

Sulfur-Containing Heterocycles Derived by Reaction of ω -Keto Amides with Lawesson's Reagent

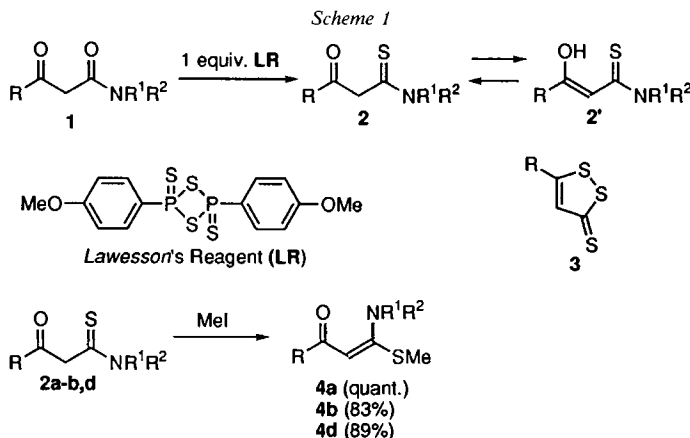
by Takehiko Nishio

Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki, 305-8571 Japan

The reaction of ω -keto amides with Lawesson's reagent (LR: 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide) is described. Treatment of 3-keto amides (2-acylacetamides) **1** with LR gave the corresponding 3-keto thioamides **2**, along with 1,2-dithiole-3-thiones **3**. Treatment of 4-keto amides, 3-acyl propionamides **5**, with LR yielded five-membered heterocycles, pyrroles **6** and/or 2-aminothiophenes **7**. 5-Keto amides, 3-benzoyl butyramides **8**, reacted with LR to give dihydrothiopyran-2-thione **9** as the sole product, but in low yield. 2-Acylbenzamides **10** also reacted with LR to afford 3-mercaptoisindolin-2-ones **11** or dihydroisobenzothiophene-1-thiones **12**.

1. Introduction. – One of the best known thionation reagents is 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, known as Lawesson's reagent (LR) [1]. Use of LR for the chemical conversion of carbonyl to thiocarbonyl compounds [1] and the synthesis of thiophenes from 1,4-dicarbonyl compounds [2] as well as thiazinones and thiazine-thiones from β -(acylamino)- α,β -unsaturated esters [3] have been well-investigated. Recently, we have reported on the direct conversion of alcohols into thiols [4] by treatment of alcohols with LR and novel routes to S-containing heterocycles such as tetrahydrothiophene-2-imines, tetrahydrothiophene-2-thione, tetrahydrothiopyran-2-thiones, dihydrothiazoles, and benzothiazines by the reaction of the substrates containing two functional groups, *e.g.*, ω -hydroxy amides [5] and ω -*N*-(acylamino) alcohols [6] with LR. To extend the use of LR to other bifunctional substrates, we have investigated the reaction of ω -keto amides **1**, **5**, **8**, and **10** with LR, and our results are described in this paper.

2. Results and Discussion. – **2.1. Reaction of 3-Keto Amides 1 with LR.** The reaction of *N*-mono- and *N,N*-disubstituted 3-keto amides (2-acylacetamides) **1** with an equimolar amount of LR in toluene at reflux temperature under Ar for 30 min yielded 3-keto thioamides **2** as a mixture of keto and enol forms, along with 1,2-dithiole-3-thiones **3** (Scheme 1 and Table 1). This result is in contrast to the reaction of the *N*-unsubstituted 3-keto amides yielding phosphorus heterocycles, reported by Pedersen and Lawesson [7]. The structures of 3-keto thioamides **2** were established on the basis of their spectral data, elemental analyses, and chemical evidence (see *Exper. Part*). The 3-keto thioamides **2a**, **b**, and **d** thus obtained were treated with MeI to give the (*Z*)- β -amino- β -(methylthio)- α,β -unsaturated ketones **4a**, **b**, and **d**, respectively, in excellent yields, for which in the $^1\text{H-NMR}$ spectrum a characteristic peak appeared as a broad *singlet* at lower field (12.20–13.52 ppm) due to the amino proton, indicating an intramolecular H-bonding between the CO and RNH groups.

Table 1. Yield of Products **2** and **3**

	R	R ¹	R ²	Yield [%] ^{a)}	
				2 (2') ^{b)}	3
1a	Ph	Ph	H	65 (4:6)	20
1a ^{c)}				63 (4:6)	23
1b	Ph	PhCH ₂	H	59 (5:2)	3
1c	Ph	PhCH ₂	PhCH ₂	33 (1:1)	13
1d	Me	Ph	H	47 (6:4)	3
1d ^{c)}				trace	51

^{a)} Yield of the isolated product. ^{b)} Ratio of the keto/enol forms. ^{c)} In the presence of 2 equiv. of sulfur.

Pedersen and *Lawesson* have already reported that acetanilide **1d** and *N,N*-dimethyl-acetoacetamide reacted with **LR** in the presence of elemental sulfur to yield 1,2-dithiole-3-thiones **3** exclusively [7]. Therefore, the influence of elemental sulfur on the reaction of **1** with **LR** was investigated. The presence of elemental sulfur did not change the product distribution, when 3-keto amide **1a** was treated with **LR** in the presence of 2 equiv. of elemental sulfur. However, from the reaction of **1d** and **LR** in the presence of elemental sulfur, 5-methyl-3*H*-1,2-dithiole-3-thione **3d** was obtained as the sole product in 51 % yield; this result is identical with published one [7].

2.2. Reaction of 4- and 5-Keto Amides, **5 and **8**, Respectively, with **LR**.** 4-Keto amides (3-acylpropionamides) **5a–d** reacted with an equimolar amount of **LR** in toluene, under the same conditions as described above, to give the five-membered heterocycles, pyrroles **6a–d**, and 2-aminothiophenes **7a–d** (Scheme 2 and Table 2). The yields of **7a–b** dropped to *ca.* one third, when 0.5 equiv. of **LR** was used in this reaction. Treatment of the 4-keto amide, 3-benzoyl-*N*-(toluene-4-yl)propionamide (**5b**), with **LR** in 1,2-dimethoxyethane (DME) at reflux temperature resulted in recovery of unchanged **5b**. Treatment of 3-benzoyl-*N,N*-dibenzylpropionamide (**5e**) with **LR** under the same conditions yielded 2-(dibenzylamino)-5-phenylthiophene (**7e**) exclusively. When a solution of 3-acetyl-*N*-anilinopropionamide (**5f**) and **LR** was refluxed in toluene or benzene, 2-methyl-

Scheme 2

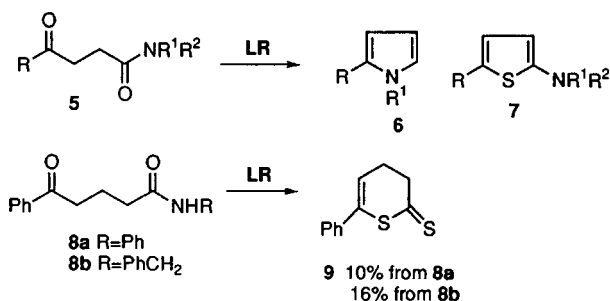


Table 2. Yield of Products 6 and 7

	R	R ¹	R ²	Solvent	Yield [%] ^{a)}	
					6	7
5a	Ph	Ph	H	Toluene	48	51
5a ^{b)}				Toluene	44	19
5b	Ph	4-CH ₃ -C ₆ H ₄	H	Toluene	35	57
5b ^{b)}				Toluene	40	18
5b				DME ^{c)}	– ^{d)}	– ^{d)}
5c	Ph	4-Cl-C ₆ H ₄	H	Toluene	36	32
5d	Ph	PhCH ₂	H	Toluene	47	13
5e	Ph	PhCH ₂	PhCH ₂	Toluene		57
5f	Me	Ph	H	Toluene	25	– ^{e)}
5f				Benzene	38	– ^{e)}

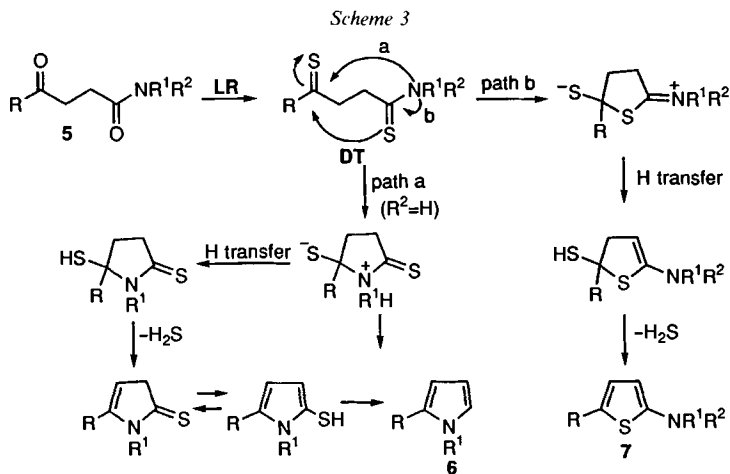
^{a)} Yield of isolated product. ^{b)} 0.5 equiv. of LR was used. ^{c)} 1,2-Dimethoxyethane was used as solvent. ^{d)} No reaction. ^{e)} Not isolated.

1-phenylpyrrole (**6f**) was obtained as the sole product in 25 and 38% yield, respectively. The structures of pyrroles **6** and 2-aminothiophenes **7** were elucidated on the basis of their spectral properties and elemental analyses.

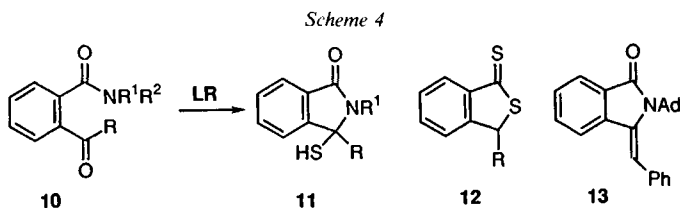
A plausible mechanism for the formation of the five-membered heterocycles **6** and **7** involves initial thionation of **5** to the corresponding 4-thioxo thioamides **DT** followed by further changes shown in Scheme 3. A subsequent intramolecular nucleophilic attack of thioamide N-atom to thiocarbonyl group leads to cyclized product, which, after elimination of H₂S, suffers desulfurization of thioxo group [8] to pyrroles **6** (Path a). On the other hand, imidothiol form of **DT** undergoes a ring closure to give 2-aminothiophenes **7** (Path b).

On treatment of 5-keto amides, 4-benzoyl-*N*-anilino butyramide (**8a**) and 4-benzoyl-*N*-benzyl butyramide (**8b**), with an equimolar amount of LR, 6-phenyl-3,4-dihydro-2*H*-thiine-2-thione (**9**) was isolated as the only isolable product, but in low yield (cf. Scheme 2).

2.3. Reaction of 2-Acylbenzamides 10 with LR. Treatment of 2-acyl-*N*-(*tert*-butyl)benzamides **10a–c** with an equimolar amount of LR in toluene at reflux temper-



ature gave 3-mercaptoisindolin-1-ones **11a–c** in 19–66% yield (Scheme 4 and Table 3). 3-Mercaptoisindolin-1-one **11b** was also obtained in 26% yield when a mixture of **10b** and **LR** was refluxed in benzene. The formation of **11** could be explained in terms of thermal cyclization of **10**, followed by preferential thionation of hydroxy to thiol groups [4][9]. A similar treatment of *N*-adamantyl-2-(2-phenylacetyl)benzamide (**10d**) with **LR** in toluene yielded *N*-adamantyl-3-benzylideneisindolin-1-one (**13**). The formation of **13** could be rationalized by elimination of H_2S from 2-mercaptoisindolin-1-one, although

Table 3. Yield of Products **11–13**

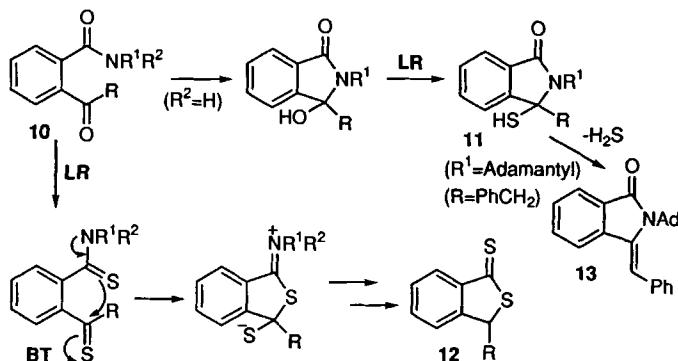
	R	R ¹	R ²	Yield [%] ^{a)}		
				11	12	13
10a	Me	<i>t</i> -Bu	H	11a 53		
10b	PhCH ₂	<i>t</i> -Bu	H	11b 19 (26) ^{b)}		
10c	Ph	<i>t</i> -Bu	H	11c 66		
10d	PhCH ₂	Adamantyl	H			22
10e	Ph	Et	Et		12a 31	
10f	PhCH ₂	Et	Et		12b 22	
10g	PhCH ₂	PhCH ₂	PhCH ₂		12b 52	

^{a)} Yield of isolated product. ^{b)} In benzene.

this compound was not isolated. 2-Acyl-*N,N*-disubstituted benzamides **10e–g** were treated with **LR** in toluene at reflux temperature to yield dihydrobenzo[*c*]thiophene-1-thiones **12a, b**.

The formation of **12** could be explained in terms of the pathway depicted in *Scheme 5*. The 2-thioacyl-thiobenzamide **BT** was formed initially by thionation of **10**. The iminium thiolate form of **BT** undergoes a ring closure and then further thionation of imino to thiocarbonyl groups [1][5], leading to the dihydrobenzo[*c*]thiophene-1-thione **12**.

Scheme 5



Experimental Part

General. Chromatography: silica gel *Merck 60* and *Wakogel C-300* for flash chromatography (FC). M.p. and b.p.: *Yanaco* micro melting-point apparatus (*MP-J3*) and a *Shibata* glass tube oven distillation apparatus (*GTO-350RD*), respectively, and are uncorrected. IR Spectra: *Hitachi 260-30* spectrophotometer, in cm^{-1} . ^1H - and ^{13}C -NMR Spectra: *JEOL FX 90Q* (90 MHz) or *JEOL EX-270* (270 MHz) spectrometers; in CDCl_3 using Me_4Si as an internal standard; δ in ppm, J in Hz.

Reaction of ω -Keto Amides 1, 5, 8, and 10 with LR: General Procedure. A soln. of ω -keto amides **1**, **5**, **8**, and **10** (2 mmol) and **LR** (2.1 mmol) in toluene (50 ml), unless otherwise noted, was heated to reflux under Ar for 15–30 min. After removal of the solvent, the residual oil was chromatographed on a silica-gel column with toluene/AcOEt 50:1–4:1 to give the products **2**, **3**, **6**, **7**, **9**, and **11–13**.

2-Benzoyl-N-phenylthioacetamide (2a; a 4:6 mixture of keto and enol form). M.p. 72–73°. IR (KBr): 3100, 1620, 1595, 1525, 1500, 1320, 770, 700. ^1H -NMR (for keto form **2a**): 4.63 (s, 2 H); 7.22–8.08 (m, 10 H); 10.97 (s, 1 H). ^1H -NMR (for enol form **2a'**): 6.26 (s, 1 H); 7.22–8.08 (m, 10 H); 8.44 (br. s, 1 H); 14.80 (br. s, 1 H). ^{13}C -NMR: 197.1 (s, C=S); 193.1 (s, C=O) for **2a**, and 191.1 (s, C=S) for **2a'**. Anal. calc. for $\text{C}_{15}\text{H}_{13}\text{NOS}$ (255.26): C 70.56, H 5.13, N 5.49; found: C 70.44, H 5.15, N 5.37.

2-Benzoyl-N-benzylthioacetamide (2b; a 5:2 mixture of keto and enol form). M.p. 83–84°. IR (KBr): 3240, 1610, 1535, 765, 740, 700. ^1H -NMR (for keto form **2b**): 4.53 (s, 2 H); 4.88 (d, $J = 5.3$, 2 H); 7.25–7.77 (m, 8 H); 8.02 (d, $J = 7.3$, 2 H); 9.42 (br. s, 1 H). ^1H -NMR (for enol form **2b'**): 4.83 (d, $J = 5.3$, 2 H); 5.97 (s, 1 H); 7.25–7.77 (m, 8 H); 8.02 (d, $J = 7.3$, 2 H); 14.51 (br. s, 1 H). ^{13}C -NMR: 196.5 (s, C=S); 194.4 (s, C=O) for **2b**, and 194.1 (s, C=S) for **2b'**. Anal. calc. for $\text{C}_{16}\text{H}_{15}\text{NOS}$ (269.29): C 71.34, H 5.61, N 5.20; found: C 71.11, H 5.60, N 5.15.

2-Benzoyl-N,N-dibenzylthioacetamide (2c; a 1:1 mixture of keto and enol form). M.p. 109–110°. IR (KBr): 1680, 1595, 1570, 1475, 765, 755, 700. ^1H -NMR (for keto form **2c**): 4.80 (s, 2 H); 5.37 (d, $J = 30.5$, 4 H); 7.16–7.61 (m, 14 H); 7.96 (d, $J = 8.3$, 1 H). ^1H -NMR (for enol form **2c'**): 4.75 (s, 4 H); 6.24 (s, 1 H); 7.16–7.61 (m, 14 H); 7.96 (d, $J = 8.3$, 1 H); 15.31 (br. s, 1 H). ^{13}C -NMR: 197.6 (s, C=S); 193.7 (s, C=O) for **2c**, and 191.2 (s, C=S) for **2c'**. Anal. calc. for $\text{C}_{23}\text{H}_{21}\text{NOS}$ (359.41): C 76.85, H 5.89, N 3.90; found: C 76.48, H 5.90, N 3.80.

3-Oxo-N-phenylbutanethioamide (**2d**; a 6:4 mixture of keto and enol form). M.p. 58–59°. IR (KBr): 3300, 1625, 1595, 1525, 1395, 1320, 780, 760, 730, 700. ¹H-NMR (for keto form **2d**): 2.33 (s, 3 H); 4.13 (s, 2 H); 7.15–7.44 (m, 4 H); 7.72–7.76 (m, 1 H); 10.85 (br. s, 1 H). ¹H-NMR (for enol form **2d'**): 1.99 (s, 3 H); 5.54 (s, 1 H); 7.15–7.44 (m, 4 H); 7.72–7.76 (m, 1 H); 8.08 (br. s, 1 H); 14.42 (br. s, 1 H). Anal. calc. for C₁₀H₁₁NOS (193.20): C 62.15, H 5.75, N 7.25; found: C 61.95, H 5.7, N 7.15.

5-Phenyl-1,2-dithiole-3-thione (**3a**). M.p. 123–124° ([7]: 126°). IR (KBr): 1500, 1480, 1445, 1320, 1305, 1285, 1185, 1025, 1015, 840, 760, 960. ¹H-NMR: 7.35–7.69 (m, 6 H). ¹³C-NMR: 126.9 (d); 129.6 (d); 131.6 (s); 132.2 (d); 136.0 (d); 172.9 (s); 215.6 (s).

5-Methyl-1,2-dithiole-3-thione (**3d**). M.p. ~32° ([7]: 33°). IR (KBr): 1510, 1420, 1315, 1180, 1145, 965. ¹H-NMR: 2.51 (s, 3 H); 7.01 (br. s, 1 H). ¹³C-NMR: 18.3 (q); 139.2 (d); 172.2 (s); 216.3 (s).

1,2-Diphenylpyrrole (**6a**). M.p. 90–91° ([10]: 92°). IR (KBr): 1590, 1495, 1460, 760, 720, 700. ¹H-NMR: 6.31–6.47 (m, 2 H); 6.90–6.95 (m, 1 H); 7.01–7.41 (m, 10 H). ¹³C-NMR: 109.3 (d); 110.7 (d); 124.4 (d); 125.7 (d); 126.2 (d); 126.5 (d); 128.0 (d); 128.2 (d); 128.9 (d); 133.0 (s); 133.8 (s); 140.5 (s).

2-Phenyl-5-(phenylamino)thiophene (**7a**). M.p. 113–114°. IR (KBr): 3390, 1600, 1535, 1500, 1465, 740, 690. ¹H-NMR: 5.61 (br. s, 1 H); 6.65 (d, *J* = 3.4, 1 H); 6.78–7.58 (m, 11 H). ¹³C-NMR: 114.8 (d); 119.2 (d); 120.1 (d); 121.6 (d); 125.2 (d); 126.9 (d); 128.8 (d); 129.3 (d); 134.5 (s); 136.7 (s); 145.3 (s). Anal. calc. for C₁₆H₁₃NS (251.29): C 76.46, H 5.21, N 5.57; found: C 76.14, H 5.21, N 5.51.

2-Phenyl-1-(toluene-4-yl)pyrrole (**6b**). B.p. 175°/3 Torr. IR (film): 1600, 1515, 1460, 1340, 820, 755, 705, 695. ¹H-NMR: 2.32 (s, 3 H); 6.29–6.45 (m, 2 H); 6.87–6.92 (m, 1 H); 6.97–7.28 (m, 9 H). ¹³C-NMR: 20.9 (q); 109.0 (d); 110.4 (d); 124.4 (d); 125.5 (d); 126.1 (d); 127.9 (d); 128.2 (d); 129.5 (d); 133.1 (s); 133.7 (s); 136.3 (s); 138.1 (s). Anal. calc. for C₁₇H₁₅N (233.30): C 87.52, H 6.48, N 6.00; found: C 87.44, H 6.58, N 6.05.

2-Phenyl-5-[(toluene-4-yl)amino]thiophene (**7b**). M.p. 128–129°. IR (KBr): 3390, 1615, 1595, 1535, 1500, 745, 685. ¹H-NMR: 2.27 (s, 3 H); 5.57 (br. s, 1 H); 6.60 (d, *J* = 3.9, 1 H); 6.81–7.57 (m, 10 H). ¹H-NMR: 20.5 (q); 115.3 (d); 117.6 (d); 121.6 (d); 125.1 (d); 126.8 (d); 128.8 (d); 129.8 (d); 134.6 (s); 135.7 (s); 142.7 (s); 146.3 (s). Anal. calc. for C₁₇H₁₅NS (265.30): C 76.96, H 5.70, N 5.28; found: C 77.00, H 5.72, N 5.29.

1-(4-Chlorophenyl)-2-phenylpyrrole (**6c**). M.p. 72–73°. IR (KBr): 1590, 1490, 1460, 1415, 830, 760, 740, 720, 700. ¹H-NMR: 6.31–6.46 (m, 2 H); 6.89–6.91 (m, 1 H); 6.99–7.34 (m, 9 H). ¹³C-NMR: 109.6 (d); 110.0 (d); 124.1 (d); 126.5 (d); 126.8 (d); 128.2 (d); 128.4 (d); 129.2 (d); 132.1 (s); 132.7 (s); 133.9 (s); 139.1 (s). Anal. calc. for C₁₆H₁₂ClN (253.72): C 75.72, H 4.77, N 5.52; found: C 75.40, H 4.80, N 5.50.

2-[(4-Chlorophenyl)amino]-5-phenylthiophene (**7c**). M.p. 129–130°. IR (KBr): 3390, 1600, 1535, 1500, 815, 800, 750, 685. ¹H-NMR: 5.63 (br. s, 1 H); 6.67 (d, *J* = 3.9, 1 H); 6.75–6.91 (m, 2 H); 7.02–7.58 (m, 8 H). ¹³C-NMR: 115.9 (d); 120.0 (d); 121.6 (d); 125.3 (d); 127.3 (d); 128.9 (d); 129.2 (d); 134.4 (s); 137.6 (s); 144.2 (s); 144.6 (s). Anal. calc. for C₁₆H₁₂ClNS (285.77): C 67.24, H 4.23, N 4.90; found: C 67.21, H 4.25, N 4.90.

1-Benzyl-2-phenylpyrrole (**6d**). B.p. 175°/3 Torr. M.p. ~25°. IR (KBr): 1600, 1495, 1465, 1450, 1300, 1070, 770, 755, 720, 705, 700. ¹H-NMR: 5.12 (s, 2 H); 6.27 (d, *J* = 2.4, 2 H); 6.73 (t, *J* = 2.4, 1 H); 6.93–7.05 (m, 2 H); 7.17–7.36 (m, 8 H). ¹³C-NMR: 50.6 (t); 108.5 (d); 108.9 (d); 122.9 (d); 126.4 (d); 126.9 (d); 127.2 (d); 128.3 (d); 128.6 (d); 128.8 (d); 133.3 (s); 134.9 (s); 138.8 (s). Anal. calc. for C₁₇H₁₅N (223.30): C 87.52, H 6.48, N 6.00; found: C 87.21, H 6.56, N 6.11.

2-(Benzylamino)-5-phenylthiophene (**7d**). M.p. ~35°. IR (KBr): 3350, 1590, 1545, 1500, 1450, 1360, 745, 725, 695. ¹H-NMR: 4.04 (br. s, 1 H); 4.27 (s, 2 H); 5.96 (d, *J* = 3.4, 1 H); 6.93 (d, *J* = 3.4, 1 H); 7.02–7.49 (m, 10 H). ¹³C-NMR: 51.9 (t); 105.0 (d); 122.3 (d); 124.5 (d); 125.9 (d); 127.6 (d); 127.8 (d); 135.0 (s); 138.5 (s); 154.4 (s). Anal. calc. for C₁₇H₁₅NS (265.30): C 76.94, H 5.70, N 5.28; found: C 76.58, H 5.51, N 5.21.

2-(Dibenzylamino)-5-phenylthiophene (**7e**). M.p. 86–87°. IR (KBr): 1590, 1545, 1505, 1435, 1360, 760, 745, 735, 695. ¹H-NMR: 4.48 (s, 4 H); 5.90 (d, *J* = 3.9, 1 H); 6.95 (d, *J* = 3.9, 1 H); 7.08–7.75 (m, 15 H). ¹³C-NMR: 56.8 (t); 104.4 (d); 122.7 (d); 124.2 (d); 125.6 (d); 127.3 (d); 127.5 (d); 127.9 (s); 128.5 (d); 128.3 (d); 128.6 (d); 135.0 (s); 137.3 (s); 157.5 (s). Anal. calc. for C₂₄H₂₁NS (355.42): C 81.09, H 5.95, N 3.94; found: C 81.29, H 6.01, N 3.95.

2-Methyl-1-phenylpyrrole (**6f**). B.p. 140°/3 Torr ([11]: 100°/4 Torr). IR (film): 1595, 1500, 1410, 1325, 760, 695. ¹H-NMR: 2.20 (s, 3 H); 5.98–6.18 (m, 1 H); 6.19 (t, *J* = 2.9, 1 H); 6.69–6.78 (m, 1 H); 7.18–7.53 (m, 5 H). ¹³C-NMR: 12.9 (q); 108.0 (d); 108.1 (d); 121.3 (d); 125.7 (d); 126.8 (d); 129.0 (d); 140.4 (s).

6-Phenyl-3,4-dihydrothiine-2-thione (**9**). B.p. > 200°/2 Torr (dec.). IR (film): 1680, 1615, 1595, 1485, 1445, 1240, 1160, 805, 750, 695. ¹H-NMR: 2.48–2.68 (m, 2 H); 3.02–3.18 (m, 2 H); 6.61 (t, *J* = 5.4, 1 H); 7.21–7.52 (m, 5 H). ¹³C-NMR: 24.5 (t); 47.2 (t); 122.1 (d); 126.0 (d); 128.8 (d); 136.2 (s); 236.7 (s). MS: 206 (*M*⁺); 173 ([*M* – SH]⁺), 147, 121, 115.

2-(tert-Butyl)-3-mercaptop-3-methylisoidolin-1-one (**11a**). M.p. 51–52°. IR (KBr): 2540, 1670, 1465, 1345, 1320, 1215, 765, 740, 700. ¹H-NMR: 1.78 (s, 9 H); 2.07 (s, 3 H); 2.58 (s, 1 H); 7.37–7.57 (m, 3 H); 7.71 (d, *J* = 7.6,

1 H). ^{13}C -NMR: 29.2 (q); 31.4 (q); 57.9 (s); 70.4 (s); 121.1 (d); 122.9 (d); 128.5 (d); 129.5 (s); 132.3 (d); 141.9 (s); 152.7 (s). Anal. calc. for $\text{C}_{13}\text{H}_{17}\text{NOS}$ (235.27): C 66.35, H 7.28, N 5.95; found: C 66.21, H 7.31, N 5.84.

3-Benzyl-2-(tert-butyl)-3-mercaptoisindolin-1-one (11b). M.p. 46–47°. IR (KBr): 2540, 1665, 1460, 1445, 1345, 1325, 1205, 740, 735, 695. ^1H -NMR: 1.69 (s, 9 H); 2.72 (s, 1 H); 3.68 (d, $J = 5.2$, 1 H); 3.92 (d, $J = 5.2$, 1 H); 6.66 (d, $J = 6.3$, 2 H); 7.02–7.12 (m, 3 H); 7.26–7.69 (m, 4 H). ^{13}C -NMR: 28.7 (q); 47.4 (t); 58.0 (s); 73.7 (s); 121.9 (d); 123.0 (d); 127.2 (d); 128.1 (d); 128.7 (d); 129.3 (d); 130.4 (s); 132.1 (d); 135.1 (d); 151.0 (s); 168.5 (s). Anal. calc. for $\text{C}_{19}\text{H}_{21}\text{NOS}$ (311.37): C 73.29, H 6.80, N 4.50; found: C 73.38, H 6.85, N 4.48.

2-(tert-Butyl)-3-mercapto-3-phenylisindolin-1-one (11c). M.p. 139–140°. IR (KBr): 2570, 1685, 1605, 1464, 1445, 1340, 1320, 1215, 760, 750, 700. ^1H -NMR: 1.54 (s, 9 H); 2.69 (s, 1 H); 7.02–7.06 (m, 1 H); 7.25–7.59 (m, 7 H); 7.73–7.89 (m, 1 H). ^{13}C -NMR: 28.7 (q); 58.0 (s); 76.2 (s); 121.8 (d); 123.0 (d); 126.0 (s); 128.2 (d); 128.3 (d); 128.7 (d); 132.5 (d); 141.2 (s); 153.7 (s); 168.7 (s). Anal. calc. for $\text{C}_{18}\text{H}_{19}\text{NOS}$ (297.34): C 72.72, H 6.44, N 4.71; found: C 72.63, H 6.43, N 4.83.

3-Phenyl-1H,3H-benzo[c]thiophene-1-thione (12a). M.p. 96–97°. IR (KBr): 1590, 1570, 1465, 1450, 1270, 1125, 1045, 900, 765, 750, 720, 700. ^1H -NMR: 5.97 (s, 1 H); 7.23–7.61 (m, 8 H); 8.10 (d, $J = 7.8$, 1 H). ^{13}C -NMR: 60.6 (d); 124.5 (d); 126.0 (d); 128.3 (d); 128.5 (d); 128.6 (d); 129.1 (d); 133.0 (d); 137.4 (s); 143.5 (s); 151.2 (s); 227.7 (s). Anal. calc. for $\text{C}_{14}\text{H}_{10}\text{S}_2$ (242.22): C 69.42, H 4.13; found: C 69.22, H 4.16.

3-Benzyl-1H,3H-benzo[c]thiophene-1-thione (12b). M.p. 82–83°. IR (KBr): 1595, 1570, 1490, 1465, 1260, 1125, 1045, 900, 770, 750, 700. ^1H -NMR: 3.04 (A of ABX, $J = 9.9$, 13.8, 1 H); 3.53 (B of ABX, $J = 5.3$, 13.8, 1 H); 5.09 (X of ABX, $J = 5.3$, 9.9, 1 H); 7.21–7.50 (m, 7 H); 7.57–7.64 (m, 1 H); 8.00–8.04 (m, 1 H). ^{13}C -NMR: 41.6 (t); 58.5 (d); 124.6 (d); 124.8 (d); 127.2 (d); 128.7 (d); 129.1 (d); 132.6 (d); 137.6 (s); 143.9 (s); 150.0 (s); 227.5 (s). Anal. calc. for $\text{C}_{15}\text{H}_{12}\text{S}_2$ (256.25): C 70.27, H 4.72; found: C 70.06, H 4.71.

2-Adamantyl-3-benzylideneisindolin-1-one (13). M.p. 72–73°. IR (KBr): 1700, 1630, 1475, 1445, 1315, 1300, 835, 770, 725, 695. ^1H -NMR: 1.65–1.85 (m, 6 H); 2.22 (br. s, 3 H); 2.70 (br. s, 5 H); 6.76 (d, $J = 7.9$, 1 H); 7.10–7.47 (m, 8 H); 7.71 (d, $J = 7.6$, 1 H). ^{13}C -NMR: 30.2 (d); 36.4 (t) 41.2 (t); 60.8 (s); 115.2 (d); 122.6 (d); 123.1 (d); 127.6 (d); 128.5 (d); 128.8 (d); 129.5 (d); 130.9 (d); 135.6 (s); 136.5 (s); 136.9 (s); 168.3 (s). Anal. calc. for $\text{C}_{25}\text{H}_{25}\text{NO}$ (355.46): C 84.47, H 7.09, N 3.94; found: C 84.11, H 7.12, N 3.95.

Methylation of 3-Keto Thioamides 2a, b, and d with MeI. To a soln. of 3-keto thioamides **2a**, **b**, and **d** (1 mmol) in acetone (15 ml) in the presence of K_2CO_3 (1.1 mmol), a soln. of MeI (2 mmol) in acetone (5 ml) was added, and then the mixture was stirred at r.t. for 2 h. The usual workup gave β -amino- β -(methylthio)- α,β -unsaturated ketones **4a**, **b**, and **d**.

3-(Methylthio)-1-phenyl-3-(phenylamino)prop-2-en-1-one (4a). M.p. 55–56° ([12]: 56–57°). IR (KBr): 1590, 1550, 1475, 1430, 1275, 740, 715, 700. ^1H -NMR: 2.41 (s, 3 H); 5.88 (s, 1 H); 7.19–7.47 (m, 8 H); 7.88–7.93 (m, 2 H); 13.52 (br. s, 1 H). ^{13}C -NMR: 14.8 (q); 88.7 (d); 125.2 (d); 126.4 (d); 127.0 (d); 128.3 (d); 129.0 (d); 130.9 (d); 138.2 (s); 140.2 (s); 167.6 (s); 186.1 (s).

3-(Benzylthio)-3-(methylthio)-1-phenylprop-2-en-1-one (4b). M.p. 65–66°. IR (KBr): 1585, 1550, 1465, 1430, 1270, 765, 740, 695. ^1H -NMR: 2.34 (s, 3 H); 4.53 (d, $J = 5.9$, 2 H); 5.68 (s, 1 H); 7.18–7.38 (m, 8 H); 7.83–7.88 (m, 2 H); 12.20 (br. s, 1 H). ^{13}C -NMR: 14.3 (q); 47.7 (t); 86.7 (d); 126.9 (d); 127.2 (d); 127.5 (d); 128.2 (d); 128.5 (d); 130.5 (d); 137.1 (s); 140.5 (s); 169.5 (s); 185.3 (s). Anal. calc. for $\text{C}_{17}\text{H}_{17}\text{NOS}$ (283.32): C 72.05, H 6.05, N 4.94; found: 71.74, H 5.91, N 4.80.

4-(Methylthio)-4-(phenylamino)but-3-en-2-one (4d). B.p. 250°/3 Torr. IR (film): 3450, 1585, 1465, 1630, 1270, 765, 740, 695. ^1H -NMR: 2.13 (s, 3 H); 2.29 (s, 3 H); 5.18 (s, 1 H); 7.16–7.36 (m, 5 H); 12.94 (br. s, 1 H). ^{13}C -NMR: 14.5 (q); 29.2 (q); 91.6 (d); 125.2 (d); 126.2 (d); 128.9 (d); 138.2 (s); 165.9 (s); 193.0 (s). Anal. calc. for $\text{C}_{11}\text{H}_{13}\text{NOS}$ (207.22): C 63.74, H 6.32, N 6.76; found: C 63.46, H 6.25, N 6.69.

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