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A convenient route for the synthesis and spectral characterization of substituted pyrazolones

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ABSTRACT

A new class of methoxy & methyl substituted pyrazolones have been synthesized by the condensation of 2-methoxy-5-methyl phenyl malonamic acid hydrazide with different ethyl aceto hydrazones by using glacial acetic acid as a catalyst. The structures of newly synthesized compounds have been confirmed from elemental analysis and spectral studies like IR.

Key words: Acid Hydrazide,Ethyl aceto hydrazones, Condensation, GAA, Pyrazolones, Spectral data.

INTRODUCTION

Pyrazolones are important nitrogen containing five membered heterocyclic compounds.Numerous pyrazolone have been found to poss ess bioactivities[1-3],a wide number of compou nds possessing pyrazolone ring structure have been reported to possess anti-inflammatory[4], analgesic[5],pesticidal[6],bactericidal[7-8],fungicidal[9] activities.Several substituted pyrazolones and th eir derivatives have been prepaired in our labo ratory[10-15].As a continuation of our previous studies on the synthesis of pyrazolones[16].herein we report on the synthesis of new methoxy and methyl substituted pyrazolones. A simple and convenient procedure is based on the condensa tion of newly synthesized acid hydrazide and ethyl aceto hydrazones in presence of glacial acetic acid.

EXPERIMENTAL

Material

Melting points were determined on Electro-thermal apparatus in open capillary tubes an d are uncorrected. All the chemicals used in the synthesis were obtained from Sigma-Aldri ch company. All the newly synthesized compou nds were recrystallised by absolute ethanol99. 9%.The purity of all the synthesized compound ds was checked by TLC on silica-gel Al plates (E-Merck) using 10% benzene/methanol as a developing agent for pyrazolones.The IR spe ctra in KBr were recorded on Perkin-Elmer Spectrum RX-1FT-IR spectrophotometer at St. John's College Agra.The identity of newly synthesized compounds was confirmed by mel tingpoints,molecular formula, molecular weight, IR spectral data. All the compounds showed sa tisfactory analytical results for C,H,N. All of the se observations are recorded in Table 1 and IR spectral data are recorded in Table 2.

Synthesis of malon (2-Methoxy-5-Methyl) Anilic acid Hydrazide (1a).

To primary amine (0.025 mole), diethyl malonate (0.05 mole) was added with the catalyst (DMF) dimethyl formamide and refluxed for 45-60 minutes, after some time, ethan ol (20 ml) was

added , and the filtrate was con centrated over a boiling water-bath , add ethan ol (20 ml) and hydrazine hydrate 99%.After co oling solid separated was recrystallised by eth anol and was identified malon (2-methoxy-5-m ethyl) anilic acid hydrazide (1a), yield 44.23%.

Synthesis of ethyl 2,3-dioxobutyrate 2- (R) phenyl hydrazone (2a-2n).

To the (R) aniline (0.025 mole) was diaz otised by adding dropwise concentrated HCl (8 ml) and distilled water (7 ml) cooled in an ice-b ath at 0°C,then the cooled (0.025 mole) aqueo us solution of sodium nitrite was added to it . The diazotised salt solution was added dropw ise in to the cooled (0°C) solution of sodium ac etate (0.12 mole) and ethyl aceto acetate (0.0 25 mole) in ethanol (25 ml).Thus the solid was separated out, filtered, washed with cold water and then dried , recrystallised with hot ethanol

General method for the synthesis of methyl and methoxy substituted pyrazolones (3a-3n).

To (1a ; 0.001 mole) dissolved in absolute ethanol (15 ml) and (2a-2n ; 0.001 mole) was added and refluxed for 4-5 hours on presence of 3-4 drops of GAA. The resulting solid was obtained during refluxing , cooled , filtered and was recrystallised with absolute ethanol.

RESULTS AND DISCUSSION

The IR spectra of the synthesized compoun ds have been recorded in the frequency re gion 4000-450 cm^{-1},these are recorded in the Table 2.

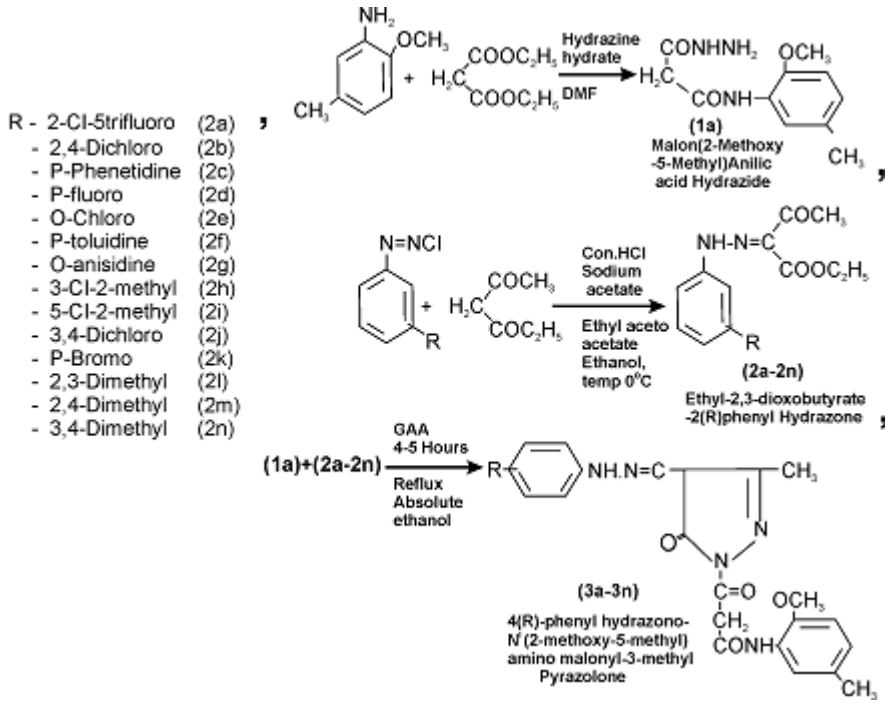
The Infrared (KBr) spectrum of 4-(R)-phenyl hydrazono-N^1(2-methoxy-5-methyl)amino ma lonyl-3-methyl pyrazolone[2a-2h] shows absorption at 3049.7-3020.5 cm^{-1} indicating the arom atic character of -CH, absorption in the range 3449.3-3425 Cm^{-1} reveals-NH stretching vibrations, absorption in the range 1610.2-1589.3 cm^{-1} reveals -C=N stretching vibrations ,abs orption in the range 1656.3-1650 cm^{-1} indicating -C=O stretching vibrations, absorption at 1432-1425.2 cm^{-1} indicating $-CH_3$ stretching vibrations,absorption in the range 1522.5-1492.3 cm^{-1} show -N-N stretching vibrations,

Table 2: IR asorption bands

Compounds code	NHcm^{-1} stretching	Ar CH cm^{-1} stretching	N=CH cm^{-1} stretching	Ar C=O cm^{-1} stretching	C=N cm^{-1} stretching	N-N cm^{-1} stretching	C-N cm^{-1} stretching	C-Cl cm^{-1} stretching	CH_3 cm^{-1} stretching
3a	3449.3	3021.7	2364.8	1651	1610.2	1522.5	1216.7	671.7	1426.6
3b	3440	3020.5	2361.3	1650	-	1521	1215.7	670.1	1425.6
3c	3432	3020.9	2361.8	1650	1592	1521.6	1215.9	670.4	1425.4
3d	3441	3046.4	2364.4	1652	1598.7	-	1229.5	666	-
3e	3433	3049.7	2362.9	1652.9	1593.1	1492.3	1233.8	670.2	1430
3f	3430	3048.4	2366.6	1652	1594.5	1492.3	1233.9	669.5	1432
3g	3425	3048	2372.0	1656.3	1589.3	1510.2	1236.7	669.2	1429
3h	3431	3020.7	2360.8	1651.6	1599	1521.1	1215.8	670.5	1425.2

Table 1: Physical & Analytical data of the Synthesized Compounds (1a,2a-2n,3a-3n)

S.No.	Compounds Code	Molecular Formula	Molecular Weight	Melting Point 0°C	Yield %	Colour	% Analytical data C cal.%	(Found)	H cal.%	(Found)	N cal.%	(Found)
1.	1a	$C_{11}H_{15}N_3O_3$	237.26	129°	44.23	white	55.68	(55.72)	6.37	(6.38)	17.71	(17.75)
2.	2a	$C_{13}H_{13}N_2O_3Cl_1F_3$	337.72	96°	64.65	pinkish yellow	45.23	(45.26)	3.88	(3.90)	08.29	(08.32)
3.	2b	$C_{12}H_{13}N_2O_3Cl_2$	304.16	91°	87.23	sunset	47.38	(47.40)	4.30	(4.31)	09.21	(09.24)
4.	2c	$C_{14}H_{16}N_2O_4$	279.31	64°	80.68	victorian gold	60.26	(60.29)	6.85	(6.87)	10.03	(10.05)
5.	2d	$C_{12}H_{14}N_2O_3F_1$	205.25	62°	69.64	earth red	70.21	(70.25)	6.87	(6.89)	13.64	(13.65)
6.	2e	$C_{12}H_{14}N_2O_3$	234.25	57°	80.99	brownish yellow	61.52	(61.53)	6.02	(6.04)	11.96	(11.98)
7.	2f	$C_{13}H_{17}N_2O_3$	249.29	58°	63.69	thar desert	62.63	(62.65)	6.87	(6.88)	11.23	(11.25)
8.	2g	$C_{13}H_{17}N_2O_4$	265.29	75°	60.17	light yellow	58.86	(58.87)	6.45	(6.46)	10.56	(10.57)
9.	2h	$C_{13}H_{16}N_2O_3Cl_1$	283.74	61°	54.44	dirty yellow	55.02	(55.03)	5.68	(5.70)	09.87	(09.89)
10.	2i	$C_{13}H_{16}N_2O_3Cl_1$	283.74	76°	83.43	sunrise	55.02	(55.04)	5.68	(5.69)	09.87	(09.90)
11.	2j	$C_{12}H_{13}N_2O_3Cl_2$	304.16	71°	96.04	sunset	47.38	(47.40)	4.30	(4.32)	09.21	(09.22)
12.	2k	$C_{12}H_{14}N_2O_3Br_1$	314.17	67°	71.34	lemon yellow	45.87	(45.92)	4.49	(4.51)	08.91	(08.93)
13.	2l	$C_{14}H_{18}N_2O_3$	263.31	66°	63.14	brazen gold	63.86	(63.88)	7.27	(7.29)	10.64	(10.62)
14.	2m	$C_{14}H_{18}N_2O_3$	263.31	93°	55.70	dark yellow	63.86	(63.90)	7.27	(7.24)	10.64	(10.61)
15.	2n	$C_{14}H_{18}N_2O_3$	263.31	62°	76.82	golden apple	63.86	(63.87)	7.27	(7.26)	10.64	(10.63)
16.	3a	$C_{22}H_{21}N_5O_4Cl_1F_3$	511.91	261°	41.11	summer sprinkle	51.62	(51.64)	4.13	(4.15)	13.68	(13.71)
17.	3b	$C_{21}H_{21}N_5O_4Cl_2$	478.35	258°	40.29	pale cream	52.73	(52.74)	4.42	(4.44)	14.64	(14.67)
18.	3c	$C_{28}H_{27}N_5O_5$	453.51	256°	46.89	sugarcane	60.91	(60.94)	6.00	(6.01)	15.44	(15.47)
19.	3d	$C_{21}H_{22}N_5O_4F_1$	427.45	244°	44.57	pale cream	59.00	(59.03)	5.19	(5.20)	16.38	(16.41)
20.	3e	$C_{21}H_{22}N_5O_4Cl_1$	443.90	252°	48.83	off white	56.82	(56.84)	4.99	(4.98)	15.78	(15.80)
21.	3f	$C_{22}H_{25}N_5O_4$	423.48	252°	56.37	dirty yellow	62.40	(62.43)	5.95	(5.98)	16.54	(16.57)
22.	3g	$C_{22}H_{25}N_5O_5$	439.48	246°	41.23	dark yellow	60.12	(60.14)	5.73	(5.76)	15.94	(15.96)
23.	3h	$C_{22}H_{24}N_5O_4Cl_1$	457.93	239°	40.96	pale cream	57.70	(57.72)	5.28	(5.30)	15.29	(15.30)
24.	3i	$C_{22}H_{24}N_5O_4Cl_1$	457.93	238°	38.26	royal ivori	57.70	(57.73)	5.28	(5.31)	15.29	(15.32)
25.	3j	$C_{21}H_{21}N_5O_4Cl_2$	478.35	244°	38.07	off white	52.73	(52.75)	4.42	(4.44)	14.64	(14.65)
26.	3k	$C_{21}H_{22}N_5O_4Br_1$	488.36	254°	37.38	limon	51.65	(51.68)	4.54	(4.57)	14.34	(14.36)
27.	3l	$C_{23}H_{27}N_5O_4$	437.51	221°	37.40	casablanca	63.14	(63.16)	6.22	(6.19)	16.00	(15.96)
28.	3m	$C_{23}H_{27}N_5O_4$	437.51	229°	38.20	off white	63.14	(63.17)	6.22	(6.20)	16.00	(15.98)
29.	3n	$C_{23}H_{27}N_5O_4$	437.51	238°	41.40	off white	63.14	(63.15)	6.22	(6.18)	16.00	(15.95)



and ab sorption at 1236.7-1215.7 cm^{-1} confirms-C-N stretching vibrations ,absorption at 671.7-666 cm^{-1} reveals -C-Cl stretching vibrations.

The above observations of the newly synthesized compounds are agreed with the assigned structure of the compounds no.3a-3h and other newly synthesized compounds (3i-3n). The pyrazolones were found to possess hig her melting points,shows the thermal stability. The study reveals absorption spectrum was in agreement with the assigned structures and colouring properties.

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