

Note

Oxidation of thiocarbamyls with lead tetraacetate

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Oxidation of a series of arylthiocarbamyls **2** to the corresponding bis-formamidinomonosulphides **3** with lead tetraacetate has been carried out. In addition sulphur is obtained.

Literature survey reveals that several workers have studied the oxidation of thioureas by different oxidants and obtained thiadiazolines¹, hector's base², and disulphides³⁻¹⁰ as the end-products.

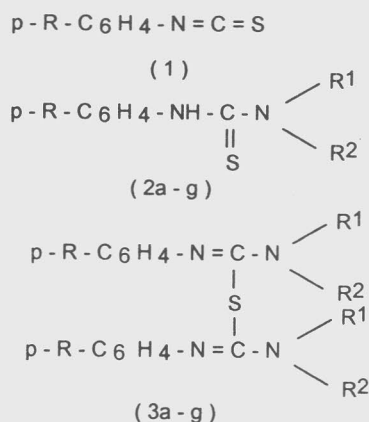
In the present work, we have synthesised piperidine, pyrrolidine and morpholine substituted thiocarbamyls by condensing arylisothiocyanates **1** with secondary cyclic amines. These products contain one secondary and one primary nitrogen atoms (-NH-CS-N<) instead of two primary nitrogen atoms in thioureas (-NH-CS-NH-). Therefore, the formation of some products different from already reported in literature was expected. Substituted bis-formamidinomonosulphides **3** and sulphur have been obtained as the reaction products (Scheme I; Table I). It may be mentioned that the formation of **3** has been proposed earlier⁴ as an intermediate product in many reactions of thioureas and it is for the first time that it could be isolated.

A tentative mechanism as shown in Scheme II can be proposed for these reactions.

Experimental Section

General. Lead tetraacetate was synthesized by treating red lead (Pb₃O₄) with acetic acid and acetic anhydride and stored in glacial acetic acid in a black-brown coloured bottle at 5°C.

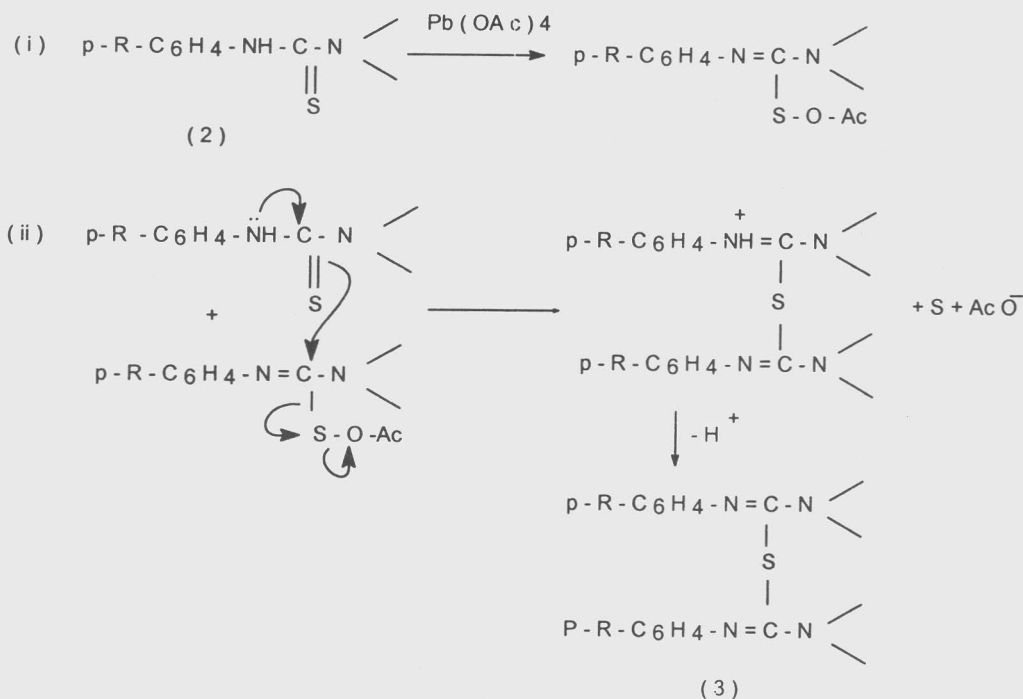
Thiocarbamyls were prepared by condensing arylisothiocyanate (1.0 mL) with secondary cyclic amines (1.0 mL) in benzene and recrystallized from ethanol.



- a: R = H, R¹R² = -(CH₂)₅⁻
 b: R = H, R¹R² = -(CH₂)₄⁻
 c: R = H, R¹R₂ = -(CH₂)₂-O-(CH₂)₂⁻
 d: R = OCH₃, R¹R² = -(CH₂)₄⁻
 e: R = OCH₃, R¹R₂ = -(CH₂)₂-O-(CH₂)₂⁻
 f: R = CH₃, R¹R² = -(CH₂)₄⁻
 g: R = CH₃, R¹R₂ = -(CH₂)₂-O-(CH₂)₂⁻

Scheme I

Oxidation of N-(N'-phenylthiocarbamyl)piperidine 2a. To a solution of **2a** piperidine (2.2 g, 0.01 mole) in benzene (120 mL) was added LTA (4.43g, 0.01 mole) during 15 min with constant shaking at room temperature. The reaction mixture was then stirred for another half an hour to complete the oxidation. A change in the colour of the reaction mixture from colourless to red-yellow was observed during the reaction. Traces of LTA were decomposed by a few drops of ethylene glycol. Thereafter the reaction mixture was washed with water, dried over anhydrous Na₂SO₄ and filtered. The solvent was distilled off and the residue (viscous product) chromatographed over silica gel. Elution with pet. ether, benzene and acetone (and their mixture) first gave yellow crystals of sulphur (m.p. 119-20°) followed by a white product which was recrystallized from ethanol to give bis-formamidinomonosulphide **3a** (430 mg, 22%), m.p. 185°. The compound gave a positive test for sulphur; IR (KBr): 3045 (aromatic



Scheme II

Table I—Physical data of various compounds prepared

Compd	Mol. formula	m.p. °C	Yield (%)	Found (%) (Calcd)		
				C	H	N
3a	C ₂₄ H ₃₀ N ₄ S	185	22	71.80 (71.03)	7.66 7.48	14.07 13.89
3b	C ₂₂ H ₂₆ N ₄ S	157	28	70.13 (69.84)	7.07 6.86	14.86 14.81
3c	C ₂₂ H ₂₆ N ₄ O ₂ S	156	35	64.73 (64.39)	6.41 6.34	13.92 13.65
3d	C ₂₄ H ₃₀ N ₄ O ₂ S	Liquid	40	66.05 (65.75)	6.81 6.84	13.00 12.78
3e	C ₂₄ H ₃₀ N ₄ O ₄ S	136	21	61.80 (61.27)	6.37 6.38	12.32 11.91
3f	C ₂₄ H ₃₀ N ₄ S	154	24	71.52 (70.93)	7.41 7.38	13.87 13.79
3g	C ₂₄ H ₃₀ N ₄ O ₂ S	Liquid	45	65.93 (65.75)	6.93 6.84	13.11 12.78

C-H, 1590, 1465, 1450 (aromatic ring), 1480 (C=N), 715 (C-S) cm⁻¹; ¹H NMR (acetone-d₆): δ 1.50 (m, 12H, 2 × $\begin{matrix} -\text{CH}_2 \\ -\text{CH}_2 \end{matrix} > \text{CH}_2$), 2.80 (d, 8H,

2 × -N $\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix}$), 6.82 - 7.45 (m, 10H, aromatic protons); MS: m/z 406 (M⁺).

Similarly the oxidation of **2b-g** gave the products **3b-g**, respectively in addition to sulphur. The characterization data of **3b** to **3g** are given in Table I. Their spectral data are as follows:

Bis-formamidinomonosulphide 3b: Shining white crystals; IR(KBr): 3040 (aromatic C-H), 1950, 1495, 1450 (aromatic ring), 1480 (C=N), 715 (C-S) cm⁻¹; ¹H NMR (acetone-d₆):

δ 1.58 (m, 8H, $2 \times \begin{matrix} -\text{CH}_2 \\ | \\ -\text{CH}_2 \end{matrix}$), 2.65 (d, 8H, $2 \times \begin{matrix} \text{CH}_2 \\ / \\ \text{N} \\ \backslash \\ \text{CH}_2 \end{matrix}$), 6.91-7.32 (m, 10H, aromatic protons); MS: m/z 378 (M^+).

Bis-formamidinomonosulphide 3c: White crystals; IR(KBr): 3045 (aromatic C-H), 1590, 1495, 1450 (aromatic ring), 1480 (C=N), 710 (C-S) cm^{-1} ; ^1H NMR (acetone- d_6): δ 2.74 (d, 8H, $2 \times \begin{matrix} \text{CH}_2 \\ / \\ \text{N} \\ \backslash \\ \text{CH}_2 \end{matrix}$), 3.52 (m, 8H, $2 \times \begin{matrix} -\text{CH}_2 \\ | \\ \text{O} \\ | \\ -\text{CH}_2 \end{matrix}$), 6.3-6.9 (m, 10H, aromatic protons); MS: m/z 410 (M^+).

Bis-formamidinomonosulphide 3d: Light yellow liquid; IR (neat): 3040 (aromatic C-H), 2960, 2930, 2880 (methyl C-H), 1590, 1495, 1450 (aromatic ring), 1480 (C=N), 1245, 1030 (C-O-C), 715 (C-S) cm^{-1} .

Bis-formamidinomonosulphide 3e: White crystals, IR (KBr): 3045 (aromatic C-H), 2960, 2930, 2880 (methyl C-H), 1590, 1495, 1450 (aromatic ring), 1480 (C=N), 1240, 1030 (C-O-C), 710 (C-S) cm^{-1} ; ^1H NMR (acetone- d_6): δ 2.84 (d, 8H, $2 \times \begin{matrix} \text{CH}_2 \\ / \\ \text{N} \\ \backslash \\ \text{CH}_2 \end{matrix}$), 3.52 (m, 8H, $2 \times \begin{matrix} -\text{CH}_2 \\ | \\ \text{O} \\ | \\ -\text{CH}_2 \end{matrix}$), 3.72 (s, 6H, $2 \times \text{OCH}_3$), 6.7-7.0 (m, 8H, aromatic protons); MS: m/z 470 (M^+).

Bis-formamidinomonosulphide 3f: White crystals; IR(KBr): 3040 (aromatic C-H), 2920,

2860 (methyl C-H) 1590, 1495, 1450 (aromatic ring), 1480 (C=N), 715 (C-S) cm^{-1} ; ^1H NMR (acetone- d_6): δ 1.59 (m, 8H, $2 \times \begin{matrix} -\text{CH}_2 \\ | \\ -\text{CH}_2 \end{matrix}$), 2.40 (s, 6H, $2 \times \text{CH}_3$), 2.65 (d, 8H, $2 \times \begin{matrix} \text{CH}_2 \\ / \\ \text{N} \\ \backslash \\ \text{CH}_2 \end{matrix}$), 6.9-7.2 (m, 8H, aromatic protons); MS: m/z 406 (M^+).

Bis-formamidinomonosulphide 3g: Light yellow liquid; IR (neat): 3045 (aromatic C-H), 2920, 2860 (methyl C-H), 1590, 1495, 1450 (aromatic ring), 1480 (C=N), 710 (C-S) cm^{-1} .

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