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## Solvent-free and room temperature synthesis of thiochromans in the presence of a catalytic amount of tungstophosphoric acid

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Abstract—Tungstophosphoric acid catalyzed rapid and good yielding reactions of  $\alpha,\beta$ -unsaturated aldehydes with arenethiols to give the corresponding 4-thioaryl-1,2,3,4-tetrahydro-1-benzothiopyrans (thiochromans) under solvent-free and room temperature conditions.

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Heteropoly acids (HPAs) have been extensively studied as acid and oxidation catalysts for many reactions and have found industrial application in several processes.<sup>1</sup> These catalysts are very important for industries associated with fine chemicals, flavours, pharmaceuticals and foods<sup>2</sup> and are also used as industrial catalysts for several liquid-phase reactions,<sup>3–6</sup> such as alcohol dehydration,<sup>7</sup> alkylation<sup>8</sup> and esterification reactions.<sup>9</sup> Polyoxometallates have found use in the field of homogeneous and heterogeneous catalysis and also in the fields of medicine, photochemistry, materials and microdevice technology.<sup>10,11</sup> Heteropoly compounds are green catalysts<sup>12</sup> that function in a variety of reaction fields and are efficient bifunctional catalysts, harmless to the environment with respect to corrosiveness, safety, quantity of waste and separability.<sup>13</sup> The Keggin-type heteropoly acids are more active and possess stronger Brønsted acidity than the usual mineral acids such as H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub><sup>14</sup> and conventional solid acids such as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>-SiO<sub>2</sub>, zeolites including HX, HY, H-ZSM-5,<sup>15,16</sup> Amberlyst-15 and Nafion-H.<sup>17</sup> Among heteropoly acids, polytungstic acids are the most widely used catalysts owing to their high acid strength, thermal stabilities, and low reducibilities.

Fused thiochromans are interesting and useful synthetic intermediates because of their strong activity towards

many kinds of reagents; the thiochroman ring system is also found in many naturally occurring biologically active compounds.<sup>18</sup> The thio-Claisen rearrangement and its modified version represent highly effective and general methods for the synthesis of intermolecular cycloaddition products from  $\alpha,\beta$ -unsaturated compounds. A number of methods for the preparation of thiochromans have been reported.<sup>19</sup> Recently, a method for selective ring formation through intermolecular cycloaddition of  $\alpha,\beta$ -unsaturated aldehydes with arenethiols in the presence of *p*-TsOH carried out at 80 °C for 3 h in anhydrous dichloroethane was reported.<sup>20</sup> The synthetic utility of these methods may, however, be considerably limited because of the use of corrosive protic acids or expensive Lewis acids, high temperatures, prolonged reaction times, multi-step reactions, etc.

Here, we report an improved, effective and rapid method for the intermolecular cycloaddition of  $\alpha$ , $\beta$ -unsaturated aldehydes and arenethiols to yield thiochromans using a catalytic amount of tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) in good yields under solvent-free and room temperature conditions (Scheme 1).



Scheme 1.

Keywords: Thiochroman;  $\alpha,\beta$ -Unsaturated aldehyde; Arenethiol; Tungstophosphoric acid; Intermolecular cycloaddition.

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Table 1. Reaction of  $\alpha,\beta$ -unsaturated aldehydes with arenethiols in the presence of catalytic amounts of  $H_3PW_{12}O_{40}$ 

Entry	Aldehyde	Ar–SH	Time (min)	Product	Yield (%) <sup>a</sup>
1	СНО	C <sub>6</sub> H <sub>5</sub>	10	SPh	76 <sup>b</sup>
2	СНО	p-MeC <sub>6</sub> H <sub>4</sub>	10	Me SAr	64 <sup>b</sup>
3	СНО	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	15	Br SAr	67 <sup>b</sup>
4	СНО	$\beta\text{-}C_{10}H_7$	15	SAr SAr	72 <sup>b</sup>
5	CHO Ph	C <sub>6</sub> H <sub>5</sub>	10	SPh	66 <sup>c</sup>
6	CHO Ph	p-MeC <sub>6</sub> H <sub>4</sub>	10	Me SAr Ph	59 <sup>b</sup>
7	CHO Ph	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	15	Br SAr	64 <sup>°</sup>
8	CHO Ph	$\beta\text{-}C_{10}H_7$	15	SAr Ph	61°

<sup>a</sup> Yields refer to isolated pure products. The products were characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data.

<sup>b</sup> Isolated by preparative thin layer chromatography.

<sup>c</sup> Isolated by recrystallization.

This reaction in the absence of tungstophosphoric acid did not proceed, but in the presence of tungstophosphoric acid (0.01 mmol, optimized), this conversion proceeded efficiently to yield the corresponding thiochromans. Tungstophosphoric acid can be recovered and reused easily, by extraction with Et<sub>2</sub>O from aqueous solution of acids and dried and dehydrated by heating at 150–130 °C under vacuum for 1–2 h, without structural degradation.<sup>21</sup> The catalyst can be prepared according to the published procedure.<sup>22</sup> Reactions carried out under solvent-free conditions have received immense popularity in recent years.<sup>23</sup> The mild reaction conditions, short reaction times, occasional enhanced selectivity and clean products are salutary features of this approach. Representative examples are given in Table 1.

The results revealed that crotonaldehyde is more efficient than cinnamaldehyde, due to electron delocalization in the benzene ring of the latter. Naphthalene derivatives also undergo the reaction. Although the details of the mechanism still remain ambiguous, the reaction may proceed through allylic cationic intermediates generated in situ.

In conclusion, the present method is a very simple, one-pot reaction, which is carried out at ambient temperature under mild and solventless conditions using tungstophosphoric acid as an effective, heterogeneous, readily available and low cost catalyst. This method is a green protocol for the synthesis of thiochromans.

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- 23. General reaction procedure: The  $\alpha,\beta$ -unsaturated aldehyde (1 mmol), thiophenol (2.5 mmol) and  $H_3PW_{12}O_{40}$ (0.01 mmol, 0.028 g) were mixed together and stirred at room temperature for 10-15 min. The reaction was monitored by TLC. NaOH (20%, 5 ml) was then added and the crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub>  $(3 \times 25 \text{ ml})$ . The organic phase was dried over MgSO<sub>4</sub> and then purified by preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate ratio was 5:1) or recrystallization from *n*-hexane or ethyl acetate. The products were characterized by IR, <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, TMS) and <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, TMS) spectroscopy. Selected spectral data: Entry 5  $(C_{21}H_{18}S_2)$ : <sup>1</sup>H NMR;  $\delta$  (ppm): 3.54 (d, J = 7.3 Hz, 1H), 5.19 (d, J = 9.3 Hz, 1H), 6.22 (dd, J = 1.8, 8.7 Hz, 1H), 6.39 (dd, J = 1.9, 8.9 Hz, 1H), 7.31–7.75 (m, 14H), <sup>13</sup>C NMR; δ (ppm): 31.42, 57.00, 59.09, 127.05–136.58; Entry 7 (C<sub>21</sub>H<sub>16</sub>S<sub>2</sub>Br<sub>2</sub>): <sup>1</sup>H NMR;  $\delta$  (ppm): 4.98 (d, J = 7.0 Hz, 1H), 6.18 (d, J = 9.2 Hz, 1H), 6.41 (dd, J = 1.7, 8.5 Hz, 1H), 6.89 (dd, J = 1.6, 8.5 Hz, 1H), 7.21–7.79 (m, 12H), <sup>13</sup>C NMR;  $\delta$  (ppm): 31.38, 57.03, 59.06, 123.08–139.04; Entry 8 ( $C_{29}H_{22}S_2$ ): <sup>1</sup>H NMR;  $\delta$  (ppm): 5.12 (d, J = 7.3 Hz, 1H), 5.73 (d, J = 9.4 Hz, 1H), 6.21 (dd, J = 2.1, 9.9 Hz, 1H), 6.78 (dd, J = 2.2, 9.9 Hz, 1H), 7.87–8.48 (m, 18H), <sup>13</sup>C NMR;  $\delta$  (ppm): 31.39, 51.63, 56.84, 126.32-133.00.