Available online at www.elixirpublishers.com (Elixir International Journal)

Organic Chemistry

Elixir Org. Chem. 48 (2012) 9414-9415

ISSN: 2229-712X

Synthesis and Characterization of 6-amino-4-(substitutedphenyl)-1-(2,4-dinitrophenyl)-3-methyl-pyrazolo[3,4-*b*]pyridine-5-carbonitrile

Shailesh P.Prajapati[1], Dasharath P. Patel[1] and Pankaj S. Patel[2,*]

[1]Department of Chemistry, Gujarat Arts & Science College, Ahmedabad.

[2]Department of Chemistry, Sheth L.H. Science College, Mansa, India.

ARTICLE INFO

Article history:

Received: 1 May 2012;

Received in revised form:

15 June 2012;

Accepted: 9 July 2012;

Keywords

Pyrazol-3-one,

Pyrazolopyridine,

Benzaldehyde,

Malononitrile.

ABSTRACT

6-amino-4-(substitutedphenyl)-1-(2,4-dinitrophenyl)-3-methyl-pyrazolo [3,4-*b*] pyridine-5-carbonitrile have been prepared by the refluxation for six hours of 4-(substitutedbenzylidene)-2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one, malononitrile and ammonium acetate in presence of ethanol. The intermediate 4-(substituted benzylidene)-2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one have been prepared by the refluxation for five hours of 2-(2,4-dinitro phenyl)-5-methyl-2,4-dihydro-pyrazol-3-one with substituted benzaldehyde in presence of glacial acetic acid. The synthesized compounds were characterized by means of their IR, ^{1}H-NMR spectral data and elemental analysis.

Introduction

Pyridine, a heterocyclic nucleus, played a pivotal role in the development of different medicinal agent and in the fild of agrochemicals. In the recent past after considering the success of novel insecticides belong to the group, neonicotinoids[1-2] like imidacloprid and nicotine, novel derivatives of pyridine have been developed and used as insecticidal agents. It is seen from the current literature that pyridine congeners are associated with different biological properties like pesticidal[3-4], insecticidal[5] and fungicidal[6] activity. Furthermore substituted derivatives of pyrazolines exhibit antimicrobial activity.[7] In view of these findings, it was contemplated to design and synthesize some new pyridine derivatives bearing pyrazolines and evaluate their antimicrobial activity.

Experimental

Melting points were taken in open capillary tube and were uncorrected. IR spectra were recorded on I.R. Spectrophotmeter of Bruker scientific Model No. Alpha E and instrument used for NMR Spectroscopy was recorded in DMSO on Bruker Advance II 400 MHz spectrometer using TMS as an internal standard. Purity of the compounds were checked by tlc on silica- G plates.

Synthesis of 2,4-di-Nitro Phenyl Pyrazolone (SP-A)

For synthesis of SP-A, Mix together (0.4M) of redistilled Ethyl acetoacetate and (0.44M) of 2,4-di-Nitro Phenyl Hydrazine in a large evaporating dish. Heat the Mixture on boiling water bath in the fume cupboard for about 2 hrs and stir from time to time with a glass road. Allow the heavy reddish syrup to cool the somewhat, add about 100 ml of ether and stir the mixture vigorously. The syrup which is insoluble in ether, will solidify within 15 minutes. Filter the solid at the pump and wash it thoroughly with ether to remove the coloured impurities. Recrystallise it from hot water or from a mixture of equal Volume of ethanol and water. The yield of the product was 76% and the product melts at 95^{0}C. Found: C(45.42%) H(3.03%) N(21.19%), Calcd. for $C_{10}H_8N_4O_5$: C(45.46%) H(3.05%) N(21.21%) IR; SP-A (cm^{-1}): 3079(=CH), 2912(-CH, Stretch),1720(>C=O), 1600(>C=N Stretch), 1499(>C=C<, aromatic ring), 1557(-N=O), 1463(-CH_3 bend), 1343(-C-N<), 1245(>N-N<).^{1}H NMR (DMSO); SP-A: 2.55, singlate (3H) (-CH3), 2.30, singlate (2H)(-CH2-), 8.16- 9.10, multiplate (3H) (Ar-H).

Preparation of 4-(substitutedbenzylidene)-2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one (SP-01-10)

A mixture of 2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one (0.01M) and substitutedbenzaldehyde (0.01M) in glacial acetic acid (25ml) was refluxed for 5 hours at a temperature of 120^{0}C. The content was poured on to crushed ice. The isolated product was filtered, dried and crystallized from ethanol. IR; SP-01 (cm^{-1}): 3028(=CH), 2913(-CH, Stretch),1676(>C=O), 1586(>C=N Stretch), 1487(>C=C<, aromatic ring), 1564(-N=O), 1407(-CH_3 bend), 1308(-C-N<), 1209(>N-N<), 752(-C-Cl). ^{1}H NMR (DMSO); SP-08: 2.5871, singlate (3H)(-CH_3), 2.4999, singlate (6H)[-N(CH_3)$_2$], 7.7571, singlate (1H)(Ar-CH=,Vinylic), 7.3732-9.0397, multiplate (7H) (Ar-H).

Preparation of 6-amino-4-(substitutedphenyl)-1-(2,4-dinitrophenyl)-3-methyl-pyrazolo [3,4-*b*]pyridine-5-carbonitrile(SP-11-20)

A mixture of 4-(substitutedbenzylidene)-2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one (0.01M) react with malononitrile (0.01M) and ammonium acetate (0.08M) in absolute alcohol (30ml) and heated under refluxed for 6 hours. The content was pourer on to crushed ice. The product was isolated and crystallized from ethyl acetate. IR ; SP-20 (cm^{-1})**:** 3344(>NH-), 3063(=C-H), 2918(-C-H, str), 2192(-C≡N), 1574(>C=N, str), 1524(>C=C<, aromatic ring), 1495(-N=O), 1414(-CH_3, bend), 1397(-C-N<), 1273(>N-N<).

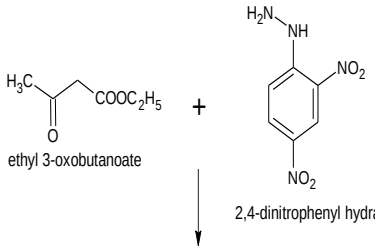
^{1}H NMR (DMSO); SP-16**:** 2.5989, singlate (3H)(-CH_3), 3.7360, singlate (3H) (-OCH_3), 4.1728, singlate (2H) (-NH_2),

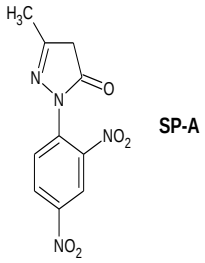
Tele:

E-mail addresses: spp.lecturer@yahoo.in

4.9762, singlate (1H)(Ar-OH), 7.8927-8.9647, multiplate (6H)(Ar-H, >CH=CH<).

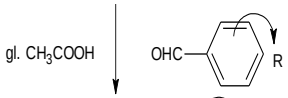
Reaction Scheme

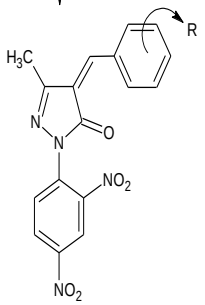




SP-A

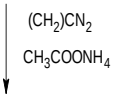
2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one

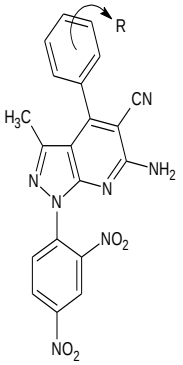




SP1-10

4-(substitutedbenzylidene)-2-(2,4-dinitrophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one





SP 11-20

6-amino-4-(substitutedphenyl)-1-(2,4-dinitrophenyl)-3-methyl-pyrazolo[3,4-*b*]pyridine-5-carbonitrile

Table. No. 1
Physical constant of 6-amino-4-(substitutedphenyl)-1-(2,4-dinitrophenyl)-3-methyl-pyrazolo [3,4-*b*]pyridine-5-carbonitrile

No.	Sub. No.	R	Molecular Formula	Mol. Wt. (gm)	Yield (%)	M.P. °C	Carbon(%)		Hydrogen(%)		Nitrogen(%)	
							Found	required	Found	required	Found	required
1	SP-11	-4-Cl	$C_{19}H_{11}ClN_6O_4$	449.80	75	250	53.37	53.40	2.66	2.69	21.76	21.80
2	SP-12	-2-Cl	$C_{19}H_{11}ClN_6O_4$	449.80	71	251	53.35	53.40	2.65	2.69	21.72	21.80
3	SP-13	-3-OCH_3,4-OCH_3	$C_{21}H_{16}N_6O_6$	475.41	70	260	55.53	55.58	3.57	3.60	20.56	20.62
4	SP-14	-H	$C_{19}H_{12}N_6O_4$	415.36	77	248	57.77	57.83	3.12	3.15	23.55	23.60
5	SP-15	-2-OH	$C_{19}H_{12}N_6O_5$	431.36	70	220	55.62	55.69	3.01	3.04	22.68	22.73
6	SP-16	-3-OCH_3,4-OH	$C_{20}H_{14}N_6O_6$	461.38	75	258	54.63	54.67	3.24	3.28	21.20	21.25
7	SP-17	-4-OH	$C_{19}H_{12}N_6O_5$	431.36	75	240	55.63	55.69	3.00	3.04	22.68	22.73
8	SP-18	-4-$N(CH_3)_2$	$C_{21}H_{17}N_7O_4$	458.42	70	241	57.59	57.64	3.90	3.96	24.39	24.44
9	SP-19	-4-OCH_3	$C_{20}H_{14}N_6O_5$	445.38	73	260	56.57	56.63	3.35	3.39	21.95	22.01
10	SP-20	-3-NO_2	$C_{19}H_{11}N_7O_6$	460.35	76	238	52.12	52.18	2.60	2.63	24.29	24.34

Acknowledgements:

The authors are thankful to the Principal Dr. A. S. Rathod, Gujarat Arts & Science College, Ahmedabad for providing research facilities. One of the author Shailesh P. Prajapati is thankful to UGC. Ganeshkhind, pune, for Teacher Research Fellowship.

References

1. Elbert A, Becker B, Hartwig J. & Erdelen C, *Pflanzenschutz Nachrichten*,44,1991,113.
2. Elbert A, Overbeck H, Iwaya K, & Tusboi S. *Proc Br Crop Prot Conf-pest Dis*,01,1990,21.
3. Kennedy A D, & Summers A L, *J Heterocyl Chem*,18,1981,409.
4. Ivoanov A B, Levin D Z, Promonecoc V K & Mortikov E S, *Zh Org Khim*,25,1989,629.
5. Holla B S, Prasanna C S, Pojjary B, Rao K S, Shridhara K & Bhat U G,*Indian J Chem*, 43B,2004,864
6. Raj M P & Rao J T, *Asain J Che*m, 25,2003,492
7. Jayant P. Singh, Vikash Tiwari, Sumer S. Chundawat, Anju Devpura, Neetu Jaitawat, Mangalshree Dulawat, Shiv S. Dulawat; *J. Chem. Bio. Phy. Sci. Sec*.A, ; 2(1), 61-66 (2012)