# Efficient Catalytic Performance of Calcined Tungstophosphoric Acid for the Claisen-Schmidt Condensation under Solvent-Free Reaction

ABDULRAHMAN I. ALHARTHI[ID]

Department of Chemistry, College of Science and Humanities in Al-Kharj, Prince Sattam Bin Abdulaziz University, P.O. Box- 83, Al-Kharj 11942, Saudi Arabia

Corresponding author: E-mail: a.alharthi@psau.edu.sa

Effect of calcination of tungstophosphoric acid catalyst was evaluated in terms of the synthesis of chalcone derivatives *via* Claisen-Schmidt condensation using the reaction of acetophenone and several substituted aldehydes. The catalyst was characterized before and after calcination by FT-IR to assess the effectiveness of the synthesis of the desired products. The calcined tungstophosphoric acid catalyst (HPW-CL) showed a better performance and high yield of Claisen-Schmidt products in a short period of time. It was also found out that the calcined tungstophosphoric acid provides a chemo selective, efficient and environmentally benign synthesis of chalcone in an excellent yield in a solvent-free system.

**Keywords: Calcination, Tungstophosphoric acid, Claisen-Schmidt condensation, Chalcone derivatives.**

## INTRODUCTION

Many efforts have been made by the chemists as well as the chemical industries over past two decades to avoid risk during the synthesis of organic compounds either at the pilot scale or the industry level. Significant use of various chemicals during the process of synthesis in order to reduce environmental pollution is designated as a green chemistry approach [1]. In recent years, researchers have been constantly trying to find new eco-friendly green solid catalysts for various organic transformation reactions [2-5]. These included tungstophosphoric acid ($H_3PW_{12}O_{40}$), a solid acid catalyst, which possesses properties of green chemistry, belongs to heteropoly acid and is therefore convenient for wide varieties of organic synthesis [6].

Structurally, it is of Keggin type, having inorganic-cage anions of the formula $XM_{12}O_{40}{}^{n-1}$, where X is a heteroatom ($P^{5+}$, $Si^{4+}$) and M is metal ion ($W^{6+}$ or $Mo^{6+}$) [7-9]. Heteropoly acids also called as polyoxometalate compounds have increasing demands recently [10-13]. Heteropoly acids have some remarkable properties in the sense that they are low toxic, environmentally friendly and cost-effective [14,15]. On the other hand, heteropoly acids behave as strong Brønsted acids due to the super acid region in it. In another way, they have effective redox properties [16]. Due to these qualities, fast multi-electron redox transformation is possible under mild reaction conditions [2]. Apart from that, heteropoly acids have a very high solubility in polar solvents and exhibit high thermal stability in a solid state [3,17,18]. Heteropoly acids have proved to be stronger than common mineral acids (HCl, $H_2SO_4$, $HNO_3$, *etc.*) in solution form. Tungstophosphoric acid is markedly stronger than any other acids in this class such as phosphomolybdic acid *etc.* [6,14,19]. Heteropoly acids also have the capability to interact with polar as well as non-polar molecules due to the pseudo liquid behaviour of the catalyst on the surface at even low temperatures [1]. It was claimed that some solid heteropoly acids and their salts, upon calcination around 300-400 ºC, developed super acids sites and acidity was found more than 100 % $H_2SO_4$ [20,21].

Formation of α,β-unsaturated ketones through C-C bond formation is known as Claisen-Schmidt condensation reaction between acetophenone and aldehydes. The product so formed is chalcone [21]. Chalcone derivatives belong to flavonoid family and are an important medicinal scaffold for varieties of pharmacological applications including anticancer [22], anti-inflam-

matory [23], antimalarial [24] and antitubercular [25]. Furthermore, they are important intermediates for useful synthesis for pharmacologically important heterocycles [3].

Conventionally, Claisen-Schmidt condensation is carried out in the presence of acid or base catalysts between aromatic aldehydes and ketones. Numerous catalysts have been used so far for the synthesis of chalcones in bases such as NaOH [26], KOH [27], LiOH·H₂O [28], Ba(OH)₂ [29] and in acids such as dry HCl [30], RuCl₃ [31], TiCl₄ [32], sulfonic acids [33], ionic liquids [4] and clay [34]. These mentioned catalysts have many shortcomings such as toxicity, corrosiveness, long reaction times, generation of undesired products and high temperature. Other drawbacks include low catalyst surface and recovery, which have their implications on the fruitful C-C bond formation during chalcone synthesis.

In this work, a comparative study between the calcined (HPW-CL) and non-calcined tungstophosphoric acid (HPW) as a catalyst for the C-C bond formation in a classical Claisen-Schmidt condensation has been carried out to the fact that the calcination increases the acidity of the catalyst which is required for this type of reactions.

## EXPERIMENTAL

All materials and chemicals were purchased from Sigma-Aldrich. FT-IR spectra for the catalyst (tungstophosphoric acid) and synthesized compounds were recorded using Thermo Scientific iD5 ATR diamond Nicolet iS 5 FT-IR Spectrometer. Data spacing was 0.482 cm$^{-1}$ with a single beam having OMINIC software. Especially designed Thermocraft incorporated tube furnace was used for calcination of the catalyst (tungstophosphoric acid). All compounds were elucidated by $^1$H and $^{13}$C NMR spectra using BRUKER-PLUS (500 MHz) with tetramethylsilane (TMS) as an internal standard.

**Calcination of tungstophosphoric acid:** An accurately 5.00 g of tungstophosphoric acid was weighed in a crucible. The crucible containing tungstophosphoric acid was put in a tube furnace at 300 ºC for 4 h in static air.

**General Procedure for the synthesis of chalcones (3a-14a) *via* Claisen-Schmidt condensation using tungstophosphoric acid**: A mixture of substituted aldehyde (2 mmol) and acetophenone (2 mmol) was stirred in the presence of calcined or non-calcined tungstophosphoric acid with varying mol % till the completion of reaction under solvent-free conditions. TLC confirmed the completion of the reaction; the mixture was filtered and washed with water to separate the catalyst (high solubility of HPW in water). The product was obtained by recrystallization with ethanol (**Scheme-I**).
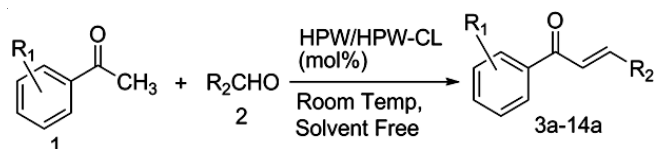


**Scheme-I:** Claisen-Schmidt condensation reaction between acetophenone and aldehydes using tungstophosphoric acid

## Spectroscopic data

**3-(Phenyl)-1-phenylprop-2-en-1-one (3a):** White, m.p.: 65 ºC, m.f. C₁₅H₁₂O; FT-IR (cm$^{-1}$, ATR): 3060 (C=C-H, Ar-H), 1660 (C=O), 1602 (C=C, Ar); $^1$H NMR (DMSO, δ ppm): 7.79-7.02 (10H, m, Ar-H), 7.05-6.96 (1H, d, *J* = 2 Hz, CH=CH), 6.68-6.24 (2H, d, *J* = 8.6 Hz, CH=CH); $^{13}$C NMR (DMSO, δ ppm): 188.40 (C=O), 148.41 (1C, CH=CH), 141.44 (1C, CH=CH), 138.35, 136.40, 133.72, 132.23, 129.43, 128.33, 124.78, 122.68, 118.05, 115.00 (Ar-C).

**3-(4-Hydroxy-3-methoxyphenyl)-1-phenylprop-2-en-1-one (4a):** Light yellow, m.p.: 82 ºC, m.f. C₁₆H₁₄O₃; FT-IR (cm$^{-1}$, ATR); 3146 (C=C-H, Ar-H), 1662 (C=O), 1585 (C=C, Ar); $^1$H NMR ( DMSO, δ, ppm): 9.23 (1H, s, OH), 7.07-7.05 (8H, m, Ar-H) 6.93-6.92 (1H, d, *J* = 2 Hz), 6.16-6.14 (2H, d, *J* = 8.3 Hz); $^{13}$C NMR (DMSO, δ, ppm): 186.44 (C=O), 145.67 (1C, CH=CH), 138.54 (1C, CH=CH), 136.40, 133.72, 129.43, 128.33, 124.78, 122.68, 118.05, 115.00 (Ar-C), 56 (1C, OCH₃).

**3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (5a):** White, m.p.: 118 ºC, m.f. C₁₅H₁₁OCl; FT-IR (cm$^{-1}$, ATR): 3196 (C=C-H, Ar-H), 1680 (C=O), 1590 (C=C, Ar); $^1$H NMR (DMSO, δ ppm): 8.15-7.27 (9H, m, Ar-H), 7.07-7.05 (1H, d, *J* = 12.9 Hz, CH=CH), 6.90-6.88 (1H, d, *J* = 12.8 Hz, CH=CH); $^{13}$C NMR (DMSO, δ ppm): 189.75 (C=O), 143.07 (1C, CH=CH), 137.83, 135.62, 134.16, 134.03, 133.79, 131.37, 131.06, 129.45, 129.37, 129.33, 129.01 (Ar-C), 123.20 (1C, CH=CH).

**3-(3-Chlorophenyl)-1-phenylprop-2-en-1-one (6a):** White, m.p.: 78 ºC, m.f. C₁₅H₁₁OCl; FT-IR (cm$^{-1}$, ATR); 3162 (C=C-H, Ar-H), 1665 (C=O), 1602 (C=C, Ar); $^1$H NMR (DMSO, δ ppm): 8.11-7.22 (9H, m, Ar-H), 7.47-7.29 (1H, d, *J* = 7.5 Hz, CH=CH), 7.28-6.89 (1H, d, *J* = 7.8 Hz, CH=CH); $^{13}$C NMR (DMSO, δ ppm): 185.47 (C=O), 148.29 (1C, CH=CH), 138.99, 136.67, 133.89, 132.33, 129.44, 129.02, 128.40, 128.19, 125.79 (Ar-C), 122.88 (1C, CH=CH).

**1-Phenyl-3-(2,3,5-trimethoxyphenyl)prop-2-en-1-one (7a):** Yellow, m.p.: 142 ºC, m.f. C₁₈H₁₈O₄; FT-IR (cm$^{-1}$, ATR); 3058 (C=C-H, Ar-H), 1669 (C=O), 1594 (C=C, Ar); $^1$H NMR (DMSO, δ ppm): 8.14-8.11 (1H, d, *J* = 15.75 Hz), 7.54-7.99 (7H, m, Ar-H), 7.45-7.44 (1H, d, *J* = 7.8 Hz); $^{13}$C NMR (DMSO, δ, ppm): 190.57 (C=O), 138.99 (1C, CH=CH), 120.78 (1C, CH=CH), 163.87, 161.92, 158.38, 132.94, 132.83, 129.74, 129.22, 128.68, 128.59, 128.42, 126.72, 106.68, 105.55 (Ar-C), 56.00 (1C, OCH₃), 55.48-56.54 (3C, OCH₃).

**1,5-Diphenylpenta-2,4-dien-1-one (8a):** Creamy white, m.p.: 110 ºC, m.f. C₁₇H₁₄O₄; FT-IR (cm$^{-1}$, ATR): 3156, 3080 (2C=C-H, Ar-H), 1664 (C=O), 1598 (C=C, Ar); $^1$H NMR (DMSO, δ ppm) 7.46-7.22 (10H, m, Ar-H), 7.05 (1H, s, =CH), 7.03-7.02 (1H, d, *J* = 2.3 Hz), 6.36 (1H, d, *J* = 1.0 Hz), 6.33 (1H, d, *J* = 0.9 Hz); $^{13}$C NMR (DMSO, δ ppm): 176.45 (C=O), 139.23 (1C, CH=CH), 121.43 (1C, CH=CH), 135.87, 130.88, 129.44, 129.14, 128.33, 128.02, 126.93, 125.66, 124.54 (Ar-C).

**3-(Indolin-3-yl)-1-phenylprop-2-en-1-one (9a):** Light brown, m.p.: 188 ºC, m.f. C₁₇H₁₅NO; FT-IR (cm$^{-1}$, ATR): 3042 (C=C-H, Ar-H), 1628 (C=O), 1611 (C=C, Ar); $^1$H NMR (DMSO, δ, ppm): 12.15 (1H, s, NH, 3-indole), 8.30-8.29 (1H, d, *J* = 3.15, 3-indole), 8.12-8.10 (1H, d, *J* = 7.65 Hz), 7.53 (1H, d, *J* = 7.9 Hz), 7.29-7.21 (9H, m, Ar-H); $^{13}$C NMR (DMSO, δ, ppm): 185.44 (C=O), 138.93 (1C, CH=CH), 137.52 (1C, CH=CH), 124.58, 123.93, 122.59, 121.29, 118.63, 112.88 (Ar-C).

**1-Phenyl-3-(1*H*-pyrrol-2-yl)prop-2-en-1-one (10a):** Brown, m.p.: 142 ºC, m.f. C₁₃H₁₁NO; FT-IR (cm$^{-1}$, ATR): 3100 (C=C-H, Ar-H), 1646 (C=O), 1583 (C=C, Ar). $^1$H NMR (DMSO, δ, ppm): 11.73 (1H, s, NH, 2-pyrrole), 8.07-8.06 (1H,

d, $J$ = 8.55, ), 8.04-8.02 (1H, d, $J$ = 8.55 Hz), 7.65-7.55 (8H, m, Ar-H); ^{13}C NMR (DMSO, δ, ppm): 188.88 (C=O), 138.79 (1C, CH=CH), 134.76 (1C, CH=CH), 133.00, 129.60, 129.17, 128.40, 124.79, 116.90, 115.05, 111.08 (Ar-C).

**1-Phenyl-3-(pyridine-2yl)prop-2-en-1one (11a):** Light yellow, m.p.: 71 ºC, m.f. $C_{11}H_{14}NO$; FT-IR (cm^{-1}, ATR): 3058 (C=C-H, Ar-H), 1669 (C=O), 1594 (C=C, Ar); ^{1}H NMR (DMSO, δ ppm): 8.49-7.09 (9H, m, Ar-H), 6.97-6.94(1H, t, $J$ = 7.3 Hz, CH=CH), 6.87-6.85(1H, t, $J$ = 6.3 Hz, CH=CH); ^{13}C NMR (DMSO, δ ppm): 186.41 (C=O), 141.49 (1C, CH=CH), 139.65, 138.76, 137.89, 135.54, 132.34, 130.90, 129.71, 128.36, 126.32 (Ar-C), 121.62 (1C, CH=CH).

**1-Phenylhex-2-en-1-one (12a):** White, m.p.: 29 ºC, m.f. $C_{12}H_{14}O$; FT-IR (cm^{-1}, ATR): 3573 (C=C-H, Ar-H), 1681 (C=O), 1597 (C=C, Ar); ^{1}H NMR (DMSO, δ ppm): 7.96-7.24 (5H, m, Ar-H), 7.22-7.16 (1H, q, $J$ = 7.1 Hz, CH=CH), 7.14-7.10 (1H, t, $J$ = 8.5 Hz, CH=CH), 2.50 (2H, s, CH$_2$), 2.36 (2H, s, CH$_2$), 0.91 (3H, s, CH$_3$); ^{13}C NMR (DMSO, δ ppm): 188.78 (C=O), 140.35 (1C, CH=CH), 138.43, 136.72, 129.47, 127.51, (Ar-C), 120.89 (1C, CH=CH), 34.45, 23.56 (2C, 2 × CH$_2$), 14.23 (1C, CH$_3$).

**1-Phenyldec-2-en-1-one (13a):** White, m.p.: 38 ºC; m.f. $C_{16}H_{22}O$. FT-IR (cm^{-1}, ATR): 3572 (C=C-H, Ar-H), 1683 (C=O), 1597 (C=C, Ar); ^{1}H NMR (DMSO, δ ppm): 7.88-7.86 (5H, m, Ar-H), 7.30-7.27 (1H, d, $J$ = 7.3 Hz, CH=CH), 7.26-7.24 (1H, d, $J$ = 8.6 Hz, CH=CH), 2.64-2.36 (12H, s, 6 × CH$_2$), 0.77 (3H, s, CH$_3$); ^{13}C NMR (DMSO, δ ppm): 191.62 (C=O), 141.53 (1C, CH=CH), 129.47, 129.03, 127.50 (Ar-C), 121.92 (1C, CH=CH), 39.94-39.44 (6C, CH$_2$), 15.18 (1C, CH$_3$).

**1-Phenylhept-2-en-1-one (14a):** Creamy white, m.p.: 42 ºC, m.f. $C_{13}H_{16}O$. FT-IR (cm^{-1}, ATR): 3572 (C=C-H, Ar-H), 1681 (C=O), 1597 (C=C, Ar); ^{1}H NMR (DMSO, δ ppm): 7.88-7.87 (2 × 1H, d, $J$ = 7.0 Hz, CH=CH), 7.30-7.25 (5H, m, Ar-H),2.99-2.50 (2H, s, 3 × CH$_2$), 0.89 (3H, s, CH$_3$); ^{13}C NMR (DMSO, δ ppm): 191.28 (C=O), 138.44 (1C, CH=CH), 133.95, 129.47, 127.52, (Ar-C), 122.54 (1C, CH=CH), 39.92-39.42 (2C, 3 × CH$_2$), 12.98 (1C, CH$_3$).

## RESULTS AND DISCUSSION

**Catalyst characterization:** From the FT-IR spectrum of non-calcined HPW, the well-defined sharp and strong absorption bands at 1073.83 and 971.99 cm^{-1} were clearly identified as P-O and W=O stretching vibrations respectively, whereas at 885.73 cm^{-1} stretching modes of vibration for W-OW were also observed (Fig. 1). These bands are a clear indication of the Keggin type structure of HPW [7,8].

When HPW was calcined, slight changes of intensity were observed. This may be due to the loss of water (Fig. 1). The W=O band was shifted from 971.99 to 963.76 cm^{-1}, whereas W-O-W band changed from 885.73 to 881.53 cm^{-1}. This revealed that the Keggin type structure of HPW was not affected by the calcination at 300 ºC and it remained intact after the calcination.

**Optimization of reaction conditions:** A model reaction was set up by taking 4-hydroxy-3-methoxy benzaldehyde (vanillin) and acetophenone as reactants to observe the performance of calcined and non-calcined tungstophosphoric acid catalyst under the solvent-free condition for effective Claisen-Schmidt condensation *via* C-C bond formation. There was no observation of any product formation in the absence of a catalyst.
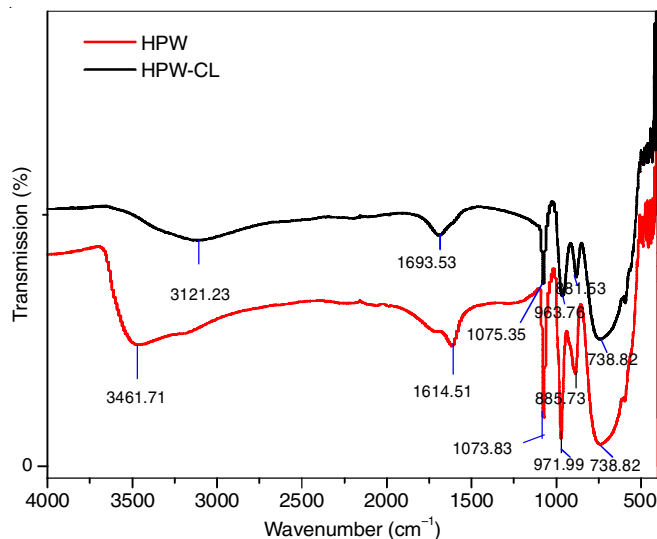


Fig. 1. FT-IR spectra of non-calcined (HPW) and calcined (HPW-CL)

Progression in percentage yields of the desired product was found increased, as the mol % of the catalyst increased by two units in each reaction. The percentage yield of product and time of completion of the reaction with each mol % of the catalyst (HPW-CL or HPW) were studied. The maximum yield (%) of 98 % was observed using 8 % of HPW-CL with the expense of 10 min only, while 10 mol % was utilized applying HPW as a catalyst to get 82 % within 45 min (Table-1, Fig. 2).

TABLE-1
OPTIMIZATION BASED ON THE AMOUNT OF CALCINED (HPW-CL) AND NON-CALCINED TUNGSTOPHOSPHORIC ACID (HPW) AND OTHER CATALYSTS FOR THE SYNTHESIS OF MODEL REACTION (**4a**) BETWEEN ACETOPHENONE (1) AND 4-HYDROXY-3-METHOXY BENZALDEHYDE (2)

| Entry[1] | Catalyst (mol %) | Yield (%)[2] | Solvents | Time (min) |
|---|---|---|---|---|
| 1 | HPW-CL (2) | 72 | – | 120 |
| 2 | HPW-CL (4) | 78 | – | 100 |
| 3 | HPW-CL (6) | 87 | – | 50 |
| 4 | HPW-CL (8) | 98 | – | 10 |
| 5 | HPW-CL (10) | 91 | – | 12 |
| 6 | HPW (2) | 51 | – | 150 |
| 7 | HPW (4) | 65 | – | 125 |
| 8 | HPW (6) | 68 | – | 80 |
| 9 | HPW (8) | 79 | – | 50 |
| 10 | HPW (10) | 82 | – | 45 |
| 11 | NaOH (10) | 45 | EtOH | 240 |
| 12 | H$_2$SO$_4$ (10) | 40 | EtOH | 300 |
| 13 | ZnCl$_2$ (10) | 50 | EtOH | 150 |

[1]Reaction conditions were optimized to 100 % conversion; [2]Isolated yield.

From the above results, the optimum mol% for HPW-CL and HPW was found 8 and 10 %, respectively. Selecting any mol% of non-calcined (HPW) as well as calcined (HPW-CL) catalysts has many differences in terms of yield and reaction completion time. The difference in these results shows that the HPW-CL acid is more efficient than HPW in relation to the C-C bond formation in Claisen-Schmidt condensation. It seems that the amount and the nature of the catalyst play significant role in the yield and time of product formation. However, it was evident that the calcination of tungstophos-
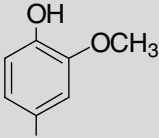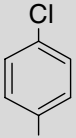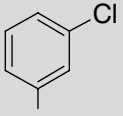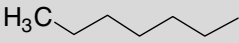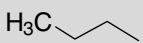
phoric acid led to enhance the activity of bronsted acid which increased the catalytic performance towards condensation reactions [6]. Furthermore, 10 mol% of NaOH, $H_2SO_4$ and $ZnCl_2$ in ethanol were used as catalysts for the reaction of Claisen Schmidt condensation. As a result, they revealed a moderate yield compare to the HPW and HPW-CL (Table-1, entries 11, 12 and 13).
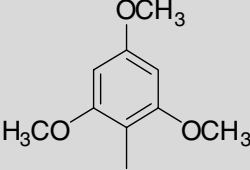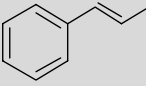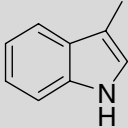
Effect of temperature was not critically observed, as there was no solvent used under catalytic reactions. Generally, room temperature to 50 ºC was considered to complete the reaction depending on reactants. It was observed that a high temperature

leads to degradation of some reactants and there was no improvement in yield. Therefore, it can be claimed that the low reaction temperature was a positive factor in the efficiency of this procedure.

To establish the scope of both forms of tungstophosphoric acid HPW-CL and HPW, various aldehydes (aromatic, heterocyclic, aliphatic) with acetophenone reactions were performed to get the product in excellent yields (Table-2). Condensation product (chalcone) was also obtained by using aromatics where heterocyclic aldehydes exhibited higher yields in a less time compared to aliphatic aldehydes under the influence of both forms of catalysts. This might be due to the hydrocarbon chain

TABLE-2
CALCINED (HPW-CL) AND NON-CALCINED (HPW) TUNGSTOPHOSPHORIC ACID (8 mol %) CATALYZED
CLAISEN-SCHMIDT CONDENSATION REACTION FOR C-C BOND FORMATION DURING CHALCONE SYNTHESIS

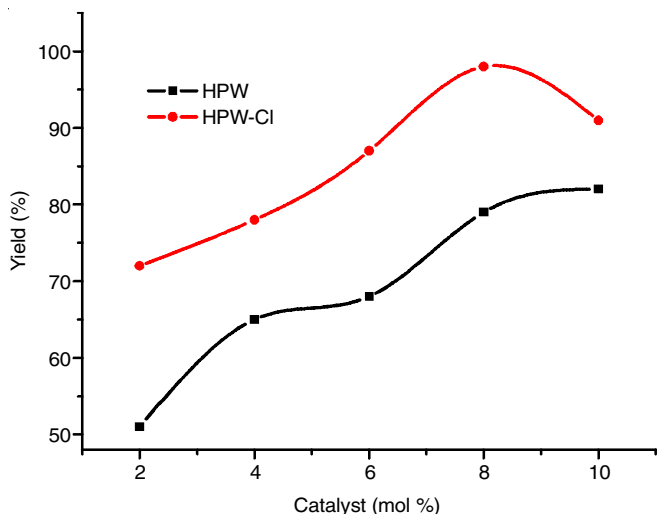| Entry | $R_1$ | $R_2$ | Product | Time (min) | | Yield (%) | |
|---|---|---|---|---|---|---|---|
| | | | | HPW-CL | HPW | HPW-CL | HPW |
| 1 | H |  | 3a | 20 | 45 | 88 | 77 |
| 2 | H |  | 4a | 10 | 40 | 98 | 88 |
| 3 | H |  | 5a | 15 | 40 | 92 | 89 |
| 4 | H |  | 6a | 15 | 60 | 85 | 70 |
| 5 | H |  | 7a | 25 | 40 | 95 | 89 |
| 6 | H |  | 8a | 30 | 85 | 86 | 62 |
| 7 | H |  | 9a | 20 | 60 | 91 | 78 |
| 8 | H |  | 10a | 20 | 55 | 97 | 75 |
| 9 | H |  | 11a | 75 | 120 | 88 | 92 |
| 10 | H |  | 12a | 50 | 80 | 75 | 65 |
| 11 | H |  | 13a | 45 | 75 | 75 | 56 |
| 12 | H |  | 14a | 60 | 100 | 72 | 60 |

Fig. 2.    Effect of mol % of catalysts HPW and HPW-CL on the yield of model compound **4a**

attached to CHO functional group that hinders towards the condensation reaction. Also, the liquid nature of aliphatic aldehydes and products after condensation were difficult to convert into the solid state resulting in a slightly lower yield.

Moreover, attempts were made to understand the effect of structure, product yield and time of reaction; however, there, could not be found any significant correlation between them except the fact that the compounds bearing aliphatic substituent were found to have a lower yield and a longer reaction time.

**Plausible mechanism:** A probable mechanism for C-C bond formation in Claisen-Schmidt condensation reaction (**3a-14a**) is presented in **Scheme-II**.
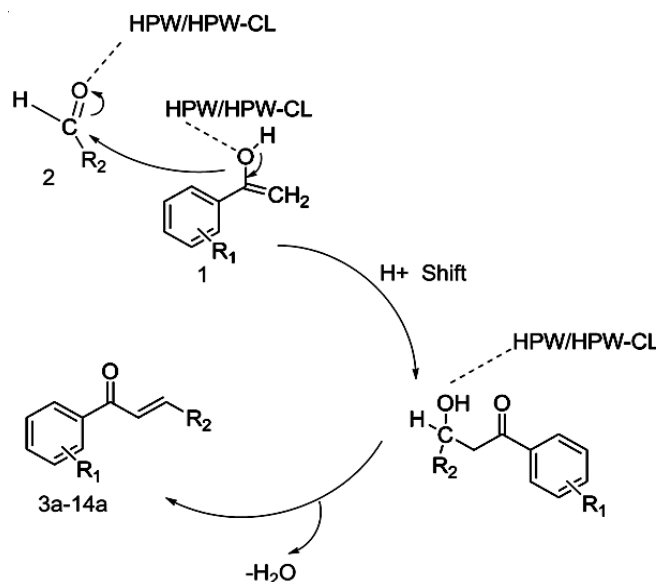


**Scheme-II:**   Plausible mechanism involved in C-C bond formation in Claisen-Schmidt condensation reaction

Either the calcined (HPW-CL) or non-calcined (HPW) catalyst activates the lone pair electron of the oxygen atom of aldehydes carbonyl groups (2), which facilitates the double bond of acetophenone (1) to attack and form β-hydroxyl compounds intermediate which finally undergoes dehydration to form the desired product **3a-14a**.

## Conclusion

This study presents an easy technique to enhance the catalytic activity of tungstophosphoric acid through calcination without any support. The calcined catalyst worked efficiently for the C-C bond formation in Claisen-Schmidt condensation under a solvent-free condition in high yield with limited time as compared to non-calcined catalyst. Thus, this method has a wider scope to improve the yield in a clean reaction state. Calcined tungstophosphoric acid could be a useful catalyst for a variety of condensation reactions, where the high demand of the acidic medium is required.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

1.  M. Dabiri and S. Bashiribod, *Molecules*, **14**, 1126 (2009); https://doi.org/10.3390/molecules14031126.
2.  J.H. Clark, *Acc. Chem. Res.*, **35**, 791 (2002); https://doi.org/10.1021/ar010072a.
3.  J.K. Rajput and G. Kaur, *Tetrahedron Lett.*, **53**, 646 (2012); https://doi.org/10.1016/j.tetlet.2011.11.109.
4.  H. Qian, D. Liu and C. Lv, *Ind. Eng. Chem. Res.*, **50**, 1146 (2011); https://doi.org/10.1021/ie101790k.
5.  J. Li, J. Feng, M. Li, Q. Wang, Y. Su and Z. Jia, *Solid State Sci.*, **21**, 1 (2013); https://doi.org/10.1016/j.solidstatesciences.2013.04.005.
6.  I.V. Kozhevnikov, *Chem. Rev.*, **98**, 171 (1998); https://doi.org/10.1021/cr960400y.
7.  L.P. Kazanskii and M.A. Fedotov, ed.: D.B. Brown, Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology, and Biology, Springer Science & Business Media, England, vol. 58, p. 383 (2012).
8.  W. Klemperer and W. Shum, *J. Am. Chem. Soc.*, **99**, 3544 (1977); https://doi.org/10.1021/ja00452a080.
9.  W. Klemperer and W. Shum, *J. Am. Chem. Soc.*, **100**, 4891 (1978); https://doi.org/10.1021/ja00483a044.
10.  T. Okuhara, N. Mizuno and M. Misono, Catalytic Chemistry of Heteropoly Compounds, In: Advances in Catalysis, Elsevier, vol. 41, pp. 113-252 (1996).
11.  A. Corma, *Chem. Rev.*, **95**, 559 (1995); https://doi.org/10.1021/cr00035a006.
12.  D. Friesen and D. Gibson, *Chem. Commun.*, **5**, 543 (1998); https://doi.org/10.1039/a800381e.
13.  M. Misono and N. Nojiri, *Appl. Catal.*, **64**, 1 (1990); https://doi.org/10.1016/S0166-9834(00)81550-X.
14.  H. Firouzabadi and A. Jafari, *J. Iran. Chem. Soc.*, **2**, 85 (2005).
15.  I.V. Kozhevnikov, *Russ. Chem. Rev.*, **56**, 811 (1987); https://doi.org/10.1070/RC1987v056n09ABEH003304.
16.  M. Misono, *Catal. Rev., Sci. Eng.*, **29**, 269 (1987); https://doi.org/10.1080/01614948708078072.
17.  M. Timofeeva, A. Demidov, A. Davydov and I. Kozhevnikov, *J. Mol. Catal.*, **79**, 21 (1993); https://doi.org/10.1016/0304-5102(93)85087-A.
18.  V. Chuvaev, K. Popov and V. Spitsyn, *Dokl. Akad. Nauk SSSR*, **255**, 892 (1980).
19.  G.A. Olah, G.K.S. Prakash and J. Sommer, Superacids, John Wiley & Sons: New York, Chichester, Brisbane, Toronto, Singapore, pp. 1073-1074 (1985).
20.  K. Nowiñska, R. Fiedorow and J. Adamiec, *J. Chem. Soc., Faraday Trans.*, **87**, 749 (1991); https://doi.org/10.1039/FT9918700749.
21.  T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.*, **74**, 247 (1992); https://doi.org/10.1016/0304-5102(92)80242-9.
22.  A. Alcantara, J.M. Marinas and J. Sinisterra, *Tetrahedron Lett.*, **28**, 1515 (1987); https://doi.org/10.1016/S0040-4039(01)81030-3.

23. Y. Xia, Z.Y. Yang, P. Xia, K.F. Bastow, Y. Nakanishi and K.H. Lee, *Bioorg. Med. Chem. Lett.*, **10**, 699 (2000); https://doi.org/10.1016/S0960-894X(00)00072-X.

24. H.K. Hsieh, L.T. Tsao, J.P. Wang and C.N. Lin, *J. Pharm. Pharmacol.*, **52**, 163 (2000); https://doi.org/10.1211/0022357001773814.

25. N. Yadav, S.K. Dixit, A. Bhattacharya, L.C. Mishra, M. Sharma, S.K. Awasthi and V.K. Bhasin, *Chem. Biol. Drug Des.*, **80**, 340 (2012); https://doi.org/10.1111/j.1747-0285.2012.01383.x.

26. M.N. Gomes, R.C. Braga, E.M. Grzelak, B.J. Neves, E. Muratov, R. Ma, L.L. Klein, S. Cho, G.R. Oliveira, S.G. Franzblau and C.H. Andrade, *Eur. J. Med. Chem.*, **137**, 126 (2017); https://doi.org/10.1016/j.ejmech.2017.05.026.

27. N.J. Lawrence, D. Rennison, A.T. McGown, S. Ducki, L.A. Gul, J.A. Hadfield and N. Khan, *J. Comb. Chem.*, **3**, 421 (2001); https://doi.org/10.1021/cc000075z.

28. X. Bu, L. Zhao and Y. Li, *Synthesis*, 1246 (1997); https://doi.org/10.1055/s-1997-1348.

29. S. Bhagat, R. Sharma, D.M. Sawant, L. Sharma and A.K. Chakraborti, *J. Mol. Catal. A Chem.*, **244**, 20 (2006); https://doi.org/10.1016/j.molcata.2005.08.039.

30. T. Narender, K.P. Reddy, Shweta, K. Srivastava, D.K. Mishra and S.K. Puri, *Org. Lett.*, **9**, 5369 (2007); https://doi.org/10.1021/ol702187m.

31. T. Szell and I. Sohar, *Can. J. Chem.*, **47**, 1254 (1969); https://doi.org/10.1139/v69-207.

32. L.J. Mazza and A. Guarna, *Synthesis*, 41 (1980); https://doi.org/10.1055/s-1980-28916.

33. T. Narender and K.P. Reddy, *Tetrahedron Lett.*, **48**, 3177 (2007); https://doi.org/10.1016/j.tetlet.2007.03.054.

34. Q. Xu, Z. Yang, D. Yin and F. Zhang, *Catal. Commun.*, **9**, 1579 (2008); https://doi.org/10.1016/j.catcom.2008.01.007.