(20) J. A. Bone, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans.* **2**, 1447 (1975); J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).
(21) In fact, (*R*)-4-*endo*- and (*R*)-4-*exo*-4-methylprotoadamantyl substrates would give essentially identical solvent-separated ion pairs, which are mirror images of the ion pairs arising from the (*S*)-4-*endo* and (*S*)-4-*exo* enantiomers.
(22) Such isomerizations of bridged intermediates are well known, for example, see J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968), and references therein.
(23) Autorenkollektiv, "Organikum", VEB Deutscher Verlag, Berlin, 1967, p 615.
(24) When concentrated HCl was used[8a] instead of H_2SO_4, some 1-methyl-2-chloroadamantane was also produced.

Roles of Heteroatoms in Solvolytic Reactions. 4. Solvolysis of the Exo and Endo Esters of 2-Thiabicyclo[2.2.1]heptan-6-ols[1]

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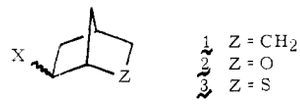
Diels–Alder cyclization of cyclopentadiene with thiophosgene yielded 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene, which was directly converted to 2-thiabicyclo[2.2.1]hept-5-ene in high yield by reduction with lithium aluminum hydride. Hydrochlorination of the olefin, followed by hydrolysis in a neutral or basic medium, gave 2-thiabicyclo[2.2.1]heptan-6-*exo*-ol in satisfactory overall yield. Acidic hydrolysis of 6-*exo*-chloro-2-thiabicyclo[2.2.1]heptane resulted in the major formation of a dimeric ether. The alcohol was oxidized with *tert*-butyl chromate, followed by reduction, to afford pure endo alcohol. Both alcohols were converted to esters, *p*-nitrobenzoate for the exo and tosylate for the endo, and the esters were solvolyzed. An exo/endo rate ratio of 3.7×10^{14} was observed, after correction for a leaving group as well as the solvent system, and 3.1×10^{10} and 1/43, respectively, for the rate ratios of the exo and endo esters against the corresponding parent carbon systems. This unusually high exo/endo rate ratio is attributed to β-S participation for the exo ester and the rate-retarding effect for the endo ester. In a product study, only an exo isomer was found as the solvolysis product from both esters. Isolation of a tricyclic episulfonium ion, 1-thioniatricyclo[1.1.1.$0^{2,6}$]heptane perchlorate, a solvolysis intermediate from the exo ester, was possible; its structure was confirmed by ^1H and ^{13}C NMR spectra.

Generally, it is well known that the amount of neighboring-group participation in solvolytic reactions varies with the spatial circumstances of molecules. C_2–C_6 interaction in the norbornyl system (**1**) has been observed in many kinetic, mechanistic, and structural studies.[3]

In the solvolysis of the 2-oxabicyclo[2.2.1]hept-6-*exo*-yl system (**2**), a relatively large amount of β-O-participation has



been observed.[4] It is considered that the structural peculiarity of the bicyclo[2.2.1]heptyl system gives rise to this unusual neighboring-group participation. Usually the effect of a β-oxygen atom resulting from direct nucleophilic participation is extremely small,[5] although the precise evaluation of the effect is difficult because of the large inductive character of oxygen.

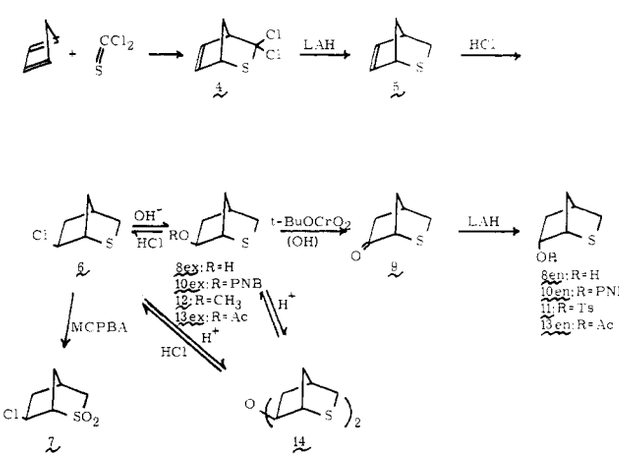
The 2-thiabicyclo[2.2.1]heptyl system (**3**) may exhibit a large amount of neighboring-group participation in solvolytic reactions and allow the isolation of a stable episulfonium ion when a carbocation is formed at the 6 position. This work was designed to examine mechanistic and structural effects in the solvolysis of the exo and endo stereoisomers of 2-thiabicyclo[2.2.1]heptan-6-ol esters and to isolate a tricyclic episulfonium ion.

Results

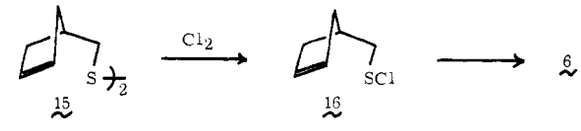
Synthesis. Originally the 2-thiabicyclo[2.2.1]heptane skeleton was prepared by Middleton[6] and several analogues were studied by Johnson and co-workers[7] in an investigation of stereochemical aspects.

As shown in Scheme I, 3,3-dichloro-2-thiabicyclo[2.2.1]-hept-5-ene (**4**), prepared according to the known procedure,[6] was directly reduced with lithium aluminum hydride ($LiAlH_4$)

Scheme I



to give 2-thiabicyclo[2.2.1]hept-5-ene (**5**) in high yield; chemical shifts of **5** in the ^1H NMR spectrum were consistent with those of reported values.[7] Hydrochlorination of the olefin (**5**) in methylene chloride with dry hydrogen chloride at −30 ~ −50 °C gave a single isomer (**6**), in which the configuration of the chlorine atom was determined to be exo on the basis of its reactivity, stereochemistry on HCl addition, and the NMR pattern of the 6-endo proton (4.74 ppm, doublets of doublet, $J_{5en,6}$ = 6.5 Hz, $J_{5ex,6}$ = 3.0 Hz) of the corresponding sulfone (**7**). This chloride was also prepared quantitatively by the intramolecular addition of sulfenyl chloride (**16**) generated in situ from the reaction of 3-cyclopentenylmethyl disulfide (**15**).[8]



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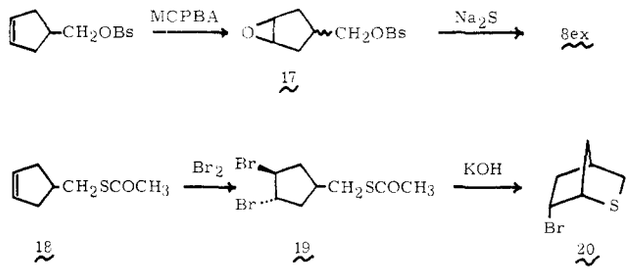
Hydrolysis of **6** in a weakly alkaline medium gave the 6-*exo*-hydroxy derivative (**8ex**) in 93% yield. When the hydrolysis was carried out without a base, a mixture of the alcohol (**8ex**) and the dimeric ether (**14**) was obtained in various ratios depending on reaction conditions used, indicating the facile conversion of **8ex** into **14** in an acidic medium.

The formation of the dimeric ether (**14**) from **8ex** was also examined by treatment of **8ex** with various concentrations of acid and by heat treatment. However, the complete conversion of **8ex** to **14** was not observed; both systems must be present in the equilibrium mixture. Treatment of **8ex** or **14** with concentrated hydrochloric acid afforded the corresponding 6-*exo*-chloro derivative (**6**).

Oxidation of β-hydroxy sulfides to the corresponding β-oxo derivatives is usually troublesome because of the high sensitivity of a sulfur atom to oxidation. The Oppenauer procedure failed. Common procedures using chromic anhydride–pyridine or *tert*-butyl chromate–pyridine in carbon tetrachloride[9] gave the desired result. However, the former procedure was accompanied with large loss of product because of difficulty in isolating product. The best yield (69%) of ketone **9** was obtained from the latter procedure. Interestingly, in the UV spectrum of **9**, a charge-transfer (CT) band at 258 (ϵ 478 in cyclohexane), 258 (ϵ 478 in acetonitrile), 260 (ϵ 589 in methanol), and 260 nm (ϵ 600 in 70% aqueous ethanol) was observed as an independent absorption.[10] The attack of a hydride on the keto group of **9** by $LiAlH_4$ or $NaBH_4$ took place exclusively on the exo side and only isomer **8ex** was obtained in moderate yield.

Infrared (IR) spectra (1×10^{-3} M solution in CCl_4) of the alcohols reveal a striking difference between the exo and endo alcohols (**8ex** and **8en**). Alcohol **8ex** exhibits an absorption at 3620 cm^{-1} due to a dissociated hydroxy group, while in **8en**, only an absorption due to an associated alcohol was observed at 3474 cm^{-1}, indicating the presence of a strong intramolecular H bond.

The exo alcohol (**8ex**) from the epoxide (**17**) has alternatively been prepared according to the following scheme by Johnson and co-workers.[7] In our experiment, however, the distillation of **8ex** under reduced pressure was accompanied by the formation of the dimeric ether (**14**) attributable to the intermolecular dehydration of the alcohol (**8ex**).

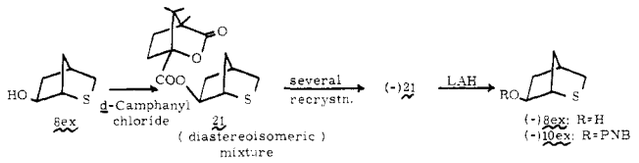


The 2-thiabicyclo[2.2.1]heptane skeleton could also be synthesized from the intramolecular nucleophilic substitution by a thiol group generated by hydrolyzing the dibromo thiolacetate (**19**) which was easily derived from the thiolacetate (**18**). Because of the great stability of 6-*endo*-bromo-2-thiabicyclo[2.2.1]heptane (**20**), with properties similar to those of 4-*endo*-bromo-6-thiabicyclo[3.2.1]octane,[11] it was not a useful compound for the stereochemical and mechanistic studies in the present systems.

The exo and endo alcohols (**8ex** and **8en**) were converted to the corresponding *p*-nitrobenzoates (**10ex** and **10en**) and the tosylate (**11**) for the endo derivative in the usual manner. ^1H NMR data of all thiabicyclic compounds are shown in Table I.

Synthesis of Optically Active 2-Thiabicyclo[2.2.1]-heptan-6-*exo*-ol. An optically active ester was needed to scrutinize the true effect of the sulfur atom in solvolysis of the 2-thiabicyclo[2.2.1]hept-6-yl system. Fortunately, if the system involves a stable episulfonium ion, the ion must be symmetrical, affording an optically inactive intermediate. Thus, the rate of the ionization step can be determined by the polarimetric method. By comparison with the recent report by Tabushi and co-workers[12] in which an attack of a solvent is a step determining the rate in solvolysis of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane (**24**), it is important to determine which step is rate determining in such systems having an effective participating group as a neighboring sulfur atom.

Scheme II



The successful optical resolution was done through the separation of diastereoisomers by repeated recrystallization, followed by the reduction of the resulting diastereoisomer of the ester with metal hydride (Scheme II).

Diastereoisomeric esters (**21**) were prepared from the alcohol (**8ex**) and *d*-camphanyl chloride derived from *d*-camphanic acid[13] in the usual manner and (−)-**21** was isolated as a single pure diastereomer after several recrystallizations from ethyl acetate. Reduction with sodium bis(methoxyethoxy)-aluminum hydride in benzene gave (−)-**8ex**, $[\alpha]^{24}_D$ −16.8 (EtOH, *c* 2.5). Routine esterification procedure yielded an *optically active ester* [(−)-**10ex**], $[\alpha]^{28}_D$ −26.2 ($CHCl_3$, *c* 2.65).[14]

Kinetics. Measurement of solvolysis rate was carried out by the titrimetric method for racemic esters;[15] hydrolysis in 80% aqueous acetone and methanolysis in methanol for **10ex** and acetolysis in acetic acid containing 1 mequiv of sodium acetate for **11**. Since the remarkable stability of the 6-endo ester (**10en**) made its rate measurement impossible, the tosylate (**11**) was used for the determination of solvolysis rate as an endo isomer. Exact rate of hydrolysis and/or methanolysis for **11** could not be determined because the decomposition of ester took place in these solvents. The rate of the optically active ester [(−)-**10ex**] was measured in the same solvents by a polarimetric procedure by which polarimetric rate constants (k_α) at 25 and 35 °C were determined.[16] The calculation of rates and physical parameters were carried out by the usual first-order expression using a computer programmed with least squares. The results of solvolysis rate are summarized in Table II along with kinetic data for 2-norbornyl (**1**) and 2-oxabicyclo[2.2.1]hept-6-yl (**2**) derivatives.

The exo ester (**10ex**) solvolyzed 3.7×10^{14} times faster than the endo isomer (**10en**) and 3.1×10^{10} times faster than the corresponding carbon system. These factors are the greatest values among β-S-participation of various systems observed until the present.

The endo isomer (**11**) underwent solvolysis 43 times slower than the *endo*-norbornyl system. This retardation might be attributed to steric hindrance in the ionizing step caused by the endo-lone pair electrons of the sulfur atom, rather than the inductive effect of sulfur.[17]

Polarimetric rate measurement of the optically active exo ester [(−)-**10ex**] provides the true rate of the ionizing step (k_1).

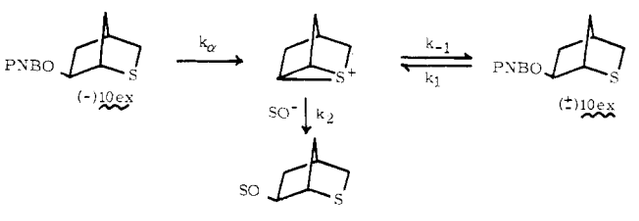
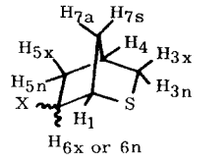


Table I. ^{1}H NMR Assignments of 2-Thiabicyclo[2.2.1]hept-6-yl Derivatives (100 MHz)[a]



registry no.	compd	1	3x	3n	4	5x	5n	6	7a	7s	other protons	J, Hz
67338-11-8	**4**	4.40 m			3.99 m	6.24 dd		6.65 dd	2.05 td	2.35 d		$J_{4,5}$ = 3.5 $J_{1,6}$ = 2.5 $J_{1\&4,7}$ = 3
						$J_{5,6}$ = 5.5 (AB)			J = 10 (AB)			
67338-12-9	**5**	4.06 m	3.22 dd	2.25 md	3.48 m	5.80 dd or		6.28 dd	1.39 md	1.61 md		$J_{4,5}$ = $J_{1,6}$ = 3 $J_{3x,4}$ = 4
			J = 9 (AB)			$J_{5,6}$ = 6 (AB)			J = 9 (AB)			
67338-13-0	**6**	3.37 bs	2.83 md	2.40 md	2.80 m	2.34 md	1.65 md	4.29 m	2.00 m			
			J = 7 (AB)			J = 11 (AB)						
67360-73-0	**7**	3.54 bs	3.04 md	2.74 md	3.00 m	2.46 qd	2.15 md	4.74 dd	2.44 m			$J_{5n,6n}$ = 7 $J_{5x,6n}$ = 3
			J = 12 (AB)			J = 14 (AB)						
67338-14-1	**8ex**	3.14 bs	2.78 md	2.35 d	2.77 m[b]	1.42 md[b]	1.82 qd	4.21 d	2.15 md	1.57 md[b]		$J_{5n,6n}$ = 6.5 $J_{5n,7}$ = 2
			J = 9 (AB)			J = 14 (AB)						
67338-15-2	**9**	3.44 bs	3.06 md	2.75 md	3.04 m	2.16 md	1.82 md		2.11 bs			
			J = 10 (AB)			J = 11 (AB)						
67338-16-3	**10ex**[c]	3.50 s	2.88 md	2.50 d	2.91 m	1.79 md	2.30 qd	5.27 d	2.17 md	1.72 md	8.23 (arom)	$J_{5n,6n}$ = 6.5
			J = 9 (AB)			J = 14 (AB)			J = 11 (AB)		J = 11 (AB)	
67338-17-4	**12**	3.32 m	2.78 md	2.36 dd	2.74 m	1.50 md	1.72 qd	3.71 md	2.04 md	1.54 md	3.30 s (CH_3)	$J_{5n,6n}$ = 7 $J_{3n,7a}$ = 1.5 $J_{5n,7s}$ = 2
			J = 9 (AB)			J = 14 (AB)			J = 11 (AB)			
67338-18-5	**13ex**	3.34 bs	*b*	*b*	2.84 m	1.64 md[b]	1.88 qd	5.00 md	2.16[b]	1.60 md	2.02 s (CH_3)	$J_{5n,6n}$ = 6.5 $J_{6n,7}$ = 2
						J = 14 (AB)			J = 11 (AB)			
67338-19-6	**14**	3.25 s	2.78 md	2.34 md	2.73 m	1.72 mdd	1.41 md	3.86 md	2.03 md	1.62 md		$J_{5n,6n}$ = 7
			J = 9 (AB)			J = 14 (AB)			J = 11 (AB)			
67338-20-9	**8en**	3.46 m	2.89 td	2.55 d	2.70 m	2.10 md	0.90 td	4.31 td	2.00 md	1.79 md		$J_{5x,6x}$ = 10 $J_{5n,6x}$ = $J_{1,6x}$ = 4
			J = 10 (AB)			J = 14 (AB)			J = 11 (AB)			
67338-21-0	**10en**	3.74 m	3.01 md	2.60 d	2.81 m	2.30 md	1.34 td	5.36 td	2.09 md	1.86 md	8.26 s	$J_{5x,6x}$ = 10 $J_{5n,6x}$ = $J_{1,6x}$ = 4
			J = 10 (AB)			J = 14 (AB)			J = 11 (AB)		(arom)	
67338-22-1	**11**	3.34 m	2.91 td	2.59 d	2.69 m	2.08 md	1.26 md	4.99 td	1.91 md	1.71 md	2.45 s (CH_3)	$J_{5x,6x}$ = 10
			J = 9 (AB)			J = 14 (AB)			J = 11 (AB)		7.59 q (arom) J = 8.5 (AB)	$J_{5n,6x}$ = $J_{1,6x}$ = 4
67338-23-2	**13en**	3.64 m	2.96 td	2.63 d	2.74 m	2.18 md	1.20 md	5.08 td	2.02 md	1.78 md	2.10 s (CH_3)	$J_{5x,6x}$ = 10 $J_{5n,6x}$ = $J_{1,6x}$ = 2.5
			J = 10 (AB)			J = 14 (AB)			J = 11 (AB)			
67338-24-3	**20**	3.51 m	2.93 td	2.62 d	2.70 m	2.34 md	1.47 qd	4.50 qd	1.95 m			$J_{5x,6x}$ = 10 $J_{5n,6x}$ = 6 $J_{1,6x}$ = 4
			J = 9 (AB)			J = 14 (AB)						

[a] All ^{1}H NMR spectra were measured in $CDCl_3$. Chemical shifts (ppm from Me_4Si) and coupling constants (Hz) were determined by the aid of shift reagent ($Eu(fod)_3$) and/or by decoupling technique. The following abbrevations are used: AB, AB pattern signal; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad singlet; dd, doublets of doublet; td, triplets of doublet; qd, quartets of doublet; md, multiplets of doublet. [b] The precise assignment could not be obtained because of overlap of signals. [c] Spectral data taken by a Varian HR-220 spectrometer (220 MHz). We thank Professors T. Yonezawa and I. Morishima, Department of Hydrocarbon Chemistry, Kyoto University, for ^{1}H NMR spectrometric analysis.

Table II. Rate Data for Solvolysis in 80% Aqueous Acetone (A), in Buffered Acetic Acid (B), and in Methanol (C)

compd	procedure	solvent	$k \times 10^6$ s^{-1} (°C)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	exo/endo rate ratio		rel rate		
10ex	titrimetric	A	420 (50)	21.4	−8.0					
			23.7 (25)							
			Ts, 7.25×10^{11}(25)[b]			3.7×10^{14}	3.1×10^{10}			
	polarimetric	A	349 (35)	14.1	−32					
			35.4 (25)							
	titrimetric	C	27.9 (25)							
	polarimetric	C	45.7 (25)							
11	titrimetric	B	303 (125)	27.4	−6.3					
			27.8 (100)							
			1.94×10^{-3} (25)[a]					1/43		
exo-2-norbornyl			Ts, 23.3 (25)[a,c]			280	1.0			
			Bs, 88.2 (25)[a,d]	21.6	−7.2	350			1.0	
endo-2-norbornyl			Ts, 8.28×10^{-2}(25)[a,c]	25.8	−4.4			1.0		
			Bs, 2.52×10^{-1} (25)[a,d]	26.0	−1.5					1.0
exo-2-oxa-6-norbornyl			Ts, 38 (25)[e]	23.4	−0.3					
			Bs, 218 (25)[e]			7×10^7			2.5	
endo-2-oxa-6-norbornyl			Bs, 2.9×10^{-6} (25)[a,e]	30.5	−9.4					1/87 000

[a] Rate extrapolation from rates at higher temperatures. [b] Rate for the tosylate calculated using a factor of $k_{Ts}(B)/k_{PNB}(A) = 3.06 \times 10^{10}$ reported by Peters [E. N. Peters, *J. Am. Chem. Soc.*, **98**, 5627 (1976)]. [c] Reference 22. [2] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952). [e] Reference 4.

Internal return of the *p*-nitrobenzoate ion forms the optically inactive exo ester (**10ex**) because the intermediary episulfonium ion is symmetrical. According to the usual treatment of kinetics, the titrimetric rate is

$$k_t = k_1 k_2/(k_{-1} + k_2)$$

Rearrangement of the equation and replacement of k_1 by k_α gives

$$k_{-1}/k_2 = k_\alpha/(k_t - 1)$$

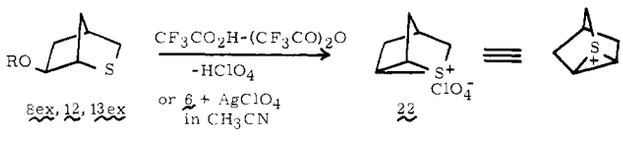
Since k_{-1}/k_2 reveals the rate ratio of internal return and solvolysis product formation, the amount of internal return in this solvolysis can be obtained.

Calculation by the introduction of the rate data observed in the present system resulted in $k_{-1}/k_2 = 33/67$ (80% aqueous acetone, 25 °C) and 39/61 (methanol, 25 °C), showing, even in the system which has a huge amount of neighboring-group participation, moderate internal return as observed in the solvolysis of carbon systems. It is concluded that the attack of solvent on an intermediary ion is not a step determining the rate, but the ionizing step determines the rate in this system.

Isolation and NMR Spectrum of the Intermediary Tricyclic Episulfonium Salt (22). Stereochemical and geometrical aspects of the 2-thiabicyclo[2.2.1]hept-6-yl system (**3**) offer the possibility of isolating a tricyclic episulfonium ion. Treatment of a solution of the chloride (**6**) in acetonitrile with 1 mequiv of silver perchlorate yielded a salt, which was found to be the tricyclic episulfonium salt (**22**) by NMR analysis. This is a common procedure for the preparation of sulfoniun salts[18] (Scheme III).

The addition of 70% perchloric acid to a solution of 6-*exo*-acetoxy-2-thiabicyclo[2.2.1]heptane (**13ex**) in trifluoroacetic acid–trifluoroacetic anhydride, followed by evaporation of the solvent, left pure **22**, which was equivalent with the salt prepared by the former method on comparison by NMR spectroscopy. The use of the other exo derivatives such as 6-hydroxy (**8ex**) and 6-methoxy (**12**) compounds also yielded the same results. This observation is a first example for trapping an episulfonium ion as a reaction intermediate.

Scheme III



The typical ^{1}H NMR and ^{13}C NMR spectra of the perchlorate (**22**) measured in trideuterionitromethane are shown in Figure 1 (Supplementary Material). Both spectra reveal that the ion (**22**) has a symmetric structure. The same spectrum was also observed in direct measurement of **6, 8ex, 12,** and **13ex** in trifluoroacetic acid.

As a reflection of the symmetric structure of the tricyclic episulfonium ion (**22**), its ^{1}H NMR spectrum was observed to be a simple pattern; in trideuterionitromethane, the protons of C_1 and C_6 resonated at 4.72 ppm as a singlet peak, that of C_4 at 3.24 ppm as a broad singlet, those of C_3 at 2.88 ppm as a sharp doublet ($J_{3,4}$ = 1.5 Hz), and those of C_5 and C_7 as an AB type pattern (J = 14 Hz) centered at 2.22 ppm. Each stereochemically different proton was split with the C_4 proton ($J_{5ex,7ex,4}$ = 2.5, $J_{5en,7en,4}$ = 0.5 Hz). The ^{13}C NMR spectrum of the salt (**22**) also reveals the four different carbon atoms, indicating the symmetric character of the ion (**22**).

Product of Solvolysis. Solvolyses for product studies were undertaken under the same conditions as used in rate measurements. After usual workup, products were analyzed by VPC. The 6-exo ester (**10ex**) yielded the 6-exo alcohol (**8ex**) in 97.6% yield. On the other hand, the 6-*exo*-acetoxy derivative (**13ex**) was obtained in 85.4% yield from the acetolysis of the 6-*endo*-tosylate (**11**).

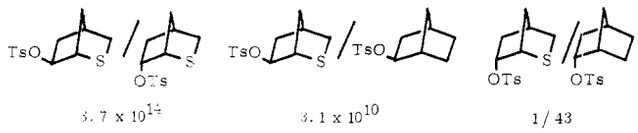
As expected from the fast rate of solvolysis of **10ex**, the reaction gave rise to an exo attack on the tricyclic episulfonium ion (**22**) by a solvent, resulting the exclusive formation of an exo derivative. The fact that only the exo product (**13ex**) was produced from the solvolysis of the less reactive **11** indicates intervention of the stable tricyclic episulfonium ion (**22**). It should be noted that no endo product nor olefin could be detected by VPC and NMR analyses.

Discussion

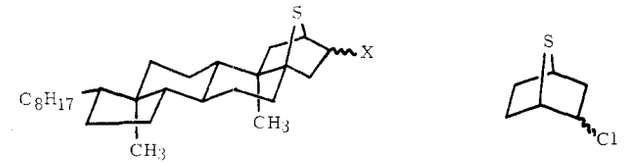
The solvolytic behaviors of the isomeric esters (**10ex** and **11**) provide valuable information on the role of a neighboring sulfur atom in solvolysis of the 2-thiabicyclo[2.2.1]hept-6-yl system. The exo isomer should have an advantage in forming a relatively stable episulfonium ion by β-S-participation.

The rate observed for the exo ester (**10ex**), 3.1×10^{10} times faster than the corresponding carbon system, reveals clearly

that the sulfur of this system highly stabilizes the transition state. An extremely high exo/endo rate ratio, 3.7×10^{14}, rises primarily from strong β-S-participation for the exo isomer (**10ex**). This value is the greatest among rate ratios of two stereoisomers observed until the present.

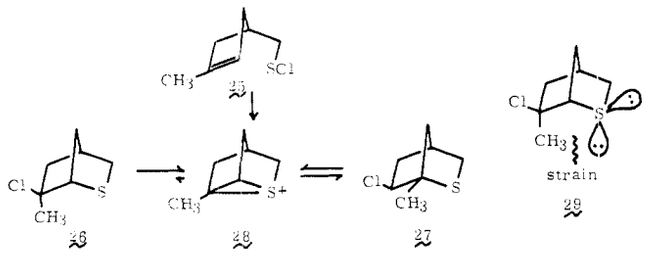


In the recent solvolytic studies of the similar systems, Tanida[19] and Tabushi[12] have examined independently the solvolytic behavior of **23** and **24**. In both systems faster rate is observed with the endo isomer: endo/exo rate ratios 1.2×10^8 (25 °C) for **23** in 70% aqueous dioxane and 4.7×10^9 (25 °C) for **24** (in acetic acid for the endo and in 50% aqueous dioxane for the exo) after correction for the solvent as well as the leaving group. Although there are observed high rate ratios of both systems, they fail to overcome the rate ratio of the 2-thiabicyclo[2.2.1]hept-6-yl system, indicating that the amount of neighboring-group participation strongly depends on the structural factors such as geometry, stereochemistry, and skeletal mobility of molecules in the transition state.[20]



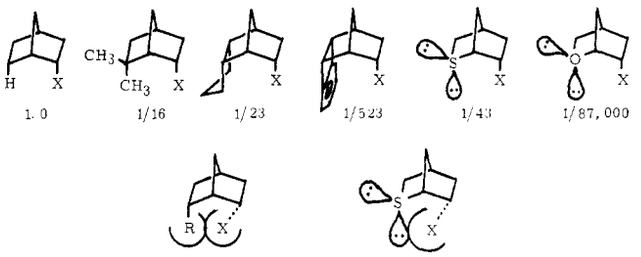
On the other hand, the endo isomer (**11**) undergoes its solvolysis somewhat slower than *endo*-2-norbornyl derivative, 1/43. This rate retardation may be attributed to the inductive character of a sulfur atom.[17]

The concept of "steric hindrance to ionization", proposed by Brown[3a] in the norbornyl system, may account for the retardation of the solvolysis rate of an endo isomer. As we reported previously,[8] the tricyclic episulfonium ion (**28**), derived



by intramolecular sulfenyl chloride addition of **25** formed in situ from the reaction of the corresponding disulfide with chlorine, should be in equilibrium with **26** and **27** at elevated temperature. However, we could not establish the presence of the tertiary chloride (**26**), although **26** is expected to be thermodynamically more stable than **27** as is usually the case with β-chloro sulfides.[21,22] The remarkable instability of the tertiary chloride (**26**) when compared with the other equilibrated isomer (**27**) indicates the presence of steric repulsion between the 6-*endo*-methyl group and the lone pair electrons of the endo side of the sulfur atom, as shown in **29**. This fact is interesting in the evaluation of the spatial requirements of lone pair electrons.

In the norbornyl system, endo-6 substituents are operative in increase of steric repulsion in ionization, and the amount of retardation depends on the spatial environment of molecules.[4,23-26] Considering the inductive rate-retarding factor of 2000 observed for solvolysis of 2-*exo*-chloro-7-oxabicyclo[2.2.1]heptane,[4] this factor being considered to be applicable to the 2-oxabicyclo[2.2.1]hept-6-*endo*-yl analogue, the factor of 1/44 attributable to steric hindrance in an ionizing step is obtained. This value is similar to that obtained for the endo isomer of the thia analogue, indicating that the steric requirement between the oxa and thia analogues, especially in relation of steric repulsion of lone pair electrons with a leaving group in the transition state, is quite equivalent.

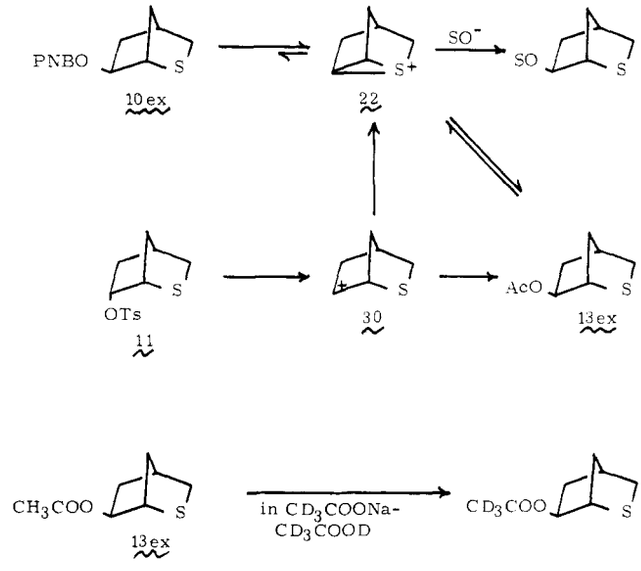


Among the solvolytic studies involving β-S-participation, an example in which a solvent-attacking step is the step determining a rate is known;[12] this may arise from a large amount of neighboring-group participation. On the basis of our results, however, the differences of rate-determining steps are not attributable to the amount of participation by neighboring groups, but to the character of the leaving groups.

The intervention of the optically inactive tricyclic episulfonium ion obtainable from the solvolysis of an ester of optically active 2-thiabicyclo[2.2.1]heptan-6-*exo*-ol makes this point unequivocal. The observation of 30–40% internal return at the first ionizing step of solvolysis, calculated from titrimetric (k_t) and polarimetric (k_α) determinations of rates, leads to the conclusion that ionization is the rate-determining step; the attack of solvent on the ion does not affect the rate.

The mechanistic considerations of solvolysis of the exo and endo esters (**10ex** and **11**) are illustrated in Scheme IV. The acetoxy group of **13ex** [the solvolysis product of the endo ester (**11**)] was readily exchangeable. The 6-*exo*-trideuterioacetoxy compound was isolated from the solvolytic reaction of the 6-*exo*-acetoxy derivative in buffered trideuterioacetic acid, so that the initially formed acetoxy product from the endo ester could be present in an equilibrium under the solvolytic condition. Thus, the presence of the direct process to **13ex** from the open carbonium ion (**30**) could not be explored independently from more plausible process via the episulfonium ion produced by overlapping of the vacant 2p orbital at the 6 position of **30** with the lone pair electrons of the sulfur atom.

Scheme IV



The intervention of the σ-sulfurane structure[18c,d,e,27,28] may be eliminated in this solvolytic reaction because of the low nucleophilic ability of a *p*-nitrobenzoate anion. The presence of σ-sulfurane as an intermediate is more plausible in reactions of β-halo sulfides.

β-Halo sulfides are often present in equilibrium with episulfonium ions even in aprotic solvents. In these cases, rates are considered to be affected by the nucleophilic character of nucleophiles and not by the ionizing ability of solvents.

Success in isolating the tricyclic episulfonium ion, 1-thioniatricyclo[1.1.1.^{2,6}]heptane perchlorate (**22**), as the intermediate ion is attributed to its structural stability when compared with usual episulfonium salts observed by Helmkamp and co-workers.[18]

The 2-thiabicyclo[2.2.1]hept-6-yl system (**3**) supplies not only matters of mechanistic interests in solvolytic reactions, but also structural interests. We are currently pursuing the role of a divalent sulfur atom in comparison with other thiabicyclic systems.

Experimental Section

All melting points are corrected and boiling points are uncorrected. IR spectra were taken on a Hitachi-Perkin-Elmer Model 225 (Grating) spectrometer. ^{1}H NMR spectra were recorded on a Varian 100-MHz spectrometer (HA-100) in deuteriochloroform and the ^{13}C NMR spectrum of the tricyclic episulfonium salt (**22**) on a JEOL FX-100 spectrometer using a 10-mm tube. Chemical shifts are indicated by parts per million from a tetramethylsilane internal standard. Mass spectra were measured on a Hitachi mass spectrometer Model RMS-4 performed with a target current of 70 μA and a chamber voltage of 70 eV. Gas chromatographic analyses were carried out with a Varian 1440 instrument equipped with a flame ionization detector and with glass tubing columns. Conditions used for analysis are given at an appropriate position.

3,3-Dichloro-2-thiabicyclo[2.2.1]hept-5-ene (4) This compound was prepared from the cycloaddition of cyclopentadiene with thiophosgene according to the procedure reported by Middleton[6] or Johnson[7] and stored in a dry-ice box.

2-Thiabicyclo[2.2.1]hept-5-ene (5). To a suspension of $LiAlH_4$ (15.5 g, 0.41 mol) in 250 mL of gently refluxing anhydrous ether was added dropwise a solution of 45 g (0.25 mol) of **4** dissolved in 150 mL of anhydrous ether. The mixture was stirred at reflux for an additional 2 h. The excess hydride was destroyed by careful addition of water. The ether solution was filtered and the residue was washed with 100 mL of ether. Both solutions were combined, dried over $MgSO_4$, and concentrated at 60 mmHg while cooling in an ice bath. Finally, the solvent was removed at room temperature to leave 25.3 g (90%) of a faint yellow oil, which solidified on cooling. The NMR spectrum of the waxy solid thus obtained was identical with that reported by Johnson and co-workers.[7] Sublimation provided pure material of a white waxy solid: mass spectrum (*m/e*) 112 (M^+), 79 ($M^+ - SH$), 66 ($C_5H_6^+$, base peak).

6-*exo*-Chloro-2-thiabicyclo[2.2.1]heptane (6). Into a solution of 11.6 g (0.103 mol) of **5** dissolved in 25 mL of anhydrous methylene chloride was passed dry hydrogen chloride gas at $-50 \sim -60$ °C. After the solution was saturated with HCl, the flow of the gas was stopped and then the mixture was stirred for 30 min at -50 °C. The light brown solution was washed three times with 50 mL of cold water, dried over anhydrous K_2CO_3, and concentrated at room temperature to give 13.6 g (89%) of a yellow oil. This crude material was spectroscopically pure and could be used as a synthetic intermediate. Distillation under reduced pressure gave a colorless oil, bp 36.5–37 °C (1 mmHg).

m-Chloroperbenzoic acid (MCPBA) oxidation of **6** yielded the corresponding sulfone derivative (**7**), which was recrystallized from ether to give white needles, mp 99.0–99.5 °C. Anal. Calcd for $C_6H_9ClO_2S$: C, 39.89; H, 5.02; Cl, 19.62; S, 17.75. Found: C, 39.82; H, 5.11; Cl, 19.51; S, 17.66.

2-Thiabicyclo[2.2.1]heptan-6-*exo*-ol (8ex). The chloro derivative (**6**) (5.2 g, 35 mmol) was dissolved in 400 mL of 50% aqueous acetone containing 2.1 g (20 mmol) of sodium carbonate and a solution was allowed to stand at room temperature for 10 h. Acetone was evaporated in vacuo and products were extracted with ether, then the extract was dried over $MgSO_4$ and concentrated to leave 4.3 g (93%) of a pale yellow viscous oil. The oil solidified under cooling. Purification was carried out by column chromatography over neutral or basic alumina because purification by sublimation or distillation resulted in formation of dimeric ether (**14**). When **6** was hydrolyzed without a base, products were contaminated with the dimeric ether (**14**); 34/66 as a ratio of **8ex/14**. Vigorous shaking of **8ex** or **14** in methylene chloride with concentrated hydrochloric acid resulted in the conversion into **6**: mass spectrum (*m/e*) 130 (M^+), 85 ($C_4H_5S^+$, base peak).

The *p*-nitrobenzoate (**10ex**) of **8ex** was prepared in the usual esterification procedure with *p*-nitrobenzoyl chloride and pyridine; recrystallization from a 4:1 mixture of hexane–benzene yielded pale yellow needles, mp 108.5–109.5 °C. Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.02; S, 11.48. Found: C, 56.02; H, 4.93; N, 4.88; S, 11.55.

2-Thiabicyclo[2.2.1]heptan-6-one (9). A cold solution of 2.15 g (16.5 mmol) of **8ex** dissolved in 30 mL of carbon tetrachloride and a *tert*-butyl chromate reagent (32 mL, 23 mmol) freshly prepared according to the reported procedure[9] were mixed and left overnight at -10 °C. To the reaction mixture, 4 mL of a saturated tartaric acid solution in ethanol was added and the mixture was stirred for 2 h at room temperature. After filtration, the filtrate was washed several times with a 5% sodium bicarbonate solution, dried over $MgSO_4$, and then evaporated to leave 1.42 g (67.1%) of a pale brown oil, which was spectroscopically pure. An attempt to obtain pure material was carried out by column chromatography over silica gel. An elution with a 1:3 mixture of hexane–benzene provided a single isomer, which was sublimed at 60–70 °C (3 mmHg) to give a colorless waxy solid: this material melted at 100–120 °C; IR ($CHCl_3$) 1740 cm^{-1} (C=O); mass spectrum (*m/e*) 128 (M^+), 85 ($C_4H_5S^+$).

The 2,4-dinitrophenylhydrazone, recrystallized from a 1:1 mixture of hexane–benzene, had mp 175–176 °C. Anal. Calcd for $C_{12}H_{12}N_4O_4S$: C, 46.75; H, 3.92; N, 18.17; S, 10.40. Found: C, 47.02; H, 3.98; N, 18.17; S, 10.21.

2-Thiabicyclo[2.2.1]heptan-6-*endo*-ol (8en). To a cold suspension of 312 mg (8.2 mmol) of $LiAlH_4$ in 40 mL of anhydrous ether was added an ethereal solution (10 mL) of 1.05 g (8.2 mmol) of **9**. The mixture was stirred at reflux for 1 h and the usual workup was carried out. Evaporation of the solvent left 850 mg (79.6%) of a white solid, which was recrystallized from hexane or pentane to afford a white waxy solid, mp 164–167 °C. Alternatively, purification by sublimation also gave the same material: mass spectrum (*m/e*) 130 (M^+), 85 ($C_4H_5S^+$, base peak).

The *p*-nitrobenzoate (**10en**) of **8en** was prepared from the reaction of **8en** with *p*-nitrobenzoyl chloride in pyridine and recrystallized from hexane to give pale yellow needles, mp 102.5–103.5 °C. Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.02; S; 11.48. Found: C, 55.78; H, 4.92; N, 4.86; S, 11.77.

The *p*-toluenesulfonate (**11**) of **8en** was prepared in the same procedure as used for the ester (**10en**). As an effort to solidify the ester (**11**) failed, the sample was purified by column chromatography over silica gel. Chromatographed material, whose purity was confirmed spectroscopically, was used for the kinetic measurements without further purification.

6,6′-*exo,exo*-Oxybis(2-thiabicyclo[2.2.1]heptane) or Di(2-thiabicyclo[2.2.1]hept-6-*exo*-yl) Ether (14). (A) To a solution of 130 mg (1mmol) of **8ex** in 2 mL of anhydrous tetrahydrofuran was added a 2 *n*-BuLi solution in hexane (0.5 mL, 1 mmol, Merck reagent) in a dry ice–acetone bath ($-30 \sim -40$ °C) under a nitrogen stream. The mixture was stirred for 30 min at -30 °C and then a solution of 148 mg (1 mmol) of **6** in 2 mL of tetrahydrofuran was added. After standing overnight at room temperature, the solution was concentrated and a residue was dissolved in 10 mL of ether. The ether solution was washed with water, dried over $MgSO_4$, and then evaporated to leave 210 mg (86.6%) of a viscous oil, which was sublimed at reduced pressure to give a waxy solid: mass spectrum (*m/e*) 242 (M^+), 129 ($C_6H_9OS^+$), 113 ($C_6H_9S^+$, base peak), 85 ($C_4H_5S^+$).

(B) In a small-scale experiment, the exo alcohol (**8ex**) containing a trace amount of *p*-toluenesulfonic acid was refluxed in benzene for 3 h. The mixture was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and then evaporated. There was obtained fairly pure dimeric ether **14** quantitatively. Spectral data were consistent with those of the product prepared according to method A.

6-*exo*-Methoxy-2-thiabicyclo[2.2.1]heptane (12). A solution of 1.1 g (8.4 mmol) of **8ex** dissolved in 30 mL of anhydrous methanol containing 30 mg of *p*-toluenesulfonic acid was refluxed for 1 h. The solution was concentrated carefully and 20 mL of ether was added. The ether solution was washed with saturated $NaHCO_3$ solution and with saturated NaCl solution, and dried over anhydrous K_2CO_3. Evaporation of the solvent under atmospheric pressure left 1.1 g (90.8%) of a pale brown oil, which was distilled to give a colorless oil: bp 50–53 °C (3 mmHg); mass spectrum (*m/e*) 144 (M^+), 112 ($M^+ - CH_3OH$), 97 ($M^+ - CH_3S$), 85 ($C_4H_5S^+$).

Likewise, by the use of dimeric ether (**14**), the same product (**12**) was obtained in a high yield. Alternatively, the methanolysis of **6** or **10ex** in methanol containing sodium methoxide gave the corresponding methoxy derivative (**12**) quantitatively.

2-Thiabicyclo[2.2.1]heptan-6-*exo*-ol Acetate (13ex). To a stirred solution of 780 mg (6 mmol) of **8ex** in 4 mL of anhydrous pyridine was added 817 mg (8 mmol) of acetic anhydride under ice cooling. The usual workup gave 940 mg (91%) of a pale yellow oil, which was spectroscopically pure. Distillation provided a colorless oil: bp 82–83 °C (2 mmHg); n^{20}_D 1.5066; IR (film) 1740, 1232 cm^{-1} ($COCOCH_3$); mass spectrum (*m/e*) 172 (M^+), 129 ($M^+ - CH_3CO$), 113 ($M^+ - CH_3COO$), 85 ($C_4H_5S^+$, base peak), 43 (CH_3CO).

2-Thiabicyclo[2.2.1]heptan-6-*endo*-ol Acetate (13en). The alochol (**8en**) (26 mg, 0.2 mmol) was acetylated in the usual manner. There was obtained 34 mg of a colorless oil, which showed to be a single peak in VPC analysis and pure in NMR spectrum. IR (film) 1733, 1243 cm^{-1} ($COCOCH_3$).

1-Thioniatricyclo[1.1.1.$0^{2,6}$]heptane Perchlorate (22). To a stirred solution of 1.5 g (10.1 mmol) of **6** dissolved in 10 mL of anhydrous acetonitrile was added dropwise a solution of 2.09 g (10.1 mmol) of silver perchlorate dissolved in 10 mL of acetonitrile under ice cooling. A solid preceipitated, which consists of a sulfonium salt and silver chloride, was assembled by filtration, and extracted three times with 50 mL of hot acetontrile. Evaporation of the solvent gave 1.77 g of a pale violet solid, which was recrystallized from acetonitrile to yield 1.32 g (61.2%) of while crystals, mp 216–218 °C dec. Anal. Calcd for $C_6H_9ClO_4S$: C, 33.89; H, 4.27; S, 15.08. Found: C, 33.85; H, 4.19; S, 15.29. The IR spectrum showed a broad band at 1100 cm^{-1} assignable to perchlorate. This compound is slightly soluble in acetonitrile and nitromethane, and insoluble in such solvents as chloroform, dichloromethane, carbon tetrachloride, dimethyl sulfoxide, dimethylformamide, tetranitromethane, and nitrobenzene.

Trapping of the Tricyclic Episulfonium Ion (22) under Solvolytic Conditions. To a stirred solution of 130 mg (1 mmol) of the exo alcohol (**8ex**) dissolved, at 0 °C, in 2 mL of a 1:1 mixture of trifluoroacetic acid and trifluoroacetic anhydride was added 0.17 mL of 60% perchloric acid solution with the aid of a microsyringe. After stirring for 30 min at 0 °C, the mixture in which small amount of colorless needles appeared was concentrated under reduced pressure to leave pale brown crystals. Decolorization of a solution of the crystals dissolved in acetonitrile with active carbon and evaporation of the solvent gave 210 mg (99%) of white crystals, which was recrystallized from acetonitrile to yield white prisms, mp 216–218 °C dec. The ^1H NMR spectrum in trideuterionitromethane showed the typical pattern of the structure of the episulfonium ion.

(−)-2-Thiabicyclo[2.2.1]heptan-6-*exo*-ol[(−)-8ex]. To a stirred solution of 11.56 g (53.4 mmol) of *d*-camphanyl chloride, derived from *d*-camphanic acid[13] [mp 202–203 °C; $[\alpha]^{25}_D$ −6.9 (EtOH, *c* 1.13)], dissolved in 100 mL of anhydrous pyridine was added dropwise a solution of 6.95 g (53.4 mmol) of the racemic alcohol (**8ex**) dissolved in 10 mL of anhydrous pyridine under ice cooling. The mixture was stirred overnight and poured into a mixture of 100 mL of concentrated hydrochloric acid and 300 g of ice. This treatment was essential to obtain the corresponding camphanic acid ester. When the mixture was poured into cold water, the yield of the ester decreased dramatically as a result of rapid hydrolysis of the ester. A viscous oil separated from the cold acidic medium was extracted with chloroform and the extract was washed twice with cold water, dried over $MgSO_4$, and then evaporated to give 14.9 g (90.3%) of a pale brown oil. Scratching the oil after adding 5 mL of ether gave 2.2 g of crystals, which were recrystallized from ethyl acetate seven times to afford 560 mg of colorless needles: mp 136–137 °C; $[\alpha]^{24}_D$ −29.2 ($CHCl_3$, *c* 3.01). Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14; S, 10.33. Found: C, 61.79; H, 7.28; S, 10.28. No more increase of $[\alpha]_D$ could be observed on further recrystallization.

The ester (530 mg, 1.7 mmol) was dissolved in 15 mL of benzene and 3.2 mL (11 mmol) of 70% sodium bis(methoxyethoxy)aluminum hydride solution in benzene was added at 5–10 °C with magnetic stirring. The solution was allowed to stand at room temperature overnight and complexes and/or an excess hydride was destroyed by careful addition of 1.2 mL of 0.5 N NaOH. The clear upper layer was decanted, dried over $MgSO_4$, and evaporated to leave 982 mg of a viscous oil, which was purified by column chromatography over alumina. Elution with benzene gave 220 mg (~100%) of a white waxy solid. This product was shown to be pure in ^1H NMR spectroscopy and thin-layer chromatography, $[\alpha]^{24}_D$ −16.8 (EtOH, *c* 2.5).

(−)-2-Thiabicyclo[2.2.1]heptan-6-*exo*-ol *p*-Nitrobenzoate [(−)-10ex]. Optically active *p*-nitrobenzoate (−)-**10ex** was prepared from the reaction of the optically active **8ex** (226 mg, 1.73 mmol) with 321 mg (1.73 mmol) of *p*-nitrobenzoyl chloride in the usual manner. Recrystallization from isopropyl ether gave 402 mg (83.1%) of pale yellow needles: mp 107–108 °C; $[\alpha]^{28}_D$ −26.2 ($CHCl_3$, *c* 2.65). Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.02; S, 11.48. Found: C, 55.86; H, 4.87; N, 4.89; S, 11.57.

Exchange of an Acetoxy Group in the Solvolysis of 2-Thiabicyclo[2.2.1]heptan-6-*exo*-ol Acetate (13ex). A solution of 17.2 mg (0.1 mmol) of **13ex** and 8.5 mg (0.1 mmol) of sodium trideuterioacetate dissolved in 2 mL of trideuterioacetic acid was heated in a sealed ampule at 125 °C. for 380 min (10 half-lives). The solution was concentrated and extracted with ether. The extract was washed with 10% sodium carbonate solution three times and then water, and dried over anhydrous potassium carbonate. Evaporation of the solvent left 12 mg of an oil whose ^1H NMR spectrum showed no methyl signal. Mass spectrum indicated a molecular ion peak at *m/e* 175 corresponded to trideuterioacetate of **8ex** and no peak at *m/e* 172.

3-Cyclopentenemethanethiol Acetate (18). To a solution of 5.5 g (48 mmol) of potassium thiolacetate dissolved in 40 mL of methanol was added a solution of 13.9 g (44 mmol) of 3-cyclopentenemethanol brosylate dissolved in 80 mL of methanol at room temperature with stirring. The mixture was stirred at 60 °C for 2 h and then evaporated. After adding 30 mL of water to a residue, the mixture was extracted with ether and the extract was washed with saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to leave 7.5 g of an oil, which was distilled under reduced pressure to afford 5 g (73%) of a colorless oil: bp 50–53 °C (3 mmHg); IR (film) 1695 cm^{-1} (CH_3COS); mass spectrum (*m/e*) 156 (M^+), 113 ($M^+ - COCH_3$).

3,4-Dibromocyclopentanemethanethiol Acetate (19). The basic procedure of bromine addition was similar to that used for the addition to 3-cyclohexanemethanethiol acetate reported by Johnson and Billman.[11] There was obtained the dibromo derivative (**18**) in 85.6% yield. Purification was carried out by column chromatopraphy over silica gel: IR (film) 1696 cm^{-1} (CH_3COS); mass spectrum (*m/e*): 194, 192 ($M^+ - CH_3CO - Br$), 113 ($M^+ - CH_3CO - 2Br$).

6-*endo*-Bromo-2-thiabicyclo[2.2.1]heptane (20). To a solution of potassium hydroxide (1.25 g, 18.8 mmol) in 30 mL of methanol was added a solution of 1.7 g (5.4 mmol) of the dibromide (**18**) dissolved in 20 mL of methanol, with stirring at room temperature, over a period of 20 min. Then the reaction was continued for 2 h and evaporated. To the residue was added 100 mL of ether and the solution was washed with water until the water layer became neutral, dried over $MgSO_4$, and evaporated to leave 910 mg (87.3%) of a pale yellow oil, which was highly pure on TLC analysis. Purification was run by silica gel column chromatography: mass spectrum (*m/e*) 194, 192 (M^+), 113 ($M^+ - Br$), 85 ($C_4H_5S^+$).

Measurement of Rates. (A) Titrimetric Method. The procedure was similar to those used for monocyclic heterocycles previously reported.[15] The 80% aqueous acetone used for the hydrolysis of the exo ester (**10ex**) was prepared by mixing 80 parts by volume of purified acetone with 20 parts of purified water at 20 °C and adjusted to yield a rate of solvolysis identical, within the experimental uncertainty of ±3%, with that observed for 1-phenylcyclohexyl *p*-nitrobenzoate. Acetic acid containing 0.01 N sodium acetate used for the acetolysis of the endo ester (**11**) was prepared according to Winstein's procedure[29] and titration was carried out with 0.01 N perchloric acid solution in acetic acid using bromophenol blue as an indicator. Rate constants were calculated by least-squares linear-regression analysis to first-order rate expression. The physical parameters were obtained by Eyring's absolute rate equation using a computer (TOSBAC 3400).

(B) Polarimetric Method. The polarimetric measurement of rates was carried out with a JASCO automatic polarimeter model DIP-SL in a micro 1-dm polarimeter tube of ~4.3 mL capacity equipped with an outer jacket. Water from a 25.00 ±0.03 °C thermostat was continuously circulated through the outer jacket during the course of the racemization runs. In each racemization rate run, solvent first brought to temperature in the 25 °C thermostat was used to dissolve the weighed quantity of the otpically active ester [(−)-**10ex**] to the mark in a 5-mL volumetric flask. The resulting 0.029–0.03 M solution was then transferred as rapidly as possible to the polarimeter tube and immersed into the thermostat. When readings were taken at appropriate intervals, the polarimeter tube was carefully located in place in the polarimeter trough. The optical rotation vanished at the completion of the reaction.

Analysis of Solvolysis Product. Solvolytic techniques were similar to those used for rate measurements. The solvolysis of the exo ester (**10ex**) was taken in 80% aqueous acetone. To a solution immersed in a temperature-controlled bath at 50 °C for more than 10 half-lives was added an equimolar amount of benzophenone as an internal standard for VPC analysis and the solution was dehydrated by adding anhydrous potassium carbonate. The resulting solution was analyzed

by VPC using a short glass column (1 ft × 1/8 in.) packed with 5% diethylene glycol adipate supported on acid-washed 80–100 mesh Chromosorb W. The column was maintained at 100 °C with a flow rate of 25 mL/min of N_2. Under the VPC condition, only one peak was observed at 28 min of retention time as a produce of solvolysis, which was consistent with that of the exo alcohol (**8ex**). Quantitative analysis by comparison with an internal standard was done by the use of a reporting integrator (Hewllet Packard Model 3880) and gave 97.6% yield as a result of a corrected value.

When the exo alcohol was analyzed using a 6 or 8 ft × 1/8 in. column, another new peak appeared. It was consistent with the dimeric ether **14**, which was attributed to the formation of **14** by thermal conversion of **8ex** on a column.

The solvolysis of the endo ester (**11**) was done in acetic acid containing an equimolar amount of sodium acetate. A solution heated in a sealed ampule at 125 °C for more than 10 half-lives was transferred to a small flask and an equal volume of water and acetone, then an equivalent of benzophenone as an internal standard for VPC analysis was added. The solution which was neutralized and dehydrated by adding anhydrous potassium carbonate was analyzed by VPC performed under the same conditions as used for the exo derivative. There was observed a single peak at 19 min retention time, which was consistent with that of the *exo*-acetate (**13ex**), and no other peaks were detected even under conditions capable of detecting at least 0.2% impurity. Quantitative analysis resulted in 85.4% yield.

Moreover, products from the two isomers (**10ex** and **11**) were isolated respectively and their structures were characterized by ^1H NMR and mass spectra.

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Registry No.—(−)-**8ex**, 67338-25-4; (−)-**8ex** *d*-camphonate, 67338-26-5; (−)-**8ex** trideuterioacetate, 67338-27-6; **9** DNP, 67338-28-7; (−)-**10ex**, 67338-29-8; **17**, 67338-30-1; **18**, 67338-31-2; **19**, 67338-32-3; **22**, 67338-34-5; *p*-nitrobenzoyl chloride, 122-04-3; *d*-camphanyl chloride, 67375-29-5; sodium trideuterioacetate, 14044-94-1; 3-cyclopentenemethanol brosylate, 18593-39-0.

Supplementary Material Available: Figure 1, showing the NMR (^1H and ^{13}C) for the tricyclic episulfonium perchlorate, **22** (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Part 3 in this series: K. Uoji, Y. Fukunaga, and S. Ikegami, *Chem. Pharm. Bull.*, **22**, 1706 (1974)
(2) Ohta Seyaku Co., Ltd., Kamijujo, Kita-ku, Tokyo, Japan.
(3) For recent reviews see: (a) H. C. Brown and P. v. R. Schleyer," The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977; (b) H. C. Brown, *Tetrahedron*, **32**, 179 (1976); (c) *Acc. Chem. Res.*, **6**, 377 (1973); (d) "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; (e) *Chem. Eng. News*, **45** (5), 87 (1967); (f) G. D. Sargent, *Carbonium Ions*, **3**, 1099–1200 (1972); (g) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965; (h) J. A. Barson, "Molecular Rearrangements", Part 1, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, pp 111–231.
(4) L. A. Spurlock and R. G. Fayter, Jr., *J. Am. Chem. Soc.*, **94**, 2707 (1972).
(5) For reviews see: (a) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964); (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, pp 16–18, 113–114.
(6) W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).
(7) C. R. Johnson, J. E. Keiser, and J. C. Sharp, *J. Org. Chem.*, **34**, 860 (1969).
(8) S. Ikegami, J. Ohishi, and Y. Shimizu, *Heterocycles*, **6**, 387 (1977); details will be reported soon.
(9) (a) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, pp 86–87; (b) E. Menini and J. K. Norymberski, *Biochem. J.*, **84**, 195 (1962).
(10) For the charge-transfer absorption of β-oxo sulfides see: L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967).
(11) C. R. Johnson and F. L. Billman, *J. Org. Chem.*, **36**, 855 (1971).
(12) I. Tabushi, Y. Tamaru, Z. Yoshida, and T. Sugimoto, *J. Am. Chem. Soc.*, **97**, 2886 (1975).
(13) O. Aschan, *Acta Soc. Sci. Fenn.*, **21** [V], 214 (1895).
(14) (a) If the exciton chirality method[14b] based on the strong $\pi \rightarrow \pi^*$ transitions of para-substituted benzoate chromophores (Me_2N, H_2N, MeO, Cl, H, CN) is applied to that of *p*-nitrobenzoate, the absolute configuration of the optically active ester [(−)-**10ex**] would be indicated, from its CD spectrum, as the structure of (−)-**10ex** shown in Scheme II. We thank Union Giken Co., Ltd., for measurement of the CD spectrum. (b) N. Harada, Mo. Ohashi, and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7349 (1968); N. Harada and K. Nakanishi, *ibid.*, **96**, 7352 (1974); N. Harada and K. Nakanishi, *Acc. Chem. Res.*, **5**, 257 (1972); N. Harada, S. L. Chen, and K. Nakanishi, *J. Am. Chem. Soc.*, **97**, 5345 (1975).
(15) S. Ikegami, T. Asai, K. Tsuneoka, S. Matsumura, and S. Akaboshi, *Tetrahdron*, **30**, 2087 (1974).
(16) For the polarimetric rates of a carbonium ion see: (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); (b) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, **77**, 5026 (1955). For a system involving β-O-participation see: (c) L. A. Paquette, I. R. Dunkin, J. P. Freeman, and P. C. Storm, *ibid.*, **94**, 8124 (1972).
(17) (a) P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, N.Y., 1968 p 35; (b) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1971, p 28.
(18) For isolation and reactivities of episulfonium ions, see: (a) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); (b) *ibid.*, **29**, 2702 (1964); (c) D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *J. Am. Chem. Soc.*, **91**, 3606 (1969); (d) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); (e) G. K. Helmkamp and D. C. Owsley, *Mech. React. Sulfur Compd.*, **4**, 37 (1969); (f) E. Carbin and G. K. Helmkamp, *Int. J. Sulfur Chem., Part A*, **2**, 129 (1972).
(19) T. Tsuji, T. Komeno, H. Itani, and H. Tanida, *J. Org. Chem.*, **36**, 1648 (1971).
(20) L. A. Paquette, G. V. Meehan, and L. D. Wise, *J. Am. Chem. Soc.*, **91**, 3231 (1969).
(21) For review see W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).
(22) For an equilibrium of cyclic systems see S. Ikegami, J. Ohishi, and Y. Shimizu, *Tetrahedron Lett.*, 3923 (1975).
(23) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); (b) *ibid.*, **74**, 1147, 1154 (1952).
(24) P v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).
(25) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Jpn.* **38**, 1318 (1965).
(26) R. Baker and J. Hudec, *Chem. Commun.*, 929 (1967).
(27) For the nomenclature and definition of σ-sulfurane, see B. M. Trost and S. D. Ziman, *J. Org. Chem.*, **38**, 932 (1973).
(28) J. A. J. M. Vincent, P. Schipper, Ae. de Groot, and H. M. Buck, *Tetrahedron Lett.*, 1989 (1975).
(29) (a) S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); (b) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).