Ultra Chemistry Vol. 8(3), 442-446 (2012).

Synthesis and fungitoxicity of 5-aryl-4-thioaryl-1-sulpho-2,3,5-triazole

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(Acceptance Date 3rd December, 2012)

Abstract

4-Arylthiosemicarbazides (I*a-e*) were prepared by mixing appropriate aromatic amines (in NH_3) with CS_2, sodium chloroacetate followed by hydrazine hydrate. These 4-arylthiosemicarbazides was added in pyridine and thionyl chloride to prepare 5-aryl-4-mercapto-1-sulpho-2,3,5-triazoles (II*a-e*). These 5-aryl-4-mercapto-1-sulpho-2,3,5-triazoles were converted to their potassium salts and further treated with appropriate aryl halide to get 5-aryl-4-thioaryl-1-sulpho-2,3,5-triazoles (III*a-y*). Fungitoxicity of the prepared compounds have been compared with Dithane M-45 a commercial fungicide, for their fungitoxic action against *Puccinia recondita* and *Ustilagonude var. maydis* and the screening results have been correlated with the structural features of the prepared compounds.

Introduction

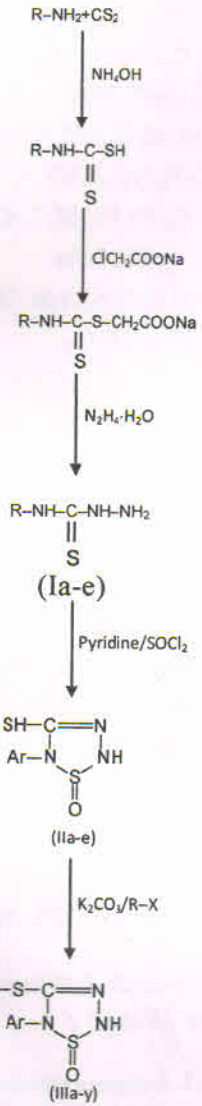
1,2,4-triazole ring is associated with various useful pesticidal activities. 3-Amino-1,2,4-triazole, commercially known as amitrole is a well known commercial herbicide[1]. 1,2,4-triazole derivatives have been patented as fungicides[2-4], herbicides[5-8] and insecticides[9-11].

Keeping the above observations in view, 5-aryl-4-thioaryl-1-sulpho-2,3,5-traizoles (III*a-y*) have been synthesized with the hope that the above compound will be pesticides of enhanced potency. Reviews clearly demonstrate that triazole ring is much associated with pesticidal activities and 2,3,5-triazole ring must be biologically active. The reaction sequence leading to the formation of title compound is antifungal activity given in the Scheme-I.

Antifungal activity :

The fungicidal activity of twenty five (III*a-y*) compounds of 5-aryl-4-thioaryl-1-sulpho-2,3,5-triazoles were evaluated against *Puccinia recondita* and *Ustilagonuda var. maydis* at 1000, 100 and 10 ppm concentrations. Dithane M-45 a standard commercial fungicide was also tested under similar condition for comparing the results.

Most of the compounds are fairly more active against *Puccina recondita* than that of *Ustilagonuda var. maydis* at higher concentration (1000 ppm) but their toxicity



R : IIIa-e = C_6H_5; f-j=4-ClC_6H_4; k-o = 2-methyl quinoline ($C_{10}H_{11}N$)

p-t = 4-methyl quinoline ($C_{11}H_{10}NO_2$),

u-y = Diethyl acetamide ($C_6H_{12}NO$)

Ar : IIIa,f,k,p,u = -C_6H_5; b,g,l,q,v = 2-ClC_6H_5, c,h,m,r,w = 4-ClC_6H_4, d,i,n,s,x = 4-$OCH_3C_6H_4$; e,j,o,y = -$C_{10}H_9$

Scheme-I

decreased considerably at lower concentration (100 and 10 ppm). The compounds III*g*, III*q* and III*v* had similar activity to mancozeb at 1000 ppm and showed 42-45% growth inhibition of both the test fungi at 10 ppm concentration.

Chloro group is more effective in increasing that fungitoxicity also varied with the fungal species but the difference was marginal.

Experimental

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

Synthesis of 4-arylthiosemicarbazide(Ia-e):

A mixture of ammonia solution (1.0 mol) and appropriate aromatic amines (1.0 mole) was placed in a flask. The mixture was cooled below 30^{0}C and Carbon disuphide (1.25 mol) was added gradually with constant stirring. Absolute ethanol (25 ml) was added to the reaction mixture and stirring continued till CS_2 had completely dissolved. After standing for two hours it was shaked with a solution of sodium chloroacetate (1.0 mol) followed by hydrazine hydrate (5 ml) 100%. The filtrate was concentrated to half its initial volume and allowed to stand. The solid obtained was separated, filtered, dried and recrystallized from ethanol.

The following synthesized compounds well agreed with the analytical data already reported in the literature.

I*a*. 4-Phenylthiosemicarbazide, m.p. 142^{0}C (reported 140^{0}C), yield 85% of theory.

I*b*. 4-(o-Chlorophenyl) thiosemicarbazide, m.p. 132^{0}C (reported 130^{0}C), yield 87% of theory.

I*c*. 4-(p-Chlorophenyl) thiosemicarbazide, m.p. 135^{0}C (reported 136^{0}C), yield 90% of theory.

I*d*. 4-(Methoxyphenyl) thiosemicarbazide, m.p. 138^{0}C, yield 89% of theory.

I*e*. 4-(1-Naphthyl) thiosemicarbazide, m.p. 140^{0}C (reported 139^{0}C), yield 87% of theory.

Synthesis of 5-aryl-4-mercapto-1-sulpho-2,3,5-triazoles (IIa-e) :

4-Arylthiosemicarbazide (0.01 mol) was added in pyridine (0.01 mol) and thionyl chloride (50 ml) in a rounded bottom flask and stirred at room temperature for 30 min and the refluxed on water bath for 2-3 hours.

The residue is poured into ice water and stirred. Yellowish product is obtained which is washed with $NaHCO_3$ solution till effervescence comes. It is then recrystallized from ethanol.

II*a* M.P. 124^{0}C, yield 75%
Found: C, 39.42; H, 3.28; N, 19.82; Molecular Formula $C_7H_7N_3OS_3$ Requires : C, 39.44; H, 3.29; N, 19.72%

II*b* M.P. 85^{0}C, yield 73%
Found: C, 33.91; H, 2.33; N, 16.81; Molecular Formula $C_7H_6N_3S_3ClO$
Requires : C, 33.94; H, 2.42; N, 16.97%

II*c* M.P. 90^{0}C, yield 76%
Found: C, 33.96; H, 2.37; N, 16.84; Molecular Formula $C_7H_6N_3S_2ClO$
Requires : C, 33.94; H, 2.42; N, 16.97%

II*d* M.P. 142^{0}C, yield 78%
Found: C, 65.35; H, 6.14; N, 28.53; Molecular Formula $C_8H_9N_3S_2O_2$
Requires : C, 65.31; H, 6.12; N, 28.57%

II*e* M.P. 153^{0}C, yield 73%
Found: C, 49.72; H, 4.18; N, 15.81; Molecular Formula $C_{11}H_{11}N_3S_2O$
Requires : C, 49.81; H, 4.15; N, 15.85%

II*a* IR (KBr):2655 (S–H), 1635 (cyclic >C=N), 1350 (–S=O) 3175 (N–H) cm^{-1}
^{1}HNMR ($CDCl_3$) δ: 3.2 (1H, s, S–H), 9.0 (1H, br, s, N–H), 7.2-7.8 (5H, m, Ar–H)

II*d* IR (KBr):2650 (S–H), 1630 (cyclic >C=N), 1350 (–S=O) 3180 (N–H) cm^{-1}
^{1}HNMR ($CDCl_3$) δ: 3.3 (1H, s, S–H), 9.1 (1H, br, s, N–H), 3.7 (3H, s, -OCH_3), 7.2-7.6 (4H, m, Ar–H)

Synthesis of 5-aryl-4-thioaryl-1-sulpho-2,3,5-traizoles (IIIa-y) :

5-Aryl-4-mercapto-1-sulpho-2,3,5-triazoles (0.01 mole) in 50 ml absolute ethanol was treated with excess amount of anhydrous potassium carbonate which furnished their potassium salts. These potassium salts are refluxed for 2-3 hours in DMF with appropriate aryl halide (0.01 mole) cooling the flask content were poured in crushed ice. Thus, obtained product was recrystallized from ethanol (Table-1).

Table-1. Characterization data of Synthesis of 5-aryl-4-thiaryl-1-sulpho-2,3,5-traizoles (III*a-y*)

Compd. No.	Ar group	R group	Yield (%)	M.P. (^{0}C)
III*a**	C_6H_5	C_6H_5	78	130
b	2-ClC_6H_4	C_6H_5	77	128
c	4-ClC_6H_4	C_6H_5	74	135
*d***	o-$CH_3C_6H_4$	C_6H_5	75	180
e	$C_{10}H_9$	C_6H_5	76	200
f	C_6H_5	4-ClC_6H_5	78	132
g	2-ClC_6H_4	4-ClC_6H_5	73	131
h	4-ClC_6H_4	4-ClC_6H_5	76	141
i	o-$CH_3C_6H_4$	4-ClC_6H_5	76	186
j	$C_{10}H_9$	4-ClC_6H_5	79	198
k	C_6H_5	$C_{10}H_{11}N$	74	135
l	2-ClC_6H_4	$C_{10}H_{11}N$	75	132
m	4-ClC_6H_4	$C_{10}H_{11}N$	76	138
n	o-$CH_3C_6H_4$	$C_{10}H_{11}N$	78	181
o	$C_{10}H_9$	$C_{10}H_{11}N$	78	202
p	C_6H_5	$C_{11}H_{10}NO_2$	79	140
q	2-ClC_6H_4	$C_{11}H_{10}NO_2$	72	137
r	4-ClC_6H_4	$C_{11}H_{10}NO_2$	73	142
s	o-$CH_3C_6H_4$	$C_{11}H_{10}NO_2$	77	183
t	$C_{10}H_9$	$C_{11}H_{10}NO_2$	79	197
u	C_6H_5	$C_6H_{12}NO$	71	131
v	2-ClC_6H_4	$C_6H_{12}NO$	72	136
w	4-ClC_6H_4	$C_6H_{12}NO$	75	144
x	o-$CH_3C_6H_4$	$C_6H_{12}NO$	74	183
y	$C_{10}H_9$	$C_6H_{12}NO$	73	201

* IR (KBr) : 1625 (cyclic >C=N), 1345 (–S=O), 3180 (N–H), 1380 (C–S–C) cm^{-1}
^{1}HNMR ($CDCl_3$) δ: 9.1 (1H, br-s, N–H), 7.0-8.0 (10H, m, Ar–H)

** IR (KBr) : 1650 (cyclic >C=N), 1355 (–S=O), 3175 (N–H), 1375 (C–S–C) cm^{-1}
^{1}HNMR ($CDCl_3$) δ: 9.2 (1H, br-s, N–H), 3.6 (3H, s, -OCH_3),
7.1-8.0 (9H, m, Ar–H)

Acknowledgement

The authors are thankful to the principal and Head of Department of Chemistry Shibli National Post Graduate College, Azamgarh (U.P.) for providing laboratory facilities and Director CDRI, Lucknow for recording IR and NMR spectra.

References

1. E.E. Deong, *Chemistry and uses of herbicides*, p 256, Reinhold publishing corporation, Newyork (1956).
2. El. Semary *et al.*, *Alexandrkia J. Pharma. Sci.* 1993, 7(2), 163-6; *Chem. Abstr.*; 1994, 121, 83189j.
3. Pees *et al.*, *PCT Int. Appl. Wo. 98,* 46608, *Chem. Abstr.*; 1998, 129, 302657.
4. Pees *et al.*, American Cyanamid Co. USA, 1999, 6297, 251, *Chem. Abstr.*; 2001, 135, 253253j.
5. Minaru *et al.*, *JPN Kokai Tokkyo Koho JP.* 09, 301, 973 (97, 301, 973); *Chem. Abstr.*; 1998, 128, 34781g.
6. Nizamuddin, Madhuri and Manoj, *J. Sci. Indi. Res.* 1999, 58(12), 1017-1020, *Chem. Abstr.*; 2000, 132, 19432y.
7. Schelterger, Layendecker, Eberhard and Siergfried, *PCT Int. Appl. WO* 1998, 0030, 450, 22pp; *Chem. Abstr.*; 2000, 133, 1743w.
8. Deihl, Robert, Trotto and Michael, *PCT. Int. Appl. WO.* 2000, 02, 06, 219, 42pp; *Chem. Abstr.*; 2002, 136, 114863h.
9. Godai *et al.*, *Indian J. Chem.*, Sect-B, 1990, *29B(2),* 176-7; *Chem. Abstr.*; 1990, 113, 40573x.
10. Nakayama *et al.*, *JPn. Kokai Tokkyo Koho JP* 61, 15, 886 (86, 15, 886); *Chem. Abstr.*; 1996, 104, 168477s.
11. Lockart *et al.*, *J. Heterocycles Chem.;* 1996, 33(3), 659-661; *Chem. Abstr.*; 1996, 125, 247740t.