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DIRECT IONIC CHLORINATION OF ALKYL SULFONES WITH SULFURYL CHLORIDE[1a]

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Abstract—The introduction of a Cl atom usually takes place at a position α to the S atom of alkyl sulfones. In this paper, a new ionic chlorination method of alkyl sulfones with sulfuryl chloride in which the most noteworthy observation was exclusive or highly selective β-chlorination of diethyl sulfone or sulfolane (tetrahydrothiophene-1,1-dioxide) is described. The most successful synthetic application of this method was exemplified by the chlorination of 7-thiabicyclo[2.2.1]heptane-7,7-dioxide, which affords 2-*exo*- and 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxides, which were difficult to obtain by the radical chlorination, probably because of the undesired homolytic SO_2–C bond fission. 2-*exo*-Chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxide, thus obtained, was selectively reduced to give 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane. A mechanism for this chlorination is also discussed.

The direct chlorination of alkyl sulfides[2] and/or sulfoxides[3] with various chlorinating agents (e.g. sulfuryl chloride, chlorine, N-chlorosuccinimide, nitrosyl chloride, iodobenzene dichloride, or t-butyl hypochlorite, etc.) is well known to occur at the α position* as exemplified in equation[2a,2b,5] (1). The lone pair electrons on the S atom seem to play an important role.[6]

Direct electrophilic chlorination of alkyl sulfones, which do not possess lone pair electrons on the S atom, has not been reported. Instead, sulfones have been chlorinated by treatment with alkyl lithium to give α-chlorosulfones[7] (Eqs 2 and 3).

RESULTS AND DISCUSSION

We have found that alkyl sulfones may be chlorinated† directly in a highly polar media‡ by using an excess of sulfuryl chloride.§ Thus, sulfolane was heated with ten molar excess of sulfuryl chloride at 60° for an appropriate time in a specially treated vessel in the dark (Experimental). Recrystallization from benzene–hexane of the pasty solid distillate (128 ~ 130°/2·0 mmHg) gave practically pure β-chlorosulfolane.

That β-chlorosulfolane (not the α-isomer) was obtained exclusively seems to be interesting and noteworthy.

Similarly, diethyl sulfone was selectively chlorinated to give β-chlorodiethyl sulfones (β 69·2%, β,β' 25·1%), along with a minor amount of α-chlorodiethyl sulfone (5·7%).

Appreciable α substitution was not observed in the chlorination of the other alkyl sulfones studied. Thus, β- (41%) and γ- (59%, based on the sulfone, used) chloro-tetrahydrothiapyran-1,1-dioxide from tetrahydrothiapyran-1,1-dioxide, and β- (43·4%), γ- (50·4%), $\beta\gamma'$- (3·7%), and γ,γ'- (2·5% based on the sulfone, used) dichloro-di-n-propyl sulfones from di-n-propyl sulfone were obtained, respectively. Butyl ethyl sulfone was chlorinated only on the Bu group to give β, γ, and δ-chlorobutyl ethyl sulfones.

Benzyl methyl sulfone was chlorinated more readily than alkyl sulfones to give exlusively nuclea-substituted products (*o*- and *p*-chlorobenzyl methyl sulfones in 46 and 54% yield, respectively, based on the sulfone used). Results are summarized in Table 1.

The present chlorination was most successfully applied to the preparation of 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane (chart 1, *cf* Eq 3), since the divalent sulfur, which showed profound anchimeric assistance,[10] completely controlled the stereochemistry of the entering groups to the *endo* position.[11]

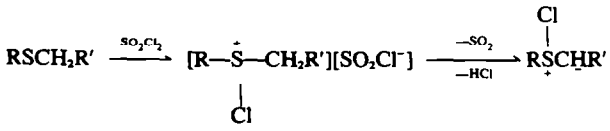
*Only one exception has been reported in the chlorination of 9-thiabicyclo[3.3.1]nonane, where 2-*endo*-chloro-9-thiabicyclo[3.3.1]nonane (β chlorination) was obtained exclusively.[4]

†Hydrocarbons are chlorinated readily by sulfuryl chloride in sulfolane; ionic mechanism have been proposed for this process.[8]

‡Substrates themselves (alkyl sulfones) are highly polar media: ϵ (dielectric constant; sulfolane) = 44 (30°). ϵ (sulfuryl chloride) = 9·2 (22°).

§Sulfuryl chloride has been used as a convenient radical chlorination reagent of hydrocarbons.[9]

¶Our preliminary experiments showed that substitution of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane with not only acetoxyl ion but also most powerful nucleophiles, thiocyanate and azide ions, occured exclusively in retention of configuration. And also, in the chlorination of 2-*endo*- and 2-*exo*-hydroxy-7-thiabicyclo[2.2.1]heptanes with dry HCl in ether (or benzene) or thionyl chloride in dioxane, only 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane was obtained.



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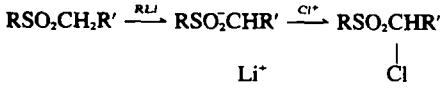

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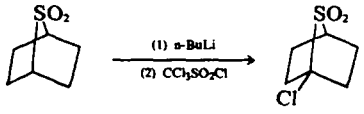

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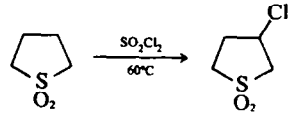

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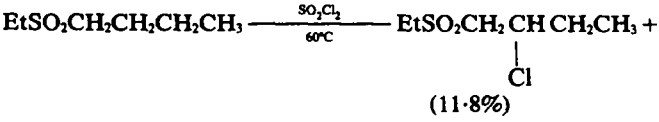

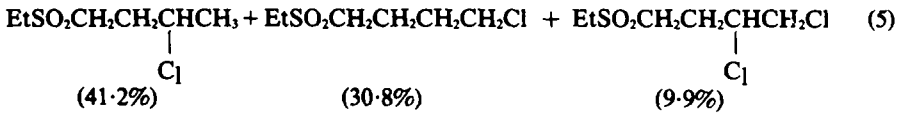

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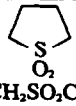
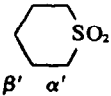
Table 1. Chlorination of alkyl sulfones with sulfuryl chloride at 60°

Sulfones	SO_2Cl_2[a]	Time (h)	Conversion (%)	Product Distribution (%)
	10	120	46	α 0, β 100
$CH_3CH_2SO_2CH_2CH_3$	5	120	22	α 5·7, β 69·2, ββ′ 25·1
	10	5[b]	33	β 58·5, γ 41·5
γ′ β′ α′ $CH_3CH_2CH_2SO_2$-	5	24	41	α 0, β 43·4, γ 50·4 βγ′ 3·7, γγ′ 2·5
$CH_2CH_2CH_3$	5	5[b]	55	α 0, β 39·5, γ 50·0, βγ′ 6·3, γγ′ 4·2
α β γ β′ α′ α β γ δ $CH_3CH_2SO_2CH_2$-$CH_2CH_2CH_3$[c]	9	120	77	α 0, β 11·8, γ 41·2, δ 30·8, γδ 9·9
	10	15	58	2-*endo* 65, 2-*exo* 18, hydrocarbons 17[d]
$PhCH_2SO_2CH_3$[e]	2	6	73	*o*-46, *p*-54

[a] Mole of SO_2Cl_2/mole of sulfone. [b] At 90°. [c] The rest of the product(s), amounted to 6·3%, was unidentified dichlorosulfone(s). [d] By weight. [e] A small amount of sulfolane was used to dissolve substrate.

Thus, 7-thiabicyclo[2.2.1]heptane-7,7-dioxide (1) was chlorinated with ten molar excess of sulfuryl chloride at 60° to give 2-*exo*- 2 (18%, based on the sulfone, used) and 2-*endo*- 3 (65%) chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxides. Physical and spectral data of 3 were identical with those of

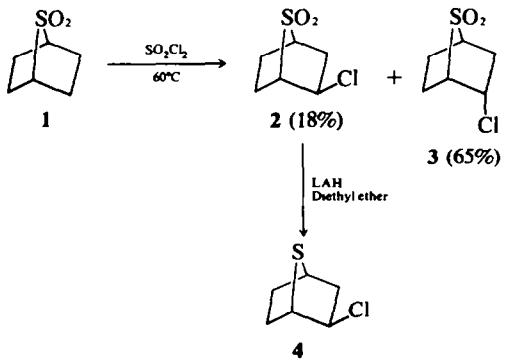
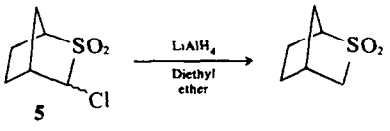


CHART I

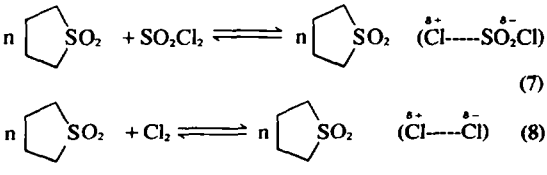
the authentic compound, prepared by the oxidation of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane.

Reduction of 2-*exo*-chlorosulfone (**2**) to 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane was achieved in quantitative yield using an excess of LAH in diethyl ether (Chart I). This makes an interesting and marked contrast to the reduction of 3-chloro-2-thiabicyclo[2.2.1]heptane-2,2-dioxide (**5**) with a large excess of LAH in diethyl ether,[11] in which chloride is preferentially reduced. (Eq 6)



(6)

Some complex formation between sulfuryl chloride and sulfolane was indicated on the bases of an appearance of a new absorption at 278 nm ($\epsilon = 650$) for sulfuryl chloride in sulfolane* (Fig 1). Similar was observed for chlorine. Thus, the absorption of chlorine at 330 nm in n-hexane was found to shift to 254 nm in sulfolane (Fig 1). These absorption bands may be interpreted as an exitation to an ionic exitated state[12] suggesting the formation of a partially charge separated SO_2Cl_2 or Cl_2 as shown in Eqs 7 and 8.



*A solution of sulfuryl chloride in n-hexane was transparent above 210 nm.

†A sulfonyl group cannot be anticipated to anchimerically assist the formation of carbonium ion as much as sulfide group does.[14]

‡The evidence of neighbouring oxygen participation was proposed by Gassman and Marshall in the acetolysis of 7,7-dimethoxybicyclo[2.2.1]heptan-*endo*-2-ol-*p*-toluenesulfonate, which had a moiety similar to **3**.[15]

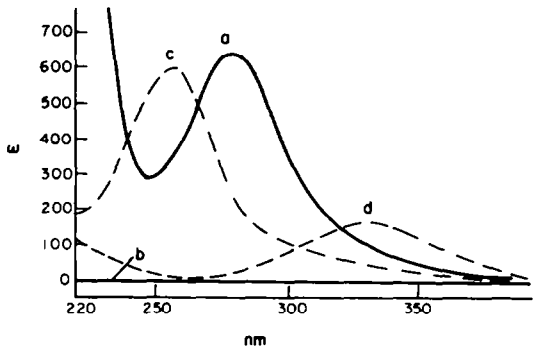
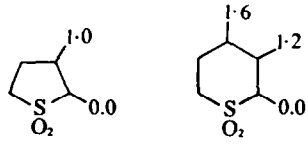


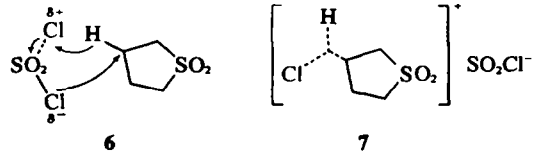
Fig 1. UV Spectra of SO_2Cl_2 and Cl_2. a. SO_2Cl_2 in sulfolane, b. SO_2Cl_2 in n-hexane, c. Cl_2 in sulfolane (ϵ; arbitrary), d. Cl_2 in n-hexane (ϵ; arbitrary).

Chloronium ion (with a partial positive charge) interacted with sulfolane (Eqs 7 and 8) seems to be the most plausible active species for this chlorination on the bases of the regio-selectivity for the chlorination of alkyl sulfones and nucleasubstitution of substituted benzenes (Table 1, 2 and 3). Thus, the qualitative comparison of the conversion at certain reaction time or the product distribution (e.g. butyl ethyl sulfone) seems to indicate that the chlorination reactivity of an alkyl group increases with increase in the length of an alkyl group of a sulfone (Table 1). This was confirmed by the relative reactivity per H atom (Eq 9), obtained in the competitive reaction of sulfolane and tetrahydrothiapyran-1,1-dioxide.



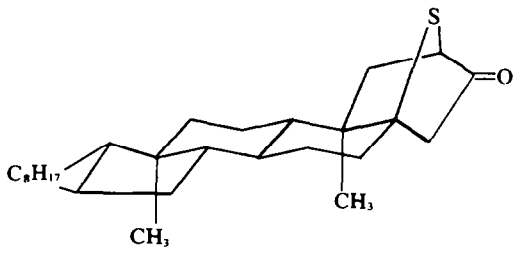
(9)

Considering a strong electron-withdrawing nature of a sulfonyl group, one may conclude that the present chlorination proceeds via cationic transition state (the hydride abstraction–chloride addition **6** or pentacoordinated carbonium ion transition state **7**).[8,13]



The product distribution of **2** and **3** (1 : 3·6) supports the mechanism. The favored *endo* chlorination may be ascribed in the overlapping of the *exo*-2p vacant orbital with the lone pair electrons on O atom as shown in **8**.†‡

However, it seems also likely that the *endo* side



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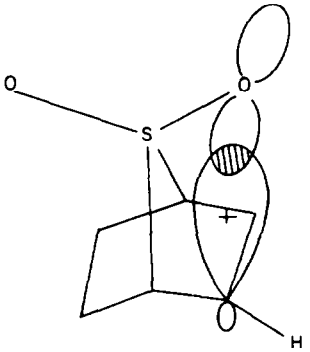
LAH, Ether → *exo*-OH + *endo*-OH (10)

66·5% 19·9%



8

attack by the chlorination species[8] is favored because of the steric repulsion* between the sulfonyl group and the chlorinating species.

The similar partial rate factors for the chlorination of toluene seem to originate from the structural similarity of the cationic active chlorination species for SO_2Cl_2 (Eq 7) and Cl_2 (Eq 8).* (Table 3).

A mechanism involving H atom abstraction may be ruled out on the bases of the following observations:

(a) The product distribution of the present reaction was found to be appreciably different from and more selective than that of the radical chlorination with sulfuryl chloride initiated by di-t-butyl peroxide (Table 2).

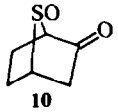
Especially in the radical chlorination of the strained sulfone (**1**), the sticky oil, with no SO_2 absorption for IR spectroscopy, was obtained as major product (~ 88%), together with the small amounts of **2** (~ 3%), **3** (~ 3%), and several unidentified chlorosulfones (~ 6%), where the oil might be formed probably via the homolytic SO_2–C bond fission.

Table 2. Chlorination of alkyl sulfones with sulfuryl chloride initiated by DTBP

Sulfones	Product distribution (%)
	α 2·6, β 97·4
$CH_3CH_2SO_2CH_2CH_3$ $CH_3CH_2CH_2SO_2$- $CH_2CH_2CH_3$	α 11·3, β 82·4, ββ′ 6·3 , α 0, β 58·0, γ 35·1, βγ 4·0, γγ′ 2·9
	2-*endo* ~ 3, 2-*exo* ~ 3, hydrocarbons ~ 88 unknown ~ 6
$PhCH_2SO_2CH_3$[a]	$PhCHClSO_2CH_3$ 100

[a] A small amount of sulfolane was used to dissolve substrate.

On the radical chlorination of benzyl methyl sulfone only the benzylic position was chlorinated under the condition similar to the present chlorination, which gave exclusively nuclea-substituted products.



10

LAH, Ether → exo-OH + endo-OH (11)

84% 16%

Table 3. Partial rate factors for the chlorination of toluene

Condition	Partial rate factor O_f	M_f	P_f
SO_2Cl_2, Sulfolane, 60°[a]	560	—	1070
Cl_2, Sulfolane, 60°[a]	600	—	1060
Cl_2, AcOH, 25°[b]	617	5·0	820
Cl_2, CH_3CN, 25°[c]	1830	9·1	6250

[a] This study. [b] Ref 18. [c] Ref 19.

(b) The quantitative formation of *o*- and *p*-chlorotoluenes was observed in the chlorination of

*Even for the considerably less bulky sulfide group, some steric repulsion was considered to explain the favored β (or *endo*) face hydride attack on the oxothiasteroid[16] (**9**) compared with the favored *exo* hydride attack on norbornanone[17] in the hydride reduction.

The similar but more selective *endo* hydride attack (probably due to the lack of hindrance by Me group in *endo* direction) was also observed in the reduction of 2-oxo-7-thianorbornane (**10**) (unpublished result).

*The complex in Eq 7 also seems to satisfy the "bulkiness" claimed in the chlorination of n-hexane or iso-octane, see Ref 8.

toluene in the present chlorination system (sulfolane and sulfuryl chloride, at room temperature in the dark) and any appreciable amount of benzyl chloride was not obtained. Partial rate factors of toluene obtained for the chlorination with SO_2Cl_2 and Cl_2 in sulfolane were shown in Table 3, together with the results in leteratures.[18,19]

EXPERIMENTAL

M. and b.ps are uncorrected. Elemental analysis was performed at the Microanalysis Center of Kyoto University. IR spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer; NMR spectra were recorded with a Varian T 60 and/or HA 100 spectrometers. Mass spectra were measured with a Hitachi RMS-4 mass spectrometer.

Commercially available sulfuryl chloride (stored in the dark under N_2) was used without further purification after repeated distillation under atmospheric pressure (69·3 ~ 69·4°) through a 10 cm Vigeux-column.

Every alkyl sulfone except for sulfolane was synthesized by the hydrogen peroxide oxidation of corresponding sulfide[20] and purified by means of the repeated recrystallization (usually from CCl_4-hexane and benzene–hexane). M.ps: 70·8 ~ 71·0° for diethyl sulfone, 29·5 ~ 30·0° for di-n-propyl sulfone, 50·5 ~ 50·9° for butyl ethyl sulfone, 99·5 ~ 100·0° for tetrahydrothiapyran-1,1-dioxide, 253·5 ~ 254·0° (in a sealed tube, with sublimation) for 7-thiabicyclo[2.2.1]heptane-7,7-dioxide and 124·5 ~ 125·0° for benzyl methyl sulfone. Sulfolane was dried over barium oxide by heating at about 100 ~ 110° for 2 days and distilled under reduced pressure (138 ~ 139°/17 mm Hg).

A reaction vessel and a reflux condenser were washed carefully and repeatedly with fuming HNO_3 and then distilled water to avoid contamination with a trace of any radical chain initiator.

Chlorination of sulfolane. In a 50 ml round bottom flask, fitted with an efficient reflux condenser connected with a $CaCl_2$ drying tube and covered with Al foil to prevent light, were added 4 g (0·033 mole) of sulfolane and 45 g (0·333 mole) of freshly distilled sulfuryl chloride. The mixture was heated at about 60° for 120 h. Excess sulfuryl chloride was distilled off and the residue, which consisted of single product and the starting sulfone on the basis of the VPC analysis, was distilled *in vacuo* (128 ~ 130°/2·5 ~ 3·0 mm Hg). Pasty solid (2·5 g) was obtained. Single recrystallization from benzene–hexane gave 2·1 g of practically pure β-chlorosulfolane, m.p. 54·2 ~ 54·4°. NMR spectrum (in $CDCl_3$) showed a quintet (J = 5·5 Hz) at δ 4·7 (one proton), a m at δ 2·9 ~ 3·8 (four protons) and a m at δ 2·4 ~ 2·8 (two protons). IR (nujor) 3040 cm^{-1} (m), 1300 cm^{-1} (s), 1130 cm^{-1} (s), 1100 cm^{-1} (s), and 915 cm^{-1} (m). (Found: C, 31·22; H, 4·67; Cl, 23·07. Calcd for $C_4H_7SO_2Cl$: C, 31·07; H, 4·56; Cl, 22·94%).

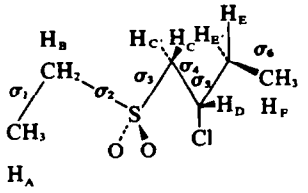
Chlorination of diethyl sulfone. Similarly, 1·2 g (0·01 mole) of diethyl sulfone was treated with 6·8 g (0·05 mole) of sulfuryl chloride at 60° for 120 h. The VPC analyses (on SiDC 550 and PEG) of the crude mixture showed the presence of three components other than the starting sulfone (78%). These products were separated by means of preparative VPC, and their structures were determined by means of NMR, IR, and mass spectra to be α-chloro- (5·7%, based on the starting sulfone, used), β-chloro- (69·2%), and β,β′-dichlorodiethyl sulfone (25·1%). β-chlorodiethyl sulfone: $\delta^{TMS}_{CDCl_3}$ 3·90 (2H, triplet, J = 6·5 Hz), 3·30 (2H, t, J = 6·5 Hz), 3·03 (2H, q, J = 7·5 Hz), and 1·41 (3H, t, J = 7·5 Hz). ν^{KBr}_{max} 1320 (s), 1300 (sh), 1135 (sh), and 1120 cm^{-1} (s). *m/e* 130 (relative intensity, 26·5%), 128 (80·6), 93 (24·2), 65 (82·4), and 63 (p^+-SO_2Et, 100). β,β′-dichlorodiethyl sulfone: $\delta^{TMS}_{CDCl_3}$ 4·17 ~ 3·87 (4H, m) and 3·70 ~ 3·40 (4H, m). ν^{KBr}_{max} 1320 (s), 1300 (sh), 1135 (sh), and 1120 cm^{-1} (s). *m/e* 130 (17·3%), 128 (49·5%), 93 (14·8%), 65 (74%), and 63 (100%). α-Chlorodiethyl sulfone: $\delta^{TMS}_{CDCl_3}$ 4·77 (1H, q, J = 7 Hz), 3·03 (2H, q, J = 6·5 Hz), 1·98 (3H, d, J = 7 Hz), and 1·43 (3H, t, J = 6·5 Hz). ν^{KBr}_{max} 1330 (s), 1300 (sh), 1158 (s), and 1130 cm^{-1} (s). *m/e* 130 (16%), 128 (37), 65 (84), 63 (100), and 62 (55).

Chlorination of tetrahydrothiapyran-1,1-dioxide. Tetrahydrothiapyran-1,1-dioxide (0·5 g, 3·7 mmole) was treated with 5·0 g (37 mmole) of sulfuryl chloride at 90° for 5 h. The product obtained via the work up described above, was determined to consist of 58·5% of β-chloro and 41·5% of γ-chloro derivatives by means of VPC (on PEG and SiDC 550, at 33% conversion). The products were purified by means of column chromatography on silica gel (eluted with benzene 10, ethanol 1), followed by preparative VPC purification. β-Chloro-tetrahydrothiapyran-1,1-dioxide crystallized on standing: m.p. 72·5 ~ 73·0°. $\delta^{TMS}_{CDCl_3}$ 4·3 (1H, t doublets, J = 4, 9 and 16·0 cs), 3·5 (1H, broad doublet, J = 12 cs), 3·3 (1H, doublet, 12 cs), 3·0 (2H, m), and 2·6 ~ 1·5 (4H, m). ν^{KBr}_{max} 1324 (m), 1296 (s), 1257 (m), 1126 (s), and 1056 cm^{-1} (m). *m/e* 170 (p^+, 5), 168 (p^+-2, 15), 135 (p^+-Cl, 7), and 133 (p^+-Cl-2, 100). γ-Chloro-tetrahydrothiapyran-1,1-dioxide: m.p. 134 ~ 135°. $\delta^{TMS}_{CDCl_3}$ 4·46 (1H, quintet, J = 3·8 cs), 3·7 ~ 2·75 (4H, m), and 2·5 (4H, m). ν^{KBr}_{max} 1338 (m), 1288 (s), 1164 (m), 1116 (s), and 1006 cm^{-1} (m). *m/e* 170 (p^+, 15), 168 (p^+-2, 60), and 133 (p^+-Cl-2, 100).

Chlorination of di-n-propyl sulfone. Di-n-propyl sulfone (1·5 g, 0·01 mole) was treated with 6·8 g (0·05 mole) of sulfuryl chloride at 60° for 24 h. The reaction percent and the product distributions were listed in Table 1. β-Chloro-di-n-propyl sulfone: $\delta^{TMS}_{CDCl_3}$ 4·43 (1H, quintet, J = 6 Hz), 3·30 (2H, t, J = 6 Hz), 3·16 ~ 2·87 (2H, m), 2·05 ~ 1·8 (2H, m), 1·70 (3H, d, J = 6 Hz), and 1·10 (3H, t, J = 6 Hz). γ-Chloro-di-n-propyl sulfone: $\delta^{TMS}_{CDCl_3}$ 3·73 (2H, t, 6 Hz), 3·06 (2H, t, 9 Hz), 3·00 (2H, t, 9 Hz), 2·46 ~ 1·65 (4H, m), and 1·10 (3H, t, J = 7 Hz). γ,γ′-dichloro-di-n-propyl sulfone and β,γ′-dichloro-di-n-propyl sulfone (the separation of these two isomers was unsatisfactory on SiDC 550, PEG, or SE 30): NMR of the α protons to chlorines of γ,γ′-dichloro-di-n-propyl sulfone showed a triplet at δ 3·70 (J = 6 Hz). The α protons to chlorines of β,γ′-dichloro-di-n-propyl sulfone showed a quintet at δ 4·58 (J = 7 Hz) and a triplet at δ 3·70 (J = 6 Hz). The ratio of β,γ′-dichloro-di-n-propyl sulfone to γ,γ′-dichloro-di-n-propyl sulfone was determined to be 1·5 on the bases of the area intensities of α protons to chlorides.

Chlorination of butyl ethyl sulfone. Butyl ethyl sulfone (1·5 g, 0·01 mole) was treated with 12·1 g (0·09 mole) of sulfuryl chloride at about 90° for 120 h. The reaction percent and product distributions were listed in Table 1. β-Chlorobutyl ethyl sulfone: $\delta^{TMS}_{CCl_4}$ (100 MH_2) 4·30 (1H, m, H_D), 3·39 (1H, d doublets, J = 7·0 and 15·0 Hz, H_C ($H_{C'}$)), 3·15 (1H, d doublets, J = 5·5 and 15·0 Hz, $H_{C'}$ (H_C)), 3·04 (2H, q, J = 7·0 Hz, H_B), 2·2 ~ 1·7 (2H, m, H_E and $H_{E'}$), 1·38 (3H, t, J = 7·0 Hz, H_A), and 1·12 (3H, t, J = 7·0 Hz, H_F).

A pair of double doublets of protons H_C and $H_{C'}$ were colapsed into a AB quartet (J = 15·0 Hz) by the saturation of proton H_D. A multiplet of protons H_E and $H_{E'}$ was



colapsed also into an AB quartet (J = 15·0 Hz) by the double saturations of protons H_D and H_F.

This information indicates that the rotation of Bu group (σ_3, σ_4, and σ_5 bonds) must be hindered at room temp by introducing Cl at the β position of Bu group. γ-Chlorobutyl ethyl sulfone: $\delta^{TMS}_{CCl_4}$ (100 MHz) 4·16 (1H, m), 3·2 ~ 2·8 (2H, m), 2·92 (2H, q, J = 7 Hz), 2·5 ~ 1·8 (2H, m), 1·60 (3H, d, J = 6 Hz), and 1·36 (3H, t, J = 7 Hz). δ-Chlorobutyl ethyl sulfone: $\delta^{TMS}_{CCl_4}$ 3·57 (2H, m), 3·2 ~ 2·7 (4H, m), 1·97 (4H, b quintet), and 1·33 (3H, t, J = 8 Hz). γ,δ-Dichlorobutyl ethyl sulfone: $\delta^{TMS}_{CCl_4}$ (100 MHz) 4·25 (1H, m), 3·85 (1H, d doublets, J = 5 and 11 Hz), 3·65 (1H, d doublets, J = 7 and 11 Hz), 3·2 ~ 2·8 (2H, m), 2·93 (2H, q, J = 7 Hz), 2·7 ~ 1·8 (2H, m), and 1·38 (3H, t, J = 7 Hz).

Chlorination of 7-thiabicyclo[2.2.1]heptane-7,7-dioxide (1). 7-Thiabicyclo[2.2.1]heptane-7,7-dioxide (1·46 g, 0·01 mole) was treated with 13·5 g (0·10 mole) of sulfuryl chloride at about 60° for 15 h. After the excess sulfuryl chloride was distilled off, the mixture (white waxy solid) was separated by means of column chromatography on silica gel. Elution with methylene chloride afforded 150 mg of oil, 581 mg of 2-*endo*-chloro-7-thiabicyclo 2-*endo*-chloro-7-thiabicyclo [[2.2.1]heptane-7,7-dioxide, of 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxide and 609 mg of the recovered sulfone (in the order of elution). 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxide was purified by the repeated column chromatography and sublimed *in vacuo* (80 ~ 85°/23 mmHg). Physical and spectral data were identical with those of the authentic sample, independently prepared by the oxidation of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane with *m*-chloroperbenzoic acid in methylene chloride. m.p. (in a sealed tube, with sublimation) 177·0 ~ 177·5°. $\delta^{TMS}_{CCl_4}$ 4·87 (1H, d triplets, J = 4 and 8 Hz), 3·07 (2H, narrow m), and 2·5 ~ 1·8 (6H, m). ν^{max}_{KBr} 1305 (s), 1156 (s), 1100 (m), 920 (m), 597 (m), 480 (m) and 425 cm^{-1} (m). 2-*exo*-Chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxide was purified by means of recrystallization from acetone after repeated column chromatography, m.p. (in a sealed tube) 199·5 ~ 200·0° (with sublimation). $\delta^{TMS}_{CCl_4}$ 4·23 (1H, d doublets, J = 6·2 and 5·7 Hz), 3·07 (2H, narrow m) and 2·7 ~ 1·6 (6H, m). ν^{max}_{KBr} 1292 (s), 1152 (s), 1085 (m), 920 (m), 595 (m), 580 (m), 438 (m), and 405 cm^{-1} (m). *m/e* 180 (P^+, 4%), 179 (p^+-1, 9), 178 (p^+-2, 53), 81 (100), 80 (87), and 79 (87). (Found: C, 39·93; H, 4·92; Cl, 19·89. Calcd for $C_6H_9SO_2Cl$: C, 39·89; H, 5·02; Cl, 19·62%).

2-exo-*Chloro-7-thiabicyclo[2.2.1]heptane*. In a 1 l. flask, fitted with an efficient condenser connected with a $CaCl_2$ drying tube, a thermometer and a dropping funnel, 300 mg (1·7 mmole) of 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane-7,7-dioxide was dissolved with 700 ml of dry diethyl ether at room temp (21°). With stirring, was added a large excess of LAH (1·5 g, 40 mmole) powder. After 15 min stirring at room temp, 5 ml of EtOAc and then dil HCl was added with external ice cooling. After usual work up 189 mg of 2-*exo*-chloro-7-thiabicyclo[2.2.1]heptane was obtained by means of preparative GLPC (yield was 77%). $\delta^{TMS}_{CCl_4}$ 4·03 (1H, d doublets, J = 3·1 and 4·0 Hz), 3·85 (2H, broad s), and 2·4 ~ 1·3 (6H, m). ν^{max}_{major} 1315 (s), 1265 (m), 1050 (m), 980 (m), 900 (s), 765 cm^{-1} (m). *m/e* 148 (p^+, relative intensity, 26%), 114 (17%), 86 (57%), 85 (100%), and 79 (44%).

Chlorination of benzyl methyl sulfone. Benzyl methyl sulfone (0·50 g, 2·9 mmole) was dissolved in 0·7 ml of sulfolane and treated with 0·80 g (5·5 mmole) of sulfuryl chloride at 60° for 6 h. The reaction percent and product distribution were listed in Table 1. *o*-Chlorobenzyl methyl sulfone: m.p. 91·0°. $\delta^{TMS}_{CDCl_3}$ 6·65 ~ 6·25 (m, 4H), 4·49 (s, 2H), and 2·81 (s, 3H). ν^{max}_{KBr} 1318 (s), 1160 (m), 1135 (s), 1110 (m), 890 (m), and 780 cm^{-1} (m). *p*-Chlorobenzyl methyl sulfone: m.p. 106·5 ~ 107·0°. $\delta^{TMS}_{CDCl_3}$ 7·36 (s, 4H), 4·21 (s, 2H), and 2·77 (s, 3H). ν^{max}_{KBr} 1310 (s), 1260 (m), 1160 (m), 1120 (s), 895 (m), and 845 cm^{-1} (m).

Into a soln of 0·5 g of benzyl methyl sulfone, 0·8 g of sulfuryl chloride and 0·7 ml of sulfolane was added a few drops of di-t-butyl peroxide at 60°. 1-Chloro-1-phenylmethyl methyl sulfone was obtained as a sole product: m.p. 105·0 ~ 105·5°. $\delta^{TMS}_{CDCl_3}$ 7·36 (s, 5H), 5·64 (s, 1H), and 2·96 (s, 3H). ν^{KBr}_{max} 1310 (s), 1140 (s), 740 (m), and 700 cm^{-1} (m).

Radical chlorination of alkyl sulfones. Into a mixture of alkyl sulfone and equimolar sulfuryl chloride heated at 60°, was added a few drops of di-t-butyl peroxide. After the vigorous evolution of SO_2 ceased, the mixture was treated as described above and the products were analyzed.

Competition reaction of sulfolane and tetrahydrothiapyran-1,1-dioxide. A mixture of 0·5 g (3·7 mmole) of tetrahydrothiapyran-1,1-dioxide and 1·3 g (11 mmole) of sulfolane was treated with two portions of 20 g (150 mmole) of sulfuryl chloride at 90° for 6 h. The conversions of sulfolane to β-chlorosulfolane and tetrahydrothiapyran-1,1-dioxide to β- and γ-chlorotetrahydrothiapyran-1,1-dioxides (the ratio of β to γ was 1·39) were determined to be 35·0% and 69·4%, respectively.

Determination of partial rate factor. Into a mixture of 2·0 g of benzene, 1·0 g of toluene and 20 ml of sulfolane, heated at 60° over a thermostated oil bath was dropped 0·3 g of sulfuryl chloride (or introduced 2·2 mmole of chlorine). After the usual treatment with sodium bicarbonate, the mixture was analyzed by VPC (PEG). The averaged value of two experiments was listed in Table 3.

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