HETEROCYCLES, Vol. 55, No. 7, 2001, pp. 1283 - 1289, Received, 16th April, 2001

A SIMPLE CONSTRUCTION OF 2-PHENYLIMINO-1,3-THIAZOLIDIN-4-ONES

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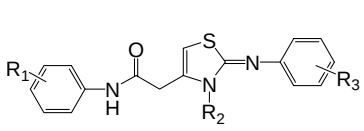
Abstract - A new methodology for the construction of 2-phenylimino-1,3-thiazolidin-4-one skeleton is described. Reaction of maleic anhydride (**5a**) or maleimides (**5b**, **5c**) with thiourea (**6**) gave the corresponding 2-imino-1,3-thiazolidin-4-ones (**7**) and (**9**) respectively. The reaction proceeded with high yield in polar solvents. In non-polar solvents at high temperature, however, isothiocyanate (**8**) was formed as a by-product presumably by the pyrolysis of thiourea (**6**). The proposed mechanism of the reaction was discussed.

INTRODUCTION

Synthetic methods available for the construction of heterocyclic molecules can be used to effect a number of valuable synthetic transformation and much of the research in heterocyclic chemistry is concerned with the development of new methods for heterocyclic ring formation. There has been an increasing interest over the past several years in the chemistry of 2-iminothiazoline derivatives, primarily due to their remarkably broad spectrum of biological activity.[1] Examples of their biological activities are agrochemical herbicides,[2] insecticides,[3] and fungicides.[4] In the previous paper,[5] we reported syntheses of 2-iminothiazolines (**1**) and (**2**), and the well known insecticide (**3**), which is effective against bee mite. It is clearly necessary to carry out structure-activity relationship studies of compound (**1**) to improve the potency and selectivity of these series of compounds as an effective fungicide. This report describes our preliminary effort toward the synthesis of new heterocyclic compounds of 1,3-thiazolidin-4-one derivative (**4**). Currently very few convenient syntheses of 1,3-thiazolidin-4-ones are available.[6]



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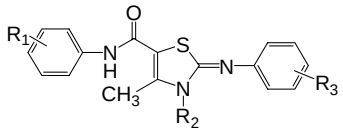

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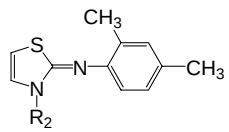

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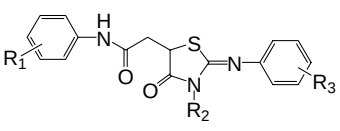

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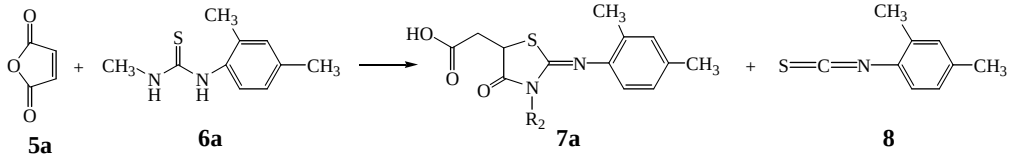
RESULTS AND DISCUSSION

To achieve the synthesis of target compounds we utilized the nucleophilic reactivity of sulfur in thiourea and electron-deficient character of olefin such as maleic anhydride (**5a**) or maleimides (**5b**, **5c**). Initially, maleic anhydride (**5a**) and substituted thiourea (**6a**) were chosen to evaluate the reactivity of both compounds (see Table 1). The starting **6a** was prepared by the reaction of methyl isothiocyanate with dimethylaniline.[7] Reaction of **6a** with **5a** in refluxing methylene chloride for 14 h afforded the corresponding 1,3-thiazolidin-4-one-5-acetic acid (**7a**) in 53% yield (entry 1). With this initial data in hand we decided to investigate conditions under which this reaction proceeds. Thus, a number of solvents were examined. Table 1 shows the yields as a function of solvent and reaction time. For instance, reaction of **6a** with **5a** in CH_3CN at 82 ^oC gave **7a** in quantitative yield (entry 5), whereas in toluene the yield was

somewhat lower (entry 7, 92%). From Table 1 it is clear that CH_3CN is the solvent of choice. Additionally, the reaction proceeded smoothly in polar solvent (entries 5, 9). In contrast, the isothiocyanate (**8**) was formed as a by-product in non-polar solvent (entries 4, 6-8) by the decomposition of thiourea (**6a**), which was confirmed by independent reaction. Thus, pyrolysis of thiourea (**6a**) in refluxing toluene for 4 h resulted in isothiocyanate (**8**) in 68% yield.

Table 1. Reaction of maleic anhydride (**5a**) with thiourea (**6a**) in various solvents

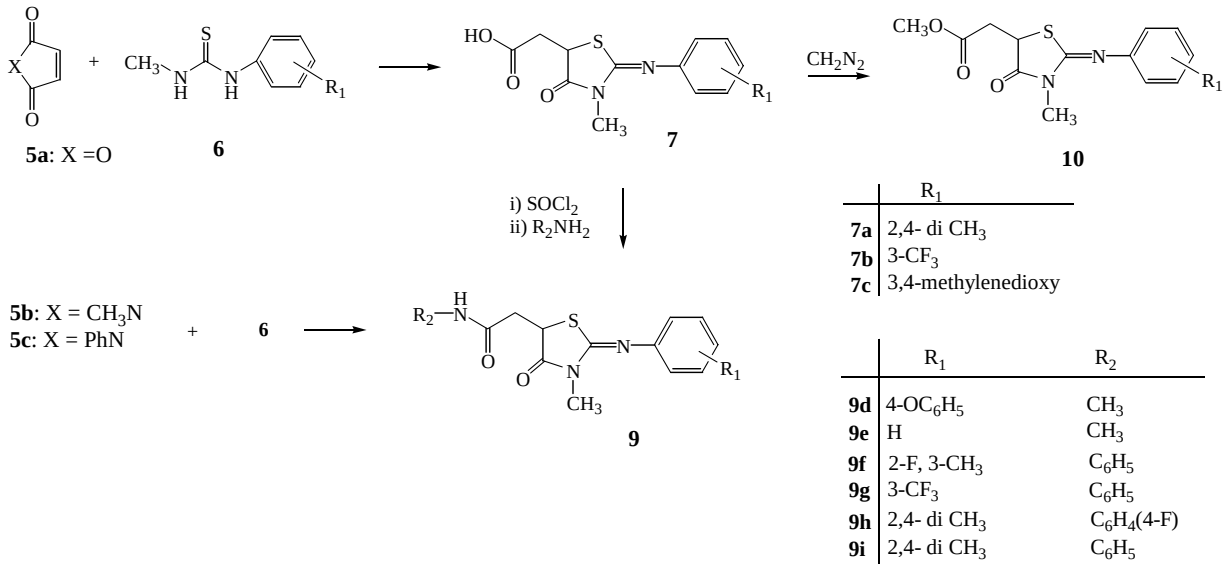


5a **6a** **7a** **8**

entry	solvent	temperature (^oC)	reaction time(h)	product ratio (%) [a]		
				6a	**7a**	**8**
1	CH_2Cl_2	40	14	47	53	0
2	acetone	56	20	27	73	0
3	C_2H_5OH	78	20	48	52	0
4	benzene	80	24	6	87	7
5	CH_3CN	82	24	0	100	0
6	1,4-dioxane	102	20	0	95	5
7	toluene	110	20	0	92	8
8	xylene	140	24	0	60	40
9	DMF	153	3	0	100	0

a: The yields were calculated by ^1H NMR spectra.

Next, we examined the reaction of various thioureas (**6**) with maleimides (**5b**) or (**5c**) to give the corresponding 1,3-thiazolidin-4-one acetamides (**9**), identical ^1H NMR spectra and TLC with those obtained from the compounds prepared by the chlorination of **7** followed by treatment of the corresponding amines respectively (see Scheme 1). As expected, treatment of the carboxylic acid (**7**) with diazomethane gave the corresponding methyl ester (**10**). Table 2 provides a list of various 2-imino-1,3-thiazolidin-4-ones that were prepared along with the yields, and melting points.



5a: X =O **6** **7** **10**

i) $SOCl_2$
ii) R_2NH_2

5b: X = CH_3N
5c: X = PhN

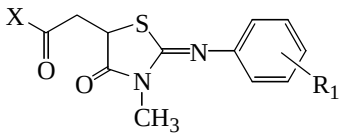
9

	R_1
7a	2,4- di CH_3
7b	3-CF_3
7c	3,4-methylenedioxy

	R_1	R_2
9d	4-OC_6H_5	CH_3
9e	H	CH_3
9f	2-F, 3-CH_3	C_6H_5
9g	3-CF_3	C_6H_5
9h	2,4- di CH_3	C_6H_4(4-F)
9i	2,4- di CH_3	C_6H_5

Scheme 1

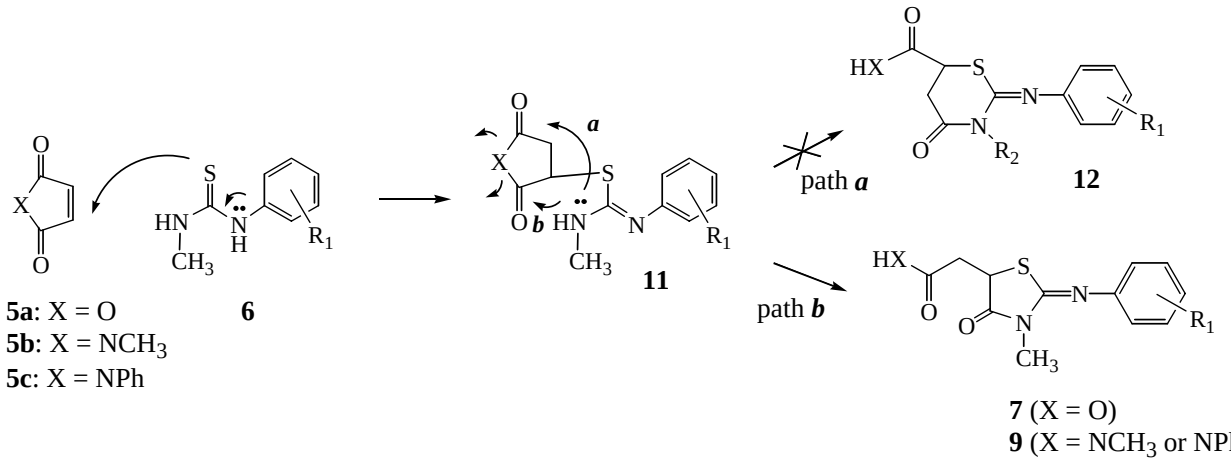
Table 2. A list of 2-imino-1,3-thiazolidin-4-ones (**7**, **9**, and **10**) prepared, the yields, and melting points.



compounds	R_1	X	solvent, reaction time	yield (%)	mp (^oC)	methods*
7a	2,4-di CH_3	OH	CH_3CN, 24 h	100	127-128	A
7b	3-CF_3	OH	CH_3CN, 24 h	100	139	A
7c	3,4-methylenedioxy	OH	Toluene, 3 h	76	135-136	A
9d	4-OC_6H_5	$NHCH_3$	Toluene, 24 h	35	178-179	B
9e	H	$NHCH_3$	CH_3CN, 24 h	43	180-181	B
9f	2-F, 3-CH_3	NHC_6H_5	CH_3CN, 24 h	76	148-151	C
9g	3-CF_3	NHC_6H_5	CH_3CN, 48 h	69	180-182	C
9h	2,4-di CH_3	NHC_6H_4(4-F)		58	176-178	D
9i	2,4-di CH_3	NHC_6H_5		78	196-197	D
10a	2,4-di CH_3	OCH_3		99	Oil	E
10c	3,4-methylenedioxy	OCH_3		73	115-116	E

* Method A: obtained by the reaction of **5a** with **6a**, **6b** or **6c**.
B: obtained by the reaction of **5b** with **6d** or **6e**.
C: obtained by the reaction of **5c** with **6f** or **6g**.
D: obtained by treatment of **7a** with thionyl chloride and then aniline derivative, respectively.
E: obtained by the reaction of **7a** or **7c** with diazomethane, respectively.

The mechanism of the reaction could be explained as follows. As shown in Scheme 2 nucleophilic 1,4-addition of the sulfur of thiourea (**6**) to maleic anhydride (**5a**) or maleimide (**5b**, **5c**) could afford iminosulfide (**11**). This unisolable intermediate (**11**) provides either 2-imino-1,3-thiazin-4-one (**12**) (path ***a***) or 1,3-thiazolidin-4-one (**7**) or (**9**) (path ***b***) as a result of an attack of the lone pair electron of the more basic



Scheme 2

methyl nitrogen on either carbonyl carbon. Since **12** was not the observed product, path ***a*** can be ruled out. All of these 1,3-thiazolidin-4-ones (**7**) or (**9**) were characterized by means of their spectral data and an X-Ray crystallographic analysis (see Figure 1 for 3,4-methylenedioxy analogue **10c**).[8] Alternatively the more basic methyl nitrogen could attack the carbonyl carbon of maleic anhydride (**5a**) or maleimides (**5b**, **5c**) to form an amide and subsequent intramolecular 1,4-addition of the sulfur to the α, β-unsaturated carbonyl yield the same product (**7**) or (**9**).

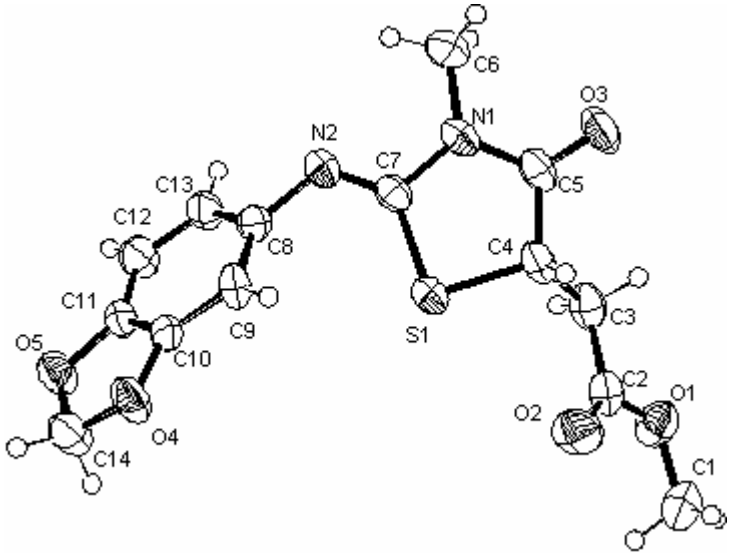


Figure 1. ORTEP plots of 3,4-methylenedioxy analogue (**10c**) with heteroatoms labeled.

EXPERIMENTAL SECTION

Melting points were determined on a Walden Precision Apparatus Electrothermal 9300 apparatus. All ^{1}H (300 MHz) and ^{13}C NMR (78.5 MHz) spectra were recorded on a Varian Gemini 300 spectrometer. Chemical shift (δ) are given in ppm and the coupling constants (*J*) in Hz. IR spectra were obtained on a Perkin-Elmer 16F-PC FT-IR and are reported in cm^{-1}. MS spectra were recorded on a Hewlet Packard 5890 series GC/MSD. Electron-impact high-resolution mass spectra (HRMS) were obtained on a JMS-700 Mass spectrometer high-resolution mass spectrometer at 70 eV.

Synthesis of 3-Methyl-2-(2,4-dimethylphenyl)imino-1,3-thiazolidin-4-one-5-acetic acid (7a) (R_1 = 2,4-di CH_3) (*General Procedure*)

A solution of maleic anhydride (**5a**) (0.98 g, 10 mmol) and thiourea (**6a**) (1.94 g, 10 mmol) in toluene (30 mL) was refluxed for 5 h. Evaporation of the solvent followed by crystallization from ethyl acetate and *n*-hexane gave **7a** as an yellow solid (2.69 g, 92 %).

mp 127-128 ℃; ^{1}H NMR ($CDCl_3$) 2.11 and 2.30 (2s, 6H, 2 x CH_3), 2.89 (dd, 1H, *J* = 9.6, 17.9, methylene CH), 3.29 (dd, 1H, *J* = 3.5, 17.9, methylene CH), 3.34 (s, 3H, N-CH_3), 4.31 (dd, 1H, *J* = 3.5, 9.6, 5-CH), 6.77-7.02 (m, 3H, ArH), 10.01 (br s, 1H, COOH); ^{13}C NMR 17.60, 20.95, 29.75, 37.67, 43.35, 119.73, 127.21, 129.56, 131.58, 134.45, 143.86, 153.90, 173.60, 175.17; IR (KBr) 2924, 1724, 1636, 1426, 1376, 1212; HRMS for $C_{14}H_{16}N_2O_3S$: Calcd 292.0881. Found, 292.0881; *Anal.* Calcd for $C_{14}H_{16}N_2O_3S$: C, 57.52, H, 5.52, N, 9.58, S, 10.97. Found, C, 57.4, H, 5.46, N, 9.47, S, 11.0.

3-Methyl-2-(3-trifluoromethylphenyl)imino-1,3-thiazolin-4-one-5-acetic acid (7b) (R_1 = 3-CF_3)

mp 139 ℃; ^{1}H NMR ($CDCl_3$) 2.92 (dd, 1H, *J* = 9.9, 18.1, methylene CH), 3.45 (s, 3H, NCH_3), 3.36 (dd, 1H, *J* = 3.5, 18.1, methylene CH), 4.37 (dd, 1H, *J* = 3.5, 9.9, 5-CH), 5.69 (br s, 1H, COOH), 7.71-7.49 (m, 4H, ArH); IR (KBr) 2907, 1732, 1634, 1588, 1428, 1240, 1210; HRMS for $C_{13}H_{11}N_2O_3F_3S$: Calcd 332.0442. Found, 332.0439.

3-Methyl-2-{(3,4-methylenedioxy)phenyl}imino-1,3-thiazolin-4-one-5-acetic acid (7c) (R_1 = 3,4-methylenedioxy)

mp 135-136 ℃; ^{1}H NMR ($CDCl_3$) 2.89 (dd, 1H, *J* = 9.8, 18.0, methylene CH), 3.31 (s, 3H, NCH_3), 3.33 (dd, 1H, *J* = 3.5, 18.0 Hz, methylene CH), 4.33 (dd, 1H, *J* = 3.5, 9.8, 5-CH), 5.96 (s, 2H, CH_2), 6.41 (d, 1H, *J* = 2.1, ArH), 6.44 (s, 1H, ArH), 6.77 (d, 2H, *J* = 2.1, ArH); IR (KBr) 3455, 1725, 1636, 1486, 1247, 1187, 1043 cm^{-1}; *Anal.* Calcd for $C_{13}H_{12}N_2O_5S$: C, 50.64, H, 3.92, N, 9.09, S, 10.40. Found, C, 50.7, H, 3.89, N, 8.96, S, 10.6.

3, *N*-Dimethyl-2-(4-phenoxyphenyl)imino-1,3-thiazolin-4-one-5-acetamide (9d) (R_1 = 4-OC_6H_5, R_2 = CH_3)

mp 178-179 ℃; ^{1}H NMR ($CDCl_3$) 2.64 (dd, 1H, *J* = 10.4, 15.5, methylene CH), 2.82 (d, 3H, *J* = 4.8, NCH_3), 3.20 (dd, 1H, *J* = 3.6, 15.5, methylene CH), 3.34 (s, 3H, 3-CH_3), 4.42 (dd, 1H, *J* = 3.6, 10.4, 5-CH), 5.50 (br s, 1H, NH), 6.95-7.36 (m, 9H, ArH); IR (KBr) 2937, 1722, 1634, 1488, 1240, 1210; HRMS for $C_{19}H_{19}N_3O_3S$: Calcd 369.1147. Found, 369.1165; *Anal.* Calcd for $C_{19}H_{19}N_3O_3S$: C, 61.77, H, 5.18, N, 11.37, S, 8.68. Found, C, 61.8, H, 5.15, N, 11.3, S, 8.71.

3, *N*-Dimethyl-2-phenylimino-1,3-thiazolin-4-one-5-acetamide (9e) (R_1 = H, R_2 = CH_3)

mp 180-181 ℃; ^{1}H NMR ($CDCl_3$) 2.63 (dd, 1H, *J* = 10.2, 15.9, methylene CH), 2.81 (d, 3H, *J* = 4.8, NCH_3), 3.18 (dd, 1H, *J* = 3.6, 15.9, methylene CH), 3.34 (s, 3H, 3-CH_3), 4.02 (dd, 1H, *J* = 3.6, 10.2, 5-CH), 5.65 (br s, 1H, NH), 6.96-7.36 (m, 5H, ArH); IR (KBr) 2927, 1716, 1636, 1591, 1426, 1378; HRMS for $C_{13}H_{15}N_3O_2S$: Calcd 277.0885. Found, 277.0880; *Anal.* Calcd for $C_{13}H_{15}N_3O_2S$: C, 56.30, H, 5.45, N, 15.15, S, 11.56. Found, C, 56.3, H, 5.41, N, 15.0, S, 11.5.

3-Methyl-2-(2-fluoro-4-methylphenyl)imino-*N*-phenyl-1,3-thiazolin-4-one-5-acetamide (9f) (R_1 = 2-F, 3-CH_3, R_2 = C_6H_5)

mp 148-151 ℃; ^{1}H NMR ($CDCl_3$) 2.31 (s, 3H, CH_3), 2.83 (dd, 1H, *J* = 10.2, 16.2, methylene CH), 3.37 (s, 3H, 3-CH_3), 3.39 (dd, 1H, *J* = 3.6, 16.2, methylene CH), 4.49 (dd, 1H, *J* = 3.6, 10.2, 5-CH), 6.83-7.76 (m, 8H, ArH), 7.44 (br s, 1H, NH); IR (KBr) 2927, 1712, 1680, 1632, 1546, 1444, 1248; HRMS for $C_{19}H_{18}N_3O_2FS$: Calcd 371.1104. Found, 371.1097.

3-Methyl-2-(3-trifluoromethylphenyl)imino-*N*-phenyl-1,3-thiazolin-4-one-5-acetamide (9g) (R_1 = 3-CF_3, R_2 = C_6H_5)

mp 180-182 ℃; ^{1}H NMR ($CDCl_3$) 2.88 (dd, 1H, *J* = 10.7, 16.6, methylene CH), 3.33 (s, 3H, 3-CH_3), 3.44 (dd, 1H, *J* = 3.2, 16.6, methylene CH), 4.46 (dd, 1H, *J* = 3.2, 10.7, 5-CH), 7.02-7.54 (m, 9H, ArH), 9.77 (br s, 1H, NH); IR (KBr) 2957, 1710, 1670, 1634, 1544, 1338, 1308, 1110; HRMS for $C_{19}H_{16}N_3O_2F_3S$: Calcd 407.0915. Found, 407.0906.

Synthesis of Methyl 3-Methyl-2-{3,4-(methylenedioxy)phenyl}imino-1,3-thiazolidin-4-one-5-acetate (10c) (R_1 = 3,4-methylenedioxy)(*General Procedure*)

A solution of 1,3-thiazolidin-4-one-5-acetatic acid (**7c**) (616 mg, 2 mmol) (R_1 = 3,4-methylenedioxy) in methylene chloride (30 mL) cooled under the ice bath was added a solution of diazomethane dissolved in ether. Evaporation of the solvent followed by crystallization from ethyl acetate and *n*-hexane gave the corresponding methyl ester.

mp 115-116 ℃; ^{1}H NMR ($CDCl_3$) 2.85 (dd, 1H, *J* = 9.9, 17.6, methylene CH), 3.27 (dd, 1H, *J* = 3.4, 17.6, methylene CH), 3.31 (s, 3H, 3-CH_3), 3.72 (s, 3H, OCH_3), 4.34 (dd, 1H, *J* = 3.4, 9.9 Hz, 5-CH), 5.97 (s, 2H, 3,4-methylenedioxy CH_2), 6.41-6.79 (m, 3H, ArH); IR (KBr) 2894, 1720(st), 1630(st), 1478, 1368, 1226, 1180, 1036; HRMS for $C_{14}H_{14}N_2O_5S$: Calcd 322.0623. Found, 322.0620; *Anal.* Calcd for $C_{14}H_{14}N_2O_5S$: C, 52.17, H, 4.38, N, 8.69, S, 9.95. Found, C, 52.3, H, 4.32, N, 8.64, S, 9.94.

Methyl 3-Methyl-2-(2,4-dimethylphenyl)imino-1,3-thiazolidin-4-one-5-acetate (10a) (R_1 = 2,4-di CH_3)

^{1}H NMR ($CDCl_3$) 2.13 and 2.30 (2s, 6H, 2 x CH_3), 2.85 (dd, 1H, *J* = 9.6, 17.5, methylene CH), 3.25 (dd,

1H, *J* = 3.6, 17.5, methylene CH), 3.35 (s, 3H, NCH_3), 3.69 (s, 3H, OCH_3), 4.33 (dd, 1H, *J* = 3.6, 9.6, 5-CH), 6.74-7.03 (m, 3H, ArH); ^{13}C NMR δ 18.01, 27.31, 30.02, 38.07, 43.97, 52.68, 119.95, 127.46, 129.85, 131.82, 134.52, 144.50, 153.76, 170.84, 173.84; IR (KBr) 2967, 1734, 1636, 1426, 1370, 1208; HRMS for $C_{15}H_{18}N_2O_3S$: Calcd 306.1038. Found 306.1040.

Synthesis of 3-Methyl-2-(2,4-dimethylphenyl)imino-*N*-(4-fluorophenyl)-1,3-thiazolidin-4-one-5-acetamide (9h) (R_1 = 2,4-di CH_3, R_2 = C_6H_4(4-F)) (*General Procedure*)

A solution of 1,3-thiazolidine-4-one-5-acetic acid (**7a**) (R_1 = 2,4-di CH_3)(584 mg, 2 mmol) in benzene (15 mL) and thionyl chloride (0.16 mL, 2.2 mmol) was refluxed for 3 h. Evaporation of the solvent gave an light brown oily residue, which was dissolved in benzene (10 mL). To a reaction mixture cooled under ice bath was added sequentially 4-fluoroaniline (0.21 mL, 2.2 mmol) and triethylamine (0.31 mL 2.2 mmol). Stirring was continued for 20 h at rt. The reaction mixture was washed sequentially with 1*N* hydrochloric acid, aqueous saturated sodium bicarbonate solution, and then water. Drying ($MgSO_4$) and evaporation of the solvent gave an light brown oil (0.743 g). Crystallization from ethyl acetate and *n*-hexane afforded **9h** (R_1 = 2,4-di CH_3, R_2 = C_6H_4(4-F)) (0.447 g, 58 %) as a light yellow needle.

mp 176-178 ℃; ^{1}H NMR ($CDCl_3$) 2.14 and 2.30 (2s, 6H, 2 x CH_3), 2.83 (dd, 1H, *J* = 9.8, 16.4, methylene CH), 3.34 (dd, 1H, *J* = 3.8, 16.4, methylene CH), 3.36 (s, 3H, NCH_3), 4.43 (dd, 1H, *J* = 3.8, 9.8, 5-CH), 6.74-7.44 (m, 7H, ArH), 7.65 (br s, 1H, NH); ^{13}C NMR 18.25, 21.49, 30.27, 40.67, 44.48, 116.11, 116.41, 120.11, 122.46, 122.56, 127.74, 130.11, 132.12, 133.94, 133.98, 134.95, 144.42, 154.34, 158.48, 161.72, 167.93, 174.94; IR (KBr) 2927, 1719, 1702, 1636, 1559, 1438, 1378; HRMS for $C_{20}H_{20}N_3O_2FS$: Calcd 385.1260. Found 385.1257.

3-Methyl-2-(2,4-dimethylphenyl)imino-*N*-phenyl-1,3-thiazolidin-4-one-5-acetamide (9i) (R_1 = 2,4-di CH_3, R_2 = C_6H_5)

yield 78 %; mp 196-197 ℃; R_f 0.42 (ethyl acetate : *n*-hexane = 1 : 4); ^{1}H NMR ($CDCl_3$): 2.14 and 2.30 (2s, 6H, 2 x CH_3), 2.84 (dd, 1H, *J* = 9.7, 16.2, methylene CH), 3.36 (dd, 1H, *J* = 3.9, 16.2, methylene CH), 3.38 (s, 3H, N-CH_3), 4.46 (dd, 1H, *J* = 3.9, 9.7, 5-CH), 6.75-7.49 (m, 8H, ArH), 7.63 (br s, 1H, NH); ^{13}C NMR: 18.02, 21.28, 30.03, 40.07, 44.33, 119.93, 120.04, 125.07, 127.52, 129.42, 129.90, 131.89, 134.68, 137.79, 144.36, 154.12, 167.68, 174.74. IR (KBr) 2925, 1722, 1692, 1625, 1545, 1430, 1363; HRMS for $C_{20}H_{21}N_3O_2S$: Calcd 367.1354. Found 367.1351; *Anal.* Calcd for $C_{20}H_{21}N_3O_2S$: C, 65.37, H, 5.76, N, 11.44, S, 8.73. Found, C, 65.5, H, 5.75, N, 11.4, S, 8.66.

Pyrolysis of *N*-methyl-*N'*-(2,4-dimethylphenyl)thiourea (6a)

A solution of **6a** (0.5 g, 2.57 mmol) in toluene (25 mL) was refluxed for 4 h. Evaporation of the solvent gave white solid residue. Crystallization from ethyl acetate and petroleum ether afforded white solids (**8**) (0.289 g, 68%, R_f = 0.47 (ethyl acetate/*n*-hexane = 4/1)). mp 29-30 ℃; ^{1}H NMR ($CDCl_3$): 2.30 and 2.34 (2s, 6H, 2 x CH_3), 6.94-7.09 (m, 3H, ArH); IR (KBr) 3445, 2917, 2088, 1780, 1646, 1386; MS, m/z 163 (M^+); *Anal.* Calcd for C_9H_9NS: C, 66.22, H, 5.56, N, 8.58, S, 19.64. Found, C, 66.2, H, 5.52, N, 8.46, S, 19.7.

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8. The X-Ray analysis was performed with the 3,4-methylenedioxy analogue (**10c**) (see Scheme 1). The data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-Ray tube and a graphite crystal monochromator. Orthorhombic space group $P2_12_12_1$ (No. 19) with a = 7.569(3) , b = 8.813(2) , c = 21.273(5) , V = 1419.0(4) Å^3, Z = 4, d_{calc} = 1.509 gcm^{-3}, μ= 0.255 mm^{-1}. A total of 1138 independent absorption-corrected reflections were collected. The structure was solved using SHELXS86 and SHELXL93 programs. The resulting structural parameters were refined to convergence of R_1 = 0.0398 for 1138 independent reflections with $I > 2\sigma(I)$ using full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms.