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Microwave Assisted Synthesis and Characterization of Oxime Derivatives of Substituted Chalcones

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Abstract: ***Present paper deals with microwave assisted green synthesis, physico-chemical studies of para substituted 2', 4'-dihydroxy chalcone oxime. The structure of the compounds were characterized by elemental analysis, molar conductance, IR, ^{1}H-, ^{13}C-NMR spectroscopic data. In the present investigation, we report synthesis of oxime derivatives of chalcones in hope of developing new compounds which might be used as analytical reagent or intermediates in synthesis of various classes of bioactive compounds.***

Keywords: Hydroxy chalcones, Chalcone oxime, Microwave irradiated synthesis, IR, NMR

1. Introduction

Synthetic and naturally occurring chalcones have been extensively studied and developed as one of the biologically and pharmaceutically important molecules [1-3]. O-hydroxychalcone and hydroxy chalcone oximes are known to be pharmacologically active and possess coordinating sites and are expected to form complexes with different metal ions and have been employed as useful analytical reagent [4]. Recently a good deal of interest has been centered on the hydroxychalcone oximes having both nitrogen of oxime group and oxygen of phenolic group for the complexation. Oximes of chalcone have been used as analytical reagents [5-9] for the gravimetric as well as spectrophotometric determination [10-11]. The versatile properties of oxygen and nitrogen donating compounds have multifarious roles in various fields as coordination [12-14], organic chemistry [15-16], agriculture [17], medical sciences [18-20] etc.

Now a days microwave induced (MWI) protocol is a well-established procedure for the synthesis of compounds due to several advantages over conventional heating methods. Microwave-irradiated (MWI) synthesis as a non-conventional technique is easy, eco-friendly and economic in comparison to the conventional method. In continuation of our earlier research works on green synthesis (MWI) of substituted chalcones [21] and keeping in view the advantages of microwave heating, the usage of hydroxychalcones in present investigation we would like to report the MWI synthesis and characterization of oxime derivatives of substituted chalcones.

2. Material and Methods

All reagents (AR grade) used were purchased from Sigma alderich and HiMedia Laboratories Ltd. Mumbai, India and used without further purification. Elemental analysis was performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. All the molar conductance of compounds in DMSO (~ 10^{-3} M) at 27± 2°C were done on direct reading electronic µP-multiparameter analyzer. The IR spectra in KBr discs were recorded on a Perkin-Elmer Spectrum Version 10.4.3. The NMR spectra were recorded on Bruker Avance 400 NMR spectrometer in DMSO using TMS as the internal standard. Microwave assisted synthesis were carried out in round bottom flask on a domestic microwave oven model MC2881SUP with rotating tray and a power source 230V. The microwave reactions were performed using on/off cycling to control the temperature. The progress and completion of the reaction was monitored by TLC on silica G gel plates using cyclohexane: ethyl acetate (7:3) solvent system using iodine vapor for detection.

3. Experimental Procedure

Para substituted 2', 4'-Dihydroxy chalcones (DHC):
The para substituted dihydroxychalcones were prepared by taking equimolar amount of dihydroxy acetophenone and p-substituted benzaldehyde in presence of base by Clainsen-Schmidt condensation [22].

Para substituted 2', 4'-dihydroxy chalcone oxime (DHCOx):
Chalcone oximes were synthesized by taking mixture of (0.001M) of DHC, hydroxylamine hydrochloride (0.015M) and sodium acetate (0.5ml) in ethanol (5ml). The covered flask was microwaves irradiated at 200W for 120-150 seconds. On cooling, the solid formed was collected by filtration, washed with water and dried. The resulting product was then recrystallized from ethanol and finally dried over anhydrous $CaCl_2$ in desiccator with high yield, and kept in air tight container. Synthesized products were analyzed and characterized. Analytical and physical data is given in Table 1.

4. Result and Discussion

The synthesized compounds were very pale coloured and stable. Yield were excellent. Elemental analysis showed that the percentage of the elements were found experimentally in agreement with the calculated values in all compounds. Through this analysis, it has been observed that molar conductance value of 10^{-3} M solution of the compounds in DMSO correspond to 5-10 $mScm^2mol^{-1}$ which were very low suggesting their non-electrolytic nature [23-24]. Proposed structure for substituted DHCOx is given in Figure 1. The constitution of newly synthesized compounds was supported by elemental analysis, IR, ^{1}HNMR, and ^{13}CNMR.

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IR spectral studies

The IR spectra of compounds were recorded within the range 4000-450 cm^{-1}. Assignments of the infrared spectral bands are based on literature [25]. On comparing the spectra of the chalcone (3300-3275 cm^{-1}) and the IR spectrum of oxime derivatives of chalcone shows broad and strong band between 3430-3355 cm^{-1} which may be due to phenolic –OH groups [26] and –OH moiety of N-OH group. The N-OH is also confirmed by bending band at 1071.08-1011.40 cm^{-1}. The ketonic (>C=O) stretching frequency of the DHC at 1681.75-1603 cm^{-1} is lowered to 1595-1582 cm^{-1} in DHCOx due to formation of (> C=N). Strong bands at 3019.62 cm^{-1} and 2923.91 cm^{-1} may be assigned to aromatic C-H stretching and aliphatic C-H stretching respectively at nearly same position in chalcones as well as in oxime. The medium intensity band appearing around 1595-1510 cm^{-1} in the chalcones and the oximes are assigned to (C=C, aliphatic).

^{1}H- and ^{13}C-NMR spectra

^{1}H-NMR spectra of the chalcone derivatives were recorded at RT in CDCl3/DMSO-d6 in the range 0-15 (ppm). A doublet resonated at δ 7.55 ppm and a δ 7.98-7.94 were attributed to H-α and H-β respectively, which coupled in a *trans*-relationship with each other. A singlet appeared at δ 10.60-11.35 ppm corresponding to one phenolic proton was assigned to 2'-OH and another singlet at δ 12.59-12.73 ppm for 4'-OH ligand. A singlet of single appeared at δ 7.44-7.75 ppm, a doublets of single at δ 7.28-7.73 and at δ 6.38 ppm were ascribed for H-3', H–5' and H-6' respectively. Another doublet signals of single centered at δ 6.91-6.39 ppm and δ 7.61-7.44 ppm were attributed to H-3, H-5 and H-2, H-6 respectively. The signal at δ 10.20 ppm (s, 1H) corresponding to the N=OH proton.

The ^{13}C–NMR spectrum displayed a deshielded carbon signal at δ 160-163 ppm indicated for C=N group. The signal resonated at δ 164.8-165.0 ppm, δ 133.6, δ 164.2 and δ 128.8 were assigned to quaternary carbons of C-4', C-4, C-1' and C-1 respectively. The olefinic carbons C_{α} and C_{β} were observed at δ 121.3-128.0 ppm and δ 145.1-147.7 ppm respectively. Remaining signals were assigned to the rest of the aromatic carbons in the molecule.

5. Conclusion

In this work, the synthesis of chalcones and their oxime derivatives by microwave irradiation method showed that the reaction time decreased from hours to minutes and with higher yields of the products. The various physico-chemical data confirmed the formation and stoichiometry of compounds. Further studies like complexation, biocidal activities and on the scope of application of the compounds is going on. These findings might be useful in the optimization of DHCOx as lead for future development of an agent for synthesis of new complexes and various pharmacological activities.

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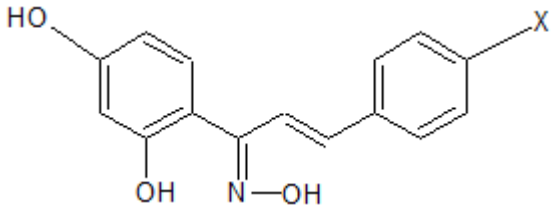

X= F, Cl, Br

Figure: 1

Table 1: Physical and analytical data of the synthesize compounds

S. No.	Compound	Yield %	Time (sec.)	Molar Conduction ($mScm^2mol^{-1}$)	Elemental analysis in %					
					C		H		N	
					Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
1	$C_{15}H_{12}O_3NF$	80	150	5.66	65.93	66.04	4.43	4.51	5.13	5.61
2	$C_{15}H_{12}O_3NCl$	88	130	6.63	62.19	62.32	4.17	4.24	4.83	4.89
3	$C_{15}H_{12}O_3NBr$	78	150	9.82	53.91	66.51	3.62	4.69	4.19	5.46

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