Russian Journal of Organic Chemistry, Vol. 40, No. 10, 2004, pp. 1526–1527. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 10, 2004, pp. 1574–1575.

Transformation of 3,4-Bis(formylamino)pyridine into 4-Nitro-1,2,3-triazolo[4,5-*c*]pyridine 2-Oxide in the Reaction with Nitrating Mixture

Yu. M. Yutilov and N. N. Smolyar

Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, ul. R. Lyuksemburg 70, Donetsk, 83114 Ukraine
e-mail: yutilov@skif.net

Received October 29, 2003

Abstract—Treatment of 3,4-bis(formylamino)pyridine with a mixture of concentrated nitric and sulfuric acids unexpectedly afforded 4-nitro-1,2,3-triazolo[4,5-*c*]pyridine 2-oxide. Reduction of the latter with iron in acetic acid gave previously known 4-amino-1,2,3-triazolo[4,5-*c*]pyridine.

We previously reported on the nitration of 1,3-dihydro-2*H*-imidazo[4,5-*c*]pyridin-2-one (**I**) which led to formation of the corresponding 4-nitro derivative **II** in almost quantitative yield [1, 2]. This reaction was the first example of introduction of a nitro group into imidazo[4,5-*c*]pyridine molecule. The imidazole nitrogen atoms in **I** are contiguous to the carbonyl carbon atom; as a result, protonation of both imidazole and probably pyridine ring in sulfuric acid medium is suppressed, and compound **I** exhibits a high reactivity toward both nitration and halogenation [3]. Taking these data into account, we examined the nitration of fairly accessible 3,4-bis(formylamino)pyridine (**III**) [4, 5] which may be regarded as a simple model of imidazolone **I**.

The reaction of compound **III** with excess nitric acid (d = 1.52) in concentrated sulfuric acid under conditions analogous to those reported in [6] gave a light yellow product which decomposed with explosion on heating above 225°C. The product is soluble in aqueous alkalies and in DMSO and DMF on heating. Its elemental composition corresponded to the formula $C_5H_3N_5O_3$. Strong absorption bands in the IR spectrum at 1310, 1365, and 1540 cm^{-1} indicated the presence of an *N*-oxide moiety and a nitro group. The ^1H NMR spectrum of the isolated product contained two doublets at δ 7.72 and 8.04 ppm from protons in the pyridine ring (^3J = 6.0 Hz). According to the mass spectral data, the molecular weight of this compound (M 181) coincided with that calculated for 4-nitro-1,2,3-triazolo[4,5-*c*]pyridine 2-oxide (**IVA**). Presumably, *N*-oxide **IVA** exists in tautomeric equilibrium with N–OH structure **IVB** (Scheme 1).

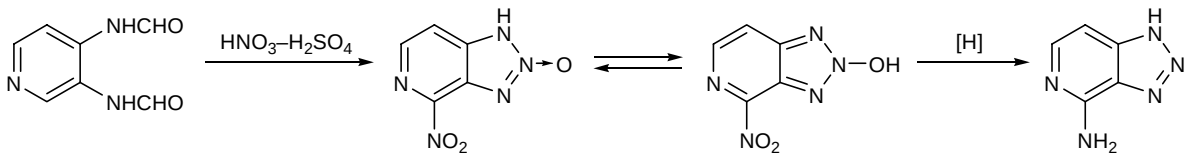
Fragmentation of compound **IV** under electron impact is likely to include successive elimination of the nitro group and hydroxy group (Scheme 2) in a way similar to that described in [7].

The reduction of nitro compound **IV** with iron in acetic acid [8] gave 4-amino-1,2,3-triazolo[4,5-*c*]pyridine (**V**) which was identical in the IR and ^1H NMR spectra with an authentic sample prepared from 4-chloro-1,2,3-triazolo[4,5-*c*]pyridine [8].

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz) in DMSO-d_6 using HMDS as internal reference. The IR spectra

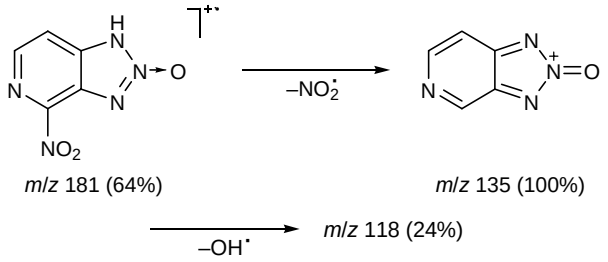
Scheme 1.



III **IVA** **IVB** **V**

1070-4280/04/4010-1526 © 2004 MAIK "Nauka/Interperiodica"

Scheme 2.



were measured on a Specord 75IR spectrophotometer from samples pelleted with KBr. The mass spectrum was obtained on a Varian 311-A mass spectrometer. The purity of the products was checked by TLC on Silufol UV-254 plates using chloroform–ethanol as eluent (development with UV light or iodine vapor).

4-Nitro-1,2,3-triazolo[4,5-*c*]pyridine 2-oxide (IV). 3,4-Bis(formylamino)pyridine (**III**), 1.65 g (10 mmol), was dissolved in 15 ml of cold concentrated sulfuric acid, the solution was cooled to 0–5°C, 2 ml (48 mmol) of concentrated nitric acid (d = 1.52) was added in portions under stirring, and the mixture was stirred for 1 h at 0–5°C. The mixture was then heated to 50–60°C, kept for 2 h at that temperature, cooled, and poured onto ice. The light yellow precipitate was filtered off, washed with a small amount of ice water, dried, and recrystallized from dimethyl sulfoxide. Yield 1.0 g (53%), mp >225°C (decomposes with explosion). IR spectrum, ν, cm^{-1}: 1310 (N→O), 1365 (NO_2, sym.), 1540 (NO_2, asym.). ^{1}H NMR spectrum, δ, ppm: 7.72 d (1H, 7-H, J = 6.0 Hz), 8.04 d (1H, 6-H, J = 6.0 Hz). Mass spectrum, m/z (I_{rel}, %): 181 (64) $[M]^+$, 135 (100), 118 (24). Found, %: C 33.05; H 1.62; N 38.81. $C_5H_3N_5O_3$. Calculated, %: C 33.16; H 1.67; N 38.67.

4-Amino-1,2,3-triazolo[4,5-*c*]pyridine (V). A mixture of 1.0 g (5.5 mmol) of 4-nitro-1,2,3-triazolo[4,5-*c*]pyridine 2-oxide (**IV**) and 2.5 g of iron in 35 ml of glacial acetic acid was heated for 3–4 h. The mixture was cooled and filtered, the filtrate was evaporated to dryness, the residue was treated with 25% aqueous ammonia and the solution was evaporated to dryness. The residue was extracted with ethanol, and the solvent was distilled off from the extract. Yield 0.5 g (67%), mp >325°C (decomp.) [9]. IR spectrum, ν, cm^{-1}: 1690, 1650, 1625. ^{1}H NMR spectrum, δ, ppm: 6.83 d (1H, 7-H, J = 6.0 Hz), 7.35 br.s (2H, NH_2), 7.68 d (1H, 6-H, J = 6.0 Hz), 12.05 s (1H, 1-H). Found, %: C 44.23; H 3.71; N 51.60. $C_5H_5N_5$. Calculated, %: C 44.44; H 3.75; N 51.73.

REFERENCES

1. Yutilov, Yu.M. and Svertilova, I.A., *Khim. Geterotsikl. Soedin*., 1973, p. 138.
2. Yutilov, Yu.M. and Svertilova, I.A., *Khim. Geterotsikl. Soedin*., 1986, p. 97.
3. Yutilov, Yu.M. and Svertilova, I.A., *Khim. Geterotsikl. Soedin*., 1994, p. 1076.
4. EP Patent Appl. no. 260613, 1988; *Chem. Abstr*., 1988, vol. 109, no. 73438c.
5. US Patent no. 4804658, 1989; *Ref. Zh., Khim*., 1989, no. 23O107P.
6. Rusinov, V.L. and Chupakhin, O.N., *Nitroaziny* (Nitro Azines), Novosibirsk: Nauka, 1991, p. 10.
7. Terent'ev, P.B. and Stankyavichus, A.P., *Mass spektrometricheskii analiz biologicheski aktivnykh azotistykh osnovanii* (Mass Spectrometric Analysis of Biologically Active Nitrogenous Bases), Vil'nyus: Mokslas, 1987, p. 140.
8. Hertog, H.J. and Overhoff, J., *Recl. Trav. Chim. Pays–Bas*, 1950, vol. 69, p. 468.
9. Temple, C., Smith, B.H., and Montogomery, J.A., *J. Org. Chem*., 1972, vol. 37, p. 3601.