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Aluminum dodecatungstophosphate ($AlPW_{12}O_{40}$) as a non-hygroscopic Lewis acid catalyst for the efficient Friedel–Crafts acylation of aromatic compounds under solvent-less conditions

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Abstract—Stable and non-hygroscopic aluminum dodecatungstophosphate ($AlPW_{12}O_{40}$), which is prepared easily from cheap and commercially available compounds was found to be an effective catalyst for Friedel–Crafts acylation reactions using carboxylic acids, acetic anhydride and benzoyl chloride in the absence of solvent under mild reaction conditions.

1. Introduction

Heteropolyacids (HPAs) show very high catalytic activity for some acid-catalyzed reactions. They have been used for hydration of alkenes[1–3] and polymerization of tetrahydrofuran.[4–6] Strong Brønsted acidity[7,8] and the softness of the heteropoly anions are responsible for their high catalytic activities in these reactions.[9] HPAs are usually solids that are insoluble in non-polar solvents but highly soluble in polar ones. The use of HPAs in non-polar solvents improves product selectivity and also provides easy separation of them.[4] Heterogeneous catalysis has become attractive in view of the increasingly strict environmental legislation, in view of their isolation and separation from the reaction media. Solid acid catalysts are harmless to the environment with respect to corrosiveness, safety, quantity of waste, and separability with certainly some exceptions.

Cesium salts of HPAs are good examples of active and useful solid acid catalysts. They exhibit an excellent performance in several organic reactions owing to their high surface acidity and also probably to their unique basicity.[10,11] The catalytic activities of solid acids are usually suppressed significantly in the presence of water. Hence, although H-ZSM-5 has a high Si:Al ratio is known to have fair tolerance in aqueous solutions.[12] It has been demonstrated that the acidic cesium salts of HPAs are very water-tolerant catalysts for hydration of olefins[13] and hydrolysis of esters.[14] This nature was assigned to moderate hydrophobicity of the catalysts.[15]

We have recently started to study new catalytic applications of heteropoly acids in organic reactions.[16a–h]

Friedel–Crafts acylation of aromatic compounds is the most important and practical route for the synthesis of aromatic ketones that are used in manufacturing of fine chemicals as well as pharmaceuticals.[17] The acylating agents for the synthesis of aromatic ketones by Friedel–Crafts reactions are mostly acid anhydrides or acyl chlorides. For this purpose, varieties of catalysts have been reported.[18,19] A literature survey indicates that the use of carboxylic acids, as acylating agents, are scarcely reported.[20] Using carboxylic acids as acylating agents is a superior method with respect to the procedures utilizing acyl chlorides and anhydrides for the preparation of aryl ketones. Carboxylic acids are stable and more available compounds and their handlings are much easier than their corresponding acyl chlorides and anhydrides.

Now, we introduce aluminum dodecatungstophosphate ($AlPW_{12}O_{40}$) as a stable, non-hygroscopic, easily available, cheap and highly effective catalyst for Friedel–Crafts acylation of aromatic compounds using carboxylic acids, acetic anhydride and benzoyl chloride as acylating agents.

Keywords: Freidel–Crafts acylation; Poly oxometalate; Aluminum dodecatungstophosphate; Solvent-free.

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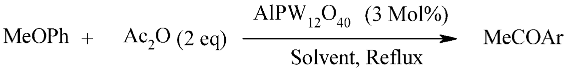
2. Results and discussion

2.1. Acylation of aromatic compounds with acetic anhydride catalyzed by $AlPW_{12}O_{40}$

The reaction of acetic anhydride and aromatic compounds by Friedel–Crafts acylation reactions is the most practical route for the synthesis of methyl aryl ketones. Investigation of the application of $AlPW_{12}O_{40}$ as an easily available, cheap and non-hygroscopic Lewis acid for this purpose is of practical importance. In order to optimize the reaction conditions, acylation of anisole with acetic anhydride in the presence of different molar ratios of $AlPW_{12}O_{40}$ and various solvents were studied (Scheme 1).

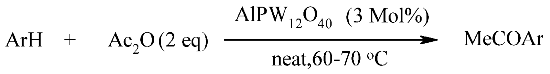


$$\text{MeOPh} + \text{Ac}_2\text{O (2 eq)} \xrightarrow[\text{Solvent, Reflux}]{\text{AlPW}_{12}\text{O}_{40}\ \text{(3 Mol\%)}} \text{MeCOAr}$$

Scheme 1.

The results of this investigation are shown in Table 1. The results indicate that the most suitable solvent for this purpose is *n*-hexane in which the catalyst reacts under completely heterogeneous conditions and the best result was obtained when no solvent was used.

The optimum ratio of the catalyst was found to be 3 mol% with respect to anisole for the reaction conducted in *n*-hexane or solvent-less conditions. The optimized molar ratio of acetic anhydride was found to be 2 mol equivalents with respect to 1 mol equivalent of anisole under similar reaction conditions (Scheme 2).



$$\text{ArH} + \text{Ac}_2\text{O (2 eq)} \xrightarrow[\text{neat,60-70 °C}]{\text{AlPW}_{12}\text{O}_{40}\ \text{(3 Mol\%)}} \text{MeCOAr}$$

Scheme 2.

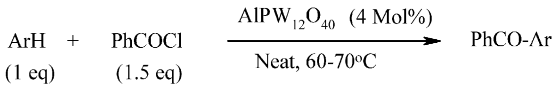
This reaction condition was applied for the preparation of different aryl ketones from electron rich aromatic compounds with success. The results of this study are tabulated in Table 2.

In order to show the efficiency and the catalytic activity of $AlPW_{12}O_{40}$ for the acylation of anisole with acetic anhydride, we have tabulated our results in Table 3 with some other recently used Lewis acids such as $Sc(OTf)_3$, $Bi(OTf)_3$ and $In(OTf)_3$.

The results show that aluminum dodecatungstophosphate is a more efficient and more effective catalyst than the triflates used for similar reaction and also does not require aqueous workup which makes the process of the isolation of the product much easier and not a time-consuming process.

2.2. Benzoylation of aromatic compounds with benzoyl chloride in the presence of $AlPW_{12}O_{40}$

We have studied optimization of the reaction conditions for the benzoylation of anisole under solvent-free conditions (Scheme 3).



$$\underset{\text{(1 eq)}}{\text{ArH}} + \underset{\text{(1.5 eq)}}{\text{PhCOCl}} \xrightarrow[\text{Neat, 60-70°C}]{\text{AlPW}_{12}\text{O}_{40}\ \text{(4 Mol\%)}} \text{PhCO-Ar}$$

Scheme 3.

It was found that the reaction was complete after 2 h by using of 4 mol% of the catalyst at 60–70 °C to produce *ortho* and *para* isomers (1:4 ratio). We applied similar reaction conditions for the preparation of other aryl ketones using different aromatic compounds. The reactions proceeded well and the desired products were isolated in excellent yields (Table 4). We have observed that the rate of acylation and benzoylation of 1,3-dimethoxy benzene was slower than anisole. Para acylation or benzoylation of anisole do not encounter that much steric resistance against the approach of bulky Lewis acid complex and acylium ions from the para position. However, in 1,3-dimethoxy benzene the situation is quiet different and the bulky complex should only approach from the ortho position of OMe groups which encounters ortho steric effects. This effect causes retardation in the rates of the reactions. Bezoylation of anthracene under solvent-free conditions was sluggish in the presence of this catalyst and gave a low yield. However, 9-benzoylanthracene was isolated in 88% yield when the reaction in *n*-hexane was heated under reflux conditions. We also applied similar reaction conditions for benzoylation of naphthalene. This reaction was not successful and a mixture of 1 and 2 substituted benzoyl naphthalenes in low yields plus unreacted starting material was isolated. Benzoylation of benzene under similar reaction conditions failed. However, this reaction was successful in a sealed tube at 120 °C overnight with 10 mol% of $AlPW_{12}O_{40}$ (97% GC yield).

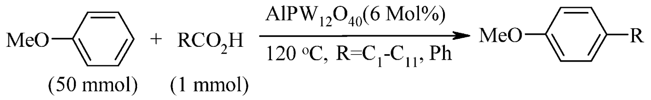
2.3. Direct acylation of anisole with carboxylic acids in the presence of $AlPW_{12}O_{40}$ as a reusable catalyst

We have also studied acylation of anisole with carboxylic acids in the presence of 6 mol% of $AlPW_{12}O_{40}$ at 120 °C (Scheme 4).

Table 1. Effect of solvents upon Friedel–Crafts acylation of anisole catalyzed by $AlPW_{12}O_{40}$

Entry	Solvent	Temp. (°C)	*T* (h)	Conv. (%)[a]
1	CH_2Cl_2	40	5	63
2	$CHCl_3$	62	3	76
3	CH_3CN	82	3	38
4	CH_3NO_2	100	4	63
5	*n*-Hexane	69	2.5	93
6	None	60	1	100

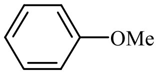
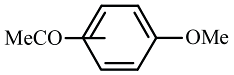
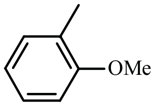
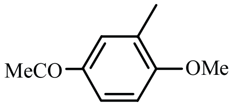
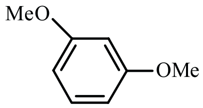
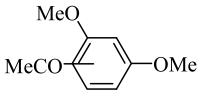
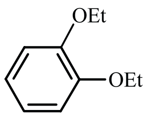
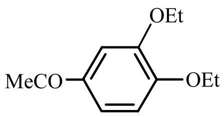
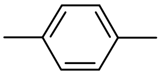
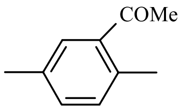
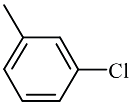
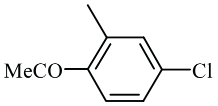
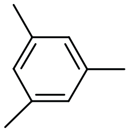
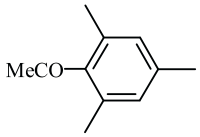
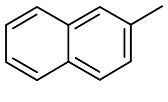
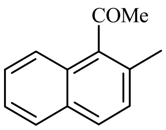
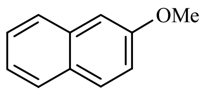
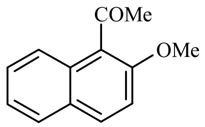
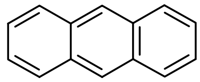
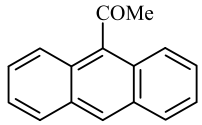
[a] Conversion was determined by GC analysis.



Scheme 4.

This acylation was carried out with different carboxylic acids (C_2–C_{12}) in good yields (Table 5). In this study, it was observed that by increasing the chain length of the carboxylic acids from C_2 to C_{12} the regioselectivity of the reactions increased and *p*-isomers were mostly produced. We have not also observed any ester formation in any of the reactions we conducted in the presence of $AlPW_{12}O_{40}$. We have found that this catalyst is reusable for these reactions and can be easily recovered from the reaction mixture by simple filtration followed by washing the mixture by *n*-hexane/EtOAc (1:1). Drying of the catalyst was performed at 120 °C under vacuum overnight. We have used the recovered catalyst for the reaction of anisole with hexanoic acid with success five times without noticeable change in its catalytic activity. In Table 6, the results are compiled in order to show the effectiveness of $AlPW_{12}O_{40}$ with respect to the recently reported catalysts $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and HZSM-5 for acylation of anisole with different carboxylic acids. The results show that $AlPW_{12}O_{40}$ promotes the reactions more effectively than the reported catalysts.

Table 2. Acylation of aromatic compounds with acetic anhydride catalyzed by $AlPW_{12}O_{40}$

Entry	ArH	Time (h)	Product	Yield[a] (%)	Ref.
1		0.75		94 (*Ortho*:*Para* = 12:88)	18p,t
2		0.25		95	18k,y
3		2		88[b]	18k
4		0.6		93	19a
5		6		91	18n
6		2.5		92[c]	18f
7		5.5		90	18l
8		4		85	18j
9		1.6		91	18i
10		2.6		90[d]	18i

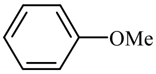
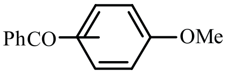
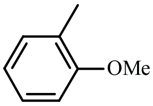
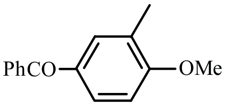
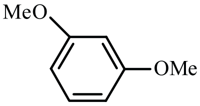
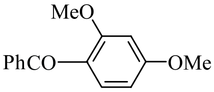
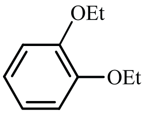
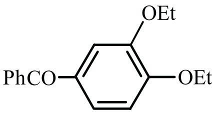
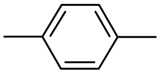
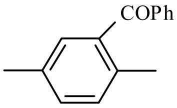
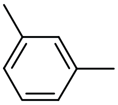
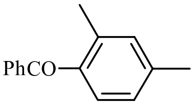
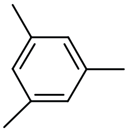
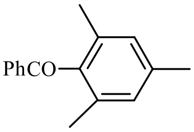
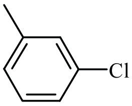
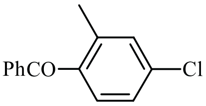
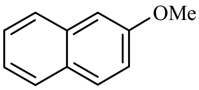
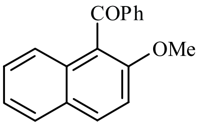
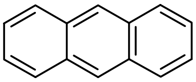
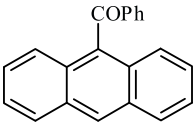
[a] Isolated yields and the purity of the products were determined by ^1H NMR spectroscopy and the ratio of the isomers was determined by GC.
[b] 2,6-Dimethoxyacetophenone was also detected in 12% yield.
[c] Other regioisomers were detected in 8%.
[d] Ac_2O (4 equiv/mol) was used.

Table 3. Comparison of the results used for the acylation of anisole with acetic anhydride catalyzed by $AlPW_{12}O_{40}$ and some other catalysts

Entry	Catalyst	Mol%	Temp. (°C)	*T* (h)	Yield (%)	Ref.
1	$Sc(OTf)_3$	20	50	18	99	18l
2	$Sc(OTf)_3$	20	50	2[a]	90	18n
3	$Bi(OTf)_3$	5	50	2	80	18p
4	$In(OTf)_3$	1	50	1[b]	96	18w
5	$AlPW_{12}O_{40}$	3	60	0.8	94	—[c]

[a] 2 equiv of $LiClO_4$ was used as an additive.
[b] 1 equiv of $LiClO_4$ was used as an additive.
[c] Results are shown in Table 2.

Table 4. Benzoylation of aromatic compounds with benzoyl chloride catalyzed by $AlPW_{12}O_{40}$

Entry	ArH	Time (h)	Product	Yield[a]	Ref.
1		2		94 (*Ortho*:*Para* = 1:4)	18p,t
2		1		97	18k
3		3.5		90[b]	18d
4		2		90	19b
5		4.5		91	18u
6		3.5		92[c]	18q,v
7		2.5		91	18q
8		3		92[d]	18f
9		1.7		94	18a
10		4		88[e]	18x

[a] Isolated yields and the purity of the products were determined by ^1H NMR spectroscopy and the ratio of the isomers was determined by GC.
[b] Formation of 2,6-dimethoxybenzophenone was detected in 10%.
[c] Formation of 2,6-dimethylbenzophenone was detected in 8%.
[d] Other regioisomers were detected in 7%.
[e] Reaction was carried out in 2 mL of *n*-hexane under reflux conditions.

Table 5. Acylation of anisole with carboxylic acids catalyzed by reusable $AlPW_{12}O_{40}$ at 120 °C[a]

Entry	Acid	Time (h)	Yield (%)[b] Ref. 20b
1	Acetic	3	85[c]
2	Propionic	3.5	88[d]
3	Butyric	5	87
4	Hexanoic	3	0[e]
5	Hexanoic	1.5	91
6	Octanoic	4	85
7	Dodecanoic	8	90
8	Benzoic	10	92

[a] The catalyst was filtered, washed with *n*-hexane: ethyl acetate, dried at 120 °C/(−20) Torr/overnight and reused.
[b] Isolated yield based on carboxylic acid conversion determined by ^1H NMR spectroscopy and GC analysis.
[c] 12% regioisomer was determined.
[d] 8% regioisomer was detected.
[e] Reaction was carried out in the presence of 1 g silica gel.

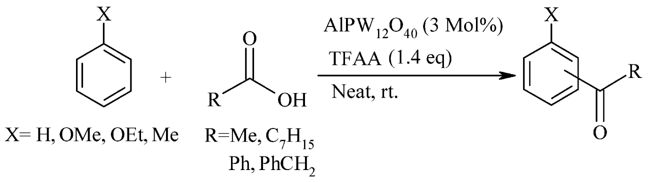
Table 6. Comparison of some of the results obtained using $AlPW_{12}O_{40}$ with some other catalysts used for acylation of anisole with carboxylic acids[a]

Acid	Cat.	Yield (%) (*para*-product)
Acetic	HZSM-5	0.025
	40%CsPW/SiO_2	62
	$AlPW_{12}O_{40}$	73
Hexanoic	HZSM-5	19.92
	40%CsPW/SiO_2	63.2
	$AlPW_{12}O_{40}$	91
Octanoic	HZSM-5	4
	40%CsPW/SiO_2	32.9
	$AlPW_{12}O_{40}$	85
Dodecanoic	HZSM-5	0
	40%CsPW/SiO_2	24.8
	$AlPW_{12}O_{40}$	91

[a] The results were extracted from Ref. 20b,c.

2.4. Acylation of aromatic compounds with carboxylic acids in the presence of trifluoroacetic anhydride catalyzed with $AlPW_{12}O_{40}$ at room temperature

In this part of our studies, we have found that with 3 mol% of $AlPW_{12}O_{40}$ in the presence of trifluoroacetic anhydride (1.4 equiv) acylation of anisole proceeded easily in 0.25 h in an excellent yield (Scheme 5).



Scheme 5.

In order to show the effect of the catalyst in this reaction, we performed acylation of anisole with acetic acid in the presence of trifluoroacetic anhydride (1.4 equiv) at room temperature in the absence of the catalyst. We have observed that the corresponding ketone was produced in 88% yield (GC) after 4 h (Table 7, entry 1) whereas the desired ketone was isolated in 94% yield after 0.25 h in the presence of the catalyst (Table 7, entry 2). We also tried the reaction of anisole with TFAA in the presence of the catalyst. We observed that the reaction did not proceed at all even after 24 h. We have found that this is a general method and can be applied easily to a wide range of liquid and crystalline carboxylic acids. Therefore, acylation of anisole was conducted with acetic acid, octanoic acid, phenyl acetic acid and benzoic acid in the presence of $AlPW_{12}O_{40}$ (3 mol%) and trifluoroacetic anhydride in excellent yields (Table 7, entries 1–5). 2-Methylanisole was also acylated with these acids in the presence of this catalyst and the anhydride in excellent yields (90–96%) with high regioselectivity (Table 7, entries 9–12). 1,2-Diethoxybenzene reacted with the above acids under similar reaction conditions to give the desired compounds as the sole products of these reactions in 91–94% yields (Table 7, entries 13–16). We also tried acylation of anthracene with acetic acid, phenyl acetic acid and benzoic acid. The reactions were slow and needed higher temperatures therefore, the reactions were performed at 50 °C and the desired ketones were isolated in 69–78% yields (Table 7 entries 17–19). The reaction of 2-methylnaphthalene with acetic acid was also conducted at 50 °C in the presence of the catalyst and trifluoroacetic anhydride. This reaction was sluggish and after prolonged reaction times the desired ketone was isolated in only 53% yield (Table 7 entry 20). The reaction of 2-methoxynaphthalene with acetic acid, octanoic acid, phenyl acetic acid and benzoic acid went smoothly at room temperature in excellent yields (Table 7, entries 21–24). Acylation of furan and pyrrole is not a straightforward reaction and usually in the presence of acid catalysts undergo polymerization reactions. We found that $AlPW_{12}O_{40}$ is a suitable catalyst for such important acylation reactions.

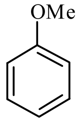
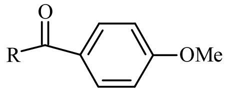
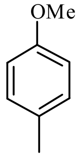
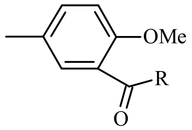
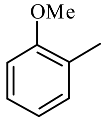
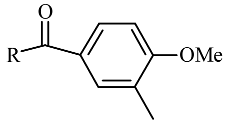
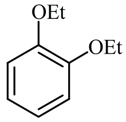
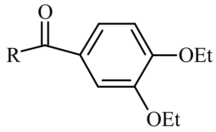
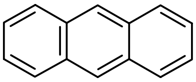
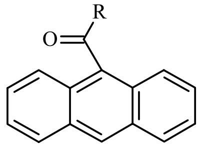
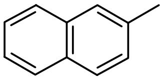
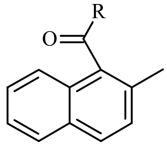
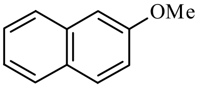
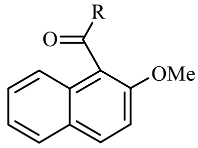
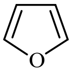
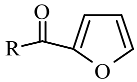
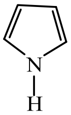
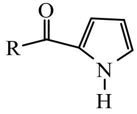
Acylation of furan with acetic acid, phenyl acetic acid and benzoic acid was conducted in the presence of TFAA and $AlPW_{12}O_{40}$ at 0 °C successfully in 94–98% isolated yield (Table 7, entries 25–27).

Acylation of pyrrole also conducted smoothly in the presence of TFAA, $AlPW_{12}O_{40}$ with acetic and benzoic acids at −23 °C. The desired pyrrole ketones were isolated in 92–98% yield (Table 7, entry 28–29). The formation of any polymeric materials was not observed in these reactions.

3. Conclusion

$AlPW_{12}O_{40}$ is a cheap, easily available, non-hygroscopic, heterogeneous, non-corrosive and environmentally benign compound. In this work it has been used as an effective catalyst for the efficient preparation of ketones via Friedel–Crafts acylation reactions with acetic anhydride, benzoyl chloride and with a range of easily available caboxylic acids in the presence of triflouroacetic anhydride. This general method can be applied easily to a wide range of liquid and crystalline carboxylic acids. The method has many advantages such as cheapness and availability of reactants and also non-aqueous and easy work-up of the reaction due to the heterogeneous conditions. The isolation of products was easily accomplished by a simple extraction and evaporation of the organic solvent.

Table 7. $AlPW_{12}O_{40}$ catalyzed acylation of aromatic compounds with compounds with carboxylic acids in the presence of trifluoroacetic anhydride

Entry	ArH	RCO_2H	Product	Time (h)	Yield (%)[a]	Ref.
1		R=Me		4	88[b,c]	18p,t
2		R=Me		0.25	94[c]	18p,t
3		R=C_7H_{15}		1.5	91	20b,d
4		R=$PhCH_2$		2	94	18w
5		R=Ph		2.5	96	18p,t
6		R=Me		2	97	18y
7		R=$PhCH_2$		2.5	90	18c
8		R=Ph		3.75	91	18k
9		R=Me		0.12	96	18y
10		R=$PhCH_2$		0.4	92	18c
11		R=C_7H_{15}		0.34	93	—
12		R=Ph		0.75	90	18k
13		R=Me		0.65	93	19a
14		R=C_7H_{15}		1.5	94	—
15		R=$PhCH_2$		2.5	91	—
16		R=Ph		3.5	91	19b
17		R=Me		2.5	78[d]	18i
18		R=$PhCH_2$		10	71[d]	18b
19		R=Ph		8.5	69[d]	18x
20		R=Me		2	53[e]	18j
21		R=Me		0.25	98	18i
22		R=C_7H_{15}		0.34	95	18m
23		R=$PhCH_2$		2	90	18m
24		R=Ph		8	88	18a
25		R=Me		1.25	94[f]	18n
26		R=$PhCH_2$		1.5	95[f]	19c
27		R=Ph		2.5	98[f]	18g
28		R=Me		0.25	92[g,h]	18h
29		R=Ph		0.4	98[g]	18h

[a] Isolated yields and the purity of the products were determined by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy and GC.
[b] Reaction was performed without using $AlPW_{12}O_{40}$.
[c] 8% of regioisomer was detected.
[d] Reaction was carried out in 2 mL *n*-hexane at 50 °C.
[e] Reaction was carried out at 50 °C.
[f] Reaction was carried out at 0 °C with 2 equiv of furan.
[g] Reaction was carried out in 2 mL *n*-hexane at −23 °C.
[h] 8% 3-acetyl pyrrole was detected by GC.

4. Experimental

4.1. General remarks

Chemicals were purchased from Fluka or Merck and $AlPW_{12}O_{40}$ was prepared from $H_3PW_{12}O_{40}$ and aluminium nitrate according to the literature method.[21] Aromatic compounds, carboxylic acids, acetic anhydride and acyl chloride were purified by distillation or recrystallization before use. The purity determination of the products was accomplished by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. The FTIR spectra were recorded on a Shimadzu model 8300 instrument. The NMR spectra were recorded on a Bruker Advance DPX 250 MHz spectrometer and in all cases $CDCl_3$ was used as a solvent and TMS as an internal standard.

4.2. Typical procedure for acylation of anisole with acetic anhydride; a

Anisole (2 mmol, 0.216 g), acetic anhydride (4 mmol, 0.408 g) and $AlPW_{12}O_{40}$ (0.06 mmol, 0.232 g) were combined, and the mixture was stirred at 60–70 °C for 45 min (Table 3). After completion of the reaction (monitored by TLC and GC), Et_2O (10 mL) and powder of sodium hydrogen carbonate (0.8 g) was added to the mixture in order to destroy the unreacted acetic anhydride. The solid phase was isolated and washed with Et_2O (2× 5 mL). Evaporation of the combined ethereal solutions afforded the almost pure product in 94% yield (0.504 g).

4.3. Typical procedure for benzoylation of anisole with benzoyl chloride

Anisole (2 mmol, 0.216 g), benzoyl chloride (3 mmol, 0.421 g) and $AlPW_{12}O_{40}$ (0.08 mmol, 0.232 g) were combined and the mixture was stirred at 60–70 °C for 2 h (Table 4, entry 1). After completion of the reaction (monitored by TLC and GC), Et_2O (10 mL) and powder of sodium hydrogen carbonate (0.8 g) was added to the reaction mixture in order to destroy the unreacted benzoyl chloride. The solid phase was recovered by filtration and was washed with Et_2O (2×5 mL). Evaporation of the combined ethereal solutions afforded the almost pure product in 94% yield (0.796 g).

4.4. General procedure for acylation of anisole with carboxylic acids

To a mixture of carboxylic acid (2 mmol) and anisole (100 mmol), $AlPW_{12}O_{40}$ (12 mol%, 0.362 g) was added and the reaction mixture was stirred at 120 °C for the appropriate reaction times (Table 5). After completion of the reaction (monitored by TLC and GC), the catalyst was filtered. The unreacted anisole was separated by vacuum distillation and the desired ketone was isolated with high purity (GC) in good yield.

4.5. General procedure for acylation of aromatic compounds using carboxylic acids and triflouroacetic anhydride (TFAA) catalyzed with $AlPW_{12}O_{40}$

Aromatic compound (2 mmol), carboxylic acid (2 mmol), trifluoroacetic anhydride (2.8 mmol, 0.39 mL) and $AlPW_{12}O_{40}$ (0.03 mmol, 0.174 g) were mixed together and stirred by a magnetic stirrer at room temperature for the appropriate reaction times (Table 7). After completion of the reaction (monitored by TLC and GC), Et_2O (10 mL) and powder of sodium hydrogen carbonate (1.2–1.5 g) was added to destroy the unreacted TFAA or carboxylic acid. The solid phase was recovered by filtration and was washed with Et_2O (2×5 mL). Evaporation of the combined ethereal solutions afforded the highly pure product.

4.6. Spectral data of the unknown ketones prepared by the presented protocol

4.6.1. Table 7 entry 11: $R=C_7H_{15}$. Colourless viscous oil, [Found: C, 77.38; H, 9.65. $C_{16}H_{24}O_2$ requires C, 77.41; H, 9.65%]. Bp (*P*/32 mmHg) = 218 °C IR (KBr) (ν C=O) = 1610, 1691 cm^{-1} δ_H (250 MHz, $CDCl_3$) 7.83–7.77 (2H, m, Ph), 6.83 (1H, d, $J=8.4$ Hz), 2.92 (t, 2H, $^2J_{HH}=12$ Hz, –$COCH_2CH_2$), 2.25 (s, 3H), 1.67 (m, 2H), 1.56 (m, 2H), 1.42 (m, 2H), 1.36 (m, 2H), 1.21 (m, 2H), 0.88 (t, 3H, $^2J_{HH}=7.5$ Hz, CH_3CH_2). ^{13}C NMR: δ (ppm) = 199.53, 161.59, 130.7, 129.72, 128.1, 126.6, 109.15, 55.4, 38.2, 31.7, 29.4, 24.7, 22.6, 16.2, 14.1. MS (20 eV): *m*/*z* (%) = 248 (M^+, 3.1), 177 (6.9), 164 (71.5), 150 (10.1), 149 (100), 91 (23.5), 41 (16.2).

4.6.2. Table 7 entry 14: $R=C_7H_{15}$. Light yellow solid, mp = 43 °C, [Found: C, 73.94; H, 9.57. $C_{18}H_{28}O_3$ requires C, 73.97; H, 9.58%] **IR** (KBr) (ν C=O) = 1677 cm^{-1}, δ_H (250 MHz, $CDCl_3$) 6.5–7.4 (m, 3H, Ph), 4.08 (q, 4H), 2.9 (t, 2H, $^2J_{HH}=12$ Hz, –$COCH_2CH_2$), 1.5 (t, 6H, $^2J_{HH}=15$ Hz, OCH_2CH_3), 1.71 (m, 2H), 1.41 (m, 2H), 1.3 (m, 2H), 1.18 (m, 2H), 0.98 (m, 2H), 0.81 (t, 3H, $^2J_{HH}=7.5$ Hz, CH_3CH_2). δ_C (63 MHz, $CDCl_3$) = 196.6, 153.2, 148.8, 144, 130.4, 122.9, 120, 115, 112.4, 64, 42, 32, 30, 23, 15, 14, MS (20 eV): *m*/*z* (%) = 292 (M^+, 10.8), 221 (8.6), 208 (100), 193 (73.2), 180 (14.8), 165 (38.4), 137 (36.3), 109 (17.5), 81 (14), 57 (16.1).

4.6.3. Table 7 entry 15: $R=PhCH_2$. Yellow solid, mp = 82 °C, [Found: C, 76.1; H, 7.02. $C_{18}H_{20}O_3$ requires C, 76.05; H, 7.04%] IR (KBr) (ν C=O) = 1700, 1596 $cm^{-1}\delta_H$ (250 MHz, $CDCl_3$) 7.34–7.2 (5H, m, Ph), 7.62 (1H, d, $J=8.37$ Hz), 7.46 (1H, s),6.86 (1H, d, $J=8.4$ Hz), 4.22 (2H, s), 4.08–4.19 (4H, m, –OCH_2CH_3), 1.5–1.41 (6H, m, OCH_2CH_3). δ_C (63 MHz, $CDCl_3$) = 196.3, 148, 144, 135.1, 131, 130, 129.3, 128, 126, 120, 114, 64.4, 45.13, 14.6. MS (20 eV): *m*/*z* (%) = 284 (M^+, 3.3), 194 (12.5), 193 (100), 165 (32.1), 137 (27.3), 109 (10.4), 91 (19.5).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2004.09.049

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