**Silica Sulphuric Acid: An Efficient Reusable, Heterogeneous Acidic Media for Synthesis of Flavones (2-aryl-4H-chromen-4-one) by Cyclocondensation of o-hydroxyphenyl aryl-1, 3-propanediones**

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**ABSTRACT**

Cyclocondensation of o-hydroxyphenyl aryl-1, 3-propanediones is a key step for the synthesis of flavones. In this work we report a very simple procedure for this conversion by using reusable, heterogeneous acidic media silica sulphuric acid with high efficiency.

**Keywords:** Cyclocondensation, Flavones, Heterogeneous, o-Hydroxyphenyl aryl-1, 3-propanediones, Silica sulphuric acid.

**INTRODUCTION**

Flavones are widely spread in nature and are having various biological activities. Flavonoid derivatives exhibit antihypertension, antitumour, antioxidant, antifungal, antiallergic, anticoagulative, and vasorelaxant activities. Therefore synthesis of flavones has enormous importance in pharmaceutical field. Flavones are abundant in fruits, vegetables, nuts, seeds, and flowers and are regular part of our diet.

Flavones are synthesized by methods like Allan-Robinson method, Algar-Flynn-Oymanda method, Baker-Venkataraman Rearrangement etc. Cyclocondensation of o-hydroxyphenyl aryl-1, 3-propanediones gives flavone. Generally, this transformation is carried out in acidic media. Some of the reported methods for this cyclocondensation include use of sulphuric acid in glacial acetic acid, CuCl₂ in ethanol, ionic liquid under microwave irradiation, FeCl₃ catalyzed synthesis of flavones at room temperature. Flavones have been synthesized from o-hydroxyphenyl aryl-1, 3-propanediones using many solid phase catalysts like silica supported NaHSO₄ and silica supported Well-Dowson acid catalysts. To the best of our knowledge silica sulphuric acid has not been utilized for the conversion of o-hydroxyphenyl aryl-1, 3-propanediones to flavones.

The use of traditional acidic catalysts like sulphuric, phosphoric acid etc. causes pollution and corrosion in the environment. The use of heterogeneous acid media overcomes these hazards. Silica sulphuric acid has been used as solid acid catalyst for many chemical transformations like synthesis of oxazolines and imidazolines, acetylation of aldehydes and sugars, synthesis of substituted pyroles, Fischer’s esterification, synthesis of benzimidazoles, thionitriles and disulphides. The wide use of this catalyst in chemical reactions is due to the ease of handling, enhanced reaction rate and simple work up in most cases. Silica sulphuric acid is synthesized at room temperature easily by treatment of silica gel with chlorosulphonic acid. Preparation of this acidic media is an easy process and without any work up as HCl gas escapes on addition of chlorosulphonic acid.

Here in we report the use of heterogeneous and reusable acidic media silica sulphuric acid for the synthesis of flavones from cyclocondensation of 1-(2-Hydroxy phenyl)-3-arylp propane-1, 3-dione as delineated in Scheme.

**MATERIALS AND METHODS**

All ¹H NMR (300 MHz) spectra were recorded on Bruker AVANCE spectrometer (Bruker BioSpin AG, Fällanden, Switzerland; 300 MHz). FT-Infrared spectra were recorded on a Perkin Elmer (Model-Frontier) spectrometer (Waltham, MA, USA). Silica gel of commercial source (60–120 mesh) was used for preparation of catalyst. All melting points are uncorrected. A mortar and pestle of porcelain was used for all reactions.

**General procedure for synthesis of acidic media**

Silica gel (60–120mesh) (30.0 g) was taken in two necked round bottom flask. Chlorosulfonic acid (6.0 ml) is added dropwise in 30 minutes time interval. Rapidly generated HCl gas was neutralized by NaOH solution. Once the addition is over, the reaction mixture is shaken for another 30 minutes.

**Reaction**

\[
\text{SiO}_2\text{OH} + \text{Cl}_2\text{O}_7 \xrightarrow{\text{RT}} \text{SiO}_2\text{O}_2\text{O}_7 + \text{HCl}
\]

**Synthesis of compounds 1a to 1j**

Compounds 1a-1j have been synthesized as per literature procedure.

**Synthesis of compounds 2a to 2j**

1-(2-Hydroxy phenyl)-3-arylp propane-1, 3-dione 1a-1j (0.002M) were ground with 5.0 g silica sulphuric acid in a mortar with pestle. Reaction mixture was shaken for some time and kept for 9 hours at room temperature.
Completion of reaction was monitored by TLC. After the completion of reaction, 25.0 ml of ethyl acetate was added to reaction mixture and filtered the mixture to remove the silica sulphuric acid. Ethyl acetate was recovered under reduced pressure to obtain compounds 2a-2j as delineated in Table 1. 

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**RESULTS AND DISCUSSION**

An efficient procedure for the cyclocondensation of 1-(2-Hydroxy phenyl)-3-arylp propane-1, 3-dione under solvent free conditions at room temperature has been described which involves grinding of 1-(2-Hydroxy phenyl)-3-arylp propane-1, 3-dione with silica sulphuric acid media previously prepared by literature procedure. The product is separated just by adding appropriate organic solvent and silica sulphuric acid is recovered by simple filtration of the reaction mixture.

Silica sulphuric acid reuse and recovery

Reusability is one of the important aspects of using heterogeneous media, therefore we tried some experiments for reusability of the silica sulphuric acid. After the completion of the reaction, the product was dissolved in organic solvent and silica sulphuric acid was filtered. Repeated washings with the organic solvent were given to remove the trace amount of product. Silica sulphuric acid was dried at 60°C and again used for the conversion (1a & 1d) to (2a & 2d) respectively, successively five times without significantly affecting its activity as delineated in Table 2.

**CONCLUSION**

In conclusion, the present method for the synthesis of flavones (2-aryl-4H-chromen-4-one) from corresponding 1-(2-Hydroxy phenyl)-3-arylp propane-1, 3-dione is simple, highly efficient and green method. Being mild and eco-friendly method, we can use it as an alternative method to the known literature methods.

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