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Catalytic Performance of Preyssler Anion in Selective Oximation of Aromatic Aldehydes

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Preyssler catalyst, $H_{14}[NaP_5W_{30}O_{110}]$, catalyzes the aldoximation of aromatic aldehydes for the synthesis of Z-isomers in conventional manner and under microwave irradiation. Both pure acid and silica-supported catalysts were used and their activities compared with common catalysts such as K_2CO_3 and $CuSO_4$. The Preyssler is the catalyst for this reaction.

Key Words: Catalyst, Heteroployacid, Preyssler, Oxime.

INTRODUCTION

In organic chemistry, oximes are very important because they are useful intermediates in organic synthesis[1]. Hydroxylamine hydrochloride can be added to the carbonyl group to form oximes that are important chiefly for the characterization and identification of aldehydes and ketones[1]. They contain a carbon-nitrogen double bond resulting from elimination of a molecule of water from the initial addition products in an acidic medium. These reactions usually produce a mixture of Z and E isomeric aldoximes that can be separated using chromatography or re-crystalization techniques[2-5]. Thus there is a high interest for research towards finding catalytic systems for selective conversion of aldehydes to oximes.

A literature survey show these reactions can be carried out using conventional catalysts such as K_2CO_3, $CuSO_4$, HCl, CH_3COOH, H_2SO_4, NH_3/H_2O and amberlyst A-21[6-10].

In view of green chemistry, the replacement of these hazardous and polluting catalysts by green solid acid catalysts is one of the preferential requirement of the chemists.

The use of heteropoly acids (HPAs) as solid acid catalysts for organic synthesis processes is developing and synthesis of a wide variety of compounds has been reported by using them[11]. Among the numerous heteropoly acids, Keggin structures have been received much attention[12,13]. Recently, dodecamolybdo and tungstophosphoric acids with Keggin structures have been used in oxime sythesis[14].

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With respect to the catalytic performance of heteropoly acids can be varied with change of structure, heteroatom, metal and counter cation. There is still a good scope for research towards finding the better heteropoly acids with exclusive properties surpassing the other structures.

Among a wide variety of heteropoly acids, Preyssler acid, $H_{14}[NaP_5W_{30}O_{110}]$ is one of the largest known polyanions and is much better than the other heteropoly acids because of following advantages: (**1**) high Bronsted acidity with 14 acidic protons, (**2**) high thermal stability and (**3**) high hydrolytic stability (pH = 0-12).

Recently, we have attempted for developing of applications of Preyssler catalyst in a wide variety of organic reactions[15]. In continuation of our works on catalytic applications of heteropoly acids[16] and extending the applications of Preyssler catalyst and seeking to use new catalysts for selective organic reactions, in the present work, the performance and capability of Preyssler acid and silica-supported Preyssler have been studied for the selective synthesis of Z-isomers of oximes. The reactions have been performed under solvent free conditions, in the presence of solvent, in reflux conditions and under microwave irradiation.

EXPERIMENTAL

Preyssler catalyst as bulk form and silica supported were synthesized according to our earlier work[15a]. All of the chemicals were purchased from commercial sources. IR spectra were obtained with a Brucker 500 scientific spectrometer. GC-Mass analysis was performed on a GC-mass model: 5973 network mass selective detector, GC 6890 Egilent mass spectra were obtained with a Massens Poektro meter CH-7A Varin MAT Bremen spectrometer. H NMR spectra were recorded on a FT NMR Bruker 100 MHZ Aspect 3000 spectrometer.

Oximation of aromatic aldeydes

General procedure: Catalyst was added to a mixture of hydroxylamine hydrochloride (3 mmol) and aromatic aldehyde (2 mmol). The reaction progress was monitored by TLC or GC. After refluxing for 5 min, the reaction mixture was cooled and washed with Et_2O. The mixture was poured into ice-water and extracted with Et_2O. All the products were characterized by comparison of their melting points and spectroscopic data with those of authentic samples.

RESULTS AND DISCUSSION

Oximation of aldehydes with hydroxylamine hydrochloride was performed, using $H_{14}[NaP_5W_{30}O_{110}]$ under microwave irradiation and thermal conditions.

Both bulk and silica supported forms were used. The results under thermal conditions are shown in Table-1. Data in Table-1 show that $H_{14}[NaP_5W_{30}O_{110}]$ catalyzes the formation of Z-oximes as major product in excellent yield for 5 min. This study was also extended to other common catalysts such as K_2CO_3 and $CuSO_4$ in order to compare the catalytic activities.

TABLE-1
YIELDS (%) OF Z-OXIMES IN SOLVENT FREE CONDITIONS IN THE PRESENCE OF PREYSSLER CATALYST AS BULK AND SILICA SUPPORTED
(ABBERIVATED AS $H_{14}P_5$ AND $H_{14}P_5/SiO_2$)

Entry	Aldehyde	$H_{14}P_5$	$H_{14}P_5/SiO_2$ 10 %	$H_{14}P_5/SiO_2$ 20 %	$H_{14}P_5/SiO_2$ 30 %	K_2SO_4	$CuSO_4$	m.p. (Lit.)
1	4-Chloro benzaldehyde	95	53	63	75	70	Trace	143 (145[17])
2	4-Nitro benzaldehyde	93	43	52	68	68	Trace	126 (129[18])
3	2-Hydroxy benzaldehyde	89	39	51	60	56	Trace	59 (63[19])
4	3-Chloro benzaldehyde	86	28	40	55	53	Trace	153 (150[19,20])
5	4-Bromo benzaldehyde	80	45	55	69	48	Trace	132 (130[19,20])
6	4-Methyl benzaldehyde	73	28	36	52	40	Trace	80 (80[19])

A comparison for yields of aldoximes under solvent free conditions shows that, the highest yield has been achieved in the presence of $H_{14}[NaP_5W_{30}O_{110}]$ as catalyst. Furthermore, the supported polyacid with different loadings (10-30 %) is less active than the unsupported one, which indicates that there is a direct interaction between the heteropoly acid and the support surface, possibly *via* an acid-base reaction.

The interaction between the heteropoly acid and the silica OH surface groups therefore will decrease the acidity. No improvements in the reaction yields were observed by the increasing the amount of the loading percentage (> 30 %).

In environment protection, solvent free microwave reactions, in the presence of supported catalysis have been attracted much attention[17]. We examined the catalytic activity of the supported Preyssler under microwave irradiation. The results are shown in Table-2.

TABLE-2
YIELDS (%) OF ALDOXIMATION OF ALDEHYDES UNDER MICROWAVE IRRADIATION

Entry	Aldehyde	$H_{14}P_5/SiO_2$ 10 %	$H_{14}P_5/SiO_2$ 20 %	$H_{14}P_5/SiO_2$ 30 %
1	4-Chloro benzaldehyde	40	59	71
2	4-Nitro benzaldehyde	26	44	56
3	2-Hydroxy benzaldehyde	30	36	50
4	3-Chloro benzaldehyde	15	27	47
5	4-Bromo benzaldehyde	13	27	43
6	4-Methyl benzaldehyde	Trace	Trace	21

As we can see, the silica supported Preyssler catalyst, in solvent free conditions, renders effective the aldehyde oximation to Z-oximes, under microwave irradiation, in 1-2 min. In order to have a proper comparison, all reactions were performed under similar times and powers. The results show that, yields of Z-oximes are different under microwave irradiation and selected aldehydes show different behaviours. It is proposed that this behavior is due to loss factor of the aldehydes[15b].

The effect of solvent for the oximation of 4-chloro benzaldehyde was studied. The results in Table-3 show that the yields are less and the times are higher, when the oximation was carried out in solvent.

TABLE-3
YIELDS OF OXIMATION OF 4-CHLOROBENZALDEHYDE IN DIFFERENT SOLVENTS

Solvent	$CHCl_3$	CH_3CN	CH_2Cl_2	CCl_4	EtOH
Time (min), yield (%)	20 (78)	15 (82)	30 (70)	25 (65)	30 (63)

In order to know whether the catalysts would succumb to poisoning and loss of catalytic activity during the reaction, the catalyst was recovered after the reaction and reused as catalyst. These studies are performed with bulk and supported catalyst. It is found that Preyssler catalyst can be reused several times without any appreciable loss of activity. This result pointing to the stability and retention capability of this useful polyanion.

In conclusion, in mild conditions, very short reaction time and solvent free conditions we have implemented the catalytic activity of inexpensive, eco-friendly, recyclable and easily prepared Preyssler catalyst in selective formation of Z-isomer of oximes.

While this reaction has been studied with different catalysts, it had not been performed with Preyssler acid with high thermal and hydrolytic stability throughout a wide pH range. Simple experimental set up and procedure makes this method a useful addition to other methodologies.

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