Chemo- and Stereoselective Monobenzoylation of 1,2-Diols Catalyzed by Organotin Compounds

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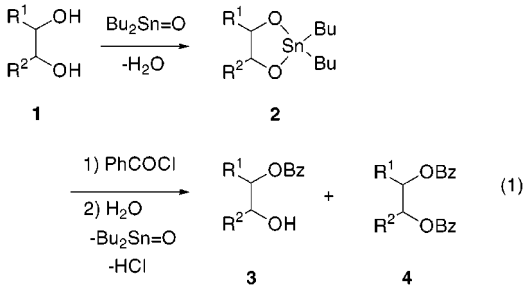
Received September 2, 1999

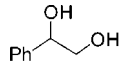
A new facile method for monoacylation of diols has been developed. A variety of cyclic and acyclic diols, in particular 1,2-diols, were selectively monobenzoylated in good yields by the reaction with benzoyl chloride in the presence of a catalytic amount of dimethyltin dichloride and inorganic bases such as potassium carbonate. Furthermore, the method was successfully applied to a kinetic resolution of racemic 1-phenyl-1,2-ethanediol using a chiral organotin catalyst. The ee was dependent on the kind of base, water as an additive, and the reaction temperature.

Introduction

Selective protection of a hydroxyl group of polyols is very important in organic synthesis.[1−4] Furthermore, provided that the protecting method has some kind of stereoselectivities, the method would be more useful in organic synthesis. It is well-known that dibutyltin oxide readily reacts with 1,2-diols **1** to form stannylene acetals **2**, which can be benzoylated to give monobenzoylated products **3** (eq 1).[5−9]



The method, however, possesses some drawbacks. Namely, **2** must be prepared by heating a mixture of **1** and dibutyltin oxide for extended periods of time prior to the benzoylation because of the slow dehydration reaction between **1** and dibutyltin oxide.[5] This imposes the use of more than an equimolar amount of dibutyltin oxide, which complicates the purification process of the products and makes the large-scale production of monobenzoylated products **3** difficult. Recently, a microwave irradiation method has been reported to reduce the amount of dibutyltin oxide. However, this method still possesses disadvantages in that a microwave apparatus is required and the irradiation conditions might be drastic.[10−12] Moreover, dibenzoates **4** are often formed as byproducts in the benzoylation of **1** using dibutyltin oxide.[11]



1j

Figure 1. Racemic 1-phenyl-1,2-ethanediol (**1j**).

We preliminarily reported a very convenient method for the monobenzoylation of **1**, which was achievable in a one-pot procedure with less than 0.01 molar equivalents of tin catalysts under mild conditions.[13,14] The report briefly described the characteristics of the method such as the high yields of **3**, an excellent 1,2-diol-selectivity with a minimized formation of **4**. Furthermore, as an application of the method, we succeeded in a first catalytic system for nonenzymatic kinetic resolution of racemic 1-phenyl-1,2-ethanediol (**1j**, Figure 1).[15] The method was based on the selective activation of 1,2-diols by a chiral organotin catalyst, and therefore the process possessed not only a high enantioselectivity but also a high chemoselectivity.

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10.1021/jo991394j CCC: $19.00
Published on Web 01/26/2000

Table 1. Monobenzoylation of 1a with PhCOCl Catalyzed by Organotin Compounds[a]

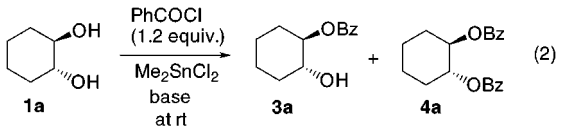
run	organotin compound	mol %	base	solvent	reaction time (h)	yield (%)[b,c] 3a	4a
1	none		Et_3N	THF	24	34	6
2	none		DMAP	THF	24	56	31
3	none		DMAP	CH_2Cl_2	24	30	34
4[d]	none		K_2CO_3	THF	24	37	0
5	$Bu_2Sn{=}O$	1	K_2CO_3	THF	12	83	0
6	Bu_2SnCl_2	1	K_2CO_3	THF	12	78	0
7	Ph_2SnCl_2	1	K_2CO_3	THF	12	55	0
8	Me_2SnCl_2	1	none	THF	24	0	0
9	Me_2SnCl_2	10	K_2CO_3	THF	12	>99	0
10	Me_2SnCl_2	1	K_2CO_3	THF	12	>99	0
11	Me_2SnCl_2	1	K_2CO_3	CH_2Cl_2	12	>99	0
12	Me_2SnCl_2	1	K_2CO_3	MeCN	12	>99	0
13	Me_2SnCl_2	1	K_2CO_3	Et_2O	12	>99	0
14	Me_2SnCl_2	1	Na_2CO_3	THF	12	>99	0
15	Me_2SnCl_2	0.5	K_2CO_3	THF	24	93	0
16	Me_2SnCl_2	0.1	K_2CO_3	THF	72	82	0
17	Me_2SnCl_2	1	Et_3N	THF	3	93	trace
18	Me_2SnCl_2	1	DMAP	THF	24	54	32
19	Me_2SnCl_2	1	KOAc	THF	24	trace	0
20	Me_2SnCl_2	1	$NaHCO_3$	THF	24	72	0
21	Bu_3SnCl	1	K_2CO_3	THF	12	33	0
22	$BuSnCl_3$	1	K_2CO_3	THF	12	37	0

[a] General conditions: **1a** (1.0 mmol), Me_2SnCl_2 (0.01 mmol), K_2CO_3 (2.0 mmol) in THF (5 mL), then PhCOCl (1.2 mmol); see Experimental Section. [b] Isolated yield. [c] Starting diol remained in the cases of low yields. [d] Equimolar amount of PhCOCl was used.

We present herein the full detail of the chemo- and stereoselective monobenzoylation of 1,2-diols using organotin compounds.

Results and Discussion

Monobenzoylation of *trans*-1,2-Cyclohexanediol. To exploit an efficient method for the monobenzoylation of 1,2-diols **1** using a catalyst, we first studied a benzoylation of *trans*-1,2-cyclohexanediol (**1a**) as a representative of **1** under various conditions (eq 2).



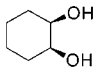
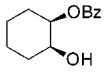
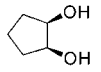
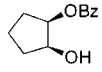
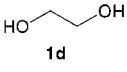
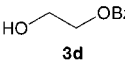
(2)

We surveyed a variety of organotin compounds as catalysts and examined the effect of the amount of the catalysts, the kind of bases and solvents on the yield of monobenzoylated product **3a**, and the ratio of **3a** to dibenzoylated product **4a**. The results are shown in Table 1.

The results clearly show the effect of dialkyltin compounds (runs 5−20 except 8 and 19). The absence of organotin compounds (runs 1−4) and the presence of trialkyl- (run 21) or monoalkyltin compounds (run 22) resulted in low yields of **3a**. Among dialkyltin compounds, dimethyltin dichloride gave the best result (compare runs 10−14 with runs 5−7). The yield of **3a** decreased as the amount of dimethyltin dichloride decreased (runs 9, 10, 15, and 16).

The results also show the importance of the bases used. Namely, in the absence of a base, attempted monobenzoylation in the presence of dimethyltin dichloride did not afford **3a** (runs 8 and 19). When (4-dimethylamino)-pyridine (DMAP) was used as a base, a large amount of **4a** was generated irrespective of the presence of dimethyltin catalyst (runs 2, 3 and 18). This may be due to the effective acylation catalysis ability of DMAP. Sodium bicarbonate resulted in a relatively moderate yield (run 20). Although triethylamine afforded 93% of **3a** within 3 h by using 1 mol % of dimethyltin dichloride, a trace amount of **4a** was observed (run 17), whereas potassium or sodium carbonate required longer reaction time but showed a complete selectivity. Thus, potassium or sodium carbonate was found to be a suitable base for the reaction. Tetrahydrofuran (THF) was recommended as a solvent, while dichloromethane (run 11), acetonitrile (run 12), and ether (run 13) were also usable.[16]

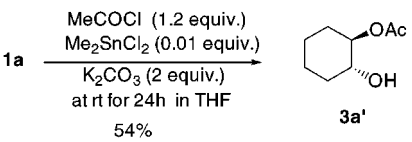
Table 2. Monobenzoylation of Various Diols 1b−h Catalyzed by Me_2SnCl_2[a]

Run	Diol 1b-h	Me_2SnCl_2 (mol%)	Product 3	Isolated Yield(%) of 3	4[b]
1	 1b	1	 3b	>99	**4b** 0
2	 1c	1	 3c	>99	**4c** 0
3	 1d	1	 3d	>99	**4d** 0
4[c]	$HO(CH_2)_3OH$ 1e	1	$HO(CH_2)_3OBz$ 3e	67	**4e** trace
5[c]	$HO(CH_2)_4OH$ 1f	1	$HO(CH_2)_4OBz$ 3f	51	**4f** 0
6[c]	1f	10	3f	65	**4f** 0
7[c]	$HO(CH_2)_5OH$ 1g	10	$HO(CH_2)_5OBz$ 3g	46	**4g** 6
8[c]	$HO(CH_2)_6OH$ 1h	10	$HO(CH_2)_6OBz$ 3h	48	**4h** 4

[a] General conditions: **1b−h** (1.0 mmol), Me_2SnCl_2 (0.01 mmol), K_2CO_3 (2.0 mmol) in THF (5 mL), then PhCOCl (1.2 mmol); see Experimental Section. [b] The corresponding dibenzoate. [c] Starting diol remained.

A typical experimental procedure is as follows: Diol **1a** (1.0 mmol) was dissolved in THF (5 mL) with a catalytic amount of dimethyltin dichloride (0.01 mmol) in the presence of potassium carbonate (2.0 mmol). Benzoyl chloride (1.2 mmol) was added to the mixture, and the solution was stirred at room temperature until **1a** disappeared (checked by thin-layer chromatography). After a usual workup, monobenzoylated product **3a** was obtained in a quantitative yield.

The acylation of diols also took place in a similar way to benzoylation by using other acyl chlorides, though the yields were less satisfactory. For example, **1a** was acylated by acetyl chloride to give **3a′** in 54% yield (eq 3).



(3)

Monobenzoylation of 1,*n*-Diols. Under the best reaction conditions described above, 1,2-diols **1b−d** and

(16) Although the chemical yields in the monobenzoylation of **1a** using dimethyltin dichloride were almost similar for these solvents, the use of THF gave the highest ee of **3j** in the benzoylation of racemic **1j**.

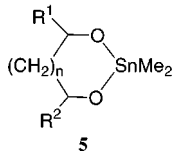


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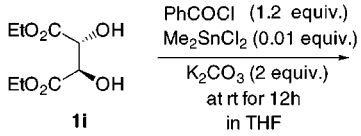
Figure 2.

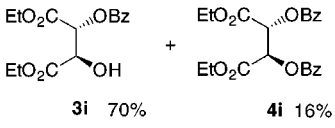
1,*n*-diols **1e**−**h** were benzoylated (Table 2). Cyclic and acyclic 1,2-diols **1b**−**d** were monobenzoylated with almost perfect selectivity in the presence of 1 mol % of dimethyltin dichloride (runs 1−3). 1,3-Propanediol (**1e**) was also monobenzoylated with a high selectivity, but the yield was less than those in cases of 1,2-diols (run 4). Furthermore, the yields of **3** decreased as the number of *n* in 1,*n*-diols increased (runs 3−8).

In contrast to the high selectivity observed in those 1,2- and 1,*n*-diols with respect to mono- and dibenzoylation, the benzoylation of diethyl L-tartrate (**1i**) gave the monobenzoylated product **3i** in 70% yield with a significant amount (16%) of the dibenzoylated product **4i** (eq 4). The low selectivity concerning the mono- and dibenzoylation may be due to the high acidity of the hydroxyl groups of **1i**.[17]



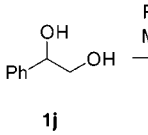
1i

PhCOCl (1.2 equiv.)
Me_2SnCl_2 (0.01 equiv.)
K_2CO_3 (2 equiv.)
at rt for 12h
in THF



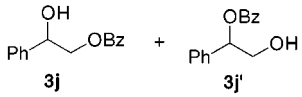
3i 70% **4i** 16% (4)

Regioselectivity of Unsymmetrical Diols 1j−**l.** Our tin-catalyzed benzoylation was applied to unsymmetrical diols **1j**−**l**. 1-Phenyl-1,2-ethanediol (**1j**) afforded the monobenzoylated product **3j** in good yield, though a small amount of the regioisomer **3j′** was formed in low yield (eq 5).



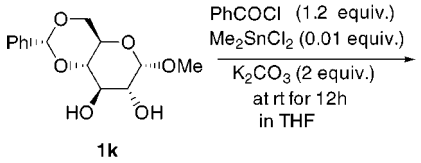
1j

PhCOCl (1.2 equiv.)
Me_2SnCl_2 (0.01 equiv.)
K_2CO_3 (2 equiv.)
at rt for 12h
in THF



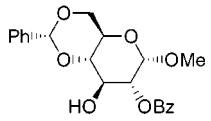
3j 90% **3j'** 5% (5)

On the other hand, a benzoylation of a glucose derivative **1k** selectively occurred at the 2-hydroxyl group (eq 6).



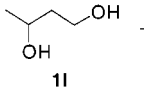
1k

PhCOCl (1.2 equiv.)
Me_2SnCl_2 (0.01 equiv.)
K_2CO_3 (2 equiv.)
at rt for 12h
in THF



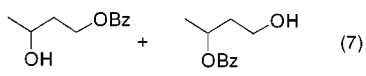
3k 92% (6)

In a case of an unsymmetrical 1,3-diol **1l**, a selectivity similar to that of **1j** was observed (eq 7).



1l

PhCOCl (1.2 equiv.)
Me_2SnCl_2 (0.01 equiv.)
K_2CO_3 (2 equiv.)
at rt for 12h
in THF

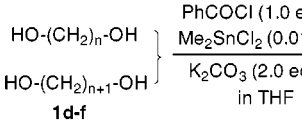


3l 63% **3l'** 6% (7)

Chemoselectivities; Competitive Reaction. To see the chemoselectivity in the tin-catalyzed benzoylation reaction, we carried out competitive reactions between 1,2-diol **1a** and *n*-butanol and between 1,*n*-diols. In a competitive reaction between **1a** and *n*-butanol, **1a** was selectively benzoylated even in the presence of 5 molar equivalents of *n*-butanol to give **3a** in 89% yield (eq 8). Thus, *n*-butanol was found to be actually inert for the benzoylation under the reaction conditions.

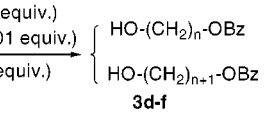
1a + n-BuOH (5 equiv.) → PhCOCl (1.2 equiv.), Me_2SnCl_2 (0.01 equiv.), K_2CO_3 (2 equiv.), at rt for 5h, in THF → **3a** 89% (8)

Furthermore, when an equimolar amount of 1,2-ethanediol (**1d**) and 1,3-propanediol (**1e**) was subjected to the monobenzoylation reaction, **1d** was predominantly monobenzoylated to give **3d** (eq 9). On the other hand, the difference of yields between **3e** and **3f** was not significant in a competitive reaction between 1,3-diol **1e** and 1,4-diol **1f** under the same reaction condition (eq 9).



1d-f

PhCOCl (1.0 equiv.)
Me_2SnCl_2 (0.01 equiv.)
K_2CO_3 (2.0 equiv.)
in THF



3d-f (9)

	diols	yield (%) of monobenzoylated products	ratio of products
n = 2	**1d/1e**	99	**3d/3e** = 93/7
n = 3	**1e/1f**	87	**3e/3f** = 68/32

Interestingly, when an equimolar mixture of *trans*-1,2-cyclohexanediol (**1a**) and diethyl L-tartrate (**1i**) was subjected to the benzoylation reaction, only **1i** was benzoylated to afford a mixture of **3i** in 64% and **4i** in 14%, respectively (eq 10).

There was no significant difference between cyclic-1,2-diols and acyclic-1,2-diols as exemplified by the benzo-

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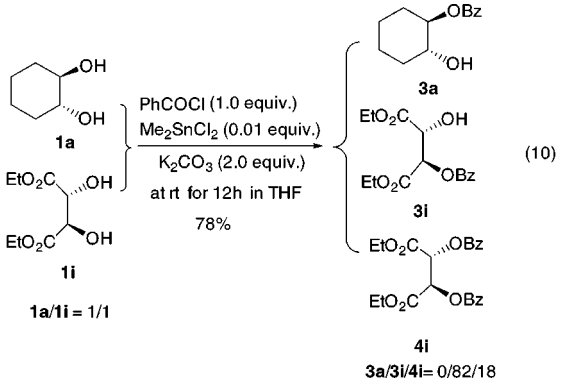
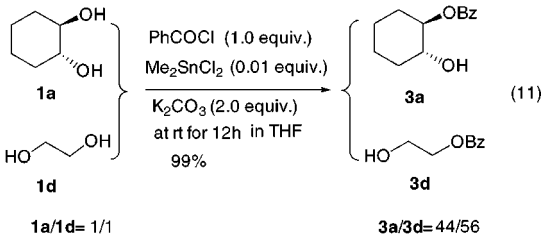
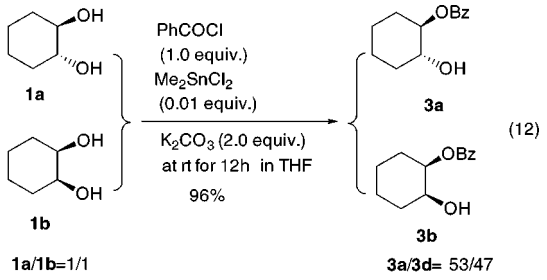


ylation of a mixture of an equimolar amount of 1,2-diols **1a** and **1d** (eq 11).

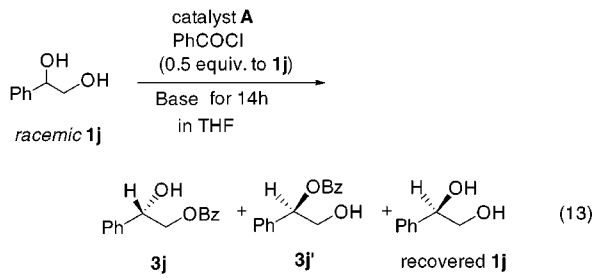


These observations strongly suggest that the reaction proceeds via formation of dimethylstannylene acetal **5** (Figure 2), and a formation of the five-membered intermediate ($n = 0$) should be kinetically more favored than that of the other membered stanylene acetals ($n > 0$). This feature might lead to the high 1,2-diol selectivity that is very useful for synthetic utilization of this benzoylation method.

Stereoselectivity. There was almost no difference in the benzoylation between *trans*- and *cis*-1,2-cyclohexanediols **1a,b** (eq 12).



However, an interesting result was obtained in the benzoylation of **1j** (eq 13) using a chiral tin catalyst, (*S*)-4,4-dibromo-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin (**A**, Figure 3),[18] which was synthesized according to the reported method.[19,20]



The benzoylation of racemic **1j** using a chiral catalyst **A** was carried out under a variety of conditions, and the

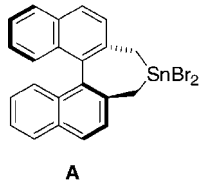


Figure 3.

Table 3. Kinetic Resolution of Diol 1j by Benzoylation with a Catalyst A[a]

run	**A** (mol %)	H_2O (μL)	base[b]	temp (°C)	%ee[c,d] (yields %[e]) of **3j**[f]	s[g]
1	0	0	Et_3N	r.t.	~0 (40)	
2	0	0	Na_2CO_3	r.t.	~0 (23)	
3	0.25	0	Et_3N	−20	~0 (43)	
4	0.25	0	Na_2CO_3	r.t.	32 (31)	2.2
5	0.25	100	Na_2CO_3	r.t.	58 (42)	5.6
6	0.25	1000	Na_2CO_3	r.t.	23 (16)	1.7
7	0.25	100	Et_3N	r.t.	13 (19)	1.3
8	0.25	100	Na_2CO_3	0	75 (54)	18.6
9	0.25	100	Na_2CO_3	−10	86 (38)	22.4
10	0.25	100	Na_2CO_3	−20	84 (41)	20.7
11	0.25	100	Na_2CO_3	−30	79 (28)	11.5
12	0.25	100	Na_2CO_3	−40	32 (10)	2.0

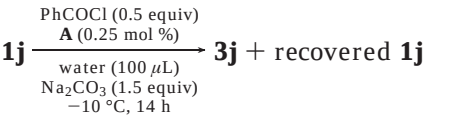
[a] General conditions: see Experimental Section. [b] 1.5 equiv of **1j** was used. [c] Determined by CSP HPLC analysis (for **3j**, Chiralcel OB column; 254 nm; *n*-hexane:*i*-PrOH = 9:1). [d] Corrected value based on the ee of used **A** (91%). [e] Isolated yield based on starting **1j**. [f] (*S*)-isomer was obtained. [g] Selectivity: see ref 22.

results are summarized in Table 3. The main product was the (*S*)-enantiomer-enriched 2-benzoyloxy-1-phenylethanol ((*S*)-**3j**), of which an ee was determined by CSP HPLC analysis. The absolute configuration of (*S*)-**3j** was confirmed by its alkaline hydrolysis followed by comparison of the specific rotation of the resulting **1j** with that of authentic sample.[21] The recovered **1j** was enriched with (*R*)-enantiomer in 56−80% yields. There appeared a small amount of 1-benzoylated diol **3j′** (0~10%) but no dibenzoylated product.

The results showed the remarkable effects of a chiral tin catalyst **A**, the kind of base, and water on the ee of **3j**. Namely, the absence of **A** in the reaction system did not cause any resolution of **1j** (runs 1 and 2), though **3j** was formed in moderate yields. Theoretically, the maximum yield is 50% since the amount of benzoyl chloride was 0.5 equiv to that of **1j**. On the other hand, the presence of **A** afforded a result with a resolution of **1j** (runs 4−12). The use of sodium carbonate was one of the critical factors for getting a satisfactory result. Although triethylamine gave an unsuccessful result with respect to the ee of **3j** (run 3), sodium carbonate as a suspended state gave an appreciable degree of ee (32%) of **3j** (run 4). The other factor for the kinetic resolution was the presence of water. The selectivity observed in run 4 was improved to 58% ee if a small amount of water was added (run 5). However, the ee decreased in the presence of a large amount of water (run 6), where sodium carbonate was completely dissolved to give a homogeneous solution. In contrast with sodium carbonate, triethylamine was not effective even though water was present (run 7).

Although the selectivity (*s* value)[22] was not much varied in the temperature range of 0 to −30 °C (runs 8−11), the yield of **3j** dropped when the reaction was carried out at −30 °C (run 11), and the reaction at −40 °C resulted in both low ee and low yield (run 12). The best selectivity was obtained when the reaction was

Table 4. Effects of Solvents on the Monobenzoylation of 1j[a]



run	solvent (5 mL)	ee %[b,c] (yield %)[d] of **3j**	s^e
1	THF	84 (41)	20.7
2	DME	56 (39)	5.0
3	MeCN	74 (22)	8.2
4	CH_2Cl_2	13 (12)	1.3

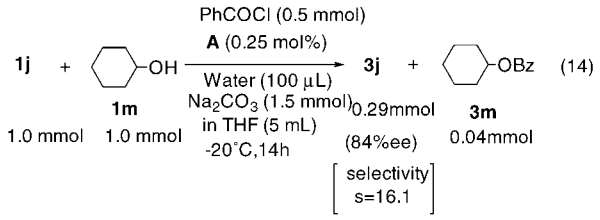
[a] General conditions: See Experimental Section. [b] Determined by Chiral Column HPLC. [c] Corrected based on the ee of used **A** (91%). [d] Isolated yield. [e] Selectivity; see ref 22.

performed using sodium carbonate in the presence of a small amount of water at −10 °C (run 9).

The other factor affecting the selectivity of the kinetic resolution was the kind of solvent. The results carried out in several solvents are shown in Table 4.

The benzoylation of **1j** in dichloromethane was sluggish and afforded poor results in both the ee and chemical yield of **3j** (run 4), whereas relatively high ee was observed by the use of polar solvents such as acetonitrile, THF, or DME (runs 1−3). The best result was obtained by using THF (run 1). Although the reason the ee of **3j** was enhanced by polar solvents has not been clear yet, an ability of solvents to coordinate with the tin atom of **A** may be important.

The catalyst **A** also showed a high 1,2-diol selectivity as dimethyltin dichloride did. That is, **1j** was efficiently resolved even in the presence of an equimolar amount of cyclohexanol (**1m**), and the ee of **3j** obtained in the reaction was almost not affected by the presence of **1m**, though a small amount of cyclohexyl benzoate (**3m**) was formed (eq 14).



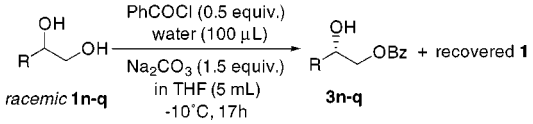
This method could be applied to various 1-substituted 1,2-ethanediols **1n**−**q**. The results are summarized in Table 5.

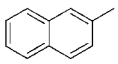
A-catalyzed monobenzoylation of terminal 1,2-diols **1n**−**q** afforded (*S*)-enantiomer-enriched 2-benzoylated diols **3n**−**q** in moderate selectivity. Only a trace amount of 1-benzoylated diols was observed under the experimental conditions. Other patterns of 1,2-diols such as **1a** afforded disappointing results under similar reaction conditions.

Mechanism for Kinetic Resolution. The resolution reaction may involve two crucial steps: a formation of stannylene acetal **2** by the reaction of **1** with a chiral tin catalyst **A** (first step), and a benzoylation of **2** with benzoyl chloride (second step) (Scheme 1). A formation of **2** is supported by the high chemoselective formation of **3j** with a high ee from a mixture of **1j** and **1m** (eq 14).

Since the observed ee was strongly dependent on the base (Table 3) and it has been well-documented that stannylene acetals are easily acylated without bases by

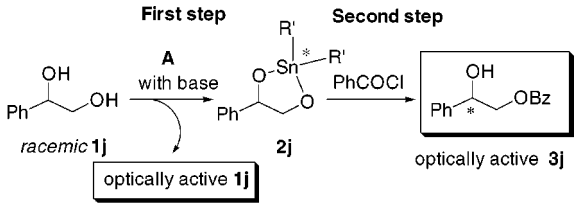
Table 5. Kinetic Resolution of Diol 1n−q by Benzoylation with a Catalyst A[a]



run	R	1	3	%ee[b,c] (yield %)[d] of 3	s^e
1		**1n**	**3n**	64 (25)	5.6
2		**1o**	**3o**	72 (41)	10.0
3	$CH_3(CH_2)_9$-	**1p**	**3p**	59 (35)	5.2
4	C_2H_5-	**1q**	**3q**	44 (35)	3.2

[a] General conditions: see Experimental Section. [b] Determined by CSP HPLC analysis. [c] (*S*)-Isomer was enriched. [d] Isolated yield. [e] See ref 22.

Scheme 1. Enantioselective Benzoylation Using a Chiral Catalyst A



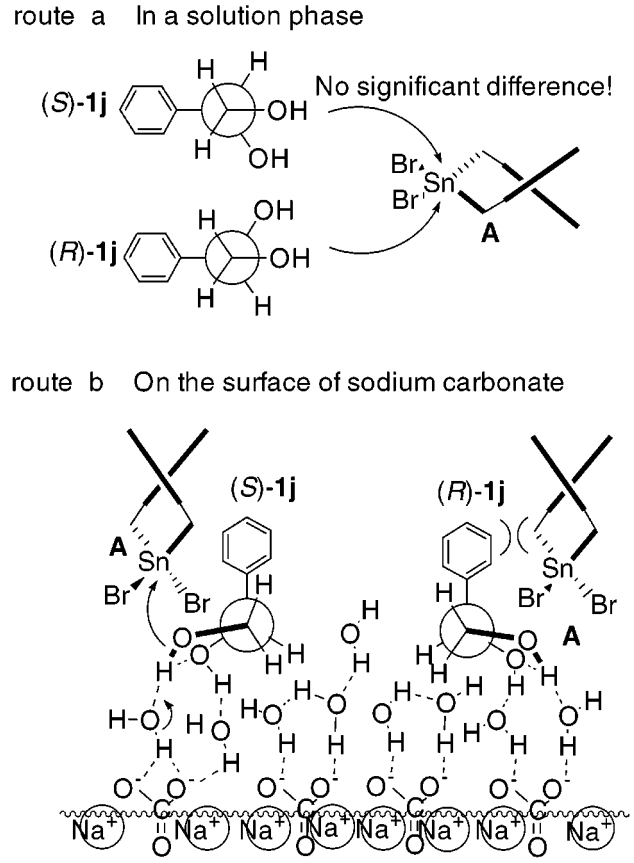
various acid chlorides,[5] the first step may be responsible for the enantio discrimination of racemic **1j**, which may occur on the surface of sodium carbonate.

Thus, we propose a mechanism for the kinetic resolution of **1j** using **A** as depicted in Scheme 2. That is, when amine is used as a base, stannylene acetals **2j** may be formed in a solution phase (THF) in a manner in which **A** approaches the primary hydroxyl group of **1j** from a direction as far away as possible from a bulky phenyl group (route a in Scheme 2). According to this hypothesis, there seems to be no significant difference between the accessibility of **A** toward (*S*)-**1j** and (*R*)-**1j**.

On the contrary, when sodium carbonate is used as a base, the hydrophilic 1,2-diol moiety of **1j** may be adsorbed on the surface of the sodium carbonate, directing the hydrophobic phenyl group toward the solution phase (THF) (route b in Scheme 2). In the presence of a small amount of water, a thin aqueous phase is formed on the surface of the sodium carbonate and, as the result, the adsorption of **1j** is assisted by hydrogen bonding as depicted in Scheme 2. Provided that this hypothesis is true, **A** should approach from the solution phase in a manner in which a steric repulsion between **A** and phenyl group is as small as possible. Thus, the discrimination of (*S*)-**1j** from (*R*)-**1j** takes place since a steric repulsion between the methylene group of **A** and phenyl group of (*S*)-**1j** is less than that between **A** and (*R*)-**1j**.

The role of THF on the kinetic resolution is not clear. One of working hypotheses is that a coordination of THF on the tin atom of **A** may increase the bulkiness of **A**, which works to increase the enantioselectivity in the monobenzoylation of **1j**.

Scheme 2. Enantioselective Benzoylation of 1j on the Surface of Na_2CO_3



In conclusion, we reported a chemo- and stereoselective monobenzoylation of diols. The extremely high 1,2-diol selectivity of this reaction may be very useful in organic synthesis. Especially, the reaction required only a catalytic amount of organotin compound. Furthermore, it was demonstrated that a chiral oragnotin compound **A** could work as an efficient catalyst for kinetic resolution of terminal 1,2-diols with the assistance of metal carbonate and a small amount of water. Since the catalyst **A** works with not only 1,2-diol selective but also stereoselective manner, this method would be a promising protocol for kinetic resolution of diols.

Although the speculated mechanism can explain the observed stereoselectivity of the reaction, further study has to be carried out to make the mechanism more clear. Designing of new organotin reagents and application of this catalytic system to further complex polyols are now under investigation.

Experimental Section

GC analyses were obtained by using a GC-12A from Shimadzu Seisakusho Inc. ^{1}H NMR spectra were measured on a Varian Gemini 200, 300, or 500 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL IMS-DX 300 instrument. IR spectra were obtained on a Shimadzu FTIR-8100A.

Materials. MeCN and CH_2Cl_2 were distilled over P_2O_5. Freshly distilled THF and ether were used after drying over sodium metal. Organotin compounds ($Bu_2Sn{=}O$, Bu_2SnCl_2, Ph_2SnCl_2, Me_2SnCl_2, Bu_3SnCl, and $BuSnCl_3$), benzoyl chloride, acetyl chloride, Et_3N, and 4-(dimethylamino)pyridine (DMAP) were commercially available and used without further purification. Diols **1a**−**l** were also commercially available. K_2CO_3 and Na_2CO_3 were used after being pulverized as small as possible with a mill. Monobenzoylated products **3a**,[23] **3b**,[24] **3c**,[24] **3d**,[25] **3e**,[26] **3f**,[25] **3g**,[27] **3h**,[28] **3i**,[10] **3j**,[8] **3j′**,[8] **3k**,[29] **3l**,[10] and **3l′**,[10] monoacetylated product **3′a**,[30] and dibenzoylated products **4a**,[31] **4g**,[32] **4h**,[33] and **4i**[10] are known compounds, and only ^{1}H NMR and/or IR spectra data for monobenzoylated compounds **3** are presented here.

General Procedure (Monobenzoylation of 1,2-Diol). To a solution of diol (1 mmol) in tetrahydrofuran (THF, 5 mL) were added a catalytic amount of dimethyltin dichloride (0.1−10 mol %), K_2CO_3 (2 mmol), and benzoyl chloride (1.2 mmol), successively, at room temperature. The mixture was stirred at room temperature for 3−72 h. Then the mixture was poured into water and extracted three times with CH_2Cl_2 (30 mL). The organic layers were combined, and the solvent was evaporated in vacuo to give a residue, which was almost a pure monobenzoylated product. Further purification of the crude products was carried out by silica gel short-column chromatography to afford the benzoylated products.

***trans*-2-Hydroxycyclohexyl Benzoate (3a).**[23] IR (neat) 3450, 2940, 2863, 1719, 1451, 1321, 1275, 1113, 1071, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22−1.53 (m, 4H), 1.60−1.84 (m, 2H), 2.00−2.25 (m, 2H), 2.50 (br s, 1H), 3.67−3.80 (m, 1H), 4.79−4.91 (m, 1H), 7.43−7.60 (m, 3H), 8.07−8.10 (m, 2H).

***cis*-2-Hydroxycyclohexyl Benzoate (3b).**[24] IR (neat) 3480, 2940, 2865, 1711, 1451, 1316, 1287, 1111, 984, 716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31−1.55 (m, 2H), 1.56−1.90 (m, 4H), 1.90−2.16 (m, 3H), 3.95−3.97 (m, 1H), 5.21−5.23 (m, 1H), 7.42−7.44 (m, 2H), 7.54−7.57 (m, 1H), 8.04−8.08 (m, 2H).

***cis*-2-Hydroxycyclopentyl Benzoate (3c).**[24] IR (neat) 3490, 2971, 1694, 1451, 1271, 1117, 1026, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55−2.14 (m, 6H), 2.25 (br s, 1H), 4.25−4.33 (m, 1H), 5.19−5.25 (m, 1H), 7.48−7.48 (m, 2H), 7.55−7.58 (m, 1H), 8.04−8.07 (m, 2H).

2-Hydroxyethyl Benzoate (3d).[25] IR (neat) 3440, 2953, 1722, 1603, 1452, 1315, 1124, 1070, 1028, 907, 718 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (br s, 1H), 3.95 (t, 2H, J = 4.7 Hz), 4.45 (t, 2H, J = 4.7 Hz) 7.40−7.47 (m, 2H), 7.50−7.59 (m, 1H), 8.01−8.08 (m, 2H).

3-Hydroxypropyl Benzoate (3e).[26] IR (neat) 3420, 2961, 2890, 1725, 1452, 1391, 1316, 1177, 1100, 718 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (quint, 2H, J = 6.1 Hz), 2.23 (br s, 1H), 3.78 (t, 1H, J = 6.1 Hz), 4.49 (t, 1H, J = 6.1 Hz) 7.44−7.47 (m, 2H), 7.55−7.57 (m, 1H), 8.03−8.06 (m, 2H).

4-Hydroxybutyl 1-Benzoate (3f).[25] IR (neat) 3410, 2951, 1722, 1453, 1316, 1177, 1070, 943, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57−2.01 (m, 4H), 2.48, (br s, 1H), 3.73 (t, 2H, J = 6.4 Hz), 4.37 (t, 2H, J = 6.4 Hz) 7.44−7.47 (m, 2H), 7.55−7.57 (m, 1H), 8.03−8.10 (m, 2H).

5-Hydroxypentyl 1-Benzoate (3g).[27] IR (neat) 3410, 2950, 1725, 1453, 1180, 1075, 945, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40−1.71 (m, 4H), 1.71−1.92 (m, 2H), 2.15 (s, 1H), 3.66 (t, 2H, J = 6.4 Hz), 4.33 (t, 2H, J = 6.4 Hz) 7.40−7.47 (m, 2H), 7.50−7.60 (m, 1H), 8.00−8.10 (m, 2H).

6-Hydroxyhexyl 1-Benzoate (3h).[28] IR (neat) 3410, 2955, 1722, 1453, 1180, 1075, 943, 712 cm^{-1}; ^{1}H NMR (300 MHz,

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(33) Meth-Cohn, O.; Smith, D. I. *J. Chem. Soc., Perkin Trans. 1* **1982**, 261−270.

$CDCl_3$) δ 1.35−1.68 (m, 6H), 1.71−1.90 (m, 2H), 2.09 (s, 1H), 3.64 (t, 2H, J = 6.4 Hz), 4.32 (t, 2H, J = 6.4 Hz) 7.40−7.49 (m, 2H), 7.50−7.60 (m, 1H), 8.00−8.10 (m, 2H).

Monobenzoylated Diethyl L-Tartrate (3i).[10] IR (neat) 3500, 3010, 1732, 1260 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.1 Hz), 1.31 (t, 3H, J = 7.1 Hz), 2.40−3.30 (br, 1H), 4.17−4.38 (m, 4H), 4.87 (d, 1H, J = 2.3 Hz), 5.67 (d, 1H, J = 2.3 Hz), 7.37−7.52 (m, 2H), 7.53−7.65 (m, 1H), 7.99−8.09 (m, 2H).

2-Hydroxy-2-phenylethyl Benzoate (3j).[8] IR (neat) 3470, 1705, 1451, 1318, 1291, 1127, 1065, 708 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 2.60 (br s, 1H), 4.43 (dd, 1H, J = 7.0, 11.0 Hz), 4.55 (dd, 1H, J = 4.0, 11.0 Hz), 5.13 (dd, 1H, J = 4.0, 7.0 Hz), 7.30−7.65 (m, 8H), 8.04−8.10 (m, 2H).

2-Hydroxy-1-phenylethyl Benzoate (3j′).[8] IR (neat) 3430, 2934, 1717, 1453, 1318, 1117, 1026, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (br s, 1H), 3.90−4.20 (m, 2H), 6.11 (dd, 1H, J = 7.4, 7.7 Hz), 7.30−7.65 (m, 8H), 8.10−8.15 (m, 2H).

Methyl 2-Benzoyl-4,6-*O*-benzylidene-α-D-glucoside (3k).[29] IR (neat) 3498, 2986, 1723, 1453, 1379, 1281, 1109, 1071, 995, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 1H), 3.39 (s, 3H), 3.62 (t, 1H, J = 9.4 Hz), 3.79 (t, 1H, J = 10.3 Hz), 3.88−3.93 (m, 1H), 4.31−4.37 (m, 2H), 5.02−5.08 (m, 2H), 5.57 (s, 1H), 7.36−7.40 (m, 3H), 7.43−7.47 (m, 2H), 7.50−7.52 (m, 2H), 7.56−7.59 (m, 1H), 8.08−8.11 (m, 2H).

3-Hydroxybutyl 1-Benzoate (3l).[10] ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (d, 3H, J = 6.2 Hz), 1.77−2.00 (m, 2H), 2.35 (br s, 1H), 3.91−4.04 (m, 1H), 4.32−4.43 (m, 1H), 4.52−4.65 (m, 1H), 7.39−7.47 (m, 2H), 7.51−7.57 (m, 1H), 8.00−8.07 (m, 2H).

4-Hydroxybutyl 2-Benzoate (3l′).[10] ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (d, 3H, J = 7.9 Hz), 1.76−1.99 (m, 2H), 2.53 (br s, 1H), 3.62−3.73 (m, 2H), 5.31−5.42 (m, 1H) 7.47−7.50 (m, 2H), 7.55−7.60 (m, 1H), 8.01−8.07 (m, 2H).

***trans*-2-Hydroxycyclohexyl Acetate (3a′).**[30] IR (neat) 3450, 2940, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20−1.53 (m, 4H), 1.63−1.82 (m, 2H), 1.90−2.15 (m, 2H), 2.10 (s, 3H), 2.40 (br s, 1H), 3.48−3.65 (m, 1H), 4.52−4.65 (m, 1H).

General Procedure for Competitive Reactions. To a solution of diols (1.0 mmol and 1.0 mmol) in tetrahydrofuran (THF, 5 mL) were added a catalytic amount of dimethyltin dichloride (0.01 mmol), K_2CO_3 (2 mmol), and benzoyl chloride (1.0 mmol), successively, at room temperature. The reaction was carried out in a similar way to that in the monobenzoylation of a 1,2-diol. The product ratios were determined by means of ^1H NMR spectra.

(*S*)-4,4-Dibromo-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin (A).[18] **A** was prepared according to the reported method (91% ee).[19,20]

Kinetic Resolution of 1-Phenyl-1,2-ethanediol (1j). 1-Phenyl-1,2-ethanediol (1 mmol) and catalyst **A** (0.0025 mmol) were dissolved in 5 mL of THF. After a pulverized sodium carbonate (1.5 mmol) was suspended in the solution, water (100 μL) and benzoyl chloride (0.5 mmol), successively, were added at −10 °C. The reaction mixture was stirred at −10 °C for 14 h. Then, the suspension was poured into water, and the organic portion was extracted three times with ethyl acetate. The combined organic layer was dried over magnesium sulfate. After removal of solvent, the residue was separated by silica gel column chromatography (*n*-hexane:ethyl acetate = 3:1).

(*S*)-2-Benzoyloxy-1-phenylethanol (3j). $[\alpha]^{26}_D$ +8.5 (*c* 1.0, MeOH); DAICEL Chiralcel OB (0.46 cm × 25 cm); *n*-hexane:2-propanol = 9:1; wavelength, 254 nm; flow rate, 1.0 mL/min; retention time, 13, 25 min, 78% ee (uncorrected). The (*S*) configuration of **3j** was confirmed by comparison of the specific rotation of authentic samples of **1j**[21] after an alkaline hydrolysis of **3j**.

(*S*)-(2-Naphthyl)-2-hydroxyethyl Benzoate (3n). White solid, mp 90−97 °C; $[\alpha]^{21}_D$ +4.9 (*c* 0.48, MeOH); IR (KBr) 2361, 2341 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.51 (1H, dd, J = 8.0, 11.6 Hz), 4.62 (1H, dd, J = 3.6, 11.6 Hz), 5.28 (1H, dd, J = 3.6, 8.0 Hz), 7.40−7.65 (6H, m), 7.81−8.09 (6H, m); DAICEL Chiralpak AS (0.46 cm × 25 cm); *n*-hexane:2-propanol = 9:1; wavelength, 254 nm; flow rate, 0.8 mL/min; retention time, 16, 19 min; 64% ee; HRMS calcd for $C_{19}H_{16}O_3$ 292.1099, found 292.1129. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.12; H, 5.62.

(*S*)-(1-Naphthyl)-2-hydroxyethyl Benzoate (3o). White solid, mp 99−103 °C; $[\alpha]_D^{24}$ −6.5 (*c* 0.5, MeOH); IR (KBr) 3510, 3404, 3059, 1705, 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.51 (1H, dd, J = 8.0, 11.6 Hz), 4.63 (1H, dd, J = 3.6, 11.6 Hz), 5.28 (1H, dd, J = 3.6, 8.0 Hz), 7.37−7.54 (6H, m), 7.81−7.89 (4H, m), 8.02−8.06 (2H, m); DAICEL Chiralpak AS (0.46 cm ø × 25 cm); *n*-hexane:2-propanol = 9:1; wavelength, 254 nm; flow rate, 1.0 mL/min; retention time, 16, 20 min; 72% ee; HRMS calcd for $C_{19}H_{16}O_3$ 292.1099, found 292.1134. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.18; H, 5.61.

(*S*)-2-Hydroxydodecyl Benzoate (3p). White solid, mp 35−37 °C; $[\alpha]^{24}_D$ +1.9 (*c* 0.49, MeOH); IR (KBr) 3501, 2953, 2920, 2849, 1697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.5 Hz), 4.23 (2H, s), 7.42−7.50 (2H, m), 7.55−7.60 (1H, m), 8.04−8.09 (2H, m); DAICEL Chiralpak AS (0.46 cm × 25 cm); *n*-hexane:2-propanol = 98:2; wavelength, 254 nm; flow rate, 1.0 mL/min; retention time, 11, 16 min; 59% ee; HRMS calcd for $C_{19}H_{30}O_3$ 306.2195, found 306.2203. Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.70; H, 9.71.

(*S*)-2-Hydroxybutyl Benzoate (3q). Colorless oil, $[\alpha]^{20}_D$ +3.7 (*c* 1.0, MeOH); IR (neat) 3450, 2966, 2880, 1718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (3H, t, J = 7.5 Hz), 1.54−2.27 (2H, m), 3.92 (1H, dd, J = 3.4, 6.8 Hz), 4.24 (1H, dd, J = 6.8, 11.8 Hz), 4.40 (1H, dd, J = 3.4, 11.8 Hz), 7.40−7.48 (2H, m), 7.54−7.58 (1H, m), 8.03−8.08 (2H, m); DAICEL Chiralcel OJ (0.46 cm × 25 cm); *n*-hexane:2-propanol = 98:2; wavelength, 254 nm, flow rate, 1.0 mL/min; retention time, 45, 48 min; 40% ee; HRMS calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0918. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.02; H, 7.43.All benzoylated products **3j** and **3n**−**q** were converted to corresponding diols by alkaline hydrolysis. Then the absolute configurations of the diols were confirmed by comparison of their specific rotation with authentic data (**1j**,[21] **1n**,[34] **1o**,[35] **1p**,[36] and **1q**[34]).

Acknowledgment. This study was supported by Grant-in-Aid for Scientific Research on Priority Areas, No. 706: Dynamic Control of Stereochemistry and No.11771414 from the Ministry of Education, Science, and Culture, Japan, and one of the authors (T.M.) also thanks Daicel Chemical Industries for general financial support.

JO991394J

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