Asian Journal of Chemistry Vol. 8, No. 1 (1996), 155–159

Oxidation of Diarylthiocarbamides with Lead Tetraacetate

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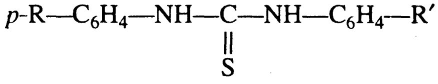
Oxidation of a series of diarylthiocarbamides with lead tetraacetate has been carried out leading to the formation of corresponding S-acetoxy-diarylthiocarbamides

INTRODUCTION

Literature survey revealed that several workers have studied the oxidation of thiocarbamides by different oxidants.[1–8] In the present work, authors have synthesised diarylthiocarbamides (II) by the condensation of arylisothiocyanates (I) with substituted aromatic amines, and have carried out their oxidation with lead tetraacetate (LTA). The oxidation resulted in the conversion of diarylthiocarbamides to the corresponding S-acetoxy diarylthiocarbamides (III). Sulphur and a gummy mass which was unable to crystallize were also obtained in these reactions (Scheme A).

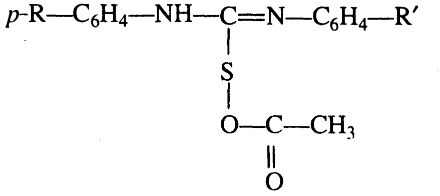
(I): $p\text{-R—C}_6\text{H}_4\text{—N}{=}\text{C}{=}\text{S}$

(IIa-g):



$$p\text{-R—C}_6\text{H}_4\text{—NH—}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{—NH—C}_6\text{H}_4\text{—R}'$$

(IIIa-g):



$$p\text{-R—C}_6\text{H}_4\text{—NH—}\underset{\underset{\underset{\underset{\text{O—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—CH}_3}{|}}{\text{S}}}{|}}{\text{C}}{=}\text{N—C}_6\text{H}_4\text{—R}'$$

(IIa, IIIa): R=H, R′=H

(IIb, IIIb): R=H, R′=OCH_3

(IIc, IIIc): R=H, R′=CH_3

(IId, IIId): R=H, R′=Cl

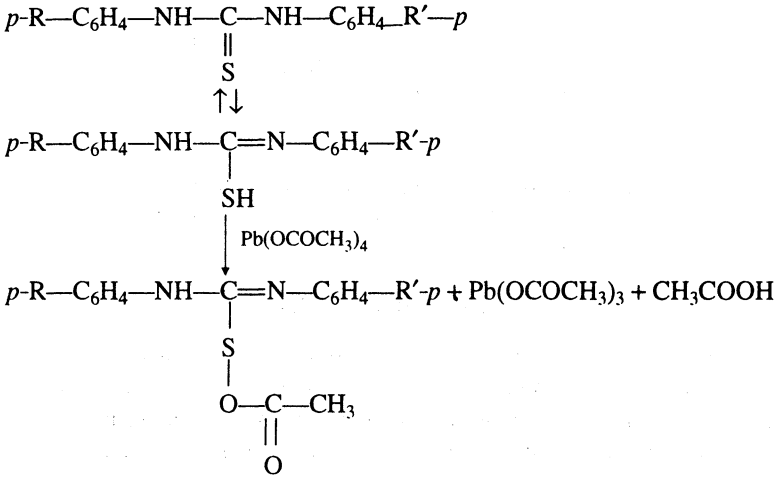
(IIe, IIIe): R=OCH_3, R′=OCH_3

(IIf, IIIf): R=CH_3, R′=CH_3

(IIg, IIIg): R=Cl, R′=Cl

Scheme-A

The following tentative mechanism can be outlined for these reactions (Scheme-B).



$$p\text{-R—C}_6\text{H}_4\text{—NH—}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{—NH—C}_6\text{H}_4\text{—R}'\text{—}p$$

$$\uparrow\downarrow$$

$$p\text{-R—C}_6\text{H}_4\text{—NH—}\underset{\underset{\text{SH}}{|}}{\text{C}}\text{=N—C}_6\text{H}_4\text{—R}'\text{-}p$$

$$\Big\downarrow \text{Pb(OCOCH}_3)_4$$

$$p\text{-R—C}_6\text{H}_4\text{—NH—}\underset{\underset{\text{S—O—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—CH}_3}{|}}{\text{C}}\text{=N—C}_6\text{H}_4\text{—R}'\text{-}p + \text{Pb(OCOCH}_3)_3 + \text{CH}_3\text{COOH}$$

Scheme-B

EXPERIMENTAL

Lead tetraacetate was synthesised by red lead oxide (Pb_3O_4),. acetic acid, acetic anhydride and stored in glacial acetic acid in a black-brown coloured bottle at 5°C. Thiocarbamides were prepared by condensing arylisothiocyanates (1.0 mol) with substituted aromatic amines (1.0 mol) in ethanol and were recrystallized from ethanol. Physical data of compounds (IIIa-g) are presented in Table-1.

TABLE-1
PHYSICAL DATA OF VARIOUS COMPOUNDS PREPARED

Reactent		Product				% Found (Calcd.)		
Compd.	m.p. (°C)	Comp.	Mol formula	m.p. (°C)	Yield (%)	C	H	N
IIa	151	IIIa	$C_{15}H_{14}N_2O_2S$	114	26	62.51 (62.93)	4.85 (4.89)	9.21 (9.79)
IIb	180	IIIb	$C_{16}H_{16}N_2O_3S$	125	37	59.82 (60.75)	5.00 (5.06)	8.73 (8.86)
IIc	141	IIIc	$C_{16}H_{16}N_2O_2S$	152	40	63.78 (64.00)	5.21 (5.33)	9.13 (9.33)
IId	151	IIId	$C_{15}H_{13}N_2O_2ClS$	Liquid	42	51.98 (52.61)	4.29 (4.38)	9.38 (9.44)
IIe	191	IIIe	$C_{17}H_{18}N_2O_4S$	232	23	58.55 (58.95)	5.18 (5.20)	7.85 (8.09)
IIf	185	IIIf	$C_{17}H_{18}N_2O_2S$	262	36.5	64.74 (64.96)	5.72 (5.73)	8.89 (8.91)
IIg	168	IIIg	$C_{15}H_{12}N_2O_2Cl_2S$	134	24	50.67 (50.70)	3.35 (3.38)	7.76 (7.88)

Oxidation of N,N′-diphenylthiocarbamide (IIa)

To a solution of N,N′-diphenylthiocarbamide (2.2 g, 0.01 mol) in benzene (100 mL) was added lead tetraacetate (4.43 g, 0.1 mol) with constant shaking for 15 min at room temperature. The reaction mixture was then stirred for another $\frac{1}{2}$ h to complete the oxidation. A change in the colour of reaction mixture from colourless to red-yellow was observed during the reaction. Traces of lead tetraacetate were decomposed by a few drops of ethylene glycol. The reaction mixture was then washed with water, dried over anhydrous Na_2SO_4 and filtered. The solvent was distilled off. The residue (viscous product) was chromatographed over silica gel. Elution with petroleum ether, bezene, acetone (and their mixture) first gave yellow needle shaped crystals of sulphur, m.p. 119–20°C, followed by a white product which was recrystallized from benzene to give S-acetoxy diphenylthiocarbamide (IIIa) (560 mg, 26%), m.p 114°C. The compound gave positive test for sulphur. Last 8–10 fractions afforded gummy masses subsequently which were rejected.

(Found: C, 62.51; H, 4.85; N, 9.21. $C_{15}H_{14}N_2O_2S$ requires C, 62.93: H, 4.89; N, 9.79%); IR (KBr) ν_{max} (cm^{-1}) 3300 (N—H stretch), 3030 (aromatic C—H stretch), 1680 (C=O stretch), 1590, 1540, 1450 (aromatic ring), 1480 (C=N stretch), 1420 (O—CO—CH_3); 680 ν(C—S); ^{1}H NMR($CdCl_3$); 1.89 (s, 3H, O—CO—CH_3) 6.9–7.4 (m, 10H, aromatic), 8.13 (s, 1H, N—H); MS: m/z 286 ($M^{+\cdot}$).

Oxidation of N-phenyl-N′-(*p*-methoxyphenyl)-thiocarbamide (IIb)

(2.58 g, 0.01 mol) N-phenyl-N′-(*p*-methoxyphenyl)-thiocarbamide in benzene (150 mL) was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur, m.p. 119°C, and a white product which was recrystallized from ethanol to give S-acetoxy-N-phenyl-N′-(*p*-methoxyphenyl)-thiocarbamide (IIIb) as shining white crystals (730 mg, 37%), m.p. 125°C. Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 59.82; H, 5.00; N, 8.73. $C_{16}H_{16}N_2O_3S$ requires C, 60.75; H, 5.06; N, 8.86%). IR (KBr) ν_{max} ($cm^{-1)}$ 3280 (N—H stretch), 3020 (aromatic C—H stretch), 3000, 2910, 2890 (methyl C—H stretch), 1670 (C=O stretch), 1600, 1560, 1460 (aromatic ring), 1480 (C=N stretch), 1420 (O—CO—CH_3), 1260, 1230, 1080 (C—O—C stretch), 680 ν (C—S); ^{1}H NMR ($CDCl_3$) 1.98 (s, 3H, O—OC—CH_3), 3.75–3.85 ν(s, 3H, OCH_3), 6.9–7.4 (m, 9H, aromatic), 8.12 (s, 1H, NH); MS: m/z 316 ($M^{+\cdot}$).

Oxidation of N-phenyl-N′-*p*-tolylthiocarbamide (IIc)

(2.24 g, 0.01 mol) of N-phenyl-N′-*p*-tolylthiocarbamide was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur, m.p. 120°C, and a white product which was recrystallized from ethanol to give S-acetoxy-N-phenyl-N′-*p*-tolylthiocarbamide (IIIc) as shining white crystals, m.p. 152°C. Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 63.78; H, 5.21; N, 9.13. $C_{16}H_{16}N_2O_2S$ requires C, 64.00; H, 5.33; N, 9.33%). IR (KBr) ν_{max} (cm^{-1}) 3200 (N—H stretch), 3010 (aromatic C—H stretch), 3000, 2900 (methyl C—H stretch), 1710 (C=O stretch), 1600, 1550, 1510, 1440 (aromatic ring), 1480 (C=N stretch), 1400 (O—CO—CH_3), 700 ν(C—S); ^{1}H NMR ($CDCl_3$) 1.96 (s, 3H, O—CO—CH_3), 2.42 (s, 3H, CH_3), 7.1–7.4 (m, 9H, aromatic), 8.28 (s, 1H, NH); MS m/z 300 ($M^{+\cdot}$).

Oxidation of N-phenyl-N′-(*p*-chlorophenyl)-thiocarbamide (IId)

(2.62 g, 0.01 mol) of N-phenyl-N′-(*p*-chlorophenyl)-thiocarbamide in benzene (150 mL) was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur m.p. 120°C, and a light yellow coloured liquid S-acetoxy-N-phenyl-N′-(*p*-chlorophenyl)-thiocarbamide, (IIId) (8.30 mg, 42%). Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 51.98; H, 4.29; N, 9.38. $C_{15}H_{13}N_2O_2ClS$ requires C, 52.61; H, 4.38; N, 9.44%). IR (KBr) ν_{max} (cm^{-1}) 3380 ν(N—H), 3.040 (aromatic ν(C—H)), 1720 ν(C=O), 1600, 1570, 1560 1450 (aromatic ring), 1480 ν(C=N), 1400 (O—CO—CH_3), 680 ν(C—S) cm^{-1}

Oxidation of N,N-bis-(4-methoxyphenyl)-thiocarbamide (IIe)

(2.88 g, 0.01 mol) of N,N′-bis-(4-methoxyphenyl)-thiocarbamide in benzene (160 mL) was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur, m.p. 20°C, and a white, product which was recrystallized from benzene to give S-acetoxy-N,N′-bis-(4-methoxyphenyl)-thiocarbamide (IIIe) as shining white crystals (460 mg, 23%), m.p. 232°C. Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 58.55; H, 5.18; N, 7.85. $C_{17}H_{18}N_2O_4S$ requires C, 58.95; H, 5.20; N 8.09%). IR (KBr) ν_{max} (cm^{-1}) 3380 ν(N—H), 3000, 2980, 2880 (aromatic C—H and methyl C—H stretch), 1660 ν(C=O), 1610, 1560, 1500, 1470 (aromatic ring), 1480 ν(C=N), 1410 (O—CO—CH_3), 1290, 1250, 1170 (C—O—C stretch), 660 ν(C—S) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.89 (s, 3H, O—CO—CH_3), 3.75 (s, 6H, 2 × OCH_3), 6.8–7.0 (m, 8H, aromatic), 8.14 (s, 1H, NH); MS: m/z 346 ($M^{+\cdot}$)

Oxidation of N,N′-bis-(4-tolyl)-thiocarbamide (IIf)

(2.56 g, 0.01 mol) of N,N′-bis-(4-tolyl)-thiocarbamide in benzene (150 mL) was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur, m.p. 120°C and a white product which was recrystallized from ethanol to give S-acetoxy-N-N′-bis-(4-tolyl)-thiocarbamide (IIIf) as shining white crystals (760 mg, 36%), m.p. 262°C. Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 64.74; H, 5.72; N, 8.89. $C_{17}H_{18}N_2O_2S$ requires C, 64.96; H, 5.73; N, 8.91%). IR (KBr) ν_{max} (cm^{-1}) 3310 (N—H stretch), 3030 (aromatic C—H stretch), 3000, 2920, 2880 (methyl C—H stretch), 1670 (C=O stretch), 1600, 1560, 1515 (aromatic ring), 1480 (C=N stretch), 1410 ν(O—C—CH_3), 670 ν(C—S); ^{1}H NMR ($CDCl_3$) 1.87 (s, 3H, O—CO—CH_3), 2.4 (s, 6H, 2×CH_3). 7.1–7.3 (m, 8H, aromatic), 8.23 (s, 1H, NH); MS: m/z 314 ($M^{+\cdot}$).

Oxidation of N,N′-bis-(4-chlorophenyl)-thiocarbamide (IIg)

(2.96 g, 0.01 mol) of N,N′ bis-(4-chlorophenyl)-thiocarbamide in benzene (200 mL) was treated with lead tetraacetate (4.43 g, 0.01 mol) as described in the previous experiment. Usual extractive work-up afforded sulphur, m.p. 119–20°C, and a white product which was recrystallized from ethanol to give S-acetoxy-N,N′-bis-(4-chlorophenyl)-thiocarbamide (IIIg) as pure white crystals (480 mg, 24%), m.p. 135°C. Last fractions afforded gummy masses subsequently which were rejected.

(Found: C, 50.67; H, 3.35; N, 7.76. $C_{15}H_{12}N_2O_2Cl_2S$ requires C, 50.70; H, 3.38; N, 7.88%). IR (KBr) ν_{max} (cm^{-1}) 3380 ν(N—H), 3040 (aromatic ν(C—H)), 2990, 2840 (methyl C—H stretch), 1720 ν(C=O), 1610, 1590, 1570, 1540 (aromatic ring), 1490 ν(C=N), 1405 ν(O—CO—CH_3), 710 ν(C—S) ^{1}H NMR ($CDCl_3$) 2.08 (s, 3H, O—CO—CH_3), 7.2–7.5 (m, 8H, aromatic), 8.21 (s, 1H, NH); MS: m/z 355 ($M^{+\cdot}$).

ACKNOWLEDGEMENTS

The authors wish to thank Dr. V.R. Shastry for providing laboratory facilities. and to RSIC, CDRI, Lucknow for providing elemental and spectral data.

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(*Received*: 24 June 1995; *Accepted*: 6 September 1995) AJC-1007