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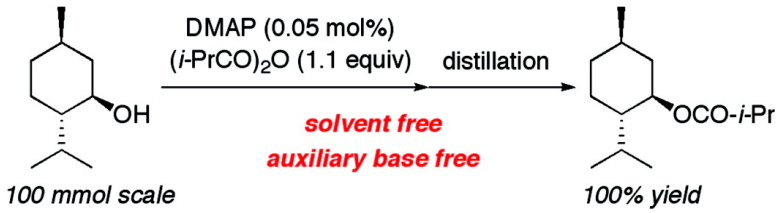

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Widely Useful DMAP-Catalyzed Esterification under Auxiliary Base- and Solvent-Free Conditions

Akira Sakakura, Kimio Kawajiri, Takuro Ohkubo, Yuji Kosugi, and Kazuaki Ishihara*

Contribution from the Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Received August 3, 2007; E-mail: ishihara@cc.nagoya-u.ac.jp

Abstract: With regard to atom economy and E-factor, catalytic condensation of carboxylic acids with equimolar amounts of alcohols is the most desirable. Although several highly active dehydration catalysts have been reported, more efficient alternatives are still strongly needed because the dehydrative esterification of tertiary alcohols, phenols, acid-sensitive alcohols, amino acids, and hardly soluble alcohols has never proceeded satisfactorily. Here we report new insights into the classical DMAP-catalyzed acylation of alcohols: surprisingly, only a 0.05−2 mol % of DMAP can efficiently promote acylation of alcohols with acid anhydrides under auxiliary base- and solvent-free conditions to give the corresponding esters in high yields. Furthermore, we achieved the recovery and reuse of commercially available polystyrene-supported DMAP without using any solvents. These serendipitous findings provide widely useful and environmentally benign esterification methods, which might be more practical and reliable than catalytic dehydrative condensation methods, in particular, for the less reactive alcohols which hardly condense with carboxylic acid directly.

Introduction

Catalytic dehydrative condensations between equimolar amounts of carboxylic acids and alcohols have been developed as atom-economically ideal synthetic methods of esters over the decade.[1] However, these methods are problematic for the esterification of sterically demanding tertiary alcohols, less nucleophilic phenols, acid-sensitive allyl alcohols, amino alcohols, and alcohols which are hardly soluble in less polar solvents. Therefore, more efficient alternatives are still in strong demand. 4-(*N*,*N*-Dimethylamino)pyridine (DMAP, **1**) is a very effective nucleophilic base catalyst for the esterification of alcohols with acid anhydrides[2−4] and other related reactions.[5,6] The **1**-catalyzed acylation with acid anhydrides is advantageous for the acylation of less reactive alcohols since the reactivity of acid anhydrides is much higher than that of carboxylic acids. However, it had been strongly believed for a long period that the classical **1**-catalyzed acylation of alcohols should be inferior to the dehydrative condensation with regard to atom economy and E-factor, because more than 1 equiv of an auxiliary base would be required as a scavenger of the carboxylic acid. In contrast, although Lewis acids such as $Sc(OTf)_3$,[7] MoO_2Cl_2,[8] and $Bi(OTf)_3$[9] can catalyze the acylation of alcohols with acid anhydrides without an auxiliary base, the substrate scope is limited because of strongly acidic conditions.

Here we report new insights into the classical **1**-catalyzed acylation of alcohols: surprisingly, only 0.05−2 mol % of **1** can efficiently promote acylation of alcohols (up to 100 mmol scale) with equimolar amounts of acid anhydrides under auxiliary base- and solvent-free conditions to give the corresponding esters quantitatively. Notably, distillable esters can be synthesized without using solvents throughout the reaction process including purification.

Results and Discussion

Effects of Solvent and Auxiliary Base on the DMAP-Catalyzed Acylations. Recently, Zipse and co-workers proposed a mechanism for the **1**-catalyzed acetylation of alcohols (Figure

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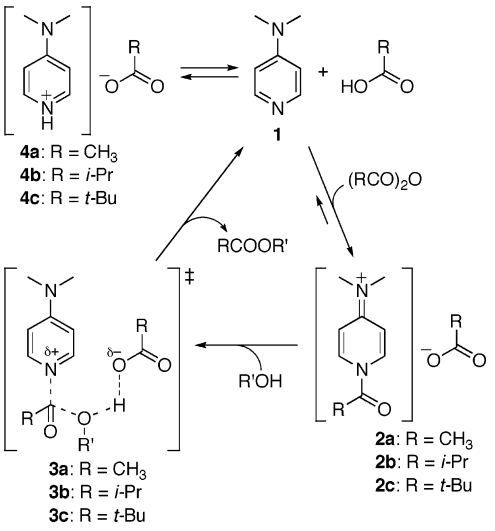

Figure 1. Proposed mechanism of the DMAP-catalyzed acylation.

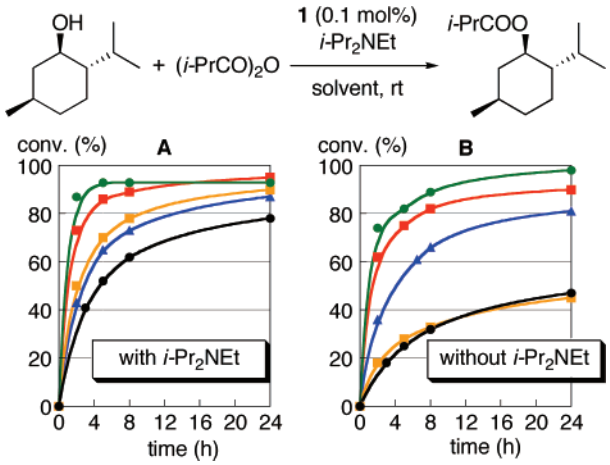

Figure 2. Solvent effect in the DMAP-catalyzed isobutyrylation of *l*-menthol. The reaction of *l*-menthol (5 mmol) was conducted with $(i\text{-PrCO})_2O$ (5 mmol) in the presence of **1** (0.1 mol %) in solvent (5 mL): green circles, no solvent; red squares, heptane; blue triangles, THF; orange squares, CH_3CN; black circles, CH_2Cl_2.

1).[10] The reaction proceeds via acetylpyridinium intermediate **2a**. In the nucleophilic addition of alcohols (R′OH) toward **2a**, acetate anion (AcO^-) abstracts the proton of alcohols. The reaction of **2a** with alcohols produces acetates (R′OAc) and the acetate salt (**4a**) of **1** via transition state **3a**. This step is thought to be the rate-determining step. In the presence of a stoichiometric amount of auxiliary base such as triethylamine, **1** is effectively regenerated (**4** → **1**).

In principle, **1**-catalyzed acylation should proceed even in the absence of an auxiliary base, since carboxylate anions rather than auxiliary bases deprotonate alcohols (Figure 1).[11] We considered that the solvent effect must play a key role in the effective regeneration of **1** without an auxiliary base. First of all, the solvent effect was examined in the **1**-catalyzed isobutyrylation of *l*-menthol (Figure 2). The reaction was conducted with isobutyric anhydride (1.0 equiv) in the presence of **1** (0.1 mol %) in several solvents. In the presence of *i*-Pr_2NEt (graph A), the reaction proceeded more smoothly in a less-polar solvent such as heptane (red line) than in a polar solvent such as acetonitrile (orange line) or dichloromethane (black line).[12] Interestingly, the reaction proceeded rapidly even without solvent (green line), as reported by Hassner and co-workers.[11a]

As expected, the **1**-catalyzed isobutyrylation proceeded smoothly even in the absence of an auxiliary base without the inactivation of **1** (graph B). Very interestingly, the reactivity of **1**-catalyzed isobutyrylation under auxiliary base-free conditions is more dependent on the solvent than in the presence of *i*-Pr_2NEt (1.0 equiv). The reaction proceeded very rapidly under solvent-free conditions (green line) or in a less-polar solvent such as heptane (red line). In contrast, the reaction in acetonitrile (orange line) or dichloromethane (black line) under base-free conditions exhibited much lower reactivity than that in the presence of *i*-Pr_2NEt. The effective regeneration of **1** in less-polar heptane might result in excellent reactivities, while polar solvent caused preferential formation of the ammonium salt **4b** under base-free conditions and decreased the reactivity. The higher reactivity under solvent-free conditions might be primarily attributed to the higher concentration, since the reaction mixture under solvent-free conditions was a little polar than that with heptane.[13]

Next, the **1**-catalyzed acetylation, isobutyrylation, and pivaloylation of *l*-menthol were examined under solvent-free conditions (graphs C, E, G) and in heptane (graphs D, F, H) (Figure 3). Solvent-free acetylation in the absence of an auxiliary base showed lower reactivity than that in the presence of *i*-Pr_2NEt despite higher concentration of *l*-menthol (3.6 M without *i*-Pr_2NEt; 2.1 M with *i*-Pr_2NEt) (graph C). The high reactivity of acetylation in the presence of *i*-Pr_2NEt would be primarily attributed to the effective promotion by *i*-Pr_2NEt. High polarity and acidity of acetic acid might decelerate the acetylation under the base- and solvent-free conditions. Actually, the use of heptane as solvent efficiently promoted the acetylation under the base-free conditions despite lower concentration *l*-menthol (3.6 M under solvent-free conditions; 0.93 M in heptane) (graph D). The reactivity of isobutyrylation was almost independent of the presence of *i*-Pr_2NEt and heptane (graphs E and F). Interestingly, under the solvent-free conditions, pivaloylation without *i*-Pr_2NEt (2.5 M *l*-menthol) gave better results than with *i*-Pr_2NEt (1.7 M *l*-menthol) (graph G). Since pivalic acid (pK_a 5.03) is a weaker acid than acetic acid (pK_a 4.76), **1** would regenerate more efficiently in pivaloylation than in acetylation under base-free conditions. Furthermore, more basic pivalate anion acted as a base to efficiently promote pivaloylation under base-free conditions. On the other hand, less-basic acetate anion did not work as an efficient base, and the reactivity of acetylation largely depended on auxiliary bases. *i*-Pr_2NEt did not promote the pivaloylation reaction, but lowered the concentration of *l*-menthol to decelerate the reaction.

DMAP-Catalyzed Acylation of Alcohols with Acid Anhydrides under Solvent- and Auxiliary Base-Free Conditions. To explore the generality and scope of **1**-catalyzed acylation under base- and solvent-free conditions, the reaction was examined with various alcohols (Table 1). Acylations of not only primary alcohols but also secondary alcohols proceeded

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(13) See Supporting Information for estimation of concentration of the reaction mixture.

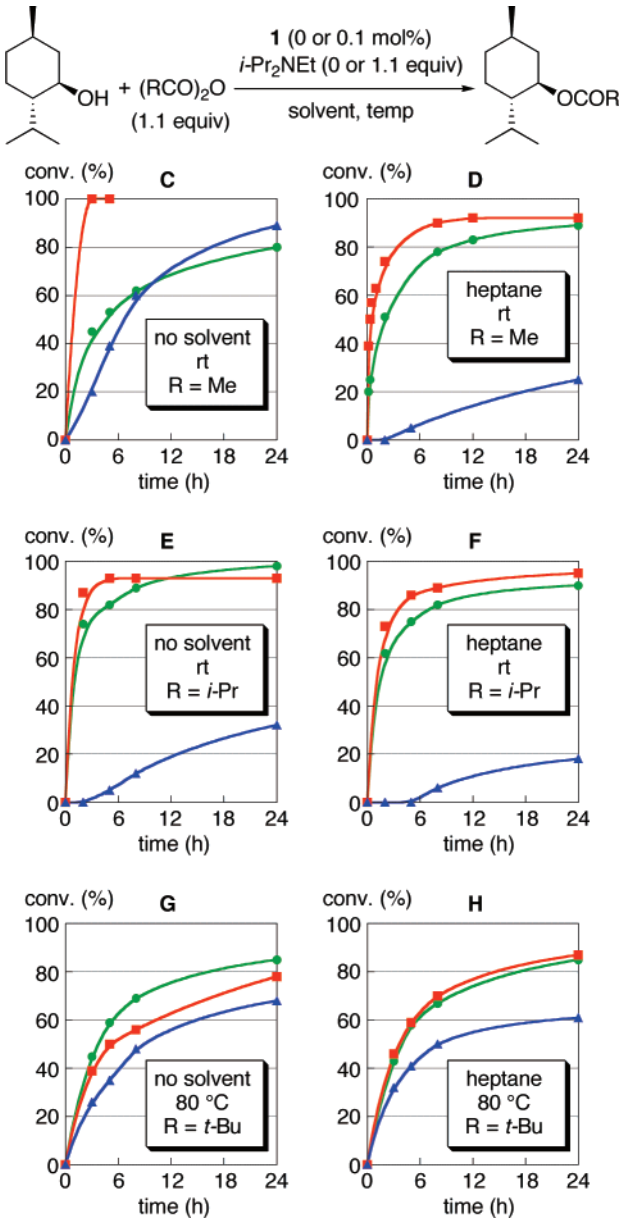
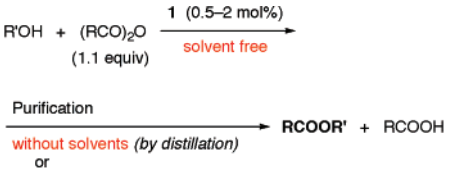


Figure 3. Effect of auxiliary base on the DMAP-catalyzed acetylation, isobutyrylation, and pivaloylation of *l*-menthol with acid anhydride. The reaction of *l*-menthol (5 mmol) was conducted with $(RCO)_2O$ (5.5 mmol) under solvent-free conditions or in heptane (5 mL): red squares, **1** (0.1 mol %) and *i*-Pr_2NEt (1.1 equiv); green circles, **1** (0.1 mol %) without *i*-Pr_2NEt; blue triangles, *i*-Pr_2NEt (1.1 equiv) without **1**.

Table 1. DMAP-Catalyzed Acylation of Alcohols with Acid Anhydrides under Base- and Solvent-Free Condition[a]

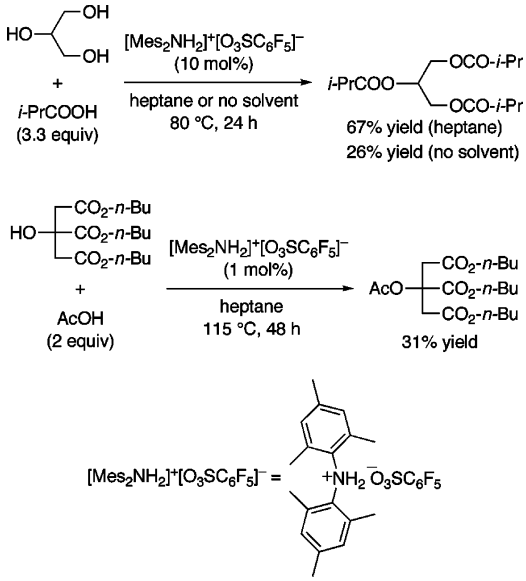


entry	product	R	conditions (°C, h)	yield (%)
1		Me	rt, 6	94
2	$RCOO(CH_2)_3Ph$	*i*-Pr	rt, 2	93
3		*t*-Bu	100, 3	96
4		Me	rt, 9	84
5[b]		*i*-Pr	rt, 9	98
6[c]	OCOR	*i*-Pr	50, 24	100
7		*t*-Bu	100, 8	90
8[d]	RCOO, OCOR, OCOR	Me	rt, 19 then 50, 3	97
9[d]		*i*-Pr	rt, 5	99
10	RCOO, OMe, RCOO, OCOR, OCOR	Me	50, 6	93
11[e]		*i*-Pr	rt, 24	100
12[e]	RCOO, RCOO, RCOO, OCOR	*i*-Pr	rt, 69	93
13	RCOO, CO_2-*n*-Bu, CO_2-*n*-Bu, CO_2-*n*-Bu	Me	100, 24	93
14		Me	100, 24	0 (53)[f]
15[g]	RCOO, Ph	Me	reflux, 24	88 (0)[f]
16		*i*-Pr	100, 24	88 (0)[f]
17	RCOO	Me	rt, 24	88
18		*i*-Pr	rt, 24	91
19	RCOO, NO_2	*i*-Pr	rt, 19	99
20	O, O-*n*-C_8H_{17}		50, 3	91
21	O, O, OMe		50, 3	94

[a] Unless otherwise noted, the reaction of alcohol (5 mmol) and acid anhydride (5.5 mmol) was conducted with **1** (0.5 mol %). [b] The reaction of *l*-menthol (50 mmol) was conducted with isobutyric anhydride (55 mmol). [c] The reaction of *l*-menthol (100 mmol) with isobutyric anhydride (110 mmol) was conducted with **1** (0.05 mol %). [d] The reaction of glycerol (5 mmol) with an acid anhydride (16.5 mmol) was conducted in the presence of **1** (1.5 mol %). [e] The reaction of methyl α-D-glucopyranoside and ascorbic acid (5 mmol) with an acid anhydride (22 mmol) was conducted in the presence of **1** (2.0 mol %). [f] Isolated yield of α-methylstyrene. [g] The reaction was conducted in heptane (5 mL, bp 98 °C).

well (entries 1−7). Importantly, esters, which could be purified by distillation, were synthesized without using solvents throughout the synthetic process: after consuming an alcohol, distillation from the reaction mixture gave a pure product along with a carboxylic acid recovered. The present protocol could be easily applied to a large-scale process, and the isobutyrylation of *l*-menthol (100 mmol) catalyzed by **1** (0.05 mol %) gave the corresponding ester in quantitative yield (entry 6). The present protocols could also be applied to acylation of polyols. Acylation of glycerol, methyl α-D-glucopyranoside and L-ascorbic acid gave the corresponding triesters or tetraesters in almost quantitative yields (entries 8−12). In contrast, Hf(IV) salts and Zr(IV) salts are not adapted to 1,2-diols owing to tight chelation with metal ions.[1c] Ester condensation between glycerol and isobutyric acid catalyzed by dimesitylammonium pentafluorobenzenesulfonate[1d−f] gave the corresponding triester in low yield because of quite low solubility of glycerol in heptane (Scheme 1). The present protocol could also work with less reactive alcohols such as tertiary alcohols and sterically demanding aromatic alcohols. The acetylation of tributyl citrate under base- and solvent-free conditions gave the corresponding acetate in 93% yield (entry 13), while ester condensation of tributyl citrate with acetic acid catalyzed by dimesitylammonium pentafluorobenzenesulfonate gave the corresponding acetate in 31% yield (Scheme 1). Acetyl tributyl citrate is a useful plasticizer. Acetylation of α,α-dimethylbenzyl alcohol gave α-methylstyrene as an elimination byproduct under solvent-free conditions, probably due to the

Scheme 1. Ester Condensation of Glycerol and Tributyl Citrate Catalyzed by *N,N*-Dimesitylammonium Pentafluorobenznensulfonate



high acidity of the reaction media (entry 14) as well as Lewis acid catalysis.[7a,b] This problem could be evaded by the use of heptane, to give the acetylation product in 88% yield along with no elimination byproduct (entry 15). It is conceivable that the lower polarity of heptane suppressed the formation of the tertiary carbocation. The acylations of 2,4,6-trimethylphenol and *p*-nitrophenol also proceeded smoothly (entries 17−19). Furthermore, acylation with 3,3-dimethylacrylic anhydride, a less reactive α,*β*-unsaturated acid anhydride, gave the corresponding esters in good isolated yields (entries 20, 21).

DMAP-Catalyzed Esterification between Alcohols and Carboxylic Acids. Next, the esterification between alcohols and carboxylic acids was examined by the mixed anhydride method using pivalic anhydride under base- and solvent-free conditions (Table 2).[7a,b,14] The reaction was thought to proceed via the corresponding mixed anhydrides. Since the counteranion of the acylpyridinium intermediate is pivalate, the reaction should proceed well even under base- and solvent-free conditions. As expected, in the presence of pivalic anhydride (1.1 equiv) and **1** (0.5 mol %), the reaction of both saturated and unsaturated carboxylic acids proceeded under base- and solvent-free conditions. After recovering pivalic acid in vacuo, the corresponding esters could be isolated without using solvents (by distillation) or with minimal solvents (passing through a short SiO_2 pad). α-Tocopherol, a sterically demanding phenol, could be converted to the linoleic acid ester, which is a serum cholesterol-lowering drug, in 88% isolated yield. Esterification of *N*-Boc-L-phenylalanine with 1-octanol gave the corresponding ester in 92% yield with complete retention of its chiral center. The reaction of glycerol and methyl α-D-glucopyranoside with oleic acid gave the corresponding triester and tetraester in respective yields of 93 and 94%.

Recover and Reuse of Polystyrene-Supported DMAP. One major problem associated with the use of soluble catalysts lies in recovery of the catalyst from the reaction medium. A simple solution is to immobilize the catalyst on a polymeric matrix.

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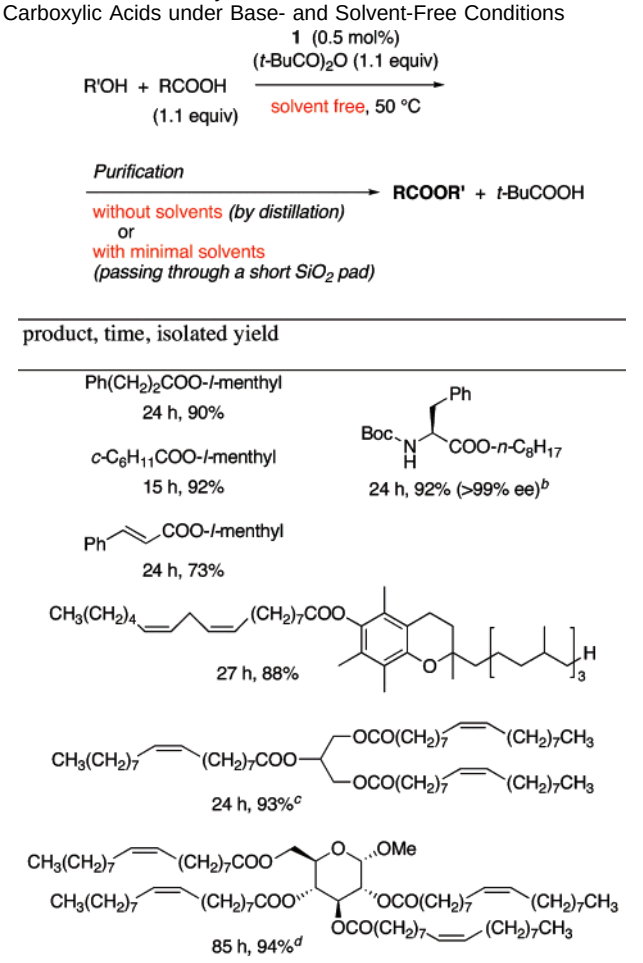
Table 2. DMAP-Catalyzed Esterification of Alcohols and Carboxylic Acids under Base- and Solvent-Free Conditions



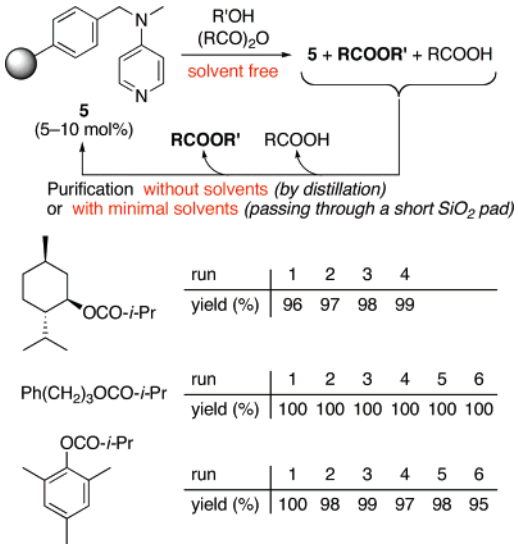
[a] Unless otherwise noted, the reaction of alcohol (1 mmol) with carboxylic acid (1.1 mmol) was conducted with **1** (0.5 mol %) and pivalic anhydride (1.1 mmol) at 50 °C. [b] Optical purity of the product. [c] The reaction of glycerol (1 mmol) and oleic acid (3.3 mmol) was conducted with **1** (1.5 mol %) and pivalic anhydride (3.3 mmol). [d] The reaction of methyl α-D-glucopyranoside (1 mmol) and oleic acid (4.4 mmol) was conducted with **1** (2.0 mol %) and pivalic anhydride (4.4 mmol).

Acylation of alcohols with isobutyric anhydride was efficiently promoted by commercially available polystyrene-supported DMAP **5** (purchased from Aldrich) under auxiliary base- and solvent-free conditions (Scheme 2). Furthermore, we achieved its recovery and reuse without any solvents: the residual salt of **5** with carboxylic acid, which was recovered by distillation, was reusable as a precatalyst, without any loss of reactivity, repeatedly. Immobilized catalyst **5** could also promote esterification of *l*-menthol with cyclohexanecarboxylic acid using pivalic acid under auxiliary base- and solvent-free conditions (Scheme 3). The recovered **5** could be reused more than three times without any loss of reactivity.

Conclusions

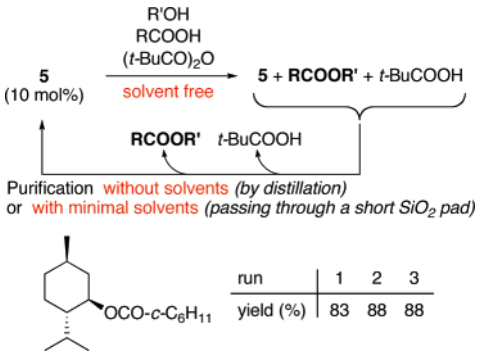
In conclusion, we have demonstrated that only 0.05−2 mol % of **1** could efficiently catalyze acylation of alcohols with acid anhydrides (1.0−1.1 equiv) under auxiliary base- and solvent-free conditions. Even less reactive alcohols, which hardly condense with carboxylic acids directly, were converted into the corresponding esters in high yields. Some esters were synthesized and isolated without using solvents throughout the

Scheme 2. Isobutyrylation of Alcohols Using Polystyrene-Supported DMAP **5** as a Recyclable Catalyst[a]



[a] The reaction of an alcohol (5 mmol) and acid anhydride (5.5 mmol) was conducted with **5** (5−10 mol %) at room temp for 12−48 h.

Scheme 3. Esterification of Alcohols with Carboxylic Acids Using **5** as a Recyclable Catalyst[a]



[a] The reaction of an alcohol (5 mmol) and an carboxylic acid (5.5 mmol) with pivalic anhydride (5.5 mmol) was conducted in the presence of **5** (10 mol %) at 50 °C for 24 h.

synthetic process. Furthermore, commercially available **5** could be recovered and reused without loss of reactivity, repeatedly. These serendipitous findings provide widely useful and highly atom-economical esterification methods, which might be more practical and reliable than catalytic dehydrative condensation, in particular, for the less reactive alcohols which hardly condense with carboxylic acid directly.

Experimental

Typical Procedure for Acylation of Alcohols with Acid Anhydrides (Table 1). To a mixture of *l*-menthol (7.81 g, 50 mmol) and DMAP (31 mg, 0.25 mmol) was added isobutyric anhydride (9.12 mL, 55 mmol) at ambient temperature. After being stirred at ambient temperature for 9 h, water (90 μL, 5.0 mmol) was added and then the mixture was stirred for 1 h. Purification by distillation under reduced pressure [bp. 98 °C at 0.0006 Torr (ULVAC VPC-050)] gave (1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)-cyclohexyl 2-methylpropanoate (11.1 g, 98% yield).

Typical Procedure for Esterification between Alcohols and Carboxylic Acids (Table 2). To a mixture of α-tocopherol (2.15 g, 5.0 mmol), linoleic acid (1.71 mL, 5.5 mmol), and DMAP (3.1 mg, 0.025 mmol) was added pivalic anhydride (1.07 mL, 5.5 mmol) at ambient temperature. After being stirred at 50 °C for 27 h, water (9 μL, 0.5 mmol) was added and the mixture was stirred at 50 °C for 1 h. The resultant mixture was concentrated under reduced pressure [ca. 0.0006 Torr (ULVAC VPC-050)] at 90 °C (bath temp) to recover the generated pivalic acid. The residue was passed through a short silica gel pad (10 g) using a mixture of hexane and ethyl acetate (100:1, 60 mL), to give α-tocopherol linoleate (3.05 g, 88% yield).

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Supporting Information Available: Experimental details, analytical data of new compounds. and ^{1}H, ^{13}C NMR data of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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