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Hypohalogenation of Functionally Substituted Acetylenic Norbornenes

M. G. Veliev[a], O. A. Sadygov[b], M. I. Shatirova[a], and Kh. M. Alimardanov[b]

[a] *Institute of Polymeric Materials, National Academy of Sciences of Azerbaidjan, ul. S. Vurguna 124, Sumgaiyt, Az5004 Azerbaidjan; e-mail: mveliyev@mail.ru*

[b] *Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaidjan, Baku, Azerbaidjan*

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Abstract—Hypohalogenation of norbornenes containing a triple bond and various functional groups in the side chain was performed using mixtures of aqueous solutions of hydrochloric or hydrobromic acid (or sodium or potassium bromide) and hydrogen peroxide. The reaction was found to involve addition of electrophilic reagent generated *in situ* (HOBr or HOCl) at the endocyclic double bond with formation of the corresponding halohydrins. The latter underwent dehydrohalogenation by the action of alklai to give *exo*-5,6-epoxybicyclo[2.2.1]heptane derivatives in high yields. Kinetic relations holding in the hypobromination process were established, and the initial rates and activation parameters were calculated.

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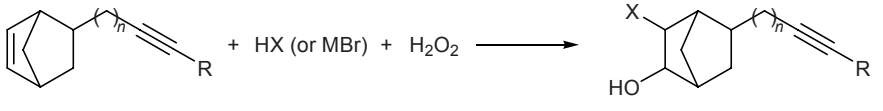
The chemistry of norbornene and its derivatives is now rapidly developing, thus opening new prospects for use of these compounds in organic synthesis [1–3]. It is known that norbornene derivatives are used in perfumery, food industry, and medicine, as well as monomers in the manufacture of valuable polymeric materials and insecticides and pesticides for agriculture [4–6]. However, the synthesis and chemical transformations of bicyclic unsaturated compounds containing a triple bond and various functional groups in the side chain have been reported only in a few publications [7–9]. Due to the presence of double and triple bonds and reactive functional groups such compounds could be brought into diverse chemical transformations [10–13]. In this work we studied hypohalogenation of bicyclo[2.2.1]hept-2-enes having a triple bond in the side chain, kinetic parameters of the process, and transformations of the resulting halohydrins.

We found that acetylenic norbornenes **Ia**–**If** and **IIa**–**IIf** react with hypochlorous and hypobromous acids *in statu nascendi* (HOCl and HOBr were generated in the system HCl or HBr/H_2O_2 or $MBr/H_2O_2/H^+$) at 10–40°C to give the corresponding halohydrins **IIIa**–**IIIf**, **IVa**–**IVf**, **Va**–**Vf**, and **VIa**–**VIf** (Scheme 1). The yields, physical constants, and elemental analyses of compounds **III**–**VI** are given in Experimental. Their structure was proved by IR and ^1H NMR spectroscopy. The IR spectra of **IIIa**–**VI** contained strong absorption bands in the regions of 3450, 3300, 2270, 2230, 2140, 1720, 1155, 805, 750, and 630 cm^{-1} due to stretching and bending vibrations of the O–H, ≡C–H, C≡C, C≡N, C=O, C–O–C, C–Br, and C–Cl bonds [14, 15]. In the upfield region of the ^1H NMR spectra of compounds **III**–**VI** we observed a multiplet at δ 1.32 ppm, corresponding to the *endo*-6-H proton, while the *exo*-6-H signal appeared as a triplet in a weaker field

Scheme 1.



Ia–If, **IIa–IIf** **IIIa–IIIf**, **IVa–IVf**, **Va–Vf**, **VIa–VIf**

III, **V**, X = Cl; **IV**, **VI**; X = Br; R = H (**a**), $HOCMe_2$ (**b**), $MeOCMe_2$ (**c**), $NCCH_2CH_2OCMe_2$ (**d**), $HOCH_2CH_2OCMe_2$ (**e**), $MeCOOCMe_2$ (**f**); **I**, **III**, **IV**, *n* = 0; **II**, **V**, **VI**, *n* = 1; M = Na, K.

Table 1. Yields of halohydrins **III**–**VI** in the hypohalogenation of compounds **Ia**–**If** and **IIa**–**IIf** at different temperatures

Compound no.	Yield, wt %							
	10°C		20°C		30°C		40°C	
	X = Cl	X = Br	X = Cl	X = Br	X = Cl	X = Br	X = Cl	X = Br
IIIa, **IVa**	70.5	72.3	75.3	78.5	80.6	86.5	83.6	91.8
IIIb, **IVb**	72.6	74.5	76.5	81.6	82.6	88.3	87.5	93.2
IIIc, **IVc**	74.2	76.6	78.3	84.5	85.7	89.5	92.6	94.3
IIId, **IVd**	71.5	73.4	75.1	80.2	80.6	85.3	90.5	90.4
IIIe, **IVe**	76.3	77.8	80.3	85.3	86.6	90.5	91.5	95.3
IIIf, **IVf**	74.6	76.0	78.6	83.0	84.7	86.6	89.4	92.1
Va, **VIa**	72.6	74.6	76.5	78.0	85.3	87.5	92.8	94.0
Vb, **VIb**	74.3	76.3	81.6	80.0	88.4	89.0	94.0	95.0
Vc, **VIc**	75.6	77.4	83.0	85.0	87.4	90.7	91.5	94.6
Vd, **VId**	73.8	76.5	77.6	79.0	82.4	84.0	87.5	89.0
Ve, **VIe**	77.5	78.6	86.2	87.3	89.8	92.7	93.7	96.0
Vf, **VIf**	75.8	78.2	84.5	86.0	89.3	91.6	92.6	95.0

(δ 2.09 ppm). The *exo*-5-H proton resonated as a multiplet centered at δ 2.75 ppm. The coupling constants $J_{6,6'}$ = 12.2–12.5, $J_{5,endo\text{-}6}$ = 5.0–5.3, and $J_{5,exo\text{-}6}$ = 9.5–9.7 Hz suggest *endo* configuration of the substituent on C^5 (large value of $J_{5,exo\text{-}6}$ and small value of $J_{5,endo\text{-}6}$). The *anti*-7-H and *syn*-7-H protons gave signals in the upfield region (δ 1.70 ppm). Signals at δ 3.65 and 3.88 ppm were assigned to protons on C^2 and C^3, respectively; the vicinal coupling constant $J_{2,3}$ is 4.5–4.7 Hz. The other proton signals were located at δ, ppm: 2.12 d (1-H), 2.31 m (4-H), 1.95 m (8-H), 2.42 t (9-H) [14, 15].

With a view to find optimal conditions for the synthesis of acetylenic chloro- and bromohydrins of the bicycloheptene series we examined influence of different parameters on the product yields. Such factors as temperature, concentration of hydrohalic acid, and intensity of stirring of the reaction mixture were found to be important. Insofar as acetylenic bicycloheptenes are almost insoluble in water, the reactions were heterogeneous, i.e., HOCl and HOBr were generated in the aqueous phase, while their addition occurred in the organic phase or at the phase boundary. Therefore, all reactions should be performed under vigorous stirring (the rate of stirring was 600–700 rpm). Raising the temperature from 10 to 40°C increased the yield of chlorohydrins **IIIa**–**IIIf** and **Va**–**Vf** from 71 do 92%; the yield of bromohydrins **IVa**–**IVf** and **VIa**–**VIf** also increased from 72 to 96% (Table 1).

The data in Table 1 show that the yields of chloro- and bromohydrins **III** and **IV** (n = 0) are lower by 2–4% than those of their analogs **V** and **VI** with a longer side chain (n = 1). The reaction selectivity and the yield of **III**–**VI** strongly depended on the hydrohalic acid concentration. At low concentration of HCl (10–15%) and HBr (6–10%) the corresponding halohydrins were formed in almost quantitative yield, whereas higher concentration of hydrohalic acids favored formation of dichloro- and dibromobicycloheptane derivatives as by-products. Presumably, increased concentration of HCl and HBr promotes their oxidation to molecular halogens which add at the double bond of the substrate with formation of dihalo derivatives (they will be the subject of our further studies).

We also tried to estimate the reactivity of the bicycloheptene fragment toward HOCl and HOBr, depending on the position and structure of the side-chain acetylenic fragment. For this purpose, we measured the kinetic parameters of the hypobromination process. The initial rates of addition of HOBr at the double bond were calculated from the GLC data on accumulation of the corresponding bromohydrins. The reaction rates were determined by graphical differentiation of the kinetic curves plotted in the coordinates product yield–time using the formula given in [16].

The relation between the logarithm of the initial rate and reciprocal temperature for the examined bicycloheptene series fits the Arrhenius equation

Table 2. Kinetic parameters of hypobromination of compounds **Ia**–**If** and **IIa**–**IIf**

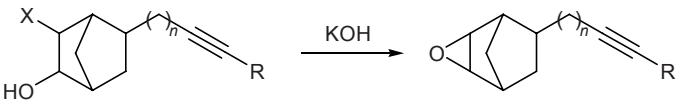
Compound no.	Initial reaction rates $w_0 \times 10^3$, l mol^{-1} min^{-1}				Activation parameters			
	10°C	20°C	30°C	40°C	E, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}$, kJ/mol
Ia	3.52	6.86	10.67	16.73	28.6	28.0	65.3	47.8
IIa	8.43	11.5	17.83	24.83	33.9	33.2	75.5	56.1
Ib	5.25	8.42	13.83	17.82	23.1	23.0	68.5	43.8
IIb	8.2	12.1	18.7	38.3	30.0	29.4	72.0	51.2
Ic	7.63	11.67	18.2	30.1	30.3	29.6	72.0	51.4
IIc	11.9	19.2	31.1	47.7	24.6	24.0	66.4	44.1
Id	6.53	10.3	16.8	23.5	25.2	24.6	66.9	44.9
IId	10.3	16.8	36.2	67.8	34.7	34.1	76.3	57.2
Ie	6.83	8.57	15.3	23.7	23.3	22.6	69.4	43.6
IIe	8.21	12.5	19.8	28.6	30.3	29.4	71.9	51.2
If	5.9	8.48	11.76	18.2	21.5	20.6	61.5	39.2
IIf	8.43	14.3	20.3	50.4	34.3	33.4	77.8	57.0

(Table 2). The initial rates and energies of activation for the formation of bromohydrins having acetylenic bonds in the β-position with respect to the bicyclic fragment are greater than those found for their analogs with a triple bond in the α-position. In the first case, the transition state is more ordered, as follows from the entropy values. Comparison of the initial reaction rates and activation parameters shows that α-acetylenic norbornenes are less reactive than their β-acetylenic analogs.

Both chloro- and bromo-substituted hydroxynorbornanes **III**–**VI** readily underwent dehydrohalogenation by the action of powdered potassium hydroxide. As a result, the corresponding epoxy derivatives **VIIa**–**VIIe** and **VIIIa**–**VIIIe** were obtained in 85–90% yield (Scheme 2). The structure of compounds **VIIa**–**VIIe** and **VIIIa**–**VIIIe** was confirmed by the IR and ^{1}H NMR data. The IR spectra of **VII** and **VIII** lacked absorption at 1635 and 3095 cm^{-1}, which is typical of HC=CH bond, but bands at 850, 910, 1245, and 3060 cm^{-1} were present due to vibrations of bonds in the oxirane ring. In the ^{1}H NMR spectra of these compounds, the *endo*-6-H proton resonated as a multiplet in a strong field, at δ 0.80 ppm, while the *exo*-6-H signal was located in a weaker field, as a multiplet at δ 1.46–1.72 ppm. The 5-H signal was a multiplet at δ 2.15 ppm. The coupling constants for the 5-H and 6-H protons were as follows: $J_{6,6'}$ = 12.2–12.4, $J_{5,6}$ = 10.3–10.5, $J_{5,6'}$ = 4.5–4.8 Hz; these findings unambiguously indicate *endo* orientation of the prop-2-yn-1-yl substituent on C^5. The *syn*-7-H (δ 1.32 ppm, m) and *anti*-7-H protons (δ 0.65 ppm, d) together with 1-H and 4-H give rise to an *ABX* spin system. The 1-H and 4-H signals appeared as an unresolved multiplet centered at δ 2.37 ppm. The 2-H and 3-H protons resonated as a doublet of doublets at δ 2.86 ppm, $J_{2,3}$ = 3.7–3.8 Hz, indicating *exo* orientation of the epoxy group. Compounds **VIIa**, **VIIb**, **VIId**, **VIIIa**, **VIIIb**, and **VIIId** were also synthesized by direct epoxidation of the corresponding norbornenes **Ia**, **Ib**, **Id**, **IIa**, **IIb**, and **IId** with peroxyacetic acid (Scheme 3); in this case, the yield was 78–80%. Samples of **VII** and **VIII** obtained by the two methods were identical in physical properties and spectral parameters.

Hydrolysis of chloro- and bromohydrins **IIIa**–**VIa** in aqueous methanol in the presence of catalytic amounts of $HgSO_4$ and H_2SO_4 gave the corresponding acetyl- and acetonyl-substituted norbornanes **IX**–**XII**

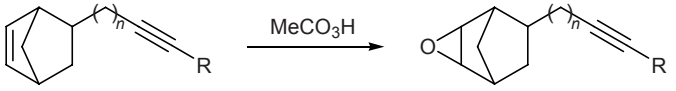
Scheme 2.



IIIa–**IIIe**, **IVa**–**IVe**, **Va**–**Ve**, **VIa**–**VIe** **VIIa**–**VIIe**, **VIIIa**–**VIIIe**

VII, n = 0; **VIII**, n = 1.

Scheme 3.



Ia, **Ib**, **Id**, **IIa**, **IIb**, **IId** **VIIa**, **VIIb**, **VIId**, **VIIIa**, **VIIIb**, **VIIId**

in almost quantitative yield. The subsequent dehydrohalogenation of **IX**–**XII** by the action of powdered potassium hydroxide led to the formation of epoxy ketones **XIII** and **XIV** (Scheme 4) whose structure was confirmed by the IR and ^{1}H NMR spectra.

Compounds **VIIa** and **VIIIa** having a terminal triple bond can be obtained in high yield by treatment of halohydrins **IIIb**–**VIb** with alkali in toluene at 40–50°C, followed by heating at 90–100°C (Scheme 5). Here, elimination of hydrogen halide was accompanied by the reverse Favorsky reaction. It should be noted that raising the temperature to 110–120°C leads to reduced yield of final products **VIIa** and **VIIIa** because of appreciable tarring, while lowering the temperature to 80–90°C also reduces the yield to 50–60% due to deceleration of the reverse Favorsky reaction. Hydrolysis of epoxides **VIIa** and **VIIIa** in 10% sulfuric acid gave acetylenic dihydroxynorbornanes **XV** and **XVI**.

Thus the results of our study showed that hypohalogenation of norbornenes having a triple bond and various functional groups in the side chain involves the endocyclic double bond in the substrate to produce the corresponding halohydrins. These compounds, as well as epoxides and diols derived therefrom, attract interest as intermediate products for the preparation of various polyfunctionalized compounds with practically useful properties.

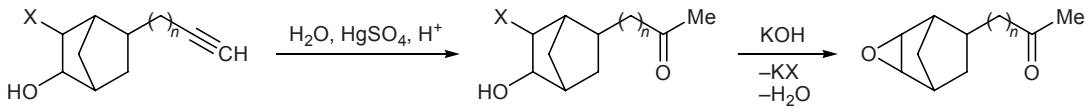
EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on a Tesla BS-487B instrument (80 MHz) from solutions in carbon tetrachloride using hexamethyldisiloxane as internal reference. Gas–liquid chromatography was performed on an LKhM-8MD-5 chromatograph equipped with a thermal conductivity detector and a 200×0.4-cm column packed with 0.5 wt % of poly(dimethylsiloxane) on NaCl; oven temperature 140°C; carrier gas helium, flow rate 60 ml/min. The initial rates and thermodynamic parameters were determined following accumulation of the corresponding bromohydrins; the calculations were performed by known equations [16].

Initial compounds **Ia**–**If** and **IIa**–**IIf** were synthesized by the Diels–Alder reactions of cyclopentadiene with the corresponding enynes [9]; their physical constants were consistent with those given in [7–12].

Halohydrins III–VIa (*general procedure***).** A 26–30% aqueous solution of hydrogen peroxide, 0.22 mol, was added from a dropping funnel at a rate of 10 g/h under stirring to a mixture of 0.2 mol of 6% aqueous HBr (or NaBr + HCl) or 10% hydrochloric acid and 0.2 mol of alkynylnorbornene **Ia**–**If** or **IIa**–**IIf**. The mixture was stirred for 5.5–6.5 h, the organic phase was separated, neutralized, and dried, and the products were isolated by vacuum distillation.

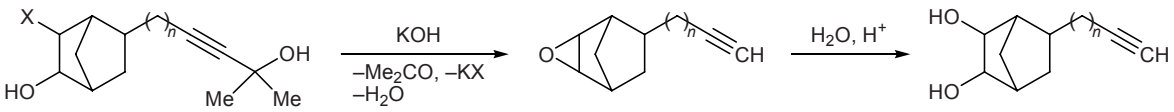
Scheme 4.



IIIa–VIa **IX–XII** **XIII**, **XIV**

IX, **XI**, X = Cl; **X**, **XII**, X = Br; **IX**, **X**, **XIII**, n = 0; **XI**, **XII**, **XIV**, n = 1.

Scheme 5.



IIIb–VIb **VIIa**, **VIIIa** **XV**, **XVI**

VIIa, **XV**, n = 0; **VIIIa**, **XVI**, n = 1; X = Cl, Br.

3-Chloro-5-ethynylbicyclo[2.2.1]heptan-2-ol (IIIa). Yield 13.2 g (75%), bp 85–86°C (10 mm), d_4^{20} = 1.1456, n_D^{20} = 1.5172. IR spectrum, ν, cm^{-1}: 3525 (O–H); 3290, 2140 (C≡CH); 850 (C–Cl), 745. ^{1}H NMR spectrum, δ, ppm: 1.53 t (1H, 1-H), 1.81 t (1H, 4-H), 1.82 d (1H, HC≡), 2.48 d (1H, 5-H), 3.47 d (1H, 2-H), 3.49 d (1H, 3-H), 4.81 br.s (1H, OH). Found, %: C 63.48; H 6.39; Cl 20.64. $C_9H_{11}ClO$. Calculated, %: C 63.35; H 6.50; Cl 20.77.

3-Chloro-5-(3-hydroxy-3-methylbut-1-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (IIIb). Yield 17.5 g (77%), bp 103–104°C (1 mm), d_4^{20} = 12.005, n_D^{20} = 1.5317. IR spectrum, ν, cm^{-1}: 3200–3550 (O–H); 2200 (C≡C); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.52 t (1H, 1-H), 2.47 m (1H, 5-H), 3.47 d (1H, 2-H), 3.49 d (1H, 3-H), 4.81 br.s (1H, OH), 5.46 br.s (1H, OH). Found, %: C 63.18; H 7.32; Cl 15.65. $C_{12}H_{17}ClO_2$. Calculated, %: C 63.01; H 7.49; Cl 15.50.

3-Chloro-5-(3-methoxy-3-methylbut-1-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (IIIc). Yield 18.9 g (78%), bp 109–110°C (1 mm), d_4^{20} = 1.1576, n_D^{20} = 1.5208. IR spectrum, ν, cm^{-1}: 3480 (O–H); 2245 (C≡C); 1125 (C–O–C); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.47 m (1H, 5-H), 3.25 s (3H, OCH_3), 3.47 d (1H, 2-H), 3.49 d (1H, 3-H). Found, %: C 64.29; H 7.80; Cl 14.79. $C_{13}H_{12}ClO_2$. Calculated, %: C 64.32; H 7.89; Cl 14.60.

3-[4-(6-Chloro-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yloxy]propanenitrile (IIId). Yield 21 g (75%), bp 137–138°C (1 mm), d_4^{20} = 1.1852, n_D^{20} = 1.5250. IR spectrum, ν, cm^{-1}: 3360 (O–H); 2235 (C≡C); 2160 (C≡N); 1140 (C–O–C); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.53 t (1H, 1-H), 2.48 d (1H, 5-H), 2.59 d (2H, CH_2CN), 3.46 d (1H, 3-H), 3.58 d (1H, 2-H), 3.75 d (2H, OCH_2), 4.81 br.s (1H, OH). Found, %: C 63.79; H 7.28; Cl 12.42; N 4.83. $C_{15}H_{20}ClNO_2$. Calculated, %: C 63.94; H 7.15; Cl 12.58; N 4.97.

3-Chloro-5-[3-(2-hydroxyethoxy)-3-methylbut-1-yn-1-yl]bicyclo[2.2.1]heptan-2-ol (IIIe). Yield 21.8 g (80%), bp 144–145°C (1 mm), d_4^{20} = 1.2116, n_D^{20} = 1.5346. IR spectrum, ν, cm^{-1}: 3600, 3350 (O–H); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.48 d (1H, 5-H), 3.47–3.49 d.d. (2H, 2-H, 3-H), 3.66 d (2H, OCH_2), 3.71 d.d (2H, CH_2O), 4.79 br.s (1H, OH), 4.81 br.s (1H, 2-OH). Found, %: C 61.78; H 7.91; Cl 13.09. $C_{14}H_{21}ClO_3$. Calculated, %: C 61.65; H 7.71; Cl 13.03.

4-(6-Chloro-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yl acetate (IIIf). Yield 19 g (71%), bp 108–109°C (1 mm), d_4^{20} = 1.1983, n_D^{20} = 1.5213. IR spectrum, ν, cm^{-1}: 3500 (O–H); 2230 (C≡C); 1720, 1080 (COO); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.67 s (6H, CH_3), 2.02 s (3H, $COCH_3$), 2.48 d (1H, 5-H), 3.47–3.49 d.d (2H, 2-H, 3-H). Found, %: C 62.28; H 6.90; Cl 13.18. $C_{14}H_{19}ClO_3$. Calculated, %: C 62.10; H 7.07; Cl 13.09.

3-Bromo-5-ethynylbicyclo[2.2.1]heptan-2-ol (IVa). Yield 16.9 g (79%), bp 94–95°C (10 mm), d_4^{20} = 1.1335, n_D^{20} = 1.5130. IR spectrum, ν, cm^{-1}: 3625, 1100 (O–H); 3300, 2130 (C≡CH); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.83 d (1H, HC≡C), 2.48 m (1H, 5-H), 3.46 t (1H, 3-H), 3.56 t (1H, 2-H). Found, %: C 50.38; H 5.01; Br 37.30. $C_9H_{11}BrO$. Calculated, %: C 50.25; H 5.16; Br 37.15.

3-Bromo-5-(3-hydroxy-3-methylbut-1-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (IVb). Yield 22.3 g (81%), bp 108–109°C (1 mm), d_4^{20} = 1.1616, n_D^{20} = 1.5213. IR spectrum, ν, cm^{-1}: 3620, 3500–3200 (O–H); 2225 (C≡C); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.48 d (1H, 5-H), 3.46 t (1H, 3-H), 3.57 t (1H, 3-H), 4.81 br.s (1H, OH), 5.46 br.s (1H, OH). Found, %: C 52.61; H 6.18; Br 29.40. $C_{12}H_{17}BrO_2$. Calculated, %: C 52.76; H 6.27; Br 29.75.

3-Bromo-5-(3-methoxy-3-methylbut-1-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (IVc). Yield 24.3 g (85%), bp 113–114°C (1 mm), d_4^{20} = 1.1316, n_D^{20} = 1.9164. IR spectrum, ν, cm^{-1}: 3460 (O–H); 2245 (C≡C); 1150 (C–O–C); 750, 680 (CBr). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 3.25 s (3H, OCH_3), 3.45 t (1H, 3-H), 3.57 t (1H, 2-H), 4.81 br.s (1H, OH). Found, %: C 54.21; H 6.79; Br 27.64. $C_{13}H_{19}BrO_2$. Calculated, %: C 54.36; H 6.67; Br 27.82.

3-[4-(6-Bromo-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yloxy]propanenitrile (IVd). Yield 26.1 g (80%), bp 143–144°C (1 mm), d_4^{20} = 1.1590, n_D^{20} = 1.5204. IR spectrum, ν, cm^{-1}: 2245 (C≡C); 2170 (C≡N); 1100 (C–O–C); 750, 680 (CBr). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.48 t (1H, 5-H), 2.58 d (2H, CH_2CN), 3.46 t (1H, 3-H), 3.58 t (1H, 2-H), 3.74 d (2H, OCH_2), 4.81 br.s (1H, OH). Found, %: C 55.08; H 6.30; Br 24.32; N 4.21. $C_{15}H_{20}BrNO_2$. Calculated, %: C 55.22; H 6.18; Br 24.49; N 4.29.

3-Bromo-5-[3-(2-hydroxyethoxy)-3-methylbut-1-yn-1-yl]bicyclo[2.2.1]heptan-2-ol (IVe). Yield 27 g (85%), bp 151–152°C (1 mm), d_4^{20} = 1.1830, n_D^{20} =

1.5280. IR spectrum, ν, cm^{-1}: 3360 (O–H); 2210 (C≡C); 750, 680 (C–Br). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 3.46 t (1H, 3-H), 3.57 t (1H, 2-OH), 3.57 d (2H, OCH_2), 3.71 d (2H, CH_2O), 4.81 br.s (1H, OH). Found, %: C 53.18; H 6.51; Br 25.05. $C_{14}H_{21}BrO_2$. Calculated, %: C 53.0; H 6.67; Br 25.19.

4-(6-Bromo-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yl acetate (IVf). Yield 23.6 g (75%), bp 114–115°C (1 mm), d_4^{20} = 1.1716, n_D^{20} = 1.5113. IR spectrum, ν, cm^{-1}: 3550 (O–H); 2260 (C≡C); 1740, 1135 (COO); 750, 680 (C–Br). ^1H NMR spectrum, δ, ppm: 1.67 s (6H, CH_3), 2.02 s (3H, OCH_3), 3.45 t (1H, 3-H), 3.57 t (1H, 2-H), 4.81 br.s (1H, OH). Found, %: C 53.20; H 6.17; Br 25.46. $C_{14}H_{19}BrO_3$. Calculated, %: C 53.34; H 6.08; Br 25.35.

3-Chloro-5-(prop-2-yn-1-yl)bicyclo[2.2.1]heptan-2-ol (Va). Yield 14 g (77%), bp 96–97°C (5 mm), d_4^{20} = 1.4330, n_D^{20} = 1.5498. IR spectrum, ν, cm^{-1}: 3600 (O–H); 3290, 2120 (C≡CH); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.41 t (1H, 5-H), 1.82 s (1H, HC≡), 1.87–2.12 d.d (2H, CH_2C≡), 3.48 d (1H, 2-H), 3.49 d (1H, 3-H). Found, %: C 65.19; H 7.22; Cl 19.01. $C_{10}H_{13}ClO$. Calculated, %: C 65.04; H 7.09; Cl 19.20.

3-Chloro-5-(4-hydroxy-4-methylpent-2-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (Vb). Yield 19.7 g (82%), bp 118–119°C (1 mm), d_4^{20} = 1.4391, n_D^{20} = 1.5642. IR spectrum, ν, cm^{-1}: 3540 (O–H); 2225 (C≡C); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.52 t (1H, 1-H), 2.07–1.82 d.d (2H, CH_2C≡), 3.47 d (1H, 2-H), 3.49 d (1H, 3-H), 4.81 br.s (1H, OH), 5.46 br.s (1H, OH). Found, %: C 64.21; H 7.78; Cl 14.76. $C_{10}H_{13}ClO$. Calculated, %: C 65.04; H 7.09; Cl 19.20.

3-Chloro-5-(4-methoxy-3-methylpent-2-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (Vc). Yield 21.2 g (83%), bp 122–123°C (1 mm), d_4^{20} = 1.3603, n_D^{20} = 1.5534. IR spectrum, ν, cm^{-1}: 3495 (O–H); 2245 (C≡C); 1150 (C–O–C); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.82–2.08 d.d (2H, CH_2C≡), 3.25 s (3H, OCH_3), 3.47 d (1H, 2-H), 3.49 d (1H, 3-H). Found, %: C 65.35; H 8.39; Cl 13.70. $C_{14}H_{21}ClO_2$. Calculated, %: C 65.49; H 8.25; Cl 13.81.

3-[5-(6-Chloro-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yloxy]propanenitrile (Vd). Yield 22.2 g (78%), bp 148–149°C (1 mm), d_4^{20} = 1.3750, n_D^{20} = 1.5523. IR spectrum, ν, cm^{-1}: 3470 (O–H); 2250 (C≡C); 2165 (C≡N); 1130 (C–O–C); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.81–2.08 d.d (2H, CH_2C≡), 2.58 d (2H, H_2CCN), 3.47–3.49 d.d (2H, 2-H, 3-H), 3.74 d.d (2H, CH_2O). Found, %: C 64.80; H 7.71; Cl 11.81; N 4.62. $C_{16}H_{22}ClNO_2$. Calculated, %: C 64.96; H 7.50; Cl 11.98; N 4.74.

3-Chloro-5-[4-(2-hydroxyethoxy)-4-methylpent-2-yn-1-yl]bicyclo[2.2.1]heptan-2-ol (Ve). Yield 24.6 g (86%), bp 153–154°C (1 mm), d_4^{20} = 1.4204, n_D^{20} = 1.5667. IR spectrum, ν, cm^{-1}: 3370 (O–H); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.82–2.07 d.d (2H, CH_2C≡), 3.56 d.d (2H, OCH_2), 3.71 d.d (2H, CH_2O), 3.78–3.49 d.d (2H, 2-H, 3-H), 4.81 br.s (1H, 2-OH). Found, %: C 62.69; H 8.20; Cl 12.49. $C_{15}H_{23}ClO_3$. Calculated, %: C 62.83; H 8.03; Cl 12.38.

5-(6-Chloro-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yl acetate (Vf). Yield 20.9 g (74%), bp 123–124°C (1 mm), d_4^{20} = 1.4112, n_D^{20} = 1.5544. IR spectrum, ν, cm^{-1}: 3600 (O–H); 2230 (C≡C); 1720, 1080 (COO); 850, 745 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.67 s (6H, CH_3), 1.86–2.07 d.d (2H, CH_2C≡), 2.02 s (3H, CH_3CO), 3.47–3.49 d.d (2H, 2-H, 3-H). Found, %: C 63.12; H 7.58; Cl 12.30. $C_{15}H_{21}ClO_3$. Calculated, %: C 63.26; H 7.43; Cl 12.45.

3-Bromo-5-(prop-2-yn-1-yl)bicyclo[2.2.1]heptan-2-ol (VIa). Yield 17.8 g (78%), bp 104–105°C (5 mm), d_4^{20} = 1.3744, n_D^{20} = 1.5389. IR spectrum, ν, cm^{-1}: 3540 (O–H); 3300, 2135 (C≡CH); 750, 680 (C–Br). ^1H NMR spectrum, δ, ppm: 1.82 d (1H, HC≡), 1.87–2.13 d.d (2H, CH_2C≡), 3.45 d (1H, 3-H), 3.58 d (1H, OH). Found, %: C 52.31; H 5.89; Br 34.74. $C_{10}H_{13}BrO$. Calculated, %: C 54.36; H 6.67; Br 27.82.

3-Bromo-5-(4-hydroxy-4-methylpent-2-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (VIb). Yield 23 g (80%), bp 123–124°C (1 mm), d_4^{20} = 1.3913, n_D^{20} = 1.5576. IR spectrum, ν, cm^{-1}: 3600, 3360 (O–H); 2235 (C≡C); 750, 680 (C–Br). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.83–2.06 d.d (2H, CH_2C≡), 3.45 d (1H, 3-H), 3.57 d (1H, 2-OH), 4.81 br.s (1H, OH). Found, %: C 54.22; H 6.55; Br 27.99. $C_{13}H_{19}BrO_2$. Calculated, %: C 54.36; H 6.67; Br 27.82.

3-Bromo-5-(4-methoxy-4-methylpent-2-yn-1-yl)-bicyclo[2.2.1]heptan-2-ol (VIc). Yield 25.6 g (85%), bp 129–130°C (1 mm), d_4^{20} = 1.3179, n_D^{20} = 1.5372. IR spectrum, ν, cm^{-1}: 3500 (O–H); 1140 (C–O–C); 750, 680 (C–Br). ^1H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.82–2.08 d.d (2H, CH_2C≡), 3.25 s (3H, CH_3O), 3.45 t (1H, 3-H), 3.57 d (1H, OH). Found, %: C 55.73; H 7.19; Br 26.36. $C_{14}H_{21}BrO_2$. Calculated, %: C 55.82; H 7.03; Br 26.53.

3-[5-(6-Bromo-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yloxy]propanenitrile (VId).

Yield 26.9 g (79%), bp 154–155°C (1 mm), d_4^{20} = 1.3376, n_D^{20} = 1.5460. IR spectrum, ν, cm^{-1}: 3600 (O–H); 2250 (C≡C); 2185 (C≡N); 1150 (C–O–C); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.41 t (1H, 2-H), 1.48 s (6H, CH_3), 1.87–2.08 d.d (2H, CH_2C≡), 2.58 d (2H, H_2CCN), 3.45 t (1H, 3-H), 3.56 t (1H, OH), 3.75 d (2H, OCH_2), 4.81 br.s (1H, OH). Found, %: C 56.34; H 6.69; Br 23.30. $C_{16}H_{22}BrNO_2$. Calculated, %: C 56.47; H 6.72; Br 23.48.

3-Bromo-5-[4-(2-hydroxyethoxy)-4-methylpent-2-yn-1-yl]bicyclo[2.2.1]heptan-2-ol (VIe). Yield 28.9 g (87%), bp 158–159°C (1 mm), d_4^{20} = 1.3785, n_D^{20} = 1.5592. IR spectrum, ν, cm^{-1}: 3520 (O–H); 3410 (O–H); 2200 (C≡C); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.41 t (1H, 2-H), 1.67 s (6H, CH_3), 1.83–3.57 d (2H, OCH_2), 2.08 d.d (2H, CH_2C≡), 3.45 t (1H, 3-H), 3.56 t (1H, 2-OH), 3.71 d (2H, CH_2O), 4.81 br.s (1H, OH). Found, %: C 54.50; H 7.15; Br 24.01. $C_{15}H_{23}BrO_3$. Calculated, %: C 54.39; H 7.0; Br 24.12.

5-(6-Bromo-5-hydroxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yl acetate (VIf). Yield 25.5 g (77%), bp 128–129°C (1 mm), d_4^{20} = 1.3704, n_D^{20} = 1.5474. IR spectrum, ν, cm^{-1}: 3600 (O–H); 2225 (C≡C); 1720, 1080 (COO); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.67 s (6H, CH_3), 1.82–2.08 d.d (2H, CH_2C≡), 2.02 s (3H, CH_3CO), 2.48 t (1H, 5-H), 3.45 t (1H, 3-H), 3.57 t (1H, OH), 4.81 br.s (1H, OH). Found, %: C 54.63; H 6.59; Br 24.11. $C_{15}H_{21}BrO_3$. Calculated, %: C 54.72; H 6.43; Br 24.27.

Acetylenic 2,3-epoxynorbornanes VIIa–VIIe and VIIIa–VIIIe (*general procedure*). Powdered potassium hydroxide, 8.4 g (0.15 mol), was added under stirring to a solution of 0.05 mol of compound **IIIa–IIIe** or **VIa–VIe** in 60 ml of anhydrous diethyl ether, maintaining the temperature at 8–10°C. The mixture was then stirred for 2 h at 12–14°C, the solvent was distilled off, and the residue was distilled under reduced pressure.

2,3-Epoxy-5-ethynylbicyclo[2.2.1]heptane (VIIa). Yield 11.4 g (85%), bp 75–76°C (10 mm), d_4^{20} = 1.0356, n_D^{20} = 1.5018. IR spectrum, ν, cm^{-1}: 3290, 2125 (C≡CH); 3060, 1245, 910, 850 (oxirane). ^{1}H NMR spectrum, δ, ppm: 1.82 d (1H, HC≡C), 2.86 d.d (2H, 2-H, 3-H). Found, %: C 81.21; H 8.02. $C_{10}H_{22}O$. Calculated, %: C 81.04; H 8.16.

4-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-ol (VIIb). Yield 16.4 g (86%), bp 95–96°C (1 mm), d_4^{20} = 1.0825, n_D^{20} = 1.5152. IR spectrum, ν, cm^{-1}: 3060 (C–H, oxirane), 2200 (C≡C), 1260, 910, 850. ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.48 t (1H, 5-H), 2.86 d.d (2H, 2-H, 3-H), 5.46 br.s (1H, OH). Found, %: C 74.82; H 8.48. $C_{12}H_{16}O_2$. Calculated, %: C 74.96; H 8.39.

2,3-Epoxy-5-(3-methoxy-3-methylbut-1-yn-1-yl)-bicyclo[2.2.1]heptane (VIIc). Yield 18.3 g (89%), bp 100–101°C (2 mm), d_4^{20} = 1.0454, n_D^{20} = 1.5046. IR spectrum, ν, cm^{-1}: 3060, 1260, 910, 850 (oxirane); 2215 (C≡C); 1090 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.47 t (1H, 5-H), 2.86 d.d (2H, 2-H, 3-H), 3.25 s (3H, CH_3O). Found, %: C 75.80; H 8.63. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.79.

3-[4-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yloxy]propanenitrile (VIId). Yield 21.5 g (87.5%), bp 129–130°C (1 mm), d_4^{20} = 1.0724, n_D^{20} = 1.5031. IR spectrum, ν, cm^{-1}: 3060, 1260, 910, 850 (oxirane); 2240 (C≡N); 1080 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 2.47 t (1H, 5-H), 2.59 d (2H, CH_2CN), 2.86 d.d (2H, 2-H, 3-H), 3.75 d (2H, CH_2O). Found, %: C 73.30; H 7.97; N 5.64. $C_{15}H_{20}NO_2$. Calculated, %: C 73.17; H 8.13; N 5.69.

2-[4-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylbut-3-yn-2-yloxy]ethanol (VIIe). Yield 20.4 g (87%), bp 136–137°C (2 mm), d_4^{20} = 1.0159, n_D^{20} = 1.5178. IR spectrum, ν, cm^{-1}: 3470 (O–H); 3060, 1260, 910, 850 (oxirane); 1145 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.77 t (1H, 1-H), 2.48 t (1H, 5-H), 2.81 t (1H, 4-H), 2.86 d.d (2H, 2-H, 3-H), 3.56 d (2H, OCH_2), 3.71 d (2H, CH_2O), 4.78 br.s (1H, OH). Found, %: C 75.78; H 9.66. $C_{14}H_{21}O_2$. Calculated, %: C 75.97; H 9.57.

2,3-Epoxy-5-(prop-2-yn-1-yl)bicyclo[2.2.1]heptane (VIIIa). Yield 13.5 g (85%), bp 82–83°C (10 mm), d_4^{20} = 0.9959, n_D^{20} = 1.4876. IR spectrum, ν, cm^{-1}: 3060, 1245, 910, 850 (oxirane); 3300, 2125 (C≡CH). ^{1}H NMR spectrum, δ, ppm: 1.76 d.d (2H, 1-H, 4-H), 1.83 s (1H, HC≡C), 1.87–2.12 d.d (2H, CH_2C≡), 2.86 d.d (2H, 2-H, 3-H). Found, %: C 81.21; H 8.02. $C_{10}H_{22}O$. Calculated, %: C 81.04; H 8.16.

5-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-ol (VIIIb). Yield 17.7 g (86%), bp 99.5–100.5°C (1 mm), d_4^{20} = 1.0413, n_D^{20} = 1.5101. IR spectrum, ν, cm^{-1}: 3400 (O–H); 3060, 1260, 910, 850 (oxirane); 2200 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.76 d.d (2H, 1-H, 4-H), 1.83–2.08 d.d (2H, CH_2C≡), 2.86 d.d (2H, 2-H, 3-H), 4.45 br.s (1H, OH), Found, %: C 75.58; H 8.70. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.79.

2,3-Epoxy-5-(4-methoxy-4-methylpent-2-yn-1-yl)bicyclo[2.2.1]heptane (VIIIc). Yield 19.8 g (90%),

bp 105–106°C (2 mm), d_4^{20} = 1.0114, n_D^{20} = 1.4896. IR spectrum, ν, cm^{-1}: 3060, 1260, 910, 850 (oxirane); 1150 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.76 d.d (2H, 1-H, 4-H), 1.82–2.08 d.d (2H, $CH_2C\equiv$), 2.86 d.d (2H, 2-H, 3-H), 3.24 s (3H, CH_3O). Found, %: C 76.48; H 9.30. $C_{14}H_{20}O_2$. Calculated, %: C 76.32; H 9.15.

3-[5-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yloxy]propanenitrile (VIIId). Yield 22.9 g (88%), bp 137–138°C (1 mm), d_4^{20} = 1.0524, n_D^{20} = 1.4883. IR spectrum, ν, cm^{-1}: 3060, 1260, 910, 850 (oxirane); 2250 (C≡N); 2200 (C≡C); 1095 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, CH_3), 1.76 d.d (2H, 1-H, 4-H), 1.83–2.08 d.d (2H, $CH_2C\equiv$), 2.58 d (2H, CH_2CN), 2.86 d.d (2H, 2-H, 3-H), 3.75 d (2H, CH_2O). Found, %: C 74.24; H 8.0; N 5.28. $C_{16}H_{21}NO_2$. Calculated, %: C 74.10; H 8.11; N 5.41.

2-[5-(5,6-Epoxybicyclo[2.2.1]hept-2-yl)-2-methylpent-3-yn-2-yloxy]ethanol (VIIIe). Yield 21.5 g (88%), bp 140–141°C (1 mm), d_4^{20} = 1.4116, n_D^{20} = 1.5032. IR spectrum, ν, cm^{-1}: 3400 (O–H); 3060, 1260, 910, 850 (oxirane); 1150 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.41 d (1H, 5-H), 1.48 s (6H, CH_3), 1.76 d.d (2H, 1-H, 4-H), 1.83–2.08 d.d (2H, $CH_2C\equiv$), 2.86 d.d (2H, 2-H, 3-H), 3.57 d.d (2H, OCH_2), 3.71 d.d (2H, C**H**$_2$OH). Found, %: C 72.40; H 8.30. $C_{15}H_{21}O_3$. Calculated, %: C 72.26; H 8.49.

Epoxidation of bicycloheptenes Ia, Ib, Id, IIa, IIb, and IId (*general procedure***).** Bicycloheptene **Ia**, **Ib**, **Id**, **IIa**, **IIb**, or **IId**, 0.27 mol, was dissolved in 50 ml of anhydrous diethyl ether, 43.5 ml of 45% peroxyacetic acid was added at 15–20°C, the mixture was kept for 4 h and treated with 100 ml of 5% aqueous sodium hydrogen carbonate, the organic phase was separated and dried over sodium sulfate, and the solvent was distilled off. Vacuum distillation of the residue gave compounds **VIIa**, **VIIb**, **VIId**, **VIIIa**, **VIIIb**, and **VIIId**. The products were identical in physical properties to samples obtained as described above.

Independent synthesis of compounds VIIa and VIIIa (*general procedure***).** Powdered potassium hydroxide, 20 g, was added in five portions under stirring to a mixture of 0.1 mol of compound **IIIb**–**VIb** and 50 ml of toluene, maintaining the temperature in the range from 40 to 50°C. The mixture was then heated to 95–100°C and was kept for 8 h at that temperature. The mixture was cooled, and the organic phase was separated, dried over sodium sulfate, and distilled under reduced pressure in the presence of hydroquinone.

2,3-Epoxy-5-ethynylbicyclo[2.2.1]heptane (VIIa). Yield 12.1 g (86%), bp 75–76°C (10 mm), d_4^{20} = 1.0360, n_D^{20} = 1.5015.

2,3-Epoxy-5-(prop-2-yn-1-yl)bicyclo[2.2.1]heptane (VIIIa). Yield 14.8 g (89%), bp 82–83°C (10 mm), d_4^{20} = 0.9964, n_D^{20} = 1.4870.

Hydrolysis of compounds IIIa–VIa (*general procedure***).** Halohydrin **IIIa**–**VIa**, 0.05 mol, was added dropwise to a solution of 0.5 g of mercury(II) sulfate in 21 ml of 7% aqueous sulfuric acid, maintaining the temperature at 26–30°C. The mixture was stirred for 0.5 h, kept for 4–5 h at 55–60°C, cooled, and extracted with diethyl ether. The extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated, and the residue was distilled under reduced pressure to isolate ketones **IX**–**XII**.

1-(6-Chloro-5-hydroxybicyclo[2.2.1]heptan-2-yl)ethanone (IX). Yield 14 g (75%), bp 95–96°C (10 mm), d_4^{20} = 1.2091, n_D^{20} = 1.5098. IR spectrum, ν, cm^{-1}: 3520 (O–H); 1725 (C=O); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.1 s (3H, CH_3CO), 3.45 d (1H, 3-H), 3.58 d (1H, OH), 4.81 br.s (1H, OH). Found, %: C 57.21; H 6.82; Cl 18.90. $C_9H_{13}ClO_2$. Calculated, %: C 57.30; H 6.95; Cl 18.79.

1-(6-Bromo-5-hydroxybicyclo[2.2.1]heptan-2-yl)ethanone (X). Yield 17 g (73%), bp 102–103°C (5 mm), d_4^{20} = 1.5243, n_D^{20} = 1.5422. IR spectrum, ν, cm^{-1}: 3600 (O–H); 1730 (C=O); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 2.08 d (1H, 1-H), 2.1 s (3H, CH_3CO), 2.49 t (1H, 2-H), 3.58 d (1H, 5-H), 4.81 br.s (1H, OH). Found, %: C 46.28; H 5.79; Br 17.32. $C_{10}H_{15}BrO_2$. Calculated, %: C 59.86; H 7.46; Br 17.49.

1-(6-Chloro-5-hydroxybicyclo[2.2.1]heptan-2-yl)propan-2-one (XI). Yield 15.9 g (79%), bp 108–109°C (10 mm), d_4^{20} = 1.1857, n_D^{20} = 1.4956. IR spectrum, ν, cm^{-1}: 3490 (O–H); 1720 (C=O); 850, 745 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.84 t (1H, 1-H), 2.1 s (3H, CH_3CO), 2.29–2.54 d.d (2H, CH_2CO), 4.81 br.s (1H, OH). Found, %: C 59.40; H 7.37; Cl 17.32. $C_{10}H_{15}ClO_2$. Calculated, %: C 59.26; H 7.46; Cl 17.49.

1-(6-Bromo-5-hydroxybicyclo[2.2.1]heptan-2-yl)propan-2-one (XII). Yield 18.9 g (76%), bp 107–108°C (5 mm), d_4^{20} = 1.4431, n_D^{20} = 1.5273. IR spectrum, ν, cm^{-1}: 3500 (O–H); 1720 (C=O); 750, 680 (C–Br). ^{1}H NMR spectrum, δ, ppm: 1.53 t (1H, 4-H),

1.84 t (1H, 1-H), 2.1 s (3H, CH_3CO), 2.29–2.55 d.d (2H, CH_2CO), 3.46 d (1H, 3-H), 3.57 d (1H, 5-H), 4.81 br.s (1H, OH). Found, %: C 48.78; H 6.03; Br 32.42. $C_{10}H_{15}BrO_2$. Calculated, %: C 48.6; H 6.19; Br 32.34.

Compounds **IX**–**XII**, 0.05 mol, were subjected to dehydrohalogenation using 0.15 mol of powdered potassium hydroxide according to the procedure described above for the synthesis of **VIIa**. As a result, epoxy ketones **XIII** and **XIV** were obtained.

1-(5,6-Epoxybicyclo[2.2.1]heptan-2-yl)ethanone (XIII). Yield 5.4 g (70%), bp 82–83°C (10 mm), d_4^{20} = 1.1105, n_D^{20} = 1.4948. IR spectrum, ν, cm^{-1}: 3060, 1245, 910, 850 (oxirane); 1740 (C=O). ^1H NMR spectrum, δ, ppm: 1.85 t (1H, 4-H), 2.09 s (3H, CH_3CO), 3.45 d (1H, 3-H), 3.57 d (1H, 2-H). Found, %: C 71.20; H 7.81. $C_9H_{12}O_2$. Calculated, %: C 71.02; H 7.95.

1-(5,6-Epoxybicyclo[2.2.1]heptan-2-yl)propan-2-one (XIV). Yield 6.1 g (74%), bp 95–96°C (10 mm), d_4^{20} = 1.0640, n_D^{20} = 1.4801. IR spectrum, ν, cm^{-1}: 3060, 1245, 910, 850 (oxirane); 1715 (C=O). ^1H NMR spectrum, δ, ppm: 2.1 s (3H, CH_3CO), 2.29–2.54 d.d (2H, CH_2CO), 3.46 d (1H, 3-H), 3.58 d (1H, 2-H). Found, %: C 72.49; H 8.32. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.49.

Hydrolysis of compounds **VIIa** and **VIIIa** gave diols **XV** and **XVI**, respectively.

5-Ethynylbicyclo[2.2.1]heptane-2,3-diol (XV). Yield 6.5 g (86%), mp 43–44°C, R_f 0.68 (hexane–EtOAc, 7:3). IR spectrum, ν, cm^{-1}: 3520 (O–H); 3295, 2125 (C≡CH). ^1H NMR spectrum, δ, ppm: 1.51–1.53 d (2H, 1-H, 4-H), 1.83 d (2H, HC≡C), 3.24 d.d (2H, 2-H, 3-H), 4.81 br.s (2H, OH). Found, %: C 71.19; H 7.80. $C_9H_{12}O_2$. Calculated, %: C 71.02; H 7.95.

5-(Prop-2-yn-1-yl)bicyclo[2.2.1]heptane-2,3-diol (XVI). Yield 7.3 g (88%), mp 49–50°C, R_f 0.69 (hexane–EtOAc, 7:3). IR spectrum, ν, cm^{-1}: 3510 (O–H); 3300, 2130 (C≡CH). ^1H NMR spectrum, δ, ppm: 1.51–1.53 d (2H, 1-H, 4-H), 1.82 s (1H, HC≡C), 1.87–1.12 d.d (2H, CH_2C≡), 4.81 br.s (2H, OH). Found, %: C 72.08; H 8.37. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.49.

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