LI.—*The Chlorination of Anilides. Part II. The Decomposition of* N-*Chloroacetanilide by Heat.*

By Alan Edwin Bradfield.

In any circumstances which are favourable to the initial production of a trace of chlorine, *N*-chloroacetanilide readily undergoes a two-stage transformation involving intermediate production of chlorine, and yields *C*-chloroacetanilides (Orton, *Rep. Brit. Assoc.*, 1910, 85); consequently, it seemed probable that the well-known and profound decomposition of the substance above its melting point followed the same course. Porter and Wilbur's recent statement (*J. Amer. Chem. Soc.*, 1927, **49**, 2145) that when *N*-chloroacetanilide is heated at 100° it undergoes a *one-stage* rearrangement, yielding " almost exclusively " *p*-chloroacetanilide, was therefore surprising.

Observations in these laboratories show that when slowly heated in an air-jacketed melting-point apparatus of the Beckmann type, *N*-chloroacetanilide melts at 87—88° to a golden liquid with a slight surface scum. If the bath temperature be maintained stationary at 100°, no apparent change takes place for 30 minutes, but the temperature of the molten chloroamide then slowly rises to 110°, and a violent reaction starts, during which the temperature momentarily rises to above 200°. Considerable darkening takes place, and, on cooling, the contents of the tube set to a mass of purple crystals. When a similar reaction takes place in a sealed tube, acid vapours are evolved on opening and the product, which melts indefinitely between 50° and 150° (Product I), has the peculiar quinone-like odour associated with the products of chlorination of acetanilide. When the sealed tubes are heated in a boiling water-bath (following Porter and Wilbur, *loc. cit.*) the rise of temperature is probably to some extent prevented (the tubes frequently burst), but the product, although lighter in colour, is of approximately the same composition (Product II). The anilides present in each product were separated as pure substances of correct melting point by methods previously recorded (Orton and W. Jones, J., 1909, **95**, 1056; Orton and Bradfield, J., 1927, 986).

	Product I. From 20 g. of *N*-chloroacetanilide in air-bath at 100°.		Product II. From 4 g. of *N*-chloroacetanilide in water-bath at 100°.	
Recovered anilides :	g.	%.	g.	%.
o-Chloroacetanilide	3·65	18·2	0·66	16·5
p-Chloroacetanilide	8·19	41·0	2·03	50·7
2 : 4-Dichloroacetanilide	1·40	7·0	0·16	4·0
Acetanilide.................	1·26	6·3	—	—
Total	14·5	72·5	2·85	71·2

The formation of 2 : 4-dichloroacetanilide indicates that, contrary to the opinion of Porter and Wilbur, chlorine appears during the reaction, as in aqueous-acetic acid solutions.

In view of the discrepancy, the following details are appended.

By titration (which indicates impurity with an accuracy of 2 parts in 1000 parts) the chlorine content of an *average* specimen of *N*-chloroacetanilide (Chattaway and Orton, J., 1899, **75**, 1046; 1901, **79**, 274) is *ca.* 20·8% (Calc.: Cl, 20·93%).* Such material does not differ in behaviour from the most carefully purified substance (Found: Cl, 20·95%). The sealed tubes (made from soft glass, 1 cm. internal diameter), which were cleaned with chromic acid, washed with water, and dried with a current of warm air, were filled to a depth of 7·5 cm. by a charge of 3 g. of *N*-chloroacetanilide, and were sealed, with precautions to avoid the entry of flame gases, at 18—20 cm. from the rounded end. The action of ultra-violet light has not been examined in these laboratories.

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* The melting point of *N*-chloroacetanilide depends on the rate of heating. The highest value observed in these laboratories is 90—90·5° with rapid heating.