ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 3, pp. 504–505. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.A. Gevorkyan, A.A. Movsisyan, Zh.L. Dzhandzhulyan, A.S. Arakelyan, K.A. Petrosyan, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 3, pp. 519–520.

LETTERS TO THE EDITOR

Alkoxymethylamines and Secondary Amine Aminals as Precursors for Aminomethylation of Acetylenes

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Received August 31, 2007

DOI: 10.1134/S1070363208030274

Analysis of published data on the Mannich reaction [1–5] shows that the problem whether well known precursors used in this reaction are suitable for acetylenes **I** is still unsolved [1–5]. Until now there is no direct experimental evidence showing whether dialkylaminomethanols R'_2NCH_2OH (**II**) are the only feasible reactants or the same role can be played by esters **III** or formals **IV**. This controversy as to the structure of precursors for acetylene aminomethylation arises from the fact that the involvement of such compounds in acetylene aminomethylation has still been considered on the basis of indirect evidence or speculations [6, 7]. However, in cases where unequivocal experimental evidence is available, it relates to reactions of compounds like butoxymethylamines with Iotsich reagents, rather than acetylenes themselves [3, 8].

We found out that both esters **III** and aminals **IV** derived from dialkylaminomethanols can be involved in acetylene aminomethylation. These reactions are performed by mixing equimolar amounts of acetylenes, esters **III** (or aminals **IV**), and trace amount of a catalyst (3–7 mg of copper iodide per 0.1 mol of acetylene) and heating the reaction mixture for some hours. The best yields (40–75%) in the reactions performed in a distillation flack with a Vigreux column 10 – 15 cm long under slow heating at temperatures 15 –40°C above the boiling point of the alcohol corresponding to ester **III** or the secondary amine corresponding to aminal **IV**, until volatiles (alcohol or secondary amine) no longer evolve. The aminomethylation products are distilled at reduced pressure. Reactions with 0.1 mol of acetylene are complete within 20–40 min. With larger amount of catalysts, much more vigorous tarring is observed.

The above procedure was used to synthesize a series of acetylene amines [in parentheses are the yields obtained with the corresponding formal **IV**).

$$\underset{\mathbf{I}}{RC{\equiv}CH} + \underset{\mathbf{II,\,III}}{R'_2NCH_2OR''} \xrightarrow{CuJ} RC{\equiv}CCH_2OR''_2$$

$$\xleftarrow{CuJ} \underset{\mathbf{I}}{RC{\equiv}CH} + \underset{\mathbf{IV}}{R'_2NCH_2OR'_2}.$$

1-Diethylamino-3-phenylprop-2-yne. Yield from diethyl(methomethyl)-, (ethoxymethyl)diethyl-, and (butoxymethyl)diethylamine 62, 68, 72–74 % (70–75%), respectively; bp 133–135°C (11 mm Hg) [9].

3-Phenyl-1-piperidylaminoprop-2-yne. Yield from (butoxymethyl)piperidine 60% (66%), bp 164°C (11 mm Hg) [9].

1-Morpholino-3-phenylprop-2-yne. Yield from (ethoxymethyl)morpholine 72% (69%), bp 168°C (11 mm Hg) [9].

4-Benzyloxy-1-diethylaminopropo-2-yne. Yield from (butoxymethyl)diethylamine 45% (34.6%), bp 170°C (11 mm Hg) [9].

1-Diethylamino-4-methylpent-2-yn-4-ol. Yield from (butoxymethyl)diethylamine 56.8% (68.6%), bp 81–82°C (2 mm Hg), n_D^{20} 1.4651. The compounds have correct elemental analyses. ^1H NMR spectra, δ_H (300 MHz): 1.05 t [6H, *J* 9.6, $N(CH_2CH_3)_2$, 1.39 s (6H, Me_2COH), 2.42 q [4H, *J* 9.6, $N(CH_2CH_3)_2$], 3.30 s (2H, $\equiv CCH_2$), 4.63 s (1H, OH).

The ^1H NMR spectra were measured on a Varian Mercury-300 spectrometer at 300 MHz in DMSO-d_6/CCl_4 (1:3), internal reference TMS.

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