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TETRAHEDRON

Thionation of ω-Hydroxy Amides with *Lawesson*'s Reagent: Synthesis of Thioenamides and Sulfur-Containing Heterocycles

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Abstract: The thionation of ω-hydroxy amides with *Lawesson*'s reagent [LR: 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide] is described. The treatment of 3-hydroxy amides **1** with **LR** exclusively gave thioenamides **2** in fair yields. The treatment of 4-hydroxy amides **5** with **LR** yielded sulfur-containing heterocycles such as tetrahydrothiophene-2-imines **6** and tetrahydrothiophene-2-thione **7a** through cyclization of intermediates, 4-mercapto amides **8**. The 5-hydroxy amides **13** also reacted with **LR** to afford tetrahydrothiopyrane-2-thione **14** as the the sole product.

Keywords: Amide-Alcohols, *Lawesson*'s Reagent, Thioenamides, Sulfur-Containing Heterocycles.

The use of 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide, commonly known as *Lawesson*'s reagent (**LR**), for the chemical conversion of carbonyls to thiocarbonyl compounds has been well investigated.[1] **LR** has also been utilized in the synthesis of five- and six-membered phosphorus-[2] and sulfur-containing heterocycles.[3] Recently, we have reported the direct conversion of alcohols into thiols by treatment of the alcohols with **LR**[4] and novel routes to sulfur-containing heterocycles by the reaction of the substrate with two functional groups such as ω-*N*-acylamino alcohols,[5] ω-hydroxy amides,[6] and ω-keto amides.[7] In this paper we report our results on the reaction of the substrates containing two functional groups, ω-hydroxy amides, with **LR**.[6]

The treatment of 3-phenyl-3-hydroxypropionamides **1a-i** with an equimolar amount of **LR** in toluene under reflux for 30 min afforded thioenamides **2a-i** in fair yields.[8] The yield of **2a** dropped to half when a 0.5 equimolar amount of **LR** was used. Neither the thionation of the amide group nor dehydration was observed using a 0.25 equimolar amount of **LR**. These results suggest that the formation of **2** can be explained in terms of the thionation of amide function and dehydration. The latter process probably involves initial conversion of the hydroxy to a thiol group, followed by loss of hydrogen sulfide to give the final products **2** (Scheme 3), since **LR** also has dehydrating effect on alcohols through thiols.[4,9] The structures of the thioenamides **2** were elucidated on the basis of their spectroscopic properties, elemental analyses, and chemical evidence. The ^{1}H NMR spectra of **2** showed two olefinic protons around δ 6.64-7.18 (d) and 7.66-7.98 (d) with the same coupling constant of 14.6-15.1 Hz, suggesting an *E*-configuration for the corresponding thioenamides **2**. The thioenamide **2a** thus obtained was treated with MeI to give *N*,4-diphenyl-2-methylthio-1-azabuta-1,3-diene (**4**) in almost quantitative yield. The thioenamides **2e** and **h** were confirmed by direct comparison of their IR and

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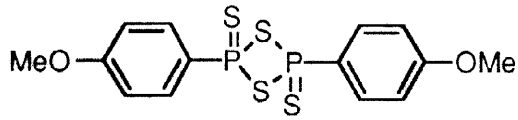
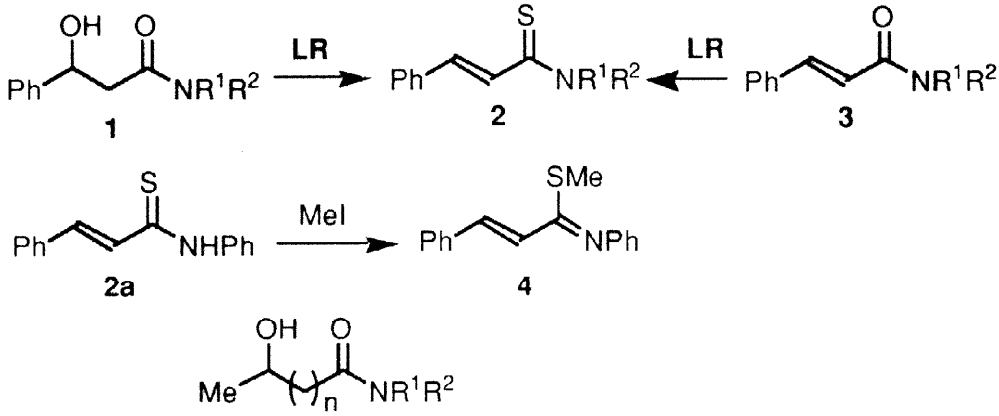
NMR spectra with those of authentic materials, which were independently prepared by thionation of the corresponding cinnamamides **3e** and **h** with **LR**. On the other hand, the reaction of 3-hydroxybutyramides **1j-k** with **LR** under similar conditions as described above leads to intractable mixtures.



Lawesson's Reagent (**LR**)



1j R^1=H, R^2=Ph, n=1 **1k** R^1=R^2=$PhCH_2$, n=1
5f R^1=H, R^2=Ph, n=2 **5g** R^1=H, R^2=$PhCH_2$, n=2

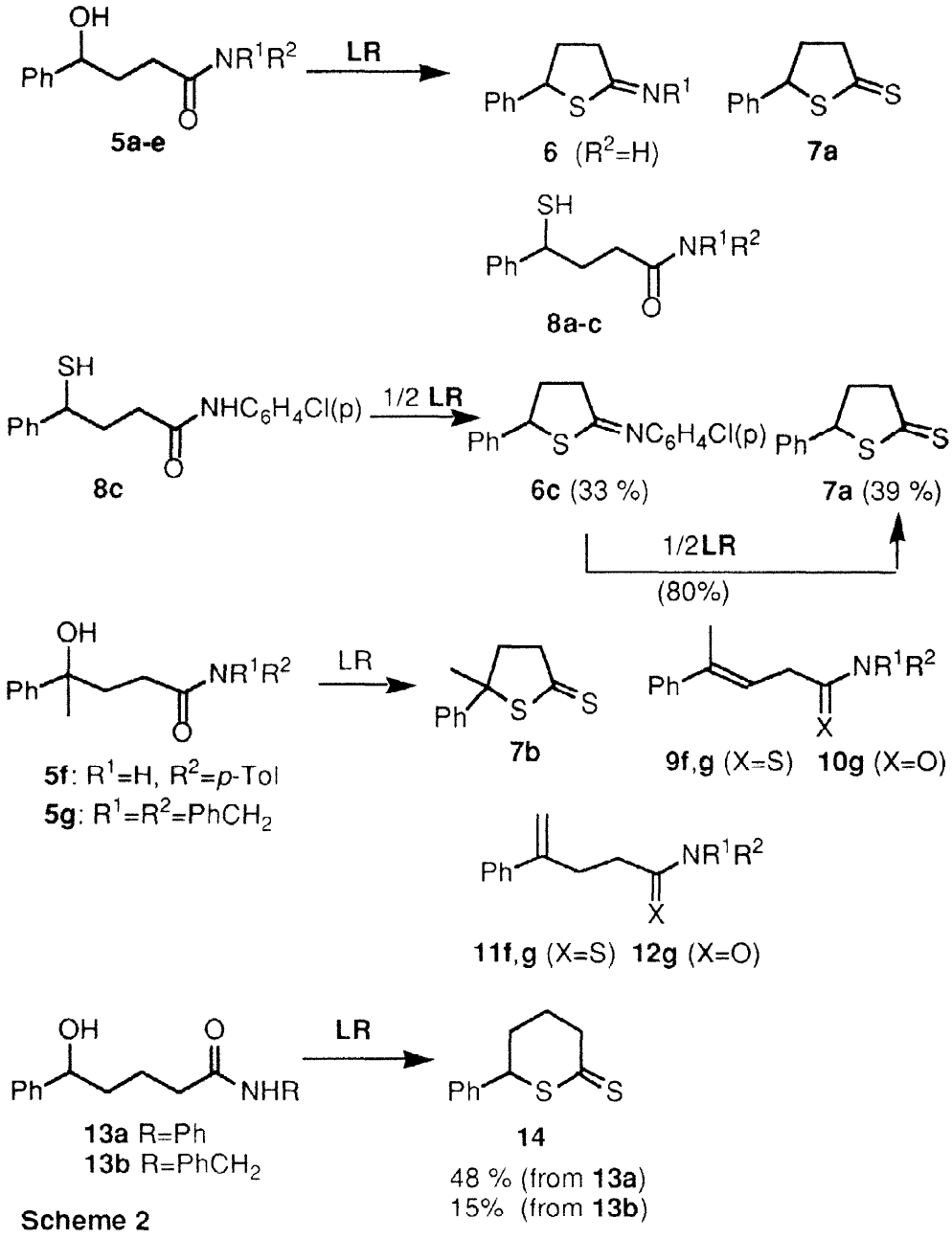
Scheme 1

Table 1. Yields of Cinnamthioamides **2** in the Reaction of 3-Hydroxy-Amides **1** with **LR**.[a]

	R^1	R^2	Molar ratio LR/1	Yield (%)[c] of **2**
1a	Ph	H	1	94
1a[b]			1	60
1a			0.5	48
1a			0.25	trace
1b	*p*-ClC_6H_4	H	1	89
1c	*p*-MeC_6H_4	H	1	69
1d	Ph	Me	1	77
1e	$PhCH_2$	H	1	97
1f	Bu^t	H	1	99
1g	Pr^i	Pr^i	1	99
1h	$PhCH_2$	$PhCH_2$	1	58
1i	-$(CH_2)_2$-O-$(CH_2)_2$-		1	86

[a]Reaction conditions: Reflux in toluene for 30 min. [b]Reflux for 10 min. [c]Isolated yield.

The Treatment of 4-phenyl-4-hydroxybutyramides **5** with an equimolar amount of **LR** gave tetrahydrothiophene-2-imines **6** and/or tetrahydrothiophene-2-thione **7a**. Interestingly, upon treatment of **5** with 0.5 equiv. of **LR**, 4-mercapto amides **8a-c** were isolated along with **6a-c** and **7a**. The 4-mercapto amide **8c** thus obtained was treated with 0.5 equiv. of **LR** under the same conditions to yield the imine **6c** and thione **7a** in 33 and 39 % yields, respectively. The imine **6c** further reacted with 0.5 equiv. of **LR** to yield the thione **7a** in 80 % yield. On the other hand, the 4-hydroxy amides **5f-g**, which are substituted with an alkyl group at 4-position, were treated with **LR** to give various products such as tetrahydrothiophene-2-thione **7b**, the dehydration products such as the alkenylthioamides **9f-g**, **11f-g** and the alkenylamides **10g**, **12g** as shown in Table 3. The structures of **6**- **12** were determined by elemental analyses as well as their spectroscopic properties. The treatment of the 4-hydroxycapronamides **5f-g** with **LR** gave unseparable mixtures.



Scheme 2

Table 2. Yields of Products **6**-**8** in the Reaction of 4-Hydroxy-Amides **5a**-**e** with LR.[a]

			Molar ratio	Yield (%)[b]		
	R^1	R^2	LR/5	**6**	**7a**	**8**
5a	Ph	H	1	51	33	-
5a			0.5	32	5	11
5b	*p*-Tol	H	1	49	48	-
5b			0.5	35	5	9
5c	*p*-ClC_6H_4	H	1	45	52	-
5c			0.5	37	5	8
5d	$PhCH_2$	H	1	32	-	-
5d			0.5	30	-	-
5e	$PhCH_2$	$PhCH_2$	1	-	22	-
5e			0.5	-	10	-

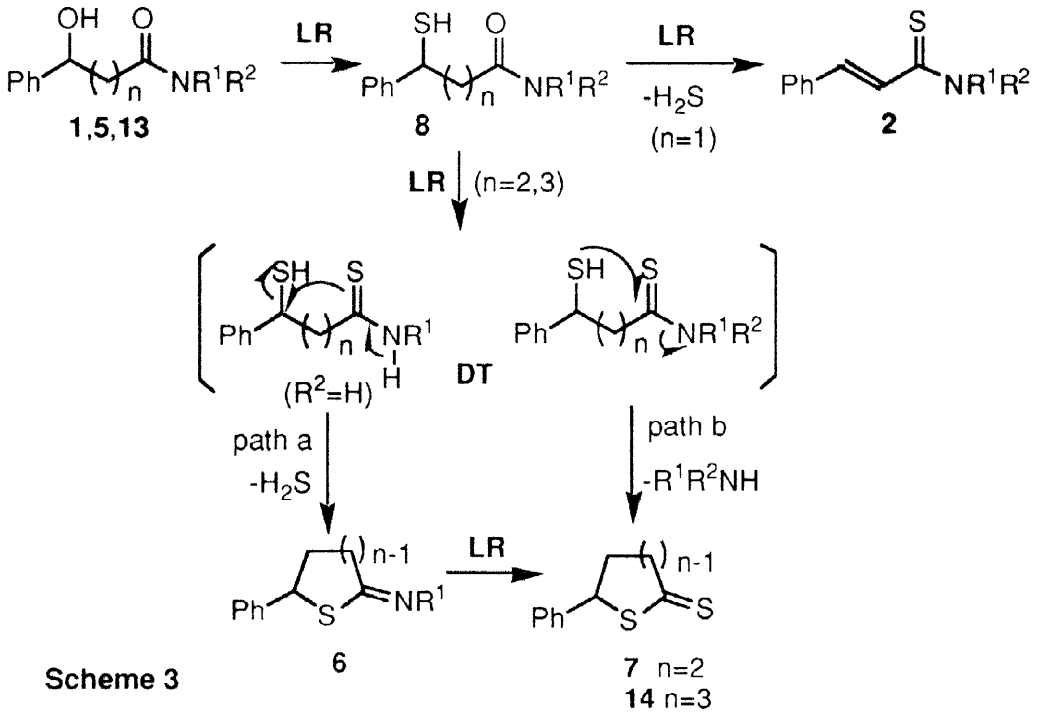
[a]Reaction conditions: Reflux in toluene for 30 min. [b]Isolated yield.

Table 3. Yields of Products **7b**, **9f-g**, **10g**, **11f-g** and **12g** in the Reaction of 4-Hydroxy-Amides **5f-g** with LR.[a]

			Molar ratio	Yield (%)[b]				
	R^1	R^2	LR/5	**7b**	**9**	**10**	**11**	**12**
5f	H	*p*-Tol	1	5	11		5	
5f			0.5	tr.	29		12	
5g	$PhCH_2$	$PhCH_2$	1		18	15		-
5g			0.5		12	31		26

[a]Reaction conditions: Reflux in toluene for 30 min. [b]Isolated yield.

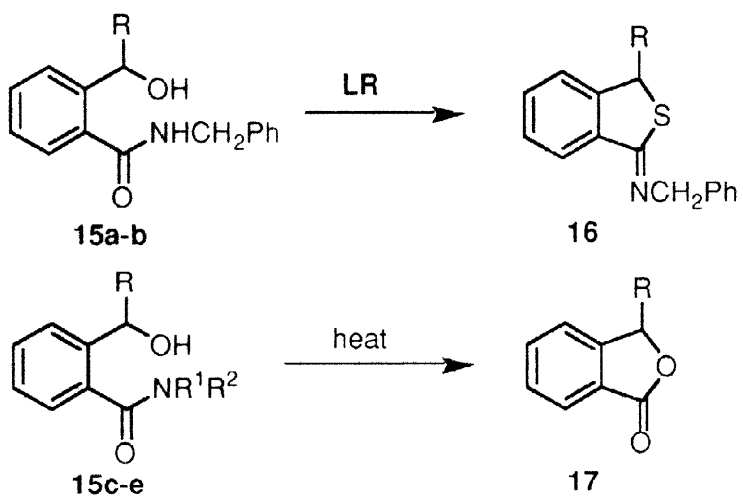
A reasonable mechanism for the formation of the tetrahydrothiophene-2-imines **6**, tetrahydrothiophene-2-thione **7** and 4-mercapto amides **8** is depicted in Scheme 3. On the basis of these findings, the hydroxy amides **5** are apparently converted to the mercapto amides **8**, which then undergo further thionation to form the corresponding mercapto thioamides **DT**. Subsequent cyclization of **DT** through the imidothiol form[3a] with the elimination of hydrogen sulfide yields the imines **6**, which then undergo further thionation to form the thiones **7** (path a). The mercapto thioamides **DT**, which involve a secondary amino function, undergo ring closure by the nucleophilic attack of SH on the thioamide carbon, followed by elimination of the amines to give **7** (path b).



Scheme 3

When the 5-hydroxy amides **13** were treated with **LR**, moderate quantities of tetrahydrothiopyrane-2-thione **14** were obtained by flash chromatography. The formation of **14** can be explained by a similar pathway as for the formation of **7**.

The *o*-(1-hydroxyalkyl)benzamides **15a-b** were treated with **LR** to give complex mixtures from which the dihydro-2-benzothiophene-1-imines **16** were isolated, but in low yields as the only isolable product. Other *o*-(1-hydroxyalkyl)benzamides **15c-e** produced phthalides **17** when heated under reflux in toluene with or without **LR**.



Scheme 4

Table 4. Yields of Dihydro-2-benzothiophene-1-benzylimines **16** in the Reaction *o*-(1-Hydroxyalkyl)benzamides **15a-b** with **LR**.[a]

	R	Molar ratio LR/15	Yield of 16 (%)[b]
15a	Me	2	8
15a		1	18
15b	Ph	2	11
15b		1	17

[a]Reaction conditions: Reflux in toluene for 30 min. [b]Isolated yield.

Table 5. Yields of Phthalides **17** in the Reaction of *o*-(1-Hydroxyalkyl)benzamides **15c-e** with **LR**.[a]

	R	R^1	R^2	Molar ratio LR/15	Reflux time (h)	Yield of 17 (%)[b]
15c	$PhCH_2$	Bu^t	H	1	0.5	26
				-	3	80
15d	Ph	$PhCH_2$	H	1	0.5	6
15d				0.5	0.5	48
15d				-	0.5	trace
15e	$PhCH_2$	Et	Et	-	5	66

[a]Reaction conditions: Reflux in toluene for 30 min. [b]Isolated yield.

EXPERIMENTAL

Melting and boiling points are uncorrected. The IR spectra were measured using a Hitachi 260-30 or JASCO FT/IR-300 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q (90 MHz) or JEOL-EX-270 (270 MHz) spectrometer using $CDCl_3$ as the solvent and tetramethysilane as the internal standard. *J* Values are given in Hz.

Reaction of ω-hydroxy amides 1, 5, 13 and 15 with LR: General procedure.

A solution of ω-hydroxy amides **1**, **5**, **13** and **15** (2 mmol) and **LR** (2 mmol), unless otherwise noted, was heated to reflux under argon for 30 min. After removal of the solvent, the residue was chromatographed on a silica-gel column with toluene-ethyl acetate 50:1-4:1 to give the products **2**, **6-12**, **14**, and **16-17**. The structures of the phthalides **17** were confirmed by a comparison of the spectral data cited in the literature.[7]

***N*-Phenylcinnamthioamide (2a)**: mp 134-135 °C (lit.[1] 134 °C); IR(KBr) 3260, 1625 cm^{-1}; ^1H NMR δ 7.00 (1H, d, *J*=15.1), 7.25-7.70 (11H, m), 7.96 (1H, br d); ^{13}C NMR δ 124.2, 127.1, 128.2, 128.9, 129.1, 130.1, 134.9, 138.2. Methylation of cinnamthioamide **2a** with MeI: To a solution of cinnamthioamide **2a** (1

mmol) in acetone (15 ml) in the presence of potassium carbonate (1.5 mmol), a solution of MeI (2 mmol) in acetone (5 ml) was added and then the mixture was stirred at room temperature for 5 h. The usual workup gave azabutadiene **4** in 97% yield.

***N*,4-Diphenyl-2-methylthio-1-azabuta-1,3-diene** (**4**): mp 87-88 °C; IR(KBr) 1620 cm^{-1}; ^1H NMR δ 2.49 (3H, s), 6.70 (1H, d, *J*=16.6), 6.78-7.44 (11H, m); ^{13}C NMR δ 12.9, 120.9, 121.2, 123.6, 127.5, 128.7, 128.8, 129.3, 135.3, 137.8, 150.5, 164.1. Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.64; H, 5.91; N, 5.47.

***N*-*p*-Chlorophenylcinnamthioamide** (**2b**): mp 193-194 °C; IR(KBr) 1625 cm^{-1}; ^1H NMR δ 7.16 (1H, d, *J*=15.1), 7.10-8.00 (9H, m), 7.97 (1H, d, *J*=15.1); ^{13}C NMR δ 126.0, 129.0, 129.6, 129.8, 130.8, 136.1, 138.9, 144.2, 187.7. Anal. Calcd. for $C_{15}H_{12}NSCl$: C, 65.81; H, 4.41; N, 5.12. Found: C, 65.68; H, 4.36; N, 5.09.

***N*-*p*-Tolylcinnamthioamide** (**2c**): mp 152-153 °C; IR(KBr) 3150, 1625 cm^{-1}; ^1H NMR δ 2.43 (3H, s), 6.99 (1H, d, *J*=15.1), 7.13-8.26 (10H, m), 9.10 (1H, br s). Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.58; H, 5.97; N, 5.53. Found: C, 75.74; H, 6.06; N, 5.54.

***N*-Methyl-*N*-phenylcinnamthioamide** (**2d**): mp 117-118 °C; IR(KBr) 1620 cm^{-1}; ^1H NMR δ 3.87 (3H, s), 6.64 (1H, d, *J*=15.1), 7.16-7.59 (10H, m), 7.93 (1H, d, *J*=15.1); ^{13}C NMR δ 45.8, 126.1, 127.8, 128.3, 128.6, 129.4, 129.8, 135.4, 143.4, 145.3, 195.4. Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 6.36; N, 5.53. Found: C, 75.62; H, 6.07; N, 5.43.

***N*-Benzylcinnamthioamide** (**2e**): mp 115-116 °C; IR(KBr) 3200, 1635 cm^{-1}; ^1H NMR δ 4.94 (2H, d, *J*=5.4), 6.82 (1H, d, *J*=15.1), 7.22-7.54 (6H, m), 7.82 (1H, d, *J*=15.1); ^{13}C NMR δ 50.3, 127.4, 128.0, 128.1, 128.4, 128.9, 129.9, 134.8, 136.3, 142.0, 194.6. Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.72; H, 6.00; N, 5.57.

***N*-*tert*-Butylcinnamthioamide** (**2f**): mp 128-129 °C; IR(KBr) 3200, 1630 cm^{-1}; ^1H NMR δ 1.64 (9H, s), 6.76 (1H, d, *J*=15.1), 7.10-7.56 (6H, m), 7.67 (1H, d, *J*=15.1); ^{13}C NMR δ 29.0, 55.9, 127.8, 128.8, 129.5, 130.1, 135.0, 139.7, 193.7. Anal. Calcd. for $C_{13}H_{17}NS$: C, 70.19; H, 7.81; N, 6.39. Found: C, 71.00; H, 7.89; N, 6.36.

***N*,*N*-Di-*iso*-propylcinnamthioamide** (**2g**): mp 114-115 °C; IR(KBr) 1615 cm^{-1}; ^1H NMR δ 1.39 (6H, d, *J*=11.2), 1.46 (6H, d, *J*=11.2), 3.94-4.40 (2H, m), 7.18 (1H, d, *J*=15.1), 7.20-7.57 (5H, m), 7.76 (1H, d, *J*=15.1); ^{13}C NMR δ 19.3, 22.6, 50.0, 53.7, 127.4, 128.7, 129.1, 135.8, 142.1, 195.1. Anal. Calcd. for $C_{15}H_{21}NS$: C, 72.88; H, 8.56; N, 5.66. Found: C, 72.91; H, 8.66; N, 5.64.

***N*,*N*-Dibenzylcinnamthioamide** (**2h**): mp 117-119 °C; IR(KBr) 1620 cm^{-1}; ^1H NMR δ, 4.84 (2H, s), 5.43 (2H, s), 7.16 (1H, d, *J*=14.6), 7.08-7.68 (15H, m), 7.97 (1H, d, *J*=14.6); ^{13}C NMR δ 53.8, 125.1, 126.4, 127.8, 128.0, 128.7, 129.2, 129.6, 135.1, 135.4, 135.7, 145.4, 197.6. Anal. Calcd. for $C_{23}H_{21}NS$: C, 80.43; N, 6.16; N, 4.08. Found: C, 80.44; H, 6.18; N, 4.10.

***N*-Morpholinocinnamthioamide** (**2i**): mp 106-107 °C; IR(KBr) 1615 cm^{-1}; ^1H NMR δ 3.50 (6H, m), 4.10-4.60 (2H, m), 7.05 (1H, d, *J*=15.1), 7.12-7.60 (5H, m), 7.68 (1H, d, *J*=15.1); ^{13}C NMR δ 50.3, 66.4, 125.0, 127.6, 128.8, 129.5, 135.3, 143.2, 195.7. Anal. Calcd. for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00. Found: C, 66.59; H, 6.46; N, 5.89.

5-Phenyldihydrothiophene-2-phenylimine (**6a**): bp 180 °C/3 Torr; mp 61.5-63 °C; IR(film) 1625

cm^{-1}; ^1H NMR δ 2.00-2.81 (2H, m), 2.90-3.25 (2H, m), 4.81 (1H, dd, *J*=5.4, 9.8), 6.95-7.50 (10H, m); ^{13}C NMR δ 35.6, 40.5, 54.8, 120.1, 124.4, 127.4, 127.8, 128.7, 129.0, 139.6, 152.1, 174.9. Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.70; H, 5.92; N, 5.39.

5-Phenyldihydrothiophene-2-thione (7a): bp 182 °C/2 Torr; mp 44-45 °C; IR(KBr) 1290, 1260, 1180, 1140, 1100 cm^{-1}; ^1H NMR δ 2.29-3.00 (2H, m), 3.06-3.48 (2H, m), 5.28 (1H, dd, *J*=5.4, 9.8), 7.24-7.45 (5H, m); ^{13}C NMR δ 39.5, 55.7, 61.2, 127.4, 128.3, 128.9, 138.0, 245.1. Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.86; H, 5.15. Found: C, 61.89; N, 5.19.

***N*-(3-Mercapto-3-phenylbutyryl)aniline (8a)**: oil; IR(film) 3440, 1675 cm^{-1}; ^1H NMR δ 1.91 (1H, d, *J*=6.3), 2.05-2.78 (4H, m), 3.89-4.04 (1H, m), 6.96-7.68 (10H, m); ^{13}C NMR δ 35.1, 35.3, 43.2, 119.9, 120.2, 126.8, 127.4, 128.7, 128.9, 137.8, 143.8, 170.4.

5-Phenyldihydrothiophene-2-*p*-tolylimine (6b): bp 210 °C/3 Torr; IR(film) 1640 cm^{-1}; ^1H NMR δ 2.30 (3H, s), 2.02-2.58 (2H, m), 2.79-3.23 (2H, m), 4.80 (1H, dd, *J*=5.4, 10.3), 6.80-7.56 (9H, m); ^{13}C NMR δ 20.9, 35.6, 40.5, 54.7, 120.0, 125.2, 127.4, 127.8, 128.6, 129.6, 134.0, 139.7, 149.5, 174.4. Anal. Calcd. for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.37; H, 6.48; N, 5.00.

***N*-(3-Mercapto-3-phenylbutyryl)-*p*-toluidine (8b)**: oil; IR(film) 3300, 2540, 1655 cm^{-1}; ^1H NMR δ 1.88 (1H, d, *J*=5.9), 2.27 (3H, s), 2.05-2.18 (4H, m), 3.80-4.08 (1H, m), 6.95-7.40 (9H, m), 8.05 (1H, br s); ^{13}C NMR δ 20.7, 35.2, 43.2, 120.1, 126.7, 127.3, 128.6, 129.2, 133.7, 135.2, 143.8, 170.4. Anal. Calcd. for $C_{17}H_{19}NOS$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.51; H, 6.60; N, 4.71.

5-Phenyldihydrothiophene-2-*p*-chlorophenylimine (6c): bp 220 °C/3 Torr; IR(film) 1630 cm^{-1}; ^1H NMR δ 2.04-2.72 (2H, m), 2.77-3.26 (2H, m), 4.80 (1H, dd, *J*=5.4, 10.3), 6.94 (2H, d, *J*=8.8), 7.10-7.48 (7H, m); ^{13}C NMR δ 35.5, 40.5, 54.9, 121.5, 127.3, 127.8, 128.6, 129.0, 129.5, 139.3, 150.4, 175.8. Anal. Calcd. for $C_{16}H_{14}NSCl$: C, 66.77; H, 4.90; N, 4.87. Found: C, 67.04; H, 5.14; N, 4.85. A solution of the product **6c** (0.5 mmol) and LR (0.25 mmol) in toluene (30 ml) was heated under reflux for 15 min under the same conditions to give **7a** (80%).

***N*-(3-Mercapto-3-phenylbutyryl)-*p*-chloroaniline (8c)**: mp 87-89 °C; IR(KBr) 3270, 3200, 2550, 1665 cm^{-1}; ^1H NMR δ 1.93 (1H, d, *J*=5.8), 2.20-2.42 (4H, m), 3.90-4.11 (1H, m), 7.18-7.46 (10H, m); ^{13}C NMR δ 35.0, 35.3, 43.2, 121.2, 126.8, 127.5, 128.8, 128.9, 138.3, 143.7, 170.3. Anal. Calcd. for $C_{16}H_{16}NOSCl$: C, 62.85; H, 5.23; N, 4.58. Found: C, 62.94; H, 5.28; N, 4.55. The compound **8c** was treated with 0.5 equiv. of LR under the same conditions for 15 min to give **6c** (33%) and **7a** (39%).

5-Phenyldihydrothiophene-2-benzylimine (6d): bp 180 °C/3 Torr; IR(film) 1630 cm^{-1}; ^1H NMR δ 1.93-2.64 (2H, m), 2.69-3.09 (2H, m), 4.43 (2H, br s), 4.78 (1H, dd, *J*=4.9, 9.8), 7.22-7.65 (10H, m); ^{13}C NMR δ 35.9, 39.9, 54.5, 61.4, 126.8, 127.5, 127.8, 128.0, 128.4, 128.7, 139.5, 140.0, 170.4. Anal. Calcd. for $C_{17}H_{17}NS$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.16; H, 6.43; N, 5.19.

5-Methyl-5-phenyldihydrothiophene-2-thione (7b): bp 185 °C/3 Torr; IR(film) 1305, 1200, 1155, 1075 cm^{-1}; ^1H NMR δ 1.98 (3H, s), 2.52-2.63 (1H, m), 2.81-2.92 (1H, m), 3.21-3.30 (2H, m), 7.25-7.50 (5H, m); ^{13}C NMR δ 29.8, 44.5, 53.5, 69.2, 125.9, 127.6, 128.7, 143.8, 145.0. Anal. Calcd. for $C_{11}H_{12}S_2$: C, 63.41; H, 5.81. Found: C, 63.29; H, 5.76.

***N*-*p*-Toly-4-phenyl-2-butenylthioamide (9f)** and ***N*-*p*-tolyl-4-phenyl-3-butenylthioamide (11f)**: The two isomers could not be completely separated. oil; IR(film) (a mixture of **9f** and **11f**) 1650, 900 cm^{-1}; ^1H NMR δ (for **9f**) 2.15 (3H, br s), 3.86 (2H, d, *J*=7.3), 6.02 (1H, dt, *J*=1.3, 7.3), 7.17-7.52 (9H, m); δ (for **11f**) 2.34 (3H, s), 2.86-2.92 (2H, m), 3.08-3.15 (2H, m), 5.20 (1H, d, *J*=1.0), 5.35 (1H, d, *J*=1.0),

7.17-7.52 (9H, m); ^{13}C NMR δ (a mixture of **9f** and **11f**) 16.4, 21.1, 35.2, 46.9, 47.8, 201.0, 203.8 and aromatic and olefinic carbon peaks.

***N*,*N*-Dibenzyl-4-phenyl-2-butenylthioamide (9g)**: bp 222 °C/3 Torr; IR(film) 1600, 1200, 1155, 1080 cm^{-1}; ^{1}H NMR δ 1.98 (3H, d, *J*=1.0), 3.90 (2H, d, *J*=6.8), 4.75 (2H, s), 5.36 (2H, s), 5.98 (1H, dt, *J*=1.0, 6.8), 7.13-7.42 (15H, m); ^{13}C NMR δ 16.5, 44.8, 53.6, 55.6, 204.5 and aromatic and olefinic carbon peaks. Anal. Calcd. for $C_{25}H_{25}NS$: C, 80.80; H, 6.78; N, 3.77. Found: C, 81.12; H, 6.66; N, 3.57.

***N*,*N*-Dibenzyl-4-phenyl-2-butenylamide (10g)** and ***N*,*N*-dibenzyl-4-phenyl-3-butenylamide (12g)**: The two isomers could not be completely separated. bp 256 °C/3 Torr; IR(film) (a mixture of **10g** and **12g**) 1650, 1605, 900 cm^{-1}; ^{1}H NMR δ (for **10g**) 1.98 (3H, d, *J*=1.0), 3.38 (2H, d, *J*=6.6), 4.50 (2H, s), 4.63 (2H, s), 6.05 (1H, br t, *J*=6.6), 7.04-7.51 (15H, m); δ (for **12g**) 2.52-2.59 (2H, m), 2.92-2.99 (2H, m), 4.32 (2H, s), 4.60 (2H, s), 5.09 (1H, d, *J*=1.0), 5.29 (1H, br s), 7.04-7.51 (15H, m). Anal. Calcd. for $C_{25}H_{25}NO$ (a mixture of **10g** and **12g**): C, 84.47; H, 7.09; N, 3.94. Found: C, 84.63; H, 7.18; N, 4.02.

6-Phenyltetrahydrothiopyrane-2-thione (14): bp 180 °C/Torr; IR(film) 1240, 1160, 1140, 1045 cm^{-1}; ^{1}H NMR δ 1.91-2.63 (4H, m), 2.99-3.41 (2H, m), 4.44-4.59 (1H, m), 7.33 (5H, s); ^{13}C NMR δ 23.2, 30.7, 49.0, 52.8, 127.6, 128.1, 128.8, 139.0, 241.7. Anal. Calcd. for $C_{11}H_{12}S_2$: C, 63.45; H, 5.81. Found: C, 63.56; H, 5.85.

3-Methyldihydro-2-benzothiophene-1-*N*-benzylimine (16a): oil; IR(film) 1625 cm^{-1}; ^{1}H NMR δ 1.71 (3H, d, *J*=6.8), 4.66 (2H, s), 4.83 (1H, q, *J*=6.8), 7.15-7.55 (8H, m), 7.94-8.04 (1H, m); ^{13}C NMR δ 23.1, 46.8, 60.7, 123.3, 124.0, 126.7, 127.7, 127.8, 128.3, 130.8, 137.2, 139.6, 149.1, 167.1; MS *m/z* 253 (M^+), 148, 130.

3-Phenyldihydro-2-benzothiophene-1-*N*-benzylimine (16b): oil; IR(film) 1625 cm^{-1}; ^{1}H NMR δ 4.69 (2H, s), 5.87 (1H, s), 7.05-7.81 (13H, m), 8.03 8.17 (1H, m); ^{13}C NMR δ 56.4, 60.3, 123.5, 125.8, 126.9, 128.0, 128.1, 128.3, 128.4, 128.9, 131.3, 137.2, 139.1, 140.3, 148.0, 168.3; MS *m/z* 315 (M^+), 224, 210, 192.

Thionation of cinnamamides 3e and h.

A solution of cinnamamides **3e**, **h** (1 mmol) and **LR** (0.5 mmol) in toluene (50 ml) was heated to reflux under argon for 15 min. After removal of the solvent, the residue was chromatographed on a silica-gel column with toluene-ethyl acetate (9:1) to yield the corresponding cinnamthioamides **2e** (82%) and **2h** (73%).

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