Synthesis and Characterization of 1- Thiocarboxamido-3, 5- diaryl –Δ^2- Pyrazolines by Green Chemistry method.

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Abstract

Chalcones (Prop-2,3-en-1-ones) (1a-e) were obtained by condensation of acetophenone with aromatic aldehydes in alkaline medium , which on microwave irradiation with thio-semicarbazide hydrochloride give 1-Thiocarboxamido-3,5- diaryl –Δ^2-Pyrazolines (2a-e). The properties of these compounds are found to be similar to the compounds obtained by usual method. The structures of these compounds were established by spectral (IR, NMR), elemental and chemical analysis.

Key Words: Microwave Synthesis, Pyrazoline

Introduction

1, 3-Diaryl-Pyrazolines show antibactercidal, cerebroprotective[1] , analgesic[2] and anti-implantation activity[3], hypoglycemic activity[4]. Due to such important roll of pyrazoline derivatives[5-12] , it was thought of interest to synthesize these compounds by acceleration of usual method using microwave radiations. This method has popularized due to concept of Green Chemistry[13], particularly solvent free conditions[14]. Microwave synthesis is one of the most popular method which is fitted among the method mentioned in the green chemistry. Hence it has been thought to prepare 3,5-diaryl- pyrazolines by Microwave irradiation with Prop-2-en-1-ones and thiosemicarbazide hydrochloride and their characterization by elemental analysis, IR, ^{1}H NMR analysis and comparison their properties with the synthesized compounds.

Experimental

The melting points of the synthesized compounds were taken in silicon oil bath with open capillary tubes and are uncorrected. IR spectra were recorded on a Nicolet-Impact 400 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC300 FNMR spectrometer (300MHz), using TMS as an internal standard. Microanalysis of nitrogen was obtained on colman 29-N analyzer. The purity of the compounds was checked by Thin Layer Chromatography on silica gel-G.

Preparation of 2'hydroxy-5'chloro-3-(4'-dimethylaminophenyl)-prop-2-en-1-one (1a)

4-dimethylaminobenzalhyde (0.1mol) and 2'-hydroxy-5'-chloro-acetophenone (0.1mol) were dissolve in ethanol at 50^0 C. To this mixture, 40% aq.NaOH (6ml) was added gradually with constant stirring. The yellow solid cake obtained, was kept overnight and then acidified with dil. HCl till acidic to litmus paper. The resulting solid was filtered, and crystallized from ethanol to get compound (1a). m. p. 158 ^{0}C, yield (74 %)

Spectral interpretation of (1a)

IR (ν_{max}) (cm^{-1}): 1643 v(C=O), 3436 cm^- v (-OH phenolic), 1549 v (-CH=CH-), 1026 v(C-N-$(CH_3)_2$), 1173 v (-C-O stretching in phenols), 730 v(C-Cl).

NMR δ ppm: 3.07 (S, 6H, N$(CH_3)_2$) , 7.32 (d, 1H =CH-), 7.91 (d, 1H =CH-), 13.73 (S, 1 H, -OH) 6.68-7.88 (m, 7H, Ar-H).

Similarly 2'-hydroxy-5'-chloro-3- aryl -prop-2-en-1-ones (1b-h) were prepared and their physical data is given in **Table-1.**

Preparation of 1 - Thiocarboxamido – 3 - (2' – hydroxyl - 5' – chlorophenyl) – 5 - (4-dimethyl aminophenyl) - Δ2-pyrazoline (2a)

Prop-2,3-en-1-one (Chalcone) (1a) mixed Thiosemicarbazide hydrochloride and irradiated with microwave radiation, in house hold 2450 Hz Microwave oven at 600 watts for 5 minutes to give 1-Thiocarboxamido-3- (2'-hydroxy-5'-chlorophenyl)-5-(4-dimethylamino phenyl)- Δ^2-pyrazoline (2a). The product was washed and recrystallized with ethanol. The structures of these compounds were confirmed by chemical and spectral analysis. m.p.232 ^{0}C, yield (71 %).

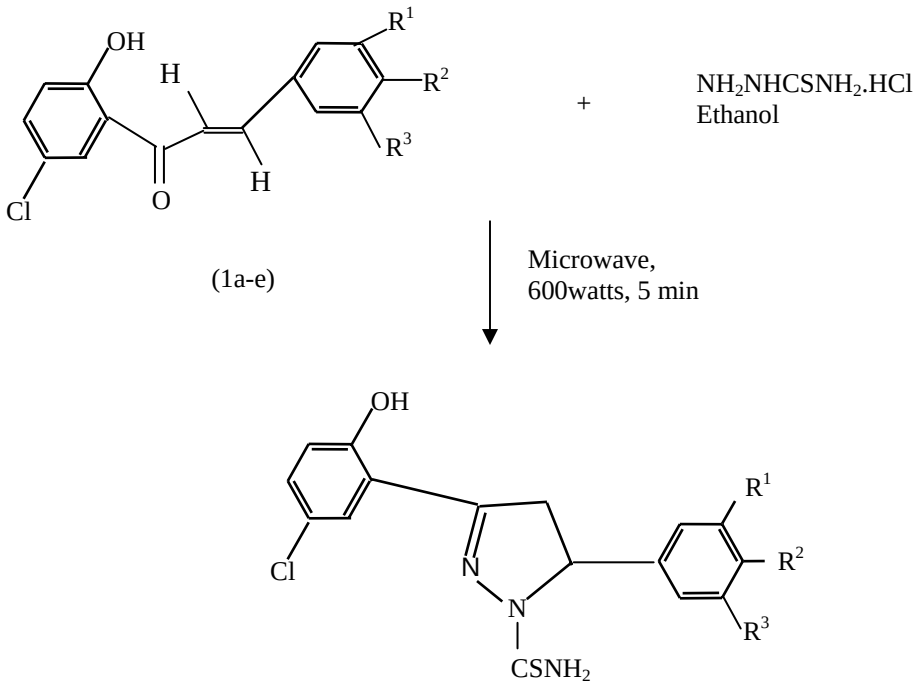
Spectral interpretation of (2a)

IR (ν_{max}) (cm^{-1}): 3448 cm^- v (-OH phenolic), 3297 v (-$CONH_2$), 1609 v(>C=N), 1646 v(-CH_2), 1026 v(-N$(CH_3)_2$), 767 v(C-Cl), 1038 v(C-N-$(CH_3)_2$)

NMR δ ppm: 3.68 (dd, 1H, >CH_B), 4.96 (t, 1H, >CH_x) , 5.97 (s, 2H, -$CSNH_2$), 6.67-7.87 (m, 7H, Ar-H), 9.87 (s, 1H , Ar-OH).

Similarly 1-Thioarboxamido-3-(2'-hydroxy-5'-chlorophenyl)-5-Aryl - Δ^2-pyrazoline (2b-h) were prepared and their physical data is given in Table-2.

Scheme



(2a-e)

R1= -H, -OCH3 , R2 = H, OCH3 , NMe2 , R3 = -H, -OCH3

Table 1 Physical Data of Synthesized Compounds.

Compound	R1	R2	R3	M.P. ^{0}C	Yield %
1a	H	NMe2	H	158	74
1b	H	H	H	162	76
1c	H	OCH3	H	171	73
1d	OCH3	OCH3	H	159	79
1e	OCH3	OCH3	OCH3	175	71

Table 2 Physical Data of Synthesized Compounds.

Compound	**R_1**	**R_2**	**R_3**	**M.P. ^{0}C**	**Yield %**	% N Found(Calculated)
2a	H	NMe2	H	224	71	14.95 (14.19)
2b	H	H	H	170	72	12.67 (13.11)
2c	H	OCH3	H	192	75	11.62 (11.52)
2d	OCH3	OCH3	H	199	70	10.73 (10.76)

2e	OCH3	OCH3	OCH3	229	76	9.96 (9.82)

Result and Discussion

Pyrazolines obtained from Chalcones (Prop-2, 3-en-1-one) and thiosemicarbazide hydrochloride (1a-h) by microwave irradiation found same characteristics to that of compounds prepared by refluxing method. The rate of the organic reaction is accelerated and product obtained in 5 minutes which was 4-6 hours in the routine method. Hence this method is quite beneficial to the usual method as it avoids water and soil pollution. % Yield of the product obtained was also found more than the usual method.

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