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Letter

Switchable Cobalt-Catalyzed α-Olefination and α-Alkylation of Nitriles with Primary Alcohols

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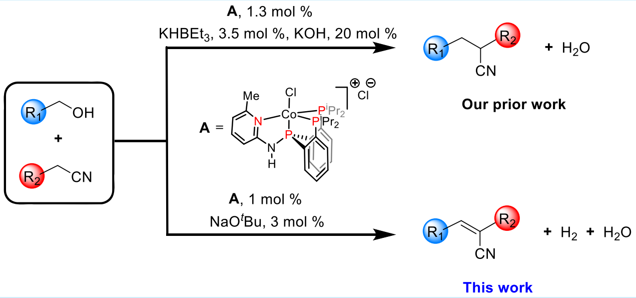
ABSTRACT: The first switchable α-olefination and α-alkylation of nitriles with primary alcohols catalyzed by a well-defined base transition-metal Co complex was presented. A broad variety of nitriles and primary alcohols are selectively and efficiently converted to the corresponding products by this method. It is noteworthy that the transformation is environmentally benign and atom efficient with H_2 and H_2O being the sole byproducts.



α,β-Substituted acrylonitriles are a family of organic compounds that are primarily applied as important building blocks, intermediates, and functional molecules for a range of products such as fragrances, dyes, polymeric materials, pharmaceuticals, natural products, etc.[1] Traditionally, the synthesis of the α,β-substituted acrylonitriles involves base-mediated condensation of carbonyl compounds and nitriles, which is normally accompanied by several competitive side-reactions, e.g., aldol reaction of aldehydes, self-condensation of nitriles, hydrolysis of nitriles to amides, etc.[2] Alternative synthetic methods of the condensation of nitriles and carbonyl compounds toward the α,β-substituted acrylonitriles have been disclosed, which, however, suffer from several issues such as low yields, the involvement of toxic reagents, generation of plentiful wastes, limited availability of the substrates, and tedious procedures.[3] Thus, there is an emerging need to develop new synthetic methods to address these challenges.

Homogeneous transition-metal-catalyzed carbon−carbon bond formation belongs to one imperative synthetic strategy for value-added products.[4] An attractive method is to utilize the cheap, low-toxic, and readily available alcohols as the alkylating agents through an acceptorless dehydrogenative coupling (ADC) process.[5,6] The typical procedure of ADC toward α,β-substituted acrylonitriles involves the dehydrogenation of primary alcohols to aldehydes, liberating H_2 to regenerate the catalytically active species. Then, the *in situ* formed aldehydes undergo condensation with the nitriles, furnishing the α,β-substituted acrylonitrile products and H_2O. Alternatively, the α,β-substituted acrylonitriles can be hydrogenated by the catalyst, leading to the saturated nitrile products. This process is recognized as the borrowing hydrogen (BH).[5,6]

There are a few examples of the synthesis of α,β-substituted acrylonitriles via the ADC process, the majority of which are based on precious transition-metal catalysts.[7] With the growing concerns on the sustainability and economy, the replacements of these precious metals with earth-abundant alternatives, e.g., Mn, Fe, Co, etc., are becoming more appealing.[8] To our best knowledge, there is just a single case disclosed by Milstein and co-workers using primary alcohols as the alkylating agents by a pincer Mn complex.[9] However, the reaction is sluggish with an average reaction time of over 40 h. Very recently, Balaraman and co-workers reported a Mn-catalyzed α-olefination of nitriles with secondary alcohols.[10] Examples of α-alkylation of nitriles with primary alcohols to saturated nitriles by base transition-metal catalysts are also limited.[11]

We have established a bench-stable Co complex (**A**) supported by a tetradentate N,P mixed-donor ligand $^{iPr}PPPN^{H}Py^{Me}$.[12a] **A** has proven to be an efficient and versatile precatalyst for secondary alcohol dehydrogenation to ketones,[12a] primary alcohol dehydrogenative self-coupling to esters,[12b] switchable couplings of primary and secondary alcohols to ketones and alcohols,[12c,d] and switchable couplings of alcohols and amines to imines and amines.[12e] We recently demonstrated that **A** can efficiently catalyze couplings of primary alcohols and nitriles to selectively form saturated nitriles[12f] (Scheme 1, top).

Encouraged by our recent studies, we herein present the cobalt-based catalytic system for the selective synthesis of α,β-substituted acrylonitriles via the ADC process with H_2 and

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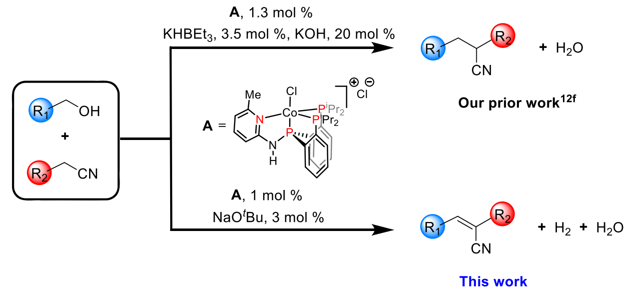
Scheme 1. Switchable α-Alkylation of Primary Alcohols with Nitriles Catalyzed by a Well-Defined Cobalt Complex A



H_2O as the only byproducts (Scheme 1, bottom). To the best of our knowledge, Co-catalyzed α-olefination of nitriles with primary alcohols has not been known so far. It is noteworthy that a short reaction time of 6 h suffices. This work also represents the first switchable α-olefination and α-alkylation of nitriles with primary alcohols to α,β-substituted acrylonitriles and nitriles, respectively, catalyzed by any base transition-metal catalyst.

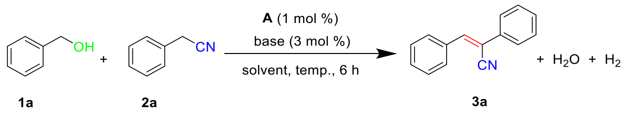
Results and Discussion

Previously, we disclosed that **A** can catalyze α-alkylation of nitriles using primary alcohols to nitriles in the presence of 20 mol % KOH and 3.5 mol % $KHBEt_3$.[12f] Mechanistic study showed that KOH plays a crucial role in the hydrogenation of the acrylonitrile intermediate to nitrile via the Meerwein−Ponndorf−Verley (MPV) pathway.[13] We surmise that at the reduced base loading, whereas the MPV process is efficiently suppressed, the reaction could be delicately controlled at the acrylonitrile level. Indeed, the reaction of benzyl alcohol (0.25 mmol) and benzyl cyanide (0.35 mmol) in the presence of 1 mol % **A** and 3 mol % KOH without $KHBEt_3$ resulted in a 67% yield of 2,3-diphenylacrylonitrile in 6 h at 140 °C (Table 1, entry 1). Intrigued by this result, we performed the optimization of the reactions. Among various types of bases, NaO^tBu was proven to be more suitable, leading to an excellent 90% NMR yield and 85% isolated yield after purification by column chromatography (Table 1, entries 1, 2, 4, and 6−8). Control experiments showed that both **A** and base are essential for the reaction (Table 1, entries 9 and 10). A temperature of 140 °C and solvents such as toluene and benzene are more favorable for the reaction (Table 1, entries 2−4, 11, and 12). Remarkably, 6 h is sufficient for the completion of the reaction (Table 1, entries 4 and 5), which is in stark contrast to the reported Mn case, where a long reaction time of about 40 h is required.[9] The ^1H NMR is on par with the *Z*-isomer. An 87% isolated yield was obtained on the 1 mmol scale reaction (Table 1, entry 13). Mercury testing suggested a homogeneous catalytic system[14] (Table 1, entry 14). H_2 was confirmed by the analysis of gas phase by GC, indicating an ADC pathway (see Supporting Information (SI)).

After obtaining the optimized reaction conditions, we then explored the substrate scope of the reaction. First, we focused on the scope of aromatic primary alcohols. Aromatic primary alcohols bearing electron-donating groups such as −OMe, −Me, $-{}^i$Pr at the *para* position transformed smoothly to give the corresponding products in good to very good 60%−87% yields with *Z*-selectivity (Table 2, entries **3b**−**3d**, **3s**, and **3t**). Similarly, aromatic primary alcohols with electron-withdrawing groups such as −Cl, −F, $-CF_3$ at the *para* position afforded desired products in good to excellent 76−92% yields (Table 2, entries **3f**−**3h**). Pleasingly, sterically hindered 2-methyl benzyl alcohol and 2-naphthyl methanol also proceeded well, leading to 81% and 82% yields, respectively (Table 2, **3e** and **3k**). Heteroaryl alcohols like piperonyl alcohol and 2-furfuryl methanol rendered the olefinic nitrile products in moderate to very good yields (Table 2, entries **3i**, **3j**, and **3u**). Next, we investigated the scope of nitriles. Pleasingly, various aromatic nitriles with various electronic properties gave the corresponding products with 60−87% yields (Table 2, entries **3h**, **3l**, **3m**, **3q**, **3r**, and **3s**). Interestingly, nitriles with pyridyl and naphthyl ring delivered the desired acrylonitriles in 73% and 89% yields, respectively (Table 2, entries **3o** and **3p**). It is noteworthy that the cyanide functionality is well tolerated (Table 2, entry **3t**). With regards to the aliphatic primary alcohols, such as 1-hexanol and 1-dodecanol, the reactions turned out to be sluggish under the standard conditions. Gratifyingly, upon doubling the loadings of **A** and NaO^tBu and prolonging the reaction time to 24 h, the reactions were significantly enhanced, revealing excellent 95% and 90% yields, respectively (Table 2, entries **3v** and **3w**). Notably, unsaturated aliphatic primary alcohols are also viable substrates with the C═C bond remaining intact (Table 2, entry **3x**). Unfortunately, benzenepropanenitrile and aliphatic nitrile were not compatible with this method (Table 2, entry **3y**).

Next, we performed a mechanistic exploration to understand this reaction. A deuterium labeling experiment using **1a-d**$_2$ and **2a** resulted in 90% D-incorporation at the β position of the nitrile group, indicating the alcohol dehydrogenation step is reversible (Scheme 2). The kinetic isotope effect (KIE) of 1.65 was obtained, which indicates that the breakage of the α-C−H bond of **1a** is moderately slow. The KIE number echoes the one from our prior study on the selective nitrile forming reaction, which is 1.88.[12f]

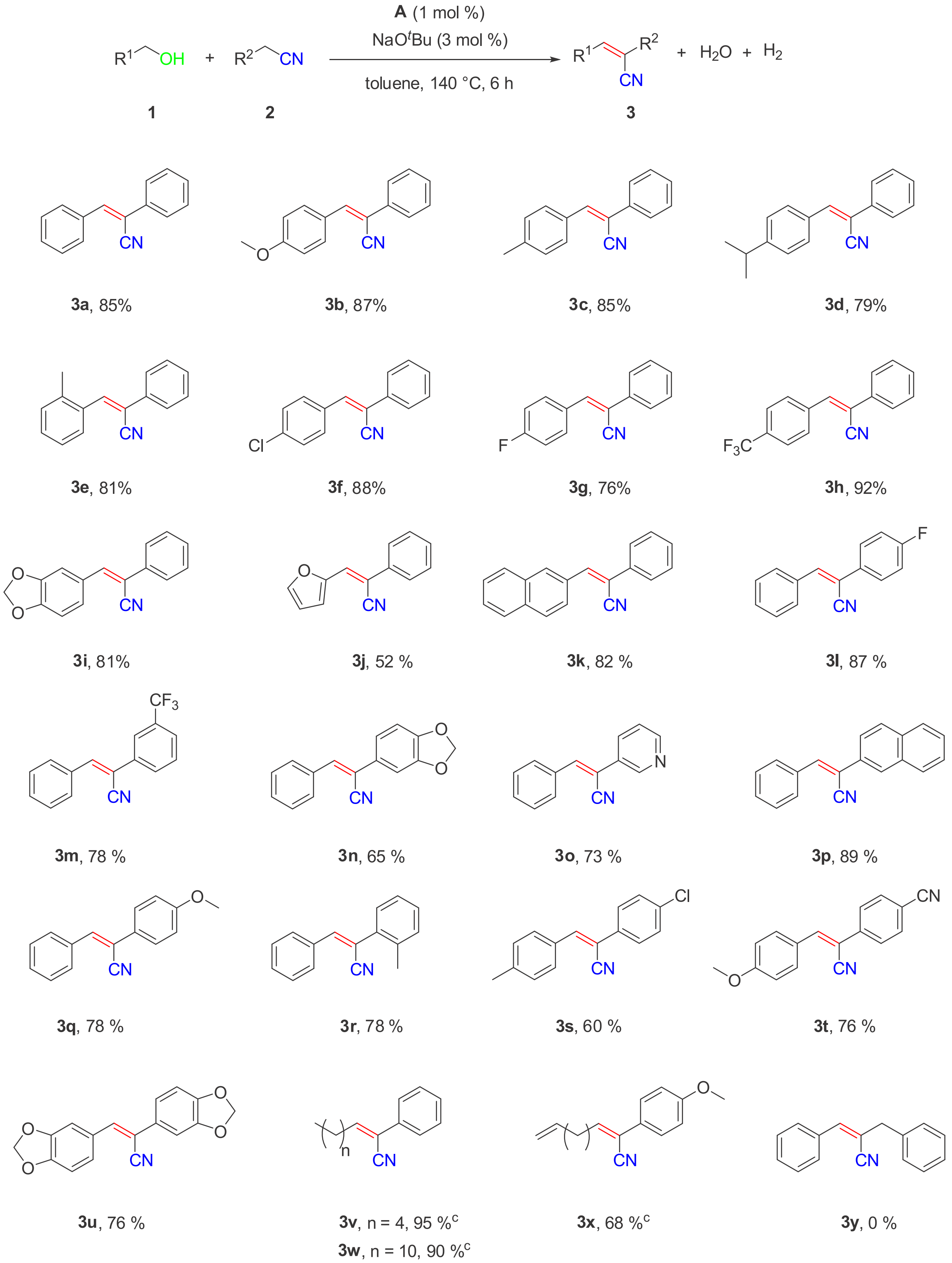
Table 1. Reaction Screening[a]



entry	cat.	base	solvent	temp (°C)	yield (%)[b]
1	**A**	KOH	toluene	140	67
2	**A**	KO^tBu	toluene	140	82
3	**A**	KO^tBu	toluene	125	52
4	**A**	NaO^tBu	toluene	140	90, 85[c]
5	**A**	NaO^tBu	toluene	140	90,[d] 86[e]
6	**A**	K_2CO_3	toluene	140	0
7	**A**	$KHBEt_3$	toluene	140	83
8	**A**	$LiHBEt_3$	toluene	140	63
9	**A**	–	toluene	140	0
10	–	NaO^tBu	toluene	140	0
11	**A**	NaO^tBu	benzene	140	90
12	**A**	NaO^tBu	THF	140	44
13[f]	**A**	NaO^tBu	toluene	140	87
14[g]	**A**	NaO^tBu	toluene	140	83

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.35 mmol), **A** (1 mol %), base (3 mol %), and solvent (1.2 mL) were heated in a reaction vessel (15 mL) with an argon balloon on top for 6 h. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield of **3a**. [d]15 h. [e]5 h. [f]Isolated yield of **3a** on the 1 mmol scale reaction. [g]Mercury (125 mg) was added to the reaction.

Table 2. α-Olefination of Nitriles with Primary Alcohols[a,b]

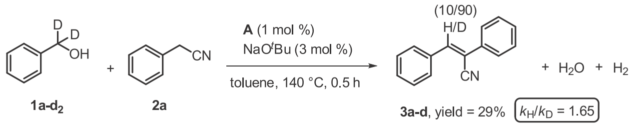


3a, 85%
3b, 87%
3c, 85%
3d, 79%
3e, 81%
3f, 88%
3g, 76%
3h, 92%
3i, 81%
3j, 52 %
3k, 82 %
3l, 87 %
3m, 78 %
3n, 65 %
3o, 73 %
3p, 89 %
3q, 78 %
3r, 78 %
3s, 60 %
3t, 76 %
3u, 76 %
3v, n = 4, 95 %[c]
3w, n = 10, 90 %[c]
3x, 68 %[c]
3y, 0 %

[a] Reaction conditions: primary alcohol (0.25 mmol), nitrile (0.35 mmol), **A** (1 mol %), NaO^{t}Bu (3 mol %), and toluene (1.2 mL) were heated at 140 °C in a reaction vessel (15 mL) with an argon balloon on top for 6 h. [b] Isolated yields. [c] **A** (2 mol %) and NaO^{t}Bu (6 mol %) for 24 h.

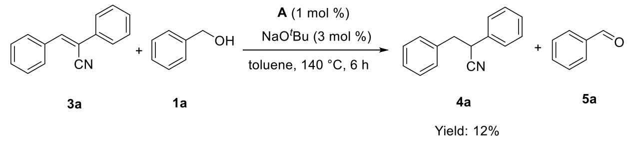
In the switchable acrylonitrile and nitrile synthesis, the base loadings play a critical and unique role in the selectivity determination. High base loadings that facilitate the MPV hydrogenation process result in the saturated nitrile

Scheme 2. Deuterium Labeling Experiment Using 1a-d_2

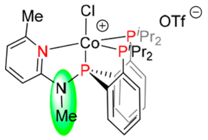


products;[12f] on the contrary, acrylonitriles are selectively formed employing a catalytic amount of base as revealed in the present work. We have successfully leveraged this strategy to achieve switchable imine/amine and ketone/alcohol synthesis based on **A**.[12c−e] The series of studies apparently demonstrate the high efficiency, selectivity, and versatility of our Co catalytic system affording a range of valuable products. In addition to the effects of the base loadings, the lack of hydrogenation ability of **A** at low base loadings is crucial for the product-switching. To test this hypothesis, the transfer hydrogenation of 2,3-diphenylacrylonitrile by benzyl alcohol was performed in the presence of 1 mol % **A** and 3 mol % of NaO^{t}Bu at 140 °C for 6 h (Scheme 3). A poor 12% yield of 2,3-diphenylpropanenitrile resulted. In stark contrast, with 20 mol % base alone, a significantly enhanced 82% yield was reached in just 15 min.[12f] These results shed light on the roles of base loadings on the selectivity. A comprehensive mechanistic study is currently underway in our laboratory.

Scheme 3. Transfer Hydrogenation of 2,3-Diphenylacrylonitrile



To explore if the metal−ligand cooperativity (MLC) participates through the N−H linker on **A**, we employed complex **B** as the precatalyst, which bears an N−Me moiety[12a] (Figure 1). Interestingly, a comparable 84% yield of **3a** was obtained, suggesting that MLC may not play a crucial role.

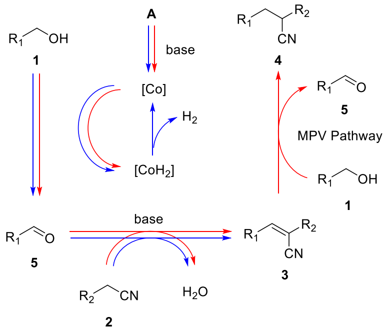


B

Figure 1. Complex **B** examined.

Previously, we have shown that **A** is capable of dehydrogenation of alcohols,[12a,b] and base alone can mediate the condensation of aldehydes and nitriles.[12f] Benzaldehydes were observed in the α-olefination of benzyl cyanide with benzyl alcohol, suggesting that the condensation is a relatively slow step. Based on the literature,[5,6] and our studies, a plausible reaction mechanism is given (Scheme 4). Initially, the Co precatalyst **A** is activated by a base through the salt elimination.[12a] The catalytically active Co species mediates the dehydrogenation of primary alcohols to form the aldehyde intermediates, which subsequently undergo the base-mediated condensation with the nitriles to yield the acrylonitriles and H_2O. Finally, the liberation of H_2 regenerates the catalyst. Alternatively, at high base loadings, the base mediated MPV process further reduces the acrylonitriles to the nitrile products.[12f]

Scheme 4. Proposed Mechanism (α-Olefination in Blue and α-Alkylation in Red)



Conclusions

We present the first Co-catalyzed switchable formations of α,β-substituted acrylonitriles and nitriles. A large variety of nitriles and primary alcohols are viable substrates with this protocol. Notably, this reaction is environmentally friendly and atom efficient with H_2 and H_2O being the sole byproducts. We anticipate that this study will contribute to the catalyst designs, especially the ones that take advantage of the earth-abundant transition metals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01553.

Experimental details, NMR spectra, and other results (PDF)

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Notes

The authors declare no competing financial interest.

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(14) A filtration experiment was performed to testify that the reaction is not mediated by nanoparticles (see SI).