XXXIX.—*Action of Acetic Acid on Phenylthiocarbimide.*

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ONE of us has shown (Trans., 1890, **57**, 67) that the product of the action of phenylthiocarbimide on benzoic acid is benzanilide, and not dibenzanilid as stated by Losanitsch. A similar reaction between phenylthiocarbimide and glacial acetic acid has been studied by Hofmann (*Ber.*, **3**, 770), who states that diacetanilide is produced with evolution of hydrogen sulphide and carbon dioxide, according to the following equation :—

This experiment was repeated by Claus and Völtzkow (*Ber.*, **14**, 445) and Gumpert (*J. pr. Chem.* [2], **32**, 294), who showed that acetanilide was the sole product formed. We have repeated Hofmann's experiment with the object of determining, if possible, the course of a reaction which might proceed in several stages, thus :

1. $2\text{C}_6\text{H}_5\cdot\text{NCS} + 4\text{C}_2\text{H}_4\text{O}_2 = (\text{C}_6\text{H}_5\cdot\text{NH})_2\text{CS} + 2(\text{C}_2\text{H}_3\text{O})_2\text{O} + \text{H}_2\text{S} + \text{CO}_2.$
2. $(\text{C}_6\text{H}_5\cdot\text{NH})_2\text{CS} + 2\text{C}_2\text{H}_4\text{O}_2 = (\text{C}_6\text{H}_5\cdot\text{NH})_2\text{CO} + (\text{C}_2\text{H}_3\text{O})_2\text{O} + \text{H}_2\text{S}.$
3. $(\text{C}_6\text{H}_5\cdot\text{NH})_2\text{CO} + 2\text{C}_2\text{H}_4\text{O}_2 = 2\text{C}_6\text{H}_5\cdot\text{NH}_2 + \text{CO}_2 + (\text{C}_2\text{H}_3\text{O})_2\text{O}.$

The aniline formed in the last reaction would then be free to combine with acetic acid and thus yield acetanilide.

It is obvious that a similar series of products might be formed by the action of water alone, with aniline as the final product.

In order to prove whether the presence of small quantities of water in the acetic acid determined the direction of the reaction, we made two experiments according to Hofmann's method, using, however, in the one case, glacial acetic acid, distilled after standing over phosphorus pentoxide, and in the other, the ordinary strong acid. The amount of acetic acid taken was, in each case, slightly in excess of that calculated from the equation given by Hofmann.

A third experiment was made at a temperature of 170° instead of at 130—140°. The first two experiments gave results which were identical. Besides hydrogen sulphide and carbon dioxide, two solid products were formed, which were readily separated by their different solubilities in alcohol. The one crystallised in plates melting at 112°, and proved to be acetanilide; the second, of which a smaller

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quantity was present, crystallised in needles melting at 235° , and was diphenylcarbamide. An analysis of the latter gave the following result:—

0.1805 gram substance gave 20.2 c.c. N at 774.6 mm. and 16° .

N found 13.52 per cent.; calculated for $(C_6H_5NH)_2CO$, 13.21 per cent.

The solid products of this reaction were free from sulphur, and therefore diphenylthiocarbamide was not formed.

In the third experiment, acetanilide alone was produced. It appears, therefore, that the formation of diphenylcarbamide is dependent on the temperature. We proved this to be the case; for when the experiment was repeated at the temperature of the steam-bath, continuing the heating for several days, a much larger quantity of the needles and a comparatively smaller quantity of the plates of acetanilide were found in the tube.

A final determination conducted at a temperature of about 70° also yielded diphenylcarbamide.

As water may be one of the substances formed in the reaction, more especially in the last stage when acetanilide is produced, it appeared of some interest to study the action of water alone on phenylthiocarbimide. This reaction takes a somewhat different course, a fact which indicates that water plays, if any, a subordinate part in breaking down the molecule.

In the experiment which is here given, the evolution of hydrogen sulphide and carbon dioxide was accompanied by the formation of diphenylthiocarbamide.

5 grams of phenylthiocarbimide were heated with 1 gram of water in a sealed tube at 150° for $3\frac{1}{2}$ hours. The resulting crystalline mass was purified and found to contain sulphur. On comparing its melting point with that of diphenylthiocarbamide prepared from aniline and carbon bisulphide, the two compounds proved to be identical, both melting at 147.5° . The reaction takes place according to the following equation:—

When diphenylthiocarbamide is in its turn heated with water under pressure to a somewhat higher temperature, the product is aniline, the rate and extent of the reaction depending mainly on the temperature to which the mixture is heated. 5 grams of diphenylthiocarbamide were heated with an equal weight of water for 6—7 hours at 150° ; but very little action took place. When, however, the temperature was raised to 170° , the whole of the thiocarbamide was converted into aniline, and hydrogen sulphide was evolved on

opening the tube. When diphenylthiocarbamide is heated with an amount of water sufficient to combine with the sulphur alone under the above conditions, a portion only of the substance is converted into aniline, the remainder being unchanged.

When dilute acetic acid was substituted for water, aniline was also formed. In no case was the presence of diphenylcarbamide detected.

If, however, diphenylthiocarbamide be heated with glacial acetic acid, diphenylcarbamide is produced. 5 grams of the thiocarbamide were heated with about 1 gram of acetic acid, dehydrated over phosphorus pentoxide, at a temperature of 130—140° for 3—4 hours. On crystallising the product from alcohol, needles of diphenylcarbamide melting at 235° were obtained.

From the above experiments, it appears very probable that the changes which occur on heating together phenylthiocarbimide and acetic acid are independent of the presence of water, and take place in two stages according to the following equations:—

We are at present engaged in the study of the bi-acid derivatives of the aromatic bases, which appear not to have been prepared.