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## Communications

### $K_5CoW_{12}O_{40} \cdot 3H_2O$ as a New and Efficient Catalyst for Preparation of Mandelates

Ezzat Rafiee, Shahram Tangestaninejad,\* Mohammad H. Habibi, and Valiollah Mirkhani

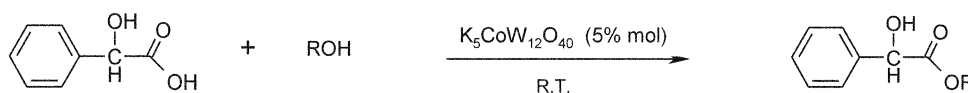
Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

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The synthesis of mandelates is very important in organic chemistry. They are used in artificial flavorings and perfumes. They are also employed as precursors for synthesis of a number of medicines and pesticides. The repellent effect against mosquitoes of certain esters (methyl, ethyl, isopropyl, butyl, isobutyl and hexyl) of *dl*-mandelic acid has been reported by Morton and co-workers.<sup>1</sup> Piper<sup>2</sup> in reporting results of entomological tests in Canada, rated ethyl mandelate as one of the best repellents against mosquitoes and black flies.

There are a few methods for preparation of mandelates in literature. Sulfuric acid,<sup>3</sup> 2,2-dimethoxypropane and sulfuric acid,<sup>4</sup> thionyl chloride,<sup>5</sup> ferric sulfate,<sup>6</sup> sodium hydrogen carbonate<sup>7</sup> and  $TiO_2/SO_4^{2-}$ <sup>8</sup> have been used as catalysts in direct esterification of mandelic acid with alcohols. However, some of these procedures are not entirely satisfactory and suffer from one or more of the following drawbacks such as corrosivity of the strong acids, tedious work up, low yields, long reaction times and side reactions such as carbonization, oxidation, etherification,



Scheme 1

Table 1. Esterification of Mandelic Acid with Alcohols Catalysed by  $K_5CoW_{12}O_{40} \cdot 3H_2O$

Entry	ROH	Temp. (°C)	Time (h)	Yield (%) <sup>a</sup>	M.P (°C)		IR (cm <sup>-1</sup> )
					Found	Reported	
1	CH <sub>3</sub> OH	Reflux	0.75	95	57-58	58 <sup>11</sup>	3445, 1741
2	C <sub>2</sub> H <sub>5</sub> OH	Reflux	1.5	95	35-36	37 <sup>11</sup>	3442, 1734
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	80	2.5	94	26-27	28 <sup>6</sup>	3440, 1735
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	80	3.5	95	Oil	Oil <sup>6</sup>	3477, 1730
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> OH	80	4	100	Oil	Oil <sup>11</sup>	3458, 1724
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> OH	80	4	85	Oil	Oil <sup>6</sup>	3480, 1730
7	Cyclohexanol	80	4	80	50-51	49-50 <sup>6</sup>	3494, 1723
8	PhCH <sub>2</sub> OH	80	1	95	92-93	93 <sup>11</sup>	3444, 1741, 1727

<sup>a</sup>Isolated yield.

\*Corresponding Author. e-mail: Tel: +98-311-7932705; Fax: +98-311-6689732; e-mail: e.rafiie@sci.ui.ac.ir

etc. As a result, there is still a need for new, mild, convenient and universally applicable methods for synthesis of mandelates.

Polyoxometalates have been proven to be good catalysts in various chemical transformations. Several features make them economically and environmentally attractive.<sup>9,10</sup> We now wish to report on  $K_5CoW_{12}O_{40} \cdot 3H_2O$ <sup>10c</sup> as an excellent and effective catalyst for direct esterification of mandelic acid (Scheme 1).

The catalytic esterification of mandelic acid (1.0 mmol) with several alcohols (5 mL) in the presence of catalytic amount of  $K_5CoW_{12}O_{40} \cdot 3H_2O$  (0.025 mmol) was performed in refluxing Solvent (Table 1, entries 1, 2) or at 80 °C (Table 1, entries 3-8), which produced the corresponding mandelates in good to excellent yields (Table 1).

We found that cobalt polyoxometalate,  $K_5CoW_{12}O_{40} \cdot 3H_2O$ , can be reused four times without a considerable loss of activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing.

In conclusion, our protocol provides a simple and effective method for esterification of mandelic acid without producing side products. In addition, recovery and industrial applicability, cheap and easy preparation of the catalyst, simple work up, low reaction times, high yields, non-corrosive and non-pollutive properties are worthy advantages of this procedure compared to the existing ones.

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