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Direct organocatalytic hydroalkoxylation of α,β-unsaturated ketones

Dhevalapally B. Ramachary* and Rumpa Mondal

School of Chemistry, University of Hyderabad, Central University (P.O.), Hyderabad 500 046, India

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Abstract—The direct addition of a variety of alcohols to in situ activated olefins was observed in the presence of mild bifunctional amine/acid catalysts. Unlike existing methods, the reactions proceed at room temperature and in the absence of transition metals. The use of simple commercially available catalysts, amines and acids makes this an attractive method for the preparation of β-alkoxy ketones, which are prevalent targets and intermediates in organic synthesis.
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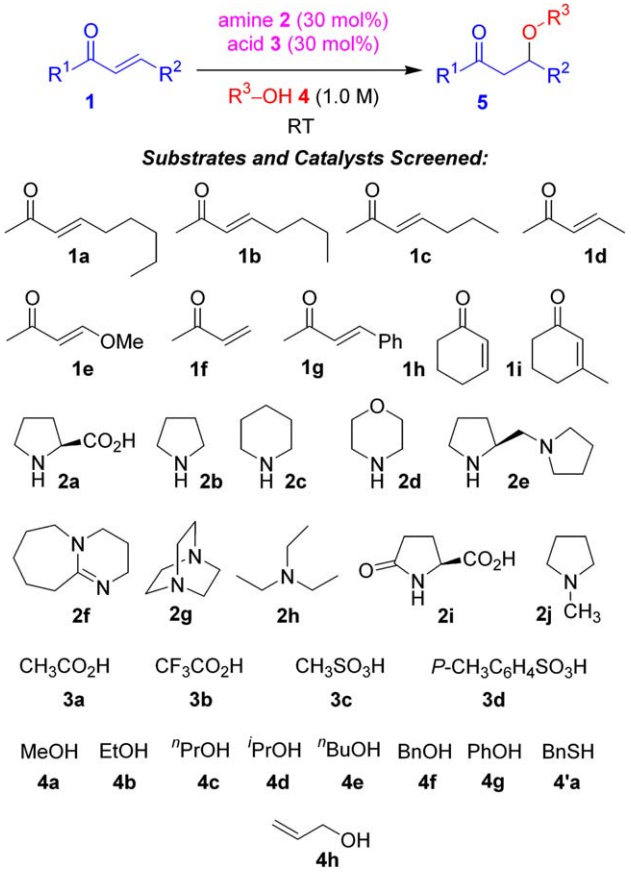
β-Hydroxy ketones and their alkoxy analogues are very important as valuable building blocks and structural motifs in a variety of natural products and in organic synthesis.[1] They are typically prepared either via aldol chemistry or sequential epoxidation and reduction of enones.[2] Direct preparation by addition of water to an enone is an attractive alternative, but only one method exists for this transformation.[3] Similarly, preparation of β-alkoxy ketones also represents a challenging problem in synthetic organic chemistry. Such hydroalkoxylation additions of alcohols to α,β-unsaturated ketones, aldehydes or esters have recently been reported to be promoted by several catalysts such as PMe_3,[3] DBU,[4] Tf_2NH,[5] $P(RNCH_2CH_2)_3N$[6] and transition metal complexes;[7] however, the hydroalkoxylation addition of alcohols to α,β-unsaturated ketones remains a challenge, mainly because of the lower reactivity of alcohols and also due to the greater number of applications of the resulting products. On the other hand, hydroalkoxylation reactions of other highly reactive heteroatom nucleophiles such as thiols[8] and amides[9] to more reactive α,β-unsaturated aldehydes via iminium ion intermediates have recently been realized by amine/acid bifunctional catalysts. In this context, we are interested in developing a novel and 'green' amine/acid bifunctional catalyst for the oxy-Michael addition reaction of less reactive alcohols to α,β-unsaturated ketones via iminium ion catalysis (Scheme 1). Herein, we report a general and green



Scheme 1. Direct organocatalytic hydroalkoxylation of α,β-unsaturated ketones.

Keywords: Amino acids; Amine/acid catalysts; Enones; Hydroalkoxylation; Organocatalysis.
* Corresponding author. Tel.: +91 40 23134816; fax: +91 40 23012460; e-mail: ramsc@uohyd.ernet.in

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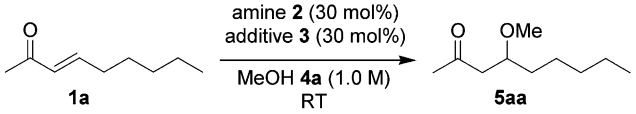
metal-free synthetic method for the hydroalkoxylation of enones and other α,β-unsaturated substrates **1** by use of an amine/acid **2/3** as a bifunctional catalyst (Scheme 1).

Recently, bifunctional amine/acid-catalysis has emerged as a powerful synthetic tool for the development of both achiral and chiral catalyzed condensations, cycloadditions, 1,2- and 1,4-additions of enals, enones and ketones with many electrophiles.[10] We reasoned that this catalysis strategy might be applicable to the in situ generation and conjugate addition of highly activated olefins if a suitable nucleophilic alcohol was present. Such a process would constitute a metal-free, green hydroalkoxylation of enones.

During our investigations on organo-catalyzed Diels–Alder[11] reactions of enones **1** in MeOH, we observed that MeOH was itself undergoing Michael addition to enones **1** under proline catalysis. In the presence of catalytic amounts of proline, we observed the direct addition of MeOH to non-3-en-2-one **1a** with moderate conversion (Table 1, entry 1).[†] A number of organic amines, amine/base and amine/acid were tested as catalysts using the hydromethoxylation of non-3-en-2-one **1a** as a benchmark, at room temperature (Table 1). Pyrrolidine/CH_3SO_3H **2b/3c** (Table 1, entries 13 and 19) were the best catalysts for hydromethoxylation of **1a** compared to other catalysts such as amines **2a–h** (Table 1, entries 5–8), acid **3c** (Table 1, entry 18) and other amine/acid bifunctional catalysts **2/3** (Table 1, entries 9–16 and entry 21). When the catalyst **2b/3c** loading was changed from 30 mol % to 10 mol % for the hydromethoxylation of enone **1a**, the product yield decreased even after longer reaction times (Table 1, entry 19). Pyroglutamic acid **2i** did not catalyze the oxy-Michael reaction of **1a** with **4a** (Table 1, entry 20) and this is a good support for iminium ion catalysis rather than for acid/base catalysis.

Next, we proceeded to investigate the scope and limitations of the hydroalkoxylation reaction of non-3-en-2-one **1a** with a range of alcohols **4a–h** and benzyl thiol **4′a** under pyrrolidine/CH_3SO_3H-catalysis at room temperature (Table 2). As shown in Table 2, larger alkyl alcohols **4c–e** furnished hydroalkoxylation products **5ac–ae** in lower yields compared to smaller alkyl alcohols **4a–b** in oxy-Michael reactions. The reason may be due to moderate steric hindrance with larger alkyl groups. Benzyl alcohol **4f** furnished hydrobenzyloxy

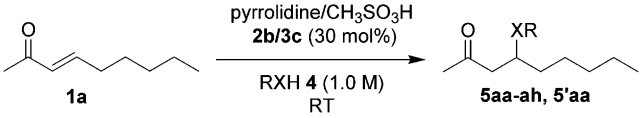
Table 1. Optimization of the organocatalytic hydromethoxylation of non-3-en-2-one **1a** with MeOH **4a**[a]



Entry	Amine **2**	Additive **3**	Time (h)	Yield[b] (%)
1	Proline **2a**	—	12	57
2[c]	Proline **2a**	DBU **2f**	5	32
3[c]	Proline **2a**	DABCO **2g**	5	20
4[c]	Proline **2a**	Et_3N **2h**	5	20
5	Pyrrolidine **2b**	—	6	23
6[d]	Piperidine **2c**	—	16	<5
7[d]	Morpholine **2d**	—	12	<5
8	Diamine **2e**	—	11	40
9	Pyrrolidine **2b**	HCl	12	20
10	Pyrrolidine **2b**	CH_3CO_2H **3a**	12	25
11	Pyrrolidine **2b**	CF_3CO_2H **3b**	12	20
12	Pyrrolidine **2b**	*p*-TSA **3d**	22	50
13	Pyrrolidine **2b**	CH_3SO_3H **3c**	17	73
14	Piperidine **2c**	CH_3SO_3H **3c**	16	70
15	Morpholine **2d**	CH_3SO_3H **3c**	12	45
16	Diamine **2e**	CH_3SO_3H **3c**	11	45
17	—	DBU **2f**	12	64
18	—	CH_3SO_3H **3c**	17	58
19[e]	Pyrrolidine **2b**	CH_3SO_3H **3c**	28	64
20[d]	Pyroglutamic acid **2i**	—	17	—
21	*N*-Methylpyrrolidine **2j**	CH_3SO_3H **3c**	8	55

[a] 30 mol % each of amine **2** and additive **3** were mixed at the same time, to this MeOH **4a** and enone **1a** were added at room temperature.
[b] Yield refers to the column purified product.
[c] Longer reaction times led to decomposition.
[d] Enone **1a** was recovered.
[e] 10 mol % each of Pyrrolidine **2b** and CH_3SO_3H **3c** was used as catalyst.

Table 2. Optimization of the organocatalytic hydroalkoxylation of non-3-en-2-one **1a** with various alcohols **4a–h** and benzyl thiol **4′a**[a]

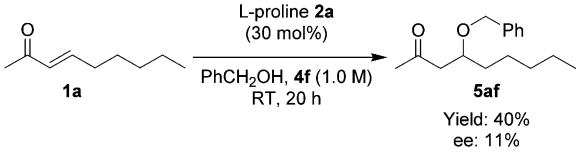


Entry	RXH	Time (h)	Product	Yield[b] (%)
1	MeOH, **4a**	17	**5aa**	73
2	EtOH, **4b**	21	**5ab**	51
3	^{n}PrOH, **4c**	37	**5ac**	48
4	^{i}PrOH, **4d**	66	**5ad**	21
5	BuOH, **4e**	37	**5ae**	<3
6	$PhCH_2OH$, **4f**	12	**5af**	45
7	PhOH, **4g**	49	**5ag**	<3
8	$CH_2{=}CHCH_2OH$, **4h**	96	**5ah**	50
9	$PhCH_2SH$, **4′a**	25	**5′aa**	77

[a] 30 mol % each of amine **2b** and additive **3c** were mixed at the same time, to this alcohol **4a–h** or thiol **4′a** and enone **1a** were added at room temperature.
[b] Yield refers to the column purified product.

[†] **Representative experimental procedure.** *Pyrrolidine/methanesulphonic acid-catalyzed hydroalkoxylation reactions of enones*: Pyrrolidine **2b** (0.15 mmol) and methanesulfonic acid **3c** (0.15 mmol) were stirred at 25 °C for 10 min, then alcoholic solvent **4** (0.5 mL) and enone **1a–i** (0.5 mmol) were added and stirring was continued at the same temperature for the time indicated in Tables 1–4. The crude reaction mixture was worked-up with aqueous NH_4Cl or $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure hydroalkoxylated products **5** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate as eluent).Many of the hydroalkoxylated products **5** are commercially available or have been described previously, and their analytical data matched with literature values. New compounds were characterized on the basis of IR, ^1H and ^{13}C NMR and analytical data (see Supplementary data).

product **5af** in moderate yield but phenol **4g** gave a poor conversion under identical conditions (Table 2, entry 7). Benzyl thiol **4′a** furnished the expected Michael product **5′aa** in a good yield (Table 2, entry 9) and allyl alcohol **4h** furnished the expected hydroallyloxylation product **5ah** in moderate yield (Table 2, entry 8). To access the asymmetric induction in these reactions, hydrobenzyloxylation of enone **1a** with benzyl alcohol **4f** under L-proline **2a** catalysis was carried out furnishing the expected product **5af** in 40% yield, but with only 11% ee as shown in Eq. 1



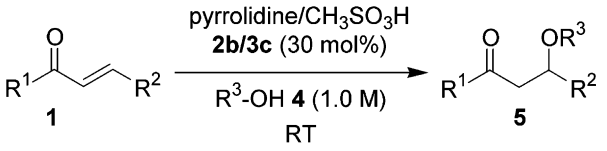
(1)

We synthesized several hydroalkoxylation products **5** from different enones **1b–i** and alcohols **4a–c** under pyrrolidine/CH_3SO_3H **2b/3c**-catalysis.[†] The results in Table 3 indicate the broad scope of this novel methodology covering a structurally diverse group of enones **1b–i** and alcohols **4a–c** with many of the yields obtained being very good, or indeed better, than previously published reactions starting from the corresponding enones **1**.

As shown in Table 3, the enones oct-3-en-2-one **1b**, hept-3-en-2-one **1c** and pent-3-en-2-one **1d** furnished hydromethoxylated **5ba–da** and hydroethoxylated **5bb–db** products from methanol and ethanol, respectively, in good yields (Table 3, entries 1–6). 4-Methoxy-but-3-en-2-one **1e** gave the useful organic intermediates, dimethyl acetal **5ea**, diethyl acetal **5eb′** and dipropyl acetal **5ec′** in very good yields by reaction with MeOH, EtOH and ^{n}PrOH, respectively, as shown in Table 3, entries 7–9. Interestingly, hydroalkoxylation of **1e** with EtOH and ^{n}PrOH furnished the unexpected acetals **5eb′** and **5ec′** as the major products rather than the expected acetals **5eb** and **5ec** which can be explained by amine/acid-catalyzed retro-Michael/Michael reactions of acetals **5eb** and **5ec** with EtOH and ^{n}PrOH, respectively. Reaction of methyl vinyl ketone **1f** with MeOH and EtOH under **2b/3c**-catalysis furnished the unexpected tandem hetero-Diels–Alder/acetalization products **6a** and **6b** in good yields rather than the expected oxy-Michael products **5fa** and **5fb** (Table 3, entries 10–11). The stereochemistries of **6a** and **6b** were established based on 2D NMR analysis. To our surprise, benzylidene acetone **1g** gave the expected oxy-Michael product **5ga** with very poor conversion and did not furnish the self-Diels–Alder[11] product **7** even after four days (Table 3, entry 12). Hydromethoxylation and hydroethoxylation of cyclohexenone **1h** furnished the expected products **5ha** and **5hb** in moderate yields (Table 3, entries 13–14), however, the reaction of 3-methylcyclohexenone **1i** did not give **5ia** or **5ib**.

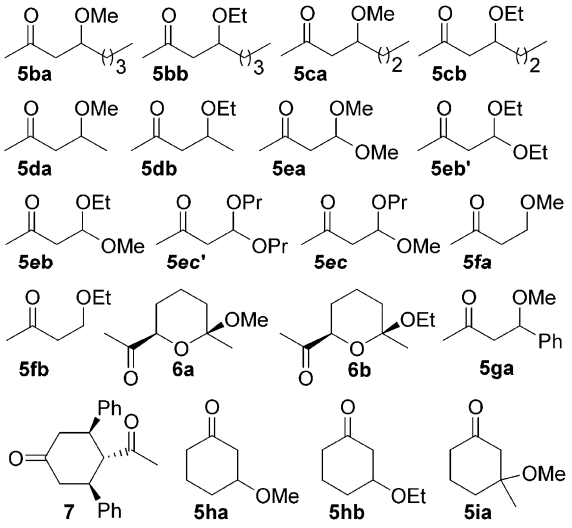
4-Ethoxypentan-2-one **5db** has been observed in the volatile components of Indian long pepper, *Piper longum Linn*., and also as a volatile metabolite in human urine.[12]

Table 3. Chemically diverse hydroalkoxylated products **5**[a]



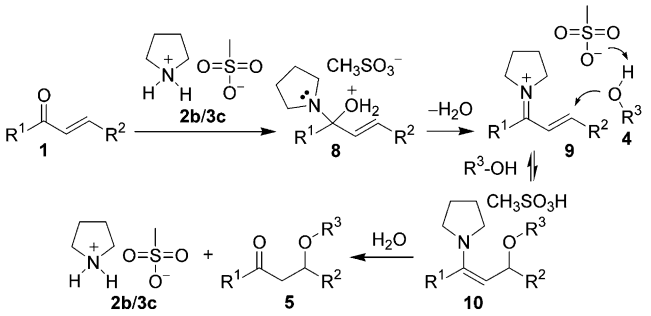
Entry	Enone	R^3–OH	Time (h)	Product	Yield[b] (%)
1	**1b**	MeOH, **4a**	23	**5ba**	65
2	**1b**	EtOH, **4b**	22	**5bb**	60
3	**1c**	MeOH, **4a**	15	**5ca**	75
4	**1c**	EtOH, **4b**	14	**5cb**	60
5	**1d**	MeOH, **4a**	17	**5da**	75
6	**1d**	EtOH, **4b**	18	**5db**	75
7	**1e**	MeOH, **4a**	28	**5ea**	99
8[c]	**1e**	EtOH, **4b**	30	**5eb**, **5eb′**	>95
9[d]	**1e**	^{n}PrOH, **4c**	25	**5ec**, **5ec′**	>95
10	**1f**	MeOH, **4a**	3	**6a**	50
11	**1f**	EtOH, **4b**	3	**6b**	50
12[e]	**1g**	MeOH, **4a**	96	**5ga**	<5
13	**1h**	MeOH, **4a**	17	**5ha**	55
14	**1h**	EtOH, **4b**	22	**5hb**	55
15[e]	**1i**	MeOH, **4a**	40	**5ia**	—

[a] See experimental section.
[b] Yield refers to the column purified product.
[c] Ratio **5eb**:**5eb′** = 1:5.6 as determined by ^{1}H and ^{13}C NMR analysis.
[d] Ratio **5ec**:**5ec′** = 1:5 as determined by ^{1}H and ^{13}C NMR analysis.
[e] Enones **1g** and **1i** were recovered.



Acetals **5ea**, **5eb′** and **5ec′** are useful intermediates in organic synthesis emphasizing the value of this green approach.

A possible reaction mechanism for the hydroalkoxylation of **1**, **4** and **2a** or **2b/3c** is illustrated in Scheme 2.[10] First, reaction of the amino acid **2a** or amine/acid-catalyst **2b/3c** with enone **1** generates the iminium cation **9** (an excellent electrophile) which undergoes a Michael type reaction with in situ activated alcohol nucleophiles **4** to generate Michael adduct **10**, which is in equilibrium with **9**. Hydrolysis of **10** furnishes the expected oxy-Michael product **5** and free catalyst amino acid **2a** or

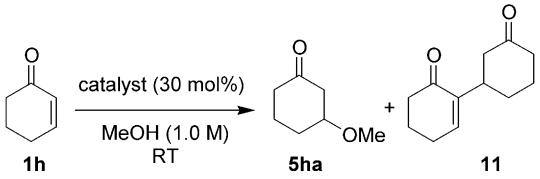


Scheme 2. Proposed reaction mechanism for the organocatalytic hydroalkoxylation of α,β-unsaturated ketones.

amine/acid **2b/3c**, which is returned to the catalytic cycle. The proposed reaction mechanism was supported by the results presented in Eq. 1 and Table 1, entries 1 and 20.

To understand the role of amine-catalysts **2** on the hydromethoxylation of cyclic enones, we screened catalysts **2a**, **2b**, **2e** and **2e/3c** for hydromethoxylation of enone **1h** at room temperature as shown in Table 4. Under proline-catalysis, enone **1h** furnished the expected oxy-Michael product **5ha** in 50% yield. Interestingly, amines **2b** and (*S*)-**2e** catalyzed the formation of the unexpected product **11** in good to moderate yields from the enone **1h** and MeOH at rt (Table 4, entries 2–3).[13] By changing the solvent MeOH to THF in the diamine **2e**-catalyzed reaction of enone **1h**, we did not observe any reaction and recovered only the starting material even after four days (Table 4, entry 4). The bifunctional catalyst, **2e/3c**-catalyzed the formation of the hydromethoxylated product **5ha** in good yield from enone **1h** with MeOH (Table 4, entry 5). Based on the above results, we propose that **11** is formed via a solvent induced amine-catalyzed Basavaiah–Baylis–Hillman reaction as shown (see Table 4).[13] Product **11** was shown to possess synergistic herbicidal effects and has been used along with 2,4,5-T and atrazine against *Chenopodium album*.[14]

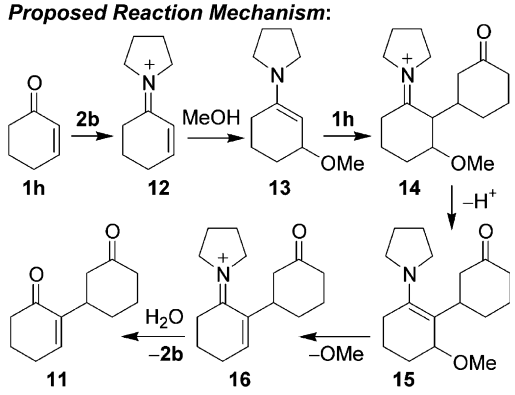
Table 4. Direct organocatalytic solvent induced Basavaiah–Baylis–Hillman reaction



Entry	Catalyst	Time (h)	Product	Yield[a]
1	**2a**	40	**5ha**	50
2	**2b**	11	**11**	50
3	**2e**	40	**11**	77
4[b]	**2e**	96	**11**	—
5	**2e/3c**	40	**5ha**	65

[a] Yield refers to the column purified product.
[b] THF used as solvent.

***Proposed Reaction Mechanism*:**



In conclusion, we have shown that the mild bifunctional amine/acid **2b/3c** catalyst, in the presence of α,β-unsaturated systems, can be used to catalyze the hydroalkoxylation of in situ activated olefins in the absence of added transition metals. Our proposed catalytic cycle suggests that this is a very practical system that could be extended to other classes of bifunctional catalysts to generate active olefins with LUMOs matched to the HOMOs of alcohols. Additionally, the possibility of using other chiral bifunctional amine/acid catalysts would further extend the applicability and practicality of this novel reactivity.

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Supplementary data

Experimental procedures and analytical data for all new compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.08.134.

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