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Solvent-free Friedel–Crafts acylation of aromatic compounds with carboxylic acids in the presence of trifluoroacetic anhydride and aluminum dodecatungstophosphate

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This article is dedicated to Professor Michael P. Cava on the occasion of his 75th birthday.

Abstract—The stable and non-hygroscopic aluminum dodecatungstophosphate (AlPW₁₂O₄₀), was found to be an effective catalyst (3 mol%) for the solvent-free Friedel–Crafts acylation of aromatic compounds with carboxylic acids in the presence of trifluoroacetic anhydride under mild reaction conditions. © 2003 Elsevier Science Ltd. All rights reserved.

Heteropolyacids (HPAs) show very high catalytic activities for acid-catalyzed reactions and have been used for the hydration of propylene¹ and isobutylene² and the polymerization of tetrahydrofuran.³ Both the strong Brønsted acidity⁴ and the softness of the heteropoly anion are responsible for such high catalytic activities.⁵ HPAs are usually insoluble in non-polar but readily soluble in polar solvents. The poor solubility of HPAs in reaction products improves product selectivity and also allows easy separation of the reactant and the product.^{3a}

Friedel-Crafts acylation of aromatic compounds is the most important and practical route for the synthesis of aromatic ketones that are used in manufacturing fine and speciality chemicals as well as pharmaceuticals.⁶ For the synthesis of aromatic ketones by Friedel-Crafts acylation reactions the acylating agents are mostly acid anhydrides or toxic acid chlorides. In the classical procedures the most familiar Lewis acid; AlCl₃ is used as a promoter which requires more than 1 equiv. of the Lewis acid due to its complexation with the aryl ketone produced in the reaction mixture. In addition, AlCl₃ is unstable in aqueous media and cannot be recovered from the reaction mixture.^{6c} In order to minimize such problems new catalytic reactions have been reported in the literature.⁷ A literature survey shows that carboxylic acids are scarcely used for Friedel-Crafts acylations.8

In continuation of our work on the catalytic properties of heteropolyacids⁹ herein, we report the use of aluminum dodecatungstophosphate (AlPW₁₂O₄₀) as a stable and effective heterogeneous catalyst (3 mol%) for the efficient acylation of aromatic compounds using carboxylic acids in the presence of trifluoroacetic anhydride (TFAA) under mild reaction conditions in the absence of solvent (Scheme 1).

The catalyst, $AIW_{12}O_{40}$ was prepared by a known procedure involving addition of aluminum nitrate¹⁰ to an aqueous solution of tungstophosphoric acid which on complete evaporation of water gave the desired compound as a white powder in quantitative yield with satisfactory analytical results. We have also used aluminum carbonate for the preparation of $AIPW_{12}O_{40}$ without any problem.

The results of the acylation reactions are presented in Table 1. Acylation of anisole was conducted by acetic or benzoic acid in the presence of trifluoroacetic anhydride catalyzed by $AlPW_{12}O_{40}$ (3 mol%) in excellent yields (Table 1, entries 1 and 2). 2-Methyl and 4-methyl anisoles were also acylated with these acids under similar reaction conditions to give the desired ketones in excellent yields (Table 1, entries 3–6).



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Scheme 1.

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Table 1. Acylation of aromatic compounds with carboxylic acids catalyzed by $AIPW_{12}O_{40}$ in the presence of trifluoroacetic anhydride

Entry	ArH	RCO ₂ H	Product	Time (h)	Yield (%) ^a
1 2	ОМе	R= Me R= Ph		0.25 2.5	94 ⁶ 96
3 4	——————————————————————————————————————	R=Me R Ph		2 3.75	97 91
5 6	<i>С</i> ОМе	R=Me R=Ph		0.12 0.75	96 90
7 8		R=Me R=Ph		0.67 3.5	93 91
9 10	OMe	R=Me R=Ph	O O O Me	2.5 8	98 88
11 12		R=Me R=Ph		2.5 8.5	78° 69°
13 14		R=Me R=Ph	R	1.25 2.5	94 ^d 98 ^d

a) Isolated yields and the purity of the products were determined by ¹HNMR spectroscopy. b) 8% of the *ortho*- isomer was detected. c) Reactions were carried out in *n*-hexane (2mL) at 50°C. d) Reactions were carried out at 0°C with furan (2 mmol).

1,2-Diethoxybenzene under similar conditions, gave the desired acetyl and benzoyl ketones as the sole products in this reaction in 93 and 91% yields, respectively (Table 1, entries 7 and 8). We have also studied the catalytic activity of $AlPW_{12}O_{40}$ for the preparation of aryl ketones from polycyclic aromatic compounds. We found that acylation and benzoylation of 2-methoxynaphthalene was successful with excellent yields at room temperature and with high regioselectivity whereas, similar reactions of anthracene needed higher temperature (50°C) and proceeded in good yields (Table 1, entries 9–12).

In all the reactions we have studied, cleavage of the O-R bond was not observed, which is usually detected using other methods.^{8a}

Furan is sensitive to acidic media and polymerizes easily under Friedel–Crafts conditions. We observed that the reaction of furan proceeded with acetic or benzoic acid in excellent yields using a catalytic amount (3 mol%) of AlPW₁₂O₄₀ in the presence of TFAA (Table 1, entries 13 and 14). Formation of polymeric materials was not observed in this reaction.

In conclusion, we have demonstrated that $AlPW_{12}O_{40}$ is a cheap, easily available, non-hygroscopic and water stable compound which can be used as an effective catalyst for the efficient preparation of aromatic ketones via Friedel–Crafts acylation reactions of aliphatic and aromatic carboxylic acids in the presence of trifluoroacetic anhydride.

In a typical procedure anisole (2 mmol, 0.216 g), benzoic acid (2 mmol, 0.244 g), trifluoroacetic anhydride (2.8 mmol, 0.39 mL) and $AlPW_{12}O_{40}$ (0.03 mmol, 0.174 g) were stirred using a magnetic stirrer at room temperature for 2.5 h (Table 1, entry 3). After completion of the reaction (monitored by TLC and GC), Et₂O (10 mL) was added to the reaction mixture and the solid material was separated by filtration. The filter cake was washed with Et₂O (2×5 mL) and the filtrates were combined and washed with saturated sodium bicarbonate solution (20 mL). The resulting ethereal solution was separated and dried over anhydrous Na₂SO₄. Evaporation of the solvent resulted in a highly pure product.

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