BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3222—3223 (1972)

Studies on the Derivatives of Thiiranes. II.[1] Ring-opening of 2-Alkoxymethylthiiranes and Their Derivatives[2]

Eiichi KAMEYAMA, Motoki NAKAJIMA,* and Tsunehiko KUWAMURA

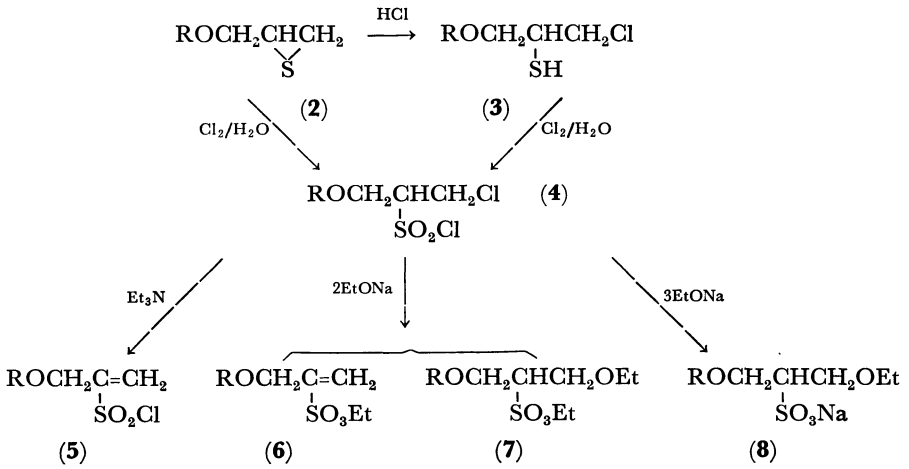
Department of Synthetic Chemistry, Faculty of Engineering, Gunma University, Tenjincho, Kiryu

(Received May 20, 1972)

2-Chloromethylthiirane (**1**)[3,4] and many other thiiranes[5-7] predominantly yield their corresponding abnormal ring-opening products. We found, however, that **1** predominantly yields a normal ring-opening product by the reaction with hydrogen chloride and chloroxidation.[8] Schwartz[9] later reported a similar results. The reaction of 2-alkoxymethylthiiranes (**2**) with some nucleophilic reagents has been found to yield a normal product.[10]

The present work was undertaken to clarify the ring-opening direction of **2** on chloroxidation and to establish a synthetic route to some alkoxylated sulfonyl compounds from **2**. The reaction of **2** with hydrogen chloride at low temperature exclusively gave a normal product, 1-alkoxy-3-chloropropane-2-thiol (**3**). On chloroxidation in water, **2** and **3** gave the same product, 1-alkoxy-3-chloropropane-2-sulfonyl chloride (**4**).

These results are similar to those for **1**. Dominance of the normal ring-opening on these reactions of **1** and **2** is seemingly due to both polar and steric effects of the substituents on the site of attack on an episulfonium ion intermediate by the nucleophile.[9]



* Present address: Kao Soap Co. Ltd., Sumidaku, Tokyo.

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Table 1. The yields, properties and analytical data of the prepared sulfonyl compounds

No.	Compd. R	Yield (%)	Bp (°C/mmHg)	n_D^{25}	Elementary analysis (calcd) C%	H%	S%	Cl%
3	Me	67	67/16	1.4827	34.57 (34.16)	6.43 (6.45)	—	—
3	Et	67	74—76/2	1.4733	39.33 (38.83)	7.17 (7.27)	—	—
4	Me	63	77—78/1	1.4870	23.10 (23.20)	4.04 (3.89)	15.03 (15.48)	34.55 (34.24)
4	Et	64	80/0.5	1.4768	26.81 (27.16)	4.46 (4.56)	14.49 (14.50)	32.13 (32.07)
5	Me	36	53/1	1.4725	28.67 (28.16)	4.23 (4.14)	18.07 (18.79)	21.10 (20.78)
5	Et	50	63/0.5	1.4670	32.27 (32.52)	4.91 (4.90)	16.67 (17.37)	—
6	Et	19	80/1	1.4426	42.88 (43.28)	8.33 (8.26)	16.07 (16.51)	—
7	Et	51	107/1	1.4375	44.52 (44.98)	8.24 (8.39)	13.54 (13.34)	— Na%
8	Et	54	—	—	34.72 (35.89)	6.59 (6.45)	13.71 (13.69)	9.82 (9.82)

On the reaction with a tertially amine and metal alkoxide at low temperature, **4** gave new olefinic sulfonyl compounds and bisalkoxy derivatives, in good yields.

The reactions are summarized in the following scheme. The yields and other data are listed in Table 1.

Although **7** and **8** could also be derived from 2-chloromethylthiirane,[1] the present route is much more advantageous with respect to the yield. Some higher homologues of **8** have been prepared by the same method and found to be highly surface active.[11]

Experimental[12]

Materials. Alkoxymethylthiiranes were prepared from the corresponding glycidylethers by the method of Bordwell and Andersen.[13] The methyl homologue, bp 54—55°C/20 mmHg, n_D^{25} 1.4775. The ethyl homologue, bp 56.5°C/20 mmHg, n_D^{25} 1.4705.

*Addition of Hydrogen Chloride to **2**.* The reactions with anhydrous hydrogen chloride were carried out by the same method as that for the addition to **1**.[1] Spectra of **3**(R: CH_3); IR(neat), 2580(SH), 1118 (C–O–C) cm^{-1}; NMR(in CCl_4), 1.95 (d, 1H, *sec.* SH), 3.30 (s, 3H, CH_3), 3.48—3.69 m, 5H, CH_2 and CH), no triplet band at 1.5—2.0 ppm assignable to a prim. thiol proton[1] could be found.

*Chloroxidation of **2** and **3**.* The thiirane **2** was added dropwise at −10—5°C to an aqueous solution saturated with chlorine. Concurrently chlorine was bubbled through the mixture at such a rate that an excess was always present. After addition of **2**, chlorine was further bubbled for 1 hr. The heavy oil layer was separated, diluted with ether and then washed successively with water, 5% bisulfite solution and water. The ether solution was distilled in a stream of nitrogen to give **4** in a good yield. Spectra of **4**(R : CH_3); IR(neat), 1380(SO_2), 1170(SO_2), 1120(C–O–C), 757(C–S) cm^{-1}; NMR (in benzene), 3.18(s, 3H, CH_3), 3.75—3.90 (m, 5H, CH_2 and CH).

Chloroxidation of **3** was similarly carried out, giving **4** in 60—70% yield.

*3-Alkoxypropene-2-sulfonyl Chloride (**5**).* An equimolar solution of triethylamine at −50—−40°C was added dropwise to an ether solution of **4**. After being stirred for 1 hr, the mixture was filtered and then distilled to give **5** in 40—50% yield. Spectra of **5**(R : CH_3); IR(neat), 3110 (=CH_2), 1630(C=C), 1370(SO_2), 1183(SO_2), 1105(C–O–C) cm^{-1}; NMR(in CCl_4), A 3.40(s, 3H, CH_3), B 4.30(t, 2H, J_{BC}=1.5, J_{BD}=1.5 Hz, $CH_3O\underline{CH_2}$–), C 6.18(q, 1H, J_{CD} =3.0 Hz, CH_2=C *trans* proton against $-SO_2Cl$), D 6.43 (q, 1H, CH_2=C *cis*).

*Reaction of **4**(R : Et) with Sodium Ethoxide.* When **4** was treated in ethanol with an equimolar solution of ethoxide, **4** remained mostly unreacted and gave a small amount of three unknown products difficult to isolate. A solution of ethoxide(0.1 mol) at −5°C was added dropwise over a period of 30 min with stirring to a solution of **4**(11 g, 0.05 mol) in ethanol(18 m*l*). After the addition, the mixture was centrifuged from the salt and distilled to give two fractions, **6** (1.8 g) and **7**(5.4 g). Spectra of **6**; IR(neat), 3120(=CH_2), 1650(C=C), 1350(SO_2), 1160(SO_2), 1105(C–O–C–), 800(C–S) cm^{-1}; NMR(in CCl_4), A 1.23(t, 3H, $C\underline{H_3}CH_2OCH_2$), B 1.38(t, 3H, $C\underline{H_3}CH_2O_3S$), C 3.57(q, 2H, J_{AC}=7.0 Hz, $CH_3C\underline{H_2}OCH_2$), D 4.14(q, 2H, J_{BD}=7.0 Hz, $CH_3C\underline{H_2}O_3S$), E 4.18(t, 2H, $EtOC\underline{H_2}$), F 6.09(t, 1H, J_{EF}=1.0, J_{FG}=1.0 Hz, CH_2=C *trans* proton against $-SO_3Et$), G 6.25(t, 1H, J_{EG} =1.0 Hz, CH_2=C *cis*).

A 3-fold molar quantity of ethoxide relative to **4** was added in the same manner. The mixture was stirred for 10 hr at 25—30°C, neutrallized, centrifuged and evaporated. The residue was recrystallized three times from acetone to yield the pure product **8**. The IR and NMR spectra of **7** and **8** agreed with those of the same products[1] derived from **1**.

11) E. Kameyama, M. Nakajima, A. Ozaki, and T. Kuwamura, *Yukagaku*, **20**, 32 (1971).

12) Boiling points are uncorrected. Measurements of 60 MHz NMR and glc analysis were carried out in the same manner as given in the previous report.[1] Chemical shifts are presented by δ from TMS.

13) F. G. Bordwell and H. M. Andersen, *J. Amer. Chem. Soc.*, **75**, 4959 (1953).