Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(1):75-77

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and Characterization of Novel Pyrazolinones by Conventional as well as Green Tools

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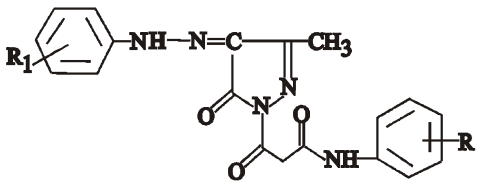
ABSTRACT

Some novel pyrazolinones were synthesized by the condensation of aryl hydrazones of ethyl aceto acetate with N-(2-chloro-4-nitro) phenyl malonamic acid hydrazide by conventional as well as microwave induced synthesis. All the compounds were characterized on the basis of I.R. spectra and elemental analysis.

Key Words: Microwave Induced Synthesis, Aryl hydrazones, Pyrazolinones.

INTRODUCTION

5-Pyrazolones are very important class of heterocycles due to their biological and pharmacological activities[1-2] which exhibit anti-inflammatory[3], herbicidal[4], fungicidal[5], bactericidal[6] and plant growth regulating properties[7]. They are also antipyretic[8] and protein kinase inhibitors[9]. Pyrazolones find use in the treatment of congestive heart failure[10]. Pyrazolinones were effective antioxident[11] for rubber and linseed oil and responsible for inhibition of odor formation in synthetic detergent[12].



4-(R_1) phenyl hydrazono-N^1-(2-chloro-4-nitro amino malonyl)-3-methyl-2-pyrazolin-5-one.

Where, R_1= 2-CH_3, 4-Cl, 4-NO_2, 4-Br, 4-OC_2H_5, 3,4-$(CH_3)_2$, 2-Cl, 3-Cl.
R= 2-Cl-4-NO_2.

EXPERIMENTAL SECTION

All reagents and solvents were procured from Sigma Aldrich. Melting points were determined in open capillaries on Electro-thermal apparatus and were uncorrected. Infrared (IR) spectra were recorded on Perkin Elmer RX-1 using KBr wafers.

General procedure for the synthesis of N-(2-chloro-4-nitro)phenyl malonamic acid hydrazide:
3 ml of 2-chloro-4-nitro aniline and 6 ml of diethylmalonate was refluxed for 1hr 15 min. when dianilide get separated, filtrate was collected in china dish and concentrated by heating on boiling water bath. Light yellow sticky mass of ethyl N-(2-chloro-4-nitro) malonamate was obtained and finally treated with petroleum ether. 2.6 gm of ethyl N-(2-chloro-4-nitro)phenyl malonamate in 20 ml of ethanol was treated with 4ml of hydrazine hydrate (98%), pale yellow crysatalline compound was obtained which was recrystallized from hot ethanol.

Synthesis of ethyl-2,3-dioxo butyrate-2-(substituted) phenyl hydrazone:
3 ml of substituted aniline was diazotized by adding conc. HCl (6ml) and diluted with 6ml distilled water and cooled to 0°C. 10ml $NaNO_2$ solution was added with constant stirring. Finally mixture of sodium acetate (1.6gm) and ethylacetoacetate (2ml) in 10ml of ethanol was added. The solid which separated was filtered, washed with cold water and recrystallised with dilute ethanol.

Table-1 Pyrazoliniones obtained by the condensation of ethyl 2,3-dioxo butyrate 2-(R) phenyl hydrazones with N-(2-chloro4-nitro) phenyl malonamic acid hydrazide

S.N.	R	Mol.Fom.	M.P. °C.	Yield %		Nitrogen%		Carbon%		Hydrgen%		I.R. v cm^{-1}.
				A	B	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	
1.	2-Cl	$C_{19}H_{14}O_5N_6Cl_2$	175	49.05	80.81	17.72	17.61	47.84	47.79	2.99	2.93	3309 cm^{-1}(NH), 1653 cm^{-1}(C=O), 1580 cm^{-1} (>C=N), 1352 cm^{-1} (CH_3,def), 3107 cm^{-1} [Ar(C-H)].
2.	4-Cl	$C_{19}H_{14}O_5N_6Cl_2$	172	50.10	83.04	17.68	17.61	47.82	47.79	2.98	2.93	3306 cm^{-1}(NH), 1644 cm^{-1}(C=O), 1569 cm^{-1} (>C=N), 1342 cm^{-1} (CH_3,def), 3101 cm^{-1} [Ar(C-H)].
3.	4-CH_3	$C_{20}H_{17}O_5N_6Cl$	196	52.07	85.34	18.13	18.04	52.61	52.57	3.79	3.72	3320 cm^{-1}(NH), 1663 cm^{-1}(C=O), 1592 cm^{-1} (>C=N), 1365 cm^{-1} (CH_3,def), 3127 cm^{-1} [Ar(C-H)].
4.	4-OC_2H_5	$C_{21}H_{19}O_6N_6Cl$	180	45.10	79.89	17.32	17.26	51.85	51.79	3.98	3.90	3313 cm^{-1}(NH), 1657 cm^{-1}(C=O), 1585 cm^{-1} (>C=N), 1358 cm^{-1} (CH_3,def), 3117 cm^{-1} [Ar(C-H)].
5.	4-NO_2	$C_{19}H_{14}O_7N_7Cl$	205	40.01	75.70	20.17	20.10	46.81	46.76	2.95	2.87	3315 cm^{-1}(NH), 1661 cm^{-1}(C=O), 1582 cm^{-1} (>C=N), 1356 cm^{-1} (CH_3,def), 3111 cm^{-1} [Ar(C-H)].
6.	4-Br	$C_{19}H_{14}O_5N_6ClBr$	185	44.80	77.90	16.18	16.10	43.79	43.72	2.75	2.68	3308 cm^{-1}(NH), 1650 cm^{-1}(C=O), 1579 cm^{-1} (>C=N), 1355 cm^{-1} (CH_3,def), 3105 cm^{-1} [Ar(C-H)].
7.	3-Cl	$C_{19}H_{14}O_5N_6Cl_2$	178	47.20	79.85	17.70	17.61	47.83	47.79	2.97	2.93	3305 cm^{-1}(NH), 1651 cm^{-1}(C=O), 1581 cm^{-1} (>C=N), 1358 cm^{-1} (CH_3,def), 3108 cm^{-1} [Ar(C-H)].
8.	2,3-$(CH_3)_2$	$C_{21}H_{14}O_5N_6Cl$	182	51.09	84.70	17.93	17.85	53.60	53.56	4.10	4.03	3322 cm^{-1}(NH), 1665 cm^{-1}(C=O), 1590 cm^{-1} (>C=N), 1362 cm^{-1} (CH_3,def), 3125 cm^{-1} [Ar(C-H)].

TABLE-II Antibacterial activity screening of some of the compounds

S. No.	compound	Concentration In H gm/ml	Sensitivity			
			Pseudomonas	*Stapphylococcus*	*E.coli*	*B.subtilis*
1.	4-(4-chloro)phenyl hydrazono-N^1-2-chloro-4-nitro-amino malonyl-3-methyl-2-pyrazolin-5-one	20	+1	R	R	R
		30	+1	R	R	R
		40	+2	R	R	R
		50	+2	R	+1	R
2.	4-(4-nitro)phenyl hydrazono-N^1-2-chloro-4-nitro-amino malonyl-3-methyl-2-pyrazolin-5-one	20	R	R	R	R
		30	R	R	R	R
		40	R	R	R	R
		50	R	R	R	R
3.	4-(4-bromo)phenyl hydrazono-N^1-2-chloro-4-nitro-amino malonyl-3-methyl-2-pyrazolin-5-one	20	R	R	R	R
		30	R	R	R	R
		40	R	+1	R	R
		50	R	+1	R	R
4.	4-(4-methyl)phenyl hydrazono-N^1-2-chloro-4-nitro-amino malonyl-3-methyl-2-pyrazolin-5-one	20	R	R	R	R
		30	R	R	R	R
		40	R	R	R	R
		50	R	R	+1	R

Synthesis of 4-(substituted)phenyl hydrazono-N^1-2-chloro-4-nitro-amino-malonyl-3-methyl-2-pyrazolin-5-one

CONVENTIONAL METHOD (A):
0.26 gm of ethyl-2,3-dioxo butyrate-2-(substituted) phenyl hydrazone (1mol) and 0.24 gm N-(2-chloro-4-nitro)phenyl malonamic acid hydrazide dissolved in 10 ml of ethanol was refluxed for 2 hrs using glacial acetic acid as catalyst and finally recrystallised from ethanol and purity has been checked by TLC using silica gel G plates in 10% methanol/benzene.

MICROWAVE METHOD (B):
Equimolar amounts of ethyl-2,3-dioxo butyrate-2-(substituted) phenyl hydrazone (1mol) and 0.24 gm N-(2-chloro-4-nitro)phenyl malonamic acid hydrazide in a trace of glacial acetic acid were mixed and irradiated at a power of 700W under microwaves for 4 min. On cooling the reaction mixture, a good yield of pyrazoliones was obtained which was recrystallized from absolute ethanol.
Increase in % yield is in following order:
Method A < Method B

RESULTS AND DISCUSSION

The results of m.p., %yield, %nitrogen, %carbon, %hydrogen were discuss in table no.1 and antibacterial activity screening of some of the compounds was discussed in table 2.

Acknowledgement
The authors thank the authorities of the CDRI, Lucknow for spectral and analytical data.

REFERENCES

[1]. S Scheibye; A A El-Barbary ; S O Lawesson; H Fritz & G Rihs; *Tetrahedron*, **1982**, 38, 3753.
[2]. A Weissberger; R H Wiley & P Wiley; The Chemistryof Heterocyclic Compounds: Pyrazolinones, pyrazolidones and derivatives, John Wiley, New York, **1964**.
[3]. S P Hiremith;K Rudresh & S R Saundan; *Indian J Chem*, **2002**, 41B, 394.
[4]. S Joerg; G Reinhold; S Otto; S H Joachim; S Robert & L Klaus; *Ger Offen*, 04 Feb. **1988**; DE 3, 625, 686 (Cl C07D 231/22); *Chem Abstr*, 108, **1988**, 167465.
[5]. P N Dhol; T E Achary; & A Nayak; *J Indian Chem Soc*, **1975**, 52, 1196.
[6]. F R Souza; V T Souaza; V Ratzlaff; L Borges; L M R Olivera; H G Bonacorso; N Zanatta; A Martina & C F Mello; *Eur J Pharma*, **2002**, 451(2), 141.
[7]. J Singh & R Tripathy; *PCT Int Appl*, **2001**, 138.
[8]. F Karci & N Ertan; *Dyes Pigments*, **2002**, 55, 99.
[9]. Y W Ho; *Dyes Pigments*, **2005**, 64, 223.
[10]. A P Spada; S L William; Campbell, F Henery; K Donald; Ernest Roarer International Overseas Inc. 17 Nov **1988**, PCT Int.
[11]. Howland, *U.S.Pat*, **1949,** 2(458) 780.
[12]. Flett, *U.S.Pat*, **1949,** 2(469) 378.