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Synthesis and study of some new 3-arylidene indolo [2, 3-b] oxazin-2-ones as potential fungicides

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Abstract

3-substituted indolo [2,3-b] oxazin-2-ones (2) have been prepared by refluxing 2-indolone-3-yl –imino alkanoic acid (1) with fused sodium acetate in acetic anhydride . The compounds prepared were screened for their fungicidal activity against *Pyricularia oryzae. Puccinia graminis, Alternaria solani* and *Phytopthora infestans.*

Introduction

Indoles itself have been found to possess a variety of biological activities such as fungicidal[1], bactericidal[2], antiviral[3], herbicidal[4] and pesticidal[5,6] activities.

Oxazinone ring is reported to have associated with antibacterial[7], herbicidal[8] and fungicidal[9] activities. Arylidene system shows various biological activities[10,11] as reported in the literature.

In the present investigation the effort has been made to synthesize heterocyclic compounds in which indole ring is fused with oxazinone ring and arylidene system. Compounds thus formed were screened for fungicidal activity against *Pyricularia oryzae, Puccina graminis, Alternaria solani* and *Phytopthora infestans*.

Experimental

Melting points of all synthesized compounds were determined in open capillary and uncorrected.IR spectra were recorded on Perkin -Elmer Spectrophoto meter in KBr disc (υ_{max} in cm^{-1}). ^{1}HMR spectra were recorded on Varian EM360 spectrometer with TMS as internal standard using DMSO d_6(chemical shift in δ, ppm) Purity of the compounds were checked by TLC on Silica gel –G plates with layer thickness of 0.3 mm. All compounds gave satisfactory C, H, N and S elemental analysis.

Synthesis of 2-[indolone-3-yl –imino] alkanoic acid (1):

It was prepared by well known method[12]. A mixture of isatin (0.1M), glycin (0.1M) and

sodium hydroxide (0.1M) were refluxed in methanol for 4 hours. The solvent was removed and water is poured into the residue to precipitate the desired product which was washed with water dried and recrystallised from ethanol.m.p.180-182^{0}C ; yield 72 %: Significant bands :IR(KBr cm^{-1}) 3475 (NH-Stretching); 3208 (OH-Stretching);1750,1720(>C=O-Stretching);1650 (>C=N -Stretching); 1548, 1518, 1508 (Aromatic ring stretching).Other compounds thus prepared are recorded in Table (1).

Synthesis of 3-arylidene indolo [2,3-b] oxazin-2-ones (2) :

It was prepared by refluxing 2-[indolone-3-yl –imino] alkanoic acid (1) (0.015M) with fused sodium acetate (0.02M) in acetic anhydride for 30 minutes. The solvent was removed and water is poured into the residue to precipitate the desired product which was washed with water dried and recrystallised from ethanol. m.p. 123^{0}C; yield (50%). Significant bands :IR(KBr cm^{-1}):1745 (>C=O-Stretching); 1620 (>C=N-Stretching); 1545,1508,1498(Aromatic ring stretching); 1288 (C-O-C Stretching); 1097 (C-N-C Stretching): ^{1}HNMR data (DMSO- d_6)δ: 3.3 (s,2H,-NHCH_2CO);6.4-7.6(m,4H,Ar-H). Other compounds thus prepared are recorded in Table (1). The synthesis of these compounds has been given in scheme-I.

SCHEME-I

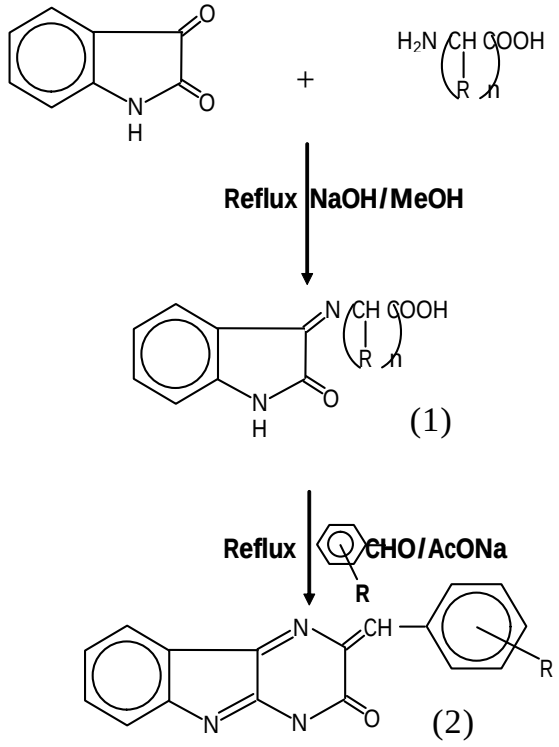

Table 1

S. No.	R	m.p. (^{0}C)	Yield (%)	Molecular Formula	Analysis			
					Carbon (%)		Hydrogen (%)	
					Found	Calc.	Found	Calc.
2a	2-CH_3	128	54	$C_{18}H_{12}O_2N_2$	75.39	75.00	2.98	3.45
2b	3-CH_3	164	62	$C_{18}H_{12}O_2N_2$	74.88	75.00	3.98	3.45
2c	4-CH_3	149	69	$C_{18}H_{12}O_2N_2$	74.32	75.00	3.11	3.45
2d	2-Cl	138	61	$C_{17}H_9O_2N_2Cl$	65.98	66.13	3.12	2.92
2e	4-Cl	154	69	$C_{17}H_9O_2N_2Cl$	66.78	66.13	2.38	2.92
2f	4-OCH_3	143	71	$C_{18}H_{12}O_3N_2$	70.69	71.05	3.59	3.95
2g	3-NO_2	133	62	$C_{17}H_9O_4N_3$	63.39	63.34	2.54	2.82
2h	4-OH	151	63	$C_{17}H_{10}O_2N_2$	70.09	70.34	3.11	3.45
2i	2,4-$(OCH_3)_2$	140	74	$C_{19}H_{14}O_4N_2$	68.01	68.26	4.89	4.19
2j	2,4-$(CH_3)_2$	161	61	$C_{19}H_{14}O_2N_2$	76.11	75.49	4.13	4.64

Evaluation of fungicidal activity:

The anti fungal activity was evaluated by agar plate technique[11] against *Pyricularia oryzae. Puccina graminis, Alternaria solani* and *Phytopthora infestans*. At concentrations 1000 ppm, 100 ppm and 10 ppm. The number of replications in each case was three. On the basis of growth recorded on 7th day of incubation the fungicidal activity of test compounds was calculated in terms of present inhibition of mycelial growth using the following formula.

$$\text{Present inhibition of mycelial growth} = \frac{dc - dt}{dc} \times 100$$

where dc = Average diameter growth of the colony in control sets on 7th day of incubation.

dt = Average diameter growth of the colony in treatment set on 7th day of incubation.

Diameter growth = apparent diameter of the colony-diameter of colony of the inoculums

The percentage inhibitions of various compounds are recorded in table -2

Table 2.

S.No.	Average % inhibition after 7 days											
	Pyricularia oryzae			*Puccinia graminis*			*Alternaria solani*			*Phytophthora infestans*		
	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
2a	62	45	26	63	46	27	64	47	28	65	48	29
2b	64	47	27	65	48	28	65	47	28	66	49	30
2c	68	49	29	69	50	29	69	51	29	67	48	27
2d	72	51	31	73	52	32	71	50	30	78	54	35
2e	74	52	32	75	53	33	74	51	31	76	54	34
2f	73	52	31	72	50	30	73	52	31	75	52	32
2g	66	48	28	67	46	26	66	46	26	69	47	29
2h	82	58	35	81	60	36	82	61	37	86	61	37
2i	80	56	32	79	65	31	80	56	32	82	57	31
2j	81	53	32	80	54	33	80	53	32	84	54	33
Carbendazim	100	78	54	100	79	55	100	78	54	100	78	55

Results and discussion

It is evident from the activity data that the all of the tested compounds have significant fungitoxicity at 1000 ppm against all the fungi but their toxicity decreased considerably at lower concentration, although compounds having serial number 2d, 2e, 2f, 2g, 2h, 2i and 2j show greater fungitoxicity against all the organisms but the result are not very spectacular except for compounds 2h, 2i and 2j.Compounds 2h and 2j found most active (>84 %) at 100 ppm. Their activity decreases with dilution.

It is also evident from the fungicidal screening data that these compounds are more active on *P. infestans* in comparison to other test fungi. It is also observed from the result that introduction of polar substituents like -NH2 group enhances the fungicidal activity.

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