

LXV.—*An Extension of the Benzoin Synthesis.*

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THE observation that benzaldehyde is readily converted into benzoin by means of potassium cyanide was first made by Zinin (*Annalen*, 1840, **31**, 329 and **34**, 186), although the details of the method as at present usually practised were suggested by Zincke (*ibid.*, 1879, **198**, 151), whilst Fischer extended it to the condensation of furfuraldehyde.

The reaction is of especial interest, first, because the potassium cyanide plays the part of a true catalytic agent, being practically unaltered in amount at the end of the operation and need be used only in relatively small quantities, and secondly, because it is one which is not applicable to the aldehydes of the fatty series.

Of the theories which have been put forward as to the mechanism of the reaction may first be mentioned those of Zincke (*Ber.*, 1876, **9**, 1772), Pomeranz (*Monatsh.*, 1900, **21**, 389), Koelichen (*Zeitsch. physikal. Chem.*, 1900, **33**, 129), and Nef (*Annalen*, 1895, **287**, 342, and 1897, **298**, 312).

Zincke assumed that mandelonitrile was formed as an intermediate product and that this, reacting with unchanged benzaldehyde, with elimination of hydrogen cyanide, yielded benzoin; but he found that benzaldehyde and hydrocyanic acid did not react to give benzoin. Pomeranz assumed a catalytic action of hydroxyl ions and Nef supposed the change to be similar in character to an aldol condensation.

The theory of Chalaney and Knoevenagel is well known (*Ber.*, 1892, **25**, 295). They suggested that a potassium derivative of benzaldehyde and mandelonitrile was formed in the first instance and these subsequently reacted in the following manner,

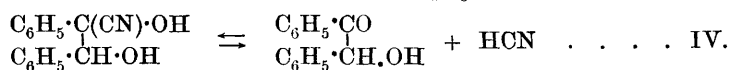
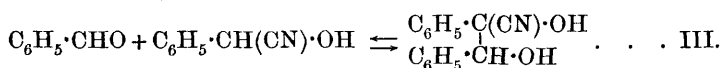
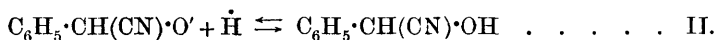
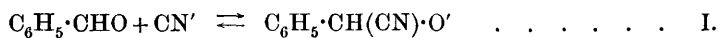
$$\text{C}_6\text{H}_5 \cdot \text{CK} : \text{O} + \text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CN} = \text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_5 + \text{KCN},$$

but the existence of this potassium compound was purely hypothetical, for no compound of this kind has been isolated, nor is there even any indirect evidence that the hydrogen atom assumed to be replaced by potassium is reactive in presence of alkalis.

In a series of papers on the additive reactions of hydrogen cyanide, one of the present authors showed that the addition of this compound to aldehydes and ketones is dependent on the presence of cyanogen ions, and suggested that a complex cyanogen ion is formed at an intermediate stage in all cases (*Trans.*, 1903, **83**, 995; 1904, **85**, 1206).

Thus in the case of benzaldehyde the complex ion $\text{C}_6\text{H}_5 \cdot \text{CH} \begin{matrix} \text{O} \\ \diagup \\ \text{CN} \end{matrix}$ was assumed to be formed in the first instance. It was further shown that

benzaldehyde yields mandelonitrile with potassium cyanide even in presence of alkali (Trans., 1903, 83, 1003), and the benzoin reaction was attributed to a reaction of benzaldehyde with mandelonitrile. The latter, being a hydroxybenzyl cyanide, contains a reactive hydrogen attached to the carbon atom between the phenyl group and the cyano-group, and in virtue of this must be capable of forming an aldol-like condensation product with aldehydes. With benzaldehyde, the product must be the unstable cyanohydrin of benzoin (*loc. cit.*, 1004). The following thus represents the suggested stages in the reaction :

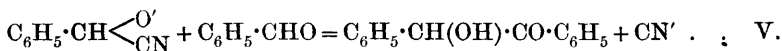


This scheme serves to explain (1) why cyanide is necessary, because, although there is no evidence that the hydrogen atom in the $\cdot\text{CH}:\text{O}$ group of aldehydes higher than formaldehyde is reactive in presence of bases, it is well recognised that in the $\cdot\text{CH}$ group between $\text{CN}\cdot$ and an aromatic nucleus, the hydrogen atom is labile and the occurrence of an aldol-like reaction between benzaldehyde and benzyl cyanide in presence of alkalis is no longer in doubt ; (2) the need for the use of potassium cyanide instead of hydrogen cyanide alone because reactions I and III do not occur with measurable speed in absence of bases ; (3) aliphatic aldehydes do not react in the same way as does benzaldehyde, because the fatty nitriles with the group $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{CH}\cdot\text{CN}$ or $\text{C}\cdot\text{CH}_2\cdot\text{CN}$ manifest relatively very little tendency to take part in the aldol and allied condensations, in comparison with those of the aromatic series.

Finally, reactions III and IV belong to well-known types, whilst direct evidence of the existence of the complex ion assumed in I and II was obtained later, when an additive compound of benzaldehyde and potassium cyanide (the potassium derivative of mandelonitrile) $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CN})\cdot\text{OK}$ was isolated (Trans., 1904, 85, 1208).

Some time after these suggestions were published, a communication from Bredig and Stern appeared (*Zeitsch. Elektrochem.*, 1904, 10, 582, *et seq.*). They described experiments on the velocity of the benzoin condensation and were able fully to establish that the reaction is brought about catalytically by the potassium cyanide, the velocity being directly proportional to the concentration of the cyanogen ion in all cases. They accepted the view that a complex ion is formed as in I above, but as they found that the velocity was not affected by the

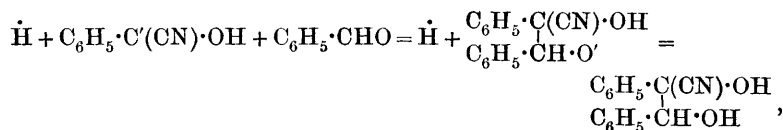
addition of excess of a base, they assumed that the change subsequent to I was as follows :



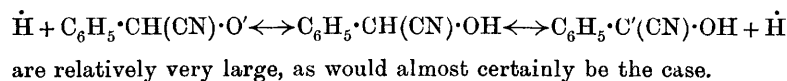
A further reason for rejecting the view expressed by III was advanced by one of these authors (Stern, *Inaugural Dissertation*, Leipzig, 1904, p. 39), namely, that above 25° the amount of the intermediate products present is extremely minute ("bei höherer Temperatur als 25° die Menge der eventuellen Zwischenproducte äusserst gering ist"), a conclusion drawn from conductivity experiments on solutions of benzaldehyde and potassium cyanide at varying temperatures.

It must here be pointed out, however, that the dependence of III on the concentration of hydroxyl ions is not more inevitable than that suggested by Bredig and Stern, nor can the second objection be sustained as conclusive. This depends on a variety of unknown circumstances and in particular on the ultimate mechanism of the aldol condensation III, which itself must be regarded as a complicated change.

If, for example, III proceeds as the result of a preliminary ionisation of mandelonitrile at the $\cdot\text{CH}\cdot$ group, followed by a union of the resulting ion with benzaldehyde in this way :

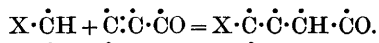


then the velocity will be proportional to the concentration of this new ion, and therefore to that of the isomeric ion as in the theory of Bredig and Stern, if the simple ion reactions

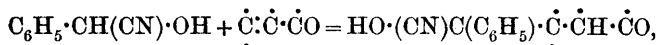


If, in accordance with Lapworth's view, mandelonitrile unites with benzaldehyde to form, in the first instance, an aldol-like product, namely, benzoincyanohydrin, in virtue of the presence of the labile hydrogen atom in the group $\cdot\text{CH}\cdot\text{CN}$, then it is to be anticipated that the nitrile will be found capable of taking part in other condensations in which substances yielding aldols in this way play a part.

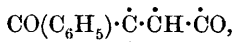
One of the most familiar reactions of such compounds is that in which they unite with $\alpha\beta$ -unsaturated ketones, &c., in accordance with the equation (where $\text{X} = \cdot\text{CO}\cdot, \cdot\text{CN}$, &c.).



Mandelonitrile might thus be expected to react with $\alpha\beta$ -unsaturated ketones as follows :



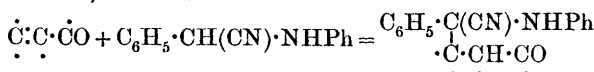
that is, yielding the cyanohydrin of a δ -diketone,



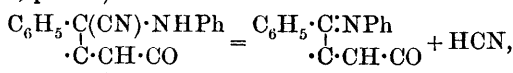
which the product might at once give by elimination of hydrogen cyanide, as in the benzoïn condensation itself.

On making experiments in this direction with mandelonitrile it was found that the latter was too unstable and that the products of its decomposition took part in by-reactions which obscured the result of the condensation and similar results attended the use of the benzoyl derivative of mandelonitrile. It was therefore decided to employ a derivative of the nitrile less easily affected by alkalis, but of exactly analogous structure, and for this purpose the aniline derivative, namely, the compound obtained by combining hydrogen cyanide with benzylideneaniline, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, was used.

Comparing the expected reactions of this compound with the reaction III and IV respectively, supposed to obtain during the benzoïn reaction, we have

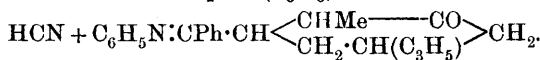
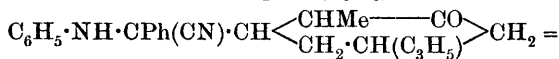
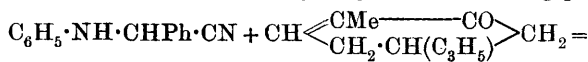


(compare III, p. 695) and

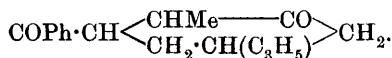


(compare IV, *loc. cit.*), that is to say, the phenylimino-derivative of the β -benzoyldihydroketone would finally be obtained.

On trying the reaction with carvone as the unsaturated ketone it was found to occur in exactly the manner anticipated, the phenylimino-derivative of β -benzoyldihydrocarvone being produced.



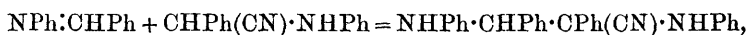
The new substance is easily hydrolysed by acids with formation of aniline and two stereoisomeric benzoyldihydrocarvones,



One of these is present in preponderating amount, and has the properties which should attach to a substance having the structure

here assigned to it. Thus, it absorbs only one molecular proportion of bromine, showing that it now contains only the carbon double linking in the *isopropenyl* group. It shows the phenomenon of mutarotation in presence of traces of alkalis indicating that it contains the group $\begin{matrix} X \\ Y \end{matrix} > \text{CH} \cdot \text{CO} \cdot$, not present in the original carvone. Further, although it could be made to unite with only one molecular proportion of hydroxylamine, its dioxime was finally isolated by the indirect process of treating the original phenylimino-compound with hydroxylamine acetate, aniline being eliminated in the process.

A by-product obtained during the condensation of benzylidene-aniline hydrocyanide with carvone is worthy of brief notice here. It has the composition of a compound of benzylideneaniline and benzylideneaniline hydrocyanide united in molecular proportions, and is almost certainly formed by a reaction again precisely analogous to the benzoin condensation proper, its formation being represented as follows,



when it is formulated as benzoincyanohydrin, in which the hydroxyl groups are replaced by aniline residues.

The above synthesis of the anil of benzoyldihydrocarvone appears to confirm the view that mandelonitrile is in reality an intermediate product in the benzoin synthesis, but at the same time it suggests an analogy with the hypothetical condensation as expressed by Bredig and Stern (given on p. 696), for in both a cyanogen ion is eliminated and the product thus found without cyanogen. It was therefore thought very desirable that other cases of the condensation of benzylideneaniline hydrocyanide with $\alpha\beta$ -unsaturated ketones should be investigated in the expectation that the intermediate cyano-compound corresponding to that postulated by Lapworth might be sufficiently stable to be isolated.

This hope was realised when, instead of carvone, benzylideneacetophenone was used. The interaction of the latter and benzylidene-aniline hydrocyanide takes place very rapidly in dilute alcoholic solution, and if the proper conditions are employed the product separates at once on addition of a little alkali into the mixed solution, and the reaction takes place in the following manner :

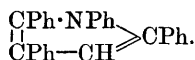


This substance, the analogue of benzoincyanohydrin, retains its hydrogen cyanide with remarkable tenacity, but, when heated above its melting point, loses the elements of hydrogen cyanide and of water. This is easily understood, as elimination of hydrogen cyanide would

lead to the formation of the aniline derivative of an open chain δ -diketone (in this instance of desylacetophenone),



but these compounds very readily pass, with loss of water, into substituted pyrroles, and the product here should therefore yield tetraphenylpyrrole,



On examination the product was, in fact, found to be identical with the substance having the structure depicted, obtained by Smith (*Trans.*, 1890, **57**, 646) on heating desylacetophenone with aniline.

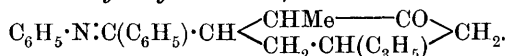
It is worthy of note that the original process for preparing this compound from benzaldehyde involved (1) the benzoin condensation, (2) the interaction of the product and acetophenone, and (3) the action of aniline on the compound so obtained. In the present case the same reactions are used, but in a different order, the benzoin condensation being brought about in a manner which throws definite light on the changes involved therein.

It should be mentioned that benzylideneaniline itself does not yield the condensation products described in this paper, the presence of cyanide and alkali being essential in both instances as in the benzoin condensation proper.

EXPERIMENTAL.

Condensation of Benzylideneaniline Hydrocyanide with Carvone.

β -Phenyliminobenzoyldihydrocarvone,



Preliminary experiments having shown that mandelonitrile was too readily decomposed by alkali to form condensation products with $\alpha\beta$ -unsaturated ketones, its aniline derivative was prepared by shaking a cold alcoholic solution of benzylideneaniline with the requisite quantity of hydrogen cyanide in presence of potassium cyanide, a method which gives a nearly quantitative yield of the hydrocyanide.

Twenty-two grams of this substance were mixed with 15 grams of carvone and an equal bulk of alcohol, and the whole warmed until a clear solution was formed. On cooling rapidly to 25° , and before the hydrocyanide had commenced to separate, 12 c.c. of a 50 per cent. solution of potassium hydroxide were added; the whole was cooled in a stream of water and allowed to remain with occasional shaking for some hours. Water was then added to the pasty product, the insoluble material being collected and washed free from alkali. When dry, the nearly solid mass was extracted with cold carbon disulphide, which

was separated by decantation and mixed with one and a half times its bulk of light petroleum in order to precipitate unchanged benzylidene-aniline hydrocyanide. The filtered solution was evaporated to about two-thirds of its original bulk and allowed to cool. Large transparent rhombs of the condensation product slowly separated and were collected and recrystallised twice from alcohol. On analysis:

0.2012 gave 0.6126 CO_2 and 0.1392 H_2O . C = 83.0; H = 7.7.

0.1998 ,, 0.6090 CO_2 ,, 0.1363 H_2O . C = 83.1; H = 7.6.

0.1918 ,, 7.0 c.c. moist nitrogen at 15° and 765 mm. N = 4.3.

$\text{C}_{23}\text{H}_{25}\text{ON}$ requires C = 83.4; H = 7.6; N = 4.2 per cent.

The molecular weight of the compound in benzene solution was determined by the cryoscopic method. The addition of 0.5063 gram of the substance to 16.68 grams of benzene caused a depression in the freezing point of 0.47° , and a subsequent addition of 0.4173 gram of the substance produced a further depression of 0.375° . The molecular weight as indicated in these experiments was 323 and 333 respectively, that calculated for a compound having the formula $\text{C}_{23}\text{H}_{25}\text{ON}$ being 331.

β -Phenyliminobenzoyldihydrocarvone is slightly soluble in light petroleum and dissolves very readily in alcohol, ether, benzene, carbon disulphide, or chloroform. It crystallises from alcohol or carbon disulphide in large, transparent, pale yellow rhombs which melt at $98.5\text{--}100^\circ$. The crystals are biaxial in character, the axial angle being wide and the double refraction strong.

For the determination of the rotatory power, 0.2500 gram dissolved and made up to 25 c.c. with absolute alcohol was examined in a 2-dcm. tube at 17° . The rotation observed was -7.38° , whence $[\alpha]_D - 369.0$.

The substance decomposes slowly at the ordinary temperature, and specimens which have been crystallised from alcohol deteriorate more rapidly than those obtained from solution in carbon disulphide. In a few months the material is converted into a viscid, transparent oil which did not crystallise. The change may be brought about rapidly by warming the compound on the water-bath.

The substance unites directly with hydrocyanic acid in presence of bases, but does not yield a well-defined semicarbazone or phenylhydrazone. With hydroxylamine, it gives an oxime of the corresponding diketone, aniline being eliminated.

The *cyanohydrin*, $\text{C}_{23}\text{H}_{25}\text{ON}, \text{HCN}$, was prepared by dissolving the foregoing phenylimine in alcohol, adding the calculated quantity of potassium cyanide dissolved in a small quantity of water, and then acidifying with acetic acid drop by drop. The crystalline material which separated was collected, washed, and dried.

The substance could only be crystallised from chloroform, and the crystals which separated contained chloroform of crystallisation. It was not found possible to expel this by heat :

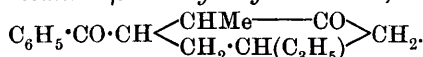
0·2102 gave 0·1243 AgCl. $\text{CHCl}_3 = 16\cdot4$.

0·5607 „ 31·9 c.c. moist nitrogen at 14° and 759 mm. N (calculated for the chloroform-free substance) = $8\cdot0$.

$\text{C}_{23}\text{H}_{25}\text{ON}, \text{HCN}$ requires N = $7\cdot8$ per cent.

The compound crystallised in minute, colourless, slender, silky needles, readily soluble in chloroform, less readily so in alcohol, ether, acetone, or carbon disulphide, and sparingly so in light petroleum.

Formation of Isomeric β -Benzoyldihydrocarvones,



The phenylimino-compound is readily hydrolysed by dilute mineral acids, and the following method furnishes a good yield of the corresponding diketone. The substance is covered with five times its weight of aqueous hydrochloric acid and warmed on the water-bath. The yellow crystals, at first, in part dissolve, but after a few minutes the clear solution becomes turbid and an oil separates; this increases in amount until all the crystals have disappeared. At the end of half an hour, the liquid is cooled, the oil collected, washed with water, and triturated with a little alcohol. A few crystals separate and the amount of these rapidly increases if a few drops of sodium hydroxide solution are added. The solid matter is then separated from the residual oil by filtration and purified by repeated crystallisation from hot alcohol :

0·2038 gave 0·5945 CO_2 and 0·1442 H_2O . C = $79\cdot6$; H = $7\cdot9$.

$\text{C}_{17}\text{H}_{20}\text{O}_2$ requires C = $79\cdot70$; H = $7\cdot8$ per cent.

The new compound dissolves readily in most of the ordinary media, with the exception of light petroleum, and separates from hot alcohol in crystals which melt at $117\text{--}118^\circ$.

The crystals are irregular, opaque plates with pectinate edges, and the optical properties could not be distinguished. After fusion between glass slips the substance solidifies rapidly just below its melting point to patches of transparent plates and few air spaces; in convergent polarised light some of these plates show a biaxial figure of small angle. The double refraction is positive in sign and weak.

For the determination of the optical activity, 0·2500 dissolved and made up to 25·1 c.c. with absolute alcohol at 18° was examined in a 2-dm. tube.

The rotation observed was constant at $-1\cdot01^\circ$, whence $[\alpha]_D - 50\cdot7$, but when a trace of sodium ethoxide was added, the rotation decreased

until at the end of a few hours it attained the value -0.80° at 18° , corresponding with $[\alpha]_D - 40.2$.

This change in rotatory power indicates the probable existence of stereoisomeric forms of the ketone, and this explains the effect of alkali on the crude, oily ketone. An isomeride was obtained from the mother liquor from which the ordinary variety had been isolated. This was deposited in prismatic needles which were separated mechanically from the pectinate crystals of the first modification, and were recrystallised from alcohol. On analysis :

0.1934 gave 0.5653 CO_2 and 0.1349 H_2O . $\text{C} = 79.7$; $\text{H} = 7.7$.

$\text{C}_{17}\text{H}_{20}\text{O}_2$ requires $\text{C} = 79.7$; $\text{H} = 7.8$ per cent.

The crystals melt at $84-86^\circ$, but further investigation of this compound was not possible, owing to the small quantity available.

The ordinary form of the diketone behaves as an unsaturated compound and at once discharges the colour of solutions of bromine in sodium acetate, or of potassium permanganate.

In order to determine how many ethylenic linkings were present, 1 gram of the substance was dissolved in acetic acid to which excess of sodium acetate was added, and then titrated with a standard solution of bromine in the same solvent ; the amount of bromine absorbed was 0.645 gram, hence 1 gram-molecule of the ketone requires 165 grams or 2 atoms of bromine, indicating the presence of one ethylenic linking. The product was an oil.

The *cyanohydrin* was prepared by adding hydrochloric acid to a solution containing the diketone and excess of potassium cyanide in dilute alcohol. On dilution with water, an oil was precipitated which slowly solidified and was purified by crystallisation from a mixture of benzene and light petroleum :

0.2053 gave 8.8 c.c. moist nitrogen at 17° and 759 mm. $\text{N} = 5.0$.

$\text{C}_{17}\text{H}_{20}\text{O}_2, \text{HCN}$ requires $\text{N} = 4.9$ per cent.

The compound dissolves freely in the usual organic media, with the exception of light petroleum, and separates from solution in rosettes of plates which sintered at 115° and melted at $117-118^\circ$.

The crystals, when examined in convergent polarized light, show, occasionally, the bisectrix of a figure of moderate angle emerging nearly normally to the field. The double refraction is negative.

The *semicarbazide* was prepared by warming the diketone with dilute alcoholic semicarbazine acetate for some hours, and was isolated by diluting the liquid, removing the precipitated matter, and crystallising from acetone. The crystals contained acetone of crystallisation, which was determined by heating some of the substance at 100° until it was constant in weight. 0.1423 lost 0.0214 acetone, or 15.0 per cent.

The nitrogen in another portion of the same specimen of the substance was determined :

0.1431 gave 14.1 c.c. moist nitrogen at 17° and 756 mm. $N = 13.4$.*
 $C_{17}H_{20}O:N_2H \cdot CO \cdot NH_2$ requires $N = 13.4$ per cent.

The semicarbazone is sparingly soluble in most of the ordinary organic solvents, and separates from acetone in crystals which, when heated rapidly, fuse at 89°, evolving acetone with effervescence. The acetone-free substance melted at 170—173°.

The *dioxime*, $C_{17}H_{20}(N \cdot OH)_2$, was obtained by heating the anil for some hours on the water-bath with a solution of three molecular proportions of free hydroxylamine in dilute alcohol; on cooling, a solid separated which was crystallised from dilute alcohol :

0.1232 gave 0.3183 CO_2 and 0.0874 H_2O . $C = 70.5$; $H = 7.9$.
 0.3321 ,, 27.3 c.c. moist nitrogen at 14.5° and 765.5 mm. $N = 9.7$.
 $C_{17}H_{22}O_2N_2$ requires $C = 71.3$; $H = 7.7$; $N = 9.8$ per cent.

The analysis indicates that aniline has been removed, and no difficulty was found in detecting aniline in the mother liquor by any of the ordinary tests.

The *dioxime* dissolves readily in hot alcohol and separates on cooling in slender, white needles melting at 138—139°.

Examination of the By-product obtained during the Preparation of Phenyliminobenzoyldihydrocarvone.

When a mixture of the hydrocyanide of benzylideneaniline and carvone was shaken with strong alkali, a sparingly soluble substance was always formed in considerable amount and was separated from the mass by means of carbon disulphide, in which it is insoluble.

It was purified by dissolving it fractionally with benzene in a Soxhlet extractor, and was finally obtained as a silky, homogeneous mass of needles :

0.2067 gave 0.6296 CO_2 and 0.1116 H_2O . $C = 83.1$; $H = 6.0$.
 0.0778 ,, 7.45 c.c. moist nitrogen at 15° and 747 mm. $N = 11.0$.
 $C_{27}H_{23}N_3$ requires $C = 83.3$; $H = 5.9$; $N = 10.8$ per cent.

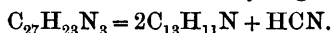
The substance is sparingly soluble in alcohol, chloroform, or acetone, and separates from hot benzene, in which it dissolves somewhat more freely, in crystals melting at 210—211°. When it is heated above its melting point, pungent aromatic fumes are evolved.

It is decomposed by hot alcoholic potassium hydroxide, yielding potassium cyanide; the liquid thus obtained, in one instance, was allowed to evaporate, when a solid was deposited which, when

* Calculated on acetone-free substance.

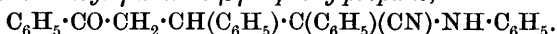
recrystallised from alcohol, separated in nacreous leaflets melting at 54°. This substance was hydrolysed by acid, giving benzaldehyde and aniline, and was proved to be benzylideneaniline, by the mixed melting point method; no other compound was obtained.

The by-product is thus formed by the union of two molecules of benzylideneaniline with one molecule of hydrogen cyanide:



*Condensation of Benzylideneaniline Hydrocyanide with
Benzylideneacetophenone.*

γ-Cyano-α-benzoyl-γ-anilino-βγ-diphenylpropane,



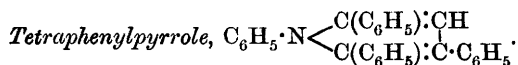
Equimolecular proportions of benzylideneacetophenone and benzylideneaniline hydrocyanide were dissolved separately in hot alcohol, the solutions were mixed and cooled rapidly to 35°, when a few drops of a 50 per cent. solution of potassium hydroxide were added, and the whole allowed to remain at the ordinary temperature until the crystalline substance which separated no longer increased in amount. The product was collected, washed with alcohol, and then with water, and was finally crystallised from boiling alcohol:

0.1994 gave 0.6095 CO₂ and 0.1040 H₂O. C = 83.4; H = 5.8.

C₂₉H₂₄ON₂ requires C = 83.7; H = 5.8 per cent.

The compound is somewhat sparingly soluble in alcohol, ethyl acetate, or acetone, and nearly insoluble in benzene, chloroform, or light petroleum. It separates from alcohol in small, glistening needles, which melt and decompose at 200°.

The crystals under the microscope are seen to be flat needles or elongated rectangular plates, having nearly a straight extinction in polarised light. Further optical characters could not be determined owing to the small size of the forms. When warmed with strong alcoholic potash the substance is in part decomposed, the odour of acetophenone may be distinguished, and the mother liquor, on treatment with ferrous sulphate, ferric chloride, and hydrochloric acid, gives a precipitate of Prussian blue.



A few grams of the preceding compound were heated in a flask over a flame until effervescence was visible, and the temperature was then maintained about this point until further action ceased; steam and hydrogen cyanide were easily recognised to be the main gaseous

products. The residue, which solidified on cooling, was purified by crystallisation from hot glacial acetic acid :

0.2022 gave 0.6685 CO_2 and 0.1044 H_2O . C = 90.2 ; H = 5.7.

$\text{C}_{28}\text{H}_{21}\text{N}$ requires C = 90.6 ; H = 5.7 per cent.

The compound melted at 197° , and further examination showed that its properties were identical in all respects with those of tetraphenylpyrrole, obtained by the action of aniline on desylacetophenone (Smith, *Trans.*, 1890, 57, 646).

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