



# Metal/catalyst/reagent free hydration of alkynes up to gram scale under temperature and pressure controlled condition



Munsaf Ali, Avinash K. Srivastava, Raj K. Joshi \*

Department of Chemistry, Malaviya National Institute of Technology, Jaipur 302017, Rajasthan, India

## ARTICLE INFO

### Article history:

Received 13 March 2018  
Revised 16 April 2018  
Accepted 18 April 2018  
Available online 22 April 2018

### Keywords:

Metal-free  
Autoclave  
Alkynes  
Hydration  
Ketone

## ABSTRACT

A new green water-mediated metal/catalyst/reagent-free methodology for hydration of alkyne is devised. The remarkable yields of various ketones were achieved when alkynes were heated at 150 °C under 11 bar pressure in an autoclave for 14 h in water-methanol solution. Outstanding functional group compatibility for both the terminal and internal alkynes was established. This methodology produces excellent yields up to gram scale under optimised reaction condition.

© 2018 Elsevier Ltd. All rights reserved.

## Introduction

Increasing the amount of product with minimising the role of catalyst and raw material is one of the critical aspects among the 12 principles of green chemistry.<sup>1</sup> There were many reports available that demonstrate the applications of green and sustainable methodologies for laboratory and industrial productions. Practising various inexpensive and environmentally benign reaction methodologies have unveiled a new era in the field of chemistry.<sup>2</sup> Optimizing reaction conditions to accomplish without any chemical activation, i.e. without using chemical reagents or catalyst to perform chemical changes; this phenomenon is interesting as well as significantly crucial from commercial and economic perspective. Reordering the physical parameters (temperature and pressure) associated with the reaction may lead to new insights in catalyst-free organic transformation. The use of autoclave technique for hydrogenation,<sup>3</sup> hydration<sup>4</sup> and various other reactions is quite common. Moreover, these methodologies outstandingly reduce the cost and formation of undesired by-products and chemical waste in the reaction.

The Wacker oxidation of alkenes and metal mediated carbonylation of alkynes is extensively used to generate the carbonyl compounds including the ketones, esters, lactone, and melamide.<sup>4,5</sup> The hydration of alkynes had developed a paramount interest world-

wide among various research groups, and it is a well-established and more advanced method for the production of ketones. Due to their diversified applications, ketones are the linchpins for various organic syntheses. Moreover, they also serve as versatile intermediates in a wide range of chemical syntheses such as natural products, drugs and other valuable industrial products.<sup>6</sup> The vast diversity of alkyne substrates are a precursor for hydration reactions, and the applications of obtained carbonyls in organic syntheses<sup>7</sup> is an essential aspect of traditional synthetic chemistry. Transition metals and other metal complexes are extensively used for hydration reactions. Before 1980's mercury compounds such as Hg(OTf)<sub>2</sub>,<sup>8a</sup> HgSO<sub>4</sub>,<sup>8b</sup> and Hg(OAc)<sub>2</sub><sup>8c</sup> were utilised for hydration reactions. While due to the toxicity and hazards to the environment; search for the green, and the economic catalyst is undergoing from many years. There is surplus literature congregated in last two decades representing alkyne hydrations from a variety of transition metals such as Pd,<sup>9</sup> Pt,<sup>10</sup> Rh,<sup>11</sup> Ru,<sup>12</sup> Au.<sup>13</sup> However, these metal catalysts are rare and not economically viable. Although some economical alternatives of metal catalyst such as Ag,<sup>14</sup> Fe,<sup>15</sup> Co,<sup>16</sup> Sn and W mix-oxides<sup>17</sup> also been reported in recent past. In some recent reports, acid catalyzed<sup>18</sup> and *para*-methoxybenzenetellurinic acid anhydride<sup>19</sup> indicates that alkyne hydration can be done by metal-free conditions. However, most of the reactions have suffered from at least one or more following drawbacks: (i) Use expensive transition metals (Ru, Rh, Pd, Pt, Au, Ir, Ag) predominantly the recovery and reusability of catalysts and the indispensable use of acid co-catalysts, additives, and promoter;

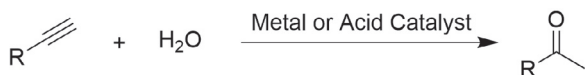
\* Corresponding author.

E-mail address: [rkjoshi.chy@mnit.ac.in](mailto:rkjoshi.chy@mnit.ac.in) (R.K. Joshi).

(ii) High price and the light sensitivity of silver salts; (iii) Narrow functional group compatibility; (iv) Large excess of acidic additive besides the metal complexes if any.

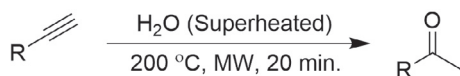
In the year 2004, Vasudevan and co-workers<sup>20</sup> reported a catalyst-free methodology which exclusively works for terminal alkynes. The alkynes in superheated water were heated at 200 °C in a microwave reactor for 20 min to produce the ketones. Although the catalyst-free alkyne hydration was reported for the first time, but, due to the harsh reaction conditions, the high temperature, unknown pressure, cannot be implemented for large scale synthesis etc. Moreover, this method was not worked for internal alkynes. All these shortfalls made this method inappropriate for the metal-free bulk synthesis of ketones.

#### Earlier Methodologies

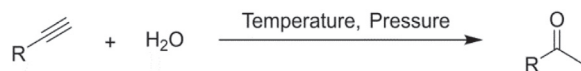


Metal Catalyst or Acid Catalyst: Au, Pd, Pt, Rh, Ru or  $\text{CF}_3\text{SO}_3\text{H}$

#### In Recent Past



#### The Present Work

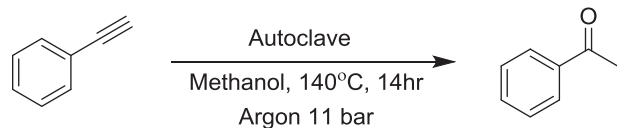


Herein, we investigated a catalyst-free methodology for hydration of terminal and internal alkyne without using any metal or acid catalyst. The present reaction is carried out in an autoclave at high temperature and pressure. Apart from the reactants, the present methodology needs only water/methanol mixture as solvent. The present method has excellent functional group compatibility and also works for both the terminal and internal alkynes and do not produce any unwanted by-product.

## Result and discussion

To follow the principles of green chemistry, we were interested in developing a metal-free reaction method for hydration of alkynes. Phenylacetylene was chosen as a model substrate for all the optimisation. After some reactions under different conditions with no results, our series of the trail is interrupted by a trace product obtained in a reaction carried out in an autoclave. Desired product acetophenone was obtained through a reaction of phenylacetylene in an autoclave at 150 °C and 11 bar of argon gas pressure in 14 h. Here, methanol was used as a solvent in the reaction. Scheme 1 represents the parameters where the desired alkyne hydration product was obtained. (Table 1, entry 9)

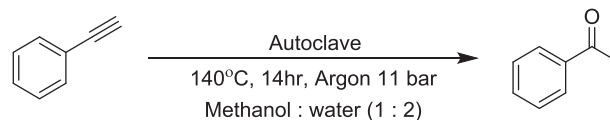
In the reaction, the inert gas pressure plays an important role. During the pressure optimisation, it was found that product yield was proportionally increased with continuously increasing pres-



Scheme 1. Temperature and pressure controlled the formation of ketones.

sure from 0 to 11 bar (Table 1, entry 1–6). Pressure below 9 bar does not initiate the reaction, while a small quantity of product was obtained at 9 bar pressure of inert gas. Increasing the pressure up to 11 bar increases the product yield. However, the further increase in pressure does not produce any change in the yield (Table 1, entry 7–8). We investigated argon, nitrogen and  $\text{CO}_2$  gas for to generate the desired pressure but irrespective of the nature of gas, the product formation was consistent and hardly brings any changes in the yield of transformed product. Since, the phenylacetylene is a volatile and low boiling liquid, at low pressure and high temperature; it vaporizes, and in the gaseous phase, it is quite rare to react with the liquid water present in the solvent mixture. While in present reaction conditions, the moderate pressure and high temperature restricted the vaporization of alkynes which make unable to convert it in its vapor form, hence, it can undergo a hydration reaction. In our opinion, it could be the best possible effect of pressure on to the reaction. The optimised value of pressure for to get the highest yield of desired product is 11 bar, while the higher pressure of inert gas does not affect the product yield and supports our proposed hypothesis. Another reason for this reaction may be the higher ionisation of water molecules at higher pressure. In the earlier reports related to the studies of ionisation of water at various pressure and temperatures<sup>21</sup> suggested that ionisation of water molecules increases at higher pressure and the ionization of water increases with the increasing temperature. Here, both the facts again support the present hypothesis of the high yield of hydrated product at a relatively high temperature and moderate to high pressure.

Table 1  
Optimization of reaction parameters with phenylacetylene.



Entry	Ar pressure (Bar)	Solvent ratio (MeOH: Water)	Temp (°C)	Time (h)	Yield <sup>a</sup> (%)
1.	00	1:2	150	14	nd
2.	9.0	1:2	150	14	23
3.	9.5	1:2	150	14	34
4.	10.0	1:2	150	14	45
5.	10.5	1:2	150	14	60
6.	11.0	1:2	150	14	79
7.	11.5	1:2	150	14	79
8.	11.0	1:2	150	14	79
9.	11.0	1:0	150	14	Trace
10.	11	0:1	150	14	nd
11.	11.0	1:1	150	14	69
12.	11.0	2:1	150	14	45
13.	11.0	1:2	150	14	79
14.	11.0	1:2	120	14	20
15.	11.0	1:2	130	14	50
16.	11.0	1:2	140	14	60
17.	11.0	1:2	150	14	79
18.	11.0	1:2	160	14	79
19.	11.0	1:2	170	14	79
20.	11.0	1:2	180	14	79
21.	11.0	1:2	150	4	nd
22.	11.0	1:2	150	8	23
23.	11.0	1:2	150	10	43
24.	11.0	1:2	150	12	67
25.	11.0	1:2	150	14	79
26.	11.0	1:2	150	16	79
27.	11.0	1:2	150	18	79
28.	11.0	1:2	150	20	79

Condition: Solvent MeOH: Water (1:2), Temperature 150 °C, 11.0 bar argon, 14 h.

<sup>a</sup> Isolated yield, nd = not detected.

Download English Version:

<https://daneshyari.com/en/article/7829214>

Download Persian Version:

<https://daneshyari.com/article/7829214>

[Daneshyari.com](https://daneshyari.com)