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Comparative Study of Synthesis of 3-Aroyl Flavanones by Using Microwave Irradiation and Conventional Method

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Abstract:
Newly substituted 3 Aroyl flavanones were synthesised by using microwave irradiation and conventional method in order to compare time required and yield. The structure of compounds was elucidate by spectral analysis (IR and NMR).
Keywords:-3-aroyl flavanone, β- Diketone.

INTRODUCTION

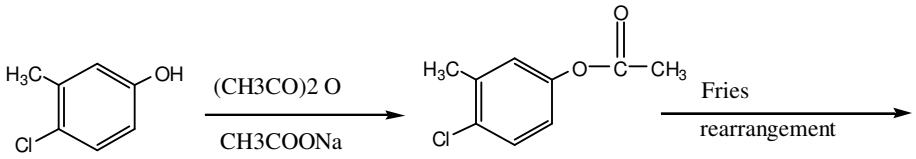
In the resent years there is much biomedical interest in flavanoids because of their lot of beneficial effects on human being. Flavanoids are naturally occurring polyphenolic compounds with flavones nucleus having anti-oxidant, anti-tumour, anti-ulcer, anti-inflammatory activities. They are available as flavanone, flavanol, isoflavane, flavones and their derivatives. The flavanoides basically possess 15 carbon skeletons (C6-C3-C6). Flavanoides are mainly found in onions, apples, red wine, blueberries, grapes and tea. Flavanones are the important class of flavanoids containing a 2-phenyl-benzopyran-4one skeleton, Flavanones are commonly found in various citrus fruits and vegetables1-3.Synthetic flavanones have attracted considerable attention because of their various pharmacological properties including antifungal4,5, antibacterial4,6,7,analgesic7, antioxidant7.Flavanones are antioxidants, preventing heart disease. They are used as a potential cancer chemopreventive agents8, 9.

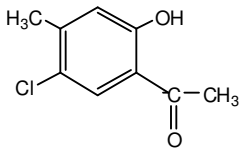
MATERIALS AND METHODS

All the laboratory chemicals and solvents required for the study were of highest purity commercially available. Melting points of all synthesised compounds were determined by melting point apparatus. The purity of synthesised compounds was checked by thin layer chromatography on silica –G layers. IR spectra were recorded on FTIR spectrophotometer using KBR pallets. NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer.

PREPARATION OF2-HYDROXY-4-METHYL-5-CHLORO ACETOPHENONE (1A).

2-hydroxy-4-methyl-5-chloro acetophenone was prepared by fries migration of p-chloro meta cresyl acetate in presence of anhydrous $AlCl_3$ which was prepared by acetylation of para chloro meta cresol in presence of acetic anhydride and sodium acetate.



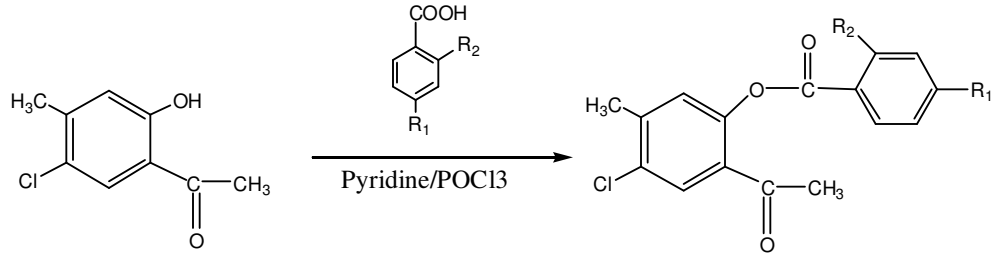


(1a)

PREPARATION OF 2-BENZOYLOXY ACETOPHENONE DERIVATIVES (2A-C)

5-chloro-2-hydroxy-4-methyl acetophenone (1) (0.04 mol) and aromatic carboxylic acid (0.05 mol) were dissolved in pyridine and pocl3 is added drop by drop with constant stirring till the viscous mass is obtained. Maintain the temperature below 100c during the addition of pocl3 to the reaction mixture. The reaction mixture is allowed to stand for overnight at room temperature .The reaction mixture is decomposed by 10% HCl. The product thus separated was filtered, washed with water followed by sodium bicarbonate (10% solution) and then again washed with water. The solid product

was crystallised from ethanol to obtained corresponding 2-benzoyloxy acetophenone.



(2a-c)

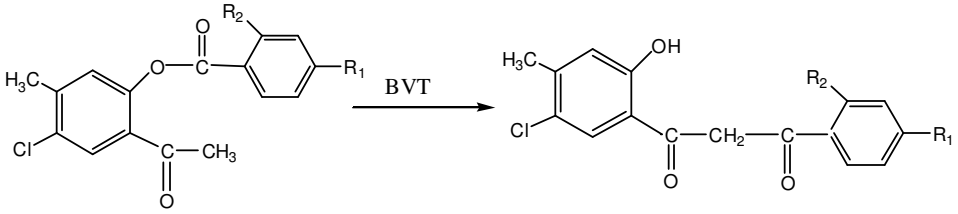
Where R_1= Cl, OCH_3, R_2 = Cl, H

The compounds prepared are (2a-c)

1. 5-chloro-2-(4'- chloro benzoyloxy)-4-methyl acetophenone (2a), m.p.120^{0}C
2. 5-chloro-2-(4'- methoxy benzoyloxy)-4-methyl acetophenone (2b), m.p.80^{0}C
3. 5-chloro-2-(2',4'-dichloro benzoyloxy)-4-methyl acetophenone (2c), m.p.105^{0}C

PREPARATION OF DIKETONES (3A-C)

2-substituted benzoyloxy acetophenones (2a-c) (0.05 mol) was dissolved in dry pyridine (40 ml). The solution was warmed up to about 600c and pulverised KOH (0.15 mol) was added slowly with constant stirring. After four hours the reaction mixture was acidified by adding ice cold dilute HCl (1:1). The solid product thus separated was filtered, washed with sodium bicarbonate solution (10%) and finally with water. It is then crystallised from ethanol acetic acid mixture.



(3a-c)

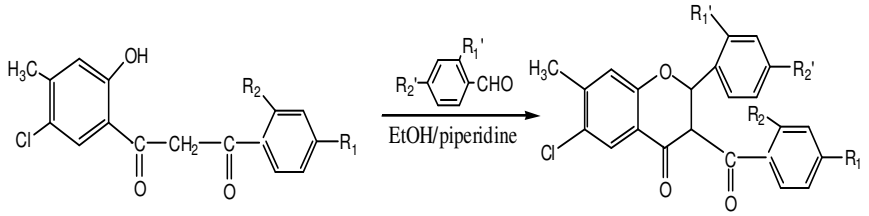
Where R_1= Cl, OCH_3, R_2 = Cl, H

The compounds prepared are (3a-c):

1. 1 -(2'-hydroxy-4'methyl-5'- chloro phenyl)-3(4'- chloro phenyl) propane 1,3-dione (3a), m.p.164^{0}C
2. 1 -(2'-hydroxy-4'methyl-5'- chloro phenyl)-3(4'- methoxy phenyl) propane 1,3-dione (3b), m.p.142^{0}C
3. 1 -(2'-hydroxy-4'methyl-5'- chloro phenyl)-3(2',4'- dichloro phenyl) propane 1,3-dione (3c), m.p.126^{0}C

PREPARATION OF 3-AROYL FLAVANONES BY CONVENTIONAL METHOD

1-(2'-hydroxy aryl)-3-aryl propane-1, 3-diones (3 a-c) (0.01 mol) and appropriate aromatic aldehyde were heated in ethanol(25ml) containing few drops of piperidine (0.5 ml) for 60 minutes.The reaction mixture on cooling gives product, which was filtered, washed with ethanol and crystallized from ethanol AcOH mixture to give product.



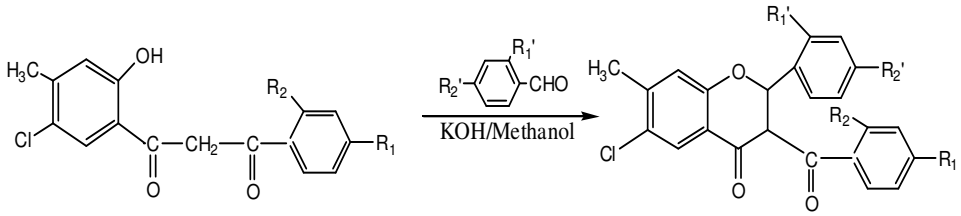
(4 a-g)

Where R_1= Cl, OCH_3, R_2 = Cl, H, R_1'= H,Cl, R_2,= H, Cl, OCH_3

PREPARATION OF 3-AROYL FLAVANONES BY MICROWAVE IRRADIATION

Synthesis of flavanone was carried out by mixing appropriate amount of 1-(2'-hydroxy aryl)-3-

aryl propane-1, 3-diones (3 a-b) (2.69 m. mol) and aromatic aldehydes (2.69 m. mol) in presence of catalytic amount of aqueous KOH in methanol and irradiating in microwave at 100 W for two minutes. The reaction mixture was cooled, poured into crushed ice and then conc. HCl was added. The mixture was left to stay at 2-3^{0}C overnight and the separated solid was collected by filtration, washed with water and recrystalized from methanol to give desired product.



Where R_1= Cl, OCH_3, R_2 = Cl, H, R_1'= H,Cl, R_2,= H, Cl, OCH_3

The compounds prepared are (4a-g):

1 2- (4'- chloro)-3-(4'-chloro benzoyl)-6-chloro-7-methyl flavanone (4a),m.p 120^{0}C
2 2-(2'-chloro)-3-(4'-chloro benzoyl)-6-chloro-7-methyl flavanone (4b), m.p. 115^{0}C
3 2- (4'-methoxy)-3-(4'-chloro benzoyl)-6-chloro-7-methyl flavanone (4c), m.p. 133^{0}C
4 2-(4'-chloro)-3-(4'-methoxy benzoyl)-6-chloro-7-methyl flavanone (4d), m.p. 145^{0}C
5 2-(2'-chloro)-3-(4'-methoxy benzoyl)-6-chloro-7 methyl flavanone (4e), m.p. 152^{0}C
6 2-(4'-chloro)-3-(2'4'-dichloro benzoyl)-6-chloro-7-methyl flavanone (4f), m.p.110^{0}C
7 2-(2'-chloro)-3-(2'4'-dichloro benzoyl)-6-chloro-7-methyl flavanone (4g),m.p. 124^{0}C

Table-Comparison of conventional method and Microwave Irradiation

Sr.No.	Compound Code	Time required for reaction		%Yield	
		conventional method	Microwave Irradiation	conventional method	Microwave Irradiation
1.	4a	1 hour	2 minutes	62%	71%
2.	4b	1 hour	2 minutes	55%	69%
3.	4c	1 hour	2 minutes	47%	61%
4.	4d	1 hour	2 minutes	40%	55%
5.	4f	1 hour	2 minutes	40%	59%
6.	4g	1 hour	2 minutes	61%	65%
7.	4h	1 hour	2 minutes	59%	73%

RESULTS AND DISCUSSIONS

In the present study we have described synthesis of some newly substituted 3-Aroyl Flavanones by both conventional method as well as by microwave irradiation. As per Table-Comparision of conventional method and Microwave Irradiation, in conventional method for synthesis of 3-Aroyl Flavanones, EtOH and piperidine was used and was refluxed for one hour for effective condensation. In contrast under microwave irradiation the reactions are completed in 2-3 minutes and afford the product in high yield.

CONCLUSION

In the present study synthesis of flavanone using microwave provide practical alternative to the existing method for the synthesis of flavanone. This method is fast and clean so found to be beneficial according to time, improved yield and environmentally sound.

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