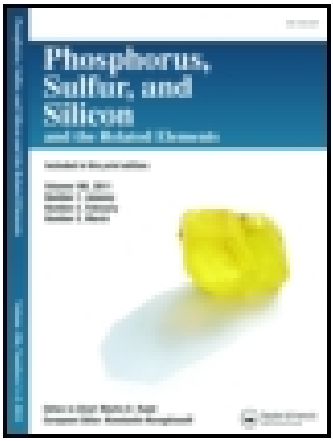


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis and Biological Activities of Novel Thiazole Derivatives of DHPMs via the N, S-dialkylation

Xiao-Fei Zhu [a] & De-Qing Shi [a]

[a] Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry , Central China Normal University , Wuhan, P. R. China

Published online: 28 Jul 2008.

To cite this article: Xiao-Fei Zhu & De-Qing Shi (2008) Synthesis and Biological Activities of Novel Thiazole Derivatives of DHPMs via the N, S-dialkylation, Phosphorus, Sulfur, and Silicon and the Related Elements, 183:8, 2020-2028, DOI: 10.1080/10426500701841680

To link to this article: http://dx.doi.org/10.1080/10426500701841680

Phosphorus, Sulfur, and Silicon, 183:2020–2028, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701841680

Synthesis and Biological Activities of Novel Thiazole Derivatives of DHPMs via the N, S-dialkylation

Xiao-Fei Zhu and De-Qing Shi
Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, P. R. China

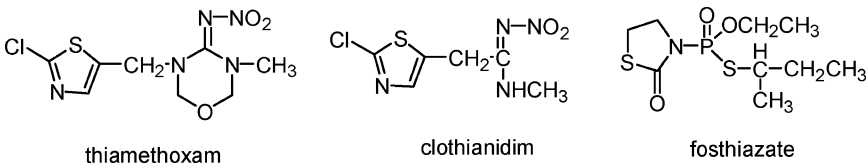
*A series of novel 1-[6-aryl-1-(2-chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl - methylsulfanyl)-4-methyl-1,6-dihydropyrimidin-5-yl]carboxylates or ethanones **2** were synthesized via the N,S-dialkylation of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) **1** using 2-chloro-5-(chloromethyl)thiazole as the alkylation reagent in one-pot reaction. The structures of the target compounds were confirmed by IR, ^{1}H NMR, EI-MS and elemental analyses, and, in the case of **2c**, by single crystal X-ray diffraction. The preliminary bioassay indicated that the title compounds **2** possess moderate to weak fungicidal and insecticidal activities.*

Keywords 3,4-Dihydropyrimidin-2(1H)-one; biological activity; N,S-dialkylation; substituted thiazole

INTRODUCTION

The Biginelli reaction involves an one-pot reaction between aldehyde, 1,3-dicarbonyl and urea or thiourea in the presence of an acidic catalyst to afford 3,4-Dihydropyrimidin-2(1H)-one (DHPM). Some DHPMs and their derivatives have attracted considerable interest due to their significant therapeutic and pharmacological properties, such as antiviral, antitumor, antibacterial and anti-inflammatory properties and so on.[1–3] There are some reports on the S-alkylation of DHPMs, and the alkylation reagents are usually benzyl and allyl halides.[4,5] However, there are few reports on the N, S-dialkylation of DHPMs in one pot reaction. Many thiazolyl containing compounds are also known to possess a wide range of biological and pharmacological

Received 29 August 2007; accepted 28 September 2007.
The authors are grateful to the Natural Science Foundation of China (grant No. 20302002) for financial support.
Address correspondence to De-Qing Shi Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China. E-mail: chshidq@mail.ccnu.edu.cn



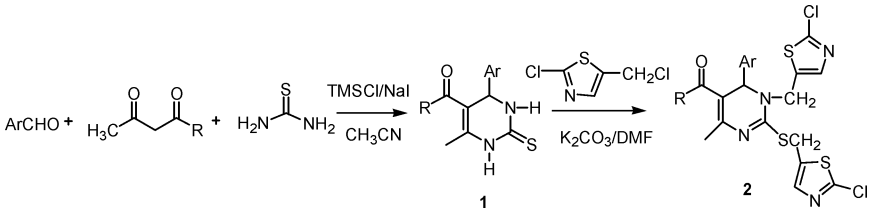
SCHEME 1

activities, as well as low toxicity toward mammals,[6–9] and some thiazolyl containing pesticides (such as thiamethoxam, clothianidim, fosthiazate, etc., (Scheme 1) have been commercialized.[10–13] As a continuation of our search for new biologically active compounds.[14–15] Herein, we hope to report a convenient synthesis of novel 1-[6-aryl-1-(2-chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-1,6-dihydropyrimidin-5-yl]carboxylates or ethanones **2** via the *N*, *S*-dialkylation of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) 1 using 2-chloro-5-(chloromethyl)thiazole as the alkylation reagent in one pot reaction as well as their biological activities.

RESULT AND DISCUSSION

We synthesized DHPMs according to an improved method.[16] DHPMs reacted with 2-chloro-5(chloromethyl)thiazole to afford pure N,S-dialkylation products in high yields and no mono S-alkylation product was detected even in the presence of excess DHPMs (3-4 equimolecular). It was found that different bases played a major role in the reactions, when triethyl amine was used, the yield was very low (about 20%) in refluxing temperature for 12 h, however, when anhydrous potassium carbonate was used, the reaction underwent very smoothly at room temperature and the yields were also good (Scheme 2).

All products were fully characterized by IR, ^{1}H NMR, EIMS and elemental analysis. All the spectral data were in accordance with the anticipated structures. In the ^{1}H NMR spectra of **2**, the two protons of



SCHEME 2

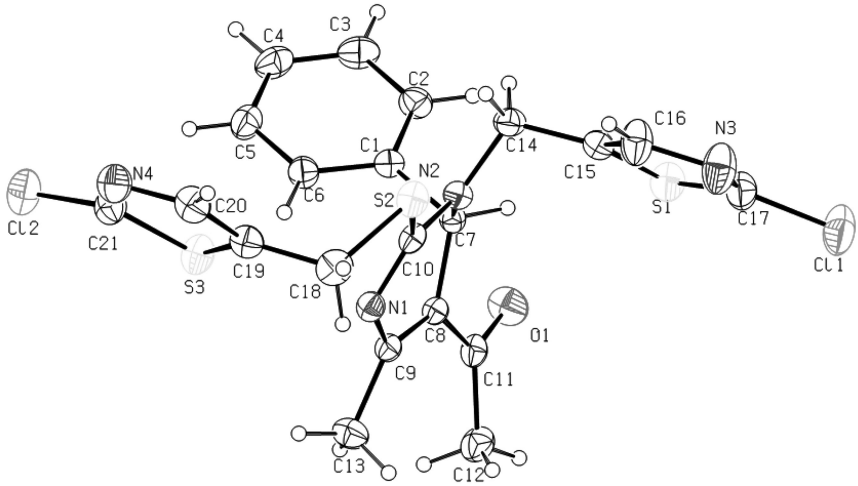


FIGURE 1 The structure of **2c**, showing displacement ellipsoids at the 50% probability level for non-H atoms.

the CH_2S moieties displayed two doublet as the result of their different chemical environments and coupling with each other, however, the two protons of the CH_2N moieties displayed as singlet and sometimes appeared as two doublet. 6-Position proton of 1,6-dihydropyrimidine exhibited as singlet. IR spectra of compounds **2** showed normal stretching absorption bands, indicating the existence of C=O ($\sim$1620 cm^{-1}), C=N ($\sim$1600 cm^{-1}). The EI mass spectra of compounds **2** revealed the existence of the molecular ion peaks and anticipant fragmentation peaks, which were in good accordance with the given structures of products.

Moreover, in order to confirm their molecular structure absolutely and investigate its regioselectivity, a single crystal of **2c** was obtained as light yellow crystals from a dichloromethane and hexane (2:1 v/v) solvent system as an example. X-ray diffraction analysis indicates that the single crystal of **2c** is monoclinic with space group P2(1)/c, cell parameters a = 10.612 (1), b = 18.741 (1), c = 12.463 (1) Å, β = 113.820 (1)°, v = 2267.6 (2) $Å^3$, z = 4, Dx = 1.492 g/cm^3, F (000) = 1048, μ = 0.59 mm^{-1} and final R = 0.047, wR = 0.134 for 4937 reflections ($I > 2\sigma(I)$). Figure 1 and Figure 2 show the molecular structure of compound **2c** and packing of the molecules in the unit cell, respectively. Intermolecular C-H...O and C-H...N and C-H...S hydrogen bonds contribute to the stability of the crystal structure (Figure 2 and Table 1). The dihydropyrimidine ring is almost planer, with a mean deviation from the plane of 0.132 (1) Å. The dihedral angles between the dihydropyrimidine ring and the

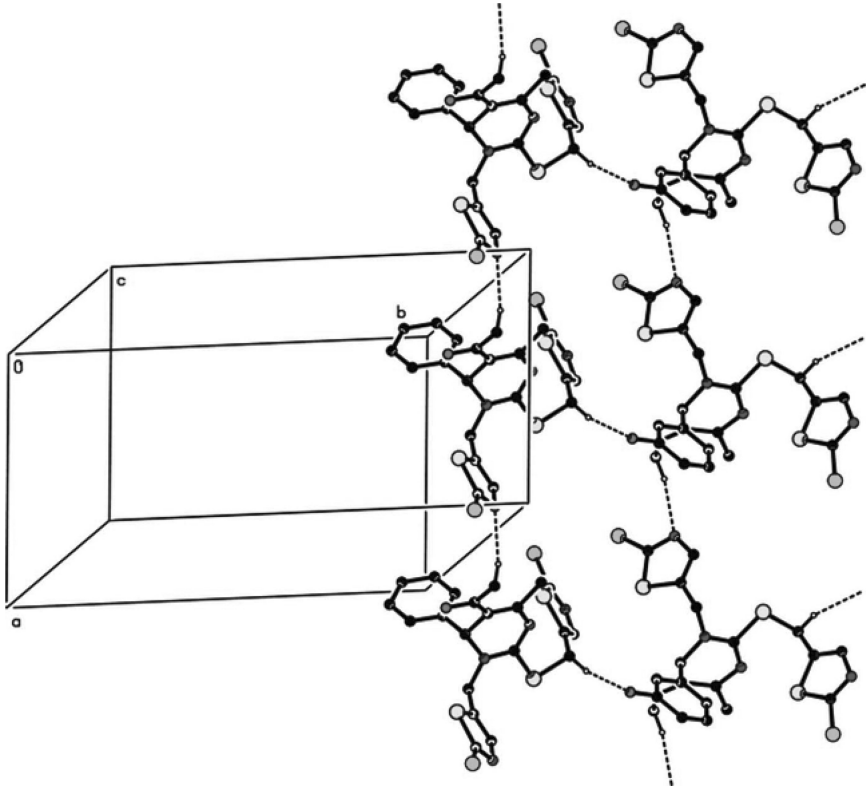


FIGURE 2 Part of the crystal packing of **2c**, Hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted.

phenyl, 1-thiazole and 2-thiazole rings are 88.5 (1), 13.6 (1) and 8.0 (1)°, respectively.

Compounds 2 were tested for insecticidal activities against aphides at the concentration of 250 mg/L according to a previously reported

TABLE I Hydrogen-Bond Geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C(18)-H(18A)...N(1)	0.97	2.39	2.799 (3)	105
C(14)-H(14A)...S(2)	0.97	2.51	2.972 (2)	109
C(7)-H(7)...O(1)	0.98	2.32	2.687 (3)	101
C(18)-H(18B)...O(1)^{i}	0.97	2.39	3.314 (3)	159
C(12)-H(12A)...N(3)^{ii}	0.96	2.45	3.390 (3)	167

Symmetry codes: (i) −x+1, y+1/2, −z+1/2 ; (ii) x−1, y, z.

TABLE II The Insecticidal and Fungicidal Activities of Compounds of 2a∼2i (Inhibitory Rate%)

Compd.	Insecticidal activity (250 mg/L) aphides	Fungicidal activity (50 mg/L) *Fusarium oxysporium*	*Rhizoctonia solani*	*Botrytis cinereapers*	*Gibberella zeae*	*Dothiorella gregaria*	*Colletotrichum gossypii*
2a	34	12	23	16	20	12	30
2b	56	40	46	40	24	16	38
2c	28	26	65	32	18	29	50
2d	25	27	16	11	39	16	30
2e	16	15	46	7	39	27	60
2f	41	45	58	40	54	69	26
2g	36	12	35	12	18	32	48
2h	47	27	26	19	36	54	48
2i	29	13	12	20	10	5	10

method.[17] The result is listed in Table II, which indicated that the title compounds 2 possess moderate to weak insecticidal activity at this dosage.

The fungicidal activities of the target compounds **2** were tested at a concentration of 50 mg/L. The six fungi used, *Fusarium oxysporium, Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria ,Colletotrichum gossypii*, belong to the group of field fungi and were isolated from corresponding crops. The activity data were listed in Table II. The preliminary bioassay indicated that the title compounds **2** possess moderate to weak inhibitory activities against the above six fungi. Further structure-activity relationships are under investigation.

In conclusion, a convenient synthesis of novel 1-[6-aryl-1-(2-chlorothiazol-5-ylmethyl)-2-(2-chlorothiazol-5-ylmethylsulfanyl)-4-methyl-1,6-dihydropyrimidin-5-yl]carboxylates or ethanones via the *N*, *S*-dialkylation of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) **1** using 2-chloro-5-(chloromethyl)thiazole as the alkylation reagent in one pot reaction was presented. It was found that only pure N,S-dialkylation products were formed even in the presence of excess DHPMs (3-4 equimolecular) and no mono S-alkylation product was detected. The results of the preliminary bioassays indicated that the title compounds **2** possess moderate to weak fungicidal and insecticidal activity.

EXPERIMENTAL

Melting points were determined with a WRS-1B digital melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian Mercury PLUS400 spectrometer with TMS as the internal reference and $CDCl_3$ as the solvent, while mass spectra were obtained with a

Finnigan TRACEMS2000 spectrometer using the EI method. IR spectra were measured by a Nicolet NEXUS470 spectrometer. Elemental analyses were performed with an Elementar Vario ELIIICHNSO elemental analyzer. X-ray diffraction analysis was performed on a Bruker SMART 1000 CCD diffractometer. DHPMs were synthesized according to the reported method.[16] All of the solvents and materials were reagent grade and purified as required.

Preparation of 1-[6-Aryl-1-(2-chlorothiazol-5-ylmethyl)-2-(2-chlorothiazol-5-ylmethylsulfanyl)-4-methyl-1,6-dihydropyrimidin-5-yl]carboxylate or Ethanone 2—General Procedure

A solution of DHPM **1** (2 mmol), 2-chloro-5-(chloromethyl)thiazole (0.67 g, 4 mmol), potassium carbonate powder (0.55 g, 4 mmol) and anhydrous DMF (15 mL) was stirred vigorously at room temperature until the reaction was complete (monitored by TLC), the solid filtered off and the filtrate concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether (1:2, *v*/*v*) as the eluent to give **2a**∼**2i** as yellow crystals.

1-[6-(4-Chlorophenyl)-1-(2-chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-1,6-dihydropyrimidin-5-yl]ethanone (2a)

Yellow crystals, yield 87%, m.p. 150–152°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.32 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 4.41 (d, J = 15.6 Hz, 1H, SCH_2), 4.56 (s, 2H, NCH_2), 4.74 (d, J = 16.0 Hz, 1H, SCH_2), 5.46 (s, 1H, CHAr), 7.20–7.29 (m, 4H, Ar-H), 7.42 (s, 1H, thiazole-H), 7.50 (s, 1H, thiazole-H); EI-MS (70 eV) *m*/*z*(%): 543 (M+1, 17.4), 542 (M+, 17.0), 410 (17.8), 163 (15.4), 131 (100), 96 (16.6), 76 (24.4); Anal. calcd for $C_{21}H_{17}Cl_3N_4OS_3$: C 46.37, H 3.15, N 10.30; found C 46.44, H 3.18, N 10.16.

1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-(4-tolyl)-1,6-dihydropyrimidin-5-yl]ethanone (2b)

Yellow crystals, yield 91%, m.p. 139–141°C; IR (KBr): 3086 (Ar-H), 1624 (C=O), 1599 (C=N), 1494, 1409 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.27 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.36 (d, J = 16.0 Hz, 1H, SCH_2), 4.54 (s, 2H, NCH_2), 4.67 (d, J = 16.4 Hz, 1H, SCH_2), 5.40 (s, 1H, CHAr), 7.10–7.18 (m, 4H, Ar-H), 7.42 (s, 1H, thiazole-H), 7.46 (s, 1H, thiazole-H); EI-MS (70 eV) *m*/*z*(%): 522 (M^+, 33.0), 431 (28.4), 227 (56.6), 163 (62.3), 139 (97.3), 113 (100), 76 (98.5); Anal. calcd. for

$C_{22}H_{20}Cl_2N_4OS_3$: C 50.47, H 3.85, N 10.70; found: C 50.29, H 3.73, N 10.54.

1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-phenyl-1,6-dihydropyrimidin-5-yl]ethanone (2c)

Yellow crystals, yield 87%, m.p. 150–152°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.27 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.37 (d, J = 16.4 Hz, 1H, SCH_2), 4.53 (s, 2H, NCH_2), 4.69 (d, J = 16 Hz, 1H, SCH_2), 5.46 (s, 1H, CHAr), 7.27–7.31 (m, 5H, Ar-H), 7.41 (s, 1H, thiazole-H), 7.47 (s, 1H, thiazole-H); Anal. Calcd for $C_{21}H_{18}Cl_2N_4OS_3$: C 49.50, H 3.56, N 11.0; found: C 49.37, H 3.60, N 11.23.

1-[1-(2-chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-6-(4-methoxyphenyl)-4-methyl-1,6-dihydropyrimidin-5-yl]ethanone (2d)

Yellow crystals, yield 90%, m.p. 129–131°C; IR (KBr): 3081 (Ar-H), 1623 (C=O), 1064 (C=N), 1495, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.25 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.43 (d, J = 15.6 Hz, 1H, SCH_2), 4.52 (s, 2H, NCH_2), 4.70 (d, J = 15.2 Hz, 1H, SCH_2), 5.38 (s, 1H, CHAr), 6.81–7.27 (m, 4H, Ar-H), 7.42 (s, 1H, thiazole-H), 7.47 (s, 1H, thiazole-H); Anal. calcd for $C_{22}H_{20}Cl_2N_4O_2S_3$: C 48.98, H 3.74, N 10.38; found: C 49.06, H 3.61, N 10.25.

1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-(thiophen-2-yl)-1,6-dihydropyrimidin-5-yl]ethanone (2e)

Yellow crystals, yield 80%, m.p. 109–110°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 4.53 (d, J = 16.8 Hz, 1H, SCH_2), 4.59 (s, 2H, NCH_2), 4.79 (d, J = 16.4 Hz, 1H, SCH_2), 5.76 (s, 1H, CHAr), 6.88-6.92 (m, 1H, Thiophene-H), 7.21 (d, J = 14.6 Hz, 2H, Thiophene-H), 7.46 (s, 2H, thiazole-H); Anal. calcd. for $C_{19}H_{16}Cl_2N_4OS_4$: C 44.27, H 3.13, N 10.87; found: C 44.14, H 3.01, N 10.69.

1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-(4-nitrophenyl)-1,6-dihydropyrimidin-5-yl]ethanone (2f)

Yellow crystals, yield 63%, m.p. 206–208°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.37 (d, J = 16 Hz, 1H, SCH_2), 4.55 (d, J = 10.8 Hz, 1H, NCH_2), 4.63 (d, J = 10.4 Hz, 1H, NCH_2), 4.75 (d, J = 16.4 Hz, 1H, SCH_2), 5.63 (s, 1H, CHAr), 7.42–7.50 (m, 4H, Ar-H), 8.14 (s, 1H, thiazole-H), 8.16 (s, 1H, thiaole-H); Anal.

calcd. for $C_{21}H_{17}Cl_2N_5O_3S_3$: C 45.49, H 3.09, N 12.63; found: C 45.67, H 3.15, N 12.78.

Ethyl 1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-(4-tolyl)-1,6-dihydropyrimidin-5-yl]carboxylate (2g)

Yellow crystals, yield 75%, m.p. 148–149°C; IR (KBr): 3091 (Ar-H), 1664 (C=O), 1602, 1558 (C=N), 1500, 1422 cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.17 (t, J = 8 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.98–4.02 (m, 2H, OCH_2), 4.30 (d, J = 15.6 Hz, 1H, SCH_2), 4.34 (d, J = 10.0 Hz, 1H, NCH_2), 4.49 (d, J = 10.4 Hz, 1H, NCH_2), 4.66 (d, J = 16.0 Hz, 1H, SCH_2), 5.25 (s, 1H, CHAr), 7.11–7.27 (m, 4H, Ar-H), 7.41 (s, 1H, thiazole-H), 7.45 (s, 1H, thiaole-H); Anal. calcd. for $C_{23}H_{22}Cl_2N_4O_2S_3$: C 49.90, H 4.01, N 10.02; found: C 60.81, H 4.07, N 9.83.

Ethyl 1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-4-methyl-6-phenyl-1,6-dihydropyrimidin-5-yl]carboxylate (2h).

Yellow crystals, yield 75%, m.p. 136–138°C; IR (KBr): 3084 (Ar-H), 1660 (C=O), 1598, 1558 (C=N), 1501, 1444 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.17 (t, J = 7.6 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.98–4.04 (m, 2H, OCH_2), 4.31 (d, J = 16.4 Hz, 1H, SCH_2), 4.45 (d, J = 10.0 Hz, 1H, NCH_2), 4.53 (d, J = 10.8 Hz, 1H, NCH_2), 4.69 (d, J = 14.8 Hz, 1H, SCH_2), 5.30 (s, 1H, CHAr), 7.27–7.34 (m, 5H, Ar-H), 7.40 (s, 1H, thiazole-H), 7.43 (s, 1H, thiaole-H); EI-MS (70 eV) m/z(%): 538 (M^+, 94), 462 (71.4), 404 (98.7), 275 (68.3), 168 (98.6), 113 (100), 87 (98.7); Anal. calcd. for $C_{22}H_{20}Cl_2N_4O_2S_3$: C 48.98, H 3.74, N 10.38; found: C 48.80, H 3.55, N 10.41.

Ethyl 1-[1-(2-Chlorothiazol-5-yl-methyl)-2-(2-chlorothiazol-5-yl-methylsulfanyl)-6-(4-methoxyphenyl)-4-methyl-1,6-dihydropyrimidin-5-yl]carboxylate (2i)

Yellow crystals, yield 80%, m.p. 118–119°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.18 (t, J = 8 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.98–4.06 (m, 2H, OCH_2), 4.36 (d, J = 15.6 Hz, 1H, SCH_2), 4.48 (d, J = 10.0 Hz, 1H, NCH_2), 4.50 (d, J = 10.8 Hz, 1H, NCH_2), 4.86 (d, J = 16.0 Hz, 1H, SCH_2), 5.22 (s, 1H, CHAr), 6.82–7.27 (m, 4H, Ar-H), 7.41 (s, 1H, thiazole-H), 7.45 (s, 1H, thiaole-H); EI-MS (70 eV) m/z(%): 568 (M^+, 14.1), 523 (12.7), 330 (19.5), 158 (22.5), 132 (100), 87 (13.1); Anal. calcd. for $C_{23}H_{22}Cl_2N_4O_3S_3$: C 48.50, H 3.89, N 9.84; found: C 48.71; H 4.02, N 9.78.

Fungicidal Activity Testing

The fungicidal activity measurement method was adapted from the one described by Molina.[18] The synthesized target compounds were dissolved in 0.5–1.0 mL of DMF to the concentration of 500 mg/L. The solutions (1 mL) were mixed rapidly with thawed potato glucose agar culture medium (9 mL) under 50°C. The mixtures were poured into Petri dishes. After the dished were cooled, the solidified plates were incubated with 4 mm mycelium disk, inverted, and incubated at 28°C for 48 h. Water was used as the blank control. Three replicates of each test were carried out. The mycelial elongation radius (mm) of fungi settlements was measured after 48 h of culture. The growth inhibitory rates were calculated with the following equation: $I = [(C - T)/C] \times 100\%$. Here, I is the growth inhibitory rate (%), and T is the treatment group fungi settlement radius (mm). The results are listed in Table II.

REFERENCES

[1] C. O. Kappe, *Tetrahedron* **49,** 6937 (1993).
[2] C. O. Kappe, *Acc. Chem. Res.*, **33,** 879 (2000).
[3] C. O. Kappe, *Eur. J. Med. Chem.*, **35,** 1043 (2000).
[4] M. M. Ghorab, S. M. Abdel-Gawad, and M. S. A. El-Gaby, *Farmaco*, **55,** 249 (2000).
[5] K. Rana, B. Kaur, and B. Kumar, *Indian J. of Chem*., **43B** (7), 1553 (2004).
[6] M. C. Liu, T. S. Lin, J. G. Cory, A. H. Cory, and A. C. Sartorelli, *J. Med. Chem*., **39,** 2586–2593 (1996).
[7] B. L. Finkelstein, M. A. Martz, C. Strock, *J. Pestic. Sci.*, **50,** 319–323 (1997).
[8] G. Y. Li X. H. Qian, J. N. Cui, Q. C. Huang, R. Zhang, and H. Guan, *J. Agric. Food Chem*., **54,** 125–129 (2006).
[9] Y. W. Jo, W. B. Im, J. K. Rhee, M. J. Shim, W. B. Kim, and E. C. Choi, *Bioorg. Med. Chem*., **12,** 5909–5915 (2004).
[10] C. D. S. Tomlin, *The Pesticide Manual* (British Crop Production Council, Hampshire, 2000) 12th ed., pp. 355–1008.
[11] S. Zhang, A. Phadke, C. Liu, X. Wang, J. Quinn, D. Chen, V. Gadhachanda, S. Li, M. Deshpande, Thiazole compounds and Methods of Use, WO 2 006 122 011, (2006).
[12] C. L. Liu, L. Li, and Z. M. Li, *Bioorg. Med. Chem.*, **12,** 2825 (2004).
[13] (a) R. P. Alexander, P. Aujla, M. J. Batchelor, D. C. Brookings, G. M. Buckley, K. V. L. Crepy, C. L. Kulisha, J. P. Turner, Fused Thiazole Derivatives as Kinase Inhibitors, WO 2 006 114 606, (2006).
(b) Li, G.; Qian, X.; Cui, J.; Huang, Q.; Zhang, R.; Liu, F. *J. Fluorine Chem*. **2006,** 127, 182.
[14] Z. G. Luo and D. Q. Shi, *J. Heterocycl. Chem*., **43,** 1021–1026 (2006).
[15] X. B. Chen, D. Q. Shi, and X. F. Zhu, *Chin. J. Chem.* **25,** 1854–1858 (2007).
[16] G. Sabitha, G. S. K. K. Reddy, C. S. Reddy, and J. S. Yadav, *Synlett*., 858–860 (2003).
[17] K. Kiriyama, S. Kagabu, and K. Nishimura, *J. Pestic. Sci.*, **29,** 43 (2004).
[18] J. Molina-Torres, C. J. Salazar-Cabrera, C. Armenta-Salinas, and E. Ramirez-Chavez, *J. Agric. Food Chem.,* **52,** 4700–4704 (2004).