A One-Pot Synthesis of 2,3-Dihydro-2-Thioxothieno[2,3-*d*]Thiazoles

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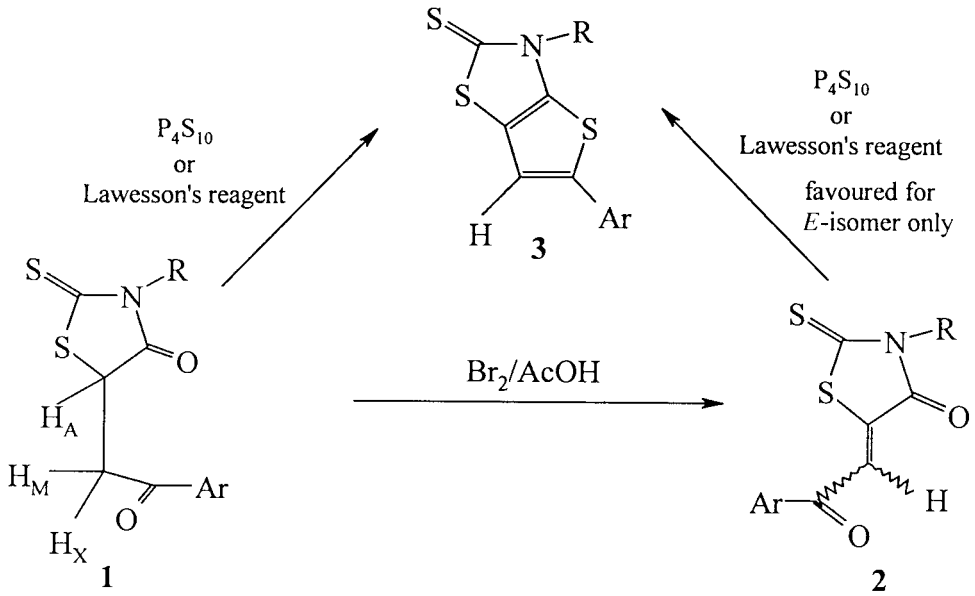
Abstract: A variety of 3,5-disubstituted-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazoles **3a–h** including alkyl-, aryl- and heteryl- substituents were synthesized in excellent yields in a one pot reaction between 3-substituted-5-(2-aryl (or heteryl)-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidines **1a–h** and either tetraphosphorous decasulfide (Method A) or Lawesson's reagent (Method B). However, fair yields of **3** were also obtained along with unknown oily products when the (*E,Z*)-5-(2-aryl-2-oxoethylidene) derivatives **2f, g** were similarly treated with the same reagents. Structures of products were supported by microanalytical and spectral evidence. A rationalization for the route of conversion is given.

Key words: 1,3-thiazolidines, thionation, 1,2-dithiines, thiazoles, fused thieno-bithienyls, sulfur, heterocycles

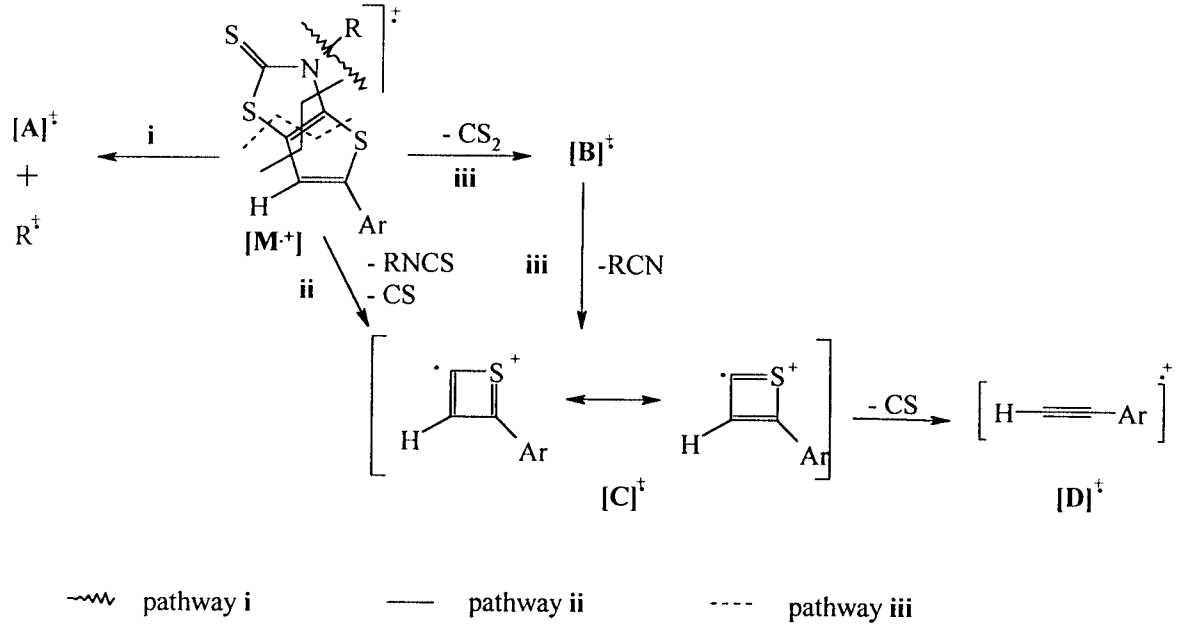
Several multistep methods have been adopted for the synthesis of thieno[2,3-*d*]thiazoles, most of them starting from thiophenes,[1–13] and few of which from thiazole derivatives.[14,15] The present work is aimed to present a new and easy one-pot synthesis of this ring system starting from the readily accessible, well crystalline compounds, namely 3-substituted-5-(2-aryl-2-oxoethyl)-2-thioxo-4-oxo-1,3-thiazolidines **1a–g,** as well as the respective 5-(2-aryl-2-oxoethylidene) derivatives **2f, g** by reacting them with tetraphosphorous decasulfide or Lawesson's reagent Scheme 1). Compounds **1a–g** were synthesized following the method of Nagase[16] by treating the respective aroylpropenoic acids with ammonium aryldithiocarbamates, whereas compounds **2f, g** were obtained by the reaction of **1f, g** with bromine in glacial acetic acid. Structures of **1** and **2** were based on analytical and spectral evidence. The AMX pattern exhibited in the ^{1}H NMR spectra of compounds **1**, has been collapsed into olefinic singlets in com-



	R	Ar
a	C_6H_5	C_6H_5
b	C_6H_5	4-MeC_6H_4
c	C_6H_5	2-Thienyl
d	4-MeC_6H_4	2-Thienyl
e	4-MeC_6H_4	4-BrC_6H_4
f	4-MeC_6H_4	4-MeC_6H_4
g	4-ClC_6H_4	4-MeC_6H_4
h	$C_6H_5CH_2$	4-BrC_6H_4

Synthesis of **3a–h**

Scheme 1



Fragmentation pathways of compounds **3a–h**

Scheme 2

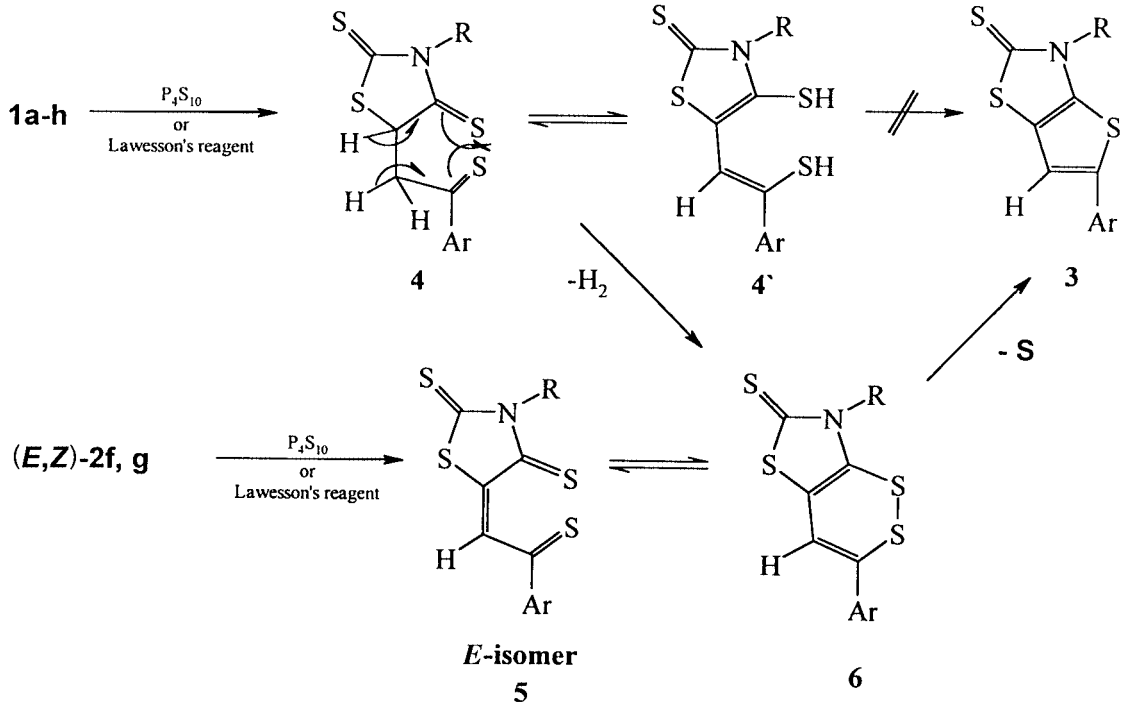
pounds **2**. Compounds **2** are undoubtedly mixtures of *E*- and *Z*-isomers and the integrated proton ratios of the olefinic singlets showed that in the cases of **2f** and **g** the *Z*-isomer constitutes 50% of (*E*,*Z*)-**2f** and 19% of (*E*,*Z*)-**2g**, respectively. Configurational assignments are based on the assumption that the olefinic protons of the *Z*-configurated isomers are more deshielded as compared with the *E*-counterparts. This relationship is an accepted assumption in the elucidation of configuration of arylidene derivatives of many heterocycles.[17]

Thus, thionation of **1a–h** and (*E*,*Z*)-**2f, g** with tetraphosphorous decasulfide or Lawesson's reagent in xylene for 3 hours produced excellent yields of the respective 3,5-disubstituted 2,3-dihydro-2-thioxothieno[2,3-*d*]thiazoles **3a–h**, in the former case, and in relatively lower yields, for the latter one. The structures of **3a–h** were deduced from microanalytical and spectral evidence. The IR spectra of **3** are devoid of any C=O absorption and the ^{1}H NMR spectra show neither the AMX pattern of **1** nor the olefinic proton of **2**. Compounds **3** show molecular ion peaks as base peaks except **3h** where the [R$^{\cdot+}$] fragment presents the base peak (Table). The abundant fragments [R$^{\cdot+}$] and [M$^{\cdot+}$-R] could be produced through the cleavage presented in pathway **i**. Although, formation of the frag-

Table EI-MS Data of 5-Substituted 3-Aryl-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazoles **3a–h**

Compound	Fragments *m*/*z* (%)					
	[M]$^{\cdot+}$	[A]$^{\cdot+}$	[B]$^{\cdot+}$	[C]$^{\cdot+}$	[D]$^{\cdot+}$	R$^{\cdot+}$
3a	325 (100)	248 (16.5)	249 (10.5)	146 (50.9)	102 (28.3)	77 (57.8)
3b	339 (100)	262 (14.8)	263 (13.4)	160 (38.9)	116 (12.9)	77 (35.7)
3c	331 (100)	254 (23.8)	255 (12.6)	152 (40.8)	108 (35.5)	77 (53)
3d	345 (100)	254 (14.2)	269 (8.9)	152 (31.2)	108 (23.7)	91 (25.1)
3e	417 (88.1) 419 (100)[a]	326 (5.8) 328 (6.6)[a]	341 (3.6) 343 (3.9)[a]	224 (18.2) 226 (17.9)[a]	180 (7.6) 182 (7.3)[a]	91 (58.5)
3f	353 (100)	262 (16.4)	277 (5)	160 (31.3)	116 (11.7)	91 (31.6)
3g	373 (100) 375 (53.5)[a]	262 (37.1)	279 (2.8)	160 (57.5)	116 (28.9)	111 (36.2) 113 (16.4)[a]
3h	417 (8.5) 419 (8.8)[a]	326 (14.0) 328 (14.1)[a]	341 (3.5) 343 (3.47)[a]	224 (20.3) 226 (20.5)[a]	180 182[a]	91 (100)

[a] M$^{\cdot+}$+ 2 peaks.

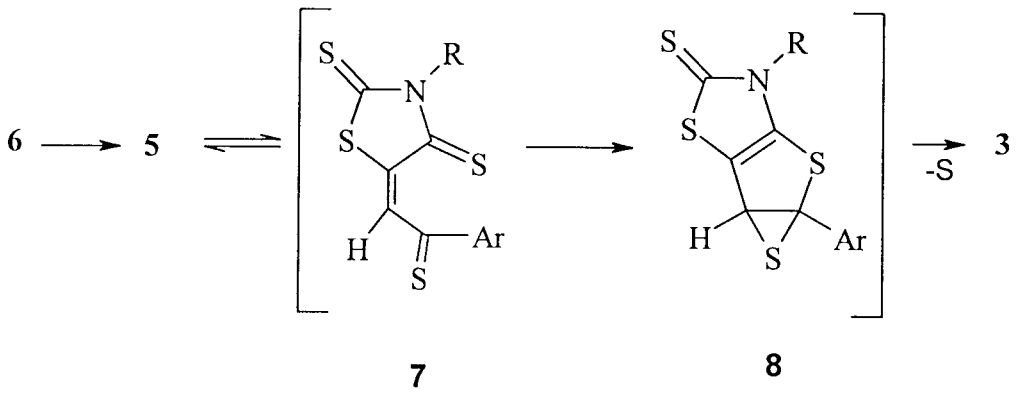


Conversion of compounds **1** and **2** into thiophenes **3**

Scheme 3

ment [$C^{\cdot+}$] could be rationalized in terms of the cleavage presented in pathway **ii**, formation via pathway **iii** is not excluded as fragments [$B^{\cdot+}$], although less abundant, are recorded in most examples. The pathways **i**–**iii** are presented in Scheme 2.

It has been postulated that the conversion of **1**, into the respective thienothiazoles **3** upon treating with tetraphosphorous decasulfide or with Lawesson's reagent has occurred via the 1,4-dithiono derivatives **4** as sulfurization of amido and enolizable carbonyl groups is well documented.[18–20] Although, the conversion **4** → **3** through the dienedithiol **4'** seems to be reasonable in terms of the ease conversion of (*Z*,*Z*)-buta-1,3-diene-1,4-dithiols into the respective thiophenes[21] by heat, the successful conversion of **2f, g** into fair yields of the respective **3** along with oily mixtures containing sulfur, shed doubt on this assumption, as the 1,4-dithioxo derivatives **5**, which are believed to be first formed, are unable to exist in the dienedithiol form **4'**. Taking into consideration the recent advances in the chemistry of 1,2-dithiines, where a sulfur atom is easily extruded either in solutions under mild conditions or under condition of the mass spectroscopic fragmentation to produce thiophenes,[21] the conversion of **4** → thiazolodithiines **6** → **3** seems probable. The conversion **4** → **6** has occurred, most likely, via a dehydrogenative single electron cyclization step.



A possible route for the sulfur extrusion from **6**

Scheme 4

The predominance of **6** versus the ring opened form **5** seems comparable with the preference of the enethiols **4'** versus the butane-1,4-dithiones **4**.

Conversion of (*E,Z*)-**2** into fair yields of **3** could be rationalized in terms of the configuration around the exocyclic double bond as only the *E*-isomers have the proper orientation to cyclize to **6** which is then converted into **3**. This is manifested experimentally in the relative higher yield of **3f** as compared with **3g** as the *E*-isomers constitute 50% and 21% of the *E,Z*-mixtures of **2f** and **2g**, respectively.

A rationalization for the sulfur extrusion from **6** is represented in Scheme **4**, in which the ring opened valence isomer **5** undergoes, in the twisted form **7,** an intramolecular $[\pi^4+\pi^2]$ cycloaddition to the episulfide in an irreversible final step. This stabilization process parallels the sulfur extrusion in thiepene via thianorcaradien.[22] Successful isolation of episulfides has been reported upon short irradiation of dithiines with visible light at −70 °C.[23]

In summary, the method presented represents a new mild, simple and convenient one pot synthesis of a variety of 3,5-disubstituted-2,3-dihydrothieno[2,3-*d*]thiazoles **3** including alkyl-, aryl- and heteryl-substitutents from the readily accessible, well crystalline compounds namely 5-(2-aryl-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidines **1**. The synthesis provides also an easy route to the fused bithienyls **3c, d** of anticipated nematocidal activity.[24]

All melting points are not corrected. IR spectra were measured on a Unicam SP1200 Spectrometer as KBr discs. Unless otherwise stated, the ^{1}H NMR spectra were measured in $CDCl_3$ on Varian Gemini 200 MHz instrument with chemical shifts (δ) expressed in ppm downfield from TMS. Mass spectra were recorded on Shimadzu GC-MS-QP1000EX Instrument operating at 70 eV. Chromatography was carried out with Reidel-de Haen Silica gel S 0.063−0.1 mm on a column with the following dimensions: length = 17 cm and diameter = 1.7 cm. TLC was performed on Merk Kieselgel 60 F_{254} aluminium backed plates. 3-Phenyl-5-(2-phenyl-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidine (**1a**) and 3-benzyl-5-[2-(4-bromophenyl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazolidine (**1h**) were synthesized according to reported methods.[25]

3-Aryl-5-(2-Aryl-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidines 1b-g; General Procedure

Ammonium aryldithiocarbamate (10.0 mmol) was added portionwise to a stirred solution of the respective 3-aroylprop-2-enoic acid[26] in EtOH (10.0 mL) and the mixture was stirred for 30 min at r.t. The solid precipitated after addition of concd HCl (3 mL) and boiling (5 min) was filtered off, washed several times with cold H_2O, air dried and recrystallized from the proper solvent to give colourless crystals of the title compounds.

3-Phenyl-5-[2-(4-methylphenyl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazolidine (1b)

Yield: 3.0 g (88%); mp 158−160 °C (toluene/MeOH).

IR: ν = 3050 (CH=CH arom), 2950, 2920, 2860 (CH), 1735, 1680 (C=O), 1235 (C=S), 810, 750, 700 cm^{-1}.

^{1}H NMR: δ = 7.872 (d, 2 H, $H_{arom,}$ J = 8.4 Hz), 7.62−7.53 (m, 3 H, C_6H_5), 7.45−7.277 (m, 4 H, H_{arom}), 4.742 (dd, 1 H, H_A, J_{AM} = 9.6, J_{AX} = 3.2 Hz), 4.107 (dd, 1 H, H_M, J_{MX} = 18.6, J_{AM} = 9.6 Hz), 3.72 (dd, 1 H, H_x, J_{MX} = 18.6, J_{AX} = 3.2 Hz), 2.43 (s, 3 H, CH_3).

Anal. calcd for $C_{18}H_{15}NO_2S_2$ (341.4): C, 63.32; H, 4.43; N, 4.10. Found: C, 63.39; H, 4.23; N, 3.85.

3-Phenyl-5-[2-(thien-2-yl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazolidine (1c)

Yield: 2.9 g (87%); mp 130−132 °C (toluene/MeOH).

IR: ν = 3040 (CH=CH arom), 2950, 2900 (CH), 1740, 1660 (C=O), 1220 (C=S), 750, 690 cm^{-1}.

^{1}H NMR: δ = 7.775 (dd, 1 H, H-3', $J_{3'-4'}$ = 5.0, $J_{3'-5'}$ = 1.0 Hz), 7.775 (dd, 1 H, H-5', $J_{4'-5'}$ = 3.5, $J_{3'-5'}$ = 1.0 Hz), 7.47−7.62 (m, 3 H, C_6H_5), 7.288 (dd, 2 H, C_6H_5, J = 7.8, 1.8 Hz), 7.18 (dd, 1 H, H-4', $J_{3'-4'}$ = 5.0, $J_{4'-5'}$ = 3.5 Hz), 4.76 (dd, 1 H, H_A, J_{AM} = 9.28, J_{AX} = 4.10 Hz), 4.05 (dd, 1 H, H_M, J_{MX} = 18, J_{AM} = 9.28 Hz), 3.71 (dd, 1 H, Hx, J_{MX} = 18.0, J_{AX} = 4.10 Hz).

Anal. calcd for $C_{15}H_{11}NO_2S_3$ (333.4): C, 54.03; H, 3.73; N, 4.2). Found: C, 54.23; H, 3.43; N, 4.20.

3-(4-Methylphenyl)-5-[2-(thien-2yl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazolidine (1d)

Yield: 2.7 g (78%); mp 141−143 °C (toluene/MeOH).

IR: ν = 3070 (CH=CH arom), 2960, 2900, 2850 (CH), 1735, 1660 (C=O), 1225 (C=S), 840 cm^{-1}.

^{1}H NMR: δ = 7.769 (dd, 1 H, H-5', $J_{4'-5'}$ = 3.8, $J_{3'-5'}$ = 1.0 Hz), 7.737 (dd, 1 H, H-3', $J_{3'-4'}$ = 5.0, $J_{3'-5'}$ = 1.0 Hz), 7.352, 7.163 (2 d, each 2 H_{arom}, J = 8.0 Hz), 7.181 (dd, 1 H, H-4', $J_{3'-4'}$ = 5.0, $J_{4'-5'}$ = 3.8 Hz), 4.731 (dd, 1 H, H_A, J_{AX} = 9.2, J_{AM} = 3.2 Hz), 4.047 (dd, 1 H, H_M, J_{MX} = 18.2, J_{AM} = 3.2 Hz), 3.697 (dd, 1 H, H_X, J_{MX} = 18.2, J_{AX} = 9.2 Hz), 2.424 (s, 3 H, CH_3).

Anal. calcd for $C_{16}H_{13}NO_2S_3$ (347.5): C, 55.31; H, 3.77; N, 4.04. Found: C, 55.15; H, 3.65; N, 4.05.

3-(4-Methylphenyl)-5-[2-(4-bromophenyl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazo-lidine (1e)

Yield: 3.65 (87%); mp 160−162 °C [$CHCl_3$/light petroleum (bp 60−80 ºC)].

IR: ν = 3050 (CH=CH arom), 2940, 2920, 2880 (CH), 1735, 1680, (C=O), 1235 (C=S), 830 cm^{-1}.

^{1}H NMR: δ = 7.84, 7.658 (2 d, each 2 H_{arom}, J = 8.8 Hz), 7.36, 7.16 (2 d, each 2 H_{arom}, J = 8.2 Hz), 4.745 (dd, 1 H, H_A, J_{AM} = 9.4, J_{AX} = 3.2 Hz), 4.09 (dd, 1 H, H_M, J_{MX} = 18.6, J_{AM} = 9.4 Hz), 3.705 (dd, 1 H, H_X, J_{MX} = 18.6, J_{AX} = 3.2 Hz), 2.405 (s, 3 H, CH_3).

Anal. calcd for $C_{18}H_{14}BrNO_2S_2$ (420.3): C, 51.43; H, 3.36; N, 3.33. Found: C, 51.60; H, 3.35; N, 3.37.

3-(4-Methylphenyl)-5-[2-(4-methylphenyl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazo-lidine (1f)

Yield: 3.1 g (87%); mp 143−145°C (toluene/MeOH).

IR: ν = 3020 (CH=CH arom), 2930, 2910 (CH), 1740, 1680, (C=O), 1240 (C=S), 810 cm^{-1}.

^{1}H NMR: δ = 7.87 (d, 2 H_{arom}, J = 8.4 Hz), 7.28, 7.37 (two central peaks of ABq, 4 H_{arom}), 7.2 (d, 2 H_{arom}, J = 8.4 Hz), 4.735 (dd, 1 H, H_A, J_{AM} = 9.6, J_{AX} = 3.2 Hz), 4.15 (dd, 1 H, H_M, J_{MX} = 18.4, J_{AM} = 9.6 Hz), 3.75 (dd, 1 H, H_X, J_{MX} = 18.4, J_{AX} = 3.2), 2.44, 2.425 (2 s, each 3 H, CH_3).

Anal. calcd for $C_{19}H_{17}NO_2S_2$ (355.5): C, 64.20; H, 4.82; N, 3.94. Found: C, 63.82; H, 4.25; N, 4.20.

3-(4-Chlorophenyl)-5-[2-(4-methylphenyl)-2-oxoethyl]-4-oxo-2-thioxo-1,3-thiazolidine (1g)

Yield: 3.25 g (87%); mp 160−162 °C (benzene/MeOH).

IR: ν = 3050 (CH=CH arom), 2940, 2910, 2860 (CH), 1725, 1675, (C=O), 1225 (C=S), 815 cm^{-1}.

^{1}H.NMR: δ = 7.87, 7.305 (2 d, each 2 H_{arom}, J = 8.2 Hz), 7.52, 7.25 (2 d, each 2 H_{arom}, J = 8.6 Hz), 4.731 (dd, 1 H, H_A, J_{AM} = 9.2,

J_{AX} = 3.0 Hz), 4.09 (dd, 1 H, H_M, J_{MX} = 18.6, J_{AM} = 9.2 Hz), 3.74 (dd, 1 H, H_X, J_{MX} = 18.6, J_{AX} = 3.0 Hz), 2.44 (s, 3 H, Me).

Anal. calcd for $C_{18}H_{14}ClNO_2S_2$ (375.9): C, 57.52; H, 3.75; N, 3.73. Found: C, 57.35; H, 3.725; N, 3.65.

(*E*,*Z*)-3-Aryl-5-(2-aryl-2-oxoethylidene)-4-oxo-2-thioxo-1,3-thiazolidines 2f and 2g

A mixture of **1f** or **1g** (3.0 mmol) and Br_2 (3.1 mmol) in glacial AcOH (50 mL) was armed gently for 5 min, during which time HBr gas ceased to evolve. The reaction mixture was concentrated (10 mL), poured into cold H_2O (100 mL) and the precipitated orange-yellow product was filtered off, washed successively with cold H_2O, air dried and recrystallized once from the proper solvent to give (*E*,*Z*)-**2** as orange crystals.

(*E*,*Z*)-3-(4-Methylphenyl)-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-2-thioxo-1,3-thiazolidine (2f)

Yield: 3.4 g (96%); mp 220−222 °C [$CHCl_3$/light petroleum (bp 40−60 °C]

IR: ν = 3060 (CH=CH arom), 1730 (br), 1680 (C=O), 1225 (C=S), 822 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.18−7.50 (m, 6 H_{arom}), 2.395−2.43 each (s, 3 H, CH_3). *E*-isomer (65%): 8.16, (d, 2 H_{arom}, *J* = 8.4 Hz), 8.125 (s, 1 H, =CH). *Z*-isomer (35%): 7.915 (d, 2 H_{arom}, *J* = 8.4 Hz), 8.25 (s, 1 H, =CH).

Anal. calcd $C_{19}H_{15}NO_2S_2$ (353.0): C, 64.57; H, 4.28; N, 3.96. Found: C, 64.42; H, 4.15; N, 3.72.

(*E*,*Z*)-3-(4-Chlorophenyl)-5-[2-(4-methylpheny)-2-oxoethylidene]-4-oxo-2-thioxo-1,3-thiazolidine (2g)

Yield: 3.55 g (95%); mp 282−284 °C (dioxane-toluene).

IR: ν = 3080 (CH=CH arom), 1725 (br), 1675 (C=O), 1220 (C=S), 830 cm^{-1}.

^1H NMR: δ = 7.32−7.54 (m, 4 H_{arom}), 2.40 (s, 3 H, CH_3). *E*-isomer (20%): 8.415, 7.815 (2 d, each 2 H_{arom}, *J* = 8.8 Hz), 8.01 (s, 1 H, =CH). *Z*-isomer (79%): 8.28, 7.69 (2 d, each 2 H_{arom}, *J* = 8.4Hz), 8.14 (s, 1 H, =CH).

Anal. calcd for $C_{18}H_{12}ClNO_2S_2$ (373.5): C, 57.83; H, 3.24; N, 3.75. Found: C, 57.58; H, 3.35; N, 3.75.

3,5-Disubstituted 2,3-Dihydro-2-thioxothieno[2,3-*d*]thiazoles 3a−h (Methods A and B)

A mixture of each of **1a−h** (3.0 mmol) and finely powdered tetraphosphorous decasulfide (0.2 g, 0.45 mmol) (Method A) or Lawesson's reagent[27,28] (1.1 g, 2.7 mmol) (Method B) was refluxed in xylene (25 mL) for 4 h and then poured into H_2O (50 mL). The organic layer was separated, washed successively with H_2O, dried ($CaCl_2$), concentrated (3 mL) and diluted with MeOH (5 mL). The precipitated solid was filtered off, air dried and recrystallized from toluene/MeOH to offer colourless crystals of the title compounds.

3,5-Diphenyl-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3a)

Yield: 2.55 g (79%, Method A), 3.0 g (92%, Method B); mp 163−165 °C.

IR: ν = 3080−3000 (CH=CH arom), 1200 (C=S), 750, 700 cm^{-1}.

^1H NMR: δ = 7.67−7.53 (m, 5 H, C_6H_5), 7.54−7.253 (m, 5 H, C_6H_5), 7.167 (s, 1 H, H-6).

Anal. calcd for $C_{17}H_{11}NS$ (325.5): C, 62.74; H, 3.41; N, 4.30. Found: C, 62.75; H, 3.375; N, 4.29.

3-Phenyl-5-(4-methylphenyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3b)

Yield: 2.95 g (87%, Method A), 3.1 g (91.45%, Method B); mp 163−165 °C.

IR: ν = 3080−3000 (CH=CH_{arom}), 1200 (C=S), 800, 750, 700 cm^{-1}.

^1H NMR: δ = 7.70−7.57 (m, 5 H, C_6H_5), 7.40, 7.215 (2 d, each 2 H_{arom}, *J* = 8.0 Hz), 7.145 (s, 1 H, H-6), 2.395 (s, 3 H, CH_3).

Anal. calcd $C_{18}H_{13}NS_3$ (339.5): C, 63.68; H, 3.86; N, 4.13. Found: C, 63.64; H, 3.71; N, 4.20.

3-Phenyl-5-(2-thienyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3c)

Yield: 2.9 g (88%, Method A), 3.15 g (95%, Method B); mp 161−163 °C.

IR: ν = 3080−3000 (CH=CH arom), 1200 (C=S), 800, 750, 700 cm^{-1}.

^1H NMR: δ = 7.7−7.5 (m, 5 H, C_6H_5), 7.255 (dd, 1 H, H-5', $J_{4'-5'}$ = 4.8, $J_{3'-5'}$ = 0.6 Hz), 7.033 (s, 1 H, H-6), 7.01 (dd, 1 H, H-4', $J_{4'-5'}$ = 4.8, $J_{3'-4'}$ = 3.8 Hz), 6.98 (dd, 1 H, H-3', $J_{3'-4'}$ = 3.8, $J_{3'-5'}$ = 0.6 Hz).

Anal. calcd for $C_{15}H_9NS_4$ (331.5): C, 54.35; H, 2.74; N, 4.23. Found: C, 54.31; H, 2.79; N, 4.21.

3-(4-Methylphenyl)-5-(2-thienyl)-2,3-dihydro-2-thioxothieno [2,3-*d*] thiazole (3d)

Yield: 3.0 g (87%, Method A), 3.15 g (91%, Mehod B); mp 190−192 °C.

IR: ν = 3080−3000 (CH=CH arom), 1200 (C=S), 800 cm^{-1}.

^1H NMR: δ = 7.44, 7.43 (two central peaks of ABq, 4 H_{arom}), 7.25 (dd, 1 H, H-5', $J_{4'-5'}$ = 5.0, $J_{3'-5'}$ = 1.2 Hz), 7.08 (dd, 1 H, H-3', $J_{3'-4'}$ = 3.4, $J_{3'-5'}$ = 1.2 Hz), 7.035 (s, 1 H, H-6), 7.01 (dd, 1 H, H-4', $J_{4'-5'}$ = 5.0, $J_{3'-4'}$ = 3.4 Hz), 2.36 (s, 3 H, CH_3).

Anal. calcd for $C_{16}H_{11}NS_4$ (345.5): C, 55.62; H, 3.21; N, 4.05. Found: C, 55.42; H, 2.93; N, 4.29.

3-(4-Methylphenyl)-5-(4-bromophenyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3e)

Yield: 3.7 g (89%, Method A), 3.9 g (93%, Method B); mp 190−192 °C.

IR: ν = 3080−3000 (CH=CH arom), 1200 (C=S), 800 cm^{-1}.

^1H NMR: δ = 7.58 (central peak of ABq, 4 H_{arom}), 7.38, 7.20 (2 d, each 2 H_{arom}, *J* = 7.8 Hz), 7.125 (s, 1 H, H-6), 2.37 (s, 3, CH_3).

Anal. calcd for $C_{18}H_{12}BrNS_3$ requires: C, 51.57; H, 2.89; N, 3.35. Found: C, 51.75; H, 3.00; N, 3.52.

3,5-Di-(4-Methylphenyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3f)

Yield: 3.0 g (85%, Method A), 3.2 g (91%, Method B); mp 176−178 °C.

IR: ν = 3030 (CH=CH arom), 1200 (C=S), 800 cm^{-1}.

^1H NMR: δ = 7.45, 7.43 (two central peaks of ABq, 4 H_{arom}), 7.37, 7.14 (2 d, each 2 H_{arom}, *J* = 8.0 Hz), 7.11 (s, 1 H, H-6), 2.46, 2.36 (2 s, each 3 H, Me).

Anal. calcd for $C_{19}H_{15}NS_3$ (353.5): C, 64.55; H, 4.28; N, 3.96. Found: C, 64.51; H, 4.21; N, 3.99.

3-(4-Chlorophenyl)-5-(4-methylphenyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3 g)

Yield: 3.15 g (85%, Method A) 3.3 g (89%, Method B), mp 182−184 °C.

IR: ν = 3070 (CH=CH, arom), 1200 (C=S), 790 cm^{-1}.

^1H NMR: δ = 7.505, 7.34 each (2 d, each 2 H_{arom}, *J* = 8.6 Hz), 7.44, 7.43 (two central peaks of ABq, 4 H_{arom}), 7.16 (s, 1 H, H-6), 2.485 (s, 3 H, CH_3).

Anal. calcd for $C_{18}H_{12}ClNS_3$ (373.9): C, 57.82; H, 3.23; N, 3.75. Found: C, 57.78; H, 3.315; N, 3.87.

3-Benzyl-5-(4-bromophenyl)-2,3-dihydro-2-thioxothieno[2,3-*d*]thiazole (3h)

Yield: 3.69g (86%), Method A), 3.75 g (90%, Method B), mp 182−184 °C.

IR: ν = 3060−3030 ($CH=CH_{arom}$), 1200 (C=S), 810, 750, 700 cm^{-1}.

^1H NMR: δ = 7.39, 7.37 (two central peaks of ABq $4H_{arom}$), 7.40−7.50 (m, 5 H, C_6H_5), 7.075 (s, 1 H, H-6), 5.53 (s, 2 H, CH_2Ph).

Anal. calcd $C_{18}H_{12}BrNS_3$ (418.4): C, 51.67; H, 2.89; N, 3.35. Found: C, 51.62; H, 2.78; N, 3.33.

Reaction of 2f and 2g with Tetraphosphorous Decasulfide or Lawesson's Reagent (Methods C and D)

A mixture of **2f** or **2g** (3.0 mmol) and finely powdered tetraphosphorous decasulfide (0.2 g, 0.45 mmol, Method C) or Lawesson's reagent[27,28] (1.1 g, 2.7 mmol, Method D) was refluxed in xylene/dioxane (25 mL, 5:1 v/v) for 4 h, and then poured into H_2O (100 mL). The reddish brown organic layer was separated, washed successively with H_2O, dried (Na_2SO_4), concentrated (to 10 mL) and chromatographed over silica gel. Elution with light petroleum (bp 60−80 °C)/EtOAc (5:1 v/v) gave first the required thienothiazole **3f** and **3g** and then the yellow oily mixtures. Separation was monitored by TLC. Separation and identification of the oily products are still in progress.

3f

Obtained from **2f**; yield: 0.15 g (43%, Method C), 0.17 g, 48%, Method D); mp 176−178 °C ($CHCl_3$/light petroleum (bp 40−60 °C), undepressed on admixture with the sample previously obtained from Methods A and B.

3g

Obtained from **2g**; yield: 0.06 g (16%, Method C), 0.075 g, 20%, Method D); mp 182−184 °C (dioxane/toluene), undepressed on admixture with the sample previously obtained from Methods A and B.

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