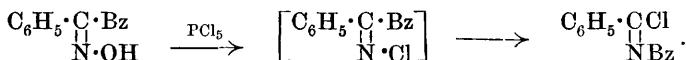


LVIII.—*The Action of Phosphorus Pentachloride on Dibenzamide.*

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BENZAMIDE has been shown by the authors (Trans., 1909, **95**, 1143) to react with phosphorus pentachloride, yielding under certain conditions the phosphorus derivative, $\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$. The behaviour of dibenzamide, as a type of aromatic secondary amide, has now been studied, and it has been shown that no phosphorus derivative is produced, but that a large yield is obtained of α -chloro-*N*-benzoylbenzimid, $\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ (m. p. 87°), which is identical with the compound (m. p. 84°) obtained by Beckmann

(*Annalen*, 1897, **296**, 279) from α -benzilmonoxime by the action of phosphorus pentachloride through the well-known rearrangement:



Preparation of α -Chloro-N-benzoylbenzimidide from Dibenzamide.

An intimate mixture of 5 grams of finely powdered dibenzamide and 7 grams of phosphorus pentachloride was treated with about 40 c.c. of dried chloroform and occasionally shaken. Hydrogen chloride was evolved, and after an hour the action was complete. The resulting chloroform solution was diluted with 50 c.c. of ether and shaken with iced water to remove phosphoryl chloride, the solution dried, and allowed to evaporate. A mass of colourless needles separated in an almost pure condition, melting at 84° , and weighing 4.7 grams (or 80 per cent. of that required by theory). On recrystallisation from light petroleum the α -chloro-N-benzoylbenzimidide was obtained in long, transparent prisms, melting at 87° .

Using ether as a solvent, instead of chloroform, in the preparation, the action is somewhat slower, and a rather smaller yield was obtained:

0.9400, by Kjeldahl's method, required 39.0 c.c. *N*/10-HCl.
N=5.8.

0.4030 gave 0.2300 AgCl. Cl=14.13.

$\text{C}_{14}\text{H}_{10}\text{ONCl}$ requires N=5.75; Cl=14.57 per cent.

On treatment with aniline in ethereal solution, it gave benzoyl-phenylbenzamidine, $\text{NPh} \cdot \text{CPh} \cdot \text{NHBz}$, melting after recrystallisation at 143° , and identical with that obtained by Beckmann (*loc. cit.*, m. p. 143°).

The following properties, not recorded by Beckmann, may be described. α -Chloro-N-benzoylbenzimidide is readily soluble in ether, benzene, acetone, or chloroform, moderately so in acetic acid, and rather sparingly so in alcohol. It decomposes on heating by simple fission into benzoyl chloride and benzonitrile. The decomposition is inappreciable at its melting point (87°), and after two and a-half hours only a slight odour of benzoyl chloride is perceptible. At higher temperatures the velocity of decomposition increases rapidly, and was measured by distilling off the benzoyl chloride and benzonitrile in a vacuum at intervals and noting the loss in weight. Precautions had to be taken to exclude traces of moisture, which leads to the formation of dibenzamide. It was found that at 100° 68 per cent. is decomposed in three hours, whilst at 130° 84 per cent. is decomposed in thirty minutes, practically complete decomposition being effected in three hours. The decomposition is not

reversible, and this was confirmed by heating molecular proportions of benzoyl chloride and benzonitrile for several hours at 100° ; no α -chloro-*N*-benzoylbenzimidide was produced. α -Chloro-*N*-benzoylbenzimidide is practically unaffected by contact with cold water or aqueous alkalis for a short time. On boiling with water, it is decomposed into benzonitrile and benzoic acid, the action apparently being preceded by fission. It is surprising that dibenzamide, which might be expected, is not produced, although it is stable under the conditions of the reaction. Beckmann, however, noted that α -chloro-*N*-benzoylbenzimidide slowly decomposes on keeping, giving dibenzamide and benzoic acid, especially when it is not quite pure. The authors have confirmed this observation, and have shown that even after careful purification the originally transparent crystals become gradually opaque, and after four or five weeks are almost completely transformed into dibenzamide, benzoic acid, and benzonitrile through the action of atmospheric moisture or ordinary water. By heating on the water-bath at about 95° in a shallow vessel exposed to air, the transformation is complete in twenty-four hours; the clear liquid slowly crystallises, and eventually completely solidifies. The yield of dibenzamide, which melted after recrystallising from alcohol at 147° , was about 60 per cent., the remainder being accounted for by simultaneous fission which takes place, giving benzoyl chloride and benzonitrile, which pass off. Again dibenzamide results, in a good yield, when α -chloro-*N*-benzoylbenzimidide is decomposed by 98 per cent. sulphuric acid; hydrogen chloride is disengaged, and dibenzamide is precipitated on subsequent dilution of the acid with water.

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