DESTRUCTION OF THE TRIAZINE RING IN 4-ALKYL-6-NITRO-7-OXO-4,7-DIHYDRO-1,2,4-TRIAZOLO[5,1-c] [1,2,4]TRIAZINES

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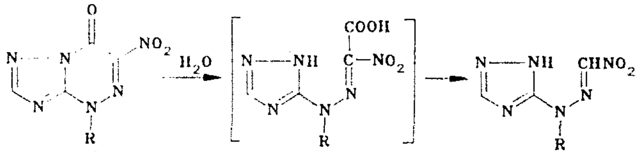
4-Alkyl-6-nitro-7-oxo-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazines I react readily with amines, thiols, and alkoxides to give the corresponding triazolo[5,1-c][1,2,4]triazines [1].

We have observed that, instead of the expected replacement of the nitro group, destruction of the triazine ring to give nitroformaldehyde alkyl(1,2,4-triazol-3-yl)hydrazones IIIa-d occurs when Ia-d are heated in water.



Ia-d II IIIa-d

I—III a $R=CH_3$; b $R=CH_2COOC_2H_5$; c $R=(CH_2)_4OCOCH_3$; d $R=$2,3,4,6-tetra-O-acetyl-β-D-glucosyl

The results of elementary analysis of the compounds obtained are in agreement with the calculated values, and the characteristics of the PMR spectra and the results of x-ray diffraction analysis for IIId confirm the Z configuration of the hydrazones.

The reaction evidently proceeds with the formation of the readily decarboxylated carboxylic acids II.

This is the first time that this sort of hydrolytic cleavage of the rather stable triazine ring has been observed. Only individual cases of the destruction of the asym-triazine ring in benzo[c]triazinones [2] and thionaphtheno[2,3-d]pyridazino[3,2-c][1,2,4]triazinones [3] by the action of alkalis, alkylamines, and hydrazine are known.

A mixture of 2.00 g (0.01 mole) of triazolotriazine Ia in 100 ml of water was refluxed for 1 h and filtered hot. It was then cooled, and the precipitated nitroformaldehyde methyl(1,2,4-triazol-3-yl)hydrazone (IIIa) was removed by filtration to give 1.48 g (87%) of a product with mp 223°C. PMR spectrum (d_6-DMSO): 3.86 (3H, s, $N—CH_3$), 8.51 (1H, broad s, 2-H), 9.18 [1H, s, $H—C(NO_2)$], 14.05 ppm (1H, broad s, NH).

A similar procedure was used to obtain **nitroformaldehyde N-ethoxycarbonyl-N-(1,2,4-triazol-3-yl)hydrazone (IIIb)** [mp 182°C. PMR spectrum (d_6-DMSO): 1.19 (3H, t, CH_3), 4.15 (2H, q, OCH_2), 4.94 (2H, s, $N—CH_2$), 8.51 (1H, broad s, 2-H), 9.29 (1H, s, $HC(NO_2)$), 14.20 ppm (1H, broad s, NH). The yield was 2.1 g (81%).], **nitroformaldehyde N-(4-acetoxybutyl)-N-(1,2,4-triazol-3-yl)hydrazone (IIIc)** [mp 116°C. PMR spectrum (d_6-DMSO): 1.35-1.96 (4H, m, $(CH_2)_2$), 1.98 (3H, s, CH_3), 4.01 (2H, t, NCH_2), 4.16 (2H, t, OCH_2), 8.53 (1H, broad s, 2-H), 9.18 (1H, s, $HC(NO_2)$), 14.15 ppm (1H, broad s, NH). The yield was 2.48 g (92%).], and **nitroformaldehyde N-2',3',4',6'-tetra-O-acetyl-β-D-glucosyl-N-(1,2,4-triazol-3-yl)hydrazone (IIId)** [mp 109°C. PMR spectrum (d_6-DMSO): 1.82, 1.93, 1.97, 2.01 (12H, s, $4CH_3CO$); 4.00-5.90 (6H, m, glycoside C—H); 6.17 (1H, d, J = 9 Hz, N—CH—O); 9.27 (1H, s, $H—C(NO_2)$; 8.52 (1H, broad s, 2-H); 14.30 ppm (1H, broad s, NH). The yield was 2.05 g (76%).].

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