Chemistry of 1,3-Glycol Derivatives. I. The Reactions of 2,4-Pentanediol Derivatives

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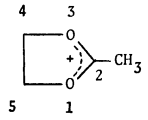
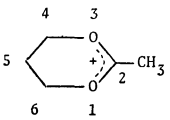
Cyclic orthoacetates of *meso*- and *dl*-2,4-pentanediol (*cis*- and *trans*-2-ethoxy-2,4,6-trimethyl-1,3-dioxane, **1**) were prepared and characterized by NMR. The stereochemical courses of the reactions of **1** with water, hydrogen chloride, trityl chloride, and acetic acid were investigated. The reactions with water gave 4-acetoxy-2-pentanol (**4**) with complete retention of configuration, while those with the other reagents gave 4-acetoxy-2-chloropentane (**3**) and 2,4-diacetoxypentane with complete inversion. Acetolyses of **3** and the tosylate of **4** gave 2,4-diacetoxypentane predominantly with retention in the absence of water. Hydrolysis of the tosylate gave **4** with almost complete inversion. These results can be explained by the mechanism that the reactions proceed mainly through acetoxonium cation intermediate involving six-membered ring. The fluoroborate salt of this acetoxonium cation was prepared and characterized by NMR.

As a case of neighboring group participation, acetoxy participation has been studied extensively by Winstein and his co-workers.[1] Participation of acetoxy group attached to the carbon α to the cationic carbon forms acetoxonium cation of five-membered ring (AcO-5 cation). Participation of the same group at the β-position should from acetoxonium cation of six-membered ring (AcO-6 cation).

AcO-5 cation





AcO-6 cation

So far, most part of the studies has been concerned with the former type of participation, and only few papers by Kovács and his co-workers[2] discussed the latter type, although the idea was reviewed by Schneider without presenting experimental data.[3]

This paper describes the preparation of *cis*- and *trans*-2-ethoxy-2,4,6-trimethyl-1,3-dioxane (*cis*- and *trans*-**1**) from *meso*- and *dl*-2,4-pentanediol (*meso*- and *dl*-**2**) and ethyl orthoacetate, and the formation of AcO-6 cation from **1**. The stereochemistry of the reactions of **1** with water, hydrogen chloride and trityl chloride is also reported together with the results of the acetolyses of 4-acetoxy-2-chloropentane (**3**) and the tosylate of 4-acetoxy-2-pentanol (**4**) which proceeded mainly through AcO-6 cation.

Preparation and Characterization of cis- *and* trans-*1*. From the reduction product of acetylacetone with sodium borohydride, *meso*- and *dl*-**2** were separated by the method of Pritchard and his co-workers.[4] The diols were converted to cyclic sulfite by the reaction with thionyl chloride and then subjected to fractional distillation. Hydrolysis of the lower boiling fraction gave pure *meso*-**2** and that of higher boiling fraction gave *dl*-isomer of 98% purity.

The method for the preparation of five-membered cyclic orthoester by Newman and his co-workers[5] was applied successfully to the present case of six-membered cyclic system. The reactions of *meso*- and *dl*-**2** with ethyl orthoacetate in benzene containing catalytic amounts of monochloroacetic acid gave *cis*-**1** and *trans*-**1** in more than 80% yields, respectively. Both *cis*-**1** and *trans*-**1** were very sensitive to atmospheric moisture and could not be stored for more than two days unless special precautions were made. However, both of them could be analyzed by gas chromatography, although slight extents of decomposition were observed.

NMR data of *cis*-**1** and *trans*-**1** are shown in Table 1.

Table 1. NMR data of **1** in deuteriochloroform

	cis-**1**			*trans*-**1**		
	δ			δ		
C_2–CH_3	1.47	s	3H	1.45	s	3H
C_4–CH_3	1.16	d	6H	1.19(e)	d	3H
C_6–CH_3				1.34(a)	d	3H
C_5H_2	1.55	m	2H	1.54	m	2H
C_4H	4.17	m	2H	4.26(a)	m	1H
C_6H				4.06(e)	m	1H
OCH_2CH_3	1.22	t	3H	1.20	t	3H
OCH_2CH_3	3.52	q	2H	3.55	q	2H

Eliel and his co-workers reported extensive studies on the conformational analyses of 1,3-dioxane system. When methyl group is attached to C_2 of 1,3-dioxane system, the equatorial position is preferred to the axial by 3.6—4.1 kcal/mol, because of the strong crowding between the axial methyl at C_2 and hydrogens or methyl groups at C_4 and C_6. On the other hand, alkoxy group at C_2 prefers the axial position (by 0.35 kcal/mol in the case of 2-alkoxy-1,3-dioxane) by a substantial anomeric effect.[6] Applying these conclusion, the configurations and conformations of *cis*- and *trans*-**1** are depicted in Fig. 1. The NMR data can be explained reasonably.

The protons of two methyl groups attached to C_4 and C_6 of *cis*-**1** give only one doublet at $\delta=1.16$ because the two methyl groups are equivalent, while those of *trans*-**1** give two doublets at $\delta=1.19$ and 1.34. Two methyl groups of *cis*-**1** must be equatorial, since the signals should be observed at much lower fields, if they were axial. Protons at C_4 and C_6 of *cis*-**1** give only one multiplet at 4.17 because they are equivalent, while those of *trans*-**1** give two multiplets at 4.06 and 4.26. In general, the diaxial repulsion in dioxane system is larger than that in cyclohexane system because of the shorter length of C–O bond than that of C–C. It appears, therefore, to be unnecessary to consider the possibility that all of the two methyl and ethoxy groups

are axial, since the steric effects will prevent the formation of such a highly strained compound. Since Eliel suggested that 2,2-*trans*-4,6-tetramethyl-1,3-dioxane takes skew boat conformation predominantly, the same conformation must be considered in the case of *trans*-**1**. To discriminate the chair and skew boat conformations, it is necessary to determine the coupling constants between C_4–H and C_5–H and C_5–H and C_6–H exactly. From the spectrum obtained, however, it is difficult to estimate these coupling constants. Whether the chair form or the skew boat form is preferred cannot be discussed at present. NMR data can be explained reasonably in terms of both conformations. In the case of *cis*-**1**, skew boat conformation appears to be unlikely because of the strong 1,3-repulsions.

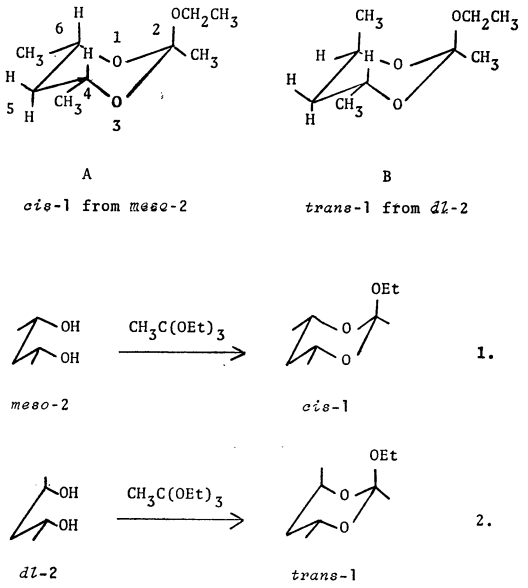


Fig. 1. Conformations and configurations of *cis*-**1** and *trans*-**1** and the stereochemistry of the formation of *cis*-**1** and *trans*-**1**.

Stereochemistry of the Reaction of **1** *with Water, Hydrogen Chloride, and Trityl Chloride.* Although a number of cyclic orthoester has been prepared by Newman and his co-workers, it appears that the stereochemistry of the nucleophilic substitution has been studied only for those with trityl chloride and trimethylsilyl chloride in methylene chloride by the same authors which proceeded with inversion. They explained the results by assuming the ionization of the substrates to AcO-5 cations and the subsequent attack of the nucleophile on the cations.[5] We have examined the stereochemical courses of the reactions of **1** with several kinds of reagent.

Treatments of *cis*- and *trans*-**1** with water–ethanol mixture (20: 80 by volume) at room temperature gave *erythro*- and *threo*-4-acetoxy-2-pentanol (**4**) in almost quantitative yields, respectively. The results show that the reactions proceeded with complete retention. On the other hand, the reactions of the same *cis*- and *trans*-**1** with trityl chloride (under reflux) or hydrogen chloride (at 0 °C) in methylene chloride gave *threo*- and *erythro*-4-acetoxy-2-chloropentane (**3**) also in almost quantitative yields, respectively. It is clear that the reactions proceeded with complete inversion. The sharp contrast of the stereochemical courses mentioned above makes it clear that the mechanism of the reactions with water–ethanol mixture is different from those with trityl chloride or hydrogen chloride in methylene chloride.

Since the stereochemistry of the latter reactions is the same as that of the case of five-membered cyclic orthoester by Newman, it appears that the mechanism is also the same.

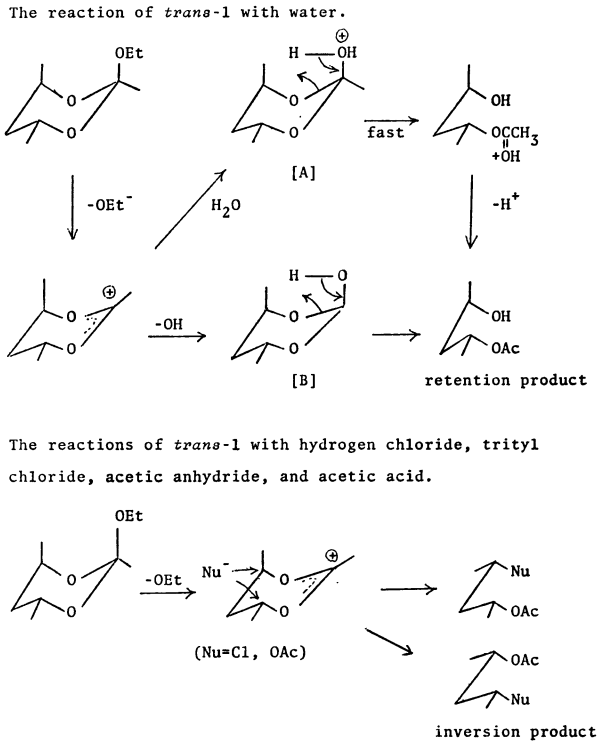


Fig. 2. Mechanisms of the reactions of *trans*-**1** (*cis*-isomer follows the same mechanism).

The most probable mechanism to explain the retentive course of the reaction with water–ethanol mixture is depicted in Fig. 2. If the product **4** is obtained by the reaction of water or hydroxide ion with the AcO-6 cation from **1** as in the cases of hydrogen chloride and trityl chloride, the stereochemistry should be inversion. The mechanism proposed to explain the results of retention assumes the ionization of **1** to form AcO-6 cation, the subsequent reaction with water or hydroxide ion to yield oxonium ion type intermediate (A) or its deprotonated type (B), and the collapse of A or B to form the final product **4** by bond reconstruction involving proton transfer. Since the stereochemistry of the reaction with the same water–ethanol (20: 80 by volume) mixture containing 2 M NaOH was also complete retention, it appears that both reaction routes through A and B are operative.

The steric courses of the reactions of **1** with several other reagents were examined qualitatively by analyzing the reaction mixtures at room temperature directly by gas-chromatography. Acetic anhydride which was completely free from water gave 2,4-diacetoxypentane

Table 2. Solvolyses of **3** and **5**.

Substrate	Reaction medium	Temp °C	Time h	Product			
				6		**4**	
				dl	*meso*	*threo*	*erythro*
erythro-**5** (0.1 M)	98% EtOH–KOAc (0.2 M)	100	1	8	trace	75	6
threo-**5** (0.2 M)	98% EtOH–KOAc (0.2 M)	100	1	—	4	2	86
erythro-**5** (1 M)	Ac_2O-KOAc (1 M)	130	1	22	78		
erythro-**5** (1 M)	HOAc[a])–Ac_2O(2 M)–KOAc (1.5 M)	115	1	8	92		
threo-**5** (1 M)	HOAc[a])–Ac_2O(2 M)–KOAc (1.5 M)	100	2	87	13		
erythro-**3** (1 M)	HOAc[a])–Ac_2O(2 M)–KOAc(1.5 M)	140	4	20	80		
threo-**3** (1 M)	HOAc[a])–Ac_2O(2 M)–KOAc(1.5 M)	140	4	70	30		
threo-**3** (0.1 M)	HOAc[b])–Ac_2O(0.2 M)–KOAc(0.2 M)	130	7	trace	30	—	70
			13	7	76	—	17

a) Dry acetic acid. b) Moist acetic acid.

(**6**) with complete inversion. Acetic anhydride–acetic acid (50: 50 by volume) mixture which was prepared without special precaution to remove the trace amount of water gave retention product of **4**. The results with acetic acid were not reproducible. From run to run, the product ratios of **4** (with retention) and **6** (with inversion) changed from 70 :30 to 30: 70. It appears that the difficulty of removing trace amount of water would be responsible for such observations. Since the acetylation of the produced **4**, which proceeds gradually under the conditions, gives **6** with retention, the product analyses after sufficient reaction times give the results as if the steric course of the direct acetolysis is affected by the presence of trace amount of water. The same change of the steric course by the presence of water reported by Winstein and his co-workers[1]) may be explained by the same way. It is concluded that the reaction of **1** with water is much faster than those with other reagents and proceeds through the intermediate A or B.

Solvolyses of 4-Acetoxy-2-chloropentane (3) and 4-Acetoxy-2-pentyl tosylate (5). The steric courses of the solvolyses of **3** and **5** which are expected to proceed through AcO-6 cation have been studied by comparing with the results of the reactions of **1** mentioned above. The starting materials of *erythro*- and *threo*-**3** and -**5** were prepared by chlorination and tosylation of the half esters **4**, which were obtained by the hydrolyses of *cis*- and *trans*-**1**, respectively. The results of solvolyses are summarized in Table 2.

The reactions proceeded to give 2,4-diacetoxypentane (**6**) and **4** with no detectable amount of by-product, and were almost complete under the conditions described. By gas-chromatography, the product distributions were determined.

In 98% ethanol containing potassium acetate, *erythro*- and *threo*-**5** gave *threo*- and *erythro*-**4** as the main products with inversion, respectively. Since the solvolyses of these compounds through planar carbonium ion without participation should form the same 50: 50 mixtures of *threo*- and *erythro*-**4**, the mechanism depicted in Fig. 3 appears to be the most probable. Formations of AcO-6 cations with inversion and the subsequent reactions with water, which have been shown to give the retention products, should result in the formation of inversion products. The formations of the retention products in **4** and the inversion products in **6** appear to show the solvolysis without participation proceeded as a minor reaction.

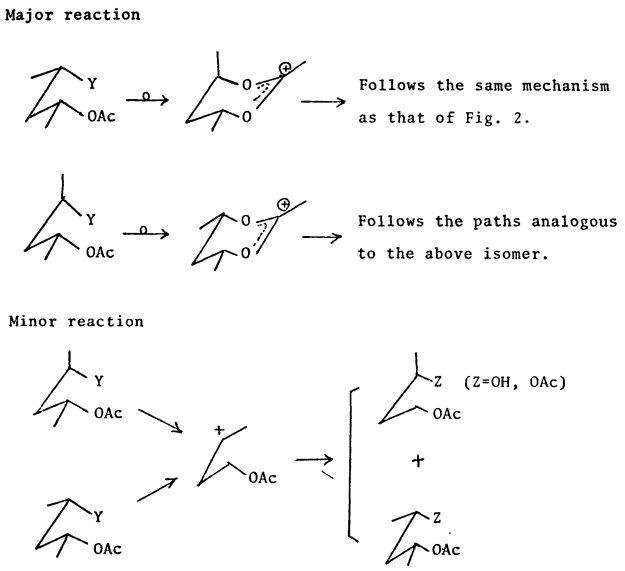


Fig. 3. Mechanism of the solvolysis of 4-acetoxy-2-pentanol derivatives.

The main products of the acetolyses of *erythro*- and *threo*-**5** in dry acetic anhydride and acetic anhydride–acetic acid mixtures containing potassium acetate were *meso*- and *dl*-**6** with retention, respectively. Double inversions in AcO-6 cation formation and the subsequent reaction of the cation with acetate ion explain the

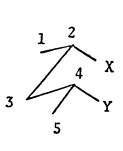
results reasonably. Here again, however, the acetolysis without participation as a minor reaction appears to be operative, since the products with inversion were obtained as the minor products. In moist acetic acid–acetic anhydride mixture, the primary main product of the reaction of *threo*-**3** was *erythro*-**4** with inversion showing that the reaction of water with AcO-6 cation is very fast as already mentioned. After a sufficient reaction time, the main product became *meso*-**6** by the acetylation of **4** under the condition. Undoubtedly, the acetylation does not change the configuration of the substrate since the bond breaking of C–OH is not involved in this reaction step. It is concluded, therefore, that the AcO-6 cation formation which was assumed in the reactions of steroid[7] and (2-acetoxycyclohexyl)-methyl cation system[2] is also important in the solvolysis of acyclic 1-acetoxy-3-ol system and that the presence of water changes the steric course of the reaction.

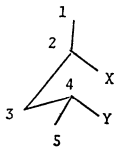
Structural assignments of 2, 3, 4, 5, and 6. The structural assignments of *erythro* and *threo* or *meso* and *dl* of the substrates and products can be made by converting them to **2** or **6** whose physical constants (mp) are known. By NMR, however, the discriminations are possible also. Methylene signal of *dl*-**6** is a doublet (J=8 Hz) of doublet (J=6 Hz), while that of *meso*-isomer is a doublet (J=14 Hz) of triplet (J=6 Hz). This difference is due to the fact that the *dl*-isomer is more symmetrical than *meso* about the the central carbon C_3. According to this principle, the assignments of the other compounds have been made. In the case of **4**, methylene signal of *threo*-isomer was a triplet (J=9 Hz) of doublet (J=3 Hz) at δ 1.61, while the signals of the *erythro* were two pairs of multiplet at δ 1.57 and 1.85. The relationship between the symmetry of the structure and the shape of the signal can be applied to the case of methine proton too. The methine signals of **5** at C_2 and C_4 should be different, since the substituents are different, although they are very similar. In the case of *erythro*-isomer, the two methine protons gave a sextet at δ 4.96 and a broad multiplet at δ 4.92 and those of *threo* gave a triplet-like signal at δ 1.79. NMR data are summarized in Table 3.

Preparation of Fluoroborate salt of 2,4,6-Trimethyl-1,3-dioxane-2-ylium Cation. Many kinds of 1,3-dioxolan-2-ylium cation (AcO-5 cation type) salt have been prepared by various methods.[8] On AcO-6 type cation salt, however, only few papers are found in the literature.[9] We have prepared the fluoroborate salt of the present AcO-6 cation.

Dropwise addition of boron trifluoride–ether complex to ether solution of **1** at room temperature resulted in the formation of oily drops which became colorless crystals after standing for several days in refrigerator. The crystals were so hygroscopic that elemental analysis and IR and mp measurements by usual methods were difficult. The raw crystals, just after filtration, were dissolved into dry nitrobenzene and subjected to NMR measurement. In Fig. 4, the spectra of the salt and

Table 3. NMR data of **2**, **3**, **4**, **5**, and **6**, δ in ppm





			C^1H_3	C^5H_3	C^2H	C^4H	C^3H_2CO	CH_3CO
2	X=OH Y=OH	*meso*	1.18 d		3.99 broad m		1.55 m	
		dl	1.21 d		4.13 sextet		1.58 t	
3	X=Cl Y=OAc	*erythro*	1.53 d	1.25 d	4.03 m	5.07 m	1.80 (1H) m 2.13 (1H) m	2.02 s
		threo	1.51 d	1.24 d	4.03 m	5.08 m	1.86 m	2.01 s
4	X=OH Y=OAc	*erythro*	1.21 d	1.26 d	3.88 sextet	5.05 sextet	1.57 (1H) d of t 1.85 (1H) d of t	2.04 s
		threo	1.19 d	1.27 d	3.75 m	5.15 m	1.61 t of d	2.08 s
5	X=OTs Y=OAc	*erythro*[a]	1.17 d	1.31 d	4.69 m	4.92 m	b)	2.05 s
		threo[c]	1.19 d	1.35 d	4.83 broad sextet		1.79 broad t-like	1.98 s
6	X=OAc Y=OAc	*meso*	1.24 d		4.98 sextet		b)	2.04 s
		dl	1.22 d		4.91 sextet		1.75 d of d	2.02 s

a) CH_3 bonded to phenyl, 2.50. b) Because of the overlapping with the peak of acetyl protons, the signals could not be determined. c) CH_3 bonded to phenyl, 2.47.

precursor **1** are shown. In the former, the signals due to ethoxy group disappeared and all signals shifted to lower fields as compared to the corresponding signals of **1**. The shifts are especially remarkable in those of C_2-methyl protons and C_4 and C_6 methine protons. In the case of the cation from *trans*-**1**, methyl protons attached to C_4 and C_6 gave only one doublet at δ 1.87 and two methine protons of the same C_4 and C_6 gave also only one multiplet at δ 5.67. It appears that the rapid flattering of the six-membered ring resulted in such observations. In the case of the cation from *cis*-**1** the flattering is considered to be difficult because the diaxial form should be much less stable than the di-equatorial form by the strong steric crowding.

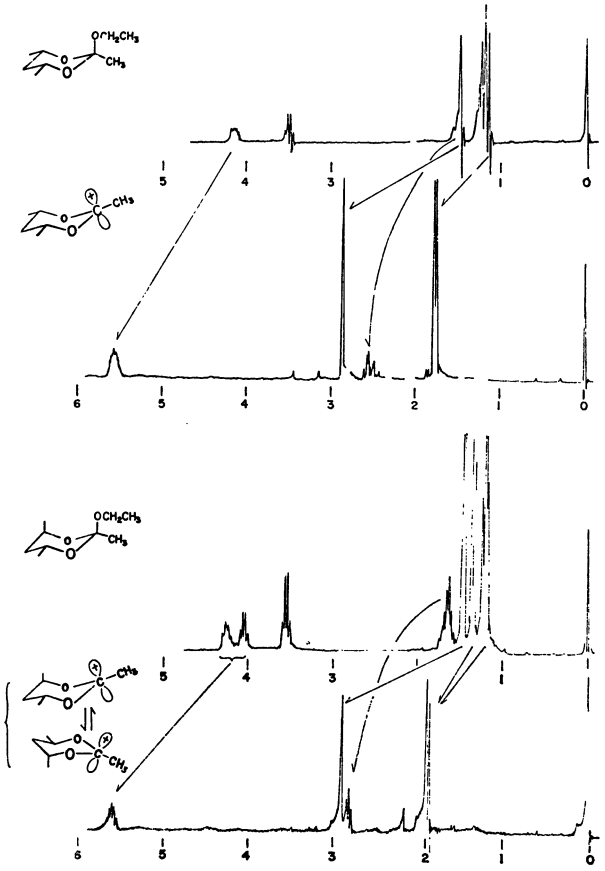


Fig. 4. NMR spectra of *cis*- and *trans*-**1** and fluroborate salts of the corresponding cations.

TABLE 4. NMR DATA OF FLUOROBORATES OF *cis*- AND *trans*-2,4,6-TRIMETHYL-1,3-DIOXANE-2-YLIUM CATIONS

	Cation from *cis*-**1**			Cation from *trans*-**1**		
	δ ppm			δ ppm		
C_2–CH_3	2.97	s	3H	2.93	s	3H
C_4–CH_3, C_6–CH_3	1.83	d	6H	1.87	d	6H
C_5H_2	2.58	m	2H	2.84	m	2H
C_4H, C_6H	5.78	m	2H	5.67	m	2H

Experimental

Preparation of dl-*and* meso-**2**. According to the method reported by Pritchard *et al.*, 2,4-pentanediol, which was obtained by sodium borohydride reduction of acetylacetone, was converted to cyclic sulfite by equivalent amount of thionyl chloride. Fractional distillation gave *cis*-(bp 57.8 °C/6 Torr) and *trans*-sulfite fraction (bp 65.4 °C/6 Torr). Analyses by gas-chromatography (EGSS-X 1m column) showed that the purities were 96 and more than 98%, respectively. Hydrolyses of the both fractions gave *meso*-**2** (bp 85—87 °C/7 Torr) and *dl*-**2** (99—100 °C/11 Torr, mp 47.5—49 °C), respectively.

Preparation of cis- *and* trans-**1**. Into a benzene (50 ml) solution containing 11.4 g of *meso*-**2** and catalytic amount (ca. 100 mg) of monochloroacetic acid, 25 g of freshly distilled ethyl orthoacetate were added under stirring. After refluxing for 3 h, benzene and ethanol formed were removed. Distillation under vacuum gave *cis*-**1** (bp 81—83 °C/40 Torr, 15.1 g). IR (liquid film): 1255 (s, ν_{as} C–O–C), 1195 (m), 1150 (m), 1120 (m), 1100 (sh), 1060 (s, ν_s C–O–C) cm^{-1}.

By the same method, *trans*-**1** was obtained from *dl*-**2** in 87% yield (bp 82.5 °C/40 Torr). IR (liquid film): 1245 (s, ν_{as} C–O–C), 1180 (m), 1150 (m), 1140 (sh), 1115, and 1055 (s, ν_s C–O–C) cm^{-1}.

Reaction of **1** *with Water*. Into 80 ml of 80% ethanol, 27.9 g of *cis*-**1** were added under stirring at room temperature After 1 h, ethanol was distilled off from the reaction mixture. Ether extract of the residue was washed with aqueous saturated sodium chloride solution, dried with sodium sulfate and then distilled to give *erythro*-**4** (bp 107—109 °C/22 Torr) in 94% yield (22.2 g). Analysis by glc. with EGSS-X column showed that the purity was more than 98%. IR in CCl_4: ν_{OH}, 3620 (sh), 3480 (br); ν_{CO}, 1740 (br), 1720 (sh); 1150, 1110 (br), 1035, 1020, 955 cm^{-1}.

From 17.3 g of *trans*-**1**, 13.0 g (90% yield) of *threo*-**4** of more than 96% purity were obtained by the same procedure. IR in CCl_4: ν_{OH}, 3630 (w), 3520 (br); ν_{CO}, 1740 (sh), 1720; 1280 (sh), 1260, 1250, 1150, 1020, 1010, 970, and 940 cm^{-1}.

The half esters of *erythro*- and *threo*-**4** were converted to *meso*- and *dl*-**6** by acetylation with acetyl chloride in pyridine, respectively. The physical constants and IR and NMR spectra were identical with those of the authentic samples which were prepared from *meso*- and *dl*-**2** by the reported method.[10]

Reaction of **1** *with Hydrogen Chloride*. Into a methylene chloride (50 ml) solution of *cis*-**1** (3.5 g), dry hydrogen chloride (0.04 mmol, 2 equivalents) was added at 0 °C. After 30 min, the reaction mixture was washed with water, dried with sodium sulfate and subjected to distillation. *threo*-**3** was obtained (2.3 g, 70% yield, bp 82—84 °C/22 Torr). Analysis by GLC showed that no detectable amount of by-product was formed. By the same experimental method, the reaction of *trans*-**1** gave *erythro*-**3** in 68% yield (83.5—86.5 °C/25 Torr).

Reaction of **1** *with Trityl Chloride*. A mixture containing 3.48 g of *cis*-**1**, 5.58 g of trityl chloride and 50 ml of methylene chloride was kept at 42 °C for 3.5 h. Distillation of the reaction mixture gave 2.75 g of *threo*-**3** (83% yield). By the same experimental procedure, *erythro*-**3** (2.70 g) was obtained from *trans*-**1**. Both products were shown to contain no other products by GLC. The IR and NMR spectra were identical with those of the products obtained by acetylation of *erythro*- and *threo*-**4**, respectively.

Preparation of **3**. Thionyl chloride (3.8 g) was added to an ether (15 ml) solution of *threo*-**4** (2.48 g). The mixture was heated under reflux for 2 h, washed with saturated aqueous solution of sodium hydrogencarbonate, extracted with ether, dried, and distilled. The product was *threo*-**3**, bp 82—84 °C/22 Torr, 1.83 g (65 % yield).

Similarly, *erythro*-**3**, bp 82—83 °C/22 Torr, was obtained from *erythro*-**2** in 78% yield.

Preparation of **5**. Into pyridine (50 ml) solution of

Table 5. Analytical data

		Calcd for			Observed		
		C	H	Cl, S	C	H	Cl, S
cis-**1**	$C_9H_{18}O_3$	62.04	10.41		61.85	10.33	
trans-**1**					62.06	10.65	
meso-**2**	$C_5H_{10}O_2$	57.66	11.61		57.85	11.58	
dl-**2**					57.69	11.64	
erythro-**3**	$C_7H_{13}O_2Cl$	51.07	7.96	21.54	51.34	8.03	21.57
threo-**3**					51.29	7.85	21.51
erythro-**4**	$C_7H_{14}O_3$	57.51	9.65		57.57	9.81	
threo-**4**					57.81	9.72	
erythro-**5**	$C_{14}H_{20}O_5S$	55.98	6.71	10.67	55.95	6.82	10.56
threo-**5**					56.02	6.89	10.66

erythro-**4** (2.96 g), *p*-toluenesulfonyl chloride (6.1 g) was added dropwise under cooling with ice bath. The mixture was kept in refrigerator (−15—−18 °C) for two days, poured into ice-water, extracted with ether and dried with K_2CO_3–Na_2SO_4. When ether was removed, oily product was obtained. This product was dissolved into 200 ml of petroleum ether, heated to about 40 °C and filtered to remove impurities. After standing in refrigerator for 24 h, crystals formed were collected and recrystallized from the same solvent, mp 32—34 °C (5.15 g, 86% yield). The structure of *erythro*-**5** was confirmed by NMR spectrum. From *threo*-**4**, *threo*-**5**, mp 60—61 °C, was obtained in 82% yield similarly.

Solvolysis Reactions. The reactions were carried out in ampoules. The experimental procedure was analogous to that of the reaction of **1** with water.

Preparation of 2,4,6,-trimethyl-1,3-dioxane-2-ylium fluoroborate. Into 15 ml of dry ether, 5.55 g of *cis*-**1** was dissolved. Boron trifluoride–ether complex (5.2 g) was added slowly. The mixture was kept in refrigerator for two days. Removing ether, 6.48 g of the salt were obtained and characterized by NMR. The same procedure gave the salt of *trans*-isomer.

NMR spectra were recorded on a Varian Associates HR-220 at 220 MHz at room temperature. Gas-chromatograph analyses were carried out with YANACO GC-550 TPH. IR spectra were recorded on HITACHI EPI-G2.

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