

XXXVI.—*Fission of the Pyridine Nucleus during Reduction. Part II. The Preparation of Glutardialdoxime.*

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THE suggestion (J., 1924, **125**, 3041) that the initial product of the action of sodium and alcohol on pyridine is 1 : 4-dihydropyridine has now been confirmed, for, although this has not been isolated, if the solution is treated with hydroxylamine, ammonia is evolved, and a good yield (70%) of glutaraldehydedioxime obtained. This value is obviously too low, since some of the dihydro-compound is further reduced. The initial reduction product, therefore, is largely, if not entirely, 1 : 4-dihydropyridine.

Further work on glutardialdehyde and its homologues is in progress.

EXPERIMENTAL.

Pyridine, b. p. 115–116°, was heated at 80° with 4% potassium permanganate solution until a pink colour persisted. The purified base was separated by distillation, dried over caustic soda, and boiled with powdered calcium carbide. The alcohol was boiled with powdered calcium carbide and fractionated through a column filled with freshly-broken lumps of the same material.

Glutardialdoxime.—No ammonia was evolved when pyridine (80 g.) in boiling alcohol (400 c.c.) was treated with sodium (24 g.). Hydroxylamine hydrochloride (36 g.) in dry alcohol was added, and the mixture boiled for a few minutes, when ammonia was evolved copiously. The remainder of the sodium was precipitated by addition of the requisite quantity of hydrochloric acid diluted with alcohol. After 2 hours' boiling, the sodium chloride was removed and the filtrate distilled until only 80 c.c. remained. The oxime separated slowly and a further quantity was obtained from the mother-liquor (yield 28 g. or 65% calculated on the hydroxylamine); m. p. 175° after recrystallisation from water or pyridine. It may be sublimed without decomposition. Its identity was established by analysis (Found: N = 21.2; calc. 21.05%), by its reactions, and by reduction to pentamethylenediamine (some piperidine was also produced). Boiling with hydrochloric acid gave pyridine (compare Braun and Danziger, *Ber.*, 1913, **46**, 103). When amyl alcohol was used for the reduction, little hydrogen was evolved, and the yield, calculated on the assumption that the sodium liberated the theoretical quantity of hydrogen and that only 1 : 4-dihydropyridine was produced, varied from 68–72%. Excess of hydroxylamine was used in these cases.

Glutardialdehyde was obtained from the oxime by the method used by Harries in the case of succindialdehyde. Both the glass-like polymeride and the unimolecular form described by Harries and Tank (*Ber.*, 1908, **41**, 1705) were obtained.

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