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Synthesis of 3,5-disubstituted Pyrazoles and their Derivatives

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ABSTRACT

2-Acetylthiophene condenses with different aromatic aldehyde in ethanol in the presence of aqueous NaOH to give 1-(2'-thienyl)-3-(substituted phenyl)-2-propen-1-one (Ia-e) which reacts with hydrazine hydrate in ethanol to give pyrazoline (IIa-e) and also treated with DMSO in presence of catalytic amount of iodine to give pyrazole (II'a-e) Similarly, 1-phenyl pyrazoline (IIIa-e) treated with DMSO/I_2 to give 1-phenyl pyrazole(III' a-e), 1-(2,4-dinitro phenyl) pyrazoline (IVa-e) treated with DMSO/I_2 to give 1-(2,4-dinitro phenyl) pyrazole(IV'a-e), 1-carboxamido pyrazoline (Va-e) treated with DMSO/I_2 to give 1-carboxamido pyrazole (V'a-e), 1-acetyl pyrazoline (VIa-e) treated with DMSO/I_2 to give 1-acetyl pyrazole (VI'a-e), 1-benzoyl pyrazoline (VIIa-e) treated with DMSO/I_2 to give 1-benzoyl pyrazole (VII'a-e) and 1-nitroso pyrazoline (VIIIa-e) treated with DMSO/I_2 to give 1-nitroso pyrazole (VIII'a-e). Characterization and structural elucidation was carried out on the basis of melting points determination, analytical and spectral studies.

Key words: Pyrazoles, synthesis, structural study.

INTRODUCTION

Pyrazole is the name given by Knorr to the class of organic compounds consisting of unsaturated five membered ring containing adjacent nitrogen atoms. Pyrazoles are known to have antitubercular[1], insecticidal[2], hypolipidemic[3], herbicides[4], antiaggregating[5], anaesthetic[5], analgesic[5,7], antiparasitic[6], anti-inflammatory[7], antifungal[8], anti-angiogenic[9] agent.

Chalcone reacts with hydrazine hydrate in ethanol to give pyrazoline. Pyrazoline[10], 1-phenyl pyrazoline[11-13], 1-(2,4-dinitrophenyl) pyrazoline[13], 1-carboxamido pyrazoline[12], 1-acetyl pyrazoline[11-17], 1-benzoyl pyrazoline[11-16] and 1-nitroso pyrazoline[12] were dissolved in DMSO medium to this catalytic amount of iodine was added. After refluxed the solid separated was washed with 20% sodium thiosulphate to remove iodine to get different pyrazoles[18-20] such as 1-phenyl pyrazole[20-23], 1-(2,4-

dinitro phenyl) pyrazole[20], 1-carboxamido pyrazole[24], 1-acetyl pyrazole[13-19], 1-benzoyl pyrazole[13,19] and 1-nitroso pyrazole. Recently a synthesis of fused pyrazoles have been reported[25]. Literature survey indiated that 1-substituted-3-(2'-thienyl)-5-(substituted phenyl)-pyrazoles and their derivatives have not been prepared from 1-substituted-3-(2'-thienyl)-5-(substituted phenyl)-Δ^2-pyrazolines. Hence it was thought interesting to prepare pyrazoles and their derivatives from 1-substituted-3-(2'-thienyl)-5-(substituted phenyl)-Δ^2-pyrazolines.

EXPERIMENTAL

Chalcone required for the synthesis of pyrazoline were prepared by earliner known method[10,26-27] and also pyrazoles were prepared from pyrazoline by known method[18]. Melting points were determined in an open capillary tubes and uncorrected. IR spectra were recorded on shimadzu spectrophotometer. PMR spretra were recorded in $CDCl_3$ on a varian mercury YH-300NMR spectrophotometer using TMS as an internal reference (Chemical shifts in δ ppm down field from TMS). Purity of the compounds was checked by TLC on silica gel G-coated plates.

Synthesis of 1-H-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (II'a)

1-H-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (IIa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-H-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (II'a). Yield 72%, m.p. 145°C, Colour-Brown.

IR (KBr) cm^{-1} : 3408.33 (N-H), 3022.55 (Ar, C-H), 1666.55 (C=N), 1228.70 (C-N), 1138.04 (C-$N(CH_3)_2$), 671.25 (C-S).

PMR ($CDCl_3$) δ: 2.9 (s, 6H, -$N(CH_3)_2$), 6.9-7.55 (m, 8H, Ar-H and heteroaromatic H) 9.5 (s, 1H, -NH)

Synthesis of 1-phenyl-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (III'a)

1-phenyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (IIIa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-phenyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (III'a). Yield 63%, m.p. 150°C, Colour-Dark Brown.

IR (KBr) cm^{-1}: 3080.28 (Ar,C-H), 1643.41 (C=N), 1230.63 (C-N), 1132.25(C-$N(CH_3)_2$), 615.31 (C-S).

PMR ($CDCl_3$) δ : 3.0 (s, 6H, -$N(CH_3)_2$), 6.9-8.1 (m, 13H, Ar-H and heteroaromatic H)

Synthesis of 1-(2,4-dinitro phenyl)-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (IV'a)

1-(2,4-dinitro phenyl)-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (IVa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-(2,4-dinitro phenyl)-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (IV'a). Yield 71%, m.p. 215°C, Colour-Light Gry.

IR (KBr) cm^{-1} : 3111.28 (Ar,C-H), 1610.61 (C=N), 1528.20, 1346.36 (-NO_2 Asym. And Sym.), 1224.84 (C-N), 1134.18 (C-N-$(CH_3)_2$), 673.18 (C-S).

PMR ($CDCl_3$) δ: 2.9 (s, 6H, -$N(CH_3)_2$), 6.7-7.7 (m, 11H, Ar-H and heteroaromatic H)

Synthesis of 1-carboxamido-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (V'a)

1-carboxamido-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (Va) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to

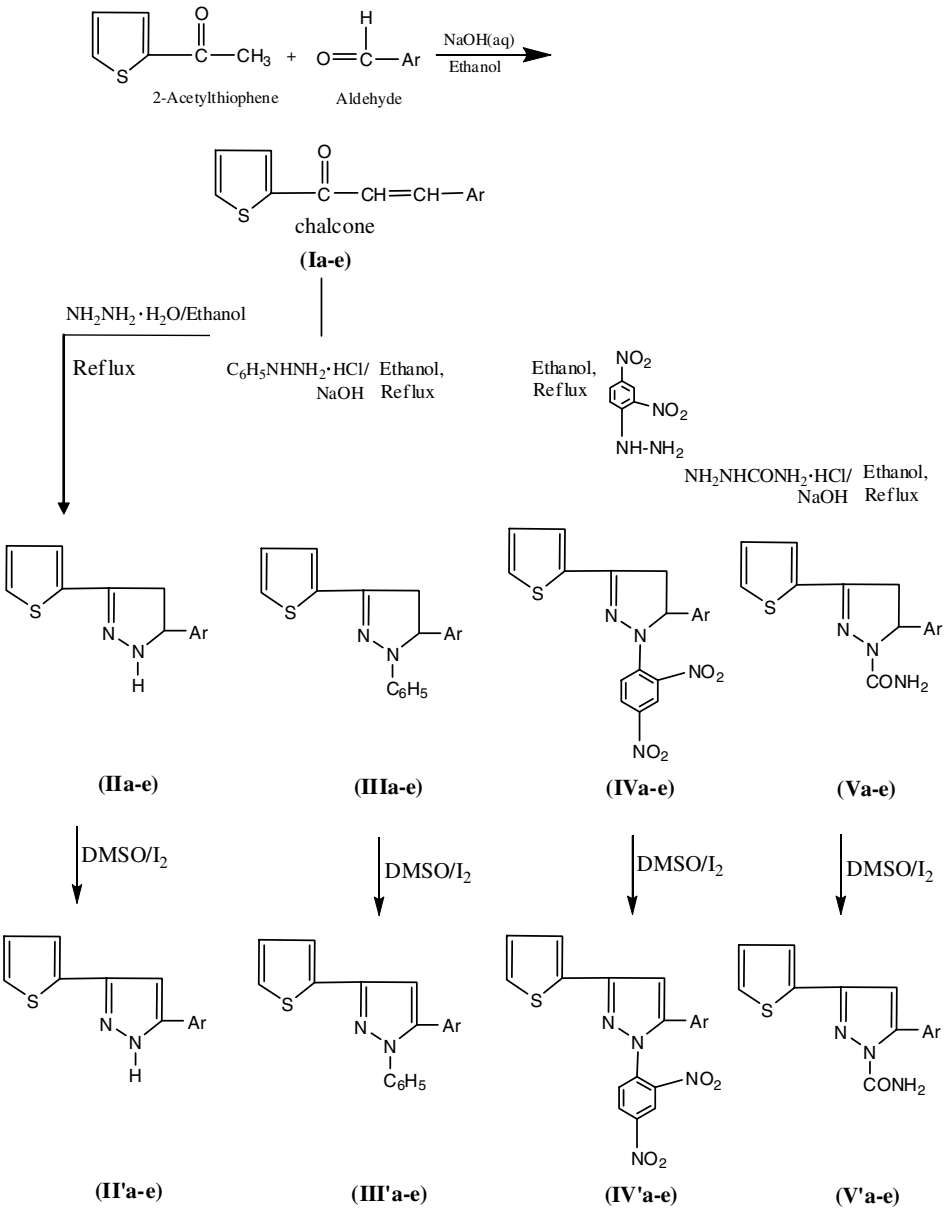
get 1-carboxamido-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (V'a). Yield 68%, m.p. 110°C, Colour- Light Yellow.

IR (KBr) cm^{-1} : 3335.03 (-CO<u>NH</u>$_2$), 3086.21 (Ar, C-H), 1643.41 (C=N), 1668.24, 1605.01 (-<u>CO</u>NH$_2$), 1234.48 (C-N), 1139.97 (C-N-$(CH_3)_2$), 615.31 (C-S).

PMR ($CDCl_3$) δ: 3.0 (s, 6H, -N$(CH_3)_2$), 6.1 (br, 2H, -CONH$_2$), 6.6-7.4 (m, 8H, Ar-H and heteroaromatic H)

Synthesis of 1-acetyl-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VI'a)

1-acetyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (VIa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine

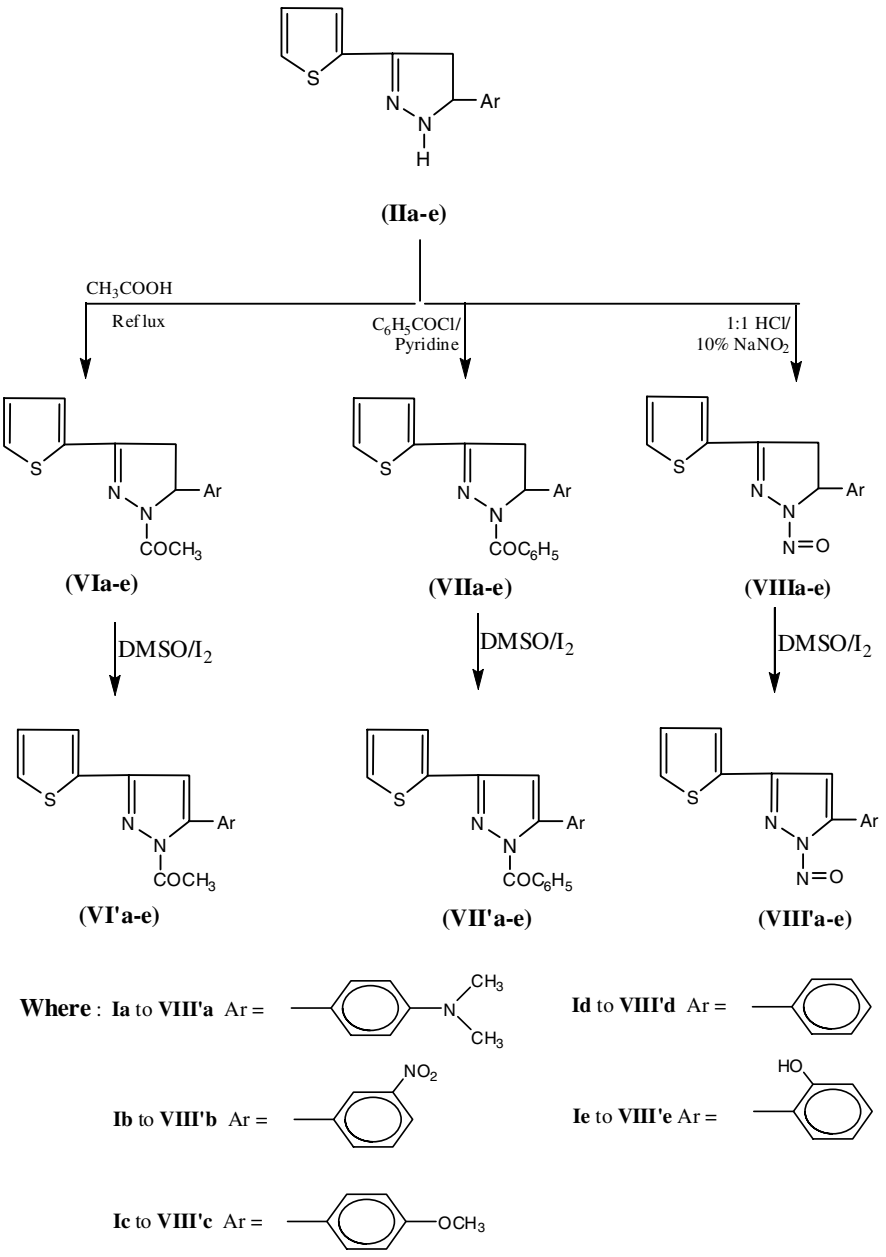


Scheme 1:

(0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-acetyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VI'a). Yield 78%, m.p. 260°C, Colour-Blackish.

IR (KBr) cm^{-1} : 2924.18 (Ar, C-H), 1664.62, 1640.11 (N-C=O and C=O), 1535.05 (C=N), 1197.83 (C-N), 1111.03 (C-N-$(CH_3)_2$), 613.38 (C-S).

PMR ($CDCl_3$) δ: 2.5 (s, 3H, -$COCH_3$), 2.85 (s, 6H, -$N(CH_3)_2$), 6.8-7.6 (m, 8H, Ar-H and heteroaromatic H)



Scheme 2:

Synthesis of 1-benzoyl-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VII'a)

1-benzoyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (VIIa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-benzoyl-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VII'a). Yield 74%, m.p. 165°C, Colour- Light Grey.

IR (KBr) cm^{-1} : 3006.04 (Ar, C-H), 1722.45, 1670.41 (N-C=O and C=O), 1610.08 (C=N), 1319.35 (C-N), 1062.81 (C-N-$(CH_3)_2$), 613.38 (C-S).

PMR ($CDCl_3$) δ: 2.95 (s, 6H, -N$(CH_3)_2$), 6.5-7.9 (m, 13H, Ar-H and heteroaromatic H)

Synthesis of 1-nitroso-3-(2'thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VIII'a)

1-nitroso-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-Δ^2-pyrazoline (VIIIa) (0.01M) was dissolved in DMSO (20 ml). To this catalytic amount of iodine (0.2 gm) was added. The reaction mixture was refluxed for one hour, cooled and diluted with water. The solid thus separated was washed with 20% sodium thiosulphate to remove iodine. The product obtained was crystallised from ethanol to get 1-nitroso-3-(2'-thienyl)-5-(4"-dimethylamino phenyl)-pyrazole (VIII'a). Yield 65%, m.p. 135°C, Colour- Brown.

IR (KBr) cm^{-1} : 3090.07 (Ar, C-H), 1585.54 (C=N), 1519.96 (N=O), 1437.02 (N-N=O and C=O), 1180.47 (C-N), 1069.66 (C-N-$(CH_3)_2$), 709.83 (C-S).

PMR ($CDCl_3$) δ: 3.05 (s, 6H, -N$(CH_3)_2$), 6.7-7.5 (m, 8H, Ar-H and heteroaromatic H)

Table 1 : Characterization data of pyrazoles and their derivatives

S. No.	Code	Molecular Formula	Molecular Weight	Colour	m.p. °C	Elemental Analysis % Calculated (Found)			
						C	H	N	S
1	II'a	$C_{15}H_{15}N_3S$	269	Browm	145°C	66.91 (60.46)	5.57 (5.50)	15.60 (15.40)	11.89 (11.72)
2	II'b	$C_{13}H_9N_3O_2S$	277	Light Grey	105°C	57.56 (57.10)	3.32 (3.29)	15.49 (15.32)	11.80 (11.64)
3	II'c	$C_{14}H_{12}N_2OS$	256	Light Brown	100°C	65.62 (65.14)	4.68 (4.59)	10.93 (10.80)	12.50 (12.35)
4	II'd	$C_{13}H_{10}N_2S$	226	Dark Brown	95°C	69.02 (68.61)	4.42 (4.39)	12.38 (12.24)	14.15 (13.97)
5	II'e	$C_{13}H_{10}N_2OS$	242	Greenish	125°C	64.46 (64.01)	4.13 (4.06)	11.57 (11.38)	13.22 (13.06)
6	III'a	$C_{21}H_{19}N_3S$	345	Dark Brown	150°C	73.04 (72.62)	5.50 (5.42)	12.17 (12.01)	9.27 (9.12)
7	III'b	$C_{19}H_{13}N_3O_2S$	347	Brown	85°C	65.70 (65.18)	3.74 (3.67)	12.10 (11.91)	9.22 (9.04)
8	III'c	$C_{20}H_{16}N_2OS$	332	Blackish	90°C	72.27 (71.84)	4.81 (4.78)	8.43 (8.28)	9.63 (9.45)
9	III'd	$C_{19}H_{14}N_2S$	302	Grey	135°C	75.49 (75.02)	4.63 (4.54)	9.27 (9.11)	10.59 (10.42)
10	III'e	$C_{19}H_{14}N_2OS$	318	Dark Brown	115°C	71.69 (71.21)	4.40 (4.33)	8.80 (8.64)	10.06 (9.90)

11	IV'a	$C_{21}H_{17}N_5O_4S$	435	Light Grey	215°C	57.93 (57.48)	3.90 (3.83)	16.09 (15.91)	7.35 (7.22)
12	IV'b	$C_{19}H_{11}N_5O_6S$	437	Brown	120°C	52.17 (51.65)	2.51 (2.45)	16.01 (15.82)	7.32 (7.16)
13	IV'c	$C_{20}H_{14}N_4O_5S$	422	Light Brown	95°C	56.87 (56.35)	3.31 (3.23)	13.27 (13.11)	7.58 (7.45)
14	IV'd	$C_{19}H_{12}N_4O_4S$	392	Dark Brown	100°C	58.16 (57.71)	3.06 (2.99)	14.28 (14.12)	8.16 (7.98)
15	IV'e	$C_{19}H_{12}N_4O_5S$	408	Brown	190°C	55.88 (55.37)	2.94 (2.88)	13.72 (13.59)	7.84 (7.61)
16	V'a	$C_{16}H_{16}N_4OS$	312	Light Yellow	110°C	61.53 (61.09)	5.12 (5.03)	17.94 (17.73)	10.25 (10.09)
17	V'b	$C_{14}H_{10}N_4O_3S$	314	Blackish	270°C	53.50 (53.14)	3.18 (3.10)	17.83 (17.66)	10.19 (10.02)
18	V'c	$C_{15}H_{13}N_3O_2S$	299	Light Brown	90°C	60.20 (59.70)	4.34 (4.24)	14.04 (13.88)	10.70 (10.52)
19	V'd	$C_{14}H_{11}N_3OS$	269	Light Brown	130°C	62.45 (62.02)	4.08 (4.00)	15.61 (15.45)	11.89 (11.70)
20	V'e	$C_{14}H_{11}N_3O_2S$	285	Reddish Brown	120°C	58.94 (58.56)	3.85 (3.76)	14.73 (14.57)	11.22 (11.03)
21	VI'a	$C_{17}H_{17}N_3OS$	311	Blackish	260°C	65.59 (65.14)	5.46 (5.35)	13.50 (13.35)	10.28 (10.15)
22	VI'b	$C_{15}H_{11}N_3O_3S$	313	Brown	130°C	57.50 (57.07)	3.51 (3.44)	13.41 (13.24)	10.22 (10.08)
23	VI'c	$C_{16}H_{14}N_2O_2S$	298	Dark Brown	135°C	64.42 (63.96)	4.69 (4.60)	9.49 (9.36)	10.73 (10.59)
24	VI'd	$C_{15}H_{12}N_2OS$	268	Blackish	140°C	67.16 (66.73)	4.47 (4.37)	10.44 (10.29)	11.94 (11.79)
25	VI'e	$C_{15}H_{12}N_2O_2S$	284	Grey	230°C	63.38 (62.86)	4.22 (4.11)	9.85 (9.72)	11.26 (11.10)
26	VII' a	$C_{22}H_{19}N_3OS$	373	Light Grey	165°C	70.77 (70.24)	5.09 (4.99)	11.26 (11.12)	8.57 (8.44)
27	VII'b	$C_{20}H_{13}N_3O_3S$	375	Light Grey	135°C	64.00 (63.53)	3.46 (3.37)	11.20 (11.06)	8.53 (8.39)
28	VII'c	$C_{21}H_{16}N_2O_2S$	360	Brown	120°C	70.00 (69.58)	4.44 (4.36)	7.77 (7.63)	8.88 (8.73)
29	VII'd	$C_{20}H_{14}N_2OS$	330	Brown	170°C	72.72 (72.19)	4.24 (4.18)	8.48 (8.32)	9.69 (9.54)
30	VII'e	$C_{20}H_{14}N_2O_2S$	346	Blackish	105°C	69.36 (68.83)	4.04 (3.95)	8.09 (7.95)	9.24 (9.05)
31	VIII'a	$C_{15}H_{14}N_4OS$	298	Brown	135°C	60.40 (59.91)	4.69 (4.60)	18.79 (18.60)	10.73 (10.56)
32	VIII'b	$C_{13}H_8N_4O_3S$	300	Blackish	220°C	51.00 (50.54)	2.66 (2.59)	18.79 (18.60)	10.73 (10.56)
33	VIII'c	$C_{14}H_{11}N_3O_2S$	285	Grey	130°C	58.94 (58.42)	3.85 (3.76)	14.73 (14.57)	11.22 (11.03)
34	VIII'd	$C_{13}H_9N_3OS$	255	Light Brown	90°C	61.17 (60.68)	3.52 (3.47)	16.47 (16.28)	12.54 (12.36)
35	VIII'e	$C_{13}H_9N_3O_2S$	271	Grey	115°C	57.56 (57.01)	3.32 (3.27)	15.49 (15.28)	11.80 (11.61)

Similarly, the other members of the series were also prepared in this manner and their characterization data are given in table-1

RESULTS AND DISCUSSION

The structures of synthesized pyrazoles (II'a, III'a, IV'a and V'a) have been established an the basis of analytical data. The IR spectra of II'a showed the presence of band for ν N-H, Ar C-H, C=N, C-N, and C-S. The PMR data showed the peaks for CH_3, multiplate for Ar-H and heteroaromatic H as well as peak for N-H also. The structure of other derivatives (VI'a to VIII'a) were determined in a similar way.

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