

SHORT
COMMUNICATIONS

Selective Noncatalytic Hydration of *N*-(1,1-Dimethyl-2-propynyl)-acetamide to *N*-(1,1-Dimethyl-2-oxopropyl)acetamide

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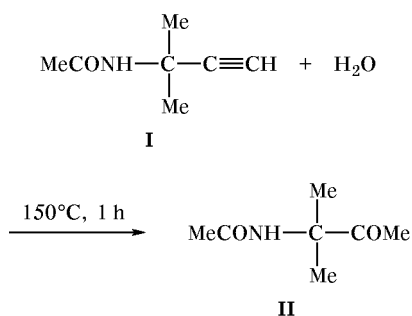
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It is known that addition of water to nonactivated acetylenes occurs as a rule in the presence of catalysts (this reaction was exhaustively discussed in [1]). In superbasic media hydration trimerization of acetylene is possible to give 2-vinyloxy-1,3-butadiene [2]. The hydration is strongly facilitated when heteroatoms having unshared electron pairs (e.g., nitrogen, oxygen, or sulfur) either are present directly at the triple bond or are conjugated with it through a double bond [3].

We have found that a functionally substituted nonactivated acetylene derivative, *N*-(1,1-dimethyl-2-propynyl)acetamide (**I**), undergoes selective hydration with retention of the amide moiety on heating with water under pressure in the absence of a catalyst. The yield of *N*-(1,1-dimethyl-2-oxopropyl)acetamide (**II**) is 59% (unoptimized).



Up to now, the hydration of amide **I** to **II** was carried out in the presence of sulfuric acid [4] or in

acid aqueous solutions of mercury salts [5]. The above reaction is a rare case of noncatalytic hydration of an unactivated triple bond, which extends the existing views on fundamental acetylene reactions. From the preparative viewpoint, this reaction opens a direct route to amidoketones like **II** which are highly potent synthetic intermediates.

***N*-(1,1-Dimethyl-2-oxopropyl)acetamide (II).** A mixture of 0.5 g (4 mmol) of amide **I** and 50 ml of water was heated for 1 h at 150°C in a high-pressure reactor. The mixture was cooled, 10 g of potassium carbonate was added, and the mixture was extracted with ether. The extract was dried over calcined KCO₃ and evaporated to obtain 0.34 g (59%) of amidoketone **II**. Colorless crystals, mp 100–101°C (from hexane); published data [5]: mp 109–111°C. IR spectrum (KBr), ν , cm⁻¹: 3420 (NH), 3273 (NH), 3067, 2984, 2938, 2855, 1715 (C=O), 1642 (C=O), 1546, 1436, 1383, 1360, 1305, 1218, 1178, 1128, 1030, 1008, 963, 728, 611, 551. ¹H NMR spectrum, δ , ppm: 6.55 (NH), 2.18 and 1.98 [CH₃C(O)C, CH₃C(O)N], 1.46 [(CH₃)₂C]. ¹³C NMR spectrum, δ_{C} , ppm: 209.23 (CH₃C=O), 170.17 (NC=O), 61.00 [C(CH₃)₂], 23.68 [(CH₃)₂], 23.52 and 23.14 [CH₃C(O)C, CH₃C(O)N]. Found, %: C 58.76; H 9.13; N 9.75. C₇H₁₃NO₂. Calculated, %: C 58.72; H 9.15; N 9.78.

The ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DPX-400 instrument at 400.13 and 100.61 MHz, respectively.

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