

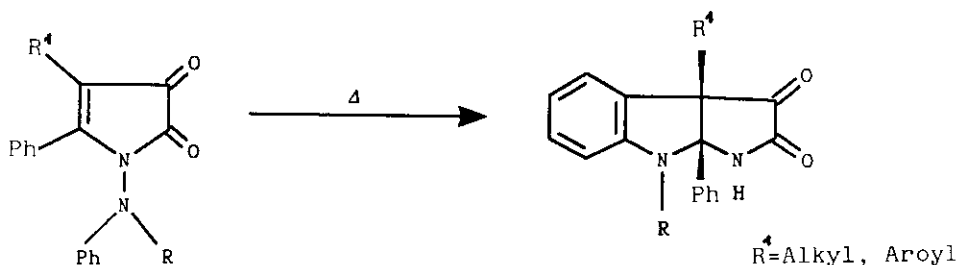
EXPECTED AND UNEXPECTED REACTIONS OF *N,N*-DIPHENYLHYDRAZONES  
WITH CHLOROCARBONYLSULFENYL CHLORIDE<sup>1</sup>

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**Abstract** - The *N,N*-diphenylhydrazones (1) and chlorocarbonylsulfenyl chloride cyclize to give the thiazolones (2), with the benzoyl derivative (1i) the 1,3-oxathiolone (3) is obtained. At low temperatures the hydrazines (1f, g, i), are selectively oxidized affording  $\alpha$ -oxohydrazones (4). From all thiazolones (2a, d) only can be rearranged into the indole derivatives (6) via a Fischer-indolization process.

4,5-Disubstituted 1-diphenylaminopyrrole-2,3-diones, obtained from cyclocondensation reactions of *N,N*-diphenylhydrazones and oxalyl chloride can easily undergo a thermal Fischer-indolization to pyrrolo[2,3-*b*]indoles.<sup>3</sup> This heterocyclic system is the basic molecular skeleton of the alkaloid physostigmine, which has found strong interest in the treatment of Alzheimer disease.<sup>4</sup>

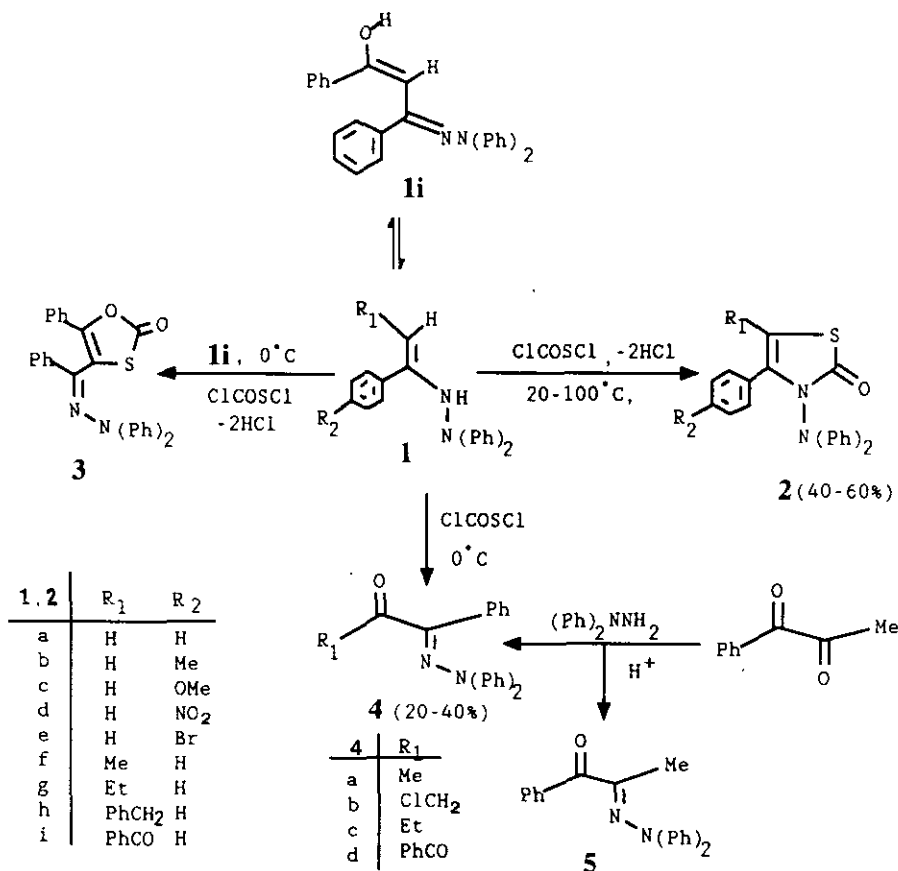


In order to proof the scope and limitations of that particular Fischer indole synthesis we now tried to use the thiazolones (2), made from the corresponding hydrazones (1) and chlorocarbonylsulfenyl chloride, in that rearrangement.

Chlorocarbonylsulfenyl chloride itself was found to be a suitable cyclization reagent,<sup>5</sup> in particular to prepare heterocyclic systems possessing biological activity in the herbicide and insecticide area.<sup>6</sup> The synthesis of the thiazolones (2) has to be seen from that aspect too.

Chlorocarbonylsulfenyl chloride is easily prepared from trichloromethanesulfenyl chloride and purified by distillation.<sup>7</sup> The cyclocondensation reaction of the diphenylhydrazones (1a-e,h) and chlorocarbonylsulfenyl chloride clearly give the expected thiazolones (2a-e,h) in moderate yields (40-60%). Structural confirmation of 2 is based on the ir and nmr spectroscopic data besides elemental analysis. All compounds (2) exhibit one single C=O absorption at 1670-1685 $\text{cm}^{-1}$ . In the <sup>1</sup>H nmr spectra, the singlets at 6.1-6.4 ppm are assigned to the olefinic protons at C-4. As an example, from the <sup>13</sup>C nmr spectrum of 2a, the signals at 170.05 ppm (d, <sup>3</sup>J=5.4 Hz, C-2) and 96.7 ppm (d, <sup>1</sup>J=187.5 Hz, C-4) strongly support the structural proposal. In addition, no =C-C=O connectivity<sup>8</sup> has been observed, thus outruling the isomeric 1,2-thiazolone-3 structure.

From the hydrazone (**1i**) the cyclization product was found to be an 1,3-oxathiolone derivative (**3**), deduced from its ir and  $^{13}\text{C}$  nmr spectra: Ir (KBr):  $1745\text{ cm}^{-1}$ , C=O;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ): 169.0 ppm (s, C=O), 144.0 ppm (t, 2.2 Hz, C=N), 139.1 ppm (t, 2.0 Hz, C-5), 110.0 ppm (s, C-4). Obviously the hydrazone (**1i**) preferably reacts from its OH- tautomeric form.



Surprisingly, with the hydrazones (**1f, g, i**), a distinct influence of reaction conditions on the specific reaction pathway has been observed: while at elevated temperatures ( $50\text{--}60^\circ\text{C}$ ), the thiazolones (**2f, g**) and the oxathiolone (**3**), respectively, are formed, at low temperature ( $0^\circ\text{C}$ ) the  $\alpha$ -oxohydrazones (**4**) are the predominating reaction products. Their structural confirmation was based on spectroscopic data (see *Experimental part*) as well as on an independent synthesis, e.g. **4a**, from 1-phenyl-1,2-propanedione and *N,N*-diphenylhydrazine. Originally a mixture of the two isomeric hydrazones (**4a**) and (**5**) (ratio 1:1) was obtained, which then could be separated by simple fractional crystallization from ethanol. **4a** was found to be identical by mp, tlc and ir spectrum with the corresponding compound obtained from **1f** and chlorocarbonylsulfonyl chloride as described above.

In order to achieve some more insight into the scope and mechanism of that surprising oxidation reaction several further experiments have been carried out:

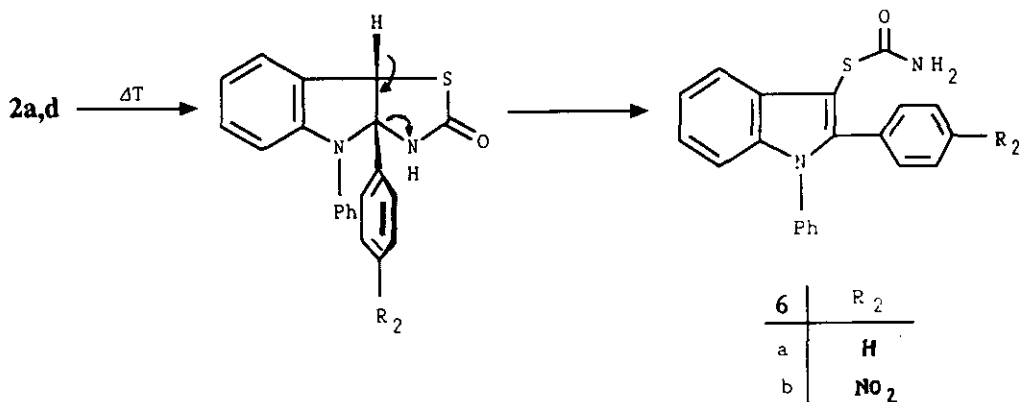
- Under a strict  $\text{N}_2$ -atmosphere no oxidation products (**4**) were formed.
- Performing the reaction in the dark does not have any influence on the formation of **4**.
- Using acetyl chloride, oxalyl chloride and chloroacetyl chloride instead of chlorocarbonylsulfonyl chloride under various reaction conditions the corresponding  $\alpha$ -oxohydrazones were obtained too. Similar results were found when the acid chlorides were exchanged to dibenzoyl peroxide. The yields are within the same scale or

somewhat lower (with acetyl chloride and dibenzoyl peroxide).

d) Starting with the corresponding ketones instead of their hydrazones (**1f, g, i**), no oxidation product could be detected.

Summarizing these experimental findings one can conclude that the reactions **1**→**4** obviously get the oxygen needed from air and they most likely proceed via a radical mechanism. Similar  $\alpha$ -oxidation products have been observed with methylene-blue sensitized photooxidation of *N,N*-diphenylhydrazones.<sup>9</sup> But it is really remarkable, that these oxidation reactions involving acid chlorides obviously don't need any additional radical initiation step like  $h\nu$ , heat or peroxides.

All thiazolones (**2**) have been tried to undergo the thermal Fischer-indolization reaction. Only **2a, d** could successfully be rearranged into the indole derivatives (**6**). The opening of the thiazolone ring during that indolization process can clearly be deduced from the <sup>13</sup>C nmr spectrum of **6a, b**: There are no signals in the  $sp^3$ -carbon region, the carbonyls are found at 170.5, 170.3 ppm respectively. (The signals of all other quaternary carbons see *Experimental Part*.)



Obviously C-4 in the thiazolones (**2**) must have high electron deficiency, otherwise the new C-C bond can not be formed. This in principle agrees well with the general mechanistic consideration on the Fischer-indole synthesis affording a [3,3]sigmatropic shift as rate determining step.<sup>10</sup> Cleavage of the thiazolo[2,3-*b*]indole intermediate to **6** corresponds well to the last step of the Fischer-indolization, namely, elimination of NH<sub>3</sub>. It has also been observed with similar pyrrolo[2,3-*b*]indole systems, having a hydrogen at C-3a.<sup>3d</sup> In general, compared to the pyrrole-2,3-diones, the thiazol-2-ones, where one C=O group is displaced by sulfur, exhibit less reactivity in that indolization rearrangement, due to a higher electron density at C-4.

#### EXPERIMENTAL PART

Melting points were determined on a Tottoli Apparatus and are uncorrected. Elemental Analyses were performed with a Carlo Erba Elemental Analyzer. Ir spectra were recorded on a Perkin-Elmer 421. <sup>1</sup>H and <sup>13</sup>C nmr spectra were obtained on a Varian 200 gemini spectrometer with TMS as an internal standard. The Ms spectrum of **4d** was recorded on a Varian MAT 212 spectrometer.

#### Synthesis of **2a-e**: General Procedure

0.2 g (0.7 mmol) of the acetophenone-*N,N*-diphenylhydrazones<sup>3d</sup>, dissolved (1a-d) or suspended (1e) in 50 ml of dry ether, were kept at 0°-20°C and 0.3 ml (3.6 mmol) of ClCOSCl<sup>7</sup> (molar ratio 1:5) were added dropwise with stirring during 30 min. After 4-7 h at 20°-30°C, the ether was removed and the residue was recrystallized from a suitable solvent.

**1-Diphenylamino-5-phenyl-1,3-thiazol-2-one (2a)**

0.14 g (58%); mp 170°C (ethanol); ir(KBr): 1675cm<sup>-1</sup>; <sup>13</sup>C nmr(CDCl<sub>3</sub>) δ : 96.7,119.8,123.8,128.5, 128.54, 130.4,138.4,144.6,170.05; Anal. Calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>OS: C, 73.26; H, 4.65; N, 8.14; Found: C, 73.27; H, 4.64; N, 8.06.

**1-Diphenylamino-5-(*p*-methyl)phenyl-1,3-thiazol-2-one (2b)**

0.13 g (55%); mp 206°C (toluene); ir(KBr): 1670cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ : 2.30(3H, s, CH<sub>3</sub>); 6.12(1H, s, =CH); 6.9-7.4(14H, m, ArH); Anal. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: C, 73.74; H, 5.03; N, 7.82; Found: C, 73.89; H, 5.18; N, 7.44.

**1-Diphenylamino-5-(*p*-methoxy)phenyl-1,3-thiazol-2-one (2c)**

0.12 g (50%); mp 198°C (toluene); ir(KBr): 1670cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ : 3.79(3H, s, OCH<sub>3</sub>); 6.09 (1H, s, =CH); 6.7-7.4 (14H, m, Ar-H); Anal. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: C, 70.59; H, 4.81; N, 7.49; Found: C, 70.83; H, 4.90; N, 7.30.

**1-Diphenylamino-5-(*p*-nitro)phenyl-1,3-thiazol-2-one (2d)**

0.15 g (64%); mp 190°C (toluene); ir(KBr): 1686cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ : 6.40(1H, s, =CH); 6.9-8.3(14H, m, Ar-H); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S: C, 64.78; H, 3.86; N, 10.80; Found: C, 64.92; H, 4.04; N, 10.4.

**1-Diphenylamino-5-(*p*-bromo)phenyl-1,3-thiazol-2-one (2e)**

0.13 g (56%); mp 202°C (benzene); ir(KBr): 1673cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ : 6.20(1H, s, =CH); 6.9-7.5(14H, m, Ar-H); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>OBrS: C, 59.57; H, 3.55; N, 6.62; S, 7.57; Found: C, 60.23; H, 3.70; N, 6.23; S, 7.17.

**Synthesis of 2f-h: General Procedure**

0.2 g (0.65 mmol) of the hydrazones<sup>3a</sup> 1f-h were dissolved in 20 ml benzene and refluxed for 3 h. 0.2 ml (2.4 mmol) of ClCOSCl were added at once and reflux was continued for additional 1.5-2.5 h. Then the solvent was removed in vacuo. The residue was purified by silica gel chromatography (column or preparative thin layer chromatography, CH<sub>2</sub>Cl<sub>2</sub> as eluant), the substances obtained then recrystallized from ethanol.

**1-Diphenylamino-4-methyl-5-phenyl-1,3-thiazol-2-one (2f)**

0.1 g (42%); mp 148°C (ethanol); ir(KBr): 1682 cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ : 2.12(3H, s, =CH<sub>3</sub>); 6.8-7.5 (15H, m, Ar-H); Anal. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: C, 73.74; H, 5.03; N, 7.82; S, 8.94; Found C, 73.68; H, 5.02; N, 7.68; S, 8.93.

**1-Diphenylamino-4-ethyl-5-phenyl-1,3-thiazol-2-one (2g)**

0.09 g (37%); mp 118°C (ethanol); ir(KBr): 1681 cm<sup>-1</sup>; <sup>1</sup>H nmr(DMSO) δ : 1.12 (3H, t, J=7 Hz, CH<sub>3</sub>); 2.50 (2H, q, J=7 Hz, CH<sub>2</sub>); 6.7-7.5 (15H, m, Ar-H); Anal. Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: C, 74.19; H, 5.38; N, 7.53; Found: C, 73.50; H, 5.32; N, 7.34.

**1-Diphenylamino-4-benzyl-5-phenyl-1,3-thiazol-2-one (2h)**

0.1 g (43%); mp 146°C (ethanol); ir(KBr): 1676 cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ: 3.82 (2H, s, CH<sub>2</sub>); 6.7-7.6 (20H, m, Ar-H); Anal. Calcd for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>OS: C, 77.42; H, 5.07; N, 6.45; Found: C, 77.32; H, 5.11; N, 6.45.

**4-Diphenylhydrazonobenzoyl-5-phenyl-1,3-oxathiol-2-one (3)**

Dissolve 0.4 g (1 mmol) of dibenzoylmethane-*N,N*-diphenylhydrazone in 20 ml of ether, add 0.3 ml (3.6 mmol) of ClCOSCl dropwise under cooling, and keep stirring for 5 h until a precipitate is formed. After suction the crude product is crystallized from ethanol.

0.16 g (35%); mp 164°C (ethanol); ir(KBr): 1745 cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ: 6.85-7.84 (m, Ar-H); <sup>13</sup>C nmr(CDCl<sub>3</sub>) δ: 122.2, 124.9, 126.3, 126.8, 127.3, 128.7, 128.9, 129.1, 129.6, 129.9, 136.7, 139.1, 144.0, 146.3, 169.0; Anal. Calcd for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: C, 75.00; H, 4.46; N, 6.25; S, 7.14; Found: C, 74.70; H, 4.60; N, 6.13; S, 7.05.

**1,3-Diphenyl-3-(2,2-diphenylhydrazono)propane-1,2-dione (4d)**

The ether filtrate of compound (3) was separated by silica gel preparative thin layer chromatography (CH<sub>2</sub>Cl<sub>2</sub> as eluant). The pure compound was eluted with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from *n*-butanol.

0.12 g (29%); mp 178°C(*n*-butanol); ir(KBr): 1670 cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ: 6.70-8.15(m, Ar-H); ms(m/z, %): 404 (M<sup>+</sup>, 70), 299 (M<sup>+</sup>-benzoyl, 60), 271(299-CO, 12), 168 [(Ph)<sub>2</sub>N<sup>+</sup>, 100], 105 (benzoyl, 27); Anal. Calcd for C<sub>27</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 80.20; H, 4.95; N, 6.93; Found: C, 78.90; H, 4.66; N, 6.77.

**Formation of 4a and 4b:**

0.4 g (1.2 mmol) of propiophenone-*N,N*-diphenylhydrazone was dissolved in 25 ml of ether, 0.3 ml (3.6 mmol) of ClCOSCl were added dropwise with cooling to 0°C and stirring within 30 min. After stirring overnight and suction, the crude mixture of products was separated by silica gel preparative thin layer chromatography (eluant: CH<sub>2</sub>Cl<sub>2</sub>). Pure 4a and 4b were obtained after recrystallization from ethanol.

**3-(2,2-Diphenylhydrazono)-3-phenylpropan-2-one (4a)**

0.17 g 2 (41%); mp 166°C (ethanol); ir(KBr): 1670 cm<sup>-1</sup>; <sup>1</sup>H nmr(CDCl<sub>3</sub>) δ: 2.68(3H, s, CH<sub>3</sub>); 6.5-7.3 (15H, m, Ar-H); <sup>13</sup>C nmr(CDCl<sub>3</sub>) δ: 28.1, 125.1, 127.2, 129.2, 129.4, 131.0, 131.3, 135.2, 147.3, 148.1, 200.4; Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O: C, 80.25; H, 5.73; N, 8.92; Found: C, 80.47; H, 5.41; N, 8.85.

**1-Chloro-3-(2,2-*N,N*-diphenylhydrazono)-3-phenylpropan-2-one (4b)**

0.08 g (17%); mp 169°C (ethanol); ir(KBr): 1690 cm<sup>-1</sup>; <sup>13</sup>C nmr(CDCl<sub>3</sub>) δ: 47.2, 123.5, 126.1, 127.6, 128.1, 129.4, 129.6, 132.5, 143.3, 145.0, 190.8; Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>OCl: C, 72.41; H, 4.88; N, 8.04; Cl, 10.05; Found: C, 72.19; H, 4.86; N, 7.98; Cl, 10.18.

**4-(2,2-Diphenylhydrazono)-4-phenylbutan-3-one (4e)**

0.2 ml (2.4 mmol) of ClCOSCl were added dropwise with cooling (ice/NaCl) to a well stirred solution of 0.34 g (1.08 mmol) butyrophenone-*N,N*-diphenylhydrazone in 20 ml of ether. After 5 h the solvent is removed and again 5 ml of ether are added. After suction the crude product was purified by silica gel preparative thin layer chromatography (eluant: CH<sub>2</sub>Cl<sub>2</sub>) and recrystallized from ethanol.

0.14 g (39%); mp 136°C (ethanol); ir(KBr): 1662 cm<sup>-1</sup>; <sup>1</sup>H nmr(DMSO-*d*<sub>6</sub>) δ: 1.11(3H, t, J=7.3 Hz, CH<sub>3</sub>); 3.15(2H, q, J=7.3 Hz, CH<sub>2</sub>); 6.7-7.3(15H, m, Ar-H); Anal. Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O: C, 80.49; H, 6.10; N, 8.54; Found: C, 80.26; H, 6.03; N, 8.41.

### Synthesis of the $\alpha$ -oxohydrazones 4a and 5:

0.4 g (2.7 mmol) of 1-phenyl-1,2-propanedione and a catalytic amount of *p*-toluenesulfonic acid were heated at 90-100°C for 40 min. After cooling, the crude residue was dissolved in ether and some heterogenic impurities were filtered off. The ether solution was washed with water twice, the ether was removed and methanol was added to the residue. After suction, the crude product was recrystallized from ethanol, yielding pure 4a 0.2 g (26%). The filtrate was kept at room temperature for several hours, then 5 precipitated.

5: 0.22 g (29%); mp 87-9°C(ethanol); ir(KBr): 1638 cm<sup>-1</sup>; Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O: C, 80.25; H, 5.73; N, 8.92; Found: C, 80.30; H, 5.60; N, 8.87.

### 3-Carbamoylthio-1,2-diphenylindole (6a)

0.2 g (0.58 mmol) of 1a were heated at 180°C in a metal bath for 5 min. After cooling, ether was added to the precipitate. The crude product was recrystallized from benzene (with charcoal).

0.06 g (30%); mp 260°C(benzene); ir(KBr): 1648, 3120, 3400 cm<sup>-1</sup>; <sup>1</sup>H nmr(DMSO-d<sub>6</sub>)  $\delta$ : 6.80-7.41(14H, m, Ar-H), 8.35 (2H, s, NH<sub>2</sub>); <sup>13</sup>C nmr(DMSO-d<sub>6</sub>)  $\delta$ : 113.5, 115.9, 117.8, 120.2, 122.1, 142.1, 143.5, 170.5; Anal. Calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>OS: C, 73.26; H, 4.65; N, 8.14; Found: C, 73.59; H, 4.69; N, 7.90.

### 3-Carbamoylthio-2-*p*-nitrophenyl-1-phenylindole (6b)

0.4 g (1 mmol) of 1d were refluxed in decaline (10 ml) for 10 min. After cooling, the precipitate formed was purified by silica gel preparative thin layer chromatography (eluant: CH<sub>2</sub>Cl<sub>2</sub> /acetone 4.5:0.5) and recrystallized from benzene.

0.14 g (35%); mp 268°C(benzene); ir(KBr): 1655, 3140, 3460 cm<sup>-1</sup>; <sup>1</sup>H nmr(DMSO-d<sub>6</sub>)  $\delta$ : 6.90-8.30(13H, m, Ar-H), 11.80(2H, s, NH<sub>2</sub>); <sup>13</sup>C nmr(DMSO-d<sub>6</sub>)  $\delta$ : 122.6, 125.2, 125.5, 125.8, 129.6, 130.5, 131.3, 135.9, 146.8, 148.5, 170.3; Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S: C, 64.78; H, 3.86; N, 10.80; Found: C, 64.40; H, 4.13; N, 10.67.

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