

**162.** *ω-Trichloro- and ω-Dichloro-α-picoline.*

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It is shown that *ω-trichloro-α-picoline* is produced when *α-picoline* is chlorinated in glacial acetic acid containing excess of potassium acetate. *ω-Trichloro-α-picoline* can be (1) hydrolysed to picolinic acid, (2) reduced to *ω-dichloro-α-picoline*, which on hydrolysis yields pyridine-2-aldehyde.

SELL (J., 1905, **87**, 799; 1908, **93**, 1993) has shown that the action of chlorine on an aqueous solution of *α-picoline* hydrochloride yields as a main product 3 : 4 : 5 :  $\omega$  :  $\omega$  :  $\omega$ -hexachloro-*α-picoline*, together with some 3 : 5 :  $\omega$  :  $\omega$  :  $\omega$ -pentachloro-*α-picoline*. We have so modified the conditions as to limit chlorination to the side chain (cf. Hammick, J., 1926, 1302) and have thus opened up a route by hydrolysis to picolinic acid and its aldehyde. When chlorine is passed into a solution of *α-picoline* in glacial acetic acid heavily buffered with potassium acetate, a halogenated product is obtained, from which *ω-trichloro-α-picoline* can be separated by distillation under diminished pressure in yields of about 25%, calculated on the original base. When the amount of chlorine necessary for disubstitution only is passed in, the  $\omega$ -chlorinated product obtained is again mainly the  $\omega$ -trichloro-derivative, picoline being recoverable unchanged; picoline thus behaves as does quinaldine under analogous conditions (Hammick, *loc. cit.*).

*ω-Trichloro-α-picoline* can be reduced to the *dichloro*-compound by stannous chloride, though the amount of reducing agent necessary is considerably more (about twice) than the calculated quantity. In this respect also *ω-trichloro-α-picoline* resembles the corresponding quinaldine derivative.

*ω-Trichloro- and ω-dichloro-α-picoline* are hydrolysable to picolinic acid and to pyridine-2-aldehyde respectively. They are, however, rather unstable liquids, that resinify on keeping (particularly the dichloro-compound) and on heating.

## EXPERIMENTAL.

*ω-Trichloro-α-picoline*.—100 G. (1 mol.) of *α-picoline* in 500 c.c. of glacial acetic acid were heated on the water-bath with 300 g. (3 mols.) of potassium acetate. In the course of about 10 hours, 210 g. (3 mols.) of chlorine were led into the hot mixture; potassium chloride separated. The oil obtained on pouring into water was separated and distilled in steam. The colourless oil that came over was washed with sodium bicarbonate solution, taken up in ether, and dried over anhydrous sodium sulphate. On removal of the ether 62 g. of chlorinated product were obtained, which gave on distillation at 15 mm., 55 g. of b. p. 112—115°. The yield of *ω-trichloro-α-picoline* was about 25%, considerable loss occurring during the steam and other distillations, tarry and resinous products being formed (Found: Cl, 53.6, 54.2.  $C_6H_4NCl_3$  requires Cl, 54.2%). The hydrolysis of this substance to picolinic acid (see below) shows that the three chlorine atoms are substituted in the side chain.

*ω-Trichloro-α-picoline* is soluble in concentrated hydrochloric acid but separates on dilution.

It appears to be less basic than  $\alpha$ -picoline and no picrate could be prepared. When a solution of it in glacial acetic acid is distilled under diminished pressure, a liquid comes over at 125—126°/15—16 mm. that solidifies on standing; m. p. *ca.* 127°. The properties of this substance showed that it is  $\omega$ -trichloro- $\alpha$ -picoline acetate.

*Hydrolysis of  $\omega$ -Trichloro- $\alpha$ -picoline.*— $\omega$ -Trichloro- $\alpha$ -picoline (10 g.) was refluxed with 100 c.c. of 30% sulphuric acid for 8 hours. The mixture was then distilled in steam to remove a small quantity of unchanged material and evaporated to about 40 c.c. On standing after the addition of a slight excess of a saturated solution of copper acetate, the characteristic violet copper salt of picolinic acid separated. This was washed, the acid liberated from it by the action of hydrogen sulphide, and the filtered solution evaporated to dryness. The solid was recrystallised from alcohol, m. p. 133° (Weidel, *Ber.*, 1879, 12, 1992). Yield, 2.2 g.

*$\omega$ -Dichloro- $\alpha$ -picoline.*—Attempts to prepare this compound by regulating the supply of chlorine were unsuccessful. Thus 70 g. (2 mols.) of chlorine were passed into 50 g. of  $\alpha$ -picoline in buffered (3 mols. of potassium acetate) acetic acid and yielded 30 g. of oil which on fractionation gave 14 g. of  $\omega$ -trichloro- $\alpha$ -picoline and 5 g. of a liquid, b. p. 100—103°/16 mm., with a chlorine content of 48.7%. This corresponds to a roughly equimolecular mixture of di- and tri-chloro-derivatives. Unchanged  $\alpha$ -picoline was recovered from the original reaction mixture.  $\omega$ -Dichloro- $\alpha$ -picoline was therefore obtained by the reduction of  $\omega$ -trichloro- $\alpha$ -picoline.  $\omega$ -Trichloro- $\alpha$ -picoline (7.5 g.; 1 mol.) in 30 c.c. of acetone was treated with 17.1 g. (2 mols.) of stannous chloride in 100 c.c. of acetone containing 10 c.c. of concentrated hydrochloric acid. The mixture was heated under reflux for 1 hour, poured into water, and distilled in steam. The colourless oil that came over was taken up in ether and dried over anhydrous sodium sulphate; 3 g. of product were obtained, b. p. 90—92°/15—16 mm. (Found: Cl, 44.2.  $C_6H_5NCl_2$  requires Cl, 43.9%).

*Hydrolysis of  $\omega$ -Dichloro- $\alpha$ -picoline.*—Hydrolysis can be affected by the method described above for  $\omega$ -trichloro- $\alpha$ -picoline; for the rapid removal of chlorine from small quantities the following method was used:  $\omega$ -Dichloro- $\alpha$ -picoline (2 g.) in 100 c.c. of alcohol was treated with 13 g. of silver nitrate in a small quantity of water. The mixture was refluxed for  $\frac{1}{2}$  hour, excess of dilute hydrochloric acid added, and the alcohol removed by steam distillation. Excess of chalk was now added to the solution, which, after filtration, was again distilled in steam. The distillate was made acid with hydrochloric acid and evaporated until the crystalline hydrochloride separated. This was made alkaline with a paste of potassium carbonate and water and extracted with ether. After drying with anhydrous sodium sulphate, the ether was removed, to leave about 0.5 g. of pyridine-2-aldehyde, b. p. 181°. The identity of this substance was further confirmed by the preparation of its bisulphite compound, which sublimed at *ca.* 160° (Harries and Lenart, *Annalen*, 1915, 410, 95). We also prepared a 2:4-dinitrophenyl-hydrazone, m. p. 213°, unchanged on admixture with a specimen made from authentic pyridine-2-aldehyde (Found: C, 49.95; H, 3.0; N, 24.1.  $C_{12}H_8O_4N_5$  requires C, 50.2; H, 3.1; N, 24.4%). We find that the *p*-nitrophenylhydrazone melts sharply at 245°, not indefinitely at 230—235° as stated by Harries and Lenart (*loc. cit.*).

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