ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 7, p. 1175. © Pleiades Publishing, Inc., 2006. Original Russian Text © A.A. Gevorkyan, A.S. Arakelyan, A.A. Movsisyan, Zh.L. Dzhandzulyan, K.A. Petrosyan, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 7, p. 1223.

LETTERS TO THE EDITOR

Improved Procedure of Acetylene Aminomethylation

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Received December 30, 2005

DOI: 10.1134/S1070363206070310

Propragylic amines are the reagents widely applied in organic synthesis. They become much more significant after discovery of the cyclization of quarternary ammonium salts obtained from them affording various polycyclic compounds [1]. Among the methods for preparation of propargyl amines one of the most useful is the Mannich aminomethylation of 1-alkynes. As a rule, this reaction is conducted using dioxane or alcohol as solvents to achieve yield about 50–70% [2–7]. The main disadvantage of this method is long reaction duration and use of organic solvents. To obtain products in a high yield, sometimes the reaction mixture should be heated for 8 to 60 h [2–7].

We found that aminomethylation of acyetylenes can be considerably accelerated (the reaction duration is 4-6 h only) when the reaction is conducted not alongside the common procedure (in a solvent, e.g., 15–30 ml of dioxane per 0.1 mol of acetylenic compound [2–7]), but without any solvent, by reaction of acetylenic compound with small excess of paraormaldehyde and secondary amine (1.1 to 1.3 mol per 1 mole of acetylenic compound) in the presence of a few drops of suspension formed from oversaturated solution of cuprous chloride in DMF (1 g of the salt in 3.5 ml of the solvent). This reagent mixture upon heating in the temperature range 95 to 105°C for 4–6 h the yields aminomethylation repeatedly from 70 to 80%.

$$R-C \equiv CH + CH_2 = O + HNR'_2$$

$$\xrightarrow{CuCl} R-C \equiv CCH_2NR'_2.$$

By this procedure we synthesized the following series of acetylenic amines: **1-diethylamino-3-phe-nyl-2-propyne**, bp 133–135°C (11 mm Hg) yield 70–

80% [4]; **1-diethylamino-4-benzyloxy-2-propyne**, bp 170–172°C (11 mm Hg), yield 69%; **1-piperidino-3-phenyl-2-propyne**, bp 160–165 °C (11 mm Hg), yield 72.4% [6]; **1-morpholino-3-phenyl-2-propyne**, bp 165–168 °C (11 mm Hg), yield 75.6% [6]. Structure of each amine was confirmed additionally by the data of ¹H NMR spectroscopy.

Under these conditions propargyl alcohol formed polymeric substance, as we reported earlier [5], and dimethylethynylcarbinol returned unchanged [3]. The reasons for such failure are under study.

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