TETRABUTYLAMMONIUM HEXATUNGSTATE $[TBA]_2[W_6O_{19}]$: A NOVEL HETEROGENEOUS CATALYST FOR ONE-POT SYNTHESIS OF HANTZSCH 1,4-DIHYDROPYRIDINES IN SOLVENT-FREE CONDITIONS

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ABSTRACT

A new method for one pot synthesis of Hantzsch 1,4-dihyropyridines was achieved by the reaction of aromatic aldehydes, ethyl acetoacetate and ammonium acetate at 80 ºC in the presence of an isopoly tungstate ,tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$, as an effective and environmentally friendly catalyst. An important advantage of this catalyst is the ease of separating it from the reaction mixture, as well as the fact that it could be recycled a number of times.

Keywords: tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$, Hantzsch, 1,4-dihydropyridines, solvent-free conditions

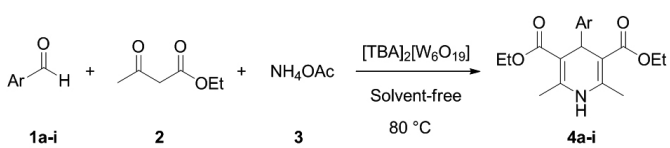
INTRODUCTION

Dihydropyridines are of importance in biological systems as a class of useful drugs, particularly as anti-oxidants. Some of the representative compounds of this class possess acaricidal, insecticidal, bactericidal and herbicidal activities [1]. Dihydropyridine drugs, namely nifedipine, nicardipine and amlodipine, are cardiovascular agents for the treatment of hypertension [2,3]. A number of dihydropyridine derivatives are employed as potential drug candidates for the treatment of congestive heart failure [4]. In human body the main metabolic route of dihydropyridine drugs involve their oxidation to pyridines catalyzed by cytochrome-450 in liver [5]. Recently, dihydropyridines are used as organocatalysts for asymmetric reactions such as hydrogenation of quinolines in the synthesis of alkaloids [6], asymmetric reductive amination of aldehydes [7] and hydrogenation of α,β-unsaturated aldehydes and ketones [8,9].

1,4-Dihydropyridines are generally synthesized by Hantzsch reaction which involves the condensation of aldehydes, β-ketoester and ammonia or ammonium acetate. A number of improved methods have been reported in the literature for this condensation which involve the use of microwave [10], ultrasound irradiation in ionic liquid [11], trifluoroethanol [12], $AlCl_3.6H_2O$ [13], K_2CO_3 [14], PPh_3 [15], silica gel/$NaHSO_4$ [16]. Many of these procedures suffer from lack of selectivity, unsatisfactory yields, being costly, toxicity of the reagents, or required special conditions. To avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time, recyclability, and simple reaction working-up for the synthesis of 1,4-dihydropyridines is of prime interest.

Polyoxometalates (POMs), constituting a large class of metal oxide molecules, are known to have a variety of sizes, structures, electrochemical properties, and chemical reactivities [17]. POMs has been extensively studied because they have many practical applications such as catalysis [18,19], molecular materials [20], and corrosion inhibition [21]. In recent decades, uses of some POMs as catalysts for fine organic synthetic processes have been developed and are important for industries related with fine chemicals [22], including flavors, pharmaceuticals and food industries [23].

Prompted by these findings and interest on the development of novel synthetic methodologies in organic reactions [24-30], in this paper a solvent-free synthesis of Hantzsch 1,4-dihydropyridines catalyzed by tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$, an isopoly tungstate, as green and effective catalyst is reported (Scheme 1).



Scheme 1. Synthesis of Hantzsch 1,4-dihydropyridines catalyzed by $[TBA]_2[W_6O_{19}]$.

EXPERIMENTAL

Chemicals and apparatus

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the known literature [31]. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained using a 4300 Shimadzu spectrophotometer as KBr disks. The ^{1}H NMR (400 & 500 MHz) spectra were recorded with Bruker 400 & 500 spectrometers.

Synthesis of tetrabutylammonium hexatungestate $[TBA]_2[W_6O_{19}]$

A mixture of sodium tungestate dihydate, $Na_2WO_4.2H_2O$, (99%, 0.1 mol, 33 g), acetic anhydride (40 ml) and N,N-dimethylformamide (30 ml) is heated at 100 °C for 3 h to obtain a white cream. Then a solution of acetic anhydride (20 ml) and HCl (12 N, 18 ml) in N,N-dimethylformamide (DMF) (50 ml) is added with stirring, and the resulting mixture is filtered off to eliminate the undissolved white solid. A solution of tetrabutylammonium bromide (0.047 mol, 15.1 g) in methanol (50 ml) is added with rapid stirring to give a white precipitate. This suspension is stirred for 5 min and the product is filtered. Recrystallization from a minimum amount of hot dimethyl sulfoxide (DMSO) gives colorless diamond-shaped crystals [31].

General procedure for the synthesis of 1,4-dihydropyridines

In a 50 ml round-bottom flask, an aromatic aldehyde **1a-i** (2 mmol), ethyl acetoacetate **2** (4 mmol) and ammonium acetate **3** (2 mmol) were stirred in presence of $[TBA]_2[W_6O_{19}]$ (0.04 g) in solvent-free condition at 80 ºC for 15-25 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and then hot ethanol was added. The catalyst was seperated by filteration, dried and reused in next reactions. Ethanol was removed and cold water was then added. The product was extracted with ethyl acetate, washed with 10% $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, concentrated under vacuum and was then rubbed in ice bath for a few minutes. The crude product was collected and recrystallized from ethanol to give pure 1,4-dihydropyridine derivatives.

The IR spectral data for fresh and used catalyst

FT-IR (KBr disc): υ (fresh catalyst) 2964.54, 1467.80, 975.06, 812.10, 586.27, 444.55; used catalyst (after third run for product **4a**) 2964.40, 1470.58, 974.85, 812.07, 585.72, 444.66 $cm^{-}1$.

The IR and ^{1}H NMR spectral data for products 4a-i

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (4a): FT-IR (KBr disc): υ 3342, 3061, 2982, 1688, 1651, 1489, 1453, 1372, 1300, 1211, 1124, 1092, 1050, 1020 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, δppm): 1.25 (t, J = 7.0 Hz, 6H, $2CH_3$), 2.37 (s, 6H, $2CH_3$), 4.07-4.18 (m, 4H, $2CH_2$), 5.03 (s, 1H, CH), 5.58 (s br, 1H, NH), 7.13-7.34 (m, 5H, Aromatic).

Diethyl 2,6-dimethyl-4-(4-fluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4b): FT-IR (KBr disc): υ 3343, 3068, 2985, 1687, 1652, 1507, 1489, 1372, 1301, 1211, 1124, 1091, 1049, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δppm): 1.24 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.35 (s, 6H, $2CH_3$), 4.04-4.19

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(m, 4H, $2CH_2$), 4.99 (s, 1H, CH), 5.67 (s br, 1H, NH), 6.90 (t, J = 8.8 Hz, 2H, Aromatic), 7.22-7.29 (m, 2H, Aromatic).

Diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4c): FT-IR (KBr disc): υ 3358, 2988, 1696, 1652, 1487, 1371, 1299, 1213, 1118, 1093, 1052, 1016 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.25 (t, J = 7.0 Hz, 6H, $2CH_3$), 2.36 (s, 6H, $2CH_3$), 4.05-4.18 (m, 4H, $2CH_2$), 4.99 (s, 1H, CH), 5.66 (s br, 1H, NH), 7.19 (d, J = 8.3 Hz, 2H, Aromatic), 7.24 (d, J = 8.3 Hz, 2H, Aromatic).

Diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4d): FT-IR (KBr disc): υ 3361, 2984, 1694, 1651, 1486, 1370, 1299, 1213, 1118, 1096, 1052, 1013 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.36 (s, 6H, $2CH_3$), 4.06-4.17 (m, 4H, $2CH_2$), 4.97 (s, 1H, CH), 5.62 (s br, 1H, NH), 7.19 (d, J = 8.4 Hz, 2H, Aromatic), 7.35 (d, J = 8.4 Hz, 2H, Aromatic).

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4e): FT-IR (KBr disc): υ 3345, 2990, 1705, 1645, 1525, 1488, 1371, 1347, 1301, 1213, 1119, 1052, 1022 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.25 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.40 (s, 6H, $2CH_3$), 4.05-4.20 (m, 4H, $2CH_2$), 5.13 (s, 1H, CH), 5.74 (s br, 1H, NH), 7.40 (t, J = 7.9 Hz, 1H, Aromatic), 7.67 (dt, J = 7.6, 1.3 Hz, 1H, Aromatic), 8.00-8.05 (m, 1H, Aromatic), 8.16 (t, J = 2.0 Hz, 1H, Aromatic).

Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4f): FT-IR (KBr disc): υ 3321, 2979, 1702, 1649, 1518, 1489, 1372, 1347, 1302, 1214, 1120, 1095, 1050, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$), 4.07-4.17 (m, 4H, $2CH_2$), 5.13 (s, 1H, CH), 5.72 (s br, 1H, NH), 7.48 (d, J = 8.7 Hz, 2H, Aromatic), 8.11 (d, J = 8.7 Hz, 2H, Aromatic).

Diethyl 2,6-dimethyl-4-(4-hydroxyphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4g): FT-IR (KBr disc): υ 3435, 3342, 2984, 1689, 1650, 1510, 1490, 1372, 1302, 1210, 1121, 1089, 1032 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, δppm): 1.14 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.25 (s, 6H, $2CH_3$), 3.90-4.10 (m, 4H, $2CH_2$), 4.75 (s, 1H, CH), 6.58 (d, J = 8.4 Hz, 2H, Aromatic), 6.94 (d, J = 8.4 Hz, 2H, Aromatic), 8.73 (s, 1H, NH or OH), 9.10 (s br, 1H, NH or OH).

Diethyl 2,6-dimethyl-4-(4-methylphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4h): FT-IR (KBr disc): υ 3360, 3093, 2988, 1698, 1653, 1487, 1369, 1299, 1213, 1118, 1097, 1053, 1019 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.26 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.31 (s, 3H, CH_3), 2.36 (s, 6H, $2CH_3$), 4.07-4.17 (m, 4H, $2CH_2$), 4.99 (s, 1H, CH), 5.60 (s br, 1H, NH), 7.04 (d, J = 7.8 Hz, 2H, Aromatic), 7.20 (d, J = 7.8 Hz, 2H, Aromatic).

Diethyl 2,6-dimethyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4i): FT-IR (KBr disc): υ 3343, 3096, 2984, 1690, 1650, 1509, 1491, 1372, 1302, 1254, 1210, 1141, 1122, 1089, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δppm): 1.26 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.36 (s, 6H, $2CH_3$), 3.78 (s, 3H, OCH_3), 4.07-4.17 (m, 4H, $2CH_2$), 4.97 (s, 1H, CH), 5.59 (s br, 1H, NH), 6.78 (d, J = 8.7 Hz, 2H, Aromatic), 7.23 (d, J = 8.7 Hz, 2H, Aromatic).

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, the synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **4a** was used as a model reaction. Therefore, a mixture of benzaldehyde (2 mmol), ethyl acetoacetate (4 mmol), and ammonium acetate (2 mmol) was heated on the oil bath under various reaction conditions.

The efficiency of the reaction is mainly affected by the amount of $[TBA]_2[W_6O_{19}]$ (Table 1). It showed that no product could be detected in the absence of this catalyst (entry 1), which indicated that the catalyst should be absolutely necessary for this condensation reaction. When the amount of $[TBA]_2[W_6O_{19}]$ was increased, a ramp in the yield of the product **4a** was observed. The optimal amount of $[TBA]_2[W_6O_{19}]$ was 0.04 g (entry 5), the higher amount of the catalyst did not increase the yield (entry 6).

Table 1. Effect of the amounts of $[TBA]_2[W_6O_{19}]$ on the model reaction[a]

Entry	Catalyst (g)	Time (min)	Yield (%)[b]
1	None	180	0
2	0.01	90	55
3	0.02	60	67
4	0.03	40	74
5	0.04	20	83
6	0.05	20	83

[a] Benzaldehyde (2 mmol), ethyl acetoacetate (4 mmol) and ammonium acetate (2 mmol) at 80°C.

[b] Isolated yields

Also, the reaction was carried out in various solvents. As shown in Table 2, in comparison to conventional methods the yields of the reaction under solvent-free conditions are higher and the reaction times are shorter.

Table 2. Synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **4a** in the presence of $[TBA]_2[W_6O_{19}]$ (0.04 g) in different solvents[a]

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)[b]
1	MeOH	64	90	58
2	EtOH	78	80	55
3	$PhCH_3$	110	70	63
4	CH_2Cl_2	40	100	68
5	$CHCl_3$	61	100	60
6	Solvent-free	80	20	83

[a] Benzaldehyde (2 mmol), ethyl acetoacetate (4 mmol) and ammonium acetate (2 mmol).

[b] Isolated yields

The effect of temperature was studied by carrying out the same model reaction in the presence of 0.04 g of the catalyst and at different temperatures in solvent-free conditions (Table 3). It was observed that yield is a function of temperature, so the yield increased as the reaction temperature was raised and at 80 ºC the product **4a** was obtained in high yield. So in other studies all reactions carried out at 80 ºC in the presence of 0.04 g of $[TBA]_2[W_6O_{19}]$ under solvent-free conditions.

Table 3. Synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **4a** in the presence of $[TBA]_2[W_6O_{19}]$ (0.04 g) at different temperatures in solvent-free conditions[a]

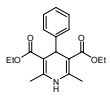
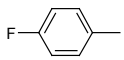
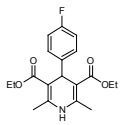
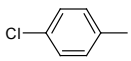
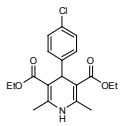
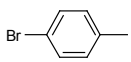
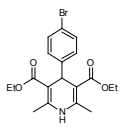
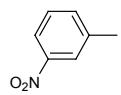
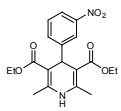
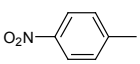
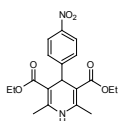
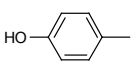
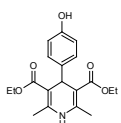
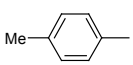
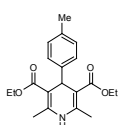
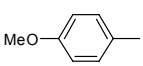
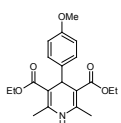
Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	25	90	25
2	50	40	43
3	65	30	62
4	80	20	83
5	90	20	83

[a] Benzaldehyde (2 mmol), ethyl acetoacetate (4 mmol) and ammonium acetate (2 mmol).

[b] Isolated yields

To show the generality of this method, the optimized system used for the synthesis of other 1,4-dihydropyridine derivatives with various aromatic aldehydes, ethyl acetoacetate and ammonium acetate (Table 4). In all cases the expected products were obtained in excellent yields in short reaction times.

Table 4. Synthesis of Hantzsch 1,4-dihydropyridines **4a-i** using $[TBA]_2[W_6O_{19}]$ as catalyst under optimized conditions[a]

Entry	Ar	Products[b]	Time (min)	Yield (%)[c]	m.p. (ºC)	
					Found	Reported
1		 **4a**	20	83	157-159	154-156 [10]
2		 **4b**	15	90	151-153	155-157 [10]
3		 **4c**	15	94	144-145	145-147 [14]
4		 **4d**	15	90	162-164	160-162 [11]
5		 **4e**	15	91	166-168	163-165 [14]
6		 **4f**	15	90	129-130	130-132 [11]
7		 **4g**	20	87	230-233	230-232 [11]
8		 **4h**	20	88	136-138	136-138 [14]
9		 **4i**	25	90	157-159	158-160 [14]

[a] Aryl aldehyde (2 mmol), ethyl acetoacetate (4 mmol), ammonium acetate (2 mmol), $[TBA]_2[W_6O_{19}]$ (0.04 g) at 80°C in solvent-free conditions.

[b] All the products were characterized by IR spectral data and comparision of their melting points with those of authentic samples. Also, the structures of some products were confirmed by ^1H NMR spectral data.

[c] Isolated yields

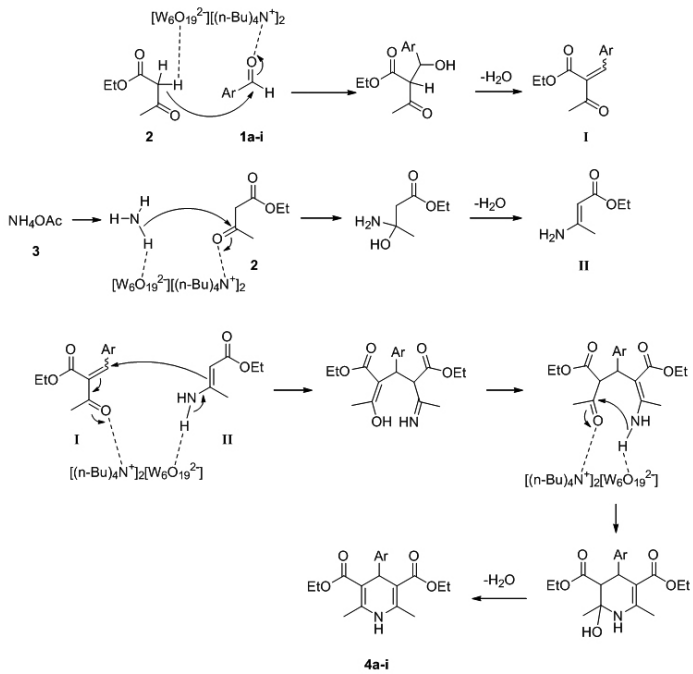
Reusability of the catalyst was also investigated. The catalyst was recovered according to the procedure mentioned in experimental section and reused for next reactions. The obtained results are summarized in Table 5. As it is shown in this table, the catalyst could be used at least three times without significant reduction in its activity.

Table 5: The comparison of efficiency of $[TBA]_2[W_6O_{19}]$ in the synthesis of 1,4-dihydropyridines after three times

Product	Ar	Yield/%[a]/run		
		First	Second	Third
4a	C_6H_5	83	81	80
4e	3-$O_2NC_6H_4$	91	90	89
4i	4-$MeOC_6H_4$	90	90	89

[a] Isolated yields

A reaction mechanism is proposed in Scheme 2. Based on Davoodnia's suggestion [31], $[TBA]_2[W_6O_{19}]$ can play a dual role. It is proposed that the tetrabutylammonium ion $[(n\text{-}Bu)_4N^+]$ induces polarization of carbonyl groups. On the other hands, terminal oxygen atoms or the bridging oxygen atom in polyoxometalate anion ,$W_6O_{19}^{2-}$, are slightly basic and can promote the reactions. Therefore, $[TBA]_2[W_6O_{19}]$ can activate the reactants and also some intermediates in this reaction. Therefore, as shown, it is proposed that $[TBA]_2[W_6O_{19}]$ facilitates the formation of the intermediates [**I**] and [**II**] that then react together to give the final products **4a-i**.



Scheme 2. Proposed mechanism for the formation of 1,4-dihydropyridines in the presence of $[TBA]_2[W_6O_{19}]$ as catalyst

CONCLUSIONS

In conclusion, in this paper a new catalytic method for the synthesis of Hantzsch 1,4-dihydropyridines using aryl aldehydes, ethyl acetoacetate and ammonium acetate in the presence of $[TBA]_2[W_6O_{19}]$ as catalyst has been reported. Good to excellent yields, short reaction times, simple operation and easy work-up are some advantages of this protocol. The catalyst can be recycled after a simple work-up, and used at least three times in the reactions without substantial reduction in its catalytic activity.

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