OPTIMIZATION OF THE SYNTHESIS OF 2-PHENYL-1,2,3-TRIAZOLE

G. F. Myachina^{1*}, T. G. Ermakova¹, N. P. Kuznetsova¹, R. G. Sultangareev¹,

L. I. Larina¹, L. V. Klyba¹, G. T. Suchanov², and B. A. Trofimov¹

The synthesis of 2-phenyl-1,2,3-triazole by the cyclization of glyoxal phenylosazone in high-boiling solvents in the presence of copper triflate catalyst has been optimized. The structure of the product was confirmed by data of IR, ¹H, ¹³C, and ¹⁵N NMR spectroscopy, mass spectrometry, and elemental analysis.

Keywords: aniline, glyoxal bis(phenylhydrazone), 2-phenyl-1,2,3-triazole, cyclization.

2-Phenyl-1,2,3-triazole is a promising starting material for the synthesis of 4-nitro-1,2,3-triazole, which is energetically a reactive material as a component of explosive compositions, reactive fuel [1]. Previously, the synthesis of 2-phenyl-1,2,3-triazole was reported [2, 3] by the cyclization of glyoxal phenylosazone in the presence of Cu₂SO₄ at 75-80°C (yield was 50-59%). Later the possibility of synthesizing 2-phenyl-1,2,3-triazole was shown by heating glyoxal phenylosazone to 180-210°C with a catalytic amount of CuCl (yield was 66.6%) [4], and also using a combined catalyst CuCl/CaCl₂ (yield was 75%) [5].

With the aim of optimizing the synthesis of 2-phenyl-1,2,3-triazole (2) (increase of yield, purity of product, and acceleration of the process) we have studied the cyclization of glyoxal phenylosazone 1 using copper triflate, $Cu(OSO_2CF_3)_2$, and also high-boiling solvents: *o*-xylene, toluene, and ethylene glycol [6]. The synthesis of the 1,2,3-triazole 2 was effected according to the following scheme:



* To whom correspondence should be addressed, e-mail: myachina@irioch.irk.ru.

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¹Irkutsk A. E. Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033, Russia.

²Institute of Problems of Chemical and Energetic Technologies, Siberian Branch of the Russian Academy of Sciences, Biisk 659322, Russia; e-mail: admin@ipcet.ru.

Reaction time, h	Yield 2, %*	Reaction time, h	Yield 2 , %* ²	Reaction time, h	Yield 2 , %* ³
0.5 1.0 1.5 2.5 5.0 6.0	20 25 34 50 85 100	0.5 1.0 2.0 5.5	65 75 85 100	0.5 1.0 1.4 2.0	85 90 95 100

TABLE 1. Dependence of the Yield of Compound 2 on the Time of Cyclization of Substance 1 in Various Solvents (according to data of 1 H NMR spectroscopy)

* Solvent toluene, reaction temp. 110°C.

*² Solvent o-xylene, reaction temp.140°C.

*³ Solvent ethylene glycol, reaction temp. 190°C.

The effect of the amount of catalyst on the yield of compound 2 on cyclization of substance 1 (without using solvent) was investigated previously in [6]. It was established that the optimum catalyst content in the reaction mixture was 5%, which was used in the present work.

In the presence of copper triflate in high-boiling solvents the cyclization of the initial compound **1** began at 100° C with subsequent self-heating to the boiling point of the solvent. The reaction kinetics was studied using the ¹H NMR method (by the relative change of integral intensities of compounds **1** and **2**). It was established that after 0.5 h the cyclization of substance **1** was effected in toluene by 20, *o*-xylene by 65, and ethylene glycol by 85%. The end of the reaction was reached after 6, 5.5, and 2 h respectively (Table 1). Reaction proceeds rapidly in a medium of ethylene glycol (2 h), which is obviously caused by the high boiling point of the solvent (190°C). In toluene, cyclization of compound **1** is complete after 6 h, but the reaction temperature is significantly lower (110°C).

In the process of cyclizing substance 1 aniline 3 was formed together with the desired product 2. Product 2 (first fraction) was isolated by column chromatography in a high degree of purity (99.96-100%, according to data of chromato-mass spectrometry). The structure of product 2 was confirmed by data of IR, ¹H, ¹³C, and ¹⁵N NMR spectroscopy, mass spectrometry, and elemental analysis.

A resonance signal was observed in the ¹H NMR spectra of compound **2** for the protons of the triazole ring at 8.11 ppm and resonance signals were also observed for the protons of the phenyl fragment. In the ¹³C NMR spectra there were resonance signals for the carbon atoms of the phenyl ring, and also a resonance signal for atoms C-4,5 of the triazole ring (136.47 ppm). The two-dimensional H^1-N^{15} HMBC (I) spectrum indicates the presence of two signals for nitrogen at 58.6 and 120.2 ppm, assigned respectively to the N-1,3 and N-2 atoms. In fact a cross peak was observed in the ¹H-¹⁵N 2D spectrum for atoms N-1,3 with the protons of the triazole ring, and also a cross peak for the N-2 atom both with the protons of the triazole ring and with the *ortho* and *meta* protons of the phenyl ring.

The use of a new catalyst (copper triflate) and high-boiling solvents (toluene, o-xylene, ethylene glycol) therefore enabled us to optimize the reaction process and to obtain 1,2,3-triazole **2** with a high degree of purity (99.9%), in high yield (82-90%), and also to simplify its isolation stage.

EXPERIMENTAL

The IR spectra were obtained on a Bruker IFS-25 instrument in a microlayer. The ¹H, ¹³C, and ¹⁵N NMR spectra were recorded on Bruker DPX-400 and AV-400 spectrometers (400, 101 and 40 MHz

respectively) in DMSO-d₆ at 25°C. Chemical shifts for ¹H and ¹³C NMR were measured relative to TMS. Chemical shifts for ¹⁵N NMR were measured relative to nitromethane with a precision of 0.1 ppm using the 2D procedure for ¹H–¹⁵N NMR HMBC. The mass spectra after electron ionization (70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument (quadrupole mass-analyzer, mass detection range 34-650 a.m.u.). Chromatographic separation was carried out on a SPB-5 ms capillary column (60 m×0.25 mm×0.25 µm), carrier gas helium, flow rate 0.7 ml/min, evaporator and ion source temperature was 250°C, pressure 250 kPa, programing mode: from 70 to 250°C at 10 deg/min. A check on the progress of reactions and the homogeneity of synthesized compounds was effected by TLC on Silufol UV–254 plates (visualization with a UV lamp). Preparative separation was carried out by column chromatography on LSL254 silica gel (5/40 µ).

Glyoxal Bis(phenylhydrazone) (1) was obtained by the known procedure of [7]. ¹H NMR spectrum, δ , ppm (*J*, Hz): 6.75 (2H, t, *J* = 8.1, *p*-C₆H₅); 6.97 (4H, d, *J* = 8.1, *o*-C₆H₅); 7.20 (4H, t, *J* = 8.1, m-C₆H₅); 7.64 (2H, s, =CH); 10.36 (2H, br. s, NH). ¹³C NMR spectrum, δ , ppm: 111.98 (*o*-C₆H₅); 118.97 (*p*-C₆H₅); 129.17 (*m*-C₆H₅); 144.84 (*ipso*-C₆H₅); 136.95 (=CH).

2-Phenyl-1,2,3-triazole (2). A mixture of compound **1** (1 g, 0.042 mmol) and copper triflate $Cu(OSO_2CF_3)_2$ (0.05g, 0.14 mmol) in toluene (10 ml) was stirred and boiled in a stream of argon at 110°C for 5 h. The solvent was evaporated under reduced pressure (15 mm Hg). The oily residue was chromatographed on a column of silica gel in the system hexane–ether, 1:2. Compound **2** (0.55 g, 90%) was isolated having bp 96°C (10 mm Hg), n_D^{20} 1.5875, R_f 0.94 (eluent hexane–ether, 1:2). Found, %: C 66.23; H 5.09; N 28.55. $C_8H_7N_3$. Calculated, %: C 66.21; H 4.83; N 28.97.

The kinetics of the process was studied by taking out test samples after definite time intervals (Table 1).

Compound **2** was obtained in *o*-xylene or ethylene glycol at the boiling point of the solvent (see Table 1) and isolated analogously to the first synthesis. IR spectrum, v, cm⁻¹: 3139, 3124, 1410, 1376, 1260 (C–H triazole ring), 694, 755, 1476, 3036, 3059, 3080 (C₆H₅). ¹H NMR spectrum, δ , ppm (*J*, Hz): 7.41 (1H, t, *J* = 8.0, *p*-C₆H₅); 7.55 (2H, t, *J* = 8, *m*-C₆H₅); 8.03 (2H, d, *J* = 8.0, *o*-C₆H₅); 8.11 (2H, s, H-4,5). ¹³C NMR spectrum, δ , ppm: 118.50 (*o*-C₆H₅); 127.75 (*p*-C₆H₅); 129.73 (*m*-C₆H₅); 136.47 (C-4,5); 139.31 (*ipso*-C₆H₅). Mass spectrum, *m/z* (*I*_{rel}, %): 145 [M]⁺⁺ (99), 118 [M-HCN]⁺⁺ (17), 91 [NPh]⁺⁺ (100), 77 [Ph]⁺⁺ (11), 64 (39), 63 (22), 59 (15), 51 [C₄H₃]⁺ (27).

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