

# $H_6P_2W_{18}O_{62} \cdot 24H_2O$ as an efficient and recyclable catalyst for the ecofriendly preparation of $\beta$ -aminocrotonates

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**Abstract:**  $H_6P_2W_{18}O_{62} \cdot 24H_2O$  bulk- and silica-supported catalysts were found to be efficient and recyclable catalysts for the synthesis of a series of  $\beta$ -aminocrotonates using toluene as the solvent or under no solvent reaction conditions. Several substituted  $\beta$ -aminocrotonates can be prepared in very good yields and purity by direct reaction of amines and 1,3-dicarbonyl compounds in the presence of a catalytic amount of bulk- and silica-gel-supported  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ . The title compounds were prepared in very good yields using both methodologies, and no secondary products were detected. The procedure using no reaction solvent resulted in a clean and useful alternative, which has the advantages of a greener methodology with operative simplicity, the use of a reusable and noncorrosive solid catalyst, soft reaction conditions, low reaction times, and good yields.

**Key words:**  $\beta$ -aminocrotonates, supported heteropolyacids, Wells–Dawson, solvent-free.

**Résumé :** On a observé que le  $H_6P_2W_{18}O_{62} \cdot 24H_2O$  seul ou sur un support de silice est un catalyseur efficace et réutilisable pour la synthèse d'une série de  $\beta$ -crotonates, dans des conditions sans solvant ou en présence de toluène comme solvant. On a ainsi été en mesure de préparer plusieurs  $\beta$ -aminocrotonates, propres et avec de bons rendements en procédant à une réaction d'amine avec des composés 1,3-dicarbonylés, en présence d'une quantité catalytique de  $H_6P_2W_{18}O_{62} \cdot 24H_2O$  seul ou sur un support de silice. Les produits mentionnés dans le titre ont été préparés avec de très bons rendements en utilisant l'une ou l'autre des deux technologies et il n'a pas été possible de détecter la présence de produits secondaires. L'utilisation de la variante de la réaction sans solvant est une alternative utile et propre qui présente l'avantage d'être plus écologique, d'opération simple, faisant appel à un catalyseur solide réutilisable et non corrosif, à des conditions réactionnelles douces, de faibles temps de réaction et de bons rendements. [Traduit par la Rédaction]

**Mots-clés :**  $\beta$ -aminocrotonates, hétéropolyacides sur un support, Wells–Dawson, sans solvant.

## Introduction

Organic transformations using heterogeneous acid catalysis are very important for the development of a sustainable chemical procedure because of cost-effectiveness, better selectivity, and operational simplicity.<sup>1</sup> Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture, thereby eliminating the need for separation through distillation or extraction. In many cases, they can be reused without appreciable loss of the catalytic activity.<sup>2</sup>

Catalysis by heteropolyacids (HPAs) and related compounds is a field of increasing importance worldwide. Numerous developments are being carried out in basic research as well as in fine chemistry processes. HPAs possess a very strong acidity, and they exhibit the characteristic features of bulk-type catalysis (pseudoliquid bulk type), in which the reagent molecules are absorbed between the polyanions (rather than in a polyanion) in the ionic crystal by replacing crystallization water or expanding the lattice, and the reaction occurs there.<sup>3</sup> We recently reported the use of HPA catalyst  $H_6P_2W_{18}O_{62} \cdot 24H_2O$  with a Wells–Dawson structure to different organic transformation reactions. Among them, phenol methoxymethyl ether<sup>4</sup> and acylal deprotection,<sup>5</sup> alcohol, phenol, amine, and thiol acylation,<sup>6</sup> and heterocyclic synthesis such as flavones, chromones, coumarins, dihydrocoumarins,<sup>7</sup> and pyridines.<sup>8</sup>

On the other hand,  $\beta$ -aminocrotonate derivatives are versatile intermediates for the synthesis of many heterocycles, for example,

pyridines, pyrimidines, and pyrazoles,<sup>9–12</sup> 1,4-dihydropyridines and 3,4-dihydropyrimidines,<sup>13,14</sup> tetrasubstituted thiophenes,<sup>15</sup> pyrroles,<sup>16</sup> and  $\beta$ -amino acid derivatives.<sup>17</sup> Also,  $\beta$ -aminocrotonates have been previously evaluated as bioactive compounds with potent oral anticonvulsant activity similar to phenytoin, carbamazepine, and lamotrigine.<sup>18</sup>

The most general preparation of  $\beta$ -aminocrotonates involves the reaction of a carbonyl compound with an amine in an aromatic hydrocarbon solvent, with azeotropic removal of formed water.<sup>19,20</sup> Other procedures include the use of iodine under solvent-free conditions,<sup>21</sup> and montmorillonite clay  $K_{10}$ , silica, or *p*-toluenesulfonic acid (PTSA) under microwave irradiation.<sup>22</sup> Also, some HPAs have been used under heterogeneous and solvent-free conditions.<sup>2,23</sup>

Continuing with our studies on green methodologies using HPAs as recyclable catalysts, we now present our findings about two new methodologies for the catalytic preparation of  $\beta$ -aminocrotonates using a bulk- and silica-supported Wells–Dawson HPA with toluene as solvent and under no solvent reaction conditions (Scheme 1).

## Experimental

### Preparation of catalysts

The employed catalyst,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$  (WD), was prepared by the Drechsel method from an  $\alpha/\beta$   $K_6P_2W_{18}O_{62} \cdot 10H_2O$  isomer mixture.<sup>24</sup> This Dawson-type salt was prepared according to the technique reported by Lyon et al.<sup>25</sup> The WD silica-supported cata-

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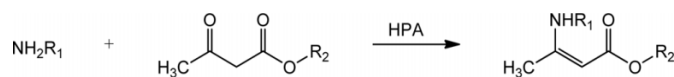
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**Scheme 1.** General preparation of  $\beta$ -aminocrotonates.

lyst was obtained by wet impregnation of Grace Davison silica (grade 59, specific area 250 m<sup>2</sup>/g) with an aqueous solution of the synthesized WD: Catalysts containing 0.1, 0.2, 0.4, or 0.6 g/g of WD acid were prepared on SiO<sub>2</sub> (0.1WDSiO<sub>2</sub>, 0.2WDSiO<sub>2</sub>, 0.4WDSiO<sub>2</sub>, or 0.6WDSiO<sub>2</sub>, respectively). Then, samples were dried at room temperature in a vacuum desiccator for 8 h.<sup>3</sup>

**Catalyst characterization**

Bulk- and silica-supported catalysts were characterized by IR spectroscopy with Fourier transform infrared (FTIR) Bruker IFS 66 equipment. <sup>31</sup>P magic-angle spinning nuclear magnetic resonance (MAS-NMR) measurements were recorded with Bruker MSL-300 equipment operating at frequencies of 121.496 MHz. A sample holder with a 5 mm diameter and 17 mm height was used. The spin rate was 2.1 kHz and several hundred pulse responses were collected. Chemical shifts were expressed in parts per million (ppm) with respect to 85% H<sub>3</sub>PO<sub>4</sub> as an external standard for <sup>31</sup>P NMR.

**Catalytic tests**

We used a bulk catalyst in solvent-free conditions and a supported catalyst using toluene as the solvent for the synthesis of a representative  $\beta$ -aminocrotonate from aniline and methyl acetoacetate. For that purpose, four silica-supported catalysts with different loadings of Wells–Dawson acid were tested. Measurements at different reaction temperatures were also made. The variation of the product yield with the molar ratio of materials was analyzed, and additional runs were made to see whether it was possible to reuse the catalysts.

**General procedures for the preparation of  $\beta$ -aminocrotonates**

All starting materials are commercial products. The reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates. All the yields were calculated from pure products. All products were identified by comparison of physical data (TLC and NMR) with those reported. <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra were recorded at room temperature on a Bruker AC 200 using tetramethylsilane (TMS) as an internal standard.

**Supported catalyst using toluene as solvent**

A mixture of 1 mmol of aniline or substituted anilines, 1 mmol of ethyl or methyl acetoacetate, with 3 mL toluene and 1 mmol% of catalyst (0.4WDSiO<sub>2</sub>) was stirred at reflux temperature for the appropriate amount of time. The progress of the reaction was checked by TLC on silica with a fluorescent indicator, monitoring the fading out of the aniline when the developed chromatogram was exposed to UV light (254 nm). The reaction mixture was filtered and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> (0.01 g). Evaporation of the solvent followed by chromatography on silica gave the pure substituted or nonsubstituted methyl and ethyl  $\beta$ -arylaminoacronates.

**Bulk catalyst using no reaction solvent**

A mixture of 1 mmol of aniline or substituted anilines, 1 mmol of  $\beta$ -ketoester, and 1 mmol % of catalyst (WD) was stirred at 80 °C for the appropriate time. The progress of the reaction was checked by TLC. After completion of the reaction, hot toluene was added (2.5 mL) and the catalyst was filtered. The extracts were combined; their solvents were evaporated and then concentrated in vacuum. Chromatography on silica gave the pure substituted or nonsubstituted methyl and ethyl  $\beta$ -aminocrotonates.

**Results and discussion****Catalyst characterization**

In previous papers,<sup>26–29</sup> bulk and supported catalysts were characterized by <sup>31</sup>P MAS-NMR, FTIR, and X-ray diffraction (XRD) measurements. The obtained results have been summarized in the following paragraph. It is known that pure WD acid has two equivalent phosphorus atoms and, consequently, it has only one peak (at –12.8 ppm) in the <sup>31</sup>P MAS-NMR spectrum.<sup>26</sup> In the case of supported catalysts, a main peak with a chemical shift of –12.7 ppm and two new small signals close to –12 and –11 ppm were detected in the <sup>31</sup>P MAS-NMR spectra. Those results indicate that WD keeps its heteropolyoxoanion structure after the impregnation and drying steps when it is supported on SiO<sub>2</sub> using a WD loading in the range of 0.1–0.6 g WD/g SiO<sub>2</sub>. The two new signals could be related to the presence of H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> species strongly interacting with the Si–OH groups of the support, and to lacunary species such as P<sub>2</sub>W<sub>21</sub>O<sub>71</sub><sup>6–</sup>, respectively.<sup>27,28</sup>

The FTIR characterization also shows that after impregnation, the acid maintains its Dawson structure. The characteristic bands of the HPA with a Dawson structure are 1091 (stretching frequency of the PO<sub>4</sub> tetrahedron), 963 (W=O terminal bonds), 911, and 778 cm<sup>–1</sup> (“inter” and “intra” W–O–W bridges, respectively). It can be observed that catalysts supported on SiO<sub>2</sub> using a WD loading in the range of 0.1–0.6 g WD/g SiO<sub>2</sub> display the same characteristic bands. Nevertheless, for these supported samples, a broadening of the band at 1091 cm<sup>–1</sup> (stretching frequency of the PO<sub>4</sub> tetrahedron) must be noted. This fact can be due to a loss of tetrahedron symmetry because of the interaction between WO<sub>6</sub> octahedra and silanol groups of the support. A slight shift of the 778 cm<sup>–1</sup> band (intra W–O–W bridges) could also be observed, which could be attributed to the same effect.<sup>29</sup>

**Catalytic tests**

A range of catalytic tests were performed to analyze the effect of the reaction temperature, charges of WD on SiO<sub>2</sub>, molar ratio of reactants, amount of catalyst and its reuse on the reaction yield and its selectivity. With that purpose, the general reaction presented in Scheme 1 was taken, for both methods, with aniline and methyl acetoacetate as starting materials.

**Effect of reaction temperature**

It is well-known that procedures without reaction solvent usually show higher yields than reactions with solvent. To determine the ideal reaction temperature for each method, the effect of reaction temperature was evaluated. Figure 1 shows that, in both cases, the conversion is higher as temperature increases. According to the results obtained, the reactions using toluene presented good product yields at 110 °C, and the reactions carried out without reaction solvent presented excellent product yields at 80 °C.

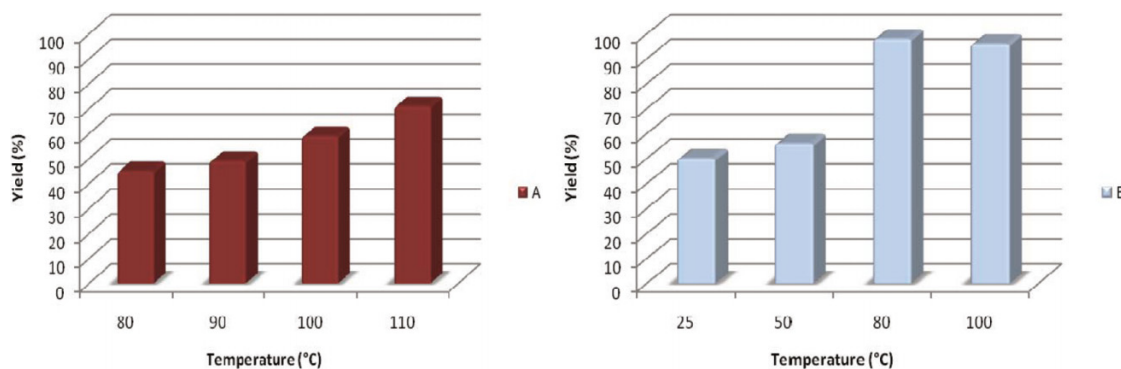
**Effect of the charges of WD on SiO<sub>2</sub>**

The catalytic activity of catalysts containing 0.1, 0.2, 0.4, or 0.6 g/g of WD acid supported on SiO<sub>2</sub> was evaluated at the ideal reaction temperature. As can be observed in Fig. 2, performing the reaction with toluene at 110 °C and in a reaction time of 2 h, an increase in WD loading produces a conversion increment following the sequence of 0.1WDSiO<sub>2</sub> < 0.2WDSiO<sub>2</sub> < 0.6WDSiO<sub>2</sub> < 0.4WDSiO<sub>2</sub>. These results are similar to those obtained by using these catalysts in flavones synthesis.<sup>28</sup> The best catalytic conversion by a gram of catalyst was shown by 0.4WDSiO<sub>2</sub>, and it was used to study the effect of other parameters on the catalyst activity.

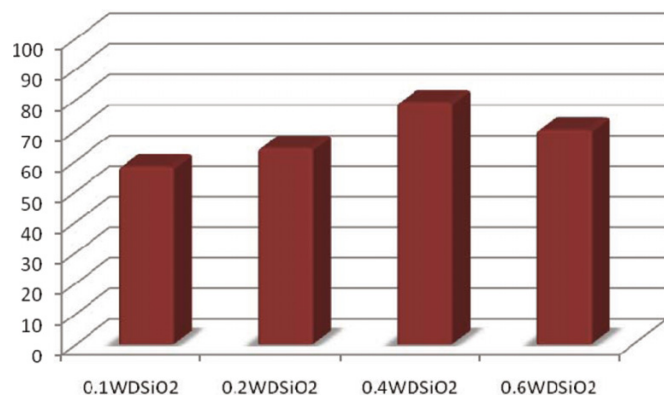
**Effect of the amount of catalyst**

The effect of different amounts of catalyst on the product yield (%) was studied. The catalytic activity of bulk WD was evaluated under no solvent reaction conditions at 80 °C. On the other hand, 0.4WDSiO<sub>2</sub> was evaluated under solvent conditions of 110 °C in

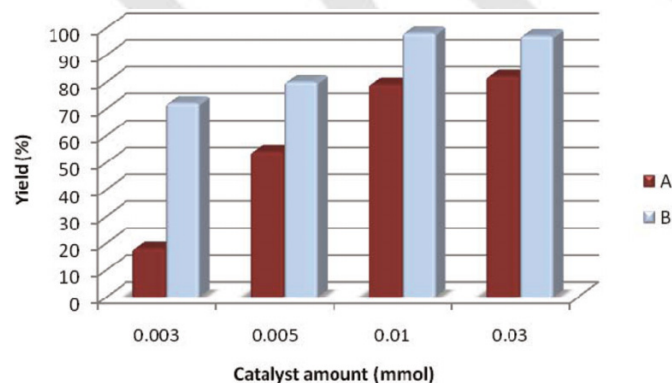
**Fig. 1.** The effect of temperature on methyl  $\beta$ -aminocrotonate yield with toluene and under no solvent reaction conditions. Method A reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; bulk WD, 1 mmol %; toluene, 3 mL; reaction time: 120 min. Method B reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; bulk WD, 1 mmol %; without reaction solvent; reaction time: 15 min. WD,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ .



**Fig. 2.** The effect of silica-supported catalyst on methyl  $\beta$ -aminocrotonate yield. Reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; supported WD, 1 mmol % “active phase”; temperature, 110 °C; toluene, 3 mL; reaction time: 120 min. WD,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ .



**Fig. 3.** The effect of the amount of active phase catalyst on methyl  $\beta$ -aminocrotonate yield. Method A reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; 0.4WDSiO<sub>2</sub> “active phase”, 1 mmol %; temperature, 110 °C; toluene, 3 mL; reaction time: 120 min. Method B reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; bulk WD, 1 mmol %; temperature, 80 °C; without reaction solvent; reaction time: 15 min. WD,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ .



toluene. The results are shown in Fig. 3. For supported catalysts the difference between 1 and 3 mmol % of 0.4WDSiO<sub>2</sub> is less than 5% and, in the case of using no reaction solvent, there is no difference between 1 and 3 mmol % of the bulk catalyst.

**Table 1.** Effect of the molar ratio of substrates on methyl  $\beta$ -aminocrotonate yield.

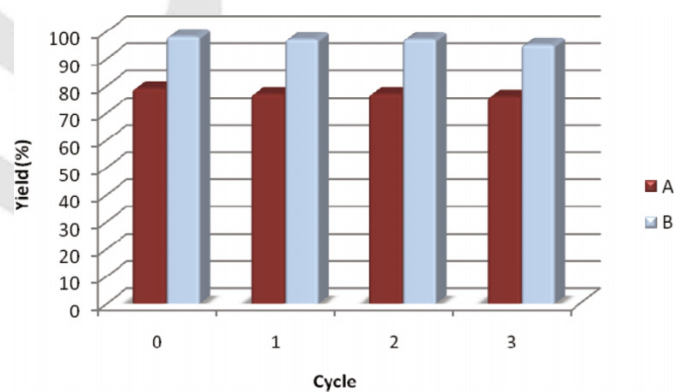
Entry	Molar ratio <sup>a</sup>	Yield (%) <sup>b</sup>
1	1:3	84
2	1:1.5	82
3	1:0.1	79
4	1.5:1	79
5	3:1	81

**Note:** Reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; 0.4WDSiO<sub>2</sub> “active phase”, 1 mmol %; temperature, 110 °C; toluene, 3 mL; reaction time: 120 min. WD,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ .

<sup>a</sup>Aniline : methyl acetoacetate.

<sup>b</sup>Isolated yield.

**Fig. 4.** Catalyst reuse on methyl  $\beta$ -aminocrotonate synthesis. Method A reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; 0.4WDSiO<sub>2</sub> “active phase”, 1 mmol %; temperature, 110 °C; toluene, 3 mL; reaction time: 120 min. Method B reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; bulk WD, 1 mmol %; temperature, 80 °C; without reaction solvent; reaction time: 15 min. WD,  $H_6P_2W_{18}O_{62} \cdot 24H_2O$ .



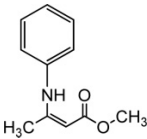
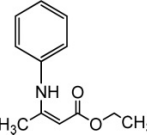
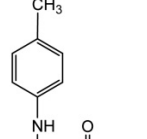
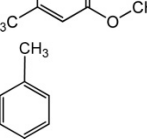
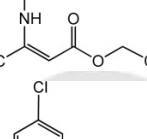
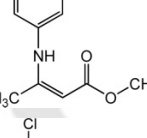
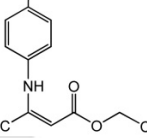
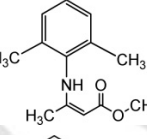
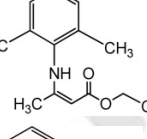
#### Effect of the molar ratio of substrates

To optimize the molar ratio between starting materials, this relationship was evaluated with toluene and 0.4WDSiO<sub>2</sub> at 110 °C. In general, the attained yields employing different molar ratios of substrates were very similar. Therefore, a molar ratio of 1:1 (Table 1, entry 3) is appropriate for the synthesis of  $\beta$ -aminocrotonates.

#### Recycling of the catalyst

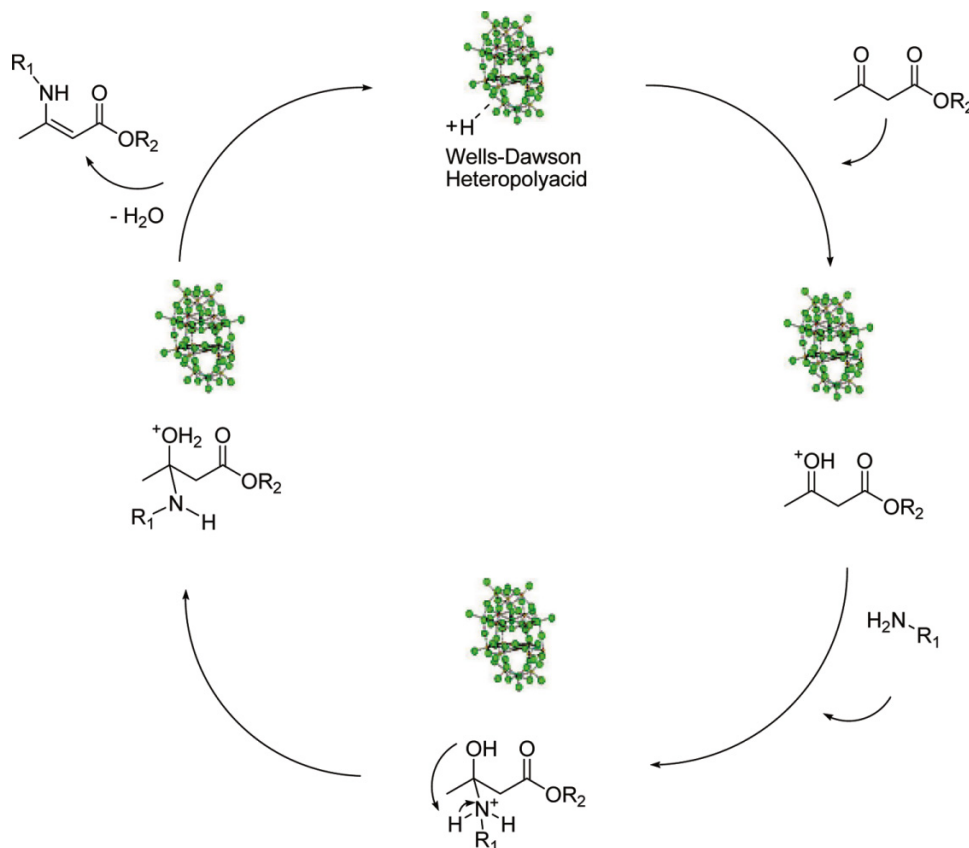
Recycling of bulk WD and 0.4WDSiO<sub>2</sub> was studied under two conditions: using toluene as the reaction solvent and using no reaction solvent. After the completion of each reaction, the cata-

**Table 2.** Synthesis of methyl and ethyl  $\beta$ -aminocrotonates.

Entry	Aniline	Acetoacetate	Product	Method A			Method B		
				Time (min)	Yield (%) <sup>a</sup>	PMI	Time (min)	Yield (%) <sup>a</sup>	PMI
1	Aniline	Methyl		120	79	19.8	15	98	12.99
2		Ethyl		120	77	19.05	15	93	12.77
3	4-Methylaniline	Methyl		120	81	18.13	210	60	19.84
4		Ethyl		120	79	17.46	—	—	—
5	4-Chloroaniline	Methyl		—	—	—	180	70	15.57
6		Ethyl		180	82	15.51	—	—	—
7	2,6-Dimethylaniline	Methyl		240	76	18.19	15	93	12.06
8		Ethyl		240	75	17.31	—	—	—
9	2-Naphthylamine	Methyl		120	84	15.05	15	95	10.83

**Note:** Method A reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; 0.4WDSiO<sub>2</sub> "active phase", 1 mmol %; temperature, 110 °C; toluene, 3 mL. Method B reaction conditions: aniline, 1 mmol; methyl acetoacetate, 1 mmol; bulk WD, 1 mmol %; temperature, 80 °C; without reaction solvent. PMI, process mass intensity; WD, H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·24H<sub>2</sub>O.

<sup>a</sup>Isolated yield.

**Scheme 2.** Plausible mechanism for the synthesis of  $\beta$ -aminocrotonates using Wells–Dawson heteropolyacid.

lyst was recovered and reused three times. As is shown in Fig. 4, the catalysts maintain their activity under both methods.

#### Preparation of $\beta$ -aminocrotonates

Finally, the reaction was extended to various amines and  $\beta$ -dicarbonyl compounds as substrates by using the catalytic amount (1 mmol %) of bulk WD and 0.4WDSiO<sub>2</sub> as active catalysts. Bulk WD was used without reaction solvent at 80 °C, and 0.4WDSiO<sub>2</sub> was used in toluene at 110 °C. The molar ratio between reactants was 1:1. The results are summarized in Table 2. In both cases, the desired products were obtained with high selectivity, almost free of secondary products. Although both methods showed rate enhancements, high yields, and relatively short reaction times, bulk WD under no solvent reaction conditions appears to be more convenient. To quantify how much “greener” one method is than the other one, the process mass intensity (PMI) was calculated for each reaction product, for both methods. Results presented in Table 2 advertise that method B is greener than method A.

The probable mechanism for the synthesis of  $\beta$ -aminocrotonates has been described in refs. 30 and 31. A general mechanism has been proposed for the synthesis of  $\beta$ -aminocrotonates using WD as the catalyst (Scheme 2). The nucleophilic attack of substituted aniline to the  $\beta$ -dicarbonyl compound is catalyzed by acidic sites; this addition is followed by elimination of water and further regeneration of protons. In our case, the acidic sites are provided by the WD HPA.

#### Conclusion

Wells–Dawson heteropolyacids have been found to be selective, active, and recyclable catalysts for  $\beta$ -aminocrotonates preparation. For comparative purposes, the reaction was carried out in different reaction media: with toluene as the solvent and under no solvent reaction conditions. In most of the cases, conditions

without reaction solvent reduced reaction times and increased yields. Also, the method without a reaction solvent uses less energy than the method with toluene as the solvent. It is possible to say that method B is greener than method A, and it is easily demonstrated by their PMI values.

In recent experiments, it was found that it is possible to synthesize more sophisticated molecules, such as nonsymmetrical 1,4-dihydropyridines, from  $\beta$ -aminocrotonates with good yields and in short reaction times.

#### Supplementary data

Supplementary data are available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2012-0157>.

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