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SYNTHESIS OF SOME NOVEL 5(1'-ARYLPYRAZOL-4'-YL) 1,3,4-OXADIAZOLES

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Various 1-aryl-pyrazole-4-carboxaldehyde benzylhydrazones were cyclized with polyphosphoric acid to give 5(1'-arylpyrazole-4'-yl) 1,3,4-oxadiazoles (3-8) in good yields. Confirmation of their structures was based on the results of elemental analyses, infrared and proton magnetic resonance spectra.

Key words: Hydrazones, Pyrazole-4-carboxaldehydes, Cyclizations.

Introduction

Synthesis of many pyrazolyl-1,3,4-oxadiazoles and pyrazolyl imidazoles and pyrazolyl 1,2,4- and 1,2,5-oxadiazoles have been reported (Cusmano and Ruccia, 1957, London and Young, 1963, Van Meeteren and Van der Plas, 1969) but not much work has been done on pyrazolyl derivatives of 1,3,4-oxadiazoles and their other isomers. However, some derivatives of 1,3,4-oxadiazole (1) have been reported (Mokhtar and Farhat, 1991) while some 1,2,4-oxadiazole isomer were synthesized (Steler *et al* 1992) as selective herbicides. It was therefore of interest to prepare derivatives of 1,3,4-oxadiazoles from readily available 1-arylpyrazoles.

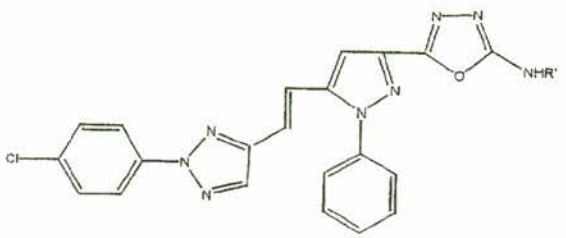
Materials and Methods

The proton resonance spectra (PMR) were obtained on Bucker AM-500 spectrometer (TMS as internal standard). The infrared atomic spectra (IR) were taken by a Hitachi 270-30 spectrometer. The solid samples were measured either in potassium bromide disks. Melting points were determined with Gallenkamp melting point apparatus and are uncorrected. The elemental analysis was performed by HEJ Research Institute of Chemistry, University of Karachi, Karachi, Pakistan.

General procedure for the synthesis of 5(1'aryl-pyrazole-4-yl) 1,3,4-oxadiazoles. An equimolar mixture (0.05 moles) of 1-arylpyrazole-4-carboxaldehyde and benzhydrazide with few drops of hydrochloric acid in 25 ml reactified alcohol was heated under reflux for 2 h. After cooling, water was added to the reaction mixture, filtered, dried to give the corresponding hydrazone. This was heated with polyphosphoric acid (15 ml) upto 150°C for 15 minutes. After cooling, the reaction mixture was poured over crushed ice. The precipitates formed were filtered, dried and crystalized from aqueous ethanol to give the compounds (**3-8**). The results of their analyses and spectra are presented in Table 1 and 2.

Results and Discussion

2-(1'-arylpyrazol-4'-yl)-1,3,4-oxadiazole (**3-8**) were prepared by a slight modification of the method used for the synthesis of 2,5-diphenyl-1,3,4-oxadiazole (Stofie, 1903; Fischer and Burton, 1985). The condensation product obtained from a reaction between 1-arylpyrazole-4-carboxaldehyde (Finar and



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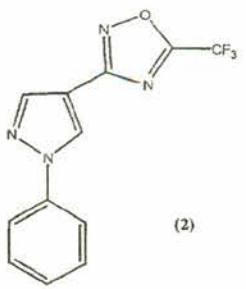

(2)

R' = C_4H_9, $CH_2C_6H_5$, C_6H_5, $C_6H_4CH_3$ (P)

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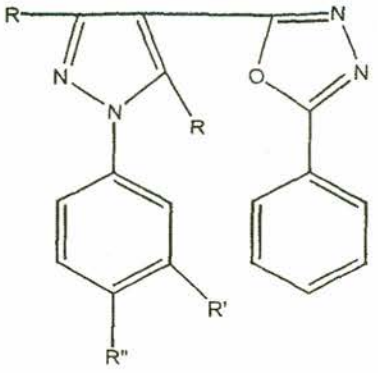
Table 1
Elemental analyses of 1-(arylpyrazole-4'-yl)-1,3,4-oxadiazoles

Comp. No.	m.p.(°C)	Yield (%)	Molecular formula	Calculated (%)			Found (%)		
				C	H	N	C	H	N
3	188-190	65	$C_{19}H_{16}N_4O$	72.15	5.06	17.06	71.24	5.90	17.05
4	235.237	64	$C_{19}H_{15}BrN_4O$	57.72	3.79	13.62	56.88	4.52	13.76
5	210.212	60	$C_{19}H_{15}BrN_4O$	57.72	3.79	13.62	58.03	3.42	13.96
6	283.285	56.	$C_{17}H_{14}N_4O$	70.34	4.82	19.20	70.74	4.51	20.01
7	220-222	58	$C_{19}H_{15}ClN_4O$	64.50	5.09	15.80	63.99	4.52	15.45
8	140-142	58	$C_{19}H_{15}ClN_4O$	64.50	5.09	15.80	64.83	4.52	16.06



3-8

3. R = CH_3 R' = R" = H
4. R = CH_3 R' = H R" = Br
5. R = CH_3 R' = Br R" = H
6. R = R" = H R' = CH_3
7. R = CH_3 R' = Cl R" = H
8. R = CH_3 R' = H R" = Cl

Table 2
Spectroscopic data of 1-(arylpyrazol-4'-yl)-1, 3,4-oxadiazoles

Comp. No.	I.R. (nujol) cm^{-1}	PMR δ Aromatic	($CDCl_3$) methyl
3	1620, 1600, 1485, 1370, 1095	8.80 - 7.30 10H. m.	2.60 - 2.50 6H, S, 2X CH_3
4	1620, 1610, 1485, 1355, 1210	9.10 - 7.20 9H, m.	2.70 - 2.50 6H, S, 2X CH_3
5	1610, 1550, 1500, 1485, 1370, 1095, 1060	8.70 - 7.50 9H, m.	2.70 - 2.50 6H, S, 2X CH_3
6	1650, 1600, 1370, 1150	8.10 - 7.20 11H, m.	2.50 H, S, 2XCH_3
7	1640, 1600, 1485, 1090, 1010	8.70 - 7.30 9H, m.	2.70 - 2.50 6H, S, 2X CH_3
8	1600, 1550, 1500, 1485, 1095	8.20 - 7.40 9H, m.	2.60 - 2.50 6H, S, 2X CH_3

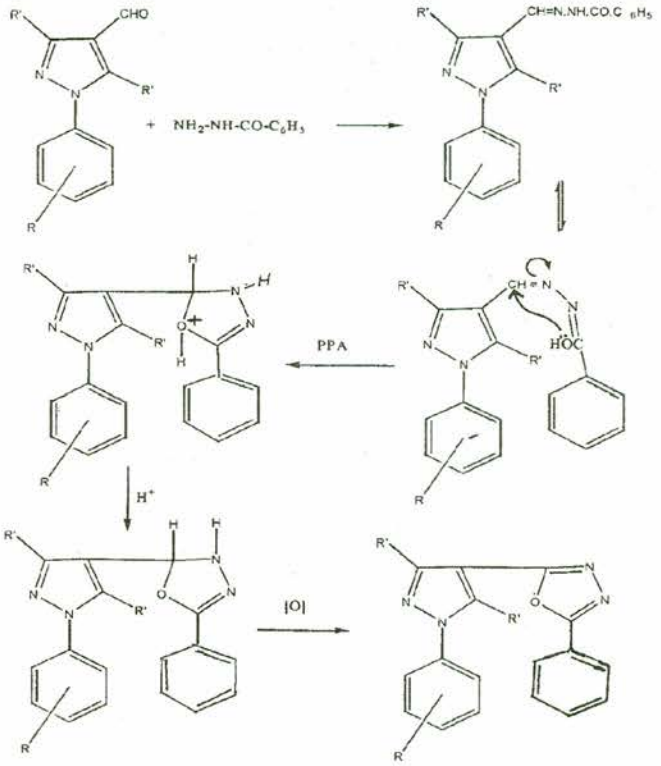


Chart 1

Lord 1967) and benzhydrazide, was cyclized with polyphosphoric acid at 150°C to give corresponding 5-(1'aryl pyrazol-4'-yl)-1,3,4-oxadiazoles. Elemental analysis of 5-(1'aryl pyrazol-4-yl)-1,3,4-oxadiazole, compounds (**3-8**), is given in Table 1 while spectroscopic data is presented in Table 2.

In IR spectra, aromatic (C=C) absorptions were observed at 1650-1500 cm^{-1} and aromatic (C-H) bond appeared at 1317 cm^{-1} and 1355 cm^{-1}. Absorption bands at 1260-1010 cm^{-1} indicated the presence of a cyclic bond (-C-O-C-) present in a 1,3, 4-oxadizole ring.

PMR spectra gave multiple singlets at δ 9.10-7.20 for aromatic protons and singles at δ 2.70-2.50 for (-CH_3) protons. No peaks due to a possible dihydro products were observed.

A possible mechanism for the formation of 1,3,4-oxadiazoles is presented in the Chart 1. The aromatization of the oxadiazole ring may take place by aerial oxidation of the intermediates formed during the cyclizatiom.

References

Cusmano S, Ruccia M 1957 Nitrosoimidazoles v. action of hydroxylamine on 4(or 5)-nitroso-2, 5(or 4)-diphenylimidazole. *Gazz Chim Ital* **86** 187.

Finar I L, Lord G H 1957 Formylation of the pyrazole nucleus. *J Chem Soc* 3314.

Fischer E, Burton C 1885. *Ber* **18** 2135.

London J D, Young L B 1963 Extrusion of sulphur VI. Novel ring contraction giving pyridazines and pyrazoles. *J Chem Soc* 5496-5502.

Mokhtar H M, Farahat O O 1991 Synthesis of nitrogenous compounds. Part IV. *Pak J Sci Ind Res* **34**(1).

Steller J, Gehring R, Schallner O, Tiefjrn K 1992 1-Aryl-4-azolylpyrazole. A new class of selective herbicides, private Communication.

Stofie R 1903. *J Prakt Chem* **68** 130.

Van Meeteren H W, Vanderplas H C 1969 Ring transformations in reactions of heterocyclic halo compounds with nucleophiles XVIII. Primidines 18 D/H exchange studies during the conversion of 2-substituted 4-chloropyrimidines into 2-substituted 4-methyl-s-triazines by treatment with potassium amide in ligand ammonia. *Res Trev Chim Pays Bas* **88** 204.