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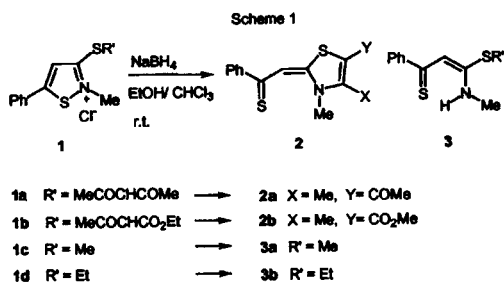
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The reactions of 1-alkylamino-1-alkylthio-3-phenylpropene-3-thiones **3** with thiophosgene and phosgene in toluene, followed by treatment of the reaction mixture with triethylamine gave 3-alkyl-2,3-dihydro-4-oxo-6-phenyl-2-thioxo- **4**, 3-alkyl-2,3-dihydro-2,4-dioxo-6-phenyl-4*H*-1,3-thiazines **5**, respectively in good to excellent yields. Similarly treatment of compounds **3** with *N*-arylimidoyl dichloride in benzene at room temperature gave 3-alkyl-2-arylimino-2,3-dihydro-4-oxo-6-phenyl-4*H*-1,3-thiazines **6** in excellent yields. The reactions of compounds **3** with oxalyl chloride in toluene gave also **5** in good yields.

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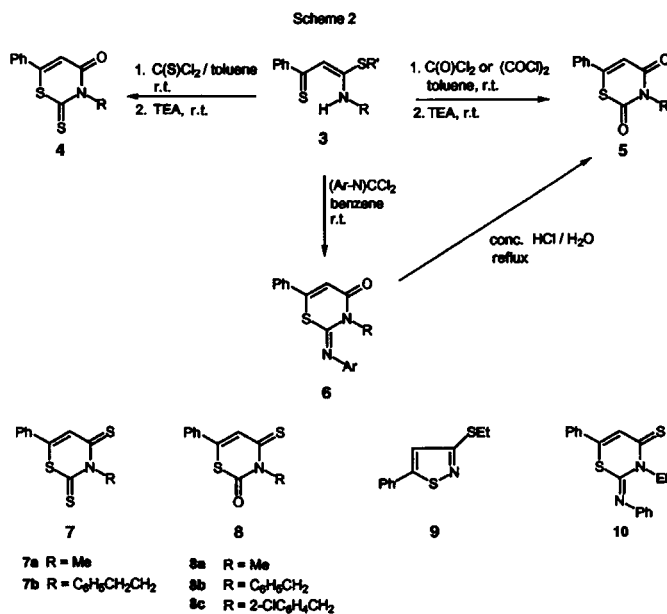
Recently we reported that the reaction of 3-alkylthio-2-methyl-5-phenylisothiazolium chlorides having two carbonyl groups bonded to methylthio group at C-3, **1a-1b**, with sodium borohydride in a mixture of chloroform and ethanol at room temperature gave 3-methyl-4,5-disubstituted-2-thiophenacylidene-1,3-thiazolines **2a-2b** [1] whereas analogous reactions of compounds **1c-1d** with a simple alkylthio group at C-3 afforded their corresponding thiophenacylketene *S,N*-acetals **3a-3b** in excellent yields under the same reaction conditions.



Apart from the reactions of phenacylketene *S,N*-acetals, which have been used as useful synthetic intermediates for various heteroatom compounds [2], only **3a** was reported to be isolated from the reaction of 2-methyl-3-methylthio-6-phenylisothiazolium iodide with benzylamine in 12% yield [3], with benzoylacetate in 10% yield [4], and with ethanolic sodium hydrosulfide in 32% yield [4]. To the best of our knowledge, no reactions have been studied on compound **3a**.

Compound **3** has a 5-atom unit consisting of 3 carbons, 1 sulfur, and 1 nitrogen. By combining 1 carbon unit to

the 5-atom unit one might achieve the synthesis of a six-membered 1,3-thiazine derivatives which have attracted much attention owing to their potential biological activities [5-7], although it has been reported less commonly that the synthesis of 1,3-thiazines are achieved by the [5 + 1] cyclization [8]. We have tried the reactions of **3** with 1 carbon units such as thiophosgene, phosgene, and imidoyl dichlorides. Herein the results we obtained are described.



## Results and Discussion.

Treatment of **3** with an equimolar amount of thiophosgene in toluene at room temperature gave immediately the

Table 1  
Reaction Conditions, Yields, and Analytical Data of 3-Alkyl-2,3-dihydro-4-oxo-6-phenyl-2-thioxo-4*H*-1,3-thiazines **4a-4k**

Substrate	R (mmole)	R'	C(S)Cl <sub>2</sub> [a] (mmole)	TEA [b] (mmole)	Product	Yield (%) [c]	mp (°C) [d]	Molecular Formula	Analyses, % Cacl'd./Found		
									C	H	N
<b>3b</b>	Me	Et	0.455	0.910	<b>4a</b>	75 [e]	113.5-114.5	C <sub>11</sub> H <sub>9</sub> NOS <sub>2</sub> (235.32)	56.15	3.85	5.95
	(0.455)								56.34	3.91	5.83
<b>3d</b>	Et	Me	0.295	0.590	<b>4b</b>	82	103.0-104.5	C <sub>12</sub> H <sub>11</sub> NOS <sub>2</sub> (249.35)	57.80	4.45	5.62
	(0.295)								57.97	4.54	5.44
<b>3i</b>	CH <sub>2</sub> =CHCH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.123	0.246	<b>4c</b>	99	103.5-104.0	C <sub>13</sub> H <sub>11</sub> NOS <sub>2</sub> (261.36)	59.74	4.24	5.36
	(0.123)								59.53	4.09	5.21
<b>3k</b>	C <sub>6</sub> H <sub>11</sub>	Me	0.241	0.482	<b>4d</b>	96	120.0-121.0	C <sub>16</sub> H <sub>17</sub> NOS <sub>2</sub> (303.44)	63.33	5.65	4.62
	(0.241)								63.10	5.72	4.58
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Me	0.234	0.468	<b>4e</b>	96	118.0-119.0	C <sub>17</sub> H <sub>13</sub> NOS <sub>2</sub> (311.42)	65.57	4.21	4.50
	(0.234)								65.47	4.35	4.36
<b>3o</b>	4-MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	0.234	0.468	<b>4f</b>	97	126.5-127.5 dec	C <sub>18</sub> H <sub>15</sub> NOS <sub>2</sub> (325.44)	66.43	4.65	4.30
	(0.234)								66.66	4.51	4.35
<b>3p</b>	4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	0.121	0.242	<b>4g</b>	92	145.0-146.0 dec	C <sub>18</sub> H <sub>18</sub> NO <sub>2</sub> S <sub>2</sub> (341.44)	63.32	4.43	4.10
	(0.121)								63.23	4.53	3.95
<b>3q</b>	2-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	0.090	0.180	<b>4h</b>	97	149.0-150.0 dec	C <sub>17</sub> H <sub>12</sub> ClNOS <sub>2</sub> (345.86)	59.04	3.50	4.05
	(0.090)								59.27	3.57	4.02
<b>3r</b>	3-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	0.239	0.479	<b>4i</b>	88	110.0-111.0 dec	C <sub>17</sub> H <sub>12</sub> ClNOS <sub>2</sub> (345.86)	59.04	3.50	4.05
	(0.239)								59.15	3.46	4.02
<b>3t</b>	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	0.073	0.146	<b>4j</b>	99	116.0-117.0 dec	C <sub>17</sub> H <sub>12</sub> ClNOS <sub>2</sub> (345.86)	59.04	3.50	4.05
	(0.073)								58.91	3.44	4.06
<b>3u</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.155	0.310	<b>4k</b>	91 [f]	123.0-124.0	C <sub>18</sub> H <sub>15</sub> NOS (325.44)	66.43	4.65	4.30
	(0.155)								66.36	4.54	4.21

[a] C(S)Cl<sub>2</sub>: Thiophosgene. [b] TEA: Triethylamine. [c] Yield of isolated compounds. [d] All compounds **4a-4k** were recrystallized from ethanol. [e] 2,3-Dihydro-2,4-dithioxo-3-methyl-6-phenyl-4*H*-1,3-thiazine (**7a**, R = Me), and 2,3-dihydro-2,4-dioxo-3-methyl-6-phenyl-4*H*-1,3-thiazine (**5a**) were isolated in 9% and 6% yields, respectively. [f] 2,3-Dihydro-2,4-dithioxo-6-phenyl-3-(2-phenylethyl)-4*H*-1,3-thiazine (**7b**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>) was isolated in 6% yield.

Table 2  
Spectroscopic Data of **4a-4k**

Product	IR ν (cm <sup>-1</sup> )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) [a] δ ppm, J (Hz)	MS m/z (%)
<b>4a</b>	1671, 1594, 1446, 1088, 850	3.83 (s, 3H, N-CH <sub>3</sub> ), 6.86 (s, 1H, =CH), 7.49-7.56 (m, 5H, ArH)	235 (M <sup>+</sup> , 63.1), 162 (43.6), 134 (100)
<b>4b</b>	1659, 1600, 1448, 1100, 842	1.33 (t, 3H, J = 7.2, CH <sub>3</sub> ), 4.65 (q, 2H, J = 7.2, CH <sub>2</sub> ), 6.81 (s, 1H, =CH), 7.48-7.54 (m, 5H, ArH)	249 (M <sup>+</sup> , 61.3), 216 (23.7), 163 (73.7), 134 (100), 121 (35.9)
<b>4c</b>	1660, 1097, 939	5.22 (d, 2H, J = 5.7, CH <sub>2</sub> ), 5.29 (d, 1H, J = 10.2, CH <sub>2</sub> -C = C- <i>H</i> <sub>cis</sub> ), 5.37 (d, 1H, J = 17.1, CH <sub>2</sub> -C = C- <i>H</i> <sub>trans</sub> ), 5.90-5.99 (m, 1H, CH <sub>2</sub> -CH=), 6.84 (s, 1H, =CH), 7.47-7.53 (m, 5H, ArH)	261 (M <sup>+</sup> , 18.6), 246 (100), 163 (48.5), 134 (88.1), 121 (34.1), 103 (22.9)
<b>4d</b>	1675, 1597, 1448, 1270	1.26-2.49 (m, 10H, cyclohexyl), 5.82-5.93 (m, 1H, NCH), 6.70 (s, 1H, =CH), 7.45-7.54 (m, 5H, ArH)	303 (M <sup>+</sup> , 25.9), 270 (20.1), 222 (100), 163 (89.9), 134 (52.4), 121 (23.9)
<b>4e</b>	1664, 1594, 1447, 1189	5.84 (s, 2H, CH <sub>2</sub> ), 6.86 (s, 1H, =CH), 7.28-7.56 (m, 10H, ArH)	303 (M <sup>+</sup> , 100), 278 (10.3), 163 (86.8), 134 (52.4), 121 (32.0)
<b>4f</b>	1670, 1599, 1446, 1194, 1105	2.34 (s, 3H, CH <sub>3</sub> ), 5.81 (s, 2H, CH <sub>2</sub> ), 6.95 (s, 1H, =CH), 7.14 (d, J = 7.8, 2H, ArH), 7.40 (d, J = 7.8, 2H, ArH), 7.48-7.53 (m, 5H, ArH)	325 (M <sup>+</sup> , 100), 163 (77.0), 134 (32.5), 121 (20.6)
<b>4g</b>	1670, 1599, 1445, 1173, 1101	3.79 (s, 3H, CH <sub>3</sub> ), 5.78 (s, 2H, CH <sub>2</sub> ), 6.84 (s, 1H, =CH), 6.85 (d, J = 7.8, 2H, ArH), 7.48-7.53 (m, 7H, ArH)	341 (M <sup>+</sup> , 50.2), 178 (31.2), 163 (60.7), 134 (19.4), 121 (100)
<b>4h</b>	1665, 1190	5.89 (s, 2H, CH <sub>2</sub> ), 6.91 (s, 1H, =CH), 6.96-6.99 (m, 1H, ArH), 7.19-7.22 (m, 2H, ArH), 7.39-7.49 (m, 1H, ArH), 7.52-7.61 (m, 5H, ArH)	310 (M <sup>+</sup> - Cl, 100), 163 (21.2), 134 (28.8), 121 (21.0)
<b>4i</b>	1667, 1190	5.79 (s, 2H, CH <sub>2</sub> ), 6.87 (s, 1H, =CH), 7.25 (s, 1H, ArH), 7.35-7.36 (m, 1H, ArH), 7.45-7.47 (m, 1H, ArH), 7.50-7.57 (m, 6H, ArH)	345 (M <sup>+</sup> , 51.5), 347 (M <sup>+</sup> + 2, 21.6), 163 (100), 134 (44.2), 121 (32.4)
<b>4j</b>	1669, 1597, 1446, 1113	5.77 (s, 2H, CH <sub>2</sub> ), 6.86 (s, 1H, =CH), 7.29 (d, J = 8.1, 2H, ArH), 7.44 (d, J = 8.1, 2H, ArH), 7.49-7.55 (m, 5H, ArH)	345 (M <sup>+</sup> , 37.7), 347 (M <sup>+</sup> +2, 16.2), 163 (100), 134 (40.4), 121 (35.4)
<b>4k</b>	1665, 1595, 1172, 1116	3.04-3.09 (m, 2H, CH <sub>2</sub> ), 4.75-4.81 (m, 2H, CH <sub>2</sub> ), 6.84 (s, 1H, =CH), 7.26-7.39 (m, 5H, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ), 7.51-7.57 (m, 5H, ArH)	325 (M <sup>+</sup> , 7.0), 221 (21.9), 163 (5.9), 134 (21.5), 121 (6.4), 104 (100)

[a] Measuring frequency: 300 MHz.

reddish salts, which disappeared gradually to give a clear solution by addition of 2 equivalents of triethylamine to the reaction mixture and eventually triethylamine hydrochloride salts were deposited. The reaction was monitored by thin layer chromatography and the spot at the origin before the addition of triethylamine disappeared concomitantly with the appearance of a new spot corresponding to 3-alkyl-2,3-dihydro-4-oxo-6-phenyl-2-thioxo-4*H*-1,3-thiazines **4** after the addition of triethylamine. The structures of **4** were assigned based on spec-

in toluene at room temperature afforded 3-alkyl-2,3-dihydro-2,4-dioxo-6-phenyl-4*H*-1,3-thiazines **5**.

The yields and analytical data of the compounds **5** are summarized in Table 3 and their spectroscopic data in Table 4.

Interestingly the same compounds **5a-5k** were obtained by the reactions of compounds **3** with oxalyl chloride in toluene in the presence of triethylamine at room temperature except for the reaction of **3d** (R = C<sub>6</sub>H<sub>11</sub>, R' = Me) which gave only a complex mixture and no **5d** was isolated

Table 3  
Reaction Conditions, Yields, and Analytical Data of 3-Alkyl-2,3-dihydro-2,4-dioxo-6-phenyl-4*H*-1,3-thiazines (**5a-5k**)

Substrate	R (mmole)	R'	C(O)Cl <sub>2</sub> [a] (mmole)	(COCl) <sub>2</sub> [b] (mmole)	TEA [c] (mmole)	Product	Yield (%) [d]	mp (°C)[e]	Molecular Formula or Lit mp (°C)	Analyses, %		
										Cacl'd./Found	C	H
<b>3b</b>	Me (0.168) (0.337)	Et	0.200	0.337	0.337 0.674	<b>5a</b>	68 -41[f]	125-126	120 [7]			
<b>3d</b>	Et (0.716) (0.337)	Me	0.800	0.337	1.432 0.674	<b>5b</b>	54 48	97-98	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub> S (233.28)	61.78	4.75	6.00
										61.61	4.81	6.12
<b>3i</b>	CH <sub>2</sub> =CHCH <sub>2</sub> (0.240) (0.200)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.266	0.200	0.480 0.400	<b>5c</b>	85 94	93-94	C <sub>13</sub> H <sub>11</sub> NO <sub>2</sub> S (245.30)	63.66	4.52	5.71
										63.47	4.63	5.66
<b>3k</b>	C <sub>6</sub> H <sub>11</sub> (0.138) (0.309)	Me	0.160	0.309	0.276 0.618	<b>5d</b>	76 0	170.5-171.0 dec	C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub> S (287.38)	66.87	5.96	4.87
										66.68	5.79	4.75
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (0.134) (0.267)	Me	0.160	0.267	0.276 0.534	<b>5e</b>	88 76 [g]	135-136	C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub> S (295.36)	69.13	4.44	4.74
										69.25	4.49	4.79
<b>3o</b>	4-MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (0.191) (0.255)	Me	0.200	0.255	0.380 0.510	<b>5f</b>	90 81	151-152	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> S (309.38)	69.88	4.89	4.53
										69.76	4.79	4.42
<b>3p</b>	4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (0.182) (0.212)	Me	0.192	0.212	0.364 0.424	<b>5g</b>	93 77	163.5-164.0	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub> S (325.38)	66.44	4.65	4.30
										66.52	4.71	4.09
<b>3q</b>	2-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (0.090) (0.269)	Me	0.090	0.269	0.180 0.534	<b>5h</b>	84 56 [h]	164-165	C <sub>17</sub> H <sub>12</sub> ClNO <sub>2</sub> S (329.80)	61.91	3.67	4.25
										62.00	3.64	4.20
<b>3r</b>	3-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (0.120) (0.180)	Me	0.200	0.180	0.239 0.359	<b>5i</b>	89 84	133-134	C <sub>17</sub> H <sub>12</sub> ClNO <sub>2</sub> S (329.80)	61.91	3.67	4.25
										61.86	3.61	4.22
<b>3t</b>	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (0.200) (0.172)	Me	0.240	0.172	0.400 0.344	<b>5j</b>	96 88	161-162	C <sub>17</sub> H <sub>12</sub> ClNO <sub>2</sub> S (329.80)	61.91	3.67	4.25
										61.93	3.65	4.13
<b>3u</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> (0.175) (0.191)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0.184	0.191	0.350 0.380	<b>5k</b>	92 80	143-144	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> S (309.38)	69.88	4.89	4.53
										69.85	4.91	4.49

[a] C(O)Cl<sub>2</sub>: Phosgene. [b] (COCl)<sub>2</sub>: Oxalyl chloride. [c] TEA: Triethylamine. [d] Yield of isolated compounds. [e] All compounds **5a-5k** were recrystallized from ethanol. [f] A minute amount of 2,3-dihydro-3-methyl-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazine (**8a**, R = Me) and 3-ethylthio-5-phenylisothiazole (**9**) were isolated. [g] 3-Benzyl-2,3-dihydro-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazine (**8b**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) was isolated in 14% yield. [h] 3-(2-Chlorobenzyl)-2,3-dihydro-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazine (**8c**, R = 2-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) was isolated in 16% yield.

troscopic and elemental analysis data. The yields and analytical data of the compounds **4** are summarized in Table 1 and their spectroscopic data in Table 2. Similar reactions of compounds **3** with an equimolar amount of phosgene, followed by treatment with 2 equivalents of triethylamine

(Table 3). Besides this, the yields of **5a-5k** obtained from the reaction with oxalyl chloride are generally slightly lower than those obtained from the reaction with phosgene. The use of oxalyl chloride is a good choice in place of the hazardous phosgene. The reaction of **3a** with

Table 4  
Spectroscopic Data of **5a-5k**

Product	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) [a] $\delta$ ppm, J (Hz)	MS m/z (%)
<b>5a</b>	1679, 1639, 1349, 1043	3.45 (s, 3H, N-CH <sub>3</sub> ), 6.78 (s, 1H, =CH), 7.49-7.57 (m, 5H, ArH)	219 (M <sup>+</sup> , 43.5) 162 (53.5), 134 (100)
<b>5b</b>	1688, 1639, 1354,	1.27 (t, 3H, J = 7.2, CH <sub>3</sub> ), 4.13 (q, 2H, J = 7.2, CH <sub>2</sub> ), 6.74 (s, 1H, =CH), 7.48-7.56 (m, 5H, ArH)	233 (M <sup>+</sup> , 17.3), 162 (38.4), 134 (100)
<b>5c</b>	1675, 1653, 1640 1599, 1363, 1316	4.68 (d, 2H, J = 5.7, CH <sub>2</sub> ), 5.25 (d, 1H, J = 9.9, CH <sub>2</sub> -C=C- <i>H</i> <sub>cis</sub> ), 5.32 (d, 1H, J = 17.1, CH <sub>2</sub> -C=C- <i>H</i> <sub>trans</sub> ), 5.84-5.95 (m, 1H, CH <sub>2</sub> -CH=), 6.76 (s, 1H, =CH), 7.46-7.57 (m, 5H, ArH)	245 (M <sup>+</sup> , 7.1), 217 (7.9), 162 (53.9), 134 (100), 121 (11.3)
<b>5d</b>	1676, 1636, 1328,	1.26-1.41 (m, 3H), 1.66-1.70 (m, 3H), 1.83-1.88 (m, 2H), 2.34-2.40 (m, 2H), 4.87-4.91 (m, 1H), 6.69 (s, 1H, =CH), 7.44-7.56 (m, 5H, ArH)	287 (M <sup>+</sup> , 0.5), 206 (100), 162 (20.1), 134 (54.5)
<b>5e</b>	1679, 1640, 1440, 1326, 1168	5.26 (s, 2H, CH <sub>2</sub> ), 6.76 (s, 1H, =CH), 7.27-7.56 (m, 10H, ArH)	295 (M <sup>+</sup> , 44.2), 267 (16.0), 162 (64.7), 134 (100), 121 (22.6), 106 (50.0)
<b>5f</b>	1675, 1636, 1375, 1327	2.33 (s, 3H, CH <sub>3</sub> ), 5.21 (s, 2H, CH <sub>2</sub> ), 6.75 (s, 1H, =CH), 7.14 (d, J = 7.5, 2H, ArH), 7.39 (d, J = 7.5, 2H, ArH), 7.50-7.54 (m, 5H, ArH)	309 (M <sup>+</sup> , 74.5), 281 (28.3), 162 (56.4), 134 (98.0), 120 (100), 105 (71.4)
<b>5g</b>	1674, 1641, 1322, 1250	3.79 (s, 3H, CH <sub>3</sub> ), 5.19 (s, 2H, CH <sub>2</sub> ), 6.75 (s, 1H, =CH), 6.86 (d, J = 8.4, 2H, ArH), 7.47 (d, J = 8.4, 2H, ArH), 7.48-7.53 (m, 5H, ArH)	325 (M <sup>+</sup> , 27.1), 162 (22.4), 134 (31.7), 121 (100)
<b>5h</b>	1674, 1636, 1337 1165	5.38 (s, 2H, CH <sub>2</sub> ), 6.82 (s, 1H, =CH), 7.06-7.09 (m, 1H, ArH), 7.20-7.23 (m, 2H, ArH), 7.38-7.41 (m, 1H, ArH), 7.49-7.61 (m, 5H, ArH)	294 (M <sup>+</sup> - Cl, 100), 162 (13.5), 134 (60.7),
<b>5i</b>	1675, 1636, 1592 1369, 1321	5.21 (s, 2H, CH <sub>2</sub> ), 6.77 (s, 1H, =CH), 7.36-7.37 (m, 1H, ArH), 7.47-7.56 (m, 8H, ArH)	329 (M <sup>+</sup> , 19.8), 331 (M <sup>++</sup> 2, 7.6), 162 (79.9), 134 (100), 121 (17.9)
<b>5j</b>	1675, 1641, 1594 1375, 1327	5.21 (s, 2H, CH <sub>2</sub> ), 6.76 (s, 1H, =CH), 7.30 (d, J = 8.4, 2H, ArH), 7.44 (d, J = 8.4, 2H, ArH), 7.49-7.55 (m, 5H, ArH)	329 (M <sup>+</sup> , 32.7), 331 (M <sup>++</sup> 2, 12.5), 301 (13.8), 162 (82.1), 134 (100), 121 (23.8)
<b>5k</b>	1684, 1646, 1617 1341	2.93-2.99 (m, 2H, CH <sub>2</sub> ), 4.26-4.31 (m, 2H, N-CH <sub>2</sub> ), 6.76 (s, 1H, =CH), 7.31-7.36 (m, 5H, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ), 7.50-7.58 (m, 5H, ArH)	309 (M <sup>+</sup> , 1.4), 275 (1.1) 134 (27.8), 104 (100)

[a] Measuring frequency: 300 MHz.

Table 5  
Reaction Conditions, Yields, and Analytical Data of 3-Alkyl-2-arylimino-2,3-dihydro-4-oxo-6-phenyl-4*H*-1,3-thiazines **6a-6p**

Substrate	R (mmole)	R'	Ar [a] (mmole)	Time (hours)	Product	Yield (%) [b]	mp (°C) [c]	Molecular Formula	Analyses, % Cacl'd./Found		
									C	H	N
<b>3a</b>	Me (0.229)	Me	Ph (0.494)	20	<b>6a</b>	94	105-106	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> OS (294.37)	69.36	4.79	9.59
									69.28	4.83	9.44
<b>3f</b>	Et (0.203)	CH <sub>2</sub> =CHCH <sub>2</sub>	Ph (0.577)	17	<b>6b</b>	75	86-88	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> OS (308.40)	70.10	5.23	9.08
									69.87	5.18	8.96
<b>3g</b>	Et (0.201)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Ph (0.402)	40	<b>6b</b>	61 [d]					
<b>3j</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (0.145)	Me	Ph (1.050)	10 [e]	<b>6c</b>	100 [f]	71-73	C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> OS (350.48)	71.97	6.33	7.99
									71.88	6.13	7.84
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (0.134)	Me	Ph (0.905)	47	<b>6d</b>	93	123-125	C <sub>23</sub> H <sub>18</sub> N <sub>2</sub> OS (370.47)	74.57	4.90	7.56
									74.38	4.83	7.47
<b>3c</b>	Me (0.147)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-MeC <sub>6</sub> H <sub>4</sub> (0.365)	2	<b>6e</b>	100	140-142	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> OS (308.40)	70.10	5.23	9.08
									69.92	5.02	9.01
<b>3e</b>	Et (0.155)	Et	4-MeC <sub>6</sub> H <sub>4</sub> (0.862)	2	<b>6f</b>	98	115-117	C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> OS (322.42)	70.78	5.63	8.69
									70.69	5.77	8.58
<b>3j</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (0.168)	Me	4-MeC <sub>6</sub> H <sub>4</sub> (0.912)	3	<b>6g</b>	94	68-70	C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> OS (364.50)	72.49	6.64	7.69
									72.26	6.73	7.54
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (0.126)	Me	4-MeC <sub>6</sub> H <sub>4</sub> (0.688)	20	<b>6h</b>	92	117-118	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> OS (384.50)	74.97	5.24	7.29
									74.98	5.25	7.26
<b>3c</b>	Me (0.368)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> (0.774)	16	<b>6i</b>	88	137-139	C <sub>17</sub> H <sub>13</sub> BrN <sub>2</sub> OS (373.27)	54.70	3.51	7.51
									54.47	3.30	7.46

Table 5 (continued)

<b>3g</b>	Et (0.164)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> (0.411)	48	<b>6j</b>	83	119-120	C <sub>18</sub> H <sub>15</sub> BrN <sub>2</sub> OS (387.30)	55.82 55.79	3.90 3.92	7.23 7.29
<b>3j</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (0.135)	Me	4-BrC <sub>6</sub> H <sub>4</sub> (1.110)	3.5	<b>6k</b>	89	72-74	C <sub>21</sub> H <sub>21</sub> BrN <sub>2</sub> OS (429.37)	58.74 58.83	4.93 4.91	6.52 6.43
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (0.147)	Me	4-BrC <sub>6</sub> H <sub>4</sub> (0.738)	8	<b>6l</b>	86	129-131	C <sub>23</sub> H <sub>17</sub> BrN <sub>2</sub> OS (449.36)	61.48 61.41	3.81 3.74	6.23 6.35
<b>3c</b>	Me (0.182)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-ClC <sub>6</sub> H <sub>4</sub> (0.483)	5	<b>6m</b>	98	133-135	C <sub>17</sub> H <sub>13</sub> ClN <sub>2</sub> OS (328.82)	62.10 61.98	3.98 3.94	8.52 8.49
<b>3g</b>	Et (0.106)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-ClC <sub>6</sub> H <sub>4</sub> (0.312)	18	<b>6n</b>	99	125-127	C <sub>18</sub> H <sub>15</sub> ClN <sub>2</sub> OS (342.84)	63.06 63.14	4.41 4.40	8.17 8.22
<b>3j</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (0.158)	Me	4-ClC <sub>6</sub> H <sub>4</sub> (0.866)	2	<b>6o</b>	82	62-64	C <sub>21</sub> H <sub>21</sub> ClN <sub>2</sub> OS (384.92)	65.53 65.31	5.50 5.43	7.28 7.15
<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (0.145)	Me	4-ClC <sub>6</sub> H <sub>4</sub> (0.721)	42	<b>6p</b>	79	136-138	C <sub>23</sub> H <sub>17</sub> ClN <sub>2</sub> OS (404.91)	68.23 68.36	4.23 4.02	6.92 6.88

[a] Ar: Aryl group of *N*-arylimidoyl dichlorides. [b] Yield of isolated compounds. [c] All compounds **6a-6p** were recrystallized from ethanol except for **6c**, **6g**, **6l**, and **6o**, which were recrystallized from acetonitrile. [d] 2,3-Dihydro-3-ethyl-6-phenyl-2-phenylimino-4-thioxo-4*H*-1,3-thiazine (**10**) was isolated in 15% yield and compound **3g** was recovered in 11% yield. [e] Minute. [f] Apart from the other reactions, 7.2 equivalents of *N*-phenylimidoyl dichloride were used.

Table 6  
Spectroscopic data of **6a-6p**

Product	IR ν (cm <sup>-1</sup> )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) [a] δ ppm, J (Hz)	MS m/z (%)
<b>6a</b>	1660, 1615, 1580, 1349, 1201, 1038	3.63 (s, 3H, N-CH <sub>3</sub> ), 6.62 (s, 1H, =CH) 6.65-7.45 (m, 10H, ArH)	294 (M <sup>+</sup> , 12.0), 132 (100), 91 (4.1), 77 (10.7)
<b>6b</b>	1664, 1619, 1582, 1370, 1327, 1058	1.35 (t, 3H, CH <sub>3</sub> ), 4.35 (q, 2H, CH <sub>2</sub> ), 6.56 (s, 1H, =CH), 6.63-7.49 (m, 10H, ArH)	308 (M <sup>+</sup> , 25.3), 163 (1.9), 146 (100), 134 (41.2), 91 (24.5), 77 (28.0)
<b>6c</b>	1664, 1620, 1583, 1389, 1366, 1331, 1073	0.79-1.92 (m, 9H, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ), 4.25 (t, 2H, N-CH <sub>2</sub> ), 6.52 (s, 1H, =CH), 6.79-7.48 (m, 10H, ArH)	350 (M <sup>+</sup> , 52.8), 279 (100), 258 (34.4), 132 (4.5)
<b>6d</b>	1660, 1620, 1583, 1574, 1376, 1362, 1322, 1179, 1073	5.46 (s, 2H, CH <sub>2</sub> ), 6.59 (s, 1H, =CH), 6.75-7.59 (m, 10H, ArH)	370 (M <sup>+</sup> , 10.5), 207 (100), 163 (8.7), 134 (29.6), 91 (84.9), 77 (13.4)
<b>6e</b>	1668, 1620, 1585, 1354, 1202, 1042	2.32 (s, 3H, CH <sub>3</sub> ), 3.58 (s, 3H, N-CH <sub>3</sub> ), 6.52 (s, 1H, =CH), 6.72-7.40 (m, 9H, ArH)	308 (M <sup>+</sup> , 82.0), 146 (100), 91 (6.6)
<b>6f</b>	1662, 1619, 1586, 1371, 1331, 1190, 1058	1.32 (s, 3H, CH <sub>3</sub> ), 2.31 (s, 3H, CH <sub>3</sub> ), 4.31 (q, 2H, N-CH <sub>2</sub> ), 6.52 (s, 1H, =CH), 6.72-7.45 (m, 9H, ArH)	322 (M <sup>+</sup> , 93.7), 160 (100), 132 (29.7), 145 (20.0)
<b>6g</b>	1664, 1612, 1580, 1386, 1365, 1183, 1065	0.72-1.94 (m, 9H, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ), 2.35 (s, 3H, CH <sub>3</sub> ), 4.25 (t, 2H, N-CH <sub>2</sub> ), 6.54 (s, 1H, =CH), 6.70-7.48 (m, 9H, ArH)	364 (M <sup>+</sup> , 100), 293 (89.8), 258 (43.1), 132 (38.0)
<b>6h</b>	1669, 1620, 1587, 1379, 1322, 1178, 1075	2.31 (s, 3H, CH <sub>3</sub> ), 5.48 (t, 2H, N-CH <sub>2</sub> ), 6.58 (s, 1H, =CH), 6.66-7.57 (m, 9H, ArH)	384 (M <sup>+</sup> , 100), 221 (96.7), 91 (33.2)
<b>6i</b>	1675, 1620, 1588, 1352, 1314, 1202, 1042	3.56 (s, 3H, CH <sub>3</sub> ), 6.60 (s, 1H, =CH), 6.70-7.59 (m, 9H, ArH)	374 (M <sup>++</sup> 2, 1.9), 372 (M <sup>+</sup> , 1.6), 166 (100), 163 (36.1), 134 (55.0), 90 (17.9), 77 (7.5)
<b>6j</b>	1672, 1617, 1589, 1386, 1370, 1334, 1196, 1092, 1060	1.33 (s, 3H, CH <sub>3</sub> ), 4.32 (q, 2H, CH <sub>2</sub> ), 6.58 (s, 1H, =CH), 6.70-7.63 (m, 9H, ArH)	388 (M <sup>++</sup> 2, 5.6), 386 (M <sup>+</sup> , 3.9), 152 (100), 163 (75.7), 134 (96.1), 90 (48.4), 77 (6.8)
<b>6k</b>	1662, 1615, 1583, 1368, 1333, 1178, 1092, 1070	0.72-1.94 (m, 9H, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ), 4.24 (t, 2H, N-CH <sub>2</sub> ), 6.55 (s, 1H, =CH), 6.70-7.51 (m, 9H, ArH)	430 (M <sup>++</sup> 2, 54.3), 428 (M <sup>+</sup> , 52.9), 384 (100), 258 (75.7), 163 (43.2)
<b>6l</b>	1668, 1620, 1586, 1372, 1322, 1174, 1098, 1072	5.48 (s, 2H, CH <sub>2</sub> ), 6.60 (s, 1H, =CH), 6.68-7.59 (m, 9H, ArH)	450 (M <sup>++</sup> 2, 6.1), 448 (M <sup>+</sup> , 5.0), 163 (27.3), 134 (42.9), 91 (100), 77 (8.1)
<b>6m</b>	1669, 1618, 1612, 1581, 1572, 1350, 1201, 1041	3.59 (s, 3H, CH <sub>3</sub> ), 6.61 (s, 1H, =CH), 6.61-7.46 (m, 9H, ArH)	340 (M <sup>++</sup> 2, 3.2), 328 (M <sup>+</sup> , 11.3), 166 (100), 134 (34.6), 90 (9.9), 77 (3.0)
<b>6n</b>	1670, 1615, 1585, 1383, 1370, 1333, 1060	1.32 (s, 3H, CH <sub>3</sub> ), 4.32 (q, 2H, CH <sub>2</sub> ), 6.56 (s, 1H, =CH), 6.73-7.48 (m, 9H, ArH)	344 (M <sup>++</sup> 2, 7.5), 342 (M <sup>+</sup> , 20.0), 163 (37.9), 152 (100), 134 (80.7), 90 (22.8), 77 (8.0)
<b>6o</b>	1660, 1612, 1582, 1382, 1369, 1334, 1179, 1092, 1017	0.72-1.91 (m, 9H, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ), 4.22 (t, 2H, N-CH <sub>2</sub> ), 6.58 (s, 1H, =CH), 6.72-7.49 (m, 9H, ArH)	386 (M <sup>++</sup> 2, 23.5), 384 (M <sup>+</sup> , 23.6), 313 (100), 258 (48.8), 163 (46.0)
<b>6p</b>	1667, 1614, 1583, 1380, 1330, 1177, 1166, 1094, 1016	5.47 (s, 2H, CH <sub>2</sub> ), 6.60 (s, 1H, =CH), 6.68-7.59 (m, 9H, ArH)	406 (M <sup>++</sup> 2, 3.3), 404 (M <sup>+</sup> , 8.2), 163 (29.2), 134 (40.8), 91 (100), 77 (8.0)

[a] Measuring frequency: 80 MHz.

an equimolar amount of *N*-arylimidoyl dichloride in benzene did not proceed at room temperature but gave complex mixtures at reflux. By employing 2 equivalents of *N*-arylimidoyl dichloride at room temperature 3-alkyl-2-arylimino-2,3-dihydro-4-oxo-4*H*-1,3-thiazines **6** were obtained in good to excellent yields. The yields and analytical data of compounds **6** are summarized in Table 5 and their spectroscopic data in Table 6.

Compounds **4**, **5**, and **6** have been synthesized basically by two different methods. The most widely used method is a [3 + 3] cyclization [8] being achieved by the reaction of three-carbon precursors such as acetylenic acids and their esters,  $\beta$ -propiolactones, and acrylic acids with dithiocarbamic acids or thioureas as the N-C-S fragment. However, the success of additions of either dithiocarbamic acids or thiourea derivatives to  $\beta$ -substituted propiolic acids or their esters seems to be very much dependant on either the  $\beta$ -substituents and/or whether the propiolic acid is acid itself or its esters. The second method involves the isomerization of 2-thioxo-1,3-oxazines [9] which are prepared by the reactions of  $\beta$ -propiolactones with ammonium thiocyanate in acetone. However, this method appears to be less versatile because of the availability of appropriate  $\beta$ -propiolactones.

## EXPERIMENTAL

All solvents were dried by standard methods. Thiophenacylketene *S,N*-acetals **3** were prepared according to the literature [1]. Thiophosgene was purchased from Aldrich. The 8*M* solution of phosgene in tetrahydrofuran was prepared by bubbling phosgene into tetrahydrofuran at  $-78^\circ$ . *N*-Phenyl [10], *N*-(*p*-tolyl)- [11], *N*-(*p*-chlorophenyl)- [11], and *N*-(*p*-bromophenyl)imidoyl dichlorides [11] were prepared by known procedures. Triethylamine was from Aldrich. Column chromatography was performed on silica gel (Merck, 70-230 or 230-400 mesh). Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were measured on a Bruker AC 80 and a Varian Gemini-300 300 MHz spectrometers using tetramethylsilane as an internal standard in deuteriochloroform. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer in potassium bromide discs. Mass spectra were obtained using HP 5890 A (GC) with HP 5970 (MSD) mass spectrometer. Microanalyses were performed by Perkin-Elmer 240 DS and Carlo Erbra 1106.

General Procedure for the Synthesis of 3-Alkyl-2,3-dihydro-4-oxo-6-phenyl-2-thioxo-4*H*-1,3-thiazines **4a-4k**.

To a stirred solution of 1-alkylamino-1-alkylthio-3-phenylpropene-3-thione (**3**) (0.1-0.3 mmole) in toluene (10 ml) was dropwise added thiophosgene (0.1-0.3 mmole) in toluene (10 ml) by using a microsyringe. Reddish precipitates were immediately formed. Upon addition of triethylamine (0.2-0.6 mmole) by using a microsyringe to the solution having the reddish precipitates, the precipitates disappeared and triethylamine hydrochloride salts began to form. The reaction mixture was

treated with water (10 ml) and extracted with chloroform (2 x 15 ml). The extract was dried on magnesium sulfate and evaporated to dryness to give the residue, which was chromatographed on a silica gel (70-230 mesh) column (8 x 2 cm) with a mixture of methylene chloride and *n*-hexane (v:v, 1:1). In each case, consult Table 1 for reaction conditions, yields and analytical data of **4a-4k** and Table 2 for their spectroscopic data.

2,3-Dihydro-2,4-dithioxo-3-methyl-6-phenyl-4*H*-1,3-thiazine (**7a**).

Chromatography of the reaction mixture obtained from the reaction of 1-ethylthio-1-methylamino-3-phenylpropene-3-thione (**3b**) with thiophosgene (refer to **4a** in Table 1 for the reaction conditions) using a mixture of methylene chloride and *n*-hexane (v:v, 1:1) as an eluent gave **7a** (10 mg, 0.038 mmole). Pure **7a** was obtained as a reddish granular solid by recrystallization from ethanol, mp 118-119 $^\circ$ ;  $^1\text{H}$  nmr (deuteriochloroform, 300 MHz):  $\delta$  4.34 (s, 3H, N-CH<sub>3</sub>), 7.48-7.58 (m, 5ArH), 7.74 (s, 1H, =CH); ir (potassium bromide): 1558, 1492, 1292, 1132, 1064, 759, 684, 655 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 251 (100) (M<sup>+</sup>), 218 (46), 178 (35), 121 (89).

Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>NS<sub>3</sub>: C, 52.56; H, 3.61; N, 5.57. Found: C, 52.42; H, 3.69; N, 5.52.

Continuous elution with the same solvent mixture gave **4a** (80 mg, 0.340 mmole, 75%) and 2,3-dihydro-2,4-dioxo-3-methyl-6-phenyl-4*H*-1,3-thiazine (**5a**) (6 mg, 0.027 mmole, 6%). Pure **5a** was obtained as a brownish granular solid by recrystallization from ethanol, mp 121-122.5 $^\circ$ ;  $^1\text{H}$  nmr (deuteriochloroform, 300 MHz):  $\delta$  3.45 (s, 3H, N-CH<sub>3</sub>), 6.78 (s, 1H, =CH), 7.49-7.57 (m, 5H, ArH); ir (potassium bromide): 1679, 1639, 1349, 1043 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 219 (43.5) (M<sup>+</sup>), 162 (53.5), 134 (100).

Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 60.26; H, 4.14; N, 6.39. Found: C, 60.19; H, 4.12; N, 6.41.

2,3-Dihydro-2,4-dithioxo-6-phenyl-3-(2-phenylethyl)-4*H*-1,3-thiazine (**7b**).

Chromatography of the reaction mixture obtained from the reaction of 1-benzylthio-1-phenylethylamino-3-phenylpropene-3-thione (**3u**) with thiophosgene (refer to **4k** in Table 1 for the reaction conditions) using a mixture of methylene chloride and *n*-hexane (v:v, 1:1) as an eluent gave **7b** (3 mg, 0.009 mmole, 6%). Pure **7b** was obtained as a reddish needle type of solids by recrystallization from ethanol, mp 119-120 $^\circ$ ;  $^1\text{H}$  nmr (deuteriochloroform, 300 MHz):  $\delta$  3.19-3.24 (m, 2H, CH<sub>2</sub>), 5.30-5.36 (m, 2H, N-CH<sub>2</sub>), 7.32-7.58 (m, 10H, ArH), 7.72 (s, 1H, =CH); ir (potassium bromide): 1560, 1495, 1346, 1177, 1121, 762, 694 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 341 (48.1) (M<sup>+</sup>), 308 (16.72), 236 (100), 178 (23.54), 121 (67.53).

Anal. Calcd. for C<sub>18</sub>H<sub>15</sub>NS<sub>3</sub>: C, 63.31; H, 4.43; N, 4.10. Found: C, 63.38; H, 4.29; N, 4.02.

Continuous elution with the same solvent mixture gave a mixture of unidentifiable compounds (20 mg) and **4k**.

General Procedure for the Synthesis of 3-Alkyl-2,3-dihydro-2,4-dioxo-6-phenyl-4*H*-1,3-thiazines **5a-5k**.

To a stirred 8*M* solution of phosgene in tetrahydrofuran (0.2 mmole) diluted with toluene (2 ml) was added dropwise compound **3**, which immediately gave a pale brown solid. The pale brown solid dissolved by dropwise addition of triethylamine (0.4 mmole) by using a microsyringe was followed by the formation of triethylamine hydrochloride salts. The reaction mixture was stirred for an additional 15 minutes, followed by addition of

water (5 ml), and extracted with diethyl ether (2 x 5 ml). The organic layer was washed with water (2 x 5 ml), and dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (230-400 mesh) column (8 x 2 cm) with a mixture of methylene chloride and *n*-hexane (v:v, 2:1). In each case, consult Table 3 for yields and analytical data of **5a-5k** and Table 4 for their spectroscopic data.

#### General Procedure for the Synthesis of **5a-5k** using Oxalyl Chloride.

To a stirred solution of oxalyl chloride (0.3 mmole) in toluene (1 ml) by a microsyringe was added dropwise a solution of compound **3** (0.3 mmole) in toluene (6 ml), which gave immediately a brown solid. Upon addition of triethylamine (0.7 mmole) by using a microsyringe to the reaction mixture, the color of the solution turned dark with the disappearance of the brown solid and triethylamine hydrochloride salts were formed. The mixture was stirred for an additional 10 minutes, followed by addition of water (7 ml), and extracted with diethyl ether (3 x 5 ml). The organic layer was washed with water twice, and dried over anhydrous magnesium sulfate. Evaporation of the solvent under the reduced pressure gave a dark residue, which was chromatographed on a silica gel (230-400 mesh) column (8 x 2 cm). Elution with a mixture of methylene chloride and *n*-hexane (v:v, 2:1) gave a small amount of 3-alkyl-2,3-dihydro-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazines **8** and 3-alkylthio-5-phenylisothiazole **9**. Continuous elution with the same solvent mixture gave **5**. In each case, consult Table 3 for reaction conditions, yields and analytical data of **5a-5k**.

#### 3-Benzyl-2,3-dihydro-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazine (**8b**).

Chromatography of the reaction mixture obtained from the reaction of 1-benzylamino-1-methylthio-3-phenylpropene-3-thione (**3m**) with oxalyl chloride and triethylamine (refer to **5e** in Table 3 for reaction conditions) using a mixture of methylene chloride and *n*-hexane (v:v, 2:1) as an eluent gave **8b** (12 mg, 0.039 mmole, 14%). Pure **8b** was obtained as pale red granular type solid by recrystallization from ethanol, mp 119-119.5°; <sup>1</sup>H nmr (deuteriochloroform, 300 MHz): δ 5.87 (s, 2H, CH<sub>2</sub>), 7.28-7.63 (m, 10H, ArH), 7.64 (s, 1H, =CH); ir (potassium bromide): 1657, 1564, 1495, 1294, 1163, 960, 762 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 311 (100) (M<sup>+</sup>), 283 (36.8), 250 (76.4), 121 (68.5), 91 (94.5).

*Anal.* Calcd. for C<sub>17</sub>H<sub>13</sub>NOS<sub>2</sub>: C, 65.57; H, 4.21; N, 4.50. Found: C, 65.48; H, 4.29; N, 4.32.

Continuous elution with the same solvent mixture gave **5e**.

#### 3-(2-Chlorobenzyl)-2,3-dihydro-2-oxo-6-phenyl-4-thioxo-4*H*-1,3-thiazine (**8c**).

Chromatography of the reaction mixture obtained from the reaction of 1-(2-chlorobenzylamino)-1-methylthio-3-phenylpropene-3-thione (**3q**) with oxalyl chloride and triethylamine (refer to **5h** in Table 3 for reaction conditions) using a mixture of methylene chloride and *n*-hexane (v:v, 2:1) as an eluent gave **8c** (15 mg, 0.043 mmole, 16%). Pure **8c** was obtained as a yellowish solid by recrystallization from ethanol, mp 162-163°; <sup>1</sup>H nmr (deuteriochloroform, 300 MHz): δ 5.90 (s, 2H, CH<sub>2</sub>), 6.98-7.63 (m, 9H, ArH), 7.66 (s, 1H, =CH); ir (potassium bromide): 1652, 1571, 1336, 1174, 756 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 310 (100) (M<sup>+</sup>-Cl), 282 (19.9), 121 (25.4).

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>ClNOS<sub>2</sub>: C, 59.04; H, 3.50; N, 4.05. Found: C, 58.88; H, 3.69; N, 3.97.

Continuous elution with the same eluent gave **5h**.

#### General Procedure for the Synthesis of 3-Alkyl-2-arylimino-2,3-dihydro-4-oxo-6-phenyl-4*H*-1,3-thiazines **6a-6p**.

A mixture of **3** (0.2 mmole) and *N*-arylimidoyl dichloride (0.5 mmole) in dried benzene (10 ml) was vigorously stirred at room temperature until compound **3** had disappeared on thin layer chromatography. The color of the solution turned from deep yellow to pale yellow. After the solvent was evaporated under reduced pressure, the residue was chromatographed on a silica gel (230-400 mesh) column (8 x 2 cm). Elution with *n*-hexane, followed by methylene chloride gave compound **6**. In each case, consult Table 5 for reaction conditions, yields, and analytical data of **6a-6p** and Table 6 for their spectroscopic data.

#### 2,3-Dihydro-3-ethyl-6-phenyl-2-phenylimino-4-thioxo-4*H*-1,3-thiazine (**10a**).

Chromatography of the reaction mixture obtained from the reaction of 1-benzylthio-1-ethylamino-3-phenylpropene-3-thione (**3g**) with *N*-phenylimidoyl chloride (refer to **6b** in Table 5 for the reaction conditions) using a mixture of methylene chloride and *n*-hexane (v:v, 1:1) as an eluent gave **10a** (10 mg, 0.296 mmole, 15%). Pure **10a** was obtained as a yellow solid by recrystallization from ethanol, mp 98-100°; <sup>1</sup>H nmr (deuteriochloroform, 80 MHz): δ 1.43 (t, 3H, CH<sub>3</sub>), 4.95 (q, 2H, CH<sub>2</sub>), 6.82-7.52 (m, 10H, ArH), 7.64 (s, 1H, =CH); ir (methylene chloride): 1588, 1570, 1424, 1384, 1196, 1105, 762 cm<sup>-1</sup>; ms: (70 eV) *m/z* (%) 324 (53.2) (M<sup>+</sup>), 221 (76.3), 178 (64.6), 121 (100).

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>: C, 66.63; H, 4.97; N, 8.63. Found: C, 66.51; H, 5.03; N, 8.46.

Continuous elution with methylene chloride gave **3g** (7 mg, 0.022 mmole, 11%). Elution with methylene chloride gave **6b**.

#### 2-(4-Bromophenylimino)-2,3-Dihydro-3-methyl-4-oxo-6-phenyl-4*H*-1,3-thiazine (**6i**).

A stirred solution of 1-benzylthio-1-methylamino-3-phenylpropene-3-thione (**3c**) with *N*-(4-bromophenyl)imidoyl dichloride (refer to **6i** in Table 5 for reaction conditions) gave a mixture of white solids, which were filtered and identified as **6i** (51 mg, 0.137 mmole). Evaporation of the filtrate, followed by chromatography, using a mixture of methylene chloride and *n*-hexane (v:v, 1:1) as an eluent gave an unknown compound (13 mg). Elution next with methylene chloride gave **6i** (70 mg, 0.188 mmole).

#### General Procedure for the Hydrolysis of **6**.

To a solution of **6** in ethanol was added concentrated hydrochloric acid, which was refluxed until compound **6** had completely disappeared. The solvent was evaporated and the residue was extracted with methylene chloride, which was washed with aqueous sodium bicarbonate (4 x 50 ml), followed by water (2 x 50 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave crude compound **5**, which was recrystallized from ethanol.

#### Hydrolysis of 2,3-Dihydro-4-oxo-3-(*n*-pentyl)-6-phenyl-2-phenylimino-4*H*-1,3-thiazine (**6c**).

A solution of **6c** (160 mg, 0.457 mmole) in ethanol (50 ml) in the presence of hydrochloric acid (10 ml) was refluxed for 15

hours to give **5i** (116 mg, 0.421 mmole, 92%). Pure **5i** was obtained by recrystallization from ethanol, mp 84-85°; <sup>1</sup>H nmr (deuteriochloroform, 80 MHz): δ 0.70-1.78 (m, 9H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 4.03 (t, 2H, N-CH<sub>2</sub>), 6.68 (s, 1H, =CH), 7.51 (s, 5H, ArH); ir (methylene chloride): 1685, 1633, 1451, 1355, 1187, 884, 770 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>S: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.27; H, 6.35; N, 4.98.

#### Hydrolysis of **6i**.

A solution of **6i** (20 mg, 0.0536 mmole) in ethanol (40 ml) in the presence of hydrochloric acid (2 ml) was refluxed for 4 hours to give 2,4-dioxo-3-methyl-6-phenyl-4*H*-1,3-thiazine (**5a**) (10 mg, 0.0447 mmole, 83%).

Hydrolysis of 2-(4-bromophenylimino)-2,3-dihydro-3-ethyl-4-oxo-6-phenyl-4*H*-1,3-thiazine (**6j**).

A solution of **6j** (27 mg, 0.0697 mmole) in ethanol (40 ml) in the presence of hydrochloric acid (2 ml) was refluxed for 15 hours to give 2,3-dihydro-2,4-dioxo-3-ethyl-6-phenyl-4*H*-1,3-thiazine (**5b**) (15 mg, 0.0693 mmole, 94%).

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