HYDROLYTIC CONVERSIONS OF 2,4-DIAZIDO-6-ALKOXY-s-TRIAZINES

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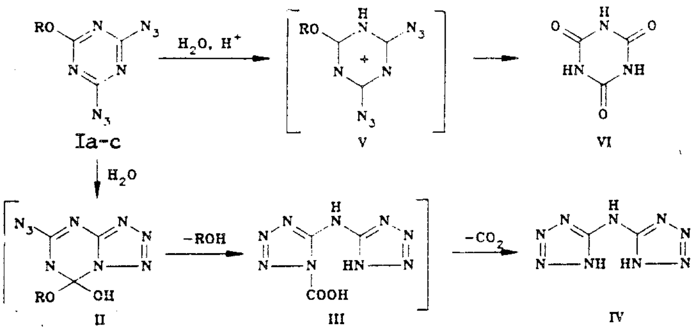
2,4,6-Triazido- and 2,4,6-trialkoxy-s-triazines [1] and [2] are hydrolyzed upon heating in aqueous base or acid to form cyanuric acid.

While studying the hydrolysis of s-triazines containing both alkoxy and azido groups we have discovered a novel s-triazine ring transformation. Thus heating the 2,4-diazido-6-alkoxy-1,3,5-triazines Ia-c in water leads to elimination of a ring carbon atom together with the attached alkoxy group to form bis(tetrazol-5-yl)amine (IV) in 55-60 % yield. The molecular weight of IV was determined mass spectrometrically and agreed with that calculated. As a result of the molecular symmetry the NMR signals for both of the tetrazole ^{13}C atoms show a single chemical shift at 153.46 ppm. The IR spectrum of crystalline bis(tetrazol-5-yl)amine, like that of 5-aminotetrazole, shows a series of characteristic peaks in the regions 700-800, 900-1100, and 1500-1600 cm^{-1}, typifying the tetrazole ring [3]. The melting point, solubility, and salt formation with ammonia for compound IV agreed with those reported for bis(tetrazol-5-yl)amine reported in the literature [4].



I a $R=CH_3$, b $R=CH_2CN$, c $R=C_2H_5$

Heating 2,4-diazido-6-alkoxy-s-triazines in the presence of acids leads to 2,4,6-trioxohexahydro-1,3,5-triazine (VI) in near to quantitative yield.

The course of the hydrolytic conversion is apparently governed by the tendency of I to undergo azide-tetrazole tautomerism. In fact, since in acid media the protonation of the triazine ring hinders the cyclization of the azide group to the annelated tetrazole, hydrolysis of I proceeds in the usual manner to cyanuric acid. However, in neutral media, there is evidently formed a covalent tetrazolotriazine hydrate II which undergoes fission of the N_4—C_5 bond and thus to the final bistetrazolylamine IV via a further series of stages. A similar C—N bond fission is known for the covalent hydrates of tetrazolo[1,5-c]quinazolines [5].

This transformation of 2,4-diazido-6-alkoxy-s-triazines is a new and convenient method for synthesizing the previously difficult to obtain bis(tetrazol-5-yl)amine which, in turn, can be used as the starting material for the polyazaheterocyclic systems [6].

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