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COMMUNICATION

Metal-Free Transesterification Catalyzed by Tetramethylammonium Methyl Carbonate

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Environmentally benign metal-free tetramethylammonium methyl carbonate is effective as a catalyst for the chemoselective, scalable, and reusable transesterification of various esters and alcohols in common organic solvents. *In situ*-generated highly active species, tetramethylammonium alkoxides, can greatly avoid the self-decomposition at ≤110 °C, and reusable. In particular, chelating substrates, such as amino alcohols, diols, triols, sugar derivatives, alkaloids, α-amino acid esters, etc., which deactivate conventional metal salt catalysts, can be used. A 100 gram scale biodiesel production was also demonstrated.

The transesterification of carboxylic esters with alcohols is an indispensable synthetic method in organic chemistry.[1] However, modern transesterification still often requires the use of harmful, colored, and/or expensive metal salt catalysts, such as highly regarded Al(III),[2] Sb(III),[3] Ti(IV),[4] Sn(IV),[5] Sm(III),[6] Hf(IV),[7] Zr(IV),[7] Y(III),[8] La(III),[9,10] Zn(II),[11] Fe(III),[12] and Co(II)[13] species.[14] Moreover, these metal salt catalysts have another serious drawback; i.e., they mostly cannot be used with chelating substrates (Fig. 1a), and thus alcoholysis in alcohol-solvents has been usually conducted.[1–14] To overcome this obstacle to the synthesis of highly functionalized esters from equimolar amounts of esters and alcohols in common organic solvents, quaternary ammonium salt catalysts, which would be regardless of chelation, might be promissing.[15–17] However, it is known that ammonium alkoxides ($[R_4N]^+[OR']^-$) are usually unstable and moisture sensitive due to their strong basicity.[18] Therefore, it is difficult to apply them directly as catalysts for transesterification. In contrast, $[R_4N]^+[OCO_2Me]^-$ are easy to handle due to their stability.[10e] Here we describe a transesterification by a catalytic use of *in situ*-generated $[R_4N]^+[OR']^-$ from $[R_4N]^+[OCO_2Me]^-$ **3** and R'OH (substrate) (Fig. 1b). Although $[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ **2a**[19,20a–c] and DABCO-derived ammonium methyl carbonate[20d] have already been known as effective catalysts for the transesterification of DMC (dimethyl carbonate) as a solvent, no one has yet reported the substrate generality including functionalized esters and alcohols,[20e] since the instability of conventional phosphonium salts (and ammonium salts) without excess DMC would not allow the application to transesterification in common solvents. Nevertheless, we made a great effort to investigate the stability and activity of onium salts, and finally found a great potential of the onium salts as transesterification catalysts. In particular, a new catalyst $[Me_4N]^+[OCO_2Me]^-$ **3d**, which is much more active than **2a**, successfully addressed the challenging problems so far unsolved by metal salt catalysts.

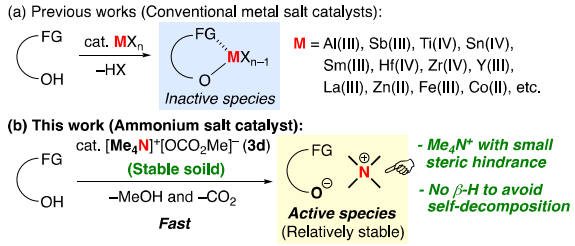

Fig. 1 Outline of catalysts for transesterification.

Table 1 shows a probe reaction of methyl salicylate **4a** and benzyl alcohol **5a** in a Soxhlet thimble under azeotropic reflux conditions of *n*-hexane (bp. 69 °C), where MS 5Å was used to remove methanol (see the Electronic supplementary information (ESI) for a reactor). Our previous La(III) catalyst system with $La(NO_3)_3{\cdot}H_2O$–$[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ (**1•2a**$_2$)[10e] was not effective with chelating **4a**, and product **6a** was obtained in 1% yield (entry 1). In contrast, phosphonium salt **2a** alone was much more effective than **1•2a**$_2$, and **6a** was obtained in 87% yield (entry 2). This excellent catalytic performance might strongly depend on chelating **4a**, since **1•2a**$_2$ was much better than **2a** alone for non-chelating substrates.[10e] Moreover, when we used ammonium salt $[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ **3a** in place of **2a**, **6a** was obtained

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†Electronic Supplementary Information (ESI) available: Experimental procedure, characterization data, additional control experiments, copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/x0xx00000x

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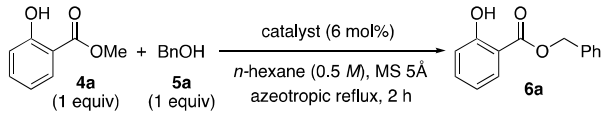
Table 1 Screening of catalysts[a]



Entry	Catalyst	Yield (%)
1	1/2 $La(NO_3)_3 \bullet H_2O$ (**1**) + $[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ (**2a**)	1
2	$[Me(n\text{-octyl})_3P]^+[OCO_2Me]^-$ (**2a**)	87 (71)[b]
3	$[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (**3a**)	90 (78)[b]
4	**3a** (1 mol%)	90[c] (90)[c,d]

[a] The reaction was carried out with **4a** (2 mmol), **5a** (2 mmol), and catalyst (6 mol%) in *n*-hexane (bp. 69 °C) at 90 °C (bath temperature) for 2 h. A Soxhlet extractor containing MS 5Å was used under azeotropic reflux conditions. [b] Yield of **6a** for 30 min. [c] Reaction was carried out with 1 mol% of **3a** for 5 h. [d] MS 5Å was reused in another reaction after removal of MeOH under reduced pressure.

in 90% yield (entry 3). Based on the yields for a shorter reaction time (0.5 h), **3a** was more active than **2a** (entries 2 and 3). The catalyst loading of **3a** could be reduced to 1 mol% (entry 4).[21,22] Moreover, MS 5Å could be reused without deterioration in a next reaction after removal of MeOH under reduced pressure (entry 4, parenthesis).

In this reaction, the $[OCO_2Me]^-$ moiety of **2a** and **3a** would quickly react with **5a**, and irreversibly provide methanol, CO_2, and $[Me(n\text{-octyl})_3P]^+[OBn]^-$ or $[Me(n\text{-octyl})_3N]^+[OBn]^-$ as active species *in situ* (Fig. 2, also see the ESI for ^{1}H NMR experiments). $[Me(n\text{-octyl})_3N]^+[OBn]^-$ would form a simple ion-pair, whereas $[Me(n\text{-octyl})_3P]^+[OBn]^-$ would form a stable pentacoordinated phosphorane[23] (Fig. 2). Therefore, the nucleophilicity of $[Me(n\text{-octyl})_3P]^+[OBn]^-$ would be weakened. A cationic nitrogen center of $[Me(n\text{-octyl})_3N]^+$ cannot directly activate an ester, but α-H moieties might act as Brønsted acids (Fig. 2, right).[24]

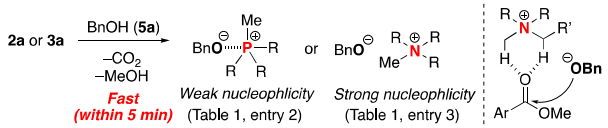
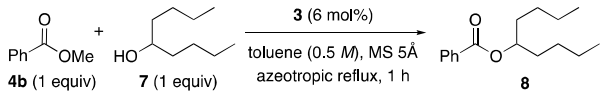


Fig. 2 Active species *in situ* from **2a** or **3a**.

However, during the initial investigation[21] of the substrate scope regardless of chelating or non-chelating substrates, catalyst **3a** was not effective for some low-reactive 2°-alcohols, such as sterically hindered **7**, as shown in Table 2. Indeed, **3a** decomposed to $Me(n\text{-octyl})_2N$ (81%) via the Hofmann elimination of β-H and $(n\text{-octyl})_3N$ (19%) via an S_N2 reaction on the Me group (entry 1, also see Fig. 3).[18] To avoid these decomposition pathways, we examined $[Me_2(n\text{-octyl})_2N]^+[OCO_2Me]^-$ **3b** (entry 2), $[Me_3(n\text{-octyl})N]^+[OCO_2Me]^-$ **3c** (entry 3), and $[Me_4N]^+[OCO_2Me]^-$ **3d** (entry 4), which have fewer β-H moieties than **3a**. In particular, **3d** has no β-H moiety. As a result, the yield of **8** was increased in the order **3a** (26%) < **3b** (57%) < **3c** (64%) < **3d** (85%). This order also might seem to be due to the bulkiness of the catalysts. However,

Table 2 Screening of ammonium salt catalysts **3**[a]



Entry	Catalyst	Yield (%)
1	$[Me(n\text{-octyl})_3N]^+[OCO_2Me]^-$ (**3a**)	26
2	$[Me_2(n\text{-octyl})_2N]^+[OCO_2Me]^-$ (**3b**)	57
3	$[Me_3(n\text{-octyl})N]^+[OCO_2Me]^-$ (**3c**)	64
4	$[Me_4N]^+[OCO_2Me]^-$ (**3d**)	85
5	$[Et_4N]^+[OCO_2Me]^-$ (**3e**)	0
6	$[Me_4N]^+[OCO_2H]^-$ (**3f**)	6
7	$[Me_4N]^+[OH]^-$ (**3g**)	17
8	$[Me_4N]^+[Cl]^-$ (**3h**)	0

[a] The reaction was carried out with **4b** (2 mmol), **7** (2 mmol), and catalyst (6 mol%) in toluene (bp. 110 °C) at 140 °C (bath temperature) for 1 h. The same reactor system was used as in Table 1.

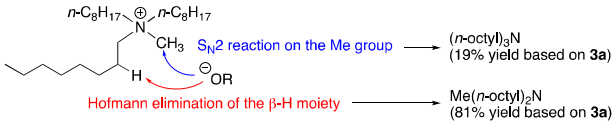


Fig. 3 Decomposition of **3a** (Table 2, entry 1).

$[Et_4N]^+[OCO_2Me]^-$ **3e**, which is slightly more sterically hindered than **3d** but has twelve β-H, showed no catalytic activity due to the severe Hofmann elimination (entry 5). Although we cannot completely exclude the effect of the steric factor of the alkyl moieties in catalysts **3a–e**, the Me group without β-H on the nitrogen should be essential for increasing the yields.[25] Moreover, the $[OCO_2Me]^-$ moiety should also be important, since $[Me_4N]^+[OCO_2H]^-$ **3f**, $[Me_4N]^+[OH]^-$ **3g**, and $[Me_4N]^+[Cl]^-$ **3h** showed poor catalytic activity (entries 6–8). Catalyst **3f** might be led to **3g** *in situ*, which would react with **4b** to generate $PhCO_2H$ and then neutralized inactive species $[Me_4N]^+[OCOPh]^-$. $[Me_4N]^+[Cl]^-$ **3h** would be inherently neutralized and unlikely to play a role in this catalysis. Notably, white powdery **3d** was dissolved and showed homogeneous states in the reaction mixture. However, when the reaction mixture was cooled at 0 °C, the **3d**-derived viscous deposit was generated. In this regard, we examined the reuse of catalyst **3d** (1 mol%) in the reaction of **4b** (6 mmol) with **5b** (6 mmol) in *n*-hexane (Scheme 1). After the reaction, a clear solution was divided from the mixture at 0 °C. Then, *n*-hexane, **4b**, and **5**

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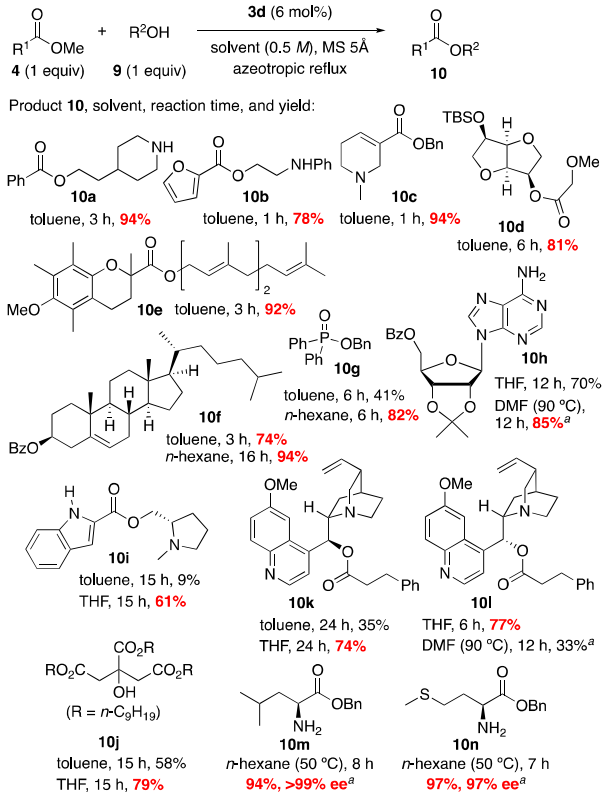
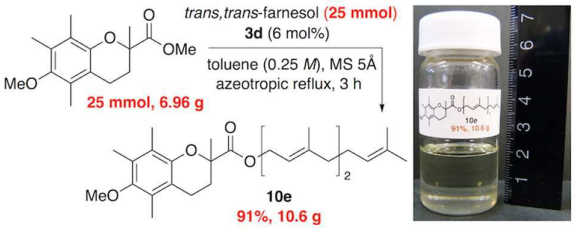
Scheme 1 Recovery and reuse of the catalyst in gram scale synthesis of **6b**.

b were added, and the reaction restarted. Overall, **3d** was recovered and reused for the same reaction three times. Thus, all crude products were combined and purified to give 5.48 g (96% yield) of **6b**.[26]

With the optimized catalyst **3d** in hand, we demonstrated the substrate scope by taking advantage of tolerance for highly chelating substrates, which are difficult to apply in metal salt catalysis (Scheme 2). As a result, amino alcohols could be used, and chemoselective *O*-acylation proceeded in toluene to give **10a** in 94% yield and **10b** in 78% yield. A pyridine alkaloid-analogue **10c**, (+)-D-isosorbide-derivative **10d**, and α-tocotrienol (vitamin E) **10e**[27] could also be obtained in high yields with the use of **3d** in toluene. Remarkably, 25 mmol-scale synthesis could be achieved (Scheme 3), and **10e** was obtained in 91% yield (10.6 g). Moreover, catalyst **3d** was effective for the synthesis of cholesterol-derivative **10f**, but the reaction stopped within 3 h when the yield was moderate (74%), probably due to the decomposition of **3d**. To avoid a possible S_N2 reaction on the Me group of catalyst **3d**, we used *n*-hexane (bp. 69 °C) in place of toluene (bp. 110 °C) under azeotropic reflux conditions. As a result, the yield was improved to 94%, although a prolonged reaction time (16 h) was needed. For the synthesis of phosphoric acid ester **10g**, *n*-hexane was again better than toluene. Moreover, nucleic



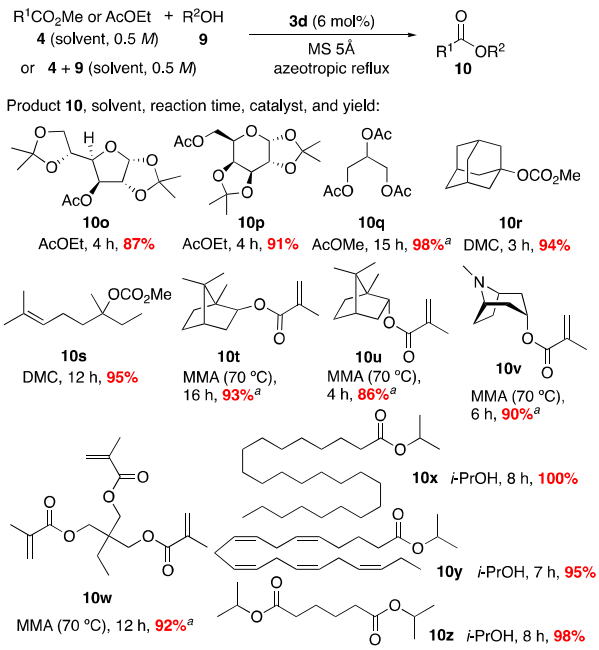
Scheme 2 **3d**-Catalyzed transesterification. [a] Powdered MS 5Å was used.



Scheme 3 Ten gram (10 g) scale synthesis of α-tocotrienol **10e**.

acid-analogue **10h**, which is hardly soluble in toluene and *n*-hexane, was successfully obtained in solvating DMF (*N*,*N*-dimethylformamide) at 90 °C. Indol/prolinol-derivative **10i**, citric acid-derivative **10j**, quinine- and quinidine-derivatives **10k** and **10l** were obtained in improved yields when the solvent was changed to solvating THF (tetrahydrofuran). Moreover, the chemoselective transesterification of chelating *N*-unprotected optically active α-amino acid esters has been scarcely reported.[28] Fortunately, **3d**-catalyzed transesterification of methyl esters of L-leucine and L-methionine proceeded, and **10m** and **10n** were obtained respectively without a serious loss of enantio-purity. Overall, unlike with conventional metal salt catalysts, we could use common solvents in the present transesterification.

We next examined the **3d**-catalyzed transesterification in substrates used as solvents (Scheme 4), since inexpensive ethyl acetate (EtOAc), methyl acetate (MeOAc), DMC, methyl meth-acrylate (MMA), and 2-propanol (*i*-PrOH) are often used as solvents in transesterification, particularly in industry. EtOAc and MeOAc could be used for chelating sugar-derivatives and a



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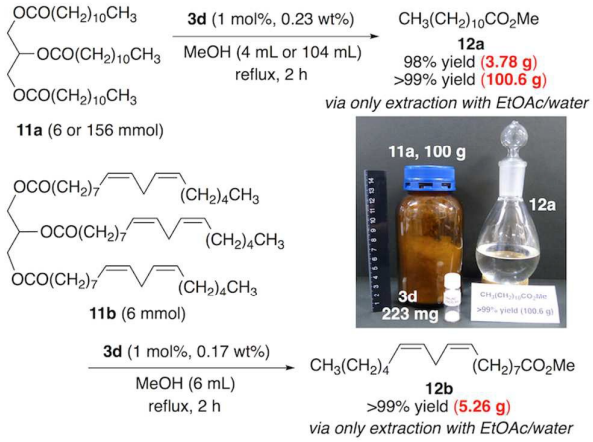
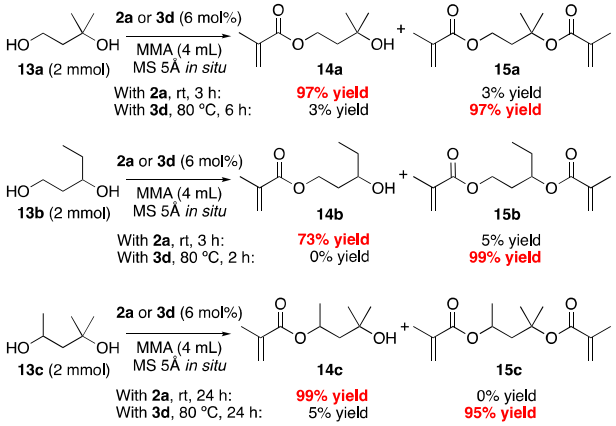
Scheme 4 **3d**-Catalyzed transesterification with ester or alcohol as a solvent. [a] Powdered MS 5Å was used.



Scheme 5 Biodiesel production with model substrates **11**.



Scheme 6 Selective transesterification of with MMA.

triol (see **10o–q**). DMC was used for tertiary alcohols (see **10r** and **10s**). Synthetically useful borneol-, isoborneol-, and tropine-derived acrylates, which can be used in synthetic resins and refractive lenses, were successfully synthesized in MMA (see **10t–v**). Moreover, *i*-PrOH could be used as asolvent for the convenient synthesis of highly fatty acid esters **10x** and **10y** and oily diester **10z** as a cosmetic moisturizing ingredient.

Biodiesel is known as a mixture of methyl ester of fatty acids, and made from renewable resources such as triglycerides in vegetable oils and animal fats by methanolysis.[29] In this regard, transesterification of model substrates of triglyceride, such as trilaurin **11a** and trilinolein **11b**, was examined (Scheme 5). In spite of chelating intermediates, such as mono- and diglycerides, and released glycerol, reaction proceeded smoothly with the use of 1 mol% of catalyst **3d** (i.e.; 0.23 wt. % for **11a** and 0.17 wt. % for **11b**), and the corresponding methyl laurate **12a** and methyl linolenate **12b** were respectively obtained in multi-gram scale almost quantitatively. The catalyst and released glycerol were completely removed by routine extraction without silica gel column chromatography. Remarkably, a >100 gram scale synthesis of **12a** was performed without serious problems.[30]

Finally, we could control the chemoselective di- and mono-transesterification of unsymmetrical 1,3-diols, by using ammonium and phoshponium salts, respectively. 1,3-Diol-derived crosslinkable bis(methacrylate) monomers have wide applications to electronic, coating, and photoresist materials.[31] However, since the intramolecular transesterification would occur reversibly, chemoselective control is difficult.[32] In this regard, we finally used unsymmetrical 1°/3°-, 1°/2°-, and 2°/3°-diols **13** with MMA (Scheme 6). Highly active ammonium salt **3d** promoted the transesterification reaction of diols **13a–c** to give diesters **15a–c** exclusively. In contrast, much less active phosphonium salt **2a** instead of **3d** provided monoesters **14a–c** exclusively.

Conclusions

In summary, we have developed metal free $[Me_4N]^+[OCO_2Me]^-$ for the transesterification of various functionalized esters and alcohols. In particular, unlike conventional metal salt catalysts, chelating substrates could be used in common solvents. Moreover, biodiesel production, chemoselective transesterification, gram-scale reaction, and catalyst recycling were demonstrated for environmentally benign use in the laboratory as well as in industrial process chemistry.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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