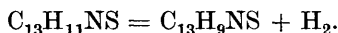


CCXLVII.—*The Thermal Decomposition of Thiobenzanilide.*

By ARTHUR WILLIAM CHAPMAN.

IT is on record (Jacobson, *Ber.*, 1886, **19**, 1067) that thiobenzanilide decomposes when distilled, yielding hydrogen sulphide and 1-phenylbenzthiazole (I). As the thermal decomposition of the *S*-phenyl ether of thiobenzanilide (*N*-phenylbenziminophenyl thioether) had recently been investigated (J., 1926, 2296), it appeared desirable to study the decomposition of the parent thiobenzanilide in greater detail, and, after a preliminary trial had confirmed the original statement that hydrogen sulphide and 1-phenylbenzthiazole were produced, experiments were carried out to determine if possible the precise mechanism of the change.

The simplest reaction by which 1-phenylbenzthiazole might be produced is the following :

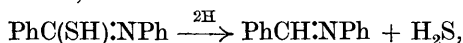


Experiment showed that hydrogen is not evolved in the decomposition, so if this reaction does take place, all the hydrogen is absorbed by some reducible material.

Under certain conditions, thioanilides are readily oxidised to thiazoles (compare Jacobson, *loc. cit.*) and the formation of thiazole in this case might be attributed to atmospheric oxidation. The

reaction, however, proceeds equally well in an atmosphere of an inert gas, so the oxygen of the air plays no part in the decomposition.

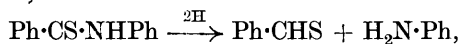
The hydrogen sulphide is not produced by direct reduction of the thioanilide thus,



since neither benzalaniline nor benzaldehyde was detected among the products of the reaction.

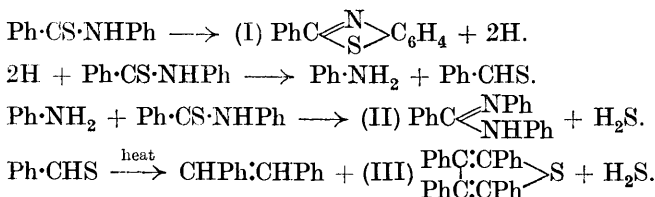
Separation of all the products of decomposition was attempted and *s*-diphenylbenzenylamidine (II) (yield, 11—19%), stilbene, and tetraphenylthiophen (III) were isolated in addition to hydrogen sulphide (37—40%) and 1-phenylbenzthiazole (38—58%). The quantities of stilbene and tetraphenylthiophen formed could not be determined.

The presence of the amidine indicated that aniline was present at some stage of the process. The yield was not affected by careful drying of the material before heating, and the formation of the amidine could therefore not be attributed to hydrolysis of the anilide. Aniline could, however, be formed by reduction of the thioanilide thus,



the necessary hydrogen being furnished from the production of the thiazole. The thiobenzaldehyde would then decompose (compare Baumann and Klett, *Ber.*, 1891, **24**, 3307), yielding hydrogen sulphide, stilbene, and tetraphenylthiophen, all of which were actually isolated.

It appears very probable that this view of the decomposition is the correct one, as it is also in agreement with the yields of products isolated in the separations. The complete series of reactions can be represented by the scheme :



EXPERIMENTAL.

Numerous experiments were performed the results of which were all in agreement. Thiobenzanilide (5 g.) was placed in a large test-tube heated in an oil-bath and fitted with inlet and outlet tubes to enable the air to be replaced by carbon dioxide or nitrogen. The

exit tube was connected in series to a cooled U-tube, so that any volatile liquid product might be condensed and observed, and, in the experiments for the detection of hydrogen, to a nitrometer, or, in the other quantitative experiments, to a series of wash-bottles containing standard iodine solution to absorb hydrogen sulphide.

Decomposition occurred at 250° and brisk evolution of gas took place at 270° and above, the gaseous product being swept out by the current of nitrogen or carbon dioxide. The bath was maintained in different experiments at various temperatures between 250° and 310°. Above 270°, the decomposition was practically complete in an hour, but at 250° about half the material could be recovered unchanged at the end of that time.

The hydrogen sulphide formed was estimated by titration of the iodine solution in the absorption vessels. A trace of non-aqueous liquid, insufficient for examination, condensed in the connecting tube. It was probably aniline, as Jacobson detected a trace of aniline among the products obtained under his conditions. The residue in the tube was a very dark brown oil which crystallised on cooling. It was dissolved in ether, and the solution extracted repeatedly with dilute aqueous sodium hydroxide. The alkaline extract yielded unchanged thiobenzanilide on acidification. The ethereal solution was then evaporated, the residue extracted several times with hot concentrated hydrochloric acid, and the extract poured into five times its volume of water. A voluminous precipitate of 1-phenylbenzthiazole was produced which on crystallisation from alcohol gave colourless needles, m. p. 113—114°. When the aqueous acid filtrate was made alkaline with sodium hydroxide, *s*-diphenylbenzenylamidine was precipitated (long prisms, m. p. 145° after crystallisation from alcohol). The identity of every substance isolated in this investigation was confirmed by direct comparison and mixed melting-point determinations with an authentic specimen prepared by a known method.

The residue insoluble in hydrochloric acid was dark brown, oily above 100°, and hard and crystalline at room temperature. It represented about 20% of the weight of the original thiobenzanilide. After a number of attempted separations had indicated the nature of the material, the following method of purification was adopted, the residue from several batches of heated thiobenzanilide being used. Part of the material was submitted to steam-distillation; a small quantity of white solid distilled over, which on crystallisation from alcohol gave colourless scales, m. p. 114—121° (120° when mixed with stilbene). Further purification of this small specimen was not attempted. The remainder of the residue was distilled (b. p. 300° to above 400°), and the distillate crystallised from

alcohol. Slender needles of tetraphenylthiophen (m. p. 184—185°; very sparingly soluble in alcohol) were obtained. The mother-liquors were evaporated to dryness and the residue was taken up in carbon disulphide and treated with a slight excess of bromine. A precipitate of α -stilbene dibromide was immediately produced, which was purified by washing with absolute alcohol, in which it was very sparingly soluble (m. p. 237° decomp.).

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