Indole β-Nucleophilic Substitution. Part 6.[1] Photochemical Transformations of Oxepino[3,2-*b*]indolones

Godfred L. Humphrey, Lesley Dalton, and John A. Joule *
Chemistry Department, Manchester University, Manchester M13 9PL
David I. C. Scopes
Glaxo Group Research Ltd., Ware, Hertfordshire SG12 0DJ

[2]Benzoxepino[4,3-*b*]indol-11-ones and pyrido[*x'*,*y'*:5,6]oxepino[3,2-*b*]indol-5-ones are transformed in the presence of light into indole-spiro(2-alkyl-2-aroyl)-3-ones. These, in the presence of air, in alcohol as solvent (or in some cases with alcoholic sodium alkoxide) are further converted into indolo[1,2-*b*]isoquinoline-6,12-diones and aza-analogues respectively.

We have described [2] the use of intramolecular indole β-nucleophilic substitution for the synthesis of pyrido- and benzo-oxepino[3,2-*b*]indoles. We report here that these high melting, highly crystalline substances are labile to daylight, an observation first made in the case of (1a) which on storage as the solid in a colourless glass bottle became a darker yellow.

When the pyrido-oxepinoindoles (1a) and (1b) in ethanol solution were exposed to daylight, in air for *ca.* 48 h, they were transformed into new yellow products showing exactly mutually comparable u.v./visible absorption spectra different from those of the starting materials. Each product had a molecular formula corresponding to two hydrogen atoms less than its starting material and although their n.m.r. spectra witnessed the continued presence of the original aromatic and heteroaromatic C-protons as well as those corresponding to R in (1), both the signals for the proton originally at C-12 and the N-hydrogen were absent. Further, it was clear from the chemical shifts of the protons of R in the product from (1a) that the R group was now attached to a trigonal carbon.

Reduction of the dehydro-product from (1b) with sodium borohydride provided helpful structural information, since the tetrahydro-derivative produced could be shown by n.m.r. decoupling experiments to contain the unit CH(OH)CH·CH, the relevant C-hydrogen signals being at τ 4.66, 5.51, and 5.66 respectively.

The situation was initially made more complex when it was found that the de-aza-analogue (2a), under comparable conditions, was transformed not into a dehydro-derivative, but into a yellow material isomeric with starting material but showing completely different u.v./visible absorption from either starting material or the dehydro-photo-products from (1a) and (1b). However, treatment of this isomeric substance with sodium methoxide in hot methanol in the presence of air, in a process which was shown *not* to require light, transformed it rapidly into a dehydro-compound which now showed u.v./visible absorption exactly comparable with that of the dehydro-photo-products derived from (1a) and (1b).

As with the dehydro-compound from (1b), the de-aza-analogue was reduced by sodium borohydride to a tetrahydro-derivative, n.m.r. spectroscopic investigation of which revealed the presence of the sequence CH(OH)·CH·CH_2, τ 4.82, 5.86, and 6.76 respectively for the C-hydrogens atoms.

It was at this point that our attention came to work by Hooper [3] in which condensation of 2-formylbenzoic acid with 3-acetoxy-1-acetylindole produced, unambiguously, the indolo-isoquinolinedione (3a). Hooper showed that this was reduced by sodium borohydride to a tetrahydro-derivative (4). A comparison of data published [3] for (3a) and (4) and the information obtained for the product derived from (2a) by light and then methoxide treatments and its borohydride reduction product, strongly suggested their identity with (3a) and (4) and this was confirmed by a direct comparison with samples kindly provided by Dr. Hooper.

It follows that the photo-dehydro-products in the pyrido-series have structures (5a) and (5b) respectively and that the reduction product of (5b) has structure (6).

Turning to the question of the structure of the initial isomeric photo-product from (2a) one must explain the two i.r. carbonyl stretching bands at 1 680 and 1 615 cm^{-1}, the n.m.r. non-equivalence of the methylene protons, represented by an AB system at τ 6.45 and 6.67, at considerably higher field than the methylene singlet (τ 4.66) in (2a), and finally the easy transformation into (3a) with methoxide in the presence of air. These data lead to the spirocyclic dione structure (7a). The transformation into (3a) can be seen to involve methoxide cleavage of the non-enolisable 1,3-diketone system generating (8), lactamisation involving the indolic nitrogen and aerial oxidation of the indoxyl to complete the sequence, though it is possible that the last two steps may take place in reverse order.

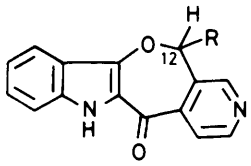
It seemed reasonable to suppose that (5a) and (5b) were being formed *via* comparable spiro-diketones, alcoholysis of which is sufficiently rapid in neutral ethanol to allow progress through to (5a) and (5b). The extra electron-withdrawing effect of the pyridine ring can account for the difference and consistent with this was the observation that nitro-benzoxepino-indole (2b) was converted directly into (3b) in ethanol in the presence of air and light.

There was an obvious way in which to test these ideas, namely to expose pyrido-oxepino-indoles to light but in the absence of nucleophilic solvent. In the cases of (1a) and (1b) although light brought a rapid change to these substrates dissolved in dry THF, the spiro-products proved too unstable to isolate or characterise. However from (1c) and from the isomeric pyrido-oxepino-indole (9) in dry THF the spiro-diones (10) and (11) could indeed be isolated, though they too were very sensitive; they could be characterised by rapidly measuring their n.m.r. spectra. Further, (10) and (11) were transformed very easily, by briefly refluxing in ethanol, into the diones (5c) and (12) respectively.

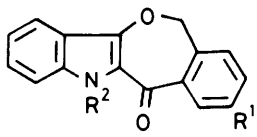
The photocatalysed isomerisation to a spiro-dione was shown not to involve radical abstraction of N-hydrogen by the ready formation of (7b) and (7c) from the *N*-methyl-oxepino-indoles (2c) and (2d). Refluxing methanol converted (7c) rapidly into the ester (13). The photo-isomerisation seems to be best viewed as a 1,3-sigmatropic rearrangement of carbon [C-12 in (1)] from oxygen to the indole-α-carbon.

Experimental

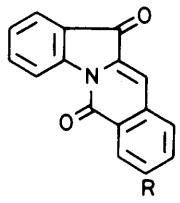
3-(α-Hydroxybenzyl)-4-pyridyl 1-Phenylsulphonylindol-2-yl Ketone.—2-Lithio-1-phenylsulphonylindole [from 1-phenylsulphonylindole (9.84 g) and n-butyl-lithium (26 ml; 1.5M in



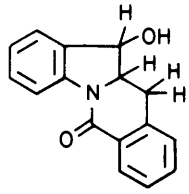
(1) R
a; Me
b; Ph
c; H



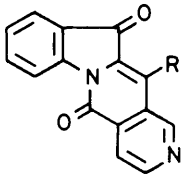
(2) R^1 R^2
a; H H
b; NO_2 H
c; H Me
d; NO_2 Me



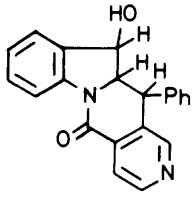
(3) R
a; H
b; NO_2



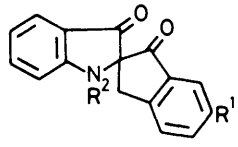
(4)



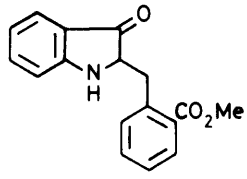
(5) R
a; Me
b; Ph
c; H



(6)



(7) R^1 R^2
a; H H
b; H Me
c; NO_2 Me



(8)

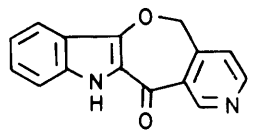
hexane)] in THF (300 ml) was treated with 3-(α-hydroxybenzyl)pyridine-4-carboxylic acid lactone [4] (8.07 g) in THF (100 ml) at −78 °C. The red solution was allowed to come to room temperature during 1 h. Evaporation of solvent was followed by partitioning between water and ether; the organic layer gave a crude product containing some 1-phenylsulphonylindole. It was dissolved in chloroform and extracted into 2M-hydrochloric acid (some of the hydrochloride precipitated as a red tar). The aqueous layer and tar were basified with potassium carbonate and extracted with ether to give the *hydroxy-ketone* as a pale yellow foam (16.26 g), pure by t.l.c. analysis, $\nu_{max.}$ (EtOH) 221, 260, and 308 nm; $\nu_{max.}$ ($CHCl_3$) 3 450m, 3 040w, and 1 660s cm^{-1}; *m/z* 468 (M^+, 0.9%), 327(8), 310(24), 309(37), 287(6), 233(9), 210(100), 105(17), and 77(29) [Found (by mass spectrometry): *M*, 468.113. $C_{27}H_{20}N_2O_4S$ requires *M*, 468.114].

12-*Phenylpyrido*[4′,3′:5,6]*oxepino*[3,2-b]*indol*-5(6H,12H)-*one* (1b).–3-(α-Hydroxybenzyl)-4-pyridyl 1-phenylsulphonylindol-2-yl ketone (15.33 g) in methanol (150 ml) was heated under reflux with aqueous sodium hydroxide (4M: 75 ml) for 10 min. Cooling produced a mustard coloured precipitate (7.49 g) of the *oxepinoindole* (1b), purified by crystallisation from acetone, m.p. 214—219 °C, $\lambda_{max.}$ (EtOH) 241, 260sh, 345sh, and 414 nm (log ε 4.32, 4.10, 3.60, and 3.48); $\nu_{max.}$ ($CHCl_3$) 3 450m and 1 620s cm^{-1}; τ($CDCl_3$) 1.14 (1 H, d, *J* 8 Hz, 9-H), 1.48 (1 H, s, 11-H), 2.06 (1 H, d, *J* 8 Hz, 1-H), 2.2—3.3 (12 H, m, ArH), and 3.09 (1 H, s, 12-H); *m/z* 326 (M^+, 100%), 325(18), 324(15), 323(19), 310(13), 309(20), 297(31), 269(12), 249(49), and 221(19) (Found: C, 76.8; H, 4.4; N, 8.3. $C_{21}H_{14}N_2O_2$ requires C, 77.3; H, 4.3; N, 8.6%).

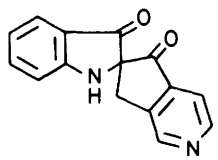
12-*Methylindolo*[1,2-b][2,6]*naphthyridine*-5,11-*dione* (5a).—The oxepinoindole [5] (1a) (300 mg) was stirred in solution in ethanol (450 ml) in daylight for 48 h. The ethanol was evaporated and the residual orange-brown foam crystallised from methanol to afford the *lactam* (5a) (150 mg), m.p. 285—287 °C, $\lambda_{max.}$ (EtOH) 230, 250sh, 256, 274sh, 281, 314sh, 326, 343sh, and 403 nm (log ε 4.33, 4.38, 4.42, 4.12, 4.04, 4.04, 4.02, and 4.14); $\nu_{max.}$ (Nujol) 1 705s and 1 620s cm^{-1}; τ ($CDCl_3$) 0.63 (1 H, s, 1-H), 1.06 (1 H, d, *J* 6 Hz, 3-H), 1.68 (1 H, d, *J* 6 Hz, 4-H), 2.25 (1 H, d, *J* 7 Hz, 10-H), 2.12 (1 H, d, *J* 7 Hz, 7-H), 2.17 (1 H, t, *J* 7 Hz, ArH), 2.25 (1 H, t, *J* 7 Hz, ArH), and 7.05 (3 H, s, CH_3); *m/z* 262 (M^+, 100%), 233(10), and 205(20) (Found: C, 72.8; H, 4.1; N, 10.0. $C_{16}H_{10}N_2O_2$ requires C, 73.3; H, 3.8; N, 10.7%).

12-*Phenylindolo*[1,2-b][2,6]*naphthyridine*-5,11-*dione* (5b).—The oxepinoindole (1b) (2.3 g) was stirred in solution in ethanol (500 ml) in daylight for 48 h. The ethanol was evaporated and the residual brown foam crystallised from methanol to give the *lactam* (5b) (0.87 g), m.p. 222—224 °C, $\lambda_{max.}$ (EtOH) 230, 250sh, 255, 268sh, 277sh, 322sh, 328, 337sh, and 403 nm (log ε 4.47, 4.44, 4.47, 4.43, 4.13, 4.09, 4.13, 4.09, 4.07, and 4.15), $\nu_{max.}$ (Nujol) 1 720s and 1 690s cm^{-1}; τ ($CDCl_3$) 1.19 (1 H, d, *J* 6 Hz, 3-H), 1.28 (2 H, m, ArH), 1.32 (1 H, d, *J* 6 Hz, 4-H), 2.32 (2 H, m, ArH), and 2.50—2.72 (6 H, m, ArH); *m/z* 324 (M^+, 70%), 323(100), 307(5), 297(8), and 295(6) (Found: C, 77.8; H, 3.7; N, 8.4%. $C_{20}H_{11}N_2O_2$ requires C, 77.8; H, 3.8; N, 8.6%).

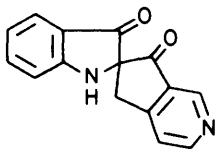
Spiro[*indene*-2,2′-*indole*]-1,3′-*dione* (7a).—The oxepinoindole [5] (2a) (280 mg) was stirred in ethanol (350 ml) in daylight for 48 h. The ethanol was evaporated and the residual orange foam purified by chromatography over silica when toluene–ether (20 : 1) eluted material which crystallised from methanol to give the *spiro-dione* (7a) (140 mg), m.p. 189—193 °C, $\lambda_{max.}$ (EtOH) 237, 250sh, 330, and 390 nm (log ε 4.38, 4.34, 3.65, and 3.54); $\nu_{max.}$ (Nujol) 3 350m and 1 680s cm^{-1}; τ [$CDCl_3$–$(CD_3)_2SO$] 2.27 (2 H, m, ArH), 2.38 (1 H, d, *J* 7 Hz, ArH), 2.48—2.57 (3 H, m, ArH), 2.73 (1 H, s, NH), 2.95 (1 H, d, *J* 7 Hz, ArH), 3.18 (1 H, t, *J* 7 Hz, ArH), 6.45 (1 H, d,



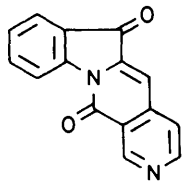
(9)



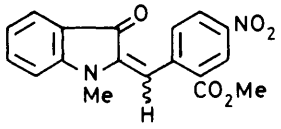
(10)



(11)



(12)



(13)

J 15 Hz, C*H*$_A$H$_B$), and 6.67 (1 H, d, *J* 15 Hz, CH$_A$*H*$_B$); *m/z* 249 (*M*$^+$, 100%), 232(26), 220(53), 193(27), and 165(19) (Found: C, 76.8; H, 4.4; N, 5.6. $C_{16}H_{11}NO_2$ requires C, 77.0; H, 4.5; N, 5.6%).

Indolo[1,2-b]*isoquinoline*-6,12-*dione* (3a).—The spiro-dione (7a) (70 mg) was heated with sodium methoxide in methanol (0.3M; 20 ml) in air for 2 min. The methanol was evaporated, water (50 ml) added, and the yellow solid filtered off, dried, and crystallised from methanol, to give the lactam (3a), m.p. 241—243 °C (lit.,[3] 241—242 °C) identical in all aspects with an authentic sample.

11,11a-*Dihydro*-11-*hydroxy*-12-*phenylindolo*[1,2-b][2,6]-*naphthyridine*-5(12H)-*one* (6).—The dione (5b) (150 mg) was reduced with sodium borohydride (1.5 g), added in portions at 0 °C to a deoxygenated solution in ethanol (400 ml). After 18 h at room temperature the solvent was evaporated and the residue partitioned between chloroform and dilute hydrochloric acid. The aqueous acidic layer was basified and extracted with chloroform to give a green foam purified by crystallisation from methanol, to give the *alcohol* (6), m.p. 249—253 °C, $\lambda_{max.}$ 230sh, 285, and 322 nm (log ε 3.70, 3.65, and 3.65); $\nu_{max.}$ (Nujol) 3 160m and 1 650s cm^{-1}; τ ($CDCl_3$) 1.24 (1 H, d, *J* 6 Hz, 3-H), 1.57 (1 H, d, *J* 9 Hz, 7-H), 1.82 (1 H, s, 1-H), 1.94 (1 H, d, *J* 6 Hz, 4-H), 2.46—2.62 (5 H, m, ArH), 2.74—2.81 (3 H, m, ArH), 4.66 (1 H, d, *J* 6 Hz, 11-H), 5.51 (1 H, dd, *J* 12, 6 Hz, 11a-H), and 5.66 (1 H, d, *J* 12 Hz, 12-H); *m/z* 328 (*M*$^+$, 85%), 310(25), 195(100), 167(50), 166(40), and 139(45) [Found (by mass spectrometry), *M*, 328.121; 195.067. $C_{21}H_{15}N_2O_2$ requires *M*, 328.121; $C_{13}H_9NO$ requires 195.068].

8-*Nitroindolo*[1,2-b]*isoquinoline*-6,12-*dione* (3b).—The nitro-oxepinoindole [1] (2b) (20 mg) was dissolved in methanol (30 ml) and left in daylight for 6 h. The methanol was evaporated to give, quantitatively, the *nitro-dione* (3b) as yellow crystals, m.p. 265—270 °C (from methanol), $\lambda_{max.}$ (EtOH) 228, 248, 283, 324sh, 330, 346, and 415 nm (log ε 4.20, 4.23, 3.73, 4.18, 3.76, 3.66, and 3.80); ν (Nujol) 1 700s and 1 660s cm^{-1}; τ [$(CD_3)_2SO$] 1.03 (1 H, s, 7-H), 1.41 (2 H, d, *J* 9 Hz, ArH), 1.74 (1 H, d, *J* 9 Hz, 1-H), 2.13 (1 H, d, *J* 9 Hz, 4-H), 2.14 (1 H, t, *J* 9 Hz, ArH), 2.20 (1 H, s, 11-H), and 2.54 (1 H, t, *J* 9 Hz, ArH); *m/z* 292 (*M*$^+$, 100%), 262(11), 246(38), 234(2), 218(5), 206(6), and 190(33) (Found: C, 65.4; H, 2.8; N, 9.4%. $C_{16}H_8N_2O_4$ requires C, 65.7; H, 2.7; N, 9.6%).

Indolo[1,2-b][2,6]*naphthyridine*-5,11-*dione* (5c).—The pyrido-oxepinoindole [2] (1c) (50 mg) was dissolved in tetrahydrofuran (20 ml) and left in the daylight for 1 h. The solvent was evaporated under reduced pressure and the residue [an orange oil, $\lambda_{max.}$ (THF) 252sh, 301, and 375 nm (log ε 4.02, 3.63, and 3.54); τ ($CDCl_3$) 1.00 (1 H, s, py-α-H), 1.28 (1 H, d, *J* 6 Hz, py-α-H), 2.30—2.50 (3 H, m, ArH), 2.98 (1 H, d, *J* 8 Hz, ArH), 3.10 (1 H, t, *J* 8 Hz, ArH), 4.76 (1 H, bs, NH), 6.36 (1 H, d, *J* 17 Hz, C*H*$_A$H$_B$), and 6.72 (1 H, d, *J* 17 Hz, CH$_A$*H*$_B$)] immediately dissolved in ethanol (20 ml) and heated on a steam-bath for 15 min. The solvent was evaporated under reduced pressure to leave an orange oil, which was purified by chromatography over silica, when ethyl acetate eluted the pure *lactam* (5c) (20 mg), m.p. 249—252 °C (from ethanol); $\lambda_{max.}$ (EtOH) 229, 244sh, 252, 266sh, 276sh, 316sh, 324, 332sh, and 404 nm (log ε 4.58, 4.57, 4.59, 4.29, 4.18, 4.16, 4.17, 4.16, and 4.45); $\nu_{max.}$ (Nujol) 1 725 and 1 675 cm^{-1}; τ ($CDCl_3$) 0.78 (1 H, s, 9-H), 1.03 (1 H, d, *J* 5 Hz, 7-H), 1.20 (1 H, d, *J* 8 Hz, 1-H), 1.63 (1 H, d, *J* 5 Hz, 6-H), 2.02 (1 H, d, *J* 8 Hz, 4-H), 2.16 (1 H, t, *J* 8 Hz, ArH), 2.42 (1 H, s, 10-H), and 2.52 (1 H,t, *J* 8 Hz, ArH); *m/z* 248 (*M*$^+$, 100%), 220(22), 192(7), and 164(10) (Found: C, 72.7; H, 3.2; N, 10.55. $C_{15}H_8N_2O_3$ requires C, 72.6; H, 3.2; N, 11.3%).

Indolo[1,2-b][2,7]*naphthyridine*-5,11-*dione* (12).—The pyrido-oxepinoindole [2] (9) (40 mg) was dissolved in tetrahydrofuran (20 ml) and left in daylight for 1 h. The solvent was evaporated under reduced pressure and the residue [an orange oil, $\lambda_{max.}$ (THF), 252sh, 303, and 375 nm (log ε 3.96, 3.58, and 3.52); τ ($CDCl_3$), 1.12 (1 H, s), 1.30 (1 H, d, *J* 6 Hz), 2.40—2.65 (3 H, m), 2.95—3.30 (2 H, m), 4.40 (1 H, bs), 6.39 (1 H, d, *J* 17 Hz), and 6.76 (1 H, d, *J* 17 Hz)] immediately dissolved in ethanol (20 ml) and heated on a steam-bath for 15 min. The solvent was evaporated under reduced pressure to leave an orange oil, which was purified by chromatography over silica when ethyl acetate eluted the pure *lactam* (12) (15 mg), m.p. 245—248 °C (from methanol), $\lambda_{max.}$ (EtOH) 233, 244, 269, 290sh, 300sh, 309, 316sh, 332sh, and 405 nm (log ε 4.52, 4.57, 4.12, 4.05, 4.12, 4.17, 4.13, 3.90, and 4.03); $\nu_{max.}$ (Nujol) 1 705s and 1 660s cm^{-1}; τ ($CDCl_3$) 0.2 (1 H, s, 6-H), 1.03 (1 H, d, *J* 4 Hz, 8-H), 1.21 (1 H, d, *J* 7 Hz, 1-H), 2.03 (1 H, d, *J* 7 Hz, 4-H), 2.16 (1 H, t, *J* 7 Hz, ArH), 2.34 (1 H, d, *J* 4 Hz, 9-H), 2.54 (1 H, t, *J* 7 Hz, ArH), and 2.58 (1 H, s, 10-H); *m/z* 248 (*M*$^+$, 100%), 220(21), 192(7), and 165(8) (Found: C, 72.6; H, 3.1; N, 11.05. $C_{15}H_8N_2O_2$ requires C, 72.6; H, 3.2; N, 11.3%).

1′-*Methylspiro*[*indene*-2,2′-*indole*]-1,3′-*dione* (7b).—The oxepinoindole (2c) (520 mg) was stirred in ethanol (300 ml) in daylight for 12 h. The ethanol was evaporated and the residual yellow crystals recrystallised from methanol to give the *spiro-dione* (7b) (500 mg), m.p. 187—189 °C, $\lambda_{max.}$ (EtOH) 230, 241, 251sh, 299, and 407 nm (log ε 4.36, 4.39, 4.34, 4.66, and 4.42); $\nu_{max.}$ (Nujol) 1 680s and 1 650s cm^{-1}; τ ($CDCl_3$) 2.33 (1 H, d, *J* 7 Hz, 1-H), 2.34 (1 H, t, *J* 7 Hz, ArH), 2.40—2.62 (6 H, m, ArH), and 4.50 (1 H, d, *J* 13 Hz, C*H*$_A$H$_B$), 4.72 (1 H, d, *J* 13 Hz, CH$_A$*H*$_B$), and 7.12 (3 H, s, NMe); *m/z* 263 (*M*$^+$, 95%), 246(6), 243(100), and 220(34) (Found: C, 77.4; H, 5.0; N, 5.3. $C_{17}H_{13}NO_2$ requires C, 77.6; H, 5.0; N, 5.3%).

1'-Methyl-6-nitrospiro[indene-2,2'-indole]-1,3'-dione (7c).—The nitro-benzo-oxepinoindole [1] (2d) (30 mg) in tetrahydrofuran (10 ml) was left in the daylight for 12 h. The solvent was evaporated to yield quantitatively the *nitro-spiro-dione* (7c) as a yellow crystalline material, m.p. 198—204 °C, $\lambda_{max.}$ ($CHCl_3$) 260sh, 280sh, and 407 nm (log ε 3.96, 3.73, and 3.53); $\nu_{max.}$ (Nujol) 1 735s and 1 685s cm^{-1}; τ ($CDCl_3$) 1.41 (1 H, s, ArH), 1.46 (1 H, d, *J* 9 Hz, ArH), 2.19 (1 H, d, *J* 9 Hz, ArH), 2.41 (1 H, d, *J* 9 Hz, ArH), 2.42 (1 H, t, *J* 9 Hz, ArH), 3.02 (1 H, d, *J* 9 Hz, ArH), 3.15 (1 H, t, *J* 9 Hz, ArH), 6.38 (1 H, d, *J* 20 Hz, CH_AH_B), 6.60 (1 H, d, *J* 20 Hz, CH_AH_B), and 7.03 (3 H, s, NMe); *m/z* 308 (M^+, 100%), 279(57), and 233(32) [Found (by mass spectrometry): *M*, 308.078. $C_{17}H_{12}N_2O_4$ requires *M*, 308.079].

2-[(2-Methoxycarbonyl-4-nitrophenyl)methylene]-1-methylindolin-3-one (13).—The nitro-dione (7c) (50 mg) in solution in methanol (20 ml) was heated under reflux for 2 min. The resultant purple solution was evaporated under reduced pressure to yield the *ester* (13) as a purple solid (55 mg), which recrystallised from glacial acetic acid to give pure material (25 mg), m.p. 185—190 °C, $\lambda_{max.}$ (EtOH), 214, 232sh, 266, 320, 335sh, and 505 nm (log ε 4.20, 4.15, 4.13, 3.90, 3.87, and 3.57); $\nu_{max.}$ (Nujol) 1 725s and 1 690s cm^{-1}; τ [$(CD_3)_2CO$] 1.15 (1 H, s, 3-H), 1.56 (1 H, d, *J* 9 Hz, 5-H), 1.73 (1 H, d, *J* 9 Hz, ArH), 2.33 (1 H, t, *J* 8 Hz, ArH), 2.41 (1 H, d, *J* 8 Hz, ArH), 2.77 (1 H, d, *J* 8 Hz, ArH), 2.94 (1 H, s, C:CH), 3.02 (1 H, t, *J* 8 Hz, ArH), 6.02 (3 H, s, OMe), and 6.51 (3 H, s, NMe); *m/z* 338 (M^+, 23%), 279(100), and 233(38) (Found: C, 63.8; H, 4.2; N, 8.1. $C_{18}H_{14}N_2O_5$ requires C, 63.9; H, 4.1; N, 8.3%).

Acknowledgements

G. L. H. and L. D. thank the S.E.R.C. for maintenance grants. Part of this work (G. L. H.) was undertaken as part of an S.E.R.C. CASE award and we thank Glaxo Group Research Ltd., Ware for their interest and support.

References

1 Part 5, W. R. Ashcroft, L. Dalton, M. G. Beal, and J. A. Joule, *J. Chem. Soc., Perkin Trans. 1*, 1983, preceding paper.
2 For several examples and a discussion of the process see M. G. Beal, W. R. Ashcroft, M. M. Cooper, and J. A. Joule, *J. Chem. Soc., Perkin Trans. 1*, 1982, 435.
3 M. Hooper and W. N. Pitkethly, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1607.
4 A. I. Meyers and R. A. Gabel, *Tetrahedron Lett.*, 1978, 227.
5 M. M. Cooper, G. J. Hignett, and J. A. Joule, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3008.

Received 13*th April* 1983; *Paper* 3/586