3. A. F. Khlebnikov, M. S. Novikov, and R. R. Kostikov, Zh. Org. Khim., 22, 1706 (1986).
4. M. Sugiura and Y. Hamada, Yakugaku Zasshi, 99, 1229 (1979); Ref. Zh. Khim., 21Zh203 (1980).

PYRIMIDINE RING TRANSFORMATIONS TO 6-NITROAZOLO[1,5-a]PYRIMIDINES – A ONE-STEP SYNTHESIS OF AZOLYLAMINO DERIVATIVES OF NITROPYRIDINE

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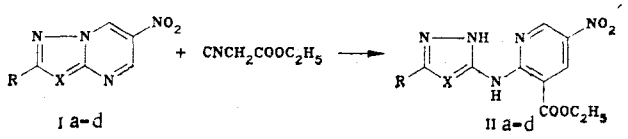
UDC 547.859.3.04'785.5'792.3'822.7.07

We have discovered the first case of a transformation of condensed pyrimidine derivatives with nitrogen in a bridge position by the action of a nucleophile. Heating of 6-nitroazolo-[1,5-a]pyrimidines Ia-d with a cyanoacetic ester forms the pyridine derivatives IIa-d. The structure of the latter compounds is evidence that the conversion of the ring to the triazopyrimidine I is different from similar reactions of uncondensed pyrimidines [1, 2]; it proceeds without elimination of the $N_{(1)}$–$C_{(2)}$ segment of the pyrimidine, and presumes attack by the nitrile nitrogen at the nodal carbon of the starting compound.



I a-d II a-d

I, II a,c,d R=H, b R=CH_3; a,b X=N, c X=$CCOOC_2H_5$, d X=CNO_2

The molecular weight determined by mass spectrometry and the elemental composition of the transformation products agrees with the calculated values. The IR and PMR spectral data permit them to be identified as the 2-(5-azolylamino)carbonyl-5-nitro-3-ethoxypyridines IIa-d. X-ray diffraction analysis of compound IIb confirms the proposed structure.

Compound IIa, mp 275-278°, yield 54%; IIb, mp 300°, yield 60%; IIc, mp 232-233°, yield 48%; IId, mp 256-275°, yield 65%. The IR spectra show absorption bands of the valence vibrations of nitro (1330-1350 and 1570-1595 cm^{-1}), carbonyl (1680-1700 cm^{-1}), and amino groups (3100-3300 cm^{-1}). In a typical PMR spectrum (compound IIb) there are signals of methyl (2.29 ppm, s, 3H), carbethoxy (1.38 ppm, t, 3H; 4.43 ppm q, 2H, J = 6 Hz), pyridine (8.83 ppm, d, 1H; 9.18 ppm, d, 1H, J = 3 Hz), and NH (10.90 ppm, br. s, 12.40 ppm, br.s) protons.

LITERATURE CITED

1. H. C. Van der Plas, Tetrahedron, 41, 237 (1985).
2. V. N. Charushin and H. C. Van der Plas, Recl. Trav. Chim., 102, 373 (1983).

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0009-3122/87/2306-0709$12.50 ©1987 Plenum Publishing Corporation