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Studying the role of sodium hydrogen sulfate stabilized on nanosilica for preparing some coumarin derivatives in the solution and under solvent-free conditions

Abdolreza Abri[a,]*, Mostafa Ebrahilou[b]

[a,b]Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz, Iran

*Corresponding author. Tel.: +98 (41) 31452187; Fax number: +98 (41) 34327541

E-mail: ar.abri@azaruniv.edu

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Abstract

Coumarin and its derivatives are the most important components of several bioactive compounds such as anticoagulants, anti-HIVs, anti-tumors, anti-oxidants, anti-anxieties, anti-inflammatories, hypnotics, helminthicides, and insecticides. Derivatives of 2H-Chromen-2-one, or coumarins, are synthesized mainly through pechmann condensation reactions. This condensation involves phenol derivatives and β -ketoesters that occur in the presence of an acidic catalyst under reflux, but the yield of coumarin derivatives obtained in this method is very low and the reaction time is long. Although a lot of modified methods have been proposed, each one of them has some disadvantages, such as hard conditions, low efficiency, long time, expensive reagents, formation of byproducts, and difficulty of recycling and reusing the catalyst. In this research, an efficient method is offered for synthesis of some coumarin derivatives using pechmann condensation reactions in the presence of phenol and ethyl acetoacetate with sodium hydrogen sulfate stabilized on nanosilica as the catalyst. This method has advantages, such as high yields, short reaction time, simple purification.

Keywords: Pechmann condensation, sodium hydrogen sulfate, nano silica, coumarins, sol-gel

Introduction

Coumarin or 2H-chromen-2-one is a colorless and crystalline substance belonging to the benzo-pyrene family and mostly is found as phenol in several herbs, especially with high concentrations in tonka beans and vanilla. This compound is used as a freshener in perfumery and also as an additive in food but it is banned due to liver toxicity. Coumarin was also used as an anticoagulant like dihydrochloride after laboratory synthesis in 1868. Warfarin is a trademark of this drug (containing coumarin), which is used as an anticoagulant [1,2]. Among the pharmaceutical activities of coumarin and its derivatives, hypnotic activity, helminthicide, insecticide and anticoagulant, anti-inflammatory, anti-tumor, and antibacterial can be mentioned [3-6].

Due to the importance of coumarin and its derivatives, different methods have been proposed for the synthesis of these compounds; among these methods, the condensation reactions of pechmann, perkin, reformatsky, witting, claisen, and others can be mentioned. Pechmann condensation reaction has been interesting due to its convenient synthesis. These reactions are carried out with phenolic derivatives and β- ketoesters in the presence of acidic reagents such as chloric acid, sulfuric acid, acetic acid, etc. These reactions are not considered extensively due to the long reaction time, high temperature, and contamination caused by the excessive acid in the environment.

During recent years, Lewis acids such as $AlCl_3$, Yb $(OTf)_3$, $ZrCl_4$, etc. have been utilized, some of which are sensitive to moisture and require specific conditions for reaction. Moreover, their reaction needs high temperature and long time to be carried out. Researchers have recently used catalysts containing metallic hydrogen sulfate as a source of protonated acids and lewis acids, which are inexpensive and stable, and their reactions are carried out in heterogeneous environments [7-9].

Importance of green chemistry has led to creation of environmentally friendly methods for synthesis of chemical compounds. In this regard, the use of solid acids as heterogeneous catalysts has expanded due to their easy application, convenient separation, reusability, and prevention of chemical waste production [10-13]. Among these, bronsted acidic nanocatalysts functionalized with sulfonic acid (SO_3H) have shown high activity in organic reactions and are a good alternative for mineral liquid acids [14-20].

Unlike homogeneous catalysts, heterogeneous catalysts are easily separated from the reaction mixture and do not cause impurities. In order to compensate lack of active surface in these compounds, using a substrate as a support is essential for catalysts.

Although the active surface of nanocatalysts is much higher than conventional catalysts, the active surface of a nanocatalyst is always lower than a homogeneous catalyst (a homogeneous catalyst with its dissolution is in full contact with the reaction content). In contrast, catalytic nanoparticles are not solvated in the solution due to their larger dimensions than those of homogeneous catalyst particles, and can be easily separated. High active surface along with the ability to separate the catalyst at the end

of the reaction causes formation of a bridge between homogenous and heterogeneous catalysts. The complex manufacturing process of some nanocatalysts may be considered costly, but this can be neglected as the amount of catalyst and the energy and time needed to react decrease in the nanotechnology.

Experimental

Chemicals and instruments

All chemicals and solvents used in this study are purchased from Merck and Aldrich Companies and have been used without further purification. In order to investigate the reaction progress, a thin film of chromatography (TLC) with an aluminum plate and silica gel F254 60 and ultraviolet light have been used. The melting temperature of the synthesized products was measured with the thermoscientefic melting point of 9100. The IR spectrum has been reported by the bruker infrared spectrometer model PS15 and using a potassium bromide pallet. Also, ^{1}H NMR spectra were obtained by the broker spectrospin with the power of 400 MHz and ^{13}C NMR spectra were recorded with a 75 MHz bruker spectrospinn device.

In this research, all reactions (both with solvent and without solvent) were carried out at room temperature under mild conditions, and all solvents used were carefully dried using standard methods.

Nano Silica Preparation Method

100 ml of methanol and 750 ml of 25% ammonia are poured in a 250 ml balloon. Then, 1.92 g of distilled water is added to the mixture. After 15 minutes of stirring in the magnetic stirrer, 10.41 g of the tetraethoxysilane compound is added dropwise. After 3 days, the resulting unclear mixture is extracted using petroleum ether. Then, using a centrifuge, a gelatinous compound is formed, which is obtained in the form of a white powder by drying at 60-70 ° C nanosilica.

preparation of $NaHSO_4$ .SiO_2 (nano)

0.1 g of nanosilica is mixed with 0.2 g of the $NaHSO_4.H_2O$ solution and 1 ml of distilled water was added to it and thein it was stirred for 2-3 hours. The mixture is then dried at 120 °C for 2-3 hours and the catalyst is obtained.

General Method for the Synthesis of Coumarin Derivatives

In a 10 ml balloon, 1 ml of phenol derivative, 1 ml of ethyl acetoacetate, and 0.05 gr of sodium hydrogen sulphate stabilized on the nanosilica were mixed and about 3 ml of acetonitrile was added to it. The reaction mixture was stirred at room temperature and the reaction progress was controlled by a thin layer of chromatography in an n-hexane and ethyl acetate solvent. After completion of the initial phenol combination and separating the catalyst, some ice was crushed and the reaction mixture was poured onto it, and then it was stirred and filtered. After evaporation of the solvent under the filter, the obtained solid is recrystallized using hot ethanol. The remaining solids on a filter are dried and rinsed with a completely cold ethanol and then, they are filtered.

Spectral data of some resulted products

Table 4, row 11

4,5,6,7-Tetramethyl-2H-chromen-2-one (11): Yellow solid; m.p.: 164–165 °C; IR (KBr) ν_{max} (cm^{-1}): 1673 (ester C=O stretch), 1604 (C−C=C stretch); ^{1}H-NMR (DMSO-d6) δ: 2.14 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.24 (m, 1H), 7.23 (s, 1H); ^{13}C-NMR (DMSO-d6) δ: 14.3, 17.5, 21.6, 23.5, 114.3, 117.2, 121.6, 125.5, 131.5, 133.8, 152.2, 158.5. MS (m/z): 202 (M+); Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.30; H, 7.03%. %. Found: C, 77.19; H, 6.87%.

Table 4, row 12

6-Ethyl-4-methyl-2H-chromen-2-one (12): Yellow solid. m.p.: 159–160 °C. IR (KBr) ν_{max} (cm^{-1}): 1660 (ester C=O stretch), 1580 (C−C=C stretch). ^{1}H-NMR (DMSO-d6) δ: 1.82 (t, J = 7.2, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.64 (q, J = 7.2, 2H, CH_2), 5.90 (m, 1H), 7.11 (d, J = 8.5, 1H), 7.34 (dd, J = 8.5, 2.2, 1H), 7.40 (s (br), 1H); ^{13}C-NMR (DMSO-d6) δ: 16.7, 18.9, 22.3, 115.2, 118.5, 123.4, 124.9, 130.7, 135.2, 155.4, 161.3. MS (m/z): 188 (M+). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. Found: C, 77.28; H, 6.39%.

Table 4, row 13

6-Isopropyl-4-methyl-2H-chromen-2-one (13): Yellow solid; m.p.: 167–169 °C. IR (KBr) ν_{max} (cm^{-1}): 1657 (ester C=O stretch), 1580 (C−C=C stretch). ^{1}H-NMR (DMSO-d6) δ: 1.63 (d, J = 6.5, 1H, CH), 2.42 (s, 3H, CH_3), 2.93 (q, J = 6.5, 6H, $2CH_3$), 5.87 (m, 1H), 7.13 (d, J = 8.3, 1H), 7.32 (dd, J = 8.3, 2.3, 1H), 7.42 (s (br), 1H); ^{13}C-NMR (DMSO-d6) δ: 14.5, 15.2, 18.2, 24.7, 116.3, 119.0, 122.6, 126.4, 133.2, 137.6, 157.4, 163.3. MS (m/z): 202 (M+). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%. Found: C, 76.56; H, 6.69%.

Results and Discussion

Preparation of nanosilica using sol-gel method

Sol-gel method is one of the several methods that can be used to synthesize various nanoparticles. This method starts with the formation of a homogeneous cell from the starting material and then, the cell is converted into a gel through chemical stimulation. Then, the solvent is removed from the gel structure and dried using one of the common methods. Depending on the drying method, the product will have different properties. Depending on the application that the gel is synthesized for, the solvent deposition can be different. Different types of dry gels have a variety of applications in coating surfaces, insulation of buildings, special cloths, etc. In the meantime, if the gel is powdered with special mills, particles in the nanoscale can be achieved.

The sol-gel process is a bottom-up synthesis method. In this process, the resulting product contains a number of irreversible chemical reactions. In fact, these reactions result in formation of the primary homogeneous soluble molecules called cells, which turn to an unlimited, heavy, and three-dimensional polymeric molecule called a gel. The hydrolytic reaction, the condensation reaction which follows the hydrolytic reaction, and the final product obtained are summarized in Figure 1.

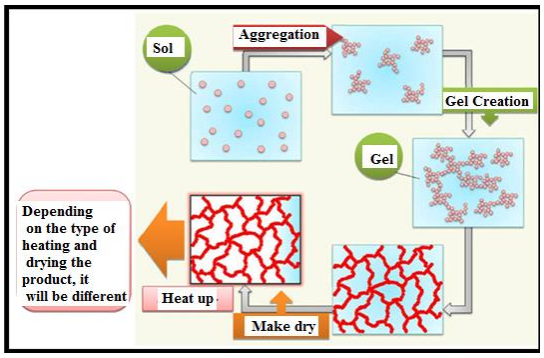


Figure 1. Sol-gel and hydrolysis process

In the sol-gel process, converting a cell to the gel state is often performed by changing the pH or solution concentration. The main reasons for using the cell-gel process are production of a high-purity product, distribution of the fine particle size, and achievement of uniform nanostructures at low temperatures. The sol-gel method is often used to prepare nano-metal oxides.

In a scientific resource, synthetic nanosilica has been synthesized using the mineral compound of sodium silicate, halosilane compounds, and organo-silanes such as tetraethyl ortho-silane or tetraethoxysilane (TEOS) with the formula of $Si(OC_2H_5)_4$ and tetramethoxysilane (TMOS) [21].

Two classes of techniques have been developed for the formation of silica nanoparticles: sol-gel method and micro-emulsion method. The pathway of micro-emulsion is the same as the sol-gel pathway. In these systems, surfactants are added to the nanoparticle cell system. Surfactants create a coating on nanoparticles in a way that the internal core contains nanoparticles and the surface layer of the surfactant. The micro-emulsion pathway is really appropriate for preparation of particles with a small diameter, narrow size distribution, and high surface area [22-23].

Importance of using hydrogen sulfate to be stabilized on nanoparticles

Several reactions such as Friedel-Craft, sterification, aldol condensation, oxidation, etc. are carried out under acidic conditions. In these types of reactions, different acids are used for acidification, including mineral acids such as HCl, H_3PO_4, and H_2SO_4, lewis acids such as $ALCl_3$ and $FeCl_3$, and organic-metal compounds. In the meantime, their application is limited by problems such as lack of easy access, slipping, difficult transportation conditions, high corrosion, and toxicity of most of the minerals.

Therefore, chemists have sought to eliminate the problems of using them by introducing and using compounds that can be a successor to the previous cases in addition to having high acidity. In recent years, the use of metal hydrogen sulfates such as Al, Na, K, Mg, and Fe has been considerably expanded. Hydrogen sulfates are solid compounds, so working with them is easier. These compounds with proper acidity appeared strongly in most reactions, so that in most of the cases, the reactions are performed with very good to excellent efficiency and less byproducts; also, product retrieval is performed through a simple method. In some cases, in the absence of a solvent, it is possible to produce products whose efficiency is even higher than the solution phase and this method has no environmental problems resulted from using the solvent [24-28].

By passing from microscale to nanoscale, some physical and chemical properties are observed, two of the most important of which are: an increase in the ratio of the surface area to volume and the entry of particle size into the domain of quantum effects. Increasing the surface greatly increases the reactivity of nanoscale materials because the number of molecules or atoms in the bulk is very high, so that these particles tend to aggregate. In some cases, in order to maintain the desired properties of the nanomaterials to prevent further reactions, a stabilizer should be

added to resist against erosion, fatigue, and corrosion.

By using these materials in production of nanocomposites, stronger chemical bonds can be formed between the support and particles and their strength is increased. Consequently, transformation of composite into nanocomposite increases strength. On the other hand, increasing the surface of the particles reduces the surface pressure and leads to a change in the distance between the particles and the distance between the atoms of the particles.

Nanomaterial components can have the combined properties of both of the components and act better because of interaction between the support surface and the filler particles. Among these materials, layer silicates and clay particles have been interesting and were studied more because of their availability and harmlessness in the environment. In the meantime, silica has been more interesting due to its smooth structure, high surface area, functionality, and having nanoscale pores [63]. By adding particles, the nanoscale properties of the material will improve when:

(1) there is enough interaction between nanoparticles and the support.

(2) there is proper dispersion of particles between the support.

Due to high importance of synthesizing coumarin derivatives (2-H-chromen-2-one) as a drug, whose biological properties have been mentioned, and since the methods of improving preparation of this compound are being updated, we tried to synthesize some of the 2H-chromium-2-one derivatives in the presence of the catalyst of hydrogen sulfate stabilized on nanosilica particles. This method has a lot of advantages, including environmental compatibility, short reaction time, easy recovery and reuse of the catalyst, and high product efficiency.

The basis of this research is studying the speed and efficiency of the Pechmann condensation reaction to synthesize some of the coumarin derivatives in the presence of sodium hydrogen sulfate catalyst stabilized with nanosilica.

In order to obtain a correct ratio of the catalyst, solvent, and optimal conditions, the resorcinol and ethyl acetoacetate reactions were investigated. In order to optimize the catalyst, various amounts of sodium hydrogen sulfate and nanosilica were mixed and used in successive experiments. The best result was obtained when 0.1 g of nanosilica was mixed with 0.2 g of sodium hydrogen sulfate (Table 1).

Table 1. Optimization of the amount of catalyst components

The amount in gram	Catalyst components
0.1 gr	SiO_2(nano)
0.2 gr	$NaHSO_4$

The size of the nanosilica particle prepared by the sol-gel method was measured by the SEM device and its size was 19.53 nm (Figure 2). After stabilizing sodium hydrogen sulfate on silica nanoparticles, the particle size increased to 27.34 nm, indicating the correct stabilization of sodium hydrogen sulfate on nanosilica (Figure 3).

Figure 2. The SEM image of nanosilica particles

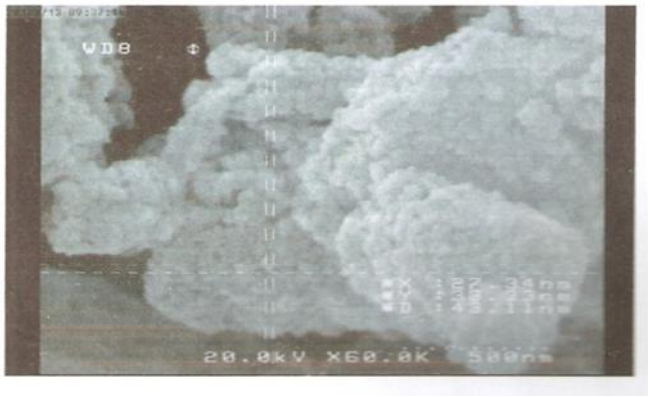


Figure3. The SEM image of nanosilica particles supported by sodium hydrogen sulfate

The general method for synthesizing coumarin derivatives through Pechmann method is as follows (Figure 4).

To select the appropriate solvent for this reaction, several solvents were tested in the presence of 0.3 g of catalyst. Acetonitrile was selected as the optimum solvent with 85% efficiency at 25 min (Table 2).

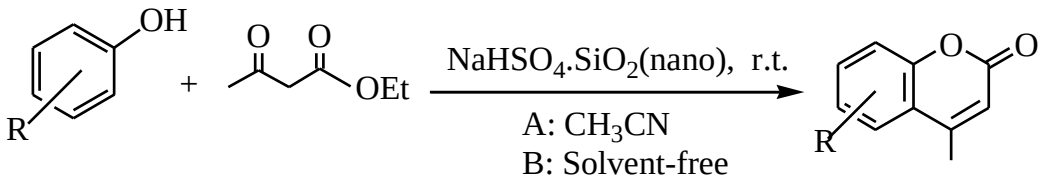


Figure 4. Synthesis of Coumarin Derivatives by Pechmann Method in the Presence of Sodium Hydrogen Sulphate Stabilizad on Nanosilica in Solvent and Solvent-free Conditions

Table2. The optimal condition for solvent

No	Solvent	Reaction Condition	Time (min)	Recovery (%)
1	Dichloromethane	Room Temperature	120	45
2	Acetonitrile	Room Temperature	25	85
3	Ethanol	Room Temperature	45	67
4	Acetone	Room Temperature	-	-
5	DMF	Room Temperature	240	22

The sign (-) indicates that the reaction did not occur

After choosing the solvent, it is time to select the optimal amount of catalyst. Different amounts of catalysts were investigated in an optimum solvent. The reaction efficiency reached its highest value by using 0.05 gr of the catalyst. Any increase or decrease in the optimum amount of catalyst did not have an ascending effect on the reaction speed (Table 3).

Table 3. The optimal conditions for the amount of catalyst in the acetonitrile solvent

No	Reaction Condition	Amount of catalyst (mole percent)	Time (min)	Recovery (%)
1	Room Temperature	0.01	65	85
2	Room Temperature	0.03	35	80
3	Room Temperature	0.05	25	90
4	Room Temperature	0.001	60	45
5	Room Temperature	0.003	120	52

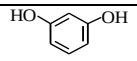
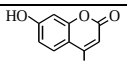
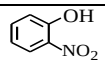
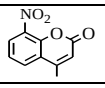
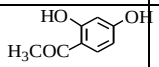
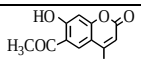
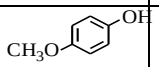
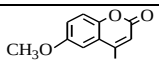
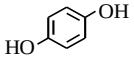
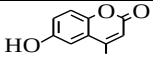
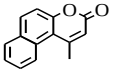
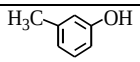
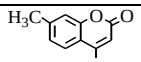
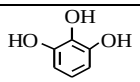
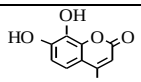
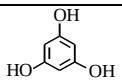
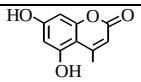
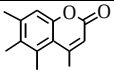
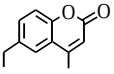
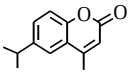
After optimizing the conditions, the reaction of various derivatives of coumarin in optimal conditions was investigated and the results are shown in Table 4. According to the results, this method can be performed with a good to excellent yield for all of the phenolic compounds with electron-donating and electron-accepting groups and even with two or three groups of hydroxyl, and it seems that the above mentioned groups do not considerably affect reaction efficiency. These results show that the effect of a catalyst with nano-substrate and wide surface accelerates preparation of coumarins in a way that the effect of accepting and donating the substitutions is insignificant compared to it.

In Table 5, the efficiency of the method proposed for synthesizing coumarin derivatives has been compared with other published articles. According to table 5, sodium hydrogen sulfate catalyst stabilized with nanosilica provides better time and efficiency at ambient temperature for performing this reaction (Table 5, rows 5 and 6), while other catalysts offer a long time, low yield, and high temperatures (Table 5, rows 1 to 4).

Regarding the mechanism presented in Fig. 5, it seems that the hydrogen sulfate anion stabilized on a vast surface of the nanosilica has a high yield and can simultaneously play double roles. First, it accelerates the tautomeric balance of the enole to ketone and second, it causes adsorption of the electron in the oxygen anion of the carbonyl group in this stage. Then, the ring is closed by attacking of

the electron pair of oxygen to the carbonyl group and removing a water molecule, and in the final step, the final product will be achieved by recovering the catalyst.

Table 4. The results obtained for synthesis of coumarins in the presence of sodium hydrogen sulfate stabilized with nanosilica

No	Raw Materials	Product	With Solvent		Solvent-free		Melting Point	
			Time (min)	Yield[A] (Percent)	Time (min)	Yield[B] (Percent)	Observed	Reported
1			25	85	10	85	187-188	183-189 [29]
2			15	80	8	90	183-184	183-185 [29]
3			30	85	20	80	165-166	164-165
4			35	85	10	85	169-170	165 [29]
5			20	90	8	90	246-247	243-247 [29]
6			35	88	15	90	140-151	154-155 [29]
7			20	85	10	90	181-182	180-181 [29]
8			30	85	15	85	130-132	131-133 [29]
9			40	80	25	85	237-238	236-239 [30]
10			30	95	10	95	280-282	283-284 [29]
11			13	80	8	80	164-165	165-165 [29]
12			10	85	5	85	159-160	160-162 [29]
13			10	80	10	80	167-169	168-170 [29]

A: reaction conditions: Phenol (1 mmol), ethyl acetate (1 mmol), 0.05 gr of catalyst, 3 ml of acetonitrile (under solvent conditions), at ambient temperature; The reaction is carried out in the absence of solvent with the same molar conditions. B: Separation Recovery

Table 5. Comparison of this method with other reported methods for synthesis of coumarins using resorcinol

No	Catalyst	Amount of catalyst (mole percent)	Condition	Time (min)	Recovery (%)	References
1	Oxalic acid	10	Silvent-free/80°C	30	95	[31]
2	Nanoreactors	7	Silvent-free/130°C	120	67	[31]
3	FeF_3	0.05 gr	Ethanol/Reflux	1.5	93	[30]
4	PFPAT	10	Toluene/110°C	180	90	[31]
5	$NaHSO_4$-SiO_2	3	Acetonitrile/Reflx	60	95	[32]
6	NP-HSO_4	0.05 gr	Acetonitrile/Room temperature	22	85	Present study
7	NP-HSO_4	0.05 gr	Solvent-free/Room temperature	10	85	Present study

Conclusion

Due to the high importance of synthesis of coumarin derivatives (2-H- chromen-2- one) as a drug, whose biological properties were mentioned, and since the preparation methods of this compound are improving continuously, we sought to synthesize some of the 2-H-chromen-2- one derivatives in the presence of a hydrogen sulfate catalyzer immobilized on nanosilica particles. This method has several advantages including environmental compatibility, short reaction time, easy recovery, catalyst reuseability (at least 3 times), and high yield.

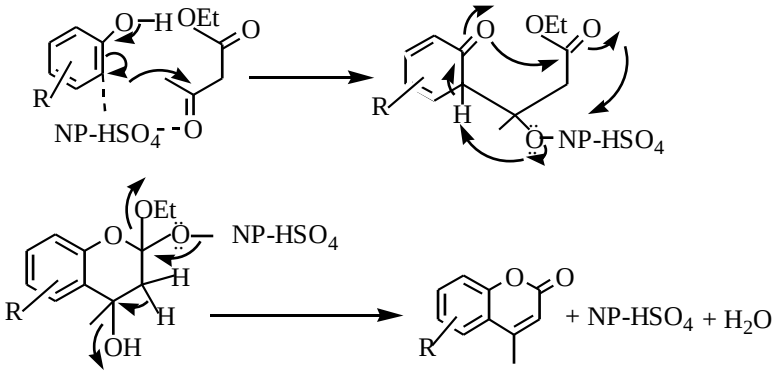


Figure 5. |Preparation mechanism of coumarins using sodium hydrogen sulfate reagent stabilized on nanosilica (NP-HSO_4)

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