SYNTHESIS OF 1,3-DIKETONES BY BAKER VENKATARAMAN REARRANGEMENT AND ITS APPLICATION IN THE SYNTHESIS OF FLAVONES.

NAME: ABIGAIL BIBIANA PINHEIRO

ROLL NO: CH-18-064

DISSERTATION (CGO-500)

Project guide: Siddhali .V. Girkar

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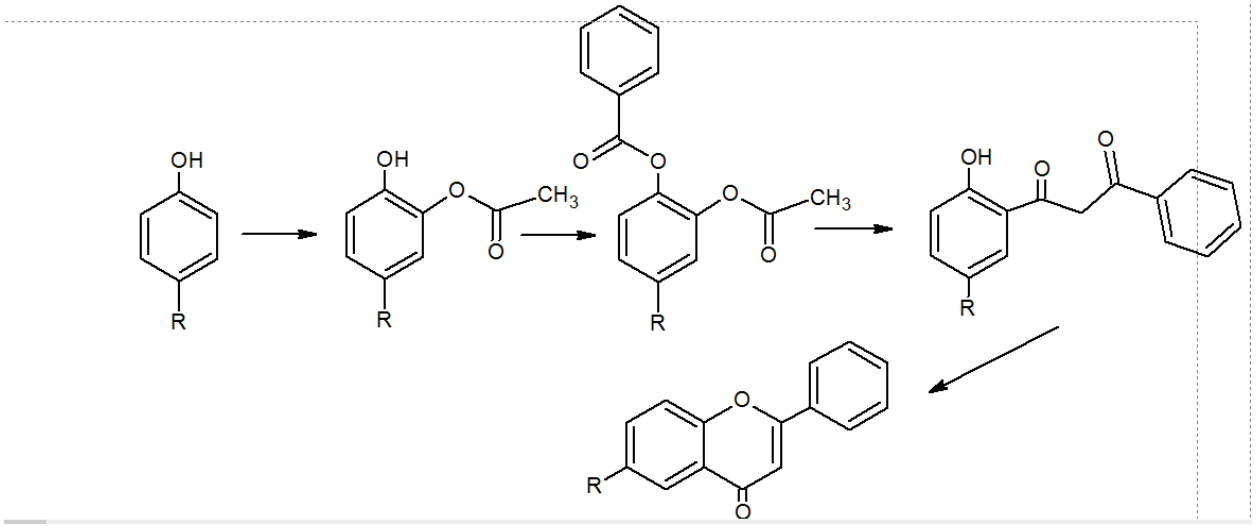
INTRODUCTION

Ortho hydroxyl aryl ketone is a versatile acylated scaffold of biological and medicinal interest. It is the synthetic intermediate in the synthesis of biologically active compounds as well as pharmaceuticals.

General reaction scheme



1, 3-Diketones and ß-keto esters are fundamentally important compounds in synthetic organic chemistry and represent one of the most important class of organic compounds, since they are applied as key structural blocks in organic syntheses, exhibit different kinds of biological activities, and display a broad range of ionophoric properties. These structural motifs are widely represented in natural products, pharmaceuticals, and other biologically relevant compounds in either their native or derivatized form. Included among such compounds, are those having antioxidant, antitumor, antimicrobial, antiviral, and antifungal activity. Till date, there are many reports for the synthesis of 1, 3-diketones by oxidation of aldol-type compounds, hydroxylation of alkynones, oxidative cleavege of 1, 4-dienes, and so on. The method most frequently used for 1, 3-diketone Synthesis is the Claisen condensation, which comprises the C-acylation of the α-position of ketones in the form of their metal enolates, enamines or silyl ethers, with or without a catalyst. To appear as an acylating agent one of the following compounds could be required: acyl halides and acid esters, including formates and oxalates, and acid anhydrides, dialkyl carbonates, methoxymagnesium methyl carbonate, *N*-acylimidazoles, acyl cyanides, and acyl benzotriazoles.

The synthesis of 1, 3-diketones has attracted much interest from synthetic chemists and many advances have been reported in this area.

From the β-diketones, flavones are synthesised. Chalcone is a starting material for the synthesis of flavones. Flavones are important class of flavonoids having wide range of biological activities like antioxidant, anti-inflammatory, anti-oestrogenic, antimicrobial, anti-allergic, antioxidant, vascular, antitumor and cytotoxic activities. First cyclin dependent kinase inhibitor, flavopiridol which is a flavone is approved as orphan drug in Europe for the treatment of relapsed chronic lymphocytic leukemia. So these structural motifs may show potential activity to wide therapeutic conditions. Thereby synthesis of flavone is an important aspect in medicinal chemistry. This flavonoids are found to be naturally occurring in different fruits, vegetables, flowers, grains, bark, roots, stem, tea, etc.

Till now there are 4000 and more flavonoids present. They are known as secondary metabolites, and act as a defender against predator, parasites in plants. They are also found to be responsible for attractive colours in flower, fruits and leaves. Using different substituted 1,3-diketones were prepared.

The synthesis involves the solvent-free solid state trituration methods involved Claisen-Schmidt reaction between acetophenone derivatives and substituted benzaldehydes in the presence of NaOH. Flavones (flavus=yellow), are a class of flavonoids based on the backbone of 2-phenylchromen-4-one. They are mainly found in cereals and herbs. Chalcones and dihydrochalcones are classes of flavonoids that consist of two phenolic groups which are connected by an open three carbon bridge.

Flavones are biologically active compounds. It is an important class of naturally occurring heterocyclic compounds belonging to the flavonoid group. These exhibit a wide range of biological properties such as antioxidant, anti-infective, anti-inflammatory, anticancerous etc. Due to these profound biological activities, there is a continued interest in developing new synthetic approaches for their synthesis, a number of methods are available for the preparation of flavones but still, their preparation from ß-diketones *via* Baker-Venkataraman is the most accepted method. This method consists of cyclodehydration of ß-diketones to flavones which is an acid reaction.

The crutial feature of 1, 3 diketones is keto-enol tautomerism, the presence of the keto and enol form in equilibrium.

Properties of flavones include yellow solid, soluble in water, ethanol and dilute acid. They precipitate out with lead salt.

ADVANTAGES

The formation of 2-aroyloxyacetophenones/ 2-cinnamoyloxyacetophenones followed by their Baker-Venkataraman rearrangement takes place simultaneously in a single step. It is a green procedure as it avoids the use of organic solvents at any stage of the reaction.

DISADVANTAGES

Only a limited number of procedures for a direct synthesis of 1, 3-diketones from ketones has been reported, because 1,3-diketones synthesized from acid chlorides or esters with various metal enolates of ketones have a problem in their chemoselectivity owing to the higher acidity of the R-hydrogen of 1,3diketones than that of starting ketones.

In addition, the regioselectivity also became a problem, when metal enolates of aliphatic ketones were used as starting materials which have R-hydrogens at both sides of the carbonyl group.

USES OF β-DIKETONES & FLAVONES

Due to the presence of two carbonyl groups β-diketones are valuable substrates in many chemical syntheses.

A) For the preparation of ketoimines by condensation with amines

B)Thioketones and various heterocyclic compounds (pyrimidine derivatives).

They are often used as catalysts of reactions such as olefin oxidation and epoxidation.

They are employed as fuel additives.

Owing to their complexing properties, they have also been used in environmental protection e.g. for metal chelation in sewage.

1, 3- diketones are used in the perfume and cosmetic industries or as a chelating agent in the solvent extraction of metals.

In addition to their biological significance, 1, 3-diketones and β-keto esters are used to facilitate many other highly useful synthetic transformations, including alkylation reactions and the preparation of heterocycles.

Flavones exhibit a wide range of functions in physiology, biochemistry, and ecology

In UV-protection, flower coloration, interspecies interaction, and plant defence. Moreover, for a long time flavonoid pattern are useful tools in phylogenetic studies. Other highly remarkably properties of certain flavonoids are their nutritional values and medicinal benefits to humans, represented among others by antioxidant, anticancer activities.

Ways to synthesis:

There are two ways of synthesizing o-hydroxy aryl ketones:

a) Conventional (Fries Rearrangement)
b) Green method (microwave)

Fries rearrangement is named after German scientist Karl Theophil Fries. The rearrangement involves transformation of aryl ester into ortho and para carbonyl compounds in the presence of Lewis acid $AlCl_3$. It involves the use of acid chloride or acid anhydride as acylating agent.

Green method involves the use of microwave chemistry. Microwave chemistry is science of applying microwave radiation to chemical reactions. It helps in providing uniform and selective heating accelerating reaction rate. Green method involves use of different aliphatic acids and Lewis acid as catalyst.

Further the hydroxyl aryl ketone is converted into 1, 3-diketone which involves Baker-Venkataraman Rearrangement. It is named after the scientist Wilson Baker and Krishnaswamy Venkataraman. The rearrangement involves the reaction of 2-hydroxy acetophenone with base to form 1, 3-diketone via intramolecular acyl transfer. The 1, 3-diketone is found to exhibit varying degree of pharmacological activities like anti-bacterial, antiviral, antioxidant antitumor, sunscreen agent. This 1, 3-diketone is a major substrate in the synthesis of flavones chemistry.

LITERATURE REVIEW:

SYNTHESIS OF 1, 3 diketones

For the synthesis 1, 3 dikeones several research papers were reviewed. These include:

a)Solid phase Baker-Venkataraman rearrangement solvent-free condition using grinding technique.

A very simple and highly efficient eco-friendly procedure for Baker_Venkataraman rearrangement has now been developed which involves the grinding of 2-aryloxyacetophenones/2-cinnamoyloxyacetophenones with pulverized potassium hydroxide in a mortar by a pestle and avoids the use of organic solvents at any stage of the reaction.

In this paper the reaction is generally carried out by heating 2-aryloxyacetophenones with pulverized potassium hydroxide in pyridine medium or by heating with barium hydroxide in dimethyl sulfoxide medium. The above transformation was also carried out in aqueous benzene biphase medium using phase transfer catalysis. Other bases which have been used for this rearrangement include sodamide and sodium hydride. Much emphasis has being placed on the development of the procedures which avoid the use of hazardous and toxic chemicals. In continuation of the work to develop the green procedures for the organic reactions under solvent-free conditions, a simple and efficient procedure for the Baker-Venkataraman rearrangement which involves the grinding of 2-aryloxyaceto-phenones with pulverized potassium hydroxide under grinding conditions in a mortar and pestle at room temperature in the absence of any solvent (Scheme 1). The moisture absorbed by the potassium hydroxide appeared to be sufficient for the formation of a homogeneous mixture and the reaction requires a very short duration (15 min.) for completion. The product was recovered simply by acidification of the reaction mixture in cold water. Attempt was also made using other bases such as barium hydroxide, calcium hydroxide, and calcium oxide which proved to be futile. (Dinesh Sharma, 2009).

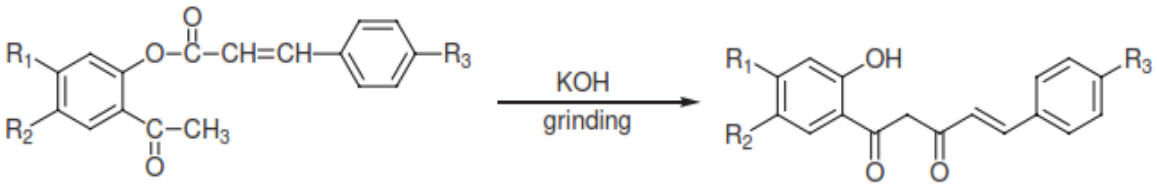


Figure 1 General procedure for the synthesis of 2-hydroxybenzoylcinnamoylmethanes.

b) A highly efficient one step green procedure for baker Venkataraman rearrangement in aqueous medium.

This paper describes a green synthesis route. A highly efficient procedure for the synthesis of 2-hydroxydibenzoylmethanes and 2-hydroxybenzoylcinnamoylmethanes is described.

2-Hydroxyacetophenones on reaction with aroyl chloride/ cinnamoyl chloride and potassium carbonate homogenized with few drops of water on microwave irradiation give required ß-diketones directly. This is a single step process and it does not involve the use of any solvent throughout the reaction.

Use of microwave heating has been employed in a number of reactions in this paper where water is being used as a solvent.

A highly rapid aqueous mediated one step green synthesis of these 2- hydroxyl dibenzoylmethanes and 2-hydroxybenzoylcinnamoyl methanes has been reported.

A mixture of substituted 2-hydroxyacetophenone aroyl chloride/ cinnamoyl chloride and potassium carbonate homogenized with 8-10 drops of water was subjected to microwave irradiation for 30 sec. The completion of reaction was checked by thin layer chromatography. The reaction mixture was diluted with ice cold water, acidified with conc. HCl (pH 5.5- 6.0), solid that separated was filtered, washed with water and recrystallized from aqueous ethanol to afford 2-hydroxydibenzoylmethane/2-hydroxybenzoylcinnamoylmethane. (Makrandi, 2012)

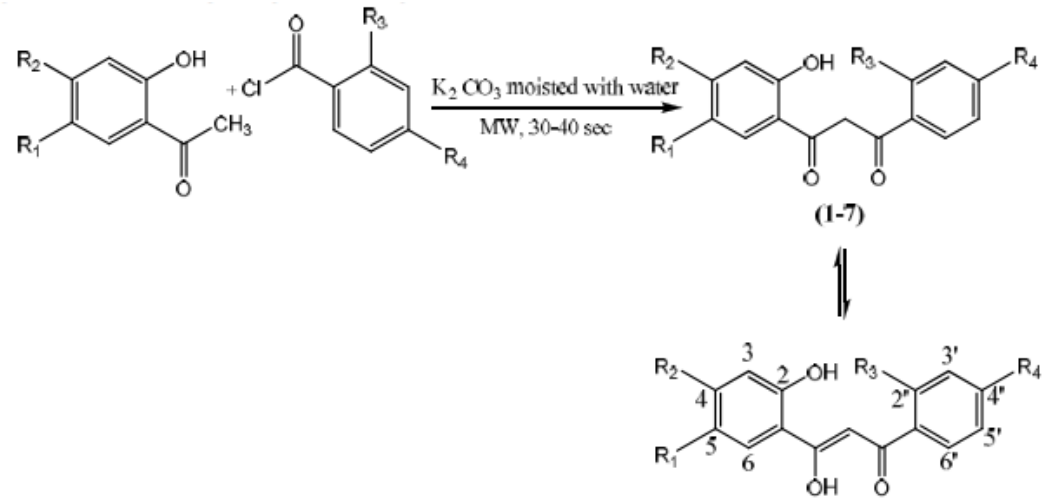


Figure 2 Synthesis of 2-hyroxydibenzoylmethanes

c) Direct Synthesis of 1,3-Diketones by Rh-Catalyzed Reductive α -Acylation of Enones.

1, 3-Diketones were synthesized from α,β-unsaturated ketones by treatment with acid chlorides and Et_2Zn in the presence of $RhCl(PPh_3)_3$. This is a very simple and extremely chemoselective reaction to give the adduct at the α-position of α, β-unsaturated ketones.

This paper also throws light on a simple and novel synthesis of 1, 3-diketones using a Rh catalyst.

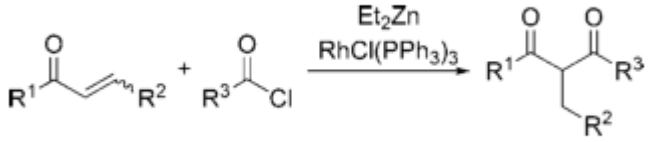


Figure 3 General eaquation for synthesis of 1,3-diketones

In the Rh-catalyzed R-fluoroalkylation, we found that a rhodium hydride complex, which formed from $RhCl(PPh_3)_3$ with Et_2Zn, played an important role, and clarified the reaction mechanism by using a deuterated Zn reagent.

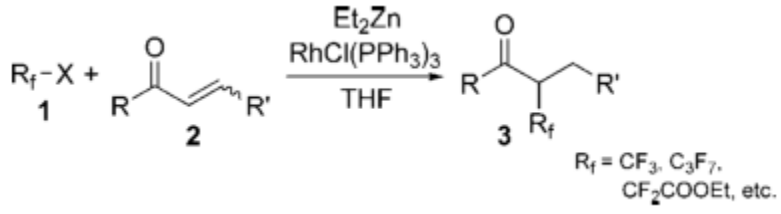


Figure 4: Rh-Catalyzed α-Fluoroalkylation Reaction

Based on this result, it was expected that if the reaction would proceed by using acid chloride instead of R1-X, the acyl group could be introduced at the R-position of α, β -unsaturated ketones to give the 1,3-diketones reductively (Equation5). Using the previous condition, this reaction of methyl vinyl ketone with benzoyl chloride was examined As expected, the reaction proceeded and gave the desired product in a moderate yield. (Kazuyuki Sato, 2008).

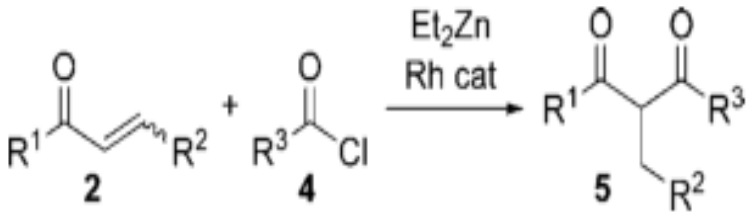


Figure 5 Rh-Catalyzed Reductive α-Acylation of α,β -unsaturated ketones.

d) Synthesis of 1,3-Diketones and #-Keto Thioesters via Soft Enolization.

This paper sites the reaction in which ketones and thioesters undergo soft enolization and acylation using crude acid chlorides on treatment with $MgBr_2 \cdot OEt_2$ and *i*-Pr_2NEt to give 1, 3-diketones and keto thioesters, respectively. This report also shows that the use of crude acid chlorides adds efficiency and cost reduction by avoiding the need to purify and/or purchase them. The process was conducted in a direct fashion that does not require prior enolate formation, further enhancing its efficiency and making it very easy to carry out. The method is suitable for large scale applications. (Sabrina O. Aderibigbe, 2019).

Synthesis of 1, 3 diketones was carried out using carboxylic acid as starting materials.

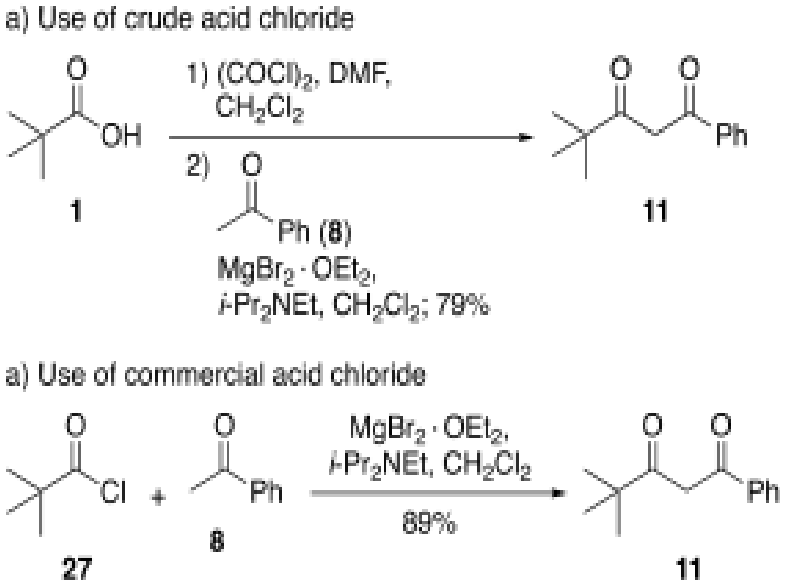


Figure 6 synthesis of 1,3 diketones using carboxylic acid and acid chloride.

e) Solvent-Free Synthesis of Functionalized Flavones under Microwave Irradiation.

The microwave-assisted synthesis offers considerable advantages over conventional heating because of rapid heating and substantial rate of a wide range of organic reactions. Cleaner reactions are also commonly achieved, together with improvement in yield and selectivity. The increasing demand of clean and efficient chemical synthesis makes solvent-free reactions, which when combined with microwave irradiation give a more eco-friendly approach required from both economic and environmental standpoints. It is because of with this demand that different reports on the use of microwaves to enhance several solvent-free reactions have been published by our group. Recently there have been several reports on the application of microwave irradiation to the synthesis of flavonoids and 4-substituted coumarins; however, no attention has been paid to the development of a two-component single-stepped reaction reported the reaction between phenols and α-ketoesters to yield flavones under very harsh conditions (250 °C for long reaction times) and extended this method to a wide number or flavones, despite the low yield in these thermal cyclocondensations. (Julio A. Seijas, 2004).

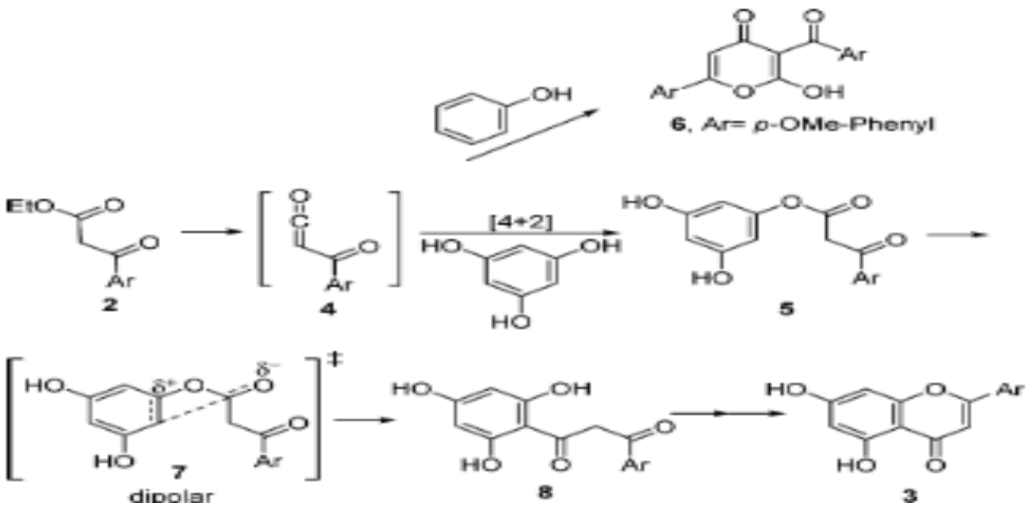


Figure 7 synthesis of flavones from 1,3-diketones.

The experimental setup is always simple, just mixing the phenol and the α-ketoester in an open test tube and irradiating with microwaves (800 W output) without any solvent or solid. Reactions can be performed either under temperature control (240 °C) with no significant differences in reaction times or yields.

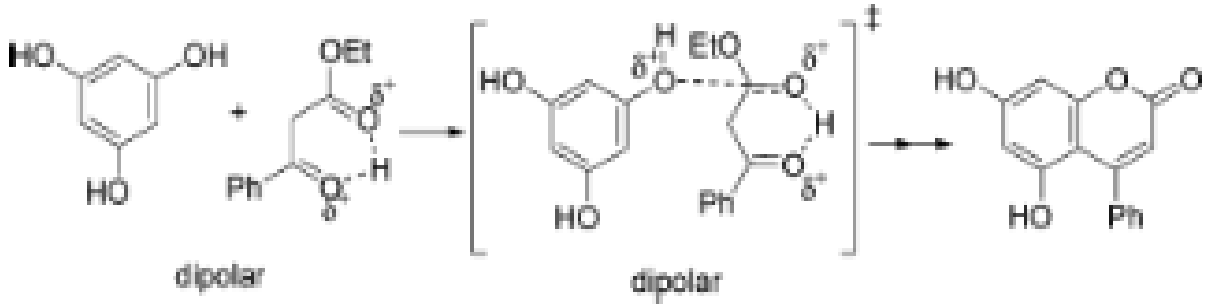


Figure 8 synthesis of flavones from 1,3-diketones

In summary, in this report they developed an efficient solvent free method for the synthesis of flavones, where the irradiation with microwaves proves to be an efficient enhancer for the access to these bioactive compounds.

f) Synthesis of flavones from 2-hydroxy acetophenone and aromatic aldehyde derivatives by conventional methods and green chemistry approach.

The reaction of 2-hydroxy acetophenone with substituted aromatic aldehydes produced chalcone by trituration (NaOH) and conventional methods (KOH/EtOH), which upon further cyclization with dimethyl sulfoxide/I2resulted to form flavone derivatives.

The purity of compounds was ascertained by melting point and thin-layer chromatography. The synthesized compounds was characterized by mass, infrared, and ^{1}H nuclear magnetic resonance spectral analysis.

In general, chalcones were prepared by Claisen-Schmidt condensation of electrophilic substituted benzaldehyde with substituted acetophenone as nucleophile in the presence of bases such as NaOH, KOH, Ba(OH), LiOH, NaH, hydrotalcites, Zeolites, Na_2CO_3 K_2CO_3 , magnesium t-butoxide, alumina, MgO, KF/natural phosphate, calcined NaNO-natural phosphates, and piperidine. Chalcones are also prepared by ultrasonic vibration and microwave irradiation techniques [17-19]. Green chemistry is the need of the day and hence it was planned to synthesize some chalcones in an eco-friendly way without using solvents.

The remaining chalcone was planned to synthesize by taking KOH as a base. Using these chalcone derivatives, it was contemplated to synthesis some flavone derivatives from the corresponding chalcone by using dimethyl sulfoxide (DMSO)/I_2**.** (Charotar University of Science and Technology, 2016)**.**

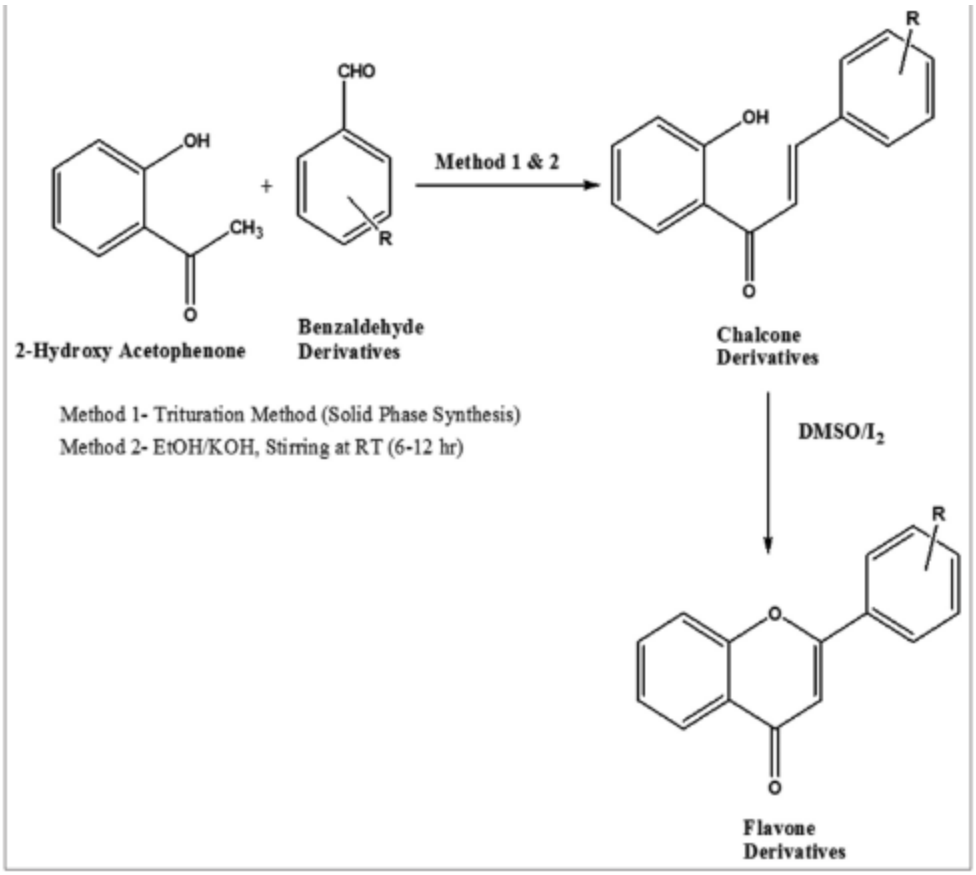
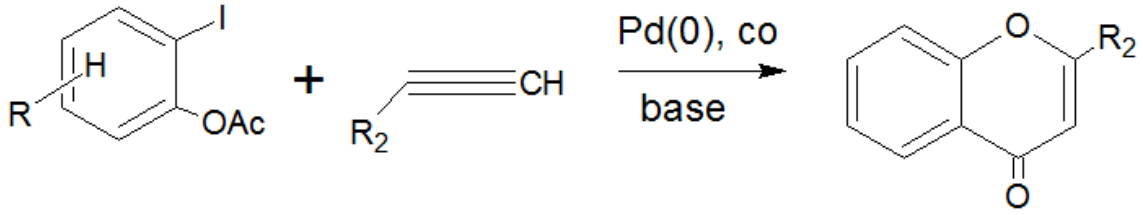


Figure 9 Synthesis of chalcones by trituration and conventional method and flavones.

Basic reactions for the synthesis of flavones:

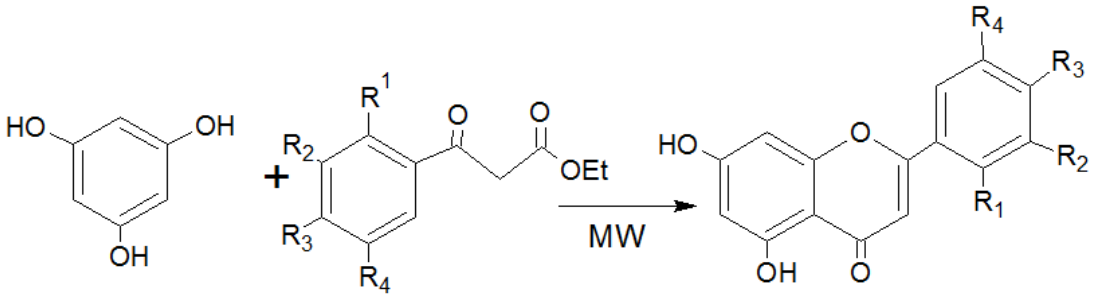
g) Palladium catalysed symthesis is carried out in the presence of basic environment by Hua and Yang,

Regiospecific carbonylative annulation of o-iodophenol acetates and acetylenes mediated by palladium-thiourea-dppp complex in the presence of base at 40^0C under a ballon pressure of CO generates diversified flavones in high yields. This newly developed synthetic technology provides highly efficient method for potential application to the combinatioral synthesis of those heterocycles on the solid support.



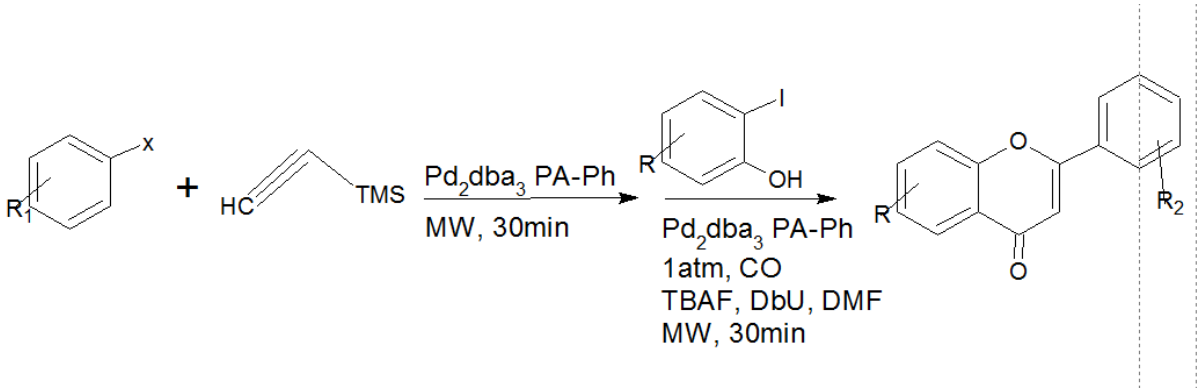
h) Solvent free synthesis flavones is carried out by Julia & co-workers.

Eco-friendly direct solvent-free synthesis of flavones is achieved by microwave irradiation of phloroglucinol and beta-ketoesters. Heating with microwave under classical conditions was shown to be higher yielding, cleaner and faster. The reaction goes through a cycloaddition of an alpha-oxo ketene intermediate followed by uncatalysed thermal Fries rearrangement.



i) Flavones via a micro-assisted, one pot Sonogashira carbonylation annulations reaction used by E. Awuah& A. Capretta.

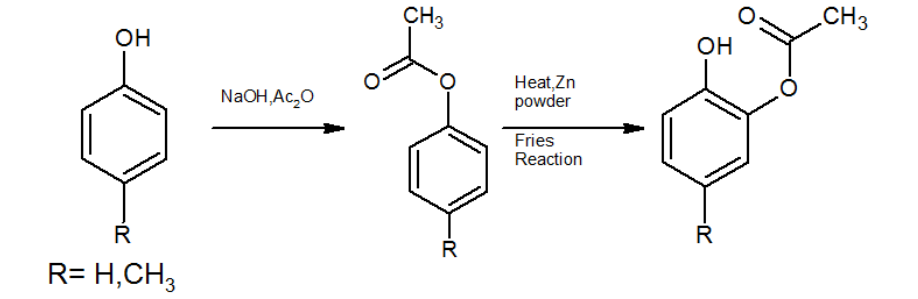
Palladium complexes of 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane are shown to be effective catalytic systems facilitating the sequential application of a microwave-assisted Sonogashira and carbonylative annulations reaction for the preparation of substituted flavones.


X
R1
+
HC
TMS
Pd2dba3 PA-Ph
MW, 30min
I
R
OH
Pd2dba3 PA-Ph
1atm, CO
TBAF, DbU, DMF
MW, 30min
O
R
R2
O

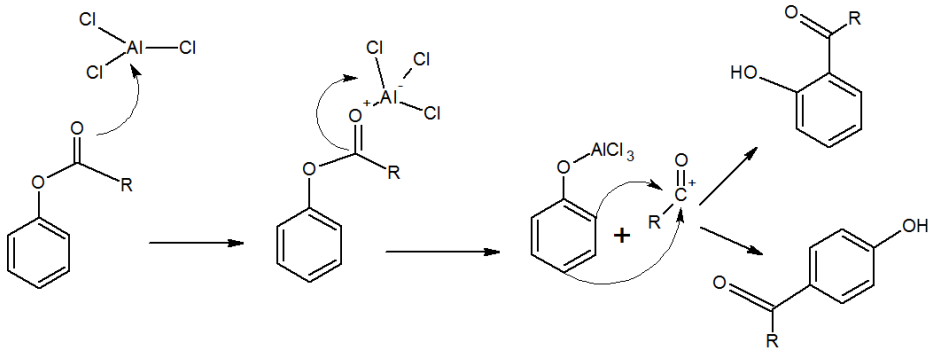
PRESENT WORK

Wide range of biological property of flavones has resulted intense synthetic efforts towards the synthesis of various flavones. There are a number of methods reported for the synthesis of flavones in the literature. Many publications in the literature having been illustrating different synthetic strategies of flavones, but a majority of these methods fall into the category of either oxidative cyclization of various substituted 2-hydroxychalcones or cyclodehydration of substituted 1-(2-hydroxyphenyl-1,3-dione using glacial acetic acid and sulphuric acid.

Step 1: o-acylation of different phenols



MECHANISM:



Procedure I: (for 4-bromophenol, o-cresol, 4-chlorophenol).

Different phenols were acylated in the presence of NaOH and acetic anhydride to give different p-substituted phenyl acetates. This esters when heated under oil bath conditions in the presence of Zn powder as a catalyst gave different p-substituted o-hydroxy acetophenones.

Procedure II:ultrasonication method. (for resorcinol, o-nitrophenol, p-nitrophenol.

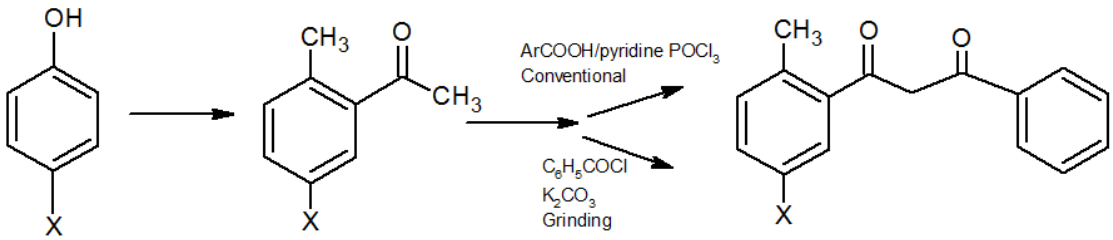
A mixture of substituted phenol, acetic acid and methane sulphonic acid was irradiated under sonochemical conditions at 33KHz for 1-2minutes. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was poured in cold water and extracted with chloroform. After evaporating the solvent the hydroxylacetophenone was obtained.

Procedure III:Conventional method for synthesis of resacetophenone using $ZnCl_2$. (for resorcinol).

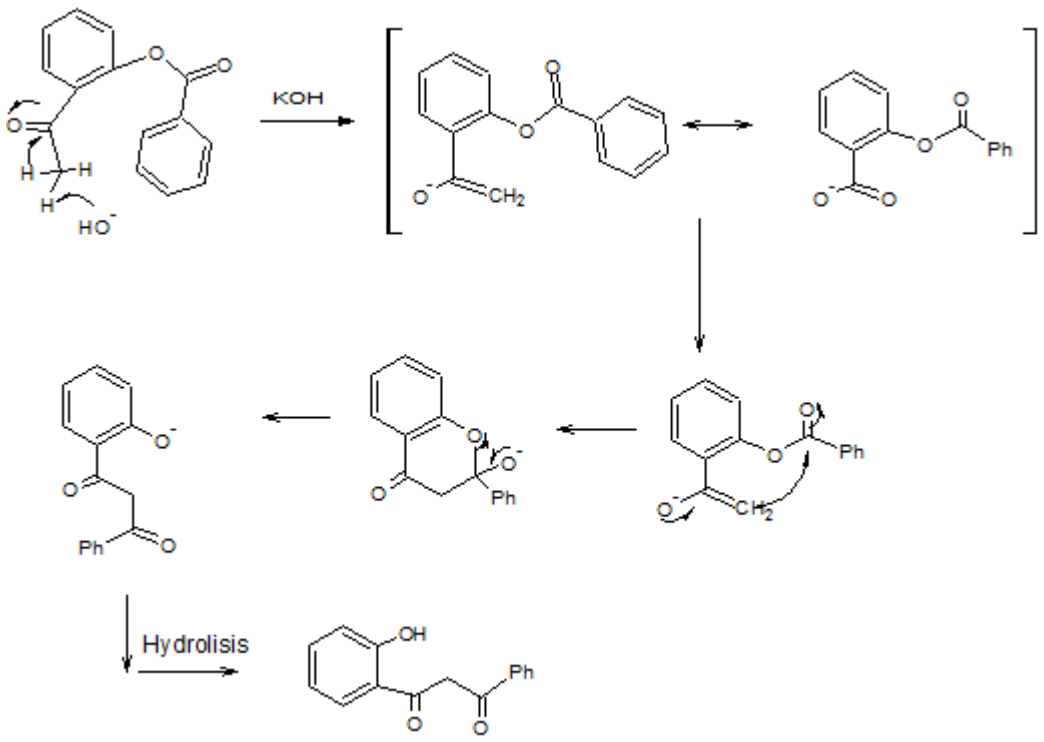
Anhydrous $ZnCl_2$ was dissolved with the help of heat in glacial acetic acid which had been placed in the beacker. To this hot mixture resorcinol was added with constant stirring. The solution was heated on a sand bath until it just began to boil. The flame was removed and the reaction was allowed to complete itself at a temperature not in excess of 159^{o}C after standing on the sand bath without further heating for 20 minutes. The solution was diluted with a mixture of conc. HCl and water. The dark red solution was placed in an ice bath and cooled. The resulting precipitate was collected and washed from Zn salt with 1:3 HCl in three times.

Step 2: Conversion of different substituted o-hydroxyacetophenone into 1,3-diketone.

Procedure I:

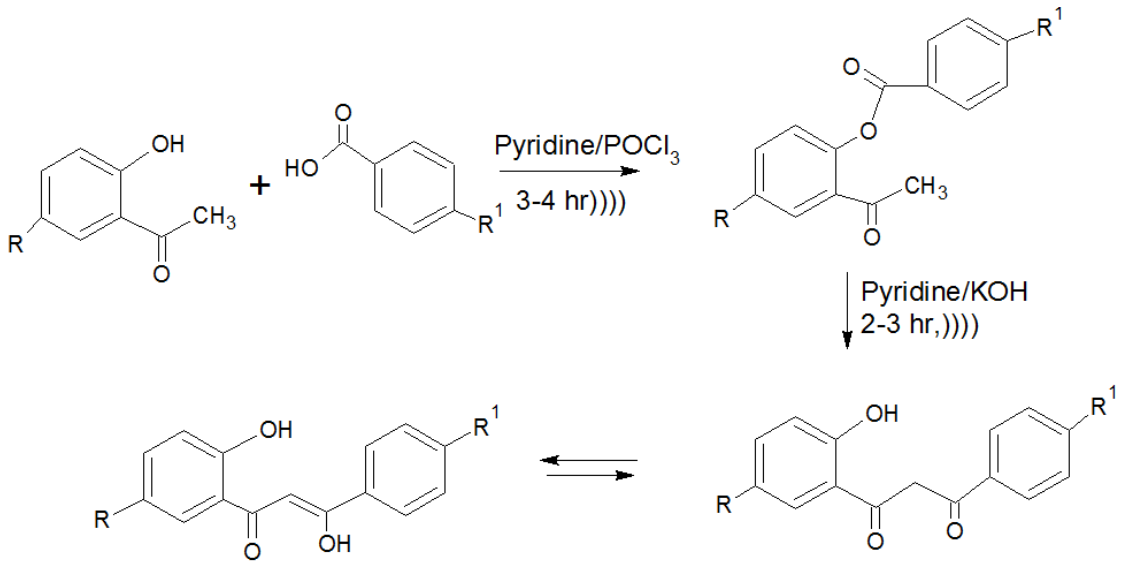


MECHANISM:



In the first step different substituted o-benzoloxy acetophenone were synthesized from reaction of different p-substituted o-hydroxy acetophenone with benzoyl chloride in the presence of dry pyridine. In the second step o-benzoyloxy acetophenone and dry pyridine were warmed and powdered KOH was added. The mixture was stirred and on acidification gave o-hydroxybenzoylmethane.

Procedure II:



a) Preparation of acetylphenyl benzoate.

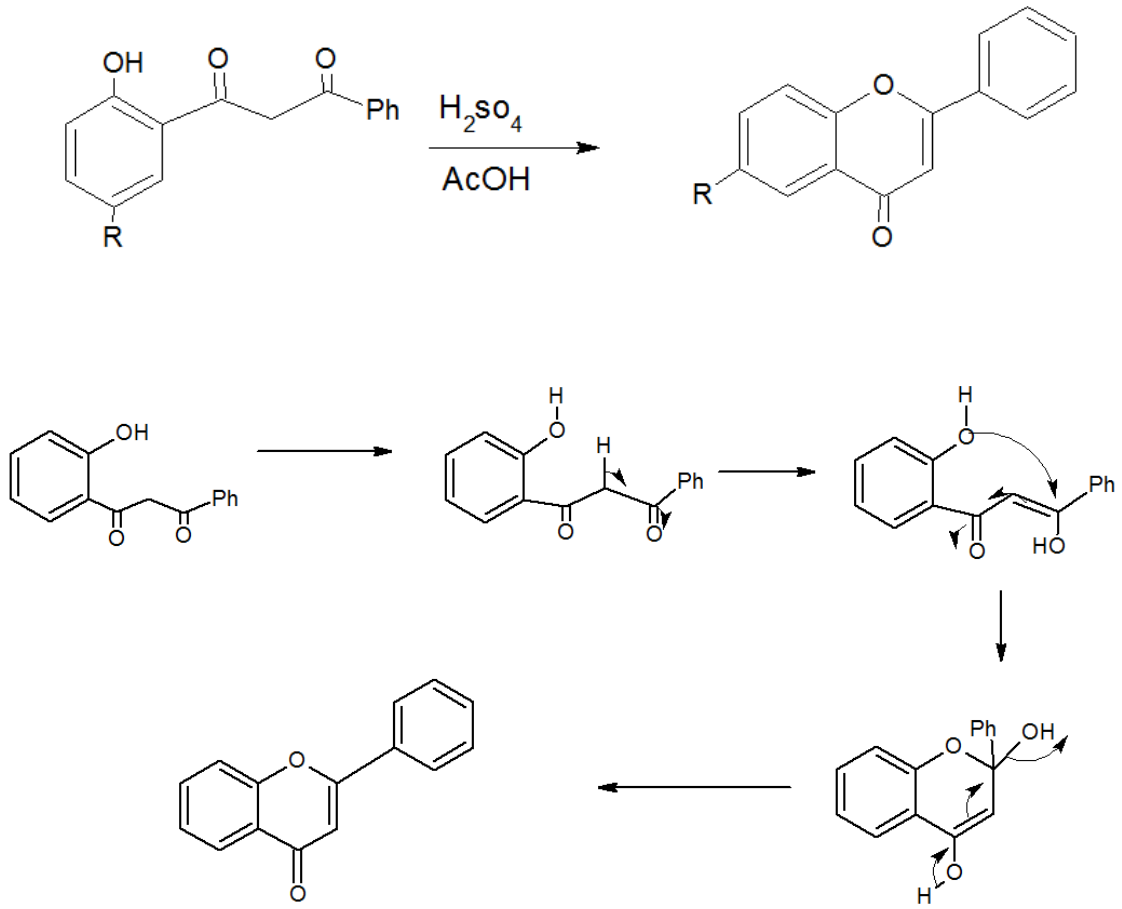
To a mixture of o-hydroxyacetophenone and 4-methoxy benzoic acid dry pyridine and $POCl_3$ were added dropwise with constant stirring at 0^oC. The reaction mixture was irradiated for about 4hrs under ultrasound. After completion of the reaction the reaction mixture was poured in HCl containing crushed ice and the solid obtained was filtered and washed with ice cold methanol and then water.

b) Preparation of 1, 3- diketone.

Compound obtained was dissolved in dry pyridine. To this powdered KOH was added and the reaction mixture was irradiated for 3hrs under ultrasound. After completion of the reaction the reaction mixture was poured in ice cold water and acidified with conc.HCl. The product obtained was filtered off and recrystallised to obtain pure product.

Step3: cyclisation of 1,3-diketones to flavones

The 1, 3-diketone was refluxed with glacial acetic acid and concentrated sulphuric acid for about an hour to obtain the final product flavones. The product was recrystallised using water.


OH
O
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H_2so_4
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Ph
HO
Ph
OH
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H
O

EXPERIMENTAL WORK:

a) O-acylaiton of phenols

Procedure I: (for 4-bromophenol, o-cresol, 4-chlorophenol).

1g of different phenols in 5mL of 10% sodium hydroxide solutions were taken in 50 mL round bottom flask. To this 10.0 g of crushed ice and 1.1 mL of acetic anhydride were added. The mixture was vigorously mixed for about 15 minutes. The ester separated out as colourless crystals which were washed with water. The product was recrystallised.

Procedure II:ultrasonication method. (for resorcinol, o-nitrophenol, p-nitrophenol.

A mixture of 5mmol of substituted phenol, 1mL of acetic acid and 0.5mmol of methane sulphonic acid was irradiated under sonochemical conditions at 33KHz for 1-2minutes. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was poured in cold water and extracted with chloroform. After evaporating the solvent the hydroxylacetophenone was obtained.

Procedure III:Conventional method for synthesis of resacetophenone using $ZnCl_2$. (for resorcinol).

7.5g of anhydrous $ZnCl_2$ was dissolved with the help of heat in 7.5mL of glacial acetic acid which had been placed in a 250mL beaker. To this hot mixture 5g of resorcinol was added with constant stirring. The solution was heated on a sand bath until it just began to boil. The flame was removed and the reaction was allowed to complete itself at a temperature not in excess of 159^{o}C after standing on the sand bath without further heating for 20 minutes. The solution was diluted with a mixture of 11.35mL of conc. HCl and 11.35mL of water. The dark red solution was placed in an ice bath and cooled. The resulting precipitate was collected and washed from Zn salt with 1:3 HCl in three times.

b) Fries rearrangement

Procedure I:

Substrate (5mmol), zinc powder (5mmol) and N,N- DMF(2.5mmol) were taken in a borosil beaker(50 mL). The mixture was mixed properly with the help of a glass rod and placed in a

pre-heated oil bath for the approximate time and at the specified temperature. The reaction mixture was cooled to room temperature and diluted with DMF (5ml). Tt was filtered with ice cold water (100mL) was added to the filtrate. The product was obtained by recrystallisation with ethyl acetate.

To this 1.5mL of benzoyl chloride was added and swirled. 1,6g of K_2CO_3 was added. Further the mixture was homogenized with 8-10 drops of water and heated under microwave radiation for 30seconds. The mixture was diluted with ice cold water and acidified with HCl. After addition the solid separated out and it was filtetred using water.

Procedure II:

a) **Preparation of acetylphenyl benzoate.**

To a mixture of 1.36g of o-hydroxyacetophenone and 1.52g of 4-methoxy benzoic acid 5mL of dry pyridine and 1mL of $POCl_3$ were added dropwise with constant stirring at 0^oC. The reaction mixture was irradiated for about 4 hrs under ultrasound. After completion of the reaction the reaction mixture was poured in 100mL HCl containing crushed ice and the solid obtained was filtered and washed with 10mL of ice cold methanol and then water.

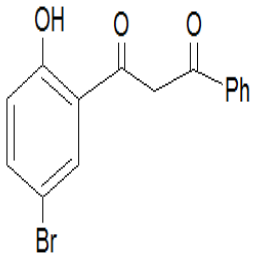
b) **Preparation of 1,3- diketone.**

Compound obtained was dissolved in 10mL of dry pyridine. To this 1.12g of powdered KOH was added and the reaction mixture was irradiated for 3 hrs under ultrasound. After completion of the reaction the reaction mixture was poured in ice cold water and acidified with conc.HCl. The product obtained was filtered off and recrystallised to obtain pure product.

RESULTS AND DISCUSSION

The following compounds were synthesized and analysed by IR spectroscopy and physical constants determined.

1.



IUPAC name: 1-(5-bromo-2-hydroxyphenyl)-3-phenylpropane-1,3-dione

Nature: white solid

Melting point: 100^{o}C-103 ^{o}C

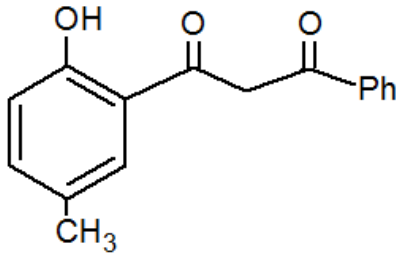
IR spectra: (KBr)cm-1: 3200cm-1 (O-H stretch), 1700(carbonyl C=O), 1600cm-1 and

1450cm-1 (aromatic C=C), 690cm-1-515cm-1 (C-Br).

2. p-chlorophenol only o-acylation product formed.

3. 4-aminophenol o-acylation product not formed.

4.



IUPAC name: 1-(2-hydroxy-5-methylphenyl)-3-phenylpropane-1,3-dione

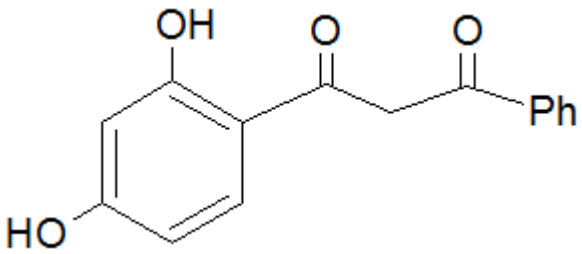
Nature: yellow solid

Melting point:88^{o}C

Yield: 90%

IR spectra details (KBr), cm-1: 3000cm-1 (0-H stretch), 1690cm-1 (C=O), 1590cm-1 and 1460cm-1 (aromatic C=C).

5.

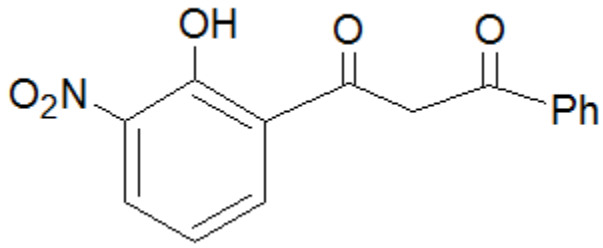


IUPAC name: 1-(2, 4-dihydroxyphenyl)-3-phenylpropane-1,3-dione

Melting point: 120 ^{o}C

IR spectra: (KBr) cm-1: 3200cm-1 (O-H stretch), 1700(carbonyl C=O), 1600cm-1 and 1450cm-1(aromatic C=C), 690cm-1-515cm-1.

6.



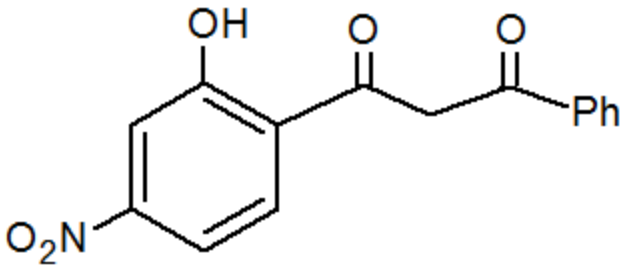
-

IUPAC name: 1-(2-hydroxy-3-nitrophenyl)-3-phenylpropane-1,3-dione

Melting point: 107 ^{o}C -110 ^{o}C

IR spectra: (KBr) cm-1: 3200cm-1 (O-H stretch), 1700(carbonyl C=O), 1600cm-1 and 1450cm-1(aromatic C=C), 1600cm-1- 1400cm-1 (C-NO_2 stretch).

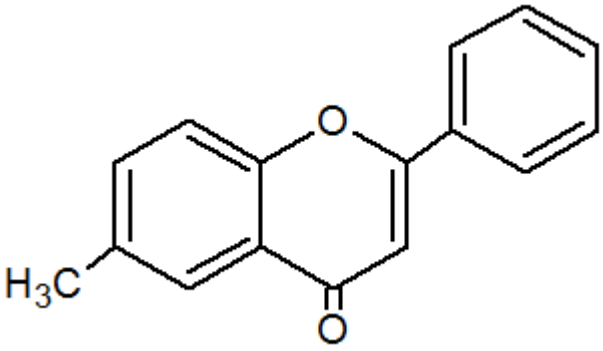
7.



IUPAC name: 1-(2-hydroxy-4-nitrophenyl)-3-phenylpropane-1,3-dione

IR spectra: (KBr) cm-1: 3200cm-1 (O-H stretch), 1700(carbonyl C=O), 1600cm-1 and 1450cm-1(aromatic C=C), 1600cm-1- 1400cm-1 (C-NO_2 stretch).

8.



IUPAC Name: 6-methyl-2-phenyl-4*H*-1-benzopyran-4-one

Nature: white solid

Melting point: 119^0C

Yield: 85%

IR spectra details (KBr) cm-1: 1590cm-1 and 1450cm-1(aromatic C=C stretch), 1700cm-1(carbonyl C=O stretch), 1200cm-1 (C-O stretch).

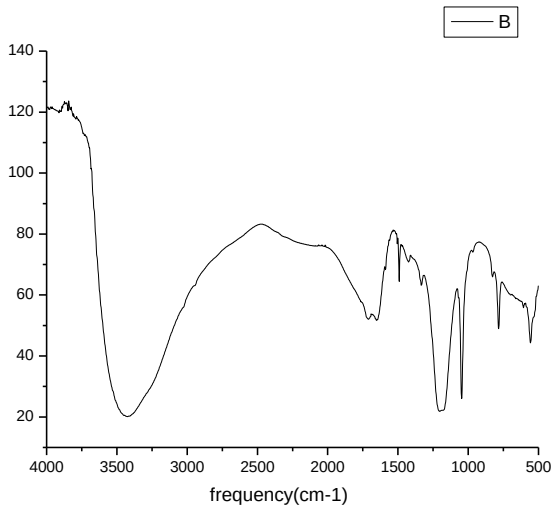
CONCLUSION:

In this study we reported the synthesis of hydoxy aryl ketone by using different substituted phenols via Fries rearrangement. Further the synthesis of 1, 3-diketone using the traditional Baker-Venkataraman rearrangement via conventional and green method. Out of which green method was found to give good yield with high purity. These were characterized using IR spectroscopy.

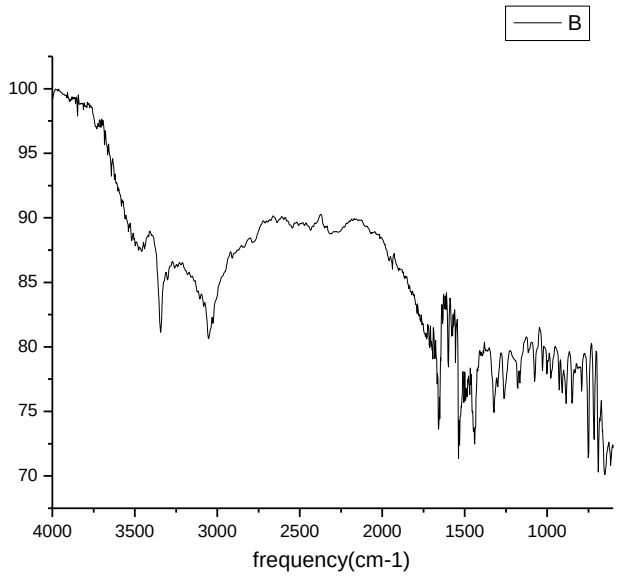
SPECTRAL ATTACHMENTS:

o-acylation products of:

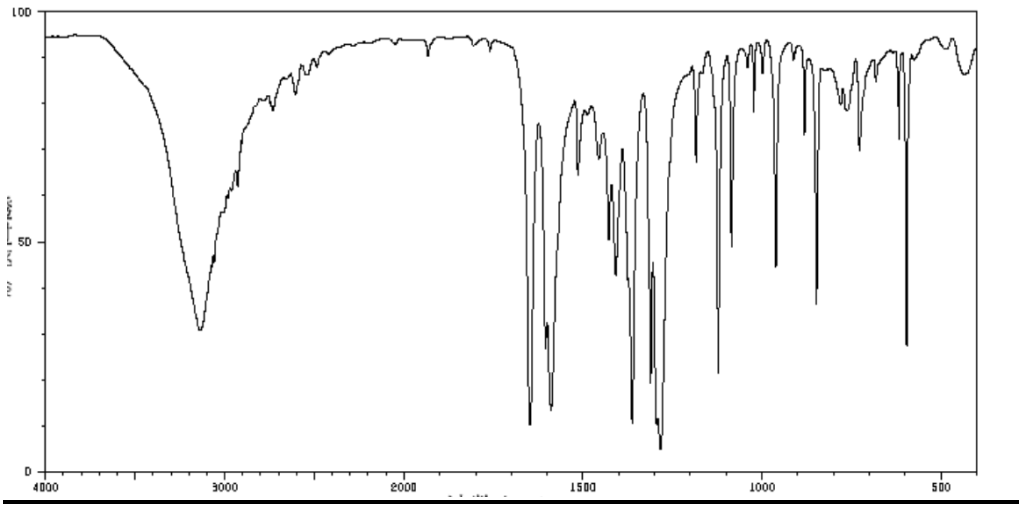
1. **p-bromophenol**



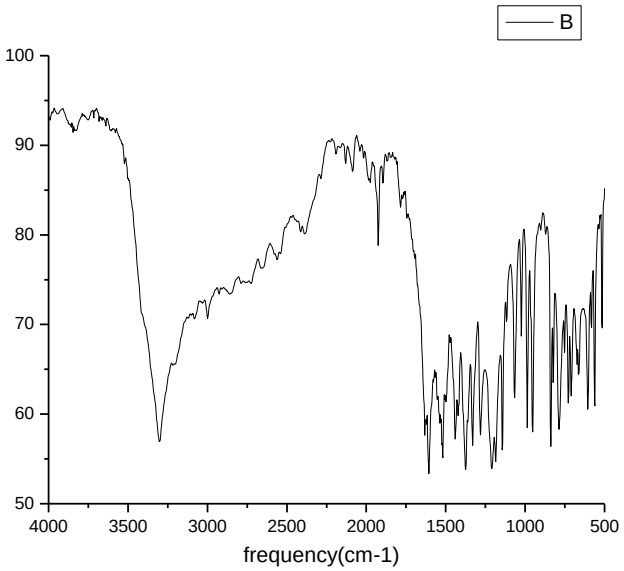
2. **p-chlorophenol**



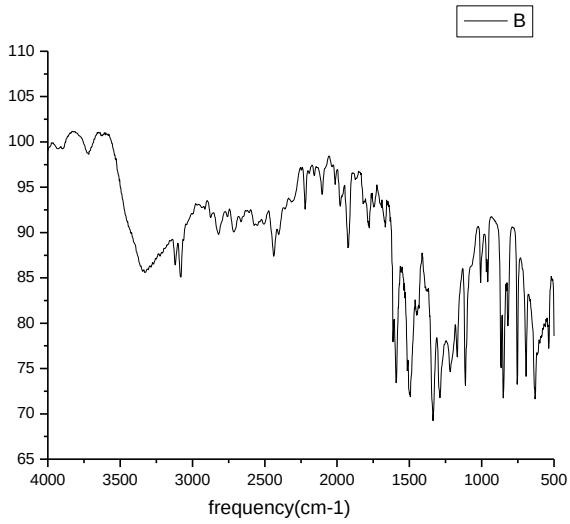
3. **4-aminophenol o-acylation product not formed.**
4. **p-cresol**



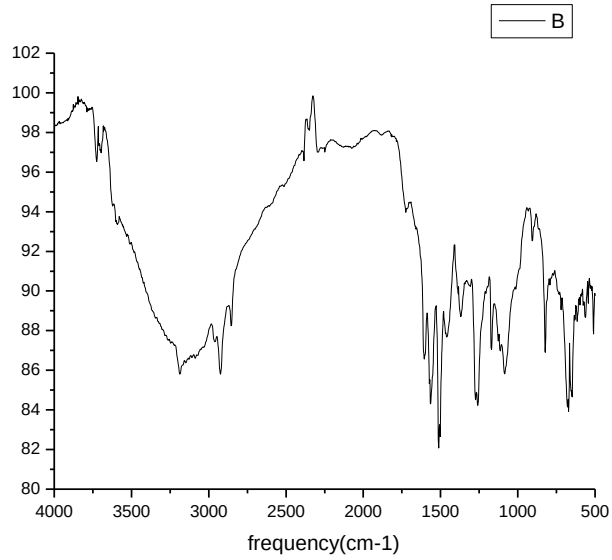
5. **resorcinol**



6. O-nitrophenol

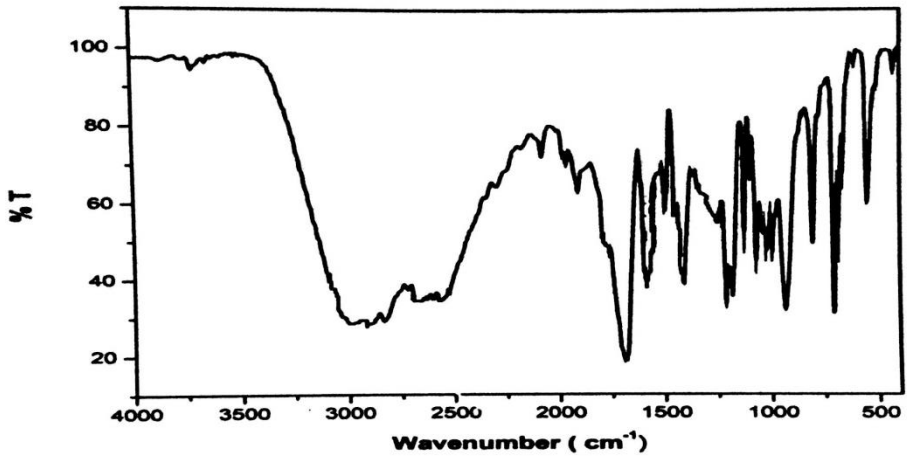


7. p-nitrophenol



Diketone of:

p-cresol



Flavone of:

p-cresol

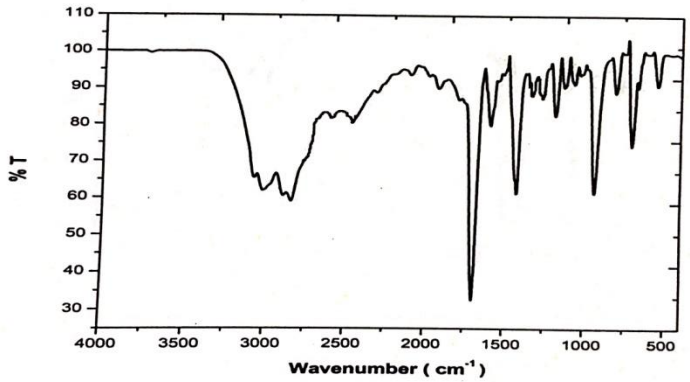


Fig. 4 6-methyl-2-phenyl-4*H*-1-Benzopyran-4-one

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