Heterocyclic Letters
Vol. 5 | No.3 |391-394 | May-July| 2015
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

ALUM CATALYSED SOLVENT FREE SYNTHESIS OF COUMARIN CHALCONE UNDER MICROWAVE IRRADIATION METHOD

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Abstract: 3-acetyl-4-hydroxy coumarins (**1**) condensed with heterocyclic aldehydes (**2**a-e) in presence of alum catalyst under solvent free condition in microwave irradiation method and synthesis of series of chalcone (**3**a-j) in ecofriendly, green condition with excellent yield. All the compounds are characterizes by IR, NMR, Mass and CHN analysis.

Keywords: Coumarin chalcone, green synthesis, solvent free condition, alum catalyst.

Introduction

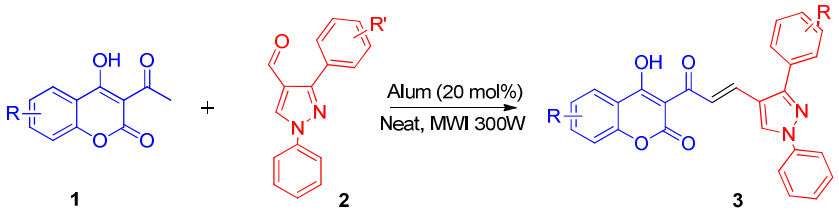
Coumarin [i] and its derivatives are one of the most important class in organic chemistry, due to its versatile biological activities like anti-tumor [ii], anti-inflammatory, anti-oxidant [iii], anti-septic and optical brightener [iv].
Coumarin-chalcone derivatives exhibits excellent biological activities, such as anti-inflammatory [v] and anti-microbial activities [vi], etc. In continuation of our research interest towards the synthesis of coumarin derivatives [vii-viii], we report the synthesis of chalcone of coumarins in presence of an ecofriendly alum catalyst [ix-xi] in solvent free condition under microwave irradiation [xii] techniques in very short time of interval.

Experimental

The melting points of the compounds were determined in open head capillary and are uncorrected. The IR spectra of the compounds were recorded in the region of 4000-400 cm-1 by using KBr pallet on FT-IR Perkin spectrophotometer. H^1 NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in DMSO-d_6. The values of chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thin layer chromatography (TLC).

General procedure for the synthesis of Chalcone derivatives of 3-acetyl-4-hydroxy coumarin:

Equimolar amount of 3-acetyl-4-hydroxy coumarin, pyrazole aldehydes (1 mmol) and alum catalyst (20 mol%) was subjected to microwave irradiation for appropriate time (Table 1) at 300 W, the progress of reaction was monitor by TLC, after completion of reaction, reaction mixture cool to room temperature and water was added (20 ml), solid was separated out, recrystalised from proper solvent to obtained desire product.



Reaction Scheme: Synthesis of Coumarin chalcone

(3a) IR (KBr) cm-1: 3616, 3124, 2970, 2827, 1479, 1443, 1371, 1282, 1215, 998, 962, 704, ^{1}H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.32-2.34 (s, 3H), 7.03-7.05 (d, 2H), 7.30-7.32 (d, 1H), 7.44- 7.46 (dd, 3H), 7.50-7.52 (dd, 2H), 7.58-7.60 (m, 3H), 7.79-7.81 (d, 2H), 7.89-7.91 (dd, 1H), 8.24-8.26 (s, 1H)

(3b) IR (KBr) cm-1 : 3591, 3126, 3057, 2993, 2951, 2833, 1727, 1497, 1432, 1332, 1227, 1220, 1180, 1003, 908, 748, 684, 1H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.34-2.36 (s, 3H), 3.78-3.80 (s, 3H), 7.02-7.05 (dd, 2H), 7.11-7.13 (d, 1H), 7.29- 7.31 (t, 1H), 7.44-7.50 (m, 5H), 7.58-7.61 (t, 3H), 7.89-7.91 (dd, 1H), 8.06-8.08 (dd, 1H), 8.43-8.45 (s, 1H)

(3c) IR (KBr) cm-1:3616, 3560, 3036, 2981, 2892, 1707, 1489, 1453, 1372, 1281, 1246, 1205, 997, 961, 735. 1H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.35-2.36 (s, 6H), 7.05-7.09 (d, 2H), 7.28-7.30 (m, 3H), 7.44-7.46 (dd, 2H), 7.50-7.52 (dd, 3H), 7.58-7.60 (dd, 2H), 7.67-7.69 (dd, 2H), 8.40-8.42 (s, 1H)

(3f) IR (KBr) cm-1: 3589, 3524, 3097, 3059, 2949, 2833, 1708, 1618, 1593, 1529, 1440, 1336, 1282, 977, 842, 750, 1H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.34- 2.36 (s, 3H), 3.78-3.80 (s, 3H), 7.05-7.08 (m, 4H), 7.28-7.30 (t, 1H), 7.43-7.45 (m, 4H), 7.73-7.75 (d, 2H), 7.86-7.88 (m, 2H), 8.05-8.09 (dd, 1H), 8.43-8.45 (s, 1H)

(3g) IR (KBr) cm-1 : 3606, 3540, 3026, 2980, 2891, 1717, 1479, 1443, 1371, 1282, 1236, 1215, 998, 962, 704, 1H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.35-2.37 (s, 3H), 7.03-7.05 (d, 2H), 7.30-7.32 (d, 1H), 7.44-7.46 (dd, 3H), 7.50-7.52 (dd, 2H), 7.58-7.60 (m, 3H), 7.79-7.81 (d, 2H), 7.89- 7.91 (dd, 1H), 8.24-8.26 (s, 1H)

(3h) IR (KBr) cm-1: 3616, 3560, 3036, 2981, 2892, 1707, 1489, 1453, 1372, 1281, 1246, 1205, 997, 961, 735, 1H NMR 400 MHz: (DMSO-d_6, δ ppm): 2.35-2.36 (s, 6H), 7.05-7.09 (d, 2H), 7.28-7.30 (m, 3H), 7.44-7.46 (dd, 2H), 7.50-7.52 (dd, 3H), 7.58-7.60 (dd, 2H), 7.67-7.69 (dd, 2H), 8.40-8.42 (s, 1H)

Result and Discussion

Keeping focus on green protocol, we select alum as efficient catalyst for cross Aldol condensation, as another part of eco-friendly reaction condition we used microwave irradiation as source of energy. Reaction proceeds with two substantial steps first optimization of percentage of alum used in reaction and secondly microwave power require for the best conversion.

We observed that isolation of yield in very short time of microwave irradiation at 300 W, on this basis we were optimized the reaction condition, then we carried out same synthesis in different concentration of alum under solvent free condition, we conclude that 20 mol% is a very good concentration of alum catalyst under microwave irradiation techniques for synthesis of chalcone derivatives of coumarins. (Table 2)

Table 1. Physical data of Chalcone derivatives.

Comp.	R and R'	Molecular Formula	M.p. (Lit.) in °C	Yield [a]	Time (MWI)
3a	6-CH_3 and H	$C_{28}H_{20}N_2O_4$	219-220,(221)[xii]	95%	5 min.
3b	6-CH_3 and 2 –OCH_3	$C_{29}H_{22}N_2O_5$	214-215,(213) [xii]	92%	5 min.
3c	6-CH_3 and 4-CH_3	$C_{29}H_{22}N_2O_4$	227-228,(231) [xii]	94%	5 min.
3d	6-CH_3 and 4-NO_2	$C_{28}H_{19}N_3O_6$	221-222,(225) [xii]	83%	5 min.
3e	6-CH_3 and 4-Cl	$C_{28}H_{19}ClN_2O_4$	225-226,(229) [xii]	89%	5 min.
3f	7-CH_3 and 2-OCH_3	$C_{29}H_{22}N_2O_5$	208-209,(205) [xii]	93%	5 min.
3g	7-CH_3 and H	$C_{28}H_{20}N_2O_4$	180-181,(181) [xii]	90%	5 min.
3h	7-CH_3 and 4-CH_3	$C_{29}H_{22}N_2O_4$	189-190,(191) [xii]	91%	5 min.
3i	7-CH_3 and 4-NO_2	$C_{28}H_{19}N_3O_6$	205-206,(201) [xii]	81%	5 min.
3j	7-CH_3 and 4-Cl	$C_{28}H_{19}ClN_2O_4$	188-189,(185) [xii]	87%	5 min.

[a]*Isolated yield*

Table 2. Optimization of % of alum catalyst for synthesis of chalcone derivatives of coumarins under solvent free conditions.

Entry	Alum catalyst (mol %)	Time of MWI	Yield [a]
1.	10	3 min.	55%
2.	15	3 min	69%
3.	**20**	**3 min**	**78 %**
4.	25	3 min	78%
5.	30	3 min	76%
6.	35	3 min	71%

[a]*Isolated yield*

Table 3. **Optimization of microwave irradiation time for synthesis of chalcone derivatives under solvent free and alum catalyzed condition**

Entry	Alum catalyst (mol %)	Time of MWI	Yield [a]
1.	20%	1 min.	55%
2.	20%	2 min.	64%
3.	20%	3 min.	78%
4.	20%	4 min.	83%
5.	**20%**	**5 min.**	**95%**
6.	20%	6 min.	90%

[a]*Isolated yield*

In next step, we optimized microwave irradiation time for same reaction condition and concluded that 5 min. irradiation of microwave time is very good for chalcone yield that is 95% (Table 3, Entry 5)

Conclusion

In conclusion we report the synthesis of coumarin chalcone from 4-hydroxy-3-acetyl coumarin and pyrazole aldehydes in alum (20 mol %) catalyzed under solvent free condition by microwave assistant techniques. This procedure is greener, simple and efficient with excellent yield under solvent free condition.

Acknowledgement

Authors are thankful to the Principal, Yashwant Mahavidhyalaya, Nanded for constant encouragement and providing necessary facilities for this work and one of the author (Chavan O.S.) is thankful to UGC, New Delhi, for providing financial Assessment.

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Received on April 13, 2015.