

Synthesis of 2,3-Dihydro-1,3,4-thiadiazole, Thiazole, and Triazolo[4,3-*a*]pyrimidine Derivatives from Ethyl Benzoylacetate

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ABSTRACT: Thiophene and thiazole derivatives can be obtained from potassium salt of ethyl 3-oxo-3-phenyl-2-[(phenylamino)thioxomethyl]propanoate and ethyl chloroacetate in *N,N*-dimethylformamide solution under different conditions. 2,3-Dihydro-1,3,4-thiadiazoles and triazolo[4,3-*a*]pyrimidine were obtained from reaction of hydrazonoyl halides with each of thioanilide and pyrimidine-2-thione, respectively. Structures of the newly synthesized compounds were elucidated on the basis of elemental analysis, spectral data, and alternative synthesis route whenever possible. © 2004 Wiley Periodicals, Inc. *Heteroatom Chem* 15:107–113, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10222

INTRODUCTION

Thiazoles have found wide use as accelerators in rubber vulcanization and also as antioxidants [1,2]. Also, thioanilides are versatile reagents, which have been used as synthetic intermediate for heterocyclic compounds, which possess expected biological activity [3–6]. As an extension of our study [7–10] and as a part of our program aiming at the synthesis of different thiophenes, thiazoles, and 2,3-dihydro-1,3,4-thiadiazoles, we report here the reactivity of potassium ethyl (2*Z*)-3-(phenylamino)-

2-(phenylcarbonyl)-3-sulfanyprop-2-enoate (**1**) toward ethyl chloroacetate and hydrazonoyl halides.

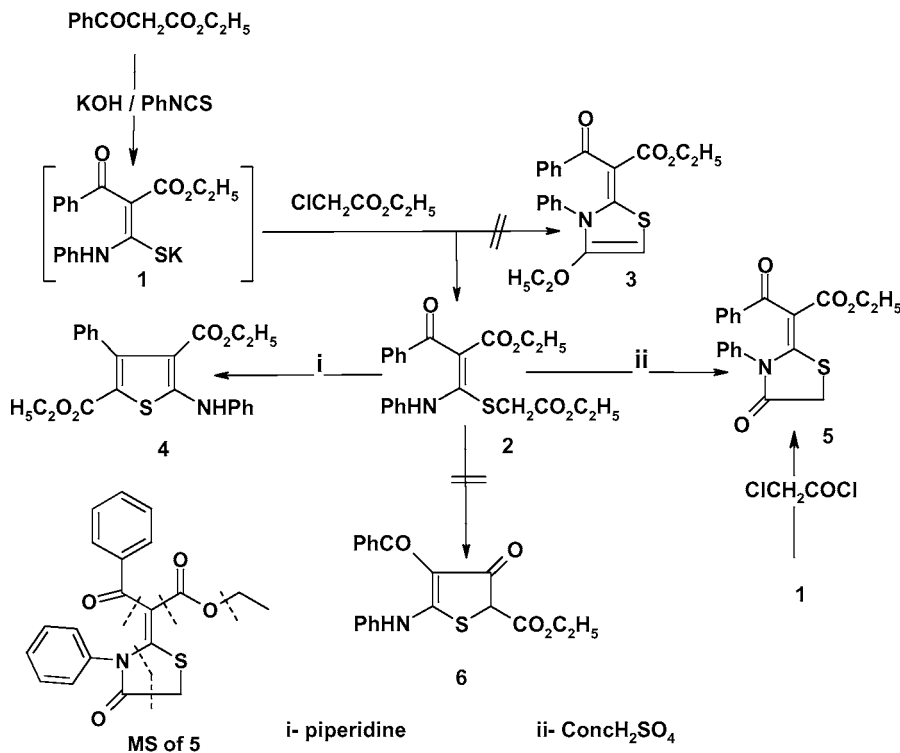
RESULTS AND DISCUSSION

Ethyl 2-(4-ethoxy-3-phenyl(1,3-thiazolin-2-ylidene))-3-oxo-3-phenylpropanoate (**3**) was claimed to be obtained from the reaction of ethyl chloroacetate with **1**, the identity of the product from this reactions has to be reinvestigated. The reaction of **1** with ethyl chloroacetate in *N,N*-dimethylformamide afforded ethyl (2*Z*)-3-[(ethoxycarbonyl)-methylthio]-3-(phenylamino)-2-(phenylcarbonyl)prop-2-enoate (**2**) and not **3** [11]. Structure of **2** was confirmed on the basis of elemental analyses, spectra, and chemical transformation. Thus, ¹H NMR spectrum showed signals at δ = 0.88 (t, 3H, CH₂CH₃), 1.25 (t, 3H, CH₂CH₃), 3.54 (s, 2H, SCH₂), 3.98 (q, 2H, CH₂CH₃), 4.20 (q, 2H, CH₂CH₃), 7.25–7.58 (m, 10H, ArH's), and 10.33 (s, 1H, NH). Its IR (cm⁻¹) spectrum showed bands at 3456 (NH), 1743, 1666 (CO's), and 1542 (C=C).

Compound **2** was converted to ethyl 5-(ethoxycarbonyl)-4-phenyl-2-(phenylamino)thiophene-3-carboxylate (**4**) by boiling in ethanol containing catalytic amount of piperidine, and ethyl 3-oxo-2-[4-oxo-3-phenyl(1,3-thiazolidin-2-ylidene)]-3-phenylpropanoate (**5**) by treatment with conc. sulfuric acid (Scheme 1).

Structures **4** and **5** were confirmed on the basis of elemental analyses, spectra, and alternative synthesis. ¹H NMR spectrum of **4** showed signals at δ = 0.77 (t, 3H, CH₂CH₃), 1.02 (t, 3H, CH₂CH₃), 3.95 (q, 2H,

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SCHEME 1

CH_2CH_3), 4.04 (q, 2H, CH_2CH_3), 7.16–7.45 (m, 10H, ArH's), and 10.54 (s, br, 1H, NH). Its IR (cm^{-1}) revealed bands at 3163 (NH), 1712, 1666 (CO's), and 1596 ($\text{C}=\text{C}$). ^1H NMR spectrum of **5** showed signals at $\delta = 1.01$ (t, 3H, CH_2CH_3), 3.89 (s, 2H, CH_2), 4.13 (q, 2H, CH_2CH_3), and 6.82–7.46 (m, 10H, ArH's). Its IR (cm^{-1}) revealed bands at 1712, 1666 (CO's), and 1596 ($\text{C}=\text{C}$). MS spectrum of **5** showed peaks m/e 367, 291, 262, 234, 227, 190, 144, 105, and 77. More evidence for structure **5** was obtained via reaction of **1** with chloroacetyl chloride, which afforded identical product in all respects (mp., mixed mp., and spectra) with compound **5**, and structure **6** was ruled out.

Also, compound **1** reacted with *C*-ethoxycarbonyl-*N*-phenylhydrazonoyl chloride **7a** to afford **9a** and ethyl 2-[5-(ethoxycarbonyl)-3-phenyl(1,3,4-thiadiazolin-2-ylidene)]-3-oxophenylpropanoate (**10a**) not as claimed [11] (Scheme 2). The reaction takes place through intermediate **8**, which converted to **10** via elimination of aniline [12] or **9** via elimination of probably **11**. Structure **9a** was elucidated on the basis of elemental analyses, spectral data, and authentic sample [12]. ^1H NMR spectrum of **10a** showed signals at $\delta = 0.85$ (t, 3H, CH_2CH_3), 1.39 (t, 3H, CH_2CH_3), 3.59 (q, 2H, CH_2CH_3), 4.47 (q, 2H, CH_2CH_3), and 7.26–7.47 (m, 10H, ArH's). Mass spectrum of **10a** showed peaks at m/z 424, 351, 291, 270, 219, 146, 105, and 77. Analogy, *C*-acetyl-*N*-

phenylhydrazonoyl chloride reacted with **1** to afford **9b** and **10b**.

Compound **5** reacted with arenediazonium chloride in pyridine to give ethyl 2-[5-[aza(aryl-amino)methylene]-4-oxo-3-phenyl(1,3-thiazolidin-2-ylidene)]-3-oxo-3-phenylpropanoate (**13a** and **13b**) (Scheme 3). Structure of **13** was confirmed on the basis of elemental analysis and spectral data. Thus, ^1H NMR spectrum of **13b** showed signals at $\delta = 1.03$ (t, 3H, CH_2CH_3), 2.31 (s, 3H, $4\text{-CH}_3\text{C}_6\text{H}_4$), 4.14 (q, 2H, CH_2CH_3), 6.91–8.04 (m, 14H, ArH's), and 10.92 (s, 1H, NH).

Compound **5** reacted with the appropriate (methylene)methane-1,1-dicarbonitrile in reflux ethanol containing catalytic amount of piperidine to yield ethyl 3-oxo-2-[4-oxo-3-phenyl-5-(arylmethylene)(1,3-thiazolidin-2-ylidene)]-3-phenylpropanoates (**16**) and not ethyl 2-[5-amino-6-cyano-3,7-diphenyl(3,4,7,3a,7a-pentahydro-4-oxabenzothiazol-2-ylidene)]-3-oxo-3-phenylpropanoates **15** on the basis of elemental analysis, spectral data, and alternative synthesis. Thus, ^1H NMR spectrum of **16b** showed signals at $\delta = 1.03$ (t, 3H, CH_2CH_3), 2.43 (s, 3H, $4\text{-CH}_3\text{C}_6\text{H}_4$), 4.12 (q, 2H, CH_2CH_3), and 7.26–7.75 (m, 15H, ArH's and $=\text{CH}$). Its IR (cm^{-1}) revealed bands at 3028, 2900 (CH), 1706, 1693, 1674 (CO's), and 1596 ($\text{C}=\text{C}$) and no bands at 3100–3300 and 2000–2300 attributed the absence of each of

NH₂ and CN groups [13]. MS spectrum of **16c** revealed peaks *m/e* at 490, 489, 418, 416, 339, 338, 314, 312, 248, 247, 169, 168, 133, 266, 105, and 77.

Compound **5** reacts with the appropriate aldehydes in ethanol containing catalytic amount of piperidine afforded identical product in all respects (mp., mixed mp., and spectra) with the appropriate **16a–d** (Scheme 3).

In contrast, compound **5** reacted with (2-furylmethylene)methane-1,1-dicarbonitrile in reflux ethanol in presence of catalytic amount of piperidine to give ethyl 2-[(7R)-5-amino-6-cyano-7(2-furyl)-3-phenyl(4H-pyrano[2,3-*d*]1,3-thiazolidin-2-ylidene)]-3-oxo-3-phenylpropanoate (**15a**). Structure of the latter was confirmed on the basis of elemental analysis and spectral data. Its ¹H NMR spectrum showed signals at δ = 0.91 (t, 3H, CH₂CH₃), 4.04 (q, 2H, CH₂CH₃), 6.42 (s, 1H, pyran C-4), 6.49–7.53 (m, 13H, ArH's and furan protons), and 8.12 (s, br, 2H, NH₂).

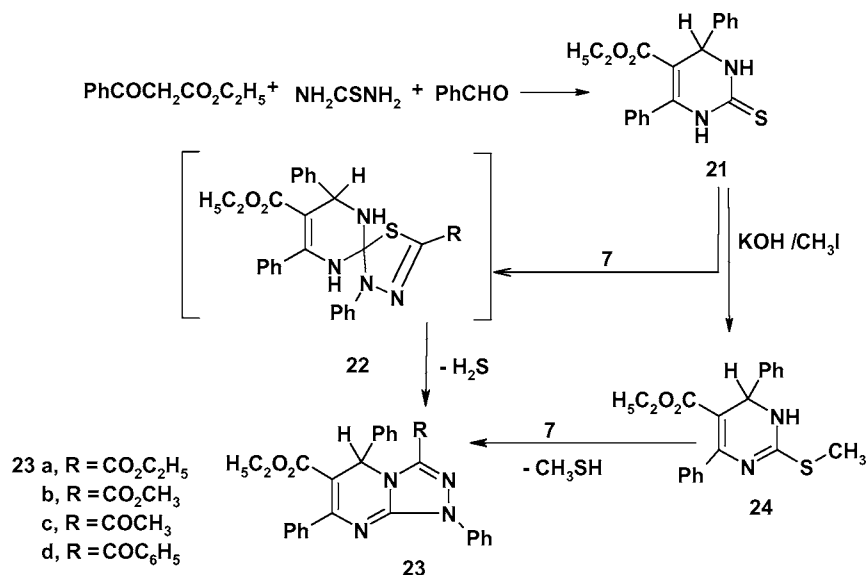
Also, treatment of **5** with phenyl isothiocyanate in presence of potassium hydroxide to give thioanilide **17**, which converted to 2,3-dihydro-1,3,4-thiadiazoles **20a–d**, respectively via its reaction with the appropriate hydrazoneyl halides **7a–d** (Scheme 3). Structure **20** was confirmed on the basis of elemental analysis, spectral data, and alternative route. ¹H NMR spectrum of **20b** showed signals at δ = 1.24 (t, 3H, CH₂CH₃), 2.41 (s, 3H, CH₃CO), 4.19 (q, 2H, CH₂CH₃), and 6.84–7.81 (m, 15H, ArH's).

Also, methyl carbodithioate **18** (which was prepared via reaction of **5** with carbon disulfide in *N,N*-dimethylformamide solution containing potassium

hydroxide followed by iodomethane) reacted with **7b** in ethanolic triethylamine to give product identical in all respects (mp., mixed mp., and spectra) with **20b**.

Finally, the appropriate hydrazoneyl chloride **7a** reacts with ethyl 4,6-diphenyl-2-thioxo-1,3,6-trihydropyrimidine-5-carboxylate **21** [14] in refluxed chloroform solution in presence of triethylamine to give ethyl 5-(ethoxycarbonyl)-1,4,6-trihydro-4,3a-dihydro-1,2,4-triazolino[4,3-*a*]pyrimidine-3-carboxylate (**23a**). Structure of **23** was elucidated on the basis of elemental analysis, spectral data, and alternative synthesis. ¹H NMR spectrum of **23a** showed signals at δ = 0.92 (t, 3H, CH₂CH₃), 1.30 (t, 3H, CH₂CH₃), 3.90 (q, 2H, CH₂CH₃), 4.39 (q, 2H, CH₂CH₃), 5.68 (s, 1H, pyrimidine C-4), and 6.85–8.25 (m, 15H, ArH's). Thus, ethyl 2-methylthio-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (**24**), which was prepared via methylation of **21** with iodomethane in presence of sodium methoxide, reacted with **7a** to give identical product in all respects (mp., mixed mp., and spectra) with **23a** (Scheme 4). Similarly, the appropriate hydrazoneyl halides **7b–d** react with **21** or **24** to afford **23b–d** respectively.

The formation of **23** can be explained via 1,3-dipolar cycloaddition or 1,3-addition of nitrile imide (prepared in situ from hydrazoneyl halides **7** with triethylamine or sodium ethoxide) to C=S of pyrimidine-2-thione **21** to give intermediate **22**, with ring opening and ring closure to afford the final products **23** by elimination of hydrogen sulfide (Scheme 4).



SCHEME 4

EXPERIMENTAL

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FT-IR 8201 PC spectrophotometer. ^1H NMR spectra were recorded in CDCl_3 and $(\text{CD}_3)_2\text{SO}$ solutions on a Varian Gemini 300 MHz spectrometer and chemical shifts were expressed in δ units using TMS as internal reference. Mass spectra were recorded on a GC-MS, HB, 5988A. Elemental analyses were carried out at the Microanalytical Center of the Cairo University. Hydrazonoyl halides **7a–d** were prepared as previously reported [15–19].

Ethyl (2Z)-3-[(Ethoxycarbonyl)methylthio]-3-(phenylamino)-2-(phenylcarbonyl)prop-2-enoate (2)

A mixture of ethyl benzoylacetate (1.92 g, 0.01 mol), phenyl isothiocyanate (1.35 g, 0.01 mol), and potassium hydroxide (0.56 g, 0.01 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h at room temperature. Ethyl chloroacetate (1.2 g, 0.01 mol) was added and stirring was continued for 2 h. The reaction mixture was diluted with water and the solid precipitate was collected and crystallized from ethanol to give **2** (Table 1).

Ethyl 5-(Ethoxycarbonyl)-4-phenyl-2-(phenylamino)thiophene-3-carboxylate (4)

Compound **2** (1 g) was refluxed in ethanol (20 ml) containing 2 drops of piperidine for 1 h. The reaction mixture was cooled and the resulting solid was collected and crystallized from ethanol to give **4** (Table 1).

Ethyl 3-Oxo-2-[4-oxo-3-phenyl(1,3-thiazolidin-2-ylidene)]-3-phenylpropanoate (5)

Method A. A mixture of ethyl benzoylacetate (1.92 g, 0.01 mol), phenyl isothiocyanate (1.35 g, 0.01 mol), and potassium hydroxide (0.56 g, 0.01 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h at room temperature. Chloroacetylchloride (1.12 g, 0.01 mol) was added and stirring was continued for 2 h. The reaction mixture was diluted with water, the solid precipitate was collected and crystallized from ethanol to give **5** (Table 1).

Method B. A mixture of **2** (1 g) in conc. sulfuric acid (10 ml) was stirred for 1 h at room temperature, and then poured onto crushed ice (30 g). The resulting solid was collected by filtration, washed with water, and crystallized from ethanol to give **5**.

TABLE 1 Characterization Data of the Newly Synthesized Compounds

Compd. No.	mp. ($^{\circ}\text{C}$), Solvent	Color, Yield (%)	Mol. Formula (Mol. Wt.)	Calcd ^a (%)			
				C	H	N	S
2	137–140, EtOH	White, 55	$\text{C}_{22}\text{H}_{23}\text{NO}_5\text{S}$ (413.50)	63.91 (64.00)	5.61 (5.70)	3.39 (3.40)	7.75 (7.80)
4	98–100, EtOH	White, 75	$\text{C}_{22}\text{H}_{21}\text{NO}_4\text{S}$ (395.48)	66.82 (66.80)	5.35 (5.30)	3.54 (3.50)	8.11 (8.10)
5	175–177, EtOH	Yellow, 79	$\text{C}_{20}\text{H}_{17}\text{NO}_4\text{S}$ (367.43)	65.38 (65.20)	4.66 (4.50)	3.81 (3.70)	8.73 (8.60)
10a	143–146, EtOH	Yellow, 80	$\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_5\text{S}$ (424.48)	62.25 (62.30)	4.75 (4.60)	6.60 (6.50)	7.55 (7.50)
10b	197–198, EtOH	Yellow, 75	$\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ (394.45)	63.95 (63.80)	4.60 (4.40)	7.10 (6.90)	8.13 (8.10)
13a	208–210, EtOH	Brown, 75	$\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$ (471.54)	66.23 (66.20)	4.49 (4.30)	8.91 (8.80)	6.80 (6.60)
13b	242–244, EtOH	Orange, 73	$\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4\text{S}$ (485.57)	66.79 (66.80)	4.77 (4.80)	8.65 (8.70)	6.60 (6.60)
15a	255–257, EtOH	Brown, 77	$\text{C}_{28}\text{H}_{21}\text{N}_3\text{O}_5\text{S}$ (511.56)	65.74 (65.60)	4.14 (4.00)	8.21 (8.30)	6.27 (6.40)
16a	219–220, Dioxane	Yellow, 85	$\text{C}_{27}\text{H}_{21}\text{NO}_4\text{S}$ (455.54)	71.19 (71.00)	4.65 (4.60)	3.07 (3.00)	7.04 (7.00)
16b	257–260, Dioxane	Yellow, 83	$\text{C}_{28}\text{H}_{23}\text{NO}_4\text{S}$ (469.56)	71.62 (71.60)	4.94 (4.90)	2.98 (3.00)	6.83 (6.80)
16c	265–267, Dioxane	Yellow, 87	$\text{C}_{27}\text{H}_{20}\text{ClNO}_4\text{S}$ (489.98)	66.19 (66.00)	4.11 (4.00)	2.86 (2.90)	6.54 (6.50)
16d	237–239, Dioxane	Orange, 85	$\text{C}_{25}\text{H}_{19}\text{NO}_4\text{S}_2$ (461.56)	65.06 (65.00)	4.15 (4.00)	3.03 (3.00)	13.89 (14.00)
17	153–155, EtOH	Orange, 75	$\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$ (502.62)	64.52 (64.30)	4.41 (4.20)	5.57 (5.50)	12.76 (12.50)
18	285–286, DMF	Yellow, 56	$\text{C}_{23}\text{H}_{19}\text{NO}_4\text{S}_3$ (457.59)	57.75 (57.60)	4.19 (4.00)	3.06 (3.00)	21.02 (21.00)
19	165–167, EtOH	Yellow, 80	$\text{C}_{23}\text{H}_{21}\text{NO}_4\text{S}_3$ (471.62)	58.58 (58.50)	4.49 (4.40)	2.97 (3.00)	20.40 (20.40)
20a	265–266, EtOH	Yellow, 85	$\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_6\text{S}_2$ (599.69)	62.09 (62.00)	4.20 (4.00)	7.01 (7.00)	10.69 (10.60)
20b	257–260, AcOH	Orange, 75	$\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_5\text{S}_2$ (569.66)	63.25 (63.20)	4.07 (4.10)	7.38 (7.20)	11.26 (11.20)
20c	278–280, DMF	Violet, 85	$\text{C}_{35}\text{H}_{25}\text{N}_3\text{O}_5\text{S}_2$ (631.73)	66.55 (66.30)	3.99 (4.00)	6.65 (6.40)	10.15 (10.00)
20d	283–285, DMF	Yellow, 83	$\text{C}_{35}\text{H}_{26}\text{N}_4\text{O}_5\text{S}_2$ (646.75)	65.00 (65.00)	4.05 (4.00)	8.66 (8.60)	9.92 (9.90)
23a	146–148, EtOH	Yellow, 85	$\text{C}_{29}\text{H}_{26}\text{N}_4\text{O}_4$ (494.55)	70.43 (70.30)	5.30 (5.20)	11.33 (11.20)	
23b	129–130, EtOH	Yellow, 80	$\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}_4$ (480.53)	69.99 (70.00)	5.03 (5.00)	11.66 (11.60)	
23c	149–151, EtOH	Yellow, 83	$\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}_3$ (464.53)	72.40 (72.30)	5.21 (5.10)	12.06 (12.00)	
23d	159–161, EtOH	Orange, 75	$\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_3$ (526.00)	75.27 (75.10)	4.98 (5.00)	10.64 (10.60)	
24	156–157, EtOH	White, 80	$\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ (352.46)	68.16 (68.00)	5.72 (5.60)	7.95 (8.00)	9.10 (9.00)

^aThe values given in parentheses indicate found value.

Ethyl 2-[5-Substituted-3-phenyl(1,3,4-thiadiazolin-2-ylidene)]-3-oxophenylpropanoates 10a,b

A mixture of ethyl benzoylacetate (1.92 g, 0.01 mol), phenyl isothiocyanate (1.35 g, 0.01 mol), and potassium hydroxide (0.56 g, 0.01 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h at room temperature. The appropriate hydrazoneyl chlorides **7a,b** (0.01 mol) was added and stirring was continued for 4 h. The reaction mixture was diluted with water; the resulting solid was collected to give **9a** and **10a**, and the filtrate was diluted with water to give **9b** and **10b**, respectively (Table 1).

Ethyl 2-{5-[Aza(arylamino)methylene]-4-oxo-3-phenyl(1,3-thiazolidin-2-ylidene)}-3-oxo-3-phenylpropanoates 13a,b

An aqueous solution of the appropriate arenediazonium chloride (0.005 mol) was added portionwise to a stirred solution of **5** (1.8 g, 0.005 mol) in pyridine (30 ml) at 0°C. The reaction mixture was stirred for 3 h, the resulting solid was collected, washed with water, and crystallized from ethanol to give **13a,b** respectively (Table 1).

Ethyl 3-Oxo-2-[4-oxo-3-phenyl-5-(arylmethylene)-(1,3-thiazolidin-2-ylidene)]-3-phenylpropanoates 16a-d

A mixture of **5** (1.8 g, 0.005 mol) and the appropriate aldehydes (0.005 mol) in ethanol (20 ml) containing catalytic amount of piperidine was refluxed for 1 h. The resulting solid was collected and crystallized from dioxane to give **16a-d** (Table 1).

Ethyl 3-Oxo-2-[4-oxo-3-phenyl-5-[(phenylamino)thioxomethyl](1,3-thiazolidin-2-ylidene)]-3-phenylpropanoate (17)

A mixture of **5** (1.8 g, 0.005 mol), phenyl isothiocyanate (0.65 g, 0.005 mol), and potassium hydroxide (0.28 g, 0.005 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h. The reaction mixture was diluted with water and acidified with acetic acid. The solid was collected and crystallized from ethanol to give **17** (Table 1).

Methyl Carbodithioates 18 and 19

A mixture of **5** (1.8 g, 0.005 mol), carbon disulfide (0.38 g, 0.005 mol), and potassium hydroxide (0.28 g, 0.005 mol) or (0.56 g, 0.01 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h. Iodomethane (0.7 g, 0.005 mol) or (1.4 g, 0.01 mol)

was added and stirring was continued for 2 h. The reaction mixture was diluted with water; the so formed solid was collected and crystallized from ethanol to give **18** and **19**, respectively (Table 1).

2,3-Dihydro-1,3,4-thiadiazoles 20a-d

A mixture of **5** (1.8 g, 0.005 mol), phenyl isothiocyanate (0.65 g, 0.005 mol), and potassium hydroxide (0.28 g, 0.005 mol) in *N,N*-dimethylformamide (20 ml) was stirred for 3 h at room temperature. The appropriate hydrazoneyl halides **7a-d** (0.005 mol) was added and stirring was continued for 2 h. The reaction mixture was diluted with water and the resulting solid was collected and crystallized from the proper solvent to afford 2,3-dihydro-1,3,4-thiadiazoles **20a-d**, respectively (Table 1).

Ethyl 2-Methylthio-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (24)

Iodomethane (0.006 mol) was added portionwise with stirring to a mixture of compound **21** (0.005 mol) and sodium ethoxide solution [prepared by dissolving sodium metal (0.11 g atom, 0.005 mol)] in ethanol (20 ml) for 4 h. The reaction mixture was left overnight at room temperature and then the precipitate was collected and crystallized from ethanol to give **24** (cf. Table 1). Its ¹H NMR spectrum showed signals at δ = 1.30 (t, 3H, CH₂CH₃), 2.00 (s, 3H, CH₃), 4.20 (q, 2H, CH₂CH₃), 4.59 (s, 1H), 7.04–7.30 (m, 10H, ArH's), and 9.56 (s, 1H, NH).

Ethyl 5-Substituted-1,4,6-trihydro-4,3a-dihydro-1,2,4-triazolino[4,3-a]pyrimidine-3-carboxylates 23a-d

Method A. A mixture of **21**, the appropriate hydrazoneyl halides **7a-d**, and triethylamine (0.005 mol, each) in chloroform (20 ml) was refluxed for 10 h, then the solvent was evaporated under reduced pressure. The oil residue was triturated with ethanol (10 ml). The resulting solid was collected and crystallized from ethanol to give **23a-d** (Table 1).

Method B. A mixture of **24**, the appropriate hydrazoneyl halides **7a-d**, and triethylamine (0.005 mol, each) in ethanol was refluxed for 2 h. The resulting solid was collected and crystallized from ethanol to give **23a-d**, respectively (Table 1).

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