AN EXPEDITIOUS AND ENVIRONMENTALLY BENIGN SYNTHESIS OF SUBSTITUTED 1,3-DIPHENYL PROP-2-EN-1-ONE

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Abstract

Chalcones exhibit a number of medicinal applications. They are outstanding intermediates for synthesizing various heterocyclic compounds. In this method, chloro chalcones were prepared by Claisen-Schmidt reaction of aromatic ketones with aromatic aldehydes in the presence of solid KOH utilizing microwave irradiations. The reaction is perfect with shorter reaction time, amiable reaction condition, environment friendly, economically viable, fantastic yields as compared to other traditional methods. The structures of the synthesized compounds have been confirmed on the basis of their IR and [1]HNMR spectroscopic techniques.

Keywords: Claisen-Schmidt reaction, Microwave irradiation, IR, [1]HNMR.

INTRODUCTION

Chalcones are important precursors in the biosynthesis of flavones and flavanones and are usually synthesized from acetophenones and benzaldehydes via the Claisen-Schmidt condensation, using base in a polar solvent. Chalcones, 1,3-diphenylpropenones (Figure 1), constitute one of the significant classes of flavonoids with widespread distribution in vegetables, fruits, tea and soya[1,2]. The name “Chalcones” was given by Kostanecki and Tambor. Other names for chalcone are benzalacetophenone and phenyl styrryl ketone.

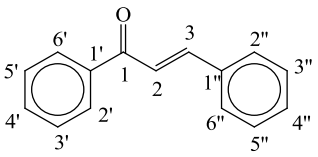


Figure 1. The general structure and numbering of chalcones.

Chalcones are not just vital precursors for the synthesis of numerous biologically active molecules but also form a noteworthy component of the natural products. Chalcones as well as their synthetic analogues show incredible medicinal properties.[3-4] There are various methods available for the synthesis of chalcones. Flavonoids are "the most common group of polyphenolic compounds in the human diet and are found universally in plants". Flavonoids have a place with large group of abundant plant secondary metabolites, which can be found in vascular plants, for example, ferns, conifers and flowering plants.[5-7] The diverse pharmacological properties of chalcones and their heterocyclic analogues, such as anticancer[8-10], and shows many more medicinal applications[11] which makes them very important scaffold in the field of medicinal chemistry. Foods with a high flavonoid

content include onions, blueberries and other berries, parsley, black tea, green tea and oolong tea, bananas, all citrus fruits, red wine, sea-buckthorns, and dark chocolate.

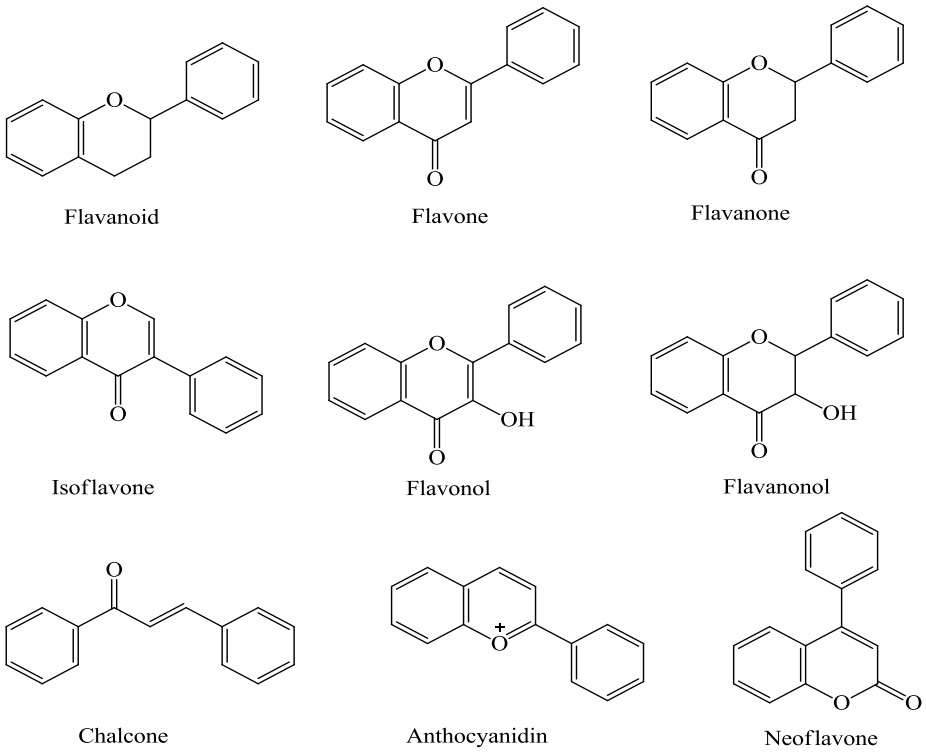


Figure 2. Examples of common flavonoids and their derivatives.

MATERIAL AND METHODS FOR THE SYNTHESIS

The starting materials were obtained from Merck and used without further purification. Melting points were uncorrected and determined in open capillary tubes. The purity of the products was checked by thin layer chromatography (TLC) on pre-coated sheets of silica gel-G of 0.25 mm thickness. IR spectra were recorded (in KBr palates) on FTIR Shimadzu spectrometer. ^{1}H NMR spectra were recorded in DMSO-d6 on Bruker Advance 400 MHz spectrometer using TMS as an internal standard.

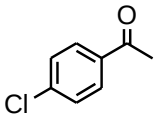
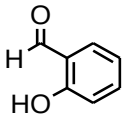
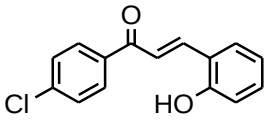
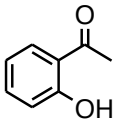
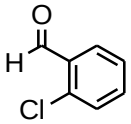
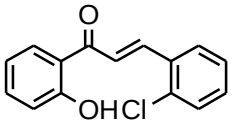
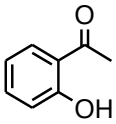
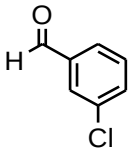
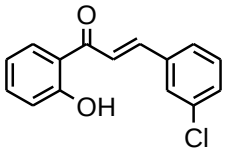
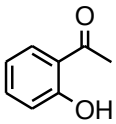
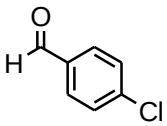
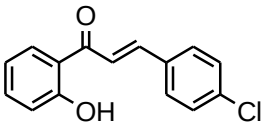
Procedure used for the synthesis of chalcones

A mixture of 0.01 moles substituted acetophenone and 0.01 moles of substituted aromatic aldehyde were added in 50 ml two neck flat bottom flask. The mixture was stirred well to get homogeneous solution and then 0.02 moles of KOH were added to the reaction mixture. The reaction mixture was exposed to microwave irradiation for 10-20minutes. The completion of the reaction was confirmed by TLC (Hexane+Ethyl acetate). The reaction mixture was diluted with cold-water and acidified with 5% aqueous HCl. The obtained solid products were filtered, dried and recrystallized from methanol.

Table: 1-Synthesized chalcones

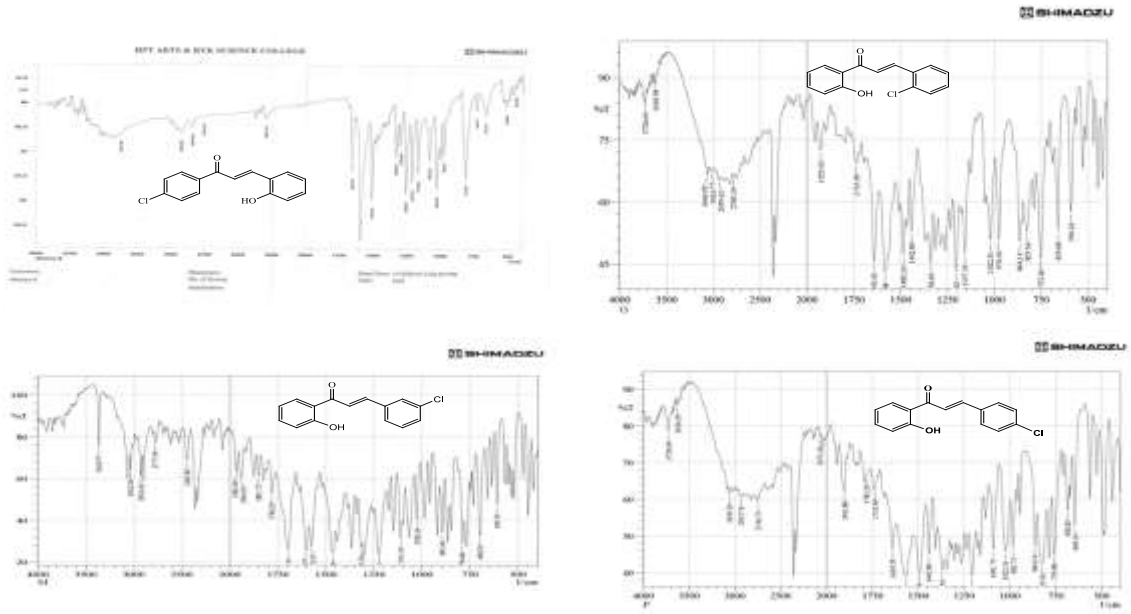
Sr. No.	Substituted acetophenone	Substituted benzaldehyde	Name of the chalcone
1.	p-chloro-acetophenone	Salicyaldehyde	(E)-1-(4-chlorophenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one
2.	o-hydroxy-acetophenone	o-chloro-banzaldehyde	(E)-3-(2-chlorophenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one
3.	o-hydroxy-acetophenone	m-chloro-banzaldehyde	(E)-3-(3-chlorophenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one
4.	o-hydroxy-acetophenone	p-chloro-banzaldehyde	(E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one

Table: 2- Physico-Chemical data of substituted chalcones.

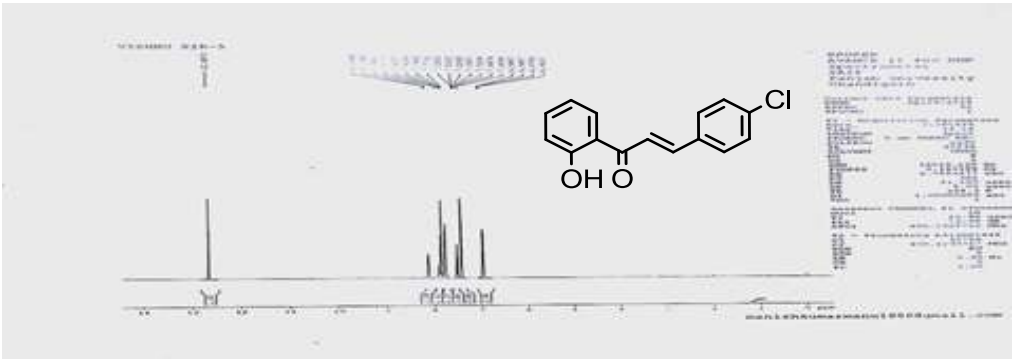
Symbol	Ketone	Aldehyde	Chalcone	Time (min)	Yield (%)	M.P (°C)
1.				16	75	100
2.				13	78	80
3.				15	73	140
4.				19	84	75

Spectral Analysis

1. IR Spectral analysis



2. 1HNMR Spectral analysis



RESULT AND DISCUSSION:

In all synthesized chalcones, the carbonyl stretching frequency is lowered than its normal value. This lowering is due to conjugation with the two phenyl rings. Also, there is decrease in olefinic double bond stretching frequency. The frequency near to 960 cm^{-1} in all synthesized chalcones indicates trans stereochemistry to olefinic double bond. The hydroxyl group stretching frequency is observed at 3600-3300 cm^{-1}. Other frequencies are also observed as expected and specified in following information. ^{1}HNMR spectrum shows ten proton signal (eight aromatic and two olefinic) at 6.9-8.14δ and hydroxyl proton signal at 12.7 ppm. The high chemical shift value of hydroxyl proton is due to intramolecular hydrogen bonding with carbonyl group.

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