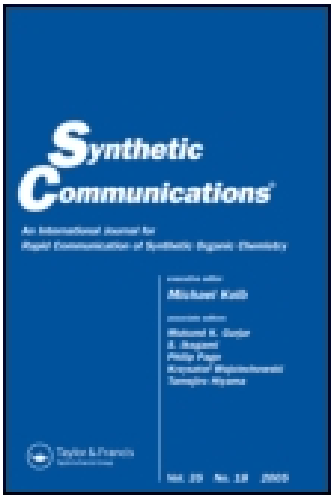


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

$H_{14}[NaP_5W_{30}O_{110}]$ as a Heterogeneous Recyclable Catalyst for the Synthesis of 6,8-Dimethyl-3-aryl-[1,2,4]triazolo[3,4-b][1,3,4]thiazepine Derivatives

Rahim Hekmatshoar [a], Sodeh Sadjadi [a], Samaheh Sadjadi [a], Majid M. Heravi [a] & Fatemeh F. Bamoharram [b]

[a] Department of Chemistry, School of Science, Alzahra University, Vanak, Tehran, Iran

[b] Department of Chemistry, School of Sciences, Azad University, Khorasan Branch, Mashad, Iran

Published online: 17 May 2010.

To cite this article: Rahim Hekmatshoar, Sodeh Sadjadi, Samaheh Sadjadi, Majid M. Heravi & Fatemeh F. Bamoharram (2010) $H_{14}[NaP_5W_{30}O_{110}]$ as a Heterogeneous Recyclable Catalyst for the Synthesis of 6,8-Dimethyl-3-aryl-[1,2,4]triazolo[3,4-b][1,3,4]thiazepine Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:12, 1778-1783, DOI: 10.1080/00397910903161785

To link to this article: http://dx.doi.org/10.1080/00397910903161785

Synthetic Communications®, 40: 1778–1783, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903161785

Taylor & Francis
Taylor & Francis Group

$H_{14}[NaP_5W_{30}O_{110}]$ AS A HETEROGENEOUS RECYCLABLE CATALYST FOR THE SYNTHESIS OF 6,8-DIMETHYL-3-ARYL-[1,2,4]TRIAZOLO[3,4-*b*][1,3,4]THIAZEPINE DERIVATIVES

Rahim Hekmatshoar,[1] Sodeh Sadjadi,[1] Samaheh Sadjadi,[1] Majid M. Heravi,[1] and Fatemeh F. Bamoharram[2]

[1]*Department of Chemistry, School of Science, Alzahra University, Vanak, Tehran, Iran*

[2]*Department of Chemistry, School of Sciences, Azad University, Khorasan Branch, Mashad, Iran*

6,8-Dimethyl-3-aryl-[1,2,4]triazolo[3,4-b][1,3,4]thiazepine derivatives were synthesized by cyclodehydration of 3-aryl-4-amino-5-mercapto-1,2,4-triazole with 2,4-pentanedione in the presence of a catalytic amount of Preyssler catalyst under very mild conditions.

Keywords: 3-Aryl-4-amino-5-mercapto-1,2,4-triazole; heteropolyacids; 2,4-pentanedione; Preyssler catalyst

INTRODUCTION

In recent years, some fused heterocycles have been found to possess many unique properties in the synthesis of condensed *S*-triazole heterocycles and have attracted a great deal of attention from chemists and pharmacologists because of their broad spectra of biological activities such as antifungal, antibacterial, hypotensive, and central nervous system–depressant activities.[1] Various methods have been reported for the synthesis of fused heterocyclic compounds using mineral acids such as H_2SO_4 and polyphosphoric acid.

These catalysts have their own disadvantages and drawbacks. They generate pollution, require great care in handling, have safety issues, cause corrosion, and need tedious workup procedures. Strong solid acids and solid acids based on supported transition-metal oxides are suitable for replacement of liquid acids to decrease these disadvantages.[2]

Recently, Nizamuddin et al. prepared some substituted 1,2,4-triazolo[3,4-*b*]-[1,3,4]thiadiazepines (II) by cyclodehydration of 3-aryl-4-amino-5-mercapto-1,2,4-triazole (I) with 2,4-pentanedione by refluxing in acetic acid.[3] All compounds were screened[3] for their fungicidal activity against *Aspergillus niger* and *Helminthosporium*

Received April 19, 2009.

Address correspondence to Rahim Hekmatshoar, Department of Chemistry, School of Science, Alzahra University, Vanak, Tehran, Iran. E-mail: rhekmatus@yahoo.com

oryzae at 1000, 100, and 10 ppm. In general, all compounds showed moderate activity. The greatest antifungal activity was observed only in compound IIa.

Heteropolyacids (HPAs), supported or in bulk form, are very interesting solid acid catalysts and can act as green and ecofriendly catalysts. HPAs are widely used as catalysts for the synthesis of fine and specific chemicals.[4] Being stronger acids, they generally exhibit higher catalyst activities than conventional catalysts such as mineral acids, ion exchange resins, mixed oxides, and zeolites.

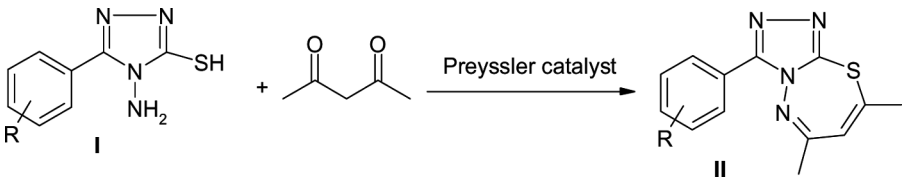
Catalysis by HPAs and related compounds is a field of increasing importance worldwide. The reactions in which they can be used, from dehydration, cyclization, and esterification to amine oxidation and olefin epoxidation, find wide application in industrial chemical production, such as fragrances, pharmaceuticals, and foods.[5–8] The application of Preyssler catalyst is mostly limited, and only a few demonstrations of catalytic activity have been reported.[9] The important advantages of this HPA are strong Brønsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH 0–12), reusability, safety, little waste, easy separability, low corrosiveness, high oxidation potential, and environmental friendliness along with its unique structure.

Recently, we have explored the application of the Preyssler catalyst in various organic reactions.[10,11] In this article, we report an improved catalytic and general approach for the synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepine derivatives, using Pressyler's anion (Scheme 1).

The performance of this catalyst as pure acid and supported on silica was compared with a Keggin type, $H_3[PW_{12}O_{40}]$, and traditional acids in homogeneous conditions.

The reactions were in most cases completed within 1.5 h as evidenced by thin-layer chromatography (TLC). The effect of temperature was studied by carrying out the model reaction in solvent-free condition and at different temperatures in the presence of these catalysts (room temperature, 45, and 90 °C). Interestingly, in the presence of classical acids such as H_2SO_4, only a trace of product was observed at 45 °C. When these reactions were carried out at 90 °C, the products were obtained in moderate yields. In the presence of HPAs as pure acid and in supported form, it was observed (Table 1) that yield is a function of temperature; the yield increased as the reaction temperature was raised.

The results showed that the greatest yields of the products were achieved when $H_{14}[NaP_5W_{30}O_{110}]$ was used as catalyst. Comparison of the catalysts in Table 1 showed that $H_{14}[NaP_5W_{30}O_{110}]$ is the catalyst of choice. Comparison of supported and unsupported catalysts showed that, in all cases, the supported polyacid is less active than the unsupported one. One plausible interpretation of this observation



Scheme 1. Synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepine derivatives.

Table 1. Catalytic synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepine (IIa) with 3-aryl-4-amino-5-mercapto-1,2,4-triazole (Ia) and 2,4-pentanedione (refluxed at 45 and 90 °C for 1.5 h in solvent-free conditions) and the comparison of efficiency of HPAs in synthesis of 6,8-dimethyl-3-aryl-[1,2,4] triazolo[3,4-*b*][1,3,4]thiazepine (IIa) after four times

		Percentage yield				
			90 °C			
Entry	Catalyst	45 °C	1	2	3	4
1	$H_{14}[NaP_5W_{30}O_{110}]$	65	87	85	83	80
2	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$	58	85	83	80	78
3	$H_3PW_{12}O_{40}$	51	78	75	72	70
4	$H_3PW_{12}O_{40}/SiO_2$	46	71	69	66	64
5	H_2SO_4	Trace	68	—	—	—
6	H_2SO_4/SiO_2	Trace	61	—	—	—

is that in the supported type, there are polyanion–support interactions of an acid–base nature. Some protons of the polyacid and some basic sites of the support (for example, hydroxyl groups) can interact. This would lead to diminished availability of hydrogens as a result of this extra ionic interaction.[12] Interestingly, this behavior is similar to that of Keggin HPAs. However, when $H_3[PW_{12}O_{40}]$ was used instead of $H_{14}[NaP_5W_{30}O_{110}]$, the yield of product was decreased. The results point out that the catalytic effectiveness may be enhanced as the number of tungsten atoms (or the number of protons) is increased. Both possibilities stand to reason. The larger number of protons may lower the activation barrier for the cyclocondensation reaction. In addition, the large anion also provides many sites on the oval-shaped molecule that are likely to render the catalyst effective. Interestingly, the comparison of Preyssler's anion, with its exclusive properties, with Keggin HPA, H_2SO_4, and supported silica sulfuric acid showed that the activity is the most for $H_{14}[NaP_5W_{30}O_{110}]$. The catalytic activity is increased in the following order: $H_{14}[NaP_5W_{30}O_{110}] > H_{14}[NaP_5W_{30}O_{110}]/SiO_2 > H_3[PW_{12}O_{40}] > H_3[PW_{12}O_{40}]/SiO_2 > H_2SO_4 > H_2SO_4/SiO_2$.

To establish the generality of this method, we investigated the cyclocondensation of various substituted 3-aryl-4-amino-5-mercapto-1,2,4-triazole with 2,4-pentanedione. The reaction of various 3-aryl-4-amino-5-mercapto-1,2,4-triazole with 2,4-pentanedione afforded the corresponding 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*]-[1,3,4]thiazepine derivatives in 78–93% yields (Table 2). The reaction was compatible with various electron-donating (Me and OMe) and electron-withdrawing (Cl and NO_2) substituents.

Consequently, we investigated the catalytic activity of recycled Preyssler catalyst in the reaction of 3-aryl-4-amino-5-mercapto-1,2,4-triazole and 2,4-pentanedione. The catalyst was filtered from the reaction, washed with diethyl ether, and dried in an oven. It could be reused without appreciable loss of activity.

As shown in Table 1, Preyssler catalyst could be reused at least four times without significant loss of activity. Our experiments exhibited that the infrared (IR) spectrum of the used Preyssler catalyst was consistent with that of the unused one.

Table 2. Synthesis of IIa–e under different reaction conditions in the reaction of 3-aryl-4-amino-5-mercapto-1,2,4-triazole and 2,4-pentanedione

Entry	Compound	R	Method A yield (%)	Method B[7] yield (%)	Mp (°C)[7]
1	IIa	4-Cl	87	68	152
2	IIb	4-NO_2	90	70	110
3	IIc	4-CH_3	89	64	64
4	IId	3-CH_3	78	59	118
5	IIe	3-OCH_3	93	82	178

Notes. Method A: refluxed at 90 °C for 1.5 h in solvent-free conditions in the presence of Preyssler catalyst. Method B: refluxed in acetic acid for 4 h.

Finally, the efficacy of the present method for the synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepine derivatives was compared with other reported procedures (Table 2).[3] It revealed that $H_{14}[NaP_5W_{30}O_{110}]$ is an efficient, environmentally benign catalyst in the synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo [3,4-*b*][1,3,4]thiazepine derivatives.

In summary, we describe a convenient and efficient protocol for the synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepine derivatives via condensation of 3-aryl-4-amino-5-mercapto-1,2,4-triazole with derivatives with 2,4-pentanedione using $H_{14}[NaP_5W_{30}O_{110}]$ as a green recyclable and heterogeneous catalyst (Table 2). The simple experimental procedure combined with ease of recovery and reuse of this catalyst make this procedure quite simple, more convenient, and environmentally benign.

EXPERIMENTAL

Catalyst Preparation

Phosphotungstic acid and molybdophosphoric acid were purchased from Merck Company. $H_3PW_{12}O_{40}/SiO_2$ was prepared by the known procedure.[13]

Preyssler-type HPA was prepared by passage of a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50 W × 8 in the H^+ form and evaporation of the elute under a vacuum.

Supported HPA catalyst was synthesized according to our previous report[14] by impregnating a support in the form of powder (SiO_2) with an aqueous solution of the H_{14}-P_5 (50% equivalent weight). After stirring the mixture, the solvent was evaporated, and the catalyst was dried at 120 °C and calcinated at 250 °C in a furnace prior to use.

Typical Experimental Procedure

The starting compounds 3-aryl-4-amino-5-mercapto-1,2,4-triazole (I) were prepared by employing our published procedures.[15] A mixture of 3-aryl-4-amino-5-mercapto-1,2,4-triazole (I, 1 mmol), 2,4-pentanedione (1 mmol), and catalyst (0.01 mmol) was refluxed at 90 °C for 1.5 h in solvent-free condition. After completion of the reaction, the mixture was cooled and diluted with chloroform, and the catalyst

was removed by simple filtration (the catalyst is not soluble in chloroform). After evaporation of solvent, the reaction mixture was poured over cold water with stirring. The resulting solid was filtered, washed with cold water, and recrystallized from ethanol.

All products were known and characterized by comparison of their physical and spectra data with those already reported.[3]

ACKNOWLEDGMENT

The authors are thankful to Alzahra Research Council for the partial financial support.

REFERENCES

1. Eweiss, N. F.; Bahajaj, A. A. Synthesis of heterocycles, part VII: Synthesis and antimicrobial activity of some 7*H*-s-triazolo[3,4-*b*][1,3,4]thiadiazine and s-triazolo[3,4-*b*][1,3,4]thiadiazole derivatives. *J. Heterocycl. Chem.* **1987**, *24*, 1173–1182.
2. (a) Heravi, M. M.; Kivanloo, A.; Rahimzadeh, M.; Bakavoli, M.; Ghassemzaeh, M. Pd–Cu–catalyzed heterocyclization during Sonogashira coupling: Synthesis of 3-benzylthiazolo[3,2-*a*]benzimidazole. *Tetrahedron Lett.* **2004**, *45*, 5747–5749; (b) Heravi, M. M.; Kivanloo, A.; Rahimzadeh, M.; Bakavoli, M.; Ghassemzaeh, M.; Neumüller, B. Regioselective synthesis of 6-benzylthiazolo[3,2-*b*]1,2,4-triazoles during Sonogashira coupling. *Tetrahedron Lett.* **2005**, *46*, 1607–1610.
3. Tiwari, N.; Singh, K.; Nizamuddin, N. Synthesis of [1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazepines and [1,2,4]triazolo[3,4-*b*][1,3,4]benzothiadiazocines. *Indian J. Heterocycl. Chem.* **1993**, *2*, 195–198.
4. Mizuno, N.; Misono, M. Heteropolyanions in catalysis. *J. Mol. Catal.* **1994**, *86*, 319–342.
5. Izumi, Y.; Urabe, K.; Onaka, M. *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; Kadansha: Tokyo, 1992.
6. Kozhevinkov, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem. Rev.* **1998**, *98*, 171–198.
7. (a) Kozhevinkov, I. V. Catalysis for fine chemicals. In *Catalysis by Polyoxometalates*; John Wiley and Sons: New York, 2002; (b) Misono, M.; Nojiri, N. Recent progress in catalytic technology in Japan. *Appl. Catal.* **1990**, *64*, 1–30.
8. Timofeeva, M. N. Acid catalysis by heteropoly acids. *Appl. Catal.* **2003**, *256*, 19–35.
9. Harrup, M. K.; Hill, C. L. Polyoxometalate catalysis of the aerobic oxidation of hydrogen sulfide to sulfur. *Inorg. Chem.* **1994**, *33*, 5448–5455.
10. (a) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Jahangir, M.; Gharib, A. Preyssler catalyst, $[NaP_5W_{30}O_{110}]^{14-}$: A green, efficient, and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols. *Appl. Catal.* **2006**, *302*, 42–47; (b) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Gharib, A.; Jahangir, M. A catalytic method for synthesis of γ-butyrolactone, ε-caprolactone, and 2-cumaranone in the presence of Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$, as a green and reusable catalyst. *J. Mol. Catal.* **2006**, *252*, 90–95.
11. (a) Heravi, M. M.; Motamedi, R.; Seifi, N.; Bamoharram, F. F. Catalytic synthesis of 6-aryl-1*H*-pyrazolo[3,4-d]pyrimidin-4[5*H*]-ones by heteropolyacid: $H_{14}[NaP_5W_{30}O_{110}]$ and $H_3PW_{12}O_{40}$. *J. Mol. Catal.* **2006**, *249*, 1–3; (b) Heravi, M. M.; Bakhtiari, K.; Bamoharram, F. F. 12-Molybdophosphoric acid: A recyclable catalyst for the synthesis of Biginelli-type 3,4-dihydropyrimidine-2(1*H*)-ones. *Catal. Commun.* **2006**, *7*, 373–376;

(c) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Takakoli, N. N-Oxidation of pyridine carboxylic acids using hydrogen peroxide catalyzed by a green heteropolyacid catalyst: Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$. *J. Mol. Catal.* **2006**, *252*, 219–225; (d) Heravi, M. M.; Bakhtiari, K.; Bamoharram, F. F. An efficient and chemoselective synthesis of acylals from aromatic aldehydes and their regeneration, catalyzed by 12-molybdophosphoric acid. *Catal. Commun.* **2006**, *7*, 499–501.

12. Lefebvre, F. ^{31}P MAS NMR study of $H_3PW_{12}O_{40}$ supported on silica: Formation of $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$. *J. Chem. Soc., Chem. Commun.* **1992**, *10*, 756–757.
13. Kozhevnikov, I. V.; Kloetstra, K. R.; Sinnema, A.; Zandbergen, H. W.; Van Bekkum, H. Study of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve and amorphous silica. *J. Mol. Catal.* **1996**, *114*, 287–298.
14. Alizadeh, M. H.; Razavi, H.; Bamoharram, F. F.; Hassanzadeh, M. K. Novel catalytic acetylation of alcohols with Preyssler's anion, $[NaP_5Wa_{30}O_{110}]^{14-1}$. *Kinet. Catal.* **2003**, *44*, 524–528.
15. (a) Sharfi, T.; Heravi, M. M.; Ghassemzadeh, M.; Neumuller, B. Synthesis, characterization, and crystal structure of the dimeric silver(I) complex containing 4-amino-5-methyl-2*H*-1,2,4-triazole-3(4*H*)-thione. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2297–2299; (b) Ghassemzadeh, M.; Tabatabaee, M.; Pouramin, M. M.; Heravi, M. M.; Eslami, A.; Neumuller, B. Synthesis and characterization of a novel 1,2,4-thiotriazine derivative (CAMTTO), and copper(I) and silver(I) complexes thereof (CAMTTO = {(4-[(4-chlorobenzylidene)-amino]-6-methyl-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2*H*)-5-one)}. *Z. Anorg. Allg. Chem.* **2006**, *632*, 786–792.