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Chemistry of 1,3-Glycol Derivatives. IV. Mechanism of the Solvolyses of 2,4-Pentanediol Derivatives and the Reactions of the Proposed Intermediate Acetoxonium Ions with Carbanions and Hydride

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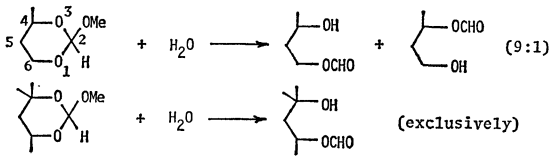
Regio- and stereochemical studies of the solvolyses of various kinds of 2,4-pentanediol derivatives, including 2-acetoxy-4-tosylates, cyclic orthoformates and orthoacetates, have been done and the previously proposed mechanism has been partially revised. The reactions of the proposed intermediate acetoxonium ions with carbanions and with a hydride ion have also been studied.

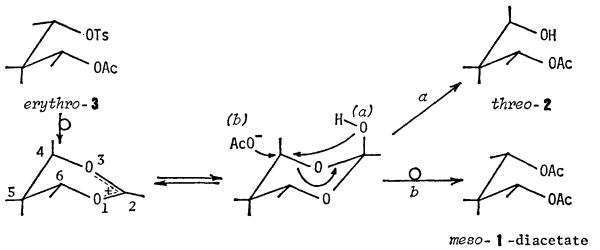
In a previous paper,[1] some of us reported that the hydrolyses of *threo*- and *erythro*-3-acetoxy-1-methylbutyl chlorides or tosylates proceeded with inversion of configuration, while the acetolyses of the same substrates proceeded with retention of configuration; we proposed a mechanism involving a formation of a cyclic acetoxonium ion (1,3-dioxan-2-ylium ion). Further studies with the related substrates, however, have shown that a part of the proposed mechanism should be modified. This paper describes these additional results, together with the chemical behavior of the above acetoxonium ion towards several kinds of carbanions and a hydride ion.

Hydrolyses of *erythro*- and *threo*-3-acetoxy-1,2,2-trimethylbutyl tosylates (*erythro*- and *threo*-**3**) proceeded with almost complete inversion of configuration. Refluxing of *erythro*-**3** (0.45 M, 1 M=1 mol dm^{-3}) solution in ethanol–water (98:2) containing potassium acetate (0.45 M) gave a product consisting of *threo*-4-acetoxy-3,3-dimethyl-2-pentanol (*threo*-**2**, 98%), its *erythro* isomer (*erythro*-**2**, trace), and *meso*-3,3-dimethyl-2,4-pentanediol diacetate (**1**-diacetate, 2%). Under the same conditions, *threo*-**3** gave a product consisting of *erythro*-**2** (90%), *threo*-**2** (trace), and *dl*-**1**-diacetate (10%).

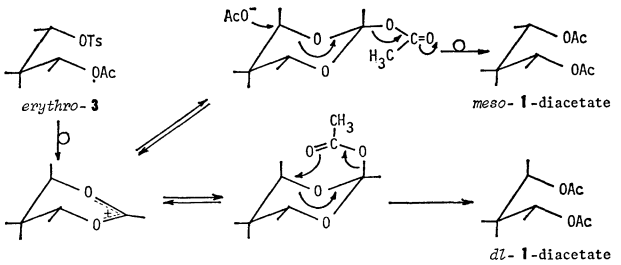
Acetolyses of **3** proceeded with retention of configuration, although the specificities were lower than those in the hydrolyses. *erythro*-**3** gave *meso*- and *dl*-**1**-diacetates in a ratio of 75:25, while *threo*-**3** gave a mixture of *meso*- and *dl*-**1**-diacetates and unidentified products in a ratio of 35:50:15.

These stereochemical results are qualitatively the same as the previous results with unsubstituted 2,4-pentanediol derivatives, supporting the mechanism proposed previously. However, the results of the hydrolyses of the cyclic orthoformates of 1,3-butanediol and 2-methyl-2,4-pentanediol, which should proceed through the same intermediates as those of **3**, have shown that the substitution with hydroxyl groups occurred at the more substituted carbons and that the proposed mechanism should thus be partially modified.





Scheme 1. Mechanism of hydrolysis of *erythro*-**3**.



Scheme 2. Mechanism of acetolysis of *erythro*-**3**.

The previous mechanism assumed the heterolytic bond breaking of C^2–C^3 in the cyclic intermediate in Scheme 1. Instead, the bond breaking of C^4–O^3 or C^6–O^1 is more plausible, since the methyl substitution at C^4 or C^6 will make the latter type of breaking easier. Although the final decision requires a tracer experiment with isotopic oxygen, the revised mechanism can explain the results obtained so far.

As was proposed previously, the stereochemistry of the hydrolysis and acetolysis are determined by the relative rates of S_Ni and S_N2 reactions in the cyclic intermediate.

In the case of hydrolysis (Scheme 1), a cyclic intermediate with an axial hydroxyl group at C^2 can be formed preferentially because the antiparallel attack of a nucleophile to the dioxocarbonium ion will be preferred,[2] and the axial hydroxy compound thus formed is also more stable than the equatorial isomer because of the anomeric effect of hydroxyl oxygen.[3] This intermediate leads to the formation of the inversion product. In the case of acetolysis (Scheme 2), the steric hindrance of acetoxyl group against the anomeric effect prevents the formation of the intermediate with the axial acetoxyl group at C^2 and results in the formation of the one with the equatorial acetoxyl group. In the latter type of intermediate, the bond reconstruction by S_Ni path does not proceed.

As a result, the S_N2 attack of acetate ion becomes predominant and results in the formation of the retention product through double inversion.

The lower specificity observed in the acetolysis of the present substrate **3** than in the previous case without two methyl groups at C^3 can be explained by the slower S_N2 attack of acetate ion due to the steric hindrance.

The nature of the by-products appears to support the mechanism also. The minor products in the hydrolysis of **3** included the diacetate with retention of configuration, showing that the S_N2 attacks of acetate ion are operative also in this case, although the extent was small. Why the acetolysis of *threo*-**3** gave a considerable amount of unidentified products, while *erythro*-**3** gave no such products, is discussed later.

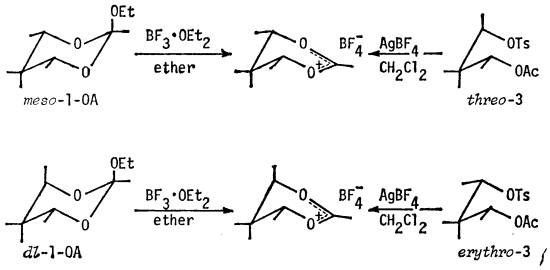
The solvolysis of cyclic orthoacetate (**1**-OA), which is expected to proceed through the formation of the same intermediate, should give the same results as those of **3**. This presumption was confirmed by the following experiments. Reaction of *meso*-**1**-OA with 80% aqueous ethanol gave *erythro*-**2**, while *dl*-**1**-OA gave *threo*-**2**. The yields were almost quantitative and no other products could be detected. Reaction of *dl*-**1**-OA with acetic acid gave a mixture of *meso*-**1** diacetate (75%) and *dl*-**1** diacetate (25%), while *meso*-**1**-OA gave a mixture of *meso*-**1** diacetate (35%), *dl*-**1** diacetate (50%) and unidentified products (15%).

The above-mentioned considerations have been extended to the case of 1,1-bis(1-hydroxyethyl)cyclopropane which is formally formed by combining the two methyl carbons attached to C^3 of **1** to form a cyclopropane ring. Hydrolyses of the orthoacetates of *meso*- and *dl*-isomers gave the *erythro*- and *threo*-diol monoacetates with excellent yields, respectively, showing that the reactions proceeded with retention of configuration as in the case of **3**, and that the solvolyses do not involve the formation of cyclopropylcarbinyl type cation, since no rearrangement products could be detected.

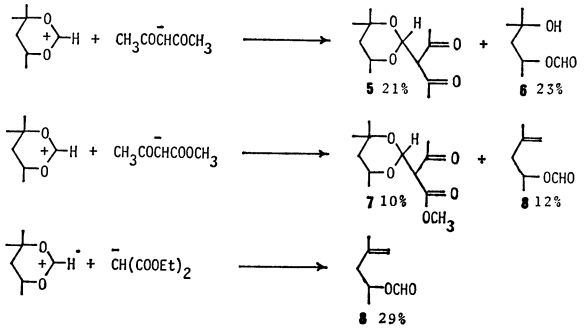
For reference, several kinds of cyclic orthoformates and orthoacetates of 1,3-diols and their acetoxonium ion salts were prepared; these are listed in Table 1. The preparation of the acetoxonium salt from 1,3-propanediol was unsuccessful. The salts were very sensitive to atmospheric moisture. The crystalline salt from *meso*-**1** was much more unstable than that from *dl*-**1** and decomposed, giving colored materials, within several hours after isolation. This instability of the former may be the reason why the acetolyses of *meso*-**1**-OA and *threo*-**3** gave considerable amounts of unidentified products in contrast with the clean-cut results of the other isomers.

The following results show clearly that the solvolyses of **3** and cyclic **1**-OA proceed through the same intermediate. Addition of $BF_3 \cdot OEt_2$ to an ether solution of **1**-OA formed a crystalline salt of the acetoxonium ion. The same salt was obtained by the addition of $AgBF_4$ to a dichloromethane solution of **3** (see Scheme 3).[4] The identity was confirmed by NMR spectra.

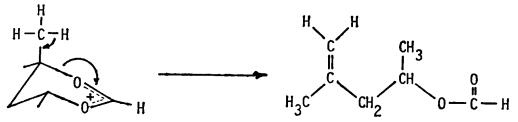
Acetoxonium ion is a stable carbonium ion. No trial of trapping this carbonium ion with an anionic



Scheme 3. Preparation of acetoxonium ion from cyclic orthoester and acetoxytosylate.



Scheme 4. Reactions of acetoxonium ions with carbanions.



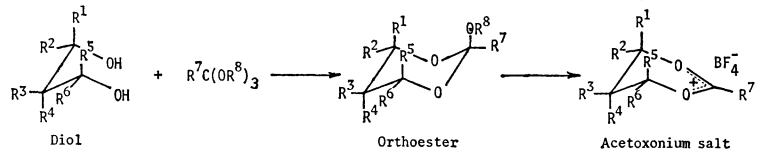
Scheme 5.

species of carbanion or with a hydride ion has been reported. Using the crystalline salt obtained above, these reactions have been examined.

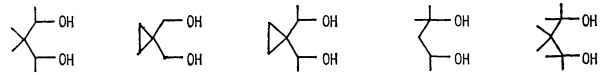
For experimental convenience, the salts obtained from the orthoformate (**4**-OF) and the orthoacetate (**4**-OA) of 2-methyl-2,4-pentanediol were used as the substrate. The experimental difficulty was the purification of the acetoxonium salts. The removal of the excess $BF_3 \cdot OEt_2$, which was added to precipitate the salts from ether solutions of **4**-OA and **4**-OF, was essential to obtain the products, since BF_3 reacted with the active methylene compounds to form inactive addition products. Repeated washing with ether was required. To avoid the effects of atmospheric moisture, the weights of the starting salts before washing were used as the bases of the yield calculations; therefore, the yields are only qualitative. The results are shown in Scheme 4.

The reaction of the salt from **4**-OF with sodium salt of 2,4-pentanedione in refluxing ether for 4—5 h gave a condensation product, 2-(1-acetyl-2-oxopropyl)-4,4,6-trimethyl-1,3-dioxane (**5**), and the hydrolysis product of the acetoxonium salt, 3-hydroxy-1,3-dimethylbutyl formate (**6**). By the reaction with sodium salt of methyl acetoacetate, the expected product of 2-(1-methoxycarbonyl-2-oxopropyl)-4,4,6-trimethyl-1,3-dioxane (**7**) was obtained, together with 1,3-dimethyl-3-butenyl formate (**8**). The reaction with sodium salt of diethyl malonate gave only **8** but no condensation product.

TABLE 1. NMR DATA OF ORTHOESTERS AND THE CORRESPONDING ACETOXONIUM SALTS[a)]

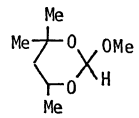
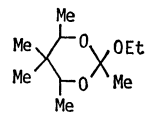
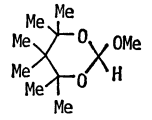
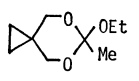
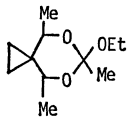


	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	Solvent
dl-**1**-OA	H	CH_3	CH_3	CH_3	CH_3	H	CH_3	CH_2CH_3	
	4.00(q)	1.08(d)	[0.78(s)	0.91(s)][b)]	1.21(s)	3.55(q)	1.45(s)	3.55(q), 1.20(t)	$CDCl_3$
Salt	5.37(q)	1.78(d)	1.28(s)		1.78(s)	5.37(q)	2.95(s)		$C_6H_5NO_2$
meso-**1**-OA	H	CH_3	CH_3	CH_3	H	CH_3	CH_3	CH_2CH_3	
	3.93(q)	1.08(d)	[0.73(s),	0.86(s)][b)]	3.93(q)	1.08(s)	1.46(s)	3.50(q), 1.24(t)	$CDCl_3$
Salt	5.45(q)	1.65(d)	[1.16(s),	1.22(s)][b)]	5.45(q)	1.65(s)	2.91(s)		$C_6H_5NO_2$
9-OA	H	H	$-CH_2CH_2-$		H	H	CH_3	CH_2CH_3	
	4.46(d)	2.93(d)	[0.31(m),	0.63(m)][b)]	4.46(d)	2.93(d)	1.52(s)	3.54(q), 1.26(t)	$CDCl_3$
Salt	5.20(s)		1.32(s)		5.20(s)		2.91(s)		$C_6H_5NO_2$
dl-**10**-OA	H	CH_3	$-CH_2CH_2-$		CH_3	H	CH_3	CH_2CH_3	
	4.46(q)	0.91(d)	[0.23—0.69(m)][b)]		1.28(d)	3.51(q)	1.47(s)	3.51(q), 1.28(t)	$CDCl_3$
Salt	Too unstable								
meso-**10**-OA	H	CH_3	$-CH_2CH_2-$		H	H	CH_3	CH_2CH_3	
	4.71(q)	0.89(d)	[0.27(m),	0.68(m)][b)]	4.71(q)	0.89(d)	1.51(s)	3.55(q), 1.29(t)	$CDCl_3$
Salt	Too unstable								
11-OF[c)]	CH_3	CH_3	H	H	H	CH_3	H	CH_3	
	1.2—1.4		1.54(m)		4.0	1.2—1.4	5.39(s)	3.33(s)	$CDCl_3$
					4.32		5.45(s)	3.47(s)	
Salt	[1.91(s),	1.98(s)][b)]	2.90(m)		5.73(m)	1.79(s)	d)		$C_6H_5NO_2$
11-OA[c)]	CH_3	CH_3	H	H	H	CH_3	CH_3	CH_2CH_3	
	[1.45(s),	1.75(s)][b)]	1.45—1.75(m)		4.57(m)	1.45—1.75	1.75(s)	3.62(q), 1.45(t)	$CDCl_3$
Salt	[1.91(s),	1.98(s)][b)]	2.68—2.86(m)		5.90(m)	1·79(d)	2.90(s)		$C_6H_5NO_2$
12-OF	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	H	CH_3	
	[1.28(s),	1.42(s)][b)]	[0.87(s),	1.07(s)][b)]	[1.28(s),	1.42(s)][b)]	5.46(s)	3.36(s)	$CDCl_3$
Salt	1.75(s)		1.19(s)		1.75(s)		d)		$C_6H_5NO_2$

Diol 

a) The chemical shifts are given in δ from TMS. b) Discrimination of axial and equatorial was unsuccessful. c) A mixture of *cis*- and *trans*-isomers. d) Hidden in a solvent region.

Table 2. Analytical data of orthoesters

			Calcd (%)	Found (%)
	**11**-OF	$C_8H_{16}O_3$ bp 64 °C/ 11 mmHg	C, 59.96; H, 10.07	C, 59.87; H, 9.93
	**1**-OA	$C_{11}H_{22}O_3$	C, 65.97; H, 10.96	
		cis, bp 88—90 °C/19.5 mmHg		C, 65.52; H, 11.25
		trans, bp 84—85 °C/14.8 mmHg		C, 65.60; H, 10.71
	**12**-OF	bp 126 °C/13 mmHg	Too unstable to analyze	
	**9**-OA	$C_9H_{16}O_3$ bp 98—99 °C/39 mmHg	C, 62.82; H, 9.66	C, 62.76; H, 9.36
	**10**-OA	$C_{11}H_{20}O_3$	C, 65.97; H, 10.07	
		cis, bp 90 °C/13 mmHg		C, 65.83; H, 10.09
		trans, bp 95—97 °C/13 mmHg		C, 66.19; H, 9.93

These results show that the condensation and the deprotonation proceeded in parallel and that the preferences depend on the reagents. The deprotonation could proceed as depicted in Scheme 5. This was consistent with the fact that the less bulky carbanions gave the condensation products and deprotonation was preferred in the case of more bulky carbanions.

The salt from **4**-OA was also treated with the carbanion, but no condensation nor deprotonation could be observed even after prolonged reaction times. The reason why the reactions did not proceed is still unclear.[5]

A trapping of the carbonium ion with hydride ion was examined by a reaction of 6-methyl-5,7-dioxaspiro-[2.5]octan-6-ylium salt with sodium borohydride. The reaction in DMF gave the same acetal (**9**-OA) as that prepared by the acetallisation of the corresponding diol (**9**).

Experimental

The IR spectra were recorded on a Hitachi EPI-G2 apparatus. The NMR spectra were taken on a Varian HR-220 apparatus at 220 MHz in $CDCl_3$ unless otherwise noted, with TMS as an internal standard.

Materials. 1,3-Propanediol, 1,3-butanediol, and 2-methyl-2,4-pentanediol were commercially available and distilled before use. Preparations of the diols containing cyclopropane rings were reported previously.[1,6]

Preparations of Stereoisomers of ***1***, ***2***, *and* ***3***. By a reaction of 2,4-pentanedione (261 g) with methyl iodide (452 g) in acetone (600 ml) containing potassium carbonate (356 g) under reflux for 6.5 h and the usual work-up, 3-methyl-2,4-pentanedione, bp 65.0—65.5 °C/20 mmHg,† was obtained in a yield of 83%. The product (223 g) was again methylated by refluxing with methyl iodide (331 g) in acetone (600 ml) containing potassium carbonate (300 g) for 30 h. After the usual work-up, 3,3-dimethyl-2,4-pentanedione, bp 58.0—58.5 °C/12 mmHg, was obtained in a yield of 82%.

† 1 mmHg ≈ 133.322 Pa.

Into this dione (99 g) solution in ethanol (150 g), sodium borohydride (47 g) solution in water (150 g) containing sodium hydroxide (0.8 g) was added slowly under cooling in an ice-bath. After standing overnight, the solution was neutralized with hydrochloric acid. After removal of inorganic crystals, the diol layer was separated from the water layer. The latter was extracted with chloroform, and the chloroform solution was combined with the diol layer. After adding glycerol (100 ml), the solution was distilled to give 3,3-dimethyl-2,4-pentanediol (80 g). As in the case of 2,4-pentanediol,[1] the reaction of the diol with thionyl chloride gave cyclic sulfite. Distillation gave the *cis*-form, bp 63—64 °C/4.5 mmHg, and the *trans*-form, bp 78—78.5 °C/4.5 mmHg, but the complete separation was difficult even with a high reflux ratio. In contrast, a recrystallization worked well, since the *cis*-isomer was solid, while the *trans*-form was liquid. Recrystallization from petroleum ether at −18 °C gave pure *cis*-isomer, mp 32—32.5 °C. Alkaline hydrolyses of the *cis*- and *trans*-isomers with 20% aqueous sodium hydroxide gave *meso*-**1** (bp 118 °C/16 mmHg; NMR δ= 0.70 (s, 3H), 0.87 (s, 3H), 1.14 (d, 6H, J=6.8), and 3.78 (q, 2H)) and *dl*-**1** (bp 115 °C/16 mmHg; NMR δ=0.87 (s, 6H), 1.16 (d, 6H), and 3.79 (2H)).

The structures of the diols were confirmed by NMR analyses of the corresponding cyclic acetals of benzaldehyde, which were prepared as in the reported case of 2,4-pentanediol.[1] Acetal of *meso*-**1**: bp 122—123 °C/8 mmHg; NMR δ=0.78 (s, 3H), 1.00 (s, 3H), 1.20 (d, 6H), 3.67 (q, 2H) and 5.52 (s, 1H). Found: C, 76.04; H, 9.01%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%. Acetal of *dl*-**1**: NMR δ=0.75 (s, 3H), 1.14 (d, 3H), 1.24 (s, 3H), 1.41 (d, 3H), 3.81 (q, 1H), 5.85 (s, 1H) and 5.90 (q, 1H). Found: C, 76.26; H, 9.36%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

According to the method reported previously,[1,6] the diols were converted to the cyclic orthoacetates (see Tables 1 and 2). *meso*-**1**-OA (8.8 g) was stirred into a water (5 g)–ethanol (20 g) mixture at room temperature for 1 h. After removal of ethanol, the reaction mixture was extracted with ether, washed with saturated aqueous sodium chloride solution, dried over sodium sulfate, and then distilled to give *erythro*-**2** (6.7 g), bp 79—80 °C/4.5 mmHg. GLC analy-

sis showed that the purity was more than 99%. NMR δ=0.81 (s, 3H), 0.92 (s, 3H), 1.12 (d, 3H), 1.16 (d, 3H), 2.02 (s, 3H), 3.68 (q, 1H), 4.93 (q, 1H); IR $\nu_{C=O}$ 1740, 1720 (sh); ν_{C-O} 1270, 1255 cm^{-1}. Found: C, 62.10; H, 10.56%. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41%. Similarly, *dl*-**1**-OA gave *threo*-**2** in a yield of 90%, bp 84.0—84.5 °C/5.6 mmHg; NMR δ=0.81 (s, 3H), 0.85 (s, 3H), 1.10 (d, 3H), 1.18 (d, 3H), 2.05 (s, 3H), 3.56 (q, 1H), 5.00 (q, 1H); IR $\nu_{C=O}$ 1725, 1710; ν_{C-O} 1265, 1250 cm^{-1}. Found: C, 62.08; H, 10.57%. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41%.

Into an anhydrous pyridine (25 ml) solution of *erythro*-**2** (6 g), *p*-toluenesulfonyl chloride (6.84 g) was added. After the mixture was kept in a refrigerator for 3 d, crystalline pyridine hydrochloride was filtered off. The filtrate was treated with ice–water and then the pH of the solution was adjusted to 5 by addition of cold hydrochloric acid. The solution was extracted with ether. After drying over K_2CO_3–Na_2SO_4, the ether was removed. To the residue, petroleum ether (70 ml) was added. After filtration, the filtrate was kept in a refrigerator to give crystals (9.4 g). After recrystallization from petroleum ether, pure *erythro*-**3** was obtained, mp 72.0—72.5 °C; NMR δ=0.83 (s, 3H), 0.88 (s, 3H), 1.09 (d, 3H), 1.23 (d, 3H), 2.04 (s, 3H), 2.45 (s, 3H), 4.62 (q, 1H), 4.80 (q, 1H), 7.36 (d, 2H), 7.81 (d, 2H). Found: C, 58.66; H, 7.65; S, 9.92%. Calcd for $C_{16}H_{24}O_5S$: C, 58.51; H, 7.37; S, 9.76%. *threo*-**3** was prepared by the same procedure, mp 59.5—60.0 °C; NMR δ= 0.82 (s, 3H), 0.87 (s, 3H), 1.14 (d, 3H), 1.26 (d, 3H), 2.04 (s, 3H), 2.43 (s, 3H), 4.77 (q, 1H), 4.79 (q, 1H), 7.31 (d, 2H), 7.78 (d, 2H). Found: C, 58.39; H, 7.15; S, 9.72%. Calcd for $C_{16}H_{24}O_5S$: C, 58.51; H, 7.37; S, 9.76%.

Solvolyses of **3**. The reaction procedure was analogous to that previously reported.[1] The product ratios were determined by GLC (EGSS-X 1 m column) using 1-methylnaphthalene as an internal standard.

Hydrolyses of Orthoformates of 1,3-Butanediol and 2-Methyl-2,4-pentanediol. The primary hydrolysis products of these substrates are hydroxy formates which are readily hydrolyzed further to glycols. In order to determine the primary products, the following procedure was used. Orthoformate of 2-methyl-2,4-pentanediol (24 g) was stirred into a mixture of carbon tetrachloride (100 ml) and water (20 ml) at room temperature for 4 h. The carbon tetrachloride layer was distilled after evaporation of the solvent to give 3-hydroxy-1,3-dimethylbutyl formate in a yield of 50%, bp 88.5—91.5 °C/10 mmHg; NMR δ=1.23 (s, 3H), 1.79 (m, 2H), 2.23 (s, 1H), 5.20 (m, 1H), and 8.0 (s, 1H). Found: C, 58.01; H, 9.63%. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65%. The rather low yield was due to the hydrolysis to the diol. The hydrolysis of orthoformate of 1,3-butanediol did not proceed at room temperature and required refluxing for 1 h. The product was obtained from the water layer by distillation, bp 99.5—101 °C/18 mmHg. This was a mixture of 3-hydroxybutyl formate and 3-hydroxy-1-methylpropyl formate in a ratio of 9:1. The ratio was determined by NMR. NMR of the former: δ=1.20 (d, 3H), 1.70 (m, 2H), 2.46 (s, 1H), 3.50—4.43 (m, 2H), and 8.0 (s, 1H). NMR of the latter: δ=1.30 (d, 3H), 1.70 (m, 2H), 2.46 (s, 1H), 3.50—4.43 (m, 2H), 5.20 (1H), and 8.0 (s, 1H).

Authentic Samples of meso- *and* dl-**1** *Diacetates.* According to the conventional method, the diacetates were prepared by the reactions of the diols with acetyl chloride (6 mole equivalent) in pyridine. *meso*-**1**-diacetate, bp 114.0—114.5 °C/18.5 mmHg; NMR δ=0.89 (s, 3H), 0.94 (s, 3H), 1.15 (d, 6H), 2.08 (s, 3H), and 4.95 (q, 2H); IR $\nu_{C=O}$ 1735, 1730; ν_{C-O} 1260, 1235 cm^{-1}. Found: C, 61.14; H, 9.30%. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32%. *dl*-**1**-diacetate, bp 106—107 °C/15.5 mmHg; NMR δ=0.91 (s, 6H), 1.16 (d, 6H), 2.03 (s, 6H), and 4.91 (q, 2H). Found: C, 60.93; H, 9.36%. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32%.

Preparation of Acetoxonium Salts. The following example shows the typical experimental procedure. Into a *meso*-**1**-OA (1.1 g) solution in dry ether (5 ml), $BF_3 \cdot OEt_2$ (1.2 g) was added slowly. After allowing the mixture to stand for 24 h at room temperature, crystals of the salt had been formed. The crystals were separated by filtration using a sintered glass filter, dissolved in dry nitrobenzene and subjected to NMR measurement. The crystals were very sensitive to atmospheric moisture and not stable enough to allow us to perform elemental analyses and IR measurements.

Reactions of Acetoxonium Ion with Carbanions. To a solution of 4-OF (16 g) in dry ether (100 ml) was added $BF_3 \cdot OEt_2$ (21 g). The resulting crystals were ground in ether and washed three times with dry ether. The crystals and sodium acetylacetonate (12 g) were added to ether (200 ml) and refluxed for 4 h. After filtering the inorganic crystals formed, the reaction mixture was distilled to give 3-hydroxy-1,3-dimethylbutyl formate, bp 79.5—80 °C/13 mmHg, 3.4 g; and **5**, bp 126—133 °C/13 mmHg, 4.7 g; NMR δ=0.89 (d, 3H), 0.93 (s, 3H), 0.98 (m, 2H), 1.03 (s, 3H), 1.78 (s, 6H), 3.07 (d, 1H), 3.04 (t, 1H), and 4.21 (d, 1H); IR $\nu_{C=O}$ 1725, 1710 cm^{-1}. Found: C, 62.87; H, 8.52%. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77%.

Similarly, the reaction with the sodium salt of methyl acetoacetate gave **8**, bp 64—65 °C/60 mmHg; NMR δ= 1.30 (d, 3H), 1.91 (s, 3H), 2.25 (s, 3H), 2.32 (q, 1H), 5.11 (d, 2H), 5.45 (s, 1H); and **7**, bp 92—93 °C/2 mmHg; NMR δ=0.92—1.08 (11H), 1.35 (s, 3H), 2.00 (s, 3H), 3.30 (m, 1H), 3.06 (m, 1H), 4.41 (s, 1H). Found: C, 59.74; H, 8.34%. Calcd for $C_{12}H_{20}O_5$: C, 59.02; H, 8.25%.

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5) In the case of the acetoxonium ion from **4**-OA, the referee, to whom the authors' thanks are due, suggested that the deprotonation might occur at the 2-methyl group giving 2-methylene-4,4,6-trimethyl-1,3-dioxane, which would decompose in the subsequent reaction. This sequence of reaction looked like a plausible one, but none of the products expected from these reactions could be detected by GLC analysis of the reaction mixture.

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