BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1244—1245(1972)

Studies on the Derivatives of Thiiranes. I. Synthesis of Some New Sulfonyl Compounds from 2-Chloromethylthiirane

Tsunehiko KUWAMURA, Eiichi KAMEYAMA, and Motoki NAKAJIMA*

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

(Received August 23, 1971)

A number of investigations have been published on the ring-opening reactions of unsymmetrical thiiranes.[1] In order to synthesize a reactive aliphatic suflonyl compound, we allowed 2-chloromethylthiirane (**1**) to react with hydrogen chloride and chlorine in water, and confirmed that ring-cleavage of **1** took place preferentially at the primary carbon-sulfur bond giving predominantly the normal products as shown in Scheme 1.[2] This is in accord with the result of Schwartz[3] but contrary to the earlier observations.[4,5]

We have investigated the reactions of 1,3-dichloropropane-2-sulfonyl chloride (**3**) with bases of various basicities, and obtained several new olefinic sulfonyl compounds and their derivatives as shown in Scheme 1. Physical properties and analytical data of these compounds are listed in Table 1. Vinyl compounds **4** and **5** obtained in high yields in these reactions have two reactive substituents which differ from each other in reactivity. They could be used as new monomers for synthesis of reactive polymers and interesting intermediates for derivatives of sulfonic acid.

Experimental

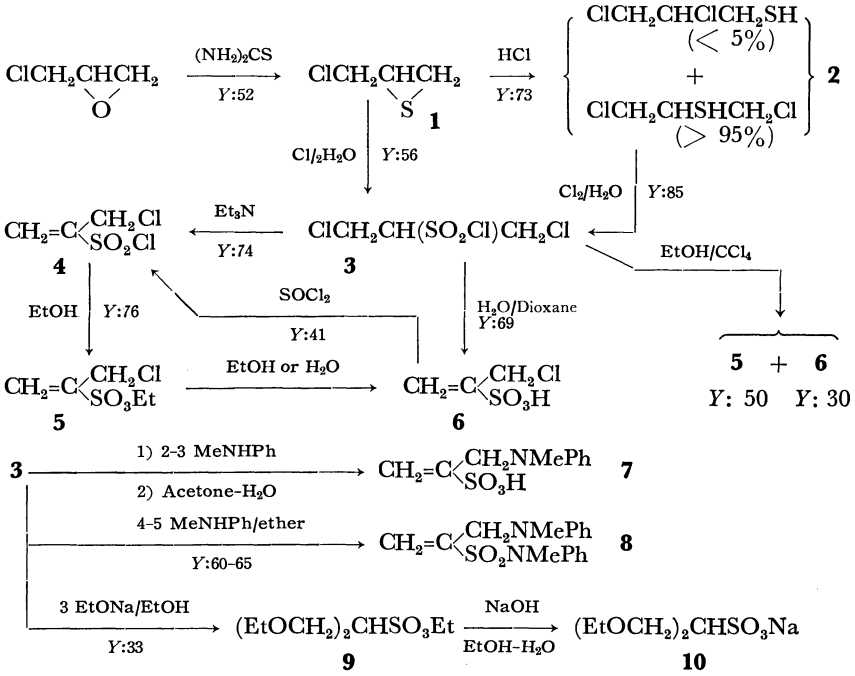
All the boiling points and melting points are uncorrected. The NMR spectra were taken on a Varian A-60D or HA-100 Spectrophotometer in carbon tetrachloride unless otherwise stated. Chemical shifts are presented in terms of δ value. All the liquid products were purified by fractional distillation *in vacuo* in a stream of N_2 to obtain a single peak on glc.

Material. Compound **1** was prepared by the method of Culvenor and his coworkers,[6] bp 79—81°C/114 mmHg, n_D^{10} 1.5297, d_4^{10} 1.2277.

Addition of Hydrogen Chloride to 1. Into **1** (40 g) was gradually introduced gaseous HCl with stirring at 5—10°C. After an equimolar amount (13.1 g) of HCl had been taken out, bubbling was continued at 10°C for 1 hr. Removal of excess HCl and distillation of the residue gave 38.8 g of **2**, bp 104—106°C/88 mmHg, n_D^{10} 1.5301, d_4^{10} 1.3338.

Found: C, 25.12; H, 4.18; Cl, 49.7; S, 22.0%. Cacld for $C_3H_6Cl_2S$; C, 24.82; H, 4.17; Cl, 48.9; S, 22.1%.

IR (neat), 2580 (SH), 1425, 1285, 870, and 845 cm^{-1}; 100 MHz NMR, 2.10 (d, 1H, *sec* SH), 1.63 (t, small, *prim* SH), 3.20 (m, 1H, CH), 3.70 (q, 2H, CH_2), 3.94 (q, 2H,



Scheme 1.

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

1) M. Sander, *Chem. Rev.*, **66**, 297 (1966).

2) T. Kuwamura, E. Kameyama, M. Nakajima, S. Mishiba, and Y. Onoguchi, presented at the Annual Meetings of the Chemical Society of Japan, March, 1967 (Tokyo), Lect. No. 4S111.

3) N. V. Schwartz, *J. Org. Chem.*, **33**, 2895 (1968).

4) W. Davies and W. E. Savige, *J. Chem. Soc.*, **1951**, 774.

5) J. M. Stewart, *J. Org. Chem.*, **29**, 1655 (1964).

6) C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, **1952**, 1050.

Table 1. Physical properties and analytical data of the sulfonyl compounds

Compound	No.	Bp (°C/mmHg)	Mp (°C)	n_D^{20}	Elementary analysis (calcd)				
					C%	H%	N%	S%	Cl%
$(ClCH_2)_2CHSO_2Cl$	**3**	85 — 87/1	—	1.5140	17.26 (17.04)	2.45 (2.38)	— —	15.0 (15.1)	49.0 (50.3)
$CH_2=C(CH_2Cl)(SO_2Cl)$	**4**	89.0/15	—	—	20.76 (20.59)	2.64 (2.30)	— —	17.7 (18.3)	39.1 (40.5)
$CH_2=C(CH_2Cl)(SO_3Et)$	**5**	87.5— 88.5/0.5	—	1.4665	32.20 (32.53)	4.66 (4.91)	— —	17.6 (16.9)	— —
$CH_2=C(CH_2Cl)(SO_3H)$	**6**	142 —143.5/1.5	—	1.4927	23.28 (23.01)	3.44 (3.22)	— —	19.2 (20.5)	22.5 (22.6)
$CH_2=C(CH_2Cl)(SO_3Na)$	—	—	—	—	— —	— —	— —	17.6 (17.9)	20.1 (19.9)
S-Benzyl thiuronium salt of **6**	—	—	85.2— 86.0 (from $ClCH_2CH_2Cl$)	—	41.43 (40.93)	4.71 (4.68)	8.37 (8.68)	— —	— —
$CH_2=C(CH_2NMePh)(SO_3H)$	**7**	—	182.5—183.5 (from ethanol)	—	— —	— —	6.17 (6.16)	14.3 (14.1)	— —
$CH_2=C(CH_2NMePh)(SO_3Na)$	—	—	—	—	— —	— —	5.60 (5.62)	12.3 (12.9)	— —
S-Benzyl thiuronium salt of **7**	—	—	149 —150 (from acetone)	—	55.00 (54.94)	5.99 (5.89)	10.8 (10.7)	16.2 (16.3)	— —
$CH_2=C(CH_2NMePh)(SO_2NMePh)$	**8**	—	97.2— 97.5 (from ether)	—	— —	— —	8.75 (8.85)	10.0 (10.1)	— —
$(EtOCH_2)_2CHSO_3Et$	**9**	118.5—120/2	—	1.4419[a]	44.83 (44.98)	8.07 (8.39)	— —	12.9 (13.3)	— —
$(EtOCH_2)_2CHSO_3Na$	**10**	—	—	—	— —	— —	— —	13.8 (13.7)	— —

a) At 10°C.

CH_2). From the NMR spectrum the ratio of 2-thiol *vs.* 1-thiol in the product was determined to be 98: 2. By treatment of **1** with concd. HCl,[4] **2** containing 5 mol% of 1-thiol was obtained in 50—55% yields.

1,3-Dichloropropane-2-sulfonyl Chloride (3). The reaction of **1** and **2** containing 2% 1-thiol with chlorine in water was carried out under similar conditions to those of the method of Stewart[5] for the oxidation of **1**. From both materials the identical product **3** (d_4^{20} 1.6014) was obtained in good yields. IR (neat), 1379 (SO_2), 1169 (SO_2), 774 (C–S) cm^{-1}; 100 MHz NMR (in benzene), A 3.04 (m, 1H, CH), B 3.40 (q, 2H, CH_2), C 3.57 (q, 2H, CH_2), J_{BC}=12.5, J_{AB}=6.0, J_{AC}=4.0 Hz.

3-Chloropropene-2-sulfonyl Chloride (4). To an ether solution of **3** cooled to −75°C was added dropwise an equimolar amount of triethylamine. The mixture was stirred for 2 hr and filtered. Distillation of the filtrate gave **4** in 74% yield. IR (neat), 3126, 1375 (SO_2), 1182 (SO_2), 1154, 974, 758 (C–S) cm^{-1}; 60 MHz NMR, A 4.41 (q, 2H, $C\underline{H}_2Cl$), B 6.35 (m, 1H, CH_2=C *cis* proton against $-CH_2Cl$), C 6.58 (m, 1H, CH_2=C *trans*), J_{AB}=1.7, J_{BC}=2.0, J_{AC}=1.0 Hz. An identical product was also obtained in 41% yield by the treatment of **6** with an excess of thionyl chloride.

Ethyl 3-Chloropropene-2-sulfonate (5). Ethanolysis of **4** in ether gave **5** in 76% yield. IR (in CCl_4), 3114, 1636 (C=C), 1369 (SO_2), 1133—1191 (SO_2), 1001 (C–O), 915 (S–O) cm^{-1}; 60 MHz NMR, A 4.16 (q, 2H, $C\underline{H}_2CH_3$), B 4.30 (q, 2H, CH_2Cl), C 6.25 (q, 1H, CH_2=C *cis* proton against $-CH_2Cl$), D 6.40 (q, 1H, CH_2=C *trans*), J_{BC}=1.5, J_{BD}=0.7, J_{CD}=1.9 Hz.

3-Chloropropene-2-sulfonic Acid (6). Hydrolysis of **3** in dioxane and distillation of the reaction mixture gave a heavy oil **6** in 69% yield, identical with the hydrolysis product of **5**. 60 MHz NMR (in $CDCl_3$), 4.13 (q, 2H, CH_2Cl), 6.17 (q, 1H, CH_2=C *cis* proton against $-CH_2Cl$), 6.41 (q, 1H, CH_2=C *trans*), 11.02 (s, 1H, SO_3H).

Ethanolysis of 3. A solution of **3** (10.6 g), ethanol (13.8 g) and carbon tetrachloride (23 m*l*) was refluxed for 20 hr. After removal of the solvent, the residue was fractionally distilled to yield two fractions, 4.5 g of **5** and 2.4 g of **6**.

Reaction of 3 with N-*Methylaniline.* Aniline (10.6 g) was added dropwise to an ether solution of **3** (7.0 g) cooled to −65°C. The mixture was gradually warmed up to room temperature, stirred for 10 hr and then filtered. Removal of ether from the filtrate gave a paste-like residue. The residue was dissolved in acetone–water (volume ratio, 10: 1), and the resulting solution was allowed to stand to give 5.0 g (45%) of **7**. IR (KBr), 3460 (OH), 3050, 2890, 1240 (SO_2), 1165 (SO_2), 1030, 725 (phenyl) cm^{-1}. 60 MHz NMR (in D_2O) of Na salt of *7*, 3.05 (s, 3H, NCH_3), 4.30 (s, 2H, CH_2N), 5.28 (s, 1H, CH_2=C *trans* proton against $-SO_2Na$), 5.88 (s, 1H, CH_2=C *cis*). In the case of a 4—5 molar ratio (the aniline: **3**), concentration of the filtrate from the reaction mixture gave another crystalline product **8** in 60—65% yield.

Reaction of 3 with Sodium Ethoxide. To a solution of **3** (21.2 g) in ethanol was added dropwise with stirring an ethanol solution of sodium ethoxide (7.13 g of metallic sodium) at −3—4°C. The mixture was neutralized, filtered and then distilled to yield 8.0 g (33%) of a colorless oil **9**. IR (neat), 1375, 1345 (SO_2), 1165 (SO_2), 1110 (C–O–C), 1000 (C–O), 920 (S–O) cm^{-1}. 60 MHz NMR (in $CDCl_3$), 1.17 (t, 6H, $C\underline{H}_3CH_2$–OCH_2), 1.31 (t, 3H, $C\underline{H}_3CH_2O_3S$), 3.50 (q, 4H, $CH_3C\underline{H}_2OCH_2$), 3.80 (d, 4H, $EtOC\underline{H}_2$), 3.43 (m, 1H, CH), 4.27 (q, 2H, $CH_3C\underline{H}_2O_3S$).

Hydrolysis of **9** with alcohol–NaOH gave **10**. IR (KBr), 1185 (broad, SO_2), 1110 (C–O–C), 1050 (S–O) cm^{-1}. 60 MHz NMR (in D_2O), 1.35 (t, 6H, CH_3), 3.41 (m, 1H, CH), 3.77 (q, 4H, $C\underline{H}_2CH_3$), 4.02 (d, 4H, $EtOC\underline{H}_2$).

The authors wish to thank Dr. M. C. Woods for providing facility for NMR measurement and his helpful advice on the analysis of NMR spectra. They are also indebted to E. Fuchita and N. Shimizu for their assistance in the experiment.