

Oxidation of Pyrazolines with Manganese Dioxide

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Manuscript received 5 August 1985, revised 29 December 1986, accepted 21 April 1987

Pyrazolines have been oxidised with manganese dioxide in chloroform at room temperature to give pyrazoles in good yields.

PYRAZOLINES have been oxidised by several reagents, such as lead dioxide¹, mercuric oxide¹ and bromine^{1,2}, potassium permanganate^{3,3}, chromic oxide¹ and silvernitrate⁴. In a recent study, Gladstone and Norman⁵ have shown that pyrazolines can be oxidised to pyrazoles using lead tetraacetate. Bhatnagar and George⁶ reported the oxidation of 1,3,5-trisubstituted-pyrazolines with active manganese dioxide to the corresponding pyrazoles. During the course of the present investigation, five pyrazolines were synthesised and oxidised with active manganese dioxide in chloroform medium to the corresponding pyrazoles in good yields. Since the pyrazolines 3-(2-hydroxyphenyl)-5-(3,4-dimethoxyphenyl)-2-pyrazoline (**1a**) and 3-(2-hydroxy-5-methylphenyl)-5-(3,4-dimethoxyphenyl)-2-pyrazoline (**1b**) have not been reported, these were synthesised from the corresponding chalcones by the method of Kallay *et al.*⁷.

Experimental

All m.ps. are uncorrected. Ir spectra (KBr) were recorded on a Perkin-Elmer 137 spectrophotometer. Active manganese dioxide⁸ and chalcones⁹ were prepared by known methods.

General procedure for preparation of pyrazolines: 3-(2-Hydroxyphenyl)-5-(3,4-dimethoxyphenyl)-2-pyrazoline (**1a**): 2'-Hydroxy-3,4-dimethoxychalcone (5 g) in ethanol (100 ml) was refluxed with hydrazine

hydrate (32.3 ml, 80%) for 3 h. On cooling, colourless needles separated from the reaction mixture. The mother liquor afforded a second crop of the needles. It was crystallised from ethanol (5.2 g), m.p. 108-9°. Other compounds were prepared by similar procedure.

Ir spectra of the pyrazoline **1a** showed peaks ν_{\max} 3 520 (phenolic OH), 1 620 (C=N), 1 600, 1 500, 1 450, 1 420, 1 325, 1 310, 1 275, 1 250, 1 180, 1 110, 1 065, 1 040, 1 010, 940, 890, 860, 825, 800 and 750 cm^{-1} ; the pyrazoline **1b** ν_{\max} 3 440 (phenolic OH), 1 610 (C=N), 1 595, 1 500, 1 450, 1 425, 1 350, 1 270, 1 250, 1 230, 1 180, 1 140, 1 112, 1 070, 1 030, 960, 930, 880, 860, 830, 790 and 750 cm^{-1} .

Oxidation of pyrazolines with active manganese dioxide: The pyrazolines were shaken with manganese dioxide (1:3) in chloroform at room temperature for 2 h. The residue obtained after the removal of inorganic material and solvent was examined on tlc. Two spots were resolved—one of these was found to be due to the starting substance and the other due to the oxidation product in each case. These compounds were separated by column chromatography. Starting substances were confirmed by m.p., m.m.p. and co-tlc with authentic samples of pyrazolines in each case.

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF PYRAZOLINES (I)

Compd no	Compd	M p. °C	Yield %	Mol. formula	Analysis % : Found/(Calcd.)		
					C	H	N
1a	3-(2-Hydroxyphenyl)-5-(3,4-dimethoxyphenyl)-2-pyrazoline	108-9	104	C ₁₇ H ₁₆ N ₂ O ₃	68.05 (68.59)	6.17 (6.04)	9.26 (9.39)
1b	3-(2-Hydroxy-5-methylphenyl)-5-(3,4-dimethoxyphenyl)-2-pyrazoline	124-5	87.5	C ₁₈ H ₂₀ N ₂ O ₃	69.10 (69.38)	6.42 (6.41)	8.81 (8.97)
1c	3-(o-Hydroxyphenyl)-5-phenyl-pyrazoline	89-90	92	C ₁₅ H ₁₄ N ₂ O	75.60 (75.63)	5.91 (5.88)	11.72 (11.76)
1d	3-(o-Hydroxyphenyl)-5-(p-methoxyphenyl)pyrazoline	101-2	95.6	C ₁₆ H ₁₆ O ₃ N ₂	71.69 (71.64)	5.91 (5.96)	10.20 (10.44)
1e	3-(2-Hydroxy-5-methylphenyl)-5-(4-methoxyphenyl)pyrazoline	113-4	88.3	C ₁₇ H ₁₈ N ₂ O ₃	72.31 (72.34)	6.30 (6.38)	10.00 (9.92)

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TABLE 2—ANALYTICAL AND PHYSICAL DATA OF PYRAZOLES (2)

Compd. no.	Compd.	M.p. °C	Mol. formula	Analysis % : Found/(Calcd.)		
				C	H	N
2a	3(5)-(2-Hydroxyphenyl)-5(3)-(3,4-dimethoxyphenyl)pyrazole	150-1	C ₁₇ H ₁₆ N ₂ O ₄	68.59 (68.91)	5.60 (5.40)	9.41 (9.46)
2b	3(5)-(2-Hydroxy-5-methylphenyl)-5(3)-(3,4-dimethoxyphenyl)pyrazole	184-5	C ₁₈ H ₁₈ N ₂ O ₄	69.40 (69.67)	6.10 (5.80)	8.91 (9.03)
2c	3-(o-Hydroxyphenyl)-5-phenylpyrazole	144	C ₁₅ H ₁₁ N ₂ O	76.21 (76.27)	6.00 (5.08)	11.20 (11.85)
2d	3-(o-Hydroxyphenyl)-5-(p-methoxyphenyl)pyrazole	147-8	C ₁₆ H ₁₄ N ₂ O ₂	72.20 (72.18)	5.31 (5.26)	10.70 (10.52)
2e	3-(2-Hydroxy-5-methylphenyl)-5-(4-methoxyphenyl)pyrazole	170	C ₁₇ H ₁₆ N ₂ O ₂	72.80 (72.86)	6.00 (5.71)	10.10 (10.00)

Results and Discussion

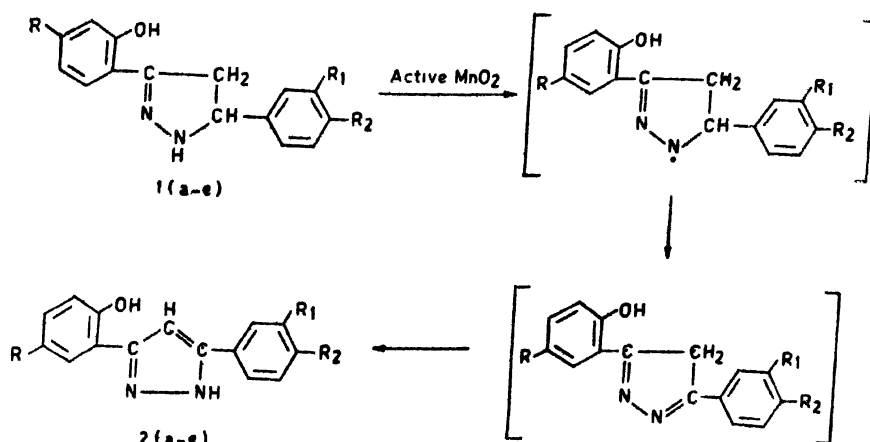
Each pyrazolines afforded the corresponding pyrazoles which were characterised on the basis of m.p., m.m.p., elemental analysis, ir and nmr spectral studies.

Ir spectrum of the pyrazoles (2) showed peaks :
 2c ν_{\max} 3 350, 3 120, 1 610, 1 535, 1 505, 1 490, 1 450, 1 380, 1 260, 1 240, 1 180, 1 110, 1 045, 1 030, 970, 900, 825, 760, 745, 725, 695, 685 and 600 cm^{-1} ;
 2d ν_{\max} 3 330, 1 620, 1 590, 1 585, 1 500, 1 465, 1 448, 1 415, 1 395, 1 270, 1 236, 1 175, 1 151, 1 090, 1 050, 1 020, 970, 930, 825, 790, 740, 710 and 675 cm^{-1} ;
 2e ν_{\max} 3 430, 1 615, 1 530, 1 505, 1 450, 1 435, 1 420, 1 300, 1 275, 1 240, 1 175, 1 130, 1 105,

1 050, 1 025, 975, 960, 835, 810, 770, 700 and 660 cm^{-1} .

The proton signals in the nmr spectra of the pyrazole 2d have been correlated with the various groups present in the molecule as follows : multiplets in the range τ 2.6-3.66 (9H) are because of aromatic and ethylenic protons, whereas OCH_3 group gives a singlet at τ 6.56 (3H). The nmr spectra of the pyrazole 2e show multiplets in the range τ 2.5-3.8 (8H) due to aromatic and ethylenic protons ; and singlets at τ 6.6 (3H) and 8.16 (3H) are because of OCH_3 and CH_3 groups, respectively.

A probable path for this reaction is shown in Chart 1.



- 1a, R=H, R₁=OCH₃, R₂=OCH₃.
 1b, R=CH₃, R₁=R₂=OCH₃.
 1c, R=R₁=R₂=H.
 1d, R=R₁=H, R₂=OCH₃.
 1e, R=CH₃, R₁=H, R₂=OCH₃.
 2a, R=H, R₁=R₂=OCH₃.
 2b, R=CH₃, R₁=R₂=OCH₃.
 2c, R=R₁=R₂=H.
 2d, R=R₁=H, R₂=OCH₃.
 2e, R=CH₃, R₁=H, R₂=OCH₃.

Chart 1

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