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Efficient acylation and transesterification catalyzed by dilithium tetra-*tert*-butylzincate at low temperatures

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ABSTRACT

The acylation and transesterification of alcohols with vinyl acetate and carboxylic esters were investigated in the presence of a catalytic amount (1–10 mol %) of dilithium tetra-*tert*-butylzincate (TBZL) as a catalyst. The acylation proceeded quantitatively at 0 °C within 1 h. The transesterification occurred for a wide range of combinations of esters and alcohols at 0 to –40 °C. To the best of our knowledge, this is the first successful transesterification at such low temperatures. The time–conversion plots for the transesterification show that the reaction reached equilibrium within 5 min at 0 °C. The reaction proceeded quantitatively by addition of molecular sieves 4A. In addition, the transesterification proceeded even in the presence of H₂O and amines.

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Introduction

Transesterification is a useful method for preparing various esters.¹ Acids² and bases³ are commonly used as catalysts to promote these reactions. However, severe conditions are generally required, that is, a high reaction temperature, long reaction time, and large amount of catalyst. Consequently, thermally sensitive functional groups undergo undesirable side reactions during the transesterification.

Effective catalysts for promoting transesterification at room temperature have been developed;^{4–9} for example, nitrogen–heterocyclic carbenes catalyze transesterification of carboxylic esters and acylation with vinyl acetate.⁴ The reactions are complete within a few hours, using catalytic amounts (0.5–5.0 mol %) of the carbenes. Et₂Zn (10 mol %) catalyzes transesterification (acylation) of benzyl alcohol (BnOH) with vinyl acetate at room temperature in the presence of *N*-phenyldiethanolamine (*N*-PDEA, 5 mol %).⁷ A μ -oxo-tetranuclear zinc cluster catalyzes acylation of alcohols under reflux conditions even in the presence of amine compounds, which could impede the reaction.¹⁰

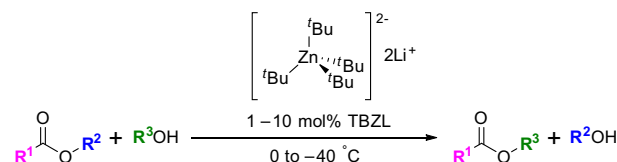
Uchiyama and coworkers¹¹ reported that dilithium tetra-*tert*-butylzincate (TBZL) catalyzed allylations of haloaromatics via halogen–zinc exchange reactions. No protection is required for haloaromatics containing a broad range of functional groups, because of the unusually low basicity of TBZL.^{11b,c} The high chemoselectivity of TBZL enables direct polymerization of *N*-isopropylacrylamide in aqueous media.^{11a,b}

Recently, we reported that TBZL catalyzed ring-opening polymerization of ϵ -caprolactone.^{11g} In a subsequent study of the copolymerization of ϵ -caprolactone with 2-hydroxyethyl methacrylate (HEMA), TBZL was found to act not only as an anionic initiator but also as a transesterification catalyst.¹² This finding led us to investigate the acylation and transesterification of alcohols with vinyl acetate and carboxylic esters in the presence of a catalytic amount (1–10 mol %) of TBZL (Scheme 1).

Results and discussion

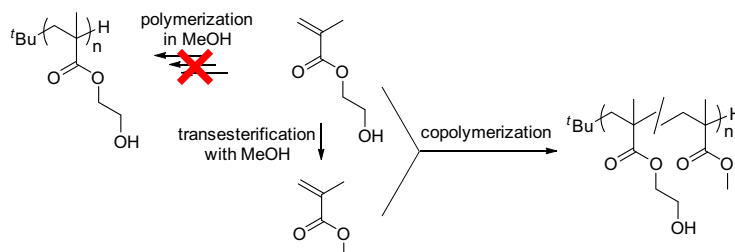
Homopolymerization of HEMA with TBZL in MeOH gave a copolymer composed of two monomeric units, HEMA and methyl methacrylate (Fig. S1). This result indicates that polymerization accompanies transesterification of HEMA with MeOH at 30 °C (Scheme 2). It is interesting to note that the reaction proceeded at a moderate temperature.

The acylation of BnOH with vinyl acetate was examined to investigate the transesterification catalytic ability of TBZL¹³ (Table 1).¹⁴ Irreversible transesterification proceeded quantitatively with



Scheme 1. Acylation and transesterification of alcohols with vinyl acetate and carboxylic esters in the presence of TBZL.

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Scheme 2. Anionic polymerization of HEMA with TBZL in MeOH at 30 °C for 1 h, giving copolymer of HEMA and methyl methacrylate.

Table 1

Acylation of alcohols with vinyl acetate in Presence of TBZL or Et₂Zn with *N*-phenyldiethanolamine (PDEA) as a catalyst^a

Run	Catalyst (mol %)	Solvent	Temp. (°C)	Time (h)	Conv. (%) ^b
1	TBZL (10)	Toluene	25	1	>99
2	TBZL (10)	THF	25	1	>99
3	TBZL (10)	Toluene	0	1	>99
4	TBZL (10)	THF	0	1	>99
5	TBZL (10)	<i>n</i> -Hexane	0	1	>99
6	TBZL (10)	Bulk	0	1	>99
7	TBZL (1)	Toluene	0	0.5	58
8	TBZL (1)	Toluene	0	1	87
9	TBZL (1)	Toluene	0	1.5	>99
10	Et ₂ Zn (10) + <i>N</i> -PDEA (5)	Toluene	25	1	>99
11	Et ₂ Zn (10) + <i>N</i> -PDEA (5)	THF	25	1	35
12	Et ₂ Zn (10) + <i>N</i> -PDEA (5)	Toluene	0	1	67
13	Et ₂ Zn (10) + <i>N</i> -PDEA (5)	THF	0	1	6
14 ^c	TBZL (2)	Bulk	0	1	>99

^a Vinyl acetate (5.0 mmol), benzyl alcohol (1.0 mmol), solvent (2.0 mL).

^b Conversion was determined by intensities of Ph-CH₂-O- proton signals of benzyl alcohol and that of benzyl acetate.

^c ^tPrOH was used as an alcohol instead of benzyl alcohol.

10 mol % TBZL in toluene or THF at 25 °C within 1 h (Runs 1 and 2). Decreasing the reaction temperature to 0 °C or changing the solvent scarcely affected the reaction (Runs 3–6). These results are comparable to those for reactions catalyzed by Et₂Zn combined with a *N*-PDEA (Runs 10–13).^{7a,7b} A decrease in the amount of TBZL to 1 mol % gave quantitative conversion within 1.5 h (Runs 7–9). Acylation of secondary alcohols such as ^tPrOH with vinyl acetate also proceeded smoothly in bulk at 0 °C and were complete within 1 h (Run 14 and Fig. S2). These results show that TBZL is a better catalyst than those reported so far.

Irreversible transesterification proceeded quantitatively for the acylation of a wide range of alcohols, except for 3-amino-1-propanol, with vinyl acetate catalyzed by TBZL (Table 2). The acylation of 3-amino-1-propanol was failed because immediate amidation and subsequent cyclization occurred before addition of TBZL due to high reactivity of vinyl acetate with amino group (Run 7).

The transesterification occurred for a wide range of combinations of esters and alcohols, except for ^tBuOH, PhOH, and ^tBuOAc (Table 3).¹⁵ Half the amount of EtOAc was converted to MeOAc in the transesterification of an equimolar mixture of EtOAc and MeOH (Run 1). The time–conversion plots for the transesterification show that the reaction reached equilibrium within 5 min at 0 °C or within 60 min at –20 °C (Fig. 1).¹⁶ The transesterification proceeded at a practical rate even at –40 °C. To the best of our

Table 2

Acylation of alcohols with vinyl acetate catalyzed by TBZL in Toluene^a

Run	ROH	Product ^b (isolated yield)
1	BnOH	>99 %
2	1-hexanol	>99 %
3	2-ethoxyethanol	>99 %
4 ^c	1,4-butanediol	>99 %
5	2,2,2-trichloroethanol	>99 %
6	geraniol	>99 % (>99 %)
7	3-amino-1-propanol	mixture (~ 1 : 1)

^a Vinyl acetate (5.0 mmol), alcohol (1.0 mmol), TBZL (0.1 mmol), Toluene (2.0 mL); 0 °C, 1 h.

^b Conversion was determined by NMR.

^c Vinyl acetate (10.0 mmol).

knowledge, this is the first successful transesterification at such low temperatures.

Removal of the product alcohol should shift the equilibrium toward complete transesterification; Molecular sieves 4A was therefore added to the mixtures of MeOAc and BnOH at 0 °C to adsorb the MeOH produced via transesterification.¹⁷ The reaction proceeded quantitatively, regardless of the feed ratio of MeOAc to BnOH (Fig. 2). Similar results were observed using MeOBz instead of MeOAc.

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