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Cooperative N-Heterocyclic Carbene/Brønsted Acid Catalysis for the Tail-to-Tail (Co)dimerization of Methacrylonitrile

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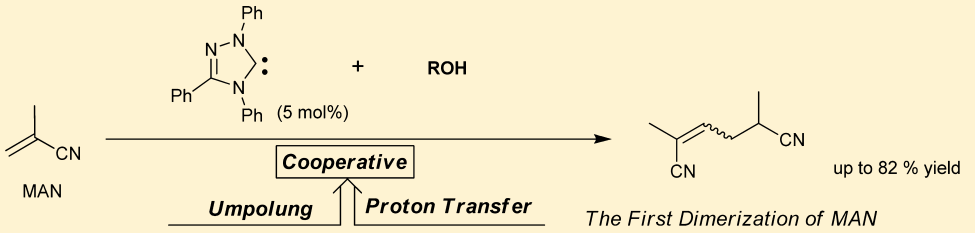
Supporting Information



The First Dimerization of MAN

ABSTRACT: The first tail-to-tail dimerization of methacrylonitrile (MAN) has been realized by the cooperative use of N-heterocyclic carbene (NHC) and Brønsted acid catalysts, producing 2,5-dimethylhex-2-enedinitrile with the *E*/*Z* ratio of 24:76. Although the NHC alone was not effective for the catalysis, the addition of alcohols resulted in the significant increase of the dimer yield up to 82% in the presence of 5 mol % NHC. Detailed experimental studies including the ESI-MS analysis of the intermediates, stoichiometric (co)dimerizations, and deuterium-labeling experiments revealed the mechanistic aspects of the proton transfer, isomerization, umpolung, and rate-limiting steps, allowing us to observe several mechanistic differences between the dimerization of MAN and that of methyl methacrylate. The stoichiometric reactions in the presence and absence of an alcohol suggest that the alcohol additives play a role in promoting the intermolecular proton transfers from the deoxy-Breslow intermediate to the regenerated NHC in the second half of the catalytic cycle. In addition, the codimerizations of MAN with *n*-butyl methacrylate (*n*-BuMA) have been studied. While the dimerization of *n*-BuMA was sluggish in the presence of an alcohol, the catalytic activity for the codimerization was enhanced by the cooperative systems.

INTRODUCTION

Bifunctional compounds, such as dicarboxylic acids and diamines, are important monomers for the synthesis of condensation polymers. The catalytic tail-to-tail (co)-dimerizations of functionalized olefins are attractive routes to access a variety of such monomers and are mostly promoted by transition metal-based systems.[1] For example, the precursors of adipic acid and hexamethylendiamine can be synthesized from the dimerizations of methyl acrylate and acrylonitrile, respectively, catalyzed by a variety of Pd,[2] Rh,[3] Ru,[4,5] and other metal[6] complexes, followed by hydrogenation. In contrast, the dimerizations of disubstituted olefins are generally difficult. Indeed, there are only a few reports on the dimerization of methyl methacrylate (MMA) catalyzed by Pd[7] and Ru[8] and, to our surprise, no example of that of methacrylonitrile (MAN). Because the polymers made from methyl-substituted monomers exhibit distinct properties from the nonsubstituted variants in terms of thermal stability, crystallinity, and solubility, the dimerization of such disubstituted olefins is an important issue that needs to be addressed.

N-Heterocyclic carbenes (NHCs)[9] have received a great deal of scientific attention as organocatalysts for the umpolung reactions of aldehydes via the Breslow intermediates.[10] The cooperative NHC and Lewis acid catalysis, involving dual-activation using metal and organic catalysts, has been found to offer interesting opportunities for the discovery of new reactions.[11] Since the first report by Scheidt et al.,[12] various Lewis acids, $Mg(OtBu)_2$,[12] $Ti(OiPr)_4$,[13] $Fe(OTf)_2$,[14] $Sc(OTf)_2$[15] and LiCl,[16] have been employed to improve the reactivity of the Breslow intermediates and/or substrate. In addition to Lewis acids, a few examples of the cooperative NHC and Brønsted acid catalytic systems have been reported by Rovis and Chi. They propose that Brønsted acids, such as catechols and carboxylic acids, promote proton transfer to form the Breslow intermediate,[17] the dual activation of the intermediate and electrophilic substrates,[18] and the intermediate transformation from homoenolates to enolates.[19]

Previously, we[20] and Glorius[21] independently developed the tail-to-tail dimerization of methacrylates catalyzed by NHC. This catalysis involves the umpolung of Michael acceptors through the deoxy-Breslow intermediates.[22] Recently, the reaction mechanism has been investigated both experimentally and computationally by us[23] and Chen,[24] in which we have revealed the reversibility, proton transfer mechanism, and rate-determining steps. Since the first report of the intramolecular reaction by Fu in 2006,[25] several other examples involving the umpolung reaction of Michael acceptors, such as the tautomerization of vinyl

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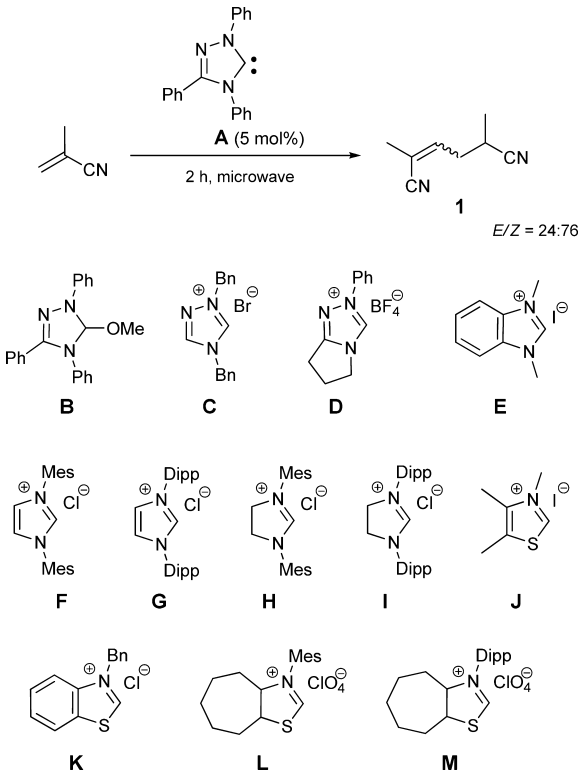
sulfones,[26] the stoichiometric three-component reaction,[27] and the cyclotetramerization of acrylates,[28] have appeared. However, the reaction scope is still not broad, and in particular, the substrate scope of the dimerization is limited to methacrylates. Glorius et al. previously attempted the dimerization of MAN catalyzed by the NHC precursor with DBU at 80 °C in 1,4-dioxane, but they documented that MAN was not suitable for the umpolung, not providing the homodimer.[21] However, on the basis of this negative reactivity, they carried out the selective codimerizations of MAN and *n*-butyl methacrylate (*n*-BuMA) to give a mixture of isomers of codimers with a low *E*/*Z* selectivity through the double bond migration. Because MAN shows a electrophilic reactivity only slightly higher than that of methacrylates, we envisioned that the detailed survey of the reaction conditions may lead to the first dimerization of MAN. We now report the cooperative NHC and alcohol catalytic systems for the (co)dimerization of MAN and the detailed experimental mechanistic studies.

RESULTS AND DISCUSSION

Tail-to-Tail Dimerization of MAN by Cooperative NHC and Alcohol Catalysts. We previously reported that the tail-to-tail dimerization of MMA at 80 °C in bulk or in solutions affords the corresponding dimer with an *E*/*Z* ratio of 95:5 in 86% yield. Under similar conditions, the initial experiments for the dimerization of MAN were carried out in bulk or in 1,4-dioxane for 2 h using 5 mol % NHC (**A**) or NHC precursors (**B**−**M**) (Table 1) using a sealed vial under microwave irradiation to increase the reaction temperature above the boiling point of MAN. Although the dimerization catalyzed by the isolated triazole NHC **A** did not proceed at 60 °C (entry 1), increasing the temperature to 80 and 100 °C resulted in the formation of the tail-to-tail MAN dimer **1** in 8% and 9% yields, respectively, with very low conversions (entries 2−4). The combinations of other NHC precursors **C**−**M** and DBU or K_2CO_3, generating NHCs in situ, did not give **1** (entries 5 and 6). This catalytic specificity was also observed in the dimerization of MMA. It is noteworthy that the methanol adduct **B**, which is converted to NHC **A** and methanol by heating, increased the yield of **1** to 18% and 26% yields (entries 7 and 8). This finding prompted us to add alcohols to the reaction system. Expectedly, similar improvements were found in the dimerizations in the presence of an equimolar amount of various alcohols for **A**. (entries 9−11 in Table 1, and entry 6 in Table S1, Supporting Information). The use of 5 and 10 equiv of alcohols enhanced the dimerization to give **1** in 62% and 58% yields (72% and 63% conversions), respectively (entries 12 and 13 in Table 1; see also entries 7 and 8 in Table S1). Further studies on the effects of the additives were then performed. The phenols, such as 2-naphthol and hydroquinone, as the additives gave **1** in nearly 20% yields (entries 15 and16). However, the addition of H_2O, carboxylic acids, bases, and Lewis acids, which were previously employed in the cooperative NHC catalysis,[11−13,15,16] were not effective (entries 14 and 17−24; see also entries 9−12 in Table S1). This suggests that the cyano group in MAN was not activated by the Lewis acids. Collectively, we hypothesized that alcohol additives would promote intermolecular proton transfers to lead to an efficient catalytic turnover.

When the combination of aliphatic alcohols and phenols was used as additives, the catalytic activities were improved (Table 2). The addition of 5.0 equiv of *i*-PrOH and 0.2 equiv of 2-naphthol for **A** provided **1** in 82% yield, in which the turnover number (TON) of the NHC catalyst was 8.2. A variety of combinations of

Table 1. Tail-to-Tail Dimerization of MAN[a]



entry	NHC	additive (equiv[b])	solvent[c]	temp (°C)	yield[d] (%)
1	**A**		–	60	0
2	**A**		–	80	8
3	**A**		–	100	9
4	**A**		DOX	100	8
5[e]	**C**−**M**	DBU (1.0)	DOX	100	0
6[e]	**C**−**M**	K_2CO_3 (1.0)	DOX	100	0
7	**B**		–	80	18
8	**B**		–	100	26
9	**A**	*i*-PrOH (1.0)	–	100	31
10	**A**	*t*-BuOH (1.0)	–	100	21
11	**A**	*n*-BuOH (1.0)	–	100	38
12	**A**	*n*-BuOH (5.0)	–	100	62
13	**A**	*n*-BuOH (10.0)	–	100	58
14	**A**	H_2O (1.0)	–	100	0
15	**A**	2-naphthol (1.0)	–	100	21
16	**A**	hydroquinone (1.0)	–	100	20
17	**A**	benzoic acid (1.0)	–	100	5
18	**A**	adipic acid (0.5)	–	100	5
19	**A**	LiCl (1.0)	–	100	10
20	**A**	$Sc(OTf)_3$ (1.0)	–	100	0
21	**A**	$Mg(OTf)_2$ (1.0)	–	100	10
22	**A**	$Mg(OtBu)_2$ (1.0)	–	100	<1
23	**A**	DBU (1.0)	–	100	0
24	**A**	K_2CO_3 (1.0)	–	100	13

[a]5.5 mmol of MAN and 5 mol % of NHC or NHC precursors, microwave irradiation for 2 h. [b]Equivalent relative to NHC. [c]1.0 mL of 1,4-dioxane or in bulk. [d]Isolated yield. [e]For 6 h.

alcohols afforded **1** in good yields (entries 2−5 in Table 2, see also entries 1−9 in Table S2, Supporting Information). With the catalyst loading of 2.5 mol %, **1** was obtained in 48% yield, however, with the higher TON of 10.6 (entry 6). We varied the reaction temperature, time, and amount of alcohols, but further improvements were not achieved (entries 7−10 in Table 2 and

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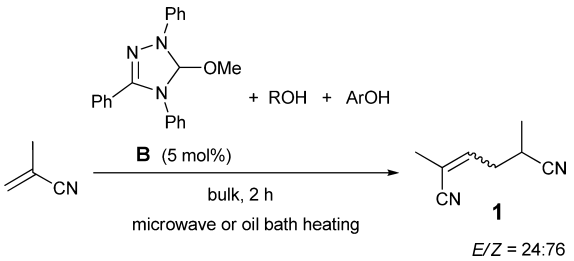
Table 2. Optimization of the Tail-to-Tail Dimerization of MAN in the Presence of Alcohols[a]



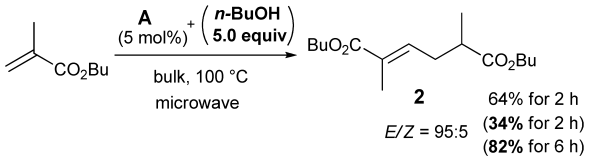
entry	B (mol %)	ROH (5.0 equiv[b])	ArOH (0.2 equiv[b])	temp (°C)	heating[c]	time (h)	yield[d] (%)
1	5.0	*i*-PrOH	2-naphthol	100	MW	2	82 (89[f])
2	5.0	EtOH	2-naphthol	100	MW	2	70
3	5.0	*t*-BuOH	2-naphthol	100	MW	2	75
4	5.0	*i*-PrOH	4-methoxyphenol	100	MW	2	77
5	5.0	*i*-PrOH	hydroquinone	100	MW	2	82
6	2.5	*i*-PrOH	2-naphthol	100	MW	2	48 (53[f])
7	5.0	*i*-PrOH	2-naphthol[e]	100	MW	2	62
8	5.0	*i*-PrOH	2-naphthol	100	MW	6	59
9	5.0	*i*-PrOH	2-naphthol	80	MW	2	51
10	5.0	*i*-PrOH	2-naphthol	120	MW	2	55
11	5.0	*i*-PrOH	2-naphthol	100	OB	2	64
12	5.0	*i*-PrOH	2-naphthol	120	OB	2	75

[a]5.5 mmol of MAN, 0.27 mmol of **B**, 1.4 mmol of ROH, amd 0.05 mmol of ArOH in bulk for 2 h. [b]Relative to **B**. [c]MW: microwave, OB: oil bath heating. [d]Isolated yield. [e]1.0 equiv to **B**. [f]Conversion of MAN determined by ^{1}H NMR.

Table S2). We then performed the reaction by oil bath heating in the same type of microwave vial. The reaction smoothly proceeded and produced **1** in good yields, i.e., 64% at 100 °C and 75% at 120 °C (entries 11 and 12). Therefore, nonthermal microwave effects were not observed in this reaction. The *E*/*Z* ratios of **1** were almost constant at 24:76, irrespective of the reaction conditions, while our previous report showed that those of the methacrylates were *E*/*Z* = 88−98:2−12.[20] The DFT calculations support that the *Z* isomer is favored (see Supporting Information).

Mechanistic Studies of the Dimerization of MAN. We evaluated the effect of alcohols on the dimerization of *n*-butyl methacrylate (*n*-BuMA). The reaction of *n*-BuMA with 5 mol % **A** for 2 h gave dimer **2** with an *E*/*Z* ratio of 95:5 in 64% yield, while in the presence of *n*-BuOH (5.0 equiv related to **A**), the reaction was sluggish and produced **2** in 34% yield for 2 h (Scheme 1). This result is in contrast to the dimerization of MAN (entries 3 and 12 in Table 1). Although the dimerization of MMA has been proved to proceed through intermolecular proton transfers,[23] the alcohol additive, in this case, exerts detrimental effects on the catalytic turnover. This interesting difference in the effect of alcohols between these two major substrates prompted us to investigate in detail the mechanistic aspects of the dimerization of MAN and the codimerization of MAN with *n*-BuMA.

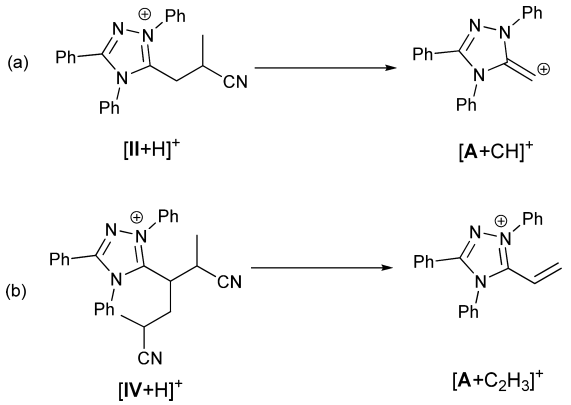
Scheme 1. Dimerization of *n*-BuMA in the Presence or Absence of *n*-BuOH[a]



[a]5.0 equiv of *n*-BuOH relative to **A** was used. The values in parentheses indicate the yields in the dimerization in the presence of *n*-BuOH.

When the dimerizations of MAN were performed under the optimal conditions for 10 and 20 min and then quenched by HCl, dimer **1** was obtained in 30% and 46% isolated yields, respectively. The ESI-MS spectra of both crude product mixtures showed signals corresponding to the proton adducts of intermediates **II** and **IV** (Scheme 2). When the dimerization was not quenched by HCl, the peak due to **IV** was not observed, suggesting that **IV** was relatively unstable. The MS/MS spectra of the $[\mathbf{II} + H]^+$ and $[\mathbf{IV} + H]^+$ showed corresponding fragments of $[\mathbf{A} + CH]^+$ and $[\mathbf{A} + C_2H_3]^+$, respectively, in a way similar to the MS analysis of the MMA dimerization. Thus, the dimerization of MAN proceeds through intermediates similar to those for the dimerization of MMA.

Scheme 2. ESI-MS/MS Fragmentation of Intermediates II and IV



When the reaction of MAN with 100 mol % **A** in 1,4-dioxane was carried out by oil bath heating at 80 °C for 5 min, followed by the addition of HCl, the adduct of the deoxy-Breslow

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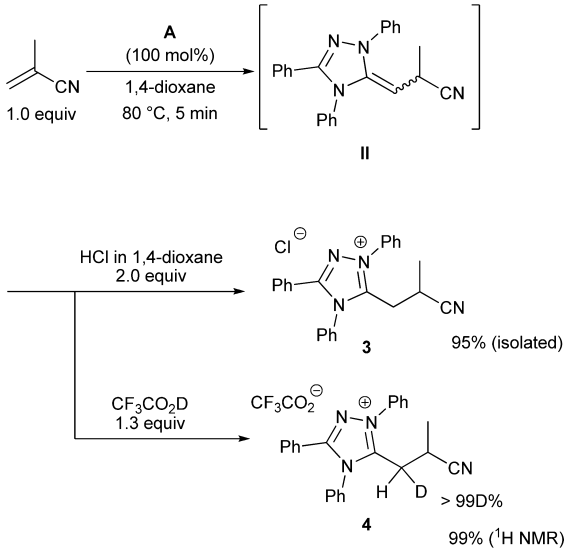
intermediates **3** was obtained in 95% yield (Scheme 3). The addition of CF_3CO_2D instead gave the adduct **4** with the

Scheme 3. Stoichiometric Reaction of MAN with A Quenched by HCl or CF_3CO_2D



selective deuterium incorporation at the β-carbon, supporting the formation of **II** in situ. These experiments indicated that the reaction of MAN with **A** to form **II** is more rapid than the subsequent Michael addition (**II** → **III** in Figure 1). This kinetics

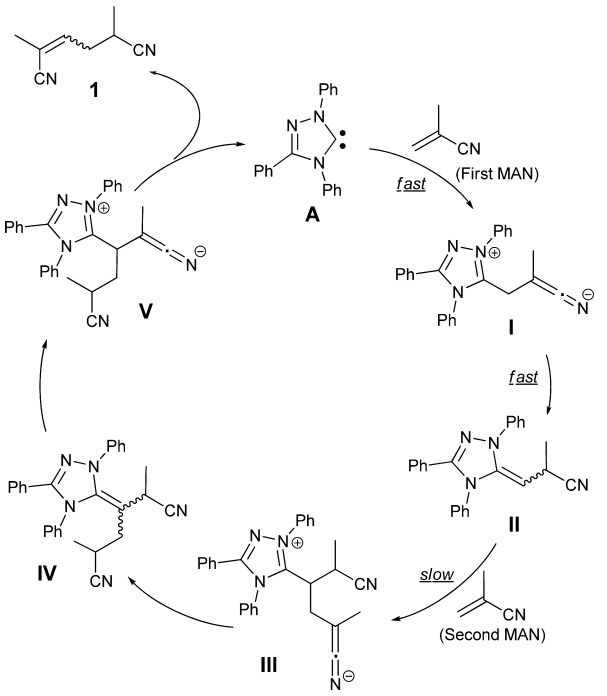
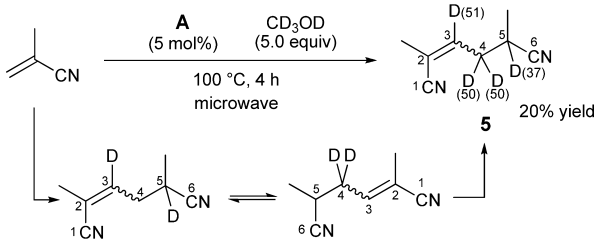


Figure 1. Reaction mechanism.

in the first half of the catalytic cycle is similar to that of the dimerization of MMA. On the basis of the results of the ESI-MS analysis and the stoichiometric reactions, we propose the reaction mechanism shown in Figure 1.

To gain insight into the proton transfer mechanisms, we performed the dimerization of MAN in the presence of CD_3OD (5.0 equiv relative to **A**) (Scheme 4). Dimer **5** was obtained in 20% yield with the deuterium incorporation at C3, C4, and C5,

Scheme 4. Dimerization of MAN in the Presence of CD_3OD through Double-Bond Migration[a]



[a]The values in parentheses indicate the percentage of deuterium incorporations.

indicating intermolecular proton transfers without exchanges between the α-methyl and alkenyl protons of MAN. We previously reported that the deuterium incorporations at C3 and C5, but not C4, were observed in the dimerization of MMA under similar conditions. This indicates that the double-bond migration in the MAN dimer consisting of the migrations of the allylic and α-protons (or deuteriums) resulted in the deuterium incorporation at C4 under these conditions.[29]

Codimerization of MAN with *n*-BuMA and Effects of Alcohol Additives. Glorius et al. previously demonstrated the codimerization of MAN and *n*-BuMA at a molar ratio of MAN/*n*-BuMA = 2:1. We then performed the codimerizations of MAN with an equimolar amount of *n*-BuMA in the presence or absence of *n*-BuOH to elucidate the role of alcohols and to compare the reactivity of the two substrates (Scheme 5). The codimerization in the presence of 10 mol % **A** produced homodimers **1** and **2** and codimers **6** and **7**. It is noteworthy that the alcohol additive was also found to improve the catalysis. Indeed, the addition of *n*-BuOH increased the yields of all dimers from 30% to 87%. In particular, the yields of **1** and **6** increased from 3% and 13% to 24% and 37%, respectively. Because the double-bond isomerization of **6** or **7** was not observed in the stoichiometric reactions (See Schemes 7 and 8), we assumed that the isomerization would not take place under the catalytic conditions.

The catalytic codimerizations of MAN with *n*-BuMA were performed for 1 min and quenched by the addition of HCl (Scheme 6). Adducts **3** and **8** were obtained in 45% and 28% ^{1}H NMR yields based on **A**, respectively, without the formation of the dimers. Adduct **3** was produced more rapidly than **8** because of the higher electrophilicity of MAN than *n*-BuMA. Although the yield of **3** slightly increased in the presence of *n*-BuOH, no significant difference was found. Thus, we reason that the alcohol additives hardly affect the first half of the catalytic cycle (**A** → **II** in Figure 1).

We then performed the stoichiometric reactions of intermediates **II** or **VII**, which are quantitatively formed in situ (Scheme 3 and ref 23), with MAN or *n*-BuMA.[29] The reaction of **II** with an equimolar amount of *n*-BuMA gave codimer **6** in 24% yield, and the addition of *n*-BuOH improved the yield to 48% (Scheme 7). The regenerated **A** catalyzed the homodimerization of the unreacted *n*-BuMA to give **2** in 17% and 15% yields, respectively, in the presence and absence of *n*-BuOH. Interestingly, the reaction of **II** with MAN gave only a trace amount of **1**, but the addition of *n*-BuOH significantly increased the yield to 46%. In contrast, no significant effects of the alcohol in the reactions of intermediate **VII**, generated from *n*-BuMA,

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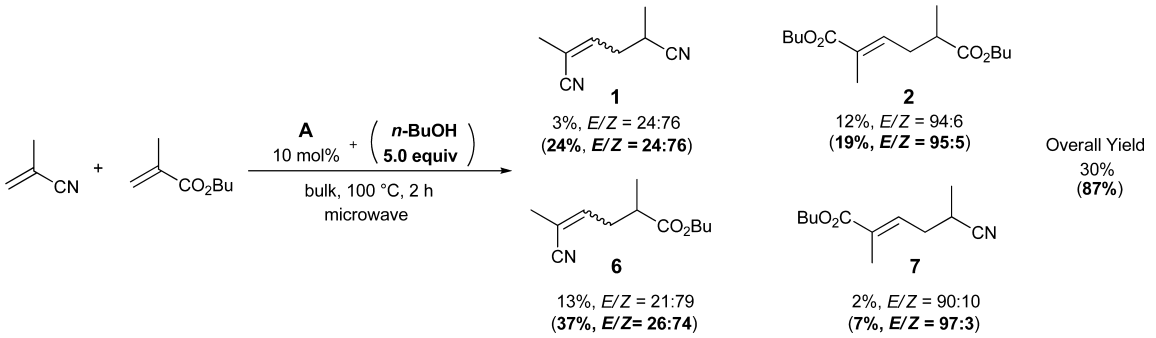
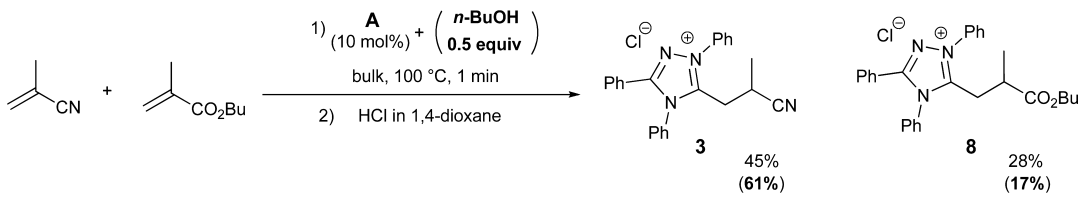
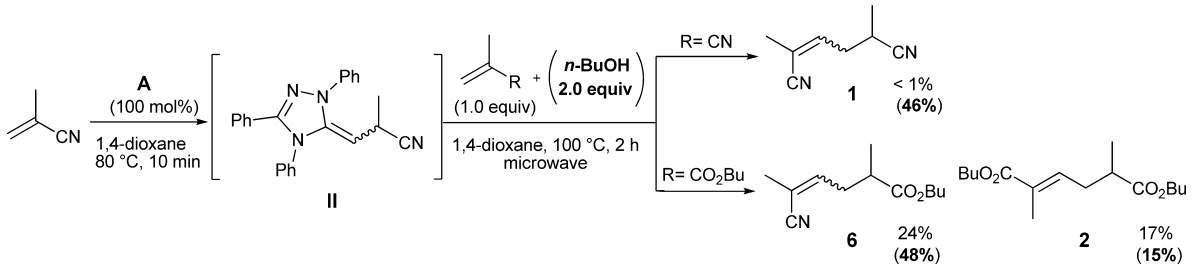
Scheme 5. Catalytic Codimerizations of MAN and *n*-BuMA



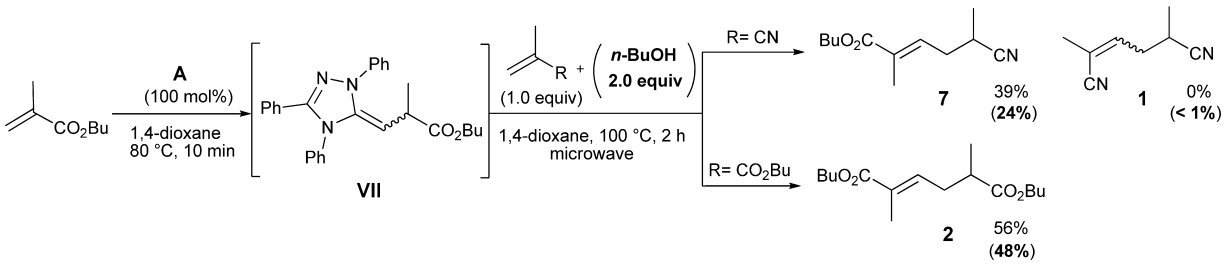
Scheme 6. Short-Time Reaction of MAN and *n*-BuMA with 10 mol % of A



Scheme 7. Stoichiometric Reactions of II with MAN or *n*-BuMA

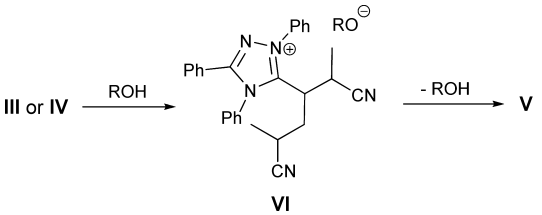


Scheme 8. Stoichiometric Reactions of VII with MAN or *n*-BuMA



were found (Scheme 8). These results indicated that the alcohol contributes to the second half of the catalytic cycle in the dimerization of MAN (**II** → **A** in Figure 1). During the catalytic codimerization, intermediate **II** is formed more rapidly than **VII**, but, in the absence of the alcohol, the subsequent reaction of **II** with MAN or *n*-BuMA is slow, resulting in the low overall catalytic activity. It is reasonable to assume that the alcohols promoted the proton transfer processes (**III** → **V**) to regenerate **A**, leading to the efficient catalytic turnover. We speculated that the reaction of intermediates **III** or **IV** with alcohols gives intermediary species **VI**, which subsequently undergoes the elimination of the alcohol to form **V** (Scheme 9).

Scheme 9. Speculative Mechanism of the Proton Transfer Assisted by Alcohol in the Dimerization of MAN



■ CONCLUSIONS

We have shown that the first dimerization of MAN was achieved by the cooperative NHC and alcohol catalyst. During the course of the optimization of the reaction conditions, a three-component catalyst system of aliphatic alcohols and phenols (5 and 0.2 equiv for NHC, respectively) with 5 mol % of the triazole NHC was found to afford the dimer in 82% yield. The cooperative system is also effective for the codimerization of MAN with *n*-BuMA. We propose that alcohol additives promote

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the intermolecular proton transfers in the second half of the catalytic cycle. Similar to the dimerization of methacrylates, that of MAN involves (1) the key deoxy-Breslow and dimeric intermediates (**II** and **VI**) and (2) intermolecular proton transfers. In addition, (3) the reaction of the deoxy-Breslow intermediate with MAN to form the C−C bond is the rate-limiting step. The differences are as follows: (1) the double-bond migration in the MAN dimer is involved, (2) the *E*/*Z* selectivity is much lower, and most interestingly, (3) the alcohol additive promotes the catalytic turnover. The cooperative systems involving the umpolung can create new opportunities for the bond-forming process of a wide variety of Michael acceptors.

EXPERIMENTAL SECTION

General. All reactions were performed under nitrogen atmosphere. Under the microwave heating, the reaction temperature was measured by a surface sensor. NHC precursors were prepared according to previous literature (**A**,[30] **B**,[30] **C**,[31] **D**,[32] **E**,[33] **F**,[34] **G**,[34] **H**,[34] **I**,[34] **J**,[35] **L**,[36] **M**[36]). MAN was distilled from $CaCl_2$ and subsequently from CaH_2 under reduced pressure and stored over 3 Å molecular sieves. *n*-BuMA, *n*-BuOH, *tert*-butyl alcohol and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were distilled from CaH_2 under reduced pressure. Triethylamine, *i*-PrOH, and 1,4-dioxane were distilled from CaH_2. Methanol was distilled from Mg. 2-Naphtol, hydroquinone, 4-methoxyphenol, biphenyl, and benzoic acid were recrystallized from the mixture of ethanol and toluene before use. Other chemicals were used as received. Microwave irradiation experiments were performed using a Biotage Initiator 2.5 instrument, under the following menu selections; prestirring: off, absorption level: very high, fixed hold on time: on. ^{1}H and ^{13}C NMR spectra were recorded on 600 MHz (600 MHz for ^{1}H, 150 MHz for ^{13}C) or 400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C) NMR spectrometers. Chemical shift values in ^{1}H and ^{13}C NMR spectra are relative to internal TMS standard (0.0 ppm for ^{1}H) or $CDCl_3$ resonance (77.1 ppm for ^{13}C). Electrospray ionization mass spectrometry (ESI-MS) and tandem mass spectrometry (ESI-MS/MS) were performed on a tandem quadrupole orthogonal acceleration time-of-flight instrument equipped with a Z-spray nanoelectrospray ionization source. GC analysis was carried out on an instrument equipped with a flame ionization detector and a Zebron ZB-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Phenomenex). All of the dimers were characterized by GC. The GC yields of the products and the conversions of substrates were estimated using biphenyl as an internal standard. The (co)dimers (**1**, **2**, **5**−**7**) were obtained as transparent liquids purified by Kugelrohr distillation under reduced pressure (<1 Torr) at 110 °C for **1**and **5**, 180 °C for **2**, 130 °C for **6**, and 230 °C for **7**.

The calculations of **1** (*E* and *Z*) were carried out with the density functional theory (DFT) in the Gaussian 09 program.[37] Geometry optimizations and vibrational frequencies (to make zero-point corrections) were calculated using the B3LYP[38,39] method at the 6-31+G(d,p) level. A series of single-point calculations were performed with the basis sets B3LYP/6-311+G(3df,2p), B3LYP/6-311++G(d,p), and B3LYP/6-31+G(d, p) on the optimized geometry.

Tail-to-Tail Dimerization of Methacrylonitrile (Table 1, Entry 12). In a two-necked flask equipped with a three-way stopcock, NHC precursor **B** (90 mg, 0.27 mmol) was heated at 100 °C for 12 h under vacuum conditions to produce NHC **A**. MAN (0.36 g, 5.4 mmol) and *n*-BuOH (100 mg, 1.35 mmol) were then added to this flask at room temperature. The mixture was transferred to a 0.5−2 mL microwave vial, which was then sealed and heated with microwave irradiation at 100 °C for 2 h. The reaction mixture was subjected to Kugelrohr distillation under reduced pressure to give **1** (0.22 g, 1.7 mmol) in 62% isolated yield.

*2,5-Dimethylhex-2-enedinitrile (**1**) (E/Z = 24:76).* ^{1}H NMR (600 MHz, $CDCl_3$) (*E*) *δ*: 1.54 (d, *J* = 7.4 Hz, 3H), 1.94 (s, 3H), 2.46−2.52 (m, 2H), 3.03−3.04 (m, 1H), 6.35 (dd, *J* = 7.7, 7.5 Hz, 1H), (*Z*) *δ*: 1.38 (d, *J* = 7.1 Hz, 3H), 2.01 (s, 3H), 2.62−2.67 (m, 2H), 2.77−2.79 (m, 1H), 6.22 (dd, *J* = 7.6, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$); (*E*) *δ*: 15.3, 17.4, 24.7, 32.4, 113.3, 115.6, 119.7, 141.7, (*Z*) *δ*: 17.6, 20.2, 24.9, 35.2, 113.6, 117.3, 121.6, 141.7. HRMS (ESI) *m*/*z*: calcd for $C_8H_{11}N_2$ $[M + H]^+$ 135.0922, found 135.0923. IR (neat, cm^{-1}): 2987, 2943, 2241, 2218, 1644, 1454, 1384, 1327, 1120, 1048, 910, 867.

Stoichiometric Reaction of MAN and NHC A (Scheme 3). To a solution of **A**, generated from **B** (100 mg, 0.30 mmol) in 1,4-dioxane (0.6 mL), was added MAN (20 mg, 0.30 mmol) at 80 °C, and the mixture was stirred for 5 min. The reaction was quenched by HCl in 1,4-dioxane (1.0 mL, 3.0 mol/L). The crude product was purified by silica gel column chromatography using CH_2Cl_2/MeOH (7:1) as the eluent to give **3** (0.11 g, 0.29 mmol) in 95% yield.

*5-(2-Cyanopropyl)-1,3,4-triphenyl-4H-1,2,4-triazol-1-ium Chloride (**3**).* Mp = 108−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.14 (d, *J* = 7.1 Hz, 3H), 2.53−2.56 (m, 1H), 3.34 (dd, *J* = 10.9, 10.7 Hz, 1H), 4.19 (dd, *J* = 5.6, 5.6 Hz, 1H), 7.47−8.53 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 18.2, 22.4, 30.5, 120.0, 122.3, 126.6, 128.9, 129.4, 130.3, 131.4, 132.1, 132.2, 134.7, 152.5, 153.6. HRMS (ESI) *m*/*z*: calcd for $C_{24}H_{21}N_4$ $[M - Cl]^+$: 365.1766, found: 365.1768. IR (neat, cm^{-1}): 3353, 3052, 2243, 2175, 1556, 1377, 1294, 1260, 927, 760, 739, 694

Dimerization of MAN in the Presence of CD_3OD (Scheme 4). NHC **B** (97 mg, 0.29 mmol), CD_3OD (0.21 g, 5.8 mmol), and MAN (0.39 g, 5.8 mmol) were added into a 0.5−2.0 mL microwave vial, which was then sealed and heated with microwave irradiation at 100 °C for 2 h. Kugelrohr distillation under reduced pressure gave **5** (78 mg, 0.58 mmol) in 20% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.37 (d, *J* = 6.2 Hz, 3.0H), 2.01 (s, 3.0H), 2.58−2.63 (m, 1.0H), 2.73−2.80 (m, 0.61H), 6.22 (brs, 0.50H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 17.5, 20.2, 24.5, 24.6, 24.7, 24.8, 34.7, 35.0, 35.1, 35.2, 113.5, 117.3, 121.5, 141.1, 141.3, 141.5, 141.6, 141.7. HRMS (ESI) *m*/*z*; calcd for $C_8H_{11}N_2$ $[M + H]^+$ 135.0916, found 135.0913; calcd for $C_8H_{10}DN_2$ $[M + H]^+$ 136.9079, found 136.0980; calcd for $C_8H_9D_2N_2$ $[M + H]^+$ 137.1040, found 137.1041; calcd for $C_8H_8D_3N_2$ $[M + H]^+$ 138.1108, found 138.1103; calcd for $C_8H_7D_4N_2$ $[M + H]^+$ 139.1169, found 139.1160.

Catalytic Codimerization of MAN and *n*-BuMA (Scheme 5). To a 0.5−2.0 mL microwave vial were added NHC **A**, generated from **B** (80 mg, 0.24 mmol), and a mixture of MAN (0.16 g, 2.4 mmol), *n*-BuMA (0.34 g, 2.4 mmol), and *n*-BuOH (89 mg, 1.2 mmol) at room temperature. The vial was sealed and heated with microwave irradiation at 100 °C for 2 h. Biphenyl (40 mg, 0.26 mmol) was then added as a GC standard. The yields and the *E*/*Z* ratios of dimers **1**, **2**, **6**, and **7** were determined from GC analysis.

Short-Time Reaction of MAN and *n*-BuMA with A under Catalytic Condition (Scheme 6). NHC **A** (72 mg, 0.24 mmol) was added to a mixture of MAN (0.16 g, 2.4 mmol), *n*-BuMA (0.34 g, 2.4 mmol), and *n*-BuOH (89 mg, 1.2 mmol) under oil bath heating at 100 °C. The reaction mixture was stirred for 1 min and then quenched with HCl in 1,4-dioxane. The mixture was dried in vacuo and subjected to ^{1}H NMR measurement in $CDCl_3$. The yields of **3** and **8** were determined from the integration ratio of the aromatic signals to the methylene signals.

Stoichiometric Reactions of II with *n*-BuMA (Scheme 7). To a solution of **A**, generated from **B** (100 mg, 0.30 mmol), in 1,4-dioxane (0.6 mL) was added MAN (20 mg, 0.30 mmol) at 80 °C, and the mixture was stirred for 10 min. After the volatiles were removed under reduced pressure, *n*-BuMA (43 mg, 0.30 mmol), *n*-BuOH (45 mg, 0.60 mmol), and 1,4-dioxane (0.3 mL) were added at room temperature. The mixture was transferred to a 0.2−0.5 mL microwave vial, which was then sealed and heated with microwave irradiation at 100 °C for 2 h. Kugelrohr distillation under reduced pressure gave **6** (30 mg, 0.14 mmol) in 48% isolated yield. The reactions shown in Scheme 8 were similarly conducted. For the ^{1}H and ^{13}C NMR, HRMS, and IR data of **6** and **7**, see ref 21.

ASSOCIATED CONTENT

Supporting Information

Supplementary tables, results of DFT calculations, and copies of ^{1}H, ^{13}C, and 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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