PHOTOLYSIS OF 2-AZIDO-3,4,6-TRICHLORO-5-CYANOPYRIDINE

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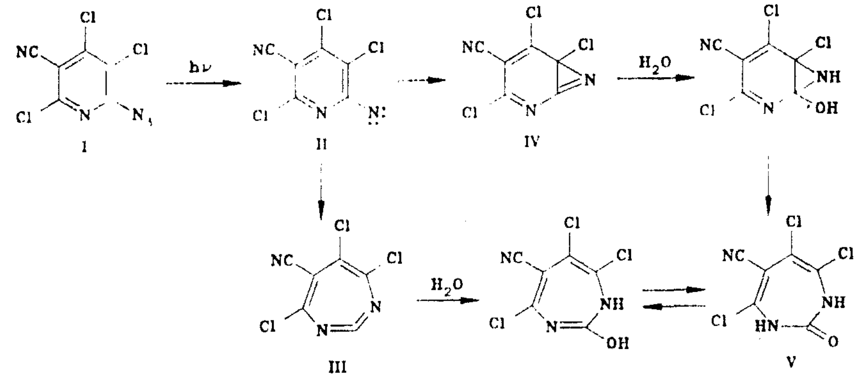
The photolysis of aryl and hetaryl azides is accompanied by the elimination of a molecule of nitrogen with subsequent ring expansion [1] or contraction [2].

To study the photolytic transformations of pyridyl azides with acceptor substituents we carried out the photolysis of 2-azido-3,4,6-trichloro-5-cyanopyridine (I) [3]. The reaction was accomplished in aqueous dioxane solution at room temperature and was complete after 1.5 h; the product was 4,5,7-trichloro-6-cyano-1H-1,3-diazepin-2(3H)-one (V), which was obtained in 72% yield.



Under these conditions nitrene II is probably converted to diazacycloheptatetraene III (see [1]) or to bicyclic azirine IV (see [4]), while subsequent reaction with a molecule of water leads to diazepinone V.

4,5,7-Trichloro-6-cyano-1H-1,3-diazepin-2(3H)-one (V). A solution of 0.25 g (1 mmole) of azide I in 10 ml of aqueous dioxane (5% H_2O) was irradiated at room temperature with the full beam of a DRSh-1000 Hg lamp for 1.5 h. The solvent was then evaporated, and the residue was washed with hot benzene to give a chromatographically pure, crystalline, beige substance [R_f 0.61 in a benzene—ethyl acetate (5:2) system] with mp 164-166°C (dec.). IR spectrum (KBr): 3230 (NH), 3150 (NH), 2228 ($C\equiv N$), 1723 ($C=O$), 1608 cm^{-1} ($C=C$). UV spectrum (C_2H_5OH), λ_{max}, nm ($\log\varepsilon$): 226 (4.14), 299 (3.26). Mass spectrum, m/z (I, %): 237 (23, $M^{+\cdot}$), 202 (30), 194 (65), 176 (32), 174 (48), 147 (13), 138 (20), 132 (19), 111 (10), 97 (13), 77 (70), 62 (63), 51 (22), 36 (100). The yield was 1.7 g (72%).

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