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CYCLIZATION OF 5-DIAZOIMIDAZOLE-4-CARBONITRILE

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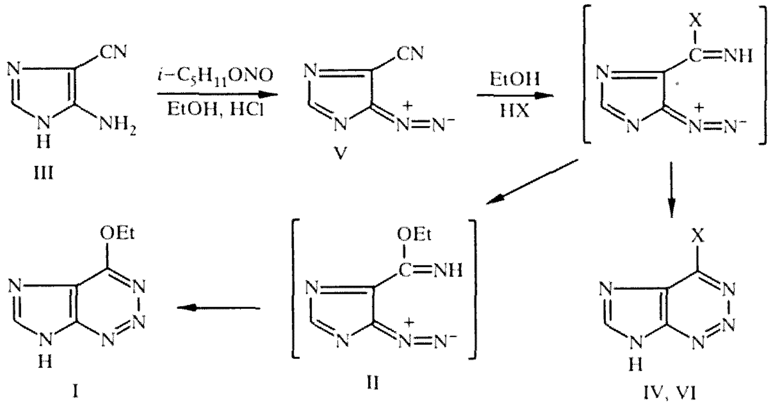
In an attempt to prepare 4-ethoxyimidazo[4,5-*d*]-1,2,3-triazine (I) or the corresponding diazocompound (II) by diazotization of 5-aminoimidazole-4-carbonitrile (III) with isoamyl nitrite in absolute ethanol containing hydrogen chloride we unexpectedly isolated 4-chloroimidazo[4,5-*d*]-1,2,3-triazine (IV) in quantitative yield. The same product was formed from a saturated chloroform solution of 5-diazoimidazole-4-carbonitrile (V) with dry hydrogen chloride. 4-Bromoimidazo[4,5-*d*]-1,2,3-triazine (VI) was formed analogously with hydrogen bromide. We have previously observed the reverse reaction, the opening of the triazine ring of IV on heating with water to give the diazoimidazole V [1].



IV X = Cl, VI X = Br

Cyclization of benzo- and pyridothieno-3-cyano-2-diazonium chlorides to derivatives of the corresponding chloro-1,2,3-triazines has been reported [2, 3] but the authors considered that the cyclization was unique and occurred as a result of the influence of the sulfur atom.

We have now observed that ring closure of heterocyclic *o*-diazonitriles into condensed 4-halogeno-1,2,3-triazines is more general than had been previously supposed [2, 3] and is not limited to compounds containing sulfur.

Compound IV ($C_4H_2ClN_5$). A. A solution of aminonitrile III (0.5 g, 3.4 mmol) in absolute ethanol (3 ml) was added dropwise at 0-2°C to a solution of isoamyl nitrite (1.2, ml 9 mmol) in ethanol saturated with HCl (5 ml). The mixture was stirred for 10 min and filtered. The precipitate was washed with ether and water, and dried in vacuum over KOH to give IV (0.52 g, 98%), m.p. 105°C. The product was identical with a sample of compound IV prepared previously [1] (m.p., electronic spectrum, TLC).

B. Dry HCl was passed through a solution of the diazonitrile V (3.45 mmol) in dry chloroform (100 ml) at 0-2°C for 15 min. The solution was evaporated to dryness in vacuum, the residue was suspended in water, filtered, and dried in vacuum over KOH. Yield 74%. The product was identical in all respects to compound IV prepared by method A.

Compound VI ($C_4H_2BrN_5 \cdot H_2O$) was prepared analogously to the imidazotriazine IV by method B. Yield 75%, m.p. 95-96°C. UV spectrum (water)(λ_{max}, (lgε)): 202 (4.14), 261 nm (3.22). Vibrations for diazo and cyano groups were absent from the IR spectrum (KBr disc), R_f 0.5 (propanol-0.2 N ammonia, 3:1) 0.4 (9:1 chloroform–ethanol).

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