#### CHATTAWAY AND SWINTON:

## CXXIX.-N-Chloro-derivatives of Benzylidene-diamides.

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THE benzylidene-diamides which are produced when benzaldehyde is heated with amides, although very easily decomposed with regeneration of the aldehyde and amide, yield *N*-chloro-derivatives with hypochlorous acid. From benzylidenediacetamide the dichloro-compound has been prepared, but from benzylidenedibenzamide only the monochloro-derivative has been obtained, this, on account of its sparing solubility, being easily isolated. These compounds show the usual general characteristics of chloroamino-derivatives. They are easily hydrolysed, even on long exposure at the ordinary temperature to moist air, benzaldehyde and *N*-chloro-acetamide or -benzamide being formed.

They react vigorously with warm concentrated potassium hydroxide solution, benzaldehyde, potassium carbonate, and a primary amine being produced. Probably hydrolysis as above first takes place, the chloro-amide subsequently undergoing the Hofmann transformation under the influence of the alkali hydroxide.

There seems no reason whatever to assume that an alkyl isocyanate is formed as an intermediate product in this and similar reactions, the normal course of which appears to be a Beckmann transformation, followed by progressive hydrolysis, thus:

 $R \cdot CO \cdot NHCl \rightarrow Cl \cdot CO \cdot NHR \rightarrow$ 

 $KO \cdot CO \cdot NHR \longrightarrow CO(OK)_2 + NH_2R.$ 

Under suitable conditions an isocyanate can be produced, thus:

 $Cl \cdot CO \cdot NHR \longrightarrow HCl + CO:NR$ ,

but its production is by no means a necessary step in the reactions which precede the amine formation.

## N-Lichlorobenzylidenediacetamide, C<sub>6</sub>H<sub>5</sub>·CH(NCl·CO·CH<sub>8</sub>)<sub>2</sub>.

Benzylidenediacetamide is best prepared by boiling for about ten minutes equivalent quantities of acetamide and benzaldehyde until water vapour ceases to be evolved. Longer heating considerably diminishes the yield. On cooling, the substance solidifies, and is easily purified by crystallisation from alcohol, from which it separates in long, hair-like crystals melting at  $245^{\circ}$  (Bülow, *Ber.*, 1893, **26**, 1974, gives  $240-241^{\circ}$ ). The dichloro-derivative is prepared by suspending benzylidenediacetamide in chloroform, and shaking with excess of a saturated solution of bleaching powder acidified with acetic acid until a clear chloroform solution is

## N-CHLORO-DERIVATIVES OF BENZYLIDENE-DIAMIDES. 1207

obtained. On separating this and evaporating off the solvent at a low temperature, the dichloro-derivative is left as an oil, which solidifies after being kept for some hours in a desiccator. It can be recrystallised from a mixture of chloroform and petroleum, from which it separates in colourless, short prisms melting at  $74-75^{\circ}$ .

It was analysed by dissolving a weighed quantity in acetic acid, adding potassium iodide, and titrating the liberated iodine with standard thiosulphate:

0.3008 liberated I = 43.6 c.c. N/10-I. Cl = 25.69.

 $C_{11}H_{12}O_2N_2Cl_2$  requires Cl = 25.78 per cent.

Dr. J. Drugman has examined the crystals, and describes them as follows:

Monoclinic:  $a:b:c=2.163:1:3.041; \beta=106.56'$ .

Forms observed: c = (001), a = (100), m = (110),  $n = (10\overline{1})$ ; prismatic || the *b*-axis.

The measurements are only approximate, as the faces are rarely well developed.



Cleavage  $\parallel$  (100); good. Optic axes in the plane of symmetry. One axis is visible on (001) towards acute edge a'/c; on (100) a bisectrix is seen towards the obtuse edge a/c, and an optic axis towards the acute edge a/c'.

N-Dichlorobenzylidenediacetamide reacts vigorously with alkali hydroxides. When a concentrated aqueous solution of potassium hydroxide is poured over the finely powdered solid, violent action accompanied by the evolution of much heat sets in. On distilling in a current of steam, a little benzaldehyde and methylamine are obtained. An odour recalling that of pyridine is noticeable during the distillation. The compound to which this is due, whatever its nature, is, however, formed in too small an amount for identification. On acidifying the alkaline residue after distillation, a quantity of benzoic acid separates.

### 1208 N-CHLORO-DERIVATIVES OF BENZYLIDENE-DIAMIDES.

# $\begin{array}{c} \text{N-Chlorobenzylidenedibenzamide,} \\ \text{C}_6\text{H}_5\text{-}\text{CH} < & \text{NCl}\text{-}\text{CO}\text{-}\text{C}_6\text{H}_5 \\ \text{NH}\text{-}\text{CO}\text{-}\text{C}_6\text{H}_5 \end{array}$

Benzylidenedibenzamide is best obtained exactly as the diacetamide by heating a mixture of equivalent quantities of benzaldehyde and benzamide to boiling for five to ten minutes until water ceases to be evolved. The product, which is very sparingly soluble, is crystallised from alcohol, separating in silky needles melting at 228°.

On account of the sparing solubility of benzylidenedibenzamide in dilute acetic acid, the action of hypochlorous acid on it is so slow that if sufficiently prolonged to convert the compound into the dichloro-derivative so much hydrolysis occurs that little besides benzoic acid and nitrogen chloride is obtained. The monochloroderivative was obtained as follows: Five grams of benzylidenedibenzamide were dissolved in warm glacial acetic acid, and the solution was added to an excess of a solution of bleaching powder, so that the benzylidenedibenzamide was precipitated in a very fine state of division; 80 c.c. of chloroform were added, and the whole was vigorously shaken until the solid had nearly all dissolved. The chloroform solution was then separated, and well shaken with fresh bleaching powder solution slightly acidified with acetic acid. It was finally separated, dried, and the solvent evaporated. Chlorobenzylidenedibenzamide was left as a white solid, which was recrystallised from a mixture of chloroform and light petroleum.

N-Chlorobenzylidenedibenzamide crystallises from chloroform in rosettes of thin, needle-shaped crystals melting at 117°, and decomposing with evolution of gas at 140—150°. It was analysed as described above:

0.3072 liberated I = 16.1 c.c. N/10-I. Cl = 9.29.

 $C_{21}H_{17}O_2N_2Cl$  requires Cl = 9.72 per cent.

When heated with concentrated aqueous potassium hydroxide, a reaction similar to that with dichlorobenzylidenediacetamide occurs, but it is not at all violent, benzaldehyde, aniline, potassium carbonate, and benzamide being produced. Potassium hydroxide has, under similar conditions, little or no action on the benzylidenediamides.

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