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

G. B. Pande[1,*] and S. G. Shirodkar[2]
Department of Chemistry, Netaji Subhashchandra Bose College, Nanded-431601(M.S.)
*E-mail : girishbpande@gmail.com

ABSTRACT
Synthesis of flavones using the catalyst DIB 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-one diacetoxyiodobenzene.

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[1]. 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, isolation of new flavones and newer methods of synthesis continue to appear.[2-4] 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, antiallergic and antiplatelet activity.[9-14]

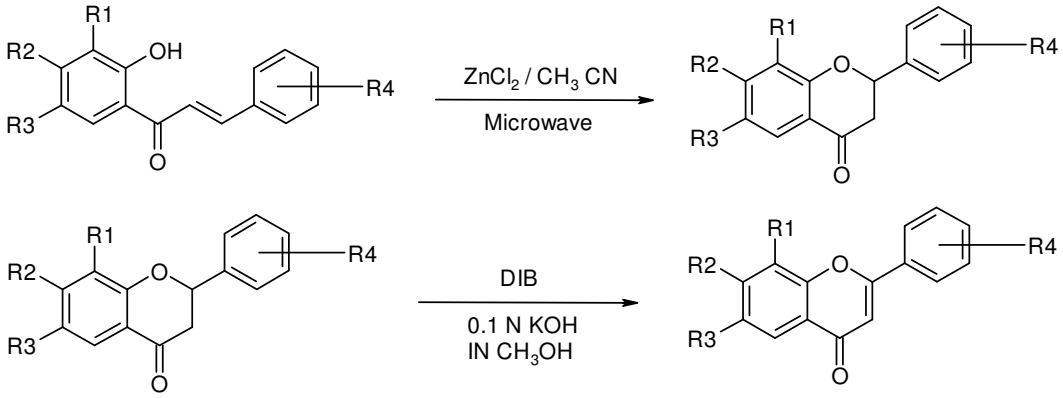
EXPERIMENTAL

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.

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

A solution of substituted 2-phenyl chroman-4-one and diacetoxy iodobenzene in 0.1N KOH was irradiated for 4-5 min. in microwave. The progress of reaction was monitored by TLC. The reaction mixture was cooled and to the cold reaction mixture, an aqueous sodium thiosulphate solution (20%) was added until the solution was colourless, followed by ice-cold water (5ml). A solid get separated out was filtered; dried, and crystallized from dilute alcohol, gave 2-phenyl chroman-4-one. 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-1

RESULTS AND DISCUSSION

Synthesis of flavones using the catalyst DIB 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.

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.

Table-1: Analytical data of substituted 2-Phenyl-chromen-4-one

S. No.	Compound	M.P.	Time		Yield (%)	
			CM	MW	CM	MW
1.	2-phenyl-chromen-4-one	97	3 hrs	4 min.	78	82
2.	6-Chloro-2-phenyl-chromen-4-one	198	3 hrs	4 min.	75	80
3.	6-Methyl-2-phenyl-chromen-4-one	202	3.5 hrs	4 min	78	85
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 hrs	5 min.	70	85
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
14.	6-chloro-2-(2-nitro-phenyl)-chromen-4-one	192	4 hrs	4 min.	65	75
15.	6-Methyl-2-(2-nitro-phenyl)-chromen-4-one	201	5 hrs	5 min.	70	80
16.	8-Bromo-6-chloro-7-methyl-2-naphthalen-2-yl-chromen-4-one	184	5 hrs	5 min.	65	75
17.	8-Bromo-6-chloro-7-methyl-2-(3,4,5-trimethoxy-phenyl)-chromen-4-one	210	5 hrs	5 min.	65	80
18.	8-Bromo-6-chloro-2-naphthalen-2-yl-chromen-4-	170	5 hrs	5 min.	70	75

	one					
19.	2-(4-Methoxy-phenyl)-chromen-4-one	220	6 hrs	4.5 min	70	85
20.	7-Methoxy-2-(4-methoxy-phenyl)-chromen-4-one	252	6 hrs	5 min	72	84
21.	2-(4-Chloro-phenyl)-chromen-4-one	215	5.5 hrs	5.5 min	70	80

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 and given in the Table-2.

Table-2: Spectral Analysis

Compound :	**8-Bromo-6-chloro-7-methyl-2-naphthalen-2-yl-chromen-4-one**
IR (v max) cm^{-1}	1640(C=O), 1546(C=C), 1450, 800, 765.
^{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)
MS : m/z (% rel. intensity)	444(M^+), 426, 400, 383, 371, 319, 248, 176, 152(100), 127, 113, 69, 57.
Compound:	**8-Bromo-6-chloro-7-methyl-2-(3,4,5-trimethoxy-phenyl)-chromen-4-one**
IR (v max) cm^{-1}	1640(C=O), 1560(C=C), 1450, 871, 669.
^{1}H NMR ($CDCL_3$)	δ2.5 (s, 3H, CH_3) δ3.7 (s, 3H, OCH_3) δ3.9, (s, 6H, 2×OCH_3) δ7.3 (s, 1H, 3-H Pyrone), δ7.8-8.1 (m, 3H, Ar-H)
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**
IR (v max) cm^{-1}	1660(C=O), 1560(C=C), 765, 669.
^{1}H NMR ($CDCL_3$)	δ6.7 (s, 1H, 3-H Pyrone), δ7.5-8.3 (m, 9H, Ar-H)
MS : m/z (% rel. intensity)	386(M^+,), 369, 213, 179, 152(100), 126, 78, 63.
Compound :	**2-(4-Methoxy-phenyl)-chromen-4-one**
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* = 8.7 Hz, 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 DIB for dehydrogenation is far superior for the above discussed methodology as DIB 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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