

Synthesis of 3-(4''-Substituted Phenyl)-5-(4'-Substituted Phenyl)- Δ^2 -Pyrazolines and Their Derivatives

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4-Substituted acetophenone (**Ia–b**) condenses with substituted benzaldehyde in ethanol in presence of pulverised KOH to give 4-substituted chalcone and 4'-substituted chalcone (**IIa–d**); (**IIa–d**) react with hydrazine hydrate in ethanol to give pyrazolines (**IIIa–d**). Pyrazolines (**IIIa–d**) react with acetic acid to form 1-acetyl pyrazoline (**IVa–d**), pyrazoline reacts with benzoyl chloride in pyridine to give 1-benzoyl pyrazoline (**Va–d**). Also pyrazoline reacts with sodium nitrite to give 1-nitroso pyrazoline (**VIa–d**). Characterisation and structural elucidation were done on the basis of chemical, analytical and spectral analysis.

Key words: Synthesis, substituted pyrazolines, derivatives, characterization..

INTRODUCTION

Pyrazolines are known to have bacterial¹, fungicidal² and insecticidal³ properties. Some pyrazolines are also reported to have anti-inflammatory, antidiabetic, anaesthetic and analgesic properties^{4–7}. Pyrazoline and its derivatives have been reported to show biological activities^{8–10}. Recently Ali *et al.*¹¹ have reported the synthesis of isomeric Δ^2 -pyrazolines and its derivatives from 2'-hydroxychalcone. It was thought interesting to prepare some new pyrazolines and their derivatives from 4'-chlorochalcone and 4'-nitrochalcone.

Chalcone reacts with hydrazine hydrate in ethanol to give pyrazoline. Pyrazoline reacts with acetic acid to give 1-acetyl pyrazoline^{12–15}. Similarly pyrazoline reacts with benzoyl chloride in pyridine to give 1-benzoyl pyrazoline^{12–15}. Pyrazoline reacts with sodium nitrite to give 1-nitroso-pyrazoline^{15, 16}. Literature survey indicates that pyrazoline and its derivatives have not been prepared from 4'-chlorochalcone and 4'-nitrochalcone. Hence it was thought interesting to prepare pyrazolines and its derivatives. Chalcones have been prepared by known methods¹⁷.

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EXPERIMENTAL

Synthesis of 1-H-3-(4''-chlorophenyl)-5-(4'-anisyl)- Δ^2 -pyrazoline (IIIa)

4-Chloro-4'-methoxychalcone (IIa) (0.01 mole) and 99% hydrazinehydrate (0.012 mole) in ethanol (50 mL) were refluxed for 2 h. The mixture was then concentrated and allowed to cool; the resulting solid was filtered, washed with ethanol and crystallised from ethanol to give pale yellow solid (IIIa), yield 75%, m.p. 93°C.

Properties of the compound (IIIa)

The compound (IIIa) is pale yellow, crystalline solid, m.p. 93°C. The analytical results indicate that the m.f. of the compound is $C_{16}H_{15}N_2OCl$. The R_f value in benzene is found to be 0.68 in silica gel-G plate with a layer of thickness 0.3 mm. It does not give blue coloration with concentrated H_2SO_4 ,

showing the absence of $\begin{array}{c} O \\ || \\ -C-CH=CH- \end{array}$ linkage. IR spectrum of the compound was recorded in Nujol: 3380 ($-NH-$ stretching), 1550–1540 ($-C=N$ of pyrazoline), 1240 (C–N stretching), 1400 ($-CH_2$ of pyrazoline), 1310 ($-OCH_3$ stretching), 790 cm^{-1} (C–Cl stretching). PMR was recorded in ($CDCl_3$): 3.80 δ (s, 3H, $-OCH_3$), 3.60 δ (dd, 1H, CHH_A), 3.48 δ (dd, 1H, $-CH_BH$), 4.90 δ (dd, 1H, $-CH_X$), 6.8–7.6 δ (m, 8H, Ar–H) and 7.8 δ (s, 1H, NH).

Synthesis of 1-acetyl-3-(4''-chlorophenyl)-5-(4'-anisyl)- Δ^2 -pyrazoline (IVa)

A mixture of pyrazoline (IIIa) (0.01 mole) and acetic acid (10 mL) was refluxed for 2 h. The reaction mixture was then concentrated. On cooling the resulting solid was filtered, washed with ethanol and crystallised from ethanol to get white solid (IVa), yield 76%, m.p. 128°C.

Properties of the compound (IVa)

The compound (IVa) is a white crystalline solid, m.p. 128°C. The analytical results indicate that the m.f. of the compound is $C_{18}H_{17}N_2O_2Cl$. The R_f value in benzene is found to be 0.76 in silica gel-G plate with a layer of thickness 0.3 mm. It gives blue coloration with concentrated H_2SO_4 , showing the absence of

$\begin{array}{c} O \\ || \\ -C-CH=CH- \end{array}$ linkage. IR spectrum of the compound was recorded in Nujol: 3000 (Ar–H), 1680–1670 (C=O and N–C=O stretching), 1640–1630 (C=N of pyrazoline), 1230 (C–N stretching), 1310 ($-OCH_3$ stretching), 740 cm^{-1} ($-C-Cl$ stretching). PMR was recorded in ($CDCl_3$): 2.8 δ (s, 3H, $-COCH_3$), 3.14 δ (dd, 1H, CHH_A), 3.6 δ (dd, 1H, CH_BH), 3.58 δ (s, 3H, $-OCH_3$), 5.56 δ (dd, 1H, $-CH_X$), 6.48–7.4 δ (m, 8H, Ar–H).

Synthesis of 1-benzoyl-3-(4''-chlorophenyl)-5-(4'-anisyl)- Δ^2 -pyrazoline (Va)

A mixture of pyrazoline (IIIa) (0.01 mole) and benzoyl chloride (0.01 mole) was dissolved in dry pyridine (10 mL) and stirred at room temperature for 1 h. The reaction mixture was treated with cold dil. HCl (2 N). The resulting solid was filtered, washed successively with water, cold NaOH (2%) and water. The crude solid was crystallised from acetic acid to get yellow coloured solid (Va), yield 80%, m.p. 166°C.

Properties of the compound (Va)

The compound (Va) is a yellow crystalline solid, m.p. 166°C. The analytical results indicate that the m.f. of the compound is $C_{23}H_{19}N_2O_2Cl$. The R_f value in benzene is found to be 0.79 in silica gel-G plate with layer of thickness 0.3 mm. It gives blue coloration with concentrated H_2SO_4 , showing the absence of

$\begin{array}{c} O \\ || \\ -C-CH=CH- \end{array}$ linkage. IR spectrum of the compound was recorded in Nujol: 1670–1660 ($-C=O$ and $N-C=O$ stretching), 1650–1640 ($-CH_2$ of pyrazoline), 1310 ($-OCH_3$ stretching), 1220 ($C-N$ stretching), 740 cm^{-1} ($-C-Cl$ stretching). PMR was recorded in ($CDCl_3$): 3.25 δ (dd, 1H, CHH_A), 3.6 δ (dd, 1H, CH_BH), 3.8 δ (s, 3H, $-OCH_3$), 4.5 δ (dd, 1H, $-CH_X$), and 6.7–7.8 δ (m, 13H, Ar—H).

Synthesis of 1-nitroso-3-(4''-chlorophenyl)-5-(4'-anisyl)- Δ^2 -pyrazoline (VIa)

A mixture of pyrazoline (IIIa) (0.002 mole) was dissolved in 1 : 1 HCl (2 mL) and then cooled in ice-cold bath. Cold 10% sodium nitrite solution (6 mL) was added dropwise with constant stirring. The mixture was further stirred for 30 min at room temperature. The resulting solid separated, crystallised from ethanol to get brown coloured solid (VIa), yield 82%, m.p. 121°C.

Properties of the compound (VIa)

The compound (VIa) is a brown crystalline solid, m.p. 121°C. The analytical results indicate that the m.f. of the compound is $C_{16}H_{14}N_3O_2Cl$. The R_f value in benzene is found to be 0.82 in silica gel-G plate with layer of thickness 0.3 mm. It gives blue coloration with concentrated H_2SO_4 , showing the absence of

$\begin{array}{c} O \\ || \\ -C-CH=CH- \end{array}$ linkage. IR spectrum of the compound was recorded in Nujol: 1550 ($N=O$ stretching), 1560–1620 ($C=N$ of pyrazoline), 1450 ($N-N=O$ stretching)¹⁸, 1330 ($-OCH_3$ stretching), 1220 ($-C-N$ stretching), 740 cm^{-1} ($-C-Cl$ stretching). PMR was recorded in ($CDCl_3$): 3.80 δ (s, 3H, $-OCH_3$), 3.60 δ (dd, 1H, CHH_A), 3.48 δ (dd, 1H, CH_BH), 4.90 δ (dd, 1H, $-CH_X$), and 6.8–7.8 δ (m, 8H, Ar—H).

Similarly other pyrazolines and their derivatives were prepared and listed in Table-1.

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