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# Catalyst- and acid-free Markovnikov hydration of alkynes in a sustainable $H_2O$ /ethyl lactate system



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# ABSTRACT

An efficient and sustainable protocol for the hydration of alkynes has been developed under metal/acid/catalyst/ ligand-free conditions in a water/ethyl lactate mixture. The hydrogen-bond network in the ethyl lactate and water mixture plays a crucial and decisive role in activating the alkynes for hydration to afford the corresponding methyl ketones. This strategy gives the Markovnikov (ketone) addition product selectively over other possible products. The essential role of hydrogen bonding has been confirmed by experimental and theoretical techniques. A probable mechanism has been suggested by various control tests. The efficacy of the method has been further explored for the competent production of value-added  $\alpha_A\beta$ -unsaturated carbonyl compounds through the reaction of aldehydes with alkynes as ketonic surrogates. The environmentally benign hydration method takes place under mild conditions, has broad functional-group compatibility, and uses the ethyl lactate/water (1:3) medium as a "green alternative" in the absence of any hazardous, harmful, or expensive substances.

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#### 1. Introduction

The development of atom-economic and selective organic transformations is one of the most demanding tasks for chemists in modern scenarios [1]. The selective addition of H<sub>2</sub>O to unsaturated bonds provides a platform for the construction of most prevalent feedstocks [2]. In particular, the straight conversion of alkynes into carbonyl compounds by hydration demonstrates high atom economy and synthetic aptitude [3]. The vital and crucial event in alkyne hydration is the effective activation of the alkyne and subsequent quick addition of a water molecule. Hydration of alkynes is traditionally catalyzed by HgO-BF<sub>3</sub> (the Hennion–Nieuwland reaction) or HgO–H<sub>2</sub>SO<sub>4</sub> (the Kucherov reaction) in a strongly acidic environment [4]. Although these procedures give good yields, pollution issues related to taking care of and disposing of toxic Hg salts have restricted their use for broad applications in largescale industrial syntheses of value-added carbonyl compounds. To overcome the disadvantages of the strongly acidic conditions and the use of poisonous Hg salts, a variety of transition-metal catalysts containing Rh, Pd, Ru, Cu, Pt, Ir, Fe, Ag, Sn—W, Co, Ga, Au, and Os, as well as other metal centers, have been widely studied for the hydration of alkynes to form carbonyl compounds [5-8].

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Cautious scrutiny of the documented methodologies illustrates that all existing processes for the hydration of alkynes have restricted efficiency because of the use of transition-metal complexes, which are toxic and expensive catalysts, and the additional steps for the synthesis of catalyst requiring hazardous and undesirable additives. In addition, strongly acidic conditions have been used to promote the hydration reaction [9]. Although some less hazardous acids have been used to improve the reaction conditions, they still lack adaptability. In all cases, a catalyst or acid was needed for further activation of the alkynes for hydration. Moreover, it is extremely hard to perform hydration of alkynes in an acid- or catalyst-free environment because of the poor nucleophilicity of water molecules and requirement for appropriate activation procedures. To our knowledge, only two reports are available describing the use of water in supercritical conditions and water with a toxic volatile organic solvent for catalyst-free hydration of alkynes [10]. These methods required specific experimental tools with tedious conditions to maintain a high temperature and pressure for the reaction under microwave irradiation or an inert atmosphere. Therefore, there is rising demand for the development of an acid- or catalyst-free greener protocol for the hydration of alkynes.

Ethyl lactate (EL) is a biomass-derived platform solvent, which is nontoxic, potentially cheap, and entirely biodegradable [11]. As a result of the excellent compatibility of EL with water, EL and water mixtures have been significantly used in organic synthesis. Recently, we suggested a crucial and unprecedented role of hydrogen bonding and hydrophobicity in aqueous-mediated synthesis [12].



Scheme 1. Strategies toward alkyne hydration methods.

Inspired by this work and our earlier studies [13], we demonstrate that hydration of alkynes can be performed very efficiently in the presence of water by tuning its properties with EL under metal/acid/ catalyst/ligand-free conditions. We anticipate that the hydrogen-bond network in the EL and water mixture plays a crucial and decisive role in activating the substrate for hydration of the alkyne. Product formation in the hydration of alkynes is strongly dependent on the reaction parameters, which raises the issue of regioselectivity. Both types of product, that is, the Markovnikov (ketones) and anti-Markovnikov (aldehydes) products, have been reported under various conditions [14]. Our method is highly regioselective and forms Markovnikov-type products. Furthermore, the efficacy of the protocol has also been ensured for the competent production of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds by the reaction of aldehydes with alkynes as ketonic surrogates (Scheme 1).

#### 2. Results and discussion

We first examined the possibility of an aqueous method for the hydration of alkynes under catalyst- and acid-free conditions at 110 °C by using phenyl acetylene as a model substrate. In this trial, formation of the desired product was not observed because of the poor nucleophilicity of the water. Hence, there is a great need for an alternative green system that appropriately activates the substrate.

Fascinated by the solvent-tuning approach with a biomass-based sustainable solvent, we performed the model reaction by employing EL as a co-solvent with water in assorted ratios (Table 1). We found that a 1:3 ratio of EL:H<sub>2</sub>O gave the desired product 2i in excellent yield relative to other proportions for the EL and water mixture. From these results, we observed that a larger amount of water was necessary in the EL/H<sub>2</sub>O system for alkyne hydration.

The distinctive role of EL in promoting the hydration of alkynes in aqueous media can be attributed to its ability to alter the intermolecular hydrogen bonding of water molecules [15]. In a pure EL phase, strong intramolecular hydrogen bonding between the hydroxy and carbonyl groups of the EL molecules enables them to interact with phenyl acetylene.

When EL is added to an aqueous reaction mixture, the intramolecular hydrogen bonding vies with the intermolecular hydrogen bonding of the water molecules and forms a complex hydrogen-bonding network that provides specific assistance to the mixture. EL molecules have four key sites through which they can connect with H<sub>2</sub>O molecules (Scheme 2): (a) the hydroxy oxygen atom (complex 1), (b) the hydroxy hydrogen and keto oxygen atoms (complex 2), (c) the keto oxygen atom (complex 3), and (d) the alkoxy oxygen atom. As a result of the steric hindrance of the alkoxy group in EL, the latter is a less favorable site for hydrogen bonding, which led us to exclude the probability of the development of complex 4.

Table 1

Screening of the hydration of phenyl acetylene to form 2i under various conditions<sup>a</sup>.

Entry	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	72	57
2	EL	72	48
3	EL:H <sub>2</sub> O (1:1)	72	41
4	EL:H <sub>2</sub> O (2:1)	72	32
5	EL:H <sub>2</sub> O (3:1)	72	28
6	EL:H <sub>2</sub> O (1:2)	72	64
7	EL:H <sub>2</sub> O (1:3)	24	84
8	EL:H <sub>2</sub> O (1:4)	24	84
9	$EL:H_2O(1:3)^{c}$	72	56
10	$EL:H_2O(1:3)^d$	72	72
11	EL:H <sub>2</sub> O (1:3) <sup>e</sup>	72	81
12	$CH_3CN:H_2O(1:3)$	72	-
13	DMF:H <sub>2</sub> O (1:3)	72	-
14	$CH_2Cl_2:H_2O(1:3)$	72	-
15	MeOH:H <sub>2</sub> O (1:3)	72	26
16	$EtOH:H_2O(1:3)$	72	24
17	iPrOH:H <sub>2</sub> O (1:3)	72	21
18	EtOAc:H <sub>2</sub> O (1:3)	72	30
19	Salicylic acid (SA):H <sub>2</sub> O (1:3)	72	-

<sup>a</sup> Reactions were performed with phenyl acetylene (2 mmol) in various solvents at 110 °C.

Isolated vield.

Reaction at 70 °C.

d Reaction at 90 °C.

Reaction at 120 °C.



Scheme 2. Hydrogen bonding in water and EL.

Table 2	
Interaction energies of the three complexes corrected with the BSSE and ZPE.	

	$E_{\text{complex}}(au)$	$E_{\rm EL+W}$ (au)	BSSE (au)	$\Delta ZPE$ (au)	E <sub>int</sub> (au)	$E_{\rm int}$ (kcal mol <sup>-1</sup> )
Complex 1	-498.8392	-498.8296	0.0010	0.0029	-0.0057	-3.6071
Complex 2	-498.8421	-498.8296	0.0014	0.0041	-0.0070	-4.3718
Complex 3	-498.8385	-498.8296	0.0008	0.0025	-0.0056	-3.5207



Fig. 1. Structures of complexes 1-3 (along with atom numbering) optimized at the B3LYP/6-311++G(d,p) level of theory.

The interaction energies ( $E_{int}$ ) [16] of the three complexes were determined as the difference between the energy of the complex ( $E_{complex}$ ) and the added energies of EL and H<sub>2</sub>O ( $E_{EL}$  and  $E_W$ , respectively; Table 2, Fig. 1). The energies were corrected by incorporating the basis set superposition error (BSSE) computed by utilizing the counterpoise procedure [17] and zero-point energy (ZPE).

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{EL}} + E_{\text{W}}) + \text{BSSE} + \Delta \text{ZPE}$$

in which  $\Delta ZPE = ZPE_{complex} - (ZPE_{EL} + ZPE_W)$ 

The interaction energy calculations summarized in Table 2 show that complex 2 is the most stable among the three complexes with  $E_{\text{int}} = -4.3718$  kcal mol<sup>-1</sup>. NBO analysis (see Table 3) indicates that, in all three complexes, the atomic charge on H in the X–H···Y hydrogen bond increases upon hydrogen-bond formation ( $\Delta q > 0$ ), whereas

those on X and Y decrease ( $\Delta q < 0$ ). This shows the presence of an Hbond [16]. Furthermore, we note interactions between the lone pair of the H-bond acceptor and the anti-bonding orbital of the H-bond donor ( $n_0 \rightarrow \sigma^*_{0-H}$ ). The stabilization energy (*E*(2)) reveals the strength of the hydrogen-bonding interaction [16,18,19]. Based on the E(2) values, it can be inferred that  $n^{(2)}_{019} \rightarrow \sigma^*_{010-H11}$  is the relatively stronger interaction and, hence, complex 2 is relatively more stable than complexes 1 and 3.

Through the above calculations, we established that complex 2 is the most contributing hydrogen-bonding network in the mixture. This hydrogen-bonding network activates the water molecule and brings it extremely close to the phenyl acetylene molecule for the hydration reaction. These hydrogen-bonding interactions predominantly occur with a higher water concentration relative to the EL concentration [15]. A few reports are available for the hydrogen-

#### Table 3

Hyperconjugative interactions, stabilization energies, *E*(2), and variations in the charges of atoms X, Y, and H with H-bond formation.

Complex	X–H $\cdots$ Y bond	Interaction	E(2) (kcal mol <sup>-1</sup> )	$\Delta q_{\rm X}$	$\Delta q_{ m H}$	$\Delta q_{ m Y}$
1	$O_{19}-H_{20}\cdots O_{10}$	$n_{O10}^{(1)} \rightarrow \sigma^*_{O19-H20}$	4.09	-0.0356	0.0268	-0.0283
	$O_{19}-H_{20}\cdots O_{10}$	$n_{O10}^{(2)} \rightarrow \sigma^*_{O19-H20}$	3.59	-0.0356	0.0268	-0.0283
2	$O_{10}-H_{11}\cdots O_{19}$	$n_{O19}^{(1)} \rightarrow \sigma^*_{O10-H11}$	0.13	-0.0356	0.0124	-0.0447
	$O_{10}$ - $H_{11}$ ··· $O_{19}$	$n_{O19}^{(2)} \rightarrow \sigma^*_{O10-H11}$	9.99	-0.0356	0.0124	-0.0447
	0 <sub>19</sub> -H <sub>20</sub> ···0 <sub>2</sub>	$n_{O2}^{(1)} \rightarrow \sigma^{*}_{O19-H20}$	2.57	-0.0447	0.0386	-0.0335
	$O_{19}-H_{20}\cdots O_{2}$	$n_{02}^{(2)} \rightarrow \sigma^*_{019-H20}$	5.41	- 0.0447	0.0386	-0.0335
3	$O_{19}-H_{20}\cdots O_{2}$	$n_{O2}^{(1)} \rightarrow \sigma^*_{O19-H20}$	2.75	-0.0360	0.0266	-0.0440
	$0_{19} - H_{20} \cdots 0_2$	$n_{02}^{(2)} \rightarrow \sigma^*_{019-H20}$	3.09	-0.0360	0.0266	-0.0440



Scheme 3. Control experiments.

bond-driven activation of alkynes [20] for nucleophilic addition, but the hydration of alkynes remains unexplored under these conditions.

To further confirm the specific assistance of the EL/H<sub>2</sub>O system, various aqueous systems with other co-solvents were studied. Aqueous mixtures of alcohols produced moderate yields of desired product (Table 1, entries 15–17). Similar results were found with an aqueous mixture of an ester (Table 1, entry 18). These outcomes confirmed the synergic effect of the hydroxy and ester carbonyl groups of the EL molecules in the EL/H<sub>2</sub>O system. No hydration of alkyne to form the corresponding methyl ketone was observed in the presence of an H<sub>2</sub>O/ salicylic acid system (Table 1, entry 19). Salicylic acid has predominantly strong intramolecular H-bonding and is not involved in strong intermolecular hydrogen bonding with the water molecules. As a result of this. SA was unable to activate the water molecules for alkvne hvdration. Moreover, the desired product was not formed in aqueous mixtures of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and DMF (Table 1, entries 12–14). The effect of temperature on the reaction was also examined (Table 1, entries 9-11). At lower temperatures, inferior yields of the product were observed. The conversion was extraordinarily enhanced by increasing the reaction temperature. The optimum temperature for the reaction was found to be 110 °C. Further increases in temperature did not advance the outcome to a significant amount.



**Fig. 2.** Gibb's free energy profiles calculated for the addition pathway. The relative energy values with respect to the sum of the energies of reactants ( $\sum E(EL + H_2O + PhCCH)$ ) in kcal mol<sup>-1</sup> are given for each reaction point.

product was formed when the reaction was performed with D<sub>2</sub>O in-

stead of H<sub>2</sub>O under analogous conditions (Scheme 3c). However, a lower yield of the desired compound was detected with D<sub>2</sub>O because

of the less effective H-bonding relative to that of H<sub>2</sub>O [12]. This test

shows that both hydrogen atoms participate in the reaction. Any associ-

ation of the hydroxy group of the EL molecule direct to the phenyl acetylene is ruled out because only deuterated product is formed. We did



Scheme 4. Probable mechanism.

In control experiments, the addition of a radical scavenger (TEMPO) did not affect the yield of the reaction (Scheme 3a). Furthermore, no products from the radical pathway were obtained under these conditions. These results ruled out the possibility of a radical mechanism. The reaction was also carried out under an inert atmosphere (Scheme 3b). An excellent yield of desired product was obtained, which ruled out the probable involvement of any oxidative pathway. Deuterated

#### Table 4

Scope of the alkyne hydration reaction<sup>a</sup>.



<sup>a</sup> Reactions were performed with aryl alkyne (2 mmol) in the EL:H<sub>2</sub>O (1:3) system at 110  $^{\circ}$ C. <sup>a</sup>Reactions were performed with aryl alkyne (2 mmol) in the EL:H<sub>2</sub>O (1:3) system at 110  $^{\circ}$ C.

not observe any peak of a vinylic ether in the GC–MS spectrum, which confirms that there is no direct participation of EL molecules in the reaction.

For further confirmation of the formation of hydrogen bonds in the reaction mixture, NMR experiments were carried out [21] (see the ESI). We prepared the samples, that is,  $H_2O$  + phenyl acetylene, EL + phenyl acetylene, and EL +  $H_2O$  + phenyl acetylene, and recorded their <sup>13</sup>C NMR spectra. If the phenyl acetylene molecules interacted with any of these solvent systems, a downfield shifting of the triple-bond carbon atoms would be observed in the <sup>13</sup>C NMR spectra. As anticipated, the NMR spectrum of the EL +  $H_2O$  + phenyl acetylene sample shows downfield shifting of phenyl acetylene triple-bond carbon atoms 1 and 2 from  $\delta$  = 83.62 and 80.52 ppm to  $\delta$  = 83.93 and 80.81, respectively. The other two samples did not show any significant downfield shifting of the triple-bond carbon atoms. These experiments confirm the possible hydrogen-bonding interaction between the alkyne molecules and the EL/H<sub>2</sub>O mixture.

Hydration of alkynes is regioselective. Both types of product, that is, Markovnikov (ketones) and anti-Markovnikov (aldehydes), have been reported under various conditions [14]. From the theoretical calculations, we observed that the transition state associated with Markovnikov addition is more stable than the transition state of antiMarkovnikov addition in the present case (Fig. 2). However, it should be noted that the activation energy ( $E_a$ ) of the anti-Markovnikov route is only slightly higher (~1.6 kcal mol<sup>-1</sup>) than that of the Markovnikov pathway. Based on the  $E_a$  values and the energies of the products, it can be inferred that the Markovnikov product is both kinetically and thermodynamically controlled.

Therefore, in the present case, only Markovnikov adducts (ketones) have been regioselectively formed. A literature survey indicated that the hydration of alkynes also competes with the formation of homocoupled alkynes [22]. The present protocol gave exclusively Markovnikov adducts (ketones). The formation of homocoupled alkynes was not observed in the current case. Based on the above observation, we propose that the hydrogen-bonding network between the EL and H<sub>2</sub>O molecules interacts with the alkyne *via* a hydrogen-bond donor-acceptor interaction and brings the H<sub>2</sub>O molecules into close proximity of the alkynes to form enolic intermediates. Subsequent tautomerization of the enolic intermediates gives the final product **2i** (Scheme 4).

After confirming our hypothesis, the hydration of a diversity of aromatic terminal alkynes with different functional groups was accomplished, and the outcomes are presented in Table 4. Alkyne electronic density is expected to be a key contributor for establishing H-bonding.

#### Table 5

Synthetic application of the procedure for the production of  $\alpha_{A}\beta$ -unsaturated carbonyl compounds<sup>a</sup>.



<sup>a</sup> Reactions were performed with benzaldehyde (2 mmol) and phenyl acetylene (2 mmol) in the EL:H<sub>2</sub>O (1:3) system at 110 °C. <sup>a</sup>Reactions were performed with benzaldehyde (2 mmol) and phenyl acetylene (2 mmol) in the EL:H<sub>2</sub>O (1:3) system at 110 °C.

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As a consequence, aryl alkynes with strong electron-donating groups generated the final compounds in outstanding yields under the optimized conditions. Electron-withdrawing groups on aryl alkynes needed longer reaction times for the transformation to the analogous aryl ketones in good yield. Moreover, aliphatic and internal alkynes were inert under the employed conditions. Further investigation is under way in our laboratory.

Encouraged by these outcomes, we extended the synthetic scope of the above procedure for the synthesis of value-added  $\alpha,\beta$ -unsaturated carbonyl compounds [23]. According to the existing literature procedures [24], the synthesis of these compounds requires a base, an acid, or a catalyst. We successfully applied the above protocol for the production of  $\alpha,\beta$ -unsaturated carbonyl compounds through the reaction of aldehydes with alkynes as ketonic surrogates. In a tentative experiment, benzaldehyde (2 mmol) and phenyl acetylene (2 mmol) were submitted to the optimized reaction conditions. After 48 h,  $\alpha,\beta$ -unsaturated compound **3i** was isolated in good yield. The reaction tolerated a wide variety of groups on the phenyl ring and gave the analogous compounds in excellent yields (Table 5). All of these reactions were accomplished in 48–60 h.

In a successive mechanism, the alkyne molecule first undergoes a hydration reaction and produces the corresponding methyl ketone. The hydrogen-bonding network between the EL and H<sub>2</sub>O molecules activates the aldehyde molecule through cooperative hydrogen bonding and facilitates the Claisen–Schmidt condensation [25] with the resulting methyl ketone to construct the desired  $\alpha$ , $\beta$ -unsaturated carbonyl compound. Overall, the reaction follows the hydration/condensation sequence.

### 3. Experimental section

3.1. General

See the ESI.

#### 3.2. Computational details

The ground-state equilibrium structures of the hydrogen-bonded complexes were optimized by using the DFT functional B3LYP [26] with the 6-311++G(d,p) basis set. To estimate the strength of intermolecular H-bonding in these complexes, NBO analysis is conducted at the same level of theory. Furthermore, to understand whether the addition reaction of complex 2 to phenyl acetylene follows the Markovnikov or anti-Markovnikov pathway, the two plausible transition states were optimized by using the Berny algorithm. An intrinsic reaction coordinate scan was conducted to confirm that the obtained transition states associate the reactants and products in the potential energy surface. The reactants, products, and transition states were optimized at the B3LYP/6-31G(d) theoretical level. All analyses were achieved in the gas-phase by utilizing the Gaussian 09 rev A.02 [27] program package.

# 3.3. General process for alkyne hydration to form compounds 2

Alkynes (2 mmol) were added to a stirred 35 mL solution of EL:H<sub>2</sub>O (1:3). The reaction mixture was stirred at 110 °C for a suitable time. After successful conversion, the resultant solution was cooled to room temperature and extracted with ethyl acetate (4–6 mL). The combined organic phases were dehydrated over anhydrous sodium sulfate and filtered. The filtered solution was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane:EtOAc as the eluent) to provide the pure desired product.

3.4. General process for the production of  $\alpha_{\!\!\!\!,}\beta$  -unsaturated carbonyl compounds 3

Alkynes (2 mmol) and aldehydes (2 mmol) were added to a stirred 35 mL solution of EL:H<sub>2</sub>O (1:3). The reaction mixture was stirred at 110 °C for a suitable time. After successful conversion, the resultant solution was cooled to room temperature and extracted with ethyl acetate (4–6 mL). The combined organic phases were dehydrated over anhydrous sodium sulfate and filtered. The filtered solution was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane:EtOAc as the eluent) to give the pure desired product.

# 4. Conclusions

In summary, we have shown regioselective Markovnikov-type alkyne hydration in an ethyl lactate/water (1:3) medium. By various experimental and theoretical techniques, the critical role of the hydrogen-bonding network in the ethyl lactate and water mixture for the hydration of alkynes has been established. This strategy was also used for the production of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds through the reaction of aldehydes with alkynes as ketonic surrogates. Broad substrate applicability and excellent yields without the addition of metals, catalysts, acids, and additives make the process eye-catching. To widen the application of the above procedure and understand the mechanism of this system in more detail, further work is ongoing in our laboratory and will be reported in due course.

### Author statement

A.D. and V.P. developed the idea; V.P. designed the concept; P.S. completed review of literature, V.P. and P.S. analyzed the results; P.S. was involved in the data analysis, P.S. and V.P. completed the manuscript CMJ and SRV analyze and conclude computational details. All the authors discussed the results and commented on the paper.

#### **Declaration of Competing Interest**

There are no conflicts to declare.

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#### Appendix A. Supplementary data

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