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Microwave assisted sulphated titania catalyzed aldol condensation: Synthesis of some (*E*) 3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones under solvent-free conditions

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ABSTRACT

A series of titled chalcones were synthesized by aldol condensation between 2-naphthaldehyde and various substituted acetophenones using solid acidic solid sulphated titania catalyst under microwave irradiation. The yields of these chalcones are more than 90 %. The synthesized chalcones are characterized by their physical constants, analytical and spectroscopic data.

***Keywords*:** Aldol condensation; Sulphated titania, Microwave irradiation; 2-propen-1-ones

1. INTRODUCTION

Chalcones or α,β-unsaturated ketones are enones [1]. They possess vinyl and carbonyl group adjacently and aryl or alkyl group in both of the ends [2]. They exist as *E* s-cis and s-trans conformers [3]. These conformers were confirmed by IR and NMR spectra [4]. Presence of vinyl, carbonyl and the polar substituents in the aryl rings of chalcones shows an important biological activities [5] such as antimicrobial [6], antidepressants [7], antiplosmodial [8], anti-aids [9] and insect antifeedant activities [10,11].

Various solvent-free and solvent assited methods are available for synthesis of chalcones. Many catalysts were applied for synthesis of chalcones using either solvent assisted or solvent-free methods such as EtOH-NaOH [12], MeOH-KOH [13], EtOH-KOH [14], $MgCl_2$ [15], silica-sulphuric acid [16], anhydrous zinc chloride [17], clay [18], Hydrotalcite [19], ground chemistry catalysts-grinding the reactants with sodium hydroxide [10], aqueous alkali in lower temperature [20], solid sulphonic acid from bamboo [21], barium hydroxide [22] anhydrous sodium bicarbonate [23], microwave assisted synthesis [24], fly-ash:water [25], fly-ash:H_2SO_4 [26], fly-ash:PTS [27], NaOH-CTABr [11], SiO_2-H_3PO_4 [28], $SOCl_2$ [29] and sulfated titania [30].

Within the above view, there is no report available for synthesis of titled compound by sulphated titania assisted aldol condensation of 2-naphthaldehyde and substituted acetophenones under microwave irradiation.

Therefore the authors have taken efforts for solvent-free synthesis of titled compounds and recorded their IR and NMR spectra for characterization.

2. EXPERIMENTAL

2. 1. General

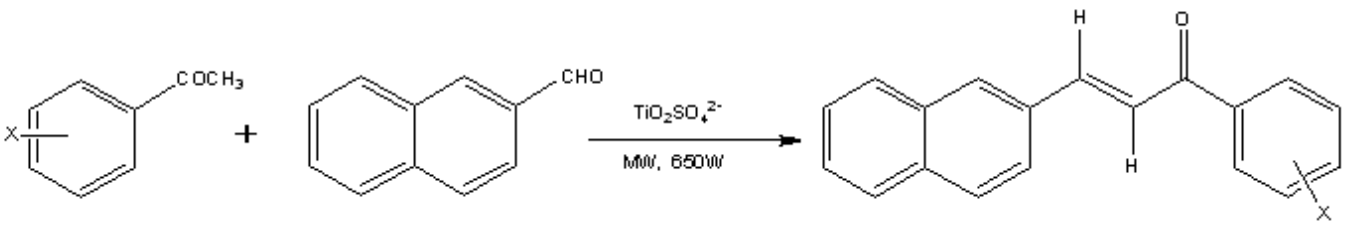
All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones were determined in open glass capillaries on SUNTEX melting point apparatus and are uncorrected. The UV spectra of all synthesized chalcones were recorded in ELICO-BL222 SPECTROMETER (λ_{max} nm) in spectral grade methanol.

Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer has been used for recording NMR spectra, operating at 400 MHz has been utilized for recording ^{1}H spectra and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Mass spectra were recorded on a SIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

2. 2. General procedure for synthesis of (*E*)-3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones

Appropriate quantities of substituted acetophenones (2 mmol) and 2-naphthaldehyde (2 mmol) and 0.15 g of sulfated titania were taken in a 50 mL beaker and closed with the lid. This mixture was subjected to microwave irradiation for 2-4 minutes at 650 W (Scheme 1) (Samsung, Microwave Oven, 100-700 W).

After completion of the reaction, dichloromethane (20 mL) was added, followed by simple filtration. The filtrate was concentrated and the obtained solid was purified by re-crystallization. The synthesized chalcones were characterized by their physical constants, UV, IR, ^{1}H and ^{13}C NMR and Mass spectral data. Analytical and Mass spectral data are presented in Table 1.



Entry	1	2	3	4	5	6	7	8	9	10	11
X	H	4-Br	4-Cl	4-F	2-OH	4-I	4-OCH_3	4-CH_3	2-NO_2	3-NO_2	4-NO_2

Scheme 1. Synthesis of (*E*)-3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones.

Table 1. Physical constants, analytical and mass fragments (m/z) data of (*E*)-3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones.

Entry	X	M.F.	M.W.	Yield (%)	m.p. (◦C)	Mass (m/z)
1	H	$C_{19}H_{14}O$	258	94	111-112 (111-112)[31]	258[M^+]
2	4-Br	$C_{19}H_{13}BrO$	337	91	98-99 (96-98)[31]	337[M^+], 339[M^{2+}]
3	4-Cl	$C_{19}H_{13}ClO$	219	92	116-117 (116-117)[32]	219[M^+], 221[M^{2+}]
4	4-F	$C_{19}H_{13}FO$	276	90	105-106 (105-106)[32]	276[M^+], 278[M^{2+}]
5	2-OH	$C_{19}H_{14}O_2$	274	93	88-89	274[M^+]
6	4-I	$C_{19}H_{13}IO$	384	92	118-119 (115-116)[33]	384[M^+], 386[M^{2+}]
7	4-OCH_3	$C_{20}H_{16}O_2$	288	95	122-123	288[M^+]
8	4-CH_3	$C_{20}H_{16}O$	272	90	112-113	272[M^+]
9	2-NO_2	$C_{19}H_{13}NO_3$	303	90	132-133	303[M^+]
10	3-NO_2	$C_{19}H_{13}NO_3$	303	90	127-128	303[M^+]
11	4-NO_2	$C_{19}H_{13}NO_3$	303	90	119-120 (199-122)[33]	303[M^+]

3. RESULTS AND DISCUSSION

In our organic chemistry research laboratory, we attempts to synthesize aryl chalcone derivatives by crossed-aldol condensation of electron withdrawing as well as electron donating group substituted acetophenone and benzaldehydes in the presence of vigorous acidic catalyst sulphated titania in microwave irradiation.

Hence the authors have synthesized the chalcone derivatives by the reaction between 2 mmol of 2-naphthaldehyde, 2 mmol substituted acetophenones in microwave irradiation with 0.15 g of sulphated titania catalyst (Scheme 1).

During the course of this reaction sulphated titania catalyzes aldol-condensation between aryl ketone and aldehydes and elimination of water gave the chalcones. The yields of the chalcones in this reaction are more than 90 %.

This condensation follows acid catalyzed mechanism. The spectroscopic data of synthesized chalcones are presented in Tables 2 and 3. These data are supported for the formation of chalcones [34-47].

Table 2. Infrared spectral data (ν, cm^{-1}) of (*E*)-3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones.

Entry	X	CO *s-cis*	CO *s-trans*	CH_{ip}	CH_{op}	$CH{=}CH_{op}$	$C{=}C_{op}$
1	H	1659.82	1602.30	1209.31	702.37	1087.08	688.76
2	4-Br	1679.91	1634.24	1212.20	750.28	1017.35	691.86
3	4-Cl	1659.39	1598.43	1206.09	814.40	1012.04	687.68
4	4-F	1661.55	1602.11	1207.88	781.53	1018.27	693.75
5	2-OH	1654.64	1602.11	1258.11	739.99	1074.79	685.65
6	4-I	1661.28	1609.06	1185.52	729.60	1027.43	683.13
7	4-OCH_3	1658.91	1604.11	1206.97	749.59	1029.51	673.24
8	4-CH_3	1658.33	1600.33	1209.14	731.63	1010.58	677.15
9	2-NO_2	1658.59	1592.57	1176.17	816.30	1007.20	674.17
10	3-NO_2	1677.41	1634.21	1161.21	876.74	1017.14	655.16
11	4-NO_2	1678.54	1632.41	1148.24	868.32	1056.82	673.26

Table 3. NMR spectral data (δ, ppm) of (*E*)-3-(2-naphthyl)-1-(substituted phenyl)-2-propen-1-ones.

Entry	X	H_α	H_β	CO	C_α	C_β
1	H	7.622	8.936	188.85	123.64	145.19
2	4-Br	7.002	7.958	188.56	125.55	136.90
3	4-Cl	7.843	8.057	189.04	123.49	134.71
4	4-F	7.657	8.075	188.00	123.32	134.18
5	2-OH	7.987	8.024	189.71	123.61	134.50
6	4-I	7.437	7.878	188.17	124.75	139.65
7	4-OCH_3	7.670	7.760	188.75	123.74	144.11
8	4-CH_3	7.684	7.945	190.03	123.73	144.53
9	2-NO_2	7.620	8.019	189.08	123.62	134.5
10	3-NO_2	7.869	8.041	189.39	125.71	145.56
11	4-NO_2	7.871	8.132	189.78	125.69	144.97

4. CONCLUSIONS

About eleven titled chalcones were synthesized by aldol condensation between 2-naphthaldehyde and various substituted acetophenones using solid acidic solid sulphated titania catalyst under microwave irradiation. The yields of these chalcones are more than 90 %. The synthesized chalcones are characterized by their physical constants, analytical and spectroscopic data. These data are supported for the formation of chalcones.

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