

ON SOME CHINOLINE SUBSTITUTION-PRODUCTS.

BY H. ENDEMANN, PH. D.

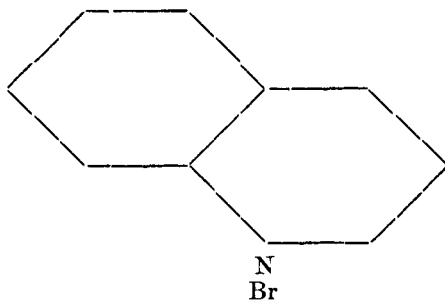
Between two and three years ago I made an investigation testing chinoline and some of its products with regard to its properties, when treated with bromine, chlorine and hypochlorous acid.

I found that free chinoline reacts by preference with 4 chlorine atoms ; the formation of a dichlorchinoline being the result, however ; monochlorchinolines are formed, but in smaller quantity.

Using one molecule of chinoline in ether solution and adding thereto 1 molecule of HClO , likewise in ether solution, a reaction soon sets in, which is marked by a growing turbidity of the liquid caused by a separation of water.

After the water had subsided, the ether solution was freed from ether by distillation and the residue was examined. As result it was found that practically one-half of the chinoline had entirely escaped the reaction, while the other half had been converted into a dichlorchinoline, as was proved by analysis.

Tetrahydrochinoline hydrochlorate in water solution, when shaken with a solution of bromine in water, yielded at ordinary temperatures, as end-product, a dibromtetrahydrochinoline. The substance had lost its basic properties to such marked degree that I considered that one bromine atom which had entered the composition must be in direct connection with the nitrogen atom thus :



Repeating the same experiment, with methyltetrahydrochinoline, a monobromtetrahydromethylchinoline was obtained. The analysis of the product gave 33.8 % bromine. The result is the same if, instead, the bromine is first dissolved in NaHO and then

liberated by H_2SO_4 . Ether dissolves from the acid solution, the monobrom- compound. The water solution yields to ether yet another compound, after it has been made alkaline, which substance, however, has not been examined.

In order to ascertain where the bromine had entered the chinoline molecule, I modified the process, so as to arrive, if possible, at a compound, which could be easily distinguished by a simple chemical reaction.

The orthoxymethyltetrahydrochinoline, when treated with ferric chloride was then known to produce a dark red color; the para- compound, which I prepared for the purpose, produced a green coloration; the corresponding meta- compounds I have not compared.

In order to prepare an analogous compound, I proceeded as follows: I prepared the acetyl compound of tetrahydrochinoline, dissolved it in ether and shook the ether solution with so much bromine in water solution as would produce a monobrom- substitution product. The layer of ether was removed, and the water solution repeatedly shaken with ether.

After uniting all the ether solutions, the ether was distilled off, and the residue boiled with a strong hydrochloric acid in order to split off the acetyl group.

On cooling, the mass became almost solid, with crystals of monobromtetrahydrochinoline hydrochlorate. This salt is quite difficultly soluble in water containing free hydrochloric acid, and can, therefore, easily be separated from impurities. Pure water decomposes the salt in part into free hydrochloric acid and monobromtetrahydrochinoline.

Alkali separates the free base (melting pt. $33^\circ C$). The hydrochlorate examined for bromine gave 31.86 % Br., calculated 32.19 % Br. If the free base be dissolved in methyl or ethyl alcohol, and be mixed with sodium methylate or ethylate in calculated quantity, and heated in a sealed tube to $140^\circ C$, even for a long time, no reaction ensues. If the temperature be raised to $180^\circ C$, the bromine can be replaced in part by either oxymethyl or oxyethyl, but the reaction can never be brought to an end owing to the high pressure, which is produced by the simultaneous formation of gases, especially in the case of the methyl compound. It is best, therefore, not to prolong the heating too far and to be content with a partial reaction.

If the contents of the tubes, after filtration and evaporation of the alcohol, are treated with hydrochloric acid, an easily soluble hydrochlorate and the difficultly soluble hydrochlorate of the monobrom- compound, are formed, and these can easily be separated. The solution containing the easily soluble hydrochlorate yields, on addition of an alkali, the free base, as an oil which is best separated from the liquid by means of ether, from which it is recovered by distilling the ether off. These bases, whether produced by means of ordinary alcohol or methyl alcohol, produce, with a solution of Fe_2Cl_6 , a deep indigo-blue color, which gradually disappears, leaving a mixture of a brownish color.

The hydrochlorate of the methylated base gave 18.6 % of hydrochloric acid—calculated 18.3 %.

0.2635 of the hydrochlorate precipitated with Ag NO_3 gave 0.145 $\text{Ag} = 0.049 \text{HCl}$.

Platinum chloride gives, in a solution of the hydrochlorates of these bases, at first a yellow precipitate, but soon, especially with an excess of platinum chloride, the solution turns blue, and finally, again yellow. When the bases are heated in a closed tube with hydrochloric acid, the resulting base fails to give the reaction with $\text{Fe}_2 \text{Cl}_6$, which is evidently due to the removal of the methyl or ethyl group from the compounds and their replacement by hydrogen. The base thus obtained is not soluble in excess of alkali, which would prove that the bromine substitution had not taken place in the benzol nucleus.

The iron reaction with the compound thus obtained results in the production of a dark, amber-colored liquid. The very unsatisfactory yield of the compounds in question, by the method described, suggested the melting with soda at 180°C ., and subsequent conversion of the oxy- compound into the methyl ether. But the reaction went differently from expectation. Most of the monobrom- compound was converted into hydrochinoline, which is formed by the removal of H Br . from 2 molecules of the compound and union of the two resulting molecules. The hydrochlorate of hydrochinoline was obtained by evaporating a solution of the base in excess of hydrochloric acid under the air pump, over lime and sulphuric acid, and the quantity of hydrochloric acid therein was determined by dissolving in water, to which some dilute nitric acid had been added, since the salt is partly decomposed by

water, and then precipitating with silver nitrate. 0.0945 of the hydrochlorate gave 0.065 Ag.

Alkalies liberate the base as an amorphous precipitate with a melting point close to 160°C.

From these reactions, I should judge that the substitution of the bromine for the hydrogen in the original compound, had taken place on the pyridine nucleus of the tetrahydrochinoline.