Novel Route to 4,5,6,7-Tetrahydroindoles and Pyrroles

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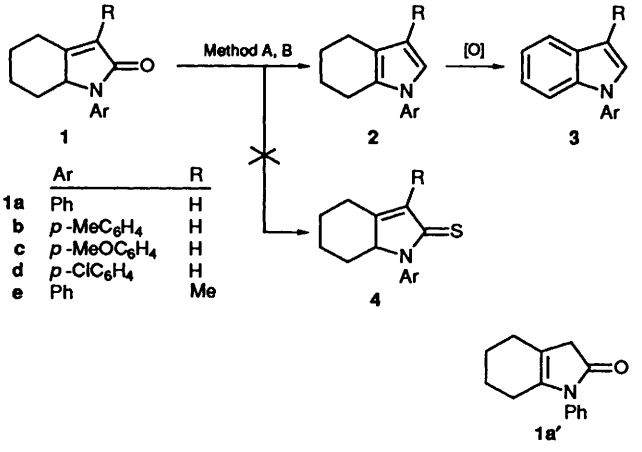
Treatment of cyclic unsaturated amides, 1,4,5,6,7,7a-hexahydro-2*H*-indol-2-ones **1**, with Lawesson's reagent [2,4-bis-(*p*-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide] yielded unexpected products, 4,5,6,7-tetrahydroindoles **2**, in moderate yield. Reduction of compounds **1** with diisobutylaluminium hydride also gave compounds **2** in good yield. In contrast, treatment of monocyclic 1,5-dihydropyrrol-2-ones **5** with Lawesson's reagent gave the thionation products, 1,5-dihydropyrrole-2-thiones **7**, as main products, along with pyrroles **6**.

2,4-Bis-(*p*-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide, generally called Lawesson's reagent (LR),[1] is known to be a superior reagent for the conversion of a wide variety of carbonyl compounds, including amide and ester carbonyls, into thiocarbonyl compounds. In the course of our studies on the reactivity of cyclic thioamide systems,[2] we found that 3-hydroxyisoindolin-1-ones reacted with LR to give isoindoline-1-thiones in good yield by the direct thionation of the amide carbonyl and reductive elimination of the hydroxy group.[3] We also reported a novel transformation of alcohols to thiols by treatment of various alcohols with LR.[4] We report now a novel synthesis of 4,5,6,7-tetrahydroindoles **2** and pyrroles 6 by the reactions of hexahydro-2*H*-indol-2-ones **1** and dihydropyrrol-2-ones **5** with LR. Furthermore, we report an efficient method for the preparation of tetrahydroindoles **2** by the partial reduction of amides **1** with diisobutylaluminium hydride (DIBAH).



Scheme 1 Method A: LR, benzene–DME. Method B: DIBAH, THF

Results and Discussion

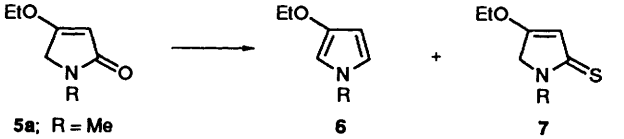
A mixture of 1-phenyl-1,4,5,6,7,7a-hexahydro-2*H*-indol-2-one **1a** and LR (2 mol equiv.) in a mixed benzene–1,2-dimethoxyethane (DME) solution was heated to reflux under argon for 15 min to yield an unexpected product, 1-phenyl-4,5,6,7-tetrahydroindole **2a** in 55% yield. The thionation product, 1-phenyl-1,4,5,6,7,7a-hexahydro-2*H*-indole-2-thione **4a**, could not be isolated even when fewer mol equivalents of LR were used. The structure of compound **2a** was elucidated on the basis of spectroscopic and elemental analysis data. The ^{1}H NMR spectrum of compound **2a** shows two doublets, at δ 6.09 (1 H) and 6.75 (1 H), with the same coupling constant (J 2.4 Hz) assignable to ring protons at C-3 and -2. The ^{13}C NMR spectrum of compound **2a** displays four triplets, at δ_C 23.3, 23.5 (× 2), and 23.6, in addition to aromatic carbon signals (δ_C 119.0–140.3) and no thiocarbonyl carbon signal around δ_C 200 appeared. In a similar manner, 1,4,5,6,7,7a-hexahydro-2*H*-indol-2-ones **1b–e** reacted with LR to yield the corresponding tetrahydroindoles **2b–e** in moderate yield (Table 1). Further proof of the structure of the tetrahydroindoles **2** was achieved by the oxidation of these compounds **2** to indoles **3** (Scheme 1). The tetrahydroindoles **2a, e** thus obtained were oxidized with chloranil to yield indoles **3a, e**, whose structures were confirmed by direct comparison of their IR and NMR spectra with those of authentic samples.[2d]

On the other hand, treatment of monocyclic unsaturated amides, 1,5-dihydropyrrol-2-ones **5**, with LR gave the thionation products, 1,5-dihydropyrrole-2-thiones **7**, as main products (27–64%), along with pyrroles **6** (11–32%) (Scheme 2) (see Table 2). The structure of products **7** and **6** was confirmed by spectral and elemental analysis data (see Experimental section). The ^{13}C NMR spectra of compounds **7** showed C=S resonances at δ_C 195.5–195.7.

Table 1 Yields of 4,5,6,7-tetrahydroindoles **2** and indoles **3**

		Yield (%)[a]			
	Method[b]	**2**			**3**
1a	A	55	(12,[c]	33[d])	52
	B	80			
1b	A	52			
	B	73			
1c	A	27			
	B	77			
1d	A	35			
	B	64			
1e	A	30			48
	B	40			

[a] Isolated yield. [b] Method A: LR, reflux in benzene–DME. Method B: DIBAH in THF. [c] 0.5 mol equiv. of LR was used. [d] 1 mol equiv. of LR was used.



5a; R = Me **6** **7**

5b; R = Ph

5c; R = *p*-MeC$_6$H$_4$

Scheme 2 *Reagent:* LR

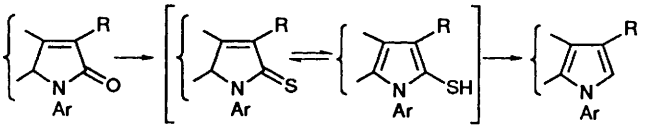
The reaction mechanism almost certainly involves initial thionation of amides **1**, **5** to thioamide (**4**, **7**) or thiol species (**4'**, **7'**), which then suffer reductive elimination of the thiol group

Table 2 Yields of pyrroles **6** and 2*H*-pyrrole-2-thiones **7**

	Molar quotient LR/5	Yield (%)[a] 6	7
5a	1	*b*	50
	2	*b*	29
5b	0.5	22	55
	0.5[c]	11	64
	1	34	35
	2	32	41
5c	0.5	20	28
	1	19	27

[a] Isolated yield. [b] Not detected. [c] DME was used as solvent.

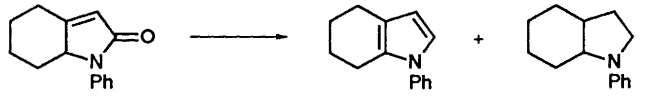
(Scheme 3). This is supported by the observation that the yield of the indole **2a** increases with an increase in the ratio LR: indol-2-one in the reaction of compound **1a** with LR (see Table 1).



1, 5 **4, 7** **4', 7'** **2, 6**

Scheme 3 *Reagent:* LR

There have been only a few reports on the synthesis of indoles by the reduction of indol-2-ones.[5] DIBAH is known to be an excellent partial reducing reagent of unsaturated amides and lactams (selective reduction of amide carbonyl).[6] Therefore we carried out the reduction of compounds **1** with DIBAH. Hexahydro-2*H*-indol-2-ones **1a–e** were treated with an excess of DIBAH to give the corresponding tetrahydroindoles **2** in good yield. On the other hand, reduction of compound **1a** with lithium aluminium hydride (LAH)[7] gave a mixture of tetrahydroindoles **2a** and the hexahydroindoline **8** (Scheme 4) since LAH has been reported to be a less selective reducing agent for the amide carbonyl of unsaturated amides and lactams.[5b,c] The analogous reduction of unsaturated 1,5-dihydropyrrol-2-ones with DIBAH to pyrroles was reported by Kochhar and Pinnick.[6b] The reaction described here would be a simple method for the synthesis of 4,5,6,7-tetrahydroindoles **2** and indoles **3**.



1a **2a** (20%) **8** (21%)

Scheme 4 *Reagents:* LAH, Et_2O

Experimental

M.p.s and b.p.s were measured with a Yanaco micro-melting point apparatus and Buchi Kugelrohr distillation apparatus, respectively, and are uncorrected. IR spectra were determined with JASCO IR-1 and Hitachi 260–30 spectrophotometers. ^1H and ^{13}C NMR spectra were run on JEOL FX-100 (100 MHz) or FX-90 Q (90 MHz) spectrometers in $CDCl_3$ as solvent with tetramethylsilane as internal standard. *J*-Values are given in Hz. Silica gel (Merck 60 or Wakogel C-300 for flash chromatography) was used for column chromatography.

Materials.—1,4,5,6,7,7a-Hexahydro-2*H*-indol-2-ones **1** were prepared by a modification of a previously reported literature method,[7] the 1,5-dihydropyrrol-2-one **5** was prepared according to a literature method,[6b] and the dihydropyrrol-2-ones **5b** and **5c** were prepared by a modification of this method. The structure of '1-phenyltetrahydroindolin-2-one' was stated to be **1a'** (m.p. 122–122.5 °C) in the literature.[7] However, on the basis of spectral data, especially the ^{13}C NMR spectrum, with four methylene (δ_C 23.0, 27.6, 28.4, 33.4), a methine (δ_C 62.4), two olefinic (δ_C 118.6, 162.1), and a carbonyl (δ_C 170.1) carbon peaks in addition to aromatic carbon ones, its structure should be revised as **1a**.

1-*Phenyl*-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1a**. M.p. 112–113 °C (from $CHCl_3$–hexane) (Found: C, 78.55; H, 7.1; N, 6.5. $C_{14}H_{15}NO$ requires C, 78.85; H, 7.1; N, 6.55%); ν_{max}(KBr)/cm^{-1} 1670 and 1640; δ_H 0.88–2.44 (7 H, m), 2.73–2.87 (1 H, m), 4.27–4.43 (1 H, m), 5.85 (1 H, s) and 7.05–7.56 (5 H, m); δ_C 23.0 (t), 27.6 (t), 28.4 (t), 33.4 (t), 62.4 (d), 118.6 (d), 121.5 (d), 124.2 (d), 128.8 (d), 137.3 (s), 162.1 (s) and 170.1 (s).

1-(p-*Tolyl*)-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1b**. M.p. 115–116 °C (from $CHCl_3$–hexane) (Found: C, 79.2; H, 7.55; N, 6.05. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%); ν_{max}(KBr)/cm^{-1} 1670 and 1615; δ_H 0.84–2.50 (7 H, m), 2.32 (3 H, s), 2.72–2.88 (1 H, m), 4.22–4.38 (1 H, m), 5.84 (1 H, s) and 7.12–7.41 (4 H, m); δ_C 20.9 (q), 23.1 (t), 27.7 (t), 28.4 (t), 33.6 (t), 62.7 (d), 118.9 (d), 121.8 (d), 129.5 (d), 134.1 (s), 134.8 (s), 162.0 (s) and 171.2 (s).

1-(p-*Methoxyphenyl*)-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1c**. M.p. 107–108 °C (from $CHCl_3$–hexane) (Found: C, 74.15; H, 7.05; N, 5.7. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05, N, 5.75%); ν_{max}(KBr)/cm^{-1} 1685; δ_H 0.97–2.43 (7 H, m), 2.72–2.85 (1 H, m), 3.78 (3 H, s), 4.17–4.34 (1 H, m), 5.84 (1 H, s), 6.82–6.98 (2 H, m) and 7.28–7.44 (2 H, m); δ_C 23.1 (t), 27.7 (t), 28.5 (t), 33.7 (t), 55.5 (q), 63.1 (d), 114.3 (d), 118.7 (d), 124.0 (d), 130.4 (s), 156.8 (s), 162.0 (s) and 172.0 (s).

1-(p-*Chlorophenyl*)-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1d**. M.p. 124–125 °C (from $CHCl_3$–hexane) (Found: C, 67.6; H, 5.65; N, 5.65. $C_{14}H_{14}ClNO$ requires C, 67.85; H, 5.7; N, 5.65%); ν_{max}(KBr)/cm^{-1} 1665; δ_H 0.85-2.45 (7 H, m), 2.74–2.88 (1 H, m), 4.24–4.41 (1 H, m), 5.85 (1 H, s) and 7.25–7.53 (4 H, m); δ_C 23.1 (t), 27.7 (t), 28.5 (t), 33.5 (t), 62.4 (d), 118.8 (d), 122.4 (d), 129.0 (d), 129.4 (s), 136.0 (s), 162.4 (s) and 170.1 (s).

3-*Methyl*-1-*phenyl*-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1e**. M.p. 93–94 °C (from $CHCl_3$–hexane) (Found: C, 79.1; H, 7.55; N, 6.1. $C_{15}H_{17}NO$, requires C, 79.25; H, 7.55; N, 6.15%); ν_{max}(KBr)/cm^{-1} 1670; δ_H 0.88 (7 H, m), 1.85 (3 H, s), 2.76–2.91 (1 H, m), 4.15–4.32 (1 H, m) and 7.00–7.60 (5 H, m); δ_C 8.4 (q), 23.5 (t), 26.2 (t), 27.4 (t), 33.4 (t), 61.0 (d), 121.2 (d), 124.0 (d), 125.1 (s), 128.9 (d), 137.8 (s), 153.0 (s) and 170.9 (s).

4-*Ethoxy*-1-*phenyl*-1,5-*dihydropyrrol*-2-*one* **5b**. M.p. 105–106 °C (from $CHCl_3$–hexane) (Found: C, 70.95; H, 6.45; N, 6.7. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.45; N, 6.9%); ν_{max}(KBr)/cm^{-1} 1685 and 1635; δ_H 1.41 (3 H, t), 4.04 (2 H, q), 4.24 (2 H, s), 5.11 (1 H, s), 6.96–7.13 (1 H, m), 7.22–7.43 (2 H, m) and 7.55–7.69 (2 H, m); δ_C 14.1 (q), 50.8 (t), 67.3 (t), 95.7 (d), 118.3 (d), 123.1 (d), 129.0 (d), 139.4 (s), 170.8 (s) and 171.6 (s).

4-*Ethoxy*-1-(p-*tolyl*)-1,5-*dihydropyrrol*-2-*one* **5c**. M.p. 131–132 °C (from $CHCl_3$–hexane) (Found: C, 71.85; H, 7.0; N, 6.4. $C_{13}H_{15}NO_2$ requires C, 71.85; H, 6.95; N, 6.45%); ν_{max}(KBr)/cm^{-1} 1665 and 1620; δ_H 1.41 (3 H, t), 2.30 (3 H, s), 4.03 (2 H, q), 4.20 (2 H, s), 5.10 (1 H, s), 7.13 (2 H, d, *J* 8.3) and 7.49 (2 H, d, *J* 8.3); δ_C 13.9 (q), 20.5 (q), 50.8 (t), 67.0 (t), 95.5 (d), 118.3 (d), 129.4 (d), 132.6 (s), 136.7 (s), 170.5 (s) and 171.4 (s).

Reaction of the Hexahydro-2H-*indol*-2-*ones* **1** *with LR. General Procedure.*—A solution of amide **1** (1 mmol) and LR (2 mmol) in benzene–DME (9:3 cm^3) was heated under reflux for 15 min. After removal of the solvent under reduced pressure, the residual oil was chromatographed on a silica gel column with benzene–hexane (1:4) as eluent to yield the corresponding tetrahydroindoles **2**.

1-*Phenyl*-4,5,6,7-*tetrahydroindole* **2a**. B.p. 100 °C at 2 mmHg

(Found: C, 84.85; H, 7.6; N, 7.0. $C_{14}H_{15}N$ requires C, 85.2; H, 7.65; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1600, 1500, 1310 and 690; δ_H 1.71–1.88 (4 H, m), 2.57 (4 H, br s), 6.09 (1 H, d, *J* 2.4), 6.75 (1 H, d, *J* 2.4) and 7.15–7.50 (5 H, m); δ_C 23.3 (t), 23.5 (t), 23.6 (t), 108.1 (d), 119.0 (s), 119.8 (d), 124.5 (d), 126.0 (d), 128.0 (s), 129.0 (s) and 140.3 (s).

1-(p-*Tolyl*)-4,5,6,7-*tetrahydroindole* **2b**. B.p. 90 °C at 2 mmHg (Found: C, 85.25; N, 8.1; N, 6.6. $C_{15}H_{17}N$ requires C, 85.1; H, 8.1; N, 6.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1510, 1480, 1305 and 820; δ_H 1.71–1.82 (4 H, m), 2.37 (3 H, s), 2.56 (4 H, br s), 6.07 (1 H, d, *J* 2.4), 6.72 (1 H, d, *J* 2.4), 7.18 (3 H, s) and 7.20 (1 H, s); δ_C 20.9 (q), 23.3 (t), 23.5 (t), 23.6 (t), 107.8 (d), 118.7 (s), 119.8 (d), 124.4 (d), 128.1 (s), 129.6 (d), 135.8 (s) and 137.8 (s).

1-(p-*Methoxyphenyl*)-4,5,6,7-*tetrahydroindole* **2c**. B.p. 90 °C at 2 mmHg (Found: C, 79.25; H, 7.55; N, 6.15. $C_{15}H_{17}NO$ requires C, 78.9; H, 7.5; N, 6.05%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1510, 1460, 1440 and 835; δ_H 1.76 (4 H, br s), 2.51–2.56 (4 H, m), 3.81 (3 H, s), 6.05 (1 H, d, *J* 2.9), 6.69 (1 H, d, *J* 2.9), 6.69 (2 H, d, *J* 9.0) and 6.91 (2 H, d, *J* 9.0).

1-(p-*Chlorophenyl*)-4,5,6,7-*tetrahydroindole* **2d**. B.p. 90 °C at 2 mmHg (Found: C, 72.55; H, 6.1; N, 6.05. $C_{14}H_{14}ClN$ requires C, 72.4; H, 6.15; N, 5.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1600, 1490, 1310, 1090 and 835; δ_H 1.71–1.83 (4 H, m), 2.54 (4 H, br s), 6.08 (1 H, d, *J* 3.0), 6.71 (1 H, d, *J* 3.0) and 7.13–7.49 (4 H, m); δ_C 23.2 (t), 23.3 (t), 23.6 (t), 108.5 (d), 119.4 (s), 119.7 (d), 125.5 (d), 128.0 (s), 129.2 (d), 131.6 (s) and 137.7 (s).

3-Methyl-1-phenyl-4,5,6,7-tetrahydroindole **2e**. B.p. 110 °C at 2 mmHg; $\nu_{max}(CDCl_3)/cm^{-1}$ 1600, 1505, 1400, 1380 and 695; δ_H 1.70–1.81 (4 H, m), 2.04 (3 H, s), 2.44–2.53 (4 H, m), 6.56 (1 H, s) and 7.17–7.36 (5 H, m); δ_C 9.8 (q), 21.6 (t), 23.3 (t), 23.6 (t), 117.4 (d), 117.6 (s), 118.9 (s), 124.1 (d), 125.5 (d), 127.8 (s), 128.9 (d) and 140.3 (s).

Oxidation of the Tetrahydroindoles **2a** *and* **2e** *to Indoles* **3a** *and* **3e**.—A mixture of a tetrahydroindole **2** (200 mg) and chloranil (2.5 mol equiv) in toluene (30 cm^3) was refluxed under argon for 20 h. Usual work-up gave the corresponding indole **3**. The structure of the products **3** was confirmed by direct comparison of their IR and NMR spectra with those of authentic samples.[2d]

Reduction of the Hexahydro-2H-*indol*-2-*ones* **1** *with DIBAH*.—To a solution of an amide **1** (200 mg) in tetrahydrofuran (THF) (20 cm^3) at 0 °C was added a solution of DIBAH (3 mol equiv.) in THF (1.5 cm^3) under argon. The stirred mixture was allowed to warm to room temperature and was stirred for 2 h, then poured into 1 mol dm^{-3} aq. NaOH and extracted with dichloromethane. The extract was dried over $MgSO_4$ and concentrated, and the residue was chromatographed on a silica gel column with benzene–hexane (1:4) to give the corresponding tetrahydroindole **2**.

Reduction of 1-*Phenyl*-1,4,5,6,7,7a-*hexahydro*-2H-*indol*-2-*one* **1a** *with LAH*.—A solution of amide **1a** (200 mg) and LAH (4 mol equiv.) in diethyl ether (20 cm^3) was refluxed for 2 h. Usual work-up gave the tetrahydroindole **2a** (20%) and the pyrrolidine **8** (21%), whose stereochemistry could not be determined from its spectral data (^1H NMR) because of spectral complexity.

1-*Phenylperhydroindoline* **8**. B.p. 145 °C at 2 mmHg (Found: C, 83.65; H, 9.75; N, 6.95. $C_{14}H_{19}N$ requires C, 83.55; H, 9.5; N, 6.95%); ν_{max}(film)/cm^{-1} 1590, 1495, 1365, 740 and 685; δ_H 1.00–2.45 (11 H, m), 3.09–3.47 (2 H, m), 3.55–3.78 (1 H, m), 6.45–6.72 (3 H, m) and 7.08–7.34 (2 H, m); δ_C 21.3 (t), 23.8 (t), 26.4 (t), 26.7 (t), 26.9 (t), 37.7 (d), 46.6 (t), 57.3 (d), 111.2 (d), 114.7 (d), 129.2 (d) and 147.1 (s).

Reaction of the 1,5-*Dihydro*-2H-*pyrrol*-2-*ones* **5** *with LR. General Procedure*.—A solution of a pyrrolone **5** (1 mmol) and LR (0.5–2 mol equiv.) in toluene or DME (30 cm^3) was heated under reflux for 10 min under argon. Usual work-up gave the corresponding pyrrole **6** and 1,5-dihydropyrrole-2-thione **7**.

4-*Ethoxy*-1-*methyl*-1,5-*dihydro*-2H-*pyrrole*-2-*thione* **7a**. M.p. 103–104 °C (from $CHCl_3$–hexane) (Found: C, 53.45; H, 7.1; N, 8.9. $C_7H_{11}NS$ requires C, 53.5; H, 7.15; N, 8.9%); ν_{max}(KBr)/cm^{-1} 1590, 1490, 1475, 1380 and 1340; δ_H 1.40 (3 H, t), 3.30 (3 H, s), 4.00 (2 H, q), 4.16 (2 H, s) and 5.61 (1 H, s); δ_C 14.1 (q), 33.3 (q), 59.1 (t), 67.4 (t), 106.6 (d), 171.3 (s) and 197.5 (s).

4-*Ethoxy*-1-*phenylpyrrole* **6b**. B.p. 145 °C at 3 mmHg (Found: C, 76.75; H, 7.0; N, 7.45. $C_{12}H_{13}NO$ requires C, 77.0; H, 7.0; N, 7.5%); ν_{max}(film)/cm^{-1} 3130, 1595, 1560, 1505, 750, 735 and 685; δ_H 1.39 (3 H, t), 3.95 (2 H, q), 6.02–6.08 (1 H, m), 6.62–6.67 (1 H, m), 6.84–6.91 (1 H, m) and 7.06–7.48 (5 H, m); δ_C 15.0 (q), 66.0 (t), 100.7 (d), 101.4 (d), 116.9 (d), 119.5 (d), 124.9 (d), 129.5 (d), 140.9 (s) and 149.6 (s).

4-*Ethoxy*-1-*phenyl*-1,5-*dihydro*-2H-*pyrrole*-2-*thione* **7b**. M.p. 144–145 °C (from $CHCl_3$–hexane) (Found: C, 65.65; H, 6.0; N, 6.4. $C_{12}H_{13}NOS$ requires C, 65.7; H, 6.0; N, 6.4%); ν_{max}(KBr)/cm^{-1} 1595, 1575, 1485, 785, 770 and 700; δ_H 1.42 (3 H, t), 4.06 (2 H, q), 4.55 (2 H, s), 5.78 (1 H, s) and 7.18–7.66 (5 H, m); δ_C 14.2 (q), 59.8 (t), 67.9 (t), 108.4 (d), 125.0 (d), 126.0 (d), 128.9 (d), 139.4 (s), 171.4 (s) and 197.7 (s).

4-*Ethoxy*-1-(p-*tolyl*)*pyrrole* **6c**. B.p. 140 °C at 3 mmHg (Found: C, 77.3; H, 7.55; N, 6.95. $C_{13}H_{15}NO_2$ requires C, 77.6; H, 7.5; N, 7.0%); ν_{max}(film)/cm^{-1} 1610, 1590, 1560, 1520, 815 and 735; δ_H 1.38 (3 H, t), 2.31 (3 H, s), 3.93 (2 H, q), 6.02 (1 H, dd, *J* 2.0 and 2.9), 6.60 (1 H, t, *J* 2.0), 6.81 (1 H, t, *J* 2.9) and 7.16 (4 H, s); δ_C 14.9 (q), 20.6 (q), 65.9 (t), 100.1 (d), 101.4 (d), 116.8 (d), 119.4 (d), 129.9 (d), 134.4 (s), 138.5 (s) and 149.3 (s).

4-*Ethoxy*-1-(p-*tolyl*)-1,5-*dihydro*-2H-*pyrrole*-2-*thione* **7c**. M.p. 121–122 °C (from $CHCl_3$–hexane) (Found: C, 67.15; H, 6.55; N, 5.95. $C_{13}H_{15}NOS$ requires C, 66.9; H, 6.5; N, 6.0%); ν_{max}(KBr)/cm^{-1} 1605, 1505, 1435, 800 and 720; δ_H 1.42 (3 H, t), 2.35 (3 H, s), 4.05 (2 H, q), 4.51 (2 H, s), 5.76 (1 H, s), 7.21 (2 H, d, *J* 8.3) and 7.44 (2 H, d, *J* 8.3); δ_C 14.0 (q), 21.0 (q), 59.9 (t), 67.5 (t), 108.1 (d), 125.0 (d), 129.4 (d), 136.8 (s), 171.2 (s) and 197.5 (s).

References

1 M. P. Cava and M. I. Levinson, *Tetrahedron*, 1985, **41**, 5061.

2 (*a*) T. Nishio, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1225; (*b*) T. Nishio, M. Fujisawa and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2523; (*c*) T. Nishio, N. Okuda, C. Kashima and Y. Omote, *J. Chem. Soc., Chem. Commun.*, 1988, 572; (*d*) T. Nishio, *J. Org. Chem.*, 1988, **53**, 1323; (*e*) T. Nishio, N. Okuda and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1663; (*f*) T. Nishio, N. Okuda and C. Kashima, *J. Chem. Soc., Perkin Trans. 1*, 1991, 141.

3 T. Nishio, N. Okuda, Y. Mori and C. Kashima, *Synthesis*, 1989, 396.

4 T. Nishio, *J. Chem. Soc., Chem. Commun.*, 1989, 205.

5 (*a*) R. J. Sundberg, in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, 1984, vol. 4, p. 313; (*b*) R. J. Sundberg, in *The Chemistry of Indoles*, Academic Press, New York, 1970; (*c*) T. Nishio, N. Okuda and C. Kashima, *Helv. Chim. Acta*, 1990, **73**, 1719.

6 (*a*) E. Winterfeldt, *Synthesis*, 1975, 617; (*b*) K. Kochhar and H. W. Pinnick, *J. Org. Chem.*, 1984, **49**, 3222.

7 A. Bertho and H. Kurzmann, *Chem. Ber.*, 1957, **90**, 2319.

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