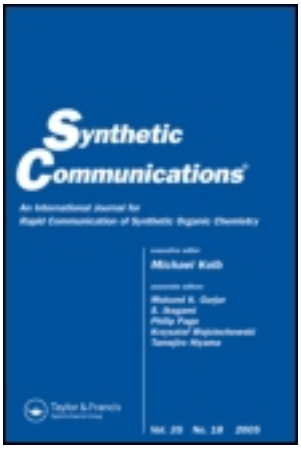

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 21 Aug 2006.

To cite this article: B. Y. Giri , B. L. A. Prabhavathi Devi , K. N. Gangadhar , K. Narasimha Rao , N. Lingaiah , P. S. Sai Prasad & R. B. N. Prasad (2006) Selective Esterification of Aliphatic Carboxylic Acids in the Presence of Aromatic Carboxylic Acids Over Monoammonium Salt of 12-Tungstophosphoric Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:1, 7-11, DOI: 10.1080/00397910500328266

To link to this article: http://dx.doi.org/10.1080/00397910500328266

Synthetic Communications®, 36: 7–11, 2006

ISSN 0039-7911 print/1532-2432 online
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Abstract: Monoammonium salt of 12-tungstophosphoric acid [$(NH_4)H_2PW_{12}O_{40}$] was found to be a practical and useful heterogeneous catalyst for an efficient and selective esterification of aliphatic carboxylic acids with alcohols in the presence of aromatic carboxylic acids. The heteropoly acid–based heterogeneous catalyst has the advantages of a simple workup procedure, water insolubility, and good activity.

Keywords: Alcohol, ammonium salt of 12-tungstophosphoric acid, carboxylic acid, esterification, heterogeneous catalyst

Received in India July 7, 2005
IICT Communication No. 040417.
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INTRODUCTION

The selective esterification of aliphatic carboxylic acid, either alone or in the presence of aromatic carboxylic acid, is a very useful synthetic reaction. Different methods are reported[1] for the selective esterification of aliphatic carboxylic acids; however, most of these methods are associated with several drawbacks such as complex, expensive, and hazardous reagents. Because there is high demand for environmentally clean processes, the chemical industry is forced to look for alternative materials that are safer. In this context, there are a few reports on the usage of nonhazardous catalytic systems such as $NiCl_6 \cdot 6H_2O$,[2] $NaHSO_4 \cdot SiO_2$[3] and Fe^{3+}-K10 montmorillonite clay,[4] which offer selective esterification of aliphatic carboxylic acids.

The acidity of heteropoly acid varies with its structure; however, the acid strength can be tuned to suit a particular demand by introducing the heteroatom. Generally heteropoly acids are very soluble in polar solvents; however, transformation into their insoluble salts can be achieved, which can then be used as heterogeneous catalysts. Various 12-tungtophosphoric acids[5] were utilized for the acetylation, esterification, and etherification reactions without much selectivity. In an attempt to prepare heterogeneous catalysts, fully and partially proton-exchanged ammonium salt of 12-tungstophosphoric acid catalysts [$(NH_4)_3PW_{12}O_{40}$ and $(NH_4)H_2PW_{12}O_{40}$] were prepared and studied for their esterification activity.[6]

RESULTS AND DISCUSSION

The present study reports the first application of a heteropoly acid catalyst (i.e., monoammonium salt of 12-tungstophosphoric acid) as an efficient catalyst for the selective esterification of aliphatic carboxylic acids (Scheme 1).

Esterification of hexanoic, heptanoic, nonoic, and palmitic acids with methanol, ethanol, and isopropanol gave the corresponding esters in good yields (92–97%) in a 6-h period. Prolonged reaction time (12 h) could improve the yields almost quantitatively. The unsaturated (entries 7 and 8, Table 1) and other functional groups such as Cl and NO_2 (entries 11 and 12, Table 1) were tolerated during the esterification. Similarly, esterification of phenyl acetic acid with methanol, ethanol, and benzyl alcohol afforded corresponding esters, whereas no reaction was observed with benzoic acid and

$$RCOOH + R^1OH \xrightarrow[\text{Reflux}]{(NH_4)H_2PW_{12}O_{40}} RCOOR^1 + H_2O$$

Scheme 1.

Table 1. Esterification of aliphatic and aromatic carboxylic acids with alcohols[a]

Entry	Carboxylic acid	Product	Time (h)	Yield (%)[b]	
				Aliphatic carboxylic ester	Aromatic carboxylic esters
1	CH_3-$(CH_2)_5$-COOH	CH_3-$(CH_2)_5$-$COOCH_3$	6	96 (99)[c]	—
2	CH_3-$(CH_2)_5$-COOH	CH_3-$(CH_2)_5$-$COOC_2H_5$	6	95 (98)	—
3	CH_3-$(CH_2)_7$-COOH	CH_3-$(CH_2)_7$-$COOCH_3$	6	97 (99)	—
4	CH_3-$(CH_2)_7$-COOH	CH_3-$(CH_2)_7$-$COOC_2H_5$	6	94 (98)	—
5	CH_3-$(CH_2)_{14}$-COOH	CH_3-$(CH_2)_{14}$-$COOCH_3$	6	96 (100)	—
6	CH_3-$(CH_2)_{14}$-COOH	CH_3-$(CH_2)_{14}$-$COOC_2H_5$	6	92 (98)	—
7	CH_2═CH-$(CH_2)_8$-COOH	CH_2═CH-$(CH_2)_8$-$COOCH_3$	6	96 (100)	—
8	CH_2═CH-$(CH_2)_8$-COOH	CH_2═CH-$(CH_2)_8$-$COOC_2H_5$	6	94 (98)	—
9	C_6H_5-CH_2-COOH	C_6H_5-CH_2-$COOCH_3$	6	95 (99)	—
10	C_6H_5-CH_2-COOH	C_6H_5-CH_2-$COOC_2H_5$	6	92 (97)	—
11	4-(Cl)-C_6H_4-CH_2-COOH	4-(Cl)-C_6H_4-CH_2-$COOCH_3$	6	95 (98)	—
12	4-(Cl)-C_6H_4-CH_2-COOH	4-(Cl)-C_6H_4-CH_2-$COOC_2H_5$	6	94 (98)	—
13	CH_3-$(CH_2)_{14}$-COOH	CH_3-$(CH_2)_{14}$-$COOCH_2$ -C_6H_5	6	92 (97)	—
14	C_6H_5-CH_2-COOH	C_6H_5-CH_2-$COOCH_2$ -C_6H_5	6	93 (98)	—
15	C_6H_5-COOH	C_6H_5-$COOCH_3$	12	—	0
16	C_6H_5-COOH	C_6H_5-$COOC_2H_5$	12	—	0
17	4-(NO_2)-C_6H_4-COOH	4-(NO_2)-C_6H_4-$COOCH_3$	12	—	0
18	4-(NO_2)-C_6H_4-COOH	4-(NO_2)-C_6H_4-$COOC_2H_5$	12	—	0

[a]Reaction conditions: carboxylic acid (5 g), alcohol (10 mL), catalyst (0.25 g, 5 wt.% of the acid), reflux temperature. All the products were characterized by ^{1}H NMR and GC.

[b]Isolated yield.

[c]Figures in parenthesis are the yields after 12 h.

4-nitro benzoic acid (entries 15 and 18, Table 1). The unique selectivity of the present reaction was well demonstrated by a competition experiment (Table 2) with an equimolar mixture of aliphatic carboxylic acid and benzoic acid with methanol, ethanol, and isopropanol, which afforded only the aliphatic carboxylic esters in 98–99% yield.

In conclusion, aliphatic carboxylic esters can be prepared by a facile and selective esterification using an efficient and water-insoluble monoammonium salt of 12-tungstophosphoric acid catalyst.

EXPERIMENTAL

General Procedure for the Preparation of the Catalyst

Monoammonium salt of 12-tungstophosphoric acid was prepared[6] by simple ion exchange of 12-tungstophosphoric acid with a required amount of ammonium carbonate in aqueous medium. Ammonium carbonate solution (0.167 g, 0.0017 mol, dissolved in 10 mL of distilled water) was added dropwise to an aqueous solution of 12-tungstophosphoric acid (10 g, 0.0035 mol, dissolved in 50 mL of distilled water) at 80°C under stirring. The reaction mixture was stirred at 80°C for 3 h, evaporated to dryness, and kept overnight at 120°C. The catalyst was calcined in air at 350°C for 4 h.

General Procedure for Esterification

A mixture of carboxylic acid (5 g), alcohol (10 mL), and the monoammonium salt of 12-tungstophosphoric acid catalyst (5 wt.% of the acid, 250 mg) were

Table 2. Esterification of aliphatic carboxylic acids in presence of aromatic carboxylic acids

			Yield (%)[a]	
Entry	Carboxylic acid	Alcohol	Aliphatic carboxylic ester	Aromatic carboxylic esters
1	C_6H_5-CH_2-COOH and C_6H_5-COOH	CH_3-OH	99	0
2	4-(Cl)-C_6H_4-CH_2-COOH and C_6H_5-COOH	CH_3-OH	98	0
3	C_6H_5-CH_2-COOH and 4-(NO_2)-C_6H_4-COOH	CH_3-CH_2-OH	98	0

[a]Isolated yield after 12 h.

refluxed, filtered, and concentrated. The residue was purified over silica gel to get pure ester. All the products were known compounds and were easily identified by comparison of their spectral data with those of authentic samples.

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