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Synthesis of 1-H-3-(2″-Hydroxy-3″-substitued-5″-Chlorophenyl)-5-(2′-Furyl)-2-Pyrazoles and Their Derivatives

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2-Hydroxy-3-substituted - 5-chlorophenyl - β-(2′-furyl)-acrylophenone dibromide (**Ia–c**) reacts with hydrazine hydrate in ethanol and yields pyrazole (**IIa–c**). Similarly, β-(2′-furyl)-acrylophenone dibromide (**Ia–c**) reacts with phenylhydrazine hydrochloride in ethanol medium and gives 1-phenyl-pyrazole (**IIIa–c**). Pyrazole (**IIa–c**) reacts with acetic acid to form 1-acetyl pyrazole (**IVa–c**). Also pyrazole (**IIa–c**) on reaction with benzoylchloride in pyridine gives 1-benzoylpyrazole (**Va–c**). Characterisation and structural elucidation were done on the basis of chemical reactions, elemental analysis and spectral data.

INTRODUCTION

o-Hydroxydibenzoyl methane and chalcone dibromide react with phenylhydrazine in pyridine and yield pyrazole[1]. Chalcone dibromide reacts with hydrazine or substituted hydrazine yields substituted pyrazoles[2–4]. The pyrazoles and pyrazolines are found in drugs and dyes[5,6]. Pyrazole[7] nucleus is five-membered heterocyclic containing two nitrogen atoms. Pyrazoles are known for their versatile physiological activities[8–11]. Herbicidal compositions containing pyrazole derivatives were prepared[12]. Pyrazoles and their derivatives[13] were prepared by the action of DMSO-I_2-H_2SO_4 and DMSO-I_2 system on pyrazolines and its derivatives. Recently we have prepared benzothiozolylamino pyrazoles[14]. Hence it was thought interesting to prepare pyrazoles and their derivatives from 2-hydroxy-3-substituted-5-chlorophenyl-β-(2′-furyl) acrylophenone dibromides.

EXPERIMENTAL

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 BrukerAC 300F spectrophotometer at 300 MHz using TMS as an internal reference (chemical shifts in δ ppm downfield from TMS). Purity of the compounds was checked on silica gel-G coated plates. β-(2′-furyl) acrylophenone dibromides were prepared by known method[15].

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Synthesis of 1-H-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole (IIa)

2-Hydroxy-5-chlorophenyl-β-(2′-furyl)-acrylophenone dibromide **(Ia)** (0.01 mol) was dissolved in ethanol (25 mL) and 90% hydrazine hydrate (0.012 mol) was added to it. The mixture was refluxed for 2 h, cooled and then diluted with water. The crude product that separated out was crystallised from ethanol to get compound **(IIa)** in 72% yield; m.p. 112°C. % Analysis: Found: C = 59.44, H = 3.05, N = 10.30; $C_{13}H_9ON_2Cl$ requires: C = 59.88, H = 3.45, N = 10.74%.

IR (KBr): 3440 cm^{-1} ν(—NH), 3190–3140 cm^{-1} ν(—OH), 1580 cm^{-1} ν(C=N), 1240 cm^{-1} ν(C—N,) 825, 880 cm^{-1} (2′-furyl), 760 cm^{-1} ν(C—Cl).

PMR ($CDCl_3$): 6.75–7.50 δ (m, 7H, Ar—H and heteroaromatic H), 10.80 δ (S, 1H, N—H), 13.30 δ (S, 1H, —OH).

Synthesis of 1-phenyl-3-(2″-hydroxy-5″-chorophenyl)-5-(2′-furyl)-2-pyrazole (IIIa)

To a solution 2-hydroxy-5-chlorophenyl-β-(2′-furyl)-acrylophenone dibromide **(Ia)** (0.01 mol) in ethanol (25 mL) was added phenylhydrazine hydrochloride (0.012 mol) and 1–2 drops of NaOH (2 N) and refluxed for 4 h. The mixture was concentrated and allowed to cool. The resulting solid was filtered and washed with water and crystallised from ethanol to get 1-phenyl-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole **(IIIa)** in 81% yield; m.p. 166°C. % Analysis: Found: C = 67.38, H = 3.50, N = 8.02; $C_{19}H_{13}O_2N_2Cl$ requires: C = 67.75, H = 3.86, N = 8.32%.

UV (Methanol): λ_{max} 220 nm and 260 nm corresponding to π–π^* and n–π^* transitions.

IR (KBr): 3150–3070 cm^{-1} ν(—OH), 1598–1582 cm^{-1} ν(C=N), 1230 cm^{-1} ν(C—N), 875, 830 cm^{-1} (2′-furyl) and 780 cm^{-1} ν(C—Cl).

PMR ($CDCl_3$): 6.9–7.4 δ (m, 12H, Ar—H and heteroaromatic H), 12.48 δ (s, 1H, —OH).

Synthesis of 1-acetyl-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole (IVa)

A mixture of pyrazole **(IIa)** (0.01 mol) and acetic acid (10 mL) was refluxed for 2 h. The reaction mixture was concentrated. On cooling the resulting solid obtained was filtered, washed with water and crystallised from ethanol to get 1-acetyl-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole **(IVa)** in 76% yield m.p. 116°C. % Analysis: Found: C = 59.10, H = 3.20, N = 9.00; $C_{15}H_{11}O_3N_2Cl$ requires: C = 59.50, H = 3.63, N = 9.25%.

IR (KBr): 3080–3000 cm^{-1} ν(—OH), 1680, 1640 cm^{-1} ν(N—C=O and C=O), 1620 cm^{-1} ν(C=N), 1240 cm^{-1} ν(C—N), 870, 840 cm^{-1} ν(2′-furyl) and 740 cm^{-1} ν(C—Cl).

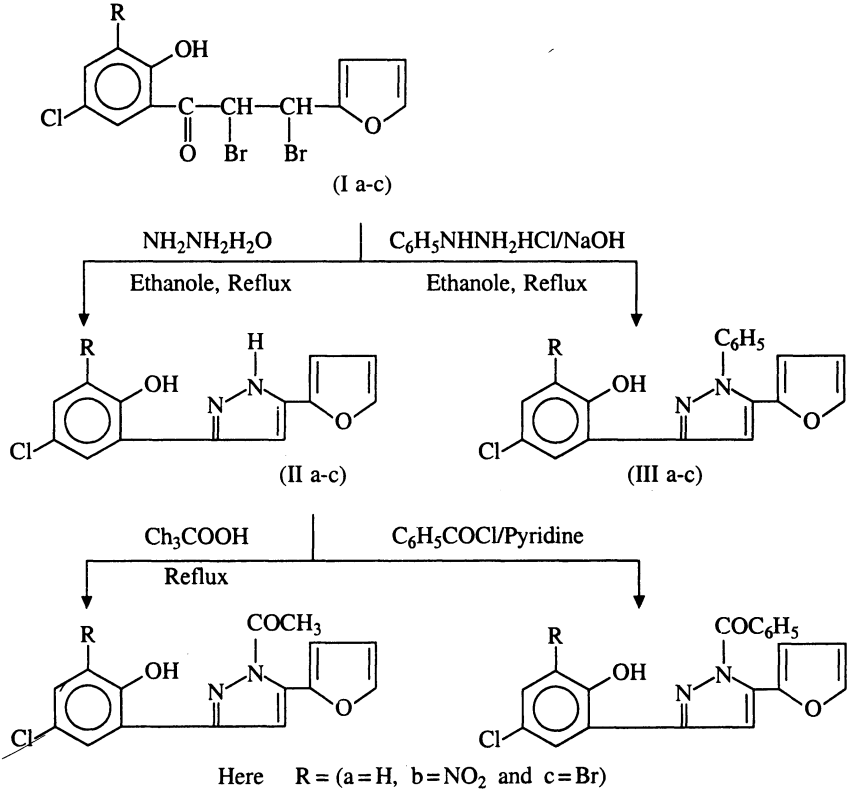
PMR ($CDCl_3$): 2.7 δ (S, 3H, $COCH_3$), 6.28–8.1 δ (m, 7H, Ar—H and heteroaromatic H), 12 δ (S, 1H, —OH).

Synthesis of 1-benzoyl-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole (Va)

A mixture of pyrazole **(IIa)** (0.01 mol) and benzoylchloride (0.01 mol) was dissolved in dry pyridine (10 mL) and stirred at room temperature for 1 h, after which the reaction mixture was treated with cold dilute HCl (2 N). The resulting solid was filtered, washed successively with water, cold NaOH (2%) and water. The crude mass was crystallised from acetic acid to get 1-benzoyl-3-(2″-hydroxy-5″-chlorophenyl)-5-(2′-furyl)-2-pyrazole **(Va)** in 75% yield; m.p. 122–24°C. % Analysis: Found: C = 65.66, H = 3.28, N = 6.20; $C_{20}H_{13}O_3N_2Cl$ requires: C = 65.84, H = 3.56, N = 7.68%.

IR (KBr): 3140–3060 cm^{-1} ν(br, —OH), 1675, 1635 cm^{-1} ν(C=O and N—C=O), 3140–3060 cm^{-1} ν(C=N), 1230 cm^{-1} ν(C—N), 880, 835 cm^{-1} ν(2′-furyl) and 730 cm^{-1}ν (C—Cl).

PMR ($CDCl_3$): 6.5–8.22 δ (m, 12H, Ar—H and heteroatomic H), 12 δ (S, 1H, —OH).



Here R = (a = H, b = NO_2 and c = Br)

The other members of the series were also prepared in a similar manner and their characterization data are given in Table-1.

TABLE-1
CHARACTERIZATION DATA OF PYRAZOLES AND THEIR DERIVATIVES

Compound No.	R	Yield (%)	m.p. (°C)	m.f.	% Analysis, Found (Calcd.)		
					C	H	N
IIb	NO_2	67	130	$C_{13}H_8O_4N_3Cl$	50.86 (51.06)	2.42 (2.61)	13.33 (13.74)
IIc	Br	74	138	$C_{13}H_{18}O_2N_2ClBr$	45.50 (45.94)	1.97 (2.35)	8.00 (8.24)
IIIb	NO_2	73	187–88	$C_{19}H_{12}O_4N_3Cl$	59.45 (59.76)	2.88 (3.14)	10.70 (11.00)
IIIc	Br	69	159	$C_{19}H_{12}O_2N_2ClBr$	54.55 (54.87)	2.46 (2.88)	6.24 (6.73)
IVb	NO_2	67	134	$C_{15}H_{10}O_5N_3Cl$	51.30 (51.79)	2.54 (2.87)	11.86 (12.08)
IVc	Br	71	145	$C_{15}H_{10}O_3N_2ClBr$	46.85 (47.18)	2.48 (2.62)	7.00 (7.33)
Vb	NO_2	50	135	$C_{20}H_{12}O_5N_3Cl$	58.22 (58.60)	2.47 (2.93)	5.92 (6.31)
Vc	Br	66	150	$C_{20}H_{12}O_3N_2ClBr$	54.03 (54.11)	2.66 (2.70)	5.92 (6.31)

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