 428) succeeded in transforming ethyl succinylsuccinate into its di-imino-derivative by fusing this ethyl salt with dry ammonium acetate, a method which had been introduced shortly before by Knorr (*Ber.*, 1886, 19, 46). On applying this reaction to ethyl cyano-*o*-toluoylacetate,

a compound which has been prepared by Haller (*Ber.*, 1888, 21, 644) by the action of *o*-toluoyl chloride on the sodium derivative of ethyl cyanoacetate, it was found that its transformation into the imino-derivative could be partially effected by heating it in a sealed tube with dry ammonium acetate for several hours. The transformation is, however, only partial, and the conditions are difficult to regulate, since a slight variation in the temperature of the reaction brings about either a complete decomposition of both the keto- and the imino-ethyl salts or leaves the former entirely unacted on. Those conditions which are described in the experimental portion were found to give the best results; the yield, however, rarely exceeded 15 per cent. of the theoretical amount. Ethyl β -imino- α -cyano- β -*o*-tolylpropionate (V) is quantitatively converted into ethyl 1:3-naphthylenediamine-2-carboxylate (VI) on treatment with cold concentrated sulphuric acid:

but the change does not take place quite so readily as in the case of ethyl β -imino- α -cyano- γ -phenylbutyrate dealt with in the previous paper. Thus it is necessary to leave the ethyl salt in contact with the strong acid for a slightly longer time before its transformation in the derivative of naphthalene is completely effected.

The identity of the product with ethyl 1:3-naphthylenediamine-2-carboxylate prepared by the action of concentrated sulphuric acid on ethyl β -imino- α -cyano- γ -phenylbutyrate (Trans., 1906, 89, 1920) is shown not only by the fact that the two compounds possess the same melting point, but also by the fact that on hydrolysis they are both converted in the same 1:3-naphthylenediamine-2-carboxylic acid (VII), which on heating above its melting point is transformed into 1:3-naphthylenediamine (VIII):

The second compound chosen to illustrate the application of the second generalisation given on p. 579 was β -imino- α -cyano- α -phenyl- β -*o*-tolylethane (XI):

which should be produced by the interaction of *o*-toluonitrile (IX) and benzyl cyanide (X) in the presence of sodium ethoxide.

It is remarkable that this condensation should proceed with much greater readiness than the corresponding condensation of *o*-toluonitrile with ethyl cyanoacetate, and not only is this the case, but the by-products corresponding with those formed in the condensation of benzyl cyanide with its sodium derivative (compare Trans., 1906, 89, 1930) are entirely absent when the condensation is carried out under the experimental conditions given on p. 588, and are apparently not formed even when the time of heating is increased beyond these limits. Since β -imino- α -cyano- α -phenyl- β -*o*-tolylethane prepared by this means could not be obtained in a solid condition even after being purified by fractional distillation, it was thought that it might be β -imino- α -cyano- α -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(:\text{NH})\cdot\text{CH}(\text{CN})\text{Ph}$, which had been formed by the condensation of benzyl cyanide with its sodium derivative and which it closely resembled both in appearance and properties, and that *o*-toluonitrile had not entered at all into the reaction.

This question was, however, answered by hydrolysing the imino-compound by means of alcoholic potash, when the formation of a

mixture of *o*-toluic and phenylacetic acids, a method for the separation of which is given on p. 589, clearly showed that the condensation product was β -imino- α -cyano- α -phenyl- β -*o*-tolylethane, since the hydrolysis had evidently taken place in accordance with the scheme:

Cold concentrated sulphuric acid instantly transforms β -imino- α -cyano- α -phenyl- β -*o*-tolylethane (XII) into 1:3-diamino-2-phenylnaphthalene (XIII):

The compound formed being identical with 1:3-diamino-2-phenylnaphthalene derived by the action of concentrated sulphuric acid on β -imino- α -cyano- α -diphenylpropane (compare *Trans.*, 1906, 89, 1934).

During the course of these investigations two other condensations were studied, partly because the conditions of the formation of the condensation products were of importance in connexion with the condensations dealt with in this paper and partly because we wished to ascertain the action of concentrated sulphuric acid on imino-cyano-compounds containing a benzene ring to which a side-chain of less than three carbon atoms was attached and which had no substituting methyl group in the ortho-position in the benzene nucleus.

The first condensation investigated was that of benzonitrile with the sodium compound of ethyl cyanoacetate, which was studied in order to ascertain whether the failure of *o*-toluonitrile to enter into condensation with this ethyl salt was shared by other nitriles containing the nitrile group directly attached to the benzene ring. It was found, however, that a good yield of ethyl β -imino- α -cyano- β -phenylpropionate (IV) was obtained by this means, the reaction proceeding in accordance with the equation given on p. 579.

The other condensation was that of benzonitrile with the sodium derivative of benzyl cyanide, which was found to proceed in much the same way as the corresponding condensation of benzyl cyanide with its sodium derivative. In the condensation of benzyl cyanide with its sodium derivative it was shown that the product, after heating the condensing constituents on the water-bath for two hours, consisted of a mixture of about equal proportions of β -imino- α -cyano- α -diphenyl-

propane, α -cyano- α -dibenzylketone, and cyanbenzylidene (compare Trans., 1906, 89, 1931), ethylamine being at the same time eliminated.

The condensation of benzonitrile with the sodium compound of benzyl cyanide proceeds in precisely the same way, and after heating the constituents on the water-bath for two hours the product, which had a strong odour of ethylamine, was found to consist of about equal quantities of β -imino- α -cyano- $\alpha\beta$ -diphenylethane,

formed by the direct condensation of the two nitriles, cyanodeoxybenzoin, $\text{CPh}\cdot\text{CHPh}\cdot\text{CN}$, formed by the "alcoholysis" of the imino-compound, and 6-amino-2:4:5-triphenylpyrimidine,

formed by the condensation of two molecular proportions of benzonitrile with one of benzyl cyanide. It is remarkable that the corresponding condensation of *o*-toluonitrile with the sodium compound of benzyl cyanide already referred to on p. 581 should yield none of these secondary products, but should proceed directly with the formation of the true condensation product.

When ethyl β -imino- α -cyano- β -phenylpropionate (XIV) is treated with cold concentrated sulphuric acid no immediate reaction takes place although the solution becomes deep red. There is therefore no apparent tendency for this compound to be converted into the di-imino-hydrindene derivative in accordance with the equation :

When left in contact with the strong acid for some days the ethyl salt is completely converted into benzoylacetamide (XV), which can be obtained by pouring the strong acid solution into water :

The same reaction is shown by β -imino- α -cyano- $\alpha\beta$ -diphenylethane (XVI), which does not immediately react with concentrated sulphuric acid, but is completely converted after standing in the cold for three days into benzoylphenylacetamide (XVII). This product is also formed when the strong acid solution is poured into water.

There is, therefore, apparently no tendency for these compounds to be converted into derivatives of hydrindene although the formation in

each of the above instances of a red condensation product, which was, however, too small for further investigation, seems to show that the reaction proceeds partly in that direction.

Experiments are, however, in progress which show that the action of concentrated sulphuric acid on nitriles gives rise to a definite addition product the formation of which may be probably represented by the general equation:

In some cases, the details of which it is hoped will shortly be placed before the Society, these sulphuric acid addition products have been isolated as crystalline compounds which are found to be extremely reactive substances. The transformation of nitriles into the amides of the corresponding acids which has been observed by many investigators is, we find, caused by the action of water on the sulphuric acid addition product thus:

If, however, there is a tendency for the compound to enter into ring formation then sulphuric acid is eliminated thus:

In the two compounds ethyl β -imino- α -cyano- β -phenylpropionate (XIV) and β -imino- α -cyano- $\alpha\beta$ -diphenylethane (XVI) it is this addition product with sulphuric acid which on treatment with water yields the amide, and it is therefore probable that on further investigation the conditions under which sulphuric acid is eliminated and the ring formed will be discovered. A complete study of the action of concentrated sulphuric acid on the nitriles and the conditions under which sulphuric acid is eliminated from them with the formation of carbon rings is in progress.

Ethyl-β-imino α-cyano-β-o-tolylpropionate,
 $C_6H_4Me \cdot C(:NH) \cdot CH(CN) \cdot CO_2Et.$

(1) *Condensation of o-Toluenitrile with the Sodium Derivative of Ethyl Cyanoacetate.*—This condensation was effected in the following manner. 11·5 Grams of sodium were dissolved in 140 grams of absolute alcohol and the solution mixed with 57 grams of ethyl cyanoacetate, and subsequently with 59 grams of *o*-toluenitrile. The mixture was then heated on the water-bath until the white sodium derivative had completely dissolved, when it was transferred to a convenient number of thick-walled glass flasks which had been blown from ordinary Carius tubing. When these flasks had been three-parts filled with the liquid they were sealed in the ordinary way and heated in a paraffin bath at 120° for twenty-four hours. After cooling, the flasks were opened and the viscid gelatinous contents dissolved in dilute hydrochloric acid, the oil which then separated being extracted by means of ether. The ethereal solution was washed thoroughly with water and then with dilute aqueous sodium carbonate, being finally evaporated free from ether and the residue distilled with steam. By this means the whole of the unchanged *o*-toluenitrile was removed from the product, the residue, which solidified on cooling, being then separated by filtration. The ethyl salt was crystallised from absolute alcohol, being obtained in this way in white, glistening prisms melting at 135°:

0·1881 gave 0·4667 CO₂ and 0·1055 H₂O. C = 67·67; H = 6·23.

C₁₃H₁₄O₂N₂ requires C = 67·8; H = 6·1 per cent.

The yield of β-imino-α-cyano-β-*o*-tolylpropionate obtained by this process is exceedingly small, being scarcely 5 per cent. of the theoretical amount. Since no better yield was obtained by varying the conditions of the experiment, the following process was tried with slightly better success.

(2) *Action of Ammonium Acetate on Ethyl Cyano-*o*-toluoylacetate.*—Ethyl cyano-*o*-toluoylacetate has been prepared by Haller (*Ber.*, 1888, 21, 664) by the action of *o*-toluoyl chloride on the sodium compound of ethyl cyanoacetate. The details of the preparation of this substance which we found most convenient were as follows. Sixty grams of ethyl cyanoacetate were added to a solution of 11·5 grams of sodium dissolved in 140 grams of absolute alcohol and the white sodium derivative which separated on cooling filtered by the aid of the pump. After being washed with dry ether, the sodium compound was transferred to a large flask, ether added, and then, gradually, 77 grams of *o*-toluoyl chloride. A vigorous reaction started as soon as the acid chloride was added, and several times during the process of the addition

the contents of the flask had to be cooled under running water. When all the chloride had been added the ethereal solution was mixed with water, separated in the funnel, and after being thoroughly washed with water and dilute aqueous sodium carbonate, dried and evaporated free from ether. The oily residue, on being distilled under diminished pressure, passed over almost constantly at $180\text{--}181^\circ$ (20 mm.) as a viscous, colourless oil which slowly solidified on standing. The solid was spread on a porous plate and crystallised from dilute alcohol, being obtained in colourless, glistening plates melting at 37° :

0.1789 gave 0.4420 CO_2 and 0.0931 H_2O . $\text{C} = 67.38$; $\text{H} = 5.78$.

$\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C} = 67.5$; $\text{H} = 5.6$ per cent.

The conversion of ethyl cyano-*o*-toluoylacetate into the corresponding imino-compound was effected by the action of ammonium acetate, the process being much the same as that employed by v. Baeyer (*Ber.*, 1886, 19, 428) for the preparation of the di-imide of ethyl succinylsuccinate from ethyl succinylsuccinate, although in the present instance the change takes place with much greater difficulty, and the yield of the imino-compound is not nearly so satisfactory.

Twenty grams of ethyl salt were dissolved in 200 grams of dry melted ammonium acetate and the mixture heated in a sealed Carius tube at 120° for six hours. After this time the tube was opened and the liquid contents poured into cold water, when, on standing, a solid crystalline substance separated. This was collected, dried, and recrystallised twice from absolute alcohol, being thus obtained in white, glistening prisms melting at 135° :

0.1890 gave 0.4672 CO_2 and 0.1061 H_2O . $\text{C} = 67.41$; $\text{H} = 6.23$.

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

The compound was identical with ethyl β -imino- α -cyano- β -*o*-tolylpropionate prepared from *o*-toluonitrile and ethyl sodiocyanoacetate in the manner already described, and, although the yield of the ethyl salt is greater when working through the toluoylacetate than by direct condensation, yet in the former case it is far from satisfactory, being only 15 per cent. of the theoretical quantity from the amount of ethyl cyano-*o*-toluoylacetate used. In fact, the ethyl imino-salt appears to be an exceedingly difficult compound to prepare in any quantity.

Ethyl β -imino- α -cyano- β -*o*-tolylpropionate is readily soluble in hot alcohol and benzene, but sparingly so in these solvents in the cold; it is practically insoluble in light petroleum. The ethyl salt is not acted on by cold dilute aqueous alkalis, a fact which serves to distinguish it from the corresponding toluoyl derivative which is readily dissolved by these reagents.

*Hydrolysis of Ethyl β -Imino- α -cyano- β -*o*-tolylpropionate.*—As in the cases of similar ethyl imino-salts already dealt with, the constitution

of the above substance was determined by means of alkaline hydrolysis previous to its transformation into the naphthalene ring in order that its formula might be established beyond question. The hydrolysis, which, as was to be expected, yielded a mixture of *o*-toluic and malonic acids, was carried out as follows. Seven grams of the ethyl salt were dissolved in a solution of 8 grams of potash dissolved in absolute methyl alcohol, and the solution heated on the water-bath until the odour of ammonia ceased to be apparent, and until a test portion on dilution with water remained clear, when it was poured into an evaporating basin and freed from methyl alcohol by evaporation on the water-bath. The solid residue was then dissolved in water and the solution acidified with hydrochloric acid, the oil which then separated and which rapidly solidified being separated by filtration. It crystallised from water in long, colourless needles melting at 102° , and was proved by the following analysis to be *o*-toluic acid :

0.2103 gave 0.5455 CO_2 and 0.1097 H_2O . $\text{C} = 70.74$; $\text{H} = 5.79$.

$\text{C}_8\text{H}_8\text{O}_2$ requires $\text{C} = 70.6$; $\text{H} = 5.9$ per cent.

The aqueous solution, after being filtered from the above acid, was extracted with ether in order to remove the last traces of *o*-toluic acid and was then evaporated to dryness on the water-bath, the solid residue being subsequently extracted in a Soxhlet apparatus with ether. The ethereal solution, after being dried, was evaporated free from ether, leaving a solid residue which, since it melted at 132° with decomposition and gave acetic acid on distillation, evidently consisted of malonic acid.

Formation of Ethyl 1:3-Naphthylenediamine-2-carboxylate from Ethyl β -Imino- α -cyano- β -o-tolylpropionate.—In order to effect this transformation 10 grams of the ethyl salt were added gradually to 30 grams of concentrated sulphuric acid cooled in ice. The solid rapidly dissolved and the solution became greenish-yellow in colour. It was allowed to stand for ten minutes after the last portion of the ethyl salt had been added, and was then poured on ice, when a clear yellow solution was obtained from which a yellow, crystalline precipitate separated on standing. This was collected by filtration, dissolved in a little cold water, the solution rendered alkaline with ammonia, and the resulting yellow precipitate collected by filtration. It crystallised from ether in golden-yellow plates melting at 108° :

0.2232 gave 0.5547 CO_2 and 0.1251 H_2O . $\text{C} = 67.77$; $\text{H} = 6.22$.

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

This substance was proved to be identical with ethyl 1:3-naphthylenediamine-2-carboxylate prepared by the action of concentrated sulphuric acid on ethyl β -imino- α -cyano- γ -phenylbutyrate, not only by direct comparison with this substance, but also by the fact that on

hydrolysis with methyl-alcoholic potash it was converted into 1:3-naphthylenediamine-2-carboxylic acid melting at 85° with decomposition, which in its turn was transformed into 1:3-naphthylenediamine melting at 96°, on heating at 100° (compare Trans., 1906, 89, 1920 *et. seq.*).

β-Imino-*α*-cyano-*α*-phenyl-*β*-*o*-tolylethane.—The condensation between benzyl cyanide and *o*-toluonitrile was effected in the following way. 11.5 Grams of sodium were dissolved in 140 grams of alcohol, the solution mixed with 59 grams of benzyl cyanide and then with 60 grams of *o*-toluonitrile. After the mixture had been heated on the water-bath for two and a half hours, water was added, and the oil which then separated extracted with ether. The ethereal solution after being washed with water was thoroughly shaken with hydrochloric acid (3:1)*, and finally with dilute aqueous sodium carbonate solution. It was then, without drying, freed from ether by evaporation, and the residue distilled in a current of steam.

When the product had been freed from unchanged benzyl cyanide and *o*-toluonitrile by this means, the residual oil was again extracted with ether, the ethereal solution dried and evaporated free from ether, the brown oil which remained being distilled under diminished pressure. Practically the whole of the product distilled constantly at 275° (20 mm.) as a viscous oil which did not show any tendency to crystallise:

0.1992 gave 0.6008 CO₂ and 0.1071 H₂O. C = 82.25; H = 5.97.

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

It is possible that traces of *β*-imino-*α*-cyano-*αγ*-diphenylpropane, formed by the condensation of benzyl cyanide with its sodium derivative (compare Trans., 1906, 89, 1930), may be mixed with this product and hence prevent it from crystallising. The compound seemed to be, however, a perfectly homogeneous substance distilling without any tendency to decompose under a pressure of 20 mm., whereas *β*-imino-*α*-cyano-*αγ*-diphenylpropane as already mentioned (*loc. cit.*) has to be rapidly distilled in small quantities under this pressure, otherwise decomposition sets in. *β*-Imino-*α*-cyano-*α*-phenyl-*β*-*o*-tolylethane, therefore, like its isomeride, appears to be a liquid under ordinary conditions.

Hydrolysis of β-Imino-*α*-cyano-*α*-phenyl-*β*-*o*-tolylethane.—The constitution of this substance was determined in the usual way by alkaline hydrolysis. Ten grams of the imino-compound were mixed with an alcoholic solution of 10 grams of potash and the mixture heated on the water-bath until a test portion on diluting with water remained

* To remove any pyrimidine derivative which may have been produced (compare Trans., 1906, 89, 1931). In this case, however, no third layer was formed, indicating that no derivative of pyrimidine was present.

clear. The alcohol was then completely eliminated by evaporation on the water-bath and the product, after being diluted with water, acidified with hydrochloric acid. The solid acids which were precipitated by this means were collected by filtration. They were separated by taking advantage of the fact that the calcium salt of *o*-toluic acid is less soluble in alcohol than the calcium salt of phenylacetic acid. The separation was effected as follows. The mixed acids were dissolved in water, and the solution mixed with excess of pure calcium carbonate. As soon as all effervescence had ceased the aqueous solution was separated from the unchanged carbonate by filtration and evaporated to a small bulk on the water-bath. When crystallisation commenced the solution was allowed to cool, and the mixed calcium salts which then crystallised out were separated by filtration and dried on a porous plate. For the purpose of separation the salts were dissolved in hot 90 per cent. alcohol (sp. gr. 0.81) and the solution allowed to cool. The calcium salt which then separated was collected and again recrystallised from alcohol, the process being repeated a third time, when a product was obtained which on reconversion into the acid gave a solid which melted at 100—102°. It was finally purified by recrystallisation from water and obtained in long needles melting at 104°, which from the following analysis evidently consisted of *o*-toluic acid:

0.2106 gave 0.5218 CO₂ and 0.1235 H₂O. C = 67.51; H = 6.51.

C₇H₈O₂ requires C = 67.8; H = 6.4 per cent.

The calcium salt obtained on evaporating the mother liquors from the above separation to dryness was again treated in the same way, yielding a further quantity of the calcium salt of *o*-toluic acid. The ultimate residues were then reconverted into the acid, yielding a product which melted at 76° and which possessed the characteristic appearance and odour of phenylacetic acid.

Formation of 1:3-Diamino-2-phenylnaphthalene from β-Imino-α-cyano-α-phenyl-β-o-tolyethane.

In order to effect this transformation 20 grams of the imino-compound were added gradually to three times its weight of well-cooled, concentrated sulphuric acid.

The solution, which became greenish-yellow in colour, was allowed to stand for two minutes after the last quantity of the imino-compound had been added, and was then poured into a large volume of water. The solution thus obtained, after being filtered to remove a small quantity of insoluble matter, was rendered alkaline with ammonia, and the resulting copious precipitate isolated by filtration. By crystallisa-

tion from methyl alcohol the base was obtained in glistening plates melting at 116° :

0.2085 gave 0.6265 CO_2 and 0.1137 H_2O . $\text{C} = 81.95$; $\text{H} = 6.05$.

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

This base was proved to be identical with that derived from β -imino- α -cyano- α -diphenylpropane (Trans., 1906, 89, 1934), not only by direct comparison with the substance, but also by the fact that on treatment with acetyl chloride it was converted into the same diacetyl derivative melting at 267° .

Ethyl β -Imino- α -cyano- β -phenylpropionate.

The condensation between benzonitrile and the sodium compound of ethyl cyanoacetate was effected in the following way. 11.5 Grams of sodium were dissolved in 140 grams of alcohol and the solution mixed with 57 grams of ethyl cyanoacetate, and then with 52 grams of benzonitrile, the whole being heated on the water-bath for ten hours. At the end of this time the contents of the flask had become almost solid, owing to the formation of a brown, gelatinous solid. Water was added, and the solution after being strongly acidified with hydrochloric acid was extracted thoroughly with ether.

The ethereal extract was washed with water and then with dilute sodium carbonate solution, being finally evaporated free from ether and distilled in a current of steam until all unchanged benzonitrile had passed over. The residue, which consisted of a dark brown, heavy oil, solidified on cooling. It was collected by filtration and crystallised from alcohol, being obtained in lustrous plates melting at 125° :

0.1945 gave 0.4744 CO_2 and 0.1007 H_2O . $\text{C} = 66.52$; $\text{H} = 5.71$.

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

The compound closely resembles both in appearance and properties its next higher homologue, ethyl β -imino- α -cyano- γ -phenylbutyrate, and also melts at the same temperature as this substance. Its constitution was determined by hydrolysing it with an alcoholic solution of potash, the hydrolysis being effected by boiling the ethyl salt with a methyl-alcoholic solution of $1\frac{1}{2}$ times the calculated quantity of potash until a test portion was completely soluble in water; the alcohol was then evaporated and the residue, after being diluted with water, acidified by means of hydrochloric acid. The white, crystalline precipitate which then separated was collected by the aid of the pump and recrystallised from hot water. It melted at 121° and gave all the reactions of benzoic acid. The aqueous solution was evaporated to dryness and the residue extracted in a Soxhlet apparatus with ether. The dried ethereal solution on evaporation yielded malonic acid melting at 132° .

Action of Concentrated Sulphuric Acid on Ethyl β -Imino- α -cyano- β -phenylpropionate.

Concentrated sulphuric acid has no immediate action on ethyl β -imino- α -cyano- β -phenylpropionate, and the ethyl salt can be dissolved in the strong acid without apparent change, since it can be recovered on pouring the solution into water. If, however, the solution is left to stand for some days, the ethyl salt is converted into benzoyl-acetamide. Ten grams of the imino-compound were added gradually to three times its weight of concentrated sulphuric acid, and the solution, after standing for three days, poured into a large volume of water. The solution became deep red, and a red, flocculent precipitate separated on standing. This was collected by filtration, but the quantity proved too small for further investigation. The filtrate was rendered alkaline with ammonia and extracted with ether, the ethereal solution being dried and evaporated free from ether. The residual solid was crystallised from a little water and obtained in lustrous plates melting at $114-115^\circ$ with evolution of gas at 160° :

0.1661 gave 0.4037 CO_2 and 0.0831 H_2O . C = 66.28 ; H = 5.56.

$\text{C}_9\text{H}_9\text{O}_2\text{N}$ requires C = 66.3 ; H = 5.5 per cent.

The compound is evidently identical with benzoylacetamide,

which Obrégia (*Annalen*, 1891, 266, 332) prepared by the action of concentrated sulphuric acid on ω -cyanoacetophenone and described as melting at $111-113^\circ$.

Condensation of the Sodium Compound of Benzyl Cyanide with Benzonitrile.

The interaction of benzyl cyanide and benzonitrile in the presence of metallic sodium has already been studied by a number of investigators. The object of the present experiments was to determine whether the condensation between these two nitriles in the presence of sodium ethoxide would proceed in the same way as the corresponding condensation of benzyl cyanide with its sodium derivative (compare *Trans.*, 1906, 89, 1930).

11.5 Grams of sodium were dissolved in 140 grams of alcohol and a mixture of 58 grams of benzyl cyanide and 52 grams of benzonitrile added, the whole being heated on the water-bath for three hours. During the time of heating the odour of ethylamine was very strong, showing that the imino-group was being "hydrolysed" in the same manner as in the corresponding experiment with benzyl cyanide. After being heated for the time stated, the contents of the flask, which were

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quite solid, were treated with water and extracted with ether, the ethereal solution after being washed with water and dilute sodium carbonate solution evaporated free from ether, and the residue distilled in a current of steam. When all the unchanged benzyl cyanide and benzonitrile had passed over, the viscid, oily residue was extracted by means of ether, and the ethereal solution thoroughly shaken with a mixture of three parts of concentrated hydrochloric acid to one of water. By this means a large quantity of a semi-solid hydrochloride which was extracted from the ethereal solution was separated in the funnel and converted into the free base by treatment with sodium carbonate solution. The white product thus obtained gave, on crystallisation from alcohol, fine, white needles melting at 177° :

0.1563 gave 0.4698 CO_2 and 0.0782 H_2O . $\text{C} = 81.98$; $\text{H} = 5.55$.

$\text{C}_{22}\text{H}_{17}\text{N}_3$ requires $\text{C} = 81.7$; $\text{H} = 5.3$ per cent.

This substance is evidently identical with 6-amino-2:4:5-triphenyl pyrimidine, $\text{CPh} \begin{smallmatrix} \text{C}(\text{NH}_2) \cdot \text{N} \\ \text{CPh} = \text{N} \end{smallmatrix} \text{CPh}$, prepared by Wache (*J. pr. Chem.*, 1889, [ii], 39, 253) by the action of benzonitrile on the sodium compound of dibenzyl cyanide.

The ethereal solution, after the separation of the hydrochloride of the above base, was dried and the ether evaporated. The solid residue after crystallisation twice from alcohol was obtained in colourless plates melting at 146° :

0.1719 gave 0.5167 CO_2 and 0.850 H_2O . $\text{C} = 81.96$; $\text{H} = 5.52$.

$\text{C}_{15}\text{H}_{12}\text{N}_2$ requires $\text{C} = 81.8$; $\text{H} = 5.4$ per cent.

This compound is evidently β -imino- α -cyano- $\alpha\beta$ -diphenylethane, identical with the compound prepared by E. v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 116) by the action of ammonia on cyanodeoxybenzoin and by Walther and Schickler (*J. pr. Chem.*, 1897, [ii], 55, 320) by the action of sodium on a mixture of benzyl cyanide and benzonitrile in ethereal solution.

The alcoholic mother liquors from the recrystallisation of the above imino-compound were evaporated to a small bulk, when a further quantity of β -imino- α -cyano- $\alpha\beta$ -diphenylethane was obtained. The ultimate filtrate was then evaporated to dryness and the solid residue crystallised from light petroleum (b. p. 60 — 70°), yielding white needles melting at 90° :

0.1812 gave 0.5408 CO_2 and 0.851 H_2O . $\text{C} = 81.38$; $\text{H} = 5.21$.

$\text{C}_{15}\text{H}_{11}\text{ON}$ requires $\text{C} = 81.4$; $\text{H} = 5.0$ per cent.

This compound is evidently α -cyanodeoxybenzoin,

first prepared by E. v. Meyer (*loc. cit.*) by the interaction of

ethyl benzoate and benzyl cyanide in the presence of sodium ethoxide.

Action of Concentrated Sulphuric Acid on β -Imino- α -cyano- $\alpha\beta$ -diphenylethane.

The action of concentrated sulphuric acid on the imino-compound does not lead to the closing of the ring, but only transforms the nitrile into the amide of the corresponding ketone.

Five grams of the imino-compound were dissolved in three times its weight of concentrated sulphuric acid and the solution allowed to stand in the cold for forty-eight hours. On pouring the acid into water a clear solution was obtained, from which a crystalline precipitate separated on standing.

This was collected by filtration and recrystallised from alcohol, being obtained in small needles melting at 178° :

0.1626 gave 0.4484 CO_2 and 0.0866 H_2O . $\text{C} = 75.21$; $\text{H} = 5.96$.

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 75.3$; $\text{H} = 5.8$ per cent.

This compound is evidently identical with benzoylphenylacetamide, $\text{COPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$, which Walther and Schickler (*J. pr. Chem.*, 1897, [ii], 55, 314) prepared by the action of concentrated sulphuric acid on α -cyanodeoxybenzoin and described as melting at 172 – 173° .

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