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NOTE

Solvent-Free Synthesis of N-aryl-β-Enaminones Under Microwave Irradiation

GUANGYONG XIE[1,2,3,*], LONG LI[2], GONGYI LIU[2], LU LEI[2] and AIQING ZHANG[2]

[1]Key Laboratory of Rubber-Plastics of Ministry of Education/Shandong Provincial Key Laboratory of Rubber -plastics, Qingdao University of Science & Technology, Qingdao 266042, P.R. China
[2]Key Laboratory of Catalysis and Materials Science of Hubei Province, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, P.R. China
[3]Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, P.R. China

*Corresponding author: Tel: +86 27 67842752; E-mail: xxgyy@hotmail.com

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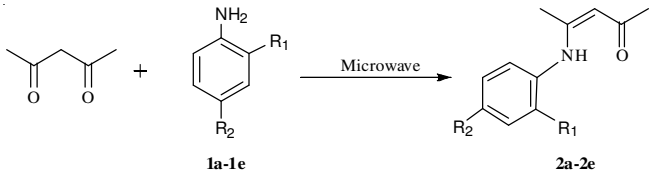
A series of N-aryl-β-enaminones were efficiently prepared by acetylacetone reacted with substituted anilines in high yields without additional solvent under microwave irradiation. The most yields can reach over 80 %. Compared with traditional routes, this method needs only 15 min and simpler after-treatment procedures while owns higher yields.

Keywords: N-aryl-β-enaminones, Acetylacetone, Microwave, Solvent-free Synthesis.

β-Enaminone compounds are very important intermediates for organic synthesis and have received considerable attentions in recent years, which can be used for the synthesis of some compounds having biological or pharmacological activity, such as α- or β-amino acids, polypeptide, alkaloid, pyrazole, *etc*.[1-3]. β-Enaminone with aryl group on N-atom, *i.e*. N-aryl-β-enaminone, can also chelate with transition metals to obtain complexes, which can usually be used for the catalysts of olefin polymerization or oligomerization[4].

Traditionally, β-enaminone compounds can be prepared by the condensation of β-diketones with amines catalyzed by proton acid catalysts[5,6], which usually needs organic solvents and high temperature to reflux and remove the generated water. These methods would lead to low yield, complicated after-treatment, high energy consumption and serious environmental pollution, *etc*. Better results can be obtained when solid Lewis acid catalysts[7-9] were used, but the yields for N-aryl-β-enaminones are much lower.

Microwave has been widely adopted for the synthesis of organic compounds. Since the mid-1980s, a large number of studies have demonstrated that an acceleration of chemical rates can be achieved by employing high-density microwave irradiation instead of traditional sources of heat. Recently we synthesized a series of N-aryl-β-enaminones in good yields without any supernumerary solvents under microwave irradiation, which was followed as **Scheme-I**. Compared with other traditional routes, this method needs less reaction time, easier after-treatment and can obtain higher yields.



a: R_1=CH_3, R_2=H; b: R_1=F, R_2=H; c: R_1=H, R_2=F
d: R_1=F, R_2=F; e: R_1=Cl, R_2=H

Scheme-I: Synthesis of N-aryl-β-enaminones under microwave irradiation

Acetylacetone and substituted anilines were purchased from Acros Organics or Aldrich Chemical Co. without further purification. The melting points were determined on a X6 microscopic warming apparatus and are uncorrected. ^{1}H NMR spectra of the compounds were recorded on a Bruker Avance III 400 MHz spectrometer with tetramethylsilane as an internal standard. IR spectra of the compounds were collected on a Nicolet Nexus470 FT-IR spectrometer. Elemental analyses were carried out using Vario EL 111.

General procedure for the synthesis of N-aryl-β-enaminones (2a-2e): The mixtures of acetylacetone (10 mmol), substituted aniline (10 mmol) and three drops acetic acid in the 100 mL flask were reacted 15 min under controlled microwave heating, then the mixtures were diluted with 10 mL

dilute hydrochloric acid and extracted three times with 10 mL diethyl ether. The collected solutions of diethyl ether were dried over anhydrous Na_2SO_4 and then the solvent was evaporated to obtain crude product, which was further purified by recrystal in methanol. Experiments results are presented in Table-1. Spectroscopic data of **2a-2e** are given below.

2a: m.p. 38-40 °C, ^{1}H NMR (400 MHz, $CDCl_3$), δ12.35 (s, 1H, NH), 7.19 (m, 4H, Ph), 5.21 (s, 1H, CH), 2.29 (s, 3H, $PhCH_3$), 2.12 (s, 3H, $CHCOCH_3$), 1.88 (s, 3H, $CHCNCH_3$). IR (KBr, ν_{max}, cm^{-1}): 3432 (N-H), 1597 (C=O), 1560 (C=C). Anal. calcd. (%) for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found (%): C, 76.07; H, 7.78; N, 7.44.

2b: m.p. 47-49 °C, ^{1}H NMR (400 MHz, $CDCl_3$), δ12.25 (s,1H, NH), 7.18 (m, 4H, Ph), 5.26 (s, 1H, CH), 2.11 (s, 3H, $CHCOCH_3$), 1.94 (s, 3H, $CHCNCH_3$). IR (KBr, ν_{max}, cm^{-1}): 3439 (N-H),1616 (C=O), 1569 (C=C). Anal. calcd. (%) for $C_{11}H_{12}NOF$: C, 68.38; H, 6.26; N, 7.25. Found (%): C, 68.12; H, 6.28; N, 7.34.

2c: m.p. 44-45 °C, ^{1}HNMR (400 MHz, $CDCl_3$), δ12.26 (s, 1H, NH), 7.07 (m, 4H, Ph), 5.20 (s, 1H, CH), 2.10 (s, 3H, $CHCOCH_3$), 1.93 (s, 3H, $CHCNCH_3$). IR (KBr, ν_{max}, cm^{-1}): 3447 (N-H), 1609 (C=O), 1570 (C=C). Anal. calcd. (%) for $C_{11}H_{12}NOF$: C, 68.38; H, 6.26; N, 7.25. Found (%): C, 68.43; H, 6.18; N, 7.20.

2d: m.p. 44-46 °C, ^{1}HNMR (400 MHz, $CDCl_3$), δ12.08 (s, 1H, NH), 6.84-7.16 (m, 3H, Ph), 5.26(s, 1H, CH), 2.10 (s, 3H, $CHCOCH_3$), 1.88 (s, 3H, $CHCNCH_3$). IR (KBr, ν_{max}, cm^{-1}): 3439 (N-H), 1609 (C=O), 1568 (C=C). Anal. calcd. (%) for $C_{11}H_{11}NOF_2$: C, 62.55; H, 5.25; N, 6.63. Found (5): C, 62.66; H, 5.37; N, 6.45.

2e: m.p. 65-66 °C, ^{1}HNMR (400 MHz, $CDCl_3$), δ12.41 (s, 1H, NH), 7.13-7.44 (m, 4H, Ph), 5.26 (s, 1H, CH), 2.12 (s, 3H, $CHCOCH_3$), 1.94 (s, 3H, $CHCNCH_3$). IR(KBr), ν, cm^{-1}: 3447 (N-H), 1604 (C=O), 1558 (C=C). Anal. calcd. For $C_{11}H_{12}NOCl$: C, 63.01; H, 5.77; N, 6.68. Found: C, 63.21; H, 5.82; N, 6.83.

The title compounds were characterized by ^{1}H NMR, IR and element analysis and the structures were confirmed.

From Table-1, it can be seen that N-aryl-β-enaminones can be prepared easily in a short time promoted by microwave with the yields up to 84 %. Compared with other traditional routes, this method needs less reaction time and simpler after-treatment while obtains higher yields. The powers of microwave, reaction times and substituted groups can affect the yields of products. Firstly, the reaction times can be condensed greatly in comparison with the traditional methods, which usually need several hours and thus the energy can be saved greatly. For *o*-methyl substituted N-aryl-β-enaminones, the yield of **2a** can reach 84.1 % with only 15 min and the yields would decrease as increasing or decreasing reaction times (Entry 1-3). Secondly, the microwave powers can also affect the reaction activities. When the power increases from 490 watt to 700 watt, a little reduction of yield would appear. Thirdly, the substituted groups on amines have great influences upon the yields of N-aryl-β-enaminones. From entry 2 and 5-8, it can be found that the N-aryl-β-enaminones with electron-donating groups would obtain higher yields, while the electron-withdrawing groups would decrease the yields of N-aryl-β-enaminones greatly. Furthermore, the *ortho* electron-withdrawing groups have more obvious reduction upon the yields than the *para*-ones and more electron-withdrawing groups can reduce the yields further.

TABLE-1
SYNTHESIS OF N-ARYL-β-ENAMINONES UNDER MICROWAVE IRRADIATION

Entry	Product	Power (watt)	Time (min)	Yield (%)
1	2a	490	10	78.3
2	2a	490	15	84.1
3	2a	490	20	79.7
4	2a	700	15	81.2
5	2b	490	15	66.4
6	2c	490	15	80.5
7	2d	490	15	62.6
8	2e	490	15	59.9

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