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2,2-DISUBSTITUTED PROPIONIC ANHYDRIDES: EFFECTIVE COUPLING REAGENTS FOR THE KINETIC RESOLUTION OF SECONDARY BENZYLIC ALCOHOLS USING BTM

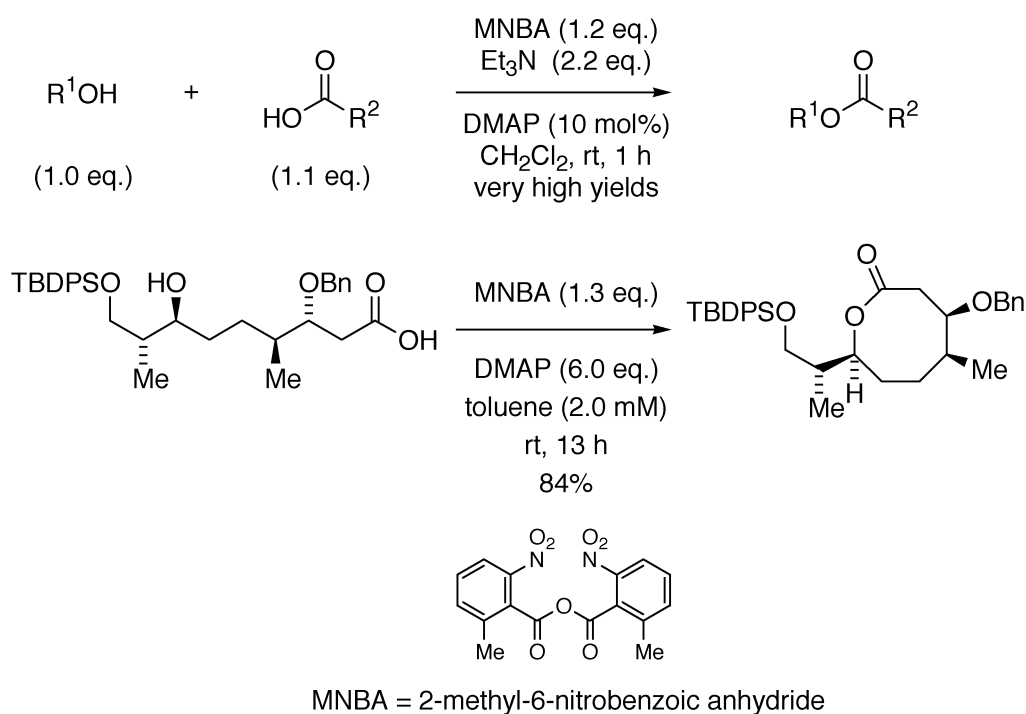
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Abstract – A variety of optically active benzylic alcohols possessing aliphatic substituents at the C-1 position are produced by the kinetic resolution of racemic secondary alcohols using free carboxylic acids with 2,2-disubstituted propionic anhydrides and (+)-benzotetramisole (BTM). Evaluation of the efficiency of this asymmetric esterification using several anhydrides derived from aliphatic carboxylic acids were carried out by comparing the efficiencies of the kinetic resolution of (±)-1-phenyl-1-propanol. It was found that not only pivalic anhydride is a very widely usable reagent to produce the corresponding esters with high ee's in the presence of BTM, but other 2,2-disubstituted propionic anhydrides, such as 2-methyl-2-phenylpropionic anhydride (MPPRA) and 2,2-diphenylpropionic anhydride (DPPRA), are also applicable as effective coupling reagents for producing the optically active esters and alcohols with high selectivities. This protocol directly provides chiral carboxylic esters from free carboxylic acids and racemic secondary alcohols by utilizing the transacylation process to generate mixed anhydrides from the acid components and sterically hindered carboxylic anhydrides.

The authors dedicate this paper to Professor Emeritus Keiichiro Fukumoto on the celebration of his 75th birthday.

In recent years, several effective methods for the kinetic resolution of racemic alcohols with acyl halides or carboxylic anhydrides to produce the corresponding optically active secondary alcohols have been developed.^{1,2} On the other hand, we have established the direct coupling reactions of free carboxylic acids with alcohols or amines using substituted benzoic anhydrides to produce the desired carboxylic acid derivatives.³ For example, nearly equimolar amounts of carboxylic acids and alcohols (or ω -hydroxycarboxylic acids) react in the presence of 2-methyl-6-nitrobenzoic anhydride (MNBA) with nucleophilic catalysts, such as 4-(dimethylamino)pyridine (DMAP) or 4-(dimethylamino)pyridine *N*-oxide (DMAPO), to produce the corresponding carboxylic esters (or lactones) in high yields as shown in **Scheme 1**.

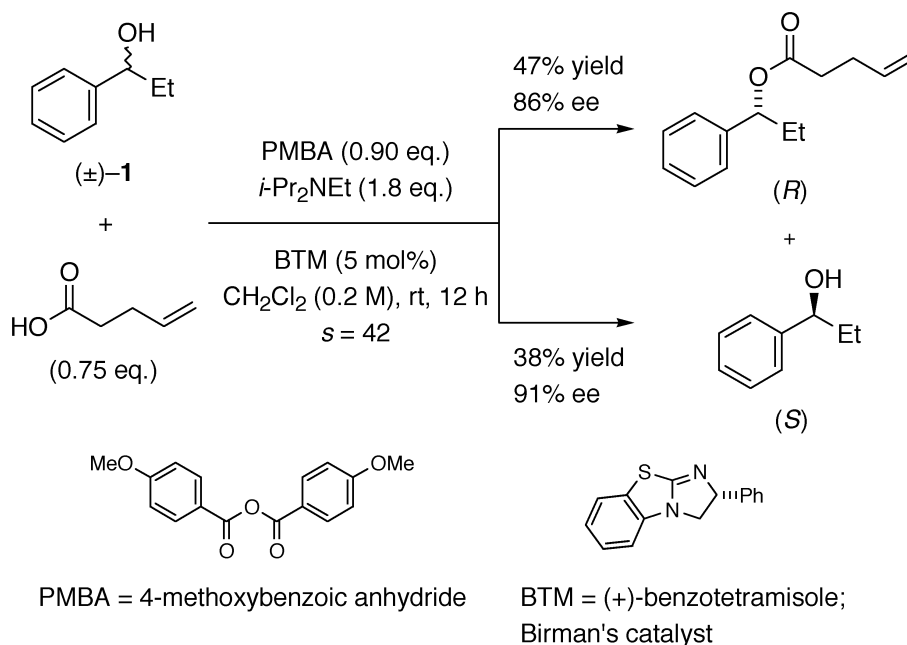


Scheme 1. Effective Synthesis of Carboxylic Esters and Lactones Using MNBA

During the course of our research to use benzoic anhydride and its relatives as effective coupling reagents, a novel and useful kinetic resolution of racemic secondary alcohols with free and achiral carboxylic acids by the promotion of symmetric benzoic anhydrides and chiral catalysts was successfully developed in 2007 (**Scheme 2**).⁴ In this reaction, the tetramisole-type chiral reagents, such as (+)-benzotetramisole (BTM), created by Birman⁵ effectively promoted the kinetic resolution of the racemic 1-phenyl alkanols in the presence of benzoic anhydride (Bz₂O) or 4-methoxybenzoic anhydride (PMBA); however, unsatisfactory chemoselectivities of the desired aliphatic esters to the benzoic esters were sometimes observed in the reaction using bulky carboxylic acids.

Because we had examined only several substituted aromatic anhydrides as coupling reagents in the preliminary research on the kinetic resolution of racemic alcohols, we planned to develop more effective reaction for providing the optically active 1-phenyl alkanols with high enantio- and chemoselectivities

starting from racemic alcohols with free carboxylic acids using our mixed anhydride formation technology.



Scheme 2. Asymmetric Esterification of Racemic Secondary Alcohols with Free Carboxylic Acids Using PMBA Catalyzed by BTM

First, the reactions of the racemic 1-phenyl-1-propanol ($(\pm)\text{-1}$) and 3-phenylpropionic acid with several typical symmetric anhydrides were chosen as model cases for the optimization of the coupling reagent structure (**Table 1**). Similar to the results in the preliminary studies of the kinetic resolution of secondary alcohols,⁴ it was found that PMBA and Bz_2O were very useful dehydration promoters to afford the desired carboxylic esters in high ee's (Entries 3, and 4), but MNBA, a very powerful coupling reagent especially for lactonization, has a structure unsuitable for the kinetic resolution of the racemic alcohols (Entry 1). We further tried to introduce other substituents on the 2- and 6-positions of the aromatic rings of the benzoic anhydride to provide a hindrance near the carboxyl groups; however, only a trace amount of the desired carboxylic ester was obtained when the reaction was carried out in the presence of 2,4,6-trimethylbenzoic anhydride as shown by Entry 2. Next, we focused on utilizing saturated carboxylic anhydrides, such as cyclohexane carboxylic anhydride, because it is assumed that these compounds have the appropriate steric bulkiness near the local carbonyl groups in the mixed anhydrides formed in situ. Actually, the desired (R)-ester **2** was obtained in 30% yield with a high enantioselectivity (90% ee) as described in Entry 5, but the chemoselectivity of **2** over **3** was unsatisfactory (72 / 28). We next planned to use pivalic anhydride (Piv_2O) or trifluoroacetic anhydride (TFAA) as shown in Entries 6 and 7, and it was then discovered that the former anhydride very effectively accelerated the desirable reaction for providing the optically active **2** with a high enantioselectivity (91% ee, s -value = 47) and with an excellent chemoselectivity (**2** / **3** = >99 / <1, 42%

chemical yield of **2**, not detected forming **3** by HPLC). Based on the results as shown in **Table 1**, it was also determined that the esterification using Piv₂O as a coupling reagent gave better chemical yield of the optically active ester **2** than that of the reaction promoted by PMBA (Compare results in Entries 6 and 3).

Table 1. Kinetic Resolution of (±)-1-Phenyl-1-propanol Using Several Kinds of Symmetric Anhydrides

(±)-1 Ph(CH₂)₂CO₂H (0.5 eq.) Anhydride (0.6 eq.) <i>i</i>-Pr₂NEt (1.2 eq.) BTM (5 mol%) CH₂Cl₂ (0.2 M), rt, 12 h 2 + (S)-1 BTM = R² = Ph(CH₂)₂; (<i>R</i>)-2 R² = X; 3						
Entry	Anhydride	Yield of 2 [%]	2 / 3 ^a	Yield of 1 [%]	ee (2 ; 1) [%]	<i>s</i>
1	MNBA	38	99 / 1 ^b	62	3 ; 2	1
2		<1	—	95	— ; 2	—
3	PMBA	37	97 / 3 ^c	51	90 ; 57	32
4		47	98 / 2 ^d	47	87 ; 86	39
5		30	72 / 28 ^e	45	90 ; 56	32
6	Piv ₂ O	42	>99 / <1 ^f	44	91 ; 77	47
7	TFAA	16	N/A ^g	75	83 ; 17	13
8	none	0	—	93	— ; 1	—

a) Alkyl group in the acyl part (R² = X) in **3** is as follows;

b) X = 2-Me-6-NO₂C₆H₃; c) X = 4-MeO-C₆H₄; d) X = Ph; e) X = *c*-Hex; f) X = *t*-Bu.

g) 1-Phenyl-1-propyl trifluoroacetate (X = CF₃) was not detected due to its instability.

Next, several 2,2-disubstituted propionic anhydrides and those derivatives were examined as coupling reagents for the kinetic resolution of (±)-**1** as depicted in **Table 2**. Substitution of the methyl group(s)

Table 2. Kinetic Resolution of (±)-1-Phenyl-1-propanol Using Several 2,2-Disubstituted Propionic Anhydrides and Other Bulky Anhydrides

(±)-1 Ph(CH₂)₂CO₂H (0.5 eq.) Anhydride (0.6 eq.) <i>i</i>-Pr₂NEt (1.2 eq.) BTM (5 mol%) CH₂Cl₂ (0.2 M), rt, 12 h R² = Ph(CH₂)₂; (<i>R</i>)-2 R² = X; 3 BTM =						
Entry	Anhydride	Yield of 2 [%]	2 / 3 ^a	Yield of 1 [%]	ee (2 ; 1) [%]	<i>s</i>
1		42	>99 / <1 ^b	44	91 ; 77	47
2		43	>99 / <1 ^c	50	85 ; 70	27
3		34	>99 / <1 ^d	50	89 ; 67	34
4		21	>99 / <1 ^e	68	93 ; 19	34
5		24	>99 / <1 ^f	61	92 ; 27	31
6		27	>99 / <1 ^g	62	93 ; 39	40
7		41	88 / 12 ^h	56	91 ; 60	37
8		0	—	80	— ; 0	—

a) Alkyl group in the acyl part (R² = X) in **3** is as follows;b) X = *t*-Bu; c) X = CMe₂Ph; d) X = CMePh₂; e) X = CPh₃; f) X = 1-methylcyclohexyl;

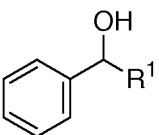
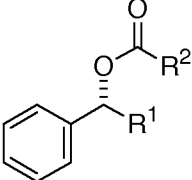
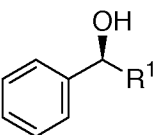
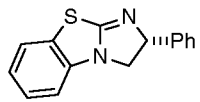
g) X = 1-phenylcyclopentyl; h) 1-adamantyl.

by phenyl group(s) at the α -position afforded results similar to that for the reaction using Piv₂O (Entries 2 and 3; cf. 1), but triphenylacetic anhydride (TPHAA) reduced the reactivity which lowered the chemical yield of (*R*)-**2** (Entry 4). Other anhydrides having peculiar structures, such as 1-methylcyclohexanecarboxylic anhydride and 1-phenylcyclopentanecarboxylic anhydride, also gave slightly lower yields of the desired ester **2** and afforded similar good chemo- and enantioselectivities compared to those of the reaction using TPHAA (Entries 5 and 6). Although the use of 1-adamantanecarboxylic anhydride produced the desired (*R*)-ester **2** with a high enantioselectivity (91% ee, *s*-value = 37), the ratio of the amount of resulting **2** to that of **3** was insufficient (88 / 12 in Entry 7). It was noted that the use of dicyclohexylacetic anhydride did not produce the target compound **2** at all and almost of all the unreacted alcohol ($\pm$)-**1** was recovered as shown in Entry 8 because of extremely low reactivity of the anhydride.

A variety of examples of the kinetic resolution of benzylic alcohols **4** possessing aliphatic substituents at the C-1 position with typical aliphatic carboxylic acids by promotion with 2,2-disubstituted propionic anhydrides and BTM is listed in **Table 3**. We generally employed Piv₂O as the coupling reagent for the present asymmetric ester-forming reaction because Piv₂O is widely used in the conventional mixed anhydride method to produce the corresponding carboxylic esters and amides from the free carboxylic acids. All reactions afforded very good results and the corresponding (*R*)-carboxylic esters **5** and the recovered (*S*)-alcohol **4** were obtained in high ee (*s* = >26, Entries 1-14). By changing the sterically hindrance of the substituents R¹ at the C-1 position of the benzylic alcohols, it was proved that larger groups afforded better enantioselectivities (Compare results in Entries 1, 3, 10, and 13; Entries 2, 4, 11, and 14). All the *s*-values in Entries 3-7 are excellent (*s* = 39-47), therefore, it is postulated that there is not a very large steric effect on the alkyl substituent of the carboxylic acid parts in the reaction using Piv₂O. However, when methoxyacetic acid was used as an acid component in this reaction under the influence of Piv₂O, an unsatisfactory chemoselectivity of **5** over the corresponding pivalate **6** (29 / 71) was observed as shown in Entry 8. Fortunately, the chemoselectivity was improved by employing more bulky carboxylic anhydrides, such as 2-methyl-2-phenylpropionic anhydride (MPPRA), as shown in Entry 15. When the kinetic resolution of the racemic 2-methyl-1-phenyl-1-propanol was carried out using 3-phenylpropionic acid with Piv₂O (Entry 11), the desired ester was obtained in 44% yield with a very high enantioselectivity (99.7% ee) that revealed an excellent *s*-value (*s* = 1580). Furthermore, it was also determined that MPPRA and 2,2-diphenylpropionic anhydride (DPPRA) function as suitable coupling reagents in the reaction of 1-phenyl-1-propanol or 2,2-dimethyl-1-phenyl-1-propanol with free carboxylic acids giving the desired products with high enantioselectivities (Entries 16-19; *s* = 25-41).

Typical procedure for the synthesis of optically active esters from racemic secondary alcohols using pivalic anhydride with BTM is described: To a solution of pivalic anhydride (36.5 μ L, 0.180 mmol) and 3-phenylpropionic acid (22.5 mg, 0.150 mmol) in dichloromethane (1.5 mL) at room temperature were added diisopropylethylamine (62.9 μ L, 0.360 mmol), BTM (3.8 mg, 0.015 mmol) and ($\pm$)-2-methyl-1-phenyl-1-propanol (**4**, R¹ = *i*-Pr) (45.0 mg, 0.300 mmol). The mixture was stirred for

Table 3. Synthesis of a Variety of Optically Active Carboxylic Esters and Alcohols

 (±)-4 RCO₂H (0.5 eq.) Piv₂O (0.6 eq.) <i>i</i>-Pr₂NEt (1.2 eq.) BTM (5 mol%) CH₂Cl₂ (0.2 M), rt, 12 h  5 +  (S)-4 BTM =  R² = R; (5) R² = <i>t</i>-Bu; (6)						
Entry	R ¹	R	5 / 6	Yield (5 ; 4) [%]	ee (5 ; 4) [%]	<i>s</i>
1	Me	Et	>99 / <1	40 ; 37	85 ; 70	26
2	Me	Ph(CH ₂) ₂	>99 / <1	42 ; 41	89 ; 65	33
3	Et	Et	>99 / <1	38 ; 47	89 ; 79	43
4	Et	Ph(CH ₂) ₂	>99 / <1	42 ; 44	91 ; 77	47
5	Et	Ph(CH ₂) ₃	>99 / <1	44 ; 53	90 ; 72	41
6	Et	Me ₂ CH(CH ₂) ₂	>99 / <1	41 ; 53	90 ; 71	40
7	Et	CH ₂ =CH(CH ₂) ₂	>99 / <1	48 ; 42	89 ; 74	39
8	Et	MeOCH ₂	29 / 71	10 ; 44	87 ; 60	26
9	Et	<i>o</i> -C ₆ H ₁₁	>99 / <1	39 ; 52	95 ; 60	73
10	<i>i</i> -Pr	Et	>99 / <1	42 ; 50	91 ; 82	53
11	<i>i</i> -Pr	Ph(CH ₂) ₂	>99 / <1	44 ; 56	99.7 ; 77	1580
12	<i>i</i> -Pr	<i>o</i> -C ₆ H ₁₁	>99 / <1	34 ; 64	89 ; 47	28
13	<i>t</i> -Bu	Et	>99 / <1	32 ; 60	97 ; 48	101
14	<i>t</i> -Bu	Ph(CH ₂) ₂	>99 / <1	41 ; 47	95 ; 70	81
15 ^a	Et	MeOCH ₂	>99 / <1 ^b	25 ; 75	78 ; 25	11
16 ^a	Et	Ph(CH ₂) ₂	>99 / <1 ^b	43 ; 50	85 ; 70	27
17 ^a	<i>t</i> -Bu	Et	>99 / <1 ^b	29 ; 69	93 ; 43	41
18 ^c	Et	Ph(CH ₂) ₂	>99 / <1 ^d	34 ; 50	89 ; 67	34
19 ^{c,e}	<i>t</i> -Bu	Et	>99 / <1 ^d	32 ; 60	88 ; 46	25

a) 2-Methyl-2-phenylpropionic anhydride (MPPRA) was used as the coupling reagent instead of Piv₂O.

b) Alkyl group in the acyl part (R²) in **6** is not *t*-Bu but PhMe₂C in this case.

c) 2,2-Diphenylpropionic anhydride (DPPRA) was used as the coupling reagent instead of Piv₂O.

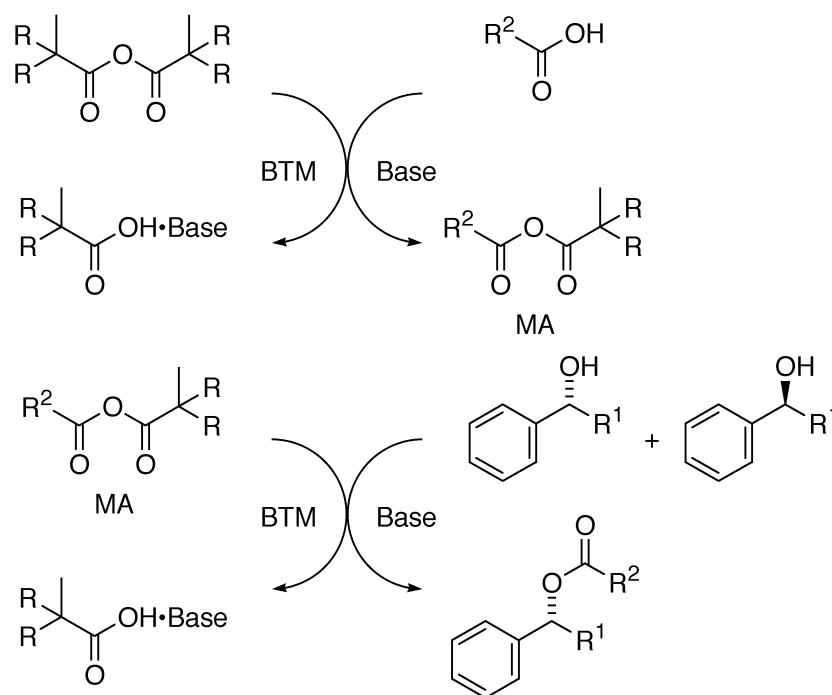
d) Alkyl group in the acyl part (R²) in **6** is not *t*-Bu but Ph₂MeC in this case.

e) Ten mol% of BTM was used.

12 h at rt, and then quenched with saturated aqueous sodium hydrogencarbonate. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography on silica gel to afford the corresponding ester **5** (37.3 mg, 44%, 99.7% ee) and the recovered optically active alcohol **4** (25.2 mg, 56%, 77% ee). [$s = 1580$, Table 3, Entry 11] **(R)-2-Methyl-1-phenylpropyl 3-phenylpropanoate** ((*R*)-**5**, $R^1 = i\text{-Pr}$): HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.5 mL/min); $t_R = 10.2$ min (99.85%), $t_R = 13.9$ min (0.15%); IR (neat): 3030, 1734, 1604, 1496, 751, 699 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.28–7.02 (m, 10H, Ph), 5.41 (d, $J = 7.5$ Hz, 1H, 1-H), 2.88 (t, $J = 7.5$ Hz, 2H, 2'-H), 2.65–2.53 (m, 2H, 3'-H), 2.07–1.83 (m, 1H, 2-H), 0.85 (d, $J = 7.0$ Hz, 3H, Me), 0.70 (d, $J = 7.0$ Hz, 3H, Me); ^{13}C NMR (CDCl_3): δ 172.1, 140.4, 139.6, 128.4, 128.2, 128.1, 127.6, 127.0, 126.2, 81.0, 36.0, 33.4, 30.9, 18.6, 18.4; HR MS: calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 305.1512, found 305.1520.

The assumed reaction pathway is illustrated in **Scheme 3**. First, a mixed anhydride (MA) forms as a key intermediate in situ from the 2,2-disubstituted propionic anhydride and free carboxylic acid by the promotion of basic catalysts. Actually, when 3-phenylpropionic acid was treated with Piv_2O in the presence of triethylamine with BTM under the standard reaction conditions, the facile formation of the mixed anhydride was observed by a ^1H NMR experiment ($\text{Piv}_2\text{O} : \text{MA} = \text{ca. } 5 : 1$). Furthermore, we initially generated the MA by the reaction of 3-phenylpropionic acid with pivaloyl chloride in the presence of a stoichiometric amount of diisopropylethylamine prior to use it as a reagent for the kinetic resolution of ($\pm$)-**1** catalyzed by BTM. According to the hypothesis on the reaction mechanism described in **Scheme 3**, we succeeded to obtain the desired ester **2** with good enantioselectivity (90% ee, 44% chemical yield) by the treatment of the MA with BTM and ($\pm$)-**1**. The unreacted alcohol **1** was recovered in 53% yield with 62% ee so that high s -value ($s = 35$) was obtained in this stepwise procedure for the kinetic resolution of ($\pm$)-**1** similar to the result of the direct esterification of 3-phenylpropionic acid using Piv_2O ($s = 47$, **Table 2**, Entry 1). In the second cycle, the mixed anhydride will be activated by BTM which then reacts with a half amount of the nucleophilic alcohol to afford the desired chiral carboxylic ester with a high ee. On the other hand, the remaining half of the nucleophile would be recovered as an enantiomer of the consumed alcohol. The first cycle does not include the chiral induction stage, and the efficiency of the kinetic resolution totally depends on the structure of the intermediary mixed anhydride; therefore, the second cycle should be the stereo-determining step in this multiple transacylation process.

In summary, we have developed a method for providing the optically active benzylic alcohols possessing a variety of aliphatic substituents at the C-1 position by the kinetic resolution of racemic alcohols using free carboxylic acids with 2,2-disubstituted propionic anhydrides and BTM. Evaluation of the efficiency of the asymmetric esterification using several anhydrides derived from aliphatic carboxylic acids were carried out by comparing the efficiencies of the kinetic resolution of ($\pm$)-1-phenyl-1-propanol. It was found that not only Piv_2O was a very widely usable reagent to produce the corresponding esters in



Scheme 3. Proposed Reaction Pathway of the Kinetic Resolution

high ee in the presence of BTM, but several kinds of 2,2-disubstituted propionic anhydrides, such as MPPRA and DPPRA, were also applicable as effective coupling reagents for generating the optically active esters and alcohols with high ee's under mild reaction conditions. This protocol directly produces chiral carboxylic esters from the free carboxylic acids and racemic secondary alcohols by utilizing the transacylation process to generate mixed anhydrides from the acid components and sterically hindered carboxylic anhydrides under the influence of chiral catalysts. Further studies of the present method to provide chiral carboxylic acid derivatives and other applications of this new protocol for the syntheses of useful complex molecules are now in progress.

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