LXIX.—*A Condensation Product of Mandelonitrile.*

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By saturating a solution of mandelonitrile (benzaldehydecyanhydrin) in absolute ether with gaseous hydrogen chloride, Minovici (*Ber.*, 1899, **32**, 2206) obtained a yellow compound of the formula $C_{16}H_{12}ON_2$:—

Minovici found the melting point of this substance at 200—203°. It was not hydrolysed by heating either with potassium hydroxide or with hydrochloric acid. It formed an unstable hydrochloride, which was at once decomposed in contact with water or alcohol, liberating the base. The author suggests, as a possible constitution,

but admits that this formula is not in keeping with the reactions of the compound.

Minovici has failed to notice that this compound is identical with a substance which Japp and Miller (*Trans.*, 1887, **51**, 29) obtained, along with other products, by dissolving benzil in alcohol, adding a considerable excess of anhydrous hydrocyanic acid, and saturating the liquid with gaseous hydrogen chloride. They point out that the compound contains in its molecule an atom of oxygen less than benzildihydrocyanide :

but they were unable to prepare the substance by the action of alcoholic hydrogen chloride on pure benzildihydrocyanide. They found the melting point at 196—197°. The yield was very small.

Minovici's reaction explains the mode of formation of this substance in the process described by Japp and Miller. Under the influence of the alcoholic hydrocyanic acid a portion of the benzil is converted into a mixture of benzaldehyde and ethyl benzoate (compare Michael and Palmer, *Amer. Chem. J.*, 1885, **7**, 189); and the benzaldehyde then

interacts with the hydrocyanic acid to form mandelonitrile, which is finally transformed by the hydrogen chloride into the compound $C_{16}H_{12}ON_2$, as in Minovici's reaction. The formation of ethyl benzoate was observed by Japp and Miller (*loc. cit.*).

A careful comparison of the substance obtained by Minovici's method with one of Japp and Miller's original preparations showed that the two were identical. We confirmed in both cases the melting point $196-197^\circ$ given by Japp and Miller. Minovici gives $200-203^\circ$.

The reactions of the compound lead us to regard it as 3-keto-2:5-diphenyl-3:4-dihydro-1:4-diazine, formed according to the scheme

It is somewhat difficult to give an account of the precise mechanism of the process in which the substance is produced, and we therefore confine ourselves to stating the reaction in the foregoing summary form.

The ketonic formula appears more probable than the tautomeric enolic form, because the former accounts better for the facts (1) that the compound cannot be acetylated, and (2) that, when it is reduced with hydriodic acid, the oxygen atom is replaced by 2 atoms of hydrogen; whereas, if a hydroxyl group were replaced by a hydrogen atom, the resulting diazine would not be further reduced. As regards the latter point, Staedel and Kleinschmidt, it is true, claim to have reduced 2:5-diphenyl-1:4-diazine ("isoindole") by the action of hydriodic acid to a yellow, basic compound (*Ber.*, 1878, 11, 1746); but we have entirely failed to confirm this result (*vide infra*).

We find that when the condensation compound is distilled with zinc

(m. p. $194-195^\circ$), a compound first obtained by Staedel and Rügheimer by the action of ammonia on ω -chloroacetophenone (*Ber.*, 1876, 9, 563), but of which the correct composition and constitution were ascertained later by L. Wolff (*Ber.*, 1887, 20, 432).*

* Wolff, however, in accordance with the view at that time prevailing on the subject of the constitution of diazines of this type, formulated the compound with a para-bond between the two nitrogen atoms.

If, on the other hand, the condensation compound is reduced by heating it with hydriodic acid and red phosphorus, it yields a compound of the formula $C_{16}H_{14}N_2$ (m. p. 162—163°), which we regard

That it is not a 1 : 4-dihydro-compound is indicated by the fact that on distillation it does not part with hydrogen yielding 2 : 5-diphenyl-1 : 4-diazine. We were unable to acetylate this substance.

Of the numerous reactions which we tried with the condensation product, only the two foregoing gave positive results.

Attempts to obtain the condensation product by acting on mandelonitrile with other dehydrating agents did not give the desired result. Thus acetic anhydride to which a few drops of sulphuric acid had been added converted mandelonitrile in the cold, with liberation of hydrocyanic acid, into a compound melting at 239—240° and having the formula $C_{27}H_{26}O_6N_2$. The yield of this substance is greatly increased by previously adding to the mandelonitrile half its molecular proportion of benzaldehyde. It is formed according to the equation :

and its constitution may be represented by the formula

The reaction in which it is formed is thus analogous to that discovered by Hepp and Spiess (*Ber.*, 1876, 9, 1425) in which acetaldehyde and benzonitrile, under the influence of concentrated sulphuric acid, yield ethylenedibenzamide, $CH_3 \cdot CH(NH \cdot CO \cdot C_6H_5)_2$. Heated with water at 180° the compound $C_{27}H_{26}O_6N_2$ was hydrolysed, yielding benzaldehyde, mandelic acid and acetic acid.

EXPERIMENTAL.

(m. p. 196—197°).

Comparison of the Compound $C_{16}H_{12}ON_2$ obtained by Minovici's Method with that described by Japp and Miller.—We prepared a quantity of the compound $C_{16}H_{12}ON_2$ by Minovici's method of saturating

a solution of mandelonitrile in *absolute* ether with gaseous hydrogen chloride (*Ber.*, 1899, 32, 2206). The product was purified by boiling it in alcoholic solution with animal charcoal and afterwards recrystallising it repeatedly from alcohol. It was compared with a specimen of the substance of the same formula prepared by Japp and Miller from benzil by the method already described.

Both preparations melted at 196—197°, and showed no depression of melting point when mixed. Both crystallised in flat, pointed, lustrous, yellow needles showing straight extinction. Both dissolved in concentrated sulphuric acid giving an orange-yellow coloration. They were therefore identical.

Both products had been previously analysed by their discoverers.

We have already given our reasons for assigning to the compound the constitution of a 3-keto-2:5-diphenyl-3:4-dihydro-1:4-diazine.

As, of the two methods for preparing the compound, that of Minovici is both the simpler and gives the better—although a far from satisfactory—yield, it was employed in obtaining the material required for the following reactions.

The compound could not be acetylated either by boiling it for several hours with excess of a mixture of acetic anhydride and anhydrous sodium acetate, or by allowing it to stand in the cold with acetic anhydride containing a few drops of concentrated sulphuric acid, nor did it yield a nitroso-derivative on adding solid sodium nitrite to its solution in glacial acetic acid.

Distillation of the Compound $C_{16}H_{12}ON_2$ (m. p. 196—197°) *with Zinc Dust: Formation of 2:5-Diphenyl-1:4-diazine,*

—Eight grams of the compound $C_{16}H_{12}ON_2$ were distilled with zinc dust in four portions—2 grams of substance mixed with 20 grams of zinc dust being used for each distillation. The united alcoholic extracts of the distillates were concentrated, and the solution was nucleated with a trace of dust of 2:5-diphenyl-1:4-diazine, prepared by the action of alcoholic ammonia on ω -bromoacetophenone (Staedel and Kleinschmidt, *Ber.*, 1880, 13, 836; compare also Braun and Victor Meyer, *Ber.*, 1888, 21, 1279). The impure crystalline substance which was thus deposited was washed with cold ether and recrystallised thrice from boiling alcohol. It melted constantly at 194—195°. The quantity was unfortunately too small for analysis, but, as the properties of the substance pointed to its being 2:5-diphenyl-1:4-diazine, we identified it by comparison with a specimen of the latter

compound prepared by Staedel and Kleinschmidt's method just referred to. Both preparations consisted of yellow, lustrous crystals, which, under the microscope, appeared as broad, flat, pointed prisms showing straight extinction, or four-sided plates, frequently overlapping, extinguishing parallel to the diagonal. Both melted at 194—195°, and, when mixed together, showed no depression of melting point. Both dissolved in concentrated sulphuric acid with a reddish-yellow colour, and were precipitated on diluting the solution with water.

The substance is therefore 2:5-diphenyl-1:4-diazine.

Reduction of the Compound $C_{16}H_{12}ON_2$ (m. p. 196—197°) *with Hydriodic Acid: Formation of 2:5-Diphenyl-3:4-dihydro-1:4-diazine,*

of hydriodic acid (sp. gr. 1·7), and 0·5 gram of red phosphorus were heated in a sealed tube at 200° for 6 hours. There was great pressure on opening the tube, which contained a brittle black mass. The contents of the tube were diluted with water, the acid liquid was decanted, and the remaining black solid was shaken with ether, in which it entirely dissolved. The ethereal solution was shaken with an aqueous solution of sulphur dioxide, which caused the separation of a brown oil; this was run off; it solidified on standing. The solid was digested on the water-bath with a solution of sodium carbonate, and purified by crystallisation from benzene with the addition of light petroleum. It was thus obtained in slender, white needles melting at 162—163°. A further quantity of the same compound was obtained from the ethereal solution.

Analysis gave figures agreeing with the formula of 2:5-diphenyl-3:4-dihydro-1:4-diazine:—

0·1792 gave 0·5349 CO_2 and 0·0985 H_2O . C=81·40; H=6·10.

0·2569 „ 25·6 c.c. moist nitrogen at 13° and 770 mm. N=11·94.

$C_{16}H_{14}N_2$ requires C=82·05; H=5·98; N=11·96 per cent.

In a previous reduction experiment in which the same proportions were employed and the tube was also heated for 6 hours, but at a temperature of only 150°, there was obtained, along with the foregoing product, a substance which crystallised from benzene, on addition of light petroleum, in slender, white needles melting at 182—184°. It contained iodine, which was not removed on adding aqueous sodium hydroxide to an alcoholic solution of the substance. It was not further examined.

2:5-Diphenyl-3:4-dihydro-1:4-diazine was distilled under reduced pressure in the hope that it might part with hydrogen and yield 2:5-diphenyl-1:4-diazine; but only unchanged substance could be isolated from the distillate.

An attempt to acetylate it by allowing it to stand at the ordinary temperature with acetic anhydride to which a few drops of sulphuric acid had been added, also led to no result. The substance was recovered unchanged.

Attempt to reduce 2:5-Diphenyl-1:4-diazine.—Staedel and Kleinschmidt (*Ber.*, 1878, 11, 1746) state that “isoindole” (2:5-diphenyl-1:4-diazine) can be reduced with hydriodic acid to a yellow basic compound melting at 125° which yields an acetyl derivative crystallising in clear yellow needles melting at 190°. No analyses are given, and, so far as we can discover, nothing further has ever been published on the subject.

In view of the well-known difficulty of reducing paradiazines, we thought it of interest to test the correctness of the foregoing statements. We therefore heated 2:5-diphenyl-1:4-diazine (prepared by the action of alcoholic ammonia on ω -bromoacetophenone) with excess of hydriodic acid (sp. gr. 1.7) and red phosphorus for 6 hours at 200°. The tube contained a dark mass, from which we succeeded in isolating a very small quantity of a yellowish-brown, non-basic oil, which could not be induced to crystallise. Nearly the whole of the diazine was recovered unchanged.

Action of Acetic Anhydride containing a little Sulphuric Acid on a Mixture of Benzaldehyde and Mandelonitrile.—In the first experiment in which the substance about to be described was obtained, no benzaldehyde was added to the mixture, a part of the mandelonitrile breaking up in the process into benzaldehyde and hydrocyanic acid. By adding benzaldehyde to start with, the yield is greatly increased.

Ten grams of benzaldehyde and 25 grams of mandelonitrile were mixed and slowly added to 35 c.c. of acetic anhydride containing 7 drops of concentrated sulphuric acid. On standing for some time the mixture deposited slender needles, the quantity of which gradually increased. At the end of six weeks the mixture was poured into water and digested on the water-bath, first with water, then with a solution of sodium carbonate, and finally with a little alcohol. The white residue was then recrystallised from boiling glacial acetic acid, in which it is moderately soluble. It was thus obtained in slender, colourless needles, showing straight extinction and melting constantly at 239—240°. The substance has the constitution

0.1468 gave 0.3661 CO_2 and 0.0724 H_2O . $\text{C} = 68.01$; $\text{H} = 5.48$.

0.3102 „ 15.8 c.c. moist nitrogen at 15° and 768 mm. $\text{N} = 6.03$.

$\text{C}_{27}\text{H}_{26}\text{O}_6\text{N}_2$ requires $\text{C} = 68.35$; $\text{H} = 5.48$; $\text{N} = 5.92$ per cent.

A quantity of this substance was heated with water in a sealed tube at 180° for 8 hours. The organic products of hydrolysis were benzaldehyde, mandelic acid, and acetic acid. The benzaldehyde was identified by its smell, and by converting it into benzalazine (m. p. 93°) ; the mandelic acid by the mixture melting-point test ; and the acetic acid by the ethyl acetate reaction.

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