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Catalytical Synthesis of Dicoumarols Using Silica-Supported Preyssler Nanoparticles (SPN), $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$

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Abstract: A new and efficient method for the synthesis of dicoumarol (3,3'-methylene-bis-4-hydroxycoumarin) in the presence of catalytic amounts of silica-supported Preyssler nanoparticles (SPN) is reported. The catalyst performs very well in comparison with other heteropolyacids catalysts. An important advantage of this catalyst is the ease of separating it from the reaction mixture, as well as the fact that it could be recycled a number of times.

Keywords: Dicoumarol, Silica-Supported Preyssler, Nanoparticles, Recyclable, Catalyst, Heteropolyacids

1. Introduction

Biscoumarins have generally been synthesized by refluxing 4-hydroxycoumarin and various aldehydes in acetic acid or ethanol for several hours [1]. Biscoumarins have also been synthesized under microwave [2] and ultrasound [3] irradiations. Recently, some condensations have been introduced for the synthesis of biscoumarins using molecular iodine [4], piperidine [5], DBU [6], DBSA [7], $LiClO_4$ [8], SDS [9], $Zn(Proline)_2$ [10], TBAB [11], ionic liquids [12] and nanoparticles [13]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have been enormous potential as anticoagulants [14, 15]. 3, 3'-methylene-bis-(4-hydroxycoumarin), commonly known as dicoumarol, occurs naturally in moldy clover [16]. It is the haemorrhagic agent responsible for the sweet clover disease of cattle and has also been employed for the prevention and treatment of thrombosis [17]. Dicoumarol is also a starting material for the synthesis of various furocoumarins and benzopyrans [18]. A number of biscoumarin have been found to be ureases inhibitors [19]. Dicoumarol (3,3'-methylene-bis-4-hydroxycoumarin) is a naturally coumarin-based compound which has long been used as an oral anticoagulant drug. It is metabolically produced from coumarin which was first isolated from both of the Tonka bean (*Dipteryx odorata*) and the sweet clover (*Melilotus alba and Melilotus officinalis*) [20]. It is now known to be present in many other plants. Dicoumarol derivative, warfarin (3-(α-acetonyl benzyl)-4-hydroxycoumarin), is commonly used as a natural anticoagulant for the prevention and treatment of excessive blood-clotting disorder [21]. The biological synthesis of dicoumarol occurs during the spoilage of cured hay, whereby, coumarin is oxidised to 4-hydroxycoumarin which, when coupled with formaldehyde, leads to the production of dicoumarol (Figure 1).

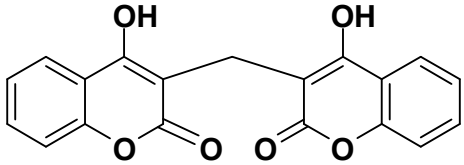


Figure 1. *Structure of Dicoumarol (3,3'-methylenebis-4-hydroxycoumarin).*

Many dicoumarols and coumarin derivatives have also shown a variety of pharmaceutical activities such as antiinflammatory, antibacterial, antiviral, anticancer, anti-HIV, and antiproliferative properties [22-28]. Therefore, dicoumarols have received much attention for medical and pharmaceutical applications. Dicoumarols and coumarin-based inhibitors exhibit a broad spectrum of activity against gram-positive bacteria [29, 30]. They have been shown to impede the growth of several bacteria strains, for instance, *Staphylococcus aureus*, *Bacillus anthracis, and Streptococcus pyogenes*. Another interesting property of dicoumarols lies in the effective anticancer activity [31]. Particularly, several evidences have shown that dicoumarol appears to be the most potent inhibitor which competes with NAD(P)H coenzyme for binding to the two-electron reduction quinone oxidoreductase [32], nitroreductase [33], azo-dyes azoreductase [34], and a ubiquitous flavoprotein found widely in various organisms.

Heteropolyacids (HPAs) are applied both in bulk or supported forms, with a homogeneous and heterogeneous catalysis being possible. Heteroplyacids (HPAs) have many advantages that make them environmentally attractive in the academic, industrial and economical signification. These are useful acids and oxidation catalysts in various reactions since their catalytic features can be varied at a molecular level [35]. Heteropolyacids catalyze a wide variety of reactions in homogeneous or heterogeneous (liquid-solid, gas-solid or liquid-liquid biphasic) systems, offering strong options for more efficient and cleaner processing compared to conventional mineral acids [36-40]. Being stronger acids, heteropolyacids will have significantly higher catalytic activity than the conventional catalysts such as mineral acids, mixed-oxides, zeolites, etc. In particular, in organic media, the molar catalytic activity of heteropolyacid is often 100-1000 times higher than that of H_2SO_4 [38-39]. It was shown that HPAs in the solid state are pure Bronsted acids and stronger acids than the conventional solid acids such as SiO_2-Al_2O_3, H_3PO_4, HNO_3, H_2SO_4, HX and HY zeolites [41] and HPAs efficient and environmentally friendly catalysts for organic reactions. HPAs will be expected as an alternative acid catalyst to improve several organic processes which employ conventional acids [42]. Heteropolyacids (HPAs) have been extensively used as green solid acids and oxidation catalysts for many reactions and gained applications in industrial practice of both electrophilic catalysis and oxidation reactions [43]. In aqueous solution HPA such as PW, SiW, Preyssler's anion $[NaP_5W_{30}O_{110}]^{14-}$ and PMo are strong fully dissociated acids. These compounds have several advantages as the catalysts which make them economically and environmentally attractive. The major disadvantage of HPAs, as the catalyst lies in their low hydrolytic stability which is very important in catalytic processes. Preyssler's anion has an excellent hydrolytic stability (pH 0-12). This stability demonstrates its functionality over a wide range of pH. If one applies the principles proposed for green chemistry, the Preyssler catalyst will be introduced as a promising candidate for green catalysts. This catalyst is green with respect to corrosiveness, safety, quantity of waste, and separability [44-50].

2. Experimental

2.1. Materials and Instruments

All chemicals were obtained from Merck and used as received. ^{1}H NMR spectra were recorded on a FT NMR Bruker 300 MHz spectrometer and ^{1}H NMR and ^{13}C NMR spectra were recorded at 298 K. Melting points were recorded on an Electrothermal type 9100 melting point apparatus andwere uncorrected. Chemical shifts were reported in ppm (δ-scale) relative to internal standard TMS (0.00 ppm); the solvent was used as a reference. The IR spectra were obtained with a Buck 500 scientific spectrometer (KBr pellets). The products were identified by comparison of their mp., IR and NMR spectra with those of authentic samples. Column chromatography was performed using EM silica gel 60 (300-400 mesh).

2.2. Preparation of Preyssler and Other Catalyst

The Keggin type heteropolyacids, $H_3[PMo_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$ were acquired from commercial sources. $H_{14}[NaP_5W_{30}O_{110}]$, $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_7[PMo_8V_4O_{40}]$ and Wells-Dawson, $H_6[P_2W_{18}O_{62}]$ were prepared according to the literature [42, 43, 51-53].

Silica-supported Preyssler nanostructures were obtained through a microemulsion method. Supported heteropolyacid catalysts were prepared by impregnating a support in the form of powder (nano-SiO_2) with an aqueous solution of the heteropolyacid with different concentrations. Samples were dried at 120-140°C, and the catalysts were calcined at 220°C in a furnace prior to use. $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ nanoparticles. Potassium salt of Preyssler's anion was prepared according to the procedure developed in our laboratory [42-50]. Preyssler HPAs, H_{14}-P_5, was prepared as follows: 33 g $Na_2WO_4.2H_2O$ were dissolved in 45 mL of water and mixed at 45 °C for 30 min. Then, this solution was cooled to room temperature, and 25 mL of concentrated phosphoric acid was added. The resulting yellow solution was refluxed for 5 h. The solution was brought to room temperature, diluted with water and then during stirring, 10 g of KCl was added. The mixture was stirred and then heated up to dryness. The product was dissolved in warm water and upon cooling to room temperature white crystals was formed. The free acid was prepared by passage of a solution of the potassium salt in water through a column of resin and evaporation of the elute to dryness under vacuum. Silica-supported Preyssler nanoparticles were prepared according to our previous work [42-50]. For synthesis of supported catalyst, a solution of surfactant in cyclohexane (0.2 M) was added to a solution of Preyssler acid in a specified amount of water. The molar ratio of water to surfactant was selected as 3, 5 and 7. Then, tetraethoxysilan was added into the microemulsion phase. After mixing for various times (8, 12,

18, 25 and 30 h) at room temperature, dispersed Preyssler acid/SiO_2 nano structures were centrifuged (1500 rpm) 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 [42-50] was 30 h. Although micro emulsion procedure has been used by some authors, this method has never been reported for the synthesis of Preyssler nanostructures with different morphologies. The analytical results are presented in terms of the P_5W_{30} stoichiometry revealed by the crystallographic measurements. Anal. Calcd (Found) for $H_{14}[NaP_5W_{30}O_{110}].58H_2O$: 1.57 (1.74); Na, 0.27 (0.21); P, 1.82 (1.86); W, 64.80 (64.82).

2.3. General Procedure for the Preparation of the Synthesis of Dicoumarols

A mixture of 4-hydroxycoumarin (2 mmol, 0.325 g), substituted aromatic aldehydes (1 mmol, 0.106 g), and silica-supported Preyssler nanoparticles (SPN), (0.05 g) was stirred at reflux in 5 mL ethanol-water mixture (1:1) for prepare time. The completion of reaction was monitored by TLC. After the reaction completion, then to separate nanocatalyst by filteration method and upon its cooling, the solid material was precipitated from the solution. The precipitates were filtered off, washed with water, and were recrystalized from EtOH to obtain pure 3,3-arylidene bis(4-hydroxy-2*H*chromen-2-ones) derivatives as yellow&white solids (93%-97% yields). Finally the products were recrystallized from ethanol to give the desired pure products (3a-g).

Selected spectral data

3,3'-(phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3a):

IR (KBr) ν_{max}/cm^{-1}: 2365, 1675, 1607, 1564, 1490, 1350, 1100 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.12 (s, 1H), 7.11-8.06 (m, 13H), 11.32 (s, 1H), 11.50 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 36.05, 103.72, 105.45, 116.52, 117.90, 124.25, 124.75, 126.34, 126.70, 128.49, 132.75, 135.04, 151.20, 164.45, 165.67, 166.75, 169.12. Anal. Calcd. For $C_{25}H_{16}O_6$; C, 72.81; H, 3.91%; found C, 72.17; H, 3.19%.

3,3'-((4-chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3b):

IR (KBr) ν_{max}/cm^{-1}: 2605, 1670, 1565, 1490, 1304. ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.05 (s, 1H), 7.10-8.05 (m, 12H), 11.02 (s, 1H), 11.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 35.21, 108.95, 115.87, 116.60, 123.68, 123.88, 127.87, 128.22, 130.77, 132.23, 136.93, 151.90, 164.16, 165.17. Anal. Calcd. For $C_{25}H_{15}ClO_6$; C, 67.20; H, 3.38%; found C, 66.97; H, 3.12%.

3,3'-((2-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3c):

IR (KBr) ν_{max}/cm^{-1}: 2600, 1656, 1610, 1525, 1357, 1305. ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.14 (s, 1H), 7.23-8.10 (m, 12H), 11.52 (s, 1H), 11.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 33.83, 103.65, 116.24, 116.45, 124.30, 124.58, 124.60, 127.94, 129.45, 131.07, 132.16, 132.80, 149.67, 152.33, 164.86, 166.45. Anal. Calcd. For $C_{25}H_{15}NO_8$; C, 65.65; H, 3.31%; found C, 64.93; H, 3.22%.

3,3'-((4-methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3d):

IR (KBr) ν_{max}/cm^{-1}: 2626, 1672, 1565, 1507, 1350, 1255. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.60 (s, 6H), 6.05 (s, 1H, CH), 7.10-8.05 (m, 12H), 11.03 (s, 1H), 11.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.87, 28.20, 31.48, 34.56, 49.95, 127.80, 128.37, 129.30, 131.29, 141.65, 158.07, 161.53, 186.70, 195.27. Anal. Calcd. For $C_{26}H_{18}O_7$; C, 70.58; H, 4.10%; found C, 70.13; H, 4.01%.

3,3'-((4-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3e)

IR (KBr) ν_{max}/cm^{-1}: 3440, 3071, 2360, 1660, 1616, 1603, 1565, 1518, 1495, 1348, 1308, 1266, 1181, 1107, 907, 825, 765; ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.10 (s, 1H, Ar-CH), 7.42-7.43 (m, 6H), 7.67(t, 2H, J = 7.8 Hz), 8.03 (d, 1H, J = 7.6 Hz), 8.10 (d, 1H, J = 7.2 Hz), 8.17 (d, 2H, J = 8.9 Hz), 11.36 (s, 1H, OH), 11.58 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.83, 161.92, 152.54, 150.58, 144.91, 128.36, 125.47, 123.39, 116.37, 100.25, 36.41. Anal. Calcd. For $C_{25}H_{15}NO_8$; C, 65.65; H, 3.31; N, 3.06% found C, 65.38; H, 3.22; N, 3.20%.

3,3'-((4-bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3f)

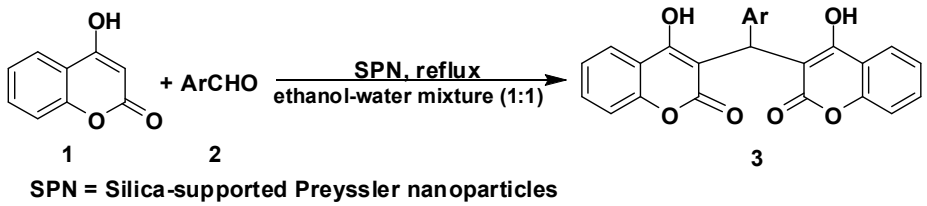
IR (KBr) ν_{max}/cm^{-1}: 3445, 3070, 2727, 2610, 2363, 1667, 1619, 1605, 1560, 1489, 1353, 1308, 1265, 1180, 1095, 907, 822, 765; ^1H NMR (300 MHz, $CDCl_3$): δ_H 6.03 (s, 1H, Ar-CH), 7.12 (d, 2H, J = 8.2 Hz), 7.31-7.44 (m, 6H), 7.65 (dt, 2H, J = 8.0 and 1.5 Hz), 7.97 (d, 1H, J = 7.7 Hz), 8.05 (d, 1H, J =7.8 Hz), 11.30 (s, 1H, OH), 11.55 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.81, 161.93, 152.56, 143.43, 131.55, 131.24, 125.45, 123.36, 128.33, 120.12, 116.34, 100.25, 36.44. Anal. Calcd. For $C_{25}H_{15}BrO_6$; C, 61.12; H, 3.08%; found C, 60.12; H, 4.11%.

3,3'-((3-hydroxy-4-methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3g)

IR (KBr) ν_{max}/cm^{-1}: 3457, 2360, 1665, 1616, 1605, 1516, 1453, 1350, 1271, 1212, 1185, 1094, 909, 798, 766; ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.76 (s, 3H, OCH_3), 5.56 (s, 1H, OH), 6.05 (s, 1H, Ar-CH), 6.65 (s, 1H), 6.70 (d, 1H, J =8.4Hz), 6.87 (d, 1H, J = 8.3Hz), 7.35-7.40 (m, 4H), 7.64 (t, 2H, J = 7.6 Hz), 8.01 (d, 2H, 9 Hz), 11.26 (s, 1H, OH), 11.50 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 146.70, 144.57, 132.85, 126.86, 124.87, 124.34, 119.50, 116.63, 114.45, 109.46, 56.10, 35.78. Anal. Calcd. For $C_{26}H_{18}O_8$; C, 68.12; H, 3.96%; found C, 67.89; H, 3.90%.

3. Results and Discussion

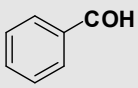
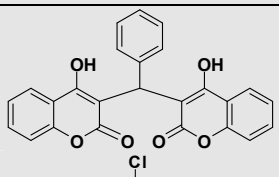
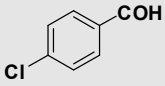
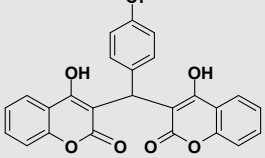
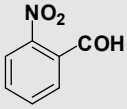
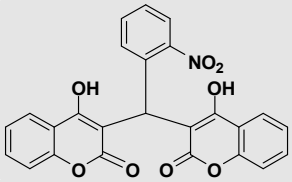
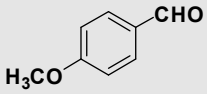
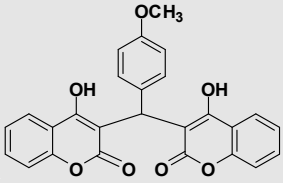
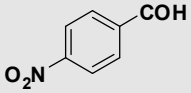
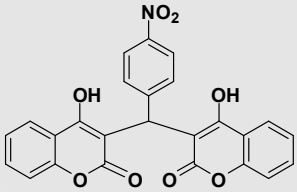
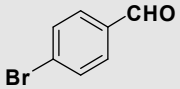
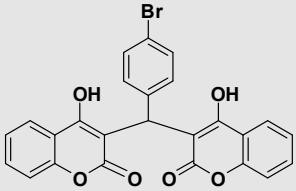
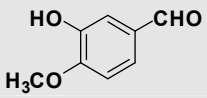
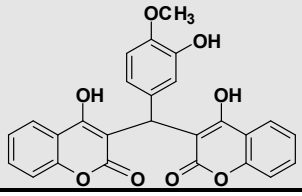
In our interest in green chemistry and in particular the development of nonhazardous methods using silica-supported Preyssler nanoparticles as a catalyst, we wish to report an easy and efficient procedure for the synthesis of dicoumarols (3) in good yields from aromatic aldehydes (1) catalyzed by silica-supported Preyssler nanoparticles (SPN) (Scheme 1).



Scheme 1. *Synthesis of dicoumarols (**3**) from 4-hydroxycoumarin (**1**) and benzaldehydes (**2**) in presence of silica-supported Preyssler nanoparticles (SPN), under reflux conditions.*

To our delight, the target compounds were obtained in excellent yield in the above mentioned method for all the combinations. The yields of the synthesis of dicoumarols with silica-supported Preyssler nanoparticles (SPN) are given in Table 1.

Table 1. *Synthesis of dicoumarols (**3**) from 4-hydroxycoumarin (**1**) in presence of silica-supported Preyssler nanoparticles (SPN), under reflux conditions.*

Entry	Aldehyde	Production	Time (h)	[a]Yield (%)	m.p.^{O}C	
					Found	Reported
1			5	95	216-218	215 [54]
2			5	94	254-257	252-258 [55]
3			5	93	203-205	200-202 [54]
4			5	94	264-266	266-268 [55]
5			5	97	234-235	232-234 [55]
6			5	91	264-266	265-267 [55]
7			5	94	226-229	-

[a]Isolated yield.

Initially, benzaldehyde was selected as a probe aldehyde to optimize the reaction conditions.

3.1. Effects of Various Solvents

In generally, the crude products obtained were of high purity (> 95% by ^{1}H NMR). In order to optimize the silica-supported Preyssler nanoparticles (SPN) catalyzed reactions, we have evaluate the reaction of 4-hydroxycoumarin and benzaldehyde to afford 3a in various other organic solvents such as H_2O, C_2H_5OH, CH_3OH, CH_2Cl_2, CCl_4, DMF, DMSO, THF, $CHCl_3$ and CH_3CN at reflux conditions for prepare times, and percentage of yields are little and poor with compare to the ethanol-water mixture (1:1) protocol (Table 2, entry 1).

Table 2. *Synthesis of dicoumarol (**3**) in presence of silica-supported Preyssler nanoparticles (SPN), and various solvents under reflux conditions.*

Entry	Solvent	Time (h)	[a]Yield (%)
1	C_2H_5OH-H_2O mixture (1:1)	5	95
2	C_2H_5OH	5.5	80
3	H_2O	5	84
4	CH_3OH	8	76
5	CH_2Cl_2	9	69
6	CCl_4	8	51
7	DMF	9	56
8	DMSO	8	57
9	THF	8	61
10	$CHCl_3$	8	66
11	CH_3N	9	58

[a]Isolated yield.

3.2. Effects of Various Catalysts

To compare the catalytic effect of the normal Preyssler catalyst with the silica-supported Preyssler nanoparticles (SPN) and other various heteropolyacids catalysts in the synthesis of dicoumarol a control experiment was carried out for both catalysts under the same conditions. The results of this comparison are reported in Table 3. It is clear that in these reactions the efficiency of silica-supported Preyssler nanoparticles (SPN), $(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$ is slightly higher than that of the conventional Preyssler bulk and other heteropolyacids catalysts. Results indicated that the reaction did not go to completion in the absence of catalyst even after extended reaction times.

Table 3. *Comparison of the efficiency of silica-supported Preyssler nanoparticles (SPN), Preyssler bulk and various heteropolyacids catalysts (0.05 g) in the synthesis of dicoumarol under reflux conditions for 5 h.*

Entry	Catalyst	[a]Yield (%)
1	$(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$ (SPN)	95
2	$H_{14}[NaP_5W_{30}O_{110}]$	93
3	$H_3[PMo_{12}O_{40}]$	61
4	$H_3[PW_{12}O_{40}]$	67
5	$H_4[SiW_{12}O_{40}]$	64
6	$H_4[SiMo_{12}O_{40}])$	53
7	$H_4[PMo_{11}VO_{40}]$	70
8	$H_5[PMo_{10}V_2O_{40}]$	75
9	$H_6[PMo_9V_3O_{40}]$	79
10	$H_7[PMo_8V_4O_{40}]$	82
11	$H_6[P_2W_{18}O_{62}]$	85
12	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(10%)	32
13	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(20%)	46
14	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(30%)	61
15	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(40%)	73
16	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(50%)	82
17	Free	0

[a]Isolated yield.

Silica-supported Preyssler nanoparticles (SPN) catalyst is well known as catalyst because of its advantages, such as low corrosivity, simple handling and it is inexpensive. It has been widely used as an efficient catalyst in several organic reactions. Silica-supported Preyssler nanoparticles (SPN) catalyst was used as a source of H+ to catalyze this reaction and found to be a good catalyst for the synthesis of dicoumarol. The hetropolyacids of the series H3+xPMo12-xVxO40 (x=1-4) showed good to excellent catalytic behaviors in methanol or ethanol. The results are shown in Table 4. H7[PMo8V4O40] catalyzes efficiently the synthesis of dicoumarol giving a total yield of 82% in methanol or ethanol. The yield with this catalyst was found to be decreased from 70% to 82% (Table 3, entries 7-10). In other words, the activities of the H3+xPMo12-xVxO40 (x=1-4) catalysts in the synthesis of dicoumarol in methanol or ethanol were found to decrease in the following order: H7[PMo8V4O40]>H6[PMo9V3O40]>H5[PMo10V2O40]>H4[PMo11VO40]. The Keggin anion have an assembly of 12 corner-shared octahedral MoO6 from trimetallic groups [Mo3O13] around a heteroatom tetrahedron PO4 [56]. The introduction of vanadium(V) into the Keggin framework of [PMo12O40]3- is beneficial for catalysis reactions [53]. Preyssler's anion, [NaP5W30O110]14-, has an approximate D5h symmetry and consists of a cyclic assembly of five {PW6O22} units. A sodium ion is located within the polyanion on the five fold axis and 1.25 above the pseudo mirror plane that contains the five phosphorus atoms, but the presence of the sodium cation reduces the overall anion symmetry from D5h to C5v [45,57,58]. Preyssler polyanion as a large anion can provide many "sites" on the oval-shaped molecule that are likely to render the catalyst effective. The central sodium ion lies not on the equator of the anion but in a plane roughly defined by the oxygen atoms of the phosphate groups. The morphology of the Preyssler nanostructures was found to depend strongly on the reaction conditions, such as concentration and time. The sizes and morphology of the products were controlled by changing the water:sodium bis(2-ethylhexyl)sulphosuccinate molar ratio/s and the reaction times. For short reaction times, the tubular structure was found to prevail, whereas spherical shapes dominated for longer times. Spherical particles of about 20 nm diameter were obtained at a molar ratio (water to sulphosuccinate) of 3:1 after 30 h, while the tubular morphology was obtained at a molar ratio of 3:1 and various times ranging from 12 h up to about 30 h. The molar ratio has been studied in various ranges and the results showed that higher molar ratios are unfavourable. The samples were analysed by tunneling electron microscopy (TEM), [49,50]. A mixture of nanowire (tubular shape) and nanospherical structures was obtained at ratio 3:1 and 12 h. The fraction of tubular shapes increased up to about 18 h. The heteropolyacid H14[NaP5W30O110] on the

SiO2 nanoparticles was confirmed by infrared (IR) spectroscopy. IR spectroscopy demonstrates that H14[NaP5W30O110] is preserved in the HPA/SiO2 nanoparticles [49,50]. The antisymmetric stretching wavenumber of the terminal oxygen-containing group is observed at 960 cm-1 and the antisymmetric P-O stretching wavenumber is noted at 1080 and 1165 cm-1 [49,50]. The prominent P-O bands at 960, 1080 and 1165 cm-1 are consistent with a C5v symmetry anion. It could therefore be confirmed that the heteropolyacid H14[NaP5W30O110] was successfully immobilized onto the SiO2 nanoparticles. Scanning electron microscopy (SEM) pictures of samples and X-ray diffraction (XRD) patterns of the synthesized samples were taken. The patterns of the spherical synthesized products contain a broad peak centered at 52 Å [49,50]. Analogous diffraction patterns have been observed for other synthesized samples. As the particle size of the nanomaterial decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, due to quantum size effects, nanometre-sized particles can exhibit unique properties. TEM and IR studies showed that the heteropolyacid stayed intact on the nanoparticles after it was recycled several times in the reaction reported below [49,50]. Bleeding of the heteropolyacid was found to be negligible by weighing the catalyst again after it was recycled five times [42-50].

3.3. Effects of Catalyst Amount

Table 4. *The effects of using different amounts of silica-supported Preyssler nanoparticles (SPN) catalyst in the synthesis of dicoumarol under reflux conditions.*

Entry	Catalyst amount (g)	Time (h)	[a]Yield (%)
1	0.01	5	90
2	0.03	5	94
3	0.05	5	95
4	0.08	5	95
5	0.09	5	95

[a]Isolated yield.

To obtain the optimum amount of catalyst for this reaction, various amounts of catalysts for the reaction were used. In Table 4 the results of various amounts of catalysts are summarized.

3.4. Catalyst Recycling

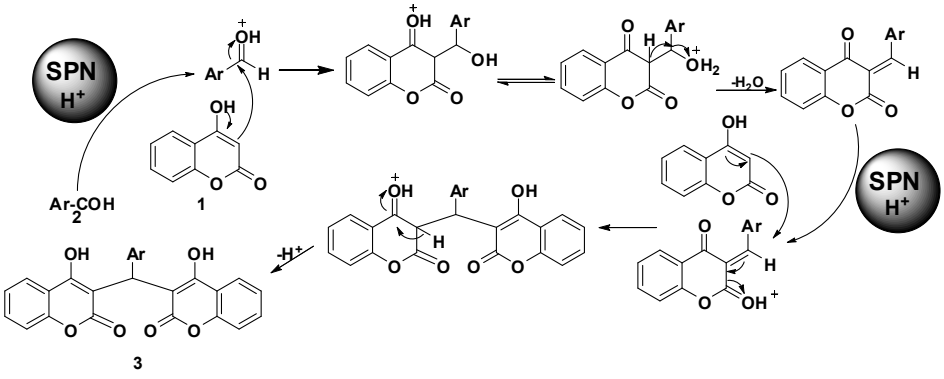
At the end of the reaction, the catalyst was recovered by a simple filtration. The recycled catalyst was washed with dichloromethane and subjected to a fifth run of the reaction process. To ensure that the catalyst did not dissolve in solvent the filtered catalysts were weighed before reusing. The results show that this catalyst is not soluble in solvent, and that bleeding at most is minimal. At the end of the reaction, the catalyst was recovered by water and re-used in the same reaction. The recycled catalyst was used without observation of appreciable lost in its catalytic activity. The reusability of the catalyst was also investigated. The results indicated that the catalyst can be recovered without structural degradation (Table 5).

Table 5. *Recycling of a silica-supported Preyssler nanoparticles (SPN) catalyst in the synthesis of dicoumarol (3a) under reflux conditions.*

Run	[a]Yield (%)
1	95
2	94
3	94
4	93
5	92.5

[a]Isolated yields and yields obtained in the first, second, third, fourth and fifth reuse of the catalyst.

In this regard, we found that the condensation between 4-hydroxycoumarin (1) and benzaldehyde 2 in the presence of catalytic amounts of silica-supported Preyssler nanoparticles (SPN) in a mixture of ethanol-water mixture (1:1) as solvent under reflux produces new and known dicoumarols 3 (Scheme 1). Here, there is a plausible mechanism of the synthesis of dicoumarols using silica-supported Preyssler nanoparticles (SPN), (Scheme 2).



Scheme 2. *Plaausible mechanism of the synthesis of dicoumarols using silica-supported Preyssler nanoparticles (SPN).*

4. Conclusion

This method demonstrates the applicability of silica-supported Preyssler nanoparticles (SPN) for those reactions that require solid catalysts with strong acidic properties. In addition, simple experimental setup and procedure makes this method a useful addition to the present methodologies. The present study demonstrates that silica-supported Preyssler nanoparticles (SPN) is an effective solid acid and heterogeneous catalyst for the preparation of dicoumarols.

Among different forms of Preyssler catalysts used, SiO_2 supported Preyssler nanoparticles (SPN) shows higher activity compared to the Preyssler and other heteropolyacids catalysts. With using silica-supported Preyssler nanoparticles (SPN) type heteropolyacid, as an eco-friendly, inexpensive and efficient catalyst. The high yields, relatively short reaction times, the simplicity of the operation and an easy work-up procedure are some advantages of this protocol.

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