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Synthesis and Crop Protective Activities of Some Novel Derivatives of 3-substituted-1,2,4-triazolo [3,4-b][1,3,4] thiadiazoles

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Abstract

To discover new 1,3,4-thiadiazoles derivatives which may possess significant biological activities, we synthesized a series of novel 3-Substituted-1,2,4-triazolo[3,4-b][1,3,4] thiadiazoles. All the synthesized title compounds were characterized by elemental analysis, IR, ^{1}H-NMR. Crop protective activity tests showed that these compounds have remarkable effects on the growth of crop.

Keywords: 1,2,4–triazolo[3,4–b][1,3,4]thiadiazoles, crop production, NMR, thiosemicarbazide.

Introduction

The task of our days is to improve the state of nutrition, this can be achieved by a bundle of means. One important tool is the used of crop protectants to enhance the crop production. There are several records of the mass destruction of crops caused by weeds. It has been estimated that about 10% of the total world crop i.e. lost annually because of the weeds. This decrease in the total food output in the present context of the population growth will be a dangerous signal in many parts of the world[1,2]. In this struggle, chemical crop protectants especially organic chemicals, have played a very significant role. Spectacular success has been achieved in the area of agriculture by the use of organic herbicides of various type. The task of our days is to improve the state of nutrition, this can be achieved by a bundle of means. One important tool is the used of crop protectants to enhance the crop production. There are several records of the mass destruction of crops caused by weeds. It has been estimated that about 10%

of the total world crop i.e. lost annually because of the weeds. This decrease in the total food output in the present context of the population growth will be a dangerous signal in many parts of the world.

3-Substituted-1,2,4-triazolo[3,4-b][1,3,4] thiadiazoles activity[3-6] of which have been well stressed. Derivatives of 1, 2, 4-triazole are also well known for their use as agrochemicals[7].Derivatives of bisthiazolo-1,2,4-triazole has been reported as potential herbicide[8].We have now synthesized a series of 3-Substituted-1,2,4-triazolo[3,4-b][1,3,4] thiadiazoles then confirmed their structures by elemental analysis, IR and NMR, determined crop protective effects of all the title compounds.

Experimental

Materials and Methods

All the chemicals and solvents used were reagent grade. Thiosemicarbazide was Aldrich product.

Analytical Methods and Physical Measurements

Microanalysis of carbon, hydrogen and nitrogen were done at CDRI, Lucknow. Sulfur was estimated as barium sulfate. The standard technique of melting point determination using sulfuric acid bath. The IR spectra of the complexes were recorded in the region 4000-200 cm^{-1} in pressed KBr pellets medium on a Perkin-Elmer 621 and Beckmann Acculab-9 spectrophotometers. ^1H NMR (300.1 MHz) spectra were recorded on a Bruker spectrometer in DMSO-d_6 as a solvent using tetramethylsilane (Me_4Si) as internal standard. Chemical shifts (δ) are reported in ppm.

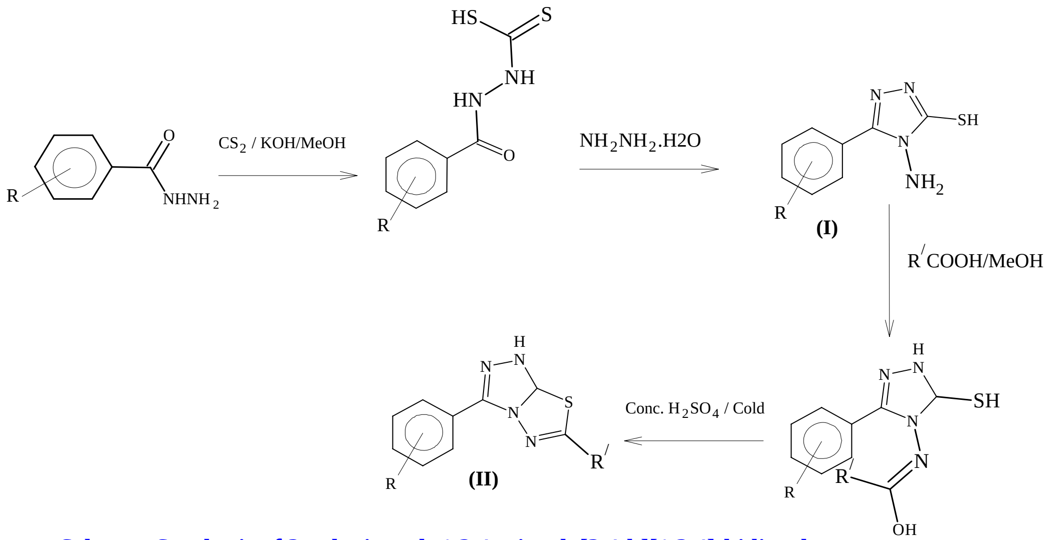
Preparation of 3-Substituted-1,2,4-triazolo[3,4-b][1,3,4] thiadiazoles.

i. 4-Amino-5-substituted phenyl-3-mercapto-1,2,4-triazoles: These compounds were prepared according to the method Hoggrrath et al. (compound I)

ii. 3-Aryl/aryloxy-1,2,4-triazolo[3,4–b] [1,3,4] thiadiazoles: 3-substituted aryl-5-mercapto-4(1-hydroxyalkane nitrite)-1,2,4-triazole (0.01 M) was added in small quantities with stirring in the conc. H_2SO_4 (A.R. 0.015 M) in cold water. After addition was completed the residue was left for 2 hours. In cold water was then added to this paste mass and neutralized by ammonia. (compound II)

Results and Discussion

The reaction proceeds according to the following equation:



Scheme: Synthesis of 3-substituted -1,2,4-triazolo[3,4-b][1,3,4]thidiazoles

IR Spectra: The C=C stretching vibration bands are observed at about 1460~1510 cm^{-1}. The presence of N-H and C=O absorption bands in the IR spectra also confirmed that the title compounds[9,10]. These bands appear at 1680~1720 cm^{-1} (C=O) and 320~3250 cm^{-1}(N-H)[11]. The stretching vibration bands of OH group are at 3220~3530 cm^{-1}. The characteristic stretching vibrations of the products are at 1600~1640 cm^{-1} (C=N), 740~750 cm^{-1}(C=Cl)[12]. The absorbance band of S-H stretching vibration (2500-2650 cm^{-1}) was observed[13].

^{1}H-NMR Spectra: In the ^{1}H-NMR spectra of triazolothiadiazines (I), the characteristic downfield signal at δ 8.70 ppm attributed to the -N=C-SH (-NH-C=S of the tautomer) in compound II is present, as is a sharp signal at δ 7.50 ppm attributable to the N-NH_2 group in the parent triazole[14]. In the spectra of the title compounds, the signal at δ 3.40~4.12 ppm is attributed to the CH_2 and OH. Resonance peaks at δ 7.20~8.12 ppm are attributed to the aromatic ring protons. In all the title compounds (II), additional resonances assigned to the –CH=N- (δ 9.25—10.10 ppm) were observed, which confirmed the condensation between the amino group and the carbonyl group[15]. A downfield signal appearing at δ 12.31-12.81 ppm is attributed to the -NH-C=S moiety whereas the chemical shifts (δ values) of the SH protons are at less than 4.0 ppm, in general[16]. The remaining protons resonated as multiplets in the aromatic region (δ 6.90-8.40 ppm). The triazole NH protons also showed downfield δ values (12 ppm or so)[17,18].

Crop Protective Activity: Al the samples were formulated as aqueous emulsion containing 6% of DMF and 0.3% of surfactant mixture. Each 15 mL of test solution was applied pre-emergently to the 1/1500 acre ppt. in which weed seeds listed as Digiteria Ciliaris(D.C.)-common grass, Chenopodium album(C.A.)-common pigweed and Nicotiana tabacum(N.T.)-tobacco. The treated pot which are kept in green-house were examined usually after three weeks[19]. The crop protectivity was evaluated by zero to five rating system. The pots were sprayed by 5.0 mL test solution. The crop protectivity data are given in table II.

Table I

R	R'	Molecular Formula	M.P. (^{o}C)	Yield(%)	Anal./% Found (calc.) C	H	N
H	2-OHC$_6$H$_4$	$C_{15}H_{12}N_4O_2S$	161	60	61.2 (61.1)	3.4 (3.3)	19.1 (19.0)
H	4-OCH$_3$C$_6$H$_4$	$C_{16}H_{14}N_4O_2S$	133	62	62.3 (62.2)	3.9 (3.8)	18.2 (18.1)
H	4-ClC$_6$H$_4$	$C_{15}H_{11}N_4OSCl$	171	59	57.6 (57.5)	2.9 (2.8)	17.9 (17.7)
H	OCH$_2$C$_6$H$_5$	$C_{17}H_{14}N_4O_2S$	180	68	62.3 (62.2)	3.9 (3.8)	18.2 (18.2)
H	4-ClOCH$_2$C$_6$H$_4$	$C_{16}H_{13}N_4O_2SCl$	174	63	56.1 (56.0)	3.2 (3.1)	16.4 (16.3)
4-CH$_3$	4-ClC$_6$H$_4$	$C_{16}H_{14}N_4OSCl$	176	60	58.8 (58.7)	3.4 (3.4)	17.2 (17.1)
4-CH$_3$	2,4-Cl$_2$C$_6$H$_3$	$C_{16}H_{13}N_4OSCl_2$	185	59	53.2 (53.1)	2.8 (2.7)	15.5 (15.4)
4-CH$_3$	OCH$_2$C$_6$H$_5$	$C_{17}H_{15}N_4O_2S$	145	65	63.4 (63.3)	4.4 (4.3)	17.4 (17.2)
4-CH$_3$	3-CH$_2$OCH$_2$C$_6$H$_4$	$C_{18}H_{18}N_4O_2S$	136	68	64.4 (64.3)	4.8 (4.7)	16.7 (16.6)
4-OCH$_3$	2-OHC$_6$H$_4$	$C_{16}H_{14}N_4O_3S$	168	65	59.3 (59.2)	3.7 (3.6)	17.3 (17.2)
4-OCH$_3$	4-ClC$_6$H$_4$	$C_{16}H_{13}N_4O_2SCl$	151	61	53.3 (53.2)	3.6 (3.5)	15.5 (15.4)
4-OCH$_3$	4-NO$_2$C$_6$H$_4$	$C_{16}H_{13}N_5O_4S$	173	60	51.8 (51.7)	3.1 (3.0)	19.8 (19.7)
4-OCH$_3$	4-OCH$_3$C$_6$H$_4$	$C_{17}H_{16}N_4O_3S$	185	61	60.4 (60.3)	4.1 (4.0)	16.6 (16.5)
4-OCH$_3$	4-ClOCH$_2$C$_6$H$_4$	$C_{17}H_{15}N_4O_3SCl$	147	69	54.8 (54.7)	3.5 (3.4)	15.0 (14.9)

Table II

	R	R′	Foliar Treatment				Soil Treatment		
			D.C.	C.A.	N.T.	Phytotoxicity	D.C.	C.A.	N.T.
1	H	2-OHC_6H_4	1	1	1		1	1	1
2	H	4-$OCH_3C_6H_4$	1	1	1		1	1	1
3	H	4-ClC_6H_4	4	3	3	4	3	3	3
4	H	$OCH_2C_6H_5$	1	1	1		1	1	1
5	H	4-$ClOCH_2C_6H_4$	1	1	1		1	1	1
6	4-CH_3	4-ClC_6H_4	2	2	2		2	2	2
7	4-CH_3	2,4-$Cl_2C_6H_3$	1	1	1		1	1	1
8	4-CH_3	$OCH_2C_6H_5$	3	2	1		2	2	2
9	4-CH_3	3-$CH_2OCH_2C_6H_4$	2	2	1		2	1	3
10	4-OCH_3	2-OHC_6H_4	1	1	1		1	1	1
11	4-OCH_3	4-ClC_6H_4	3	3	3	4	4	3	4
12	4-OCH_3	4-$NO_2C_6H_4$	3	3	3	4	2	3	3
13	4-OCH_3	4-$OCH_3C_6H_4$	4	5	4	5	5	4	4
14	4-OCH_3	4-$ClOCH_2C_6H_4$	4	5	5	1	5	5	5
		Standard 2,4-D	5	5	5		5	5	5

Rating	5	4	3	2	1
% Control	100	99-80	79-50	49-20	19-0

Conclusion

Fourteen compounds of this category were tested for crop protectivity activity by soil and foliar treatment. The data shows that only compound no. 3,11,12 and 13 have strong crop protectivity. These have 80-90% activity against *D. Ciliaris, E. Crusgalli* and *R. Sativas* infoliar treatment which is comparable with 2,4-D tested under similar condition but the chances to it as crop protectant is less because of its phytotoxic effect against rice plant which is about 70-80%. In soil treatment compound no. 3,11,12 and 13 show 80-90% activity against *D. Ciliaris, C. Album*

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