Thionation of ω-Acylamino Ketones with *Lawesson*'s Reagent: Convenient Synthesis of 1,3-Thiazoles and 4*H*-1,3-Thiazines

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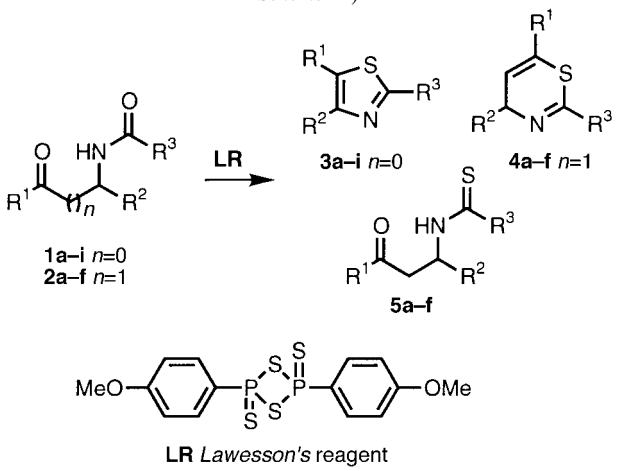
The reaction of ω-acylamino ketones with *Lawesson*'s reagent (=2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide; **LR**) is described. Treatment of 2-acylamino ketones **1** ($n=0$) with **LR** gave 1,3-thiazole derivatives **3** in good yields (*Scheme 1* and *Table 1*). The 4*H*-1,3-thiazines **4** were obtained as main products by treatment of 3-acylamino ketones **2** ($n=1$) with an equimolar amount of **LR**, while mainly the corresponding 3-(thioacyl)amino ketones **5** were isolated when 0.5 equiv. of **LR** was used. The 3-acylamino esters **7** also reacted with **LR** to give the corresponding 3-(thioacyl)amino esters **8** (*Scheme 3* and *Table 2*).

1. Introduction. – The five- and six-membered S-containing heterocycles such as thiazoles and thiazines are known to have interesting biological activities, and a number of methods for the synthesis of these compounds have been reported [1]. The 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, commonly known as *Lawesson*'s reagent (**LR**), is one of the best known thionation reagents, and its advantage has been demonstrated for the thionation of a great variety of carbonyl compounds [2]. **LR** is also utilized in the synthesis of five- and six-membered P- [3] or S-containing heterocycles [4–10]. Recently, we have reported the usage of **LR** for the direct conversion of alcohols into thiols [5] and also for the novel synthesis of S-containing heterocyclic compounds such as tetrahydrothiophen-2-imines [6], tetrahydrothiophene-2-thiones [6], dihydrothiazoles [7][8], benzothiazines [7], thiazolones [8], thiophen-2-amines [9], and 4*H*-1,3-thiazines [10]. The above syntheses were accomplished by reacting **LR** with substrates containing two functional groups such as ω-hydroxyamides [6], 2-acylamino alcohols [7], *N*-acylthreonine derivatives [8], and ω-oxoamides [9]. To extend the usage of **LR** to other multifunctional substrates, we have investigated the reaction of 2- and 3-acylamino ketones (= *N*-(2-oxoalkyl)- and *N*-(3-oxoalkyl)amides) with **LR**, and our results are described in the present paper[1]).

2. Results and Discussion. – 2.1. *Reaction of 2-Acylamino Ketones* **1** *with* **LR**. The treatment of 2-acylamino ketones **1** with an equimolar amount of **LR** in toluene at reflux temperature under Ar for 15 min yielded exclusively 1,3-thiazole derivatives **3** in good yields (*Scheme 1* and *Table 1*). Thus, the thiazoles **3e** and **3f**, which are substituted by a heterocycle such as a furyl or thienyl group at C(2), were synthesized by the reaction of 2-(2-furoyl)- and 2-(2-thienoyl)amino ketones **1e** and **1f** with **LR**. When 0.5 equiv. of **LR** was used in the reaction of **1f**, the yield of thiazole **3f** dropped, but we

[1]) See [10] for a preliminary report of part of this work.

Scheme 1 [a])



[a]) See *Table 1* for R^1–R^3.

Table 1. *Yield of Products* **3**–**5**

	n	R^1	R^2	R^3	Molar ratio	Yield [%][a])		
					LR/**1** or **2**	**3**	**4**	**5**
1a	0	Ph	H	Ph	1	**a** 70		
b	0	Ph	Me	Ph	1	**b** 70		
c	0	Ph	Me	^{t}Bu	1	**c** 92		
d	0	Ph	H	adamantyl	1	**d** 78		
e	0	Ph	H	furyl	1	**e** 69		
f	0	Ph	H	thienyl	1	**f** 51		
f[b])					0.5	**f** 12		
g	0	Ph	Me	thienyl	1	**g** 61		
h	0	Me	Me	Ph	1	**h** 87		
i	0	Me	$PhCH_2$	Ph	1	**i** 66		
2a	1	Ph	Me	Ph	1		**a** 11	**a** 34
a[c])					1		**a** 31	**a** 22
a					0.5		**a** trace	**a** 28
b	1	Ph	Ph	Ph	1		**b** 41	**b** 27
b					0.5		**b** 12	**b** 63
c	1	Ph	Ph	*p*-Tol	1		**c** 66	**c** 26
c					0.5		**c** 11	**c** 27
c[d])							**c** trace	**c** 10
d	1	Ph	Ph	4-ClC_6H_4	1		**d** 52	**d** 34
d					0.5		**d** 5	**d** 56
e	1	Ph	Ph	^{t}Bu	1		**e** 59	**e** trace
e					0.5		**e** 5	**e** 16
d	1	*p*-Tol	*p-Tol*	*p*-Tol	1		**f** 86	**f** 4
f					0.5		**f** 11	**f** 79

[a]) Yield of isolated product. [b]) 0.5 Equiv of **LR** was used. [c]) Reflux for 3 h. [d]) **2c** was refluxed in pyridine with an equimolar amount of P_4S_{10} for 30 min.

were not able to obtain the intermediate thiocarbonyl compounds such as a 2-(thioacyl)amino ketone, 2-(acylamino) thioketone, or 2-(thioacyl)amino thioketone. The structures of the 1,3-thiazoles were determined by their spectroscopic data and elemental analyses.

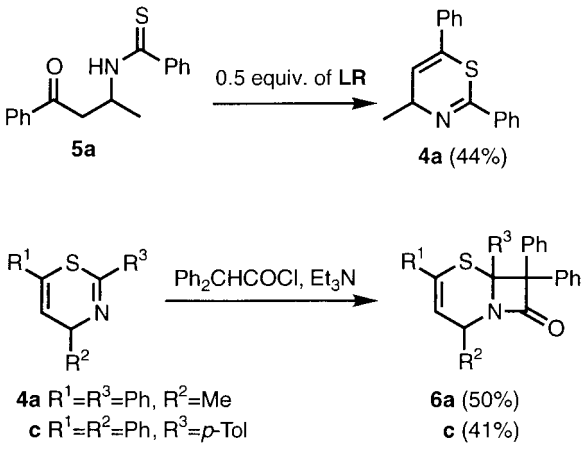
2.2. *Reaction of 3-Acylamino Ketones* **2** *with* **LR**. The treatment of 3-acylamino ketones **2** with **LR** under the same conditions as described in *Sect. 2.1* gave the 4*H*-1,3-thiazine derivatives **4** and 3-(thioacyl)amino ketones **5** (*Scheme 1* and *Table 1*). The yields of the products **3** and **4** were dependent on the molar ratio **LR**/**2**. The 4*H*-1,3-thiazines **4** were the main products when an equimolar amount of **LR** was used, while with 0.5 equiv. of **LR**, the 3-(thioacyl)amino ketones **5** were the major products. In contrast, the treatment of 3-acylamino ketone **2c** with P_4S_{10} resulted in the formation of thioamide **5c** in low yield and only a trace of 4*H*-1,3-thiazine **4c**. The thiazine **4a** was also obtained in 44% yield when 3-(thioacyl)amino ketone **5a** thus obtained was treated with 0.5 equiv. of **LR** under the same conditions (*Scheme 2*). The structures of **4** and **5** were confirmed by their spectroscopic data, microanalyses, and chemical evidence.

In the ^{1}H-NMR spectrum of 4-methyl-2,6-diphenyl-4*H*-1,3-thiazine (**4a**), the signals of Me–*C*(4) and H–*C*(5) appeared as *d*s at δ 1.67 (3 H) and 5.94 (1 H), respectively, indicating the position of the C=C bond to be between C(5) and C(6) in the thiazine ring. In the ^{13}C-NMR spectrum of the 3-(thioacyl)amino ketones **5**, the thiamide C-signals in the low-field region at δ 199.0–212.6 showed a downfield shift of *ca*. 35 ppm compared to the amide C-signals at δ 165.6–177.8 of the 3-acylamino ketones **2**, suggesting that the thionation had occurred at the amide carbonyl group.

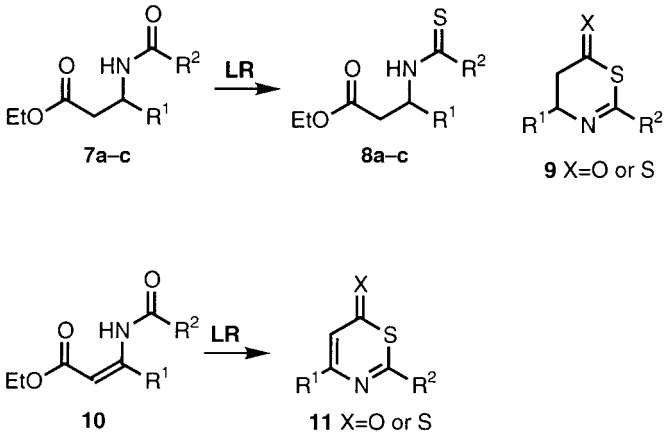
The 4*H*-1,3-thiazines **4a** and **4c** thus obtained were treated with diphenylketene to afford [2 + 2] cycloadducts, *i.e.*, the β-lactams **6a** and **6c**, respectively, in moderate yields (*Scheme 2*).

On the other hand, the treatment of 3-acylamino esters **7** with **LR** gave the 3-(thioacyl)amino esters **8** in high yields as the sole product, and the cyclized products **9** were not detected (*Scheme 3* and *Table 2*). This result is in contrast to the reaction of

Scheme 2



Scheme 3 [a])



[a]) See *Table 2* for R^1 and R^2.

Table 2. *Yield of (Thioacyl)amino Esters* **8**

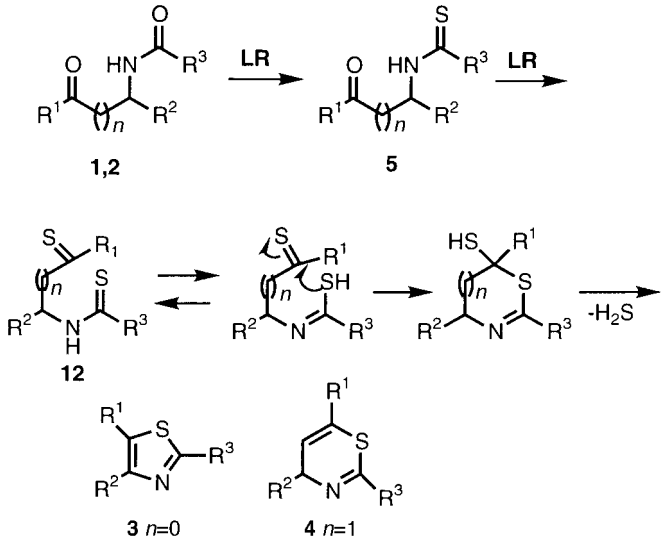
	R^1	R^2	Yield [%][a]) of **8**
7a	Ph	Me	**a** 95
b	Ph	*p*-Tol	**b** 95
b[b])			**b** 92
c	Me	*p*-Tol	**c** 78

[a]) Yield of isolated product **8**. [b]) Reflux in toluene for 5 h.

the 2,3-unsaturated 3-acylamino esters **10** yielding 6*H*-1,3-thiazin-6-ones **11** (X = O) and/or 6*H*-1,3-thiazine-6-thiones **11** (X = S), reported by *Lawesson* and his co-workers [11]. This is probably due to the low reactivity of the ester group toward **LR** [2]. It is noteworthy that the amide group seems to be more reactive toward **LR** than the carbonyl and ester groups. *Serra* and his co-workers have recently reported a similar tendency in the reaction of 2-keto amides with **LR** [12]. Furthermore, we have previously reported that the hydroxy group tends to be more reactive toward **LR** than the amide group [6][7] on treatment of *N*-acylamino alcohols with **LR**. The similar reactivity of **LR** toward hydroxy, amide carbonyl, ketone, and ester carbonyl functional groups was observed. For example, the relative reactivity for the thionation of diphenylmethanol, benzanilide, dibenzyl ketone, and ethyl benzoate with **LR** in toluene to give the corresponding diphenylmethanethiol, benzothioanilide (= *N*-phenylbenzenecarbothioamide), dibenzyl thioketone (= 1,3-diphenylpropane-2-thione), and ethyl thiobenzoate (= ethyl benzenecarbothioate), were 1:0.44:0:0 (at 80°) and 1:1:0.44:0 (at 100°).

Based on these results, a plausible mechanism for the formation of 1,3-thiazoles **3** and 4*H*-1,3-thiazines **4** can be proposed as shown in *Scheme 4*. On treatment of 2- and 3-acylamino ketones **1** and **2** with **LR**, the amide carbonyl group is initially thionated to yield the 2- and 3-(thioacyl)amino ketones **5**, which then undergo further thionation at

Scheme 4



the ketone carbonyl group to form the 2- and 3-(thioacyl)amino thioketones **12**. Subsequent ring closure of the iminothiol form of **12** under elimination of hydrogen sulfide yields 1,3-thiazoles **3** and 4*H*-1,3-thiazines **4**, respectively.

The procedure described here represents a useful method for the preparation of S-containing five- or six-membered heterocycles such as thiazoles **3** and thiazines **4**.

Experimental Part

1. *General*. Chromatography: silica gel *Wakogel C-300* and *Merck 60* 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*), resp.; uncorrected. IR Spectra: *JASCO FT/IR-300* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *JEOL JNM-EX-270* (270 MHz) or *Varian GEMINI-200* (200 MHz); in CD_3Cl with Me_4Si as an internal standard; δ in ppm, J in Hz.

2. *Reaction of ω-Acylamino Ketones* **1** *and* **2** *with* **LR**: *General Procedure.* A soln. of ω-acylamino ketone **1** or **2** (2 mmol) and **LR** (1–2 mmol) in toluene (50 ml), unless otherwise noted, was heated to reflux under Ar for 15 min. After evaporation, the residual oil was chromatographed (silica gel; toluene/AcOEt 50:1 → 4:1): products **3**–**5**. Yields in *Table 1*.

2,5-Diphenyl-1,3-thiazole (**3a**). M.p. 103–104° ([13]: 103–104°). IR (KBr): 1520, 1475, 1445, 755, 690. ^{1}H-NMR: 7.21–7.68 (*m*, 9 H); 7.84–8.05 (*m*, 2 H). ^{13}C-NMR: 126.4; 126.7; 128.3; 128.9; 129.1; 130.0; 131.4; 133.7; 139.2; 167.1.

4-Methyl-2,5-diphenyl-1,3-thiazole (**3b**). B.p. 190°/2 Torr. IR (film): 1595, 1534, 1486, 1458, 1440, 1016, 1003, 759, 690. ^{1}H-NMR: 2.55 (*s*, 3 H); 7.30–7.49 (*m*, 8 H); 7.91–7.96 (*m*, 2 H). ^{13}C-NMR: 16.3; 126.3; 127.7; 128.3; 128.7; 128.9; 129.1; 129.7; 133.2; 136.7; 148.8; 165.0. Anal. calc. for $C_{16}H_{13}NS$ (251.3): C 76.47, H 5.22, N 5.55; found: C 76.20, H 5.32, N 5.58.

*2-(*tert*-Butyl)-4-methyl-5-phenyl-1,3-thiazole* (**3c**). B.p. 195°/2 Torr. IR (film): 1600, 1541, 1488, 1458, 1363, 1257, 1071, 758, 690. ^{1}H-NMR: 1.46 (*s*, 9 H); 2.47 (*s*, 3 H); 7.34–7.44 (*m*, 5 H). ^{13}C-NMR: 16.7; 31.3; 37.9; 127.8; 129.0; 129.6; 130.8; 133.1; 147.3; 178.8. Anal. calc. for $C_{14}H_{17}NS$ (231.4): C 72.70, H 7.41, N 6.06; found: C 72.50, H 7.46, N 6.05.

2-Adamantyl-5-phenyl-1,3-thiazole (**3d**). M.p. 62–63°. IR (KBr): 1598, 1487, 1449, 1341, 1259, 1137, 1099, 869, 749, 686. ^{1}H-NMR: 1.90 (br. *s*, 6 H); 2.10 (br. *s*, 9 H); 7.25–7.46 (*m*, 3 H); 7.50–7.56 (*m*, 2 H); 7.83 (*s*, 1 H).

^{13}C-NMR: 28.6; 36.5; 39.6; 43.1; 126.6; 127.8; 128.9; 137.3; 181.0. Anal. calc. for $C_{19}H_{21}NS$ (295.4): C 77.26, H 7.17, N 4.74; found: C 77.0, H 7.34, N 4.67.

2-(Furan-2-yl)-5-phenyl-1,3-thiazole (**3e**). M.p. 69–70°. IR (KBr): 1583, 1491, 1447, 1264, 1227, 1167, 1143, 1021, 1002, 880, 862, 754. ^{1}H-NMR: 6.51–6.54 (*m*, 1 H); 7.00 (*d*, *J* = 3.3, 1 H); 7.29–7.42 (*m*, 3 H); 7.49–7.59 (*m*, 3 H); 7.96 (*s*, 1 H). ^{13}C-NMR: 108.8; 112.2; 126.5; 128.2; 129.0; 131.0; 138.5; 138.9; 143.5; 148.8; 156.9. Anal. calc. for $C_{13}H_9NOS$ (227.3): C 68.72, H 3.99, N 6.17; found: C 68.30, H 4.22, N 5.94.

4-Phenyl-2-thienyl-1,3-thiazole (**3f**). M.p. 94–95°. IR (KBr): 1542, 1480, 1451, 1410, 1159, 1150, 901, 845, 759, 727, 687. ^{1}H-NMR: 7.08 (*dd*, *J* = 3.6, 5.0, 1 H); 7.20–7.59 (*m*, 7 H); 7.91 (*s*, 1 H). ^{13}C-NMR: 126.4; 126.5; 127.6; 127.9; 128.3; 129.1; 138.7; 131.1; 137.4; 160.7. Anal. calc. for $C_{13}H_9NS_2$ (243.4): C 64.20, H 3.73, N 5.76; found: C 64.10, H 3.84, N 5.66.

4-Methyl-5-phenyl-2-thienyl-1,3-thiazole (**3g**). M.p. 73–74°. IR (KBr): 1595, 1523, 1483, 1453, 1433, 1409, 1371, 1224, 983, 914, 840, 822, 760, 716, 697. ^{1}H-NMR: 2.53 (*s*, 3 H); 7.05 (*dd*, *J* = 3.6, 5.0, 1 H); 7.34–7.49 (*m*, 7 H). ^{13}C-NMR: 16.2; 126.2; 127.3; 127.8; 128.7; 129.1; 131.4; 131.9; 148.4; 158.8. Anal. calc. for $C_{14}H_{11}NS_2$ (257.4): C 65.33, H 4.31, N 5.44; found: C 65.22, H 4.36, N 5.39.

4,5-Dimethyl-2-phenyl-1,3-thiazole (**3h**). B.p. 135°/3 Torr. ([14]: 128–130°/5 Torr; [15]: 148°/14 Torr). IR (film): 1590, 1545, 1500, 1460, 1240, 760, 685. ^{1}H-NMR: 2.36 (*s*, 6 H); 7.24–7.44 (*m*, 3 H); 7.77–7.91 (*m*, 2 H). ^{13}C-NMR: 11.4; 14.8; 126.1; 126.4; 128.8; 129.3; 134.0; 149.2; 163.3.

4-Benzyl-5-methyl-2-phenyl-1,3-thiazole (**3i**). M.p. 83–84°. IR (KBr): 1600, 1535, 1495, 1455, 975, 760, 720, 695. ^{1}H-NMR: 2.37 (*s*, 3 H); 4.10 (*s*, 2 H); 7.13–7.49 (*m*, 8 H); 7.78–7.93 (*m*, 2 H). ^{13}C-NMR: 11.5; 35.1; 126.0; 126.1; 127.8; 128.4; 128.7; 129.4; 134.0; 139.5; 151.8; 163.6. Anal. calc. for $C_{17}H_{15}NS$ (265.4): C 76.94, H 5.70, N 5.28; found: C 76.85, H 5.73, N 5.26.

*4-Methyl-2,6-diphenyl-4*H*-1,3-thiazine* (**4a**). B.p. 200°/3 Torr (dec.). IR (film): 1620, 1576, 1489, 1445, 1215, 942, 756, 691. ^{1}H-NMR: 1.67 (*d*, *J* = 6.9, 3 H); 3.86–3.96 (*m*, 1 H); 5.94 (*d*, *J* = 3.6, 1 H); 7.14–7.51 (*m*, 8 H); 7.90–7.94 (*m*, 2 H). ^{13}C-NMR: 21.3; 58.8; 122.6; 126.8; 127.0; 128.3; 128.9; 129.1; 131.4; 135.6; 137.5; 160.1. MS: 265 ($M^{+\cdot}$), 250, 152, 129. Anal. calc. for $C_{17}H_{15}NS$ (265.4): C 76.96, H 5.70, N 5.24; found: C 76.56, H 5.89, N 5.28.

N-*(1-Methyl-3-oxo-3-phenylpropyl)benzenecarbothioamide* (**5a**). B.p. 215°/3 Torr. IR (film): 3307, 1680, 1518, 1486, 1448, 1378, 1298, 1213, 1001, 980, 719. ^{1}H-NMR: 1.47 (*d*, *J* = 6.6, 3 H); 3.37 (*dd*, *J* = 5.6, 17.2, 1 H); 3.53 (*dd*, *J* = 3.6, 17.2, 1 H); 5.20–5.30 (*m*, 1 H); 7.31–7.61 (*m*, 8 H); 7.73–7.78 (*m*, 2 H); 8.70 (br. *d*, *J* = 7.6, 1 H). ^{13}C-NMR: 18.5; 41.2; 48.8; 126.6; 128.0; 128.2; 128.6; 128.8; 130.9; 133.6; 136.5; 141.5; 197.2; 199.5. Anal. calc. for $C_{17}H_{17}NOS$ (283.4): C 72.05, H 6.05, N 4.94; found: C 71.94, H 6.27, N 4.73.

*2,4,6-Triphenyl-4*H*-1,3-thiazine* (**4b**). M.p. 113–114°. IR (KBr): 1616, 1593, 1569, 1487, 1443, 1305, 1218, 979, 954, 893, 768, 755, 704, 692. ^{1}H-NMR: 5.02 (*d*, *J* = 3.6, 1 H); 6.19 (*d*, *J* = 3.6, 1 H); 7.24–7.64 (*m*, 13 H); 8.05–8.09 (*m*, 2 H). ^{13}C-NMR: 66.8; 122.5; 126.7; 127.3; 127.7; 128.0; 128.5; 128.7; 128.8; 131.1; 135.3; 136.8; 136.9; 142.9. Anal. calc. for $C_{22}H_{17}NS$ (327.4): C 80.73, H 5.23, N 4.28; found: C 80.39, H 5.48, N 4.24.

N-*(3-Oxo-1,3-diphenylpropyl)benzenecarbothioamide* (**5b**). M.p. 154–156°. IR (KBr): 3334, 1674, 1593, 1526, 1488, 1446, 1382, 1365, 1349, 1284, 1216, 1184, 943, 766, 750, 720, 687. ^{1}H-NMR: 3.62–3.72 (*m*, 1 H); 4.03 (*dd*, *J* = 4.5, 17.5, 1 H); 6.38–6.45 (*m*, 1 H); 7.22–7.61 (*m*, 11 H); 7.82 (*m*, 4 H); 9.18 (br. *s*, 1 H). ^{13}C-NMR: 41.2; 56.0; 126.6; 126.8; 127.7; 128.2; 128.5; 128.8; 131.2; 133.8; 136.5; 139.2; 141.4; 198.0; 199.3. Anal. calc. for $C_{22}H_{19}NOS$ (345.5): C 76.49, H 5.54, N 4.06; found: C 76.26, H 5.53, N 4.06.

*2-(4-Methylphenyl)-4,6-diphenyl-4*H*-1,3-thiazine* (**4c**). M.p. 83–84°. IR (KBr): 1614, 1568, 1488, 1455, 1306, 1220, 1172, 974, 898, 813, 758, 736, 689. ^{1}H-NMR: 2.37 (*s*, 3 H); 4.97 (*d*, *J* = 3.6, 1 H); 6.17 (*d*, *J* = 3.6, 1 H); 7.19–7.63 (*m*, 12 H); 7.94–8.00 (*m*, 2 H). ^{13}C-NMR: 21.9; 67.2; 122.2; 127.1; 127.7; 128.1; 128.4; 128.8; 129.0; 129.2; 129.6; 134.7; 135.8; 137.3; 141.9; 143.6; 160.0. Anal. calc. for $C_{23}H_{19}NS$ (341.5): C 80.91, H 5.61, N 4.03; found: C 80.65, H 5.61, N 4.10.

4-Methyl-N-*(3-oxo-1,3-diphenylpropyl)benzenecarbothioamide* (**5c**). M.p. 151–152°. IR (KBr): 3231, 1673, 1492, 1448, 1408, 1297, 1215, 1183, 756, 745, 701, 688. ^{1}H-NMR: 2.37 (*s*, 3 H); 3.65 (*dd*, *J* = 5.9, 17.3, 1 H); 4.03 (*dd*, *J* = 4.0, 17.3, 1 H); 6.34–6.45 (*m*, 1 H); 7.21–7.60 (*m*, 10 H); 7.76 (*d*, *J* = 8.3, 2 H); 7.91 (*d*, *J* = 8.3, 2 H); 9.14 (br. *d*, *J* = 7.6, 1 H). ^{13}C-NMR: 21.3; 41.2; 55.9; 120.5; 126.8; 127.7; 128.1; 128.7; 129.1; 133.8; 136.5; 138.6; 139.3; 141.8; 197.7; 199.3. Anal. calc. for $C_{23}H_{21}NOS$ (359.5): C 76.84, H 5.89, N 3.90; found: C 76.55, H 5.84, N 3.84.

*2-(4-Chlorophenyl)-4,6-diphenyl-4*H*-1,3-thiazine* (**4d**). M.p. 114-115°. IR (KBr): 1611, 1593, 1576, 1486, 1445, 1397, 1302, 1237, 1091, 981, 896, 828, 739, 697. ^{1}H-NMR: 4.98 (*d*, *J* = 3.5, 1 H); 6.18 (*d*, *J* = 3.5, 1 H); 7.24–7.62 (*m*, 12 H); 8.20 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR: 66.9; 121.6; 127.4; 127.6; 128.7; 128.9; 129.3; 135.1; 135.3; 136.6; 137.3; 142.8; 158.7. Anal. calc. for $C_{22}H_{16}ClNS$ (361.9): C 73.02, H 4.46, N 3.87; found: C 72.71, H 4.64, N 3.72.

4-Chloro-N-*(3-oxo-1,3-diphenylpropyl)benzenecarbothioamide* (**5d**). M.p. 137–138°. IR (KBr): 3287, 1681, 1621, 1594, 1518, 1485, 1449, 1404, 1262, 1218, 1110, 1090, 1013, 835, 752, 698. ^{1}H-NMR: 3.65 (*dd*, *J* = 5.6, 17.5,

1 H); 4.00 (*dd*, *J* = 4.1, 17.5, 1 H); 6.33 – 6.40 (*m*, 1 H); 7.21 – 7.61 (*m*, 10 H); 7.75 – 7.90 (*m*, 2 H); 7.92 (*d*, *J* = 7.3, 2 H). ^{13}C-NMR: 41.1; 56.1; 126.5; 127.8; 128.2; 128.6; 128.8; 133.9; 136.4; 137.5; 139.1; 139.7; 196.4; 199.5. Anal. calc. for $C_{22}H_{18}ClNOS$ (365.9): C 69.55, H 4.78, N 3.69; found: C 69.58, H 4.83, N 3.63.

*2-(*tert*-Butyl)-4,6-diphenyl-4*H*-1,3-thiazine* (**4e**). M.p. 79 – 80°. IR (KBr): 1636, 1560, 1489, 1457, 1362, 989, 957, 910, 766, 755, 696. ^{1}H-NMR: 1.37 (*s*, 6 H); 1.39 (*s*, 3 H); 4.58 – 4.62 (*m*, 1 H); 6.10 – 6.14 (*m*, 1 H); 7.30 – 7.45 (*m*, 6 H); 7.53 – 7.63 (*m*, 4 H). ^{13}C-NMR: 29.0; 41.8; 66.2; 122.8; 126.6; 127.0; 127.5; 128.5; 136.6; 137.2; 143.3; 147.2; 170.4. Anal. calc. for $C_{20}H_{21}NS$ (307.4): C 78.13, H 6.88, N 4.56; found: C 78.15, H 6.98, N 4.51.

*2,2-Dimethyl-*N*-(3-oxo-1,3-diphenylpropyl)propanethioamide* (**5e**). M.p. 133 – 134°. IR (KBr): 3344, 1675, 1523, 1480, 1375, 1342, 1281, 1215, 971, 752, 692. ^{1}H-NMR: 1.41 (*s*, 3 H); 1.42 (*s*, 3 H); 1.44 (*s*, 3 H); 3.47 – 3.59 (*m*, 1 H); 3.90 – 4.00 (*m*, 1 H); 6.26 – 6.33 (*m*, 1 H); 7.20 – 7.60 (*m*, 8 H); 7.87 – 7.92 (*m*, 2 H); 9.72 (br. *s*, 1 H). ^{13}C-NMR: 30.0; 40.9; 44.7; 55.2; 126.3; 127.5; 128.1; 128.7; 133.7; 136.5; 139.3; 199.7; 212.6. Anal. calc. for $C_{20}H_{23}NOS$ (325.5): C 73.81, H 7.12, N 4.30; found: C 73.66, H 7.03, N 4.33.

*2,4,6-Tris(4-methylphenyl)-4*H*-1,3-thiazine* (**4f**). M.p. 144 – 145°. IR (KBr): 1609, 1508, 1302, 1177, 946, 897, 823, 800. ^{1}H-NMR: 2.35 (*s*, 3 H); 2.38 (*s*, 6 H); 4.95 (*d*, *J* = 3.6, 1 H); 6.13 (*d*, *J* = 3.6, 1 H); 7.14 – 7.25 (*m*, 6 H); 7.47 – 7.51 (*m*, 4 H); 7.96 (*d*, *J* = 7.9, 2 H). ^{13}C-NMR: 21.2; 21.4; 66.5; 120.9; 126.5; 127.6; 127.9; 129.1; 129.3; 134.1; 134.3; 135.0; 136.8; 138.7; 140.3; 141.3; 159.4. Anal. calc. for $C_{25}H_{23}NS$ (369.5): C 81.26, H 6.28, N 3.79; found: C 81.48, H 6.25, N 3.66.

*4-Methyl-*N*-[1,3-bis(4-methylphenyl)-3-oxopropyl]benzenecarbothioamide* (**5f**). B.p. 210°/3 Torr (dec.). IR (film): 3316, 1680, 1606, 1515, 1494, 1454, 1409, 1371, 1294, 1223, 1182, 965, 950, 817, 755, 720. ^{1}H-NMR: 2.28 (*s*, 3 H); 2.37 (*s*, 3 H); 2.39 (*s*, 3 H); 3.59 (*dd*, *J* = 5.9, 17.1, 1 H); 3.98 (*dd*, *J* = 4.3, 17.1, 1 H); 6.31 – 6.38 (*m*, 1 H); 7.08 – 7.53 (*m*, 8 H); 7.74 – 7.84 (*m*, 4 H); 9.16 (br. *d*, *J* = 7.9, 1 H). ^{13}C-NMR: 21.0; 21.3; 21.7; 41.0; 55.8; 125.4; 126.8; 128.2; 128.3; 129.0; 129.1; 129.4; 134.1; 136.4; 137.3; 138.7; 141.7; 144.7; 197.5; 199.0. MS: 387 ($M^{+\cdot}$), 236, 235, 151, 135. Elemental analysis: not in accord with the calc. values since **5f** decomposed on distillation.

3. *Reaction of 4*H*-1,3-Thiazines* **4a** *and* **4c** *with Diphenyl Ketene*. To a soln. of **4a** or **4c** (2 mmol) and diphenylacetyl chloride (2 mmol) in benzene (20 ml), a soln. of Et_3N (2.2 mmol) in benzene (10 ml) was added dropwise at 0° (ice bath) under Ar, and then the mixture was stirred at r.t. for 5 h. Usual workup gave β-lactam derivatives **6a** and **6c**.

*4-Methyl-2,7,7,7a-tetraphenylazeto[2,1-*b*]-4*H*-[1,3]thiazin-6-one* (**6a**). Yield 50%. M.p. 193 – 195° (dec.). IR (KBr): 1752, 1617, 1597, 1488, 1445, 1358, 1298, 1225, 947, 758, 736, 691. ^{1}H-NMR: 1.51 (*d*, *J* = 7.0, 3 H); 4.83 (*dq*, *J* = 2.6, 7.0, 1 H); 5.83 (*d*, *J* = 2.6, 1 H); 6.97 – 7.82 (*m*, 20 H). ^{13}C-NMR: 22.6; 45.9; 77.5; 122.3; 126.8; 127.0; 127.3; 127.4; 127.5; 127.8; 128.0; 128.3; 128.4; 128.6; 134.6; 137.6; 138.2; 138.4; 139.4; 171.1. Elemental analysis: not in accord with the calc. values since **6a** decomposed upon recrystallization [16].

*7a-(4-Methylphenyl)-2,4,7,7-tetraphenylazeto[2,1-*b*]-4*H*-[1,3]thiazin-6-one* (**6c**). Yield 41%. M.p. 129 – 131° (dec.). IR (KBr): 1764, 1639, 1598, 1492, 1448, 1375, 1236, 1181, 760, 741, 697. ^{1}H-NMR: 2.10 (*s*, 3 H); 4.78 (*d*, *J* = 5.4, 1 H); 5.95 (*d*, *J* = 5.4, 1 H); 6.58 (br. *d*, *J* = 7.3, 4 H); 6.70 – 7.05 (*m*, 8 H); 7.19 – 7.59 (*m*, 8 H); 7.77 – 7.81 (*m*, 4 H). ^{13}C-NMR: 20.8; 44.0; 74.0; 78.5; 111.4; 125.7; 126.5; 127.2; 127.3; 127.5; 127.8; 127.9; 128.0; 128.4; 128.5; 128.7; 128.8; 129.4; 134.1; 134.8; 136.3; 137.3; 137.8; 141.8; 167.9. Elemental analysis: not in accord with the calc. values since **6c** decomposed upon recrystallization [16].

4. *Reaction of 3-Acylamino Esters* **7** *with* **LR**: *General Procedure*. A soln. of 3-acylamino ester **7** (2 mmol) and an equimolar amount of **LR** in toluene (30 ml) was heated to reflux under Ar for 15 min. After evaporation, the residual oil was chromatographed (silica gel; toluene/AcOEt 50 : 1 → 4 : 1): (thioacyl)amino esters **8**. Yields in *Table 2*.

Ethyl 3-Phenyl-3-[(1-thioxoethyl)amino]propanoate (**8a**). B.p. 195°/3 Torr. IR (film): 3306, 3240, 1730, 1537, 1531, 1461, 1455, 1372, 1345, 1296, 1214, 1186, 1156, 763, 700. ^{1}H-NMR: 1.16 (*t*, *J* = 7.2, 3 H); 2.59 (*s*, 3 H); 2.94 (*dd*, *J* = 6.0, 16.2, 1 H); 3.07 (*dd*, *J* = 5.0, 16.2, 1 H); 4.08 (*q*, *J* = 7.2, 4 H); 6.01 – 6.09 (*m*, 1 H); 7.25 – 7.36 (*m*, 5 H); 8.48 (br. *d*, *J* = 9.6, 1 H). ^{13}C-NMR: 14.0; 34.3; 38.1; 55.2; 61.0; 125.9; 126.4; 127.9; 128.7; 129.2; 171.4; 200.4. Anal. calc. for $C_{13}H_{17}NO_2S$ (251.3): C 62.10, H 6.82, N 5.57; found: C 61.71, H 6.75, N 5.53.

Ethyl 3-{[(4-Methylphenyl)thioxomethyl]amino}-3-phenylpropanoate (**8b**). B.p. 220°/3 Torr. IR (film): 3319, 1730, 1519, 1495, 1373, 1286, 1237, 1206, 1184, 821, 699. ^{1}H-NMR: 1.13 (*t*, *J* = 7.3, 3 H); 2.34 (*s*, 3 H); 3.00 (*dd*, *J* = 5.6, 16.2, 1 H); 3.10 (*dd*, *J* = 5.0, 16.2, 1 H); 4.05 (*q*, *J* = 7.3, 2 H); 6.18 – 6.25 (*m*, 1 H); 7.14 (*d*, *J* = 7.9, 2 H); 7.21 – 7.35 (*m*, 5 H); 7.74 (*d*, *J* = 8.2, 2 H); 9.05 (br. *d*, *J* = 8.2, 1 H). ^{13}C-NMR: 13.8; 21.1; 38.3; 55.2; 60.8; 126.2; 126.6; 127.6; 128.0; 128.6; 128.9; 138.3; 138.8; 141.6; 171.5; 197.6. Anal. calc. for $C_{19}H_{21}NO_2S$ (327.4): C 69.69, H 6.46, N 4.28; found: C 69.72, H 6.44, N 4.26.

Ethyl 3-{[(4-Methylphenyl)thioxomethyl]amino}butanoate (**8c**). B.p. 200°/3 Torr. IR (film): 3316, 1730, 1524, 1504, 1373, 1300, 1241, 1190, 1026, 988, 821. ^{1}H-NMR: 1.28 (*t*, *J* = 7.2, 3 H); 1.40 (*d*, *J* = 6.9, 3 H); 2.36 (*s*, 3 H); 2.65 (*dd*, *J* = 4.0, 16.2, 1 H); 2.84 (*dd*, *J* = 5.3, 16.2, 1 H); 4.18 (*q*, *J* = 7.2, 2 H); 5.07 – 5.14 (*m*, 1 H); 7.17

(*d*, *J* = 7.4, 2 H); 7.69 (*d*, *J* = 7.9, 2 H); 8.57 (br. *d*, *J* = 4.9, 1 H). ^{13}C-NMR: 14.0; 18.2; 21.2; 38.1; 48.1; 60.8; 126.6; 128.9; 138.7; 141.4; 172.0; 197.1. Anal. calc. for $C_{14}H_{19}NO_2S$ (265.4): C 69.69, H 6.46, N 4.28; found: C 69.72, H 6.44, N 4.26.

5. *Relative Reactivity for the Thionation of Diphenylmethanol, Benzanilide, Dibenzyl Ketone, and Ethyl Benzoate.* A mixture of diphenylmethanol (50 mg), benzanilide (50 mg), dibenzyl ketone (50 mg), or ethyl benzoate (50 mg), and **LR** (250 mg) in toluene was heated at 80° or 100° under Ar for 3 min. The relative reactivity for thionation of these compounds to the corresponding thio analogues was measured by GLC.

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