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The synthesis and evaluation of 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones and their 5-arylidene derivatives as potential agricultural fungicides†

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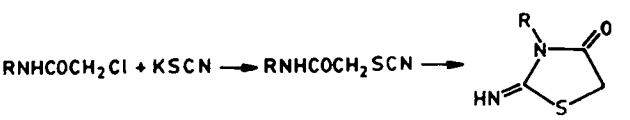
Abstract. A series of new 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones and their 5-arylidene derivatives have been synthesized from 2-amino-4-arylthiazoles as starting materials. The reaction mechanism has also been critically examined. Of all the synthetic compounds tested against the agricultural fungi *Trichoderma harzianum* and *Curvularia lunata*, two compounds, namely 2-imino-3-(4-*p*-chlorophenylthiazol-2-yl)-4-thiazolidinone and 5-benzylidine-2-imino-3-(4-*p*-tolylthiazol-2-yl)-4-thiazolidinone exhibited the most potent fungicidal effect.

Keywords. 2-Imino-3-(4-*p*-chlorophenylthiazol-2-yl)-4-thiazolidinone; 5-benzylidine-2-imino-3-(4-*p*-tolylthiazol-2-yl)-4-thiazolidinone; agricultural fungicide; *Trichoderma harzianum*; *Curvularia lunata*.

1. Introduction

Over the years, 4-thiazolidinones have enjoyed a prominent place in heterocyclic chemistry largely due to the wide ranging biological activity demonstrated by this class of compounds (Bhargava and Chaurasia 1969; Mousseron 1972; Lakhan 1982; Lakhan and Singh 1984a; Lakhan and Rai 1987; Troutman and Long 1948). An overview of the chemistry of this ring system has been dealt with in depth quite recently (Newkome and Nayak 1979). A convenient method of synthesis involves the 2,3-bond formation. Thus, 2-haloacetamides react with potassium thiocyanate to give the intermediate 2-thiocyanatoacetamides, which cyclise in anhydrous acetone to the corresponding 2-imino-4-thiazolidinones as given below (Ebetino and Gever 1962; Schröpl and Pohloudek-Fabini 1968, 1969):



(1)

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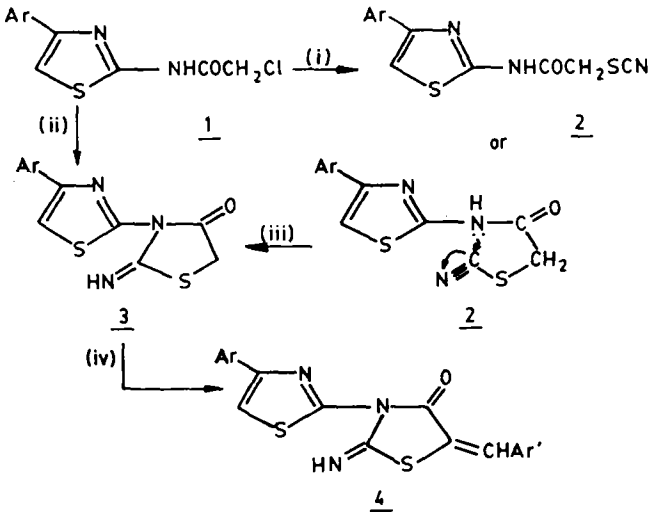
Moreover, it is well known that the thiazole moiety has significant bioligical activity in its own right (Lakhan and Singh 1984b; Bhargava *et al* 1981, 1982). We have therefore aimed at synthesizing a series of thiazol-2-yl substituted 4-thiazolidinones (3) and their 5-arylidene derivatives (4), and evaluating them as potential agricultural fungicides.

The target compounds (3 and 4) were obtained from 2-amino-4-arylthiazoles as the key intermediates (scheme 1). The interaction of substituted acetophenones, thiourea and iodine by literature methods (Dodson and King 1945; King and Hlavacek 1950; Bhargava *et al* 1982; Lakhan and Singh 1984b) gave 2-amino-4-arylthiazoles, which were reacted with chloroacetyl chloride to afford the corresponding 2-chloroacetamido-4-arylthiazoles (1). The latter on treatment with potassium thiocyanate in refluxing acetone gave the related 4-thiazolidinones (3). Condensation of 3 with different aromatic aldehydes occurred at the reactive methylene group present at position 5 of the thiazolidinones ring and resulted in the formation of 5-arylidene-2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (4). Fungicidal activity screening of 3 and 4 was accomplished by the agar growth food poison technique against *T. harzianum* and *C. lunata*. The activity has been compared with that of a commercially used fungicide 'Cuman' (80% Ziram).

2. Experimental

All melting points were determined in open capillaries with a Gallenkamp apparatus and are uncorrected. The purity of compounds was routinely checked by TLC using silica gel G (Merck). Elemental analyses (C, H and N) were carried out with a Coleman analyser. The IR spectra were recorded on Perkin-Elmer 257 and 783 grating spectrophotometers, and ^{1}H-NMR spectra on Jeol FX 90Q Fourier-transform spectrometer as $CDCl_3$ or DMSO–d_6 solutions with Me_4Si as an internal reference.



Scheme 1. Reagents: (i) and (ii) KSCN, Me_2CO, boil, 3h; (iii) DMF, 150–160°C, 4h; (iv) Ar'CHO, xylene, pyridine; 150–160°C, 3h.

2.1 *2-Amino-4-(2,4-dimethoxyphenyl) thiazole*

A mixture of 2,4-dimethoxyacetophenone (18·0 g, 0·1 mol), thiourea (15·2 g, 0·2 mol), and iodine (25·0 g, 0·2 mol) was heated in a water bath with occasional shaking for 8 h. The solid obtained was triturated with ether to remove unreacted 2,4-dimethoxyacetophenone. It was further washed with aqueous sodium thiosulphate to remove the excess iodine and then with water. The crude product was dissolved in hot water and 2-amino-4-(2,4-dimethoxyphenyl) thiazole was precipitated by the addition of ammonia. Recrystallisation from ethanol–benzene (3:1) gave 70% yield of product as brown crystals: m.p. 102°C [literature (Societe de Recherches Industrielles 1968) m.p. 102°C]; IR ν_{max}^{Nujol} 3450, 3260, 1620, 1590, 1520 cm^{-1}. ^1H NMR $\delta_{Me_4Si}^{CDCl_3}$ 3·62 and 3·70 (two singlets, 3H each, two OCH_3 groups), 5·52 (broad, 2H, NH_2), 6·92–7·84 (*m*, 4H, aromatic). Analysis–calcd. for $C_{11}H_{12}N_2O_2S$: N, 11·9; found: N, 12·0.

Other 2-amino-4-arylthiazoles were prepared by known methods (loc. cit.).

2.2 *2-Chloroacetamido-4-(2,4-dimethoxyphenyl)thiazole (1i)*

To a chilled solution of 2-amino-4-(2,4-dimethoxyphenyl)-thiazole (9·4 g, 0·04 mol) in dry benzene (50 ml), chloroacetyl chloride (5·2 g, 0·046 mol) dissolved in dry benzene (20 ml) was added dropwise with vigorous stirring. When the addition was over, the reaction mixture was refluxed on a water bath at 80° for 3 h. Benzene and excess chloroacetyl chloride were removed by distillation. The residue was washed with 5% sodium hydrogen carbonate followed by water. The crude product was dried, and recrystallized from ethanol to give colourless crystals: m.p. 126–127°C (65% yield); IR ν_{max}^{Nujol} 3400, 1650, 1550, 1500, 1100 cm^{-1}. Analysis – calcd. for $C_{13}H_{13}ClN_2O_3S$: N, 9·0; S, 10·2; found: N, 9·1; S, 10·0.

Other 2-chloroacetamino-4-arylthiazoles (1a–h) were prepared by literature methods (Sharma 1966; Bhargava *et al* 1982; Lakhan and Singh 1984b).

2.3 *2-Imino-3-[(4-p-methoxyphenyl)thiazol-2yl]-4-thiazolidinone (3f)*

A mixture of 2-chloroacetamido-4-*p*-methoxyphenylthiazole (1f; 4·0 g, 0·014 mol), potassium thiocyanate (2·0 g, 0·02 mol), and dry acetone (50 ml) was refluxed on a water bath for 3 h. Excess acetone was distilled off and the residue was agitated with water (40 ml). The solid product was filtered under suction, washed with water, and dried. It was crystallized from ethanol to afford colourless needles: m.p. 262–263°C (65% yield); IR ν_{max}^{Nujol} 3120, 1735, 1700, 1610, 1575, 1250, 745 cm^{-1}. ^1H NMR $\delta_{Me_4Si}^{Me_2SO-d_6}$ 3·75 (*s*, 3H, OCH_3), 4·00 (*s*, 2H, $>CH_2$), 6·75–7·90 (*m*, 5H, aromatic protons), 9·62 (broad, 1H, $>NH$). Analysis – calcd. for $C_{13}H_{11}N_3O_2S_2$: C, 51·1; H, 3·6; N, 13·8; S, 21·0; found: C, 51·0; H, 3·8; N, 13·9; S, 21·2.

Similarly, other 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (3a–h) were also prepared. Their melting points and characterization data are recorded in table 1.

2.4 *Reaction of 2-chloroacetamido-4-(2,4-dimethoxyphenyl)thiazole with potassium thiocyanate: Formation of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)thiazole (2i)*

A mixture of 2-chloroacetamido-4-(2,4-dimethoxyphenyl) thiazole (1i; 4·0 g, 0·013 mol), potassium thiocyanate (1·94 g, 0·02 mol), and dry acetone (50 ml) was

Table 1. 2-Imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (3).

Compd.	Substituent Ar	Yield (%)	M.P. (°C)	Formula*	% Carbon		% Nitrogen		Characteristic IR peaks (cm^{-1})
					Found	Calcd	Found	Calcd.	
3a	C_6H_5	62	240–41	$C_{12}H_9N_3OS_2$	52·5	52·4	15·2	15·3	3350, 1710, 1560, 1150
3b	p-$CH_3C_6H_4$	70	200–01	$C_{13}H_{11}N_3OS_2$	54·0	54·0	14·3	14·5	3350, 1710 1630, 1560
3c	p-ClC_6H_4	65	290–91	$C_{12}H_8ClN_3OS_2$	46·8	46·5	13·4	13·6	3400, 1700, 1590, 1530
3d	p-BrC_6H_4	55	300–01	$C_{12}H_8BrN_3OS_2$	40·9	40·7	11·6	11·9	3350, 1710, 1620, 1560
3e	m-$CH_3OC_6H_4$	58	235–36	$C_{13}H_{11}N_3O_2S_2$	51·2	51·1	13·8	13·8	3400, 1660, 1550, 1500
3f	p-$CH_3OC_6H_4$	65	262–63	$C_{13}H_{11}N_3O_2S_2$	51·0	51·1	13·9	13·8	3120, 1735, 1610, 1575
3g	m-$O_2NC_6H_4$	60	244–46	$C_{12}H_8N_4O_3S_2$	45·2	45·0	17·3	17·5	3300, 1690, 1580, 1530
3h	p-$O_2NC_6H_4$	75	188–90	$C_{12}H_8N_4O_3S_2$	44·9	45·0	17·6	17·5	3310, 1700, 1580, 1560
3i	2,4-$(CH_3O)_2C_6H_3$	60	183–84	$C_{14}H_{13}N_3O_3S_2$	49·8	50·1	12·3	12·5	3400, 1720, 1600, 1560

*Satisfactory analyses for hydrogen and sulphur were also obtained.

heated under reflux on a water bath for 6 h. The product was worked up as described above and the crude material was crystallized from ethanol to give 3·0 g of colourless crystals: m.p. 149–150°C (70% yield); IR ν_{max}^{Nujol} 3230, 2050, 1720, 1630, 1590 cm^{-1}. Analysis – calcd. for $C_{14}H_{13}N_3O_3S_2$: C, 50·1; H, 3·9; N, 12·5; S, 19·1; found: C, 50·2; H, 4·0; N, 12·3; S, 19·0.

2.5 *Thermal cyclization of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)thiazole: Formation of 2-imino-3-[4-(2,4-dimethoxyphenyl)thiazol-2-yl]-4-thiazolidinone (3i)*

Finely powdered 2·5 g of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)-thiazole 2i suspended in 25 ml dimethylformamide was refluxed in an oil bath at 150–160°C for 4 h. The solvent was removed by distillation under vacuum and the crude product crystallized from ethanol to give colourless crystals of the expected thiazolidinone: m.p. 183–184°C (60% yield); IR ν_{max}^{Nujol} 3400, 1720, 1600, 1560, 1170 cm^{-1}. Analysis – calcd. for $C_{14}H_{13}N_3O_3S_2$: C, 50·1; H, 3·9; N, 12·5; S, 19·1; found: C, 49·8; H, 3·9; N, 12·3; S, 19·5.

An attempted thermal cyclisation of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)thiazole (2i) in boiling 3-pentanone (b.p. 102°C) as solvent failed to give the desired 4-thiazolidinone. However, the starting material was isolated quantitatively.

2.6 *5-Benzylidene-2-imino-3-[(4-p-methoxyphenyl)thiazol-2-yl]-4-thiazolidinone (4f)*

A mixture of 2-imino-3-[(4-*p*-methoxyphenyl)thiazol-2-yl]-4-thiazolidinone (3f; 0·9 g, 0·027 mol), benzaldehyde (0·6 g, 0·056 mol), xylene (10 ml), and pyridine (4 drops) was heated under reflux in a paraffin bath at 150–160°C for 3 h. The solvent was removed by distillation and the residue was washed with hot water. It was crystallized from ethanol to form brown crystals: m.p. 222–223°C (60% yield); ν_{max}^{Nujol} 3350, 1730, 1590, 1520, 1190, 840 cm^{-1}. Analysis – calcd. for $C_{20}H_{15}N_3O_2S_2$: C, 61·1; H, 3·8; N, 10·7; S, 16·3; found: C, 61·4; H, 3·9; N, 10·6; S, 16·4.

Similarly, other 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (3) were condensed with benzaldehyde and/or *p*-anisaldehyde. The characterization data of the products (4) are recorded in table 2.

3. Results and discussion

The interaction of 2-chloroacetamido-4-arylthiazoles with potassium thiocyanate for 3 h in boiling acetone results in the nucleophilic displacement of chloride by the thiocyanate ion forming 2-thiocyanatoacetamido-4-arylthiazole as intermediate. The latter with a nucleophilic amino nitrogen favourably situated with respect to the electrophilic cyano group undergoes intramolecular cyclization *in situ* almost invariably. Thus, 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (3) are isolated as the end products in all the cases with one exception (i.e., with Ar = 2,4-dimethoxyphenyl).

Under identical conditions the reaction of 2-chloroacetamido-4-(2,4-dimethoxyphenyl)thiazole (1i) with KSCN gives 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)thiazole (2i) in about 70% yield. The same product is isolated when the heating period was prolonged from 3 to 6 h or the reaction temperature was raised by replacing boiling acetone (b.p. 56°C) with 3-pentanone (b.p. 102°C). The 2-thiocy-

Table 2. 5-Arylidene-2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (4).

Compd.	Substituents Ar	Substituents Ar'	Yield (%)	M.P. (°C)	Formula*	% Carbon Found	% Carbon Calc.	% Nitrogen Found	% Nitrogen Calc.	Characteristic IR peaks, cm^{-1}
4a	C_6H_5	C_6H_5	72	289–91	$C_{19}H_{13}N_3OS_2$	62·7	62·6	11·5	11·6	3300, 1700, 1580, 1150
4a'	C_6H_5	p-$CH_3OC_6H_4$	65	257–58	$C_{20}H_{15}N_3O_2S_2$	61·7	61·6	10·6	10·7	3300, 1690 1570, 1140
4b	p-$CH_3C_6H_4$	C_6H_5	58	283–84	$C_{20}H_{15}N_3OS_2$	63·4	63·7	11·4	11·1	3250, 1715, 1560, 1170
4c	p-ClC_6H_4	p-$CH_3OC_6H_4$	52	303–04	$C_{20}H_{14}ClN_3O_2S_2$	56·3	56·1	10·0	9·8	3300, 1710, 1580, 1160
4d	p-BrC_6H_4	p-$CH_3OC_6H_4$	78	263–65	$C_{20}H_{14}BrN_3O_2S_2$	50·6	50·8	9·0	8·9	3350, 1700, 1570, 1150
4e	m-$CH_3OC_6H_4$	C_6H_5	75	231–32	$C_{20}H_{15}N_3O_2S_2$	61·0	61·1	10·9	10·7	3350, 1720, 1580, 1150
4f	p-$CH_3OC_6H_4$	C_6H_5	60	222–23	$C_{20}H_{15}N_3O_2S_2$	61·4	61·1	10·6	10·7	3350, 1730, 1590, 1190
4g	m-$O_2NC_6H_4$	p-$CH_3OC_6H_4$	73	322	$C_{20}H_{14}N_4O_4S_2$	54·9	54·8*	12·7	12·8	3350, 1700, 1590, 1150
4h	p-$O_2NC_6H_4$	C_6H_5	55	271	$C_{19}H_{12}N_4O_3S_2$	55·7	55·9	13·9	13·7	3200, 1720, 1590, 1160
4h'	p-$O_2NC_6H_4$	p-$CH_3OC_6H_4$	75	264–65	$C_{20}H_{14}N_4O_4S_2$	55·0	54·8	12·6	12·8	3350, 1710 1590, 1160

*Satisfactory analyses for hydrogen and sulphur were also obtained.

anatoacetamide derivative gets cyclised into the corresponding 4-thiazolidinone (3i) by heating in a highly polar aprotic solvent DMF at 150–160°C for 4 h. The isolation of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)thiazole (2i) and its conversion into related 4-thiazolidinone (3i) by intramolecular cyclization confirms the actual intermediacy of the 2-thiocyanatoacetamide derivatives in the formation of the 4-thiazolidinones (3).

The reactive methylene group of 3 has been successfully condensed with aromatic aldehydes in the presence of pyridine yielding the related 5-arylidene derivatives (4).

The structure of the intermediates and products has been established on the basis of microanalyses and spectral data. The IR spectrum of 2-thiocyanatoacetamido-4-(2,4-dimethoxyphenyl)-thiazole (2i) in nujol shows absorption bands at 3230 cm^{-1} for N–H stretching, a strong band at 2050 cm^{-1} for SCN stretching, at 1720 cm^{-1} for carbonyl stretching, and at 1630 and 1590 cm^{-1} for the aromatic rings.

Similarly, the IR spectrum of 2-imino-3-[4-(*p*-tolylthiazol)-2-yl]-4-thiazolidinone (3b) in nujol shows absorption bands at 3350 for N–H stretch, at 1710 (C = 0 stretch), and at 1630, 1560 cm^{-1} for the aromatic rings. Its ^1H NMR spectrum in DMSO-d_6 displays a singlet of 3H intensity at δ 2·40 for the methyl protons. Another singlet is observed at δ 3·92 (2H) for the methylene protons attached to C – 5 of the thiazolidinone ring and a multiplet between 6·98 to 7·92 for the five aromatic protons. A broad signal is displayed for one proton at δ 9·52 for the imino group.

3.1 *Fungicidal activity*

The synthesized compounds 3 and 4 were screened for their potential fungicidal activity against the agricultural fungi *Trichoderma harzianum* and *Curvularia lunata* by the agar growth food poison technique at two dilutions (1:1000 and 1:5000). The percentage inhibition of growth by an inhibitor at a particular dilution is determined by comparison with growth in controls, i.e. untreated petridishes. The experiments were performed in triplicate for each dilution of the test compounds and replicates of the controls, and the results are shown in tables 3 and 4.

From the screening results it is evident that on the whole the compounds are remarkably more fungicidal than the standard chosen. In particular the fungicides 3c (table 3) and 4b (table 4) are 100% active against the experimental fungi at both the dilutions. The introduction of the benzylidene and *p*-methoxybenzylidene groups at position 5 of the 4-thiazolidinone ring shows mixed effects with regard to activity. Generally the fungicidal activity decreases, having some marginal cases where the activity remains more or less similar to that of the parent 4-thiazolidinones themselves (e.g., 4e and 4f). On the other hand, in two instances (4a and 4b) the fungicidal activities are considerably enhanced for the 5-benzylidene-4-thiazolidinones. It is also noteworthy that the compounds are more fungicidal against *Curvularia lunata* than *Trichoderma harzianum*, a trend also observed with the standard fungicide 'Cuman'.

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Table 3. Fungicidal activity results of 2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (3).
Medium: Czapek's agar, time: 5 days, temp. 25 ± 1°C

Compd.	Substituent Ar	% Inhibition at given dilutions			
		Trichoderma harzianum		*Curvularia lunata*	
		1:1000	1:5000	1:1000	1:5000
3a	C_6H_5	62	48	64	43
3b	p-$CH_3C_6H_4$	56	34	100	45
3c	p-ClC_6H_4	100	100	100	100
3d	p-BrC_6H_4	83	45	100	57
3e	m-$CH_3OC_6H_4$	60	58	80	71
3f	p-$CH_3OC_6H_4$	68	66	67	60
3g	m-$O_2NC_6H_4$	64	46	100	93
3h	p-$O_2NC_6H_4$	65	33	100	100
3i	2,4-$(CH_3O)_2C_6H_3$	100	51	100	79
	Cuman*	32	14	60	52
		(40)	(17·5)	(75)	(65)

*Values in parentheses denote the extrapolated percentage inhibition of this commercial fungicide for 100% Ziram content.

Table 4. Fungicidal activity results of 5-arylidene-2-imino-3-(4-arylthiazol-2-yl)-4-thiazolidinones (4).
Medium: Czapek's agar, time: 5 days, temp. 25 ± 1°C

Compd.	Substituents		% Inhibition at given dilutions			
			Trichoderma harzianum		*Curvularia lunata*	
	Ar	Ar′	1:1000	1:5000	1:1000	1:5000
4a	C_6H_5	C_6H_5	76	54	73	54
4a′	C_6H_5	p-$CH_3OC_6H_4$	34	18	58	36
4b	p-$CH_3C_6H_4$	C_6H_5	100	100	100	100
4c	p-ClC_6H_4	p-$CH_3OC_6H_4$	23	17	67	51
4d	p-BrC_6H_4	p-$CH_3OC_6H_4$	21	12	56	33
4e	m-$CH_3OC_6H_4$	C_6H_5	80	61	78	64
4f	p-$CH_3OC_6H_4$	C_6H_5	66	42	78	56
4g	m-$O_2NC_6H_4$	p-$CH_3OC_6H_4$	57	34	56	38
4h	p-$O_2NC_6H_4$	C_6H_5	67	46	64	40
4h′	p-$O_2NC_6H_4$	p-$CH_3OC_6H_4$	66	24	44	31
	Cuman*		32	14	60	52
			(40)	(17·5)	(75)	(65)

*Values in parentheses denote the extrapolated percentage inhibition of this commercial fungicide for 100% Ziram content.

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