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FOCUS REVIEW

N-Heterocyclic carbene-catalyzed dimerization, cyclotetramerization and polymerization of Michael acceptors

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N-Heterocyclic carbenes (NHCs), which were first isolated in the early 1990s, have received a great deal of scientific attention as ligands for transition metal complexes and organocatalysts for more than a decade. Organocatalysis by NHCs primarily involves the reaction of carbonyl compounds, particularly the umpolung of aldehydes, although we and others have been developing the reactions and the polymerizations of Michael acceptors. This review focuses on the NHC-catalyzed transformations of Michael acceptors that were developed by our research group, including (1) tail-to-tail dimerization of a wide variety of substrates, (2) cyclotetramerization of acrylates, (3) tandem oxa-Michael addition and head-to-tail dimerization of methacrolein and (4) oxa-Michael addition polymerization of hydroxyl-functionalized acrylates. For the former two reactions, the NHCs turn the β-carbon of the Michael acceptors into nucleophilic sites (umpolung), thereby generating the deoxy-Breslow intermediate and enabling bond formation between the β-carbon and electrophiles. The latter two reactions are based on the O–C bond formation between alcohols and Michael acceptors, in which the NHC catalysts act as a Lewis base. Thus, the use of NHC catalysts allowed new modes of reactivity of Michael acceptors other than the conventional addition polymerizations.
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INTRODUCTION

Carbenes have long been recognized as unstable species. In 1991, however, Arduengo *et al.* made a major breakthrough in isolating the first crystalline nucleophilic N-heterocyclic carbenes (NHCs): a 1-adamantyl and the aromatic group substituted imidazol-2-ylidenes.[1–3] They are stable both in solution and in bulk, and can be characterized by X-ray analysis. Enders *et al.* also made a significant contribution by isolating another type of NHC, a 1,2,4-triazol-5-ylidene, in 1995.[4–6] Since these early discoveries, NHCs[7] have found a wide variety of applications as ligands for transition metal complexes.[8–10] Compared with phosphine ligands, NHCs generally have a stronger electron-donating ability, and the structural design of the NHCs makes it easier to tune the electronic and steric environment. These features enable ruthenium and palladium complexes with NHC ligands to be competent catalysts for various reactions, such as olefin metathesis and cross-coupling reactions, respectively. NHCs also serve as ligands for main group element species.[11,12]

In addition to the ligand chemistry, the NHC itself acts as an organocatalyst.[13–24] The first example of an NHC-catalyzed reaction dates to Ukai *et al.* in 1943, who first reported the thiazolium salt-catalyzed benzoin condensation.[25] Breslow proposed the reaction mechanism in 1958, in which the C2 position of a thiazolium ring shows nucleophilic reactivity to benzaldehyde to generate the enaminol intermediate.[26] This is the umpolung or polarity reversal because the electrophilic aldehyde carbon is converted to a nucleophilic species. Later, this key umpolung intermediate, an acyl anion equivalent, was called the Breslow intermediate. In addition to these early studies, a major advance was made by Stetter in the 1970 s, who demonstrated the thiazolium salt-catalyzed selective reaction of an aldehyde and Michael acceptors via the Breslow intermediate, which is now called the Stetter reaction.[27] After the isolation and characterization of the NHCs by Arduengo and Enders in the 1990 s, organocatalysis using NHCs received a great deal of attention. Since the early 21st century, numerous publications have continued to appear. There have been breakthroughs, such as the asymmetric synthesis using chiral NHCs,[15,16] catalysis via homoenolate intermediates from α,β-unsaturated aldehydes,[17] reaction of the Breslow intermediates with various electrophiles[18] and polymer synthesis.[19–22] Most of the NHC-catalyzed reactions involve the nucleophilic addition of the NHC to carbonyl groups.

Our research group and others have been investigating the NHC-catalyzed reaction of Michael acceptors.[23,24] When Enders isolated the first 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT), they also showed that TPT readily adds to ethyl fumarate or ethyl maleate to form stable adducts.[4–6] A decade later, Fu *et al.*[28] found the intramolecular umpolung reaction of Michael acceptors, in which the β-carbons of the Michael acceptors are made nucleophilic by the NHC catalyst to generate the deoxy-Breslow intermediate.

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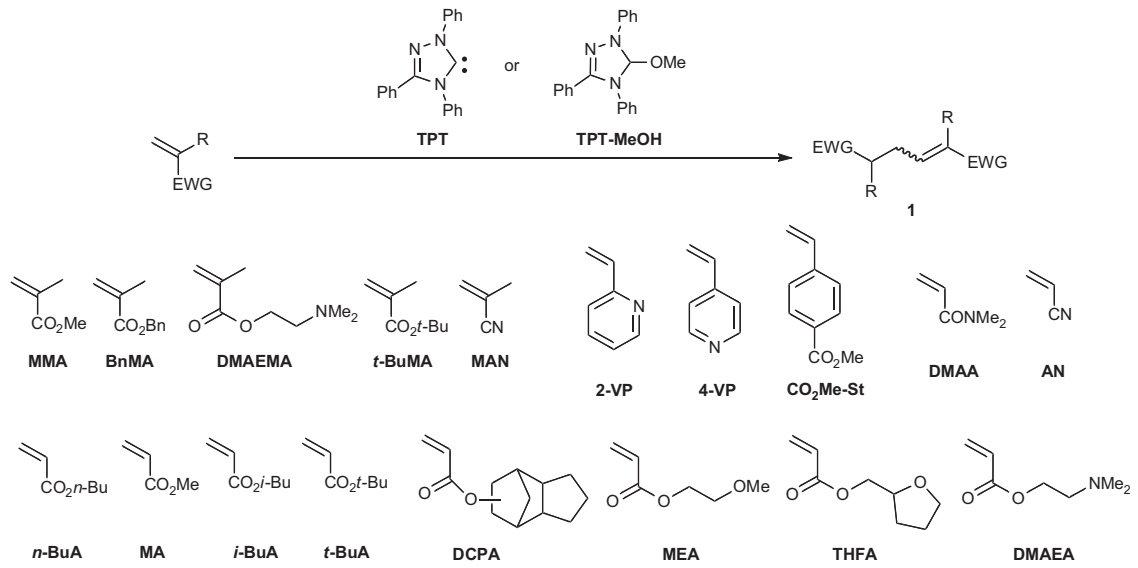


Scheme 1 Tail-to-tail dimerization of Michael acceptors catalyzed by TPT or TPT-MeOH. TPT, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene.

This demonstrated that the NHC catalysts potentially allow the bond-forming reaction between the β-carbon of the Michael acceptors and electrophiles. Other reactions initiated by the conjugate addition of the NHC to Michael acceptors, such as the aza-Morita–Baylis–Hillman reaction,[29–31] rearrangements of vinyl sulfones,[32] Rauhut–Currier reactions,[33] [4+2] cycloaddition,[34] conjugate addition and proton transfer polymerizations[35,36] and stoichiometric cyclodimerization[37] have been reported. In addition to these reactions, various types of Michael additions by NHC catalysts have recently been performed.[38–43] Among them, Scheidt and colleagues reported the oxa-Michael addition of α,β-unsaturated ketones, in which the NHCs act as Brønsted bases to activate alcohols.[39] Although the NHC-catalyzed reactions of Michael acceptors is underdeveloped compared with that of carbonyl compounds, they have gained increasing attention in this decade.

In this focused review, the NHC-catalyzed transformations of Michael acceptors developed by our research group, including tail-to-tail dimerization,[44–47] cyclotetramerization[48] and oxa-Michael addition dimerization[49] and polymerization,[50] are reviewed. NHC catalysis has provided a new mode of reactivity for Michael acceptors in addition to the conventional addition polymerization.

TAIL-TO-TAIL DIMERIZATION OF VARIOUS MICHAEL ACCEPTORS

The tail-to-tail dimerizations of Michael acceptors are analogous to benzoin condensation, that is, the dimerization of benzaldehydes, because both reactions go through the umpolung of electrophilic unsaturated carbons into nucleophiles, which enables bond formation between the carbons. The tail-to-tail dimerizations of Michael acceptors provide bifunctional compounds, such as diesters, thus allowing the synthesis of condensation polymers from conventional Michael acceptors. More than half a century since the discovery of the benzoin condensation by NHC catalyst, we and Glorius *et al.* have been independently developing tail-to-tail dimerizations. The initial reports by both groups in 2011 showed the dimerization of methacrylates,[44,51] and since then, the scope has been expanded to methacrylonitrile (MAN),[46] activated styrenes,[47,52] vinyl pyridines (VPs),[47,52] acrylates[47] and acrylonitrile[47] (Scheme 1). We now report the results of the dimerization developed by our group.

When methyl methacrylate (MMA) was reacted with 10 mol% of TPT at 80 °C for 8 h, the tail-to-tail dimer was selectively obtained in 86% isolated yield with an *E*/*Z* ratio of 95:5.[44] The NHC precursor, TPT-MeOH, thermally converted to TPT at 80 °C, is also effective, whereas other NHC precursors with bases do not work, which demonstrates the high catalyst specificity. Benzyl and *N*,*N*-dimethylaminoethyl methacrylates (BnMA and DMAEMA) undergo a similar dimerization. Although the rate of the dimerization of *t*-butyl methacrylate is relatively low, prolonging the reaction time to 24 h resulted in a high yield.

The mechanism of the dimerization of MMA was experimentally studied in detail.[45] For example, methyl methacrylate-3,3-d_2 (MMA-d_2) provides a dimer with selective deuterium incorporation at the C3, C4 and C5 positions, indicating that there is no scrambling between the deuteriums and α-methyl protons. Furthermore, the k_H/k_D value obtained by the dimerizations of MMA and MMA-d_8 is 0.81 ± 0.13, which indicates that proton transfer processes are not rate-limiting steps. In addition to these dimerizations, we performed short-time reactions, deuterium-labeling experiments, competitive, stoichiometric and cross-dimerizations, isolation and electrospray ionization mass spectrometry (ESI-MS) analysis of the proton or deuterium adducts of the key deoxy-Breslow intermediate. The results of these experiments revealed the stability of the intermediate, reversibility, rate-limiting steps and proton transfer mechanism. We then proposed the reaction mechanism, as shown in Figure 1. TPT readily adds to the β-carbon of MMA to generate the zwitterionic intermediate (**I**), and the subsequent proton transfer gives the deoxy-Breslow intermediate (**II**), which is more stable than the aldehyde-derived Breslow variants. The nucleophilic reactivity of the β-carbon of **II** is central for the umpolung reaction. The Michael addition of **II** to the second MMA allows the formation of the C–C bond between the β-carbons of MMA. This Michael addition (**II** → **III**) and the final catalyst elimination (**V** → TPT) are partially rate-limiting steps. The alkenyl protons of the first MMA undergo an intermolecular exchange and are transferred to the C3 and C5 positions of the dimer. Several mechanistic differences between this dimerization and benzoin

condensation are observed. In addition, the presence of the deoxy-Breslow intermediate **II** was supported by the selective reaction with isocyanates to form the three-component products.[53]

We then examined the dimerization of MAN, the dimer of which can be expected to be the precursor of the C6 aliphatic diamine. We initially envisioned that the dimerization of MAN, which is a slightly stronger electrophile than methacrylates, could readily proceed, but the TPT catalyst (5 mol%) alone produced the dimer in $<10\%$.

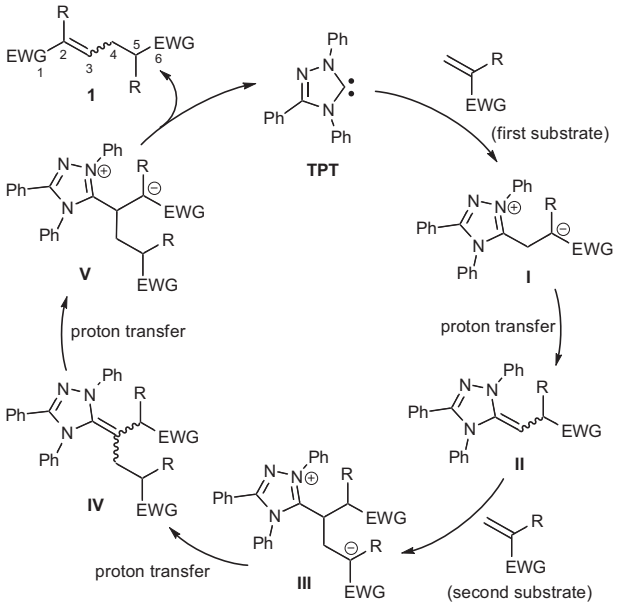


Figure 1 Proposed mechanism of the tail-to-tail dimerization of Michael acceptors.

However, the addition of alcohols, which was aimed to form the cooperative NHC/Brønsted acid catalytic system, promoted the catalytic turnover, giving the dimer in up to 82% yield.[46] Experimental studies, such as stoichiometric and cross-dimerizations with *n*-butyl methacrylate, indicated that the alcohols assisted the intermolecular proton transfers in the second half of the catalytic cycle (**III** → **V**). Similar to the dimerization of MMA, the Michael addition of **II** with a second MAN is a rate-limiting step. In addition, in contrast to the dimerization of MAN, that of *n*-butyl methacrylate using the cooperative system led to a lower yield.

Glorius *et al.*[52] first reported the dimerizations of low electrophilic substrates, VPs and activated styrenes in 2014, and we had also been performing the dimerization of the same substrates before their publication.[47] The dimerization of 2VP at 100 °C in the bulk did not occur, but increasing the reaction temperature to 150 °C gave the *trans*-dimer in a high yield within 10 min. Under these conditions, 4VP and ester-functionalized styrene (CO_2Me-St) also underwent dimerization. In contrast, no dimerization of styrene and 4-chlorostyrene occurred, which suggests the limitation of the dimerization of weak electrophilic substrates.

We next considered the dimerizations of highly reactive substrates, that is, acrylates, acrylonitrile and acrylamide.[47] The optimization of the reaction conditions was performed using *n*-butyl acrylate. Despite its high electrophilicity, the dimerization requires temperatures above 120 °C. The alcohol additives for the dimerizations of acrylates are effective, and the turnover numbers were enhanced several fold, up to 18. The results of the dimerization in the presence of CD_3OD as an additive suggest the reasonable intermolecular proton transfers. From the ESI-MS studies for the detection of the intermediates, it is proposed that the rate-limiting step involves the second half of the catalytic cycle. Under the high temperature conditions, the dimerizations of various highly reactive substrates, including bulky alkyl, ether and trialkyl amino-functionalized acrylates (MA, *i*-butyl acrylate,

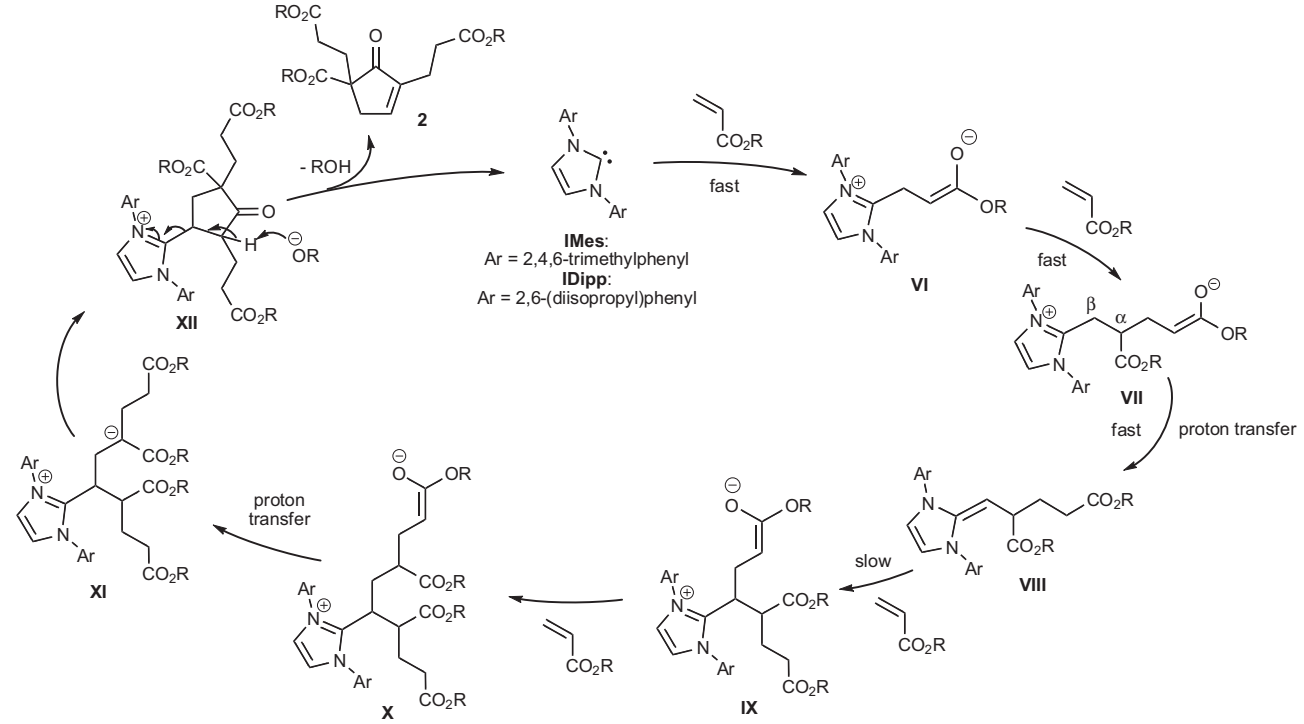
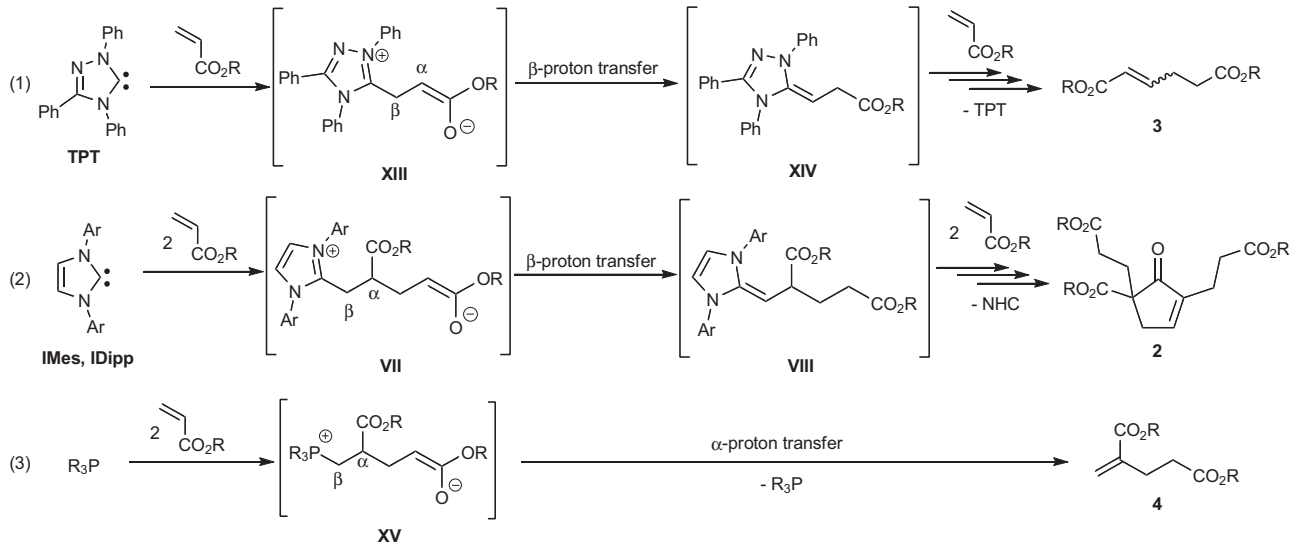


Figure 2 Proposed mechanism of the cyclotetramerization of acrylates.



Scheme 2 Mechanistic difference between the transformations of acrylates catalyzed by organic bases. (1) Tail-to-tail dimerization catalyzed by TPT. (2) Cyclotetramerization catalyzed by IMes or IDipp. (3) Rauhut–Currier reaction, a head-to-tail dimerization, catalyzed by PR_3. PR_3, trialkyl phosphine.

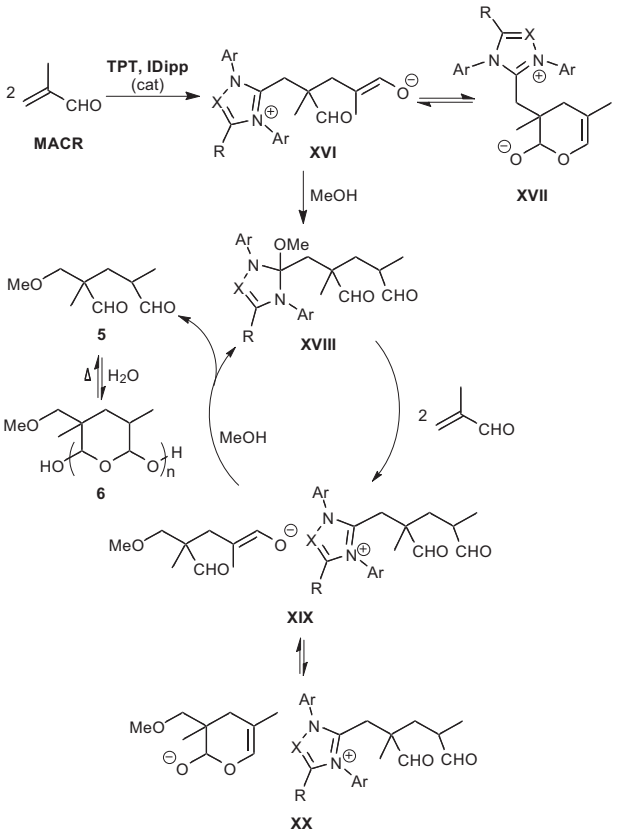


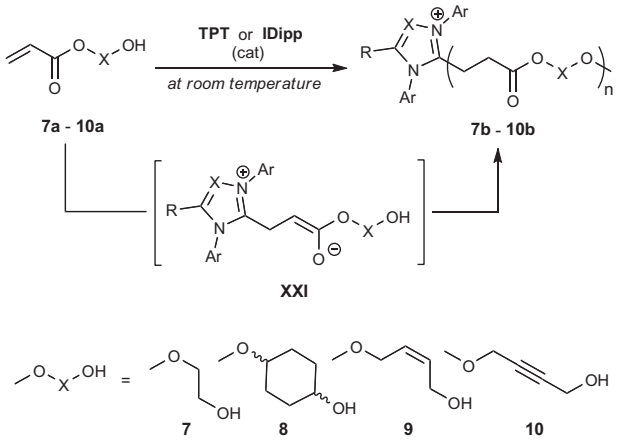
Figure 3 Proposed mechanism of oxa-Michael addition dimerization of MACR catalyzed by TPT or IDipp. MACR, methacrolein.

t-butyl acrylate, DCPA, MEA, THFA and DMAEA), *N*,*N*-dimethylacrylamide (DMAA) and acrylonitrile (AN), have become possible. A wide variety of substrates ranging from low electrophilic VPs to highly reactive acrylonitrile could be dimerized by the TPT catalyst.

CYCLOTETRAMERIZATION OF ACRYLATES

Imidazole-2-ylidenes, such as IMes and IDipp, did not catalyze the tail-to-tail dimerizations, and Zang and Chen[35] previously showed that IMes reacts with MMA to selectively form the stable deoxy-Breslow intermediate without further nucleophilic reactions. We found that IMes and IDipp catalyzed the novel cyclotetramerization of acrylates to form trisubstituted cyclopentenones (Figure 2).[48] The unprecedented tetramer of MA was identified by its nuclear magnetic resonance spectra, including two-dimensional INADEQUATE. Under the optimized conditions using 5 mol% of IMesHCl with potassium *tert*-butoxide (*t*-BuOK) in 1,4-dioxane at 80 °C, the product was obtained in 47% yield. The other substrates (ethyl, *i*-butyl and 2-methoxyethyl acrylates) also underwent this transformation under these conditions. For the mechanistic elucidation, the short-time reaction of IDipp with MA followed by the addition of CF_3CO_2X (X = H or D) indicated the *in situ* formation of the deoxy-Breslow intermediate (**VIII**). Namely, in contrast to the TPT-catalyzed dimerization, IMes or IDipp consecutively reacts with two molecules of acrylates followed by proton transfer to generate **VIII**. The ESI-MS study for the detection of the intermediates suggests the mechanism of the second half of the catalytic cycle. The Michael addition of **VIII** with two molecules of acrylates and subsequent proton transfer generates **XI**. The cyclization occurs via the nucleophilic attack of the ester enolate on the ester carbonyl, and this is followed by elimination of the alcohol and NHC to afford the cyclic tetramers **2**.

The organic bases, TPT, IMes, IDipp and trialkyl phosphine (PR_3), catalyzed distinct transformations of the acrylates, as shown in Scheme 2. These catalysts are sufficiently nucleophilic to add to the acrylates to generate the zwitterionic intermediate (**XIII**, **VII** and **XV**). For the tail-to-tail dimerization catalyzed by TPT, the β-proton of the intermediate **XIII** is transferred to generate the deoxy-Breslow intermediate (**XIV**). In the case of the cyclotetramerization catalyzed by IMes and IDipp, the dimeric zwitterionic intermediate **VII** also undergoes β-proton transfer, which leads to the deoxy-Breslow intermediate **VIII**. PR_3 catalyzes the Rauhut–Currier reaction, a head-to-tail dimerization, of acrylates. The intermediate **XV** derived from PR_3 undergoes α-proton transfer followed by the elimination of PR_3 to produce dimer **4**. The transfer of the β-proton to generate the



Scheme 3 Oxa-Michael addition polymerization of hydroxyl-functionalized acrylates catalyzed by TPT or IDipp.

phosphorus ylide intermediate is unfavorable in this case. The transfer of the α or β-protons is the difference between the NHCs and PR_3-catalyzed reactions.

OXA-MICHAEL ADDITION DIMERIZATION AND POLYMERIZATION

The conjugate addition of oxygen nucleophiles with electron-deficient alkenes, that is, the oxa-Michael addition, is an important O–C bond-forming reaction. In 2010, Scheidt and colleagues[39] showed that IMes acts as a Brønsted base catalyst for the oxa-Michael addition. Subsequently, we reported the tandem catalysis involving the oxa-Michael addition of methanol and the head-to-tail dimerization of methacrolein (MACR) catalyzed by organic bases, such as NHCs, DBU and Et_3P, to give dimer **5** (Figure 3).[49] Moderate yields were obtained, even with a low catalyst loading (0.70 mol%). In general, the NHC catalyst reacts with aldehydes to promote the umpolung, but the aldehyde group remains unreacted during this dimerization. Dimer **5** was readily converted to the oligomeric acetal product **6** by moisture in the air. This organocatalytic dimerization is specific for MACR. Other substrates (MA, dimethyl itaconate and *N*-phenyl maleimide) formed monomeric oxa-Michael adducts under the same conditions. The ESI-MS and tandem mass spectrometry (MS/MS) analysis supports the generation of the key intermediate (**XVIII**), which led us to propose the reaction mechanism as shown in Figure 3. The NHC catalysts act as Lewis bases without the direct activation of MeOH. The dimeric enolate intermediate (**XIX**) is equilibrated with the hemiacetal alkoxide (**XX**), thus resulting in selective dimerization without further Michael addition.

We then extended the oxa-Michael addition to the polymerization of hydroxyl-functionalized acrylate monomers (**7a–10a**) (Scheme 3).[50] TPT or IDipp catalyzed the polymerization at room temperature to give poly(ester-ether)s with alicyclic, alkene and alkyne groups in the main chain. Among them, the polymer (**10b**) with $M_n = 2400$ and $M_w/M_n = 3.8$ was obtained in 81% yield from the alkyne-functionalized monomer (**10a**). The nuclear magnetic resonance analysis and methanolysis of the resulting polymer (**7b**) revealed the frequency of the transesterification during the polymerization. The ESI-MS and MS/MS analysis supports the fact that the NHC is covalently linked to the C terminus of the polymer chain. We thus propose the Lewis base mechanism, which is similar to the dimerization of MACR.

The Lewis base mechanism of the oxa-Michael addition dimerization and polymerization developed by us is in contrast to the Brønsted base mechanism reported by Scheidt and colleagues.[39] We suggest that the mechanism depends on the electrophilicity of the Michael acceptors. The NHCs react with vinyl or vinylidene compounds, such as acrylates and MACR, even in the presence of alcohols, but for weak electrophilic vinylene compounds, such as β-methyl-substituted vinyl ketones, the NHCs directly activate alcohols without the nucleophilic attack on the sterically hindered β-carbons.

SUMMARY

We have demonstrated the NHC-catalyzed dimerization, cyclotetramerization and polymerization of Michael acceptors. TPT successfully catalyzed the tail-to-tail dimerization of a wide variety of substrates, ranging from (meth)acrylates and (meth)acrylonitrile to low electrophilic VPs and an activated styrene. Compared with metal-catalyzed dimerizations, this organocatalysis is superior in terms of substrate scope and functional group tolerance and is the most general procedure to synthesize tail-to-tail dimers. Because such dimers or their derivatives can be considered as bifunctional monomers, we expect that new synthetic routes to condensation polymers, such as polyesters and polyamides, from conventional vinyl monomers will be developed. In contrast, IMes catalyzed the unprecedented cyclotetramerization of acrylates through the dimeric deoxy-Breslow intermediate to afford trisubstituted cyclopentenones. TPT, IMes and PR_3 are similar nucleophiles, but they show distinct reactivity for acrylates. NHCs are effective catalysts for the oxa-Michael addition dimerization of MACR and the polymerization of hydroxyl-functionalized acrylates. It is proposed that the Michael addition of NHCs to the substrates generates zwitterionic intermediates followed by the activation of alcohols. The ESI-MS and MS/MS analyses of the intermediates are effective for determining the reaction mechanism.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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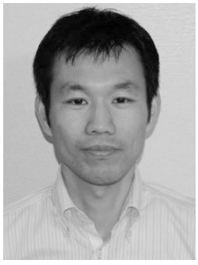

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