Synthesis of 3-Hydroperoxyindolin-2-ones and Oxidation of Sulphides to Sulphoxides by 3-Hydroperoxyindolin-2-ones

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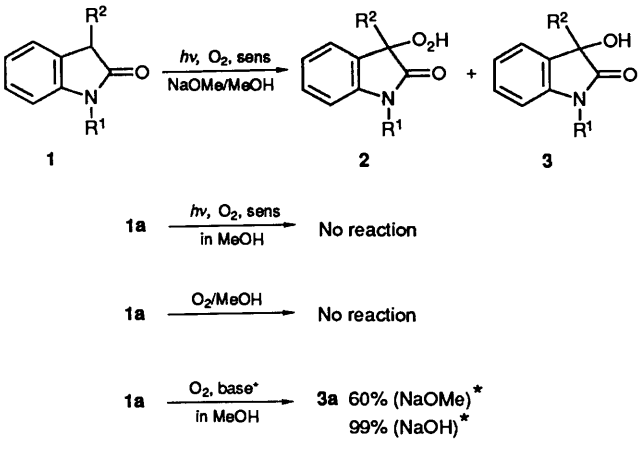
The 3-hydroperoxyindolin-2-ones **2** were prepared in moderate yields by the dye-sensitized photooxidation of the indolin-2-ones **1**. The 3-hydroperoxyindolin-2-ones **2** thus obtained oxidized a series of sulphides **4** selectively to the corresponding sulphoxides **5** without further oxidation to the sulphone.

Organic hydroperoxides such as flavin 4a-hydroperoxides and α-azohydroperoxides are well documented as oxidizing sulphides to sulphoxides.[1] However, their application is limited by their sensitivity to light[1h] and poor stability, especially in solution.[1i] We report here the synthesis of stable *N*-substituted 3-hydroperoxyindolin-2-ones **2**,[2] which are readily prepared from the indolin-2-ones **1** with singlet oxygen, and *S*-oxidation of sulphides by **2**.

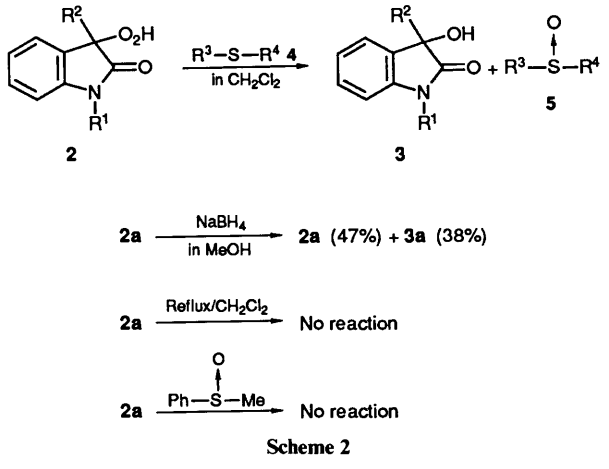
Results and Discussion

Irradiation of a solution of 3-methyl-1-phenylindolin-2-one **1a** in methanol with visible light, under an oxygen atmosphere in the presence of Rose Bengal as sensitizer and a catalytic amount of sodium methoxide, at room temperature, for 5 h gave 3-hydroperoxy-3-methyl-1-phenylindolin-2-one **2a** and 3-hydroxy-3-methyl-1-phenylindolin-2-one (dioxyindole) **3a** in 70 and 26% yields, respectively. A similar result was obtained when sodium



Scheme 1

hydroxide was used as base in the dye-sensitized photooxygenation of **1a**. The structure of **2a** was elucidated on the basis of its spectral properties and elemental analysis, and that of **3a** was confirmed by direct comparison of its IR and NMR spectra with an authentic sample.[3] Further proof of the formation of hydroperoxide **2a** was achieved by the reduction of **2a** to **3a** (38% yield) with sodium borohydride. Control experiments were conducted which demonstrated that both light and base are required to effect the formation of 3-hydroperoxyindolin-2-one **2a**. Neither compound **2a** nor compound **3a** could be obtained on air oxidation of **1a** or irradiation of an oxygenated solution of **1a** in the absence of sodium methoxide under the conditions described above. On the other hand, when **1a** was oxidized with molecular oxygen in the presence of a base such as sodium methoxide and sodium hydroxide, compound **3a** was



Scheme 2

Table 1 Yield of the hydroperoxyindolinones **2** and hydroxyindolinones **3**

Compound	R^1	R^2	Irr. time (h)	Yield (%)[a] 2	3
1a	Ph	Me	5	70 (61)[b]	26 (13)[b]
1b	Ph	Et	8	41	26
1c	Ph	Ph	2	52	47
1d	Me	Ph	4	45	31
1e	Bu	Ph	2	54	30
1f	Bu	Me	8	17	—[c]

[a] Isolated yield. [b] Sodium hydroxide was used as base. [c] Recovered **1f**: 67%.

obtained as the sole product and compound **2a** was not detected.

Several examples of the reaction of oxygen with alkaline solutions of the indolin-2-ones have been reported.[3] From 3-substituted indolin-2-ones, the corresponding 3-hydroxyindolin-2-one analogues and/or ring cleavage products were obtained. In a similar manner, the indolin-2-ones **1b–f** gave 3-hydroperoxyindolin-2-ones **2b–f** and 3-hydroxyindolin-2-ones **3b–e** (Table 1). The structures of **2** and **3** were elucidated on the basis of their spectral properties and elemental analyses. The IR spectrum of the 3-hydroperoxyindolin-2-ones **2** showed an absorption at ν 3220–3320 cm^{-1} assignable to the hydroperoxy group, while that of **3** showed absorption at ν 3350–3425 cm^{-1} due to a hydroxy group. The ^{13}C NMR spectrum of **2** showed a signal characteristic of quaternary carbon at C-3 at δ_C 84.4–88.7, while that of **3** showed it at higher field, δ_C 73.4–78.1.

The hydroperoxyindolin-2-ones **2** thus obtained are indefinitely stable in the solid state at room temperature.[2] Compound **2a** was recovered unchanged even when heated to reflux in

Table 2 Yield of hydroxyindolinones **3** and sulphoxides **5** obtained by the reaction of hydroperoxyindolinones **2** with sulphides **5**

Run	Peroxide **2**		Sulphide **4**		React. time (h)	Yield (%)[a]		
	R^1	R^2	R^3	R^4		**3**	**5**	Other
1	Ph	Me	**4a** Ph	Me	2	98	82	
2[b]	Ph	Me	**4a** Ph	Me	10	92	81	**6**[c] (tr)
3[d]	Ph	Me	**4a** Ph	Me	5	quant.	62	
4	Ph	Me	**4b** *p*-MeC_6H_4	Me	2	quant.	87	
5	Ph	Me	**4c** *p*-ClC_6H_4	Me	2	69	69	
6	Ph	Me	**4d** $PhCH_2$	$PhCH_2$	3	quant.	91	
7	Ph	Me	**4e** $PhCH_2$	Me	3	quant.	81	
8	Ph	Me	**4f** Bu	Bu	2	quant.	85	
9	Ph	Me	**4g** Bu^t	Bu^t	3	quant.	37	
10	Ph	Me	**4h** $-(CH_2)_5-$		2	quant.	95	
11	Ph	Me	**4i** $-(CH_2)_4-$		3	quant.	87	
12	Ph	Me	**4j** Me	Me	2	75	49	**7**[e] (24)
13	Ph	Me	**4k** Ph	Ph	12	35	20	**2**[f] (77)
14	Ph	Ph	**4a** Ph	Me	5	96	66	
15	Bu	Ph	**4a** Ph	Me	5	95	44	

[a] Isolated yield. [b] Molar ratio: **2**/**4** = 2. [c] Methyl phenyl sulphone. [d] Benzene was used as solvent. [e] Dimethyl sulphone. [f] Recovered.

dichloromethane for a long time. On the other hand, the thermal oxygen-atom transfer of 3-hydroperoxyindolin-2-ones **2** to sulphides **4** was observed. Compound **2a** was heated to reflux in dichloromethane in the presence of an equimolar amount of methyl phenyl sulphide (thioanisole) **4a** to yield methyl phenyl sulphoxide **5a** and the reduced product, 3-hydroxyindolin-2-one **3a** in 83 and 98% yields, respectively. Sulphone was not formed in this reaction even by treatment of hydroperoxyindolinone **2a** with sulphide **4a** in a molar ratio of 2. Further oxidation of sulphoxide to sulphone was not observed. Treatment of methyl phenyl sulphoxide **5a** with **2a** did not yield methyl phenyl sulphone and **5a** was recovered unchanged. Similarly, treatment of a dichloromethane solution of **2a** with a series of sulphides **4b–k** at reflux temperature resulted in the formation of the corresponding sulphoxides **5b–k** in 20–95% yields with concomitant of formation of hydroxyindolinone **3a**. The hydroperoxyindolinones, **2c** and **2e** also oxidized methyl phenyl sulphide **4a** to give the sulphoxide **5a**, but the yields were rather low (run 14, 15). In all cases, the sulphoxides were selectively formed (except dimethyl sulphide **4j**). The results are summarized in Table 2. The sulphoxides **5a–k** were isolated and proven to be identical with authentic samples by direct comparison of their spectral properties. Diphenyl sulphide **4k** was found to be less reactive towards oxidation by hydroperoxyindolinone **2a** (run 13). The presence of electron-donating substituents on the thioanisole accelerates its reaction with hyderoperoxyindolinone **2a** (runs 1, 4 and 5). The relative reactivity of the reaction of hydroperoxyindolinone **2a** with sulphides **4** is similar to that from the corresponding *S*-oxidation with flavin 4a-hydroperoxides[1a,c] and α-azohydroperoxides.[1d,e,g] Furthermore, the yield of di-*tert*-butyl sulphoxide **5g** was lower than that of dibutyl sulphoxide **5f**, probably due to steric reason of bulkyl *tert*-butyl groups adjacent to the reactive sulphur. These results suggest that the mechanism for the oxidation of sulphide **4** with hydroperoxyindolinones **2** involves nucleophilic attack of sulphur on the oxygen atom of **2**.[1]

Thus, 3-hydroperoxyindolin-2-ones **2** provide synthetically useful selective oxidizing reagents for sulphides to sulphoxides, since the hydroperoxyindolinones **2** are stable in the solid state and can be stored indefinitely at room temperature.

Experimental

M.p.s and b.p.s are uncorrected and measured with Yanaco micro melting point apparatus (MP-J3) and Buchi Kugelrohr distillation apparatus. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. ^1H and ^{13}C NMR spectra were run on a JEOL FX-100 spectrometer (100 MHz) in $CDCl_3$ as solvent using TMS (Me_4Si) as an internal standard unless otherwise stated. *J* Values are given in Hz. A halogen lamp was used as an irradiation source.

Materials.—Indolin-2-one **1a** was prepared according to methods previously described in the literature[4–6] and **1b–f** were prepared by a modification of these methods.

3-*Methyl*-1-*phenylindolin*-2-*one* **1a**. M.p. 70–71 °C (lit.,[4] b.p. 153–156 °C at 1.2 mmHg); ν_{max}(KBr)/cm^{-1} 1705 (C=O); δ_H 1.57 (3 H, d, *J* 7.8), 3.60 (1 H, q, *J* 7.8), 6.75–6.84 (1 H, m) and 7.04–7.63 (8 H, m); δ_C 15.7 (q), 40.7 (d), 109.2 (d), 122.8 (d), 123.8 (d), 126.5 (d), 127.7 (d), 127.9 (d), 129.5 (d), 130.4 (s), 134.6 (s), 143.8 (s) and 177.8 (s).

3-*Ethyl*-1-*phenylindolin*-2-*one* **1b**. M.p. 75–76 °C (Found: C, 80.9; H, 6.2; N, 5.85. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%); ν_{max}(KBr)/cm^{-1} 1705 (C=O); δ_H 0.97 (3 H, t), 1.98–2.26 (2 H, m), 3.59 (1 H, t, *J* 5.8), 6.75–6.84 (1 H, m) and 6.97–7.61 (8 H, m); δ_C 9.9 (q), 24.2 (t), 46.7 (d), 109.2 (d), 122.7 (d), 124.0 (d), 126.6 (d), 127.7 (d), 127.9 (d), 128.7 (s), 129.5 (d), 134.7 (s), 144.5 (s) and 177.1 (s).

1,3-*Diphenylindolin*-2-*one* **1c**. M.p. 112–113 °C (Found: C, 84.25; H, 5.3; N, 4.85. $C_{20}H_{15}NO$ requires C, 84.2; H, 5.3; N, 4.9%); ν_{max}(KBr)/cm^{-1} 1705 (C=O); δ_H 4.77 (1 H, s), 6.81–6.92 (1 H, m) and 6.97–7.61 (13 H, m); δ_C 52.1 (d), 109.5 (d), 123.1 (d), 125.3 (d), 126.5 (d), 127.6 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.9 (d), 129.5 (d), 134.6 (s), 136.7 (s), 144.4 (s) and 175.2 (s).

1-*Methyl*-3-*phenylindolin*-2-*one* **1d**. M.p. 114–116 °C (lit.,[3,7] 120 °C, 116 °C); ν_{max}(KBr)/cm^{-1} 1685 (C=O); δ_H 3.23 (3 H, s), 4.56 (1 H, s), 6.87 (1 H, d, *J* 7.3) and 6.96–7.41 (8 H, m); δ_C 26.4 (q), 52.0 (d), 109.1 (d), 122.7 (d), 125.0 (d), 127.5 (d), 128.4 (d), 128.8 (d), 136.7 (s), 144.4 (s) and 175.9 (s).

1-*Butyl*-3-*phenylindolin*-2-*one* **1e**. B.p. 170 °C at 2 mmHg (Found: C, 74.7; H, 8.2; N, 5.2. $C_{18}H_{19}NO$ requires C, 74.65; H, 8.5; N, 5.1%); ν_{max}(film)/cm^{-1} 1700 (C=O); δ_H 0.94 (3 H, t), 1.20–1.85 (4 H, m), 3.80 (2 H, t), 4.57 (1 H, s) and 6.85–7.42 (9 H, m); δ_C 13.7 (q), 20.1 (t), 29.5 (t), 39.9 (t), 52.0 (d), 108.4 (d), 122.4 (d), 125.1 (d), 127.4 (d), 128.4 (d), 128.8 (d), 129.1 (s), 136.9 (s), 143.9 (s) and 175.9 (s).

1-*Butyl*-3-*methylindolin*-2-*one* **1f**. B.p. 120 °C at 2 mmHg; m.p. 45 °C (Found: C, 77.0; H, 8.7; N, 6.65. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%); ν_{max}(film)/cm^{-1} 1705 (C=O); δ_H 0.94 (3 H, t), 1.14–1.81 (4 H, m), 1.46 (3 H, d, *J* 7.8), 3.39 (1 H, q, *J* 7.8), 3.69 (2 H, t) and 6.77–7.48 (4 H, m); δ_C 13.7 (q), 15.4 (q),

20.1 (t), 29.5 (t), 39.6 (t), 40.5 (d), 108.2 (d), 122.0 (d), 123.6 (d), 127.7 (d), 130.8 (s), 143.4 (s) and 178.4 (s).

General Procedure for the Dye-sensitized Photooxidation of the Indolin-2-ones **1**.—A solution of the indolin-2-ones **1** (200 mg) in methanol (100 cm^3) in the presence of Rose Bengal (*ca.* 2 mg) and catalytic amount of sodium methoxide (or sodium hydroxide) in a Pyrex vessel under oxygen was irradiated with a halogen lamp for 2–8 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (9:1–4:1) as eluent to yield the 3-hydroperoxyindolin-2-ones **2** and 3-hydroxyindolin-2-ones (dioxyindoles) **3**.

3-Hydroperoxy-3-methyl-1-phenylindolin-2-one **2a**. M.p. 126–127 °C (Found: C, 70.55; H, 5.15; N, 5.5. $C_{15}H_{13}NO_3$ requires C, 70.55; H, 5.15; N, 5.5%); ν_{max}(KBr)/cm^{-1} 3270, 1705; δ_H 1.65 (3 H, s), 6.76–6.85 (1 H, m), 7.05–7.60 (8 H, m) and 9.93 (1 H, br s); δ_C 20.3 (q), 84.5 (s), 109.7 (d), 123.6 (d), 123.8 (d), 128.2 (d), 128.4 (s), 129.5 (d), 129.8 (d), 133.9 (s), 143.6 (s) and 175.4 (s).

3-Hydroxy-3-methyl-1-phenylindolin-2-one **3a**. M.p. 149–150 °C (lit.,[4] 149.5–150 °C); ν_{max}(KBr)/cm^{-1} 3370 and 1700; δ_H 1.71 (3 H, s), 3.67 (1 H, br s), 6.78–6.86 (1 H, m) and 7.02–7.62 (8 H, m); δ_C 25.2 (q), 73.4 (s), 109.7 (d), 123.6 (d), 123.8 (d), 126.3 (d), 128.0 (d), 129.5 (d), 131.2 (s), 134.0 (s), 142.7 (s) and 178.1 (s).

3-Ethyl-3-hydroperoxy-1-phenylindolin-2-one **2b**. M.p. 151–152 °C (Found: C, 71.35; H, 5.6; N, 5.15. $C_{16}H_{15}NO_3$ requires C, 71.35; H, 5.6; N, 5.2); ν_{max}(KBr)/cm^{-1} 3250 and 1700; δ_H 0.84 (3 H, t, *J* 7.8), 2.07 (2 H, d of q, *J* 2.0, 7.8), 6.75–6.85 (1 H, m), 7.06–7.60 (8 H, m) and 9.85 (1 H, br s); δ_C 7.3 (q), 27.4 (t), 88.6 (s), 109.6 (d), 123.6 (d), 124.1 (d), 126.5 (d), 126.9 (s), 128.2 (d), 129.5 (d), 129.8 (d), 133.9 (s), 144.2 (s) and 175.2 (s).

3-Ethyl-3-hydroxy-1-phenylindolin-2-one **3b**. M.p. 140–141 °C (Found: C, 75.9; H, 5.9; N, 5.5. $C_{16}H_{15}NO_2$ requires C, 75.85; H, 5.95; N, 5.5%); ν_{max}(KBr)/cm^{-1} 3350 and 1700; δ_H 0.84 (3 H, t, *J* 7.8), 2.10 (2 H, q, *J* 7.8), 3.20 (1 H, br s), 6.76–6.86 (1 H, m) and 7.04–7.62 (8 H, m); δ_C 7.7 (q), 32.2 (t), 77.3 (s), 109.6 (d), 123.5 (d), 124.1 (d), 126.3 (d), 126.5 (s), 128.2 (d), 129.4 (d), 129.6 (d), 134.0 (s), 143.5 (s) and 177.7 (s).

3-Hydroperoxy-1,3-diphenylindolin-2-one **2c**. M.p. 181.5–182.5 °C (Found: C, 75.4; H, 4.65; N, 4.35. $C_{20}H_{15}NO_3$ requires C, 75.7; H, 4.75; N, 4.4%); ν_{max}(KBr)/cm^{-1} 3300 and 1700; δ_H 6.88 (1 H, dd, *J* 1.5, 6.8), 7.13–7.61 (13 H, m) and 9.22 (1 H, s).

3-Hydroxy-1,3-diphenylindolin-2-one **3c**. M.p. 165–166 °C (Found: C, 79.5; H, 4.9; N, 4.55. $C_{20}H_{15}NO_2$ requires C, 79.7; H, 5.0; N, 4.65%); ν_{max}(KBr)/cm^{-1} 3425 and 1700; δ_H 3.92 (1 H, s), 6.80–6.90 (1 H, m) and 6.98–7.62 (13 H, m); δ_C 78.1 (s), 109.9 (d), 123.9 (d), 125.3 (d), 126.4 (d), 128.3 (d), 128.6 (d), 129.6 (d), 131.4 (s), 134.0 (s), 140.4 (s), 143.4 (s) and 177.0 (s).

3-Hydroperoxy-1-methyl-3-phenylindolin-2-one **2d**. M.p. 178–179 °C (Found: C, 70.5; H, 5.15; N, 5.45. $C_{15}H_{13}NO_3$ requires C, 70.55; H, 5.15; N, 5.5%); ν_{max}(KBr)/cm^{-1} 3320 and 1695; δ_H 3.24 (3 H, s), 6.87–6.97 (1 H, m), 7.10–7.53 (8 H, m) and 8.94 (1 H, s).

3-Hydroxy-1-methyl-3-phenylindolin-2-one **3d**. M.p. 129–130 °C (lit.,[3,7] 139–141 °C, 130 °C); ν_{max}(KBr)/cm^{-1} 3350 and 1705; δ_H 3.16 (3 H, s), 4.16 (1 H, s), 6.81–6.90 (1 H, m) and 6.96–7.43 (8 H, m); δ_C 26.4 (q), 78.0 (s), 108.6 (d), 123.4 (d), 124.9 (d), 125.3 (d), 128.1 (d), 128.4 (d), 129.7 (d), 131.7 (s), 149.1 (s), 143.4 (s) and 177.6 (s).

1-Butyl-3-hydroperoxy-3-phenylindolin-2-one **2e**. M.p. 147–148 °C (Found: C, 72.4; H, 6.4; N, 4.65. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%); ν_{max}(KBr)/cm^{-1} 3250 and 1700; δ_H 0.90 (3 H, t), 1.17–1.84 (4 H, m), 3.71 (2 H, t), 6.93 (1 H, d, *J* 7.8), 7.06–7.48 (8 H, m) and 10.29 (1 H, s); δ_C 13.7 (q), 20.0 (t), 29.3 (t), 40.2 (t), 88.7 (s), 109.0 (d), 123.1 (d), 125.8 (d), 126.9 (d), 127.9 (s), 128.5 (d), 129.0 (d), 130.2 (d), 135.2 (s), 143.8 (s) and 174.8 (s).

1-Butyl-3-hydroxy-3-phenylindiolin-2-one **3e**. M.p. 117–118 °C (Found: C, 76.75; H, 6.75; N, 4.9. $C_{18}H_{19}NO_2$ requires C, 76.85; H, 6.8; 4.95%); ν_{max}(KBr)/cm^{-1} 3350 and 1695; δ_H 0.94 (3 H, t), 1.20–1.95 (4 H, m), 3.45–3.87 (2 H, m), 3.97 (1 H, s) and 6.84–7.41 (9 H, m); δ_C 13.7 (q), 20.1 (t), 29.4 (t), 40.0 (t), 77.9 (s), 109.8 (d), 123.2 (d), 125.0 (d), 125.2 (d), 128.0 (d), 128.5 (d), 129.6 (d), 132.0 (s), 140.3 (s), 142.8 (s) and 177.4 (s).

1-Butyl-3-hydroperoxy-3-methylindolin-2-one **2f**. M.p. 103–104 °C (Found: C, 66.3; H, 7.3; N, 5.9. $C_{13}H_{17}NO_3$ requires C, 66.35; H, 7.3; N, 5.95%); ν_{max}/cm^{-1} 3220 and 1700; δ_H 0.94 (3 H, t), 1.15–1.88 (4 H, m), 1.51 (3 H, s), 3.71 (2 H, t), 6.87 (1 H, br d) and 7.03–7.48 (3 H, m), δ_C 13.8 (q), 20.1 (t), 20.2 (q), 29.3 (t), 39.9 (t), 84.4 (s), 108.8 (d), 123.0 (d), 123.6 (d), 129.0 (s), 129.8 (d), 142.9 (s) and 176.0 (s).

Dye-sensitized Photooxidation of 3-Methyl-1-phenylindolin-2-one **1a**.—An oxygenated solution of **1a** (200 mg) in methanol (100 cm^3) in the presence of Rose Bengal (*ca.* 2 mg) was irradiated under the same conditions as described above for 10 h. Work-up gave no photoproducts and **1a** was recovered quantitatively.

Air Oxidation of 3-Methyl-1-phenylindolin-2-one **1a**.—Into a solution of **1a** (200 mg) in methanol (50 ml) was bubbled oxygen at room temperature for 6 h. Work-up gave no oxidized product and **1a** was recovered quantitatively.

Air Oxidation of **1a** *in the Presence of Base*.—Oxygen was bubbled through a solution of **1a** (200 mg) in methanol (50 cm^3) in the presence of catalytic amount of base (sodium hydroxide or sodium methoxide) under the conditions described above. Work-up gave 3-hydroxy-3-methyl-1-phenylindolin-2-one **3a** in 60–99% yields.

Reduction of 3-Hydroperoxy-3-methyl-1-phenylindolin-2-one **2a** *with Sodium Borohydride*.—To a solution of **2a** (128 mg) in methanol was added $NaBH_4$ (38 mg) and a mixture was stirred under argon at room temperature for 5 h. Work-up gave 1-phenyl-3-hydroxy-3-methylindolin-2-one **3a** (38%) and unchanged **2a** (47%).

Thermal Reaction of 3-Hydroperoxy-3-methyl-1-phenylindolin-2-one **2a**.—A solution of **2a** (100 mg) in dichloromethane or methanol (50 cm^3) was heated to reflux under argon for 12 h. After work-up, unchanged **2a** was recovered quantitatively.

Thermal Reaction of **2a** *in the Presence of Sulphides* **4**.—A solution of **2a** (1 mmol) and sulphide **4** (1.2 mmol) in dichloromethane (30 cm^3) was refluxed for 2–12 h under argon. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (4:1–1:1) to yield 3-hydroxyindolin-2-one **3a** and the corresponding sulphoxides **5**.

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