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A GREEN AND EFFICIENT PROTOCOL FOR THE SYNTHESIS OF CHALCONE OF 3-ACETYL PYRIDINE USING GRINDING TECHNIQUE

Chemistry

KEYWORDS: Ecofriendly 3-Acetyl pyridine, Barium hydroxide, Chalcones, Grinding.

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ABSTRACT

Here we describe the green and efficient protocol for the synthesis of chalcones of 3-acetyl pyridine by the condensation of 3-acetyl pyridine with substituted aromatic aldehydes in presence of activated barium hydroxide using grinding conditions. This is an environmentally benign procedure which not only avoids the use of hazardous organic solvents during the reaction as well as at working up stage but also gives the product in good yield.

INTRODUCTION

Chalcones represent the key structure motif in the plethora of biological active molecules including natural and synthetic product. Chalcones have immenes biosynthetic importance as the first isolevel C-15 precursors in flavoinds biosynthesis. It has been demonstrated that these compounds are the central intermediate from which most of the other flavanoids originate. Among all the flavanoids chalcones are extensively investigated because generally they are endowed with various biological activities such as –antituberculosis [1], antileishmanial [2], antitumor [3], antimitotic [4], antimalarial [5], antioxidant [6-9], antifilamentary [10], antibacterial [11], cardiovascular [12] etc.

Attempts have also been made for synthesis of chalcones of 3-acetyl pyridine but the results have not been encouraging due to longer reaction time (24 hrs), poor yields and use of hazardous chemicals [13-14].

In continuation to our work on development of green and efficient route for synthesis of organic compounds using grinding technique. We wish to report a simple and the efficient protocol for the synthesis of chalcones of 3-Acetyl pyridine by the condensation of 3-Acetyl pyridine with substituted aromatic aldehydes in presence of activated Barium hydroxide under grinding conditions which avoids the use of hazardous chemicals and solvents at any stage. [scheme1].

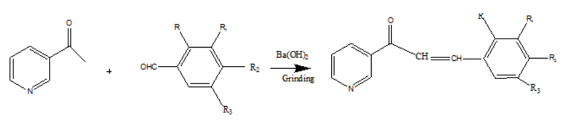
EXPERIMENTAL

Melting points were determined in capillary tube on melting point apparatus and were uncorrected. IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer.NMR spectra were recorded on Baker advance instruments using TMS as an internal standard.

RESULT AND DISCUSSION

A mixture of 3-acetyl pyridine and 2, 4 dichlorobenzaldehyde and activated barium hydroxide was ground in pestle motor and the progress of reaction was checked by TLC (Thin layer chromatography). After working out the compound thus obtained has melting point 152^{0}C and IR it showed absorption at 1676 cm ^{1}, 1609 cm ^{1}, 1582 cm ^{1},1094 cm ^{1}, which were assigned to C=O, CH=CH, C=N, C-Cl stretching. In ^{1}H NMR it showed two doublet for protons each at 7•43 and 7•24 which were assigned to =CH-Ar and CO-CH and a multiplet at 7•55, 8•77 for (Ar-H) based upon the data it was revealed that the compound was 1-(3 -pyridyl)-3-(2 ,4 -dichloro phenyl)-2-propen-1-one.

Using the above protocol the following compounds were synthesized (table 1)



I II III (a-k)

Scheme1.

Table 1

Sr. No.	R	R_1	R_2	R_3	m.pt. (◦C)	lit.m.pt. (◦C)	Yield(%)
III a	Cl	H	Cl	H	154	155 [13]	90
III b	H	H	Cl	H	165-166	167 [13]	87
III c	Cl	H	H	H	94	96 [13]	85
III d	H	H	F	H	88-89	90 [13]	80
III e	H	Br	H	H	141	140 [13]	83
III f	H	H	NO_2	H	153-154	156 [13]	85
III g	H	OCH_3	OCH_3	OCH_3	113	115 [13]	80
III h	H	NO_2	H	H	175-176	178 [14]	84
III i	OCH_3	H	OCH_3	H	154	156 [14]	82
III j	H	OCH_3	OCH_3	H	135	138 [14]	80
III k	H	H	$N(CH_3)_2$	H	143	144 [14]	81

GENERAL PROCEDURE

3-acetyl pyridine (1 m mole) substituted aldehyde (1 m mole) and activated barium hydroxide (2 m mole) was ground in motor by pestle for 15 minutes. Then the reaction mixture was kept at room temperature for 10 minutes and the completion of reaction was checked by TLC. After completion the reaction mixture was poured into crushed ice and acidified with dil HCl. The solid separated was filtered and dried and recrystallized from ethanol.

SPECTRAL CHARACTERIZATION

1-(3′-pyridyl)-3-(2″, 4″-dichloro phenyl)-2-propen-1-one. (III a)
IR (KBr) 1676 cm ^{1} (C=O), 1609 cm ^{1} (HC=CH), 1582 cm ^{1} (C=N), 1094 cm ^{1} (C-Cl);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 7•43 (1H, d, J=17Hz, =CH-Ar), 7•24 (1H, d, J=17Hz, -CO-CH=), 7•55-8•77 (7H, Ar-H).

1-(3′-pyridyl) -3-(4″-chloro phenyl)-2-propen-1-one. (III b)

IR (KBr) 1670 cm ^{1} (C=O), 1612 cm ^{1} (HC=CH), 1594 cm ^{1} (C=N), 1094 cm ^{1} (C-Cl);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 7•43 (1H, d, J=17Hz, -CO-CH=), 7•74 (1H, d, J=17Hz, =CH-Ar), 7•2-8•6 (8H, Ar-H).

1-(3′-pyridyl)-3-(2″-chloro phenyl)-2-propen-1-one. (III c)
IR (KBr) 1692 cm ^{1} (C=O), 1624 cm ^{1} (HC=CH), 1584 cm ^{1} (C=N), 1086 cm ^{1} (C-Cl);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 7•28 (1H, d, J =17Hz, -CO-CH=), 7•44 (1H, d, J=17Hz, (=CH-Ar), 7•46-8•70 (8H, Ar-H).

1-(3′-pyridyl)-3-(4″-floro phenyl)-2-propen-1-one. (III d)
IR (KBr) 1684 cm ^{1} (C=O), 1612 cm ^{1} (HC=CH), 1584 cm ^{1} (C=N), 1110 cm ^{1} (C-F);

^{1}H NMR ($CDCl_3$, **δ**, ppm): 7•26 (1H, d, J=17Hz, -CO-CH=), 7•47 (1H, d, J=17Hz, =CH-Ar), 7•08-8•74 (8H, Ar-H).

1-(3′-pyridyl)-3-(3″-Bromo phenyl)-2-propen-1-one. (III e)
IR (KBr) 1682 cm ^{1} (C=O), 1640 cm ^{1} (HC=CH), 1584 cm ^{1} (C=N), 1170 cm ^{1} (C-Br);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 6•67 (1H, d, J=17Hz, - (CO-CH=), 7•3 (1H, d, J=17Hz, =CH-Ar) 6•99-8•76 (8H, Ar-H).

1-(3′-pyridyl)-3-(4″-nitro phenyl)-2-propen-1-one. (III f)

IR (KBr) 1690 cm ^{1} (C=O), 1618 cm ^{1} (CH=CH), 1596 cm ^{1} (C=N), 1520 cm ^{1} (N=O), 1340 cm ^{1} (N=O);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 7•20 (1H, d, J=17Hz, -CO-CH=), 7•45 (1H, d, J=17Hz, =CH-Ar), 7•4-8•53 (8H, Ar-H).

1-(3′-pyridyl)-3-(3″, 4″-dimethoxy)-2-propen-1-one. (III g)
IR (KBr) 1690 cm ^{1} (C=O), 1610 cm ^{1} (HC=CH), 1585 cm ^{1} (C=N), 1210 cm ^{1} (C-O-C);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 3•95 (9H, $3_x OCH_3$), 7•20 (1H, d, J=17Hz, -CO-CH=), 7•26 (1H, d, J=17Hz, =CH-Ar) 7•20-7•28 (6H, Ar-H).

1-(3′-pyridyl)-3-(3″-nitro phenyl) -2-propen-1-one. (III h)

IR (KBr) 1690 cm ^{1} (C=O), 1610 cm ^{1} (HC=CH), 1590 cm ^{1} (C=N);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 7•50 (1H, d, J=17Hz, -CO-CH=), 7•86 (1H, d, J=17Hz, =CH-Ar), 7•65-9•20 (8H, Ar-H).

1-(3′-pyridyl)-3-(2″, 4″-dimethoxy phenyl)-2-propen-1-one. (III I)
IR (KBr) 1690 cm ^{1} (C=O), 1618 cm ^{1} (HC=CH), 1596 cm ^{1} (C=N);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 3•90 (6H, s, 2_x OCH_3), 7•50 (1H, d, J=17 Hz, -CO-CH=), 8•07 (1H, d, J=17 Hz, =CH-Ar), 6•50-9•20 (8H, Ar-H).

1-(3′-pyridyl)-3-(3″, 4″-dimethoxy phenyl)-2-propen-1-one. (III j)
IR (KBr) 1684 cm ^{1} (C=O), 1610 cm ^{1} (HC=CH), 1590 cm ^{1} (C=N), 1210 cm ^{1} (C-O-C);

^{1}H NMR ($CDCl_3$, **δ, ppm**): 3•90 (6H, s, 2_x OCH_3), 7•01 (1H, d, J=17Hz, -CO-CH=), 7•38 (1H, d, J=17Hz, =CH-Ar), 6.85-8•70 (7H, Ar-H).

1-(3′-pyridyl)-3-(4″ N, N-dimethyl phenyl)-2-propen-1-one. (III k)
IR (KBr) 1696 cm ^{1} (C=O), 1620 cm ^{1} (HC=CH), 1586 cm ^{1} (C=N), 1180 cm ^{1} (-N-$(CH_3)_2$;

^{1}H NMR ($CDCl_3$, **δ, ppm**): 3•05 (6H, s, NMe_2), 6•69 (1H, d, J=17Hz, -CO-CH=), 7•10 (1H, d, J=17Hz, =CH-Ar), 7•25-8•73 (8H, Ar-H).

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