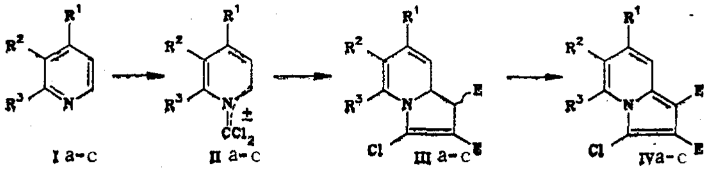
1,3-DIPOLAR CYCLOADDITION OF CYCLOIMMONIUM YLIDS THAT FORM FROM PYRIDINES AND DICHLOROCARBENE

A. F. Khlebnikov and R. R. Kostikov

UDC 547.821.2'821.411'831.1'834.2.07

When pyridines react with carbenes formed from diazo compounds [1], or when dichlorocarbene reacts with ketenimines [2,3], immonium ylids form. The reaction of pyridines with dichlorocarbene generated in alkaline medium forms a polymer [4].

We have established that when dichlorocarbene obtained by thermal decomposition of sodium trichloroacetate in chloroform in the presence of benzyltriethylammonium chloride, reacts with compounds Ia-c, the ylids IIa-c form; the latter undergo 1,3-cycloaddition with dimethyl fumarate or dimethyl maleate. The primary cycloaddition products undergo dehydrochlorination to the dihydroindolizines IIIa-c, which by reaction with 2,3-dichloro-5,6-dicyanoquinone are oxidized to the substituted indolizines IVa-c.



E=CO$_2$Me; I—IV a R^1=R^2=R^3=H; b R^1=Me, R^2=R^3=H; c R^1=H, R^2+R^3= —(CH=CH)$_2$—

To a solution of 20 mmoles of compound Ia-c, 0.5 g of benzyltriethylammonium chloride, and 10 mmoles of dimethyl fumarate (in the case of Ia) or dimethylmaleate (in the case of Ib,c) in 50 ml of chloroform at 60° was added 20 mmoles of sodium trichloroacetate over 4 h with stirring in a stream of argon. The reaction mixture was filtered and evaporated, and the residue was separated by column chromatography (silica gel 100-160 µm, hexane—ether eluent). To the fraction containing dihydroindolizine IIIa-c was added a benzene solution of 2,3-dichloro-5,6-dicyanoquinone until aromatization was complete (monitored by TLC). The mixture was filtered through silica gel and the solvent was evaporated. The residue was recrystallized from ether—hexane—chloroform mixture to give 28% of indolizine IVa, 47% of IVb, or 5% or IVc.

Dimethyl 3-chloroindolizine-1,2-dicarboxylate (IVa). Mp. 83-84°. IR spectrum (KBr): 1700, 1735 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 296 (3.81), 308 (3.93), 347 nm (3.87). PMR spectrum (CDCl$_3$): 3.92 and 4.02 (s, 3H, OMe), 6.92-7.42 and 8.18, 8.45 ppm (m, 4H, arom.).

Dimethyl 7-methyl-3-chloroindolizine-1,2-dicarboxylate (IVb). Mp 125-126°. IR spectrum (KBr): 1700, 1740 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 238 (4.36), 295 (3.89), 307 (4.01), 340 nm (3.86). PMR spectrum (CDCl$_3$): 2.42 (s, 3H, Me), 3.95 and 4.03 (s, 3H, OMe), 6.72-6.98 and 8.05-8.15 ppm (m, 3H, arom.).

Dimethyl 1-chloropyrrolo[1,2-a]quinoline-2,3-dicarboxylate (IVc). Mp 147-148°. IR spectrum (KBr): 1710, 1740 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 263 (4.63), 270 (4.60), 323 nm (3.85). PMR spectrum (CDCl$_3$): 3.98 and 4.05 (s, 3H, OMe), 7,09 and 7.97 (d.d, 2H, 9-H, 10-H, J = 8 Hz), 7.44- 7.74 and 8.49-8.68 ppm (m, 4H, arom.). Satisfactory elemental composition data were obtained for compounds IVa-c.

LITERATURE CITED

1. V. A. Nikolaev and I. K. Korobitsyna, Zh. Vses. Khim. Ova., 24, 496 (1979).
2. A.F. Khlebnikov, M. S, Novikov, and R. R. Kostikov, Zh. Org. Khim., 21, 2227 (1985).

A. A. Zhdanov Leningrad State University, Leningrad 199004. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 856, June, 1987. Original article submitted November 25, 1986.

0009-3122/87/2306-0708$12.50

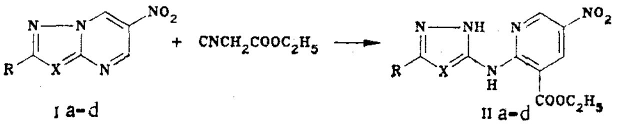
3. A. F. Khlebnikov, M. S. Novikov, and R. R. Kostikov, Zh. Org. Khim., 22, 1706 (1986).
4. M. Sugiura and Y. Hamada, Yakugaku Zasshi, 99, 1229 (1979); Ref. Zh. Khim., 21Zh203 (1980).

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

V. L. Rusinov, T. L. Pilicheva,
A. A. Tumashov, and O. N. Chupakhin

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).

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 857, June, 1987. Original article submitted December 23, 1986.

0009-3122/87/2306-0709$12.50