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Synthesis and fungitoxicity of some new 1,2,4-triazolo -1,3,4-thiadiazolo-s-triazine derivatives

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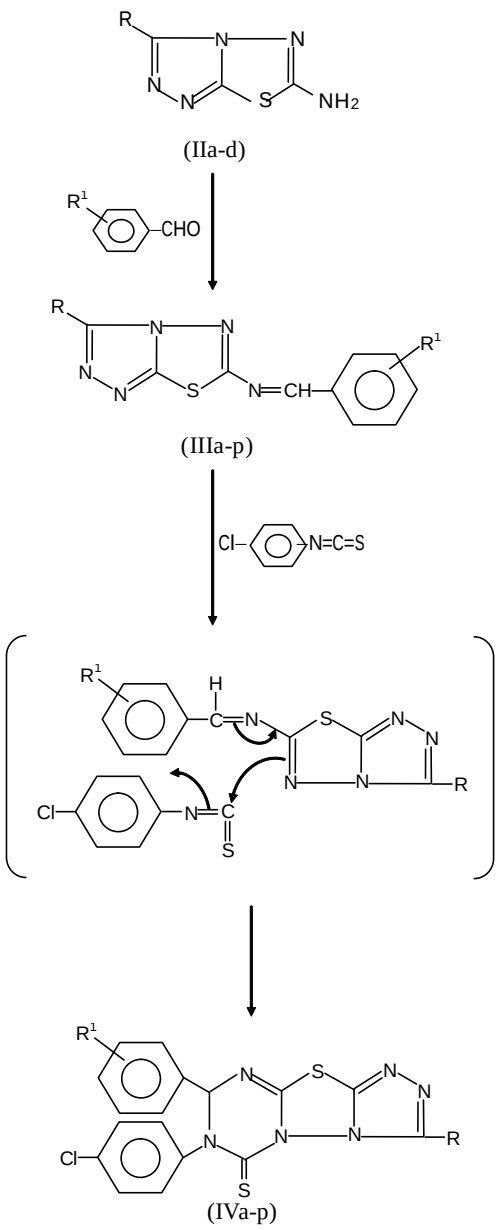
Abstract

3-Aryl-4-amino-5-mercapto-s-triazoles (I) were synthesized by the method of Reid & Heindel[1]. These were treated with cyanogen bromide in ethanol which on refluxing on a water bath (6 hrs) was neutralized with saturated aqueous solution of K_2CO_3 to give 6-amino-3-aryl-s-traizolo-[3,4-b]-1,3,4-thiadiazoles (II*a-d*), which were further treated with aromatic aldehydes to gives 6-arylidene-amino-3-aryl-s-triazolo-[3,4-b]-1,3,4-thiadi- azoles (III*a-p*) is treated with p-chlorophenylisothiocyanate to give 3,4,6-triaryl-1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazolo-[3,2-a]-1,3,5-triazine-5-thione (IV*a-p*). Fungitoxicity of the prepared compounds have been compared with Dithane M-45 a commercial fungicide, for their fungitoxic action against *Puccinia recondita* and *Ustilagonuda var. maydis* and the screening results have been correlated with the structural features of the prepared compounds.

Introduction

Recently some 1,3,4-thiadiazole derivatives were reported to possess fungicidal[2-4], herbicidal[5], bactericidal activity[6,7]. Similarly 1,3,5-traizines were also reported as potential fungicdes[8,9]. In continuation of our work[10] on fungitoxic, condensed heterocycles, in the present investigation we have fused 1,3,4-thiadiazole nucleus with 1,3,5-triazine ring to prove how far this combination could enhance the fungitoxicity. The reaction sequence leading to the formation of the title compounds have been out lined in the Scheme-I.

3-Aryl-4-amino-5-mercapto-5-triazoles (I) were prepared by the method of Reid and Heindel[1]. 6-Amino-3-aryl-s-triazolo-[3,4-b]-1,3,4-thiadiazoles (II) were synthesized by treating (I) with cyanogen bromide in ethanol followed by neutralization with saturated aqueous solution of K_2CO_3. These triazolo-thiadiazoles on treating with aromatic aldehydes in absolute ethanol on refluxing and recrystallisation gave 6-(arylidene) amino-3-aryl-s-triazolo-[3,4-b]-1,3,4-thiadiazoles (III). These Schiff's bases on treating with p-chloro-phenylisothiocyanate gave 3,4,6-triaryl-1,2,4-traizolo-[3,4-b]- 1,3,4-thiadiazolo [3,2-a]1,3,5-triazine-5-thione (IV).



R : IVa,e,i,m=-C_6H_5; b,f,j,n=4-ClC_6H_4; c,g,k,o=4-$CH_3C_6H_4$, d,l,h,p=4-$CH_3OC_6H_4$

R^1 : IVa-d=-H; e-h=-pCl; i-l=-pCH_3, m-p=-$pOCH_3$

Scheme-I

Fungicidal activity :

The fungicidal screening of the compounds (IV*a-p*) were evaluated against *Puccinia Recondita* and *Ustilagonuda var. maydis* by the usual Agar plate Technique[11] at 1000, 100 and 10 ppm conc. Dithane M-45 a commercial fungicide was also tested under similar conditions for comparing the screening results. The antifungal activity displayed by the tested compounds (IV*a-p*) significantly inhibited the mycelial growth of both tested fungi at 1000 ppm but their activity decreased markedly at lower conc. (100 & 10 ppm) compound IV*f*, IV*h*, IV*l* are more active and shows fungitoxicity of the order of Dithane M-45 at 1000 ppm concentration and also inhibited the growth of both the fungal species from 41-46% even at 10 ppm concentration. The compounds (IV*a-p*) are more potent than their precursors 6-arylidine-amino-3-aryl-s-traizolo-[3,4-b]-1,3,4-thiadiazoles due to the compact size and planarity of the molecule. Introduction of chloro group and methoxy group in the phenyl moiety of these compound increases the fungicidal activity & in fact the chloro group is more effective methoxy group.

Experimental

Melting points were determined in open glass capillaries and are incorrect. Infrared spectra in KBr were recorded either on Perkin-Elmer-157 or Hitachi-295 IR spectrometer. ^{1}HNMR spectra were recorded on a EM-360L (60 MHz) NMR spectrometer in $CDCl_3$ and DMSO-d_6 with TMS as internal reference. Chemical shifts are expressed in δ ppm.

Table 1. Characterization data of synthesis of 3,4,6-triaryl-1,2,4-triazolo [3,4-b]-1,3,4-thiadiazolo [3,2-a]-1,3,5-triazine -5-thione (IV*a-p*)

Compd. No.	Ar group	R group	Yield (%)	M.P. (^{0}C)
IV*a*[*]	C_6H_5	H	77	203
b	4-ClC_6H_4	H	75	198
c	4-$CH_3C_6H_4$	H	73	206
d	4-$CH_3OC_6H_4$	H	71	210
e	C_6H_5	p-Cl	72	201
f	4-ClC_6H_4	p-Cl	74	196
g	4-$CH_3C_6H_4$	p-Cl	71	208
h	4-$CH_3OC_6H_4$	p-Cl	73	209
i[**]	C_6H_5	p-CH_3	72	201
j	4-ClC_6H_4	p-CH_3	70	200
k	4-$CH_3C_6H_4$	p-CH_3	71	205
l	4-$CH_3OC_6H_4$	p-CH_3	82	209
m	C_6H_5	p-OCH_3	76	205
n	4-ClC_6H_4	p-OCH_3	77	203
o	4-$CH_3C_6H_4$	p-OCH_3	74	207
p	4-$CH_3OC_6H_4$	p-OCH_3	71	208

* IR (KBr) : 1620 (cyclic >C=N); 1665 (exocyclic >C=N), 1374 (C–S–C) cm^{-1}
^{1}HNMR (DMSO-d_3) δ : 3.8 (3H, S, –OCH_3); 7.3-8.1 (13H, m, Ar-H)

** IR (KBr) : 1618 (cyclic >C=N); 1670 (exocyclic >C=N), 1378 (C–S–C) cm^{-1}
^{1}HNMR (DMSO-d_3) δ : 2.4 (3H, S, –OCH_3); 7.3-8.0 (13H, m, Ar-H)

Synthesis of 3,4,6-triaryl-1,2,4-triazolo [3,4-b]-1,3,4-thiadiazolo [3,2-a]-1,3,5-triazine -5-thione (IVa-p) :

A mixture of 6-(arylidene) amino-3-aryl-s-triazolo [3,4-b]-1,3,4-thiadiazoles (IIIa-p) (0.01 mol) and p-chlorophenylisothio cyanate (0.01 mol) was refluxed in dry toluene for 6 hours and the solvent was distilled off under reduced pressure. The residue thus obtained was washed with small amount of ethanol followed by water and the product was recrystallized from ethanol.

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