

Catalytic synthesis of 1,3-diaryl-2-propene-1-ones by using heteropolyacids as heterogeneous recyclable green catalysts

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New convenient conditions for the synthesis of 1,3-diaryl-2-propene-1-ones are described. 1,3-diaryl-2-propene-1-ones were readily prepared in the presence of heteropolyacids as heterogeneous recyclable catalysts in good yields and short times.

Key words: Heteropolyacids, Aromatic aldehyde, Acetophenone, 1,3-diaryl-2-propene-1-ones, Heterogeneous, Catalyst.

INTRODUCTION

(1,3-diaryl-2-propene-1-ones), chalcones are natural substances found in a number of plants or are synthetically prepared. They display many biological activities, *viz.*, antiviral, anti-inflammatory, antimicrobial, antimetabolic, antitumor, analgesic, and antipyretic properties [1]. In addition, these compounds are of a high interest due to their use as starting materials in the synthesis of a series of heterocyclic compounds [2] like, isoxazoles, quinolinones, thiadiazines, benzofuranones, benzodiazepine, tetrahydro-2-chromens [3], flavones, etc. Moreover, these are important intermediates in many addition reactions of nucleophiles due to the inductive polarization of carbonyl group at the β -position. The main method for the synthesis of chalcones is the classical Claisen-Schmidt condensation in the presence of aqueous alkaline bases [4], Ba(OH)₂ [5], LiOH, microwave irradiation, ultrasound irradiation [6]. They are also obtained *via* the Suzuki reaction [7], Wittig reaction, Friedel-Crafts acylation with cinnamoyl chloride, or photo-fries rearrangement of phenyl cinnamates. In aldol condensation, the preparation of chalcones requires at least two-steps of aldol formation and dehydration. Jhala *et al.* synthesized chalcone using basic alumina under microwave irradiation [8]. There are numerous acid-catalyzed organic reactions and the use of solid acid catalysts is very important in several

industrial and environmental processes [9]. In recent times, inorganic solid-catalyzed organic transformations are gaining much importance due to the proven advantage of heterogeneous catalysts, such as simplified product isolation, mild reaction conditions, high selectivity, easy recovery and catalyst reuse, and reduced generation of waste byproducts [10]. The reactions catalyzed by both heterogeneous and homogeneous systems have been reviewed by many researchers [11]. The reactions in which they can be used, from dehydration, cyclization or esterification up to amine oxidation or olefin epoxidation, may find wide applications in fine chemical production, such as fragrances, pharmaceutical and food [12]. Although there are many structural types of HPAs, the majority of the catalytic applications use the most common Keggin-type HPAs [13], especially for acid catalysts, owing to their availability and chemical stability. Other catalysts such as Wells-Dawson and Preyssler heteropolyacids are already being used [14].

EXPERIMENTAL SECTION

All chemicals were obtained from Merck and were used as received. H₄[PMo₁₁VO₄₀], H₆[PMo₉V₃O₄₀] and H₅[PMo₁₀V₂O₄₀] were prepared according to the literature [15-17]. The Wells-Dawson species H₆[P₂W₁₈O₆₂] was prepared as described elsewhere [16], from an aqueous solution of α/β K₆P₂W₁₈O₆₂·10H₂O salt, which was treated with ether and concentrated (37%) HCl solution. IR spectra were obtained with a Buck Scientific 500 spectrometer. ¹H-NMR spectra were

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recorded on a Bruker 200 MHz FT-NMR. All products are known compounds and were characterized by mp, IR and ¹H NMR. Melting points were measured by the capillary tube method with an Electrothermal 9200 apparatus.

Typical procedure for preparation of 1,3-diphenyl prop-2-en-1-ones (3a-j):

A mixture of 4-hydroxy acetophenone **1a** (3 mmol), benzaldehyde **2a** (3 mmol) and H₆[P₂W₁₈O₆₂] (0.03 g) was stirred at different temperatures using water as a green solvent (10 mL) for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the catalyst was filtered off using a Buechner funnel (Ø = 6.0 cm) and washed with 20 mL dichloromethane. The filtrate was concentrated on a rotary evaporator. The reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous MgSO₄ and the solvent was evaporated to afford 1,3-diphenyl prop-2-en-1-ones, which were purified by column chromatography to afford 1,3-diphenyl prop-2-en-1-ones.

Spectral data of selected compounds:

1,3-Diphenyl prop-2-en-1-one (3a):

¹H NMR (CDCl₃, 200 MHz): δ 7.82 (1H, d, β-H, *J* = 7.50 Hz), 7.06 (1H, d, α-H, *J* = 7.50 Hz), 8.02 (dd, 2H), 7.45-7.72 (m, 8H, Ar-H, *J* = 6.94 Hz); ¹³CNMR (CDCl₃, 100 MHz): δ 120.91, 127.95, 128.43, 128.75, 129.48, 134.69, 135.66, 137.96, 145.37, 188.90. Anal. calcd for C₁₅H₁₂O: C 86.51, H 5.81; found: C 86.41, H 5.72.

1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one (3b):

¹H NMR (CDCl₃, 200 MHz): δ 7.88 (1H, d, β-H, *J* = 15.06 Hz), 6.86 (1H, d, α-H, *J* = 15.18 Hz), 6.95-7.72 (9H, m, Ar-H), 10.75 (1H, s, Ar-OH); ¹³CNMR (CDCl₃, 100 MHz): δ 116.65, 121.46, 127.96, 128.76, 130.87, 131.44, 135.70, 146.10, 165.20, 189.90. Anal. calcd for C₁₅H₁₂O₂: C 80.34, H 5.39; found: C 80.24, H 5.47.

(E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (3c):

¹H NMR (CDCl₃, 200 MHz): δ 7.79 (1H, d, β-H, *J* = 8.50 Hz), 6.56 (1H, d, α-H, *J* = 8.50 Hz), 6.65-7.89 (9H, m, Ar-H), 9.67 (1H, s, Ar-OH); ¹³CNMR (CDCl₃, 100 MHz): δ 115.90, 121.47, 127.88, 128.90, 129.67, 130.78, 134.65, 145.70, 158.23, 190.35. Anal. calcd for C₁₅H₁₂O₂: C 80.34, H 5.39; found: C 80.26, H 5.30.

3-(4-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (3d):

¹H NMR (CDCl₃, 200 MHz): δ 7.88 (1H, d, β-H, *J* = 17.52 Hz), 6.86 (1H, d, α-H, *J* = 17.62

Hz), 7.28-7.64 (8H, m, Ar-H, *J* = 8.50 Hz), 10.05 (1H, s, Ar-OH). ¹³CNMR (CDCl₃, 100 MHz): δ 115.90, 121.50, 129.47, 130.41, 130.67, 136.34, 140.87, 145.23, 158.21, 190.15. Anal. calcd for C₁₅H₁₁ClO₂: C 69.64, H 4.29; found: C 69.57, H 4.19.

3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3e):

¹H NMR (CDCl₃, 200 MHz): δ 7.80 (1H, d, β-H, *J* = 15.20 Hz), 7.16 (1H, d, α-H, *J* = 15.12 Hz), 7.4-7.74 (9H, m, Ar-H, *J* = 8.60 Hz), 10.05 (1H, s, Ar-OH). ¹³CNMR (CDCl₃, 100 MHz): δ 122.10, 128.60, 128.65, 128.89, 129.34, 133.45, 133.68, 134.68, 138.25, 145.67. Anal. calcd for C₁₅H₁₁ClO: C 74.23, H 6.59; found: C 74.10, H 6.45.

3-(4-(dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (3f):

¹H NMR (CDCl₃, 200 MHz): δ 7.90 (1H, d, β-H, *J* = 15.80 Hz), 6.85 (1H, d, α-H, *J* = 15.56 Hz), 9.25 (1H, s, Ar-OH), 3.05 (6H, s, -N(CH₃)₂), 7.05-7.80 (8H, m, Ar-H). ¹³CNMR (CDCl₃, 100 MHz): δ 45.65, 111.80, 116.65, 121.80, 125.23, 129.80, 131.60, 145.35, 150.78, 165.00. Anal. calcd for C₁₇H₁₇NO₂: C 76.38, H 6.41, N 5.24; found: C 76.24, H 6.33, N 5.16.

3-(4-(dimethylamino)phenyl)-1-(2-hydroxy-3,5-dimethylphenyl)prop-2-en-1-one (3g):

¹H NMR (CDCl₃, 200 MHz): δ 7.85 (1H, d, β-H, *J* = 14.71 Hz), 7.05 (1H, d, α-H, *J* = 14.67 Hz), 13.03 (1H, s, Ar-OH), 3.08 (6H, s, -N(CH₃)₂), 2.35 (6H, s, Ar-CH₃), 6.85-7.80 (6H, m, Ar-H). ¹³CNMR (CDCl₃, 100 MHz): δ 28.60, 44.57, 11.80, 118.75, 122.45, 124.88, 126.70, 129.75, 132.00, 134.45, 145.60, 150.35, 158.90, 193.10. Anal. calcd for C₁₉H₂₁NO₂: C 77.26, H 7.17, N 4.74; found: C 77.12, H 7.08, N 4.69.

1-(4-hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (3h):

¹H NMR (CDCl₃, 200 MHz): δ 8.20 (2H, d, Ar-H, *J* = 8.92 Hz), 7.40 (2H, d, Ar-H, *J* = 8.70 Hz), 7.05 (2H, s, Ar-H), 6.92 (1H, d, β-H, *J* = 15.83 Hz), 6.75 (1H, d, α-H, *J* = 15.83 Hz), 3.80-3.90 (9H, s, 3x OCH₃), 11.05 (1H, s, Ar-OH). ¹³CNMR (CDCl₃, 100 MHz): δ 57.70, 61.25, 104.25, 116.69, 122.20, 126.60, 131.70, 139.34, 145.56, 153.00, 164.50, 190.15. Anal. calcd for C₁₈H₁₈O₅: C 68.78, H 7.17; found: C 68.56, H 7.18.

3-(2-hydroxyphenyl)-3-oxoprop-1-enyl)-4H-chromen-4-one (3i):

¹H NMR (CDCl₃, 200 MHz): δ 7.65 (1H, d, β-H, *J* = 11.43 Hz), 7.15 (1H, d, α-H, *J* = 12.00 Hz), 12.45 (1H, s, Ar-OH), 8.65 (s, 1H), 7.10-8.05 (8H, m, Ar-H). ¹³CNMR (CDCl₃, 100 MHz): δ 109.30, 119.68, 120.45, 123.46, 123.95, 126.34, 129.20, 134.76, 135.55, 136.87, 137.80, 157.57, 163.45,

189.90. Anal. calcd for C₁₈H₁₂O₃: C 78.25, H 4.38; found: C 78.18, H 4.29.

3-(5-chloro-2-hydroxyphenyl)-3-oxoprop-1-enyl)-4H-chromen-4-one (3j) :

¹H NMR (CDCl₃, 200 MHz): δ 7.85(1H, d, β-H, *J* =11.40 Hz), 7.15(1H, d, α-H, *J* =11.32 Hz), 12.75(1H, Ar-OH), 8.55(s, 1H), 6.85-7.95(7H, m, Ar-H). ¹³CNMR (CDCl₃, 100 MHz): δ 109.25, 119.48, 123.56, 125.98, 129.90, 130.97, 134.68, 135.47, 135.40, 137.89, 158.24, 163.56, 198.57. Anal. calcd for C₁₉H₁₃ClO₃: C 70.27, H 4.03; found: C 72.47, H 3.93.

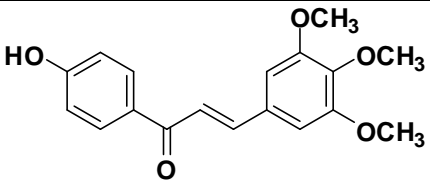
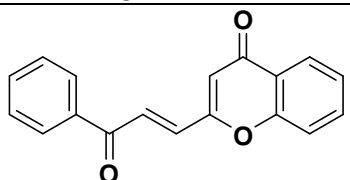
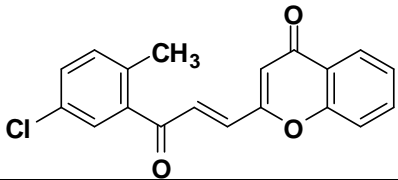
RESULTS AND DISCUSSION

In a systematic study in the presence of all catalysts, the reaction was examined with different solvents and then in the solvent of choice. The

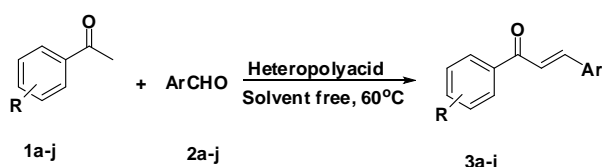
effect of the reaction temperature was also studied. Next, using the best solvent and temperature, the effect of the reaction time was studied. In a typical example we have carried out a reaction of 4-hydroxy acetophenone **1a** with benzaldehyde **2a** in the presence of Wells–Dawson type of heteropolyacids H₆[P₂W₁₈O₆₂], H₄[PMo₁₁VO₄₀], H₅[PMo₁₀V₂O₄₀] and H₆[PMo₉V₃O₄₀] at 60°C using water as a green solvent to afford the corresponding 1,3-diaryl-2-propene-1-one (**3a**) (Table 1) without any side products and in excellent yields with short reaction time (Scheme 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the usual work-up afforded pure chalcones in excellent yields (82-96%), Table 1.

Table 1. Synthesis of 1,3-diaryl-2-propene-1-ones in the presence of a Wells–Dawson, H₆[P₂W₁₈O₆₂] heteropolyacid catalyst at different temperatures using water as a green solvent

Entry	Products (3a-i)	Time (min)	Mp (°C)		^a Yield (%)		
			Found	Reported	25 °C	50 °C	60 °C
1		48	57-59	54-56	57	71	90
2		64	173-175	172-174	64	83	96
3		68	184-186	180-181	61	74	82
4		79	175-177	173-174	65	72	87
5		55	111-113	113-114	68	84	92
6		72	119-122	120-122	61	77	95
7		77	135-137	-	57	73	86

8		75	162-165	-	59	71	91
9		84	147-149	-	61	75	93
10		85	112-115	-	59	70	84

^a Isolated yields.



Scheme 1. Synthesis of 1,3-diaryl-2-propene-1-ones using heteropolyacid catalysts at 60°C and water as a green solvent

Effect of the catalyst type

Initially, we compared the catalytic performance of Keggin, $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$, $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$ with Wells–Dawson, $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ in the synthesis of 1,3-diaryl-2-propene-1-one derivatives. The results are shown in Table 2. The yield of product decreases in the following order: $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}] > \text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}] > \text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] > \text{H}_4[\text{PMo}_{11}\text{VO}_{40}] > \text{H}_2\text{SO}_4 > \text{Yb}(\text{OTf})_3 > \text{Hf}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4 > \text{Bi}(\text{OTf})_3$

Table 2. Synthesis of (E)-chalcone 3a using various heteropolyacid catalysts at 60°C and water as a green solvent

Entry	Catalyst	Time (min)	^a Yield (%)
1	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	48	90
2	$\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$	48	85
3	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	48	81
4	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	48	74
5	Free	600	-
6	$\text{Hf}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$	59	64
7	$\text{Yb}(\text{OTf})_3$	66	66
8	$\text{Bi}(\text{OTf})_3$	74	62
9	H_2SO_4	78	70

^aIsolated yields.

As can be seen, Wells–Dawson type of heteropolyacid $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$, is more effective than the other heteropoly anions and in the presence

of this catalyst the highest yields of products are obtained. The interesting feature of this polyanion compared to the other heteropolyacids is its hydrolytic stability (pH 0-12), which is very important in catalytic processes.

Comparison of $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$, $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$ with Wells–Dawson, $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$, showed that the activity was always higher for Wells–Dawson, $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$. In other words, Wells–Dawson, $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ is a better catalyst for the synthesis of 1,3-diaryl-2-propene-1-ones, and the acid strength of this solid acid catalyst is higher than that of H_2SO_4 (with serious environmental and operational problems). Heteropolyacid with a tungsten atom shows higher acidity than its molybdenum analogue [18, 19]. It seems clear that the acid strength of the protons on Wells–Dawson, $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ (tungsten atom shows higher acidity than molybdenum) is sufficient to catalyze the synthesis of 1,3-diaryl-2-propene-1-ones, and potentially all protons are active sites.

Table 3. Synthesis of 1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one 3b using various heteropolyacid catalysts and water as a green solvent at 60°C

Entry	Catalyst	Time (min)	^a Yield (%)
1	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	64	96
2	$\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$	64	91
3	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	64	84
4	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	64	80
5	Free	600	-
6	$\text{Hf}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$	61	58
7	$\text{Yb}(\text{OTf})_3$	69	63
8	$\text{Bi}(\text{OTf})_3$	79	60
9	H_2SO_4	77	68

^aIsolated yields.

Effect of the solvent

The synthesis of 1,3-diaryl-2-propene-1-one derivatives at 60°C was carried out using various common solvents such as ethanol, methanol, THF, CHCl₃ and acetonitrile. The results are shown in Table 4. With all catalysts, the highest yields of the products were obtained under solvent-free conditions (water as a green solvent). In addition, the time required for completion of the reaction was found to be shorter under solvent-free conditions (water as a green solvent).

The results (Table 4) show that the H₆[P₂W₁₈O₆₂] catalyst is better with respect to yield and reaction conditions. In all cases, the H₆[P₂W₁₈O₆₂] heteropolyacids show higher activity compared to the Keggin-type heteropolyacids, Hf[N(SO₂C₈F₁₇)₂]₄, Bi(OTf)₃, Yb(OTf)₃ and H₂SO₄ (Table 4, entries 27-29).

The reaction proceeds cleanly at 60°C, however at room temperature using a solvent it required longer reaction time (Table 2). In the absence of catalyst, the reaction did not yield any product even after long reaction time (10 h). This method not only affords the products in good yields but also avoids

the problems associated with catalyst cost, handling, safety and pollution. These catalysts are non-volatile, easy to handle and thermally robust and can be considered as ecofriendly for a variety of organic transformations. The results are presented in Table 1. In all cases, the reactions proceeded rapidly and with high efficiency at 60°C and water as a green solvent. IR spectra of the chalcones showed a characteristic band in the region near 1625 cm⁻¹ due to >C=O stretching vibrations. All chalcones showed absorption in the region 1575-1610 cm⁻¹ due to (-CH=CH-) ethylenic double bond. ¹H NMR spectra showed characteristic doublet signals near δ 6.84 and δ 7.96 due to olefinic a,b-protons. These findings are in agreement with the confirmed product.

Effect of temperature

The effect of temperature was studied by carrying out the reactions at different temperatures [25 °C, 50 °C and 60 °C]. As is shown in Table 1, by raising the reaction temperature from ambient temperature 25 °C to 60 °C, the yield of the

Table 4. Synthesis of 3a in the presence of different solvents and various heteropolyacid (HPAs) catalysts at different temperatures

Entry	Solvent	Catalyst	Temperature (°C)	Time (min)	^a Yield (%)
1	Water	H ₆ [P ₂ W ₁₈ O ₆₂]	60	48	90
2	Water	H ₆ [PMO ₉ V ₃ O ₄₀]	60	54	85
3	Water	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	44	81
4	Water	H ₄ [PMO ₁₁ VO ₄₀]	60	54	74
5	Ethanol	H ₆ [P ₂ W ₁₈ O ₆₂]	60	50	88
6	Ethanol	H ₆ [PMO ₉ V ₃ O ₄₀]	60	58	83
7	Ethanol	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	58	78
8	Ethanol	H ₄ [PMO ₁₁ VO ₄₀]	60	58	76
9	Methanol	H ₆ [P ₂ W ₁₈ O ₆₂]	60	60	86
10	Methanol	H ₆ [PMO ₉ V ₃ O ₄₀]	60	65	83
11	Methanol	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	65	77
12	Methanol	H ₄ [PMO ₁₁ VO ₄₀]	60	65	74
13	THF	H ₆ [P ₂ W ₁₈ O ₆₂]	60	89	81
14	THF	H ₆ [PMO ₉ V ₃ O ₄₀]	60	94	77
15	THF	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	94	72
16	THF	H ₄ [PMO ₁₁ VO ₄₀]	60	94	68
17	CHCl ₃	H ₆ [P ₂ W ₁₈ O ₆₂]	60	78	83
18	CHCl ₃	H ₆ [PMO ₉ V ₃ O ₄₀]	60	72	80
19	CHCl ₃	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	72	75
20	CHCl ₃	H ₄ [PMO ₁₁ VO ₄₀]	60	72	71
21	Acetonitrile	H ₆ [P ₂ W ₁₈ O ₆₂]	60	88	80
22	Acetonitrile	H ₆ [PMO ₉ V ₃ O ₄₀]	60	83	77
23	Acetonitrile	H ₅ [PMO ₁₀ V ₂ O ₄₀]	60	83	71
24	Acetonitrile	H ₄ [PMO ₁₁ VO ₄₀]	60	83	66
25	FREE	FREE	60	600	-
26	Water	Hf[N(SO ₂ C ₈ F ₁₇) ₂] ₄	60	59	64
27	Water	Yb(OTf) ₃	60	66	66
28	Water	Bi(OTf) ₃	60	74	62
29	Water	H ₂ SO ₄	60	78	70

^aIsolated yields.

reactions increased. From these results, it was concluded that 60 °C would be the optimum temperature for all reactions. The reaction proceeds very cleanly and free of side products in water as a green solvent.

Reusability of the catalyst

The catalyst was recovered after the reaction and was reused in the synthesis of 1,3-diaryl-2-propene-1-ones. Several recoveries have only slightly decreased the catalytic activity, pointing to the stability and retention capability of this useful polyanion. At the end of the reaction, the catalyst was filtered, washed with diethyl ether, dried at 130 °C for 1 h, and reused in another reaction. The recycled catalyst was used for three reactions without any appreciable loss in its catalytic activities being observed. In Table 5, the efficiency of $H_6[P_2W_{18}O_{62}]$ in the synthesis of **3a** after five recoveries is reported. As it is shown in Table 5, the first, second, third, fourth and fifth reaction using recovered $H_6[P_2W_{18}O_{62}]$ afforded similar yields.

Table 5. Reuse of the $H_6[P_2W_{18}O_{62}]$ catalyst for the synthesis of **3a**.

Entry	Run	^a Yield (%)	Time (min)
1	1	89	48
2	2	88	48
3	3	88	48
4	4	86	48
5	5	84	48

^aIsolated yields.

CONCLUSION

We have demonstrated an alternative simple procedure for the synthesis of 1,3-diaryl-2-propene-1-one derivatives using Wells–Dawson, $H_6[P_2W_{18}O_{62}]$ heteropolyacid catalyst as an ecofriendly, reusable, inexpensive and efficient catalyst. The method has advantages in terms of yield, heterogeneous nature, expenses, availability of reagents and reusability of the green catalyst, short reaction times and easy work-up procedure.

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REFERENCES

1. R. Kalirajan, S. U. Sivakumar S. Jubie, B. Gowramma B. Suresh, *Int. J. Chem. Tech. Res.*, **1**, 27 (2009).
2. S. Wang, G. Yu, J. Lu, K. XiaO, Y. Hu, H. Hu, *Synthesis*, 487 (2003).
3. S. R. Sarda, V. A. Puri, A. B. Rode, T. N. Dalawe, W. N. Jadhav, R. P. Pawar, *Arkivoc.* **16**, 242 (2007).
4. Y. Rajendra Prasad, A. Lakshmana Rao, R. Rambabu, P. Ravi Kumar, *Oriental J. Chem.* **23**, 927 (2007).
5. M. Srinivasa Rao, J. Kotesch, R. Narukulla, H. Duddeck, *Arkivoc.* **14**, 96 (2004).
6. V. Calvino, M. Picallo, A. J. López-Peinado, R. M. Martín-Aranda, C. J. Durán-Valle, *Appl. Surface Sci.*, **252**, 6071 (2006).
7. N. Eddarir, S. Catelle, Y. Bakkour, C. Ronlando, *Tetrahedron Lett.*, **44**, 5359 (2003).
8. G. Thirunarayanan G. Vanangamudi, *Arkivoc.* **12**, 58 (2004).
9. A. Corma, H. García, *Chem. Rev.* **103**, 4307 (2003).
10. B.M. Reddy, P. M. Sreekanth, P. Lakshmanan, *J. Mol. Catal. A. Chem.* **237**, 93 (2005).
11. L. Wilson, J. H. Clark, *J Pure Appl. Chem.* **72**, 1313 (2000).
12. G. Sartori, R. Ballini, F. Bigi, G. Bosica, R. Maggi, P. Righi, *Chem. Rev.* **104**, 199 (2004).
13. M. Misono, N. Nojiri, *Appl. Catal. A. Gen.* **64**, 1 (1990).
14. T. Okuhara, *Catal. Today.* **73**, 167 (2002).
15. I. V. Kozhevnikov, *Catalysts for fine chemical synthesis Catalysis by polyoxometalates*, Wiley, England, **2** (2000).
16. G. Romanelli, J. C. Autino, G. Baronetti, *Molecules*, **6**, 1006 (2001).
17. M. M. Heravi, T. Benmord. K. Bakhtiari, F. F. Bamoharram, H. A. Oskooie, *J. Mol. Catal. A: Chem.* **264**, 318 (2006).
18. I. V. Kozhevnikov, *Russ. Chem. Rev.* **56**, 811 (1987).
19. F.F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, M. Jahangir, *J. Mol. Catal.* **252**, 90 (2006).

КАТАЛИТИЧНА СИНТЕЗА НА 1,3-ДИАРИЛ-2-ПРОПЕН-1-ОНИ ИЗПОЛЗВАЙКИ ХЕТЕРОПОЛИКИСЕЛИНИ КАТО РЕЦИКЛИРУЕМ ЗЕЛЕН КАТАЛИЗАТОР

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(Резюме)

Описани са нови подходящи условия за синтезата на 1,3-диарил-2-пропен-1-они. Тези съединения лесно се получават в присъствие на хетерополикиселини като хетерогенни рециклируеми катализатори с добри добиви и за кратко време.