Reaction of Monothio-derivatives of 2-Heteroarylideneindene-1,3(2*H*)-diones with Quinones

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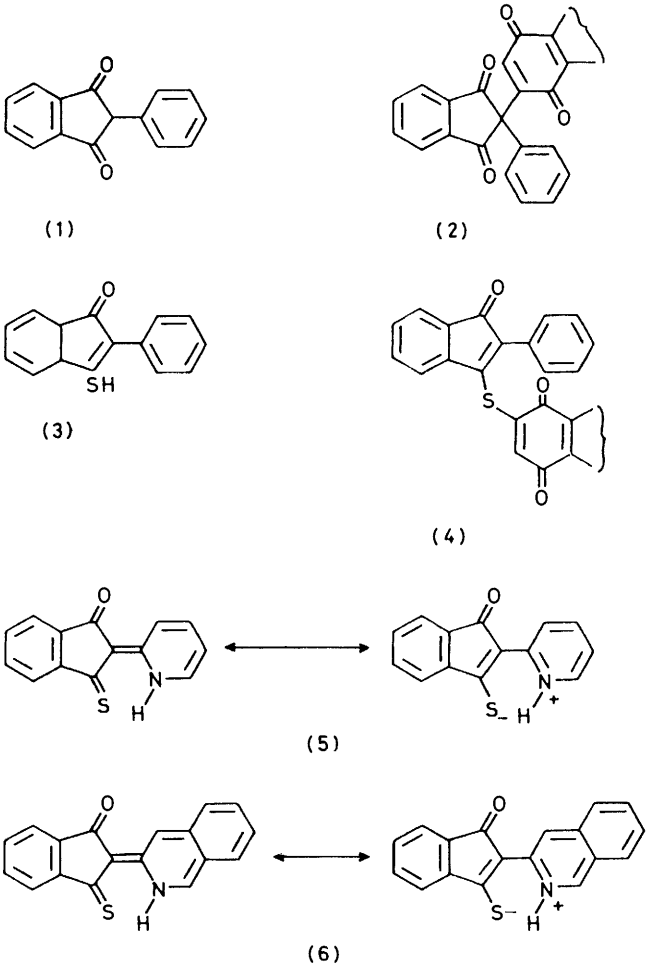
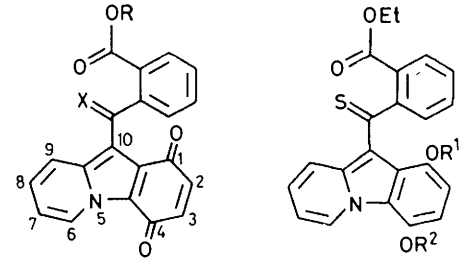
The reaction of 2,3-dihydro-2-[2(1*H*)-pyridylidene]-3-thioxoinden-1-one (5) with 1,4-benzoquinone and with 1,4-naphthoquinone in alcohols afforded thiobenzoylindolizinoquinones (7) and (12) which were characterised by spectroscopy and by oxidation and reduction reactions. In a similar reaction with 1,4-naphthoquinone the 2-isoquinolin-3-ylidene-derivative (6) afforded the pentacyclic quinone (20); the 2-quinolin-2-ylidene-derivative (18) did not undergo the reaction.

2-PHENYLINDENE-1,3(2*H*)-DIONE (1) reacts readily with 1,4-naphthoquinone and 1,4-benzoquinone forming Michael adducts which are isolated as the quinones (2).[1,2] In contrast, the monothio-derivative, 3-mercapto-2-phenylinden-1-one (3), adds *via* the thiol group forming sulphides of type (4).[3] As part of a study on the chemistry of thio-derivatives of 2-heteroarylideneinden-1,3(2*H*)-diones, we have examined the reaction of 2,3-dihydro-2-[2(1*H*)-pyridylidene]-3-thoxoinden-1-one (5)[4] and the isoquinolin-3-ylidene derivative (6) with 1,4-benzoquinone and 1,4-naphthoquinone.



Reaction of the thione (5) in ethanol with 1,4-benzoquinone yielded a purple adduct which was identified as the indolizinoquinone (7a) on the basis of its analytical, spectroscopic, and chemical properties. The use of propan-2-ol instead of ethanol in the reaction resulted in formation of compound (7b), while with 2-methylpropan-2-ol the compound (7c) was isolated in low yield. N.m.r. spectroscopy was of particular value in establishing the structures since it revealed, in addition to the alkoxy-group protons, signals at δ 6.7 (1 H, d, *J* 10 Hz) and 6.4 (1 H, d, *J* 10 Hz) attributable to the protons in a 2,3-disubstituted quinone and a signal at 9.7 (1 H, sextet) characteristic of a 3-benzoylindolizino-system[5] and assigned to the proton at *C*-6.



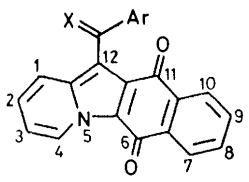
(7) X = S, a; R = Et
b; R = isopropyl
c; R = t-butyl
(8) X = O, R = Et

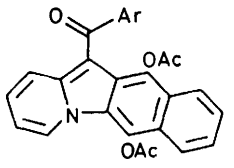
(9) $R^1 = R^2 = H$
(10) $R^1 = R^2 = Ac$
(11) $R^1 = Ac, R^2 = H$

Attempts to prepare the corresponding sulphine from compound (7a) using one equivalent of *m*-chloroperbenzoic acid were unsuccessful while oxidation to the ketone (8) was accompanied by considerable decomposition. Reduction of compound (7a) with sodium dithionite afforded the hydroquinone (9) which was converted into the diacetate (10). A monoacetate, assigned structure (11), was prepared both by treating the hydroquinone (9) with acetic anhydride and by reductive acetylation of the quinone (7a). A model of compound (9) showed that the hydroxy-group at C-4 is more hindered than that at C-1 (*cf.* ref. 6).

A similar reaction of compound (5) with 1,4-napthoquinone in ethanol and in methanol afforded, respectively, the indolizinoquinones (12a and b). In contrast to the benzoquinone (7a), oxidation of the naphthoquinone (12a) with one equivalent of *m*-chloroperbenzoic acid afforded a product which analytical and spectroscopic data showed to be the expected sulphine obtained, how-

ever, as a mixture of geometrical isomers (13a, i + ii) in the ratio 2 : 1. Oxidation of the methyl ester (12b) gave a similar result. The alkoxy-proton signals of the minor isomers were at lower field, $\Delta\delta$ 0.4, than those of the major





(12) X = S, Ar = 2′-$RO_2CC_6H_4$

(13. i + ii) X = SO, Ar = 2′-$RO_2CC_6H_4$

(14) X = O. Ar = 2′-$RO_2CC_6H_4$

a: R = Et

b: R = Me

c: R = H

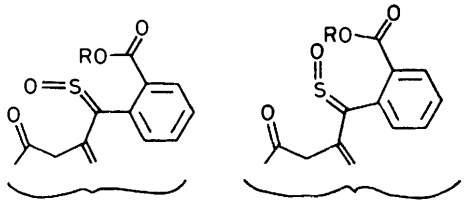
(15) Ar = 2′-$EtO_2CC_6H_4$

(17) Ar = Ph

(16) X = O. Ar = Ph

isomers. This indicates that the minor isomers possess *E*-configuration (see Figure 1) since only in the *E*-configuration can the *o*-alkyloxycarbonyl group rotate through the deshielding cone of the S=O bond of the sulphine (*cf.* ref. 7).

Irradiation of the sulphines (13a and b) in the visible region resulted in sulphur extrusion giving the corresponding ketones (14a and b) as fluorescent orange



(13i) *Z*-isomer

a; δ 0·97 (Me), 3·93 (CH_2)

b; δ 3·38 (Me)

(13ii) *E*-isomer

a; δ 1·33 (Me), 4·35 (CH_2)

b; δ 3·84 (Me)

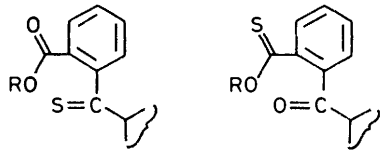
FIGURE 1

compounds. The melting point and i.r. data of the latter and of its hydrolysis product accorded with those reported for the ketones (14b and c) previously prepared [8] from 2,3-dichloro-1,4-naphthoquinone, pyridine, and isochroman-1,4-dione. The n.m.r. data of the methyl ester were also consistent with those reported and showed the lowfield absorptions at δ 9.95 and 8.6 due to H-4 and -1 respectively.

Attempted reduction and acetylation of the thiocarbonyl quinone (12a) resulted in decomposition but the corresponding carbonyl quinone (14a) was converted into the diacetate (15). Further confirmation of the structures of the compounds (14a and b) and (15) was obtained by comparison of their n.m.r., i.r., and electronic spectra with those of the known ketone (16) [9] and its diacetate (17). The spectroscopic data for compounds (16) and (17) are included with the data for new compounds in the Table.

^{13}C Spectroscopic data confirmed that the thiocarbonyl compounds had the ester–thioketone structure (i) assigned rather than the alternative thioxo-ester–ketone structure (ii) (Figure 2). A comparison of the data obtained for compounds (12a), (14a), and the known ketone (16) shows that the spectrum of compound (12a) contains an absorption at 168.2 p.p.m. corresponding to the ester carbonyl of compound (14a) and an absorption at 227.6 p.p.m., typical of a thioketone, which replaces the ketone signals (at 192 p.p.m.) of the other two compounds. Moreover the n.m.r. spectra showed a downfield shift of the ethoxy-group protons (Me, Δ 0.33; CH_2, Δ 0.17 p.p.m.) in compounds (8, 14a and b) relative to the compounds (7a, 12a and b). This shift is opposite in direction to that expected [10] for the thioxo-ester ⟶ ester conversion and thus eliminates structure (ii), in agreement with the ^{13}C result.

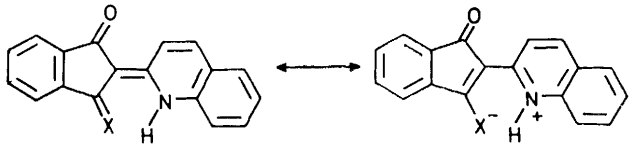
Attempted reaction of the 2-quinolinylidene derivative (18) with 1,4-naphthoquinone led only to recovery of the



(i) (ii)

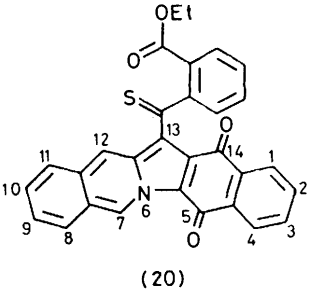
FIGURE 2

oxidised compound (19). However, the less sterically hindered isoquinolinylidene derivative (6) reacted readily with 1,4-naphthoquinone yielding the green thione (20). While the benz[5,6]indolo[1,2-*b*]isoquinoline ring system

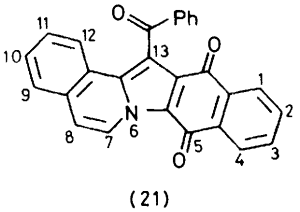


(18) X = S

(19) X = O



(20)



(21)

has not previously been reported, the benz[5,6]indolo-[2,1-*a*]isoquinoline system is well known and for comparison of spectroscopic data the compound (21) was prepared by the method described by Pratt *et al.*[9] In agreement with the structures assigned the n.m.r.

Analytical and spectroscopic data

Compound (formula)	Found (Required) (%) C	H	N	S	ν/cm⁻¹	δ(p.p.m.) (J in Hz)
(7a) ($C_{22}H_{15}NO_4S$)	67.7 (67.85	3.7 3.85	3.6 3.6	8.2 8.2)	1 710, 1 660, 1 630	9.7 (sextet, 6-H, *J* 6.7 and 1), 8.67 (sextet, 9-H, *J* 9 and 1), 7.2—8.0 (6 H, m), 6.7 (1 H, d, *J* 10), 6.45 (1 H, d, *J* 10), 3.75 (2 H, q, *J* 8), and 0.95 (3 H, t, *J* 8)
(7b) ($C_{23}H_{17}NO_4S$)	68.9 (68.5	4.4 4.25	3.8 3.5	8.1 7.95)	1 710, 1 660, 1 630	9.65 (sextet, 6-H, *J* 6.7 and 1), 8.63 (sextet, 9-H, *J* 9 and 1), 7.2—8.0 (6 H m), 6.68 (1 H, d, *J* 10), 6.38 (1 H, d, *J* 10), 4.62 (1 H, septet, *J* 6.7), and 0.95 (6 H, d, *J* 6.7)
(7c) ($C_{24}H_{19}NO_4S$)	68.6 (69.05	4.4 4.6	3.55 3.6	7.85 7.7)	1 710, 1 660, 1 630	9.74 (sextet, 6-H, *J* 6.7 and 1), 8.70 (sextet, 9-H, *J* 9 and 1), 7.2—8.0 (6 H, m), 6.72 (1 H, d, *J* 10), 6.42 (1 H, d, *J* 10), and 1.1 (9 H, s)
(8) ($C_{22}H_{15}NO_5$)	70.75 (70.8	4.3 4.05	3.7 3.75)		1 730, 1 705, 1 665	9.60 (sextet, 6-H, *J* 6.7 and 1), 8.63 (sextet, 9-H, *J* 9 and 1), 7.0—8.1 (6 H, m), 6.67 (1 H, d, *J* 10), 6.40 (1 H, d, *J* 10), 4.07 (2 H, q, *J* 8), and 1.12 (3 H, t, *J* 8)
(9) ($C_{22}H_{17}NO_4S$)	67.2 (67.5	4.5 4.4	3.4 3.6	8.0 8.2)	3 400, 1 680	10.6 (1 H, s), 9.5 (1 H, m), 6.9—8.2 (7 H, m), 6.0—6.5 (2 H, m), 4.42 (2 H, q, *J* 8), and 1.40 (3 H, t, *J* 8)
(10) ($C_{26}H_{21}NO_6S$)	65.7 (65.7	4.6 4.45	3.1 2.95	6.7 6.7)	1 760, 1 720	8.90 (sextet, 6-H), 6.5—7.8 (9 H, m), 4.05 (2 H, q, *J* 8), 2.50 (3 H, s), 2.10 (3 H, s), and 1.05 (3 H, t, *J* 8)
(11) ($C_{24}H_{19}NO_5S$)	66.95 (66.5	4.2 4.4	3.2 3.2	7.3 7.4)	1 770, 1 715	9.02 (sextet, 6-H), 6.9—8.1 (8 H, m), 6.2—6.5 (1 H, m), 4.15 (2 H, q, *J* 8), 2.53 (3 H, s), 1.09 (3 H, t, *J* 8), and 10.8 (1 H, s, OH)
(12a) ($C_{26}H_{17}NO_4S$)	71.4 (71.1	3.9 3.9	3.3 3.2	7.2 7.3)	1 715, 1 670, 1 630	9.98 (sextet, 4-H, *J* 6.7 and 1), 8.62 (sextet, 1-H, *J* 9 and 1), 7.1—8.4 (10 H, m), 3.77 (2 H, q, *J* 8), and 0.93 (3 H, t, *J* 8)
(12b) ($C_{25}H_{15}NO_4S$)	70.4 (70.6	3.7 3.55	3.3 3.3	7.8 7.5)	1 715, 1 670, 1 630	9.95 (sextet, 4-H, *J* 6.7 and 1), 8.64 (sextet, 1-H, *J* 9 and 1), 7.1—8.4 (10 H, m), and 3.28 (3 H, s)
(13a, i + ii) ($C_{26}H_{17}NO_5S$)	68.8 (68.6	3.8 3.8	3.4 3.1	7.4 7.0)	1 715, 1 670, 1 610	9.85 (m, 4-H), 7.1—8.55 (11 H, m) [4.35 (q) and 3.93 (q), 2 H, 1 : 2], [1.33 (t) and 0.97 (t), 1 : 2]
(13b, i + ii) ($C_{25}H_{15}NO_5S$)	67.7 (68.0	3.5 3.4	3.4 3.2	6.8 7.3)	1 710, 1 670, 1 630	9.85 (m, 4-H), 7.1—8.4 (11 H, m), 3.84 (s), and 3.38 (s), 3 H, 1 : 2
(14a) ($C_{26}H_{17}NO_5$)	74.0 (73.75	4.0 4.05	3.4 3.3)		1 715, 1 675, 1 625	9.96 (sextet, 4-H, *J* 6.7 and 1), 8.64 (sextet, 1-H, *J* 9 and 1), 7.1—8.3 (10 H, m), 4.10 (2 H, q, *J* 8), and 1.10 (3 H, t, *J* 8)
(15) ($C_{30}H_{23}NO_7$)	70.7 (70.7	4.5 4.55	2.8 2.75)		1 760, 1 715, 1 620	8.63 (sextet, 4-H, *J* 6.7 and 1), 6.4—8.2 (11 H, m), 4.22 (2 H, q, *J* 8), 2.33 (3 H, s), 2.31 (3 H, s), and 1.10 (3 H, t, *J* 8)
(16) †					1 670, 1 620	9.88 (sextet, 4-H, *J* 6.7 and 1) and 7.1—8.5 (12 H, m)
(17) ($C_{27}H_{19}NO_5$)	74.1 (74.2	4.4 4.3	3.2 3.2)		1 760, 1 620	8.55 (sextet, 4-H, *J* 6.7 and 1), 6.4—8.2 (12 H, m), 2.52 (3 H, s), and 2.28 (3 H, s)
(20) ($C_{30}H_{19}NO_4S$)	73.4 (73.6	3.7 3.9	3.3 2.9	6.4 6.5)	1 710, 1 670 1 620	9.48 (s, 7-H), 7.4—8.5 (13 H, m), 3.63 (2 H, q, *J* 8), and 0.78 (3 H, t, *J* 8)
(21) †					1 670, 1 620	9.58 (d, 7-H), 7.2—8.5 (14 H, m)
(22) ($C_{26}H_{17}NO_5$)	73.6 (73.75	3.8 4.05	3.7 3.3)		1 770, 1 670, 1 630	9.90 (m, 4-H), 8.60 (m, 1-H), 7.0—8.4 (10 H, m), 3.3—3.9 (2 H, m), and 1.35 (3 H, t)

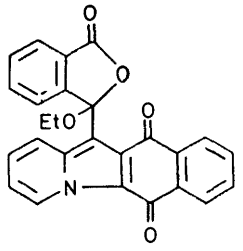
† Ref. 9.

spectrum of compound (20) showed a singlet at δ 9.48 (7-H) while that of compound (21) exhibited a doublet at δ 9.50 (7-H).

The formation of indolizinoquinones by the reaction of active methylene compounds and pyridine (or isoquinoline) with quinones has been known since 1954 [6] and there are many applications and modifications of the reaction in the literature.[9,11] Originally the reaction was carried out on 1,4-naphthoquinone but improved yields were obtained using the 2,3-dichloro-derivative. In all subsequent reports, 2,3-dichloro-1,4-naphthoquinone and *para*-chloranil have been employed in preference to the unsubstituted quinones. It is, therefore, noteworthy that compound (5) failed to react with 2,3-dichloro-naphthoquinone, presumably for steric reasons. However, a novel reaction between indene-1,3(2*H*)-dione, pyridine, ethanol, and 2,3-dichloro-1,4-naphthoquinone afforded compound (14a) in 10% yield. An isomer of compound (14a) was also isolated in low yield from this reaction. On the basis of spectroscopic data which included an i.r. absorption at 1 770 cm⁻¹ typical of a five-membered lactone and a u.v.–visible spectrum similar to that of compound (14a), structure (22) is proposed. In agreement with the structure the compound yielded the acid (14c) on hydrolysis.

In contrast with compound (5) neither the dioxo-analogue (pyrophthalone) (23) nor the dithioxo-analogue (24) reacted with 1,4-napththoquinone, presumably

reflecting the greater resonance stabilisation in their polarised forms. Likewise, attempts to cause compound (23) to react with 2,3-dichloro-1,4-naphtho-



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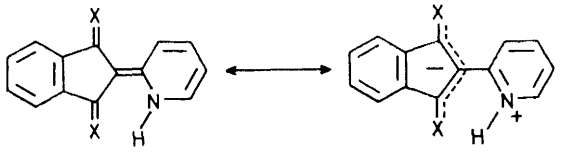
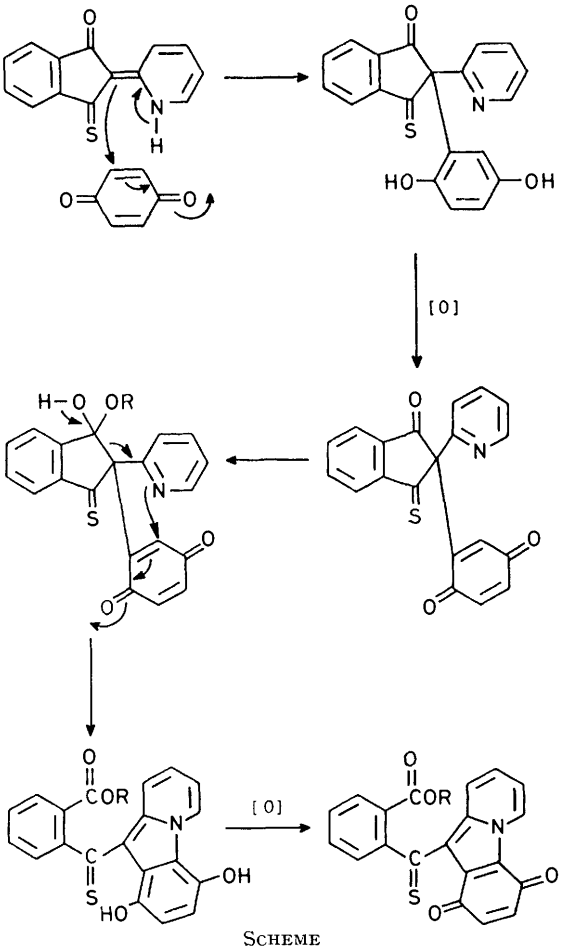


(23) X = O

(24) X = S

quinone, a reaction analogous to the condensation of 2-phenacylpyridine,[9] failed both in the presence and absence of base.



SCHEME

The reaction of 3-mercapto-2-phenylinden-1-one (3) with 1,4-naphthoquinone and 1,4-benzoquinone was re-examined. The i.r. and n.m.r. spectra of compound (3), prepared as previously described,[3] showed the presence of the thioenol group (SH, ν 2 535 cm^{-1} and δ 4.1) but no evidence of the enol tautomer (*cf.* ref. 12). The addition reactions with the quinones were carried out as before. ^{13}C N.m.r. spectra of the products showed no thiocarbonyl absorptions in agreement with the sulphide structures (4).

The formation of compounds (7a—c), (12a and b), and (20) in optimal yields requires the presence of a several molar excess of quinone. A plausible reaction mechanism is shown in the Scheme and has analogies with pathways previously described [6,11] for the preparation of indolizinoquinones. Ring-opening of 2,2-disubstituted indene-1,3-diones occurs readily, *e.g.* the 2-nitro-2-(2-pyridyl)-derivative opens on heating in alcohols.[13] An interesting feature of the present reaction is the formation of the ester rather than the thioxo-ester. In general, nucleophilic addition occurs more readily at a thiocarbonyl than at a carbonyl group.[14] An exception, however, is the reaction of tetramethyl-3-thioxocyclobutan-1-one with phenylhydrazine which proceeded at the 1-position to yield the thiocarbonylphenylhydrazone.[15] It may be that the preferential ring-opening at the keto- rather than the thioketo-position of the 3-thioxoinden-1-one is due to a steric effect.

EXPERIMENTAL

^1H n.m.r. spectra were recorded for solutions in deuteriochloroform on a Perkin-Elmer R12 60 MHz spectrometer and ^{13}C n.m.r. spectra on a JEOL PFT 100 spectrometer; chemical shifts are in p.p.m. downfield from internal Me_4Si. I.r. spectra were obtained for potassium bromide discs with a Perkin-Elmer 700 spectrometer. Preparative t.l.c. was carried out on Merck Kieselgel 60 $PF_{242+366}$ with benzene–ethyl acetate (9 : 1) as eluant. Analytical and spectroscopic data are given in the Table.

Alkyl 2-{(1,4-*Dihydro*-1,4-*dioxopyrido*[1,2-a]*indol*-10-*yl*)-*thiocarbonyl*}*benzoates* (7a—c).—A solution of the indenone (5) (500 mg) and 1,4-benzoquinone (2.0 g) in a mixture of ethanol (160 ml) and chloroform (40 ml) was heated under reflux for 4 h. The deep blue-violet solution was concentrated and the residual solid was chromatographed on a silica column and crystallised from chloroform–methanol yielding *compound* (7a) as purple crystals (273 mg; 38%), m.p. 174—176 °C; $\lambda_{max.}$ ($CHCl_3$) (log ε) 535 (3.83), 403 (3.83), 338 (3.80), 312 (3.87), 262 (4.13), and 240 (4.35); *m/e* 389.

Prepared similarly on the same scale were the *isopropyl ester* (7b), m.p. 186—188 °C (35%) and the *t-butyl ester* (7c), m.p. 143—144 °C (5%).

Ethyl 2-{(1,4-*Dihydro*-1,4-*dioxopyrido*[1,2-a]*indol*-10-*yl*)-*carbonyl*}*benzoate* (8).—A solution of compound (7a) (50 mg) in chloroform (15 ml) was stirred with a tenfold excess of *m*-chloroperbenzoic acid (222 mg) for 6 h. The solution was washed with aqueous sodium sulphite (1%; 15 ml) and aqueous sodium hydrogencarbonate (5%; 15 ml), dried, and concentrated. The residue was purified by chromatography yielding *compound* (8) as pink crystals m.p. 126—128 °C (from MeOH) (32 mg, 68%).

Ethyl 2-{(1,4-*Dihydroxypyrido*[1,2-a]*indol*-10-*yl*)*thiocarbonyl*}*benzoate* (9).—A solution of compound (7a) (300 mg) in chloroform (100 ml) was shaken with an aqueous solution of sodium dithionite (1%; 100 ml) for 10 min. The resulting red solution was washed with water, dried, and evaporated affording the *hydroquinone* (9), m.p. 210—212 °C (chloroform–hexane) (210 mg, 67%). Acetylation of compound (9) (100 mg) with sodium acetate and acetic anhydride gave the *diacetate* (10) (84 mg, 69%), m.p. 172—174 °C (from chloroform–ethanol).

Ethyl 2-{(1-*Acetoxy*-4-*hydroxypyrido*[1,2-a]*indol*-10-*yl*)-*thiocarbonyl*}*benzoate* (11).—(i) A solution of the hydroquinone (9) (120 mg) in acetic anhydride (30 ml) was heated on a steam-bath for 10 min, cooled, and added to ice–water (100 ml). The mixture was extracted with chloroform, the extracts were dried ($MgSO_4$), and the solvent evaporated yielding the *monoacetate* (11) (95 mg, 72%) as red crystals, m.p. 218—220 °C (from chloroform–methanol); $\lambda_{max.}$ (log ε) 522 (4.33), 475 (4.15), 368 (3.86), 325 (3.88), 302 (3.88), 285 (3.97), and 253 (4.53).

(ii) A solution of the quinone (7a) (50 mg) in a mixture of chloroform (10 ml), acetic anhydride (1 ml), and acetic acid (1 ml) containing iron filings (50 mg) was heated under reflux for 30 min and then added to water (100 ml). The mixture was warmed on a steam-bath for 30 min and then worked up as before yielding the monoacetate (11) (33 mg, 54%).

Ethyl 2-{(6,11-*Dihydro*-6,11-*dioxonaphth*[2,3-b]*indolizin*-12-*yl*)*thiocarbonyl*}*benzoate* (12a).—A solution of the thioxoindenone (5) (2 g) and 1,4-naphthoquinone (5 g) in a mixture of ethanol (400 ml) and chloroform (100 ml) was heated under reflux for 6 h. The solution was concentrated to 300 ml and kept overnight. The black-brown crystals which were deposited were collected and recrystallised from ethanol–chloroform affording *compound* (12a) (1.8 g, 48%), m.p. 235—237 °C; $\lambda_{max.}$ ($CHCl_3$) (log ε) 505 (4.08), 400 (3.84), 330 (4.12), 285 (s) (4.30), and 245 (4.50); δ_C 227.6 (C=S), 180.5 and 175.4 (quinone C=O), and 168.2 p.p.m. (ester C=O). A similar procedure using methanol instead of ethanol gave the *methyl ester* (12b), m.p. 253—255 °C.

Ethyl 2-{(6,11-*Dihydro*-6,11-*dioxonaphth*[2,3-b]*indolizin*-12-*yl*)*thiocarbonyl*}*benzoate* S-*Oxide* (13a; i + ii).—A solution of *m*-chloroperbenzoic acid (52 mg) in chloroform (5 ml) was added dropwise with stirring to a solution of the thione (12a) (110 mg) in chloroform (20 ml); the brown solution rapidly turned red. After 5 min the reaction mixture was washed with aqueous sodium sulphite and aqueous sodium hydrogencarbonate, dried, and evaporated to dryness. The residue was crystallised from chloroform–ethanol yielding a mixture (n.m.r.) of isomeric sulphines (13a, i + ii) as red needles (105 mg, 92%), m.p. 246—248 °C. In a similar experiment the methyl ester (12b) was converted into the mixture of sulphines (13b, i + ii), m.p. 238—240 °C.

Ethyl 2-{(6,11-*dihydro*-6,11-*dioxonaphth*[2,3-b]*indolizin*-12-*yl*)*carbonyl*}*benzoate* (14a).—A solution of the sulphines (13a, i + ii) (1.1 g) in chloroform (500 ml) was irradiated by 4 × 40-W (Philips Daylight) circular fluorescent tubes at 25 °C for 15 h. The fluorescent orange solution afforded the *ketone* (14a) (0.984 g, 96%), m.p. 194—195 °C (from ethanol–chloroform); $\lambda_{max.}$ ($CHCl_3$) (log ε) 470 (3.89), 358 (4.10), 333 (4.17), 325 (4.18), 280 (4.43), and 262 (4.59); δ_C 192.0 (aromatic ketone C=O), 180.4 and 175.2 (quinone C=O), and 167.3 (ester C=O).

Reductive acetylation of the quinone (zinc and pyridine–acetic anhydride) gave the diacetate (15) (95 mg, 39%), m.p. 233—234 °C (from chloroform–ethanol). The mixture of the sulphines (13b) was similarly oxidised to the ketone (14b), m.p. 194—195 °C (from ethanol–chloroform) (lit.,[8] 194—195 °C).

(6,11-*Dihydro*-6,11-*dioxonaphth*[2,3-b]*indolizin*-12-*yl*)-*carbonylbenzoic Acid* (14c).—A solution of the ester (14b) (138 mg) in ethanol (150 ml) was treated with aqueous sodium hydroxide (10%; 10 ml) and the mixture heated under reflux for 30 min. Acidification and work-up afforded the acid (14c) (120 mg, 93%), m.p. 267—268 °C (from chloroform–hexane) (lit.,[8] 268 °C).

6,11-*Diacetoxynaphth*[2,3-b]*indolizin*-12-*yl Phenyl Ketone* (17).—The ketone (16) prepared by the method of Pratt *et al.* had m.p. 256—259 °C (lit.,[8] 257.5 °C); $\lambda_{max.}$ $CHCl_3$ (log ε) 470 (3.91), 358 (4.01), 333 (4.16), 325 (4.20), 280 (s) (4.42), and 258 (4.64); δ_C 191.7 (aromatic ketone C=O) and 180.8 and 174.9 (quinone C=O). Reductive acetylation (zinc, pyridine–acetic anhydride) of the quinone gave the *diacetate* (17) (39%), m.p. 219—220 °C (from chloroform–ethanol).

Ethyl 2-{(5,14-*Dihydro*-5,14-*dioxobenz*[5,6]*indolo*[1,2-b]-*isoquinolin*-13-*yl*)*thiocarbonyl*}*benzoate* (20).—A solution of the isoquinolinylidene compound (6) (80 mg) and 1,4-naphthoquinone (175 mg) in a mixture of chloroform (64 ml) and ethanol (16 ml) was heated under reflux for 2 h. The solution was concentrated to half volume and kept overnight. The green crystals were collected and on recrystallisation from chloroform–ethanol gave compound (20) (80 mg, 59%), m.p. 249—250 °C; $\lambda_{max.}$ $CHCl_3$ (log ε) 595 (4.25), 475 (4.25), 450 (4.15), 435 (s) (3.92), 360 (3.99), 295 (4.69), and 260 (4.67).

Reaction of Indene-1,3(2H)-*dione*, 2,3-*Dichloro*-1,4-*naphthoquinone, and Pyridine in Ethanol.*—A solution of indene-1,3(2*H*)-dione (2.5 g), 2,3-dichloro-1,4-naphthoquinone (2.0 g), and pyridine (28 ml) in ethanol (100 ml) was refluxed for 4 h. The mixture was cooled, filtered, and evaporated to dryness. The residual solid was purified on a silica column affording a mixture of two fluorescent orange compounds (700 mg), which on separation by preparative t.l.c. gave the ketone (14a) (373 mg, 10%) and, at higher R_F value, *compound* (22) (200 mg, 6%), m.p. 257—258 °C (from chloroform–ethanol); $\lambda_{max.}$ $CHCl_3$ (log ε) 475 (3.92), 355 (3.75), 332 (s) (3.98), 323 (4.08), 288 (4.14), and 258 (4.59); δ_C 180.7 and 174.6 (quinone C=O) and 169.4 (lactone C=O).

A solution of the lactone (22) (20 mg) in aqueous ethanol (80%; 50 ml) containing potassium hydroxide (500 mg) was stirred for 2 h. Acidification and work-up afforded the acid (14c), m.p. and mixed m.p. 267—268 °C (lit.,[8] 268 °C).

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