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Synthesis and Pesticidal Activities of Some 3,5-Disubstituted Furothiazole-2-Thiones

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ABSTRACT

Several 3,5-disubstituted-furothiazole-2-thiones have been synthesised by the reaction of 3-substituted phenyl-2-thio-4-thiazolidinone with styrene oxide in the presence of tertiary amine in ethanol by refluxing 2-3-hours, and screened for their herbicidal activities against Echinochloa oryzicola, Echinochloa crus-galli, Oryza sativa, Glycine max and antifungal activities against Aspergillus niger, Pyricularia oryzae, whereas insecticidal activities against S. litura and T. urticeae of the title compounds.

Keywords: Disubstituted furothiazole, 2-thiones, thiazolidinone and pesticidal activity.

INTRODUCTION

Rhodanine is a five-membered heterocyclic ring with diverse applications particularly in biochemistry, medicinal chemistry, photochemistry, industry and coordination chemistry [1]. In a recent review, rhodanine was reported as privileged scaffold in drug discovery whose functionalization and appropriate modifications led to compounds endowed with various biological activities [2-8]. Guided by these observations and in continuation of our work on fused heterocyclic system, we synthesised the title compounds via the ring-opening of epoxide transformation cascades. The structure of these compounds was established by the IR, ^{1}HNMR spectral data and elemental analysis.

MATERIALS AND METHODS

Melting points were taken in open capillary tubes and are uncorrected. IR spectra were recorded in KBr on a Perkin-Elmer-881 spectrophotometer and ^{1}HNMR spectra on a Perkin Elmer R-32 spectrometer at 60 MHz. Procedure for one typical case for each step has been described.

3-(2-Methyl phenyl)-2-thio-4-thiazolidinone 1 (R = 2-CH_3): The required 3-(2-methylphenyl)-2-thio-4-thiazolidinone i.e. required rhodanines were prepared following the method of Sahoo et al [9] with some modification. A methanolic solution of 2-methyl aniline (24.4g, 0.2M) was treated with carbon disulphide (18.0 mL), and then ammonia solution (30.0 mL) was added below 10°C with constant stirring in ice bath. It was again stirred for three hours. The solid ammonium thiocarbazate was separated by filtration and

treated with equimolar solution of sodium chloroacetate in water, and again well stirred. Now acidified with dil. HCl and the solid mass obtained was separated out, dried and then treated with glacial acetic acid (25.0ml) by heating up to 15 min. The crystals obtained were filtered out, dried and recrystalized from ethanol. m.p. 105°C.

3,5-Disubstitued-furothiazole-2-thiones: 3,5-Disubstituted-furothiozole-2-thiones was prepared by the reaction of 3-substituted phenyl-2-thio-4-thiazolidinone (0.01M) with styrene oxide (0.01M) in the presence of tertiary amine (3.0ml) was refluxed in ethanol for 3h.

2a IR (KBr), 1250 (C-N), 1564, 1465, 1428, (aromatic ring), 1200 (C=S), 1100 (C-S-C) and 1060 cm^{-1} (C-O-C) ^{1}HNMR (DMSO-d_6); δ 7.8 (s,5H, Ar–H), δ 7.4 (s,5H,Ar–H), δ 3.5 (d, 2H, CH_2), δ 3.9 (1H, t).

2b IR (KBr), 1250 (C–N), 1560, 1462, 1426, (aromatic ring), 1199 (C =S), 1100 (C-S-C) and 1060 cm^{-1} (C-O-C) ^{1}HNMR (DMSO-d_6); δ 7.4 (s,5H, Ar–H), δ 3.5 (d,2H, CH_2), δ 3.9 (t, 1H), δ 2.4 (s 3H, CH_3), δ 6.8 (d, 1H), δ 6.8 (dd, 1H), δ 6.9 (dd, 1H), δ 6.5 (d, 1H).

2c IR (KBr), 1250 (C–N), 1560, 1461, 1422, (aromatic ring), 1200 (C =S), 1100 (C-S-C) and 1060 cm^{-1} (C-O-C). ^{1}HNMR (DMSO-d_6); δ 7.4 (s, 5H, Ar–H), δ 3.45(d, 2H, CH_2), δ 3.9(t, 1H), δ 2.3 (s 3H, CH_3), δ 6.8 (d, 1H), δ 6.4 (d, 1H).

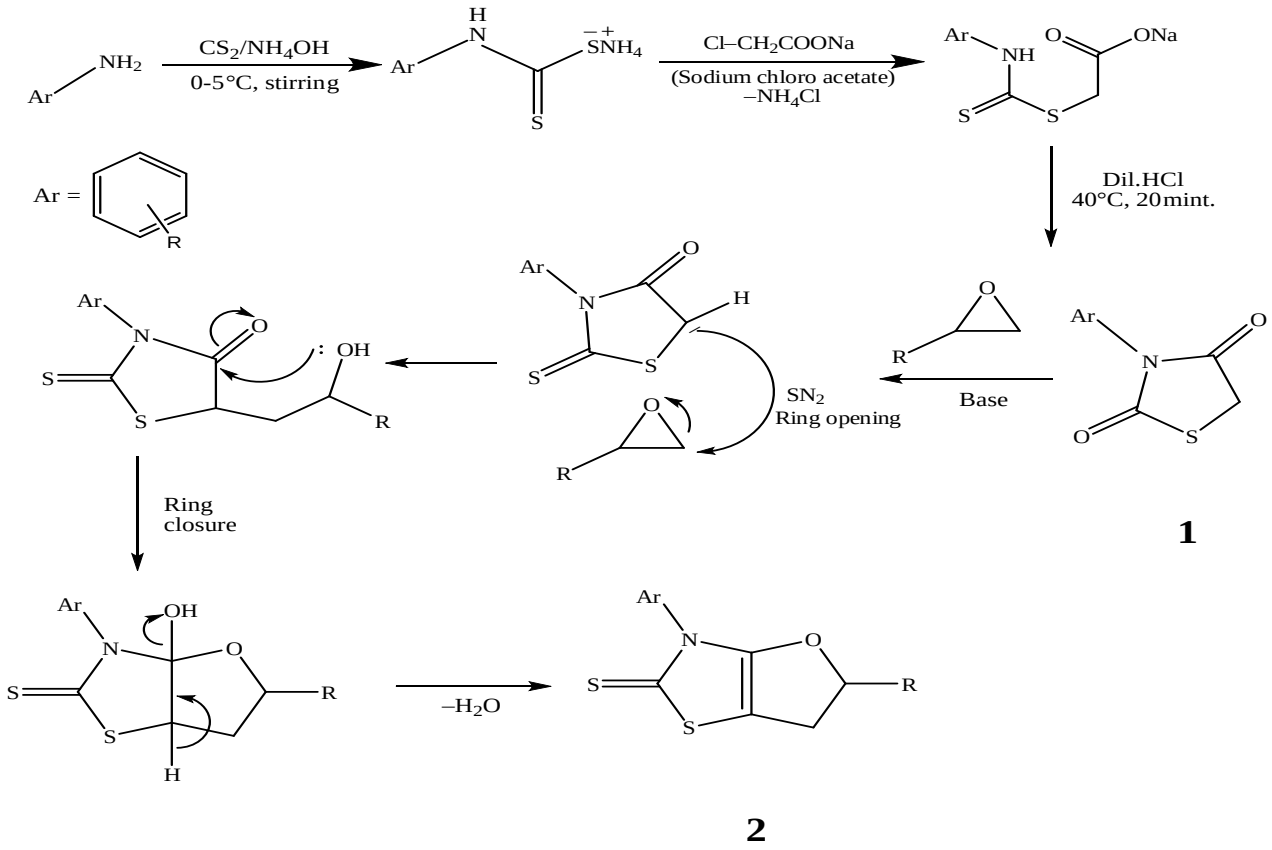
2d IR (KBr), 1250 (C–N), 1561, 1458, 1421, (aromatic ring), 1199 (C =S), 1100 (C-S-C) and 1065 cm^{-1} (C-O-C) ^{1}HNMR (DMSO-d_6); δ 7.4 (s, 5H, Ar–H), δ 3.50(d,2H, CH_2), δ 3.9 (t, 1H), δ 3.9 (s 3H, OMe), δ 6.7 (d, 1H), δ 6.8 (dd, 1H), δ 6.8 (dd, 1H), δ 6.5 (d, 1H).

2e IR (KBr), 1250, 1460, 1418, (aromatic ring), 1195 (C =S), 1100 (C-S-C) and 1060 cm^{-1} (C-O-C), 1250 (C–N). ^{1}HNMR (DMSO-d_6); δ 3.50 (d, 2H,CH_2), δ 7.4 (s, 5H, Ar–H), δ 3.9(t, 1H), δ 3.9 (s 3H, OMe), δ 6.7 (d, 1H), δ 6.5 (d, 1H).

2f IR (KBr)[1], 1258, 1455, 1423 (aromatic ring), 1195 (C =S), 1065 cm^{-1}(C-O-C) 1100 (C-S-C), 1250 (C–N). ^{1}HNMR (DMSO-d_6); δ 3.50 (d, 2H,CH_2), δ 7.4 (s,5H, Ar–H), δ 3.9 (t, 1H), δ 7.67 (d, 1H), δ 7.45 (dd, 1H), δ 7.43 (dd, 1H), δ 6.5 (d, 1H).

2g IR (KBr)[1], 1065 CM^{-1}(C-O-C), 1256, 1460, 1426, (aromatic ring), 1195 (C =S), 1100 (C-S-C), 1250 (C–N). ^{1}HNMR (DMSO-d_6); δ 3.50 (d, 2H,CH_2), δ 7.4 (s,5H, Ar–H), δ 3.9 (t, 1H), δ 7.69 (d, 1H), δ 6.5 (d, 1H).

Other such compounds were also prepared in a similar way. The Scheme was given in fig.1



2a Ar = C_6H_5, R = C_6H_5
2b Ar = 2-$CH_3C_6H_4$, R = C_6H_5
2c Ar = 4-$CH_3C_6H_4$, R = C_6H_5
2d Ar = 2-$OCH_3C_6H_4$, R = C_6H_5
2e Ar = 4-$OCH_3C_6H_4$, R = C_6H_5
2f Ar = 2-ClC_6H_4, R = C_6H_5
2g Ar = 4-ClC_6H_4, R = C_6H_5

Fig.1 Scheme

RESULTS AND DISCUSSION

The characterization data of the prepared compounds are given in table 1.

Herbicidal activity: The compounds 2c, 2e and 2g were subjected to primary post and pre-emergent herbicidal evaluation [10-12] at rate of 8.0, 4.0, 1.0 and 0.5 kg ha^{-1}. The test species are *Echinochloa oryzicola, Echinochloa crus-galli, Oryza sativa* and *Glycine max.* The detailed data on title compounds having promising herbicidal activity are given in table 2.

Fungicidal activity: All the compounds were screened for their antifungal activity by agar growth technique [13] against *Aspergillus niger* and *Pyricularia oryzae* at 1000ppm, 100 ppm and 10 ppm concentrations respectively. Amongst the tested compounds the most active compounds 2c, 2e and 2g showed activity nearly comparable 90% at 1000ppm) to that of carbendazim (98% at 1000ppm). Other compounds were founds to be moderate to poorly active. The results of further investigation on compound 2e and 2g on wider range of fungi as well as at higher dilution was not encouraging.

Table 1: Characterization data of compounds 1a-g and 2a-g.

Compd.	M.P. (Oc)	Yield (%)	Mot. formula	Found (%) C	H	(Calcd.) N
1a	140	52	$C_9H_7ONS_2$	(51.67)	(3.34)	(6.69)
				51.55	3.39	6.83
1b	110	55	$C_{10}H_9ONS_2$	(53.81)	(4.03)	(6.27)
				53.30	3.95	6.53
1c	165	49	$C_{10}H_9ONS_2$	(53.81)	(4.03)	(6.27)
				53.75	3.92	6.10
1d	130	59	$C_{10}H_9O_2NS_2$	(50.20)	(3.76)	(5.85)
				50.05	3.65	5.60
1e	165	55	$C_{10}H_9O_2NS_2$	(50.20)	(3.76)	(5.85)
				50.10	3.61	5.75
1f	140	53	$C_9H_6ONS_2Cl$	(44.35)	(2.46)	(5.74)
				44.10	2.25	5.52
1g	148	54	$C_9H_6ONS_2Cl$	(44.35)	(2.46)	(5.74)
				44.10	2.30	5.60
2a	145	61	$C_{17}H_{13}ONS_2$	(65.59)	(4.18)	(4.50)
				65.35	4.23	4.51
2b	155	60	$C_{18}H_{15}ONS_2$	(66.46)	(4.61)	(4.30)
				66.49	4.67	4.53
2c	150	60	$C_{18}H_{15}ONS_2$	(66.46)	(4.61)	(4.30)
				66.39	4.53	4.15
2d	122	62	$C_{18}H_{15}O_2NS_2$	(69.90)	(4.85)	(4.53)
				69.70	4.73	4.69
2e	165	63	$C_{18}H_{15}O_2NS_2$	(69.90)	(4.85)	(4.53)
				69.70	4.73	4.69
2f	152	58	$C_{17}H_{15}ONS_2Cl$	(49.93)	(3.67)	(3.42)
				49.81	3.48	3.29
2g	144	58	$C_{17}H_{15}ONS_2Cl$	(49.93)	(3.67)	(3.42)
				49.81	3.41	3.29

Table 2. Herbicidal activity of compounds 2c, 2e, and 2g.

Compd.	Application rate kg/ha	Post-emergence species				Pre-emergence species			
		E.or	*E.cr*	*O.sa*	*G.max*	*E.or*	*E.cr*	*O.sa*	*G.max*
2c	8.0	4	5	5	4	5	5	4	5
	4.0	5	4	4	4	4	5	4	5
	1.0	3	2	2	3	3	3	2	3
	0.5	1	2	1	1	2	2	1	1
2e	8.0	5	5	5	5	5	5	5	5
	4.0	5	4	5	5	5	4	4	5
	1.0	4	4	4	3	4	4	4	4
	0.5	4	3	3	3	4	3	4	4
2g	8.0	5	5	5	4	5	5	5	5
	4.0	4	4	4	4	4	4	4	4
	1.0	4	3	2	1	3	2	2	2
	0.5	1	1	1	1	1	1	1	1

Insecticidal activity: The compounds 2c, 2e and 2g were examined for their insecticidal activity against two insects viz. *Spodoptera litura* and *Tetranychus utriceae* by leaf dipping method [14-15] at 500 ppm. The compounds 2e and 2g showed moderate to good activity. All the tested compounds showed lower activity as compared to the standard insecticide propoxure. The detailed data on title compounds having promising insecticidal activity are given in table 3.

Table 3. Insecticidal activity of compounds 2c, 2e and 2g.

Compd.	*S. litura*	*T. utriceae*
2c	++	++
2e	+++	+++
2g	+++	+++
Propoxure	Δ	Δ

Mortality (%) is indicated by symbols (–) = 0-20%, (+) = 21-40% (++) = 41-60%, (+++) = 61-80%, Δ = 80~.

APPLICATIONS

We have synthesised 3,5-disubstituted-furothiazole-2-thiones. All these compounds have been assayed for their herbicidal activity against *Echinochloa oryzicola, Echinochloa crus-galli, Oryza sativa* and *Glycine max* antifungal activity against *Aspergillus niger, Pyricularia oryzae* whereas insecticidal activity against two insects viz. *Spodoptera litura* and *Tetranychus utriceae.*

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