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EFFECT OF o/p SUBSTITUTED CHLOROGROUP OF AROMATIC ALDEHYDE IN THE SYNTHESIS OF 3-AROYL FLAVANONE

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ABSTRACT

Flavanones are 2,3-dihydroflavones. Generally flavanones are prepared by condensation of 1,3-propanediones and aromatic aldehydes. In the present work, aromatic aldehyde was used to prepare 3-aroyl flavanones. Effect of chloro substitution in the aromatic ring of aldehyde was studied in terms of yield. Probable mechanism is also discussed. It is observed that due to introduction of chloro group in o/p position of aromatic aldehyde, the yield of product decreases due to deactivation of –CHO group for condensation with reactive methylene group.

Key words: 3-Aroyl flavanone, Chlorobenzldehyde, 1, 3-Propanedione.

INTRODUCTION

Flavanoids are diphenylpropanes that commonly occur in plants[1]. The immediate family members of flavanoid includes flavones, isoflavone, flavanol etc. 2,3-dihydro derivative of flavones are known as flavanones, which are found to possess biological activities like antioxidant, anti-inflammatory, antiviral, antibacterial ,anticarcinogenic, antifungal and antiulcer activities[2-15]. Flavanones are not yet found in nature but are synthesized by cyclization of isomeric chalcones[16] or by condensation of 1,3-propanediones with aromatic aldehydes[3]. 1,3-propanediones condenses with aromatic aldehyde through its reactive methylene group[17]. In condensation reactions of aromatic aldehyde, substitution of a group possessing inductive and mesomeric effects has been found to affect the reaction by deactivating aromatic ring for condensaton[18]. In the present work, 1-(2-hydroxy phenyl)-3-phenyl-1,3-propanedione was reacted with benzyldehyde and its o/p Chloro substituted derivatives to form various flavanones.The yield was co-related with the substitution of chloro group at ortho and para position.

EXPERIMENTAL

Materials and methods

Starting from p-cresol, 1-(2-hydroxy-5-methyl phenyl)-3-phenyl-1,3-propanedione (I) was prepared by literature method[3]. Compound (I) was allowed to react with benzaldehyde, o-chloro benzaldehyde and p-chlorobenzaldehyde in the basic medium using piperidine in ethanol. The reaction was monitored using

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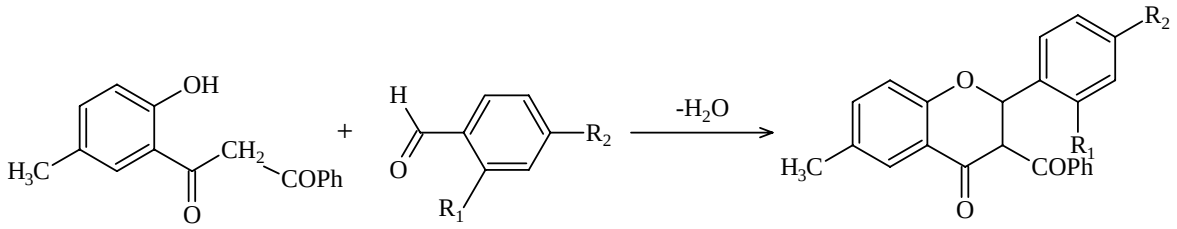
TLC technique. The compounds formed were analyzed by chemical tests, elemental analysis and spectral data.



(I) Substituted benzaldehyde **II (A, B, C)**

A = R_1–H, R_2–H

B = R_1–H, R_2–Cl

C = R_1–Cl, R_2–H

Scheme 1

RESULTS AND DISCUSSION

Colour reactions with $FeCl_3$, $KMnO_4$, aq. NaOH, H_2SO_4 and Mg-HCl agreed with colour reactions of flavanones[19]. The major absorption bands observed in IR Spectra of compounds II-A to II-C were as follows.

For 3-Benzoyl-6-methyl flavanone (II-A): 3034 cm^{-1} (Ar-H), 1697 cm^{-1} (C=O), 1313 cm^{-1} (Pyrone ring), 1290 cm^{-1} (Ar-O stretching).

For 3-benzoyl-2'-chloro-6-methyl flavanone (II-B): 3057 cm^{-1} (Ar-H), 1697 cm^{-1}(C=O), 1697 cm^{-1} (C=C), 1301 cm^{-1} (Pyrone ring), 1288 cm^{-1} (Ar-O), 1095 cm^{-1} (= C-O), 690 cm^{-1} (-C-Cl stretching).

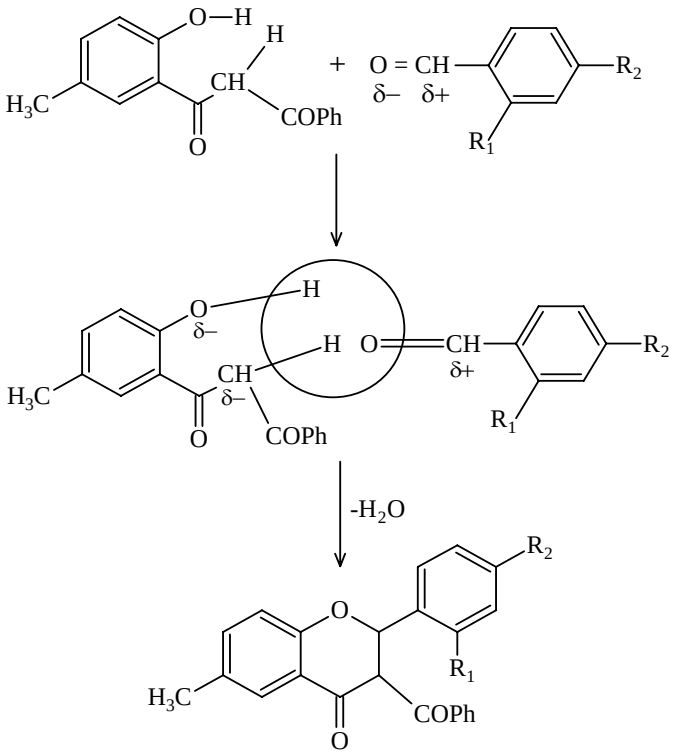
For 3-benzoyl-4'-chloro-6-methyl flavanone (II-C): 3046 cm^{-1} (Ar-H), 1690 cm^{-1} (C=O), 1678 cm^{-1} (C=C), 1311 cm^{-1} (Pyrone ring), 1275 cm^{-1} (Ar-O), 1089 cm^{-1} (=C-O), 696 cm^{-1} (-C-Cl stretching).

It was observed that yield of the product decreases due to substitution of chloro group. Further, the decrease in the yield is more in o-substituted product. The overall decrease in the yield due to Chloro substitution may be attributed to –I and +M effects of Chloro group present on o or p position. Chloro group is strongly electronegative and its electron withdrawing inductive effect deactivates the benzaldehyde group for condensation with reactive methylene group of 1,3-propanedione. Further the lower yield in the o-Chloro substituted product may be attributed to the position of Chloro group, which may offers steric hinderance.

Table 1

Compound	Yield (%)	M.P. (^oC)
II-A	58.47	146
II-B	20.66	148
II-C	15.33	142

The probable mechanism of reaction is shown in **Scheme 2**.



II (A, B, C)

Scheme 2

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