



**Table 1.** Yields, melting points, and  $MR_D$  values of compounds **I–XII**

Compd. no.	Yield, %	bp, °C (mm Hg)	$n_D^{20}$	$d_4^{20}$	$MR_D$		Found, %			Formula	Calculated, %			$R_f$
					found	calculated	C	H	Cl or S		C	H	Cl or S	
<b>I</b>	65	106 (1.3)	1.5410	1.1272	51.48	51.17	65.27	6.90	19.34	$C_{10}H_{13}OCl$	65.04	7.10	19.20	0.43
<b>II</b>	61	140 (2.8)	1.5285	1.0791	60.72	60.41	67.94	7.87	16.38	$C_{12}H_{17}OCl$	67.76	8.06	16.66	0.51
<b>III</b>	71	134–135 (4)	1.5398	1.1271	51.39	51.17	64.91	6.83	19.07	$C_{10}H_{13}OCl$	65.04	7.10	19.20	0.53
<b>IV</b>	56	145–146 (1.1)	1.6230	1.2532	61.89	61.89	70.67	5.82	16.35	$C_{13}H_{13}OCl$	70.35	5.94	16.07	0.62
<b>V</b>	68	70 (1.3)	1.5192	1.0155	44.31	44.20	80.81	8.29	–	$C_{10}H_{12}O$	81.04	8.16	–	0.68
<b>VI</b>	63	98 (3)	1.5135	0.9854	53.84	54.16	81.52	9.36	–	$C_{12}H_{16}O$	81.77	9.15	–	0.86
<b>VII</b>	74	90–91 (0.4)	1.5220	1.0266	44.03	44.20	81.17	8.03	–	$C_{10}H_{12}O$	81.04	8.16	–	0.77
<b>VIII</b>	85	154–155 (4)	1.6131	1.1430	56.07	56.04	84.42	6.29	–	$C_{13}H_{12}O$	84.75	6.57	–	0.41
<b>IX</b>	83	98 (1.3)	1.5642	1.0518	50.81	50.68	73.43	7.18	19.31	$C_{10}H_{12}S$	73.12	7.36	19.52	0.71
<b>X</b>	70	110 (2)	1.5430	1.0037	60.36	60.53	74.67	8.52	16.58	$C_{12}H_{16}S$	74.94	8.39	16.67	0.82
<b>XI</b>	71	129 (2.5)	1.5625	1.0469	50.92	50.68	73.31	7.12	19.16	$C_{10}H_{12}S$	73.12	7.36	19.52	0.75
<b>XII</b>	80	134–135 (1)	1.6508	1.1427	62.21	62.56	77.69	6.23	16.37	$C_{13}H_{12}S$	77.95	6.04	16.07	0.74

**Table 2.** Parameters of  $^1H$  NMR and IR spectra of compounds **I–XII**

Compd. no.	$^1H$ NMR spectrum ( $CCl_4$ ), $\delta$ , ppm					IR spectrum, $cm^{-1}$				
	$CH_3$ , s	$ArCH_2$ , d	$CH_2X$ , d	CH, m	Ar, s	OH	$CH_2Cl$	oxirane	thiirane	frequencies of substitution type
<b>I</b>	2.15	2.65	3.30	3.65	6.70	3400	770	–	–	840, 1790, 1960
<b>II</b>	1.30	2.60	3.25	1.85 3.70	6.75	3380	765	–	–	1790, 1910
<b>III</b>	–	2.65 t	3.30	3.50	6.95	3390	765	–	–	840, 1790, 1960
<b>IV</b>	–	2.45	3.15	4.15	6.65 7.10	3390	785	–	–	830, 1720, 1930
<b>V</b>	2.20	2.65	2.35 2.70	2.80	6.60	–	–	830, 1020, 1250	–	805, 1785, 1900
<b>VI</b>	1.30	2.60	2.25 2.60	2.75	6.70	–	–	840, 1020, 1240	–	810, 1780, 1820
<b>VII</b>	–	2.65	2.20 2.45	2.85	6.95	–	–	830, 1015, 1240	–	700, 730, 1810
<b>VIII</b>	–	3.20	2.35 2.65	3.30	7.2– 8.2	–	–	830, 1015, 1245	–	815, 1720, 1925
<b>IX</b>	2.20	2.70	2.08 2.25	2.70	6.60	–	–	–	635	820, 1700, 1910
<b>X</b>	1.20	2.60	2.10 2.30	2.75	6.75	–	–	–	625	820, 1710, 1910
<b>XI</b>	–	2.75	1.85 2.25	2.85	6.85	–	–	–	625	690, 750, 1930
<b>XII</b>	–	3.20	2.10 2.30	3.20	7–8	–	–	–	625	805, 1780, 1910

corresponding to asymmetrical, symmetrical, and pulse vibrations of the oxirane ring. Unlike the IR spectra of oxiranes, in the spectra of thiiranes **IX–XII** are present absorption bands at 625–635  $\text{cm}^{-1}$  from the stretching vibrations of the C–S bond in the three-membered thiirane ring.

In the  $^1\text{H}$  NMR spectra of 1,2-chlorohydrins **I–IV** in the strong field at 1.30–2.15 ppm appear signals of protons from methyl groups attached to aromatic rings, and doublet signals in the region 2.60–2.65 ppm correspond to the methylene protons linked to the benzene ring. The proton signals of the methylene group in compound **III** bonded to benzyl group and the neighboring methine group appear at 1.5–1.9 ppm as a quartet due to spin-spin coupling. The protons signals from the methylene groups linked to chlorine in the molecules of 1,2-chlorohydrins give rise to doublet in the 3.15–3.30 ppm region, and the signal of methine proton appears as a multiplet at 3.50–4.15 ppm.

A strong signal in the downfield part of the  $^1\text{H}$  NMR spectra (6.70–6.95 ppm) originates from aromatic protons, and naphthyl protons of compound **IV** give rise to a multiplet at 7.80–8.10 ppm. The proton signal of the hydroxy group in all studied 1,2-chlorohydrins overlapped with the resonance of  $\text{CH}_2\text{Cl}$  group as was proved by recording the spectrum in the presence of  $\text{D}_2\text{O}$ .

In the  $^1\text{H}$  NMR spectra of oxiranes **V–VIII** the protons of  $\text{CH}_2$  group in the oxirane ring give rise to two doublets at 2.20–2.35 ppm and 2.45–2.70 ppm which correspond to hydrogens located in *cis*- and *trans*-positions. The methine proton signals in the oxirane ring of compounds **V–VIII** are shifted upfield as compared with 1,2-chlorohydrins and appear at 2.70–3.30 ppm. The  $^1\text{H}$  NMR spectra of thiiranes **IX–XII** are similar in appearance to the oxirane spectra, but the proton signals of the  $\text{CH}_2$  group in the thiirane ring are shifted upfield and give two doublets in the region 1.85–2.10 and 2.70–3.20 ppm.

## EXPERIMENTAL

$^1\text{H}$  NMR spectra were recorded on spectrometer Varian T-60 at operating frequency 60 MHz from solutions in  $\text{CCl}_4$  with TMS as internal reference.  $^{13}\text{C}$  NMR spectra were registered on Varian VXR-400 instrument at operating frequency 100 MHz. IR spectra were measured on spectrophotometer Specord-75 IR from liquid films in the region 400–4000  $\text{cm}^{-1}$  (with prisms of KBr, NaCl, LiF). The progress of reactions was monitored and the purity of

compounds synthesized was checked by GLC using chromatograph Tsvet-126 equipped with a flame-ionization detector, glass column 1500  $\times$  3 mm, stationary phase 5% SE-30 on Chromaton N-AW, carrier gas nitrogen. TLC of compounds **I–XII** was performed on Silufol UV-254 plates using as eluent ethanol–hexane mixture, 1:5.

**4-Phenyl-1-chloro-2-butanol (III).** To an ethereal solution of benzylmagnesium bromide obtained by a common procedure from 0.5 mol (93 g) of benzyl bromide, 0.5 g-atom (12 g) of magnesium in 200 ml of dry ether in the presence of 2–3 iodine crystals under external cooling with an ice bath was added dropwise at stirring a solution of 1 mol (92.5 g) of 1,2-epoxy-3-chloropropane in 100 ml of dry ether. Then the reaction mixture was heated to 35°C for 2 h more at constant stirring. Then at cooling the flask with an ice bath the reaction mixture was quenched with 10% solution of hydrochloric acid till two transparent layers formed. The upper organic layer was separated, the water layer was thrice extracted with ether. The combined organic solutions were washed with water and dried with anhydrous sodium sulfate. After removing the solvent the residue was subjected to a vacuum distillation. We obtained 65.5 g of 4-phenyl-1-chloro-2-butanol (**III**). Yield of compound **III** 71%, bp – 134–135°C (4 mm Hg),  $n_{\text{D}}^{20}$  1.5398,  $d_4^{20}$  1.1271. Published data [13]: bp 158–160°C (23 mm Hg),  $n_{\text{D}}^{20}$  1.5371.

Likewise by reaction of *p*-tolyl-, *p*-isopropyl-phenyl-,  $\alpha$ -naphthylmagnesium bromides with 1,2-epoxy-3-chloropropane in a dry ether solution were prepared the corresponding 1,2-chlorohydrins **I**, **II**, **IV**. Their physical constants are listed in Table 1. 1-Chloro-3-(4-methylphenyl)-2-propanol (**I**) and 1-chloro-3-( $\alpha$ -naphthyl)-2-propanol (**IV**) were prepared as described in [13]; as mentioned in [13], the data on the constants of compounds **I**, **IV** were incorrect.

**1,2-epoxy-4-phenylbutane (VII).** To a mixture of 18.5 g (0.1 mol) of 1-chloro-4-phenyl-2-butanol and 50 ml of hexane at vigorous stirring was added dropwise 20 g of 29% NaOH solution. Then the reaction mixture was heated for 2 h to 60°C. On cooling the reaction mixture was several times washed with water till neutral washings and dried with anhydrous sodium sulfate. On removing the solvent the reaction product was subjected to vacuum distillation to obtain 11 g (24%) of compound **VII**, bp 90–91°C (0.4 mm Hg),  $n_{\text{D}}^{20}$  1.5220;  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ),  $\delta$ , ppm: 2.20, 2.45 (2H,  $\text{CH}_2$ -oxirane), 2.85 (1H, CH), 2.65 t (2H,  $\text{ArCH}_2$ ), 6.95 s (5H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  NMR spectrum

(CDCl<sub>3</sub>),  $\delta$ , ppm: 52.57 (CH), 38.49 (CH<sub>2</sub>-oxirane), 38.43 (CH<sub>2</sub>CH), 147.42 (C<sub>i</sub>), 134.30 (C<sub>p</sub>), 129.31 (C<sub>o</sub>), 127.54 (C<sub>m</sub>). Found, %: C 81.17; H 8.03. C<sub>10</sub>H<sub>8</sub>O. Calculated, %: 81.04; H 8.16.

Likewise were obtained the other oxiranes **V**, **VI**, **VIII** whose constants are given in Table 1.

**1,2-Epithio-4-phenylbutane (XI)**. Into a three-neck flask was charged 76 g (1 mol) of thiourea and 30 ml of sulfuric acid solution containing 1 g-equiv of the acid and 350 ml of water. At vigorous stirring the reaction mixture was cooled to 5–10°C and maintaining this temperature 148 g (1 mol) of 1,2-epoxy-4-phenylbutane was added dropwise within 2 h. After completion of oxirane addition the reaction mixture was stirred for 1 h at room temperature and then hydrolyzed with a solution of 106 g (1 mol) of sodium carbonate in 450 ml of water. The organic layer was separated, the water layer was twice extracted with ether. The combined organic solutions were dried with anhydrous sodium sulfate. After removing ether the reaction product was subjected to vacuum distillation to obtain 116 g (71%) of compound **XI**, bp 129°C (2.5 mm Hg),  $n_D^{20}$  1.5625; <sup>1</sup>H NMR spectrum (CCl<sub>4</sub>),  $\delta$ , ppm: 1.85, 2.25 (2H, CH<sub>2</sub>-thiirane), 2.85 m (1H, CH), 2.75 t (2H, CH<sub>2</sub>Ar), 6.85 s (5H, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 35.36 (CH), 25.94 (CH<sub>2</sub>-thiirane), 141.08 (C<sub>i</sub>), 128.41, 128.36 (C<sub>o,m</sub>), 125.97 (C<sub>p</sub>), 38.29 (CH<sub>2</sub> Ph), 35.60 (CH<sub>2</sub> CH). Found, %: C 73.31; H 7.12; S 19.16. C<sub>10</sub>H<sub>12</sub>S. Calculated, %: C 73.12; H 7.36; S 19.52.

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