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NOTES

Synthesis of 1H-3-(2′-hydroxy-4′-methoxy)-5-substituted Phenyl-2-pyrazolines

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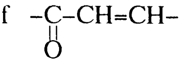
2′-Hydroxy-4′-methoxy-chalcones (1a–c) on condensation with hydrazine hydrate in ethanol gave 1H-3-(2′-hydroxy-4′-methoxy)-5-substituted phenyl-2- pyrazolines (2a–c). The reaction of (2a–c) with acetic acid gave the acetyl derivatives (3a–c) by direct and indirect method. Similarly reaction of (2a–c) with benzoyl chloride gave benzoyl derivatives (4a–c). The structures of the compounds have been supported by elemental and spectral data.

Hydrazines or substituted hydrazines reacting with 2-hydroxy-chalcones of flavanones lead to the formation of pyrazolines. Pyridine as reaction medium has been widely used[1–3]. The use of DMF[4], ethylenediamine and DMSO[5] has also been reported. Acetic acid has been used in the reaction between phenylhydrazine and benzal-acetophenone with hydrazine and acetic acid; however, N-acetyl pyrazolines are formed[3, 6]. In the present work, we report the preparation of some new pyrazolines from 2-hydroxy-4-methoxy-chalcones.

2-Hydroxy-4-methoxy-4′-methoxy-chalcone (1a) (0.01 mol) and 99% hydrazine hydrate (0.015 mol) in ethanol (50 ml) was refluxed for 2 h. The mixture was then concentrated and allowed to cool. The resulting solid was filtered, washed with ethanol and recrystallised from ethanol to give pale yellow solid, (2a). Yield *ca.* 80%, m.pt. 150°C, m.f. $C_{17}H_{18}O_3N_2$, % Found (Calcd.): C = 69.0(68.4), H = 6.0(6.0), N = 9.3(9.4).

It gives green colouration with neutral $FeCl_3$ solution indicating the presence of free phenolic –OH group and deep blue colouration with concentrated H_2SO_4 showing the absence of  $-\underset{\underset{O}{\|}}{C}-CH=CH-$ linkage.

IR bands (cm^{-1}): 3380 ν(NH), 2900–3000 ν(OH), 1540–1550 (ν(C=N) of pyrazoline), 1240–1250 ν(C–N) and 1400 (ν(CH_2) of pyrazoline).

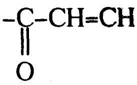
PMR ($CDCl_3$): 2.63 δ (dd, 1H, >CH<u>HA</u>, JAB = 18 Hz, JAX = 4 Hz); 3.61 δ (dd, 1H, >CH<u>BA</u>, JAB = 17 Hz, JBX = 11 Hz); 3.8 δ (S, 6H, –) CH_3; 4.8 δ (dd, H, >CH_x, JAX = 4 Hz, JBX = 11 Hz); 6.4–7.52 δ (m, 7H, Ar–H); 10.8–11.44 δ (S(br), 1H, –OH)

Hence compound, 2a, is 1H-3-(2-hydroxy-4-methoxy)-5-anisyl-2-pyrazoline. Similarly other pyrazolines were prepared (Table 1).

1-Acetyl-3-(2-hydroxy-4-methoxy)-5-anisyl-2-pyrozoline (3a)

Indirect Method

A mixture of 2a (0.001 mol) and acetic acid (10 ml) was refluxed for 2 h. The solution was then concentrated; on cooling the resulting solid was filtered, washed with water and recrystallised from ethanol. Yield 80%, m.pt. 170°C. (Found C 67.2%, H 5.72%, N 8.12%; requires C 67.5%, H 5.88%, N 8.23%); m.f. $C_{19}H_{20}O_4N_2$.

It gives green colouration with neutral $FeCl_3$ solution indicating the presence of free phenolic –OH group and deep blue colouration with concentrated H_2SO_4, showing the absence of  $-\underset{\underset{O}{\|}}{C}-CH{=}CH$ linkage.

IR bands (cm^{-1}): 3350–3400 ν(OH), 1670–1680 ν($N-COCH_3$), 1630–1640 ν(C=O, N–C=O), 1600–1610 (νC=N) of pyrazoline), 1230–1220 cm^{-1} ν(C–N).

PMR ($CDCl_3$): 2.8 δ (S, 3H, $-COCH_3$); 3.14 δ (dd, 1 H, >CHHA, JAB = 18 Hz, JAX = 4 Hz), 3.6 δ (dd, H, >CHBA, JAB = 18 Hz, JBX = 11 Hz); 3.88 δ (3, 1H, $-OCH_3$); 5.56 δ (dd, 1H, $>CH_X-$, JAY = 4 Hz, JBX = 11 Hz); 6.48–7.44 δ (m, 7H, Ar–H) 10.56 δ (S, 1H, –OH).

Similarly other acetyl derivatives were prepared (Table 1)

TABLE 1
PHYSICAL DATA OF THE COMPOUNDS

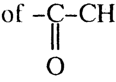
Sr. No.	R_1	R_2	M pt. (°C)	Yield %	Molecular formula
2a	$-OCH_3$	H	150	80	$C_{17}H_{18}O_3N_2$
2b	H	H	105	75	$C_{16}H_{15}O_2N_2$
2c	$-O-CH_2-O-$	–	142	78	$C_{17}H_{17}O_4N_2$
3a	$-OCH_3$	H	170	80	$C_{19}H_{20}O_4N_2$
3b	H	H	145	85	$C_{18}H_{17}O_2N_2$
3c	$-O-CH_2-O-$	–	190	90	$C_{19}H_{19}O_5N_2$
4a	$-OCH_3$	H	120	85	$C_{24}H_{22}O_4N_2$
4b	H	H	90	80	$C_{23}H_{19}O_3N_2$
4c	$-O-CH_2-O-$	–	128	90	$C_{24}H_{21}O_5N_2$

Direct method

A mixture of chalcone (2a) (0.0015 mol) and 99% hydrazone hydrate (0.002 mol) in acetic acid 15 ml was refluxed for 2 hrs. The solvent was then removed under reduced pressure and residual matter was diluted with water. The resulting solid was washed with water and recrystallised from ethanol. Yield 80%, m.pt. 170°C.

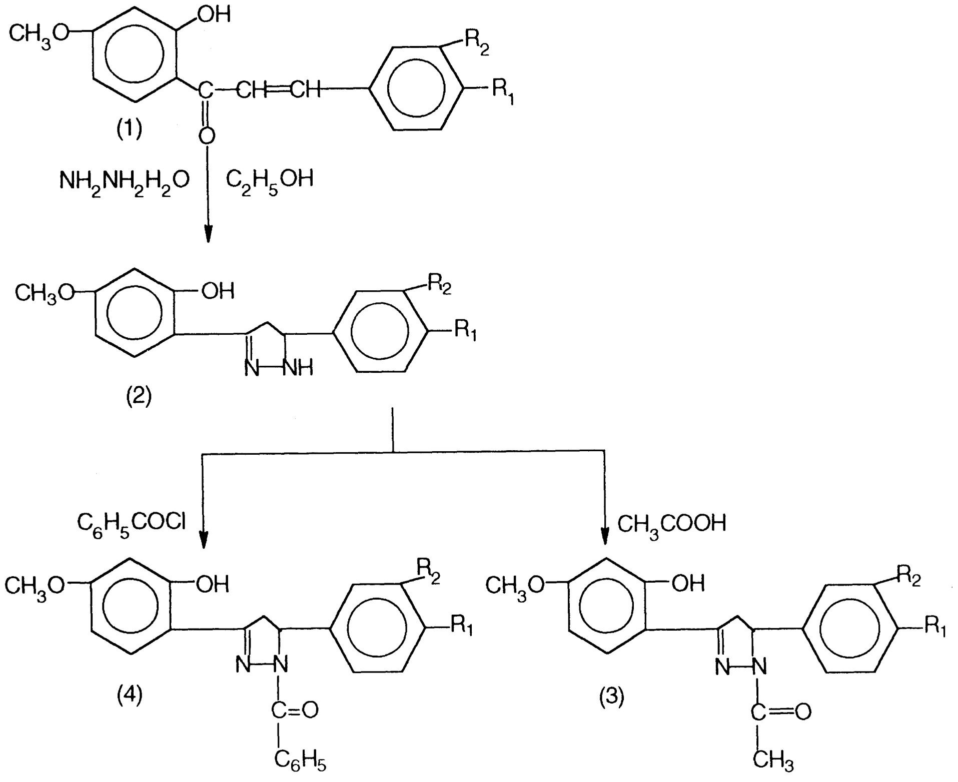
1-Benzoyl-3-(2-hydroxy-4-methoxy)-5-anisyl-2-pyrazoline (4a)

A mixture of 2a (0.001 mol) and benzoyl chloride (0.001 mol) was dissolved in dry pyridine (10 ml) and stirred at room temeprature for 1 h, after which the reaction mixture was treated with cold dilute HCl (2N). The resulting solid was filtered, washed successively with water, cold NaOH (2%) and water and crystallised from glacial acetic acid. Yield 85%, m.pt. 120°C (found C 71.82%, H 5.62%, N 6.87%; require C 71.46%, H 5.7%, N 6.9%), m.f. $C_{24}H_{22}O_4N_2$.

It gives green colouration with neutral $FeCl_3$ solution indicating the presence of free phenolic –OH group and deep blue colouration with concentrated H_2SO_4 showing the absence of  $-\underset{\underset{O}{\|}}{C}-CH=CH-$ linkage.

IR bands (cm^{-1}): 3500–3350 ν(–OH), 1670–1660 ν(C=O, N–C=O), 1650–1640 (ν(C=N) of pyrazoline), 1220–1210 cm^{-1} ν(C–N).

PMR ($CDCl_3$): 3.25 δ (dd, 1H, >CH$\underline{\text{HA}}$, JAB = 18 Hz, JAX = 4 Hz; 3.6 δ (dd, 1H, >CH$\underline{\text{BA}}$, JAB = 18 Hz, JBX = 12 Hz; 3.8 δ (s, 6H, $-OCH_3$), 4.5 δ (dd, 1H, >CHX—, JAX = 4 Hz, JBX = 11 Hz; 6.7 to 8.2 δ (m, 12H, Ar–H).



(a) $R_1 = -OCH_3$, $R_2 = H$, (b) $R_1 = R_2 = H$, (c) $R_1R_2 = -O-CH_2-O-$

Hence the compound (4a) is 1-benzoyl-3-(2-hydroxy-4-methoxy)-5-anisyl-2-pyrazoline.

Similarly other benzoyl derivatives were prepared (Table 1).

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