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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

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Published online: 11 Jul 2011.

To cite this article: Majid M. Heravi , Fatemeh F. Bamoharram & Niloofar Tavakoli-Hoseini (2011) Generation of Brønsted Acidic Ionic Liquid by Keggin Heteropoly Acid and its Application in the Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthenes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:6, 616-620, DOI: 10.1080/15533174.2011.568449

To link to this article: http://dx.doi.org/10.1080/15533174.2011.568449

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:616–620, 2011

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2011.568449

Generation of Brønsted Acidic Ionic Liquid by Keggin Heteropoly Acid and its Application in the Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthenes

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A new waterstable Brønsted acidic ionic liquid based on Keggin heteropoly acid was used as an environmentally benign catalytic medium in the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes under mild reaction conditions. The catalyst can be easily recovered and reused without appreciable loss of activity.

Keywords Brønsted acidic ionic liquid, dibenzoxanthene, green chemistry, Keggin heteropoly anion

INTRODUCTION

Recently, ionic liquids (ILs) have gained much attention as designer solvents and catalysts for a diversity of chemical applications. The reason for this interest is the enormous selection of weakly bonding anion and cation combinations, which make up this special class of low melting salts.

One of the most important ILs is SO_3H-functionalized ionic liquids. For synthesis of these ILs, first a N-alkylimidazole (or N-alkylpyrrolidine, pyridine, etc.) is reacted with 1,4-butan(or propan)sultone to obtain a solid zwitterion. This zwitterion is then protonated with a Brønsted acid such as sulfuric acid and phosphoric acid to obtain the corresponding ionic liquid. Although the mentioned IL shows satisfactory behavior, it needs hazardeus acids as starting materials.[1,2] To the best of our knowledge, protonation of such zwitterions with heteropoly acids has not yet been reported in the literature.

The principles of green chemistry have been introduced to eliminate or reduce the use of hazardous materials such as H_2SO_4 or H_3PO_4 in chemical processes. Cleaner technologies could be possible by making use of environmentally friendly materials involving the use of solid acids. It was shown that heteropolyacids (HPAs) in the solid state are pure Brønsted acids and stronger acids than conventional solid acids such as $SiO_2–Al_2O_3$, H_3PO_4, HNO_3, HF, H_2SO_4, and HX and HY zeolites.[3,4] These compounds have several advantages that make them economically and environmentally attractive. [5–7] These solid acids are “green” with respect to corrosiveness, safety, quantity of waste, and separability. Moreover, while some of the acid catalysts such as HCl, HNO_3, H_2SO_4, etc., can produce chlorated, nitrated, sulfated, etc. by-products, HPAs do not produce any of these by-products. HPAs have been extensively studied as green acid catalysts for many reactions, and found industrial applications in several processes.[8,9] Many reactions catalyzed by Brønsted and Lewis acids, but, in the presence of HPAs, proceed more effectively under milder conditions with greater selectivity, better yields, and shorter reaction times. Among HPAs, the application of Keggin structures has been extensively studied.[10–12] The Keggin structure with formula of $[XM_{12}O_{40}]^{n-}$ is shown in Figure 1.

Pursuing these studies, and in continuation of our previous works on the applications of Keggin HPAs[13–15] and ILs[16–18] in the synthesis of organic compounds, in the present work for the first time, we used $H_3PW_{12}O_{40}$ as a Brønsted acid for the synthesis of an ionic liquid and then investigated its catalytic activity in the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes.

The synthesis of xanthenes, especially dibenzoxanthenes, has received significant attention in recent years because of their wide range of biological and pharmaceutical properties, such as anti-viral,[19] anti-bacterial,[20] and anti-inflammatory[21] activities, as well as efficacy in photodynamic therapy[22] and antagonists for the paralyzing acting of zoxazolamine.[23]

EXPERIMENTAL

All compounds were known, and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrophotometer as

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Received 15 September 2010; accepted 28 January 2011.

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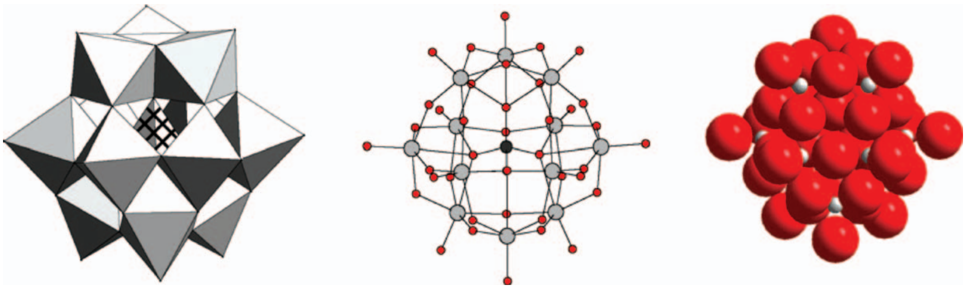


FIG. 1. The structure of the Keggin heteropoly anion [XM$_{12}$O^{40}]$^{n-}$ in polyhedral (left), ball-and-stick (middle), and space-filling (right) representations (color figure available online).

KBr disks. The ^{1}H NMR (500 MHz) spectra were recorded on Bruker DRX500 spectrometer.

Preparation of IL

Pyridine (0.2 mol) and 1,4-butane sultone (0.2 mol) were charged into a 100 mL round-bottom flask. Then, the mixture was stirred at 40°C for 10 h. The obtained white solid zwitterion was washed repeatedly with ether to remove non-ionic residues and dried in vacuum.[1] Then, $H_3PW_{12}O_{40}$, Keggin heteropoly acid was added and the mixture stirred for 20 min at 60°C to form the IL.

Preparation of 14-Aryl-14H-dibenzo[a,j]xanthene Derivatives: General Procedure

A mixture of β-naphthol (2 mmol), aromatic aldehyde (1 mmol) and IL (0.5 mL) was stirred at 100°C for 3–14 min. The progress of the reactions was monitored by TLC (ethyl acetate/n-hexane 3/8). After cooling to room temperature, water (10 mL) was added and the mixture was stirred for 5 min. The precipitated product was filtered and purified by crystallization from ethanol. The IL was recovered by evaporation of the water from the filtrate, washed with diethyl ether, dried at 50°C under vacuum for 1 h and reused in another reaction without appreciable reduction in the catalytic activity.

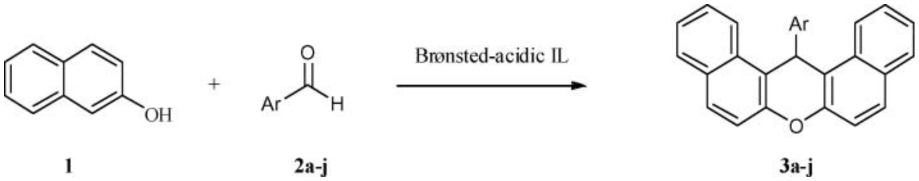
RESULTS AND DISCUSSION

14-Aryl-14H-dibenzo[a,j]xanthenes have been synthesized from the reaction of various aldehydes with β-naphthol in the presence of a new and green IL based on Keggin heteropoly acid (Scheme 1).

For preparation of this IL, first, pyridine was reacted with 1,4-butansultone to give a solid zwitterion (**1**). Interestingly, when we mixed two solids including **1** and $H_3PW_{12}O_{40}$, a liquid formed after 20 min at 60°C. It is worthwhile to mention that protonating of zwitterion (**1**) with H_2SO_4 as Brønsted acid need, longer reaction time (6 h) and higher temperature (80°C).[1,2] Therefore, $H_3PW_{12}O_{40}$ not only reduced time, but also required temperature. Figure 2A and 2B show the IR spectra of $H_3PW_{12}O_{40}$ and IL.

The [XM$_{12}$O$_{40}$] (Keggin structure) consists of one XO$_4$ tetrahedron (X = Si^{IV}, Ge^{IV}, P^{V}, ...) surrounded by four M$_3$O$_{13}$ sets (M = W^{VI}, Mo^{VI}) linked together through oxygen atoms (named M-O$_b$-M). The XO$_4$ tetrahedron is assumed to vibrate almost independently from the rest of the anion. This assumption is particularly valuable for X = P^{V}. The symmetric and asymmetric stretching of the different kinds of M-O bonds are observed in the following spectral regions: M-O$_d$ bonds (1000–960 cm^{-1}), M-O$_b$-M bridges (inter bridges between corner-sharing octahedra) (890–850 cm^{-1}), M-O$_c$-M bridges ("intra" bridges between edge-sharing octahedra, (800–760 cm^{-1}). Only the M-O$_d$ stretching can be considered as pure vibrations: the stretching involving O$_b$ or O$_c$ atoms present some bend character.[24,25]

In our study, the IR spectrum of the formed IL (Figure 2B) exhibits the characteristic frequencies of the Keggin structure in the range 1100–600 cm^{-1}. Compared with the initial Keggin structures (Figure 2A), the bands arising from the HPAs change obviously either in intensity, or in position. Comparing the IR spectrum of the IL with the IR spectrum of H$_3$[PW$_{12}$O$_{40}$] (Figure 2A and 2B), the vibrational band of the M-O$_c$-M of the Keggin is split from 793.88 into two bands, including 728.73



SCH. 1.

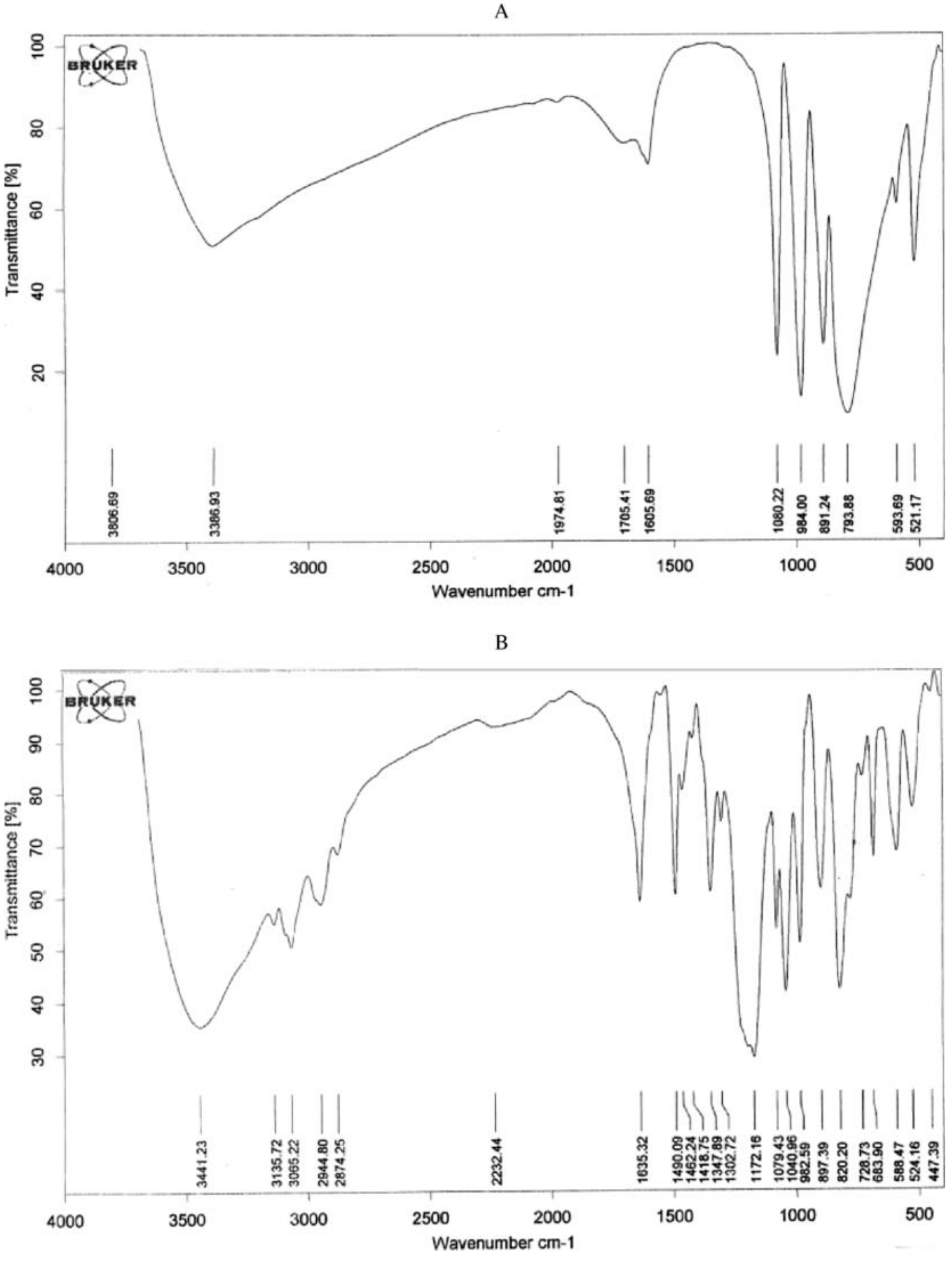


FIG. 2. (A) IR spectrum of the Keggin, $H_3\,[PW_{12}\,O_{40}]$; and (B) IR spectrum of IL formed via interaction of Keggin with **1**.

and 820.20, due to the difference in the M-O_c-M bonds. The vibrational band of the P-O is split from 1080.22 into two bands, including 1040.96 and 1079.43. This means that the inter bridges between edge-sharing octahedra (800–760 cm^{-1}) and the P-O stretchings have been affected. These results indicate that many of the bonds were strengthened and the others were weakened. It means that the HPA has a intraction with **1**.

It is suggested that the Keggin heteropoly acid, as a Brønsted acid, protonates the zwitterion to produce an acidic IL that

TABLE 1
Comparison of efficiency of various catalysts in synthesis of dibenzoxanthenes

Catalyst	Conditions	Time (h)	Yield (%)	Ref.
H_2SO_4	AcOH/80°C	73	60–90	[26]
p-Toluene sulfonic acid	$ClCH_2CH_2Cl$/reflux	15–24	83–95	[27]
Sulfamic acid	Solvent-free/125°C	6–12	90–95	[28]
I_2	Solvent-free/90°C	2.5–5	82–95	[29]
Amberlyst-15	Solvent-free/125°C	0.5–2	80–94	[30]
NaHSO4	Solvent-free/90°C	0.5–1	74–91	[31]
Preyssler[$NaP_5W_{30}O_{110}$]	Solvent-free/90°C	0.5–2	50–99	[32]
Keggin[$H_3PW_{12}O_{40}$]	EtOH/reflux	6	None	this work
[MIMPS]HSO_4	Solvent-free/100°C	0.1–0.5	85–96	[33]
[$(CH_2)_4SO_3$HPY]Keggin	Solvent-free/90°C	3–14(min)	87–98	this work

can be used as catalyst in the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes.

Our efforts were directed toward investigating the catalytic behavior of this new IL as a green medium for synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes. The synthesis of dibenzoxanthenes has been achived by the reaction of aldehydes with β-naphthol by the dehydration, and the results have been compared with the other reported methods.[26–33] The results are shown in table 1. As can be seen, the IL based on Keggin and 1 catalyzed the reaction and reduced reaction time significantly. Excellent yields and selectivity were obtained with different substrates (Table 2). A comparison between catalytic activity of Keggin and IL showed that the Keggin structure cannot catalyze reaction even after 6 h.

In order to investigate the possibility of recycling of this Brønsted acidic IL, a recovery experiment was conducted. The IL could be reused at least four times with only slight reduction in catalytic activity.

CONCLUSION

In summary, a new and green Brønsted acidic IL based on Keggin anion was successfully used as effective and green medium for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes under smooth conditions. The products were easily separated with high yields. The IL catalyst was readily recycled and reused to produce almost identical results. No organic solvent was used, resulting in eco-friendly process. The use of this new novel IL in this reaction provides a better and practical alternative to the existing procedures and provides great promise toward further useful applications. This process will pave a way for large scale applications of synthesis of dibenzoxanthenes. Further applications for other reaction systems are currently under investigation.

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TABLE 2
Synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes catalyzed by [$(CH_2)_4SO_3$HPY] Keggin

Entry	R	Time (min)	Compound	Yields (%)	Mp °C found	Reported
1	C_6H_5	9	a	94	187–189	184–185[33]
2	$2\text{-}ClC_6H_4$	3	b	98	213–215	214–215[33]
3	$4\text{-}ClC_6H_4$	4	c	96	294–296	287–288[33]
4	$4\text{-}FC_6H_4$	4	d	96	240–242	239–240[33]
5	$2\text{-}NO_2C_6H_4$	8	e	90	214–215	214–215[33]
6	$3\text{-}NO_2C_6H_4$	6	f	94	210–211	210–211[33]
7	$4\text{-}NO_2C_6H_4$	4	g	95	312–313	310–311[33]
8	$4\text{-}HOC_6H_4$	14	h	88	142–143	140[32]
9	$4\text{-}CH_3C_6H_4$	9	i	92	229–230	227–228[33]
10	$4\text{-}CH_3OC_6H_4$	14	j	87	204–206	202–203[33]

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