

Hydroalumination of Terminal β -Acetylene Alcohols with Lithium Aluminum Hydride

O. A. Garibyan, G. M. Makaryan, M. R. Ogannisyan, and Zh. A. Chobanyan

*Institute of Fine Organic Chemistry, Scientific Technological Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences of Armenia, ave. Azatutyan 26, Yerevan, 0014 Armenia
e-mail: hgaribyan@mail.ru*

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Abstract—Hydrogenation of terminal β -acetylene alcohols with lithium aluminum hydride in THF has afforded homoallylic alcohols. Decomposition of the intermediate organoaluminum complex with deuterated water, iodine, or pyridinium dibromide has evidenced about the non-regioselective hydride attack at the triple bond.

Keywords: lithium aluminum hydride, terminal β -acetylene alcohol, hydroalumination-iodination, bromination-hydroalumination, pyridinium dibromide

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Homoallylic alcohols are valuable building blocks for many natural products and biologically active compounds [1, 2]. In recent decades, numerous methods of synthesis of homoallylic alcohols have been reported [3, 4], allylation of carbonyl compounds being the most general one.

The reports on the methods of selective synthesis of multifunctional homoallylic alcohols [5–7] as well as the information about reducing the triple bond of the terminal acetylene alcohols [8–12] have been scarce; although it is obvious that modification of homoallylic alcohols with various functional groups will significantly increase their synthetic capacity.

The triple bond of the terminal α -acetylene alcohols can be easily reduced by lithium aluminum hydride (LAH) [8]. Halogenation of the intermediate organoaluminum complex indicates regioselective hydride attack at the triple bond [9]. In addition, hydrogenation of the terminal triple bond of monopropargyl glycol ether [10] and 2-methylhepta-4,6-diyne-2-ol has been known [11].

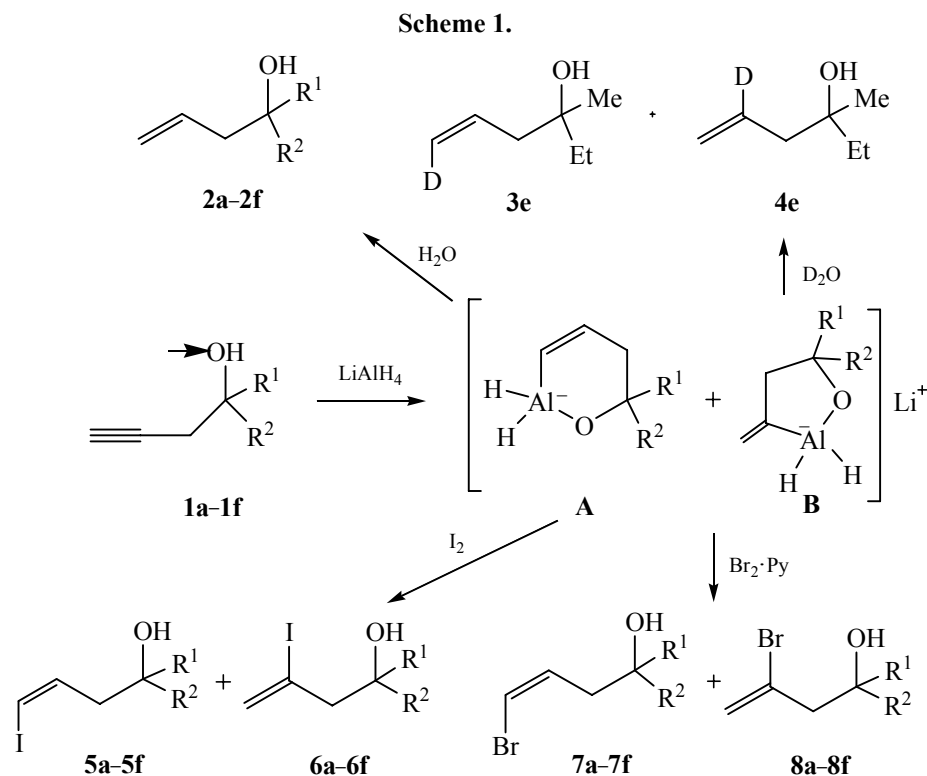
We investigated regio- and stereochemistry of hydroalumination of terminal β -acetylene alcohols with LAH. Reactions of acetylenic alcohols **1a–1f** with LAH (1 : 4) proceeded in anhydrous THF under reflux to give homoallylic alcohols **2a–2f** in high yields

(Table 1). Structure of the obtained compounds was confirmed by IR and ^1H NMR spectroscopy data (Table 2).

In order to determine the structure of the intermediate organometallic complex, the latter was decomposed with deuterated water, iodine, or pyridinium dibromide. In all the cases, a mixture of regioisomeric alkenols was obtained (Table 3). Their ^1H NMR spectral parameters are given in Table 4.

^1H NMR spectrum of the reaction mixture after decomposition with D_2O contained the signals corresponding to alcohols **3e** (doublet at 4.95 ppm, $J = 10.5$ Hz, multiplet at 5.74–5.92 ppm) and **4e** (broadened singlets at 4.96 and 4.99 ppm). The spectra of compounds **5–8** contained the signals of vinyl protons in the range of 5.68–6.82 ppm (Table 4). In the case of compounds **6** and **8**, assignment of the signals of vinyl protons in ^1H NMR spectra was made accounting for the downfield shifting the signal of the proton *trans*-positioned with respect to the halogen atom as compared with the *cis*-positioned proton. This fact is well known in the chemistry of retinoids [13].

When secondary (**1b–1d**) or tertiary (**1e** and **1f**) alcohols were introduced in the reaction instead of the primary (**1a**) one, the ratio of the formed regioisomeric alcohols changed sharply. In the case of the primary



alcohol **1a**, the ratio of regioisomers **5a**, **6a** and **7a**, **8a** was of 1 : 9, i. e., the regioisomers with the halogen atom located in the β -position with respect to the hydroxyl group (**6a** and **8a**) were predominantly formed. The secondary alcohols **1b–1d** also formed halogenated alkenols with the ratio of regioisomers **5**, **6** and **7**, **8** of 5 : 1 (Scheme 1).

In the case of the tertiary alcohols, the regioisomers ratio was of 1 : 2. In all the cases, except the products

of halogenation of alcohol **1c**, iodo- and bromo- alkenols were isolated by column chromatography. According to 1H NMR data, the double bond in compounds **5a–5f** and **7a–7f** was *cis*-configured ($^3J = 7.2–7.5$ Hz).

Only a single example of hydroalumination-iodination of the primary homopropargylic alcohol, but-3-yn-1-ol, has been known so far [12]. In this case, diisobutylaluminum hydride has been used as the

Table 1. Yields, boiling points and elemental analysis data for alkenols **2a–2f**

Comp. no.	bp, °C (mmHg)	Yield, %	R_f (Et ₂ O–hexane, 1 : 3)	Found, %		Formula	Calculated, %	
				C	H		C	H
2a	65–66 (700)	65.00	0.51	67.11	10.92	C ₄ H ₈ O	66.66	11.11
2b	74–75 (40)	74.90	0.51	71.88	12.08	C ₆ H ₁₂ O	72.00	12.00
2c	110–112 (5)	65.60	0.52	80.80	7.90	C ₁₀ H ₁₂ O	81.08	8.10
2d	70–72 (20)	60.70	0.57	74.80	12.95	C ₈ H ₁₆ O	75.00	12.58
2e	68–70 (10)	47.50	0.57	74.24	12.15	C ₇ H ₁₄ O	73.68	12.28
2f	70–71 (10)	60.80	0.55	77.60	11.64	C ₉ H ₁₆ O	77.14	11.42

Table 2. The IR and ^1H NMR spectroscopy data for alkenols **2a–2f**

Comp. no.	ν , cm^{-1}	δ , ppm (J , Hz)
2a	3300–3500 (O–H), 3095, 1610 (CH=CH ₂), 1050 (C–O)	2.50 q (2H, H ² , $J = 6.5$), 3.41 t (2H, H ¹ , $J = 6.5$), 3.41 br.s (1H, OH), 4.95 d (1H, H ⁴ , $J = 9.0$), 4.99 d (1H, H ⁴ , $J = 15.5$), 5.80–5.95 m (1H, H ³)
2b	3300–3500 (O–H), 3095, 1610 (CH=CH ₂), 1050 (C–O)	0.91 t (3H, H ¹ , $J = 7.4$), 1.31–1.66 m (2H, H ²), 2.18–2.25 m (2H, H ⁴), 2.90 br.s (1H, OH), 3.40–3.48 m (1H, H ³), 4.94 d (1H, H ⁶ , $J = 16.6$), 4.98 d (1H, H ⁶ , $J = 10.2$), 5.75–5.90 m (1H, H ⁵)
2c	3300–3500 (O–H), 3100, 1620 (CH=CH ₂), 3040, 1560, 1510, 740, 690 (benzene ring), 1100 (C–O)	2.45–2.58 m (2H, H ²), 4.54 t (1H, H ¹ , $J = 6.5$), 4.97 d (1H, H ⁴ , $J = 10.2$), 5.01 d (1H, H ⁴ , $J = 16.9$), 5.25 br.s (1H, OH), 5.72–5.83 m (1H, H ³), 7.12–7.35 m (5H, C ₆ H ₅)
2d	3550–3350 (OH), 3095, 1610 (CH=CH ₂), 1050 (C–O)	0.87 d (6H, H ⁷ , C ⁶ –CH ₃ , $J = 6.5$), 1.21–1.35 m (2H, H ⁵), 1.75–1.92 m (2H, H ³), 2.83 br.s (1H, OH), 3.42–3.50 m (1H, H ⁴), 4.94 d (1H, H ¹ , $J = 16.5$), 4.98 d (1H, H ¹ , $J = 10.0$), 5.72–5.86 m (1H, H ²)
2e	3600–3400 (OH), 3100, 1610 (CH=CH ₂), 1050 (C–O)	0.87 t (3H, H ¹ , $J = 7.5$) 1.14 s (3H, C ³ –CH ₃), 1.50 q.d (2H, H ² , $J_1 = 7.5$, $J_2 = 1.7$), 2.18 d (2H, H ⁴ , $J = 7.1$), 3.20 br.s (1H, OH), 4.95 d (1H, H ⁶ , $J = 16.2$), 4.99 d (1H, H ⁶ , $J = 7.3$), 5.72–5.80 m (1H, H ⁵)
2f	3500–3300 (OH), 3100, 1620 (CH=CH ₂), 1100 (C–O)	1.05–1.70 m (10H, cyclohexyl), 2.15 d (2H, H ¹ , $J = 6.8$), 3.50 br.s (1H, OH), 4.81 d (1H, H ³ , $J = 15.6$), 4.83 d (1H, H ³ , $J = 8.5$), 5.66–5.81 m (1H, H ²)

Table 3. Yields and elemental analysis data for alkenols **5–8**

Comp. no.	Yield, %	R_f (Et ₂ O–hexane, 1 : 3)	Found, %			Formula	Calculated, %		
			C	H	Hlg		C	H	Hlg
5a + 6a	65.00	0.59, 0.57	24.62	3.60	64.40	C ₄ H ₇ IO	24.24	3.59	64.14
5b + 6b	44.2	0.32, 0.39	32.20	4.62	56.30	C ₆ H ₁₁ IO	31.85	4.86	56.19
5c + 6c	56.8	0.58, 0.64	43.63	4.01	46.61	C ₁₀ H ₁₁ IO	43.79	4.01	46.35
5d + 6d	33.33	0.68, 0.52	37.96	5.25	50.80	C ₈ H ₁₅ IO	37.79	5.90	50.00
5e + 6e	45.50	0.68, 0.56	35.12	5.92	53.04	C ₇ H ₁₃ IO	35.00	5.41	52.91
5f + 6f	55.10	0.55, 0.61	40.83	5.98	47.38	C ₉ H ₁₅ IO	40.60	5.63	47.74
7a + 8a	52.40	0.55, 0.61	32.42	4.88	53.04	C ₄ H ₇ BrO	31.78	4.63	52.98
7b + 8b	45.70	0.69, 0.72	39.80	5.64	43.48	C ₆ H ₁₁ BrO	40.22	6.14	44.69
7c + 8c	65.0	0.55, 0.61	53.09	5.01	35.38	C ₁₀ H ₁₁ BrO	52.86	4.84	35.24
7d + 8d	24.62	0.68, 0.56	46.80	7.42	38.93	C ₈ H ₁₅ BrO	46.37	7.24	38.64
7e + 8e	55.28	0.68, 0.56	43.92	6.91	41.52	C ₇ H ₁₃ BrO	43.52	6.79	41.45
7f + 8f	67.00	0.61, 0.53	49.84	7.03	36.92	C ₉ H ₁₅ BrO	49.31	6.84	36.52

hydrogenating agent, and the produced 4-iodobut-3-yn-1-ol has the *E*-configuration of the double bond.

To establish the role of the hydroxyl group in the hydroalumination of terminal β -acetylene alcohols with lithium aluminum hydride, we replaced it with tetrahydropyranyl moiety (compound **9**). Under the studied conditions (THF, reflux, 12–14 h), the attempt

to hydrogenate the triple bond of 2-(but-3-yn-1-yloxy)tetrahydro-2*H*-pyran **9** failed. Unlike terminal homo-propargylic alcohols, in that case the triple bond was completely inert to the hydrogenation.

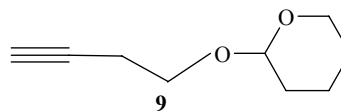


Table 4. The IR and ¹H NMR spectroscopy data for alkenols **5–7**

Comp. no.	ν , cm ⁻¹	δ , ppm (J , Hz)
5a	3500–3300 (O–H), 3100, 1630 (C=C), 1050 (C–O), 480 (C–I)	2.44 q (2H, H ² , $J = 6.4$), 2.94 br.s (1H, OH), 3.47 t (2H, H ¹ , $J = 6.4$), 6.26 d.t (1H, H ⁴ , $J_1 = 7.3$, $J_2 = 1.2$), 6.33 d.t (1H, H ³ , $J_1 = 7.3$, $J_2 = 6.4$)
5b	3550–3350 (OH), 3080, 1620 (C=C), 1050 (C–O), 490 (C–I)	0.88 t (3H, H ¹ , $J = 6.5$), 1.30–1.62 m (2H, H ²), 2.22–2.41 m (2H, H ⁴), 3.44–3.50 m (1H, H ³), 4.22 br.s (1H, OH), 6.23 d.t (1H, H ⁶ , $J_1 = 7.2$, $J_2 = 1.3$), 6.35 d.t (1H, H ⁶ , $J_1 = 7.2$, $J_2 = 6.5$)
5c+6c	3500–3300 (OH), 3100, 1610 (C=C), 1100, 1050 (C–O), 3040, 1560, 1510, 740, 690 (benzene ring), 490 (C–I)	2.32–2.50 m (2H, H ² , 5c), 3.10–3.23 and 3.31–3.39 m (2H, H ² , 6c), 3.90 br.s (1H, OH), 4.54 d.d (1H, H ¹ , $J_1 = J_2 = 6.9$, 6c), 4.75 d.d (1H, H ¹ , $J_1 = J_2 = 6.9$, 5c), 5.69 d (1H, H ⁴ , $J = 1.3$, 6c), 6.04 q (1H, H ⁴ , $J = 1.3$, 5c), 6.25 d.t (1H, H ⁴ , $J_1 = 7.5$, $J_2 = 1.2$, 5c), 6.33 d.t (1H, H ³ , $J_1 = 7.5$, $J_2 = 6.3$, 5c), 7.10–7.37 m (5H, C ₆ H ₅)
5d	3500–3300 (OH), 3100, 1610 (C=C), 1050 (C–O), 480 (C–I)	0.94 d (6H, H ⁷ , C ⁶ –CH ₃ , $J = 6.4$), 1.20–1.36 m (2H, H ⁵), 1.68–1.92 m (1H, H ⁶), 2.05–2.22 m (2H, H ³), 3.04 br.s (1H, OH), 3.57–3.65 m (1H, H ⁴), 6.23 d.t (1H, H ¹ , $J_1 = 7.2$, $J_2 = 1.3$), 6.35 d.t (1H, H ² , $J_1 = 7.2$, $J_2 = 6.5$)
5e	35300–3300 (OH), 3070, 1600 (C=C), 1050 (C–O), 490 (C–I)	0.88 t (3H, H ¹ , $J = 7.4$), 1.22 s (3H, C ³ –CH ₃), 1.25–1.44 m (2H, H ²), 2.18 d (2H, H ⁴ , $J = 6.4$), 2.97 br.s (1H, OH), 6.25 d.t (1H, H ⁶ , $J_1 = 7.3$, $J_2 = 1.4$), 6.34 d.t (1H, H ⁵ , $J_1 = 7.3$, $J_2 = 6.4$)
5f	3500–3300 (OH), 3060, 1610 (C=C), 1060 (C–O), 490 (C–I)	1.20–1.66 m (10H, cyclohexyl), 2.15 d (2H, H ¹ , $J = 6.5$), 3.03 br.s (1H, OH), 6.13 d.t (1H, H ¹ , $J_1 = 7.3$, $J_2 = 1.5$), 6.26 d.t (1H, H ² , $J_1 = 7.3$, $J_2 = 6.5$)
6a	3600–3400 (OH), 3080, 1600 (C=C), 1080 (C–O), 480 (C–I)	2.44 t (2H, H ² , $J = 6.4$), 3.43 t (2H, H ¹ , $J = 6.4$), 4.25 br.s (1H, OH), 5.71 d (1H, H ⁴ , $J = 1.2$), 6.13 d.t (1H, H ⁴ , $J_1 = 1.2$, $J_2 = 0.9$)
6b	3300–3500 (OH), 3080, 1610 (C=C), 1040 (C–O), 490 (C–I)	0.88 t (3H, H ¹ , $J = 6.4$), 1.30–1.62 m (2H, H ²), 2.10–2.42 m (2H, H ⁴), 2.95 (1H, OH), 3.42–3.48 m (1H, H ³), 5.68 d (1H, H ⁶ , $J = 1.2$), 6.13 d.t (1H, H ⁶ , $J_1 = 1.2$, $J_2 = 0.9$)
6d	3550–3350(OH), 3100, 1620 (C=C), 1090 (C–O), 480 (C–I)	0.94 d (6H, H ⁷ , C ⁶ –CH ₃ , $J = 6.5$), 1.16–1.28 m (2H, H ⁵), 1.77–1.90 m (1H, H ⁶), 3.08–3.20 m (2H, H ³), 3.31–3.50 m (1H, H ⁴), 4.12 br.s (1H, OH), 5.68 d (1H, H ¹ , $J = 1.1$), 6.11 q (1H, H ¹ , $J = 1.1$)
6e	3500–3300 (OH), 3080, 1630 (C=C), 1030 (C–O), 490 (C–I)	0.88 t (3H, H ¹ , $J = 7.4$), 1.14 s (3H, C ³ –CH ₃), 1.46 q (2H, H ² , $J = 7.4$), 2.61 s (2H, H ⁴), 3.87 br.s (1H, OH), 5.84 d (1H, H ⁶ , $J = 1.1$), 6.18 q (1H, H ⁶ , $J = 1.1$)
6f	3300–3500 (OH), 3100, 1610 (C=C), 1070 (C–O), 490 (C–I)	1.20–1.66 m (10H, cyclohexyl), 2.61 s (2H, H ²), 3.42 br.s (1H, OH), 5.83 d (1H, H ³ , $J = 1.0$), 6.15 q (1H, H ³ , $J = 1.0$)
7a	3500–3300 (OH), 3050, 1605 (C=C), 1100 (C–O), 610 (C–Br)	2.38 q (2H, H ² , $J = 6.5$), 3.02 br.s (1H, OH), 3.51 t (2H, H ¹ , $J = 6.5$), 6.24 d.t (1H, H ⁴ , $J_1 = 7.2$, $J_2 = 1.2$), 6.30 d.t (1H, H ³ , $J_1 = 7.2$, $J_2 = 6.5$)
7b	3500–3300 (OH), 3070, 1620 (C=C), 1100 (C–O), 610 (C–Br)	0.90 t (3H, H ¹ , $J = 6.5$), 1.55–1.90 m (2H, H ²), 2.23–2.31 m (2H, H ⁴), 3.08 br.s (1H, OH), 4.02 m (1H, H ³), 6.21 d.t (1H, H ⁶ , $J_1 = 6.9$, $J_2 = 1.3$), 6.27 d.t (1H, H ⁵ , $J_1 = 6.9$, $J_2 = 6.2$)
7c+8c	3550–3350 (OH), 3100, 1630 (C=C), 3040, 1560, 1510, 740, 690 (benzene ring), 1100, 1050 (C–O), 580 (C–Br)	2.31–2.47 m (2H, H ² , 7c), 2.56 br.s (1H, OH), 3.06–3.20 and 3.28–3.38 m (2H, H ² , 8c), 4.57 d.d (1H, H ¹ , $J_1 = J_2 = 6.8$, 8c), 4.88 d.d (1H, H ¹ , $J_1 = J_2 = 6.8$, 7c), 5.89 d (1H, H ⁴ , $J = 1.2$, 8c), 6.07 q (1H, H ⁴ , $J = 1.3$, 7c), 6.32 d.t (1H, H ⁴ , $J_1 = 7.5$, $J_2 = 1.3$, 8c), 6.39 d.t (1H, H ³ , $J_1 = 7.2$, $J_2 = 6.5$, 7c), 7.20–7.38 m (5H, C ₆ H ₅)
7d	3300–3500 (OH), 3050, 1630 (C=C), 1050 (C–O), 590 (C–Br)	0.95 d (6H, H ⁷ , C ⁶ –CH ₃ , $J = 6.5$), 1.20–1.32 m (2H, H ⁵), 1.65–1.87 m (1H, H ⁶), 2.12–2.28 m (2H, H ³), 3.24 br.s (1H, OH), 3.52–3.64 m (1H, H ⁴), 6.21 d.t (1H, H ¹ , $J_1 = 7.2$, $J_2 = 1.2$), 6.34 d.t (1H, H ² , $J_1 = 7.2$, $J_2 = 6.5$)

Table 4. (Contd.)

Comp. no.	ν , cm^{-1}	δ , ppm (J , Hz)
7e	3500–3300 (OH), 3080, 1610 (C=C), 1050 (C–O), 600 (C–Br)	0.88 t (3H, H^1 , $J = 6.5$), 1.06 s (3H, $C^3\text{-CH}_3$), 1.36–1.48 m (2H, H^2), 2.23 d (2H, H^4 , $J = 6.0$), 2.84 br.s (1H, OH), 6.22 d.t (1H, H^6 , $J_1 = 7.0$, $J_2 = 1.2$), 6.28 d.t (1H, H^5 , $J_1 = 7.0$, $J_2 = 6.0$)
7f	3500–3300 (OH), 3050, 1630 (C=C), 1100 (C–O), 630 (C–Br)	1.05–1.70 m (10H, cyclohexyl), 2.18 d (2H, H^1 , $J = 6.7$), 3.67 br.s (1H, OH), 6.11 d.t (1H, H^3 , $J_1 = 7.0$, $J_2 = 1.5$), 6.20 d.t (1H, H^2 , $J_1 = 7.0$, $J_2 = 6.7$)
8a	3500–3300 (OH), 3050, 1610 (C=C), 1100 (C–O), 620 (C–Br)	2.38 q (2H, H^2 , $J = 6.5$), 3.45 t (2H, H^1 , $J = 6.5$), 3.62 br.s (1H, OH), 6.53 d (1H, H^4 , $J = 1.2$), 6.82 d.t (1H, H^4 , $J_1 = 1.2$, $J_2 = 0.9$)
8b	3500–3300 (OH), 3100, 1610 (C=C), 1100 (C–O), 610 (C–Br)	0.95 t (3H, H^1 , $J = 6.4$), 1.21–1.55 m (2H, H^2), 2.44 d.d (2H, H^4 , $J_1 = 6.4$, $J_2 = 0.9$), 2.90 br.s (1H, OH), 3.40–3.48 m (1H, H^3), 5.38 d (1H, H^6 , $J = 1.2$), 5.65 d.t (1H, H^6 , $J_1 = 1.2$, $J_2 = 0.9$)
8d	3500–3300 (OH), 3060, 1620 (C=C), 1100 (C–O), 620 (C–Br)	0.94 d (6H, H^7 , $C^6\text{-CH}_3$, $J = 6.5$), 1.16–1.28 m (2H, H^5), 1.46 br.s (1H, OH), 1.77–1.90 m (1H, H^6), 2.58–2.90 m (2H, H^3), 3.31–3.50 m (1H, H^4), 5.72 d (1H, H^1 , $J = 1.0$), 6.13 q (1H, H^1 , $J = 1.0$)
8e	3500–3300 (OH), 3050, 1630 (C=C), 1100 (C–O), 590 (C–Br)	0.88 t (3H, H^1 , $J = 6.5$), 1.16 s (3H, $C^3\text{-CH}_3$), 1.41–1.52 m (2H, H^2), 2.53 s (2H, H^4), 3.87 br.s (1H, OH), 5.50 d (1H, H^6 , $J = 1.2$), 5.71 d.t (1H, H^6 , $J_1 = 1.2$, $J_2 = 0.9$)
8f	3500–3300 (OH), 3050, 1610 (C=C), 1100 (C–O), 620 (C–Br)	1.05–1.70 m (10H, cyclohexyl), 2.20 s (2H, H^1), 3.63 br.s (1H, OH), 5.38 d (1H, H^3 , $J = 1.1$), 5.58 q (1H, H^3 , $J = 1.1$)

The resistance to hydrogenation of terminal β -acetylene alcohols with the hydroxyl group protected with tetrahydropyranyl moiety, the presence of deuterium, bromine, and iodine atoms at the β - and γ -positions with respect to the hydroxyl group in the reaction products, and the *cis*-configuration of the double bond suggested that the hydride ion attack took place simultaneously via two pathways. The reported results, as well as the available data on the reduction of α -acetylene alcohols [8] indicated that the hydrogenation of terminal β -acetylene alcohols occurred through the formation of cyclic organometallic complexes **A** and **B**.

In summary, hydroalumination-halogenation of terminal β -acetylene alcohols afforded β - and γ -halogenated homoallylic alcohols that are of interest as precursors for the synthesis of β - and γ -alkylhomoallylic alcohols, components of many natural and biologically active substances.

EXPERIMENTAL

^1H NMR spectra were registered using a Varian Mercury-300 VX spectrometer in $\text{DMSO-}d_6$ (300.077 MHz) relative to internal TMS. IR spectra (thin films) were recorded using a Specord 75-IR spectrometer. GLC analysis was carried out using a

Clarus 400 instrument equipped with a flame ionization detector (Elite-Wax ETR column, 60 m \times 0.32 mm; helium as the carrier gas, pressure of the carrier gas 14.0 psi). TLC analysis was performed using Silufol UV-254 plates, eluting with a hexane-diethyl ether mixture and developing with potassium permanganate solution. L40/100 silica was used for column chromatography.

But-3-yn-1-ol **1a** was purchased from Alfa Aesar. β -Alcohols **1b–1f** were synthesized via the Reformatsky reaction of 1-bromobut-2-yne with the corresponding carbonyl compounds [14]. 2-(But-3-ynyloxy)tetrahydro-2*H*-pyran **9** was obtained by the known procedure [15].

Hydroalumination of terminal β -acetylene alcohols **1a–1f**. A solution of 50 mmol of alkynol **1a–1f** in anhydrous THF was added dropwise to a suspension of 200 mmol of lithium aluminum hydride in anhydrous THF at 0 to -5°C under nitrogen. The mixture was refluxed upon stirring during 12–13 h (5 h in the case of alcohol **1c**). The reaction progress was monitored by TLC and GLC. After cooling to 0 to -5°C , 7.6 mL of water, 7.6 mL of 15% sodium hydroxide, and 22.8 mL of water were added. The reaction mixture was stirred during 0.5 h. The formed precipitate was filtered off, and the filtrate was extracted with diethyl ether. The

extract was washed with saturated sodium chloride solution and dried with sodium sulfate. After the solvents removal, the residue was distilled. Boiling points, yields, R_f values, elemental analysis results, and IR and ^1H NMR spectroscopy for alkenols **2a–2f** are shown in Tables 1 and 2.

A mixture of deuterioalcohols **3e** and **4e** was obtained in a ratio of 1 : 2 when treating the reaction mixture with D_2O . ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 0.86 t (3H, H^1 , $J = 6.5$), 1.07 s (3H, $\text{C}^3\text{--CH}_3$), 1.37 q (2H, H^2 , $J = 6.5$), 2.10–2.14 m (2H, H^4), 3.40 br.s (1H, OH), 4.95 d (1H, H^6 , $J = 10.5$, **3e**), 5.74–5.92 m (1H, H^5 , **3e**), 4.96 br.s (1H, H^6 , **4e**), 4.99 br.s (1H, H^5 , **4e**).

Hydroalumination-iodination of terminal β -acetylene alcohols **1a–1f**. A solution of 50 mmol alk-3-yn-1-ol **1a–1f** in anhydrous THF was added dropwise to a suspension of 200 mmol of lithium aluminum hydride in anhydrous THF at 0°C under nitrogen. The reaction mixture was refluxed upon stirring during 12–13 h (6 h in the case of alcohol **1f**). After cooling to -10 to -5°C , 200 mmol of ethyl acetate was added dropwise. The reaction mixture was incubated at the same temperature during 0.5 h, and then cooled to -10°C . Next, 100 mmol of crushed iodine was added portionwise over 0.5 h. The reaction mixture was stirred during 1 h at -10 to 0°C and then treated with a saturated solution of sodium thiosulfate. The formed precipitate was filtered off, and the reaction products were extracted with diethyl ether. The extract was washed with saturated sodium thiosulfate solution, then with saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed to obtain the mixture of iodalkenols **5a–5f** and **6a–6f**. The individual isomers were isolated by column chromatography (hexane : diethyl ether = 19 : 1). Yields, R_f values, elemental analysis results, and IR and ^1H NMR spectroscopy data for iodalkenes **5a–5f** and **6a–6f** are shown in Tables 3 and 4.

Hydroalumination-bromination of terminal β -acetylene alcohols 1a–1f. A solution of 44 mmol of alk-3-yn-1-ol **1a–1f** in anhydrous THF was added dropwise to a suspension of 176 mmol of lithium aluminum hydride in anhydrous THF at 0 to -5°C under nitrogen. The reaction mixture was refluxed during 12–13 or 6 h (**1f**) upon stirring. After cooling to -10 to -5°C , 176 mmol of ethyl acetate was added dropwise. The reaction mixture was incubated at the same temperature during 0.5 h, and then a solution of

pyridinium bromide (prepared from 66 mmol of pyridine and 44 mmol of bromine) in 10 mL of THF was added dropwise. The reaction mixture was stirred during 15 min at 0 to -5°C . Next, 6.8 mL of water, 6.8 mL of 15% aqueous sodium hydroxide solution, and 20.4 mL of water were added. The formed precipitate was filtered off, and the reaction products were extracted with diethyl ether. The extract was washed with dilute hydrochloric acid, saturated solutions of sodium bicarbonate and sodium chloride, and then dried over magnesium sulfate. The solvent was removed, the residue was subject to chromatography (hexane : diethyl ether = 19 : 1). Yields, R_f values, elemental analysis results, and IR and ^1H NMR spectroscopy data for bromalkenols **7a–7f** and **8a–8f** are shown in Tables 3 and 4.

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