Oriental Journal of Chemistry Vol. **26**(4), 1517-1520 (2010)

Synthesis and structural studies of isomeric Δ^2-pyrazolines

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(Received: September 11, 2010; Accepted: October 21, 2010)

ABSTRACT

1-(2'-Thienyl)-3-(4"-dimethylamino phenyl)-2-propen-1-one(Ia-e) react with hydrazine hydrochloride in DMF medium to give isomeric 1-H pyrazolines (IIa-e), react with phenyl hydrazine hydrochloride in DMF medium to give isomeric 1-phenyl pyrazolines (IIIa-e),react with 2,4-dinitro phenyl hydrazine hydrochloride in DMF medium to give isomeric 1-(2,4-dinitro phenyl) pyrazolines (IVa-e) and also react with semicarbazide hydrochloride in DMF medium to give isomeric 1-carboxamido pyrazolines (Va-e). Characterization and structural elucidation were done on the basis of melting point determination, analytical and spectral studies.

Key words: Isomeric Δ^2-pyrazolines, synthesis, structural study.

INTRODUCTION

Furochalcones react with hydrazine hydrate in ethanol to give isomeric pyrazolines[1]. 3,5-Diaroyl-4-aroy-1-phenyl pyrazoline has been synthesized from 3-aroylflavone in pyridine[2]. The reaction of chalcone with hydrazine hydrochloride in DMF was reported to give the isomeric 3-aryl-5(2'-hydroxyphenyl)- Δ^2 -pyrazolines[3].

Chalcones react with hydrazine hydrochloride in DMF medium to give isomeric 1-H pyrazolines[1,2,3,4], react with phenyl hydrazine hydrochloride in DMF medium to give isomeric 1-phenyl pyrazolines[1,2], react with 2,4-dinitro phenyl hydrazine hydrochloride in DMF medium to give isomeric 1-(2,4-dinitro pheyl) pyrazolines and also react with semicarbazide hydrochloride in DMF medium to give isomeric 1- carboxamido pyrazolines. Literature survey indicates that the isomeric pyrazolines have not been prepared so far from 1-(2'-thieny)-3-(substituted phenyl)-2-propene-one. Hence it was thought intresting to prepare isomeric pyrazolines from 1-(2'-thienyl)-3-(substituted phenyl)-2-propen-1-one.

EXPERIMENTAL

Chalcones required for the synthesis of isomeric Δ^2-pyryzolines were prepared by earlier known method.[5,6].Melting points were determined in an open capillary tubes and are uncorrected. IR spectra were recorded on perkin-Elmer- 557 Spectrophotometer. PMR spectra were recorded in $CDCl_3$ on a Bruker Avance II 400 NMR Spectrometer at 300 MHz 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-(4'-dimethylamino phenyl)-5-(2"-thienyl) --pyrazoline (IIa).

A mixture of 1-(2'-thienyl)-3-(4''-dimethylamino phenyl)-2-propen-1-one (Ia) (0.01 mol) and hydrazine hydrochloride (0.02 mol) was refluxed in DMF (20 ml) for two hours. The reaction mixture on cooling was diluted with water and product separated was filtered and crystallised from ethanol to obtain solid 1-H-3-(4'-dimethylamino phenyl)-5-(2"-thienyl) Δ^2-pyrazoline (IIa). Yield 74%, m.p. 105^0, Colour - Light Yellow.

IR (KBr) cm^{-1} : 3401.4 (-NH), 3080.6 (Ar C-H), 1631.2 (C=N), 1434.9 (-CH_2- of pyrazoline), 1296.4 (C-N), 1055.7 (C-N$(CH_3)_2$), 696.3 (C-S).

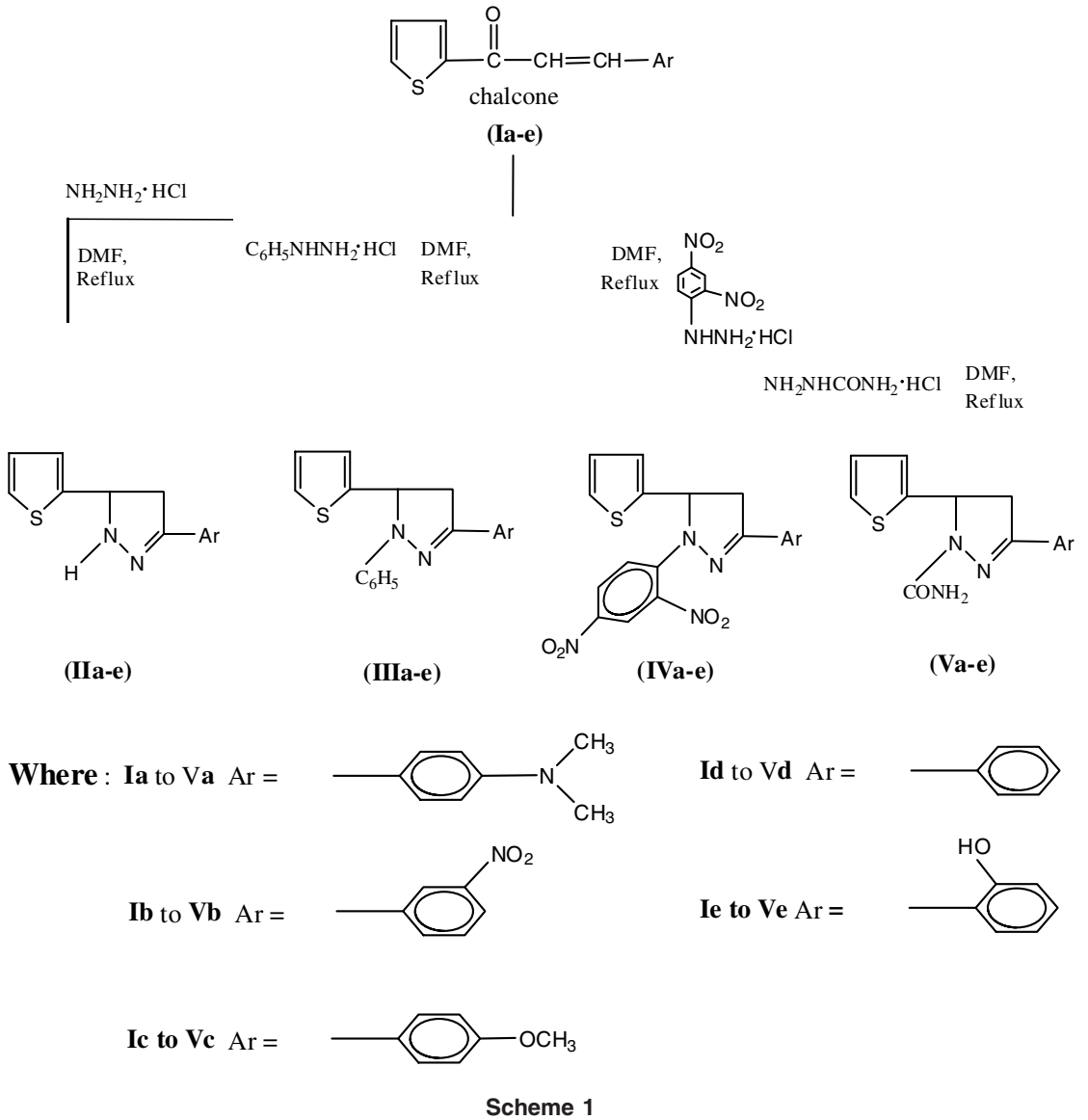
PMR ($CDCl_3$) δ : 3.0 (s, 6H, -N$(CH_3)_2$), 3.2 (dd, 1H, >CHH_A), 3.8 (dd, 1H, >CH_BH),) 5.5 (dd, 1H, >CH_X-),) 6.6-7.8 (m, 7H, Ar-H and heteroaromatic H) 8.9 (S, 1H, -NH)

Synthesis of 1-phenyl-3-(4'-dimethylamino phenyl)-5-(2"-thienyl) Δ²-pyrazoline (IIIa).

A mixture of 1-(2'-thienyl)-3-(4''-dimethylamino phenyl)-2-propen-1-one (Ia) (0.01 mol) and phenyl hydrazine hydrochloride (0.02 mol) was refluxed in DMF (20 ml) for two hours. The reaction mixture on cooling was diluted with water and product separated was filtered and crystallised from ethanol to obtain solid 1-phenyl-3-(4'-dimethylamino phenyl)-5-(2"-thienyl)--pyrazoline (IIIa). Yield 80%, m.p. 85⁰, Colour – Brown.

IR (KBr) cm^{-1} : 3100 (Ar C-H), 1611.1 (C=N), 1497.3 (-CH_2- of pyrazoline), 1352.6 (C-N), 1164.1 (C-N$(CH_3)_2$, 692.1 (C-S).

PMR ($CDCl_3$) δ : 3.05 (s, 6H, -N$(CH_3)_2$), 3.1 (dd, 1H, >CHH_A), 3.8 (dd, 1H, >CH_BH),) 5.2 (dd, 1H, >CH_X-),) 6.5-7.95 (m, 12H, Ar-H and heteroaromatic H)



Scheme 1

Table 1: Characterization data of isomeric Δ²-pyrazolines

S. No.	Code	Molecular formula	Molecular Weight	Colour	Yield %	M.P. (°C)	Elemental Analysis % Calculated (Found)			
							C	H	N	S
1	IIa	$C_{15}H_{17}N_3S$	271	Light Yellow	74	105	66.42 (65.90)	6.27 (6.16)	15.49 (15.30)	11.80 (11.64)
2	IIb	$C_{13}H_{11}N_3O_2S$	273	Blackish	78	115	57.14 (56.60)	4.02 (3.93)	15.38 (15.23)	11.72 (11.50)
3	IIc	$C_{14}H_{14}N_2OS$	258	Grey	65	300	65.11 (64.74)	5.42 (5.37)	10.85 (10.76)	12.40 (12.24)
4	IId	$C_{13}H_{12}N_2S$	228	Brown	74	100	68.42 (67.96)	5.26 (5.21)	12.28 (12.18)	14.03 (13.92)
5	IIe	$C_{13}H_{12}N_2OS$	244	Off White	68	280	63.93 (63.56)	4.91 (4.87)	11.47 (11.38)	13.11 (12.94)
6	IIIa	$C_{21}H_{21}N_3S$	347	Brown	80	85	72.62 (72.13)	6.05 (6.01)	12.10 (11.98)	9.22 (9.09)
7	IIIb	$C_{19}H_{15}N_3O_2S$	349	Light Grey	72	145	65.32 (64.93)	4.29 (4.20)	12.03 (11.95)	9.16 (9.01)
8	IIIc	$C_{20}H_{18}N_2OS$	334	Brown	64	290	71.85 (71.59)	5.38 (5.30)	8.38 (8.28)	9.58 (9.45)
9	IIId	$C_{19}H_{16}N_2S$	304	Blackish Brown	70	65°C	75.00 (74.61)	5.26 (5.19)	9.21 (9.16)	10.52 (10.40)
10	IIIe	$C_{19}H_{16}N_2OS$	320	Light Green	75	270	71.25 (70.69)	5.00 (4.94)	8.75 (8.66)	10.00 (9.81)
11	IVa	$C_{21}H_{19}N_5O_4S$	437	Bottle Green	61	90	57.66 (57.18)	4.34 (3.30)	16.01 (15.94)	7.32 (7.20)
12	IVb	$C_{19}H_{13}N_5O_6S$	439	Light Orange	78	130	51.93 (51.56)	2.96 (2.94)	15.94 (15.82)	7.28 (7.19)
13	IVc	$C_{20}H_{16}N_4O_5S$	424	Reddish Brown	72	160	56.60 (56.15)	3.77 (3.72)	13.20 (13.11)	7.54 (7.46)
14	IVd	$C_{19}H_{14}N_4O_4S$	394	Light Brown	80	110	57.86 (57.52)	3.55 (3.51)	14.21 (14.15)	8.12 (8.07)
15	IVe	$C_{19}H_{14}N_4O_5S$	410	Reddish	65	210	55.60 (55.14)	3.41 (3.35)	13.65 (13.59)	7.80 (7.74)
16	Va	$C_{16}H_{18}N_4OS$	314	Dark Yellow	72	100	61.14 (60.62)	5.73 (5.69)	17.83 (17.71)	10.19 (10.06)
17	Vb	$C_{14}H_{12}N_4O_3S$	316	Grey	78	125	53.16 (52.75)	3.79 (3.70)	17.72 (17.60)	10.12 (10.01)
18	Vc	$C_{15}H_{15}N_3O_2S$	301	Light Grey	71	270	59.80 (59.58)	4.98 (4.95)	13.95 (13.86)	10.63 (10.50)
19	Vd	$C_{14}H_{13}N_3OS$	271	Light Brown	80	75	61.99 (61.56)	4.79 (4.70)	15.49 (15.36)	11.80 (11.68)
20	Ve	$C_{14}H_{13}N_3O_2S$	287	Off White	70	285	58.53 (58.14)	4.52 (4.45)	14.63 (14.51)	11.14 (11.05)

Synthesis of 1-(2,4-dinitro phenyl)-3-(4'-dimethylamino phenyl)-5-(2"-thienyl)--pyrazoline (IVa).

A mixture of 1-(2'-thienyl)-3-(4''-dimethylamino phenyl)-2-propen-1-one (Ia) (0.01 mol) and 2,4 dinitro phenyl hydrazine hydrochloride (0.02 mol) was refluxed in DMF (20 ml) for two hours. The reaction mixture on cooling was diluted with water and product separated was filtered and crystallised from ethanol to obtain solid 1-(2,4-dinitro phenyl)-3-(4'-dimethylamino phenyl)-5-(2"-thienyl)-Δ^2-pyrazoline (IVa). Yield 61%, m.p. 90^0, Colour – Bottle Green.

IR (KBr) cm^{-1} : 3080.6 (Ar C-H), 1608.9 (C=N), 1560.7, 1413.4 (-NO_2 Asym. and Sym.), 1434.5 (-CH_2- of pyrazoline), 1230.3 (C-N), 1182.5 (C-N-$(CH_3)_2$, 696.6 (C-S).

PMR ($CDCl_3$) δ: 3.05 (s, 6H, -$N(CH_3)_2$), 3.3 (dd, 1H, >CHH_A), 3.91 (dd, 1H, >CH_BH),) 5.45 (dd, 1H, >CH_X-),) 6.6-8.6 (m, 10H, Ar-H and heteroaromatic H)

Synthesis of 1-carboxamido-3-(4'-dimethylamino phenyl)-5-(2"- thienyl)Δ^2-pyrazoline (Va).

A mixture of 1-(2'-thienyl)-3-(4''-dimethylamino phenyl)-2-propen-1-one (Ia) (0.01 mol) and semicarbazide hydrochloride (0.02 mol) was refluxed in DMF (20 ml) for two hours. The reaction mixture on cooling was diluted with water and product separated was filtered and crystallised from ethanol to obtain solid 1-carboxamido-3-(4'-dimethylamino phenyl)-5-(2"-thienyl) Δ^2-pyrazoline (XIIa). Yield 72%, m.p. 100^0, Colour – Dark Yellow.

IR (KBr) cm^{-1} : 3399.2 (-CO$\underline{NH_2}$), 3075.0 (Ar C-H), 1638.7 and 1609.9 (-$\underline{CO}NH_2$), 1565.5 (C=N), 1437.5 (-CH_2- of pyrazoline), 1351.6 (C-N), 1167.3 (C-N-$(CH_3)_2$, 698.1(C-S).

PMR ($CDCl_3$) δ : 3.1 (s, 6H, -$N(CH_3)_2$), 3.22 (dd, 1H, >CHH_A), 3.85 (dd, 1H, >CH_BH),) 5.45 (dd, 1H, >CH_X-), 6.08 (s, 2H, -$CONH_2$), 6.5-7.9 (m, 7H, Ar-H and heteroaromatic H).

Similarly, the other members of the series have been prepared in the same manner and their characterization data are given in Table 1.

RESULTS AND DISCUSSION

Isomeric Δ^2-pyrazolines have been synthesized by the interaction of chalcones (Ia-e) and hydrazine hydrochloride and substituted hydrazine hydrochlorides in DMF medium. IR Spectral values in Δ^2-pyrazolines and isomeric -pyrazolines are different and in PMR spectrum ABX pattern was seen in Δ^2-pyrazolines as well as in isomeric Δ^2- pyrazolines but values are somewhat different or greater in isomeric Δ^2- pyrazolines.

ACKNOWLEDGMENTS

Thanks of the authors are due to Principal Shri Shivaji Science College, Amravati for providing necessary facilities and to director R.S.I.C., Chandigarh and authorities of Pune University Pune for spectral and analytical data. One of the author (A.V. Ingle) is thankful to University Grants Commission, New Delhi for awarding Teacher Fellowship,

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