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Some Special Features of Hydroalumination-Iodination of Alkyne-1,4-diols

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Abstract—Hydroalumination-iodination of alkyne-1,4-diols of different structure showed that with increasing number of substituents at the C–OH group the amount of β-iodo-substituted products with respect to this group increased. In the case of symmetric secondary 1,4-diols the reaction results in a 1 : 1 mixture of stereoisomeric iodoalkenediols, and in the case of phenyl substituents the reaction proceeds regio- and stereoselectively to give an alkenediol iodine atom in the β-position to phenyl group.

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Hydroalumination of propargylic alcohols with lithium aluminum hydride followed by iodination of the resulting organometallic complex is a convenient method for the synthesis of 1-iodo- and 2-iodoallyl alcohols [1]. The hydride ion attack can be directed on the C^2 or C^3 atoms of propargyl alcohol by adding Lewis acids ($AlCl_3$) or bases (CH_3ONa) to the reaction mixture [2]. This method has been successfully applied to the synthesis of some natural isoprenoid compounds [1, 3–6].

In this work we studied stereo- and regioselectivity of hydroalumination-iodination of alkyne-1,4-diols **Ia**–**Ij**. For this purpose, various α-substituted (with respect to the triple bond) acetylenic diols were used (Table 1). Hydroalumination of diols **Ia**–**Ij** was performed at room temperature in a THF–diethyl ether mixture at the ratio substrate–lithium aluminum hydride of 1 : 4 [in the case of **Ia** a ratio was 1 : 3] (Table 2). Intermediate aluminates were quenched with powdered iodine at –5 to –10°C. As expected, the reaction afforded a mixture of regioisomeric iodoalkenediols **IIa**–**IIj**, **IIIa**–**IIIj**. The IR and ^{1}H NMR spectra indicated the formation of regioisomeric iodoalkenediols of *Z*-configuration [7]. The configuration of the double bonds was confirmed by NOESY method. For example, in the spectrum of **IId** cross peaks were observed between the protons H^2 and H^4, and in the spectrum of **IIId**, between the H^1 and H^3 protons. This shows the spatial proximity of the protons H^2, H^4 and H^3, H^1 in compounds **IId** and **IIId**, respectively. This arrangement of the protons can occur only if the double bond CH=CI is of the *Z*-configuration (see Scheme 1).

The composition and the ratio of the products of hydroalumination-iodination of alkyne-1,4-diols **Ia**–**Ij** are shown in Table 1. Regioisomers ratio was determined using ^{1}H NMR by integrating the signals of vinyl protons (see Table 3).

The results allowed to derive the following rule of thumb: the more substituents at the C–OH groups in the starting diol, the more formed a compound in which the iodine atom is located at the β-carbon atom with respect to the specified group.

For accurate assignment of the signals in the spectra of isomeric iodoalkenediols, we performed NOESY experiment by an example of **Id**. The proton signals of hydroxy groups were established after adding trifluoroacetic acid to the sample. In the NOESY spectrum there were cross peaks between the vinyl proton signal at 5.91 ppm and the signals of $C\underline{H}_2OH$ and $C\underline{H}_2CH_2CH_3$ groups at 4.02 and 1.30 ppm, respectively. There was also a coupling between the protons of iodovinyl fragment (6.09 ppm) and the protons of $C\underline{H}_2OH$ (3.62 ppm) and $C\underline{H}OH$ (3.98 ppm). These data allow assigning the signals at 5.91, 1.30, and 4.02 ppm to one isomer, and the signals at 6.09, 3.62, and 3.98 ppm to another.

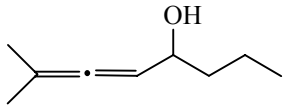
Table 1. Composition and ratio (%) of the products **II**, **III** of hydroalumination-iodination of alkyne-1,4-diols **Ia**–**Ij**

Alkynediols	Iodoalkenediols	
	II	**III**
Ia	100	–
Ib	33	67
Ic	28	72
Id	35	65
Ie	100	–
If	100	–
Ig	31	69
Ih	30	70
Ii	100	–
Ij	100	–

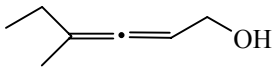
Table 2. Conditions of hydroalumination-iodination of alkyne-1,4-diols **Ia**–**Ij**

Comp. no.	Solvent	Temperature, °C	Time, h	[I] : [$LiAlH_4$]
Ia	THF	39–40	7	1 : 3
Ib	EtO–THF, 1 : 2	21–24	2	1 : 4
Ic	EtO–THF, 1 : 2	22–23	2.5	1 : 4
Id	EtO	22–25	4	1 : 4
Ie	EtO–THF, 1 : 2	22–25	2	1 : 4
If	EtO	23–25	2	1 : 4
Ig	EtO–THF, 1 : 2	23–25	2	1 : 4
Ih	EtO–THF, 1 : 5	33–35	2.5	1 : 4
Ii	EtO–THF, 1 : 2	22–24	2	1 : 4
Ij	EtO–THF, 1 : 2	22–24	2	1 : 4

When the starting alkyne-1,4-diol contained a tertiary hydroxy group adjacent to the triple bond (**Ig**, **Ih**), then hydroalumination-iodination resulted in allenic alcohols **IVg** and **IVh** along with appropriate alkenediols **IIg**, **IIh** and **IIIg**, **IIIh** (Table 4). This agrees well with the literature data on hydroalumination of alkyne-1,4-diols [8].



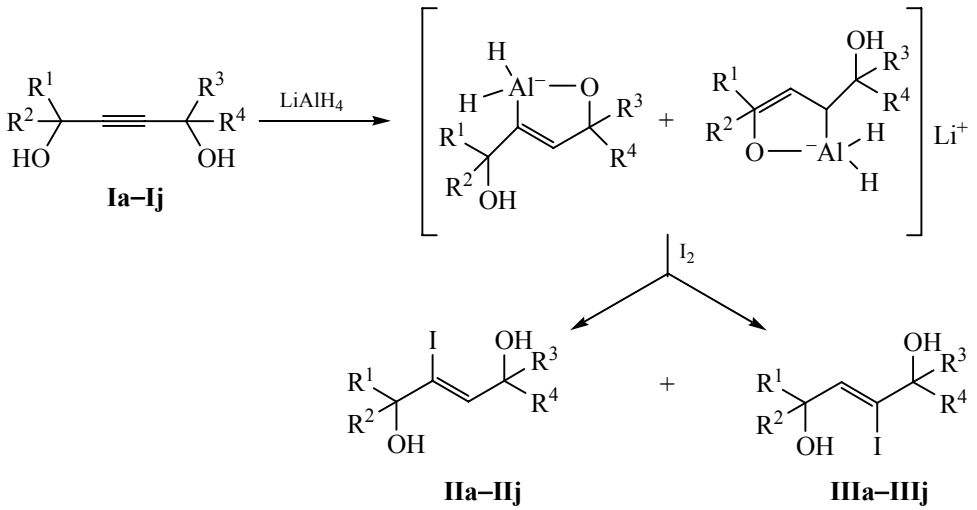
IVg



IVh

In the case of hydroalumination-iodination of symmetric secondary alkyne-1,4-diols **If**, **Ij** the formation of diols **IIf**, **IIj** with only *Z*-configuration can be expected. However, the obtained data showed that *E*-isomer also formed. According to the ^{1}H NMR data, stereoisomers ratio was ~ 1 : 1. Value of the constant (^4J) of spin-spin coupling between the vinyl proton and the proton in the α-position with respect to the iodine atom was a criterion for assigning the signals to geometric isomers. For *Z*-isomer it equals 1.0 Hz, and for *E*-isomer, 0.8 Hz. Furthermore, the signal of vinyl proton of *E*-isomer appears downfield with respect to that of *Z*-isomer [5.97 and 5.92 ppm

Scheme 1.



Ia–Ij **IIa–IIj** **IIIa–IIIj**

a, $R^1 = R^2 = R^3 = R^4 = H$; **b**, $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$; **c**, $R^1 = R^3 = R^4 = H$, $R^2 = C_2H_5$; **d**, $R^1 = R^3 = R^4 = H$, $R^2 = C_3H_7$; **e**, $R^1 = R^3 = R^4 = H$, $R^2 = C_6H_5$; **f**, $R^1 = R^3 = H$, $R^2 = R^4 = C_2H_5$; **g**, $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = C_3H_7$; **h**, $R^1 = CH_3$, $R^2 = C_2H_5$, $R^3 = R^4 = H$; **i**, $R^1 = R^3 = H$, $R^2 = R^4 = C_3H_7$; **j**, $R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^4 = C_2H_5$.

Table 3. IR and ^{1}H NMR spectra of iodoalkenediols **IIa**–**IIj**, **IIIa**–**IIId**, **IIIg** and allene alcohols **IVg**, **IVh**

Comp. no.	IR spectrum	^{1}H NMR spectrum
IIa + **IIIa**	3300–3500 (OH), 1630 (HC=CI), 1050 (C–O), 600 (C–I)	($CDCl_3$): 2.6 br.s (2H, C^1OH, C^4OH), 4.26 d (2H, H^1, *J* 1.2), 4.28 d.d (2H, H^4, J_1 4.0, J_2 1.2), 6.28 d.t (1H, H^3, J_1 4.0, J_2 1.2)
IIb + **IIIb**	3350–3500 (OH), 1625 (HC=CI), 1100, 1050 (C–O), 960 (CH=), 600 (C–I)	(DMSO-d_6–CCl_4, 1 : 3): 1.27 d (3H, H^5, *J* 6.5), 2.93 br.s (2H, C^1OH, C^4OH), 3.52 d [2H, H^1, *J* 7, (**IIb**)], 3.78 q [1H, H^4, *J* 6.5, (**IIIb**)], 3.90 s [2H, H^1, (**IIIb**)], 4.20–4.35 m [1H, H^4, *J* 6.5, (**IIb**)], 5.95 d.t [1H, H^2, J_1 7, J_2 1.2, (**IIIb**)], 6.13 t [1H, H^3, *J* 6.5, (**IIb**)]
IIc + **IIIc**	3350–3400 (OH), 1625 (HC=CI), 1100, 1050 (C–O), 960 (CH=), 600 (C–I)	($CDCl_3$): 1.22 t (3H, H^6, *J* 6.0), 1.40–1.80 m (2H, H^5), 4.15 d [2H, H^1, *J* 8.3, (**IIc**)], 4.22 s [2H, H^1, (**IIIc**)], 4.18–4.28 m (1H, H^4), 4.42 br.s (2H, C^1OH, C^4OH), 5.98 d.t [1H, H^3, J_1 7.5, J_2 1.5, (**IIIc**)], 6.22 t.d [1H, H^2, J_1 6.0, J_2 1.0, (**IIc**)]
IId + **IIId**	3300–3500 (OH), 1630 (HC=CI), 1100, 1020 (C–O), 960 (CH=), 600 (C–I)	(DMSO-d_6): 0.90 t (3H, H^7, *J* 6.8), 1.20–1.52 m (4H, H^5, H^6), 3.62 t (2H, H^4, *J* 7.1), 3.98–4.06 m [2H, H^1, (**IId**)], 4.02 s [2H, H^1, (**IIId**)], 4.50 d [1H, C^4OH, *J* 7.1, (**IIId**)], 4.56 t [1H, C^1OH, *J* 7.2, (**IId**)], 4.92 d [1H, C^4OH, *J* 7.2, (**IId**)], 5.22 t [1H, C^1OH, *J* 7.1, (**IIId**)], 5.91 d [1H, H^3, *J* 7.2, (**IIId**)], 6.09 t [1H, H^2, *J* 7.1, (**IId**)]
IIe	3300–3500 (OH), 3040, 1560, 1510, 740, 690 (monosubstituted benzene ring), 1630 (HC=CI), 1100 (C–O), 860 (CH=), 600 (C–I)	(DMSO-d_6–CCl_4, 1 : 3): 4.15 d (2H, H^4, *J* 7.0), 4.89 t (1H, H^2, *J* 7.0), 5.09 t (1H, C^4OH, *J* 7.0), 5.33 d (1H, H^1, *J* 7.0), 5.66 d (1H, C^1OH, *J* 7.0), 7.20–7.35 m (5H, C_6H_5)
IIf	3300–3500 (OH), 1640 (*Z*-HC=CI), 1630 (*E*-HC=CI), 1080, 1050 (C–O), 960 (*Z*-CH=), 850 (*E*-CH=), 600 (C–I)	($CDCl_3$): 0.90 t (6H, H^1, H^8, *J* 7.0), 1.40–1.60 m (4H, H^2, H^7), 3.56 br.s (2H, C^3OH, C^6OH), 3.63 q (1H, H^6, *J* 7.0), 4.28 t (1H, H^3, *J* 7.0), 5.92 d.d (1H, H^5, J_1 7.5, J_2 1.0, *Z*-isomer), 5.97 d.d (1H, H^5, J_1 7.5, J_2 0.8, *E*-isomer)
IIg + **IIIg**	3300–3500 (OH), 1625 (HC=CI), 1150 (C–O), 960 (CH=), 600 (C–I)	(DMSO-d_6): 0.92 t (6H, H^1, C^2CH_3, *J* 7.0), 1.15–1.60 m (4H, H^6, H^7), 1.37 s (3H, H^8), 1.55–1.63 m [1H, H^5, (**IIg**)], 4.14–4.20 m [1H, H^5, (**IIIg**)], 4.78 br.s (2H, C^2OH, C^5OH), 5.82 d [1H, H^4, *J* 7.0, (**IIg**)], 6.18 s [1H, H^3, (**IIIg**)]
IVg[a]	3300–3500 (OH), 1950 (C=C=C), 1020–1000 (C–O), 840 (C=C=CH)	(DMSO-d_6): 0.88 t (3H, H^1, *J* 6.9), 1.32–1.62 m (4H, H^2, H^3), 1.57–1.65 m (6H, H^8, C^7CH_3), 3.10 br.s (1H, OH), 4.45–4.53 m (1H, H^4), 5.58–5.65 m (1H, H^5)
IIh[a]	3300–3500 (OH), 1625 (HC=CI), 1150, 1020 (C–O), 960 (CH=), 600 (C–I)	($CDCl_3$): 0.88 t (3H, H^6, *J* 7.0), 1.22 s (3H, C^4CH_3), 1.55 and 1.78 q (2H, H^5, *J* 7.0), 4.96 d (2H, H^1, *J* 7.0), 5.10 br.s (2H, C^1OH, C^4OH), 5.24 t (1H, H^2, *J* 7.0)
IIIh[a]	3300–3500 (OH), 1620 (HC=CI), 1100, 1020, 1000 (C–O), 960 (CH=), 600 (C–I)	(DMSO-d_6): 0.88 t (3H, H^6, *J* 7.0), 1.30 s (3H, C^4CH_3), 1.55 and 1.78 q (2H, H^5, *J* 7.0), 4.0 br.s (1H, C^4OH), 4.03 s (2H, H^4), 5.28 t (1H, C^1OH, *J* 7.0), 6.33 s (1H, H^3)
IVh[a]	3300–3500 (OH), 1950 (C=C=C), 1200–1000 (C–O), 840 (C=C=CH)	(DMSO-d_6): 0.88 t (3H, H^6, *J* 7.0), 1.48–1.54 m (3H, C_4CH_3), 1.97–2.06 m (2H, H^5), 3.93 br.s (1H, OH), 4.56 d (2H, H^1, *J* 7.1), 5.75–5.80 m (1H, H^2)
IIi	3300–3500 (OH), 1640 (*Z*-HC=CI), 1630 (*E*-HC=CI), 1080, 1050 (C–O), 960 (*Z*-CH=), 850 (*E*-CH=), 600 (C–I)	(DMSO-d_6): 0.92 t (6H, H^1, H^{10}, *J* 7.0), 1.20–1.44 m (8H, H^2, H^3, H^8, H^9), 3.40–3.55 m (1H, H^7), 4.08–4.20 m (1H, H^4), 4.41 d (1H, C^7OH, *J* 6.0, *Z*-isomer), 4.46 d (1H, C^7OH, *J* 6.0, *E*-isomer), 4.82 d (1H, C^4OH, *J* 5.0, *Z*-isomer), 4.93 d (1H, C^4OH, *J* 5.0, *E*-isomer), 5.82 d.d (1H, H^6, J_1 7.5, J_2 1.0, *Z*-isomer), 5.88 d.d (1H, H^6, J_1 7.5, J_2 0.8, *E*-isomer)
IIj	3300–3500 (OH), 3040, 3020, 1590, 1510, 740, 700 (monosubstituted benzene ring), 1625 (HC=CI), 1100, 1050 (C–O), 960 (CH=), 600 (C–I)	($CDCl_3$): 0.98 t (3H, H^6, *J* 7.0), 1.56–1.74 m (2H, H^5), 2.20 br.s (2H, C^1OH, C^4OH), 4.36 d.t (1H, H^4, J_1 7.6, J_2 6.4), 5.12 d (1H, H^1, *J* 0.8), 6.21 d.d (1H, H^3, J_1 7.7, J_2 1.0), 7.15–7.45 m (5H, C_6H_5)

[a] Compounds were isolated by column chromatography.

Table 4. Yields, R_f values, and elemental analysis data of iodoalkenediols **IIa**–**IIj**, **IIIa**–**IIId**, **IIIg** and allene alcohols **IVg**, **IVh**

Comp. no.	Yield, %	R_f (Et_2O–hexane)	Found, %			Formula	Calculated, %		
			C	H	I		C	H	I
IIa	46.70	0.41 (Et_2O)	21.80	3.20	59.08	$C_4H_7IO_2$	22.43	3.27	59.35
IIb + **IIIb**	41.20	0.50 (3 : 1)	26.78	3.57	56.69	$C_5H_9IO_2$	26.31	3.97	55.70
IIc + **IIIc**	50.00	0.58 (5 : 1)	29.68	4.80	53.20	$C_6H_{11}IO_2$	29.75	4.54	52.48
IId +**IIId**	49.70	0.58 (8 : 1)	33.08	5.30	50.20	$C_7H_{13}IO_2$	32.80	5.08	49.60
IIe	57.20	0.50; 0.41 (5 : 1)	40.80	4.00	44.00	$C_{10}H_{11}IO_2$	41.38	3.79	43.79
IIf	53.10	0.72; 0.58 (5 : 1)	36.08	6.10	48.08	$C_8H_{15}IO_2$	35.55	5.55	47.03
IIg + **IIIg**	51.02	0.41; 0.30 (5 : 2)	37.98	5.93	44.69	$C_9H_{17}IO_2$	38.03	5.98	44.72
IVg[a]	19.50	0.51 (1 : 1)	77.10	11.37	–	$C_9H_{16}O$	77.14	11.43	–
IIh[a]	27.50	0.24 (4 : 1)	33.00	4.80	50.28	$C_7H_{13}IO_2$	32.81	5.08	49.61
IIIh[a]	45.30	0.30 (4 : 1)	32.79	4.91	49.89	$C_7H_{13}IO_2$	32.81	5.08	49.61
IVh[a]	20.10	0.48 (1 : 1)	74.92	10.66	–	$C_7H_{12}O$	75.00	10.71	–
IIi	51.02	0.40 (4 : 1)	40.21	6.30	42.58	$C_{10}H_{19}IO_2$	40.26	6.37	42.62
IIj	40.00	0.52 (5 : 1)	45.22	4.56	40.59	$C_{12}H_{15}IO_2$	45.30	4.75	39.89

[a] Compounds were isolated by column chromatography.

(**IIf**), 5.88 and 5.82 ppm (**IIj**)]. The IR spectrum contains the characteristic absorption bands of *E*- and *Z*-isomeric iodo-substituted alkenediols at 1630, 850 and 1640, 960 cm^{-1}, respectively.

All these facts concern alkyne-1,4-diols containing alkyl groups as substituents (**Ia**–**Id**, **If**–**Ii**). Hydroalumination-iodination of alkyne-1,4-diols containing a phenyl group (**Ie**, **Ij**) proceeded regio- and stereoselectively to give *Z*-alkenediols **IIe** and **IIj**, i.e., a iodine atom attached to the *sp*-hybridized carbon atom in the β-position relative to the phenyl group. According to the ^1H NMR data, the purity of the obtained iodo-substituted alkenediols **IIe**, **Ij** was ~97%. The same result we observed in hydroalumination-halogenation of phenylacetylene α-alcohols [9, 10]. This hydrogenation regioselectivity was due to the easy attack of the hydride ion on the *sp*-hybridized carbon atom of the triple bond in the γ-position of the phenylpropynyl group.

The starting 1,4-diols were synthesized from prop-2-yn-1-ol **V**, 2-methylbut-3-yn-2-ol **VI**, and 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran **VII**. 4-Methylhex-2-yne-1,4-diol **Ih** was obtained directly from prop-2-yn-1-ol **V**. The oxidation of the latter resulted in propiolic aldehyde **X** used further in the synthesis of diols **If**, **Ij**. 2-Methylbut-3-yn-2-ol **VI** was used in the synthesis of diols **Ig**, **Ii**. Diols **Ib**, **Ic**, **Ie** were prepared from compound **VII** (see Schemes 2–4).

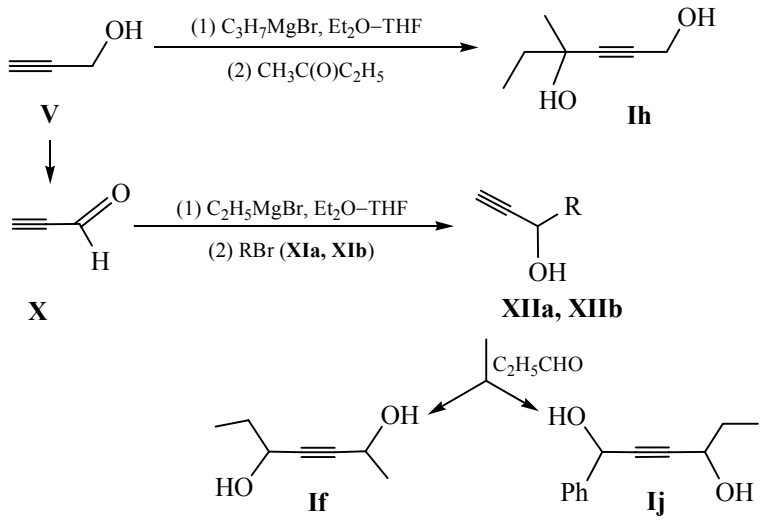
EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-VX 300 spectrometer operating at 300.077 and 75.462 MHz, respectively. $CDCl_3$, CCl_4, $CDCl_3$–CCl_4 (1 : 1), DMSO-d_6 were used as solvents. Chemical shifts were reported relative to internal reference TMS. IR spectra were registered on a Specord 75IR instrument from a thin layer. The reaction progress was monitored by TLC using Silufol UV-254 plates, eluting with hexane–diethyl ether mixture and detecting with iodine vapor or $KMnO_4$ solution.

But-2-yne-1,4-diol **Ia** was purchased from Sigma-Aldrich. Hept-2-yn-1,4-diol **Id** was synthesized by the known procedure [11].

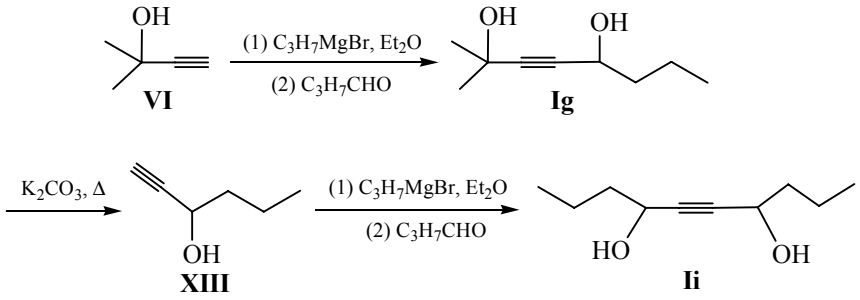
Hydroalumination-iodination of alkyne-1,4-diols (I). A solution of alkyne-1,4-diol **I** in anhydrous diethyl ether or THF was added dropwise to a mixture of lithium aluminum hydride in anhydrous diethyl ether and (or) THF at 0°C under nitrogen. After stirring, ethyl acetate ($LiAlH_4$–ethyl acetate ratio was 1 : 1) was added to the mixture at 0°C. The reaction mixture was maintained for 1 h and cooled to –10°C.

Scheme 2.

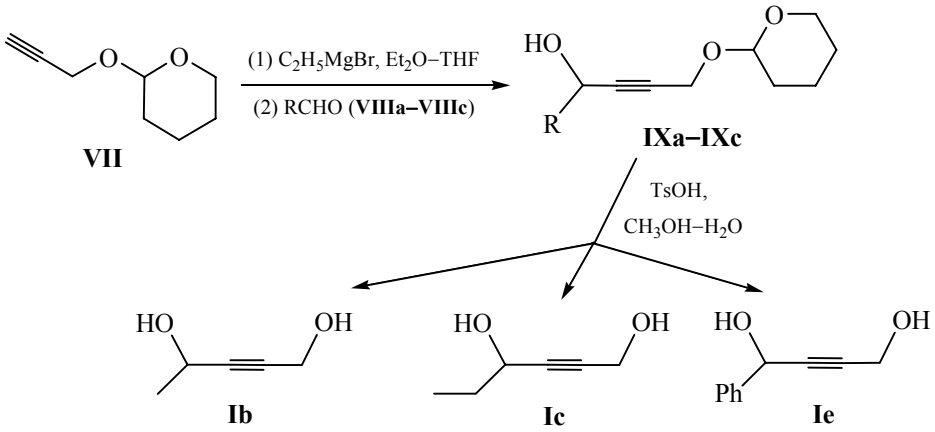


R = C_2H_5 (**a**), C_6H_5 (**b**).

Scheme 3.



Scheme 4.



R = CH_3 (**a**), C_2H_5 (**b**), C_6H_5 (**c**).

Then crushed iodine was added by portions to the mixture (substrate:iodine = 1 : 3) within 0.5 h. After stirring at –10 to 0°C for 1 h, the mixture was treated with a saturated solution of sodium thiosulfate. The precipitate was filtered off. The filtrate was extracted with diethyl ether. Then the extract was washed with saturated sodium thiosulfate solution, with brine, and dried over magnesium sulfate. After removing the

solvents, a mixture of iodoalkenediols **II** and **III** was isolated (Tables 1, 3, 4). In the case of an alkyne-1,4-diols **Ig**, **Ih**, **Ij** a mixture of isomers was separated by column chromatography [eluent hexane–diethyl ether (19 : 1)–(9 : 1)]. In the case of alkyne-1,4-diols **Ig**, **Ih**, allene alcohols **IVg** and **IVh** were isolated by chromatography along with the corresponding alkenediols **II** and **III**.

Alkynols IXa–IXc. A solution of 38 mmol of an appropriate aldehyde **VIIIa–VIIIc** in 50 mL of anhydrous diethyl ether was added dropwise to the Grignard reagent, prepared from 0.50 g-atom of magnesium, 38 mmol of ethyl bromide and 50 mmol of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran **VII** [12], in 50 mL of anhydrous ether at –5 to –10°C. The reaction mixture was stirred for 30 min and then refluxed for 4–5 h. The reaction mixture was hydrolyzed with saturated ammonium chloride solution and 10% aqueous hydrochloric acid solution at –15 to –10°C. The reaction product was extracted with diethyl ether. The ether extract was salted out, washed with saturated sodium carbonate solution and dried over magnesium sulfate. After removing the solvent, the residue was distilled in a vacuum.

5-(Tetrahydro-2*H*-pyran-2-yloxy)pent-3-yn-2-ol (IXa). Yield 40.0%, bp 130–134°C (1 mm Hg), R_f 0.44 (diethyl ether–hexane, 3 : 1). IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1240, 1160, 1100, 1060, 1040 (C–O, C–O–C). ^{1}H NMR spectrum ($CDCl_3$–CCl_4, 1 : 1), δ, ppm (*J*, Hz): 1.40 d (3H, H^5, *J* 6.5), 1.52–1.70 m (6H, $CH_2CH_2CH_2$, tetrahydropyran), 3.55 t and 3.83 t (2H, OCH_2, tetrahydropyran, *J* 6.5), 4.27 and 4.30 d (2H, H^1, *J* 1.2), 4.33 q (1H, H^4, *J* 6.5), 4.81 t (1H, OCH, tetrahydropyran, *J* 6.4). Found, %: C 65.18; H 8.61. $C_{10}H_{16}O_3$. Calculated, %: C 65.22; H 8.69.

6-(Tetrahydro-2*H*-pyran-2-yloxy)hex-4-yn-3-ol (IXb). Yield 45.0%, bp 127–130°C (2 mm Hg), R_f 0.48 (diethyl ether–hexane, 3 : 1). IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1240, 1160, 1100, 1060, 1040 (C–O, C–O–C). ^{1}H NMR spectrum ($CDCl_3$–CCl_4, 1 : 1), δ, ppm (*J*, Hz): 1.02 t (2H, H^6, *J* 6.5), 1.52–1.70 m (6H, $CH_2CH_2CH_2$, tetrahydropyran), 1.72–1.78 m (2H, H^5), 3.55 and 3.83 t (2H, OCH_2, tetrahydropyran, *J* 6.5), 4.27 d and 4.30 d (2H, H^1, *J* 1.2), 4.36 t (1H, H^4, *J* 6.5), 4.81 t (1H, OCH, tetrahydropyran, *J* 6.4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.580 (C^6), 19.117 (CH_2, tetrahydropyran), 25.540 (CH_2, tetrahydropyran), 30.369 (CH_2, tetrahydropyran), 30.927 (C^5), 54.313 (C^1), 61.925 (CH_2, tetrahydropyran), 63.793 (C^4), 80.967 (C^2), 87.074 (C^3). Found, %: C 66.66; H 9.09. $C_{11}H_{18}O_3$. Calculated, %: C 66.39; H 8.96.

4-(Tetrahydro-2*H*-pyran-2-yloxy)1phenylbut-2-yn-1-ol (IXc). Yield 35.0%, bp 108–112°C (3 mm Hg), R_f 0.47 (diethyl ether–hexane, 3 : 1). IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1570, 1550, 720, 680 (monosubstituted benzene ring), 1240, 1160, 1100, 1060, 1040, 1000 (C–O, C–O–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.40–2.00 m (6H, $CH_2CH_2CH_2$, tetrahydropyran), 2.42 br.s (1H, C^1–OH), 3.48 t and 3.92 t (2H, OCH_2, tetrahydropyran, *J* 6.5), 4.50 d and 4.78 d (2H, H^4, *J* 12.0), 4.68 s (1H, H^1), 4.72 t (1H, OCH, tetrahydropyran, *J* 6.5), 7.20–7.40 m (5H, C_6H_5). Found, %: C 73.27; H 7.21. $C_{15}H_{18}O_3$. Calculated, %: C 73.17; H 7.31.

Diols Ib, Ic, Ie. A mixture of 10.0 mmol of the corresponding compound **IXa**, **IXb**, **IXc**, 31 mL of methanol, 37 mL of diethyl ether, 3.1 mL of water, and 130 mg of *p*-toluenesulfonic acid was heated with stirring for 2–3 h. Then methanol was distilled off, and the residue was treated with a saturated potassium carbonate solution. The reaction product was extracted with diethyl ether, and the extract was dried over magnesium sulfate.

Pent-2-yne-1,4-diol (Ib) [13]. Yield 45.0%, bp 113–114°C (2 mm Hg). IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1130, 1060, 1020 (C–O). ^{1}H NMR (DMSO-d_6), δ, ppm (*J*, Hz): 1.31 t (3H, H^5, *J* 6.6), 3.39 br.s (2H, C^1OH, C^4OH), 4.05 s (2H, H^1), 4.33 q (1H, H^4, *J* 6.6). ^{13}C NMR (DMSO-d_6), δ_C, ppm: 24.183 (C^5), 48.964 (C^1), 56.172 (C^4), 81.870 (C^2), 87.096 (C^3).

Hex-2-yn-1,4-diol (Ic). Yield 41.0%, bp 109–112°C (1 mm Hg) [14]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1130, 1060, 1020 (C–O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.98 t (3H, H^6, *J* 6.5), 1.70 q (2H, H^5, *J* 6.5), 2.45 br.s (2H, C^1OH, C^4OH), 4.26 s (2H, H^1), 4.32 t (1H, H^4, *J* 6.5).

1-Phenylbut-2-yne-1,4-diol (Ie). Yield 40.8%, mp 86°C (hexane) [15]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 3040, 3020, 1580, 1560, 720, 680 (monosubstituted benzene ring), 2200 (C≡C), 1100, 1050, 1000 (C–O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.18 br.s (2H, C^1OH, C^4OH), 4.13 s (2H, H^4), 5.40 s (1H, H^1), 7.30–7.50 m (5H, C_6H_5).

4-Methylhex-2-yne-1,4-diol (Ih) was prepared analogously from the Grignard reagent prepared from

0.2 g-atom of magnesium, 200 mmol of propyl bromide, 100 mmol prop-2-yn-1-ol **V**, 50 mL of anhydrous ether and 100 mmol of methyl ethyl ketone in 45 mL of anhydrous benzene. Yield 5.17 g (40.4%), bp 120–124°C (1 mm Hg) [16]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1080, 1060 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.36 t (3H, H^6, *J* 6.5), 1.41 s (3H, C^4CH_3), 1.42–1.72 m (2H, H^5), 2.84 br.s (2H, C^1OH, C^4OH), 4.35 s (2H, H^1).

Alkynols XIIa, XIIb were prepared analogously from the Grignard reagent obtained from 0.118 g-atom of magnesium and 118 mmol of ethyl bromide **XIa** or bromobenzene **XIb**, respectively, in 70 mL of anhydrous diethyl ether and 59.2 mmol of propiolic aldehyde [17] in 15 mL of anhydrous THF.

Pent-1-yn-3-ol (XIIa). Yield 42.5%, bp 68–70°C (98 mm Hg) [18]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 3280 (≡CH), 2100 (C≡C), 1150 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.02 t (3H, H^5, *J* 6.6), 1.50–1.80 m (2H, H^4), 2.15 br.s (1H, OH), 2.38 s (1H, H^1), 4.30–4.38 m (2H, H^3).

1-Phenyl-2-yn-1-ol (XIIb). Yield 58.1%, bp 78–80°C (1 mm Hg) [18]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 3280 (≡CH), 3030, 1580, 1520, 720, 680 (monosubstituted benzene ring), 2100 (C≡C), 1150 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.16 s (1H, H^3), 3.55–3.70 m (1H, H^1), 4.12 br.s (1H, OH), 7.09–7.22 m (5H, C_6H_5).

Diols If, Ij were prepared analogously from the Grignard reagent obtained from 0.04 g-atom of magnesium and 40.4 mmol of ethyl bromide, 2.20 mmol pent-1-yn-3-ol **XIIa** or 1-phenylprop-2-yn-1-ol **XIIb** in 90 mL of anhydrous diethyl ether and 2.20 mmol of propionic aldehyde.

Oct-4-yne-3,6-diol (Ie). Yield 30.0%, bp 111–114°C (3 mm Hg) [19]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1080, 1050 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.02 t (6H, H^1, H^8, *J* 6.5), 1.60–1.80 m (4H, H^2, H^7), 2.24 br.s (2H, C^3OH, C^6OH), 4.37 t (2H, H^3, H^6, *J* 6.5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 9.580 (C^1, C^8), 31.033 (C^2, C^7), 63.785 (C^3, C^6), 86.652 (C^4, C^5).

1-Phenylhex-2-yne-1,4-diol (Ik). Yield 29.0%, bp 158–160°C (1 mm Hg) [20]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 3040, 3020, 1580, 1510, 730, 680 (monosubstituted benzene ring), 2200 (C≡C), 1080, 1050 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.02 t (3H, H^6, *J* 6.5), 1.68–1.79 m (2H, H^5), 2.64 br.s (2H, C^1OH, C^4OH), 4.28 t (1H, H^4, *J* 6.5), 5.42 s (1H, H^1), 7.30–7.56 m (5H, C_6H_5).

2-Methylhept-3-yne-2,5-diol (Ig) was prepared analogously from the Grignard reagent obtained from 0.150 g-atom of magnesium, 150 mmol of propyl bromide, 75 mmol of 3-methylbut-1-yn-3-ol **VI** in 30 mL of anhydrous diethyl ether and 75 mmol of butyraldehyde. Yield 5.6 g (47.86%), bp 123–125°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1080, 1050 (C–O). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.93 t (3H, H^8, *J* 6.5), 1.39 s (6H, H^1, C^2CH_3), 1.44–1.72 m (4H, H^6, H^7), 3.01 br.s (2H, C^2OH, C^5OH), 3.90 t (1H, H^5, *J* 6.5), 4.90 br.s (1H, C^5OH). Found, %: C 69.12; H 10.11. $C_9H_{16}O_2$. Calculated, %: C 69.23; H 10.25.

Hex-1-yn-3-ol (XIII). A Claisen flask charged with a mixture of 7.7 g (75 mmol) of 2-methylhept-3-yne-2,5-diol **Ig** and 1.5 g (10.8 mmol) of dry potassium carbonate was placed in a preheated (150°C) bath of Wood's metal. The released acetone was slowly distilled off at normal pressure, and then the fraction with bp 107–122°C (45–50 mm Hg) was isolated. This fraction was redistilled to yield 2.6 g (53.06%) of hex-1-yn-3-ol **XIII**, bp 66–67°C (38 mm Hg) [18]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 3280 (≡CH), 2100 (C≡C), 1150 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 t (3H, H^6, *J* 6.7), 1.15–1.30 m (2H, H^5), 1.32–1.52 m (2H, H^4), 1.90 s (1H, H^1), 3.58 t (1H, H^3, *J* 6.8), 4.02 br.s (1H, OH).

Dec-5-yne-4,7-diol (Ii) was prepared similarly from the Grignard reagent obtained from 1.44 g (0.060 g-atom) of magnesium, 7.38 g (60 mmol) of propyl bromide, 2.60 g (26 mmol) of hex-1-yn-3-ol **XIII** and 2.16 g (30 mmol) of butyraldehyde in 55 mL of anhydrous diethyl ether. Yield 2.2 g (49.80%), bp 143–148°C (1 mm Hg) [21]. IR spectrum, ν, cm^{-1}: 3300–3500 (OH), 2200 (C≡C), 1050, 1080 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 t (6H, H^1, H^{10}, *J* 6.5), 1.35–1.75 m (8H, H^2, H^3, H^8, H^9), 2.46 br.s (2H, $C^{4-}OH$, C^7OH), 4.45–4.55 m (2H, H^4, H^7).

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