Functionally substituted sulfur-containing compounds
12.* Reactions of 2-[(organylthio)methyl]oxiranes with aliphatic alcohols in the presence of boron trifluoride etherate

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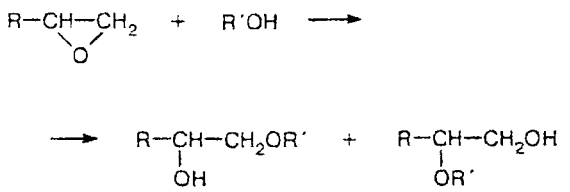
Reactions of 2-[(organylthio)methyl]oxiranes with aliphatic alcohols in the presence of catalytic amounts of $BF_3 \cdot Et_2O$ are accompanied by 1,2-migration of the organylthio group to give mixtures of 2-alkoxy-3-(organylthio)propan-1-ols and 3-alkoxy-2-(organylthio)propan-1-ols. The ratio of these isomers is significantly influenced by the structure of the alcohol and the nature of the organylthio group. The proposed reaction mechanism includes the formation of a thiiranium intermediate and its subsequent transformations.

Key words: 2-[(organylthio)methyl]oxiranes, aliphatic alcohols, boron trifluoride etherate, isomers, steric factor, thiiranium intermediate.

Epoxy compounds easily react with aliphatic alcohols in the presence of Lewis acids (*e.g.*, $BF_3 \cdot Et_2O$) to give common adducts. In the case of unsymmetrical epoxides, the reaction yields a mixture of isomers (Scheme 1) in a ratio depending on the structure of the starting reagents.[2] However, reactions involving organylthiomethyloxiranes have not been investigated so far.

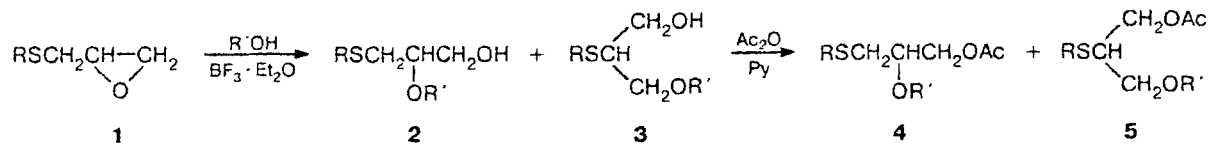
Scheme 1



Previously, we showed that the reactions of such epoxy compounds with acetic anhydride and acetyl chloride are accompanied by migration of the organylthio group.[3] It was of interest to find out whether such a migration is possible in the addition of alcohols in the presence of $BF_3 \cdot Et_2O$.

The reactions of 2-[(organylthio)methyl]oxiranes (**1**) with alcohols were carried out in a boiling alcohol with addition of $BF_3 \cdot Et_2O$, the molar epoxide : catalyst ratio being 20 : 1 (Scheme 2). The reaction products were isolated by distillation; their selected characteristics are presented in Table 1. To elucidate the influence of the nature of the organylthio group on the reaction direction, we used epoxy compounds **1** with different substituents $RSCH_2$ (R = Et, *n*-C_8H_{17}, Bu^t, $CH_2CH{=}CH_2$, $PhCH_2$, and Ph). It was found that the reaction of

Scheme 2



1: R = Et, *n*-C_8H_{17}, Bu^t, $CH_2CH{=}CH_2$, $PhCH_2$, Ph

2–5	R	R′
a	Et	Me
b	Et	Pr^i
c	Et	Bu^t
d	*n*-C_8H_{17}	Me
e	*n*-C_8H_{17}	Pr^i
f	*n*-C_8H_{17}	Bu^t
g	Bu^t	Me
h	Bu^t	Pr^i
i	$CH_2CH{=}CH_2$	Me
j	$CH_2CH{=}CH_2$	Pr^i
k	$CH_2CH{=}CH_2$	Bu^t
l	$PhCH_2$	Me
m	$PhCH_2$	Pr^i
n	$PhCH_2$	Bu^t
o	Ph	Me
p	Ph	Pr^i
q	Ph	Bu^t

* For Part 11, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 881–887, May, 2000.

1066-5285/00/4905-0879 $25.00

Table 1. Characteristics of adducts **2** and **3** and acetates **4** and **5**

Mixture of compounds	**2** : **3** or **4** : **5** [a]	Yield (%)	B.p./°C (*p*/Torr)	Found / Calculated (%)			Molecular formula
				C	H	S	
2a + **3a**	1 : 2	85	115–116 (20)	47.81 47.97	9.53 9.39	21.12 21.34	$C_6H_{14}O_2S$
2b + **3b**	3 : 7	80	74–75 (2)	53.80 53.89	10.24 10.18	18.07 17.98	$C_8H_{18}O_2S$
2c + **3c**	1 : 7	64	90–91 (3)	56.33 56.21	10.56 10.48	16.51 16.67	$C_9H_{20}O_2S$
2d + **3d**	1 : 2	80	136–138 (2)	61.32 61.49	11.24 11.18	13.60 13.68	$C_{12}H_{26}O_2S$
2e + **3e**	3 : 7	73	146–147 (2)	63.93 64.07	11.56 11.52	12.31 12.22	$C_{14}H_{26}O_2S$
2f + **3f**	1 : 7	65	150–152 (2)	65.31 65.16	11.75 11.68	11.42 11.58	$C_{15}H_{32}O_2S$
2g + **3g**	2 : 3	62	81–82 (1)	54.01 53.89	10.10 10.18	17.86 17.98	$C_8H_{18}O_2S$
2h + **3h**	3 : 5	56	96–97 (2)	58.13 58.21	10.81 10.75	15.60 15.54	$C_{10}H_{22}O_2S$
2i + **3i**	2 : 3	84	80–82 (2)	51.68 51.82	8.89 8.70	19.70 19.76	$C_7H_{14}O_2S$
2j + **3j**	3 : 5	82	96–97 (2)	56.71 56.80	9.54 9.49	16.88 16.85	$C_9H_{18}O_2S$
2k + **3k**	1 : 4	60	102–104 (2)	58.87 58.79	9.83 9.87	15.61 15.69	$C_{10}H_{20}O_2S$
2l + **3l**	2 : 3	70	131–132 (2)	62.10 62.23	7.71 7.60	15.02 15.10	$C_{11}H_{16}O_2S$
2m + **3m**	1 : 2	52	134–135 (1)	65.03 64.96	8.45 8.39	13.21 13.34	$C_{13}H_{20}O_2S$
2n + **3n**	1 : 4	41	127–128 (0.2)	66.28 66.10	8.57 8.72	12.82 12.60	$C_{14}H_{22}O_2S$
2o + **3o**	3 : 2	78	123–125 (1)	60.32 60.55	7.18 7.12	16.06 16.17	$C_{10}H_{14}O_2S$
2p + **3p**	1 : 1	72	130–132 (0.8)	63.46 63.67	7.97 8.02	14.22 14.16	$C_{12}H_{18}O_2S$
2q + **3q**	2 : 5	35	136–138 (1)	64.79 64.96	8.51 8.39	13.16 13.34	$C_{13}H_{20}O_2S$
4a + **5a**	1 : 2	94	[b]	50.14 49.97	8.21 8.39	16.31 16.68	$C_8H_{16}O_3S$
4b + **5b**	3 : 7	95	[b]	54.37 54.51	9.23 9.15	14.59 14.55	$C_{10}H_{20}O_3S$
4c + **5c**	1 : 7	93	[b]	56.50 56.37	9.38 9.46	13.80 13.68	$C_{11}H_{22}O_3S$
4d + **5d**	1 : 2	95	[b]	60.88 60.83	10.06 10.21	11.51 11.60	$C_{14}H_{28}O_3S$
4e + **5e**	3 : 7	95	[b]	63.28 63.11	10.46 10.59	10.67 10.53	$C_{16}H_{32}O_3S$
4f + **5f**	1 : 7	92	[b]	63.96 64.10	10.85 10.76	10.21 10.07	$C_{17}H_{34}O_3S$
4g + **5g**	2 : 3	93	[b]	54.64 54.51	9.21 9.15	14.28 14.55	$C_{40}H_{20}O_3S$
4h + **5h**	3 : 5	92	[b]	57.90 58.03	9.82 9.74	13.11 12.96	$C_{12}H_{24}O_3S$
4i + **5i**	2 : 3	94	[b]	52.73 52.91	7.76 7.90	15.88 15.70	$C_9H_{16}O_3S$
4j + **5j**	3 : 5	95	[b]	57.02 56.86	8.55 8.68	13.69 13.80	$C_{11}H_{20}O_3S$
4k + **5k**	1 : 4	91	[b]	58.66 58.49	9.11 9.00	13.17 13.01	$C_{12}H_{22}O_3S$
4l + **5l**	2 : 3	95	[b]	61.18 61.39	7.20 7.13	12.37 12.61	$C_{13}H_{18}O_3S$

(to be continued)

Table 1. (*continued*)

Mixture of compounds	2 : 3 or 4 : 5 [a]	Yield (%)	B.p./°C (*p*/Torr)	Found / Calculated (%) C	H	S	Molecular formula
4m + 5m	1 : 2	95	[b]	64.04 63.81	7.74 7.85	11.16 11.35	$C_{15}H_{22}O_3S$
4n + 5n	1 : 4	96	[b]	64.96 64.78	8.19 8.14	10.63 10.82	$C_{16}H_{24}O_3S$
4o + 5o	3 : 2	96	[b]	59.77 59.98	6.84 6.71	13.46 13.32	$C_{12}H_{16}O_3S$
4p + 5p	1 : 1	94	[b]	62.62 62.78	7.66 7.51	11.79 11.92	$C_{14}H_{20}O_3S$
4q + 5q	2 : 5	90	[b]	63.92 63.81	7.96 7.85	11.21 11.35	$C_{15}H_{22}O_3S$

[a] Molar ratio.
[b] Oil.

aliphatic alcohols with oxiranes **1** in the presence of $BF_3 \cdot Et_2O$ yields a mixture of two isomers, namely, 2-alkoxy-3-(organylthio)propan-1-ol (**2**) and 3-alkoxy-2-(organylthio)propan-1-ol (**3**), whose separation was not achieved by either distillation or chromatographic methods.

The isomeric composition of mixtures of **2** and **3** was determined from their ^{1}H NMR spectra. In addition, the reaction mixtures were treated with Ac_2O/Py to give the corresponding acetates **4** and **5**, whose ^{1}H NMR spectra were also recorded (see Scheme 2, Table 1). Spectral parameters are given in Tables 2 and 3. The

Table 2. Spectral parameters of adducts **2** and **3**

Mixture of compounds	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz) CH_2S (d, *J* = 7)	CHS (m)	CH_2OH (d, *J* = 6.5)	CH_2OR (d, *J* = 6.5)	CHOR′ (m)	OH (s)	R	R′
2a + 3a	3430 (OH); 1090 (C—O)	2.58	2.92	3.58	3.43	3.75	2.80	1.24 (t, 3 H, CH_3, *J* = 7.0); 2.50 (q, 2 H, CH_2S, *J* = 6.8)	3.30 (s, 3 H, CH_3O)
2b + 3b	3440 (OH); 1088 (C—O)	2.56	2.94	3.56	3.48	3.62	2.80	1.26 (t, 3 H, CH_3, *J* = 7.0); 2.52 (q, 2 H, CH_2S, *J* = 6.8)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.38 (m, 1 H, CHO)
2c + 3c	3430 (OH); 1088 (C—O)	2.58	2.86	3.58	3.45	3.84	2.80	1.26 (t, 3 H, CH_3, *J* = 7.0); 2.52 (q, 2 H, CH_2S, *J* = 6.8)	1.17 (s, 9 H, 3 CH_3)
2d + 3d	3440 (OH); 1080 (C—O)	2.56	2.86	3.72	3.60	3.73	2.80	0.87 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.48 (t, 2 H, CH_2S, *J* = 6.8)	3.32 (s, 3 H, CH_3O)
2e + 3e	3450 (OH); 1080 (C—O)	2.60	2.91	3.63	3.48	3.84	2.80	0.88 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.48 (t, 2 H, CH_2S, *J* = 6.8)	1.13 (d, 6 H, 2 CH_3, *J* = 6.0); 3.38 (m, 1 H, CHO)
2f + 3f	3430 (OH); 1090 (C—O)	2.58	2.86	3.60	3.45	3.84	2.80	0.88 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.50 (t, 2 H, CH_2S, *J* = 6.8)	1.16 (s, 9 H, 3 CH_3)

(*to be continued*)

Table 2. (*continued*)

Mixture of compounds	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz)							
		CH_2S (d, *J* = 7)	CHS (m)	CH_2OH (d, *J* = 6.5)	CH_2OR (d, *J* = 6.5)	CHOR′ (m)	OH (s)	R	R′
2g + 3g	3440 (OH); 1090 (C—O)	2.60	2.90	3.67	3.60	3.68	2.80	1.22 (s, 9 H, 3 CH_3)	3.30 (s, 3 H, CH_3O)
2h + 3h	3440 (OH); 1080 (C—O)	2.60	2.91	3.62	3.50	3.70	3.55	1.23 (s, 9 H, 3 CH_3)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.35 (m, 1 H, CHO)
2i + 3i	3450 (OH); 3078, 3062 (=C—H); 1640 (C=C); 1090 (C—O)	2.56	2.84	3.58	3.50	3.80	2.80	3.25 (t, 2 H, CH_2S, *J* = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	3.34 (s, 3 H, CH_3)
2j + 3j	3440 (OH); 3078, 3062 (=C—H); 1640 (C=C); 1085 (C—O)	2.56	2.87	3.58	3.50	3.80	2.60	3.25 (t, 2 H, CH_2S, *J* = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.35 (m, 1 H, CHO)
2k + 3k	3440 (OH); 3078, 3062 (=C—H); 1640 (C=C); 1085 (C—O)	2.58	2.88	3.56	3.48	3.78	2.80	3.26 (t, 2 H, CH_2S, *J* = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	1.17 (s, 9 H, 3 CH_3)
2l + 3l	3450 (OH); 3062, 3030 (C—H); 1500, 1460 (C—C); 1055 (C—O)	2.45	2.80	3.52	3.35	3.70	3.10	3.68 (s, 2 H, CH_2S); 7.21 (m, 5 H, C_6H_5)	3.30 (s, 3 H, CH_3O)
2m + 3m	3440 (OH); 3060, 3030 (C—H); 1500, 1460 (C—C); 1070 (C—O)	2.44	2.78	3.60	3.43	3.78	2.73	3.70 (s, 2 H, CH_2S); 7.21 (m, 5 H, C_5H_6)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.50 (m, 1 H, CHO)
2n + 3n	3450 (OH); 3063, 3030 (C—H); 1500, 1460 (C—C); 1075 (C—O)	2.46	2.81	3.56	3.43	3.77	2.85	3.72 (s, 2 H, CH_2S); 7.20 (m, 5 H, C_6H_5)	1.15 (s, 9 H, 3 CH_3)
2o + 3o	3440 (OH); 3068, 3058 (C—H); 1585 (C—C); 1090 (C—O)	3.09	3.43	3.80	3.62	3.65	2.43	7.25 (m, 5 H, C_6H_5)	3.32 (s, 3 H, CH_3O)
2p + 3p	3440 (OH); 3068, 3058 (C—H); 1585 (C—C); 1090 (C—O)	3.07	3.41	3.80	3.58	3.77	2.60	7.25 (m, 5 H, C_6H_5)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.52 (m, 1 H, CHO)
2q + 3q	3450 (OH); 3068, 3058 (C—H); 1585 (C—C); 1080 (C—O)	3.10	3.41	3.75	3.56	3.70	3.46	7.25 (m, 5 H, C_6H_5)	1.16 (s, 9 H, 3 CH_3)

Table 3. Spectral parameters of acetates **4** and **5**

Mixture of compounds	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz)								
		CH_2S (d, *J* = 7)	CHS (m)	CH_2OR' (d, *J* = 6.5)	CHOR′ (m)	CH_2OAc (d, *J* = 6) 4	5	Ac (s)	R	R′
4a + **5a**	1740 (C=O); 1230 (C—O)	2.58	2.90	3.45	3.50	4.07	4.17	2.01	1.26 (t, 3 H, CH_3, *J* = 7.0); 2.48 (q, 2 H, CH_2S, *J* = 6.8)	3.32 (s, 3 H, CH_3O)
4b + **5b**	1740 (C=O); 1230 (C—O)	2.57	2.87	3.50	3.58	4.07	4.16	2.00	1.27 (t, 3 H, CH_3, *J* = 7.0); 2.48 (q, 2 H, CH_2S, *J* = 6.8)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.38 (m, 1 H, CHO)
4c + **5c**	1740 (C=O); 1230 (C—O)	2.58	2.88	3.45	3.80	4.05	4.20	2.01	1.26 (t, 3 H, CH_3, *J* = 7.0); 2.50 (q, 2 H, CH_2S, *J* = 6.8)	1.17 (s, 9 H, 3 CH_3)
4d + **5d**	1740 (C=O); 1230 (C—O)	2.56	2.86	3.45	3.68	4.06	4.16	2.01	0.88 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.48 (t, 2 H, CH_2S, *J* = 6.8)	3.32 (s, 3 H, CH_3O)
4e + **5e**	1740 (C=O); 1230 (C—O)	2.63	2.85	3.48	3.64	4.10	4.18	2.03	0.87 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.48 (t, 2 H, CH_2S, *J* = 6.8)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.40 (m, 1 H, CHO)
4f + **5f**	1740 (C=O); 1230 (C—O)	2.58	2.90	3.46	3.82	4.05	4.18	2.00	0.87 (t, 3 H, CH_3, *J* = 7.0); 1.30 (m, 8 H, 4 CH_2); 1.42 (m, 2 H, CH_2); 1.70 (m, 2 H, CH_2); 2.48 (t, 2 H, CH_2S, *J* = 6.8)	1.17 (s, 9 H, 3 CH_3)
4g + **5g**	1740 (C=O); 1230 (C—O)	2.47	2.82	3.40	3.48	4.06	4.18	1.95	1.25 (s, 9 H, 3 CH_3)	3.34 (s, 3 H, CH_3O)
4h + **5h**	1740 (C=O); 1230 (C—O)	2.50	2.85	3.47	3.64	4.07	4.18	2.00	1.22 (s, 9 H, 3 CH_3)	1.13 (d, 6 H, 2 CH_3, *J* = 6.0); 3.40 (m, 1 H, CHO)
4i + **5i**	3075, 3060 (=C—H); 1740 (C=O); 1640 (C=C); 1233 (C—O)	2.52	2.89	3.40	3.54	4.07	4.16	2.00	3.23 (t, 2 H, CH_2S, *J* = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	3.32 (s, 3 H, CH_3O)
4j + **5j**	3075, 3060 (=C—H); 1740 (C=O); 1640 (C=C); 1230 (C—O)	2.52	2.90	3.48	3.60	4.07	4.18	2.00	3.25 (t, 2 H, CH_2S, *J* = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	1.12 (d, 6 H, 2 CH_3, *J* = 6.0); 3.40 (m, 1 H, CHO)

(to be continued)

Table 3. (*continued*)

Mixture of compounds	IR, ν/cm^{-1}	^{1}H NMR, δ (J/Hz)								
		CH_2S (d, J = 7)	CHS (m)	CH_2OR' (d, J = 6.5)	CHOR' (m)	CH_2OAc (d, J = 6) 4	CH_2OAc (d, J = 6) 5	Ac (s)	R	R'
4k + **5k**	3075, 3060 (=C—H); 1740 (C=O); 1640 (C=C); 1230 (C—O)	2.52	2.82	3.43	3.77	4.07	4.18	2.00	3.25 (t, 2 H, CH_2S, J = 6.5); 5.05 (m, 2 H, $=CH_2$); 5.70 (m, 1 H, =C—H)	1.17 (s, 9 H, 3 CH_3)
4l + **5l**	3060, 3030 (C—H); 1740 (C=O); 1500, 1460 (C—C); 1240 (C—O)	2.42	2.78	3.42	3.71	4.07	4.16	1.98	3.72 (s, 2 H, CH_2S); 7.18 (m, 5 H, C_6H_5)	3.34 (s, 3 H, CH_3O)
4m + **5m**	3065, 3030 (C—H); 1740 (C=O); 1500, 1460 (C—C); 1240 (C—O)	2.41	2.78	3.37	3.76	4.02	4.23	2.00	3.72 (s, 2 H, CH_2S); 7.22 (m, 5 H, C_6H_5)	1.12 (d, 6 H, 2 CH_3, J = 6.0); 3.45 (m, 1 H, CHO)
4n + **5n**	3060, 3030 (C—H); 1740 (C=O); 1500, 1460 (C—C); 1240 (C—O)	2.46	2.78	3.46	3.77	4.07	4.21	2.00	3.76 (s, 2 H, CH_2S); 7.27 (m, 5 H, C_6H_5)	1.16 (s, 9 H, 3 CH_3)
4o + **5o**	3068, 3058 (C—H); 1740 (C=O); 1585 (C—C); 1244 (C—O)	3.11	3.37	3.55	3.58	4.21	4.24	2.07	7.25 (m, 5 H, C_6H_5)	3.38 (s, 3 H, CH_3O)
4p + **5p**	3068, 3058 (C—H); 1740 (C=O); 1585 (C—C); 1244 (C—O)	3.07	3.47	3.56	3.77	4.18	4.31	2.06	7.25 (m, 5 H, C_6H_5)	1.12 (d, 6 H, 2 CH_3, J = 6.0); 3.43 (m, 1 H, CHO)
4q + **5q**	3070, 3055 (C—H); 1740 (C=O); 1585 (C—C); 1244 (C—O)	3.17	3.41	3.52	3.55	4.12	4.30	2.05	7.25 (m, 5 H, C_6H_5)	1.16 (s, 9 H, 3 CH_3)

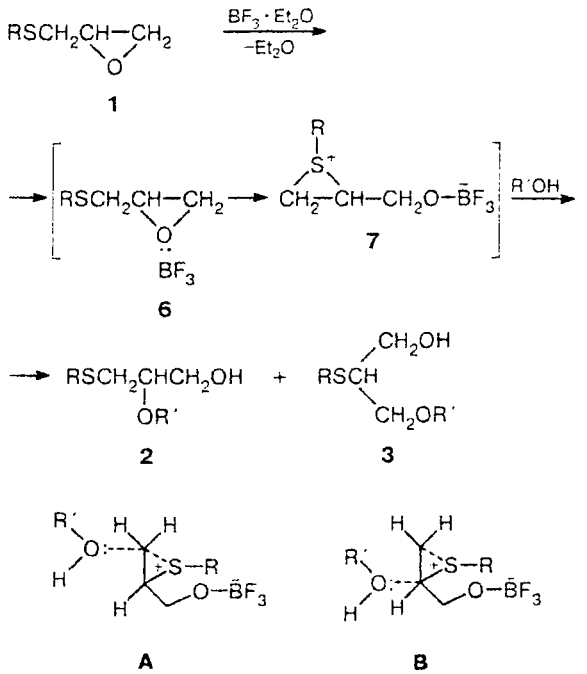
ratio of isomers **2** and **3** was found from the ratio of the signal intensities for CH_2S and CHS groups, while that of acetates **4** and **5**, from the ratio of the signal intensities for CH_2S, CHS, and CH_2OAc groups.

Thus, the observed 1,2-migration of the organylthio group seems to be a common phenomenon in the electrophilic reactions of 2-[(organylthio)methyl]oxiranes **1**.

The influence of steric factors on the ratio of isomers **2** and **3** was studied with the use of such alcohols as MeOH, Pr^iOH, and Bu^tOH. The data obtained indicate that, for all epoxy compounds **1**, the relative content of isomer **3** increases in the order Me < Pr^i ≪ Bu^t; furthermore, the relative content of isomers **2** and **3** depends on the nature of R. Note that the greatest content of isomer **3** is characteristic of aliphatic groups (R = Et, n-C_8H_{17}, or Bu^t), while the smallest one, of the Ph group.

To explain the above regularities, let us consider the reaction mechanism. One can assume that, at the first stage, epoxide **1** reacts with $BF_3 \cdot Et_2O$ to give adduct **6**, which further isomerizes into thiiranium intermediate **7** (Scheme 3). The reaction of the latter with alcohol gives a mixture of compounds **2** and **3**, because this stage is not selective and occurs through two transition states, **A** and **B**.

Scheme 3



Transition state **A** leads to isomer **3**, while transition state **B** leads to isomer **2**. The nucleophilic reactions of thiiranium compounds were studied in a series of papers.[4—7] It was shown that, in the case of an unsymmetrical thiiranium compound, the site of the attack of a nucleophile depends on the stability of the thiiranium ring. The more stable the ring, the closer the rate of rupture of the C—S bond to the rate of formation of a new bond, and hence a tighter transition state occurs. In this case, a nucleophile adds to the site most appropriate sterically. This variant favors the formation of transition state **A**. If the thiiranium ring is less stable, the rate of rupture of the C—S bond is markedly higher than that of formation of a new bond. The reaction follows the carbocationic mechanism, and a nucleophile attacks the carbon atom on which the positive charge is stabilized by the neighboring groups. In our case, this results in transition state **B**.

According to the data obtained, the strongest stabilizing effect is provided by aliphatic groups, while the weakest one by aromatic groups. Allyl and benzyl groups are intermediate between them. The lower relative content of compound **3** (R = Bu^t) in the reaction mixture as compared to products derived from the other oxiranes **1** (R = Alk) is probably due to the lower stability of intermediate **7**, because of the destabilizing steric effect of the *tert*-butyl group.

Experimental

IR spectra were recorded on a UR-20 instrument (thin film). ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in $CDCl_3$.

Reaction of 2-[(organylthio)methyl]oxiranes (1) with alcohols in the presence of $BF_3 \cdot Et_2O$ (general procedure). Epoxide **1** (20 mmol) was added to a boiling corresponding alcohol (12—15 mL) containing $BF_3 \cdot Et_2O$ (0.14 g, 1 mmol). The reaction mixture was refluxed for 30 min and then cooled to 20 °C. Ether (50 mL) was added, and the resulting solution was washed with water, 5% KF, and water again and dried over $MgSO_4$. The solvent was removed, and the residue was distilled. The selected characteristics of mixtures of isomers **2** and **3** are presented in Table 1. The spectral parameters are summarized in Table 2.

Acetylation of mixtures of adducts 2 and 3. Pyridine (15 mmol) and acetic anhydride (12 mmol) were added with stirring at 10 °C to a solution of a mixture of isomers **2** and **3** (10 mmol) in 5 mL of benzene. The reaction mixture was allowed to stand overnight at ~20 °C, whereupon it was poured into 30 mL of water. The products were extracted with benzene. The extract was washed with water, 5% HCl, and water again and dried over $MgSO_4$. The solvent was removed to give acetates **4** and **5**. Their selected characteristics are presented in Table 1. The spectral parameters are summarized in Table 3.

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Received August 11, 1999;
in revised form February 4, 2000