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Hydrogen Peroxide- or Sodium Hypochlorite-Induced Bromination of 1-Arylbut-2-enes

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Abstract—Bromination of 1-arylbut-2-enes in the system [HBr or NaBr (KBr)–HX]–H_2O_2 (or NaOCl) under relatively mild conditions leads to electrophilic addition of bromine or hypobromous acid at the side-chain double bond. Under more severe conditions, the process is accompanied by bromination of the aromatic ring. Treatment of the title compounds with peroxy acids (RCOOH–H_2O_2) gives the corresponding epoxy derivatives which react with HBr and oxygen-containing nucleophiles to produce α-bromo alcohols, diols, and diol acetates.

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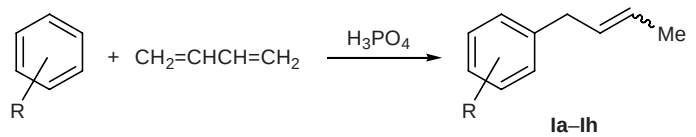
Halogen and hydroxy halogen derivatives of alkylaromatic hydrocarbons are used as starting materials in the synthesis of pharmacological agents [1], fragrant substances [2, 3], and specialty composite materials [4]. In the present article we report the results of our study on the bromination of various 1-phenylbut-2-ene derivatives and their heterophase epoxidation products with alkali metal bromides or hydrobromic acid in the presence of hydrogen peroxide or sodium hypochlorite.

Interest in conjugate electrophilic halogenation of unsaturated hydrocarbons of the aromatic series stems from convenience of these reactions as a one-step route to aromatic compounds having various substituents in the vicinal positions of the side chain, which opens the way to their subsequent transformations. Addition of hypohalous acids HOHlg across the multiple bond in aliphatic unsaturated hydrocarbons has been studied in detail. In particular, hypochlorination of ethylene and propylene underlie large-scale technologies for manufacture of epoxyethane and 1,2-epoxypropane through the corresponding chlorohydrins [5]. Electrophilic addition of halogens and hypohalous acids at a double C=C bond was considered in detail in [6]. Later publications on this topic were reviewed in [7–9]. However, bromination of unsaturated compounds of the aromatic series in the presence of hydrogen peroxide or sodium hypochlorite has received much lesser attention.

Initial 1-arylbut-2-enes were synthesized by alkenylation of benzene, toluene, chlorobenzene, anisole, phenetole, and *o*-, *m*-, and *p*-xylenes with divinyl according to the procedure described in [10, 11]. The use of phosphoric acid instead of sulfuric acid favored selective *ortho*-alkenylation (Scheme 1). The IR spectrum of 1-phenylbut-2-ene (**Ia**) contains strong absorption bands at 695 and 741 cm^{-1}, which are typical of monosubstituted benzene ring, and a band at 968 cm^{-1}, which was assigned to bending vibrations of the C–H bonds at the *trans*-configured aliphatic double bond. In the IR spectrum of butenyltoluene **Ib**, the most intense band was that located at 980 cm^{-1}; it characterizes C=C bond with *trans* orientation of the alkyl groups. This band is absent in the spectrum of the hydrogena-

Scheme 1.



Ia–Ih

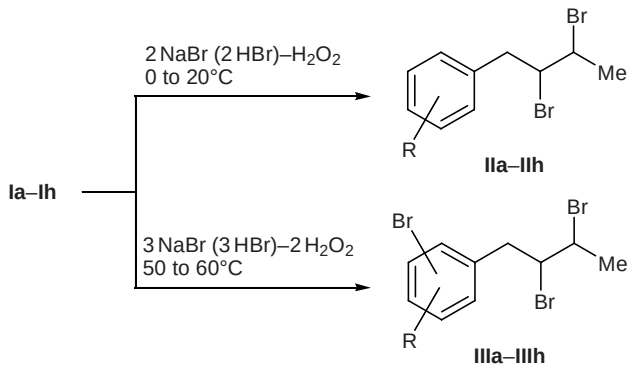
R = H (**a**), Me (**b**), Cl (**c**), MeO (**d**), EtO (**e**), 1,2-Me_2 (**f**), 1,3-Me_2 (**g**), 1,4-Me_2 (**h**).

tion product of **Ib**. In addition, the weak band at 778 cm^{-1}, which is likely to belong to the *cis* isomer, disappears from the spectrum upon hydrogenation. The presence of absorption bands at 742 and 809 cm^{-1} indicates formation of a mixture of 1,2- and 1,4-substituted isomers (62% and 33%, respectively, according to the GLC data). The IR spectrum of chlorophenyl derivative **Ic** contains bands at 742 (C–Cl) and 996 cm^{-1} (*trans*-C=C). The GLC and spectral data showed that the alkenylation products of anisole (**Id**) and phenetole (**Ie**) are mixtures of 1,2- (54–57 wt %) and 1,4-substituted isomers (37–40 wt %) [12, 13].

Isomer mixtures were also obtained by alkenylation of individual *o*-, *m*-, and *p*-xylenes with buta-1,3-diene. Products **If**–**Ih** displayed in the IR spectra a strong band at 966 cm^{-1}, which was assigned to the *trans*-butenyl group. *o*-Xylene (**If**) gave rise to a mixture of 1,2,3- (up to 33%; 817–825 cm^{-1}) and 1,2,4-substituted isomers (63%; 780–790 cm^{-1}). The major product of alkenylation of *m*-xylene (**Ig**) was 1,3,4-substituted isomer (up to 92%; 824 cm^{-1}), while the fraction of 1,2,3-substituted derivative (766 cm^{-1}) was as low as 5%. 2-(But-2-en-1-yl)-1,4-dimethylbenzene was formed as the only product in the reaction with *p*-xylene (**Ih**).

The presence of a reactive double bond in the side chain of compounds **Ia**–**Ih** provides the possibility for using them in the synthesis of various functional derivatives. We previously showed that alkylaromatic compounds undergo bromination at the aromatic ring in acid aqueous solutions of alkali metal bromides in the presence of various oxidants [14]. Depending on the conditions, compounds containing a double bond in the side chain could give rise to bromination products both at the side-chain double bond and at the aromatic ring.

Scheme 2.

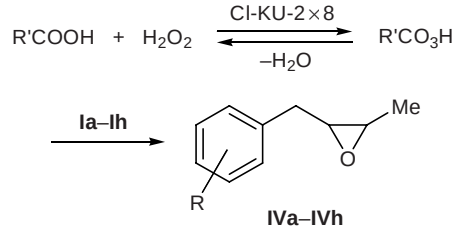


R = H (**a**), Me (**b**), Cl (**c**), MeO (**d**), EtO (**e**), 1,2-Me_2 (**f**), 1,3-Me_2 (**g**), 1,4-Me_2 (**h**).

In fact, treatment of compounds **Ia**–**Ih** with MBr (HBr)–H_2O_2 at a molar ratio of 1:2:1 at 0–20°C led to the formation of vicinal dibromides **IIa**–**IIh**, while in the presence of excess reagent [**I**–MBr (HBr)–H_2O_2 molar ratio 1:3:2] at 50–60°C bromination of the aromatic ring also occurred to give tribromo derivatives **IIIa**–**IIIh** (Scheme 2).

The structure of compounds **IIa**–**IIh** and **IIIa**–**IIIh** was confirmed by GLC, IR, and analytical data. Their IR spectra contained absorption bands at 640 and 655–680 cm^{-1} due to stretching vibrations of the C–Br bonds, whereas absorption typical of C=C bond vibrations (1600, 1608 cm^{-1}) was absent [12, 13]. Apart from products **IIa**–**IIh** and **IIIa**–**IIIh**, we detected in the reaction mixtures the corresponding bromohydrins **Va**–**Vh** (6–12.5 wt %) which were formed as a result of electrophilic addition of HOBr at the side-chain double bond. Compounds **Va**–**Vh** were synthesized by independent method, bromination of the corresponding 1-aryl-2,3-epoxybutanes. The synthesis was performed in two steps. In the first step, epoxidation of 1-arylbut-2-enes in the presence of chlorine-containing acidic cation exchanger KU-2×8 or KU-2×8n gave epoxy derivatives **IVa**–**IVh** (Scheme 3). Their structure was confirmed by elemental analysis and IR spectroscopy, as well as by determination of epoxide numbers using a solution of hydrogen chloride in acetone [15]. Comparison of the IR spectra of compounds **Ia**–**Ih** and **IVa**–**IVh** showed disappearance of strong absorption bands at 778, 968, 1600, and 1602 cm^{-1}, typical of the double bond in **I**, and appearance of new bands at 1260 and 1250 cm^{-1} due to C–O bond vibrations.

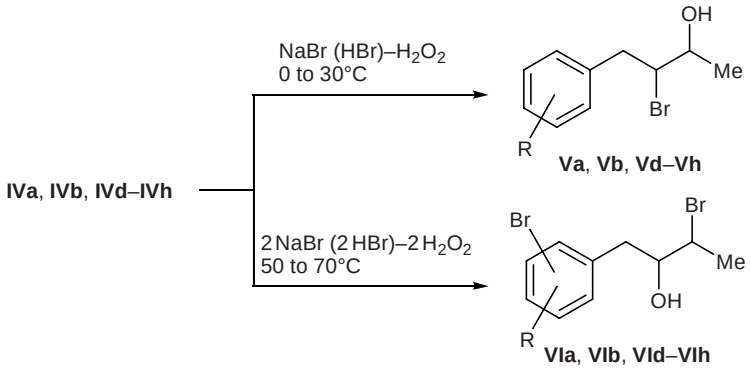
Scheme 3.



For R, see legend to Scheme 1; R′ = Me, Et.

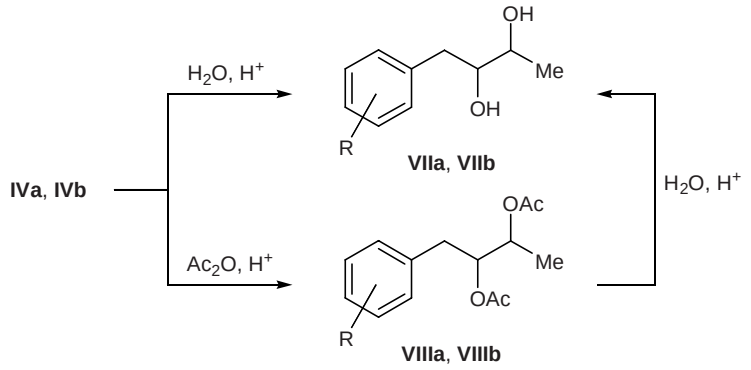
The bromination of epoxy derivatives **IVa**, **IVb**, and **IVd**–**IVh** under mild conditions [**IV**–NaBr (HBr)–H_2O_2 molar ratio 1:1:1, 0–30°C] was accompanied by opening of the oxirane ring with formation of the corresponding bromohydrins **Va**–**Vh**. Under more severe conditions [**IV**–NaBr (HBr)–H_2O_2 molar ratio 1:2:2, 50–70°C] both hydrobromination of the epoxy group

Scheme 4.



R = H (**a**), Me (**b**), MeO (**d**), EtO (**e**), 1,2-Me_2 (**f**), 1,3-Me_2 (**g**), 1,4-Me_2 (**h**).

Scheme 5.



R = H (**a**), Me (**b**).

and electrophilic bromination of the benzene ring occurred as shown in Scheme 4. Determination of the epoxide numbers [15] of the isolated products **Va**–**Vh** and **VIa**–**VIh** showed that the conversion of the oxirane ring in compounds **IVa**–**IVh** by the action of HBr was complete [16, 17]. Presumably, next followed electrophilic bromination of the aromatic ring.

By reactions of epoxides **IVa** and **IVb** with oxygen-centered nucleophiles [18, 19] we synthesized some their functional derivatives. Compounds **IVa** and **IVb** readily reacted with water and acetic anhydride in the presence of acid catalyst (RSO_3H, KU-2) to give the corresponding diols **VIIa** and **VIIb** and esters **VIIIa** and **VIIIb**; acid hydrolysis of the latter also afforded diols **VIIa** and **VIIb** (Scheme 5).

The results of the present study demonstrate that alkenylaromatic hydrocarbons can be converted, depending on the conditions, into various functionalized alkylaromatic compounds which possess useful properties and attract interest from the viewpoint of their subsequent transformations.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer. The ^1H NMR spectra were recorded on a Tesla BS-484D instrument (80 MHz) from solutions in carbon tetrachloride using hexamethyldisiloxane as internal reference. The purity and isomeric composition of the initial compounds were checked by GLC. Alkenylarenes, epoxy derivatives, and products of their transformations were analyzed using a 0.3×200-cm column packed with 12 wt % of Apiezon L on Celite (oven temperature 210–250°C), and bromination products were analyzed using a 0.3×300-cm column packed with 5% of XE-60 on Chromaton N-AW DMCS (oven temperature 140°C); carrier gas helium, flow rate 40 ml/min. The purity of compounds **IIIa**–**IIIh** was checked by TLC on Silufol UV-254 plates using benzene–dichloroethane–acetic acid (4:1.5:1 by volume) as eluent; spots were visualized under UV light. The molecular weights of compounds **IIIa**–**IIIh** were determined by cryoscopy in camphor.

(But-2-en-1-yl)benzene (Ia). A mixture of 78 g (1 mol) of benzene and 10.5 g of 86% H_3PO_4 was heated to 60°C, and 27 g (0.5 mol) of buta-1,3-diene was supplied at a rate of 6 l/h. The mixture was stirred for 3.5 h at 60°C, washed with water until neutral reaction, and dried over $MgSO_4$. Unreacted benzene was distilled off, and the residue was distilled under reduced pressure. Yield 49 g (46%, calculated on the initial benzene), bp 73–78°C (15 mm), d_4^{20} = 0.884, n_D^{20} = 1.5108; MR_D = 44.75, calcd. 44.21; iodine number 188. Found, %: C 91.1; H 9.12. $C_{10}H_{12}$. Calculated, %: C 90.84; H 9.08.

Compounds **Ib**–**Ie** were synthesized in a similar way.

1-(But-2-en-1-yl)-2-methylbenzene and 1-(but-2-en-1-yl)-4-methylbenzene (Ib). Yield 65.5 g (58%, calculated on the initial toluene), bp 192–194°C (15 mm), d_4^{20} = 0.8859, n_D^{20} = 1.5121; MR_D = 49.49, calcd. 49.47; iodine number 160. Found, %: C 90.48; H 9.73. $C_{11}H_{14}$. Calculated, %: C 90.41; H 5.58. According to the GLC data, the product contained 62% of 1,2-isomer and 33% of 1,4-isomer.

1-(But-2-en-1-yl)-2-chlorobenzene and 1-(but-2-en-1-yl)-4-chlorobenzene (Ic) were obtained from 112.5 g (1 mol) of chlorobenzene. Yield 82 g (59%), bp 80–82°C (15 mm), d_4^{20} = 1.1123, n_D^{20} = 1.5685; MR_D = 49.04, calcd. 49.18; iodine number 150. Found, %: C 72.15; H 6.8; Cl 21.62. $C_{10}N_{11}Cl$. Calculated, %: C 72.03; H 6.6; Cl 21.31. According to the GLC data, the product contained 51.6% of 1,2-isomer and 43.3% of 1,4-isomer.

1-(But-2-en-1-yl)-2-methoxybenzene and 1-(but-2-en-1-yl)-4-methoxybenzene (Id) were obtained from 162 g (1.5 mol) of anisole. Yield 117.2 g (62%), bp 109–114°C (14 mm), d_4^{20} = 0.9573, n_D^{20} = 1.5112; MR_D = 50.72, calcd. 50.57; iodine number 143. Found, %: C 81.65; H 8.76. $C_{11}H_{14}O$. Calculated, %: C 81.48; H 8.64. According to the GLC data, the product contained 40% of 1,2-isomer and 56% of 1,4-isomer.

1-(But-2-en-1-yl)-2-ethoxybenzene and 1-(but-2-en-1-yl)-4-ethoxybenzene (Ie) were obtained from 183 g (1.5 mol) of phenetole. Yield 97.7 g (47%), bp 118–120°C (15 mm), d_4^{20} = 0.9523, n_D^{20} = 1.5120; MR_D = 55.44, calcd. 55.19; iodine number 139. Found, %: C 81.63; H 8.98. $C_{12}H_{18}O$. Calculated, %: C 81.82; H 8.69. According to the GLC data, the product contained 42% of 1,2-isomer and 52% of 1,4-isomer.

1-(But-2-en-1-yl)-2,3-dimethylbenzene and 1-(but-2-en-1-yl)-3,4-dimethylbenzene (If). Buta-1,3-diene, 27 g (0.5 mol), was passed at a flow rate of 6 l/h through a mixture of 160 g (1.5 mol) of 1,2-dimethylbenzene and 18.5 g of 86% H_3PO_4. The mixture was stirred for 3.5 h at 60°C and treated as described above, and the residue was distilled under reduced pressure. Yield 122.5 g (66%), bp 105–107°C (15 mm), d_4^{20} = 0.8944, n_D^{20} = 1.5170; iodine number 154. Found, %: C 89.75; H 10.13. $C_{12}H_{16}$. Calculated, %: C 89.92; H 9.99. According to the GLC data, the product contained 56% of 1,3,4-isomer and 40% of 1,2,3-isomer.

Compounds **Ig** and **Ih** were synthesized in a similar way.

2-(But-2-en-1-yl)-1,3-dimethylbenzene and 1-(but-2-en-1-yl)-2,4-dimethylbenzene (Ig) were obtained from 160 g (1.5 mol) of 1,3-dimethylbenzene. Yield 133 g (71%), bp 102–105°C (15 mm), d_4^{20} = 0.8940, n_D^{20} = 1.5140; MR_D = 54.22, calcd. 54.65; iodine number 154. Found, %: C 90.1; H 10.08. $C_{12}H_{16}$. Calculated, %: C 89.92; H 9.9. According to the GLC data, the product contained 10% of 1,2,3-isomer and 90% of 1,2,4-isomer.

1-(But-2-en-1-yl)-1,4-dimethylbenzene (Ih) was obtained from 160 g (1.5 mol) of 1,4-dimethylbenzene. Yield 106 g (56%), bp 105–108°C (15 mm), d_4^{20} = 0.8955, n_D^{20} = 1.5146; MR_D = 56.6, calcd. 54.65; iodine number 152. Found, %: C 90.07; H 10.1. $C_{12}H_{16}$. Calculated, %: C 89.92; H 9.99.

2,3-Dibromo-1-phenylbutane (IIa). Sodium bromide, 20.3 g (0.2 mol), or potassium bromide, 24 g (0.2 mol), was dissolved in 25 ml of water, and 24 g (0.2 mol) of 33% hydrochloric acid and 13.2 g (0.1 mol) of (but-2-en-1-yl)benzene (**Ia**) were added dropwise under stirring over a period of 30 min. A 18.5% aqueous solution of sodium hypochlorite, 124.2 g (0.2 mol; 110 mol/l of active chlorine) was then added over a period of 90 min, and the mixture was heated to 30–40°C and stirred for 4 h at that temperature. When the reaction was complete, the organic phase was separated, washed, and dried over anhydrous calcium chloride. Vacuum distillation gave 28.5 g (98%) of **IIa**, bp 130°C (15 mm), d_4^{20} = 1.5901, n_D^{20} = 1.570; MR_D = 60.2, calcd. 60.44. IR spectrum: ν 670 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.71–7.01 m (5H, C_6H_5), 2.58–2.83 d (2H, CH_2) 3.65–3.68 m (3H, CH), 0.79 s (3H, CH_3), 4.01–4.21 m (2H, CHBr). Found, %: C 40.8; H 4.0; Br 54.66. $C_{12}H_{16}Br_2$. Calculated, %: C 41.1; H 4.1; Br 54.79. Analogous results were obtained with the use of 30% hydrogen

peroxide and 46% hydrobromic acid ($HBr–H_2O_2$ molar ratio 2:1) as brominating agent.

1-(2,3-Dibromobutyl)-2-methylbenzene and 1-(2,3-dibromobutyl)-4-methylbenzene (IIb) were obtained from 14.6 g (0.1 mol) of isomer mixture **Ib**. Yield 28.2 g (92%), bp 150°C (15 mm), d_4^{20} = 1.5144, n_D^{20} = 1.5711; MR_D = 65.34, calcd. 65.08. IR spectrum: ν 676 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 7.0–7.18 m (4H, C_6H_4), 0.89 s (3H, CH_3), 2.58–2.83 d (2H, CH_2), 3.65–3.68 m (3H, CH), 0.87 s (3H, CH_3), 4.0–4.22 m (2H, CHBr). Found, %: C 43.0; H 4.36; Br 52.0. $C_{11}H_{14}Br_2$. Calculated, %: C 43.13; H 4.57; Br 52.3. Analogous results were obtained with the use of 30% hydrogen peroxide and 46% hydrobromic acid ($HBr–H_2O_2$ molar ratio 2:1) as brominating agent.

1-Chloro-2-(2,3-dibromobutyl)benzene and 1-chloro-4-(2,3-dibromobutyl)benzene (IIc) were obtained from 16.8 g (0.1 mol) of isomer mixture **Ic**. Yield 29.9 g (92%). IR spectrum, ν, cm^{-1}: 1022 (C–Cl), 674 (C–Br). ^1H NMR spectrum, δ, ppm: 6.69–6.73 m (4H, C_6H_4), 2.59–2.84 d (2H, CH_2), 4.0–4.21 m (2H, CHBr), 1.79 s (3H, CH_3). Found, %: C 36.58; H 3.64; Br+Cl 59.65. $C_{11}H_{12}ClBr_2$. Calculated, %: C 36.64; H 3.66; Br+Cl 59.69.

1-(2,3-Dibromobutyl)-2-methoxybenzene and 1-(2,3-dibromobutyl)-4-methoxybenzene (IId) were obtained from 16.2 g (0.1 mol) of isomer mixture **Id**, 52 g (0.2 mol) of 46% hydrobromic acid, and 11.4 g (0.1 mol) of 30% hydrogen peroxide. Yield 22.1 g (69%), bp 155–160°C (15 mm), d_4^{20} = 1.5862, n_D^{20} = 1.5775; MR_D = 67.32, calcd. 66.72. IR spectrum: ν 678 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.69–7.2 m (4H, C_6H_4), 1.33 s (3H, CH_3), 2.87–3.13 d (2H, CH_2), 4.0–4.22 m (2H, CHBr), 1.79 s (3H, CH_3). Found, %: C 39.78; H 4.18; Br 49.45. $C_{11}H_{14}Br_2O$. Calculated, %: C 41.0; H 4.35; Br 49.69. According to the GLC data, the product contained 40% of 1,2-isomer and 56% of 1,4-isomer. Analogous results were obtained using a 26% solution of NaOCl (153 mol/l of active chlorine) as oxidant.

1-(2,3-Dibromobutyl)-2-ethoxybenzene and 1-(2,3-dibromobutyl)-4-ethoxybenzene (IIe) were obtained from 17.6 g (0.1 mol) of isomer mixture **Ie**. Yield 22 g (65%), bp 165–170°C (15 mm), d_4^{20} = 1.5142, n_D^{20} = 1.5674; MR_D = 68.49, calcd. 69.33. ^1H NMR spectrum, δ, ppm: 6.66–7.18 m (4H, C_6H_4), 3.89 m (2H, CH_2), 1.33 s (3H, CH_3), 2.87–3.12 d (2H, CH_2), 4.0–4.21 m (2H, CHBr), 0.86 s (3H, CH_3). Found %: C 42.58; H 4.65; Br 47.36. $C_{12}H_{16}Br_2O$. Calculated, %: C 42.86; H 4.76; Br 47.62. According to the GLC data, the product contained 42% of 1,2-isomer and 52% of 1,4-isomer. Analogous results were obtained with the use of 30% hydrogen peroxide and 46% hydrobromic acid ($HBr–H_2O_2$ molar ratio 2:1).

1-(2,3-Dibromobutyl)-2,3-dimethylbenzene and 1-(2,3-dibromobutyl)-3,4-dimethylbenzene (IIf) were obtained from 16 g (0.1 mol) of isomer mixture **If**. Yield 29 g (91%), bp 168°C (15 mm), d_4^{20} = 1.4946, n_D^{20} = 1.5745. IR spectrum: ν 676 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.75−6.88 m (3H, C_6H_3), 2.34 s (6H, CH_3), 2.86–3.1 d (2H, CH_2), 4.0–4.21 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: C 45.15; H 5.12; Br 50.8. $C_{12}H_{16}Br_2$. Calculated, %: C 45.0; H 5.0; Br 50.0.

1-(2,3-Dibromobutyl)-2,4-dimethylbenzene and 2-(2,3-dibromobutyl)-1,3-dimethylbenzene (IIg) were obtained from 16 g (0.1 mol) of isomer mixture **Ig**. Yield 29.6 g (92%), bp 163°C (15 mm), d_4^{20} = 1.4947, n_D^{20} = 1.5712. IR spectrum: ν 674 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.81–6.87 m (3H, C_6H_3), 2.33 s (6H, CH_3), 2.87–3.1 d (2H, CH_2), 4.0–4.2 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: C 45.23; H 5.18; Br 51.12. $C_{12}H_{16}Br_2$. Calculated, %: C 45.0; H 5.0; Br 50.0.

2-(2,3-Dibromobutyl)-1,4-dimethylbenzene (IIh) was obtained from 16 g (0.1 mol) of compound **Ih**. Yield 27.5 g (86%), bp 160°C (15 mm), d_4^{20} = 1.4943, n_D^{20} = 1.5734. IR spectrum: ν 678 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.75–6.87 m (3H, C_6H_3), 2.34 s (6H, CH_3), 2.88–3.11 d (2H, CH_2), 4.0–4.2 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: C 45.17; H 5.2; Br 51.15. $C_{12}H_{16}Br_2$. Calculated, %: C 45.0; H 5.0; Br 50.0.

1-Bromo-2-(2,3-dibromobutyl)benzene and 1-bromo-4-(2,3-dibromobutyl)benzenes (IIIa) were obtained at a substrate–MBr (HBr)–H_2O_2 molar ratio of 1:3:2 from 12.2 g (0.1 mol) of isomer mixture **Ia** at 50–60°C. Yield 32.2 g (87%), mp 75–76°C (from benzene). IR spectrum: ν 678 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.96–7.36 m (4H, C_6H_4), 2.86–3.11 d (2H, CH_2), 4.0–4.21 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: Br 49.45. *M* 370.2. $C_{10}H_{11}Br_3$. Calculated, %: Br 49.69. *M* 371.

Compounds **IIIb**–**IIIh** were synthesized in a similar way.

1-Bromo-2-(2,3-dibromobutyl)-3-methylbenzene and 1-bromo-2-(2,3-dibromobutyl)-4-methylbenzene (IIIb) were obtained from 14.2 g (0.1 mol) of isomer mixture **Ib**. Yield 34.8 g (91%), mp 70–71°C (from benzene). IR spectrum: ν 676 cm^{-1} (C–Br). ^1H NMR spectrum, δ, ppm: 6.64–6.96 m (3H, C_6H_3),

2.32 s (3H, CH_3), 2.87–3.12 d (2H, CH_2), 4.0–4.21 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: Br 62.12. *M* 383.5. $C_{11}H_{13}Br_3$. Calculated, %: Br 62.34. *M* 385.

1-Bromo-3-chloro-2-(2,3-dibromobutyl)benzene and 1-bromo-4-chloro-2-(2,3-dibromobutyl)benzene (IIIc) were obtained from 16.6 g (0.1 mol) of isomer mixture **Ic**. Yield 25.7 g (64%), mp 82–83°C (from hexane). IR spectrum, ν, cm^{-1}: 1065 (C–Cl), 674 (C–Br). Found, %: Br+Cl 67.68. *M* 403.8. $C_{10}H_{10}Br_3Cl$. Calculated, %: Br+Cl 67.94. *M* 405.5.

1-Bromo-2-(2,3-dibromobutyl)-3-methoxybenzene and 2-bromo-4-(2,3-dibromobutyl)-1-methoxybenzene (IIId) were obtained from 16.1 g (0.1 mol) of isomer mixture **Id**. Yield 29.1 g (77%), mp 61–62°C (from hexane). IR spectrum: ν 678 cm^{-1} (C–Br). ^{1}H NMR spectrum, δ, ppm: 6.95–7.12 m (3H, C_6H_3), 2.86–3.112 d (2H, CH_2), 4.0–4.21 s (2H, CH), 1.78 s (3H, CH_3). Found, %: Br 59.53. *M* 401.35. $C_{11}H_{13}Br_3O$. Calculated, %: Br 59.7. *M* 402.

1-Bromo-2-(2,3-dibromobutyl)-3-ethoxybenzene and 2-bromo-4-(2,3-dibromobutyl)-1-ethoxybenzene (IIIe) were obtained from 17.5 g (0.1 mol) of isomer mixture **Ie**. Yield 28.5 g (69%), mp 63–64°C (from hexane). IR spectrum: ν 676 cm^{-1} (C–Br). Found, %: Br 57.15. *M* 414.4. $C_{12}H_{15}Br_3O$. Calculated, %: Br 57.83. *M* 415.

1-Bromo-2-(2,3-dibromobutyl)-3,4-dimethylbenzene and 1-bromo-2-(2,3-dibromobutyl)-4,5-dimethylbenzene (IIIf) were obtained from 15.8 g (0.1 mol) of isomer mixture **If**. Yield 34.1 g (86%), mp 71–72°C (from benzene). IR spectrum: ν 678 cm^{-1} (C–Br). ^{1}H NMR spectrum, δ, ppm: 6.67–7.1 d (2H, C_6H_2), 2.33 s (6H, CH_3), 3.1–2.86 d (2H, CH_2), 3.97–4.2 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: Br 59.82. *M* 398.3. $C_{12}H_{15}Br_3$. Calculated, %: Br 60.15. *M* 399.

1-Bromo-3-(2,3-dibromobutyl)-2,3-dimethylbenzene and 2-bromo-4-(2,3-dibromobutyl)-1,3-dimethylbenzene (IIIg) were obtained from 15.8 g (0.1 mol) of isomer mixture **Ig**. Yield 31.2 g (78%), mp 68–69°C (from benzene). IR spectrum: ν 676 cm^{-1} (C–Br). ^{1}H NMR spectrum, δ, ppm: 6.70–6.80 d (2H, C_6H_2), 2.34 s (6H, CH_3), 3.11–2.87 d (2H, CH_2), 3.99–4.19 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: Br 59.75. *M* 398.1. $C_{12}H_{15}Br_3$. Calculated, %: Br 60.15. *M* 399.

1-Bromo-4-(2,3-dibromobutyl)-2,5-dimethylbenzene (IIIh) was synthesized from 15.8 g (0.1 mol) of compound **Ih**. Yield 32.1 g (71%), mp 70–71°C (from benzene). IR spectrum: ν 678 cm^{-1} (C–Br). ^{1}H NMR spectrum, δ, ppm: 6.68–7.0 d (2H, C_6H_2), 2.34 s (6H, CH_3), 3.11–2.87 d (2H, CH_2), 3.99–4.19 m (2H, CHBr), 1.78 s (3H, CH_3). Found, %: Br 59.68. *M* 398.1. $C_{12}H_{15}Br_3$. Calculated, %: Br 61.15. *M* 399.

2-Benzyl-3-methyloxirane (IVa). A mixture of 12 g (0.2 mol) of acetic acid or 14.8 g (0.2 mol) of propionic acid, 17 g (0.15 mol) of 30% hydrogen peroxide (in water or dioxane), and 3.5 g of chlorinated KU-2×8n cation exchanger (9.5% of chlorine) was heated to 50°C and stirred for 2 h at that temperature, and a solution of 13.2 g (0.1 mol) of compound **Ia** in 40 ml of toluene was added dropwise over a period of 20 min. After consumption of the required amount of H_2O_2, the mixture was filtered through a Schott filter, the organic phase was separated and washed with an aqueous solution of sodium carbonate until neutral reaction, the aqueous phase was extracted with toluene, the extract was combined with the organic phase and dried over sodium sulfate, the solvent was distilled off, and the residue was distilled under reduced pressure. Yield 12.9 g (82%), bp 72–73°C (2 mm), d_4^{20} = 0.9925, n_D^{20} = 1.5113; MR_D = 44.59, calcd. 44.5; epoxide number 10.2. IR spectrum, ν, cm^{-1}: 695 (C_6H_5); 1260, 1250 (C–O). Found, %: C 81.04; H 8.28. $C_{10}H_{12}O$. Calculated, %: C 81.06; H 8.16.

Compounds **IVb–IVh** were synthesized in a similar way.

2-Methyl-3-(2-methylbenzyl)oxirane and 2-methyl-3-(4-methylbenzyl)oxirane (IVb) were obtained from 14.6 g (0.1 mol) of isomer mixture **Ib**. Yield 13.9 g (86%), bp 71–75°C (1 mm), d_4^{20} = 0.9856, n_D^{20} = 1.5136; MR_D = 49.45, calcd. 49.15. Epoxide number 9.4. IR spectrum, ν, cm^{-1}: 746, 828 (δC_6H_4); 1260, 1250 (C–O). Found, %: C 81.39; H 9.05. $C_{11}H_{14}O$. Calculated, %: C 81.43; H 8.7. According to the GLC data, the product contained 62% of 1,2-isomer and 33% of 1,4-isomer.

2-(2-Chlorobenzyl)-3-methyloxirane and 2-(4-chlorobenzyl)-3-methyloxirane (IVc) were obtained from 16.7 g (0.1 mol) of isomer mixture **Ic**. Yield 16.4 g (90%), bp 81–83°C (15 mm), d_4^{20} = 1.131, n_D^{20} = 1.5284; MR_D = 49.75, calcd. 50.92. Epoxide number 8.5. IR spectrum, ν, cm^{-1}: 752–826 (C–Cl); 748, 805, 810 (δC_6H_4); 1260, 1250 (C–O). Found, %: C 64.56; H 6.01; Cl 18.58. $C_{10}H_{11}OCl$. Calculated, %: C 65.75; H 6.03; Cl 19.45.

2-(2-Methoxybenzyl)-3-methyloxirane and 2-(4-methoxybenzyl)-3-methyloxirane (IVd) were

obtained from 16.1 g (0.1 mol) of isomer mixture **Id**. Yield 17.2 g (90%), bp 94–96°C (15 mm), d_4^{20} = 1.0690, n_D^{20} = 1.5264; MR_D = 51.19, calcd. 50.92. Epoxide number 8.5. IR spectrum, ν, cm^{-1}: 1260, 1250 (C–O). ^1H NMR spectrum, δ, ppm: 7.0–7.19 m (4H, *o*-C_6H_4), 7.0 s (4H, *p*-C_6H_4), 2.34 s (3H, CH_3), 2.34–2.79 d (2H, CH_2), 2.71–2.92 s (2H, CHO), 1.20 s (3H, CH_3). Found, %: C 73.89; H 7.95. $C_{11}H_{14}O_2$. Calculated, %: C 74.15; H 7.85.

2-(2-Ethoxybenzyl)-3-methyloxirane and 2-(4-ethoxybenzyl)-3-methyloxirane (IVe) were obtained from 17.5 g (0.1 mol) of isomer mixture **Ie**. Yield 15.9 g (83%), bp 98–103°C (15 mm), d_4^{20} = 1.0568, n_D^{20} = 1.5223. Epoxide number 8.3. IR spectrum, ν, cm^{-1}: 1260, 1250 (C–O). ^1H NMR spectrum, δ, ppm: 6.72–7.02 m (4H, C_6H_4), 3.96 m (2H, CH_2O), 1.31–1.33 s (3H, CH_3), 2.70–2.90 s (2H, CHO), 1.20 s (3H, CH_3). Found, %: C 75.39; H 7.82. $C_{12}H_{15}O_2$. Calculated, %: C 75.69; H 7.85.

3-(2,3-Dimethylbenzyl)-3-methyloxirane and 2-(3,4-dimethylbenzyl)-3-methyloxirane (IVf) were obtained from 16 g (0.1 mol) of isomer mixture **If**. Yield 18.1 g (89%), bp 79–81°C (1 mm), d_4^{20} = 0.9778, n_D^{20} = 1.5178; MR_D = 54.14, calcd. 53.8. Epoxide number 8.6. IR spectrum, ν, cm^{-1}: 742, 772, 810, 883 (δC_6H_3); 1260, 1250 (C–O). ^1H NMR spectrum, δ, ppm: 6.78–6.91 m (3H, C_6H_3), 2.35 s (3H, CH_3), 2.56–2.80 d (2H, CH_2), 2.70–2.92 s (2H, CHO), 1.23 s (3H, CH_3). Found, %: C 82.74; H 9.04. $C_{12}H_{15}O_2$. Calculated, %: C 81.89; H 9.16.

2-(2,4-Dimethylbenzyl)-3-methyloxirane and 2-(2,6-dimethylbenzyl)-3-methyloxirane (IVg) were obtained from 16 g (0.1 mol) of isomer mixture **Ig**. Yield 15.3 g (87%), bp 91–95°C (2 mm), d_4^{20} = 0.9754, n_D^{20} = 1.5168; MR_D = 54.55, calcd. 53.8. Epoxide number 8.8. IR spectrum, ν, cm^{-1}: 1260, 1250 (C–O). ^1H NMR spectrum, δ, ppm: 6.76–7.0 m (3H, C_6H_3), 2.35 s (3H, CH_3), 2.87–3.12 d (2H, CH_2), 3.62 m (1H, CHOH), 4.80 m (1H, OH), 3.88 m (1H, CHBr), 2.70–2.92 s (2H, CHO), 1.58 s (3H, CH_3). Found, %: C 82.62; H 9.6. $C_{12}H_{15}O$. Calculated, %: C 81.89; H 9.16.

2-(2,5-Dimethylbenzyl)-3-methyloxirane (IVh) was obtained from 16 g (0.1 mol) of compound **Ih**. Yield 15.4 g (88%), bp 79–80°C (1 mm), d_4^{20} = 0.9727, n_D^{20} = 1.5160; MR_D = 54.61, calcd. 53.8. Epoxide number 8.1. IR spectrum, ν, cm^{-1}: 810, 883 (δC_6H_3); 1260, 1250 (C–O). ^1H NMR spectrum, δ, ppm: 6.75–6.89 m (3H, C_6H_3), 2.34 s (3H, CH_3), 2.54–2.78 d (2H, CH_2), 2.70–2.92 s (2H, CHO), 1.22 s (3H, CH_3). Found, %: C 81.53; H 9.27. $C_{12}H_{15}O_2$. Calculated, %: C 81.89; H 9.16.

3-Bromo-1-(2-methylphenyl)butan-2-ol and 3-bromo-1-(4-methylphenyl)butan-2-ol (Vb). A 30% solution of hydrogen peroxide, 11.3 g (0.1 mol), was added at 20°C to 16.2 g (0.1 mol) of isomer mixture **IVb**, 41 g of 20% hydrobromic acid was then added over a period of 30 min, and the mixture was stirred for 3 h. The organic phase was separated, washed with water and 3% aqueous sodium hydrogen carbonate, and dried over Na_2SO_4, the solvent was removed, and the residue was distilled under reduced pressure. Yield 22.4 g (91%), bp 109–111°C (0.5 mm), d_4^{20} = 1.4162; n_D^{20} = 1.5972; MR_D = 58.48, calcd. 58.63. IR spectrum, ν, cm^{-1}: 1100, 1755, 3625 (OH); 625, 640 (C–Br); 918, 974 (*cis* and *trans*); 770, 780, 840, 810 (δC_6H_4). ^1H NMR spectrum, δ, ppm: 6.98–7.2 m (4H, C_6H_4), 2.34 s (3H, CH_3), 2.58–2.83 d (2H, CH_2), 4.0 s (1H, C**H**OH), 4.8 br.s (1H, OH), 3.67 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 54.10; H 5.98; Br 32.64. $C_{11}H_{15}BrO$. Calculated, %: C 54.32; H 6.17; Br 32.82.

3-Bromo-1-phenylbutan-2-ol (Va) was obtained from 14.8 g (0.1 mol) of compound **IVa**. Yield 17.6 g (77%), bp 105–106°C (0.5 mm), d_4^{20} = 1.4201, n_D^{20} = 1.5856; MR_D = 54.09, calcd. 54.04. IR spectrum, ν, cm^{-1}: 676 (C–Br); 1100, 3550 (CHOH). ^1H NMR spectrum, δ, ppm: 7.11–7.26 m (5H, C_6H_5), 2.58–2.85 d (2H, CH_2), 4.0 m (1H, C**H**OH), 4.8 br.s (1H, OH), 3.68 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 52.34; H 6.98; Br 34.93. $C_{10}H_{13}BrO$. Calculated, %: C 52.4; H 5.68; Br 34.93.

3-Bromo-1-(2-methoxyphenyl)butan-2-ol and 3-bromo-1-(4-methoxyphenyl)butan-2-ol (Vd) were obtained from 17.8 g (0.1 mol) of isomer mixture **IVd**. Yield 19.5 g (75%), bp 113–115°C (0.5 mm), d_4^{20} = 1.4287, n_D^{20} = 1.5865; MR_D = 60.87, calcd. 60.33. IR spectrum, ν, cm^{-1}: 678 (C–Br); 1100, 3580 (CHOH). ^1H NMR spectrum, δ, ppm: 6.71–7.02 m (4H, C_6H_4), 3.72 s (3H, CH_3O), 2.56–3.11 d (2H, CH_2), 4.0 m (1H, C**H**OH), 3.67 m (1H, CHBr), 4.81 br.s (1H, OH), 1.22 s (3H, CH_3). Found, %: C 50.73; H 5.81; Br 30.25. $C_{11}H_{15}BrO_2$. Calculated, %: C 50.96; H 5.79; Br 30.89.

3-Bromo-1-(2-bromo-6-ethoxyphenyl)butan-2-ol and 3-bromo-1-(3-bromo-4-ethoxyphenyl)butan-2-ol (Ve) were obtained from 19.2 g (0.1 mol) of isomer mixture **IVe**. Yield 19.8 g (73%), bp 119–120°C (0.5 mm), d_4^{20} = 1.4386, n_D^{20} = 1.5736; MR_D = 62.58, calcd. 62.1. ^1H NMR spectrum, δ, ppm: 7.0–7.02 m (4H, C_6H_4), 3.98–4.01 d (2H, CH_2O), 1.31 s (3H, CH_3), 2.58–2.83 d (2H, CH_2), 4.01 m (1H, C**H**OH),

4.80 br.s (1H, OH), 3.68 m (1H, CHBr), 1.79 s (3H, CH_3). Found, %: C 53.0; H 6.10; Br 29.3. $C_{12}H_{18}O_2Br$. Calculated, %: C 52.75; H 6.23; Br 29.3.

3-Bromo-1-(2,3-dimethylphenyl)butan-2-ol and 3-bromo-1-(3,4-dimethylphenyl)butan-2-ol (Vf) were obtained from 17.6 g (0.1 mol) of isomer mixture **IVf**. Yield 21.9 g (85%), bp 114–115°C (0.5 mm), d_4^{20} = 1.4686, n_D^{20} = 1.5883; MR_D = 58.92, calcd. 58.68. IR spectrum, ν, cm^{-1}: 655, 680 (C–Br); 1100, 3615 (CHOH); 918, 974 (*cis* and *trans*); 775, 810, 865 (δC_6H_3). ^{1}H NMR spectrum, δ, ppm: 6.80–6.90 m (3H, C_6H_3), 2.35 s (6H, CH_3), 2.58–2.83 d (2H, CH_2), 3.62 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.67 m (1H, CHBr), 1.58 s (3H, CH_3). Found, %: C 56.14; H 6.48; Br 31.23. $C_{12}H_{17}BrO$. Calculated, %: C 56.03; H 6.61; Br 31.19.

3-Bromo-1-(2,4-dimethylphenyl)butan-2-ol and 3-bromo-1-(2,6-dimethylphenyl)butan-2-ol (Vg) were obtained from 17.5 g (0.1 mol) of isomer mixture **IVg**. Yield 21.5 g (84%), bp 111–113°C (0.5 mm), d_4^{20} = 1.4628, n_D^{20} = 1.5836; MR_D = 58.71, calcd. 58.68. IR spectrum, ν, cm^{-1}: 655, 680 (C–Br); 1100, 3620 (CHOH). ^{1}H NMR spectrum, δ, ppm: 6.76–7.0 m (3H, C_6H_3), 2.34 s (6H, CH_3), 2.86–3.10 d (2H, CH_2), 4.01 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.68 m (1H, CHBr), 1.59 s (3H, CH_3). Found, %: C 56.0; H 6.58; Br 31.2. $C_{12}H_{17}BrO$. Calculated, %: C 56.03; H 6.61; Br 31.16.

3-Bromo-1-(2,5-dimethylphenyl)butan-2-ol (Vh) was obtained from 17.5 g (0.1 mol) of compound **IVh**. Yield 22.2 g (86%), bp 113–116°C (0.5 mm), d_4^{20} = 1.4564, n_D^{20} = 1.5778; MR_D = 58.44, calcd. 58.67. IR spectrum, ν, cm^{-1}: 656, 680 (C–Br); 1100, 3618 (CHOH). ^{1}H NMR spectrum, δ, ppm: 6.75–6.89 m (3H, C_6H_3), 2.35 s (6H, CH_3), 2.87–3.12 d (2H, CH_2), 4.0 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.67 m (1H, CHBr), 1.57 s (3H, CH_3). Found, %: C 56.0; H 6.58; Br 31.2. $C_{12}H_{17}BrO$. Calculated, %: C 56.03; H 6.61; Br 31.19.

3-Bromo-1-(2-bromophenyl)butan-2-ol and 3-bromo-1-(4-bromophenyl)butan-2-ol (VIa) were obtained from 14.8 g (0.1 mol) of compound **IVa**, 22.6 g (0.2 mol) of 30% hydrogen peroxide, and 40 g of 46% hydrobromic acid. Yield 26.7 g (87%), mp 62–64°C (from hexane). IR spectrum, ν, cm^{-1}: 655, 680 (C–Br); 1100, 3625 (OH); 776, 810, 864 (δC_6H_3); 918, 974 (*cis* and *trans*). ^{1}H NMR spectrum, δ, ppm: 6.69–7.38 m (4H, C_6H_4), 2.59–2.84 d (2H, CH_2), 3.89–4.01 m (1H, C**H**OH), 4.8 br.s (1H, OH), 3.68 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 38.73; H 3.84; Br 52.08. *M* 307.4. $C_{10}H_{12}Br_2O$. Calculated, %: C 38.96; H 3.89; Br 51.95. *M* 308.

Compounds **VIb** and **VId–VIh** were synthesized in a similar way.

3-Bromo-1-(2-bromo-4-methylphenyl)butan-2-ol and 3-bromo-1-(3-bromo-4-methylphenyl)butan-2-ol (VIb) were obtained from 16.2 g (0.1 mol) of isomer mixture **IVb**. Yield 27.1 g (84%), mp 58–59°C. IR spectrum, ν, cm^{-1}: 776, 810, 864 (δC_6H_3); 1100, 3625 (OH); 625, 655, 680 (C–Br); 918, 974 (*cis* and *trans*). ^{1}H NMR spectrum, δ, ppm: 6.87–7.23 m (3H, C_6H_3), 2.34 s (3H, CH_3), 2.57–2.82 d (2H, CH_2), 3.89–4.0 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.68 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 41.06; H 4.38; Br 49.86. *M* 321.4. $C_{11}H_{14}Br_2O$. Calculated, %: C 41.0; H 4.35; Br 51.95. *M* 322.

3-Bromo-1-(2-bromo-6-methoxyphenyl)butan-2-ol and 4-bromo-1-(3-bromo-4-methoxyphenyl)-butan-2-ol (VId) were obtained from 17.8 g (0.1 mol) of isomer mixture **IVd**. Yield 26.6 g (79%), mp 60–61°C (from hexane). IR spectrum, ν, cm^{-1}: 625, 655, 680 (C–Br); 776, 810, 840 (δC_6H_3); 1100, 3610 (OH); 918, 974 (*cis* and *trans*). ^{1}H NMR spectrum, δ, ppm: 6.66–7.20 m (3H, C_6H_3), 2.73 s (1H, CH_3O), 2.58–2.83 d (2H, CH_2), 3.80–3.83 m (1H, C**H**OH), 3.67 m (1H, CHBr), 4.8 br.s (1H, OH), 1.78 s (3H, CH_3). Found, %: C 40.91; H 4.54; Br 45.45. *M* 336.2. $C_{11}H_{14}Br_2O_2$. Calculated, %: C 40.93; H 4.58; Br 45.62. *M* 338.

3-Bromo-1-(2-bromo-6-ethoxyphenyl)butan-2-ol and 3-bromo-1-(3-bromo-4-ethoxyphenyl)butan-2-ol (VIe) were obtained from 19.2 g (0.1 mol) of isomer mixture **IVe**. Yield 28.6 g (81%), mp 61–63°C (from hexane). IR spectrum, ν, cm^{-1}: 625, 655, 680 (C–Br); 1100, 3610 (OH); 730, 770, 810, 840 (δC_6H_3). ^{1}H NMR spectrum, δ, ppm: 6.70–7.10 m (3H, C_6H_3), 3.97 d (2H, CH_2O), 1.33 s (3H, C**H**$_3$$CH_2O$), 3.80 m (1H, C**H**OH), 3.88 m (1H, CHBr), 4.8 m (1H, OH), 1.78 s (3H, CH_3). Found, %: C 40.98; H 4.58; Br 45.68. *M* 351.2. $C_{12}H_{16}Br_2O_2$. Calculated, %: C 40.91; H 4.54; Br 45.45. *M* 352.

3-Bromo-1-(4-bromo-2,3-dimethylphenyl)butan-2-ol and 3-bromo-1-(3-bromo-4,5-dimethylphenyl)-butan-2-ol (VIf) were obtained from 17.6 g (0.1 mol) of isomer mixture **IVf**. Yield 30.7 g (92%), mp 68–69°C (from hexane). IR spectrum, ν, cm^{-1}: 650, 685 (C–Br); 1100, 3615 (OH); 918, 974 (*cis* and *trans*). ^{1}H NMR spectrum, δ, ppm: 6.70–7.07 m (2H, C_6H_2), 2.35 s (6H, CH_3), 2.88–3.12 d (2H, CH_2), 3.80 m (1H,

C**H**OH), 4.8 br.s (1H, OH), 3.89 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 42.86; H 4.76; Br 47.62. *M* 335.4. $C_{12}H_{16}Br_2O$. Calculated, %: C 42.82; H 4.74; Br 47.86. *M* 336.

3-Bromo-1-(3-bromo-2,6-dimethylphenyl)butan-2-ol and 3-bromo-1-(2-bromo-4,6-dimethylphenyl)-butan-2-ol (VIg) were obtained from 17.6 g (0.1 mol) of isomer mixture **IVg**. Yield 29.6 g (88%), mp 66–67°C (from hexane). IR spectrum, ν, cm^{-1}: 625, 655, 680 (C–Br); 1100, 3620 (OH). ^{1}H NMR spectrum, δ, ppm: 6.71–7.01 m (2H, C_6H_2), 2.35 s (6H, CH_3), 2.57–2.83 d (2H, CH_2), 4.08 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.67 m (1H, CHBr), 1.78 s (3H, CH_3). Found, %: C 42.83; H 4.73; Br 47.72. *M* 335. $C_{12}H_{12}Br_2O$. Calculated, %: C 42.86; H 4.76; Br 47.62. *M* 336.

3-Bromo-1-(3-bromo-2,5-dimethylphenyl)butan-2-ol (VIh) was obtained from 17.6 g (0.1 mol) of compound **IVh**. Yield 31.1 g (93%), mp 69–70°C (from hexane). IR spectrum, ν, cm^{-1}: 625, 655, 680 (C–Br); 1100, 3620 (OH). ^{1}H NMR spectrum, δ, ppm: 6.68–7.06 m (2H, C_6H_2), 2.35 s (6H, CH_3), 2.57–2.83 d (2H, CH_2), 4.0 m (1H, C**H**OH), 4.81 br.s (1H, OH), 3.67 m (1H, CHBr), 1.76 s (3H, CH_3). Found, %: C 42.8; H 4.72; Br 48.06. *M* 335.2. $C_{12}H_{16}Br_2O$. Calculated, %: C 42.86; H 4.76; Br 47.62. *M* 336.

1-Phenylbutane-2,3-diol (VIIa). A mixture of 14.8 g (0.1 mol) of compound **IVa**, 18 g (0.1 mol) of water, and 3.5 g of KU-2×8 cation exchanger was stirred for 4 h at 50–60°C. The product was recrystallized according to the procedure described in [16]. Yield 15.4 g (93%), mp 54–55°C. IR spectrum, ν, cm^{-1}: 1100, 3625 (OH); 918, 974 (*cis* and *trans*). ^{1}H NMR spectrum, δ, ppm: 7.12–7.26 m (5H, C_6H_5), 2.57–2.82 d (2H, CH_2), 3.67–3.46 s (2H, C**H**OH), 4.81 br.s (1H, OH), 1.21 s (2H, CH_3). Found, %: C 72.18; H 8.26. $C_{10}H_{14}O_2$. Calculated, %: C 72.29; H 8.43.

1-(2-Methylphenyl)butane-2,3-diol and 1-(4-methylphenyl)butane-2,3-diol (VIIb) were obtained in a similar way from 16 g (0.1 mol) of isomer mixture **IVb**. Yield 16.8 g, mp 65–68°C. IR spectrum, ν, cm^{-1}: 1100, 3625 (CHOH). ^{1}H NMR spectrum, δ, ppm: 7.0–7.2 m (4H, *o*-C_6H_4), 7.0 s (4H, *p*-C_6H_4), 2.57–2.83 d (2H, CH_2), 3.67–3.46 s (2H, C**H**OH), 4.81 br.s (2H, OH), 1.21 s (3H, CH_3). Found, %: C 73.02; H 8.68. $C_{11}H_{16}O_2$. Calculated, %: C 73.33; H 8.89.

1-Phenylbutane-2,3-diyl diacetate (VIIIa). A mixture of 7.4 g (0.05 mol) of compound **IVa** and 2 g of KU-2×8 cation exchanger (H form) in 25 g of benzene was cooled to 10°C, and 4.5 g (0.056 mol) of acetic anhydride was slowly added under stirring. The reaction was accompanied by slight evolution of heat. The mixture was stirred for 3 h and filtered through a Schott filter, the solvent was distilled off from the filtrate, and the residue was distilled under reduced pressure. Yield 11.9 g (94%), bp 125–128°C (3 mm), d_4^{20} = 1.083, n_D^{20} = 1.4918; MR_D = 67.01, calcd. 66.87. ^{1}H NMR spectrum, δ, ppm: 7.1–7.24 m (5H, C_6H_5), 2.64–2.90 d (2H, CH_2), 4.71–4.92 m (2H, CH), 1.38 s (3H, CH_3), 2.0 s (6H, CH_3CO). Found, %: C 67.45; H 7.38. $C_{14}H_{18}O_4$. Calculated, %: C 67.2; H 7.2.

1-(2-Methylphenyl)butane-2,3-diyl diacetate and 1-(3-methylphenyl)butane-2,3-diyl diacetate (VIIIb) were obtained in a similar way from 8.0 g (0.05 mol) of isomer mixture **IVb** and 4.5 g (0.056 mol) of acetic anhydride. Yield 12.5 g (95%), bp 128–129°C (1.5 mm), d_4^{20} = 1.0701, n_D^{20} = 1.4931; MR_D = 71.57, calcd. 71.52. ^{1}H NMR spectrum, δ, ppm: 6.86–7.17 m (4H, C_6H_4), 2.34 s (3H, CH_3), 2.65–2.90 d (2H, CH_2), 4.71–4.90 m (2H, CH), 1.39 s (3H, CH_3), 2.0 s (6H, CH_3CO). Found, %: C 68.23; H 7.46. $C_{15}H_{20}O_4$. Calculated, %: C 68.18; H 7.58.

REFERENCES

1. Soldatenko, L.T., Kolyadina, I.M., and Shendrik, I.V., *Osnovy organicheskoi khimii lekarstvennykh veshchestv* (Foundations of Organic Chemistry of Drugs), Moscow: Mir, 2003.
2. Kheifits, L.A. and Dashunin, V.M., *Dushistye veshchestva i drugie produkty dlya parfyumerii* (Fragrant Substances and Other Materials for Perfumery), Moscow: Khimiya, 1994.
3. Shulov, L.M. and Kheifits, L.A., *Dushistye veshchestva i produkty parfyumerno-kosmeticheskogo proizvodstva. Spravochnik* (Fragrant Substances and Products of Perfume and Cosmetic Industries. Reference Book), Moscow: Agropromizdat, 1990.
4. Paken, A.M., *Epoksidnye soedineniya i epoksidnye smoly* (Epoxy Compounds and Epoxy Resins), Moscow: Goskhimizdat, 1962.
5. *Okis' etilena* (Ethylene Oxide), Zimanov, P.V. and Dymenta, O.N., Eds., Moscow: Khimiya, 1967.
6. De la Mare, P.B.D. and Bolton, R., *Electrophilic Additions to Unsaturated Systems*, Amsterdam: Elsevier, 1966.
7. Boguslovskaya, L.S., *Usp. Khim.*, 1972, vol. 51, p. 1591.
8. Sergeev, G.B. and Leenson, I.A., *Usp. Khim.*, 1972, vol. 51, p. 1566.

9. Sergeev, G.B., Serguchev, Yu.A., and Smirnov, V.V., *Usp. Khim.*, 1973, vol. 52, p. 1545.
10. Mamedaliev, Yu.G., Guseinov, M.M., and Mishiev, D.E., *Dokl. Akad. Nauk Azerb. SSR*, 1963, vol. 19, p. 27; *Azerb. Khim. Zh.*, 1962, p. 19.
11. Guseinov, M.M., Mishev, D.E., and Mekhraliev, A.A., *Dokl. Akad. Nauk Azerb. SSR*, 1968, vol. 24, p. 24.
12. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.
13. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
14. Sadygov, O.A., Alimardanov, Kh.M., and Chalabiev, Ch.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 1631; Sadygov, O.A., Alimardanov, Kh.M., and Chalabiev, Ch.A., *Neftekhimiya*, 2006, vol. 46, p. 144; Sadygov, O.A., Alimardanov, Kh.M., and Chalabiev, Ch.A., *Zh. Prikl. Khim.*, 2006, vol. 79, p. 959.
15. Sorokin, M.F. and Lyalyushko, K.A., *Praktikum po khimii i tekhnologii plenkoobrazuyushchikh veshchestv* (Laboratory Course on the Chemistry and Technology of Film-Forming Substances), Moscow: Khimiya, 1971.
16. Malinovskii, M.S., *Okisi olefinov i ikh proizvodnye* (Olefin Oxides and Their Derivatives), Moscow: Goskhimizdat, 1961.
17. John, H., Raubuch, H., Rudekirch, G., and Teige, W., *J. Prakt. Chem.*, 1968, vol. 37, p. 113.
18. Salomatina, O.V., Yarovaya, O.N., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 155.
19. Kas'yan, L.I., Kas'yan, A.O., and Okovityi, S.I., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 307.