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LETTERS TO THE EDITOR

Reduction of Ethylene Glycol Monopropargyl Ether by Lithium Aluminum Hydride

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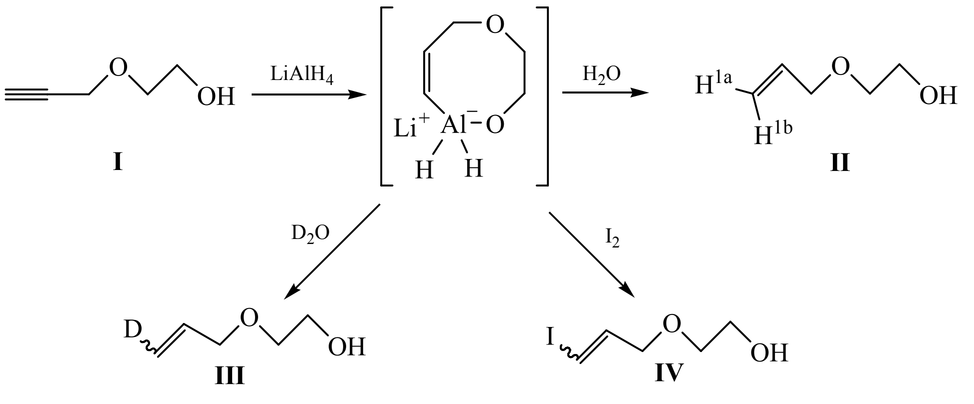
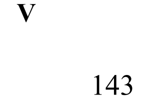
Recently we have found that 2-methyl-4,6-heptadiyne-2-ol reacted easily and selectively with lithium aluminum hydride in refluxing THF to form 2-methyl-6-hepten-4-yne-2-ol, a product of the terminal triple bond reduction [1]. In continuation of this work we studied the hydroalumination of 2-(2-propyn-1-yloxy)ethanol **I** containing oxymethylene group instead of the neighbour acetylenic group.

We have established that in contrast to the aforementioned diacetylenic alcohol, compound **I** undergoes the hydroalumination under the more rigid conditions, namely, by refluxing with lithium aluminum hydride in anhydrous 1,3-dioxane for 6 h at a reagents ratio of 1:2 followed by the hydrolysis to give 2-(allyloxy)ethanol **II** in a 78% yield.

The regio- and stereochemistry of the hydroalumination was established by the decomposition of the intermediate organometallic complex with deuterium oxide and iodine. The hydride ion was shown to attack the internal carbon atom of acetylene group. The decomposition of the intermediate organometallic complex with deuterium oxide results in a mixture of the geometric isomers of 2-[2-propen-1-yloxy]ethanol-d_1 **III**. In the ^{1}H NMR spectrum of the latter there are no signals of the H^{1A} and H^{1B} protons at 5.18 and 5.27 ppm, respectively. The spectrum contains the doublets at 4.93 (*J* 12.2) and 4.99 ppm (*J* 16.4) belonging to the H^1 protons of *Z*- and *E*-isomers (*Z*:*E* = 3:2).

Similar results were obtained in the case of the hydroalumination-iodination of ether **I**. A mixture of (*Z*)- and (*E*)-2-[(3-iodo-2-propen-1-yl)oxy]ethanols **IV** was isolated in a ratio of 3:2. The isomers ratio was determined by integrating the signals of vinyl protons at 6.32 (*J* 11.9) and 6.36 ppm (*J* 16.6) corresponding to *Z*- and *E*-isomers, respectively.





V

Based on the foregoing, we can assume that the hydroalumination proceeds through the formation of the same cyclic organometallic complex on the reduction of both α-acetylenic alcohols and isopropenylacetylene and diacetylene β-alcohols [1–3]. This is evidenced by the fact that the triple bond in the tetrahydropyranyloxy derivative **V** is not reduced under the reaction conditions.

Thus, the hydroalumination of 2-(2-propyne-1-yloxy)ethanol **I** is regiospecific: the hydride ion attacks the carbon atom of the C≡C bond nearest to the ether group. The splitting of the intermediate organometallic complex by the deuterium oxide and iodine is not stereoselective. This can be explained by the fact that in contrast to the triple bond forming eight-membered cyclic organometallic complex formed at the hydroalumination of the diacetylene β-alcohols, in the case of ethylene glycol monopropargyl ether **I** the organometallic complex is more labile, and as a consequence the electrophilic substitution does not proceed stereoselectively.

The starting monopropargyl ether of ethylene glycol **I** was synthesized by a known method [4].

2-(Allyloxy)ethanol (II). To a suspension of 1.5 g (40 mmol) of lithium aluminum hydride in 20 ml of anhydrous dioxane was added dropwise 2.0 g (20 mmol) of 2-(2-propyn-1-yloxy)ethanol **I** in 5 ml of anhydrous dioxane at –5°C. The reaction mixture was refluxed with stirring for 6 h, cooled to 0°C, and treated with 1.5 ml of water, 1.5 ml of 15% sodium hydroxide solution, and 4.5 ml of water. The precipitate was filtered off. The filtrate was extracted with diethyl ether and dried over magnesium sulfate. After the solvent removal, the residue was distilled in a vacuum. Yield 1.57 g (78.0%), bp 85–87°C (2 mm Hg). IR spectrum, ν, cm^{-1}: 930, 970, 1645, 3070 ($CH=CH_2$), 1100 (C–O–C), 3300–3500 (OH). ^1H NMR spectrum (DMSO-d_6), d_H, ppm (*J*, Hz): 2.65 br. s (1H, OH), 3.36–3.58 m (4H, $OC\underline{H}_2C\underline{H}_2OH$), 3.93 m (2H, $=CHC\underline{H}_2O$), 5.18 d. d (1H, H^{1A} , $^3J_{cis}$ 11.3, $^2J_{gem}$ 1.6), 5.27 d. d (1H, H^{1B}, $^3J_{trans}$ 16.5, $^2J_{gem}$ 1.6), 5.82–5.95 m (1H, H^2). Found, %: C 59.32; H 10.09. $C_5H_{10}O_2$. Calculated, %: C 58.80; H 9.87.

2-[2-Propen-1-yloxy]ethanol-d_1 (III). To a suspension of 0.4 g (10 mmol) of lithium aluminum hydride in 5 ml of anhydrous dioxane was added dropwise 0.5 g (5 mmol) of 2-(2-propyn-1-yloxy)ethanol **I** in 1 ml of anhydrous dioxane at –5°C. The reaction mixture was refluxed with stirring for 6 h, cooled to 0°C and added dropwise to 1 ml of D_2O. The resulting precipitate was filtered off and washed with diethyl ether. The filtrate was treated with ammonium chloride solution, dried over magnesium sulfate, and concentrated. Yield 0.3 g (58.8%). ^1H NMR spectrum ($CDCl_3$), d_H, ppm (*J*, Hz): 3.47–3.70 m (5H, $OC\underline{H}_2C\underline{H}_2O\underline{H}$), 4.19 d (2H, $=CHC\underline{H}_2O$, *J* 7.0), 4.93 d (1H, DHC=, $^3J_{cis}$ 12.2), 4.99 d (1H, DHC=, $^3J_{trans}$ 16.4), 5.68–5.81 m (1H, $=C\underline{H}CH_2O$).

2-[(3-Iodo-2-propen-1-yl)oxy]ethanol (IV). To a suspension of 3.3 g (86 mmol) of lithium aluminum hydride in 40 ml of anhydrous dioxane was added dropwise 4.3 g (43 mmol) of 2-(2-propyn-1-yloxy) ethanol **I** in 10 ml of anhydrous dioxane at –5°C. The reaction mixture was refluxed with stirring for 6 h. After cooling to 0°C, to the reaction mixture was added 7.6 g (86 mmol) of ethyl acetate. The reaction mixture was kept at 0°C for 1 h. Then to the mixture was added by portions 8.21 g (86 mmol) of powdered iodine for 0.5 h. The stirring was continued at 0°C for 1 h. After treating with the saturated sodium thiosulfate solution the precipitate was filtered off, and the organic layer was extracted with ether. The extract was washed with sodium thiosulfate solution, brine, and dried over magnesium sulfate. After the solvent removal, the product was purified by column chromatography (hexane–diethyl ether, 8:1). Yield 4.5 g (46.1%), R_f 0.52 (hexane–diethyl ether, 2:1). IR spectrum, ν, cm^{-1}: 930, 970, 1640, 3070 (CH=CHI), 1110 (C–O–C), 3300–3500 (OH). ^1H NMR spectrum ($CDCl_3$), d_H, ppm (*J*, Hz): 2.46 br. s (1H, OH), 3.27 t (2H, $OC\underline{H}_2CH_2OH$, *J* 7.0), 3.51–3.55 m (4H, $OC\underline{H}_2C\underline{H}_2OH$), 4.20 d (2H, $=CHC\underline{H}_2O$, J 7.0), 6.32 d (1H, CHI, $^3J_{trans}$ 16.6), 6.37 d (1H, CHI, $^3J_{cis}$ 11.9), 6.42–6.56 m (1H, *trans*-IHC=C$\underline{H}$), 6.62–6.92 m (1H, *cis*-IHC=C$\underline{H}$). Found, %: C 26.45; H 4.06; I 55.54. $C_5H_9IO_2$. Calculated, %: C 26.34; H 3.98; I 55.65.

2-[2-(2-Propynyl-1-oxy)ethoxy]tetrahydro-2*H*-pyran (V). To a mixture of 2.0 g (20 mmol) of 2-(2-propyn-1-yloxy) ethanol **I** and 4.2 g (50 mmol) of dihydropyran was added 20 mg of *p*-toluenesulfonic acid. The mixture was stirred for 4 days at room temperature, treated with a saturated potassium carbonate solution, extracted with diethyl ether, and dried over potassium carbonate. After the solvent removal, the residue (3.5 g) was purified by column chromatography (hexane–diethyl ether, 10:1). Yield 2.2 g (59.8%), R_f 0.41 (hexane–diethyl ether, 2:1). IR spectrum, ν, cm^{-1}: 1040, 1080, 1100, 1130, 1200, 1370, 1445 (C–O–C), 2220 (C≡C). ^1H NMR spectrum

($CDCl_3$), d_H, ppm (*J*, Hz): 1.45–1.82 m (6H, tetrahydropyran), 2.39 t (1H, HC≡C, ^4J 1.5), 3.71 t (4H, OCH_2CH_2O, ^3J 7.2), 3.79–3.82 m (2H, OCH_2-tetrahydropyranyl), 4.20 d (2H, $OC\underline{H}_2C≡CH$, ^4J 1.5), 4.62 t (1H, OCHO, ^3J 7.2).

The ^1H NMR spectra were recorded on a Varian Mercury-300VX spectrometer (300.077 MHz), internal reference TMS. The IR spectra were taken on a Specord 75IR spectrometer from thin films. TLC was performed on Silufol UV-254 plates detecting with $KMnO_4$ solution or iodine vapor. The column chromatography was performed on L 40/100 silica gel.

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