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SYNTHESIS OF BENZYLIDENEACETOPHENONE UNDER MICROWAVE IRRADIATION; GREEN CHEMISTRY

Short report

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Keywords: Benzylideneacetophenone, trans-Chalcone, Microwave Synthesis, Irradiation, Green Chemistry, NMR.

ABSTRACT

The synthetic equivalent of the natural chalcone known as benzylideneacetophenone was obtained under microwave irradiation conditions. The synthetic reaction included benzaldehyde and acetophenone as precursors. The reaction was done under alkaline conditions (NaOH). The pure compound was obtained after crystallization and was characterized by NMR techniques.

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RESUMEN

Spanish title: *Síntesis de bencilidenacetofenona por irradiación de microondas; química verde.* El equivalente sintético de la chalcona natural bencilidenacetofenona, fue sintetizada a partir de la reacción de benzaldehído y acetofenona en medio básico asistido por microondas y purificado por cristalización. La caracterización del compuesto fue realizada por RMN de ¹H y ¹³C.

INTRODUCTION

Phenolics like chalcones of natural origin are known as benzylideneacetophenones. These compounds are natural precursors of open chain flavonoids. In this category are classified chalcones whose structure consists of two benzene rings linked by a α,β -unsaturated carbonyl system bridge. The two benzene rings are named as ring A and B [1]. The range of the biological activities reported for chalcones is wide and varied including antibacterial, anti-inflammatory, antimalarial, antifungal, antiviral, antioxidant, mutagenic and cytotoxic, among the most significant [2]. Besides classical methods for synthesizing chalcones, the green chemistry approach proposes as well a variety of examples. There are current different methods, these differ in conditions implying catalysts, solvents and times of irradiation [3].

Green synthesis of chalcones obey to the Claisen-Schmidt condensation [4,5] which is easily attained with good yields depending on the nature of the reagents and desired products. Currently, there are other many tries using microwave and ultrasound techniques.

The advantages with respect to conventional methods (no MW using) are well known and include shortening of reaction times and cleaner conditions in the obtaining of the products. The product was purified by crystallization and it was identified by NMR techniques.

The present short report is a novelty regarding the microwave method used to synthesize the simplest existing chalcone (benzylideneacetophenone).

RESULTS AND DISCUSSION

The condensation reaction between acetophenone and benzaldehyde under microwave irradiation (170 W, 10 min.) and alkaline conditions (40%) in C₂H₅OH afforded yellowish crystals of compound **1** [6]. See Fig. 1. The product was re-crystallized in Cl₂CH₂ and CH₃OH (5: 95 v/v) and subsequently submitted to 1D and 2D NMR analyses. Comparison of spectral data of **1** with those published [7] permitted the identification of **1** as benzylideneacetophenone or *trans*-chalcone (IUPAC name: (*E*)-1,3-diphenylprop-2-en-1-one). Figures 2 and 3 are the ¹H and ¹³C NMR spectra of **1** which are coincident in chemical shift values and shape with the published spectra [7].

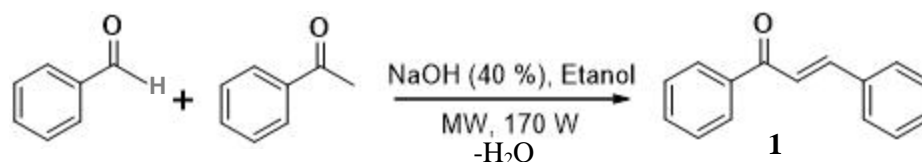


Figure 1. Microwave assisted synthesis of **1**, benzylideneacetophenone (*trans*-chalcone) by Claisen-Schmidt condensation of benzaldehyde and acetophenone

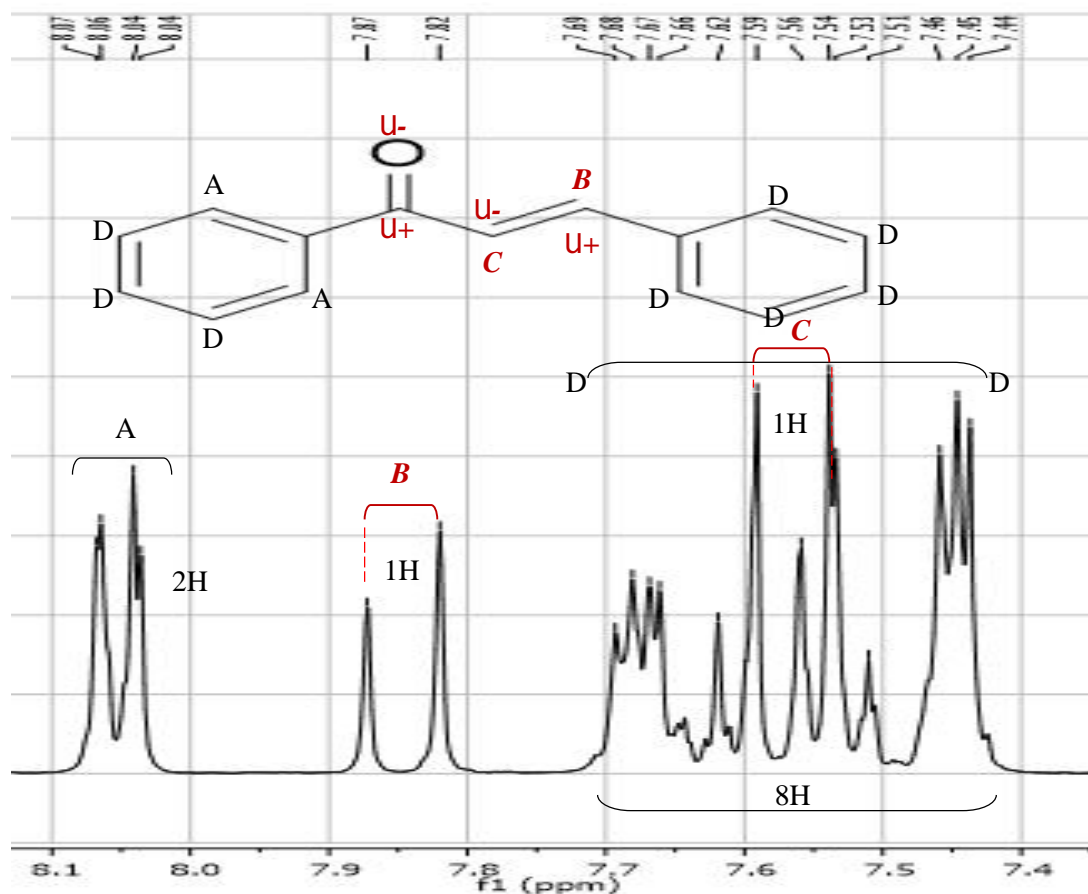


Figure 2. ¹H NMR spectrum of **1**, 300 MHz, CDCl₃, δ from TMS. Assignment by comparison with spectrum from the literature [7]

Protons A are the more deshielded due to the carbonyl's anisotropy cone. The *E* alkene presents two protons (**B** and **C**) with a wide common *J* value of 15.5 Hz, proton **B** is the more deshielded as consequence of its *S* position respect

to carbonyl. The rest of protons (D) present non-analyzable signals (300 MHz) corresponding to 8 aromatic protons distributed in both benzene rings.

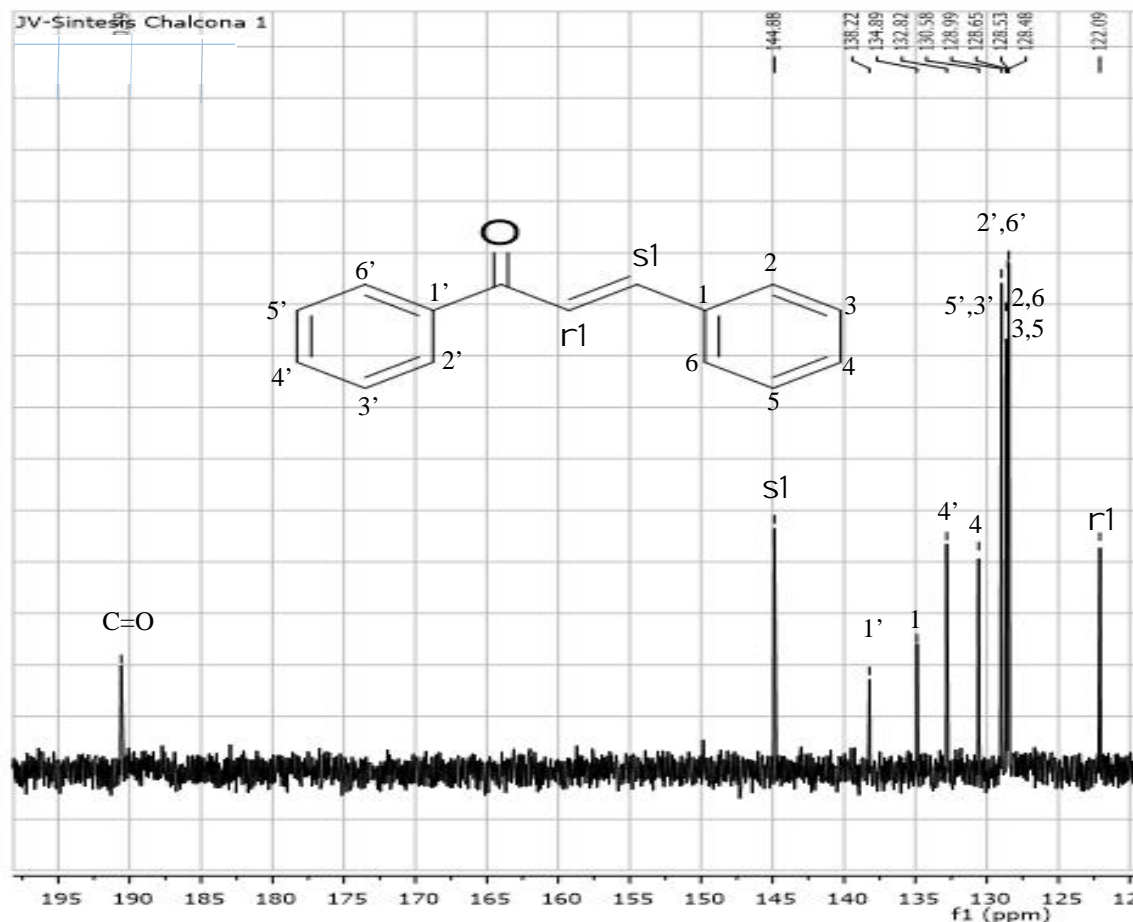


Figure 3. ^{13}C NMR spectrum of **1**, 75 MHz, CDCl_3 , δ from TMS. Assignment by comparison with spectrum from the literature [7]

Table 1. Comparison of ^{13}C chemical shift values of **1** (see Fig. 3) and those reported in the literature for trans-chalcone [7]

Atom	1 $\delta^{13}\text{C}$	1* $\delta^{13}\text{C}$
4 1	134.9 s	134.9 s
9 2	128.48 d	128.49 d
10 3	128.48 d	128.45 d
6 4	130.6 d	130.5 d
10 5	128.48 d	128.45 d
9 6	128.48 d	128.49 d
11 r1	122.1 d	122.1 d
2 s1	144.9 d	144.8 d
3 1'	138.2 s	138.2 s
8 2'	128.7 d	128.6 d
7 3'	129.0 d	128.9 d
5 4'	132.8 d	132.8 d
7 5'	129.0 d	128.9 d
8 6'	128.7 d	128.6 d
1 C=O	190.5 s	190.4 s

*[7]

1*		
ppm	Int.	Atom
190.42	463	1
144.77	433	2
138.22	264	3
134.90	493	4
132.75	398	5
130.51	398	6
128.94	851	7 *
128.60	851	8 *
128.49	1000	9 *
128.45	980	10 *
122.09	483	11

*[7], 25.16 MHz, CDCl_3

EXPERIMENTAL

General

The NMR spectra were run in a Bruker DRX300, (300 MHz ^1H , 75 MHz ^{13}C) equipment at the Department of Chemistry of UMSA, TMS was used as internal standard. Microwave device was DAEWOO DC electronics, model KOC-1B0K, power: 170 W. Synthesis monitoring by Silica gel 60 F254 TLC plates by Merck.

Chemicals

Benzaldehyde (p.a.), acetophenone (p.a.) from Sigma-Aldrich. Ethanol and NaOH commercial.

Synthesis procedure

The synthesis of benzylideneacetophenone (*trans*-chalcone, principal product) by Claisen-Schmidt condensation of benzaldehyde and acetophenone assisted by microwave application was achieved.

In a 50 mL Erlenmeyer flask 1 mL of NaOH (40%) was added together with 1 mL of ethanol and stirred until dissolution. After dissolution, 0.9 mL of benzaldehyde and 0.927 g of acetophenone were added to the reaction mixture and stirred until dissolution at room temperature. Microwave radiation (170 Watts) was applied to the flask in a microwave oven during 10 minutes with cooling of the flask in ice bath each 10 seconds. After 10 minutes of reaction 25 mL of water were added to the flask. After 24 hours of repose at room temperature, an orange precipitate was filtered and separately dissolved in ethanol 95° GL (25 mL). This solution was evaporated at reduced pressure to afford a solid which was subsequently crystallized in dichloromethane - ethanol (5 : 95 v/v) to give yellow crystals. The yield was 43%.

CONCLUSION

We achieved the so far unreported synthesis assisted by microwave irradiation of the known compound benzylideneacetophenone (*trans*-chalcone). Characterization was done by using NMR techniques. Yield was 43%. Even though the green chemistry conditions as: reduced reaction times and reduced use of non aqueous solvents were achieved, the yield of the principal product **1**, was not so encouraging. The amounts of reagents should be revised in future assays in order to increase the yield of **1**.

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