American Journal of Heterocyclic Chemistry
2015; 1(1): 6-12
Published online April 24, 2015 (http://www.sciencepublishinggroup.com/j/ajhc)
doi: 10.11648/j.ajhc.20150101.12

Catalytical Synthesis of Pyrazolines Using Nanoparticles of Preyssler Heteropolyacid Supported on Nano-SiO_2, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$: A Green and Reusable Catalyst

Ali Gharib[1, 2, *], Nader Noroozi Pesyan[3], Leila Vojdani Fard[4], Mina Roshani[1]

[1]Department of Chemistry, Islamic Azad University, Mashhad, Iran
[2]Department of Chemistry, Agricultural Researches and Services Center, Mashhad, Iran
[3]Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran
[4]Education Ministry, Education Organization of Razavi Khorasan, Mashhad, Iran

Email address:
aligharib5@yahoo.com (A. Gharib)

To cite this article:
Ali Gharib, Nader Noroozi Pesyan, Leila Vojdani Fard, Mina Roshani. Catalytical Synthesis of Pyrazolines Using Nanoparticles of Preyssler Heteropolyacid Supported on Nano-SiO_2, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$: A Green and Reusable Catalyst. *American Journal of Heterocyclic Chemistry*. Vol. 1, No. 1, 2015, pp. 6-12. doi: 10.11648/j.ajhc.20150101.12

Abstract: Different Pyrazoline derivatives were synthesized by cyclization of substituted chalcone derivatives in presence of hydrazine hydrate. A series of novel 1,3,5-triaryl pyrazoline derivatives has been synthesized by the reaction of chalcone and phenylhydrazine in the presence of Silica-supported Preyssler Nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, Preyssler $H_{14}[NaP_5W_{30}O_{110}]$ and Keggin heteropolyacids, $H_3PW_{12}O_{40}$, $H_7[PMo_8V_4O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$, $H_3[PMo_{12}O_{40}]$ as catalyst under aqueous conditions is described. The best conditions were observed using Preyssler and Silica-supported Preyssler Nanoparticles as catalysts. The catalyst is recyclable and reusable. The structures of compounds obtained were determined by IR and ^1H NMR spectra.

Keywords: Pyrazoline, Nanoparticles, Preyssler, Heteropolyacids, Catalyst, Synthesis

1. Introduction

Heterocyclic compounds have gained much importance in medicinal chemistry due to its presence in large number of pharmacologically active moieties. Among the five membered heterocyclic containing two hetero atoms in its ring structure, pyrazole is one of the most important one as large variety of biological activities have been reported for various pyrazole derivatives. Pyrazolines are well known, and important nitrogen-containing five-membered heterocyclic compounds and the pyrazoline ring protons were bonded with carbon atoms on a spatially different environment [1]. Pyrazolines are widely used and studied privileged pharmacophores in medicinal chemistry due to their synthetic and biological importance. Some studies have confirmed that pyrazoline derivatives possess antimicrobial activity and they have found to possess anti-fungal, anti-depressant, anti-convulsant, anti-inflammatory, anti-bacterial, anti-cancer, antioxidant, anti-pyretic, anti-neoplastic activities, anti-viral, anti-amoebic, acaricidal agro chemical fungicides or insecticides, anti-cholinergic, antidiabetic, anti-HIV, antimalarial, anaxiolytic, antiparasitic, anti-allergic, anti-microbial, anti-tuberculosis, tyrosinase inhibitor, hypoglycemic, hypotensive, immuno suppressive, anti-tumor [2-7]. Conventional method of synthesis of pyrazolines involves the base-catalyzed condensation of aromatic ketones to give α, β- unsaturated ketones (also called as chalcones), which undergo subsequent cyclization with hydrazine and hydrazine derivatives yielding 2- pyrazoline and 2-pyrazoline derivatives. In this method, hydrazones are formed as intermediates that can subsequently cyclized to 2-pyrazolines in presence of a suitable catalyst such as NaOH [8] or acetic acid [9]. The α,β-unsaturated ketones can play the role of versatile precursors in the synthesis of the corresponding pyrazolines [10-15]. Numerous methods have been reported for the preparation of pyrazoline compounds. Fischer and Knoevenagel in the nineteenth century studied the reaction of α,β-unsaturated aldehydes and ketones with phenyl hydrazine in acetic acid by refluxing, which became one of the most

popular methods for the preparation of 2-pyrazolines [16]. In 1998, Powers et al. [17] have reported the reaction of chalcones with phenyl hydrazine hydrochloride in the presence of sodium hydroxide and absolute ethanol at 70 °C, where the longer reaction time is the disadvantage of the reaction. K_2CO_3-mediated microwave irradiation has been shown to be an efficient method for the synthesis of pyrazolines [18]. Recently, the application of nanoparticles (NPs) as catalysts has attracted worldwide attention because of their high catalytic activity and improved selectivity [19]. Heteropolyacids as solid acid catalysts are green with respect to corrosiveness, safety, quantity of waste and separability and it is well known that the use of heteropolyacid catalysts for organic synthesis reactions can give a lot of benefits. One of the unique features that make solid heteropoly acids economically and environmentally attractive is their stability and bronsted acidity. The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds has attracted much attention, particularly in the last two decades [20]. These compounds exhibit high activity in acid-base type catalytic reactions, hence they are used in many catalytic areas as homogeneous and heterogeneous catalysts. The application of Preyssler catalysts is highly limited and only a few examples of catalytic activity have been reported [21]. The important advantages of this heteropolyacid are: strong Brønsted acidity with 14 acidic protons, high thermal stability,-high hydrolytic stability (pH 0–12), reusability, safety, quantity of waste, ease of separation, corrosiveness, high oxidation potential, and application as a green reagent along with an exclusive structure. Over the last decade, due to the unique properties of nanoparticles along with their novel properties and potential applications in different fields [22], the synthesis and characterization of catalysts with lower dimension has become an active topic of research. As the particle size decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, due to quantum size effects, nanometre-sized particles may exhibit unique properties for a wide range of applications [23]. In spite of extensive investigations on Keggin-type nanocatalysts [24], the synthesis of Preyssler-type nanocatalysts has been largely overlooked. Recently we have explored the application of a Preyssler catalyst in various organic reactions.

2. Experimental

2.1. Chemicals and Apparatus

Melting points were determined by Thieles tube method (Table 1) and were uncorrected. ^{1}H-NMR spectra were recorded on a Bruker AM 300 MHz and ^{13}C NMR (Brucker Gemini 100 MHz) spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The chemical shifts are expressed in δ (ppm). FT-IR spectrometer of Perkin Elmer was used for study. Thin layer chromatography (TLC) was done with pre-coated silica gel plates (GF254 Merck) using benzene:ethyl acetate (9.5:0.5, v/v) as the mobile phase.

2.2. Catalyst Synthesis Procedure

2.2.1. Synthesis of SiO_2 Nanoparticles

The materials used in this work include tetraethyl orthosilicate (TEOS) (Merck, 98%) as the SiO_2 precursor. Besides the main precursor, nitric acid (65%) and double distilled water were used for peptization and solvent, respectively. The sol-gel precursor solution was obtained by mixing tetraethyl orthosilicate (TEOS) and ethanol with specific molar ratios of ethanol to TEOS. The mixture was stirred using magnetic stirring.

2.2.2. Preyssler Heteropolyacid Catalyst Preparation

Preyssler catalyst, $H_{14}[NaP_5W_{30}O_{110}]$ was prepared by passage of a solution of the potassium salt (30 mL) in water (30 mL) through a column (50 cm × 1 cm) of Dowex 50w×8 in the H^+ form. The eluent was evaporated to dryness under vacuum [25, 26].

2.2.3. Synthesis Procedure of Nanoparticles of Preyssler Heteropolyacid Supported on Nano-SiO_2, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ Catalyst

To a solution of the surfactant, sodium bis(2-ethylhexyl) sulphosuccinate, in cyclohexane (0.2 mol L^{-1}), a solution of Preyssler acid in a specified amount of water was added. The molar ratio of water to surfactant was selected to be 3, 5 and 7. Tetraethoxysilane (TEOS) was then added to the micro-emulsion phase. After mixing for various times (8, 12, 18, 25 and 30 h) at room temperature, dispersed Preyssler acid/SiO_2 nanostructures were centrifuged and the particles were rinsed with acetone (4 times) and dried in a vacuum oven. The optimum ratio of water to surfactant was 3:1 and the optimum time was 30 h.

2.2.4. Preparation of Various Heteropolyacids Caralysts

The catalysts of $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_7[PMo_8V_4O_{40}]$ and Wells-Dawson, $H_6[P_2W_{18}O_{62}]$ were prepared in according to the literature [27-35]. $H_6[P_2W_{18}O_{62}]$, $H_7[PMo_8V_4O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$ and $H_3[PMo_{12}O_{40}]$ were prepared according to the literatures [35, 36]. The integrity of the synthesized heteropolyacids has been proven by comparing of spectral data with those reported in literatur [25, 29, 37, 38].

2.3. Synthesis of Substituted Pyrazoline Derivatives

2.3.1. Procedure for the Synthesis of Substituted Chalcone Derivative

A solution of sodium hydroxide (40%) in water and rectified spirit was placed in a flask provided with a mechanical stirrer. The flask was immersed in a bath of crushed ice. Substituted acetophenone (0.008 mol) was poured with constant stirring, Substituted benzaldehydes (0.008 mol) was added to the solution. The temperature of the mixture was kept at room temperature (25 ^{o}C) and stirred vigorously until the mixture was thick enough to retard the stirring (5 h). The stirrer was removed and the reaction mixture was kept at 5 ^{o}C overnight. The product was filtered

with suction on a buchner funnel, washed with cold water until the washings were neutral to litmus and then with ice cold ethanol. The crude product was recrystallized from ethanol.

2.3.2. Procedure for the Synthesis of Substituted Pyrazoline Derivatives

In a mixture of substituted chalcone (0.02 mol) in nanoparticles of Preyssler heteropolyacid supported on Nano-SiO_2, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ as catalyst (0.05 mmol), glacial acetic acid (1 mL), ethanol (60 mL), hydrazine hydrate (0.04 mol) was added drop wise in a round bottom flask. The reaction mixture was heated under reflux for appropriate time on a water bath and then the reaction was continued for a certain period of time as required for completion (monitored by TLC). The reaction mixture was then filtered to separate the catalyst and this solvent followed with addition of ice cold water at room temperature. The mixture was kept overnight at 5 ^oC. The precipitates were filtered, washed with distilled water and dried. The product was recrystallized with ethanol to get final product.

2.4. Selected Spectral Data

3-(4-Chlorophenyl)-1,5-Diphenyl-2-Pyrazoline (5a):

IR (KBr, cm^{-1}): ν 1120, 1506, 1591. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.13 (dd, *J* = 7.1, 17.0 Hz, 1H), 3.89 (dd, *J* = 12.2, 17.1 Hz, 1H), 5.30 (dd, *J* = 7.3, 12.4 Hz, 1H) 6.83-7.65 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 42.36, 61.30, 113.51, 117.25, 126.80, 126.92, 128.63, 129.16, 129.39, 130.56, 132.15, 132.18, 136.04, 139.60, 143.70, 147.38. Anal. calcd. for $C_{21}H_{17}N_2Cl$: C 84.85, H 5.72, N 9.43; found C 84.81, H 5.77, N 9.47.

5-(4-Methoxyphenyl)-1,3-Diphenyl-2-Pyrazoline (5b):

IR (KBr, cm^{-1}): ν 1120, 1263, 1511, 1595. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.11 (dd, *J* = 7.1, 17.1 Hz, 1H), 3.80 (s, 3H, OCH_3), 3.85 (dd, *J* = 12.1, 16.9 Hz, 1H), 5.26 (dd, *J* = 7.2, 12 Hz, 1H) 6.75-7.83 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 44.04, 55.63, 64.15, 113.70, 114.45, 119.56, 126.40, 127.90, 128.48, 128.87, 129.18, 130.57, 133.20, 135.02, 145.34, 147.19. Anal. calcd. for $C_{22}H_{20}N_2O$: C 84.62, H 6.41, N 8.97; found C 84.56, H 6.40, N 8.93.

5-(3-Bromophenyl)-1,3-Diphenyl-2-Pyrazoline (5c):

IR (KBr, cm^{-1}): ν 1125, 1501, 1597. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.05 (dd, *J* = 7.1, 17.0 Hz, 1H), 3.33 (dd, *J* =12.1, 16.9 Hz, 1H), 5.67 (dd, *J* = 6.9, 12.7 Hz, 1H) 6.80-7.73 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 42.36, 60.45, 113.33, 119.50, 124.22, 127.95, 128.07, 129.05, 129.15, 129.34, 130.58, 132.41, 133.18, 139.66, 145.25, 147.14. Anal. calcd. for $C_{21}H_{17}N_2Br$: C 85.85, H 5.72, N 9.43; found C 85.78, H 5.69, N 9.43.

5-(2,4-Dichlorophenyl)-1,3-Diphenyl-2-Pyrazoline (5d):

IR (KBr, cm^{-1}): ν 1115, 1501, 1587. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.01 (dd, *J* = 6.6, 17.6 Hz, 1H), 3.96 (dd, *J* =12.5, 17.5 Hz, 1H), 5.57 (dd, *J* = 6.6, 12.2 Hz, 1H), 6.69-7.70 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 41.54, 60.94, 113.51, 119.50, 124.30, 125.69, 127.42, 127.72, 128.61, 128.50, 128.59, 129.29, 129.55, 132.10, 133.92, 137.73, 144.40, 147.55. Anal. Calcd. for $C_{21}H_{16}Cl_2N_2$: C, 68.67; H, 4.39; N, 7.62. Found: C, 68.73; H, 4.39; N, 7.71%.

5-(2-Chlorophenyl)-1,3-Diphenyl-2-Pyrazoline (5e):

IR (KBr, cm^{-1}): ν 1122, 1498, 1593. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.05 (dd, *J* = 4.8, 17.6 Hz, 1H), 3.95 (dd, *J* =11.2, 17.7 Hz, 1H), 5.62 (dd, *J* = 4.7, 11.0 Hz, 1H), 6.76-7.70 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 41.71, 61.46, 113.33, 119.27, 125.90, 127.52, 127.98, 128.34, 128.55, 128.88, 129.38. 129.86, 131.40, 132.24, 139.56, 144.65, 147.48. Anal. Calcd. for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.41. Found: C, 75.83; H, 5.23; N, 8.38%.

5-(3-Chlorophenyl)-1,3-Diphenyl-2-Pyrazoline (5f):

IR (KBr, cm^{-1}): ν 1123, 1504, 1590. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.05 (dd, *J* = 6.8, 17.0 Hz, 1H), 3.41 (dd, *J* = 12.2, 17.2 Hz, 1H), 5.65 (dd, *J* = 6.9, 12.4 Hz, 1H) 6.85-7.72 (m, 14H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 42.37, 61.54, 113.58, 119.60, 124.44, 127.79, 128.07, 128.92, 129.18, 129.48, 130.67, 132.53, 133.04, 135.04, 139.67, 144.84, 147.53. Anal. calcd. for $C_{21}H_{17}N_2Cl$: C 85.85, H 5.72, N 9.43; found C 85.79, H 5.70, N 9.41.

5-(4-Chlorophenyl)-1,3-Diphenyl-2-Pyrazoline (5g):

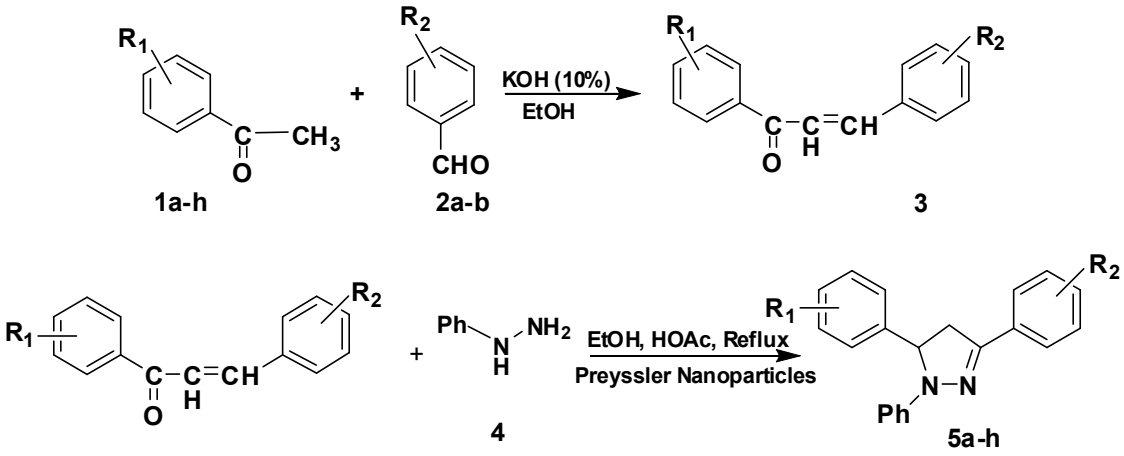
IR (KBr, cm^{-1}): ν 1121, 1493, 1595. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.01 (dd, *J* = 7.4, 17.6 Hz, 1H), 3.75 (dd, *J* = 11.6, 17.6 Hz, 1H), 5.64 (dd, *J* = 7.4, 11.6 Hz, 1H), 6.71-7.60 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 43.45, 63.85, 113.42, 119.41, 125.73, 127.37, 128.52, 128.76, 128.92, 129.30, 129.93, 132.54, 133.37, 141.10, 144.68, 146.73. Anal. Calcd. for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.41. Found: C, 75.69; H; 5.10; N, 8.49%.

5-(4-Methylphenyl)-1,3-diphenyl-2-pyrazoline (5h):

IR (KBr, cm^{-1}): ν 1115, 1496, 1590. ^1H NMR (300 MHz, $CDCl_3$): δ_H 2.35 (s, 3H, CH_3), 3.14 (dd, *J* = 7.1, 17.0 Hz, 1H), 3.852 (dd, *J* = 12.1, 17.0 Hz, 1H), 5.24 (dd, *J* = 6.9, 12 Hz, 1H) 6.77-7.70 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.67, 44.06, 64.70, 113.63, 119.46, 126.21, 128.41, 128.84, 129.31, 129.50, 130.15, 133.04, 137.66, 141.52, 145.41, 147.19. Anal. calcd. for $C_{22}H_{20}N_2$: C 84.62, H 6.41, N 8.97; found C 84.61, H 6.43, N 9.00.

3. Result and Discussion

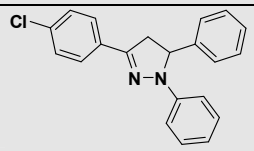
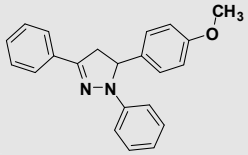
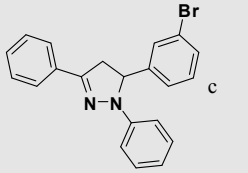
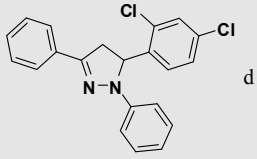
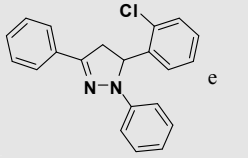
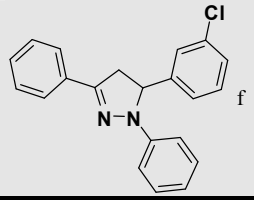
The propenones (1a-h) were then reacted with hydrazines in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst to give pyrazolines drivatives (Table 1, 5a-h) and Scheme 1.

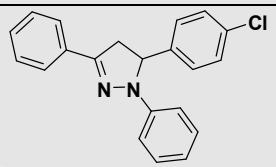
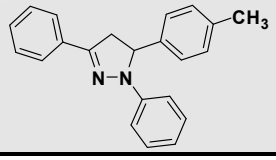


Scheme 1. *Synthesis of pyrazolines drivatives using silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst under reflux conditions.*

This reaction probably takes place via an appropriate α,β-unsaturated hydrazone intermediate followed by the attack of NH on the carbon-carbon double bond of the propenone moiety to give a pyrazoline ring.

Table 1. *Synthesis of pyrazolines using silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst and in presence of ethanol as solvent under reflux conditions.*

Entry	Product	Time (h)	[a]Yield (%)	Mp (°C)	
				Found	Reported
1	 a	3	89 (89, 88, 88,87.5) [b]	142-144	143-145[16]
2	 b	4	96(96,95.5,95.5) [b]	110-111	110-112[16]
3	 c	3.5	92	139-141	141-143[16]
4	 d	5	86	135-137	136-138 [16]
5	 e	4	88(88,87,87) [b]	132-134	134-135[16]
6	 f	4.5	92(91.5,91,91) [b]	132-135	134-136[16]

Entry	Product	Time (h)	[a]Yield (%)	Mp (°C)	
				Found	Reported
7	 g	4	94(94,93,93) [b]	132-135	133-134[16]
8	 h	3.5	99(99,98.5,98.5)[b]	129-131	128-130 [16]

[a]Isolated yields. [b]Catalyst was reused over three runs.

3.1. Catalyst Rcovery

In our experiments, the reusability of the catalyst were examined by repetitive use of the catalyst. The wet catalyst was recycled and no appreciable change in activity was noticed after three cycles (Table 1, entries 1, 2, 5-8).

3.2. Effects of the Solvent

Different organic solvents were examined for the reaction and we found that ethanol was the solvent of choice (Table 2). CH_3OH, $CHCl_3$ and THF proved to be almost as good as ethanol, with CH_2Cl_2 giving a slightly better yield than CCl_4. When the reactions were conducted in ethanol, the expected products were obtained in good yields and with better reaction times compared to organic solvents (Tables 1 and 2).

Table 2. *Solvent effects in the synthesis of 5-(4-Methylphenyl)-1,3-diphenyl-2-pyrazoline (Table 1, entry 8, product 5h) in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst.*

Entry	Solvent	Time (h)	[a]Yield (%)
1	C_2H_5OH	3.5	99
2	CH_3OH	3.5	97
3	CH_3CN	5	73
4	$CHCl_3$	5	94
5	CH_2Cl_2	5	80
6	CCl_4	6	76
7	DMF	7	69
8	DMSO	7	68
9	THF	4.5	95

[a]Isolated yield.

3.3. Effects of the Catalyst Type

Initially, we compared the catalytic performance of Preyssler and four Keggin-type heteropolyacids ($H_{14}[NaP_5W_{30}O_{110}]$, $H_7[PMo_8V_4O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$, $H_6[P_2W_{18}O_{62}]$ and $H_3[PMo_{12}O_{40}]$) catalyst, in the synthesis of 5-(4-Methylphenyl)-1,3-diphenyl-2-pyrazoline (Table 1, entry 8, product 5h). The results are shown in Table 3. The yield of product decreases in the following order:

silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$>$H_{14}[NaP_5W_{30}O_{110}]$>$H_7[PMo_8V_4O_{40}]$>$H_6[P_2W_{18}O_{62}]$>$H_6[PMo_9V_3O_{40}]$>$H_5[PMo_{10}V_2O_{40}]$>$H_4[Pmo_{11}VO_{40}]$>$H_3[PMo_{12}O_{40}]$>$H_3[PW_{12}O_{40}]$>$H_4[SiW_{12}O_{40}]$>$H_4[SiMo_{12}O_{40}]$>T*s*OH>$H_3[PMo_{12}O_{40}]$>SSA>$HClO_4$>$ZnCl_2$>$H_2SO_4$>$SiO_2$ nanoparticles> no Catalyst

As could be seen, silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst is more effective than the other catalysts, and in the presence of this catalyst the highest yields of products are obtained. The results (Table 3) show that silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst is better with respect to yield and to reaction. In all cases, the silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst shows higher activity compared with other catalysts (Table 3, Entries 2-4). This catalyst is an efficient solid acid catalyst for the synthesis of synthesis of 5-(4-Methylphenyl)-1,3-diphenyl-2-pyrazoline (Table 1, Entry 8, product 5h).

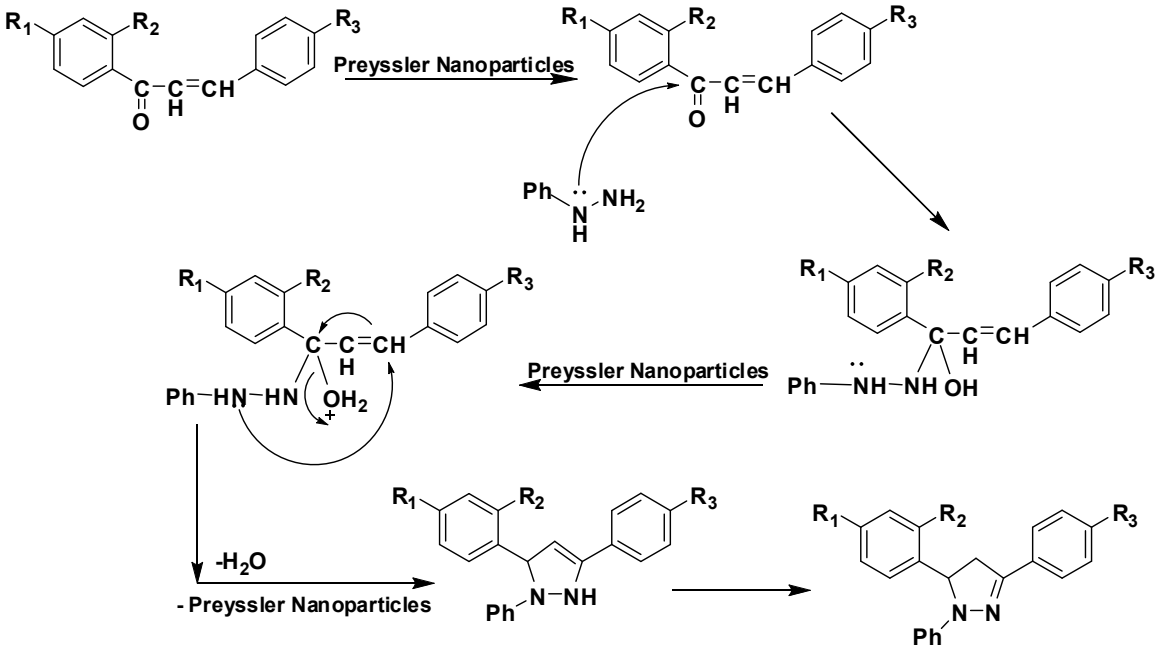
Table 3. *The effectiveness of varities catalysts in the synthesis of 5-(4-Methylphenyl)-1,3-diphenyl-2-pyrazoline (Table 1, Entry 8, product 5h) in presence of ethanol as solvent and under reflux conditions.*

Entry	Catalyst	Time (h)	[a]Yield (%)
1	Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$	3.5	99
2	$H_{14}[NaP_5W_{30}O_{110}]$	2	89
	$H_7[PMo_8V_4O_{40}]$	3	43.5
2	$H_6[PMo_9V_3O_{40}]$	3	41
3	$H_5[P\ Mo_{10}V_2O_{40}]$	3	40
4	$H_4[PMo_{11}V_1O_{40}]$	3	39
5	$H_3[PW_{12}O_{40}]$	3	37.5
6	$H_4[SiW_{12}O_{40}]$	4	34
7	$H_3[PMo_{12}O_{40}]$	4	29
8	$H_4[SiMo_{12}O_{40}]$	4	31.5
9	$H_6[P_2W_{18}O_{62}]$	4	42
10	$HClO_4$	6	19.5
11	H_2SO_4	6	10.5
12	T*s*OH	6	31
13	SSA	6	28.5
14	$ZnCl_2$	6	12
15	SiO_2 nanoparticles	7	9
16	Free	10	-

[a] Isolated yield.

A plausible mechanism for the reaction of chalcone with phenylhydrazine in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst is also

presented by Scheme 2.



Scheme 2. *Suggested mechanism for the reaction of chalcone with phenylhydrazine in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst.*

4. Conclusion

Herein is reported a relatively simple and useful method for the synthesis of pyrazolines in good yield using silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ catalyst in ethanol as solvent. This catalyst is a safe and recoverable heterogeneous system for promoting the synthesis of 1,3,5-triaryl pyrazoline. The advantages of this catalytic system is mild reaction conditions, short reaction times, high product yields, easy preparation of the catalysts, non-toxicity of the catalysts, stable, simple and clean work-up of the desired products. In addition, the catalyst can be recycled after washing ethanol followed by drying. and the catalysts can be reused several times but they will be less active. Therefore, the method is eco-friendly.

References

[1] R. H. Wiley, Ed.; "Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings; in the Chemistry of Heterocyclic Compounds;" Weissberger A, Ed.; Interscience Publishers: New York, 1967; Vol. 22, p 180.

[2] K. Suresh, B. Sandhya, D. Sushma., *Recent Patents Anti-Infect Drug Discov*. 2009, *4*, 154.

[3] Z. A. Kaplancıklı, G. Turan-Zitouni, A. Özdemir, *Phosphorus Sulfur Silicon Relat Elem*. 2007, *182*, 749.

[4] A. Özdemir, G. Turan-Zitouni, Z. A. Kaplancıklı, *European Journal Med Chem*. 2007, *42*, 403.

[5] A. Özdemir, G. Turan-Zitouni, Z. A. Kaplancıklı, *Journal Enzym Inhib Med Chem*. 2010, *25*, 565.

[6] G. Turan-Zitouni, A. Özdemir and K. Güven, *Arch Pharm Pharm Med Chem*. 2005, *338*, 96.

[7] G. Turan-Zitouni, A. Özdemir and Z. A. Kaplancıklı, *Phosphorus Sulfur Silicon Relat Elem*. 2005, *180*, 2717.

[8] B. A. Bhat, K. L. Dhar, S. C. Puri et al., *Bioorg Med Chem Lett*. 2005, *15*, 3177.

[9] R. Chawla, U. Sahoo, A. Arora et al., *Acta Pol Pharma Drug Res*. 2010, *67*, 51.

[10] R. Gupta, N. Gupta and A. Jain, *Indian Journal Chem*. 2010, *49B*, 3, 351.

[11] A. Solankee, S. Lad, S. Solankee et al., *Indian Journal Chem*. 2009, *48B*, 10, 1442.

[12] B. C. Revanasiddappa, R. Nagendr Rao, E . V. S. Subramaniyam, *E-J Chem*. 2010, *7*, 295.

[13] A. Voskiene, V. Mickevicius and G. Mikulskiene, *ARKIVOC*. 2007, *XV*, 303 .

[14] S. Kataade, U. Phalgune, S. Biswas, et al., *Indian Journal Chem*. 2008, *47B*, 6, 927.

[15] S. A. Al-Issa, N. A. L. Andis, *Journal Saudi Chem Soc*. 2005, *9*, 687.

[16] A. Levai, J. Jeko, *ARKIVOC*. 2007, *I*, 134.

[17] D. G. Powers, D. S. Casebier, D. Fokas, *Tetrahedron*. 1998, *54*, 4085.

[18] K. Kidwar, S. Kukreja and R. Thakur, *Lett Org Chem*. 2006, *3*, 135.

[19] S. Wang, Z. Wang and Z. Zha, *Dalton Trans*. 2009, 9363.

[20] M. M. Heravi, S. Sajadi, H.A. Oskooie, R. H. Shoar and F. F. Bamoharram, *Catal. Commun*. 2008, *9*, 470.

[21] H. Firouzabadi and A. A. Jafari, *J. Iranian Chem. Soc.* 2005, *2*, 85.

[22] M. M. Heravi, R. Motamedi, N. Seifi and F. F. Bamoharram, *J. Mol. Catal.,* 2006, *249*, 1.

[23] C. R. Gorla, N. W. Emanetoglu, S. Liang,W. E. Mago, Y. Lu, M. Wraback and H. Shen, *J. Appl. Phys.* 1999, *85*, 2595.

[24] J. Zhang and R. M. J. Dickson, *Phys.Rev. Lett.* 2004, *93*, 077402.

[25] M. H. Alizadeh, S. P. Harmalker, Y. Jeannin, J. Martin-Frere, M. T. Pope, *J. Am. Chem. Soc*. 1985, *107*, 2662.

[26] F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir and A. Gharib, *Appl. Catal.* 2006, *302,* 42.

[27] I. V. Kozhevnikov, *Chem. Rev.* 1998, *98*, 171.

[28] F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, M. Jahangir, *J. Mol. Catal. A: Chem.* 2006, *252*, 90.

[29] G. A. Tsigdinos, C. Hallada, *J. Inorg. Chem.* 1968, *7*, 437.

[30] Y. Mahha, A. Atlamsani, J. C. Blais, M. Tessier, J. M. Brégeault, L. Salles, *J. Mol. Catal. A: Chem.* 2005, *234*, 63.

[31] Y. Ding, Q. Gao, G. Li, H. P. Zhang, J. M. Wang, L. Yan, J. S. Suo, *J. Mol. Catal. A: Chem.* 2004, *218*, 161.

[32] a) M. Misono, *Stud. Surf. Sci. Catal.* 1993, *75*, 69. b) M. Misono, *Catal. Rev. Sci. Eng.* 1987, *29*, 269.

[33] M. Misono, N. Nojiri, *Appl. Catal.* 1990, *64*, 1.

[34] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 1996, *41*, 113.

[35] I. V. Kozhevnikov, *Appl. Catal. A: Gen.* 2003, *256*, 3.

[36] I. V. Kozhevnikov, K. I. Matveev, *Appl. Catal.* 1983, *5*, 135.

[37] Pope M T, Heteropoly and Isopoly Oxometalates*,* Springer, Berlin, 1983.

[38] G. T. Baronetti, L. Briand, U. Sedran and H. Thomas, *Appl Catal A: Gen.* 1998, *172,* 265.