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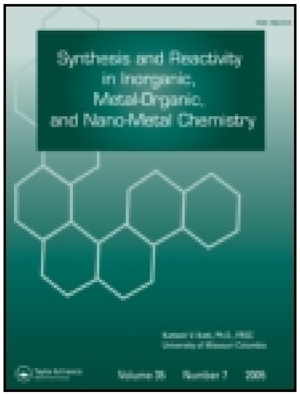

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An Efficient Method for Knoevenagel Condensation Catalyzed by Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$ as Novel and Reusable Heterogeneous Catalyst

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An Efficient Method for Knoevenagel Condensation Catalyzed by Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$ as Novel and Reusable Heterogeneous Catalyst

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Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$ has been efficiently used as catalyst for the synthesis of electrophilic alkenes *via* the Knoevenagel condensation reaction of aromatic aldehydes with malononitrile. The catalyst shows high catalytic activity with good to excellent yields of the desired products. Moreover, the catalyst could be recycled three times without noticeably decreasing the catalytic activity.

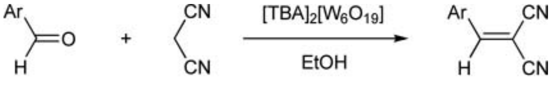
Keywords heterogeneous catalysis, Knoevenagel condensation, tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$

INTRODUCTION

The Knoevenagel condensation reaction is among the most important widely used reactions for the formation of carbon-carbon bonds.[1] In recent years, there has been a growing interest in Knoevenagel products, due to their use in the preparation of coumarin derivatives, cosmetics, perfumes and pharmaceuticals.[2–4] This condensation is generally carried out between a carbonyl group and a compound having an active methylene such as malononitrile, diethylmalonate, and ethyl cyanoacetate in the presence of a catalyst in organic solvents. Usually homogeneous base catalysts such as ammonia, primary and secondary amines, pyridine, and piperidine are used for this reaction.[1,5–7] In recent years, a number of ionic liquids[8–10] have also been reported to promote this reaction under homogeneous conditions. The use of homogeneous catalysts, however, has some major limitations such as difficulty of products separation and catalyst recovery.[11,12] As a result, one of the challenges in the field of catalysis is to replace homogeneous catalysts by easy to handle and environmentally friendly heterogeneous catalysts. Hence, the Knoevenagel reaction has also been carried out using heterogeneous catalysts such as $TiCl_4$,[13] $AlPO_4$-Al_2O_3,[14] $ZnCl_2$,[15] TiO_2,[16] Urea,[17] metal oxides,[18] fluorapatite,[19] hydroxyapatite,[20] and SiO_2/NH_4OAc.[21] In addition, electrochemically induced, microwave and ultrasound irradiation methods have been reported.[22,23] Many of these methodologies, however, suffer from disadvantages such as unsatisfactory yields, long reaction times, stoichiometric amounts of catalysts, and harsh reaction conditions. In addition, some of the catalysts are not recoverable and reusable. On the other hand, some of Lewis acidic catalysts such as $TiCl_4$ and $ZnCl_2$ are not stable in the presence of the water made from the Knoevenagel reaction itself. Thus, there is a need for development of simple, efficient, and environmentally friendly methods using new recoverable and reusable catalysts for the Knoevenagel condensation reaction.

In recent decades, uses of polyoxometalates as catalysts for fine organic synthetic processes have been developed and are important for industries related with fine chemicals,[24] including flavors, pharmaceuticals and food industries.[25] Furthermore, the Lindqvist-type metal-oxygen clusters, $M_6O_{19}{}^{2-}$ ($M =$ W, Mo), and their functionalized compounds have fascinating chemical properties, photophysical properties, and diverse practical applications.[26,27]

Prompted by these findings and interest on the development of novel synthetic methodologies in organic reactions,[28–42] in this paper an efficient and fast method for the Knoevenagel condensation reaction of aromatic aldehydes with malononitrile using tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$, an isopolytungstate, as heterogeneous catalyst is reported (Scheme 1).



1a-k **2** **3a-k**

SCH. 1. Knoevenagel condensation catalyzed by $[TBA]_2[W_6O_{19}]$

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EXPERIMENTAL

Chemicals and Apparatus

All chemicals were available commercially and used without additional purification. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ^{1}H NMR (500 MHz) spectra were recorded with a Bruker DRX500 spectrometer.

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 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 DMSO gives colorless diamond-shaped crystals.[43]

General Procedure for the Knoevenagel Condensation of Aromatic Aldehydes with Malononitrile Using $[TBA]_2[W_6O_{19}]$ as Catalyst

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol) and $[TBA]_2[W_6O_{19}]$ (0.07 g, 3.7 mol%) as catalyst in ethanol (5 mL) was heated under reflux for a few minutes. The reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration. The product was collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **3a-k** in high yields.

Recycling and Reusing of the Catalyst

Due to the fact that the catalyst was insoluble in hot ethanol, it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold ethanol, dried at 60 °C under vacuum for 1 h and reused in another reaction. The results show that there is not any significant loss of activity in using recycled catalyst after three times in the reactions.

RESULTS AND DISCUSSION

In order to evaluate the catalytic efficiency of $[TBA]_2[W_6O_{19}]$ in the Knoevenagel condensation and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of compound **3a** by the condensation of benzaldehyde (1 mmol) and malononitrile (1 mmol) in different sets of reaction conditions (Table 1). Among the tested solvents such as EtOH, MeOH, THF, $CHCl_3$, CH_3CN, and also solvent-free conditions and various amounts of the catalyst, the reaction between benzaldehyde, and malononitrile was more facile and proceeded to give the highest yield, using 0.07 g of $[TBA]_2[W_6O_{19}]$ in EtOH at reflux temperature (Table 1, entry 4).

TABLE 1
Synthesis of compound **3a** in the presence of $[TBA]_2[W_6O_{19}]$ as catalyst in different reaction conditions[a]

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield (%)[b]
1	None	EtOH	Reflux	120	Trace
2	0.05	EtOH	Reflux	7	73
3	0.07	EtOH	50	20	69
4	0.07	EtOH	Reflux	7	92
5	0.10	EtOH	Reflux	7	92
6	0.07	MeOH	Reflux	7	66
7	0.10	MeOH	Reflux	10	75
8	0.07	THF	Reflux	15	54
9	0.07	$CHCl_3$	Reflux	15	58
10	0.07	CH_3CN	Reflux	15	61
11	0.07	Solvent-free	80	30	76
12	0.10	Solvent-free	100	30	77

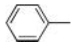
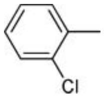
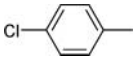
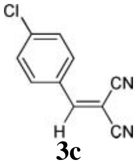
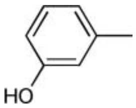
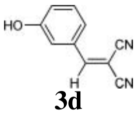
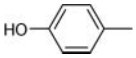
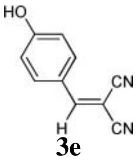
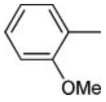
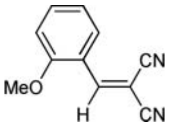
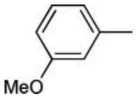
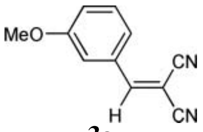
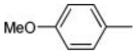
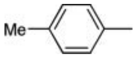
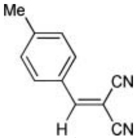
[a] 1 mmol Benzaldehyde and 1 mmol malononitrile.
[b] Isolated yields.

Encouraged by the above results, the Knoevenagel condensation reaction using various aryl aldehydes was also examined under optimized reaction conditions. As expected, high yields of products were generated smoothly in the presence of $[TBA]_2[W_6O_{19}]$ in refluxing EtOH. The results are summarized in Table 2. The results also revealed that electron-donating or -withdrawing groups on the aromatic ring did not seen to affect the reaction significantly either in the yield of the product or the rate of the reaction.

The principle advantage of the use of heterogeneous catalysts in organic transformations is their reusability. Hence, the catalytic activity of recycled $[TBA]_2[W_6O_{19}]$ in the synthesis of compound **3a** under the optimized conditions was also studied. After the completion of the reaction, the catalyst was filtered under hot condition, washed with cold ethanol, dried at 60 °C under vacuum for 1 h, and reused for the similar reaction. The catalyst could be used at least three times with only slight reduction in the catalytic activity (92% for 1st use, 90% for 2nd use, and 89% for 3rd use).

A plausible mechanism for the Knoevenagel condensation reaction using $[TBA]_2[W_6O_{19}]$ as catalyst can be depicted in scheme 2. The proposed mechanism demonstrates that $[TBA]_2[W_6O_{19}]$ has played as a dual role. Based on Kantevari's[44] and Yue's,[9] suggestions, it is proposed that the tetrabutylammonium ion $[(n\text{-}Bu)_4N^+]$ induces polarization of carbonyl group in aldehydes. On the other hands, Reinheimer and co-workers[45] reported that terminal oxygen atoms or the bridging oxygen atom in polyoxometalate anion,$W_6O_{19}{}^{2-}$, are slightly basic and can promote the reactions. Therefore,

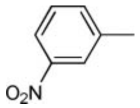
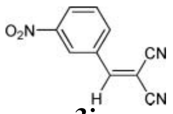
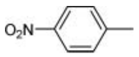
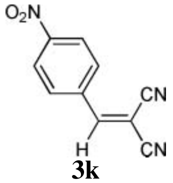
TABLE 2
The Knoevenagel condensation catalyzed by $[TBA]_2[W_6O_{19}]$[a]

Entry	Ar	Products[b]	Time (min)	Yield (%)[c]
1		 **3a**	7	92
2		 **3b**	10	89
3		 **3c**	5	91
4		 **3d**	10	88
5		 **3e**	8	87
6		 **3f**	10	88
7		 **3g**	10	90
8		 **3h**	8	89
9		 **3i**	7	86

(continued on next page)

TABLE 2

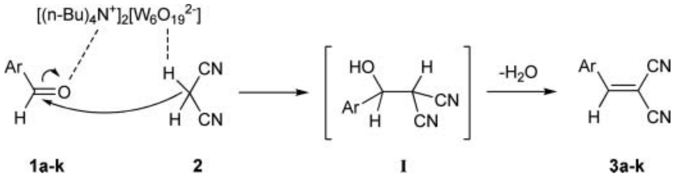
The Knoevenagel condensation catalyzed by [TBA]$_2$[W$_6$O$_{19}$]^a *(continued)*

Entry	Ar	Products^b	Time (min)	Yield (%)^c
10		 **3j**	5	89
11		 **3k**	5	92

^{a}1 mmol Benzaldehyde, 1 mmol malononitrile, and 0.07 g [TBA]$_2$[W$_6$O$_{19}$] in ethanol under reflux.

^{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 ^{1}H NMR spectral data.

^{c}Isolated yields.



SCH. 2. Plausible mechanism for the Knoevenagel condensation in the presence of [TBA]$_2$[W$_6$O$_{19}$] as catalyst

[TBA]$_2$[W$_6$O$_{19}$] can activate both reactants. Under these conditions, attempts to isolate the intermediate [**I**] failed after careful monitoring of the reactions.

CONCLUSION

In conclusion, [TBA]$_2$[W$_6$O$_{19}$] was found to be an efficient heterogeneous catalyst for the Knoevenagel condensation reaction of aromatic aldehydes with malononitrile, which gives electrophilic alkenes in high yields in refluxing ethanol. High yields, simple work-up procedure, short reaction times, and recyclability and reusability of the catalyst makes this protocol distinctly superior over to many other protocols reported earlier.

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