ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 6, Issue 2, pp: (228-231), Month: April - June 2018, Available at: www.researchpublish.com

SYNTHESIS OF SOME SUBSTITUTED BENZYLIDENE ACETOPHENONES UNDER MICROWAVE IRRADIATION

Shailendra Jain

Synthetic Organic Chemistry Laboratory, M.L.V. College, Bhilwara (Raj.) -311001, INDIA
E-mail: shailjain1@yahoo.co.in

Abstract: **Claisen–Schmidt condensation has been carried out for the synthesis of some substituted benzylidene acetophenones under microwave irradiation is based on solid phase, solvent free protocol. In the present investigation, condensation has been carried out in the presence of basic alumina, instead of normal bases like NaOH or KOH, which makes the process eco-friendly, economic and easy and becomes a part of green chemistry.**

Keywords: **Claisen-Schmidt condensation, microwave irradiation, solvent free protocol, green chemistry.**

1. INTRODUCTION

Over the years various innovative methods have been devised to speed up the chemical reactions. In the environment conscious era, the development of technology is directed towards environmentally sound and eco-friendly methods. The usage of microwave energy to accelerate the organic reactions is of increasing interest and offers several advantages over conventional techniques[1].

Synthesis of the molecules which normally requires a long time period can be achieved rapidly and conveniently in microwave oven. Less reaction time, easy work up and cleaner products are the major advantages of microwave protocol. Furthermore the reactions can be carried out under solvent free conditions which hold a strategic position as the solvents are often very toxic, problematic and expensive to use. Solvent free condition is especially suitable for microwave activation. Thus the use of microwave energy for the synthesis of organic compounds forms a part of green chemistry.

Title compounds of the present investigation are having an α,ß - unsaturated carbonyl group are one of the important biocides and versatile synthons for various chemical transformations. Chemically they can also be termed as phenylstyrylketones, benzalacetophenones, α-phenyl-β-benzoylethylene and β- phenylacrylophenone. They are popularly known as chalcones.

The chalcones having an α,ß-unsaturated ketone system, serve as important Michael acceptors.They serve as a synthon in various chemical transformations for the synthesis of a variety of biodynamic molecules such as five membered (pyrazolines, isoxazoline), six membered (pyridines, pyrimidines), and seven membered (diazepines, thiazipines) heterocyclic and carbocyclic systems[2]. These systems constitute the major share of synthetic drugs, which are capable of performing a variety of functions. A wide spectrum of pharmacological properties is associated with chalcone derivatives. Most of the chalcones are highly biologically active with a number of medicinal and pharmacological applications. Chalcones have been used as anti-HIV agents[3], cytotoxic agents[4], anticancer[5], anti-inflammatory[6] and anti-protozoal agents[7]. Keeping in view the advantages of microwave heating and the usage of chalcones as natural biocides, in the present investigation, I have carried out the synthesis of some substituted hydroxychalcones by Claisen-Schmidt condensation. This reaction is generally carried out in presence of base like NaOH or KOH which are harmful, toxic and polluting. Therefore, in the present investigation we have used basic alumina as the condensing agent which is cheap,

non-toxic and easy to use. Furthermore the reaction can be easily carried out under solvent free condition under microwave irradiation so as to minimize the pollution.

Mono and disubstituted hydroxyacetophenones were condensed with variously substituted aromatic aldehydes in presence of basic alumina to afford the desired benzylidene acetophenones in 80-85 % yields under microwave irradiations. The reaction was completed within 4-6 minutes.

2. EXPERIMENTAL

Melting points of all synthesized compounds were determined in open capillary tubes on an electro thermal apparatus and are uncorrected. The purity of the compounds was monitored by thin layer chromatography on silica gel coated aluminium plates (Merck) as adsorbent and UV light as visualizing agent. The progress of the reaction was also checked by UV-Vis spectrophotometer (UV-1700,Shimatzu). IR spectra (KBr in cm^{-1}) were recorded on a Perkin-Elmer spectrophotometer in the range of 4000-400 cm^{-1}. 1H NMR spectra were recorded on a ECS 400 MHz (JEOL) NMR spectrometer using CDCl3 as solvent and TMS as an internal standard (chemical shifts in δ ppm).Mass spectra were recorded by Xevo G2-SQ,TOF(Waters).Domestic Microwave oven (Samsung CE117ADE,output 900W, frequency 2450MHz) was used to synthesize the titled compounds.

(2 or 2,4)-Hydroxy acetophenone (1) (0.005mol), substituted benzaldehyde (2a-f) (0.005mol) and basic alumina were thoroughly mixed to form a thick paste. The paste was air dried and the residual mass was subjected to microwave irradiation for 4-6 minutes. After completion of reaction as indicated by tlc, the contents were dissolved in ethanol. Inorganic material was filtered off and then filtrate, after concentration, was left overnight to get analytical sample of the benzylidene acetophenones(3a-f) in 80-85% yields.

3. RESULTS AND DISCUSSION

Claisen-Schimdt condensation is a versatile method for the preparation of α,ß-unsaturated carbonyl compounds. The reaction is generally carried out in presence of aqueous alkali[8-14]. The concentration of the alkali generally lies between 20-60%. Other condensing agents which have been used for this reaction include activated carbons[15], ionic liquid catalyst under ultrasound irradiation[16], graphene-supported ZnO nanoparticles[17], mesoporous silica (SBA-Pr-NH_2) nano base catalyst[18] and MgO nanoparticles[19] which are quite expensive and require a lot of precautions during their use. In the present investigation I have carried out the condensation of hydroxy acetophenone and substituted aromatic aldehyde in presence of basic alumina. In comparison to above mentioned condensing agents, it is non toxic, non expensive and easy to use reagent. Furthermore its use in presence of microwave irradiation makes the process eco-friendly and economic and makes a new path in green chemical transformation. In comparison to the conventional method, yield obtained is higher and cleaner products are obtained.

The synthesized compounds show two absorption bands located 300nm (band I) and 230 nm (band II) in UV spectra, which are believed to originate due to presence of two chromophoric groups e.g., benzoyl and cinnamoyl moieties in the chalcone molecule. However, according to the accepted view band I results from the conjugation of the whole molecule. This band is dominant whereas band II is of low intensity.

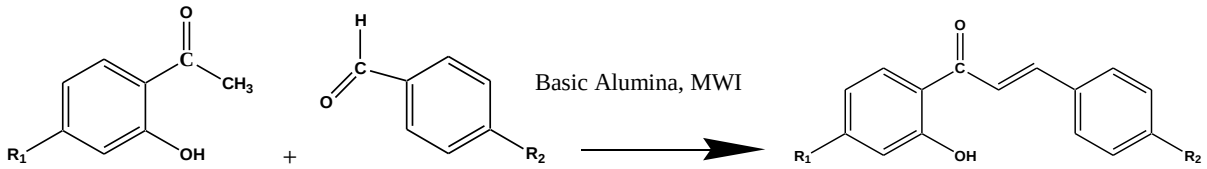
The characterization of prepared compounds has also been made by their IR spectra. Effect of intramolecular hydrogen bonding is observed in IR frequency of carbonyl group which shift the carbonyl band to lower frequency region 1640-1630 cm^{-1}.Characteristic aromatic C-H stretching band in the 3100-3000 cm^{-1} region is also observed. Medium to intense absorption peaks in the range 1600-1400 cm^{-1} are observed which are due to benzene ring vibrations. However, the number and position of these peaks depend to some extent upon the substitution of the aromatic ring as well. Two absorption peaks of medium to strong intensity occur in the region 1000-950 cm^{-1}, these may be attributed to –CH=CH- out of the plane vibrations. An intense peak at nearby 1300 cm^{-1} may be due to –CH=CH- vibration confirming the presence of trans-ethylenic structure.

The PMR spectra of synthesized chalcones exhibited protons as two doublets in the range of δ 7.6-7.7 and δ 7.8-7.9 respectively. The aromatic protons of the rings were seen in the region δ 6.7-7.0.

Mass spectral studies of synthesized compounds showed the presence of strong ions for M^+, $[M-H]^+$and $[M-CO]^+$. Fragmentation pattern took place on expected lines on either side of the carbonyl group and the fragment ions derived from it depend upon the substitution pattern of the parent compound.

ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 6, Issue 2, pp: (228-231), Month: April - June 2018, Available at: www.researchpublish.com

REACTION SCHEME:



(1) **(2a-f)** **(3a-f)**

TABLE - PHYSICAL DATA OF SYNTHESIZED COMPOUNDS

Comp.	R_1	R_2	Mol. Formula	Mol. Wt	MP	React. Time Conv. Hrs	MWI Mins	%Yield Conv.	%Yield MWI
3a	H	OH	$C_{15}H_{12}O_3$	240.25	116	5.5	4.5	62	82
3b	H	$N(CH_3)_2$	$C_{17}H_{12}NO_2$	267.32	159	5.0	4.0	58	85
3c	OH	OH	$C_{15}H_{12}O_4$	256.25	80	5.5	5.0	55	85
3d	H	Cl	$C_{15}H_{11}ClO_2$	258.70	152	7.0	6.0	48	84
3e	H	CH_3	$C_{16}H_{14}O_2$	238.28	143	8.5	5.0	56	80
3f	H	OCH_3	$C_{16}H_{14}O_3$	254.28	92	6.0	4.5	61	83

ACKNOWLEDGEMENT

Author is grateful to the Principal, M. L. V. Govt. College, Bhilwara (Raj.) for providing necessary facilities. Author is also thankful to the Director, MRC, MNIT, Jaipur for providing spectral analyses.

Author thankfully acknowledges UGC for providing financial assistance.

REFERENCES

[1] Caddick, S., *Tetrahedron*, 1995, 51, 10403.

[2] Prabhakar, V., Kondra, S. B., Ravindranath, L. K., Basha, M. S., and Latha, J., *Asian Journal of Research in Chemistry*, 2017, 10(2), , 71-84.

[3] Koran, K., Çiğdem T., Fatih, B., Suat, T., Süleyman, S. and Ahmet, O. G., *Medicinal Chemistry Research*, 2017, 26(5), 962-974.

[4] Mellado-García, M., Reyna, M., Weinstein-Oppenheimer, C., Cuellar, M. and Aguilar, L. F., *J Pharmacol Ther Forecast*, 2018,1(1), 1003.

[5] Das, M. and Kuntal M., *Journal of toxicology*, 2016, 4, 208.

[6] Li, J., Dong L., Xu, Y., Guo, Z., Liu, X., Yang, H., Lichuan W. and Lisheng, W., *Bioorganic & medicinal chemistry letters*, 2017, 27(3), 602-606.

[7] Ramírez–Prada, J., Sara M. R., Iván D. V., Crespo, M. P., Quiroga, J., Rodrigo, A., Montoya, A., Svetaz, L., Zacchino, S. and Braulio I., *European journal of medicinal chemistry*, 2017, 131, 237-254.

[8] Kohlar, E. F. and Chandwell, H. M., *Org.Synth.Coll.*, 2015, 2, 1, 8902.

[9] Yu, L., Han, M., Luan, J., Xu, L., Ding, Y. and Xu, Q., *Scientific Report*, 2016, 6, 30432.

[10] Schrafstatter, E. and Deutsch, S., *Chem. Ber.*, 1948, 81, 489.

[11] Solankee, A., and Riki T., *Chemistry International*, 2016, 2, 4, 189-200.

[12] Smith, H. E. and Paulson, M. C., *J.Am.Chem.Soc.*, 1954, 76, 4486.

[13] Martins, L., Hölderich, W., Hammer, P. and Cardoso, D. , *Catalysis*, 2010, 271, 2, 224.

[14] Chavan, B. B., Gadekar, A. S., Mehta, P. P., Vawhal, P. K., Kolsure, A. K. and Chabukswar, A. R., *Asian Journal of Biomedical and Pharmaceutical Sciences*, 2017, 6, 56, 4532.

[15] Winter, C., Jéssika N. C., Anderson B. C. A., Chaves, A. R., Indianara, C. O., Boniek, G. V., Caridad, N. P. and Alonso, C. G., *Chemical Engineering Journal*, 2016, 303, 604-610.

[16] Arafa, W. A., *Journal of Heterocyclic Chemistry*, 2018, 55, 2, 456-464.

[17] Li, Z., Hongyan, Z, Han, H., Liu, Y., Song, J., Guo, W., Chu, W. and Sun, Z., *Tetrahedron Letters*, 2017, 58, 42, 3984-3988.

[18] Ziarani, M., Ghodsi, Lashgari, N. and Badiei., A., *Current Organic Chemistry*, 2017, 21, 8 , 674-687.

[19] Gajengi, A. L., Takehiko S., and Bhalchandra M. B., *Advanced Powder Technology*, 2017, 28, 4, 1185-1192.