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Transformation of Azido Derivatives of s-Triazine into 1,2,4-Triazolylaminotetrazoles

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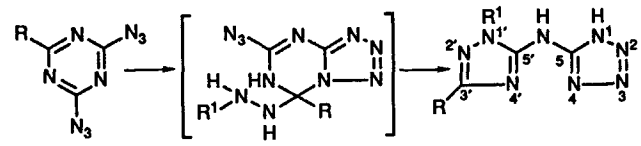
On heating 6-amino and 6-alkoxy derivatives of 2,4-diazido-s-triazine **1a–c** with hydrazine or phenylhydrazine in ethanol the corresponding triazolylaminotetrazoles **2a–d** are produced.

The type and direction of the chemical transformation of heterocyclic azido derivatives may be determined by their ability to undergo azidotetrazole tautomerism. Azidotetrazole tautomeric equilibria depend on various factors, *e.g.* solvent, pH of medium, temperature, *etc.* We have recently shown[1] that acidic hydrolysis of the azido and alkoxy groups in 2,4-diazido-6-alkoxy-s-triazines results in the formation of cyanuric acid, while heating without acid allows compounds **1** to be transformed into bis(tetrazol-5-yl)amine.

While studying the properties of s-triazine azido derivatives we found a new transformation reaction on the s-triazine ring. Heating compounds **1a–c** with hydrazine or phenylhydrazine in

ethanol resulted in the corresponding triazolylaminotetrazoles **2**.† Compounds **2a–c** were obtained as the salts with hydrazine. In order to eliminate hydrazine the saturated aqueous solutions of **2a–c** were treated with concentrated hydrochloric acid. The molecular ion peaks of compounds **2** determined by mass spectrometry proved to correspond to the estimated values. Also, the initial decay process is accompanied by the formation of ions $[M - N_3]^{\bullet+}$ and $[M - HN_3]^{\bullet+}$ which are characteristic of the mass spectrometric behaviour of tetrazoles.[2] In the ^{13}C NMR spectrum of compound **2d** measured in $[^2H_6]$DMSO the chemical shifts δ of the carbons of both the tetrazole ($C_{(5)}$ 151.9) and the triazole ($C'_{(3)}$ 157.7, $C'_{(5)}$ 151.8) rings are very similar to those for bis(tetrazol-5-yl)amine[1] and aminotriazole[3] derivatives, respectively. In addition, the chemical shifts of the aromatic ring carbons ($C''_{(1)}$ 136.3, $C''_{(2,6)}$ 120.6, $C''_{(3,5)}$ 129.2, $C''_{(4)}$ 126.4) are similar to those of the corresponding carbons of the phenyltriazoles but differ from those of phenylhydrazine,[3] which indicates that hydrazine fragments have been introduced into the 1,2,4-triazole ring.

Compounds **2** are most likely derived from splitting of the triazine ring due to nucleophilic addition of hydrazines, followed by cyclization of one of the azido groups into the tetrazole ring, cleavage of the C–N bond in the intermediate tetrazolotriazine and the intramolecular substitution of the other azido group by the hydrazine moiety, leading to formation of the triazole ring.



1a–c
a R = OMe
b R = OEt
c R = NH_2

2a–d
a R^1 = H; R = OMe
b R^1 = H; R = OEt
c R^1 = H; R = NH_2
d R^1 = Ph; R = OMe

† A typical procedure for the synthesis of triazolylaminotetrazoles **2a–d** is as follows. The corresponding diazido compound **1** (2.5 mmol) was heated with 5 mmol of hydrazine hydrate or phenylhydrazine in 5 ml of ethanol for 1 h. The reaction mixture was then cooled to 15–20 °C, yielding a crystalline precipitate of the compound **2** which was filtered off. The compounds **2a–c** were obtained as the salts with hydrazine. In order to eliminate hydrazine these salts were dissolved in water and the saturated aqueous solutions obtained were treated with concentrated hydrochloric acid to pH 1. The analytically pure compounds **2a–d** were obtained by recrystallization from the following solvents: **2a,b**: from aqueous acetic acid; **2c**: from water; **2d**: from aqueous ethanol. Melting points (°C) and yields: **2a** 265–267, 25–30%; **2b** 219–220, 30–35%; **2c** >300, 25–30%; **2d** 215–216, 30–35%

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