LX.—*Production of some Chloropyridinecarboxylic Acids.*

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AMONGST substituted pyridine compounds containing methyl or other hydrocarbon radicles (in the place of hydrogen), the hydroxy-derivatives, unfortunately, are unable to withstand the oxidising action of potassium permanganate, and, as a consequence, hydroxycarboxylic acids cannot be prepared by this means. A typical instance of this breaking down of the pyridine ring is that of methylpseudolutidostyryl, which yields methyloxamic acid when oxidised with potassium permanganate (Hantzsch, *Ber.*, 1884, 17, 1019). If, however, the hydroxy-group be replaced by chlorine, then the pyridine nucleus remains unbroken when boiled with potassium permanganate, and only the side groups are attacked with production of chlorocarboxylic acids of pyridine. The introduction of a methoxyl group also in certain cases seems to have the same effect as chlorine, for Freer and

Konigs (*Ber.*, 1885, 18, 2394), by the oxidation of methylamidocarbo-
styryl, obtained methoxypyridinedicarboxylate.

Various hydroxy- and chloro-carboxylic acids have already been in-
vestigated by one of the authors (*Trans.*, 1895, 67, 399; 1897, 71,
299, and 1897, 71, 653). The present communication is a continuation
of the same work.

When ethylic acetoacetate is treated with gaseous ammonia, ethylic
 β -amidocrotonate is formed, and when the latter compound is satu-
rated with hydrogen chloride and heated, it condenses to the ethylic
salt of an hydroxylutidinecarboxylic acid. This pyridine derivative
was used as the starting-point of the research. It was converted by
means of phosphorus pentachloride into the corresponding chloro-com-
pound, which in its turn was oxidised with potassium permanganate,
giving a chlorinated tribasic acid.

Several intermediate ethers and salts also have been investigated,
and the chlorocarbo-cinchomeronic acid has been reduced by means of
tin and hydrochloric acid to the carbocinchomeronic acid itself.

Ethylic Chlorolutidinecarboxylate.

When the hydrochloride of ethylic amidocrotonate is heated, the
chief product is an ethylic hydroxylutidinecarboxylate melting at
138—139°. This substance was treated, in quantities of about 20
grams at a time, with 24 grams of phosphorus pentachloride, and, on
warming, the reaction takes place gradually, with evolution of hydrogen
chloride.

It was found best to raise the temperature of the oil bath in which
the mixture was heated to about 180°. After the action is over, the
contents of the flask are poured into water, nearly neutralised with
caustic soda, and the ether separated by distillation in a current of
steam; the oil which passes over is dried and again distilled. It boiled
at 288—290° (corr.), and on analysis it gave the following numbers.

Found C = 56.6; H = 6.0; N = 7.0; Cl = 16.6.

$\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl}$ requires C = 56.2; H = 5.6; N = 6.5; Cl = 16.6 per cent.

This chloro-ether is an oily substance insoluble in water, and not

easily acted on by potash. About 15 grams were produced from 20 grams of the ether.

The free acid was obtained by persistent boiling with strong potash solution, and alcohol had to be added and the boiling continued before the hydrolysis was complete.

The whole was then evaporated to dryness on a water bath with excess of hydrochloric acid, and the residue treated with small quantities of water, so as to remove the potassium chloride. The acid that remained, when recrystallised from hot water, formed needles which, when pure, melted at 148° (corr.), and decomposed at about 190° .

On analysis, it gave the following results.

Found C = 50.3 and 51.3 ; H = 4.8 and 4.8 ; N = 7.6 ; Cl = 19.3.

$\text{C}_8\text{H}_8\text{NO}_2\text{Cl}$ requires C = 51.7 ; H = 4.3 ; N = 7.5 ; Cl = 19.1 per cent.

and the acid, therefore, has the formula

The oxidation of ethylic chlorolutidinecarboxylate by potassium permanganate was carried out in batches of 5 grams at a time. The ether was placed with 150 grams of water in a flask fitted with a reflux condenser, 14.8 grams of potassium permanganate were added in small quantities at a time, and the mixture boiled. The oxidation took about 7 hours to complete ; after any excess of unoxidised ether had been removed by steam distillation, the residue was filtered, and the filtrate evaporated to dryness on a water bath with a small excess of hydrochloric acid ; potassium chloride was removed from the dry residue by treating it with small quantities of water, and the insoluble residue was then recrystallised from water. The yield was not good, only about 1 gram of acid being obtained from 5 grams of the chloro-ether. This acid did not give any concordant results on analysis, and it was ultimately found to consist of the acid potassium salts of two different acids. It is curious that these salts do not seem to be decomposed when their solutions are evaporated to dryness with hydrochloric acid on the water bath.

To obtain the free acid, therefore, the lead salts were prepared, washed, and then decomposed with sulphuretted hydrogen ; on filtering off the lead sulphide and concentrating the solution on a water bath, a crystalline acid was left which, when pure, melted at about 207° , whilst from the mother liquors a second acid of lower melting point

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$C_8H_4NO_6Cl$ requires C=39.0; H=1.6; N=5.7; Cl=14.4 per cent.

$$\begin{array}{c} \text{COOH} \cdot \text{C} \text{---} \text{N} = \text{C} \text{---} \text{CH} \\ \text{COOH} \cdot \text{C} \text{---} \text{C} = \text{C} \text{---} \text{CH} \\ \text{COOH} \end{array}$$
$$\begin{array}{c}
 \text{COOH} \cdot \text{C} \text{---} \text{N} = \text{CCl} \\
 \text{COOC}_2\text{H}_5 \cdot \text{C} \text{---} \text{CH} \\
 \quad \quad \quad \text{C} = \text{COOH}
 \end{array}$$

Compound B, m. p. 169°.

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$C_8H_3Ag_2NO_6$ requires C = 22.5; H = 0.7; Ag = 50.8 per cent.

Carbocinchomeric acid or pyridinetricarboxylic acid,

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