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NOTE

Synthesis and Fungicidal Activities of Some 4-Aryl-1-aroyl-5-cyano-3-methyl pyrazolo [4,5-b], 4,5,7-trihydropyridin-6-ones Derivatives

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A series of 4-aryl-1-aroyl-5-cyano-3-methyl pyrazolo [4,5-b], 4,5,7-trihydropyridin-6-ones have been prepared. The structures of compounds were confirmed by spectral data. Ten compounds were screened for their antifungal activity against two fungi *Rhizactonia solani* and *Penicillium citrinum* and were found to be fungicidal.

Key Words: Synthesis, Fungicidal, 4-Aryl-1-aroyl-5-cyano-3-methyl pyrazolo [4,5-b], 4,5,7-trihydropyridin-6-ones.

Compounds with a pyrazole ring in its structure have been reported to show fungicidal[1, 2] and herbicidal[3] activities. Similarly compounds incorporating a pyridine ring in their structure are reported to have various bioactivities[4–6]. Keeping these facts in mind it was planned to fuse a pyridine system with pyrazole ring to give planar compact novel heterocyclic compounds having polar groups like —CN, —C═O, —NH with better pesticidal activities. The present paper deals with the synthesis and fungicidal activities of 4-aryl-1-aroyl-5-cyano-3-methyl pyrazolo [4,5-b], 4,5,7-trihydropyridin-6-ones derivatives.

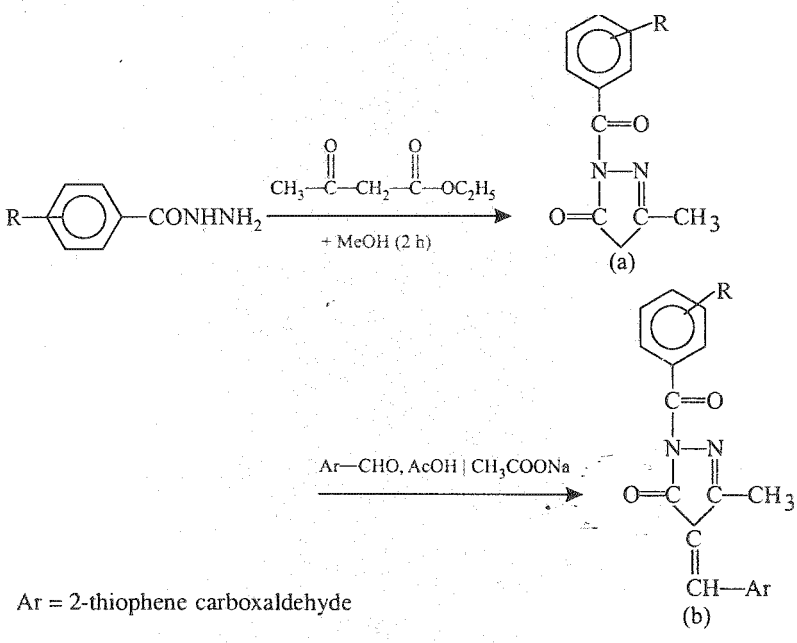
Substituted hydrazide is refluxed with ethyl aceto acetate in presence of methanol for 2 h to give compound **(a)**. These compounds were treated with araldehyde in presence of glacial acetic acid and fused sodium acetate to get compound **(B)**. Final compound 4-aryl-1-aroyl-5-cyano-3-methyl pyrazolo [4,5-b]-4,5,7-trihydropyridin-6-ones derivatives (C_{1-10}) were obtained by condensation of corresponding compound **(B)** with ethyl cyanoacetate and ammonium acetate in equimolar ratio **(Scheme-1)**.

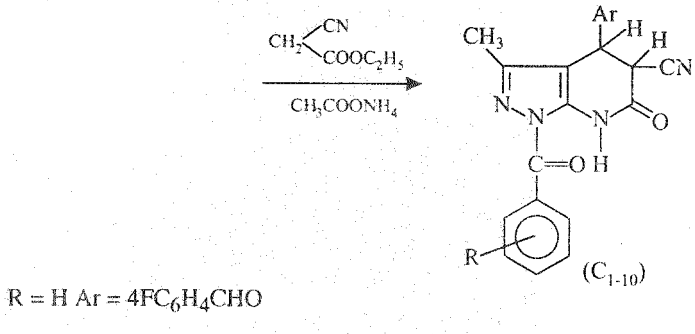
All melting points were taken in open capillary tubes and are uncorrected. IR spectra were recorded on Perkin-Elmer-710 spectrophotometer in nujol and PMR spectra on Perkin-Elmer R-32 at 90 MHz. The completion of the reaction and purity of the synthesised compounds were checked by TLC. The required hydrazines were prepared by known method.

The spectral data of one representative final compound **(C)** is given below:

IR (KBr) ν_{max}: Compound No. **(C)**; (R = H, Ar = 4-FC_4H_4CHO); 1285 ν(C═N), 1590, 1500 (aromatic ring); 1630 ν(C═N), 1690 and 1740 ν(C═O), 3290 ν(—NH). PMR (DMSO-d_6): Compound **(C)**: (R = H, Ar = 4-FC_4H_4CHO); δ 2.1 (S, 1H, —CH), 2.8 (S, 3H, CH_3), 7.4–8.7 (m, 11H, ArH), 8.7 (S, 1H, NH).

The other compounds thus prepared are given in Table-1 (C_{1-10}).





Scheme-1

TABLE-1

Comp. (C)	R	Ar
C_1	H	4-FC_4H_4CHO
C_2	4-Cl	4-FC_4H_4CHO
C_3	2-Cl	4-FC_4H_4CHO
C_4	3-CH_3	4-FC_4H_4CHO
C_5	2,4-Cl_2	4-FC_4H_4CHO
C_6	H	2-thiophenecarboxaldehyde
C_7	4-Cl	2-thiophenecarboxaldehyde
C_8	2-Cl	2-thiophenecarboxaldehyde
C_9	3-CH_3	2-thiophenecarboxaldehyde
C_{10}	2,4-Cl_2	2-thiophenecarboxaldehyde

The compounds have been screened for their fungicidal activity by agar growth technique[7] against two fungi, *viz.*, *Rhizactonia solani* and *Penicillium citrinum*.

The fungus was planted in agar growth media mixed with test compounds. The diameter of the fungus colony was measured at three different concentrations, *viz.*, 1000, 100 and 10 ppm. The inhibition of the fungus growth was determined as the difference in growth between the control plate and those treated with the test compound. The activity of the test compounds was compared with commercial fungicide carbendazim under similar conditions. The percentage inhibition was calculated as:

$$\text{Percentage inhibition} = \{(C - T)/C\} \times 100$$

C = diameter of fungus colony (in mm) in the control plate after 96 h,
T = diameter of fungus colony (in mm) in the treated plate after 96 h.

They were, however, slightly more fungicidal against *Rhizactoria solani* and *Penicillium citrinum*. IR and ^{1}H NMR spectra strongly supported the structure of final compounds (C_{1-10}). The results show that all compounds under investigation were fairly toxic against both the fungi at 1000 ppm. A careful study of their antifungal activity shows that their fungicidal activities sharply decrease on dilution (from 1000–100 ppm). In all compounds C_2 and C_5 have remarkable fungicidal activity even at 10 ppm. By considering the structure and bioactivity of these compounds it may be concluded that the presence of chlorine atom at position 4 contributes more to the fungicidal activity. The compound having a polar group like —CN, C=O, —NH attached to heterocyclic system[8] is expected to display strong pesticidal power.

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