NOTES

INDOLYL-3-ACETALDOXIME

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In connection with our work on the biosynthesis of indolyl-3-acetonitrile (1) we have prepared and characterized indolyl-3-acetaldoxime, which had been postulated (2) as the biological precursor of indolyl-3-acetonitrile, but does not appear to have been described.

EXPERIMENTAL

Indolyl-3-acetaldoxime

The sodium bisulphite adduct of indolyl-3-acetaldehyde (3) (1.310 g, 0.005 mole) was suspended in water and the pH of the mixture was adjusted to pH 8 by addition of 5% Na_2CO_3 solution. A solution of hydroxylamine hydrochloride (0.380 g, 0.0055 mole) in water, similarly adjusted to pH 8, was added, the mixture was stirred for a few minutes, filtered, and kept at 5°. After 12 hours the product (0.450 g, 52%), melting at 127–128° was filtered off. Recrystallization from chloroform gave indolyl-3-acetaldoxime as silvery plates, melting at 140–141°. (Found: C, 68.8; H, 5.9; N, 15.9. $C_{10}H_{10}N_2O$ requires: C, 69.0; H, 5.8; N, 16.1%.) Infrared absorption in Nujol (cm^{-1}): 3385 (s), 3220 (s), 1642 (m). Ultraviolet absorption (λ_{max}, $m\mu$ (log ϵ)) in ethanol: 220(4.58), 275 (shoulder) (3.83), 281(3.85), 290(3.77).

Conversion of Indolyl-3-acetaldoxime to Indolyl-3-acetonitrile

The oxime (0.210 g, 0.0012 mole) was dissolved in 5 ml acetic anhydride and allowed to stand 18 hours at room temperature. The dark mixture was treated with excess 10% NaOH solution and extracted with ether. The ether extract was dried (Na_2CO_3) and concentrated, and the residual oil was distilled at 100–110° and 2.10^{-3} mm yielding indolyl-3-acetonitrile as an oil (0.055 g, 30%) whose infrared absorption was identical with that of an authentic specimen (1). The oil crystallized on seeding with authentic indolyl-3-acetonitrile, melting point 34–36°.

The same product was obtained when $POCl_3$ was used in place of acetic anhydride.

Reduction of Indolyl-3-acetaldoxime to Tryptamine

A solution of the oxime (0.250 g, 0.00144 mole) in dry ether was added dropwise to a boiling suspension of $LiAlH_4$ in ether. After complete addition the mixture was refluxed for 1 hour, allowed to cool, decomposed by pouring into water, and acidified with 2 *M* H_2SO_4 until a clear solution was obtained, which was extracted with ether. The aqueous layer was made alkaline with 10% NaOH and some LiOH was filtered off. The filtrate was repeatedly extracted and the precipitate washed with ether. The combined ether extracts and washings were dried (NaOH), the solvent evaporated, and the oily residue distilled at 105–110° and 5.10^{-3} mm yielding tryptamine (0.132 g, 57%), melting at 116–118°, identical with an authentic specimen in melting point, mixed melting point, and infrared absorption.

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