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## "NOVEL SYNTHESIS AND CYCLIZATION REACTIONS OF 3-AMINO-2-MERCAPTOPYRROLE DERIVATIVES"

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Interaction of cyanothioformamides with chalcones gave 3-amino-2-mercaptopyrroles, which have the tautomeric structures (3-aminopyrroline-2-thiones and 3-iminopyrrolidine-2-thiones). The latter was reacted with chloroacetic acid, ethyl chloroacetate, chloroacetamide and 2,3-dichloro-1,4-naphthoquinone to give the corresponding pyrrolothiazines derivatives. On using phenylisocyanate or p-chlorobenzoyl chloride, the corresponding pyrrolothiazole derivatives could be isolated. Replacement of chalcones by maleimides furnished pyrrolopyrrolinediones.

**Keywords:** cyanothioformamides; 3-Amino-2-mercaptopyrroles; pyrrolothiazines; pyrrolothiazoles; pyrrolopyrrolinediones

### INTRODUCTION

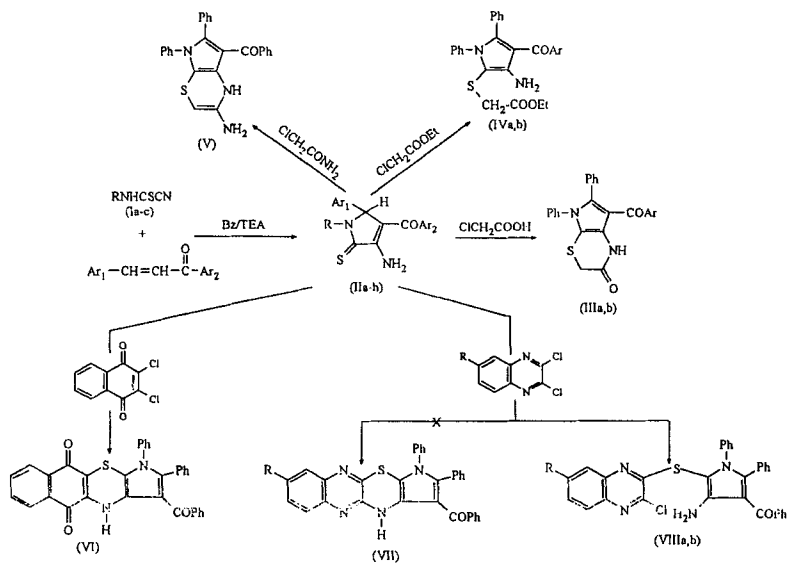
Cyanothioformamides<sup>[1-3]</sup> find extensive application in the synthesis of heterocyclic compounds as imidazoles<sup>[4]</sup>, oxazoles<sup>[5]</sup> and thiazoles<sup>[6,7]</sup>. Our interest in ring-closure reactions<sup>[8]</sup>, activated nitriles<sup>[9]</sup> and chemistry of cyanothioformamides<sup>[10-12]</sup> led us to investigate the behavior of the latter towards other electrophiles as chalcones and maleimides. This reaction produced pyrroloiminothione derivatives, which possess latent functional substituents and appear promising for further chemical transformation.

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Thus, cyanothioformamides (Ia-c)<sup>[1-3]</sup> reacted with  $\alpha,\beta$ -unsaturated ketones to give 5-aryl-4-aroyle-3-amino-1-substituted-2-pyrrolinethiones (IIa-h) which were found to have the tautomeric structures (3-iminopyrrolidine-2-thione and 3-amino-2-mercaptopyrrole) (scheme-1). The behavior of (II) towards chloroacetic acid, ethyl chloroacetate and chloroacetamide was investigated. Thus, interaction of (IIg,h) with chloroacetic acid using  $\text{Ac}_2\text{O}/\text{AcOH}$  as medium and fused  $\text{AcONa}$  as catalyst caused cyclization to give 5-benzoyl-3-oxo-6,7-diphenyl-pyrrolo[3,2-e][1,4]thiazines (IIIa,b) (scheme-1), through elimination of one mole each of  $\text{HCl}$  and  $\text{H}_2\text{O}$ . Attempted interaction of (IIg,h) with ethyl chloroacetate using absolute  $\text{EtOH}/\text{fused AcONa}$  hoping to obtain the same products (IIIa,b) was unsuccessful and instead the intermediate 1,5-diphenyl-4-aroyle-3-amino-2-mercaptoethylacetopyrrole (IVa,b) (scheme-1) were obtained. Repeating this reaction between the pyrrole (IIg) and ethyl chloroacetate using dioxan as solvent and triethylamine as catalyst caused cyclization and the pyrrolothiazine (IIIa) was obtained (m.p., m.m.p. & TLC). Interaction of (IIg) with chloroacetamide either by fusion or using dioxan as solvent and triethylamine as catalyst resulted in the formation of one isolatable product. This reaction may undergo either through elimination of one mole of both ( $\text{HCl}$  &  $\text{NH}_3$ ) to give a product identical with (IIIa) or by elimination of one mole of ( $\text{HCl}$  &  $\text{H}_2\text{O}$ ) to give (V). Analytical and spectral data showed that chloroacetamide reacted analogous of same lines as chloroacetic acid towards the pyrrole (IIg) (elimination of  $\text{HCl}$  &  $\text{H}_2\text{O}$ ) and the obtained product was 3-amino-5-benzoyl-6,7-diphenyl-pyrrolo[3,2-e][1,4]thiazine (V) (scheme-1).

The behaviour of 3-amino pyrroline-2-thione (II) towards aromatic o-dichloro compounds was investigated. Thus, interaction of (IIg) with 2,3-dichloro-1,4-naphthoquinone gave 3-benzoyl-1,2-diphenyl-pyrrolo[2,3-b]naptho[2',3'-e][1,4]thiazine-5, 10-dione (VI) (scheme-1) through elimination of 2 moles of  $\text{HCl}$ . Mass spectra of (VI) showed the molecular ion peak ( $\text{M}^+$ ; 525) which was the base peak (100%).

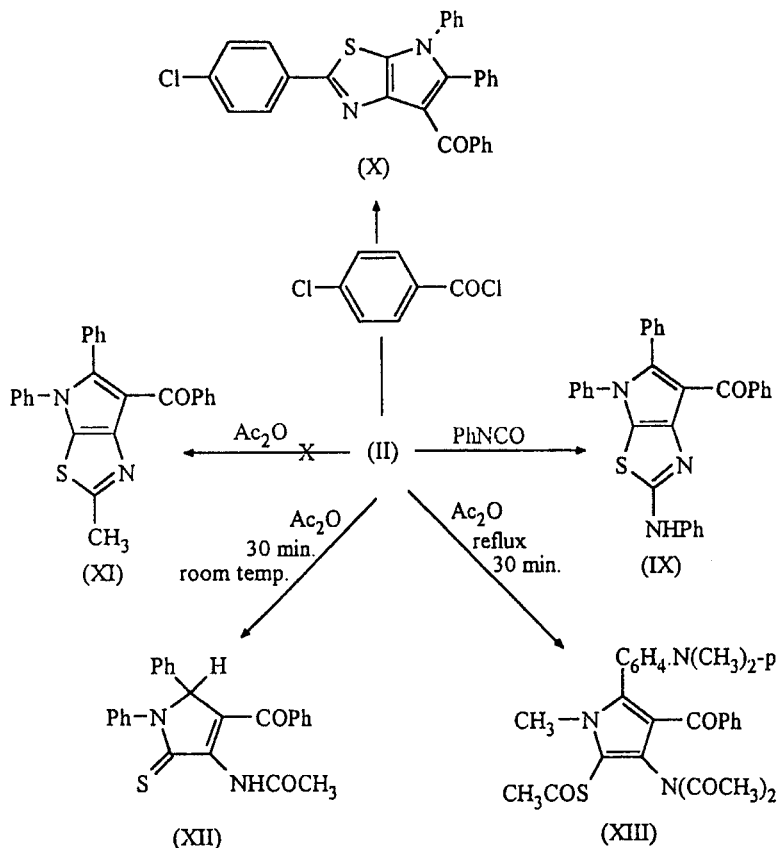
On the other hand, repeating the same reaction using 2,3-dichloroquinoxaline and its 6-methyl derivative hoping to obtain a product of type (VII) was unsuccessful and instead the intermediate sulfide (VIII) was isolated in both cases. With respect to the methyl derivative, the authors favor structure (VIIIb) over the other isomer, as the chlorine atom para to the methyl group will be less active.



SCHEME 1

The behavior of (II) towards phenylisocyanate, p-chlorobenzoyl chloride and acetic anhydride was also investigated. Thus, interaction of (IIg) with phenylisocyanate caused cyclization through addition followed by elimination of one molecule of  $\text{H}_2\text{O}$  to yield 2-anilino-4-benzoyl-5,6-diphenyl-pyrrolo[3,2-d]thiazole (IX) (scheme-2). The pyrrolothiazole structure could be also achieved through ring closure reaction between (IIg) and p-chlorobenzoyl chloride. The reaction included elimination of one mole of each  $\text{HCl}$  and  $\text{H}_2\text{O}$  to produce 4-benzoyl-2-(4'-chlorophenyl)-5,6-diphenyl-pyrrolo[3,2-d]thiazole (X) (scheme-2). Its mass spectrum exhibited the molecular ion peak ( $\text{M}^+$ ; 490) which also was the base peak (100%). Extension of this reaction to acetic anhydride hoping to obtain a pyrrolothiazole structure of type (XI) was unsuccessful and instead the monoacetyl (XII) and the triacetyl (XIII) derivatives (scheme-2) were obtained depending on the amount of  $\text{Ac}_2\text{O}$ , the reaction temperature and the reaction time. The formation of the pyrrolothiazole (X) and the failure of formation of (XI) can be attributed to the bulk of the aryl acid chloride which permits only one mole to react and prevents a second mole to participate in the reaction which gave a chance for cyclization.

These results are in complete agreement with our findings on 5-aminoimidazole-4-thiones<sup>[13]</sup> with  $\text{Ac}_2\text{O}$ .



SCHEME 2

Maleimides were used as another electrophile instead of chalcones and allowed to react with cyanothioformamides at different conditions. Thus, interaction of equimolar amounts of (IIg) and N-(p-totyl, p-anisyl, p-chlorophenyl, p-bromophenyl or p-nitrophenyl) maleimides at room temp. in benzene as solvent and triethylamine as catalyst furnished in each case one isolatable product. The assigned structures of these products were based on analytical and spectral data; they are 3-amino-1-phenyl-2-mercaptopyr-

rolo[2,3-c]pyrroline-5-aryl-4,6-diones (XIVa-e). The mechanism of their formation is illustrated in scheme-3. Repeating this reaction using N-methylcyanothioformamide and N-phenylmaleimide in boiling benzene and TEA as catalyst furnish a product of which analytical and spectral data are in agreement with structure (XV) (scheme-3). The formation of (XV) can be rationalized on the basis that a product of type (XIV), first formed then dimerized through elimination of two molecules of  $H_2S$  to give (XV). In hot benzene and TEA as catalyst, two moles of cyanothioformanilide were reacted with one mole of N-phenylmaleimide to give (XVI) (scheme-3). The mechanism of its formation proceeds initially to give a product of type (XIV), which then reacted, with a second mole of cyanothioformanilide with elimination of HCN to give (XVI).

## EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were carried out in the Microanalytical unit at Cairo University. IR spectra (KBr) were measured on a Shimadzu 440 spectrometer,  $^1H$ -NMR spectra on a JEOL FX 90 Q (90 MHz) spectrometer and mass spectra on a Shimadzu GC-MS QO 1000 EX spectrometer using a direct-inlet system.

### Cyanothioformamides (Ia-c)

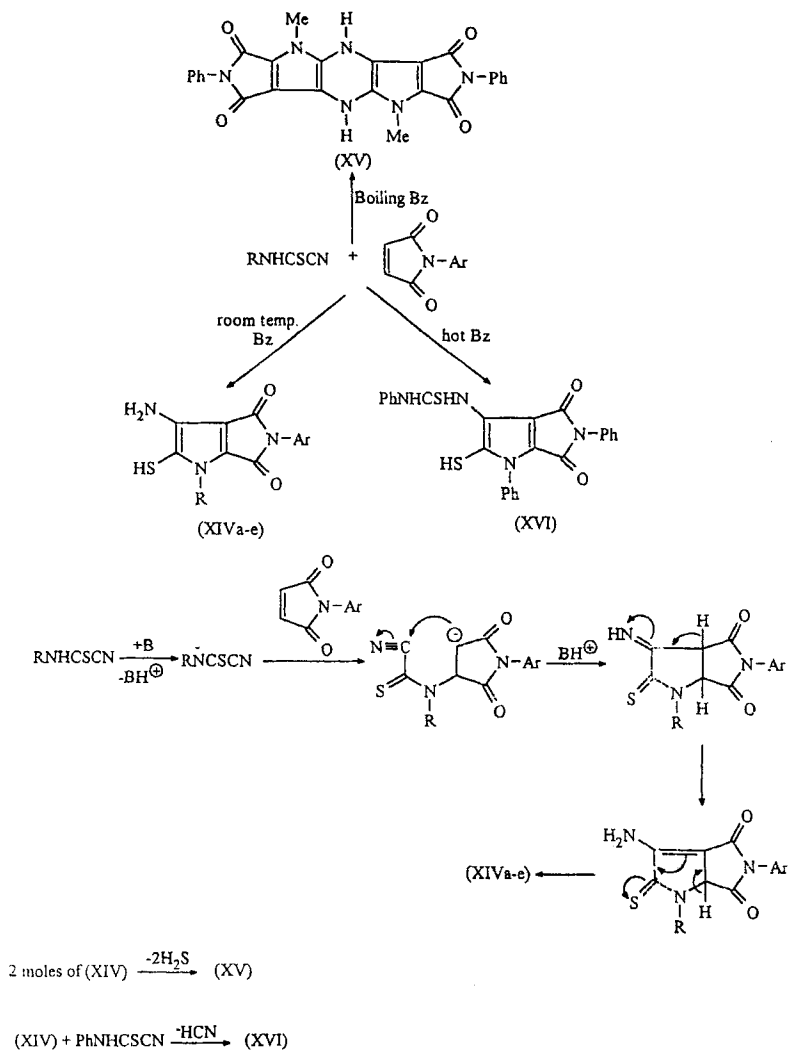
Were prepared according to the reported methods<sup>[1-3]</sup>.

### 5-Aryl-4-aryl-3-amino-1-substituted-2-pyrrolinethiones (IIa-h)

A solution of cyanothioformamide (I; 0.01 mol) in dry benzene (30 ml) was treated with an ethereal solution of the requisite  $\alpha,\beta$ -unsaturated ketone (0.01 mol) and triethylamine (0.3 ml). The reaction mixture was stirred at room temperature for 2 hr. The product that obtained after trituration with ethanol was recrystallized to give (IIa-h), Table (1), IR  $\nu_{max}/cm^{-1}$ . 3400,

3300 ( $NH_2$ ), 1630 (CO), 1490, 1300 ( $-CS-N\diagup$ ) and 2850 (aliph.CH).

$^1H$ -NMR,  $\delta_H/ppm$  ( $CD_3 COCD_3$ ) IIa; 2.9 (2H,s, $NH_2$ , disappeared by  $D_2O$ ), 3.2 (3H,s, $N-CH_3$ ), 6.1 (1H,s,C-H) and 6.9–7.7 (10H,m,Ar-H); IIe; 2.55 (2H,s, $NH_2$ ; cancelled by  $D_2O$ ), 2.65 (6H,s, $N(CH_3)_2$ ), 2.85 (3H,s, $N-CH_3$ ), 5.25 (1H,s,C-H), 5.8–6.2 (4H,q,AB-system) and 6.5–6.9



SCHEME 3

(5H,m,Ar-H). Mass spectrum of IIe: 351 ( $M^+$ , 45.2%), 246 (100%), 105 (56%) and 77 (47.8%); IIg:  $m/e$  370 ( $M^+$ , 66.7%), 265 (100%), 337 (3.0%), 293 (1.6%), 264 (7.0%), 249 (2.9%), 232 (1.3%), 162 (2.8%), 155 (1.9%) and 130 (12.3%) (scheme-4).



TABLE I Physical data of the prepared compounds

Compd No.	R	Ar <sub>1</sub>	Ar <sub>2</sub>	M.P. °C	Solvent Cryst.	Yield %	Mol. formula (Mol. wt.)	Analyses, %				TLC	
								Required/Found				Eluent (Ratio)	R <sub>f</sub>
								C	H	N	S		
IIa	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	185	E	40	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> OS (308.39)	70.09 70.20	5.23 5.10	9.08 9.00	10.39 10.80	Ea/H (1:1)	0.79
IIb	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> Br-p	163	M	65	C <sub>18</sub> H <sub>15</sub> N <sub>2</sub> OSBr (387.28)	55.82 55.90	3.90 4.00	7.23 7.10	8.28 8.20	Ea/H (1:1)	0.84
IIc	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> Cl-p	C <sub>6</sub> H <sub>5</sub>	165	E	43	C <sub>18</sub> H <sub>15</sub> N <sub>2</sub> OSCl (342.83)	63.06 63.20	4.41 4.40	8.17 8.00	9.35 9.10	Ea/H (1:1)	0.83
IId	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> Cl-p	C <sub>6</sub> H <sub>5</sub>	235	B	41	C <sub>18</sub> H <sub>15</sub> N <sub>2</sub> OSCl (342.83)	63.06 63.30	4.41 4.30	8.17 8.10	9.35 9.20	Ea/H (1:3)	0.53
IIf	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> -p	C <sub>6</sub> H <sub>5</sub>	170	E	55	C <sub>20</sub> H <sub>21</sub> N <sub>3</sub> OS (351.45)	68.35 68.20	6.02 6.00	11.96 11.70	9.12 9.00	Ea/H (1:2)	0.63
IIg	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> Cl-p	C <sub>6</sub> H <sub>5</sub>	190	E	75	C <sub>19</sub> H <sub>17</sub> N <sub>2</sub> OSCl (356.86)	63.94 64.00	4.80 4.70	7.85 7.80	8.98 9.00	Ea/H (2:3)	0.54
IIh	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	167	M	45	C <sub>23</sub> H <sub>18</sub> N <sub>2</sub> OS (370.45)	74.57 74.70	4.90 4.80	7.56 7.70	8.66 8.60	Ea/H (1:1)	0.74
IIi	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> Br-p	160	E	90	C <sub>23</sub> H <sub>17</sub> N <sub>2</sub> OSBr (449.35)	61.47 61.50	3.81 3.90	6.23 6.10	7.14 7.00	Ea/H (1:1)	0.67
IIIa			C <sub>6</sub> H <sub>5</sub>	179	B/H	80	C <sub>25</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S (410.47)	73.15 73.30	4.42 4.40	6.83 6.70	7.81 7.70	Ea/H (1:3)	0.51

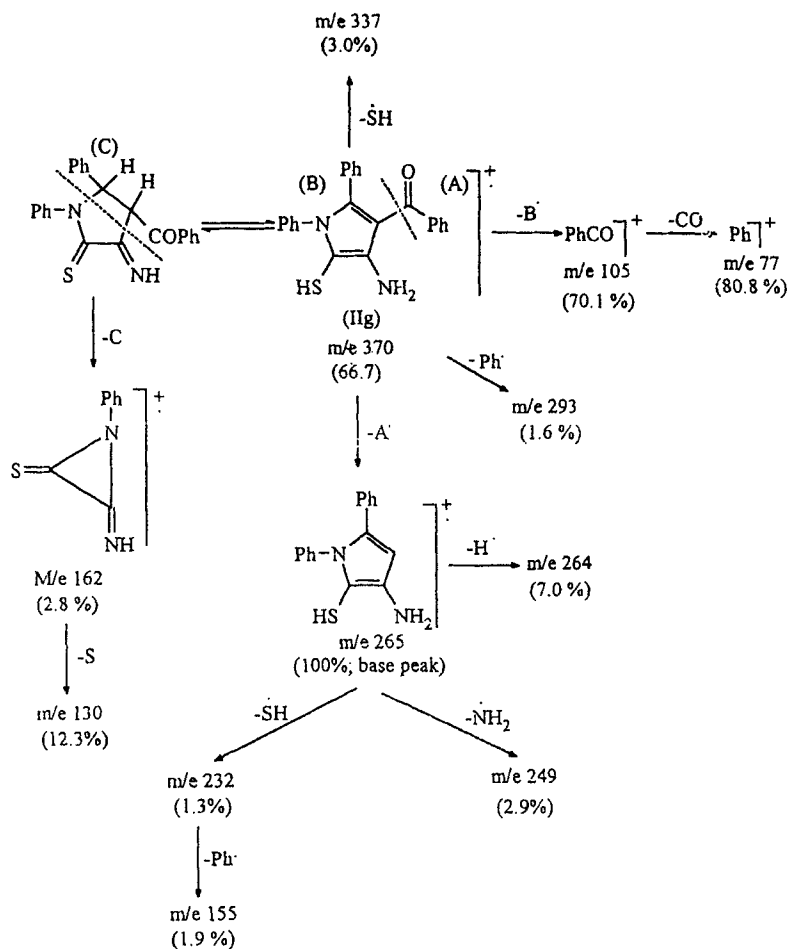
Compd No.	R	Ar <sub>1</sub>	Ar <sub>2</sub>	M.P. °C	Solvent Cryst.	Yield %	Mol. formula (Mol. wt.)	Analyses, %				TLC	
								Required/Found				Eluent (Ratio)	R <sub>f</sub>
								C	H	N	S		
IIIb			C <sub>6</sub> H <sub>4</sub> .Br-p	170	B/H	75	C <sub>23</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> SBr (489.37)	61.35 61.50	3.50 3.40	5.73 5.80	6.55 6.60	Ea/H (1:4)	0.62
IVa			C <sub>6</sub> H <sub>5</sub>	230	E/B	73	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> S (456.54)	71.03 71.30	5.30 5.20	6.14 6.00	7.02 7.10	Ea/H (1:3)	0.50
IVb			C <sub>6</sub> H <sub>4</sub> .Br-p	70	B/H	70	C <sub>27</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> SBr (535.44)	60.56 60.70	4.33 4.30	5.23 5.30	5.99 5.70	Ea/H (1:4)	0.70
V				216	E	55	C <sub>25</sub> H <sub>19</sub> N <sub>3</sub> OS (409.49)	73.32 73.50	4.68 4.50	10.26 10.30	7.83 7.70	Ea/H (3:1)	0.60
VI				130	E	70	C <sub>33</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S (524.57)	75.55 75.70	3.84 3.70	5.34 5.30	6.11 6.00	Ea/H (1:3)	0.74
VIIIb				225	B	65	C <sub>32</sub> H <sub>23</sub> N <sub>4</sub> OSCl (547.05)	70.25 70.30	4.24 4.20	10.24 10.30	5.86 5.70	Ea/H (1:3)	0.88
IX				108	C/H	67	C <sub>30</sub> H <sub>21</sub> N <sub>3</sub> OS (471.55)	76.41 76.61	4.49 4.40	8.91 8.70	6.80 6.90	Ea/H (1:1)	0.87
X				178	M	80	C <sub>30</sub> H <sub>19</sub> N <sub>2</sub> OSCl (490.98)	73.38 73.50	3.90 4.00	5.71 5.60	6.53 6.50	Ea/H (1:3)	0.47
XII				185	E	75	C <sub>25</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S (412.49)	72.79 73.00	4.89 4.80	6.79 6.60	7.77 7.60	Ea/H (2:1)	0.50
XIII				190	E	60	C <sub>26</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> S (477.56)	65.39 65.50	5.70 5.70	8.80 8.70	6.71 6.70	Ea/H (1:1)	0.62

## MERCAPTOPYRROLES

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Compd No.	R	Ar <sub>1</sub>	Ar <sub>2</sub>	M.P. °C	Solvent Cryst.	Yield %	Mol. formula (Mol. wt.)	Analyses, %					TLC	
								Required/Found				S	Eluent (Ratio)	R <sub>f</sub>
								C	H	N				
XIVa	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> .CH <sub>3</sub> -p		110	B/H	65	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> S (349.40)	65.31 65.50	4.33 4.20	12.03 12.00		9.18 9.00	Ea/H (1:3)	0.18
XIVb	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> .OCH <sub>3</sub> -p		170	B/H	60	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S (365.40)	62.45 62.50	4.14 4.00	11.50 11.50		8.78 8.60	Ea/H (1:3)	0.21
XIVc	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> .Cl-p		115	B/H	65	C <sub>18</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> SCl (369.81)	58.46 58.70	3.27 3.10	11.36 11.20		8.67 8.70	Ea/H (3:8)	0.51
XIVd	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> .Br-p		120	B/H	70	C <sub>18</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> SBr (414.27)	52.18 52.30	2.92 3.00	10.14 10.00		7.74 7.70	Ea/H (1:3)	0.37
XIVe	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> .NO <sub>2</sub> -p		150	B/H	60	C <sub>18</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub> S (380.37)	56.83 57.00	3.18 3.10	14.73 14.50		8.43 8.40	Ea/H (1:3)	0.11
XV				120	C/H	55	C <sub>26</sub> H <sub>18</sub> N <sub>6</sub> O <sub>4</sub> (478.45)	65.27 65.40	3.79 3.70	17.57 17.30			Ea/H (1:3)	0.31
XVI	C <sub>6</sub> H <sub>5</sub>			110	B	65	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> (470.55)	63.81 64.00	3.86 3.70	11.91 12.00		13.63 13.50	Ea/H (1:3)	0.28

B= Benzene; C= Chloroform; E= Ethanol; Ea= Ethyl acetate; H= n-Hexane; M= Methanol and P= Pet. ether (60-80).



SCHEME 4

### 5-Benzoyl-3-oxo-6, 7-diphenyl-pyrrolo[3,2-e][1,4]thiazines(IIIa, b)

A mixture of(IIg; 0.01 mol), chloroacetic acid (0.01 mol) and fused sodium acetate (0.5 gm) in glacial acetic acid (20 ml) was refluxed for 3 hrs. The obtained solid was recrystallized to give (IIa; Table I). Simi-

larly, (IIh; 0.01 mol) and chloroacetic acid (0.01 mol) gave (IIIb, Table I). IIIa,  $\nu_{\max}/\text{cm}^{-1}$  3250 (NH), 3025 (Ar-CH), 2910 (aliph. CH), 1707 & 1632 (CO);  $\delta_{\text{H}}/\text{ppm}$  2.3 (2H,s, S-CH<sub>2</sub>), 2.6 (1H,s,NH, cancelled by D<sub>2</sub>O) & 6.6–8 (15H,m,Ar-H);  $m/e$  410 (M<sup>+</sup>, 7.9%), 105 (100%), 396 (77.7%), 337 (22.6%) and 77 (87.9%).

### 1,5-Diphenyl-4-aryl-3-amino-2-mercaptoethylacetopyrrole (IVa,b)

A suspension of (IIg; 0.01 mol), ethyl chloroacetate (0.01 mol) and fused sodium acetate (0.5 gm) in absolute ethanol (30 ml) was refluxed for 4 hrs. The obtained solid after cooling was recrystallized to give (IVa, Table I). Similarly (IIh) and ethyl chloroacetate gave (IVb, Table I). IVa  $\nu_{\max}/\text{cm}^{-1}$ , 3440, 3330 (NH<sub>2</sub>), 3040 (Ar-CH), 2930 (aliph. CH) & 1719 (CO);  $\delta_{\text{H}}/\text{ppm}$  in CDCl<sub>3</sub>, 1.2–1.4 (3H,t,CH<sub>3</sub>), 3.1 (2H,s,S-CH<sub>2</sub>), 4.1–4.5 (2H,q,O-CH<sub>2</sub>), 5.4 (2H,s,NH<sub>2</sub>; cancelled by D<sub>2</sub>O) and 7–8.7 (15H,m,Ar-H).

A mixture of (IIg; 0.01 mol), ethyl chloroacetate (0.01 mol) and triethylamine (0.3 ml) in dioxan (30 ml) was refluxed for 4 hrs. The obtained product was recrystallized to give IIIa (m.p., m.m.p. & TLC).

### 3-Amino-5-benzoyl-6, 7-diphenyl-pyrrolo[3,2-e][1,4]thiazine (V)

#### Method (A)

A mixture of (IIg; 0.01 mol), chloroacetamide (0.01 mol) and triethylamine (0.3 ml) in dioxan (30 ml) was refluxed for 4 hrs. The obtained solid was recrystallized to give (V; Table I). IR  $\nu_{\max}/\text{cm}^{-1}$ , 3410, 3320 (NH<sub>2</sub>), 1670 (CO),  $m/e$  409 (M<sup>+</sup>, 2.4%), 410 (100%), 411 (24.6%), 349 (14.6%), 323 (2.8%) and 105 (57%).

#### Method (B)

The same reactants were fused together at 150°C for 30 min. Then triturated with ethanol and recrystallized to give (V, m.p., m.m.p. & TLC).

### 3-Benzoyl-1,2-diphenyl-pyrrolo[2,3-b]naphtho[2',3'-e][1,4]thiazine-5, 10-dione (VI)

A mixture of (IIg; 0.01 mol), 2,3-dichloro-1,4-naphthoquinone (0.01 mol) and fused sodium acetate (0.5 gm) in absolute ethanol (30 ml) was

refluxed for 3hrs. The obtained product was recrystallized to give (VI; Table I).  $\nu_{\max}/\text{cm}^{-1}$ , 3350 (NH), 1698, 1960 (CO);  $m/e$  524 ( $M^+$ ; 98.8%), 525 (100%), 317 (17.9%), 105 (50.4%) and 77 (68.9%).

### The Sulphides (VIIIa,b)

#### Method (A)

A mixture of (IIg; 0.01 mol), 2,3-dichloroquinoxaline (0.01 mol) and fused sodium acetate (0.5 gm) in absolute ethanol (30 ml) was refluxed for 3 hrs. The obtained solid was recrystallized to give (VIIIa; Table I). Similarly (IIg; 0.01 mol) and 7-methyl-2,3-dichloroquinoxaline (0.01 mol) gave (VIIIb; Table I).

#### Method (B)

A mixture of (IIg; 0.01 mol) and 2,3-dichloroquinoxaline or its 7-methyl derivative (0.01 mol) in DMF (20 ml) was refluxed for 3 hrs. then cooled and poured onto crushed ice. The obtained product was recrystallized to give (VIIIa and VIIIb; m.p., m.m.p. and TLC). VIIIb;  $\nu_{\max}/\text{cm}^{-1}$  3400, 3300 ( $\text{NH}_2$ ), 3030 (Ar-CH), 1640 (CO);  $\delta_{\text{H}}/\text{ppm}$  2.7 (3H,s, $\text{CH}_3$ ), 5.3(2H,s, $\text{NH}_2$ ; cancelled by  $\text{D}_2\text{O}$ ), 7.1–8.2(18H,m,Ar-H);  $m/e$  547 ( $M^+$ , 5.5%), 77 (100%), 548 (10.9%), 549 (6.4%), 510 (42.5%), 370 (42.8%) and 105(87%).

### 2-Anilino-4-benzoyl-5, 6-diphenyl-pyrrolo[3, 2-d]thiazole (IX)

A mixture of (IIg; 0.01 mol) and phenyl isocyanate (0.01 mol) was fused at  $120^\circ\text{C}$  for 2 hrs. The reaction mixture was cooled, triturated with light pet. ( $40\text{--}60^\circ$ ). washed with ether then recrystallized to give (IX; Table I);  $\nu_{\max}/\text{cm}^{-1}$ , 3200 (NH), 3030 (Ar-CH), 1700 (CO) & 1600 ( $\text{C}=\text{N}$ );  $\delta_{\text{H}}/\text{ppm}$  ( $\text{CDCl}_3$ ), 7.82 (20H, m, Ar-H), the NH proton underneath the aromatic protons;  $m/e$  471 ( $M^+$ , 6.6%), 77 (100%), 396 (50.8%), 370 (19.3%), 119 (68.0%), 105 (63.4%) and 91 (29.2%)

### 4-Benzoyl-2-(4'-chlorophenyl)-5,6-diphenyl-pyrrolo[3,2-d]thiazole (X)

A solution of (IIg; 0.01 mol) in p-chlorobenzoyl chloride (10 ml; excess) was refluxed for one hour. Decomposition over ice-cold water gave a solid

which recrystallized to give (X; Table I),  $\nu_{\max}/\text{cm}^{-1}$  1780 (CO), 1640 (C=N);  $\delta_{\text{H}}/\text{ppm}$  ( $\text{CDCl}_3$ ), 6.6–8.2 (19H, m, Ar-H), m/e 490 ( $\text{M}^+$ , 100%), 413 (22%), 155 (52.2%), 105 (51.4%) and 77 (28.9%).

### The monoacetyl derivative (XII)

A solution of (IIg, 0.01 mol) in  $\text{Ac}_2\text{O}$  (10 ml; excess) was stirred at room temperature for 30 min. Removal of excess  $\text{Ac}_2\text{O}$  under reduced pressure furnished a product which recrystallized to give (XII; Table I).  $\nu_{\max}/\text{cm}^{-1}$ , 3170 (NH), 1700, 1650 (CO) & 1460, 1270 ( $-\text{CS}-\text{N}^{\prime}$ );  $\delta_{\text{H}}/\text{ppm}$  ( $\text{CDCl}_3$ ), 2.7 (3H, s,  $\text{CH}_3$ ), 6.3–7.5 (16H, m, Ar-H+CH) & 9.3 (1H, s, NH, disappeared by  $\text{D}_2\text{O}$ ); m/e 412 ( $\text{M}^+$ , 8.3%), 369 (100%), 337 (12%), 321 (1.6%), 307 (2.4%), 265 (5.4%) and 105 (94.5%).

### The triacetyl derivative (XIII)

A solution of (IIg; 0.01 mol) in  $\text{Ac}_2\text{O}$  (10 ml; excess) was reflux for 30 min. and treated as above to give (XIII; Table I).  $\nu_{\max}/\text{cm}^{-1}$ , 1760, 1740, 1645 (CO) & 2900 (CH aliph.);  $\delta_{\text{H}}/\text{ppm}$  ( $\text{CDCl}_3$ ), 248 (3H, s,  $\text{CH}_3$  CO-S), 2.56 [6H, s,  $(\text{CH}_3\text{CO})_2\text{N}$ ], 3.00 [6H, s,  $\text{N}(\text{CH}_3)_2$ ], 3.70 (3H, s, N- $\text{CH}_3$ ), 6.70–6.80, 7.75–7.85 (4H, AB-system, p-phenylene) & 7.20–7.70 (5H, m, Ar-H); m/e 477 ( $\text{M}^+$ , 7.2%), 350 (100%), 435 (7.5%), 393 (24%), 351 (36.2 %), 105 (44.5%) and 77 (29.7%).

### 3-A mino-1-phenyl-2-mercapto-pyrrolo[2,3-c]pyrroline-5-aryl-4,6-diones (XIVa-e)

A mixture of cyanothioformanilide (Ic; 0.01 mol), N-arylmaleimides (0.01 mol) and triethylamine (0.3 ml) in dry benzene (50 ml) was stirred at room temp. for 2 hrs. The obtained product was treated several times with n-hexane then recrystallized to give (XIVa-e; Table I).  $\nu_{\max}/\text{cm}^{-1}$  (XIVb) 3450, 330 ( $\text{NH}_2$ ), 2900 (CH aliph.) & 1700 (CO);  $\delta_{\text{H}}/\text{ppm}$  ( $\text{CDCl}_3$ ) (XIVa) 2.5 (3H, s,  $\text{CH}_3$ ), 3.5 (2H, hump,  $\text{NH}_2$ , cancelled by  $\text{D}_2\text{O}$ ), 7.2–8.0 (9H, m, Ar-H). Mass spectrum of (XIVa) m/e 349 ( $\text{M}^+$ , 26.5%), 187 (100%), 350 (54%), 216 (69%), 161 (47%), 135 (39%) & 77 (97%); (XIVb)

m/e 365 ( $M^+$ , 43%), 77(100%), 262(14%), 217(87%) & 189(27%); (XIVd) m/e 413( $M^+$ , 24%), 77(100%), 415(21%), 253(77%), 216(37%) and 162(31%). UV,  $\lambda_{1max}$ . (320),  $\lambda_{2max}$ . (260) and XIVc,  $\lambda_{1max}$ . (312),  $\lambda_{2max}$ . (276).

### Preparation of XV

A mixture of N-methylcyanothioformamide (0.01 mol), N-phenylmaleimide (0.01 mol) and triethylamine (0.3 ml) in dry benzene (50 ml) was refluxed for 45 min. then worked as above to give (IV; Table I). IR,  $\nu_{max}/cm^{-1}$  3150 (NH), 2900 (CH aliph) & 1700 (CO); m/e 478( $M^+$ , 10%), 42(100%), 278(12%), 239(8%).

### Preparation of XVI

A mixture of cyanothioformanilide (Ic; 0.02 mole), N-phenylmaleimide (0.01 mol) and triethylamine (0.3 ml) in dry benzene (50 ml) was stirred at 50°C for one hr. then worked as above to give (XVI; Table I). IR  $\nu_{max}/cm^{-1}$  broad band around 3200 (NH) & 1715 (CO); m/e 470 ( $M^+$ , 1.9%), 363 (100%), 364 (14.7%), 362 (98%) and 135 (59%).

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