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LETTERS TO THE EDITOR

Unusual Hydroalumination-Bromination Reaction of 1,4-Butynediol

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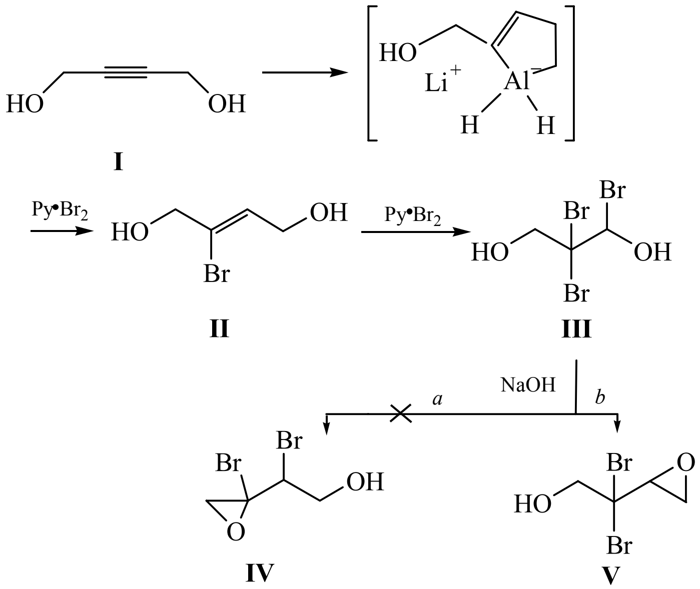
The hydroalumination-halogenation of propargyl alcohols with a lithium aluminum hydride–iodine or lithium aluminum hydride–pyridinium dibromide system followed by methylation of the obtained vinyl halides with lithium dimethyl copper is used as a convenient method for the synthesis of a variety of natural terpenoid products [1]. For the hydroalumination-bromination 1.2–1.3-fold excess of brominating agent is commonly used. Its residual amount is neutralized with a sodium hydroxide solution [2]. Use of the pyridinium dibromide complex was intended to exclude the electrophilic addition to double bonds [3]. This complex is also known to add to the triple bonds [4].

In this work we studied the hydroalumination-bromination of 1,4-butynediol **I**. For the carbon–aluminum bond cleavage we used a threefold excess of pyridinium dibromide complex as a brominating agent. However, instead of the expected 2-bromo-2-butene-1,4-diol **II** a crystalline substance was isolated from the reaction mixture. Its physicochemical and spectral data differ sharply from that of diol **II**.

Thus, in the mass spectrum of this compound there are no molecular peaks with *m*/*z* 166 and 168, which would indicate the formation of diol **II**. The number of the bromine atoms in the resulting compound was proved by the mass spectral data. The presence of the molecular peaks with *m*/*z* 248(5), 246(10) and 244(5), as well as peaks with *m*/*z* 169(9) and 167(9) indicate the presence of two bromine atoms in the molecule. The IR spectra contain the absorption bands at 3400 and 3050 cm^{-1} belonging to the hydroxy and the terminal epoxy groups, respectively.



Apparently, the reaction proceeds through several stages. In the first stage the triple bond in 1,4-butynediol **I** is hydrogenated by lithium aluminum hydride, and the resulting organometallic complex is decomposed by pyridinium dibromide to form 2-bromo-2-butene-1,4-diol **II**. Then, the second molecule of pyridinium dibromide adds to the C=CBr bond to give 2,2,3-tribromo-1,4-butanediol **III**. The latter, in turn, loses the hydrogen bromide molecule at the action of sodium hydroxide. This leads to the closure of the epoxide ring to form 2,2-dibromo-2-(2-oxyranyl)ethanol **V**. From two possible ways the path *b* is realized. This is supported by the ^{1}H NMR spectral data. The diagnostic is a singlet at 4.33 ppm belonging to the CH_2 group located near the hydroxy group.

The hydroalumination-bromination of 1,4-butynediol. To a suspension of 3.6 g (0.15 mol) of lithium aluminum hydride in 70 ml of anhydrous ether was added 2.7 g (0.03 mol) of 1,4-butynediol in 30 ml of anhydrous THF at 0°C under argon. The reaction mixture was refluxed (39–40°C) for 7 h, cooled to from 0 to –5°C, mixed with 8.8 g (0.1 mol) of ethyl acetate and stirred for 0.5 h. Then to the reaction mixture was added a solution of pyridinium dibromide prepared from 5 ml (0.1 mol) of bromine and 12 ml of pyridine in 6 ml of THF. After 0.5 h to the reaction mixture was added dropwise 3.6 ml of water, 3.6 ml of 15% sodium hydroxide solution, and 10.8 ml of water at 0°C. The precipitate was filtered off and washed with ether. The filtrate was extracted with ether, washed with dilute hydrochloric acid, with saturated sodium carbonate solution,with brine, and dried over magnesium sulfate. After the solvent removal, the residue was distilled (bp 138–140°C, 1 mm Hg). The formed crystals were washed with hexane. **2,2-Dibromo-2-(2-oxyranyl)ethanol V** was obtained in a yield of 58.4% (4.3 g), mp 128–129°C. IR spectrum, ν, cm^{-1}: 620, 890, 930, 1140, 1610, 3050, 3400. ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 3.84 d and 3.88 d (2H, CH_2 oxyrane ring, *J* 12.0), 4.33 s (2H, $C\underline{H}_2OH$), 4.39 t (1H, CH, *J* 12.0), 4.94 br. s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 56.71 (CH), 64.12 (CH_2), 65.41 (CH_2), 122.45 (CBr_2). Mass spectrum, *m/z* (I_{rel}, %): 248 (5) $[M]^+$, 246 (10) $[M]^+$, 244 (5) $[M]^+$, 169 (9) $[M - Br]^+$, 167 (9) $[M - Br]^+$, 151(17), 149 (25), 121 (29), 119 (30), 87 (18), 85(23).

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-300VX spectrometer [300.077 MHz (^{1}H), 75.462 MHz (^{13}C)] in DMSO-d_6 relative to internal TMS. The IR spectrum was registered on a Specord 75IR spectrometer in a thin layer. The mass spectrum obtained on a MX-1320 instrument at the direct injection of the sample into the ion source at ionizing voltage of 70 eV. The reaction progress was monitored by the TLC on Silufol UV-254 plates eluting with a hexane–diethyl ether mixture (2:1) and detecting with iodine vapor and $KMnO_4$ solution.

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