NEW TRANSFORMATION OF THE PYRIMIDINE RING IN 6-NITROTRIAZOLO-[1,5-a]PYRIMIDINES UNDER THE INFLUENCE OF AMINES

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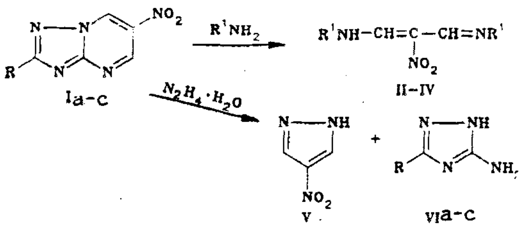
On reaction with liquid ammonia, potassium amide, hydrazine, and 1,3-ambident dinucleophiles nitropyrimidine derivatives are transformed to hetero- and carbocyclic compounds [1, 2]. The reaction commences with the formation of a covalent adduct, which is then transformed through postulated open form I or a fixed bicyclic intermediate [3].

We have observed that in the case of reaction with aromatic amines and benzylamine under relatively mild conditions destruction of the pyrimidine ring in 2-R-6-nitro-1,2,4-triazolo[1,5-a]-pyrimidines Ia-c with the formation of noncyclic compounds — 1-R^1-amino-2-nitro-3-R^1-iminopropenes II-IV — occurs, whereas the formation of 4-nitropyrazole V and 3-R-5-amino-1,2,4-tri-azoles VIa-c occurs in the reaction with hydrazine.



I, VI a R=H, b $R=CH_3$, c $R=CF_3$; II $R^1=C_6H_5$; III $R^1=C_6H_4Br$; IV $R^1=CH_2C_6H_5$

The molecular masses determined by mass spectrometry and the results of elementary analysis of II–V were in agreement with the calculated values, while the melting points and the spectral characteristics coincided with the corresponding constants of samples obtained by alternative synthesis from nitromalonaldehyde and amines [4, 5].

A mixture of 0.01 mole of 2-R-6-nitro-1,2,4-triazolo-[1,5-a]pyrimidines Ia-c and 1.86 g (0.02 mole) of aniline in 30 ml of butanol (10 ml of DMSO or DMF) was heated for 30 min at 100°C, after which it was cooled to 20°C, and compound II, with mp 90-91°C (mp 91-92°C [4]), was removed by filtration. IR spectrum: 1300, 1600 (NO_2), 3090 cm^{-1} (NH). PMR spectrum: 7.24-7.63 (10H, m, Ph), 9.14 (2H, s, CH), 13.50 ppm (1H, s, NH). Aminotriazoles VIa-c were extracted with ethyl acetate from the residues obtained after evaporation in vacuo.

Compound III, with mp 169-170°C, was similarly obtained from 6-nitro-1,2,4-triazolo[1,5-a]pyrimidine (Ia) and the corresponding amine. IR spectrum: 1320, 1595 (NO_2), 3080 cm^{-1} (NH). PMR spectrum: 7.46 (4H, d, Ar), 7.66 (4H, d, Ar), 9.11 (2H, s, CH), 13.50 ppm (1H, s, NH). Also similarly obtained was IV with mp 80°C. IR spectrum: 1320, 1610 (NO_2), 3100 cm^{-1} (NH). PMR spectrum: 4.68 (4H, s, CH_2), 7.10-7.45 (10H, m, Ph), 8.85 (2H, s, CH), 13.50 ppm (1H, s, NH). A similar procedure was also used to obtain V with mp 160°C (mp 161°C [5]). IR spectrum: 1330, 1600 (NO_2), 3120 cm^{-1} (NH). PMR spectrum: 8.50 [2H, s, 3(5)-H], 13.80 ppm (1H, s, NH).

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