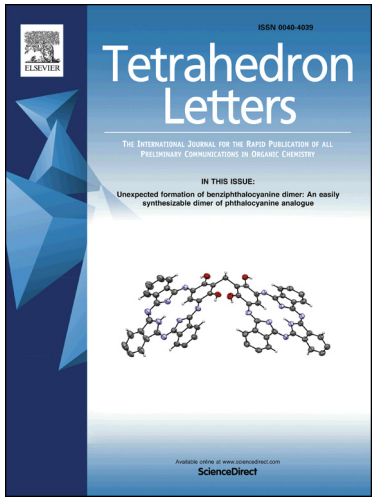

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Lewis Base-Catalyzed Cyanation of Morita-Baylis-Hillman Carbonates. Synthesis of Allylamine Derivatives

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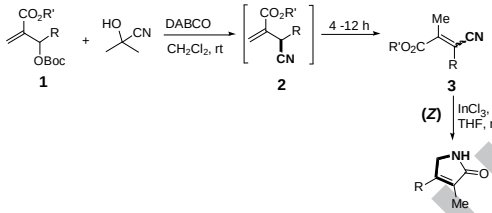

DABCO-catalyzed cyanation of MBH carbonates via 1,3-proton shift transfer is reported. The adducts of cyanation that are converted in one step to allylic amines derivatives. The salient features of this reaction include readily available starting materials, mild conditions, broad substrate scope, high efficiency and valuable further applications. The process of the 1,3-proton shift transfer was conducted by a joint research of NMR and DFT calculation.

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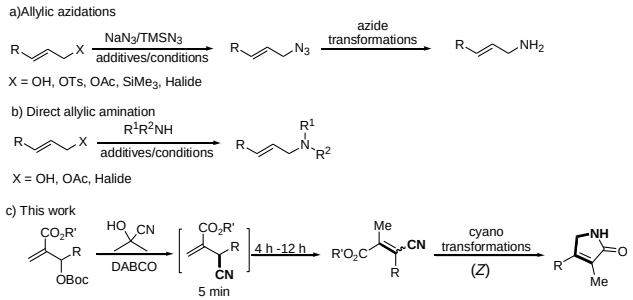
ABSTRACT

DABCO-catalyzed cyanation of MBH carbonates via 1,3-proton shift transfer is reported. The adducts of cyanation that are converted in one step to allylic amines derivatives. The salient features of this reaction include readily available starting materials, mild conditions, broad substrate scope, high efficiency and valuable further applications. The process of the 1,3-proton shift transfer was conducted by a joint research of NMR and DFT calculation.

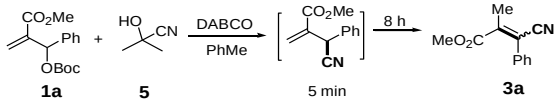
1. Introduction

Allyl amines and allylamine derivatives represent an important class of compounds due to their potency in medicinal chemistry given their activities such as chemotherapeutic agents,[1] enzyme inhibitors[2] and antifungal activities.[3] Furthermore, allylic amines are very important synthetic intermediates[4] and functional groups in many biologically active compounds and natural products.[5] Due to their significance in organic synthesis, much effort has been exerted to develop efficient methods of allylic amines or allylamine derivatives.[6] The allylamine functionality can be introduced by nucleophilic substitution at the allylic position or by direct allylic amination of olefins (Scheme 1a, b)[7]. Conversions of alcohols or a better leaving group, for instance, halide, carboxylate, carbonates, phosphonate, or sulfonate, etc. to their corresponding nitriles or azides are very important and essential in functional group transformation for the synthesis of amino groups.[8]



Scheme 1. Different approaches for the synthesis of allyl amines.

MBH adducts possess a high potential for use as synthetic intermediates; therefore, in recent years, several research groups have focused their efforts on the modification of the β-position (the alcohol moiety) of the MBH adducts. In particular, by converting the hydroxy group into a leaving group, the MBH adducts, such as acetates and carbonates, can construct a large variety of multifunctional compounds.[9] However, Among them little attention has been paid to exploring cyanide as viable nucleophilic substrates in the cyanation of MBH carbonates[10] and there are no effective methods for transforming the adducts of the cyanation to allylic amines.

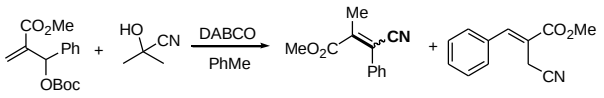


Scheme 2. Cyanation of MBH Carbonate **1a**.

Herein, we disclose a new type of organocatalytic approach towards synthetic of vinyl cyanide moieties via a procedure of DABCO promoting 1,3-proton shift transfer reaction. The significance of the present chemistry is: 1) Compared to previous work mainly with metal catalysts, this work is under metal free conditions. 2) Acetone cyanohydin as cyanide source was used which was simple, stable, easy to handle, and readily available compared with other toxicity, volatility, and hazardous handling cyanide sources such as HCN, TMSCN or KCN. 3) It is the first example of a transformation of vinyl cyanide to allylic amines derivatives. This research not only provides a new approach for

allylic amines derivatives in organic synthesis, but also offers valuable mechanistic insights into this novel 1,3-proton shift transfer reaction.

Table 1. Optimization of Reaction Conditions.[a]



1a **5** **3a** **4**

Entry	Base (mol %)	Solvent	Yield (%)[b]		(*E*/*Z*)[c]
			3a	**4**	
1	DABCO (10)	toluene	85	—	1.5:1
2	Et_3N (10)	toluene	45	—	1:1
3	DBU (10)	toluene	23	64	1.2:1
4	DMAP (10)	toluene	—	—	
5	Ph_3P (10)	toluene	—	—	
6	K_2CO_3 (10)	toluene	—	83	
7	DBACO (10)	THF	90	—	1.5:1
8	**DABCO (10)**	**CH_2Cl_2**	**96**	**—**	**1.7:1**
9	DABCO (10)	DMF	40	—	1.1:1
10	DABCO (10)	CH_3OH	—	—	
11	DABCO (10)	$CHCl_3$	92	—	1.6:1
12	DABCO (5)	CH_2Cl_2	80	—	1.7:1
13	DABCO (20)	CH_2Cl_2	96	—	1.6:1

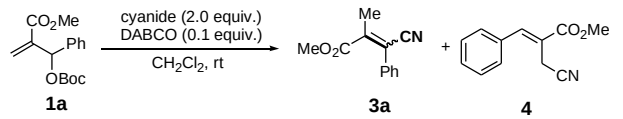
[a] Reactions were performed with MBH carbonate **1a** (0.5 mmol), acetone cyanohydin (2.0 equiv) in 1.0 mL of solvent for 2 h at room temperature.

[b] Yield after column chromatography.

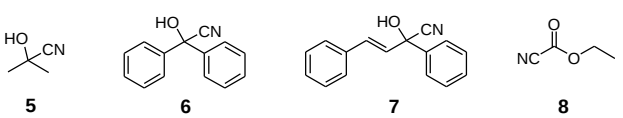
[c] E:Z ratio of the product determined by yield after column chromatography.

Our study commenced with MBH carbonate **1a** and acetone cyanohydin in the presence of 10 mol % of DABCO in toluene at room temperature. Gratifyingly, the final product of cyanation was thermodynamically-favored compound **3a** containing the vinyl cyanide moiety, a precursor of allylic amine transforming from kinetic-favored product **2** envisaged initially which could be detected in the reaction system. As indicated in Table 1, among various bases evaluated in the cyanation of MBH carbonate 1a, the strong nucleophilic base DABCO showed the best regioselectivity, affording **3a** in 85% yield (E/Z=1.5/1, Entry 1). Regioisomer **4** was obtained when using inorganic base K_2CO_3 (Entry 6). Mixture of both products were obtained employing the DBU (Entry 3). Further optimization on the other reaction conditions (including solvent and base's loading) led to the discovery that the regioisomer of **3a** was formed exclusively in 96% yield (E/Z=1.7/1) when CH_2Cl_2 was used as solvent and base's loading was 10 mol % (Entry 11).

Table 2. Different cyanide sources effect on the Cyanation of MBH Carbonates.[a]



1a **3a** **4**



5 **6** **7** **8**

Entry	Cyanide	Solvent	Yield (%)[b]		(*E*/*Z*)[c]
			3a	**4**	
1	**5**	CH_2Cl_2	96	—	1.7:1
2	**6**	CH_2Cl_2	80	—	1:1
3	**7**	CH_2Cl_2	n.r.	—	—
4	**8**	CH_2Cl_2	78	—	1.2:1
5	TMSCN	CH_2Cl_2	87	—	1:1

[a] Reactions were performed with MBH carbonate 1a (0.5 mmol), cyanide (2.0 equiv) in 1.0 mL of solvent for 2 h at room temperature.

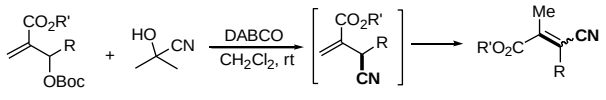
[b] Yield after column chromatography.

[c] E:Z ratio of the product determined by yield after column chromatography.

A series of other cyanide sources were screened in Table 2. In general, silyl cyanide reagent (87% yield) was found to be superior to benzophenone cyanohydrin (6; 80% yield) and 8 (78% yield) in this reaction (entries 5 vs. 2 and 4), whereas chalcone cyanohydrin **7** gave no conversion (entry 3). Of the cyanide reagents, **5** exhibited the best yield 96%.

Having identified optimized reaction conditions for the cyanation of MBH carbonate, we explored the substrate scope of this process. The results are summarized in Table 3. A variety of aromatics with electron-donating and electron-withdrawing groups in the 3-, or 4-position were tolerated (Table 2, entries 2–10). MBH carbonates bearing electron-withdrawing groups on the aromatic ring participate in the reaction, affording the cyanation products in good yields within 4 h (entries 4–7, 9–10). The substrates bearing electron-donating groups on the aromatic ring participate in the slower transformation, delivering the sequential products in excellent yields after 12 h (entries 2–3, 8). Heteroaromatic substrates were also suitable under these conditions (entries 15, 16). In addition, the reaction worked well with 1- and 2-naphthyl MBH carbonates to give the desired products **3m** and **3n** in 88% and 86%, respectively (entries 13, 14). Due to the steric effect, substrates substituted in the 2-position on the aromatic rings afforded the desired products in lower yields (entries 11, 12). The reaction also worked well by changing the ester group in the MBH carbonates, providing the corresponding product **3q** in 96% yield (entry 17). Subsequently, in the case of aliphatic substrate, the reaction proceeded smoothly at room temperature. However, the final product obtained was **2r** not transformational product even prolonged reaction time to 24 h (entry 18).

Table 3. Substrate Scope for the Cyanation of MBH Carbonates.[a]



1 **5** **2** **3**

Entry	**1** (R, R')	Product **3**	Time (h)	Yield (%)[b]	(*E*/*Z*)[c]
1	**1a** (C_6H_5, Me)	**3a**	8	97	1.7:1
2	**1b** (4-$MeOC_6H_4$, Me)	**3b**	12	94	2.3:1
3	**1c** (4-MeC_6H_4, Me)	**3c**	12	97	1.7:1
4	**1d** (4-FC_6H_4, Me)	**3d**	4	88	1.5:1
5	**1e** (4-ClC_6H_4, Me)	**3e**	4	84	1.9:1
6	**1f** (4-BrC_6H_4, Me)	**3f**	4	83	1.7:1
7	**1g** (4-$CF_3C_6H_4$, Me)	**3g**	4	81	3.2:1
8	**1h** (3-$MeOC_6H_4$, Me)	**3h**	12	96	2.0:1

9	**1i** (3-ClC_6H_4, Me)	**3i**	4	80	1.6:1
10	**1j** (3,4-$Cl_2C_6H_3$, Me)	**3j**	4	81	2.2:1
11[d]	**1k** (2-$MeOC_6H_4$, Me)	**3k**	12	60	6:1
12	**1l** (2-BrC_6H_4, Me)	**3l**	12	78	1.5:1
13	**1m** (1-Naphthyl, Me)	**3m**	8	88	1.3:1
14	**1n** (2-Naphthyl, Me)	**3n**	8	86	1.4:1
15	**1o** (2-Furanyl, Me)	**3o**	4	85	1.6:1
16	**1p** (2-thienyl, Me)	**3p**	4	84	2.3:1
17	**1q** (C_6H_5, Et)	**3q**	8	96	1.4:1
18	**1r** (isopropyl, Me)	**2r**	24	65	-

[a]Reactions were performed with MBH carbonate **1** (0.5 mmol), acetone cyanohydin (2.0 equiv), and 10 mol % of DABCO in 1.0 mL of CH_2Cl_2 for 4-24 h at room temperature.

[b]Yield after column chromatography.

[c]*E*:*Z* ratio of the product determined by yield after column chromatography.

[d]*E*:*Z* ratio of the product determined by NMR analysis.

To gain additional insight into the transformation of dynamically-favored product **2** to thermodynamically favored product **3a**, the reaction of **1a** under standard reaction conditions in $CDCl_3$ was monitored by ^1H NMR spectroscopy (Figure 1). After reacting with acetone cyanohydin for 5 min, the signals A, B, C and D were assigned to the hydrogen of MBH carbonate **1a**, which weakened gradually and disappeared after 15 min (Figure 1). The characteristic peaks E and F were assigned to **2**, which appeared and increased after 5 min along with the decrease of 1a. The peaks of **2** became weak at 2 h, and completely disappeared at 12 h as it was converted into the characteristic peaks G, H and I, J of final product **3a** (Figure 1).

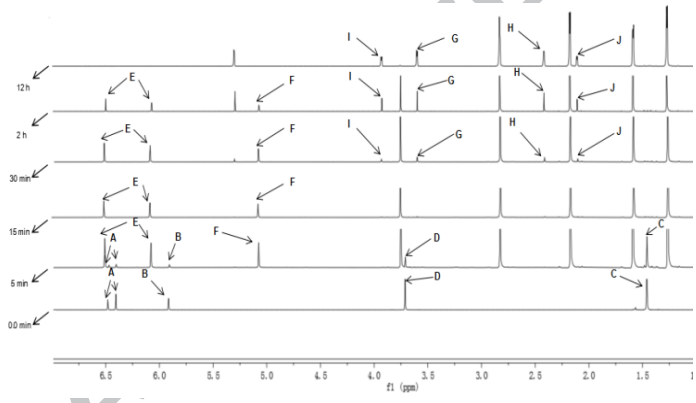


Figure 1. Dynamically-favored Product **2** Detected by NMR Analysis.

In order to explain this astonishing transformation of dynamically-favored product **2** to the thermodynamically favored product **3a**, DFT calculation was conducted on the M06-2X/6-31G(d) level (Figure 2). The combination of **2** and DABCO is endothermic by 2.8 Kcal/mol in gas phase. Then, acidic β-H was snatched by Lewis base DABCO furnishing an allylic anion **IN2**. This procedure is endothermic by 3.7 Kcal/mol. The subsequent step is the releasing of proton from proton shuttle H-DABCO to sp^2-hybidized carbon after overcoming an activation Gibbs free energy barrier of 21.6 kcal/mol to get the final product and is exergonic by -1.1 kcal/mol.

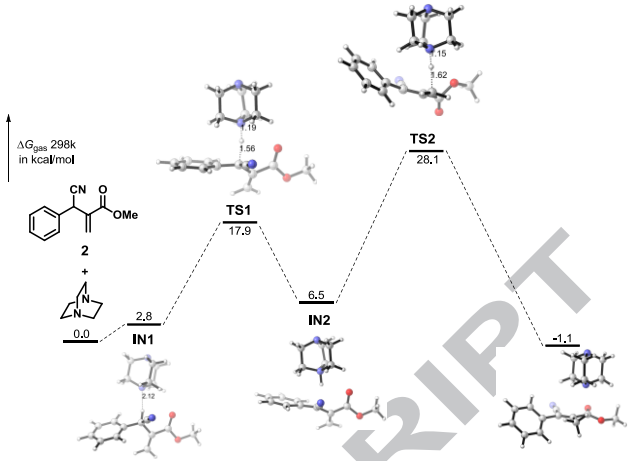
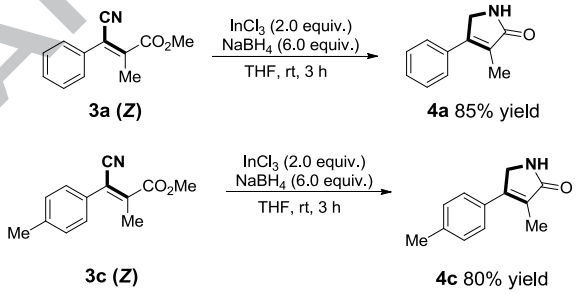
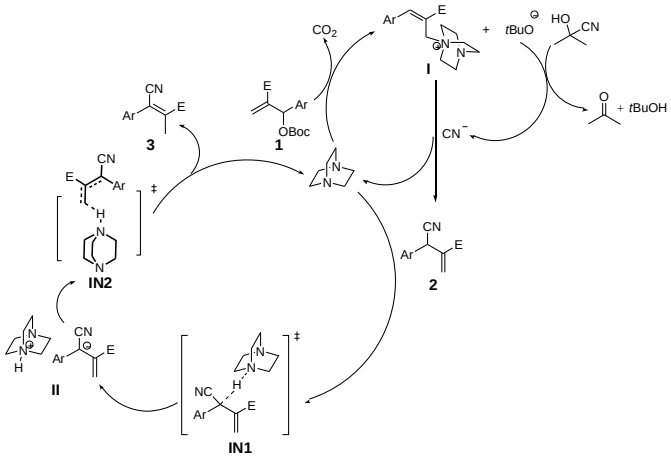


Figure 2. DFT Profile of 1,3-hydrogen Transfer

We next turned our attention to the application of the cyanation products to the synthesis of the allylic amines derivatives. The adducts **3a** and **3c** were readily transformed into corresponding unsaturated lactam **4a** and **4c** by reductive amidation using $InCl_3$ and $NaBH_4$ with good yields (Scheme 3).[11]



Scheme 3. Transformation of Cyanation Adducts **3a** and **3c** to Unsaturated Lactam **4a** and **4c**.



Scheme 4. Possible reaction mechanism for the formation of **3**.

On the basis of above experimental results, previous work and computational data,[12] a plausible reaction mechanism has been outlined in Scheme 4. The nucleophilicity of the catalyst plays an important role in the mechanism of the reaction. The reaction might be initiated with the in situ formation of a quaternary ammonium ion **I** from **1** via an addition-elimination-deprotonation process. The deprotonation of acetone cyanohydin

at -OH by in situ generated tert-butoxide anion occurs, and is followed by allylation of I to give **2**. Then in the presence of DABCO, intermediate **IN1** was formed as hydrogen-bonding interaction between the C-H of DABCO and carbonyl group of **2**. Then, acidic β-H was snatched by Lewis base DABCO furnishing an allylic anion **II**. Subsequential release of proton from proton shuttle H-DABCO to sp^2-hybidized carbon occurred after overcoming an activation Gibbs free energy to get the final product [3].

In conclusion, we have demonstrated a general and practical reaction of acetone cyanohydin with MBH carbonates via an 1,3-proton shift transfer process under metal free conditions. This novel protocol provided an efficient method for the construction of vinyl cyanide moieties, which could be easily transformed into allylamine derivatives, in good to excellent yields and regioselectivities. Remarkably, the transformation of dynamically-favored product to the thermodynamically favored product was conducted by a joint research of NMR and DFT calculation. Efforts are currently underway in our laboratory to explore medicinal applications of the products, and the results of which will be reported in due course.

Acknowledgments

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Highlights

Organocatalytic approach towards synthetic of vinyl cyanide moieties is disclosed.

A procedure of DABCO promoting 1,3-proton shift transfer reaction is mentioned.

1,3-proton shift transfer is conducted by researching of NMR and DFT calculation.

Vinyl cyanide is transformed into allylic amines derivatives.

Mechanism relies on addition-elimination-deprotonation and 1,3-proton shift transfer.