

Hypohalogenation of Vinyl- and Allylacetylenes and Some Chemical Transformations of the Products

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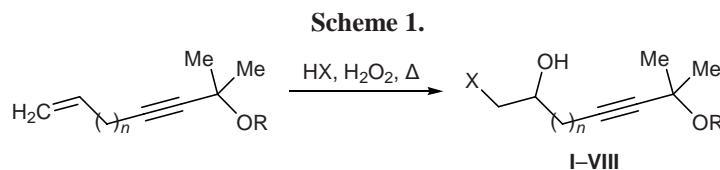
Abstract—Hypohalogenation of 2-methylhex-5-en-3-yn-2-ol, 2-methylhept-6-en-3-yn-2-ol, and their methyl ethers at 303–328 K with hydrochloric or hydrobromic acid in the presence of hydrogen peroxide involves only the double bond to produce the corresponding halohydrins in fairly high yields. Kinetic parameters of these reactions were determined, and the allylacetylenic alcohol and its methyl ether were found to be more reactive than their vinylacetylenic analogs. Acetylenic halohydrins and oxiranes derived therefrom were shown to be quite reactive compounds which may be used as building blocks in organic synthesis.

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Functionally substituted enynes are important building blocks in the synthesis of a series of biologically active compounds and analogs of natural products [1–3] such as pheromones, hormones, and prostaglandins [4–6]. In the recent years, enynes were generally synthesized by reactions of terminal alkynes with alkenyl halides in the presence of transition metal complexes [7–9]. Cross-coupling reactions of haloenynes, including those containing heteroelements, with various terminal alkynes were studied in [10–13]. Analysis of published data shows that allylacetylene derivatives have been studied to a much lesser extent than their vinylacetylene analogs. In particular, only a few data are available on the relative reactivities of vinyl- and allylacetylenic systems toward nucleophilic and electrophilic reagents (except for [2+1]- and [4+2]-cycloadditions) [14–16]. Undoubtedly, such studies would be important from both theoretical and practical viewpoints [17–20]. In continuation of our studies on the reactivity of conjugated

and nonconjugated enyne systems in various transformations [14–16, 21, 22], in the present work we examined hypohalogenation of vinyl- and allylacetylenic alcohols, as well as chemical transformations of the halohydrins thus obtained, with a view to synthesize new functionally substituted derivatives, specifically oxiranes having an alkynyl group.

We found that 2-methylhex-5-en-3-yn-2-ol, 2-methylhept-6-en-3-yn-2-ol, and their methyl ethers smoothly react at 303–328 K with HOCl and HOBr generated *in situ* from hydrochloric or hydrobromic acid and hydrogen peroxide (Scheme 1). The resulting acetylenic chloro- and bromohydrins **I–VIII** were characterized by elemental analyses, physical constants, and IR and ¹H NMR spectra. Apart from absorption bands due to stretching vibrations of C–H bonds and molecular backbone, the IR spectra of **I–VIII** contained bands in the regions 3360–3400, 2230–2250, 1120–1150, and 750–600 cm⁻¹, which were assigned to stretching vibrations of O–H, C≡C,



I–IV, $n = 0$; **V–VIII**, $n = 1$; **I, V**, X = Cl, R = H; **II, VI**, X = Cl, R = Me; **III, VII**, X = Br, R = H; **IV, VIII**, X = Br, R = Me.

C–O–C, and C–Br (C–Cl) bonds, respectively. No absorption typical of double C=C bond ($1630\text{--}1650\text{ cm}^{-1}$) and C–H bonds in terminal =CH₂ group ($3095, 1420, 915\text{ cm}^{-1}$) were present [23, 24]. In the ¹H NMR spectra of compounds **I–VIII**, protons in the geminal methyl groups resonated as a singlet at δ 1.30 ppm, signal from the hydroxy proton appeared as δ 3.85 ppm, and methoxy protons gave rise to a signal at δ 3.20 ppm. Protons in the halohydrin fragment CH₂–CH appeared as multiplets at δ 3.35–3.55 (CH₂Hlg) and δ 3.75–4.00 ppm (CH) [24, 25].

In order to estimate the relative reactivities of vinyl- and allylacetylenic alcohols and their methyl ethers in the hypohalogenation reaction and find optimal conditions for the preparation of acetylenic halohydrins, we examined the effects of different parameters on the yields of compounds **I–VIII**. It turned out that their yields depend on the temperature and hydrohalic acid concentration (Tables 1, 2). It is seen that raising the temperature from 303 to 328 K increases the yield of **I–VIII** by 13–16%. The reaction direction and product yield essentially depend on the hydrohalic acid (HCl, HBr) concentration (Table 2). Fairly high yields (up to 94%) are attained with the use of 6–10% hydrochloric acid. Further increase in the acid concentration in the range from 15 to 35 wt % leads to reduced yield (39.6% for compound **II**). Analogous results were obtained in experiments with hydrobromic acid. High yields of bromohydrins were obtained with 6% hydrobromic acid. In more concentrated hydrobromic acid, the yield of bromohydrins decreases to 43.5%, presumably due to increased contribution of the process leading to formation of molecular halogens (Scheme 2). Electrophilic addition of the latter at the vinyl or allyl double bond gives the corresponding dichloro or dibromo derivatives. In fact, the formation of dihalogen derivatives **IX–XVI** was detected in the reactions performed with 36% hydrochloric acid and 43% hydrobromic acid.

We also studied the kinetics of the above reactions and determined their activation parameters with a view

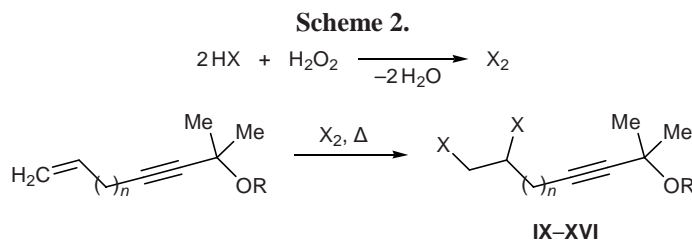
Table 1. Temperature effect on the yield of halohydrins **I–VIII**; substrate–HX–H₂O₂ ratio 1:1.2:1.2; HCl concentration 10%, HBr concentration 6%; reaction time 7.5 h; rate of addition of H₂O₂ 10 g/h

| Temperature, K | Yield, % | | | | | | | |
|----------------|----------|-----------|------------|-----------|----------|-----------|------------|-------------|
| | I | II | III | IV | V | VI | VII | VIII |
| 303 | 72.3 | 77.6 | 68.8 | 71.2 | 76.8 | 81.4 | 74.5 | 77.7 |
| 313 | 88.5 | 90.3 | 85.7 | 89.3 | 92.5 | 93.5 | 90.6 | 91.6 |
| 318 | 92.6 | 92.8 | 90.6 | 90.8 | 95.4 | 94.3 | 92.5 | 92.8 |
| 328 | 94.3 | 93.4 | 92.8 | 92.5 | 96.3 | 95.2 | 94.3 | 94.1 |

Table 2. Effect of hydrochloric acid concentration on the yield of chlorohydrins **I–IV**; substrate–HCl–H₂O₂ ratio 0.2:0.22:0.24, temperature 313 K, rate of addition of H₂O₂ 10 g/h, reaction time 8 h

| Concentration of HCl, % | Yield, % | | | |
|-------------------------|----------|-----------|------------|-----------|
| | I | II | III | VI |
| 6.0 | 78.6 | 75.2 | 80.5 | 77.4 |
| 10 | 89.6 | 90.3 | 85.7 | 89.3 |
| 15 | 67.5 | 64.6 | 72.8 | 68.7 |
| 25 | 50.6 | 48.2 | 65.7 | 52.6 |
| 36 | 44.3 | 39.6 | 50.5 | 46.7 |

to estimate the contribution of electronic factors to the reactivity of conjugated and nonconjugated enynes in the addition of HOCl and HOBr at the double bond. The rate constants were calculated using kinetic equations for bimolecular reactions [26]. All the examined enynes showed linear dependences between the logarithms of the rate constants and reciprocal temperature (see figure). On the basis of these dependences we determined the thermodynamic parameters of the reactions under study (Table 3). The rate constants for the formation of acetylenic chlorohydrins increase as the temperature rises from 303 to 328 K. The energies of activation for hypohalogenation of 2-methylhex-5-en-3-yn-2-ol and 2-methylhept-6-en-3-yn-2-ol were estimated at 62.0 and 59.3 kJ/mol, and the corresponding

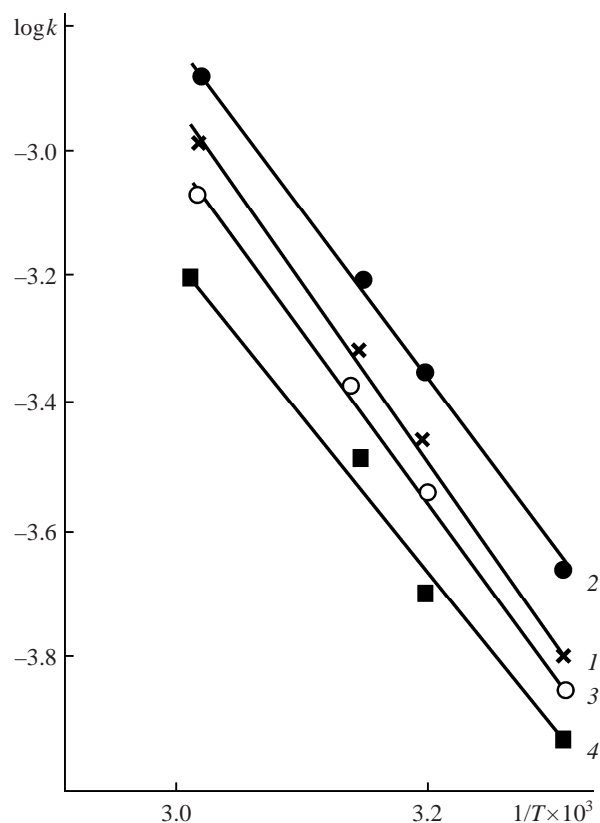


IX–XII, $n = 0$; **XIII–XVI**, $n = 1$; **IX, XIII**, X = Cl, R = H; **X, XIV**, X = Cl, R = Me; **XI, XV**, X = Br, R = H; **XII, XVI**, X = Br, R = Me.

Table 3. Rate constants and activation parameters for hypohalogenation of enynes

| Comp. no. | $k \times 10^3, \text{l mol}^{-1} \text{min}^{-1}$ | | | | $E, \text{kJ/mol}$ | $-\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$ | $\Delta H^\ddagger, \text{kJ/mol}$ | $\Delta G^\ddagger, \text{kJ/mol}$ |
|-----------|--|-------|-------|-------|--------------------|---|------------------------------------|------------------------------------|
| | 303 K | 313 K | 318 K | 328 K | | | | |
| I | 1.594 | 3.513 | 4.878 | 9.297 | 62.0 | 185.3 | 61.4 | 117.5 |
| II | 1.968 | 4.527 | 6.114 | 12.02 | 59.3 | 188.1 | 58.6 | 115.6 |
| V | 1.168 | 1.967 | 3.323 | 6.036 | 53.5 | 183.9 | 52.8 | 108.5 |
| VI | 1.693 | 2.91 | 5.784 | 8.44 | 54.3 | 182.6 | 53.7 | 109 |

values for their methyl ethers were 53.5 and 54.3 $\text{kJ} \times \text{mol}^{-1}$, respectively. The entropies of activation suggest that the transition state in the reaction with alcohols is more ordered (σ 1.39) than in the reaction with methyl ethers (σ 1.79). Reduction of the energy of activation in going from the enyne alcohols to their methyl ethers is compensated by reduction in the entropy of activation. Thus comparison of the rate constants and thermodynamic parameters shows that 2-methylhept-6-en-3-yn-2-ol and its methyl ether are more reactive than their vinylacetylenic analogs.

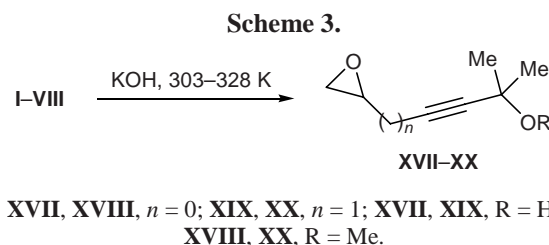


Plots of the logarithms of rate constants versus reciprocal temperature for hypohalogenation of (1) 2-methylhex-5-en-3-yn-2-ol, (2) 2-methylhept-6-en-3-yn-2-ol, (3) 5-methoxy-5-methylhex-1-en-3-yne, and (4) 6-methoxy-6-methylhept-1-en-4-yne.

Development of a convenient method for the synthesis of acetylenic mono- and diepoxy derivatives is an important problem from the practical viewpoint, for such compounds are widely used as monomers for epoxy resins and intermediate products in organic synthesis and synthesis of polymers [27–29]. As shown in [30], alkynyl-substituted oxiranes can be synthesized in two steps, the first of which is condensation of a chloro ketone with an acetylenic alcohol, and the second is alkaline treatment of the condensation product (the corresponding chlorohydrin). The most widely used method for the preparation of mono- and diepoxy derivatives is based on oxidation of appropriate unsaturated substrates with peroxy acids [31]. However, introduction of a second or third epoxy group into a molecule having a triple $\text{C} \equiv \text{C}$ bond is often accompanied by side processes, and the target product is formed in a very poor yield [31, 32].

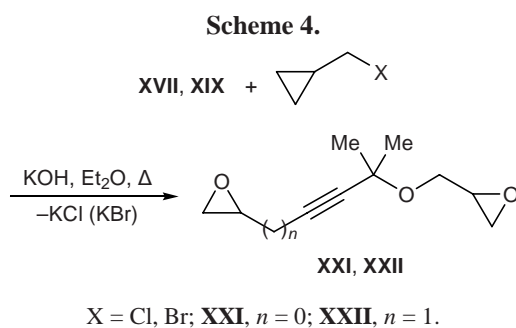
We found that both chloro and bromo alcohols **I–VIII** readily undergo dehydrohalogenation by the action of powdered potassium hydroxide to give the corresponding oxiranes **XVII–XX** in 85.5–96.7% yield (Scheme 3). The yield increases with rise in temperature from 303 to 318 K and attains 91.3 (**XVII**), 95 (**XVIII**), 96.3 (**XIX**), and 97.4% (**XX**) (Table 4). Raising the temperature above 318 K is not advisable, for the dehydrohalogenation process is accompanied by opening of the oxirane ring with formation of tars, and the yield of compounds **XVII–XX** decreases.

The structure of oxirane derivatives **XVII–XX** was confirmed by their IR and ^1H NMR spectra. The oxirane ring in compounds **XVII–XX** is characterized



by IR absorption bands at 915, 3060, and 1260–1235 cm^{-1} , belonging to vibrations of C–H bonds at the oxirane ring. According to the procedure described in [24] we determined the epoxide number for each compound: 12.2 (**XVII**), 12.0 (**XVIII**), 11.0 (**XIX**), and 10.9 (**XX**). In the ^1H NMR spectra of **XVII–XX**, protons of the CH_2 group in the oxirane ring gave two signals: a doublet at δ 2.5 ppm and a triplet at δ 2.65 ppm. The upfield signal was split due to coupling with the OCH proton (δ 3.0 ppm) with a constant J of 2.5 Hz, and the corresponding coupling constant for the downfield signal was $J = 5.0$ Hz. The geminal coupling constant for the CH_2 protons coincided with the larger vicinal constant ($^2J = 5.0$ Hz).

Chemical transformations of epoxy acetylenic compounds **XVII–XX** attract interest from both synthetic and practical viewpoints. We tried to synthesize acetylenic compounds having two oxirane rings via reaction of **XVII** and **XIX** with halomethyloxiranes. The reactions were carried out in one step: epoxy acetylenic alcohols were used without isolation from the reaction mixture. Dehydrohalogenation was accomplished by the action of potassium hydroxide in anhydrous diethyl ether, and the corresponding diepoxy derivatives **XXI** and **XXII** were obtained in 60–70% yield (Scheme 4).



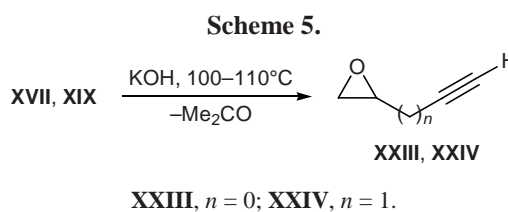
Compounds **XXI** and **XXII** displayed in the IR spectra absorption bands typical of oxirane rings (3065, 1248, 915 cm^{-1}) and disubstituted acetylenic bond (2230–2250 cm^{-1}), whereas no absorption assignable to hydroxy group was present. Their ^1H NMR spectra lacked signal at δ 3.85 ppm, typical of hydroxy proton. The epoxide numbers of compounds **XXI** and **XXII** were 17.1 and 16.0, respectively.

Epoxyalkynols **XVII** and **XIX** readily underwent the reverse Favorskii reaction in the presence of powdered potassium hydroxide at 100–110°C. Elimination of acetone molecule gave terminal epoxyalkynes **XXIII** and **XXIV** (Scheme 5). The IR spectra of

Table 4. Temperature effect on the yield of epoxy derivatives **XVII–XX**

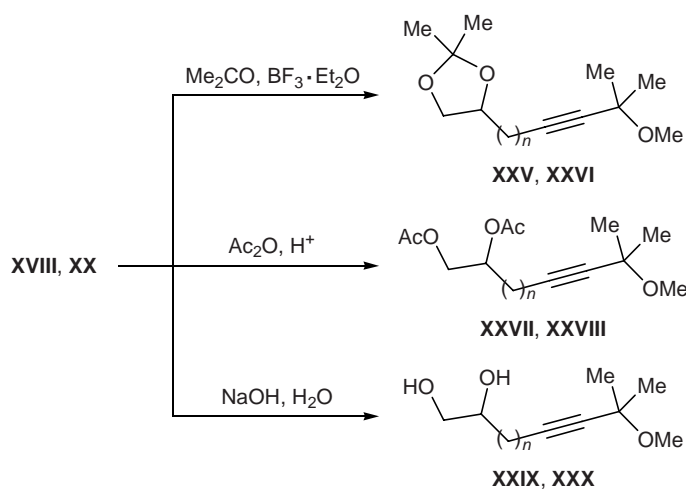
| Temperature, K | Yield, wt % | | | |
|----------------|-------------|--------------|------------|-----------|
| | XVII | XVIII | XIX | XX |
| 303 | 70 | 68.5 | 72.5 | 71.8 |
| 313 | 90.1 | 96.7 | 85.5 | 89.8 |
| 318 | 91.3 | 95.0 | 96.3 | 97.4 |
| 328 | 82.2 | 84.3 | 85.6 | 88.5 |

XXIII and **XXIV** contained no hydroxy group absorption, but strong bands typical of terminal triple $\text{C}\equiv\text{C}$ bond were present (2125 and 3310 cm^{-1}). In the ^1H NMR spectra of these compounds we observed no signals assignable to geminal methyl groups and hydroxy proton; instead, the $\equiv\text{C}\text{--H}$ signal appeared as a triplet at δ 2.21–2.24 ppm.



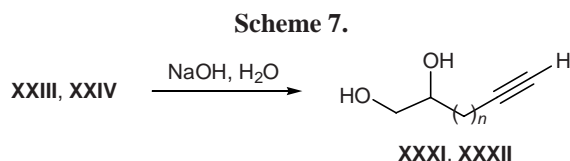
By reactions of epoxyalkynyl methyl ethers **XVIII** and **XX** with nucleophilic reagents we obtained various functional derivatives of the acetylene series. Treatment of **XVIII** and **XX** with acetone in the presence of boron trifluoride–ether complex resulted in formation of 2,2-dimethyl-1,3-dioxolanes **XXV** and **XXVI**, respectively. Compounds **XVIII** and **XX** readily reacted with acetic anhydride in the presence of sulfuric or sulfonic acid to produce diacetates **XXVII** and **XXVIII**. Alkaline hydrolysis of **XVIII** and **XX**, as well as of **XXVII** and **XXVIII**, gave diols **XXIX** and **XXX** (Scheme 6). The structure of compounds **XXV–XXX** was confirmed by the IR and ^1H NMR spectra. The absence in their IR spectra of absorption bands at 3065 and 915 cm^{-1} , which are typical of vibrations of CH_2 group in oxirane ring and asymmetric stretching vibrations of oxirane ring, respectively, indicated that the above reactions involved opening of the oxirane ring. On the other hand, strong absorption bands at 1250 and 1745 cm^{-1} were observed due to acetoxy groups. Absorption bands at 3400 and 1000–1170 cm^{-1} in the IR spectra of **XXIX** and **XXX** were assigned to stretching vibrations of associated OH groups and stretching C–O and bending O–H vibrations.

Scheme 6.



XXV, XXVII, XXIX, $n = 0$; XXVI, XXVIII, XXX, $n = 1$.

Hydrolysis of terminal epoxyalkynes **XXIII** and **XXIV** in aqueous sodium hydroxide gave 85–89% of diols **XXXI** and **XXXII** (Scheme 7). The IR and ^1H NMR spectra of **XXXI** and **XXXII** showed the absence of oxirane ring and the presence of terminal acetylenic bond and hydroxy group in their molecules.



XXXI, $n = 0$; XXXII, $n = 1$.

Thus the results of our study demonstrate that acetylenic chloro- and bromohydrins **I–VIII** can be used as starting compounds in the synthesis of new epoxy and other functionalized acetylene derivatives.

EXPERIMENTAL

The IR spectra were recorded in the range from 400–3600 cm^{-1} on a UR-20 spectrometer from neat substances (films). The ^1H NMR spectra were measured on Tesla BS-487B (80 MHz) and Tesla BS-467 instruments (60 MHz) from solutions in carbon tetrachloride using hexamethyldisiloxane as internal reference. The purity of the products was checked by TLC (Silufol UV-254 plates; benzene–diethyl ether, 3:1 to 5:1; development with iodine vapor) and by GLC using an LKhM-8 MD-5 chromatograph equipped with a thermal conductivity detector [200 \times 0.4-cm column packed with 0.5 wt % of poly(dimethylsiloxane) on

NaCl; oven temperature 140°C; carrier gas nitrogen, flow rate 60 ml/min]. The rate constants and activation parameters were calculated using kinetic equations for bimolecular reactions [23] on the basis of the kinetic data measured by GLC. Kinetic experiments were carried out in the temperature range from 303 to 328 K with equimolar amounts of the components, which ruled out side processes.

Acetylenic halohydrins I–VIII (*general procedure*). The reactions were performed maintaining the temperature with an accuracy of $\pm 0.2^\circ\text{C}$. A flask was charged at a specified temperature with 0.2–0.4 mol of 6% hydrobromic acid or 6–10% hydrochloric acid and 0.2 mol of 2-methylhex-5-en-3-yn-2-ol, 2-methylhept-6-en-3-yn-2-ol, or the corresponding methyl ether. The mixture was stirred, and 0.22 mol of a 26–30% aqueous solution of hydrogen peroxide was added from a dropping funnel at a rate of 10 g/h. The mixture was stirred for 6.5–8.5 h until complete disappearance of H_2O_2 and HOCl or HOBr (according to the permanganatometric or iodometric titration data). The resulting chloro- and bromohydrins were converted without isolation into the corresponding epoxy derivatives by adding potassium hydroxide to the reaction mixture. Individual compounds **I–VIII** were isolated as follows. The organic phase was separated, the aqueous phase was extracted with diethyl ether (2 \times 50 ml), the extracts were combined with the organic phase, neutralized by treatment with a 10% solution of sodium carbonate, and dried over magnesium sulfate, the solvent was removed, and the residue was distilled under reduced pressure.

1-Chloro-5-methylhex-3-yne-2,5-diol (I). Yield 72%, bp 109–110°C (5 mm), $n_D^{20} = 1.4895$, $d_4^{20} = 1.1326$. Found, %: C 51.60; H 6.71; Cl 21.96. $C_7H_{11}ClO_2$. Calculated, %: C 51.70; H 6.82; Cl 21.80.

1-Chloro-5-methoxy-5-methylhex-3-yn-2-ol (II). Yield 78%, bp 82–83°C (5 mm), $n_D^{20} = 1.4670$, $d_4^{20} = 1.0885$. Found, %: C 54.53; H 7.45; Cl 20.01. $C_8H_{13}ClO_2$. Calculated, %: C 54.39; H 7.41; Cl 20.07.

1-Bromo-5-methylhex-3-yne-2,5-diol (III). Yield 69%, bp 114–115°C (2.5 mm), $n_D^{20} = 1.5221$, $d_4^{20} = 1.4714$. Found, %: C 40.52; H 5.45; Br 38.52. $C_7H_{11}BrO_2$. Calculated, %: C 40.60; H 5.36; Br 38.60.

1-Bromo-5-methoxy-5-methylhex-3-yn-2-ol (IV). Yield 71%, bp 89–90°C (2 mm), $n_D^{20} = 1.4990$, $d_4^{20} = 1.3685$. Found, %: C 43.53; H 5.81; Br 36.20. $C_7H_{11}BrO_2$. Calculated, %: C 43.46; H 5.93; Br 36.14.

7-Chloro-2-methylhept-3-yne-2,6-diol (V). Yield 77%, bp 121–122°C (5 mm), $n_D^{20} = 1.4755$, $d_4^{20} = 1.1462$. Found, %: C 54.31; H 7.32; Cl 20.22. $C_8H_{13}ClO_2$. Calculated, %: C 54.39; H 7.41; Cl 20.07.

1-Chloro-6-methoxy-6-methylhept-4-yn-2-ol (VI). Yield 81%, bp 95–96°C (5 mm), $n_D^{20} = 1.4540$, $d_4^{20} = 1.0994$. Found, %: C 56.59; H 7.95; Cl 18.79. $C_9H_{15}ClO_2$. Calculated, %: C 56.69; H 7.92; Cl 18.59.

7-Bromo-2-methylhept-3-yne-2,6-diol (VII). Yield 75%, bp 126–127°C (2 mm), $n_D^{20} = 1.5075$, $d_4^{20} = 1.3834$. Found, %: C 43.32; H 5.85; Br 36.26. $C_8H_{13}BrO_2$. Calculated, %: C 43.46; H 5.93; Br 36.14.

1-Bromo-6-methoxy-6-methylhept-4-yn-2-ol (VIII). Yield 78%, bp 99–100°C (2 mm), $n_D^{20} = 1.4870$, $d_4^{20} = 1.2906$. Found, %: C 45.85; H 6.52; Br 33.83. $C_9H_{15}BrO_2$. Calculated, %: C 45.97; H 6.43; Br 33.98.

Dichloro and dibromo derivatives IX–XVI (general procedure). Hydrogen peroxide was added at a rate of 10g/h to a mixture of 0.1 mol of compound I–VIII and 0.22 mol of 43% hydrobromic acid or 36% hydrochloric acid. The mixture was stirred for 4 h at 313 K, the heavy organic layer was separated from the aqueous layer, and compounds IX–XVI were isolated by vacuum distillation.

5,6-Dichloro-2-methylhex-3-yn-2-ol (IX). Yield 78%, bp 112.5–113.5°C (4 mm), $n_D^{20} = 1.5312$, $d_4^{20} = 1.2888$. Found, %: C 46.56; H 5.42; Cl 39.23. $C_7H_{10}Cl_2O$. Calculated, %: C 46.43; H 5.57; Cl 39.16.

1,2-Dichloro-5-methoxy-5-methylhex-3-yne (X). Yield 80%, bp 86–87°C (4 mm), $n_D^{20} = 1.5087$, $d_4^{20} = 1.2071$. Found, %: C 49.38; H 6.11; Cl 36.24. $C_8H_{12}Cl_2O$. Calculated, %: C 49.25; H 6.20; Cl 36.35.

5,6-Dibromo-2-methylhex-3-yn-2-ol (XI). Yield 82%, bp 116–117°C (2 mm), $n_D^{20} = 1.5637$, $d_4^{20} = 1.7857$. Found, %: C 31.26; H 3.61; Br 59.36. $C_7H_{10}Br_2O$. Calculated, %: C 31.14; H 3.73; Br 59.20.

1,2-Dibromo-5-methoxy-5-methylhex-3-yne (XII). Yield 84%, bp 95–96°C (2.5 mm), $n_D^{20} = 1.5412$, $d_4^{20} = 1.6582$. Found, %: C 33.95; H 4.12; Br 56.20. $C_8H_{12}Br_2O$. Calculated, %: C 33.83; H 4.26; Br 56.28.

6,7-Dichloro-2-methylhept-3-yn-2-ol (XIII). Yield 80%, bp 117–118°C (2 mm), $n_D^{20} = 1.5174$, $d_4^{20} = 1.2285$. Found, %: C 49.18; H 6.27; Cl 36.47. $C_8H_{12}Cl_2O$. Calculated, %: C 49.25; H 6.20; Cl 36.35.

6,7-Dichloro-2-methoxy-2-methylhept-3-yne (XIV). Yield 82%, bp 94–95°C (2 mm), $n_D^{20} = 1.4950$, $d_4^{20} = 1.1518$. Found, %: C 51.76; H 6.65; Cl 33.83. $C_9H_{14}Cl_2O$. Calculated, %: C 51.69; H 6.75; Cl 33.91.

6,7-Dibromo-2-methylhept-3-yn-2-ol (XV). Yield 83%, bp 125–126°C (2 mm), $n_D^{20} = 1.5510$, $d_4^{20} = 1.6810$. Found, %: C 33.74; H 4.18; Br 56.36. $C_8H_{12}Br_2O$. Calculated, %: C 33.83; H 4.26; Br 56.27.

6,7-Dibromo-2-methoxy-2-methylhept-3-yne (XVI). Yield 86%, bp 104–105°C (2 mm), $n_D^{20} = 1.5270$, $d_4^{20} = 1.5646$. Found, %: C 36.16; H 4.86; Br 53.75. $C_9H_{14}Br_2O$. Calculated, %: C 33.83; H 4.26; Br 56.27.

Epoxy derivatives XVII–XX (general procedure). Compound I–VIII, 0.05 mol, was dissolved in 60 ml of diethyl ether, and powdered potassium hydroxide, 8.4 g (0.15 mol), was added under stirring and cooling (281–283 K). The mixture was stirred for 2 h at 285–287 K and subjected to appropriate treatment. Compounds XVII–XX were isolated by vacuum distillation.

2-Methyl-4-(oxiran-2-yl)but-3-yn-2-ol (XVII). Yield 90%, bp 94–95°C (5 mm), $n_D^{20} = 1.4650$, $d_4^{20} = 1.0745$. Found, %: C 66.50; H 8.01. $C_7H_{10}O_2$. Calculated, %: C 66.64; H 7.98.

2-(3-Methyl-3-methoxybut-1-yn-1-yl)oxirane (XVIII). Yield 97%, bp 66–67°C (5 mm), $n_D^{20} = 1.4520$, $d_4^{20} = 0.9638$. Found, %: C 68.52; H 8.62. $C_8H_{12}O_2$. Calculated, %: C 68.57; H 8.57.

2-Methyl-5-(oxiran-2-yl)pent-3-yn-2-ol (XIX). Yield 86%, bp 100–101°C (5 mm), $n_D^{20} = 1.4610$, $d_4^{20} = 1.0016$. Found, %: C 68.62; H 8.42. $C_8H_{12}O_2$. Calculated, %: C 68.57; H 8.57.

2-(4-Methyl-4-methoxypent-2-yn-1-yl)oxirane (XX). Yield 90%, bp 75–76°C (5 mm), $n_D^{20} = 1.4484$,

$d_4^{20} = 0.9608$. Found, %: C 70.06; H 9.20. $C_9H_{14}O_2$. Calculated, %: C 70.10; H 9.25.

2-[3-Methyl-3-(oxiran-2-ylmethoxy)but-1-yn-1-yl]oxirane (XXI). Diethyl ether, 30 ml, and chloromethyloxirane, 4 g (0.042 mol), or bromomethyloxirane, 5.8 g (0.042 mol), were added under stirring and cooling (281–283 K) to 0.1 mol of compound **XVII**. Powdered potassium hydroxide, 4.7 g, was then added, and the mixture was stirred for 2 h at 285–287 K. After appropriate treatment, compound **XXI** was isolated by vacuum distillation. Yield 61%, bp 97–98°C (1 mm), $n_D^{20} = 1.4912$, $d_4^{20} = 1.2109$. Found, %: C 65.75; H 7.88. $C_{10}H_{14}O_3$. Calculated, %: C 65.91; H 7.74.

2-[4-Methyl-4-(oxiran-2-ylmethoxy)pent-2-yn-1-yl]oxirane (XXII) was synthesized in a similar way from compound **XIX**. Yield 71%, bp 112–113°C (1 mm), $n_D^{20} = 1.4753$, $d_4^{20} = 1.0616$. Found, %: C 67.26; H 8.14. $C_{11}H_{16}O_3$. Calculated, %: C 67.32; H 8.22.

2-Ethynyloxirane (XXIII). A mixture of 6.5 g (0.05 mol) of compound **XVII** and 0.1 g of powdered potassium hydroxide was distilled in a stream of nitrogen at 333–338 K. The mixture was heated in such a way that the products gradually condensed in a pipe coil receiver. We thus obtained an equimolar mixture of acetone and compound **XXIII**. Yield 87%, bp 86–87.5°C, $n_D^{20} = 1.4265$, $d_4^{20} = 0.8935$. Found, %: C 70.65; H 5.80. C_4H_4O . Calculated, %: C 70.57; H 5.92.

2-(Prop-2-yn-1-yl)oxirane (XXIV) was obtained in a similar way from epoxy alcohol **XIX**. Yield 89%, bp 102–103°C, $n_D^{20} = 1.4207$, $d_4^{20} = 0.8610$. Found, %: C 73.28; H 7.30. C_5H_6O . Calculated, %: C 73.14; H 7.37.

4-(3-Methoxy-3-methylbut-1-yn-1-yl)-2,2-dimethyl-1,3-dioxolane (XXV). Compound **XVIII**, 4.6 g (0.032 mol), was added in portions to a mixture of 25 g of acetone and 0.2 ml of boron trifluoride–ether complex. The mixture slightly warmed up. It was left overnight and treated with a saturated solution of potassium carbonate, and the organic phase was separated, dried over magnesium sulfate, and distilled under reduced pressure. Yield 70%, bp 69–70°C (5 mm), $n_D^{20} = 1.4335$, $d_4^{20} = 0.9674$. Found, %: C 66.58; H 9.25. $C_{11}H_{18}O_3$. Calculated, %: C 66.64; H 9.15.

4-(4-Methoxy-4-methylpent-2-yn-1-yl)-2,2-dimethyl-1,3-dioxolane (XXVI) was synthesized in a similar way from compound **XX**. Yield 76%, bp 77–78°C (4 mm), $n_D^{20} = 1.4195$, $d_4^{20} = 0.9173$.

Found, %: C 67.71; H 9.66. $C_{12}H_{20}O_3$. Calculated, %: C 67.89; H 9.50.

5-Methoxy-5-methylhex-3-yne-1,2-diyl diacetate (XXVII). Acetic anhydride, 4.5 g (0.056 mol), was slowly added under stirring at 283 K to a mixture of 20 g of benzene, 7.0 g (0.05 mol) of compound **XVIII**, and 1.5 g of KU-2 cation exchanger (H-form). The addition was accompanied by slight heat evolution. The mixture was stirred for 2.5 h at 285–287 K, the catalyst was filtered off through a Schott filter, the solvent was distilled off from the filtrate, and the residue was distilled under reduced pressure. Yield 77%, bp 104–105°C (1 mm), $n_D^{20} = 1.4840$, $d_4^{20} = 1.1188$. Found, %: C 59.30; H 9.25. $C_{12}H_{18}O_5$. Calculated, %: C 59.49; H 7.49.

6-Methoxy-6-methylhept-4-yne-1,2-diyl diacetate (XXVIII) was synthesized in a similar way from compound **XX**. Yield 81%, bp 112–113°C (1 mm), $n_D^{20} = 1.0933$, $d_4^{20} = 1.0933$. Found, %: C 60.83; H 7.80. $C_{13}H_{20}O_5$. Calculated, %: C 60.92; H 7.87.

Acetylenic diols XXIX–XXXII (general procedure). Compound **XVIII**, **XX**, **XXIII**, or **XXIV**, 0.1 mol, was added to a solution of 2 g of sodium hydroxide in 15 g of water, and the mixture was stirred for 4 h at 323–333 K. The mixture was then saturated with potassium carbonate and extracted with diethyl ether, the extract was dried over calcined potassium carbonate, the solvent was removed, and the residue was distilled under reduced pressure. The product crystallized in the receiver.

5-Methoxy-5-methylhex-3-yne-1,2-diol (XXIX). Yield 82%, mp 43–44°C. Found, %: C 60.63; H 8.97. $C_8H_{14}O_3$. Calculated, %: C 60.74; H 8.92.

6-Methoxy-6-methylhept-4-yne-1,2-diol (XXX). Yield 87%, mp 48–49°C. Found, %: C 62.89; H 9.28. $C_9H_{16}O_3$. Calculated, %: C 62.76; H 9.37.

But-3-yne-1,2-diol (XXXI). Yield 85%, mp 39–40°C. Found, %: C 55.99; H 7.16. $C_4H_6O_2$. Calculated, %: C 55.80; H 7.03.

Pent-4-yne-1,2-diol (XXXII). Yield 90%, mp 44–45°C. Found, %: C 59.82; H 8.20. $C_5H_8O_2$. Calculated, %: C 59.98; H 8.05.

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