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NOTE

Synthesis and Characterization of 4-Aroyl Substituted Pyrazolines and Pyrazoles

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Some new 4-aroyl substituted pyrazolines **(IIIa–d)** and pyrazole **(IVa–d)** have been synthesized by condensation of phenyl hydrazine hydrochloride with 3-aroyl flavanones **(Ia–d)** and 3-aroyl flavones **(IIa–d)** respectively in DMF containing small amount of piperidine. Also, 4-aroyl substituted pyrazoles **(IVa–d)** have been synthesized by reaction with 4-aroyl substituted pyrazoline **(IIIa–d)** with DMSO-I_2-H_2SO_4 system or DMSO-I_2 system. Structures of the compounds have been characterized by IR spectra, PMR spectra and chemical properties.

Key Words: 4-Aroyl substituted pyrazolines, Pyrazoles.

Flavanones and flavones are reported[1–5] to react with hydrazines to furnish pyrazolines and pyrazole derivatives respectively and the reaction mechanism has also been explained[3]. Reaction of hydrazine or substituted hydrazine on chromone, thiochromone or flavone is one of the methods for the synthesis of 3-*o*-hydroxy phenyl-5-alkyl (or aryl) pyrazoles[6]. Pyrazolines and pyrazoles are found in drugs and dyes[7, 8]. Recently pyrazoline has been converted into pyrazoles with DMSO-I_2-H_2SO_4 system and DMSO-I_2 system on pyrazoline[9].

We report the synthesis of some pyrazolines **(IIIa–d)** and pyrazoles **(IVa–d)** by reacting 3-aroyl flavanones **(Ia–d)** and 3-aroyl flavones **(IIa–d)** with phenyl hydrazine hydrochloride in DMF solvent containing small amount of piperidine. 3-Aroyl flavanones **(Ia–d)** and 3-aroyl flavones **(IIa–d)** were prepared by known method[10]

Synthesis of 3-(5′-chloro-2′-hydroxy phenyl)-4-(4′-chloro benzoyl)-5-(4′-N,N′-dimethyl aminophenyl)-1-phenyl-Δ^2-pyrazoline (IIIa)

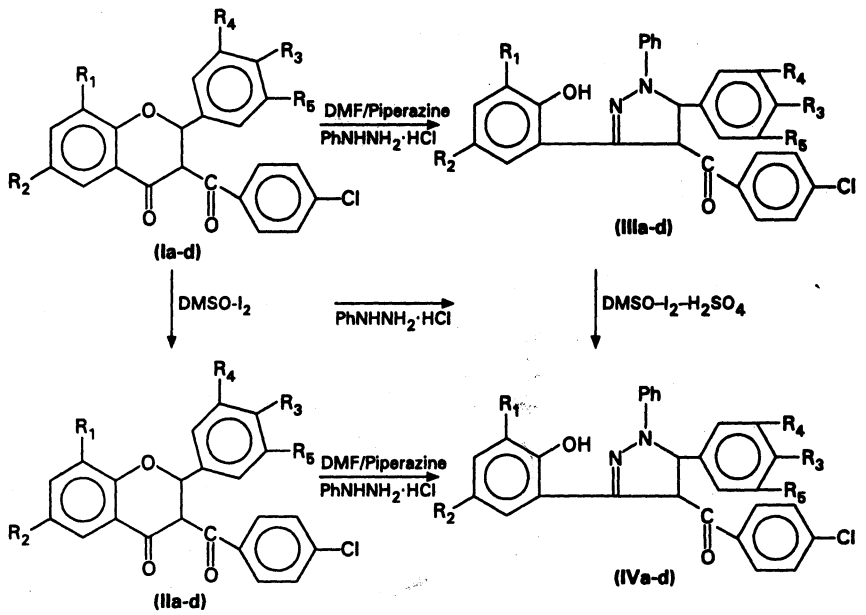
A mixture of 4′-(N,N-dimethylamino)-3-(4′-chlorobenzoyl)-6-chloro flavanone **(Ia)** (0.01 mol) and phenyl hydrazine hydrochloride (0.02 mol) in DMF (20 mL) containing few drops of piperidine (0.5 mL) were refluxed for 1.3 h. The reaction mixture was cooled, diluted with ice-cold water, filtered and crystallized from ethanol-acetic acid to obtain white crystalline compound **(IIIa)**. Yield: 70%; m.p.: 198°C; IR (Nujol): 3446 ν(O—H), 1630 ν(=N—N), 1610 ν(C=O), 1461 ν(—C=C), 1190–1284 ν(C=N) and 725 cm^{-1} ν(C—C); ^1H NMR ($CDCl_3$):

2.85δ (ppm) (s, 6H, —$N(CH_3)_2$), 3.6δ (d, 1H, —CH), 4.4δ (d, 1H, —CH), 6.7–8.03δ (m, 16H, Ar—H) and 11.92δ (s, 1H, Ar—OH).

Similary, the other compounds **(IIIb–d)** have been synthesized from **(Ib–d)** and characterized.

TABLE-1
4-AROYL SUBSTITUTED PYRAZOLINES AND 4-AROYL SUBSTITUTED PYRAZOLES

S. No.	Compd.	R_1	R_2	R_3	R_4	R_5	m.p. (°C)	Yield (%)	R_f
1	**IIIa**	H	—Cl	—$N(CH_3)_2$	—H	—H	198	70	0.26
2	**IIIb**	H	—Cl	—OH	—OCH_3	—OCH_3	221	72	0.45
3	**IIIc**	NO_2	—CH_3	—$N(CH_3)_2$	—H	—H	209	65	0.32
4	**IIId**	NO_2	—CH_3	—OH	—OCH_3	—OCH_3	230	60	0.21
5	**IVa**	H	—Cl	—$N(CH_3)_2$	—H	—H	228	70	0.26
6	**IVb**	H	—Cl	—OH	—OCH_3	—OCH_3	231	75	0.47
7	**IVc**	NO_2	—CH_3	—$N(CH_3)_2$	—H	—H	246	68	0.34
8	**IVd**	NO_2	—CH_3	—OH	—OCH_3	—OCH_3	280	64	0.33



Synthesis of 3-(5′-chloro-2′-hydroxyphenyl)-4-(4′-chlorobenzoyl)-5-(4′-dimethyl aminophenyl)-1-phenyl-pyrazole (IVa)

Mixture of 4′-(N,N-dimethylamino)-3-(4′-chlorobenzoyl)-6-chloro flavone **(IIa)** (0.01 mole) and phenyl hydrazine hydrochloride (0.02 mole) in DMF (20 mL) containing few drops of piperidine (0.5 mL) was refluxed for 1.3 h. The reaction mixture was cooled, diluted in ice-cold water, decomposed with HCl and

crystallised from ethanol-acetic acid mixture to get white crystalline solid **(IVa)**, Yield: 70%; m.p.: 228°C; IR (Nujol): 3450 ν(O—H), 1612 ν(C=O), 1571 ν(C=N), 1527 ν(C=C), 1377 ν(C—N), 1035 ν(C—O stretching in phenol) and 788 cm^{-1} ν(C—Cl); ^1H NMR ($CDCl_3$): 2.85δ (ppm) (S, 6H, —$N(CH_3)_2$), 6.63–8.16δ (m, 16H, Δr-H) and 11.92δ (s, 1H, Ar—OH).

Similary the other compounds **(IVb–d)** have been synthesized and characterized.

General procedure for the synthesis of IVa–d from IIIa–d.

4-Aroyl substituted pyrazolines **(IIIa–d)** were dissolved in (20 mL) $DMSO_4$ and crystals of iodine added. To this mixture 2–3 drops of H_2SO_4 were added and refluxed for 1/2 h, washed with $NaHCO_3$ (to remove unreacted I_2) several times and then with water and crystallized from ethanol-acetic acid to give 4-aroyl substituted pyrazoles **(IVa–d)**. The same reaction was carried out in absence of concentrated H_2SO_4 and the same product was obtained.

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