CLXXI.—*Amidechloroiodides.*

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It seemed possible that when pure dry hydrogen iodide acts on the imidechloride of benzanilide, replacement of the chlorine atom by iodine might occur, and that the resulting imide-iodide would then lose iodine and yield the dianil of benzil, thus: $\text{PhCCl:NPh} + \text{HI} = \text{PhCl:NPh} + \text{HCl}$ and $2\text{PhCl:NPh} = (\text{PhC:NPh})_2 + \text{I}_2$.

We find, however, that hydrogen iodide yields an additive compound with the imidechloride, to which we are inclined, although direct experimental evidence is wanting, to ascribe the constitution of a mixed amide halide, in this case the chloroiodide corresponding with benzanilide, $\text{PhCCl:NPh} + \text{HI} = \text{PhCClI}\cdot\text{NHPh}$.

Action of Hydrogen Iodide on Benzophenylimidechloride.

A current of pure dry hydrogen iodide, purified by means of moist amorphous phosphorus and phosphoric oxide, was passed into a solution of benzophenylimidechloride at the ordinary temperature. A lemon-yellow, microcrystalline precipitate of the amidechloroiodide was at once produced, and was filtered, washed with light petroleum, and dried in a vacuum. The substance is moderately stable, but slowly acquires a green colour on keeping, and is only sparingly soluble in organic solvents, from which it cannot be recrystallised without undergoing alteration. The maximum degree of purity can therefore only be secured by employing the imidechloride in as pure a condition as possible, the absence of phosphorus chlorides being especially necessary. The compound decomposes energetically at 106° , when hydrogen chloride and iodide are given off, leaving a dark brown residue, the composition of which has not been determined.

When warmed with alcoholic potash, benzanilide and a mixture of potassium halides are formed:

The halogens were estimated in a weighed quantity in this way.

0.2440 required 0.15012 Ag and gave 0.2650 AgCl + AgI. $\text{Cl} = 9.7$;
 $\text{I} = 37.3$.

0.3852 gave 12.8 c.c. moist nitrogen at 14° and 772 mm. $\text{N} = 4.0$.
 $\text{C}_6\text{H}_5\cdot\text{CClI}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ requires $\text{Cl} = 10.35$; $\text{I} = 37.0$; $\text{N} = 4.1$ per cent.

Considering the difficulty of purification, we think that the experi-

mental figures agree sufficiently with those calculated to establish the composition.

Benzo-p-tolylamidechloroiodide, $C_6H_5 \cdot CCl \cdot NH \cdot C_7H_7$, was prepared in a similar manner; it decomposes at 130° and resembles the phenyl analogue in all respects. On analysis, it gave $N = 6.6$ instead of the calculated $N = 6.7$ per cent.

Reactions of the Amidechloroiodides.

With water and, as already stated, with potassium hydroxide the amidechloroiodides yield the parent amide and halogen hydrides or their salts.

When benzophenylamidechloroiodide is dropped into an alcoholic solution of pure sodium ethoxide, *N*-phenylbenziminioethyl ether is formed, $PhCCl \cdot NHPh + 2NaOEt = PhC(OEt) : NPh + NaCl + NaI + HOEt$, as was shown by adding water and extracting with ether, when the ethereal extract, on evaporation, left an oil which, on boiling with dilute hydrochloric acid, gave aniline and ethyl benzoate, the characteristic products of the hydrolysis of the imino-ether. A little benz-anilide also resulted from the action of the ethoxide.

With aniline (3 mols.) in benzene solution, diphenylbenzenylamidine and aniline hydrohalides are formed. The amidine melted after crystallisation from alcohol at 129° , and gave $N = 10.4$ instead of the calculated $N = 10.3$ per cent.

It will be observed that in no case could evidence of the position of the iodine atom in the molecule be obtained from reactions of replacement. Supposing, however, that in the reactions with sodium ethoxide and aniline the compounds $PhC(OEt)_2 \cdot NHPh$ and $PhC(NHPh)_3$ had been formed, there can be no doubt (compare this vol., p. 986) that they would most readily part with alcohol and aniline, yielding the imino-ether and amidine respectively. At the same time, it must be remarked that the amidechloroiodide differs in physical properties, and particularly in respect to its stability on warming, from its congener benzophenylamidechloride, $PhCCl_2 \cdot NHPh$, a substance which parts so readily with hydrogen chloride, forming the imidechloride, that it is prepared only with great difficulty, and, so far as we know, it is not formed when hydrogen chloride acts on the imidechloride.

Our amidechloroiodides are also analogous to the imidedi-iodides prepared by Biltz from the nitriles by means of concentrated hydriodic acid solution (*Ber.*, 1892, 25, 2533). In these compounds, the hydrogen iodide is most readily dissociated from the molecule, yielding the nitriles, although benzamidedi-iodide with phenol gives benzaurine, a reaction which favours the given formula, but which could be explained in other ways, as, for example, a condensation dependent on the elimin-

ation of ammonia between benzonitrile and phenol in the presence of acid.

The amideiodides of Biltz can be easily prepared by our method. We find also that, with sodium ethoxide, benzamidedi-iodide gives benzonitrile, a reaction not examined by Biltz.

The only alternative structure for the amidechloriodide would be that of a salt of the type $\text{PhCCl}:\text{NHPhI}$, for which, however, there is no analogy, especially when the anil group is attached to so negative a residue as PhCCl .

We are at present engaged in attempts to prepare other ortho-compounds of a similar kind to those described in this note.

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