



MICROWAVE SYNTHESIS OF 1- CARBOXAMIDO-3, 5-DIARYL Δ^2 -PYRAZOLINES

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ABSTRACT

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

Key words: Microwave Synthesis, Pyrazolines.

INTRODUCTION

1,3-Diaryl-pyrazolines show cerebroprotective¹, antidepressant activity², anti-implantation activity³ and hypoglycemic activity⁴. Due to such important role of pyrazoline derivatives⁵⁻¹⁶, it was thought of interest to synthesize these compounds by acceleration of usual method using microwave radiations. This method has been popularized due to concept of Green chemistry¹⁷, particularly solvent free conditions¹⁸.

Prop-2-en-1-ones are best starting compounds of the pyrazoline derivatives and are synthesized by the usual method. Present work deals with the microwave synthesis of 3,5-diaryl- pyrazolines and their characterization by elemental analysis, IR, ¹H NMR analysis their properties were compared with the synthesized compounds.

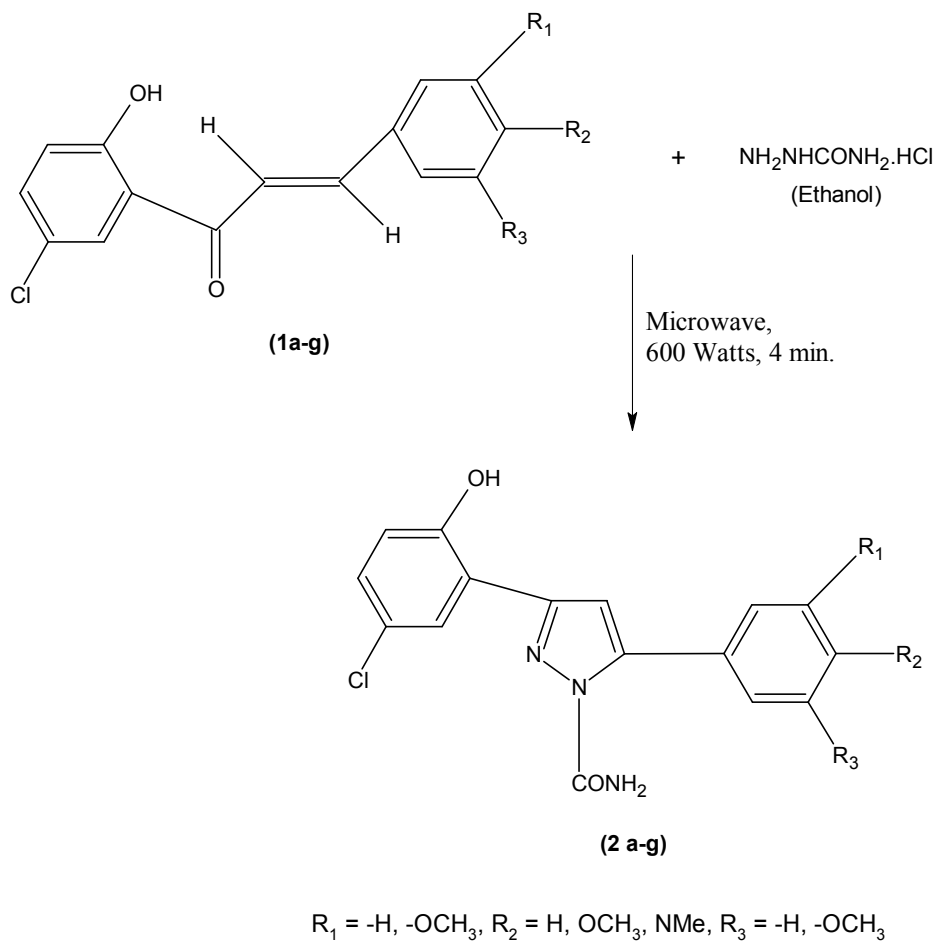
EXPERIMENTAL

The melting points of the synthesized compounds were taken in silicon oil bath with open capillary tubes and are uncorrected. The purity of the compounds was checked by thin layer chromatography on silica gel-G. IR spectra were recorded on a Nicolet-

Impact 400 FT-IR spectrometer. ^1H NMR spectra were recorded on a Bruker AC300 FNMR spectrometer (300 MHz), using TMS as an internal standard. Microanalysis of nitrogen was obtained on colman 29-N analyzer.

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

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



Scheme 1

Spectral interpretation of (1a)

IR (ν_{\max}) (cm^{-1}): 3436 ν (-OH phenolic), 1643 ν (C=O), 1549 ν (-CH=CH-), 1173 ν (-C-O stretching in phenols), 730 ν (C-Cl) and 1026 ν (C-N-(CH₃)₂),

NMR δ ppm: 3.07 (s, 6H, N(CH₃)₂), 6.68-7.88 (m, 7H, Ar-H), 7.32 (d, 1H =CH-, 7.91 (d, 1H =CH-), 13.73 (s, 1 H, -OH).

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

Preparation of 1 – carboxamido – 3 - (2' – hydroxyl - 5' – chlorophenyl) – 5 - (4 - dimethylaminophenyl) - Δ^2 -pyrazoline (2a).

Prop-2,3-en-1-one (Chalcone) (**1a**) mixed with semicarbazide hydrochloride was irradiated with microwave radiation, in house hold 2450 Hz Microwave oven at 600 watts for 4 minutes to give 1-carboxamido-3 - (2'-hydroxy-5'-chlorophenyl)-5-(4-dimethylaminophenyl)- 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 °C, yield (85 %).

Spectral interpretation of (2a)

IR (ν_{\max}) (cm^{-1}): 3446 ν (-OH phenolic), 3295 ν (-CONH₂), 1603 ν (>C=N), 1647 ν (-CH₂), 1022 ν (-N(CH₃)₂), 760 ν (C-Cl) and 1032 ν (C-N-(CH₃)₂)

NMR δ ppm: 3.67 (dd, 1H, >CH_B), 4.92 (t, 1H, >CH_X), 5.96 (s, 2H, -CONH₂), 6.69-7.89 (m, 7H, Ar-H), 9.88 (s, 1H, Ar-OH).

Similarly, 1-carboxamido-3-(2'-hydroxy-5'-chlorophenyl)-5-aryl - Δ^2 -pyrazoline (**2b-g**) were prepared and their physical data are given in Table 1.

Table 1. Physical data of synthesized compounds

Compound	R ₁	R ₂	R ₃	M. P. (°C)	Yield old (M/W)	N % Found (Calculated)
1a	H	NMe ₂	H	158	74	

Cont...

Compound	R ₁	R ₂	R ₃	M. P. (°C)	Yield old (M/W)	N % Found (Calculated)
1b	H	H	H	162	76	
1c	H	OCH ₃	H	171	73	
1d	OCH ₃	OCH ₃	H	159	79	
1e	OCH ₃	OCH ₃	OCH ₃	175	71	
1f	OCH ₃	OH	H	167	69	
1g	OCH ₃	H	H	164	76	
2a	H	NMe ₂	H	232	71 (85)	6.26 (11.19)
2b	H	H	H	194	72 (89)	3.47 (13.89)
2c	H	OCH ₃	H	240	75 (90)	15.62 (15.62)
2d	OCH ₃	OCH ₃	H	196	70 (88)	10.16 (10.36)
2e	OCH ₃	OCH ₃	OCH ₃	227	76 (92)	16.79 (16.94)
2f	OCH ₃	OH	H	212	68 (86)	13.10 (12.67)
2g	OCH ₃	H	H	207	73 (91)	13.25 (13.31)

RESULTS AND DISCUSSION

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

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REFERENCES

1. D. H. Boschelli, J. B. Kramer, S. S. Khatna, R. J. Sorenson, R. J. Connor, M. A. Ferin, C. D. Wright, M. Lesch and K. Imre, *J. Med. Chem.*, **38**, 1995, 4597; *Chem. Abstr.*, 124, 56144 (1996).
2. S. Selvi and P. T. Perimul, *Indian J. Chem.*, **41B**, 1887 (2002).
3. K. T. Potts, in *Comprehensive Heterocyclic Chemistry*, Vol. **5**, Part 4A, Pergamon Press, Oxford, (1986).
4. Erhan Palaska, Mutlu Aytemir, Tayfun Uzbay and Dilek Erol, *Euro, J. Med. Chem.*, **36**, 539 (2001).
5. Hernab and Gabliks, *J. Cancer Chemotherapy Pept*, **14**, 85 (1961).
6. Y. U. M. Batulin, *Chem. Abstr.*, **70**, 2236a (1969).
7. J. T. Drummond and G. Johnson, *J. Heterocyclic Chem.*, **12**, 1123 (1998).
8. S. S. Ganguli, M. S. Vadaria and A. R. Parikh, *J. Inst. Chem.*, **68**, 1920 (1996).
9. J. Upadhyay, U. Dave and H. Parekh, *J. Indian Chem. Soc.*, **68**, 413 (1991).
10. P. Patel, S. Koregaonkar, M. Shah and H. Parekh, *Indian J. Pharma. Sci.*, **58**, 222 (1996).
11. El-Taher Z. Sarhan, Shadia A. Mohamed, Anwar N. Mikhael and Alexandria, *J. Pharm.*
12. E. L. Sharif AMS and Y. A. Ammar, *J. Indian Chem. Soc.*, **61**, 537 (1984).
13. Y. J. Fernandes and H. Parekh, *J. Indian Chem. Soc.*, **74**, 59, 108 (1997).
14. P. Patel, S. Koregaonkar, M. Shah and H. Parekh, *Farmaco*, **51**, 59 (1996).
15. R. M. Kedar, *Asian J. Chem.*, **13(2)**, 477 (2001).
16. M. Afzal, E. Rajanarendar and K. Ramu, *Ind. J. Chem.*, **44B**, 376 (2005).
17. S. R. Cullen, S. J. Barlon, and T. W. Bastock and J. H. Clark, *J. Chem. Soc. Perkin Trans.*, **2**, 1117 (1994).

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