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Reaction of Acetylene with 2-Hydrazinoethanol

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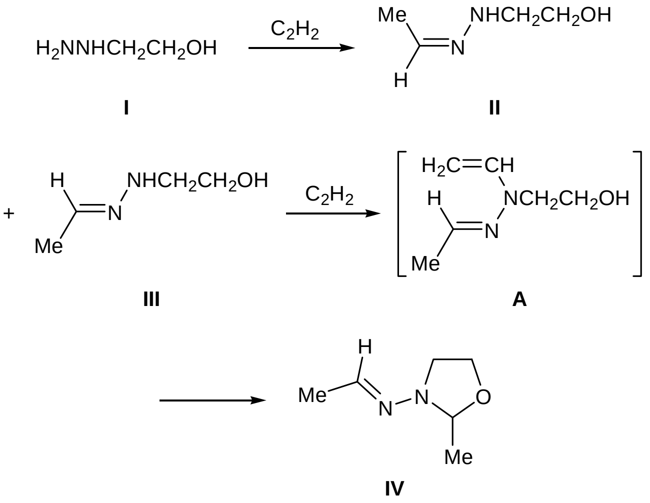
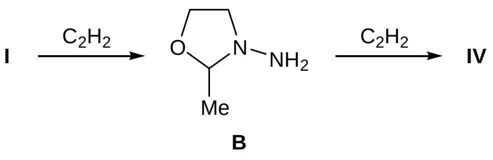
Unlike well-known reactions of acetylene with amino alcohols [1, 2], its reactions with hydrazinoethanols were not studied. We examined the reaction of 2-hydrazinoethanol (**I**) with acetylene in benzene in the presence of anhydrous cadmium acetate as catalyst. Separation of the reaction mixture by vacuum distillation gave *E*- and *Z*-isomeric acetaldehyde *N*-(2-hydroxyethyl)hydrazones **II** and **III** and *N*-(*E*)-ethylidene-2-methyloxazolidin-3-amine (**IV**). Presumably, the reaction begins with addition of the primary amino group in hydrazine **I** to acetylene to give hydrazones **II** and **III**, as in the cadmium acetate-catalyzed reactions of acetylene with primary amines [3]. The subsequent vinylation of the same nitrogen atom leads to unstable intermediate **A** which undergoes intramolecular ring closure involving the *N*-vinyl-*N*-(2-hydroxyethyl) fragment.



Insofar as no 3-aminooxazolidine **B** was detected in the reaction mixture before separation by ^{1}H NMR spectroscopy, the path of formation of hydrazone **IV** through intermediate **B** was ruled out.



It is known that *E* and *Z* izomers of unsubstituted aliphatic aldehyde hydrazones are separated by a low energy barrier and that the *E* isomer predominates in solution. The CH=N proton in the *E* isomer gives a signal in the ^{1}H NMR spectra in a weaker field relative to the corresponding signal of the *Z* isomer [3]. The ratio of compounds **II** and **III** was estimated at 2 : 3 on the basis of the CH=N signal intensity ratio. Compound **IV** was formed exclusively as *E* isomer.

***N*-(*E*)-Ethylidene-2-methyloxazolidin-3-amine (IV).** A mixture of 100 ml of benzene, 22.83 g (0.3 mol) of 2-hydrazinoethanol (**I**), and 2.28 g of anhydrous cadmium acetate in a 0.5-l steel high-pressure reactor was saturated with acetylene to a pressure of 14 atm and was then heated for 6 h at 130°C. Distillation gave 1.65 g (43%) of compound **IV**, bp 66–68°C (17 mm), d_4^{20} = 0.9807, n_D^{20} = 1.4678. IR spectrum, ν, cm^{-1}: 458, 508, 672, 783, 843, 917, 947, 990, 1033, 1100, 1132, 1165, 1180, 1217, 1283, 1317, 1380, 1442, 1450, 1608, 2708, 2752, 2835, 2874, 2908, 2972. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.37 d (3H, =CH**Me**, ^3J = 5.2), 1.90 d (3H, 2-Me, ^3J = 5.4), 2.89 d.d (1H, NCH$_2$, ^2J = 8.4, ^3J = 15.0) and 3.38 d.d (1H, NCH$_2$, ^2J = 7.3, ^3J = 14.5), 3.92 d.d (1H, OCH$_2$, ^2J = 8.1, ^3J = 13.5) and 4.06 d.d (1H, OCH$_2$, ^2J = 7.2, ^3J = 14.6), 4.48 q (1H, OCHN, *J* = 5.4), 6.83 q (1H, N=CH, *J* = 5.2). ^{13}C NMR spectrum, δ_C, ppm: 19.05 (=CH**Me**), 19.83 (2-Me), 49.78 (NCH$_2$), 64.58 (OCH$_2$), 92.35 (OCHN), 139.38 (N=CH). Found, %: C 56.47; H 9.86; N 21.33. $C_6H_{12}N_2O$. Calculated, %: C 56.23; H 9.94; N 21.86.

Acetaldehyde *N*-(2-hydroxyethyl)hydrazones II and III (a mixture of isomers) were isolated by subsequent distillation. Yield 11.1 g (36%), bp 107–112°C (13 mm), d_4^{20} = 1.0439, n_D^{20} = 1.4854. IR spectrum, ν, cm^{-1}: 453, 652, 812, 850, 917, 942, 1018, 1083, 1212, 1312, 1358, 1417, 1558, 1598, 1650, 1725, 2850, 2917, 3233–3367. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.73 d (1.2H, Me, *Z*, ^3J = 5.5), 1.85 d (1.8H, Me, *E*, ^3J = 5.3), 3.17 t (1.2H, NCH_2, *E*, ^3J = 4.7), 3.28 t (0.8H, NCH_2, *Z*, ^3J = 4.9), 3.75 m (2H, OCH_2), 6.59 q (0.4H, CH=N, *Z*, ^3J = 5.5), 7.03 q (0.6H, CH=N, *E*, ^3J = 5.3). Found, %: C 47.12; H 9.91; N 27.31. $C_4H_{10}N_2O$. Calculated, %: C 47.04; H 9.87; N 27.43.

The ^1H and ^{13}C NMR spectra were recorded at 26°C on a Bruker DPX-400 instrument (400 and 100 MHz, respectively) using $CDCl_3$ as solvent and HMDS as internal reference. The IR spectra were measured on a Specord 75IR spectrometer from thin films (neat).

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