

VIII.—*Note on Dibenzanilide.*

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THE researches of Paal and Otten (*Ber.*, **23**, 2587), and of Pictet (*Ber.*, **23**, 3011), which have recently appeared, induce me to publish the following observations, which I made some time ago. In the latter portion, I was greatly assisted by Mr. F. Brownsword, B.Sc., a former student in this laboratory.

When a mixture of phenylthiocarbimide with benzaldehyde is heated for some hours at  $190^{\circ}$ , sulphuretted hydrogen is evolved, and several products are formed. These consist mainly of benzanilide and benzaldehyde-aniline, and form a semi-solid mass from which the benzanilide may be isolated by filtration. The latter was recrystallised from alcohol and melted at  $161$ — $162^{\circ}$ . When heated in a sealed tube with concentrated hydrochloric acid, it splits up into aniline and benzoic acid. The following result was obtained on analysis:—

0.1995 gram gave 12.4 c.c. of N at  $16.5^{\circ}$  and 761.2 mm.

|        | Found. | Calculated. |
|--------|--------|-------------|
| N..... | 7.36   | 7.10        |

The reaction is a complex one, and was not studied further. A similar reaction described by Losanitsch (*Ber.*, **6**, 176), and repeated by Higgin (*Trans.*, 1882, 132), consists in heating phenylthiocarbimide with benzoic acid at  $220^{\circ}$ . A solid product melting at  $160^{\circ}$  is thus formed, which is stated to be *dibenzanilide*; but in neither paper is any analysis given. The similarity of the two reactions, and the alleged difference in the product obtained, induced me to repeat Losanitsch's experiment. The product of the reaction is a solid, crystalline mass, which, when recrystallised from alcohol, melted at  $161$ — $162^{\circ}$ .

The following result was obtained on analysis:—

0.2150 gram gave 13.4 c.c. of N at  $13.4^{\circ}$  and 775.5 mm.

|        | Found.         | Calculated for<br>benzanilide. | Calculated for<br>dibenzanilide. |
|--------|----------------|--------------------------------|----------------------------------|
| N..... | 7.60 per cent. | 7.10                           | 4.63                             |

The compound is obviously benzanilide.

In this as in all subsequent analyses, the nitrogen alone has been determined, as this suffices to establish the identity of the compound with benzanilide or dibenzanilide.

To confirm the above result, and to compare the product with dibenzanilide, I attempted to prepare the latter by the method of Gerhardt and Chiozza (*Ann. Chim. Phys.* [3], 46, 129) by heating a mixture of benzanilide and benzoyl chloride in molecular proportion at 160—180°. In doing so, I followed in detail the method of Gerhardt and Chiozza; but was entirely unsuccessful in obtaining dibenzanilide.\* The substance was purified by the method given in their paper, namely, by digesting with sodium carbonate solution, washing with water, and recrystallising the product from alcohol. Prepared in this way, the compound obtained is a white, granular mass consisting of aggregates of microscopic crystals, differing entirely in appearance from the glistening plates of benzanilide. The substance, which was evidently impure after two recrystallisations, melted at 158°, and gave the following results on analysis:—

|    |             |                     |        |                    |
|----|-------------|---------------------|--------|--------------------|
| 1. | 0.2020 gram | gave 13.1 c.c. of N | at 24° | and 759.9 mm.      |
| 2. | 0.2168      | „ „                 | 14.2   | „ „ 15.5 „ 747.8 „ |
|    |             |                     |        | Nitrogen found.    |
|    | 1           | .....               | 7.54   | per cent.          |
|    | 2           | .....               | 7.64   | „                  |

The above process was then repeated under a variety of different conditions. The mixture of benzanilide and benzoyl chloride was heated at 200°, 220°, and 230° for different periods from 3 to 12 hours, and also in sealed tubes at 180°.

In the latter case, it may be mentioned that no excess of pressure was observed on opening the tubes. This would prove that no great

\* The authors state that gaseous hydrogen chloride is evolved during the reaction, but this is not the case. The evolution of hydrogen chloride is not more apparent than when benzoyl chloride alone is heated at the same temperature in an open vessel, as I observed by placing benzoyl chloride in a flask in the same bath with the mixture. There was no marked evolution of gas in either case. Gerhardt and Chiozza obtained, as a result of one analysis, 5 per cent. of nitrogen in place of 4.6 per cent. The percentage, which I recalculated from their figures, should be 5.22 per cent. This is undoubtedly due to the fact that the benzanilide, which remains unaltered in the process, contains benzoic acid, from which it is exceedingly difficult to free it. The low melting point (137°) may also be accounted for in this way.

evolution of gas had occurred during the heating. In the many analyses made of both the impure and purified product, in not one instance did the percentage of nitrogen fall below 7 per cent.

The following are some of the results of the analyses of the products obtained at 180°.

- |    |        |      |      |       |      |      |    |       |     |        |     |
|----|--------|------|------|-------|------|------|----|-------|-----|--------|-----|
| 1. | 0·2170 | gram | gave | 13·4  | c.c. | of N | at | 16°   | and | 750    | mm. |
| 2. | 0·2068 | „    | „    | 12·65 | „    | „    | „  | 12·9° | „   | 739·85 | mm. |
| 3. | 0·2160 | „    | „    | 13·4  | „    | „    | „  | 13·5° | „   | 750·9  | „   |

|                                                                                                                           | Per cent.<br>of N found |
|---------------------------------------------------------------------------------------------------------------------------|-------------------------|
| 1. After heating in a sealed tube for 4 hours at 180° and crystallising the product three times. Melting point 158° ..... | 7·19                    |
| 2. After heating at 180° for 4–5 hours and crystallising once .....                                                       | 7·13                    |
| 3. After heating at 180° for 4–5 hours and crystallising three times .....                                                | 7·34                    |

The following experiment was then carried out:—45 grams of pure benzanilide melting at 160–160·5° were heated at 180° with 34 grams of benzoyl chloride for five hours, and the liquid product poured whilst hot into a large volume of cold water. To prevent possible decomposition of dibenzanilide, the product was digested with sodium carbonate solution in the cold, by adding, successively, small quantities of a solution of sodium carbonate until an alkaline reaction remained permanent. It was then filtered, dried, and weighed. 43 grams were obtained. The substance was then submitted to a process of recrystallisation from alcohol, and the melting point of each product determined as follows:—

*First Crystallisation.*—Granular mass, m. p. 155°, also a minute quantity of needle-shaped crystals melting at 156°.

*Second Crystallisation.*—White grains, m. p. 157–158°. A few needle-shaped crystals again formed and were carefully separated. These melted at 157°.

*Third Crystallisation.*—Appearance similar to the previous product, m. p. 157–158°. No needles were present.

*Fourth Crystallisation.*—Appearance unchanged, m. p. 157–159°. No needles.

*Fifth Crystallisation.*—The crystals were more distinctly tabular, and had the characteristic glistening appearance of benzanilide, m. p. 157–159°.

By evaporating the mother liquors from the separate crystallisations, more granular crystals mixed with a brown resinous matter

separated, and from the last mother liquor, a small amount of benzoic acid was obtained. The presence of benzoic acid is not easy to explain. The amount of brown, resinous matter increases with the temperature at which the reaction is carried out. In an experiment made at 230°, the product was very impure from this cause, and after five crystallisations from alcohol, only melted slowly at 140—151°. Under these conditions, the percentage of nitrogen in the compound was always *above* the calculated amount.

The quantity of the needle-shaped crystals was too small to allow me to do more than make a determination of the melting point. I attempted to obtain more of them by evaporating the mother liquors and dropping some of the needles into the solution to bring about crystallisation. On the assumption that benzanilide might be dimorphous, I also added a crystal or two to a saturated solution of pure benzanilide. In both cases I was unsuccessful in obtaining the needles. This compound may therefore be dibenzanilide.

The literature of the subject would be incomplete without reference to the work of Steiner on tribenzhydroxylamine (*Annalen*, **178**, 235). The author states that by heating  $\alpha$ -tribenzhydroxylamine in a closed tube, dibenzanilide is formed and carbon dioxide evolved. The evidence for this is based on the decomposition of about 1 gram of substance, which gave a volume of gas roughly corresponding to the amount required by the decomposition of the substance in the manner indicated. He admits that the product does not resemble dibenzanilide, that it does not smell of phenyl cyanate; but possesses a strong odour of bitter almonds, and is to a great extent soluble in cold ether. The residue insoluble in ether, after crystallisation, formed small needles with the melting point 161°. Steiner, finding that the melting point did not agree with that of Gerhardt and Chiozza's compound, repeated their experiment of heating together benzoyl chloride and benzanilide. The product, after recrystallisation, had the required melting point of 161°. The analysis gave 5.38 per cent. of nitrogen in place of 4.63 per cent. Like Gerhardt and Chiozza, Steiner probably obtained benzanilide containing benzoic acid.\*

The author concludes by stating that the products of decomposition of  $\alpha$ -tribenzhydroxylamine "are not wholly, apparently not even to any extent, dibenzanilide and carbon dioxide."

We may then conclude that, up to the present, dibenzanilide has

\* This experiment was again repeated in 1882 by Higgin (*Trans.*, 1882, 132), at a temperature of 230°. The author obtained needles melting at 136°, but as he only determined the percentage of carbon in the compound, viz., 79.60 (benzanilide has 79.18 and dibenzanilide 79.73 per cent.), no satisfactory conclusions can be drawn.

not been prepared, at any rate not in the pure state. The synthesis of this compound I desire to reserve for future study.

Paal and Otten, as well as Pictet, point out in the papers referred to at the beginning of this note, that by the action of benzoyl chloride on acetanilide, benzanilide and acetyl chloride are formed in theoretical quantities, and, from this and other experiments, state that, in this reaction, the acid chloride of higher molecular weight replaces that of lower molecular weight in combination with the amine. I had occasion incidentally to try and replace the amido-hydrogen atom in benzanilide by acetyl, and attempted this by heating benzanilide with acetic anhydride and a small quantity of fused sodium acetate. The benzanilide was converted into acetanilide which melted at  $112^{\circ}$ . It appears, therefore, that under these conditions the action is reversed. I intend to try this reaction with the other homologues of benzanilide.

This is an additional confirmation of the fact that the replacement of the second amido-hydrogen atom by an acid radical in aniline is not readily accomplished by the ordinary methods.

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