

SHORT
COMMUNICATIONS

Reaction of Acetylene with 2-(2-Aminoethylamino)ethanol

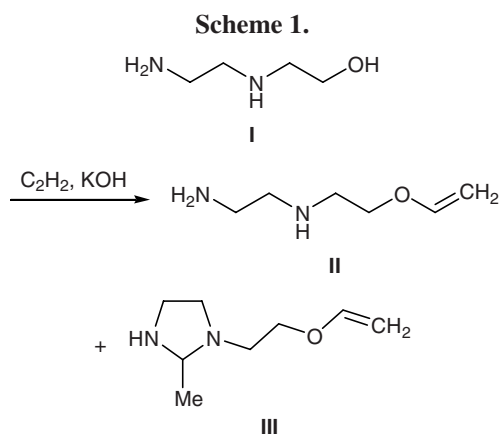
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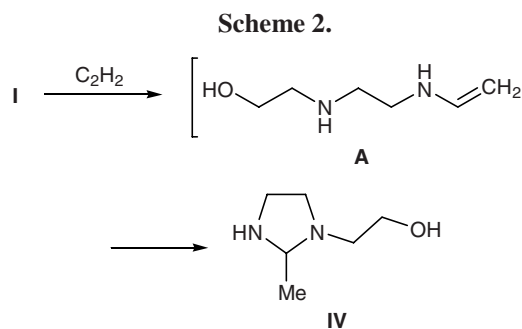
According to [1], the reaction of 2-(2-aminoethylamino)ethanol (**I**) with acetylene (150°C, 28 atm) in the presence of potassium hydroxide gives the corresponding vinyl ether **II**. We performed vinylation of compound **I** under analogous conditions and found that up to 17% of 2-methyl-1-(2-vinyloxyethyl)imidazolidine (**III**) is formed together with vinyl ether **II** (Scheme 1).



No appreciable change in the product composition was observed when the reaction was carried out in such solvents as benzene, dioxane, and DMSO. In all cases, a mixture of compounds **II** and **III** was formed, and the fraction of the latter ranged from 14 to 19% (according to the 1H NMR and GLC data). Variation of the reaction time and temperature affected only the conversion of initial amino alcohol **I**. Depending on the amount of the catalyst and temperature, the complete conversion of **I** was achieved in 7 to 16 h. Only when the amount of KOH was increased from 10 to 30 wt % relative to compound **I** and the reaction temperature was reduced to 115°C, we succeeded in obtaining almost pure vinyl ether **II**. According to the

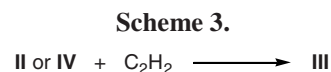
GLC data, the product contained no more than 3% of imidazolidine **III**.

The reaction of amino alcohol **I** with acetylene in the absence of a catalyst was considerably slower. The conversion of compound **I** was as low as 28% in 16 h, and the only product was 2-methyl-1-(2-hydroxyethyl)imidazolidine (**IV**). Its yield was 14% calculated on the initial amino alcohol **I** (Scheme 2).

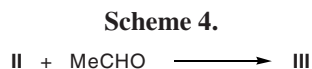


Presumably, in this case vinylation of 2-(2-aminoethylamino)ethanol (**I**) occurred at the nitrogen atom with subsequent intramolecular cyclization of unstable *N*-vinylamine **A** to imidazolidine **IV**.

Thus the reaction of acetylene with 2-(2-aminoethylamino)ethanol (**I**) in the presence of KOH involves both noncatalytic formation of imidazolidine **IV** and base-catalyzed O-vinylation of compounds **I** and **IV**. Imidazolidine **III** could also be formed via noncatalytic N-vinylation of vinyl ether **II** (Scheme 3). Insofar as the boiling points of vinyl ether **II** and imidazolidine **III** are similar and the concentration of **III** in the reaction mixture is fairly low, we failed to isolate



the latter as individual substance by vacuum distillation. Pure imidazolidine **III** was synthesized in almost quantitative yield by condensation of vinyl ether **II** with acetaldehyde (Scheme 4).



N-(2-Vinyloxyethyl)ethane-1,2-diamine (II).

A mixture of 150 ml of benzene, 20.83 g (0.2 mol) of 2-(2-aminoethylamino)ethanol (**I**), and 6.25 g of potassium hydroxide was saturated with acetylene in a 1-l steel high-pressure reactor under a pressure of 14 atm, and the mixture was heated for 6 h at 115°C. Vacuum distillation gave 12.81 g (49%) of compound **II** with bp 70–72°C (4 mm); published data [2]: bp 84–86°C (9 mm); $d_4^{20} = 0.9624$, $n_D^{20} = 1.4689$. IR spectrum, ν , cm^{-1} : 490, 505, 570, 680, 790, 940, 970, 1005, 1045, 1105, 1170, 1300, 1330, 1340, 1360, 1435, 1600, 1610, 2810, 2820, 2860, 2910, 3020, 3055, 3100, 3265, 3330. ^1H NMR spectrum, δ , ppm: 1.23 s (3H, NH, NH₂), 2.60 t (2H, CH₂NH₂, $^3J = 5.9$ Hz), 2.71 t (2H, NH₂CH₂CH₂NH, $^3J = 5.9$ Hz), 2.79 t (2H, OCH₂CH₂NH, $^3J = 5.2$ Hz), 3.70 t (2H, OCH₂, $^3J = 5.2$ Hz), 3.90 d.d (1H, *cis*-CH₂=, $^2J = 1.9$, $^3J_{cis} = 6.7$ Hz), 4.10 d.d (1H, *trans*-CH₂=, $^2J = 1.9$, $^3J_{trans} = 14.5$ Hz), 6.38 d.d (1H, OCH=, $^3J_{cis} = 6.7$, $^3J_{trans} = 14.2$ Hz). ^{13}C NMR spectrum (CDCl₃), δ_C , ppm: 41.62 (CH₂NH₂), 48.36 (OCH₂CH₂NH), 52.26 (OCH₂CH₂NHCH₂), 67.25 (OCH₂), 86.48 (=CH₂), 151.57 (OCH=). Found, %: C 55.27; H 10.86; N 21.83. C₆H₁₄N₂O. Calculated, %: C 55.35; H 10.84; N 21.52.

2-Methyl-1-(2-vinyloxyethyl)imidazolidine (III).

A solution of 13.02 g (0.1 mol) of compound **II** in 30 ml of diethyl ether was cooled to –20°C, and a solution of 4.4 g (0.1 mol) of acetaldehyde in 20 ml of diethyl ether, cooled to 0°C, was added dropwise under stirring. The mixture was treated with solid potassium carbonate and kept for 8 h at room temperature. Vacuum distillation gave 15.15 g (97%) of compound **III** with bp 60–63°C (3 mm), $d_4^{20} = 0.9781$, $n_D^{20} = 1.4768$. IR spectrum, ν , cm^{-1} : 510, 580, 600, 640, 685, 805,

930, 950, 985, 1020, 1060, 1140, 1185, 1245, 1310, 1335, 1370, 1425, 1445, 1605, 1625, 2580, 2660, 2705, 2730, 2810, 2875, 2925, 2965, 3035, 3065, 3110, 3250. ^1H NMR spectrum, δ , ppm: 1.24 d (3H, Me), 1.74 br.s (1H, NH), 2.31 m (1H, 1-CH₂), 2.45 m (1H, 1-CH₂), 2.93–3.30 m (5H, 2-H, 4-H, 5-H), 3.81 t (2H, OCH₂, $^3J = 5.9$ Hz), 4.00 d.d (1H, *cis*-CH₂=, $^2J = 1.2$, $^3J_{cis} = 6.9$ Hz), 4.18 d.d (1H, *trans*-CH₂=, $^2J = 1.2$, $^3J_{trans} = 14.4$ Hz), 6.49 d.d (1H, OCH=, $^3J_{cis} = 6.9$, $^3J_{trans} = 14.4$ Hz). ^{13}C NMR spectrum (CDCl₃), δ_C , ppm: 18.40 (Me), 43.56 (C⁴), 51.12 (1-CH₂), 53.11 (C⁵), 66.29 (OCH₂), 76.11 (C²), 86.09 (=CH₂), 151.31 (OCH=). Found, %: C 61.22; H 10.54; N 17.71. C₈H₁₆N₂O. Calculated, %: C 61.51; H 10.32; N 17.93.

2-(2-Methylimidazolidin-1-yl)ethanol (IV). A 1-l steel high-pressure reactor was charged with 150 ml of benzene and 20.83 g (0.2 mol) of 2-(2-aminoethylamino)ethanol (**I**), and the mixture was saturated with acetylene under a pressure of 14 atm and heated for 18 h at 115°C. Vacuum distillation gave 3.65 g (14%) of compound **IV**, mp 54–56°C. IR spectrum, cm^{-1} : 515, 630, 780, 865, 920, 935, 990, 1050, 1125, 1140, 1165, 1220, 1295, 1335, 1370, 1445, 1455, 1560, 1665, 2680, 2800, 2880, 2925, 2960, 3160–3305. ^1H NMR spectrum, δ , ppm: 1.19 d (3H, Me), 2.23–2.34 m (2H, 1-CH₂), 2.64–3.27 m (7H, 2-H, 3-H, 4-H, 5-H, OH), 3.57–3.66 m (2H, OCH₂). Found, %: C 55.14; H 10.96; N 21.67. C₆H₁₄N₂O. Calculated, %: C 55.35; H 10.84; N 21.52.

The ^1H and ^{13}C NMR spectra were recorded at 26°C on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively, using CDCl₃ as solvent and hexamethyldisiloxane as internal reference. The IR spectra were measured on a Specord 75IR spectrophotometer from thin films.

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