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Preyssler Heteropoly Acid: An Efficient Catalyst for One-Pot Synthesis of Bis(dihydropyrimidinone)benzenes

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Introduction

One of the most important protocols in organic synthesis are multicomponent reactions (MCRs), that involve in three or more compounds as starting materials in one-pot conditions. In these reactions, two or more synthetic steps were done in a one-pot process. Therefore, they are very fast, economical, facile, easy to work-up and eco-friendly. So, the design of new MCRs and modification of them has interested for a synthetic chemist in prepared of new compounds and drugs and the development of new multicomponent reactions is an ideal idea. One of the most famous multicomponent reactions is Biginelli; one-pot three-component condensation of an aldehyde, ethylacetoacetate and urea gave dihydropyrimidones (DHPMs)[1]. DHPMs and their derivatives show wide range of properties such as biological and pharmacological activities. Therefore, the Biginelli reaction is a well-known and straight forward procedure for organic and medicinal chemists[2].

In the last two decades, heteropoly acids (HPAs) have found numerous applications as useful and versatile acid catalysts for some acid-catalyzed reactions. HPAs are more reactive catalysts than conventional inorganic and organic acids for reactions in solution. Heteropoly acids are non-toxic, highly stable towards humidity, air stable, recyclable, compatible with the environment, ease of handling and experimental simplicity[3].

A Preyssler acid ($H_{14}NaP_5W_{30}O_{120}$) is a highly acidic catalyst from heteropoly acid family with excellent catalytic activity in a variety of acid-catalyzed reactions [3]. The Preyssler is a HPA which has significant advantages, such as 14 acidic protons, safety, high thermal and hydrolytic stability. Owing to the low surface area (7–10 m2/g) and high solubility of HPAs in polar solvents, it is preferable to use them in supported form. Then, we hope that to get better the behavior of this catalyst in organic reactions and synthesizes.

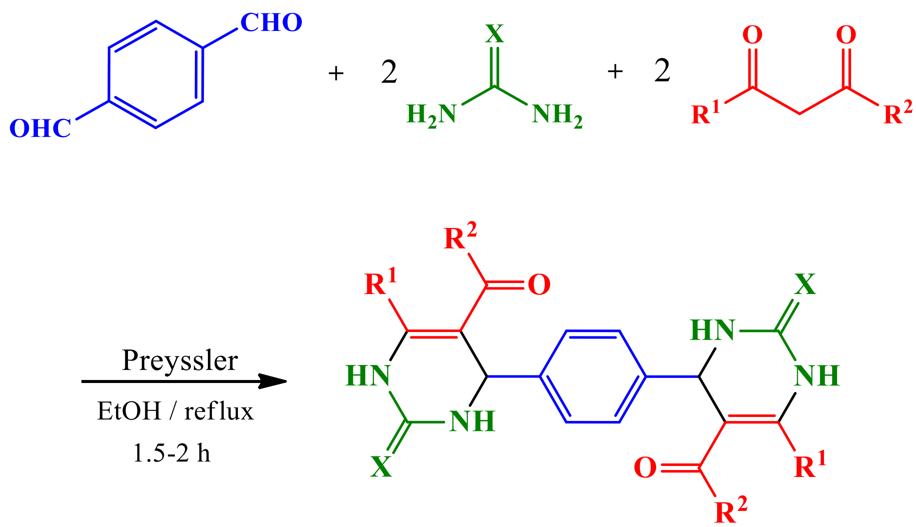
Herein, and in a continuation of our work by heteropoly acid as catalysts[4], we report a mild, practical, and highly efficient procedure using Preyssler as catalyst, for one-pot synthesis of bis(dihydropyrimidinone)benzenes through Biginelli condensation reaction of terephthaldialdehyde, 1,3-dicarbonyl compounds and urea (or thiourea) in reflux conditions in high yields in this work.

Experimental

A mixture of terephthaldialdehyde, 1,3-dicarbonyl compounds, urea (or thiourea) and Preyssler was refluxed in ethanol in oil bath for 1.5-2 hours. Then the resulting solid product was filtered and recrystalized from ethanol to give the pure products. This catalyst also showed excellent reusability in these reactions.

Results and discussion

In this research we have selected the Preyssler and used them in synthesis of bis(dihydropyrimidinone)benzenes via one-pot synthesis from terephthaldialdehyde, 1,3-dicarbonyl compounds and urea (or thiourea) under acidic conditions (Scheme 1).



Scheme 1

For a systematic comparison the reaction was performed in the presence of Preyssler and Keggin type structure ($H_3PW_{12}O_{40}$) as catalyst (the reaction is not performed in the absence of catalyst). The results are shown in Table 1. The results in this Table show a higher catalytic activity for Preyssler form in shorter times. It is suggested that as the particle size decreases, the relative number of surface atoms increases, and the catalytic activity increases.

Table 1: Synthesis of bis(dihydropyrimidinone)benzene derivatives, using catalytic amount of Preyssler and Keggin

Entry	X	R[1]	R[2]	Time(h) / Yield(%) $H_3PW_{12}O_{40}$	Time(h) / Yield(%) Preyssler
1	O	Me	Me	5 / 76	1.5 / 94
2	S	Me	Me	7 / 69	2 / 89
3	O	Me	OEt	5 / 63	1.5 / 91
4	S	Me	OEt	6 / 78	2 / 90
5	O	Me	Ph	5 / 72	2 / 92
6	O	CF_3	Me	8 / 70	2 / 85

We also studied the rate and yield of the reaction in different solvents as acetonitrile, ethanol, acetic acid and water. Therefore, ethanol was applied as acceptable solvent for this reaction.

Conclusion

In conclusion, Preyssler as an efficient, green and eco-friendly catalyst showed an excellent activity in synthesis of heterocycle compounds via the Biginelli process. We found that the Preyssler is more effective than Keggin in terms of yields and times. Simple experimental procedure as well as high yield and selectivity, makes this method useful addition to the methodologies that require green superacid solid catalyst. Also, low cost, easy availability, stability, and reusability are some of the salient features of this nano catalyst.

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