ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 3, pp. 613–614. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © S.A. Chumachenko, O.V. Shablykin, V.S. Brovarets, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 3, pp. 518–519.

LETTERS TO THE EDITOR

Reaction of 2-Methoxycarbonylamino-3,3-dichloroacrylonitrile with Phenylhydrazine in the Presence of Triethylamine

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Received October 19, 2010

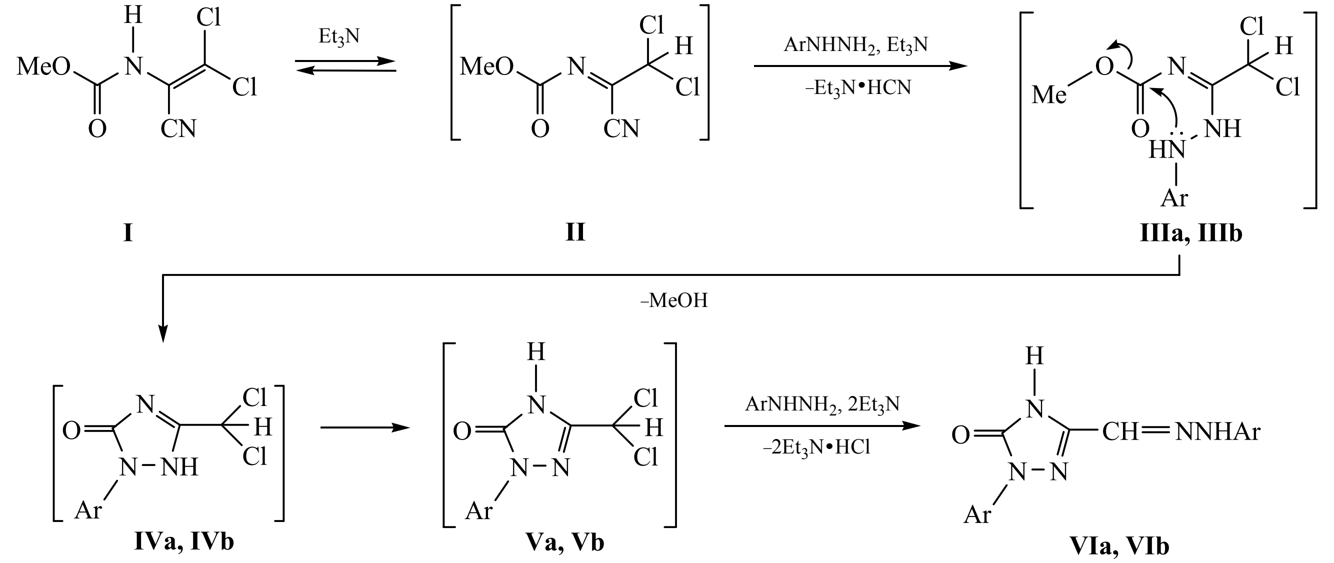
DOI: 10.1134/S1070363211030327

It was found previously that the reaction of 2-methoxycarbonylamino-3,3-dichloroacrylonitrile **I** with an excess of phenylhydrazine occurs initially through the substitution of two labile chlorine atoms by the phenylhydrazine residues followed by the intramolecular cyclization due to the addition of phenylhydrazine fragment to the cyano group to form 5-aminopyrazole [1].

As shown in the present report, these reagents react otherwise in the presence of triethylamine, giving rise to substituted triazol-5-ones **VI**. The presence of triethylamine in the reaction mixture promotes apparently the increase in the amount of the reactive *N*-methoxycarbonylimine tautomer **II**, which elimi-nates the cyanide ion under the action of aryl hyd-razines [1, 2].

1-Aryl-5-oxo-4,5-dihydro-1*H*-1,2,4-triazole-3-carbaldehyde aryl hydrazones **VI** are formed as the final products via some intermediate stages (see transformation **II**→**VI** in the scheme). The structure of compounds **VIa** and **VIb** was confirmed by the ^{1}H NMR, IR spectroscopy, mass spectrometry and X-ray diffraction studies.

1-Aryl-5-oxo-4,5-dihydro-1*H*-1,2,4-triazole-3-carbaldehyde (VIa, VIb) aryl hydrazones. To a solution of 10 mmol of **I** in 20 ml of methanol 30 mmol of triethylamine and 20 mmol of the appropriate aryl hydrazine were added. The mixture was stirred for



Ar = Ph (**a**), 4-ClC$_6$H$_4$ (**b**).

12 h at 20–25°C. Then the precipitate was filtered off, washed first with water and then with a small amount of 2-propanol.

Compound VIa. Yield 52%, mp 270–272°C (ethanol). IR spectrum, ν, cm^{-1}: 1707 (C=O), 3162 (NH), 3293 (NH). ^{1}H NMR spectrum, δ, ppm: 6.83–8.03 m ($10H_{Ar}$), 7.58 s (1H, NH), 10.92 s (1H, CH), 12.35 br.s (1H, NH). Found, %: C 64.73; H 4.72; N 25.25. *M* 278, 280. $C_{15}H_{13}N_5O$. Calculated, %: C 64.51; H 4.69; N 25.07. *M* 279.

Compound VIb. Yield 58%, mp 290–292°C (ethanol). IR spectrum, ν, cm^{-1}: 1717 (C=O), 3173 (NH), 3321 (NH). ^{1}H NMR spectrum, δ, ppm: 7.25–8.18 m ($8H_{Ar}$), 7.60 s (1H, NH), 11.10 s (1H, CH), 12.45 br.s (1H, NH). Found, %: C 51.97; H 3.21; N 20.38 Cl 20.54. *M* 346, 348. $C_{15}H_{11}Cl_2N_5O$. Calculated, %: C 51.74; H 3.18; N 20.11; Cl 20.36. *M* 347.

The IR spectra were recorded on a Vertex 70 spectrometer from KBr pellets. The ^{1}H NMR spectra were obtained on a Varian-300 spectrometer (300 Hz) in DMSO-d_6 relative to internal TMS. The mass spectra were taken on an Agilent 1100/DAD/MSD VL G1965 instrument. Melting points were measured on a Fisher-Johns device.

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