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Facile synthesis and characterization, spectral evaluation of some new 1-phenyl (2-methoxy-5-methyl)-3,5-dimethyl-4(substituted phenyl benzeneazo acetyl acetone) pyrazoles

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ABSTRACT

A facile synthesis of various 1-phenyl(2-methoxy-5-methyl)-3,5-dimethyl-4(substituted phenyl benzeneazo acetyl acetone) Pyrazoles (3a-3l) have been synthesized by the condensation of malon (2-methoxy-5-methyl) anilic acid hydrazide (1a) with selected various substituted phenyl benzeneazo acetyl acetone (2a-2l) and glacial acetic acid used as medium. The newly novel synthesized substitu ted pyrazoles have been characterized by means of their spectral studies and elemental analysis.

Key words: Acid hydrazide, substituted acetyl acetone, GAA, condensation, pyrazoles, spectral data.

INTRODUCTION

Pyrazole derivatives constitute an interesting class of organic compounds with diverse chemical, pharmacological and medicinal applications[1,2]. Pyrazoles are well known to have a wide spectrum of biological activities[3]. Many of the therapeut ically useful compounds such as phenylbutazone, oxyphenbutazone, celecoxib, are modulate on it's structure. Pyrazoles have been reported as antibacterial[4], antifungal[5], anti-convulsant[6], antidiabetic[7] activities. Some substituted pyrazoles have been found to possess anticancer activity[8]. Several pyrazoles and their derivatives have been prepaired by various workers in our laboratory[9-15].

In the present paper we would like to report the synthesis of some newly novel substituted pyrazoles derived from malon (2-methoxy-5-methyl) anilic acid hydrazide (1a) with substituted acetyl acetones (2a-2l) in alcoholic medium by using glacial acetic acid as a catalyst.

EXPERIMENTAL

Material and Methods

All the melting points were determined on Electro-thermal apparatus in open capillary tubes and are uncorrected. All the Chemicals are used in this synthesis were obtained from Sigma-Aldrich Company. The purity of newly synthesized compounds was checked by TLC on silica-gel-coated AI plates (E-Merck). The IR spectra in Kbr-disc method were recorded on Perkin-Elmer spectrum RX-1 FT-IR Spectrophotometer at Central Drug Research Institute (CDRI) Lucknow .

All the newly synthesized compounds showed satisfactory analytical results for C,H,N and identity of the newly synthesized compounds was confirmed by molecular weight, molecular formula,

m.p, yield %, colour are furnished in Table -1 and the spectral data are recorded in the Table 2.

General procedure of the synthesis of malon (2-methoxy-5-methyl) anilic acid hydrazide (1a)

To the primary amine (2-methoxy-5-methyl; 0.025 mole), diethyl malonate (0.05 mole) was added in the presence of the catalyst dimethyl formamide and the mixture was refluxed for about 45-60 minutes, ethanol 20 ml was added and concentrated over boiling water-bath, add alcohol 20 ml and hydrazine hydrate 99%, solid was recrystallized by ethanol, was identified as (1a) .

General procedure of the synthesis of substituted phenyl benzeneazo acetyl acetone (2a-2l)

To substituted aniline (0.025 mole) was diazotised by adding together with concentrated HCl (8 ml) and dis. water (7 ml) cooled in an ice-bath at maintained temperature 0°C, and then cooled aqueous solution of $NaNO_2$ (0.025 mole) was added dropwise to it, the ready diazotised salt solution was added dropwise in to the cooled maintained at 0°-2°C solution of Sodium acetate (0.12 mole) and acetyl acetone (0.025 mole) in ethanol (20 ml), thus the solid was separated out, filtered, washed with cold dis. water, recrystallized with ethanol.

General procedure of the synthesis of 1-phenyl(2-methoxy-5-methyl)-3,5-dimethyl-4(substituted phenyl benzeneazo acetyl acetone) Pyrazoles (3a-3l)

To (**1a** ; 0.001 mole)dissolved absolute ethanol (15 ml) and (**2a-2l**;0.001 mole) was added then refluxed for 3-4 hours in the presence of glacial acetic acid 4-5 drops, cooling, filtered, and the resulting solid was recrystallized by hot absolute ethanol 99%

RESULTS AND DISCUSSION

The Infrared Spectra of the newly synthesized substituted pyrazoles have been recorded in the frequency region 4000-450 cm^{-1}, in the Table-2.

The IR Spectrum of 1-phenyl (2-methoxy-5-methyl)-3,5-dimethyl-4(3-chloro-4-methoxy)phenyl benzeneazo acetyl acetone) pyrazole[3a] indicates stretching vibrations at 3283.0 cm^{-1} show -NH, stretching vibrations at 3022.0 cm^{-1} indicates the presence of -CH, stretching vibrations at 1649.6 cm^{-1} indicates the presence of aromatic C=O,stretching vibrations at 1591.2 cm^{-1} reveals the -C=C, stretching vibrations at 1216.6 cm^{-1} show C-N, stretching vibrations at 1522.8 cm^{-1} represents -N-N, stretching vibrations at 1429.7 cm^{-1} reveals the $-CH_3$ group, stretching vibrations at 670.7 cm^{-1} indicates the mono substitution ring. The above observation are agreed with the assigned structure of compounds 3a-3g and also other compounds 3h-3l. The study reveals absorption spectrum was in agreement with the assigned structure of all the newly synthesized compounds and colouring properties and show higher melting points.

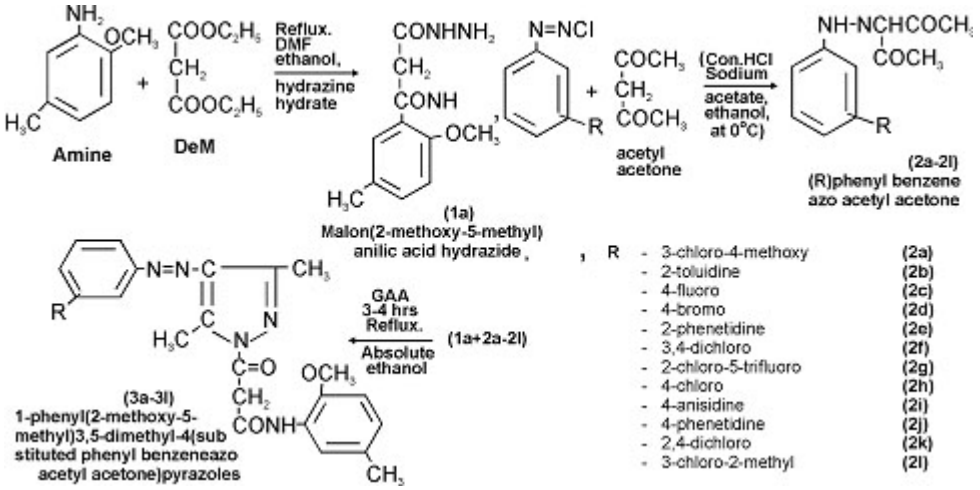

Table 1: Physical & Analytical data of Newly Synthesized Compounds

S. No.	Codes	Molecular formula	Molecular weight	% C Cal.	(Found)	% H Cal.	(Found)	% N Cal.	(Found)	Melting Point °C	Yield %	Colour
1.	1a	$C_{11}H_{15}N_3O_3$	237.26	55.68	(55.72)	6.37	(6.38)	17.71	(17.75)	129°	44.23	white
2.	2a	$C_{12}H_{14}N_2O_3Cl_1$	269.71	53.44	(53.46)	5.23	(5.24)	10.38	(10.42)	131°	73.24	sporty yellow
3.	2b	$C_{12}H_{15}N_2O_2$	219.26	65.73	(65.71)	6.90	(6.91)	12.77	(12.80)	098°	66.60	light mango yellow
4.	2c	$C_{11}H_{12}N_2O_2F_1$	223.22	55.19	(55.21)	5.41	(5.43)	12.55	(12.59)	101°	79.56	cryatalline mango yellow
5.	2d	$C_{11}H_{12}N_2O_2Br_1$	239.68	55.12	(55.14)	5.04	(5.05)	11.69	(11.72)	122°	52.22	pale cream
6.	2e	$C_{13}H_{17}N_2O_3$	249.29	62.63	(62.65)	6.87	(6.88)	11.24	(11.27)	123°	64.24	light sporty yellow
7.	2f	$C_{11}H_{11}N_2O_2Cl_2$	274.14	48.19	(48.20)	4.04	(4.06)	10.22	(10.26)	134°	73.63	wild yellow
8.	2g	$C_{12}H_{11}N_2O_2Cl_1F_3$	307.88	46.87	(46.89)	3.60	(3.62)	09.10	(09.14)	112°	72.64	light crystalline yellow
9.	2h	$C_{11}H_{12}N_2O_2Cl_1$	239.68	55.12	(55.15)	5.04	(5.06)	11.69	(11.73)	119°	66.18	milk toffee
10.	2i	$C_{12}H_{15}N_2O_3$	235.26	61.26	(61.28)	6.42	(6.43)	11.91	(11.95)	087°	65.43	mid buff yellow
11.	2j	$C_{13}H_{17}N_2O_3$	249.29	62.63	(62.66)	6.87	(6.89)	11.24	(11.29)	114°	66.82	crystalline dirty yellow
12.	2k	$C_{11}H_{11}N_2O_2Cl_2$	274.14	48.49	(48.21)	4.04	(4.05)	10.22	(10.25)	126°	98.38	light yellow
13.	2l	$C_{12}H_{14}N_2O_2Cl_1$	253.71	56.80	(56.82)	5.56	(5.57)	11.04	(11.07)	078°	93.56	light yellow
14.	3a	$C_{23}H_{27}N_5O_4Cl_1$	472.96	58.41	(58.43)	5.75	(5.77)	14.81	(14.84)	221°	39.92	dirty cream caress
15.	3b	$C_{23}H_{28}N_5O_3$	422.51	65.38	(65.40)	6.68	(6.66)	16.57	(16.60)	226°	39.25	light sandalwood
16.	3c	$C_{22}H_{25}N_5O_3F_1$	426.48	61.96	(61.99)	5.91	(5.92)	16.42	(16.46)	218°	46.52	puppy love
17.	3d	$C_{22}H_{25}N_5O_3Br_1$	487.40	54.21	(54.23)	5.17	(5.19)	14.37	(14.41)	247°	51.26	sugarcane
18.	3e	$C_{24}H_{30}N_5O_4$	452.54	63.70	(63.67)	6.68	(6.69)	15.47	(15.49)	226°	46.70	cream
19.	3f	$C_{22}H_{24}N_5O_3Cl_2$	477.39	55.35	(55.38)	5.07	(5.09)	14.67	(14.73)	225°	44.22	puppy love
20.	3g	$C_{23}H_{24}N_5O_3Cl_1F_3$	510.94	54.06	(54.08)	4.73	(4.75)	13.71	(13.74)	238°	41.91	dirty cream
21.	3h	$C_{22}H_{25}N_5O_3Cl_1$	442.94	59.65	(59.67)	5.69	(5.71)	15.81	(15.85)	232°	40.75	magnolia
22.	3i	$C_{23}H_{28}N_5O_4$	438.52	62.99	(63.02)	6.43	(6.45)	15.97	(16.02)	197°	47.88	wheat sprig
23.	3j	$C_{24}H_{30}N_5O_4$	452.54	63.70	(63.72)	6.68	(6.70)	15.47	(15.51)	214°	38.88	sugarcane
24.	3k	$C_{22}H_{24}N_5O_3Cl_2$	477.39	55.35	(55.37)	5.07	(5.08)	14.67	(14.70)	209°	49.70	basra pearl
25.	3l	$C_{23}H_{27}N_5O_3Cl_1$	456.97	60.45	(60.47)	5.95	(5.96)	15.33	(15.36)	221°	33.87	light cream

Table 2: Spectral data of Newly Synthesized Compounds (3a-3g)

S. No.	Codes	-NH cm^{-1} (-CONH)	-CH cm^{-1} Stretching	Ar C=O Stretching	C=C cm^{-1} Stretching	C-N cm^{-1} Stretching	N-N cm^{-1} Stretching	$-CH_3$ cm^{-1} Stretching	mono Substitution ring
1.	3a	3283.0	3022.0	1649.6	1591.2	1216.6	1522.8	1429.7	670.7
2.	3b	3280.9	3022.0	1650.0	1591.5	1216.3	1520.7	1427.9	671.1
3.	3c	3276.8	3021.1	1648.2	1591.1	1215.9	1524.1	1426.5	669.9
4.	3d	3282.7	3021.5	1649.6	1590.9	1216.5	1523.3	1427.8	670.7
5.	3e	3281.4	3022.1	1649.3	1590.9	1216.2	1527.3	1427.3	671.1
6.	3f	3279.9	3022.0	1649.9	1588.7	1216.0	1524.9	1426.2	670.7
7.	3g	3280.0	3021.8	1650.8	1590.0	1215.9	1526.4	1426.8	670.7

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