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NOVEL ROUTE OFDEHYDROGENATION OF 2-PHENYL-CHROMAN-4-ONE TO 2-PHENYL-CHROMEN-4-ONE USING MONTMORIILONITE K-10 CLAY

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ABSTRACT:

Synthesis of flavones using the catalyst Montmorillonite k-10 clayunder microwave irradiation has been carried out. Excellent yield was obtained in shorter reaction time as these reactions were carried out under microwave irradiation, it reduces the cost and time period of reaction.

Dehydrogenation of 2-phenyl-chroman-4-one to 2-phenyl-chromen-4-one using Montmorillonite k-10 clay is not investigated so far. Herein we wish to report a mild method for dehydrogenation in microwave which gives better yield of the product in less time

Keywords: chalcones,2-phenyl chroman-4-one,2-phenyl chromen-4-oneMontmorillonite k-10 clay

Introduction :

Though their presence being a century old[1-3], isolation[3] of new flavones and newer methods[4] of synthesis continue to appear. Their attraction as synthetic targets is due to the wide range of biological activities exhibited by them. These include leishmanicidal activity, ovipositor stimulant phytoalexins, anti-HIV, vasodilator, antiviral, antioxidants, bactericidal, DNA cleavage, anti-inflammatory, antimutagenic, antiallergic, and anticancer[5]. Some flavonoids inhibit the histamine release from human basophiles and rat mast cells[6].

Moreover, it is known that some flavonoids have a repelling property against some phytophagous insects and a subterranean termite (Coptotermes sp.) acting as antifeedant[7,8].Some flavones are also known to exhibit hypotensive and hypothermic activities,[12] antiallergic[13] and antiplatelet activity.[14]

INTRODUCTION TO CLAYS IN CHEMISTRY:

In the most general sense, clays are a type of fine-grained earth, primarily composed of aluminum and silcate minerals. Montmorillonite clays[15-17]are thought to have formed from volcanic ash during the Jurassic and later periods, and were named for the location of their discovery, Montmorillon, France, in the 1800s. These clays are now mined in regions all over the world, including Europe, Africa, Asia, South and North America, with U.S. mines in Florida, Georgia, Illinois and Texas. Montmorillonite clays have a wide variety of uses and have recently been found to have the ability to catalyze a wide range of chemical reactions. A catalyst is a chemical species that induces a chemical reaction to occur at a reasonable rate, without itself being consumed in the process; the catalyst[1-3]can typically be recovered and reused. Development of naturally benign substances like clays as catalysts for chemical reactions constitutes an exciting breakthrough in Green Chemistry and promises to reduce the amount of hazardous waste associated with the synthesis of new drug compounds[18].

EXPERIMENTAL

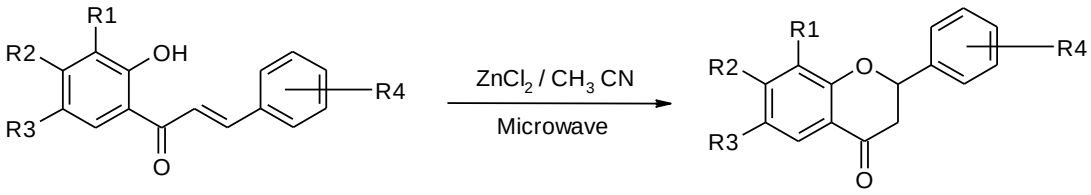
Procedure for synthesis of substituted 2-phenyl chroman-4-one:

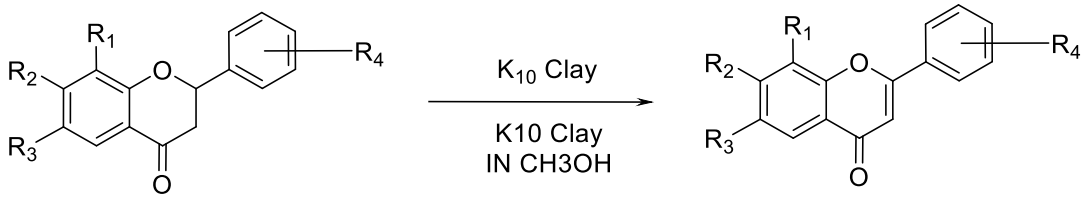
A solution of substituted 2-propen-1-one(3.0 mmoles) and Zinc chloride (3.3 mole) was subjected to microwave heating for 4 minutes. The progress of reaction was monitored by TLC. The resultant mixture was poured into saturated solution of NH_4Cl (20 ml) and extracted with methylene chloride **(Scheme - II).**

Procedure for dehydrogenation of 2-phenyl chroman-4-one:

In a solution of substituted 2-phenyl chroman-4-one a solution ofK-10 clay(2 m.mole) was added and was irradiated for 4-5 min. in microwave. The progress of reaction was monitored by TLC. A solid get separated out was filtered; dried, and crystallized from dilute alcohol, gave 2-phenyl chroman-4-one (Scheme - III). The residue obtained was purified by silica gel column chromatography (10% EtOAc–hexane) as eluent to afford the pure products.Similarly other compounds of the series were prepared by same method.

SCHEME I





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The result showed that efficiency and yield of the reaction is high as compared to other conventional methods. Yields of all isolated product after purification found to be excellent as compare to the previously reported methods. This method offers advantage in terms of simple procedure and workup, mild reaction condition and excellent yields. The ^{1}HNMR spectra of flavones showed a singlet at 6.55-6.8 due to 1H of 3H i.e. pyrone ring, it is the characteristic singlet for flavones. The multiple at 7.1-7.9 is due to aromatic protons. Such observed ^{1}HNMR data and complete absence of a peak near 13 due to orthohydroxy group.

Flavones do not give violet coloration with $FeCl_3$ solution and pink coloration with conc. H_2SO_4 and Wilson test was negative.

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2.	6-Chloro-2-phenyl-chromen-4-one	198	3 hrs	4 min.	75	80
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4.	6-Bromo-2-phenyl-chromen-4-one	199	3.5 hrs	5 min	70	85
5.	6-Iodo-2-phenyl-chromen-4-one	197	4 hrs	5 min	70	85
6.	6-Hydroxy-2-phenyl-chromen-4-one	201	4 hrs	5 min	65	80
7.	6-Chloro-2-(2-hydroxy-phenyl)-chromen-4-one	194	3 hrs	4 min	70	80
8.	2-(2-Hydroxy-phenyl)-6-methyl-chromen-4-one	197	4 hrs	4.5 min.	70	80
9.	6-Bromo-2-(2-Hydroxy-phenyl)-chromen-4-one	198	4 hrs	4 min	70	85
10.	2-(2-Hydroxy-phenyl)-6-iodo-chromen-4-one	200	4.5	5	70	85

			hrs	min.		
11.	6-Hydroxy-2-(2-hydroxy-phenyl)-chromen-4-one	199	5 hrs	5 min.	70	75
12.	2-(2-Hydroxy-phenyl)-chromen-4-one	198	3 hrs	4 min.	70	85
13.	2-(2-nitro-phenyl)-chromen-4-one	196	5 hrs	5 min.	70	85
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CM : Conventional method MW : Microwave

SPECTRAL ANALYSIS:

The structures of the products were confirmed from NMR, IR and LCMS. The representative spectral analysis for few of the products is given below. The observed values are in accordance with the literature values.

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^{1}H NMR ($CDCL_3$) : δ2.5 (s, 3H, CH_3), δ6.8 (s, 1H, 3-H Pyrone)

δ7.6-8.3 (m, 8H, Ar-H)

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152(100), 127, 113, 69, 57.

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IR (v max) cm^{-1} : 1640(C=O), 1560(C=C), 1450, 871, 669.

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MS : m/z (% rel. intensity) : 444(M^+,100), 425, 411, 397, 367, 337, 249,221, 206, 194, 179, 167, 151, 119, 103, 91,75, 63, 53.

Compound :8-Bromo-6-chloro-2-naphthalen-2-yl-chromen-4-one

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IR (v max) cm^{-1} : 3050, 2992, 1647 (C=O), 1608, 1465, 1381, 1123, 827 cm^{-1}

^{1}H NMR ($CDCL_3$) : (300 MHz, CDCl3) □8.23 (dd, *J*1 = 7.8 Hz, *J*2 = 1.5 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.66-7.72 (m, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.39-7.44 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.75 (s, 1H), 3.90 (s, 3H);

MS : m/z (% rel. intensity) : 252 (M+, 100), 251 (33), 209 (13), 132 (49)

Compound :7-Methoxy-2-(4-methoxy-phenyl)-chromen-4-one

IR (v max) cm^{-1} : 3082, 2940, 1645 (C=O), 1605, 1441, 1376, 1267, 1163, 1029

^{1}H NMR ($CDCL_3$) : 8.13 (d,*J* = 9.0 Hz,1H), 7.86 (d,*J* = 9.0 Hz,2H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.95-6.99 (m, 2H), 6.80 (s, 1H), 3.93 (s, 3H), 3.89 (s, 3H)

MS : m/z (% rel. intensity) : 281 (33), 239 (28), 132 (36)

Compound :2-(4-Chloro-phenyl)-chromen-4-one

IR (v max) cm^{-1} : 3090, 1641 (C=O), 1606, 1466, 1220, 1090, 828 cm^{-1}

^{1}H NMR ($CDCL_3$) : (300 MHz, $CDCl_3$) □8.23 (dd, *J*1 = 8.0 Hz, *J*2=1.5 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.69-7.75 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.7Hz, 2H), 7.41-7.46 (m, 1H), 6.80 (s, 1H)

MS : m/z (% rel. intensity) : 258 (M++2, 34), 256 (M+, 100), 230 (14), 228 (41), 120 (57), 92 (33)

Conclusion :

The use of K-10 clay for dehydrogenation is far superior for the above discussed methodology as K-10 clay is ecofriendly and the reaction can be carried out with mild reaction condition. The workout for the product was very simple. This methodology finds its utility even for $–OCH_3$ substituted chromen-4-one for which the problem of etherification with other method is associated.

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ECO-FRIENDLY DEHYDROGENATION OF 2-PHENYL-CHROMAN-4-ONE TO 2-PHENYL-CHROMEN-4-ONE USING K10

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ABSTRACT:

Synthesis of flavones using the catalyst K-10 clay under microwave irradiation has been carried out. Excellent yield was obtained in shorter reaction time as these reactions were carried out under microwave irradiation, it reduces the cost and time period of reaction.

Dehydrogenation of 2-phenyl-chroman-4-one to 2-phenyl-chromen-4-one using DIB is not investigated so far. Herein we wish to report a mild method for dehydrogenation in microwave which gives better yield of the product in less time

Keywords : chalcones,2-phenyl chroman-4-one,2-phenyl chromen-4-onediacetoxyiodobenzene

Introduction :

Flavonoids are substances endowed with a wide number of pharmacological activities. Among the naturally occurring oxygen heterocycles, 2-pheny1-4H-1-benzopyran-4-ones (flavones) are important and abundant group of flavononids. They possess a unique importance, as about 300 different compounds of this class have so far been isolated from natural sources and thousands of their derivatives have been synthesized.

Though their presence being a century old[2], isolation[3] of new flavones and newer methods[4] of synthesis continue to appear. Their attraction as synthetic targets is due to the wide range of biological activities exhibited by them. These include leishmanicidal activity, ovipositor stimulant phytoalexins, anti-HIV, vasodilator, antiviral, antioxidants, bactericidal, DNA cleavage, anti-inflammatory, antimutagenic, antiallergic, and anticancer[5]. Some flavonoids inhibit the histamine release from human basophiles and rat mast cells[6]. Moreover, it is known that some flavonoids have a repelling property against some phytophagous insects and a subterranean termite (Coptotermes sp.) acting as antifeedant[7,8].Some flavones are also known to exhibit hypotensive and hypothermic activities,[12] antiallergic[13] and antiplatelet activity.[14]

EXPERIMENTAL

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A solution of substituted 2-propen-1-one(3.0 mmoles) and Zinc chloride (3.3 mole) was subjected to microwave heating for 4 minutes. The progress of reaction was monitored by TLC. The resultant mixture was poured into saturated solution of NH_4Cl (20 ml) and extracted with methylene chloride **(Scheme - II).**

Procedure for dehydrogenation of 2-phenyl chroman-4-one:

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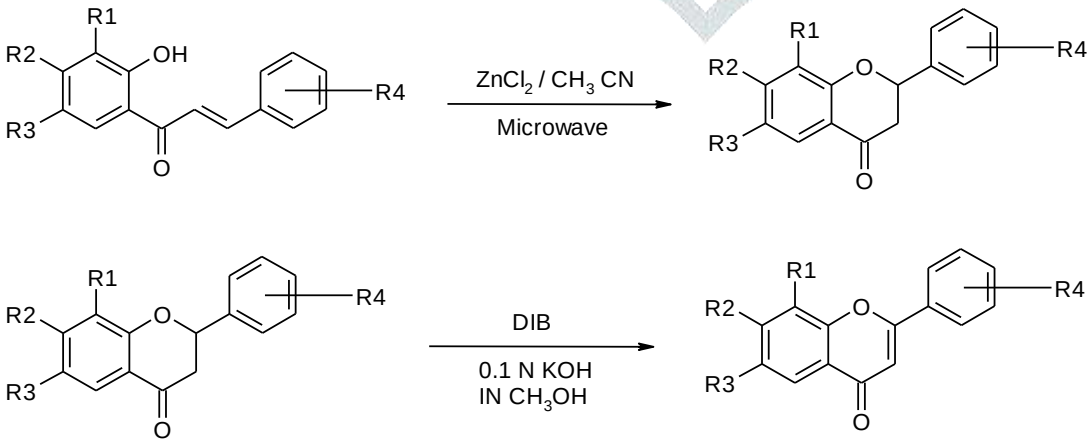

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