

# Synthesis, characterization of some new 1-phenyl (3-chloro- 4-methoxy, 2-methoxy-5-methyl)- 4(substituted) phenyl benzene-azo acetyl acetone-3,5-dimethyl pyrazoles

ALOK K. PAREEK\*, P.E. JOSEPH and DAYA S. SETH

School of Chemical Sciences, Department of Chemistry,  
ST. John's College, Agra - 282 002 (India).

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## ABSTRACT

This review introduces the synthesis of some newly 1-phenyl (3-chloro-4-methoxy, 2-methoxy-5-methyl)- 4(substituted) phenyl benzeneazo acetyl acetone-3,5-dimethyl pyrazoles (4a-4l, 5a-5l) containing different selected functional groups have been synthesized by condensing (3-chloro-4-methoxy, 2-methoxy-5-methyl) phenyl benzeneazo acetyl acetone hydrazone (1a,2a) with (R<sup>1</sup>)-malon phenyl anilic acid hydrazide (3a-3i,3j,3k,3l) in alcoholic medium, presence of glacial acetic acid as a catalyst. The identity of newly synthesized compounds were confirmed on the basis of their spectral studies viz- IR, physical properties, elemental analysis.

**Key words:** Synthesis, Substituted Acetyl Acetone Hydrazones, Substituted Acid Hydrazides, Characterization, GAA, Condensation, Pyrazoles, Spectral Analysis .

## INTRODUCTION

Pyrazole is an important class of heterocyclic compounds plays an interesting role in medicinal chemistry. Various substituted pyrazole and its derivatives containing two Nitrogen-atoms in five membered parent ring. Since a very long time the usefulness and great therapeutic value of pyrazole nucleus has been recognised and the wide range of biological activities<sup>1,2</sup>. Pyrazole ring has fairly developing area of synthetic chemistry. Besides traditional interest in the synthesis of drugs. Some pyrazole derivatives also reported to have anaesthetic properties<sup>3,4</sup> and strong anti-bacterial<sup>5,6</sup> activities. Pyrazoles possess as anti-tumor<sup>7</sup>, anti-depressant<sup>8</sup>, analgesic<sup>9</sup> agents.

Keeping these facts in view in continuation of our previous work<sup>13-15</sup>. in the present paper some new novel substituted pyrazoles have been synthesized by the condensation reaction of (R) phenyl benzene-azo acetyl acetone hydrazones with

(R<sup>1</sup>)-malon phenyl anilic acid hydrazides with few drops of glacial acetic acid.

## EXPERIMENTAL

### Material and Methods

The all melting points were determined in Electro-Thermal apparatus in open capillary tubes and are uncorrected. The chemicals are used in the synthesis were of analytical grade and obtained from Sigma-Aldrich Company. The purity of newly synthesized compounds was checked by TLC using silica-gel-coated Al-Plates (Merck), IR spectra (KBr in cm<sup>-1</sup>) were recorded on Perkin-Elmer spectrum RX-1 FT-IR spectrophotometer at ST. John's College Agra. Physical and analytical data are furnished in Table-1.

### General procedure for the synthesis of (R) phenyl benzene-azo acetyl acetone hydrazone (1a, 2a)

To the substituted amine(R;0.025 mole) was diazotised by adding concentrated HCl (8 ml)

with distilled water, cooled the solution in ice-bath at 0°C, cold aqueous solution of NaNO<sub>2</sub> (0.025 mole) was added slowly drop-wise in to the cooled diazotised solution after that it was added drop-wise in the cooled solution of sodium acetate (0.12 mole) and acetyl acetone (0.025 mole) in ethanol (25 ml), during stirring the solid product of benzene-azo acetyl acetone was separated out, filtered, washed with cold water, recrystallised by ethanol 99%, it was identified to be (R) phenyl benzene-azo acetyl acetone hydrazone (1a, 2a).

#### General procedure for the synthesis of malon (R') phenyl anilic acid hydrazide (3a-3i, 3j,3j<sub>1</sub>, 3k,3k<sub>1</sub>-3l)

To the substituted aniline (0.025 mole), freshly distilled diethyl malonate (0.05 mole) was added in presence of dimethyl formamide, reaction mixture was refluxed for about 45-60 minutes, cooling, concentrated the product over the boiling water-bath, now treated with hydrazine hydrate 99% with ethyl alcohol (20 ml), thus the obtained solid was recrystallised by hot ethanol, it was identified to be malon (R') phenyl anilic acid hydrazide (3a-3i,3j,3j<sub>1</sub>, 3k,3k<sub>1</sub>-3l)

#### General procedure for the synthesis of 1-phenyl (R)- 4 - (R') phenyl benzene-azo acetyl acetone - 3,5-dimethyl pyrazole (4a- 4l, 5a-5l)

To (1a, 2a; 0.001 mole) dissolved with absolute ethanol (15 ml) and (3a-3i,3j,3j<sub>1</sub>,3k,3k<sub>1</sub>-3l; 0.001 mole) was added in equi molar quantity (1:1), refluxed 3 hours in the presence of glacial acetic acid few drops, cooling, filtered, the resulting solid product was recrystallised by hot absolute ethanol . It was identified to be 1-phenyl (R)-4-(R')-phenyl benzene-azo acetyl acetone-3,5 -dimethyl pyrazole (4a-4l, 5a-5l).

### RESULTS AND DISCUSSION

The infrared spectra in Kbr-disc of the newly synthesized compounds have been recorded in the frequency region 4000-500 cm<sup>-1</sup>. IR spectral data are recorded in the Table-2. The infrared spectrum of compounds (3j,3k,3l) showed -NH stretching vibrations in the range 3448.0-3448.2 cm<sup>-1</sup>, stretching vibrations in the region 3020.0-3040.0 cm<sup>-1</sup> indicates the -CH str., presence of aromatic C=O confirm by the stretching vibrations in the region 1733.1-1773.9 cm<sup>-1</sup>, -CONH group are

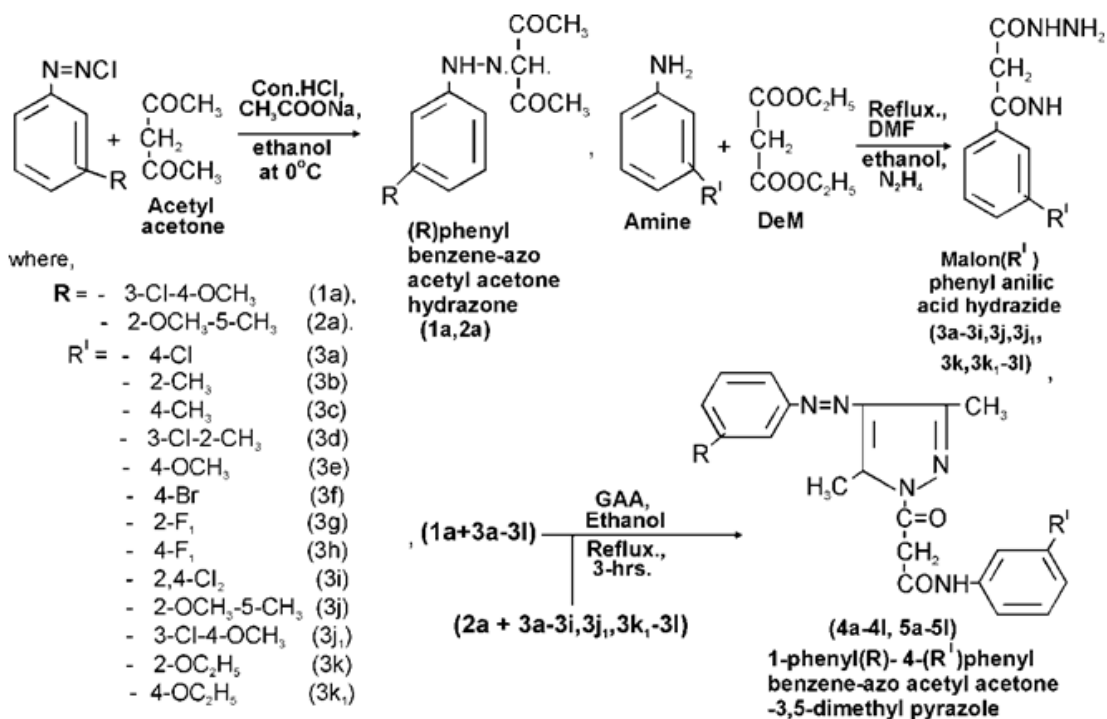


Table 1: Physical and Analytical data of newly synthesized compounds

codes	Molecular Formula	M.P °C	Yield %	Molecular Weight	% Analytical data			colour
					C cal.% (found)	H cal.% (found)	N cal.% (found)	
1a	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>1</sub>	131°	73.24	268.70	53.64 (53.66)	4.87 (4.88)	10.42 (10.46)	spoty yellow
2a	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	138°	57.73	248.28	62.88 (62.91)	6.49 (6.50)	11.28 (11.30)	deep sunset
3a	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>2</sub>	264°	53.13	460.33	54.79 (54.81)	4.16 (4.17)	15.21 (15.26)	dark limon
3b	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub>	237°	44.00	439.91	60.06 (60.08)	5.04 (5.02)	15.92 (15.95)	magnolia
3c	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub>	260°	46.73	439.91	60.06 (60.09)	5.04 (5.06)	15.92 (15.96)	wild yellow
3d	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>2</sub>	221°	48.33	474.36	55.70 (55.68)	4.46 (4.44)	14.76 (14.80)	light magnolia
3e	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>4</sub> Cl <sub>1</sub>	249°	60.28	455.91	57.96 (57.97)	4.86 (4.87)	15.36 (15.39)	sandalwood
3f	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub> Br <sub>1</sub>	252°	60.55	504.79	49.96 (49.98)	3.79 (3.81)	13.87 (13.91)	light raw silk
3g	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub> F <sub>1</sub>	243°	43.21	443.88	56.82 (56.81)	4.31 (4.32)	15.78 (15.80)	light sugarcane
3h	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub> F <sub>1</sub>	259°	54.90	443.88	56.82 (56.84)	4.31 (4.33)	15.78 (15.82)	cream caress
3i	C <sub>21</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub>	255°	45.47	494.78	50.97 (50.98)	3.66 (3.67)	14.15 (14.19)	wild yellow
3j	C <sub>23</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub> Cl <sub>1</sub>	266°	53.86	469.94	58.78 (58.79)	5.14 (5.12)	14.90 (14.95)	light garlic pod
3k	C <sub>23</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub> Cl <sub>1</sub>	261°	49.50	469.94	58.78 (58.77)	5.14 (5.11)	14.90 (14.92)	wheat sprig
3l	C <sub>22</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>2</sub> F <sub>3</sub>	248°	46.53	528.34	50.01 (50.02)	3.43 (3.41)	13.25 (13.29)	deep wild yellow
4a	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub>	266°	59.79	439.91	60.06 (60.07)	5.04 (5.05)	15.92 (15.96)	deep gold rush
4b	C <sub>23</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub>	240°	52.21	419.49	65.85 (65.84)	6.00 (6.02)	16.69 (16.72)	light promise
4c	C <sub>23</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub>	244°	58.90	419.49	65.85 (65.87)	6.00 (6.03)	16.69 (16.71)	dark orange frost
4d	C <sub>23</sub> H <sub>24</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub>	253°	57.25	453.94	60.85 (60.83)	5.32 (5.30)	15.43 (15.45)	light candy
4e	C <sub>23</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub>	243°	73.88	435.49	63.43 (63.46)	5.78 (5.80)	16.08 (16.12)	dull promise
4f	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> Br <sub>1</sub>	254°	69.61	484.37	54.55 (54.57)	4.57 (4.59)	14.46 (14.50)	dull promise
4g	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> F <sub>1</sub>	262°	56.64	423.45	62.40 (62.38)	5.23 (5.24)	16.54 (16.56)	light candy
4h	C <sub>22</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> F <sub>1</sub>	258°	62.96	423.45	62.40 (62.42)	5.23 (5.26)	16.54 (16.58)	candy
4i	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>2</sub>	260°	48.23	474.36	55.70 (55.71)	4.46 (4.45)	14.76 (14.78)	light ceramic
4j	C <sub>23</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub> Cl <sub>1</sub>	255°	57.22	469.94	58.78 (58.80)	5.14 (5.12)	14.90 (14.94)	light candy
4k	C <sub>23</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub>	249°	53.19	449.52	64.12 (64.14)	6.05 (6.07)	15.58 (15.63)	deep candy
4l	C <sub>23</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>1</sub> F <sub>3</sub>	248°	40.88	507.91	54.39 (54.41)	4.16 (4.18)	13.78 (13.82)	light candy

**Table 2: Spectral data of newly Synthesized Compounds**  
**IR absorption bands in  $\nu$   $\text{cm}^{-1}$**

codes	-NH $\text{cm}^{-1}$ stretching	-CH $\text{cm}^{-1}$ stretching	Ar C=O $\text{cm}^{-1}$ stretching	-CONH $\text{cm}^{-1}$ stretching	C=C $\text{cm}^{-1}$ stretching	N-N $\text{cm}^{-1}$ stretching	N=N $\text{cm}^{-1}$ stretching	CH <sub>2</sub> $\text{cm}^{-1}$ stretching	C-N $\text{cm}^{-1}$ stretching	mono subs.
3j	3448.2	3020.0	1773.9	1654.6	1560.3	1508.2	1492.5	1385.0	1258.0	668.2
3k	3448.0	3040.0	1733.1	1636.1	1559.5	1507.7	1458.0	1374.5	1257.6	668.2
3l	3448.2	-	1735.1	1637.3	1560.0	1508.3	1458.5	1375.5	1258.6	668.8
4h	3448.9	3020.0	1735.2	1654.4	1560.0	1508.4	1458.6	1375.5	1237.6	669.3
4j	3466.6	3027.0	1735.0	1654.0	1542.3	1508.2	1458.5	1375.2	1236.6	668.7
4k	3447.9	3053.2	1773.1	1654.1	1588.5	1507.8	1458.4	1351.3	1244.6	688.1

confirm by the stretching vibrations in the region 1636.1-1654.6  $\text{cm}^{-1}$ , 1560.0-1559.5  $\text{cm}^{-1}$  (-C=C str.), 1507.7-1508.3  $\text{cm}^{-1}$  confirm the pyrazole ring N-N, 1458.0-1492.5  $\text{cm}^{-1}$  indicates the N=N str., -CH<sub>2</sub> group is confirm by stretching vibrations in the region 1374.5-1385.0  $\text{cm}^{-1}$ , 1257.6-1258.6  $\text{cm}^{-1}$  (-C-N str.), mono substitution are present in the region 668.2-668.8  $\text{cm}^{-1}$ . These observations are lent support to the assigned structure of compounds (3j,3k,3l) and other compounds (3a-3i).

IR spectrum of newly synthesized compounds (4h,4j,4k) absorption bands in the region 3447.9-3466.6  $\text{cm}^{-1}$  indicates -NH str., while

absorption bands in the range 3020.0-3053.2  $\text{cm}^{-1}$  (-CH str.), 1735.0-1773.1  $\text{cm}^{-1}$  (aromatic -C=O), 1654.0-1654.4  $\text{cm}^{-1}$  indicates the -CONH group, 1542.3-1588.5  $\text{cm}^{-1}$  confirm the presence of -C=C str., 1507.8-1508.4  $\text{cm}^{-1}$  indicates pyrazole ring N-N str., while absorption in the range 1458.4-1458.6  $\text{cm}^{-1}$  indicates -N=N str., stretching vibrations in the region 1351.3-1375.5  $\text{cm}^{-1}$  confirm the presence of -CH<sub>2</sub> group, 1236.6-1244.6  $\text{cm}^{-1}$  (C-N str.), mono substitution are present in the region 668.7-688.1  $\text{cm}^{-1}$ . By above observations the assigned structure of newly synthesized compounds (4h, 4j,4k) was in agreement and other compounds (4a-4g,4i,4l).

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