© 2023, Centre for Advanced Research in Agricultural Sciences
Research Journal of Agricultural Sciences
Volume 14; Issue 01; pp 080–082

Open Access
ISSN: 0976-1675 (P)
ISSN: 2249-4538 (E)

Short Communication

Fungicidal Activities of Synthesized 2-Aryl-5,6-dihydro-5-thioxoimidazo-[2,1-b]-1,3,4-thiadiazol-6-ones derivatives

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***Key words*:** Arylimino, Thiadiazole, Fungicidal, Imidazole

There are so many biotic factors like pest, micro-organism and weeds are responsible for huge loss of agricultural and industrial economy. The disastrous effect of the fungi and herbs on the economy as well as on human and animal health is not being overemphasized. As a matter of fact, the biological factors which include bacteria, fungi, insects, weeds and rodents are responsible for the loss of 1/3rd of world harvest. So, they are great enemies to mankind. The 1,3,4 – thiadiazole nucleus isolated [1-2] or fused with other ring [3-8] is associated with fungicidal activities. Likewise various imidazole derivative are well known fungicides. In addition, many other imidazole derivatives have been reported [9-12] as potential fungicides. In view of above facts and the observation of Horifall and Rich [13] that the combination of C=0 and C=S function in molecule some time works better than eihter alone. In view of this fact the title compounds have been synthesized with the hope that the fusion of bio labile 1,3,4- thiadiazole and imidazole nuclei might result in fungicides of enhanced potency.

The melting points were recorded in open capillaries, may be uncorrected. The ^{1}HNMR spectra in DMSO- d_6 were obtained using TMS as internal references, while the IR spectra in KBr were obtained (cm^{-1}).

2-Aryl -5,6 – dihydro -5 –thioxoimidazo- [2,1-b] – 1,3,4 – thiadiazol-6-ones

2-Amino -5-phenyl – 1,3,4 – thiadiazole

This was prepared by the method of Kokovina *et al*. [14] by the reaction of thiosemicarbazide with carboxylic acid in presence of PPE (Poly phosphate ester). In this reaction no less than 20 g of PPE used for each 5 mmol of the carboxylic acid. To a hot solution of 5 mmol carboxylic acid in a mixture of PPE, chlorofrom and 5 mmol of thiosemicarbazide was added, the reaction mixture was refluxed for 10 hour then added 15ml of distilled water to the mixture and residue of PPE was neutralized by sodium carbonate.

2-Phenyl -5- phenylimino-5,6- dihydroimidazol-[2,1-b]- 1,3,4-thiadiazol -6- ones

A solution of trichloroacetyl chloride (0-01m) in dioxane (20ml) was added over 15 min to a stirred suspension of 2-Amino-5-phenyl-1,3,4- thiadiazole (0.01M) in dioxan (80ml). After completion the reaction mixture was refluxed for 1 hr. Then cooled to the room temperature.

Next a solution of triethylamine (0.03m) and primary phenyl amine (0.01m) in dioxan (15ml) was added with stirring and refluxing the mixture for 15 hrs. It was cooled and poured into water to yield the desired product which was crystallized from ethanol.

2-Aryl-5,6-dihydro-5-thioxoimidazol-[2,1-b]-1,3,4-thiadiazol-6-ones

This was prepared by refluxing 2- phenyl-5-phenyl imino-5,6 – dihydroimidazol-[2,1-b]-1,3,4-thiadiazol-6–ones (0.05m) with sulphur (0.05m) in CS_2 for about 20 hrs. and finally poured into water. The product thus obtained was crystallised from ethanol. The characterization data, m.p, yield is recorded in (Table 1) while the spectral data of compound 4 e recorded in (Table 1).

Fungicidal screenings

Using standard dithane M-45, a commercial fungicide, the fungicidal activity were assessed against two fungal species i.e. *Collectotrichum falcatum* and *Fusarium oxysporum* by standard agar-plate methods at 1000, 100 and 10 ppm concentrations. There were three replications in each case. The diameter of the fungal growth zone was determined after 96 hours.

By comparing the results to growth under control, the findings were reported as a percentage growth inhibition.

Thus, percentage inhibition = (C-T)/100

Where C = Diameter (in mm) of the fungal colony in control plate

T = Diameter (in mm) of the fungal Colony in treated plate

Received: 23 Oct 2022; Revised accepted: 25 Dec 2022; Published online: 11 Jan 2023

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Citation: Srivastava AK, Sharma SS, Tiwari B, Kumar A. 2023. Fungicidal activities of synthesized 2-Aryl-5,6-dihydro-5-thioxoimidazo-[2,1-b]-1,3,4-thiadiazol-6-ones derivatives. *Res. Jr. Agril Sci*. 14(1): 80-82.

According to the fungicidal results given in (Table 2), all of the tested substances shown strong to moderated activity. It is interesting to note from antifungal data that all of the tested compound [4a-e] exhibit strong antifungal activity against both fungal species i.e., *Collectotrichum falcatum* and *Fusarium oxysporum* at 1000 ppm, while their activity diminished at lower doses, i.e., 100 ppm and 10 ppm. It is significant to note that antifungal activities of title compound were enhanced by the addition of more electronegative oxophores. These substances disrupt the fungal cell wall which affect the metabolic processes of the fungi.

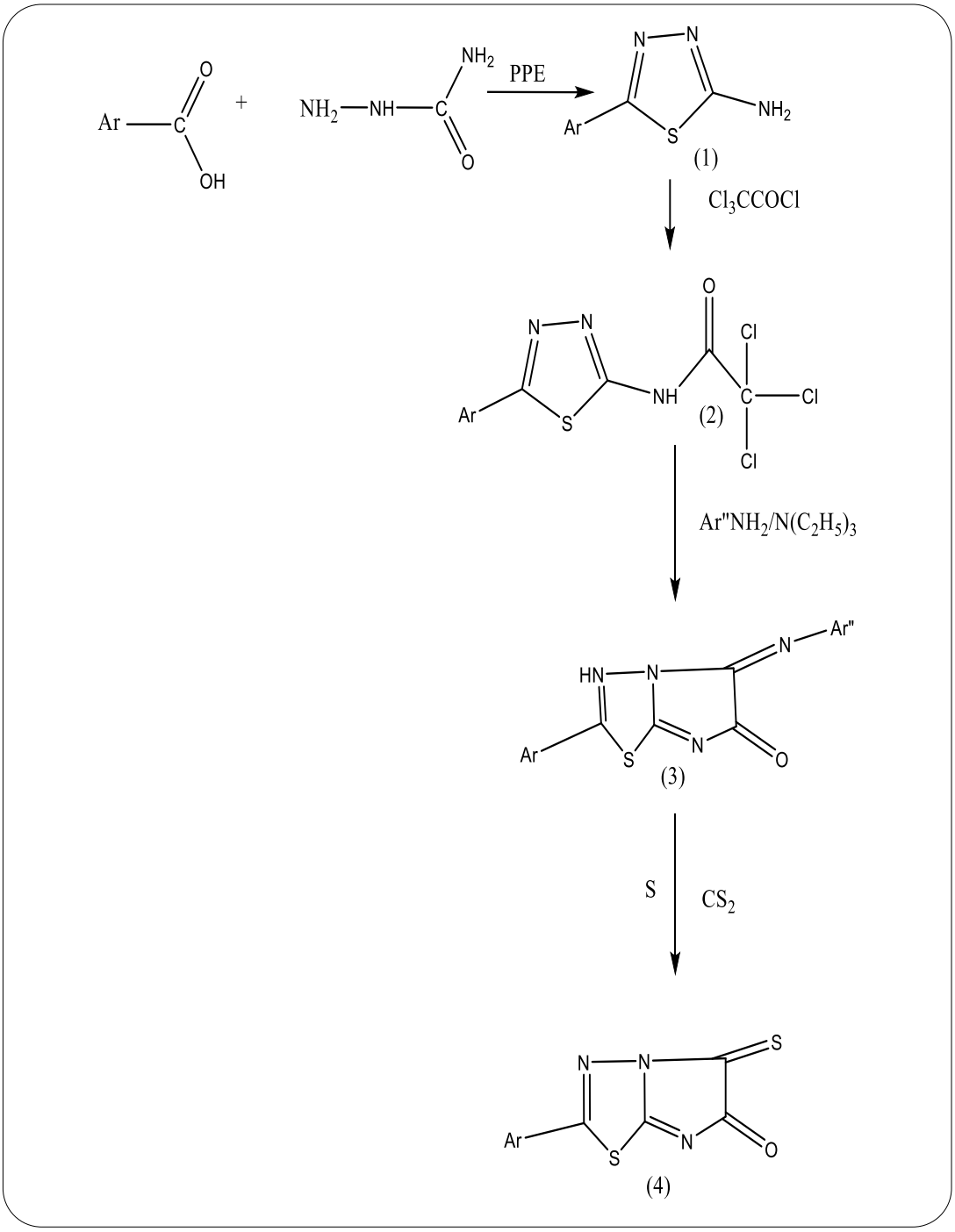

Table 1 Physical and spectral data of the title compounds

Compound	Ar	Yield (%)	M.P.	C Experimental (Calculated)	H Experimental (Calculated)	N Experimental (Calculated)
4a	C_6H_5	66	160	47.05 (48.57)	1.83 (2.04)	16.73 (16.99)
4b	2-ClC_6H_4	63	179	41.57 (42.63)	0.85 (1.43)	13.43 (14.92)
4c	2,4- $Cl_2C_6H_3$	61	183	36.57 (37.99)	0.87 (0.96)	13.12 (13.29)
4d	2-NO_2 C_6H_4	69	185	40.80 (41.09)	1.26 (1.38)	19.01 (19.17)
4e*	2-CH_3 C_6H_4	67	168	49.11 (50.56)	2.13 (2.70)	15.91 (16.08)

*IR(KBr): 1725(exocyclic C=O),1620(Endocyclic C=N),1088(Exocyclic C=S), cm^{-1}
1HNMR(DMSO-d_6);2.40(s,3H,CH_3),7.38-7.81(m,4H, ArH)

In this communication the title compounds (4a-e) were synthesized as mention in scheme 1 with a yield of 61-69%. The compounds [4a-e] were identified using elemental analysis and one compound 4e by IR and ^{1}H NMR spectral data.

The five such compounds [4a-e] have been evaluated for their antifungal activity. From the screening data in (Table 2), it is clear that most of the compounds showed significant antifungal activities at 1000ppm concentration against two fungal species i.e., *Collectotrichon falcatum* and *Fussarium oxysporum*.

On the basis of the fungi toxicity data in (Table 2) which indicate both C=O and C=S together are more effective. The compound having Cl or NO_2 group are more active.

Table 2 Fungicidal screening data of 2-Aryl-5,6-dihydro-5-thioxoimidazo-[2,1-b]-1,3,4-thiadiazol-6-ones (4a-e)

Compound No.	Average % inhibition against					
	Collectotrichon falcatum			*Fussarium oxysporum*		
	1OOO ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
4a	61	30	20	61	29	15
4b	76	57	52	74	53	49
4c	91	78	61	84	72	59
4d	81	56	39	80	52	41
4e	64	35	24	63	37	23
Dithane M-45	100	86	70	100	85	66

SUMMARY

The title compounds 2- Aryl-5,6-dihydro-5-thioxoimidazo - [2,1-b] – 1,3,4- thiadiazol -6-one [4] were prepared by refluxing 2-aryl-5-arylimino-5,6-dihydroimidazol-[2,1-b] -1,3,4-thiadiazol -6 one[3] with sulphur in CS_2 for about 20 hours. 2-Aryl-5-arylimino-5,6-dihydroimidazo-[2,1-b]-1,3,4-thiadiazol-6-one [3] were synthesized by the reaction of trichloroacetyl chloride and 2- amino -5- aryl -1,3,4 thiadiazole in dioxane followed by the treatment of the solution of tri ethylamine and primary phenyl amine in dioxane. The reaction mixture was refluxed for 15 hours. 2-Amino-5-aryl- 1,3,4-thiazole were prepared by the reaction of thiosemicarbazide with carboxylic acid in the presence of PPE (polyphosphate ester). All the title compound have been tested in vitro for their fungicidal activities against two fungal species *Colletotrichum falcatum and Fusarium oxysporum*. All the title compounds were characterized by elemental analysis and one compound by IR and 1H-NMR spectral data.

LITERATURE CITED

1. Newman H, Tomcufric SA. 1971. Synthesis of 6,6'-diethynyldiphenic anhydride. *American Cyanamid CO.U.S3, 502,284,*(1971). *Chemical Abstracts* 75: 20413.
2. Dine, Shams, Sh. AE, Hazaa AAB. 1974. *Pharmazie* 29(12): 761. *Chemical Abstracts* 82: 52647.
3. Patel HV, Fernandes PS, Yyas KA. 1990. *Ind. Jr. Chem*. 29(B): 135-141.
4. Yadav LDS, Mishra AR, Singh H. 1989. *Pesticide Science* 25: 219-225.
5. Singh S, Yadav LDS, Singh H. 1981. Synthesis and antifungal activity of some 1,3,4-thiadiazolo[3,2-a]-S-triazine-7-thiones and*N*-acyl-*N*-(5-araylkyl/aryl)-1,3,4-thiadiazol-2-yl)thiourease. *Ind. Jr. Chem*. 20B: 518.
6. Srivastava AK, Khare RK, Singh BK, Singh H. 2007. Synthesis and fungicidal activity of some 2,6-diaryl-1,3,4-thiadiazolo [3,2-b]-s-triazine-5,7-dithiones. *Ind. Jr. of Het. Chem.* 17: 109-112
7. Yadav LDS, Mishra AR, Singh H. 1988. *Jr. Agri. Food Chemistry* 36: 828-83.
8. Giri SA, Singh, Giri JPN. 1983. *Bokin Bobai*. 11(10): 575-578. *Chemical Abstracts* 100: 103294.
9. Jain K, Jain KK, Chadha VK, Handa RN. 1984. *Jr. Indian Chem. Society* 6(11/12): 1053.
10. Beard CC. 1977. *U.S. Pat*. 4(609): 164. *Chemical Abstracts* 86: 189943.
11. Beard CC. 1976. *U.S. Pat*. 3(946): 031. *Chemical Abstracts* 85: 21381.
12. Bread CC. 1976. *U.S. Pat*. 3(979): 404. *Chemical Abstracts* 86: 29815.
13. Horstall JG, Rich S. 1951. Cont. *Boyce Thompson Inst*. 16: 313. *Chemical Abstracts* 46: 11543.
14. Kokovina TS, Gadomsky SY, Terertive AA, Sanina NA. 2021. *Molecule MDPI* 2/6: 5159.