tert-butylhydroxylamine leads to an N-hydroxyamidoxime, the oxidation of which made it possible to preparatively isolate an amidoxime N-oxyl radical, viz., 4-(N-oxyl-N-tert-butylcarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide.

2. Oxidation of the radical gives a nitroso nitrone, and alkylation gives only an O-alkylation product (an ether amidoxime N-oxyl), whereas the similarly constructed amidoxime reacts to give both an O-alkylation product (an ether amidoxime) and an N-alkylation product (a nitrone).

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FUNCTIONAL SULFUR-CONTAINING COMPOUNDS. COMMUNICATION 7. REACTIONS OF 2,3-EPOXYPROPYL ALKYL SULFIDES, SULFOXIDES, AND SULFONES WITH ALKOXIDES AND AMINES

A. R. Derzhinskii, V. E. Kalugin,
and E. N. Prilezhaeva

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In a previous paper [1] we described the nucleophilic addition of mercaptans to 2,3-epoxy(epithio)propyl alkyl sulfides, sulfoxides, and sulfones and showed that the specificity of opening of the epoxide ring depends on the structure of the mercaptan and the oxidation state of the sulfur atom in the substituent.

In the present research we studied the nucleophilic addition of alcohols and amines with various structures to 2,3-epoxypropyl alkyl sulfides, sulfoxides, and sulfones. The reactions of epoxy sulfides with alkoxides [2] and with aliphatic, acyclic, and aromatic amines [3-6] have been described in the literature. It is assumed that only products of normal opening of the epoxide ring are obtained in these cases.

We have investigated the addition of alkoxides to epoxy sulfides I at 60-65°C in the corresponding alcohol. The maximum yields (90-93%) of the products of addition of primary and secondary alcohols are achieved at an epoxide:alkoxide molar ratio of 1:1.5, and the yields of products of addition of tert-butyl alcohol do not exceed 5%. Despite the assertion of Rietz and co-workers [2], the reaction of epoxides I with alkoxides does not proceed selectively and leads to mixtures of regioisomers II and III:

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TABLE 1. Characteristics of Compounds with the General Formulas $RS(O)_nCH_2CH(OH)CH_2OR^1$ and $RS(O)_nCH_2CH(OR^1)CH_2OH$

Compound*	Method of preparation	Yield, %	mp or bp (mm), °C	Found/calc., %			Empirical formula	Isomer ratio
				C	H	S		
$RSCH_2CH(OH)CH_2OR^1$ (II) and $RSCH_2CH(OR^1)CH_2OH$ (III)								(II) : (III)
(II,b, a), (IIIb,a)		93	71–72(1)	53,75/53,89	10,30/10,18	17,82/17,98	$C_8H_{18}O_2S$	1 : 1
(IIb,b), (IIIb,b)		92	58–63(0,3)	56,13/56,21	10,36/10,48	16,78/16,67	$C_9H_{20}O_2S$	1 : 1
(IIb,c), (IIIb,c)		92	98–101(1,5)	58,44/58,21	10,81/10,75	15,66/15,54	$C_{10}H_{22}O_2S$	3 : 2
(IIb,d), (IIIb,d)		70	148–149(0,1)	68,47/68,62	12,05/12,12	9,75/9,64	$C_{19}H_{40}O_2S$	1 : 1
(IIb,e), (IIIb,e)		42	133–134(1)	65,07/64,96	8,31/8,39	13,48/13,34	$C_{13}H_{20}O_2S$	2 : 1
(IIc,a), (IIIc,a)		93	115–117(1,5)	61,31/61,49	11,27/11,18	13,83/13,68	$C_{12}H_{26}O_2S$	1 : 1
(IIc,c), (IIIc,c)		92	102–104(0,8)	64,23/64,07	11.64/11,52	12,09/12,22	$C_{14}H_{30}O_2S$	3 : 2
(IIc,e), (IIIc,e)		45	176–178(1)	68,72/68,87	9,66/9,52	10,94/10,82	$C_{17}H_{28}O_2S$	2 : 1
$RS(O)CH_2CH(OH)CH_2OR^1$ (IV) and $RS(O)CH_2CH(OR^1)CH_2OH$ (V)								
(IVb,a)	A	40	Oil	49,27/49,45	9,41/9,34	16,64/16,50	$C_8H_{18}O_3S$	
(Vb,a)	A	52	52–53	49,38/49,45	9,52/9,34	16,47/16,50	$C_8H_{18}O_3S$	
(Vb,a)	B C	93 93						
(IVb,b)	A	47	Oil	51,69/51,89	9,50/9,68	14,85/15,39	$C_9H_{20}O_3S$	
(Vb,b)	A	46	63–64	52,02/51,89	9,56/9,68	15,07/15,39	$C_9H_{20}O_3S$	
(IVc,c)	A	54	Oil	54,18/54,02	10,11/9,97	14,58/14,42	$C_{10}H_{22}O_3S$	
(Vc,c)	A	38	81–82	54,07/54,02	9,83/9,97	14,32/14,42	$C_{10}H_{22}O_3S$	
	B C	66 66						
(IVc,d)	A	48	30–30,5	65,72/65,71	11,56/11,56	9,21/9,22	$C_{19}H_{40}O_3S$	
(Vc,d)	A	48	63–64	65,83/65,71	11,60/11,56	9,14/9,22	$C_{19}H_{40}O_3S$	
(IVc,e)	A	63	69–70	60,83/60,91	7,94/7,86	12,59/12,51	$C_{13}H_{20}O_3S$	
(Vc,e)	A	32	122–122,5	60,96/60,91	7,98/7,86	12,43/12,51	$C_{13}H_{20}O_3S$	
(Vc,a)	A	41	Oil	57,78/57,56	10,32/10,47	12,73/12,80	$C_{12}H_{26}O_3S$	
(IVc,a)	A	53	58–59	57,32/57,57	10,56/10,47	12,77/12,80	$C_{12}H_{26}O_3S$	
(Vc,a)	B C	90 90						
(IVc, c)	A	55	Oil	60,29/60,39	10,98/10,86	11,33/11,51	$C_{14}H_{30}O_3S$	
(Vc,c)	A	39	50,5–51	60,43/60,39	10,84/10,86	11,46/11,51	$C_{14}H_{30}O_3S$	
(Vc,c)	B C	62 62						
(IVc,e)	A	64	99–99,5	65,18/65,35	9,15/9,03	10,37/10,26	$C_{17}H_{28}O_3S$	
(Vc,e)	A	32	145–144	65,22/65,35	9,09/9,03	10,45/10,26	$C_{17}H_{28}O_3S$	
$RSO_2CH_2CH(OR^1)CH_2OH$ (VIII)								
(VIIb,a)	B C	93 93	25,5–26	45,43/45,69	8,78/8,63	12,36/12,25	$C_8H_{18}O_4S$	

TABLE 1 (continued)

Compound*	Method of preparation†	Yield, %	mp or bp (mm), °C	Found/calc., %			Empirical formula	Isomer ratio
				C	H	S		
(VIIIb,c)	B	56	Oil	50,28 50,39	9,41 9,30	13,49 13,45	$C_{10}H_{22}O_4S$	
	C	58						
(VIIIc,a)	B	90	47,5–48,5	54,15 54,11	9,91 9,84	11,96 12,04	$C_{12}H_{26}O_4S$	
(VIIIc,a)	C	90						
(VIIIc,c)	B	52	23–23,5	57,03 57,10	10,35 10,27	10,84 10,89	$C_{14}H_{30}O_4S$	
(VIIIc,c)	C	55						

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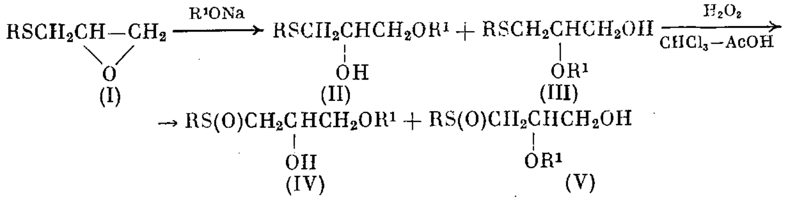
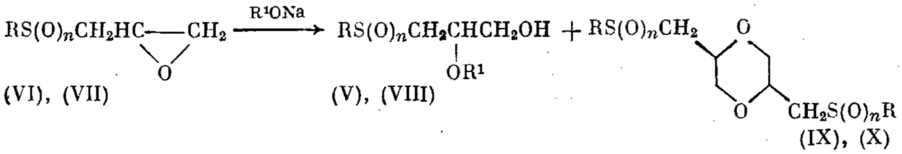
*The first index is R, and the second index is R^1: R = C_4H_9 (b), C_8H_{17} (c); R^1 = Me (a), Et (b); iso-Pr (c), $C_{12}H_{25}$ (d), Ph (e).

†Method A involves the reaction of alkoxides with epoxy sulfoxides VI and sulfones VII, and method C involves the reaction of alkoxides with unsaturated alcohols XI and XII.



We were unable to separate sulfides II and III; they were characterized in the form of mixtures (Table 1). To determine the ratios the mixtures of sulfides II and III were oxidized by the action of H_2O_2 to the corresponding sulfoxides IV and V (see Table 1). It follows from the data in Table 1 that the ratios of regioisomers II and III vary as a function of the structure of the alcohol. In the reactions with primary alcohols II:III = 1:1, whereas II:III = 3:2 in the reaction with isopropyl alcohol. The analogous reaction with sodium phenoxide in MeOH proceeds with the formation of both regioisomers in a ratio of 3:2.

Epoxy sulfoxides VI and sulfones VII react differently with primary and secondary alcohols in the presence of alkoxides. In this case the principal reaction pathway is the formation of isomers V and VIII (see Table 1) and dimeric products, viz., dioxanes IX and X.



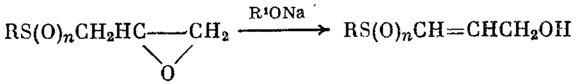
$n = 1$ (V), (VI), (IX); 2 (VII), (VIII), (X).

It has previously been shown [7] in the case of 2,3-epoxypropyl ethyl sulfone (VII, R = Et) that the epoxy sulfone can be isomerized under the influence of EtONa to 3-ethylsulfonylprop-2-en-1-ol, the subsequent addition of the alkoxide to which leads to 3-ethylsulfonyl-2-ethoxypropan-1-ol (VIII, R = R^1 = Et). We found that for the entire series of investigated compounds, both epoxy sulfoxides VI and epoxy sulfones VII, isomerization under the influence of alkoxides at an epoxide:alkoxide molar ratio of 1:0.3-2 in the first step of the process is a general reaction that leads to the formation of the corresponding unsaturated alcohols XI and XII:

TABLE 2. Characteristics of RS(O)CH=CHCH₂OH (XI) and RSO₂CH=CHCH₂OH (XII)

Compound*	Yield, %	MP, °C	Found/calc., % C	H	S	Empirical formula	trans:cis ratio
(XIa)	90	Oil	44,75 44,75	7,63 7,51	23,67 23,89	$C_5H_{10}O_2S$	4:1
(XIb)	92	»	52,04 51,82	8,95 8,70	19,61 19,76	$C_7H_{14}O_2S$	4:1
(XIc)	92	31–31,5	60,46 60,51	10,11 10,16	14,74 14,68	$C_{11}H_{22}O_2S$	12:1
(XId)	93	46–47	63,23 63,37	10,78 10,64	12,79 13,01	$C_{13}H_{26}O_2S$	19:1
(XIe)	93	57,5–58	65,70 65,64	11,12 11,02	11,75 11,68	$C_{15}H_{30}O_2S$	19:1
(XIIa) †	65	62–63	–	–	–	$C_5H_{10}O_3S$	1:0
(XIIb)	72	57,5–58	47,24 47,17	7,64 7,92	17,78 17,99	$C_7H_{14}O_3S$	1:0
(XIIc)	84	66–67	56,21 56,37	9,57 9,46	13,80 13,68	$C_{11}H_{22}O_3S$	1:0
(XIId)	86	74–76	59,56 59,50	10,14 9,98	12,13 12,22	$C_{13}H_{26}O_3S$	1:0
(XIIe)	85	82,5–83,5	61,86 62,03	10,83 10,41	10,94 11,04	$C_{15}H_{30}O_3S$	1:0

*R = Et (a), Bu (b), C_8H_{17} (c), $C_{10}H_{21}$ (d), and $C_{12}H_{25}$ (e).
†This compound was reported to have mp 62-63°C [7].



$$RS(O)_nCH_2HC\overset{}{-\!-}CH_2\ (\text{epoxide, O}) \xrightarrow{R^1ONa} RS(O)_nCH{=}CHCH_2OH$$

(VI), (VII) (XI), (XII)

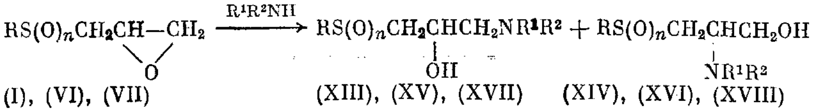
$n = 1$ (VI), (XI); 2 (VII), (XII).

The process can be stopped at the step involving the production of the unsaturated alcohols if one interrupts their subsequent reaction with the alkoxide a few seconds from the instant of mixing of the reagents for sulfones VII and after 10 min for sulfoxides VI by the addition of an equimolar amount of AcOH (Table 2). According to the PMR spectral data, sulfones XII are trans isomers. The isomerization of epoxy sulfoxides VI does not proceed stereospecifically; the ratios of the resulting cis and trans isomers depend on the length of the aliphatic chain in starting epoxides VI. Thus the ratio of the trans and cis isomers for XI (R = Et, Bu) is 4:1, whereas it is 19:1 for the higher homologs.

The reaction of unsaturated sulfones XII with alkoxides proceeds relatively rapidly (∼10 min) and leads to sulfones VIII. For the completion of the analogous reaction of sulfoxides XI with the alkoxides of primary and secondary alcohols 50 h and 20 h, respectively, are necessary. It is characteristic that the addition of alkoxides of primary, secondary, and tertiary alcohols to 3-alkylthioprop-2-en-1-ols does not occur under the indicated conditions.

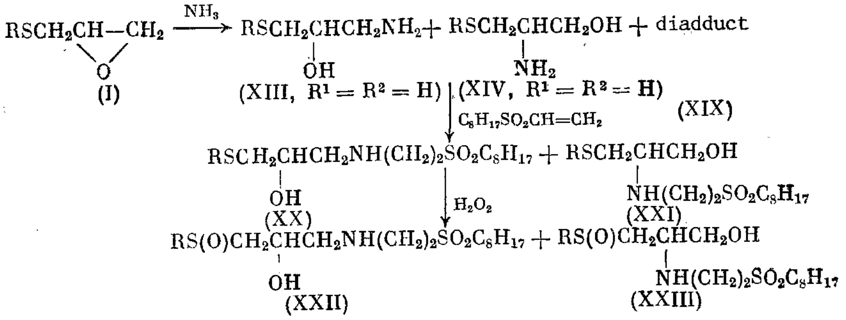
As we have already noted, dioxanes IX and X are formed along with V and VIII in the reaction of epoxides VI and VII with alkoxides. In the reaction of epoxy sulfoxides VI with the alkoxides of primary alcohols the percentage of dioxane IX is 2%, as compared with 6% in the reaction with the alkoxides of secondary alcohols. The yields of products X from epoxy sulfones VII are considerably higher: 5-7% in the reaction with alkoxides of primary alcohols, and 40% in the reaction with iso-PrONa. The process can be regulated to favor primarily the formation of dioxane X by treatment of the epoxy sulfone with aqueous alkali [1].

The reaction of epoxy compounds I, VI, and VII with amines does not proceed regiospecifically in most cases. This is manifested particularly in the addition of amines to epoxy sulfides I, which is not in agreement with the conclusions in [3-6] regarding the regiospecificity of the formation of exclusively products of normal opening of the epoxide ring.



$n = 0$ (I), (XIII), (XIV); 1 (VI), (XV), (XVI); 2 (VII), (XVII), (XVIII).

Sulfides XIII and XIV were isolated and characterized in the form of mixtures, the isomeric compositions of which were determined by oxidation to the corresponding readily separable sulfoxides XV and XVI (Table 3). The analysis of the compositions of the products of addition of ammonia to epoxy sulfides I proved to be a more complex problem. The mixture of monoamines XIII ($R^1 = R^2 = H$) and XIV ($R^1 = R^2 = H$) was separated from the diadducts by distillation in a high vacuum and treated with an equimolar amount of octyl vinyl sulfone (XIX). Amino sulfones XX and XXI, which were isolated in virtually quantitative yields, were then oxidized to sulfoxides XXII and XXIII.



We were able to separate XXII and XXIII completely and characterize them, and we were also able to determine the ratio of the starting sulfides (see Table 3).

The elucidation of the isomeric compositions of the products of the reaction of epoxy sulfoxides VI with amines was not a complicated problem, since sulfoxides XV and XVI are easily separated. In contrast to the latter, we were unable to separate sulfones XVII and XVIII, and their isomeric composition was determined by comparison of the PMR spectra of the reaction mixture and the corresponding anomalous isomer XVIII, which was obtained by alternative synthesis by the addition of the amine to 3-alkysulfonylprop-2-en-1-ol (XII):

$$C_4H_9SO_2CH{=}CHCH_2OH \xrightarrow{R^1R^2NH} C_4H_9SO_2CH_2\underset{NR^1R^2}{\underset{|}{C}}HCH_2OH$$

(XII) (XVIII)

The physicochemical characteristics of XIII-XVIII are presented in Table 3. The data on the isomer ratios provide evidence that the addition of amines to epoxides I, VI, and VII does not proceed selectively. The ratios of the regioisomers of sulfides XIII and XIV are ∿1:1 in most cases, and the formation of the normal isomer is preferred only for the reaction with diethylamine and tert-butylamine (7:3 and 3:2, respectively). The addition of amines to epoxy sulfoxides proceeds more selectively: the ratio of regioisomers XV and XVI for the reaction with diethylamine is 9:1, as compared with 2:1 for hexylamine and aniline and 3:2 for piperidine. The addition of tert-butylamine to epoxides VI is regiospecific and leads to the production of exclusively normal isomer XV ($R^1 = H$, $R^2 =$ tert-Bu).

The addition of amines to epoxy sulfones VII proceeds less selectively than the addition to epoxy sulfoxides VI: even in the case of the addition of diethylamine and tert-butylamine the ratio of regioisomers XVII and XVIII are 4:1 and 7:3, respectively (see Table 3).

Thus, on the basis of the results of our research, it may be concluded that the chemical behavior of epoxy sulfides I, sulfoxides VI, and sulfones VII and the specificity of the nucleophilic addition of alcohols and amines are determined by the oxidation state of the sulfur atom in the substituent and the nature of the addends and their structure.

EXPERIMENTAL

The IR spectra of KBr pellets of the solid substances and thin layers of the liquids were recorded with a UR-10 spectrometer. The PMR spectra of solutions of the compounds in

TABLE 3. Characteristics of Compounds with the General Formulas $RS(O)_nCH_2CH(OH)CH_2Y$ and $RS(O)_nCH_2CH(Y)CH_2OH$ [R = Et (a), Bu (b), C_8H_{17} (c), $C_{12}H_{25}$ (e)]

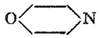
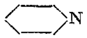
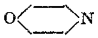
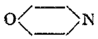
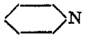
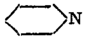
Compound	Y	Yield, %	mp or bp (mm), °C	Found/calc., % C	Found/calc., % H	Found/calc., % S	Empirical formula	Isomer ratio
			$RSCH_2CH(OH)CH_2Y$ (XIII) and $RSCH_2CH(Y)CH_2OH$ (XIV)					(XIII) : (XIV)
(XIIIa), (XIVa)	PhNH	90 *	139–140 (0,7)	62,31 62,52	8,19 8,11	15,08 15,17	$C_{11}H_{17}NOS$	1 : 1
(XIIIb), (XIVb)	NH_2	68 *	103–104 (1,5)	51,62 51,49	10,37 10,49	19,71 19,64	$C_7H_{17}NOS$	1 : 1
(XIIIb), (XIVb)	Et_2N	93 *	93–94 (1)	60,35 60,22	11,53 11,49	14,42 14,61	$C_{11}H_{25}NOS$	7 : 3
(XIIIb), (XIVb)		95 *	116–117 (1,5)	62,36 62,28	10,21 10,28	13,73 13,87	$C_{12}H_{25}NOS$	1 : 1
(XIIIb), (XIVb)		87 *	136–137 (1,5)	56,79 56,61	10,07 9,93	13,58 13,74	$C_{11}H_{23}NO_2S$	1 : 1
(XIIIb), (XIVb)	$C_6H_{13}NH$	88 *	28–32	63,03 63,10	11,74 11,81	12,93 12,96	$C_{13}H_{29}NOS$	1 : 1
(XIIIb), (XIVb)	*t*-BuNH	70 *	108–109 (1,5)	59,98 60,22	11,28 11,49	14,82 14,61	$C_{11}H_{25}NOS$	3 : 2
(XIIIb), (XIVb)	PhNH	90 *	177–178 (1,5)	65,11 65,23	8,96 8,84	13,43 13,39	$C_{13}H_{21}NOS$	1 : 1
(XIIIc), (XIVc)	NH_2	69 *	20–50	59,91 60,22	11,42 11,49	14,84 14,61	$C_{11}H_{25}NOS$	1 : 1
(XIIIc), (XIVc)		93 *	133–135 (0,3)	66,62 66,84	11,48 11,57	11,23 11,15	$C_{16}H_{33}NOS$	1 : 1
(XIIIc), (XIVc)	$C_6H_{13}NH$	90 *	40–40,5	64,01 63,90	11,56 11,67	10,09 10,03	$C_{17}H_{37}NOS$	1 : 1
(XIIIc), (XIVc)	PhNH	82 *	193–195 (0,3)	65,28 65,55	9,51 9,38	10,36 10,29	$C_{17}H_{29}NOS$	1 : 1
			$RS(O)CH_2CH(OH)CH_2Y$ (XV) and $RS(O)CH_2CH(Y)CH_2OH$ (XVI)					(XV) : (XVI)
(XVa)	PhNH	A† 62 B† 53	68–69	58,22 58,12	7,63 7,54	14,01 14,10	$C_{11}H_{17}NO_2S$	2 : 1
(XVIa)	PhNH	A 32 B 43	121–121,5	58,19 58,12	7,68 7,54	14,03 14,10	$C_{11}H_{17}NO_2S$	
(XVb)	Et_2N	A 83 B 68	Oil	56,06 56,13	10,85 10,72	13,76 13,62	$C_{11}H_{25}NO_2S$	9 : 1
(XVIb)	Et_2N	A 9 B 29	43–44	56,21 56,13	10,88 10,72	13,57 13,62	$C_{11}H_{25}NO_2S$	
(XVb)		A 55 B 48	Oil	58,44 58,26	10,11 10,19	13,17 12,96	$C_{12}H_{25}NO_2S$	3 : 2
(XVIb)		A 40 B 48	111–112	58,20 58,26	10,04 10,19	12,81 12,96	$C_{12}H_{25}NO_2S$	
(XVb)		A 56 B 48	Oil	53,12 52,98	9,51 9,30	12,81 12,86	$C_{11}H_{23}NO_3S$	3 : 2
(XVIb)		A 38 B 47	90,5–91,5	52,91 52,98	9,45 9,30	12,97 12,86	$C_{11}H_{23}NO_3S$	
(XVb)	*t*-BuNH	A 92 B 58	Oil	56,47 56,13	10,66 10,72	13,84 13,62	$C_{11}H_{25}NO_2S$	1 : 0

TABLE 3 (continued)

Compound	Y	Yield, %	mp or bp (mm), °C	Found/calc., %			Empirical formula	Isomer ratio
				C	H	S		
(XVIb)	*t*-BuNH	B 38	110–111	56,18/56,13	10,83/10,72	13,53/13,62	$C_{11}H_{25}NO_2S$	
(XVb)	PhNH	A 53 B 52	102,5–104	61,21/61,14	8,37/8,29	12,51/12,56	$C_{13}H_{21}NO_2S$	2 : 1
(XVIb)	PhNH	A 33	145–145,5	61,03/61,14	8,41/8,29	12,70/12,56	$C_{13}H_{21}NO_2S$	
(XVb)	$C_6H_{13}NH$	A 65 B 51	68–69	58,19/59,27	11,06/11,10	12,35/12,17	$C_{13}H_{29}NO_2S$	2 : 1
(XVIb)	$C_6H_{13}NH$	A 31 B 44	102,5–103,5	59,37/59,27	11,02/11,10	12,40/12,17	$C_{13}H_{29}NO_2S$	
(XVc)		A 56 B 49	Oil	63,21/63,32	11,08/10,96	10,44/10,56	$C_{16}H_{33}NO_2S$	3 : 2
(XVIc)		A 39 B 47	53–54	63,24/63,32	10,85/10,96	10,52/10,56	$C_{16}H_{33}NO_2S$	
(XVc)	PhNH	A 65 B 54	94–95	65,48/65,55	9,33/9,38	10,38/10,29	$C_{17}H_{29}NO_2S$	2 : 1
(XVIc)	PhNH	A 31 B 55	131–131,5	65,41/65,55	9,45/9,38	10,32/10,29	$C_{17}H_{29}NO_2S$	
(XVc)	$C_6H_{13}NH$	A 53 B 55	64–65	63,72/63,90	11,82/11,67	10,17/10,03	$C_{17}H_{37}NO_2S$	2 : 1
(XVIc)	$C_6H_{13}NH$	A 33 B 43	103,5–104,5	63,96/63,90	11,50/11,67	9,94/10,03	$C_{17}H_{37}NO_2S$	
(XVe)	*t*-BuNH	A 91	59–59,5	65,47/65,65	11,73/11,89	9,36/9,22	$C_{19}H_{41}NO_2S$	

		RSO$_2$CH$_2$CH(OH)CH$_2$Y (XVII)and RSO$_2$CH$_2$CH(Y)CH$_2$OH (XVIII)						(XVII) : (XVIII)
(XVIIa), (XVIIIa)	PhNH	96 *	Oil	54,17/54,30	7,19/7,04	13,27/13,18	$C_{11}H_{17}NO_3S$	2 : 1
(XVIIb), (XVIIIb)	Et_2N	97 *	»	52,29/52,56	10,14/10,02	12,56/12,76	$C_{11}H_{25}NO_3S$	4 : 1
(XVIIb), (XVIIIb)	t-BuNH	91 *	»	52,33/52,56	10,22/10,02	12,82/12,76	$C_{11}H_{25}NO_3S$	7 : 3
(XVIIIb), (XVIIb)		97 *	»	54,86/54,72	9,68/9,57	11,93/12,17	$C_{12}H_{25}NO_3S$	1 : 1
(XVIIb), (XVIIIb)	PhNH	97 *	»	57,39/57,54	7,93/7,80	11,97/11,82	$C_{13}H_{21}NO_3S$	2 : 1
(XVIIb), (XVIIIb)	$C_6H_{13}NH$	97 *	35–60	56,15/55,87	10,66/10,46	11,22/11,47	$C_{13}H_{29}NO_3S$	2 : 1
(XVIIc), (XVIIIc)	Et_2N	96 *	61–63	58,64/58,59	10,73/10,82	10,31/10,43	$C_{15}H_{33}NO_3S$	4 : 1
(XVIIc), (XVIIIc)		97 *	Oil	60,38/60,15	10,67/10,42	10,18/10,04	$C_{16}H_{33}NO_3S$	1 : 1
(XVIIc), (XVIIIc)	PhNH	96 *	86,5–87,5	62,31/62,35	8,98/8,93	9,84/9,79	$C_{17}H_{29}NO_3S$	2 : 1
(XVIIc), (XVIIIc)	$C_6H_{13}NH$	95 *	70–71	60,75/60,85	11,21/11,12	9,63/9,56	$C_{17}H_{37}NO_3S$	2 : 1
(XVIIIb)	Et_2N	C ** 87	Oil	52,23/52,56	10,14/10,02	12,97/12,76	$C_{11}H_{25}NO_3S$	
(XVIIIb)	t-BuNH·HCl	C 83	157–159	45,81/45,90	9,18/9,10	11,08/11,14	$C_{11}H_{26}ClNO_3S$	
(XVIIIb)	·HCl	C 90	Sublimes >175	48,15/48,07	8,82/8,74	10,56/10,69	$C_{12}H_{26}ClNO_3S$	
(XVIIIb)	PhNH	C 85	91,5–92,5	57,62/57,54	7,76/7,80	11,90/11,82	$C_{13}H_{21}NO_3S$	
(XVIIIb)	$C_6H_{13}NH$	C 87	92–94	55,74/55,87	10,42/10,46	11,59/11,47	$C_{13}H_{29}NO_3S$	

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*These yields are for mixtures of the isomers.

†Method A involves the addition of the amines to epoxy sulfoxide VI, method B involves oxidation of mixtures of sulfides XIII and XIV, and method C involves the addition of the amines to 3-butylsulfonylprop-2-en-1-ol (XIb).

$CDCl_3$ and CCl_4 were recorded with Varian 60-IL, Tesla BS-467 (60 MHz), and Tesla BS-497 (100 MHz) spectrometers relative to hexamethyldisiloxane (HMDS).

Addition of Alcohols to Epoxy Sulfides I in the Presence of Alkoxides. General Method. A 0.04-mole sample of I was added at 60°C in the course of 5 min to a solution of the sodium alkoxide, obtained from 30-50 ml of the alcohol and 1.4 g (0.06 g-atom) of Na, after which the mixture was stirred for 1 h and then poured into 200 ml of water. The aqueous mixture was extracted with ether, and the extract was dried over $MgSO_4$. The ether was removed by distillation, and the mixture of sulfides II and III was distilled in vacuo (see Table 1). IR spectrum of II and III (ν, cm^{-1}): 3200-3600 (OH) and 1070-1080 (CO). PMR spectrum of II and III (δ, ppm): 2.50-2.80 m (CH_2SCH_2), 3.40-3.56 d (CH_2O, $J = 4$ Hz), 3.60-3.90 m (CHO), and 3.10-3.20 s (OH). PMR spectra for the phenoxy derivatives: 4.02 d (CH_2O, $J = 5$ Hz) and 4.06-4.32 m (CHO).

Oxidation of the Mixture of Sulfides II and III. A 3-ml sample of AcOH and 1 ml (0.008 mole) of 25% H_2O_2 were added at 20°C to a solution of 0.006 mole of the mixture of sulfides II and III in 3 ml of $CHCl_3$, after which the mixture was stirred at 35°C for 30 min and then poured into 20 ml of Na_2CO_3 solution. The resulting mixture was extracted with $CHCl_3$, and the extract was washed with Na_2CO_3 solution and dried over $MgSO_4$. The solvent was removed by distillation, and the residue was chromatographed with a column packed with silica gel in a hexane—acetone gradient. Fractional crystallization of the fractions from hexane—acetone yielded pure sulfoxides IV and V (see Table 1). IR spectrum of IV and V (ν, cm^{-1}): 3200-3600 (OH), 1115-1125 (CO for V), 1050-1070 (CO for IV), and 1020 (SO). PRM spectrum of IV and V (δ, ppm): 2.60-2.90 m [$CH_2S(O)CH_2$], 4.30 m (CHO for V), and 4.20-4.50 m (CHO for IV). PMR spectra for the phenoxy derivatives: 4.02 d (CH_2O, $J = 5$ Hz) and 4.35-4.75 (CHO).

Addition of Alcohols to VI, VII, XI, and XII in the Presence of the Alkoxides. General Method. A solution of the alkoxide (from 0.02 g-atom of Na and 30 ml of the alcohol) was added to a solution of 0.02 mole of the substrate in 10 ml of the alcohol, and the mixture was stirred at 20°C until conversion was complete (10 min for VI and XI and 20-50 h for VII and XII). The precipitated dioxanes IX and X [1] were removed by filtration, and the filtrate was treated with CO_2. The alcohol was evaporated, and the residue was chromatographed with a column packed with silica gel. IR spectrum of VIII (ν, cm^{-1}): 3380 (OH); 1280, 1140 (SO_2); 1050 (CO). PMR spectrum of VIII (δ, ppm): 2.90-3.25 m ($CH_2SO_2CH_2$), 3.55-3.60 d (CH_2O, $J = 4.5$ Hz), 3.40 s (OH), and 4.10-4.40 m (CHO).

Isomerization of Epoxy Sulfoxides VI. A solution of MeONa (from 0.01 g-atom of Na and 3 ml of MeOH) was added to a solution of 0.02 mole of VI [1] in 10 ml of MeOH, after which the mixture was stirred at 20°C for 10 min and worked up as described above. IR spectrum of XI (ν, cm^{-1}): 3200-3600 (OH), 3046 (=CH), 1640 (C=C), 1090 (CO), and 1020 (SO). PMR spectrum (δ, ppm): 2.75 t (CH_2SO), 4.35 d (CH_2O, $J = 4$ Hz), 4.85-4.90 s (OH), 6.57 s ($CH{=}CH_{trans}$, $J = 0$ Hz), 6.16 d ($SOCH{=}_{cis}$, $J = 10$ Hz), and 6.28-6.42 m ($={CH}_{cis}$, $J = 10$ Hz).

Isomerization of Epoxy Sulfones VII. A solution of MeONa (from 0.01 g-atom of Na and 3 ml of MeOH) was added to a solution of 0.02 mole of VII [1] in 10 ml of MeOH. After 5 sec, 0.015 mole of AcOH was added, and the mixture was worked up as described for sulfoxides IV and V. IR spectrum of XII (ν, cm^{-1}): 3470 (OH); 3067 (=C—H); 1640 (C=C); 1290, 1130 (SO_2); 1090 (CO). PMR spectrum (δ, ppm): 3.02 t (CH_2SO_2), 4.37 d (CH_2O, $J = 4$ Hz), 3.40 s (OH), 6.55 d ($SO_2CH{=}_{trans}$, $J = 15$ Hz), and 7.00 d ($={CH}_{trans}$, $J = 15$ Hz).

Addition of Amines to Epoxy Sulfides I, Sulfoxides VI, and Sulfones VII. General Method. A mixture of 0.03 mole of epoxide I, VI, or VII with 0.045 mole of the secondary amine (or with 0.12 mole of the primary amine) was maintained at 20°C from 3 to 12 days for epoxy sulfides I or from 3 h to 4 days for epoxy sulfoxides VI and sulfones VII. The resulting sulfides XIII and XIV were isolated by distillation in vacuo, and sulfoxides XV and XVI and sulfones XVII and XVIII, after removal of the amine by distillation in vacuo, were isolated by crystallization from hexane—acetone. IR spectrum of XIII and XIV (ν, cm^{-1}): 3200-3600 (OH), 3200-3300 (NH), and 1050-1070 (CO). PMR spectrum of XIII and XIV (δ, ppm): 2.30-2.80 m (CH_2S, CH_2N), 2.80-2.96 m (CHN), 3.30-4.00 m (CH_2O, CHO), 3.20-3.96 s (OH), and 2.70-3.96 s (OH). IR spectrum of XV and XVI (ν, cm^{-1}): 3200-3600 (OH), 3280-3370 (NH), 1030-1045 (CO for XV), 1090-1120 (CO for XVI), and 1000-1020 (SO). PMR spectrum of XV and XVI (δ, ppm): 2.60-3.0 m [$CH_2S(O)CH_2$], 2.60-3.28 d (CH_2N, $J = 5.5$ Hz), 2.70-3.45 m (CHN), 4.05-4.35 d (CH_2O, $J = 4$ Hz), 3.85-4.35 m (CHO), 2.80-4.60 (OH), and 2.75-4.60 s (NH). IR spectrum of XVII and XVIII (ν, cm^{-1}): 3200-3600 (OH) 3290-3380 (NH) 1290, 1130 (SO_2) 1055-1060 (CO). PMR spectrum of XVII and XVIII (δ, ppm): 2.85-3.30 m ($CH_2SO_2CH_2$), 2.40-

2.75 d (CH_2N, J = 5.5 Hz), 2.90-3.30 (CHN), 3.46-4.25 d (CH_2O, J = 4.5 Hz), 3.88-4.62 m (CHO), 3.57-3.60 s (OH), and 3.40-3.90 s (NH).

Oxidation of Sulfides XIII and XIV. A 4-ml sample of AcOH and 0.8 ml (0.0063 mole) of 25% H_2O_2 were added at 20°C to a solution of 0.005 mole of the mixture of XIII and XIV in 4 ml of $CHCl_3$, after which the mixture was stirred at 35°C for 30 min. A solution of NaOH was added at 20-25°C until the mixture was strongly alkaline, and it was then extracted with $CHCl_3$. The extract was dried over calcined K_2CO_3, and the solvent was removed by distillation. Fractional crystallization of the residue from hexane—acetone yielded individual sulfoxides XV and XVI (see Table 3).

3-Alkylsulfonyl-2-alkyl(phenyl)aminopropan-3-ols XVIII. A mixture of 0.004 mole of 3-alkylsulfonylprop-2-en-1-ol XII and 0.006 mole of the amine in 4 ml of acetone was stirred at 20°C from 8 h to 8 days, after which the acetone and amine were removed by distillation in vacuo, and the product was crystallized from hexane—acetone (see Table 3). Some sulfones XVIII were characterized through the hydrochlorides, where were obtained by bubbling dry HCl through benzene solutions of XVIII.

3-Butylthio-1-aminopropan-2-ol (XIIIb, Y = NH_2) and 3-Butylthio-2-aminopropan-1-ol (XIVb, Y = NH_2). A 25-ml sample of a 25% solution of NH_3 (0.33 mole of NH_3) was added to a solution of 5.84 g (0.04 mole) of Ib in 45 ml of MeOH, after which the mixture was maintained at 20°C for 2 days. It was then evaporated, and the product was isolated by distillation in vacuo to give 4.4 g (68%) of a mixture of sulfides XIIIb (Y = NH_2) and XIVb (Y = NH_2) (see Table 3). Workup of the residue yielded 1.8 g of the diadduct with mp 84-85°C. Found: C 54.22; H 10.18; S 20.64%. $C_{14}H_{31}NO_2S_2$. Calculated: C 54.32; H 10.10; S 20.72%. IR spectrum (ν, cm^{-1}): 3380 (OH), 3030-3180 (NH), and 1070 (CO). PMR spectrum (δ, ppm): 2.55-2.88 m (CH_2S, CH_2N, NH), 3.47 s (OH), and 3.68-4.11 m (CHO).

3-Octylthio-1-aminopropan-2-ol (XIIIc, Y = NH_2) and 3-Octylthio-2-aminopropan-1-ol (XIVc, Y = NH_2). A 20-ml sample of 25% solution of NH_3 (0.265 mole of NH_3) was added to a solution of 5.05 g (0.025 mole) of Ic in 50 ml of MeOH, after which the mixture was maintained at 20°C for 2 days. The diadduct was removed by filtration, the filtrate was evaporated in vacuo, and the mixture of sulfides was crystallized from hexane—acetone to give 3.8 g (69%) of a mixture of XIIIc (Y = NH_2) and XIVc (Y = NH_2) (see Table 3). We also obtained 1.5 g of the diadduct with mp 87.5-88.5°C. Found: C 62.41; H 11.55; S 15.06%. $C_{22}H_{47}NO_2S_2$. Calculated: C 62.65; H 11.23; S 15.21%. IR spectrum (ν, cm^{-1}): 3360 (OH), 3030-3200 (NH), and 1070 (CO). PMR spectrum (δ, ppm): 2.52-2.90 m (CH_2S, CH_2N, NH), 3.51 s (OH), and 3.70-4.20 m (CHO).

3-Butylthio-1-[(β-octylsulfonyl)ethylamino]propan-2-ol (XXb) and 3-Butylthio-2-[(β-octylsulfonyl)ethylamino]propan-1-ol (XXIb). A 2.04-g (0.01 mole) sample of octyl vinyl sulfone (XIX) [8] was added at 20°C to a solution of 1.63 g (0.01 mole) of the mixture of sulfides XIIIb (Y = NH_2) and XIVb (Y = NH_2) in 20 ml of MeOH. After 8 h, the precipitate was removed by filtration to give 3.3 g (90%) of a mixture of XXb and XXIb with mp 94.5-95.5°C. Found: C 55.49; H 10.06; S 17.42%. $C_{17}H_{37}NO_3S_2$. Calculated: C 55.54; H 10.15; S 17.44%.

A mixture of 3-octylthio-1[(β-octylsulfonyl)ethylamino]-propan-2-ol (XXc) and 3-octylthio-2-[(β-octylsulfonyl)ethylamino]-propan-1-ol (XXIc), with mp 99.5-100°C, was similarly obtained. Found: C 59.67; H 10.83; S 15.01%. $C_{21}H_{45}NO_3S_2$. Calculated: C 59.53; H 10.71; S 15.13%. IR spectrum of XX and XXI (ν, cm^{-1}): 3200-3600 (OH); 3300 (NH); 1310, 1132 (SO_2); 1070 (CO). PMR spectrum of XX and XXI (δ, ppm): 2.38-2.82 m (CH_2S, CHN, CH_2N), 2.90-3.08 m (CH_2N), 3.15 s ($CH_2SO_2CH_2$), 3.72-3.75 d (CH_2O, J = 4 Hz), 3.52-4.00 m (CHO).

3-Butylsulfinyl-1-[(β-octylsulfonyl)ethylamine]propan-2-ol (XXIIb) and 3-Butylsulfinyl-2-[(β-octylsulfonyl)ethylamino]propan-1-ol (XXIIIb). A 3-ml sample of AcOH and 0.6 ml (0.0048 mole) of 25% H_2O_2 were added at 20°C to a solution of 1.1 g (0.003 mole) of the mixture of sulfides XXb and XXIb in 3 ml of $CHCl_3$, after which the mixture was stirred at 35°C for 30 min and worked up as described for sulfoxides XV and XVI to give 1.1 g (96%) of a mixture of XXIIb and XXIIIb, from which 0.57 g of XXIIb and 0.53 g of XXIIIb were obtained by fractional crystallization. Compound XXIIb had mp 102-102.5°C. Found: 53.35; H 9.77; S 16.64%. $C_{17}H_{37}NO_4S_2$. Calculated: C 53.22; H 9.72; S 16.72%. Compound XXIIIb had mp 127.5-128.5°C. Found: C 53.31; H 9.66; S 16.79%. $C_{17}H_{37}NO_4S_2$. Calculated: C 53.22; H 9.42; S 16.72%.

3-Octylsulfinyl-1-[(β-octylsulfonyl)ethylamino]propan-2-ol (XXIIc) and 3-cotylsulfinyl-2-[(β-octylsulfonyl)ethylamino]propan-1-ol (XXIIIc) were similarly obtained. Compound XXIIc had mp 105-106.5°C. Found: C 57.18; H 10.24; S 14.65%. $C_{21}H_{45}NO_4S_2$. Calculated: C 57.36; H 10.32; S 14.58%. Compound XXIIIc had mp 134.5-135.5°C. Found: C 57.41; H 10.38; S 14.43%. $C_{21}H_{45}NO_4S_2$. Calculated: C 57.36; H 10.32; S 14.58%. IR spectrum of XXII and XXIII (ν, cm^{-1}): 3200-3600 (OH); 3290-3310 (NH); 1020 (SO); 1310, 1132 (SO_2); 1040 (CO for XXII) 1112-1120 (CO for XXIII). PRM spectrum of XXII and XXIII (δ, ppm): 2.50-2.92 m [$CH_2S(O)CH_2$, CH_2N, NH], 3.08-3.25 m (CHN), 2.90-3.08 m (CH_2N), 3.15 s ($CH_2SO_2CH_2$), 4.23-4.25 d (CH_2O, J = 4 Hz), 4.15-4.55 m (CHO), and 3.20 s (OH).

CONCLUSIONS

1. The reaction of 2,3-epoxypropyl alkyl sulfides with primary and secondary alcohols in the presence of alkoxides leads to mixtures of normal and anomalous isomers in ratios of 1:1 and 3:2, respectively.

2. Isomerization to give 3-alkylsulfinyl(sulfonyl)prop-2-en-1-ols occurs initially in the reaction of epoxy sulfoxides and sulfones with the alkoxides of primary and secondary alcohols. The subsequent addition of the alkoxides to the unsaturated alcohols leads to 3-alkylsulfinyl(sulfonyl)prop-2-en-1-ols.

3. The addition of amines to 2,3-epoxypropyl alkyl sulfides, sulfoxides, and sulfones proceeds with the formation of mixtures of normal and anomalous regioisomers, the ratios of which depend on the oxidation state of the sulfur atom and the structure of the amine.

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