Regio- and Stereo-chemical Aspects of [2+2] Photocycloaddition Between 1-Benzoylindoles and Olefins

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The regio- and stereo-selectivities in the [2+2] photocycloaddition of a series of 1-benzoylindoles with vinyl acetate and methyl acrylate have been investigated. With some exceptions, the 1-benzoylindoles gave exclusively or predominantly the corresponding 1-acetoxy-3-benzoyl and 3-benzoyl-1-methoxycarbonyl-1,2,2a,7b-tetrahydro-3H-cyclobut[b]indoles as mixtures of stereoisomers.

1-Aroylindoles [e.g. (1a)] are known to undergo [2 + 2] photocycloaddition with olefins to give cyclobut[b]indole derivatives.[1] In connection with our interest in the use of this reaction for synthetic purposes,[2,3] we have investigated the regio- and stereo-chemical aspects of this cyclobutane ring formation reaction, and we describe here our results from the photocycloaddition reaction between substituted 1-benzoylindoles and olefins such as vinyl acetate and methyl acrylate.
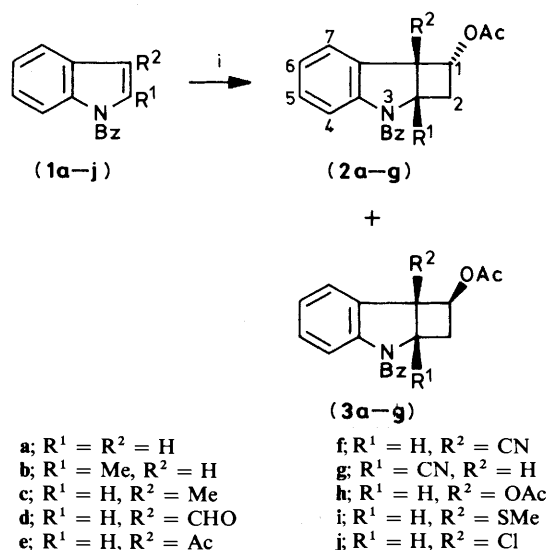
A solution of the 1-benzoylindole (1a—j) and an excess of olefin in degassed benzene, in the presence of acetophenone† as a triplet sensitizer in the case of vinyl acetate or without acetophenone in the case of methyl acrylate, was irradiated with a 350-W high-pressure mercury lamp in a Pyrex tube. The progress of the reaction was followed by t.l.c. analysis. After evaporation of the solvent, the crude material was chromatographed on silica gel to remove the sensitizer and polymeric substances.

In this manner, the indoles (1a—c), on irradiation with vinyl acetate, each afforded a mixture of the corresponding acetates, (2a—c) and (3a—c) (Scheme 1), which could not be separated by conventional means. Pure samples of the acetates were obtained by alkaline hydrolysis of the crude mixture, separation of the resulting alcohols (4a—c) and (5a—c) by column chromatography, and reacetylation (Scheme 2). The structures of the acetates were elucidated by oxidation of each alcohol to the corresponding cyclobutanone (6a—c).[1,2] The structure of the 2a-methyl derivative (6b) was deduced on the basis of the n.m.r. spectrum; the C-2 protons appeared as part of an ABX system, with the AB portion centred at δ 3.61, J_{AB} 19.5 Hz, J_{AX} 4 Hz, and J_{BX} 2 Hz, as expected for a slightly puckered four-membered
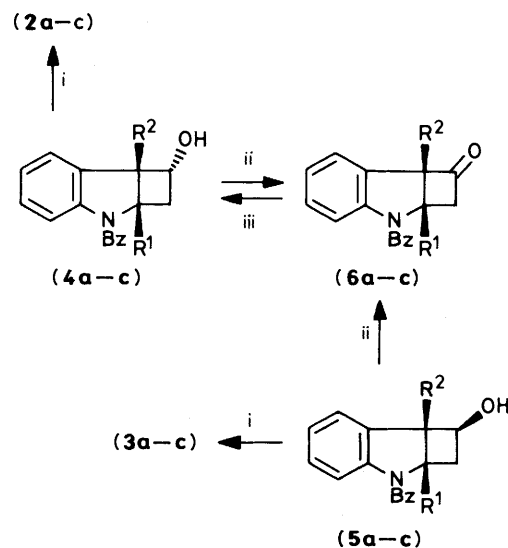
(6b)
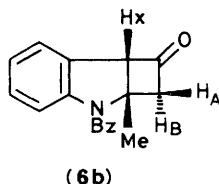
ring. The C-7b proton appears as a four-line signal at δ 4.44. The stereochemical assignment of the acetates (2a—c) and (3a—c) was based on the fact that reduction with sodium borohydride of the cyclobutanones (6a—c) gave exclusively the *endo*-alcohols (4a—c), respectively, as a result of hydride attack at the less hindered *exo*-face of the molecule.[2,4]

Irradiation of the 3-formyl derivative (1d) with vinyl acetate gave a mixture of the acetates (2d) and (3d) in the ratio 1:0.7,‡

a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = H, R^2 = Me$
d; $R^1 = H, R^2 = CHO$
e; $R^1 = H, R^2 = Ac$

f; $R^1 = H, R^2 = CN$
g; $R^1 = CN, R^2 = H$
h; $R^1 = H, R^2 = OAc$
i; $R^1 = H, R^2 = SMe$
j; $R^1 = H, R^2 = Cl$

Scheme 1. *Reagents:* i, hv, vinyl acetate

Scheme 2. *Reagents:* i, Ac_2O, C_5H_5N; ii, CrO_3; iii, $NaBH_4$

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† Direct irradiation of a benzene solution of the indoles (1d—f) and vinyl acetate also gave similar results.

‡ Compound (2d), upon irradiation under the same conditions, was recovered unchanged, indicating that no isomerisation takes place under the photolytic conditions.

Table 1. N.m.r. spectral data (δ values in CDCl₃) for (2a—f) and (3a—f) (J values in Hz)

Compd.	1-H	2-H	2a-H	7b-H	OCOMe	Others
(2a)	4.55—4.95 (m)	2.45—2.95 (m)	4.55—4.95 (m)	3.85—4.05 (m)	2.07 (s)	6.95—7.55 (8 H, m, arom) 7.65—8.1 (1 H, m, 4-H)
(3a)	4.9—5.2 (m)	2.25—2.6 (m) 2.7—3.05 (m)	4.15—4.5 (m)	4.15—4.5 (m)	1.92 (s)	6.95—7.5 (8 H, m, arom) 7.75—8.2 (1 H, m. 4-H)
(2b)	5.12 (q, J 7.5)	2.74 (dd, J 2, 7.5)		3.91 (dd, J 2, 7.5)	1.82 (s)	1.60 (3 H, s, 2a-Me) 6.25—6.5 (1 H, m, 4-H) 6.65—7.5 (8 H, m. arom)
(3b)	4.86 (ddd, J 4, 5, 7.5)	2.49 (ddd, J 2, 5, 14) 3.18 (dd, J 7.5, 14)		3.48 (bd, J ca. 4)	2.12 (s)	1.75 (3 H, s, 2a-Me) 6.15—6.35 (1 H, m, 4-H) 6.75—7.7 (8 H, m, arom)
(2c)	4.87 (t, J 8)	2.23 (ddd, J 6, 8, 14) 2.84 (ddd, J 6, 8, 14)	3.97 (bt, J ca. 6)		1.97 (s)	1.50 (3 H, s, 7b-Me) 7.0—7.55 (8 H, m, arom) 7.85—8.15 (1H, m, 4-H)
(3c)	4.97 (dd, J 4, 7)	2.4—2.7 (m)	4.32 (bdd)		2.09 (s)	1.30 (3 H, s, 7b-Me) 7.0—7.6 (8 H, m, arom) 7.75—8.1 (1 H, m. 4-H)
(2d)	4.95 (t, J 8)	2.2—3.05 (m)	4.59 (t, J 6)		2.01 (s)	7.05—7.65 (8 H, m, arom) 7.95—8.1 (1 H, m, 4-H) 9.79 (1 H, s, CHO)
(3d)	4.98 (dd, J 4, 8)	2.4—2.9 (m)	5.07 (dd, J 6, 8)		2.02 (s)	7.05—7.7 (8 H, m, arom) 7.85—8.15 (1 H, m, 4-H) 9.62 (1 H, s, CHO)
(2e)	5.25 (t, J 8)	2.1—2.5 (m) 2.84 (ddd, J 7, 8, 13)	4.44 (t, J 7)		1.98(s) or 2.04(s)	1.98 or 2.04 (3 H, s, COMe) 7.0—7.5 (8 H, m, arom) 7.9—8.1 (1 H, m, 4-H)
(3e)	5.24 (dd, J 3, 7)	2.40 (ddd, J 3, 8, 14) 2.74 (ddd, J 6, 7, 14)	5.10 (dd, J 6, 8)		2.02(s) or 2.16(s)	2.02 or 2.16 (3 H, s, COMe) 7.0—7.6 (8 H, m, arom) 7.8—8.1 (1 H, m, 4-H)
(2f)	5.30 (t, J 8)	2.44 (ddd, J 7, 8, 13.5) 3.04 (ddd, J 7, 8, 13.5)	4.72 (t, J 7)		2.03 (s)	6.95—7.6 (8 H, m, arom) 7.7—8.0 (1 H, m, 4-H)
(3f)	5.05 or 5.07ᵃ	2.75 (dd, J 5.5, 7)	5.07 or 5.05 ᵃ		2.18 (s)	6.95—7.95 (9 H, m, arom)

ᵃ The chemical shifts for 1-H and 2a-H were nearly identical, so that the coupling constants could not be determined.
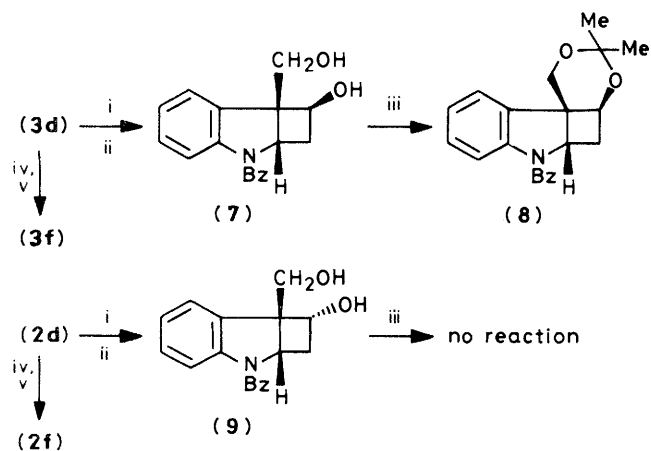
Scheme 3. Reagents: i, NaBH₄; ii, OH⁻; iii, Me₂CO, H⁺; iv, NH₂OH; v, (CF₃CO)₂O, C₅H₅N

which was separated by column chromatography on silica gel. The structures of (2d) and (3d) were confirmed by their spectroscopic data and chemical evidence. The C-2a proton of the acetates (2d) and (3d) appeared as a triplet and a doublet of doublets centred at δ 4.59 (J 6 Hz) and δ 5.07 (J 6 and 8 Hz), respectively, suggesting the presence of the acetoxy group at the 1-position rather than the 2-position. The exo stereochemistry of the 1-acetoxy group of compound (3d) was deduced by transforming it into the acetonide (8) via reduction with sodium borohydride, subsequent alkaline hydrolysis, and treatment of the resulting diol (7) with acetone in the presence of toluene-p-sulphonic acid (Scheme 3). Repetition of the same sequence starting from the isomer (2d), however, did not give the corresponding acetonide, and thus its 1-acetoxy group was assigned the endo stereochemistry.

Irradiation of the 3-acetyl derivative (1e) with vinyl acetate proceeded rapidly to give a 1:1 mixture of the adducts (2e) and (3e) which was resolved, but with difficulty, by chromatography. The structures of compounds (2e) and (3e) were deduced from comparison of the chemical shifts and coupling constants of the C-1 and C-2a protons with those of the aldehydes (2d) and (3d) (see Table 1).

Irradiation of the 3-cyano derivative (1f) with vinyl acetate gave a 1:1 mixture of the cyclobutanones (2f) and (3f) which could be separated by chromatography. The structures of (2f) and (3f) were deduced by chemical correlation with the

Table 2. N.m.r. spectral data (δ values in $CDCl_3$) for compounds (**10a**), (**10e**), (**10f**), (**10h**), (**11a—f**), (**11h—j**), (**12a**), and (**12d—f**)

| Compd.	1-H	2-H	2a-H	7b-H	OMe	Others
(**10a**)	3.1—3.4 (m)	2.3—3.9 (m)	4.5—4.7 (m)	4.05—4.25 (m)	3.72 (s)	6.3—6.5 (1 H, m, arom) 7.0—7.7 (8 H, m, arom)
(**11a**)[a]	3.0—3.25 (m)	2.5—2.8 (m)	4.6—4.9 (m)	4.05—4.25 (m)	3.70 (s)	6.9—7.5 (8 H, m, arom) 7.8—8.2 (1 H, m, 4-H)
(**12a**)	2.3—3.0 (m)	3.3—3.6 (m)	4.4—4.7 (m)	4.1—4.4 (m)	3.58 (s)	6.8—7.5 (8 H, m, arom) 7.75—8.15 (1 H, m, 4-H)
(**11b**)	2.5—3.3 (m)	2.5—3.3 (m)		3.7—3.85 (m)	3.76 (s)	1.70 (3 H, s, 2a-Me) 6.2—6.4 (1 H, m, 4-H) 6.8—7.6 (8 H, m, arom)
(**11c**)	3.21 (dd, J 4, 9)	2.27 (ddd, J 6, 9, 12) 2.79 (ddd, J 4, 8, 12)	4.36 (dd, J 6, 8)		3.72 (s)	1.28 (3 H, s, 7b-Me) 6.9—7.7 (8 H, m, arom) 7.8—8.2 (1 H, m, 4-H)
(**11d**)	3.43 (dd, J 5, 8)	2.5—2.8 (m)	5.12 (t, J 6)		3.70 (s)	6.95—7.8 (8 H, m, arom) 7.85—8.1 (1 H, m, 4-H) 9.67 (H, s, CHO)
(**12d**)	2.39 (dd, J 9.5, 12) 2.82 (dd, J 9, 12)	3.29 (ddd, J 5.5, 9, 9.5)	5.07 (d, J 5.5)		3.53 (s)	7.0—7.7 (8 H, m, arom) 7.8—8.1 (1 H, m, 4-H) 9.71 (1 H, s, CHO)
(**10e**)	3.83 (t, J 9.5)	2.35—2.9 (m)	4.61 (dd, J 6, 7)		3.61 (s)	2.00 (3 H, s, COMe) 7.0—7.7 (8 H, m, arom) 7.85—8.05 (1 H, m, 4-H)
(**11e**)	3.36 (dd, J 5, 7)	2.4—2.6 (m)	5.14 (t, J 7)		3.69 (s)	1.97 (3 H, s, COMe) 7.0—7.55 (8 H, m, arom) 7.8—8.1 (1 H, m, 4-H)
(**12e**)	2.40 (dd, J 10, 12) 2.83 (dd, J 9, 12)	3.27 (ddd, J 5.5, 9.10)	5.00 (d, J 5.5)		3.56 (s)	2.02 (3 H, s, COMe) 7.0—7.65 (8 H, m, arom) 7.8—8.05 (1 H, m, 4-H)
(**10f**)	3.74 (t, J 9.5)	2.6—2.95 (m)	4.86 (t, J 8)		3.67 (s)	7.0—8.0 (9 H, m, arom)
(**11f**)	3.42 (dd, J 4.5, 9)	2.51 (ddd, J 6, 9, 14) 2.91 (ddd, J 4.5, 8, 14)	5.07 (dd, J 6, 8)		3.82 (s)	7.05—7.7 (8 H, m, arom) 7.75—8.0 (1 H, m, 4-H)
(**12f**)	2.62 (dd, J 10, 12) 2.92 (dd, J 9, 12)	3.31 (ddd, J 6, 9.10)	5.13 (d, J 6)		3.58 (s)	7.05—7.65 (8 H, m, arom) 7.7—7.9 (1 H, m, 4-H)
(**10h**)	3.79 (t, J 10)	2.1—2.9 (m)	4.90 (t, J 8)		3.69 (s)	2.01 (3 H, s, COMe) 6.9—8.0 (9 H, m, arom)
(**11h**)	3.59 (dd, J 4, 8)	1.9—2.2 (m) 2.71 (ddd, J 4, 9, 12)	5.00 (dd, J 6, 9)		3.72 (s)	1.90 (3 H, s, COMe) 7.0—7.7 (8 H, m, arom) 7.75—8.1 (1 H, m, 4-H)
(**11i**)	3.42 (dd, J 4, 9)	2.31 (ddd, J 6, 9, 12.5) 3.01 (ddd, J 4, 8, 12.5)	4.64 (dd, J 6, 8)		3.77 (s)	1.67 (3 H, s, SMe) 7.0—7.6 (8 H, m, arom) 7.85—8.1 (1 H, m, 4-H)
(**11j**)	3.61 (dd, J 4, 8)	2.09 (ddd, J 6, 8, 12) 2.97 (ddd, J 4, 8, 12)	4.90 (dd, J 6, 8)		3.78 (s)	7.1—7.65 (8 H, m, arom) 7.9—8.15 (1 H, m, 4-H)

[a] Ref. 3b.

aldehydes (**2d**) and (**3d**): treatment of (**2d**) and (**3d**) with hydroxylamine followed by dehydration of the oximes with trifluoroacetic anhydride in pyridine[5] gave the cyanides (**2f**) and (**3f**), respectively.

The photoaddition reactions of the 3-acetoxy (**1h**) and 3-chloro derivatives (**1j**) with vinyl acetate were very slow; a mixture of adducts was obtained from (**1h**), and a complex mixture from (**1j**), both in low yield, and no further experiments were carried out. The 2-cyano (**1g**) and 3-methylthio derivatives (**1i**) did not react with vinyl acetate.

A reinvestigation of the irradiation of compound (**1a**) with methyl acrylate[3b] (Scheme 4) enabled us to isolate, in addition to the exo-1-methoxycarbonyl derivative (**11a**), two photo-adducts which were tentatively assigned the structures (**10a**) and (**12a**) on the basis of the n.m.r. spectral evidence (see Table 2).

Irradiation of the methyl derivatives (**1b**) and (**1c**) with methyl acrylate proceeded very slowly to give a mixture of two products in the ratio 1:5—7 from which only the major products (**11b**) and (**11c**) were isolated, by recrystallisation. The structures of (**11b**) and (**11c**) were established by chemical correlation with the exo-1-acetoxy derivatives (**3b**) and (**3c**): mild alkaline hydrolysis of (**11b**) and (**11c**) gave the carboxylic
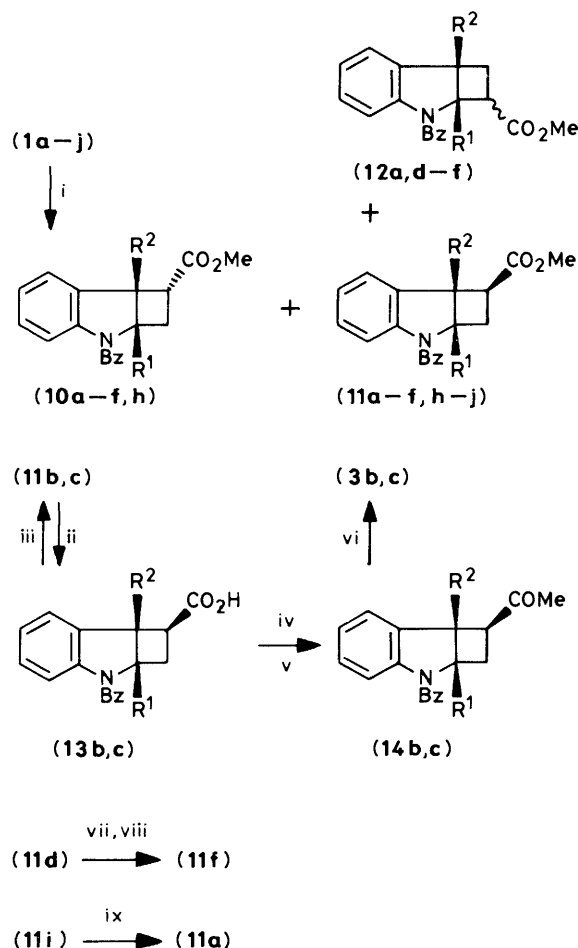
Scheme 4. Reagents: i, hv, methyl acrylate; ii, NaOH; iii, CH$_2$N$_2$; iv, SOCl$_2$; v, Me$_2$CuLi; vi, mCPBA; vii, NH$_2$OH; viii, (CF$_3$CO)$_2$O, C$_5$H$_5$N; ix, Raney Ni

Table. 3. Product distribution from the irradiation of the 1-benzoyl-indoles (1a—j) with vinyl acetate

	Time (h)	Unchanged (1) (%)	Combined yield of adducts (%)	Ratio of adducts[a] (2):(3)
(1a)	32	0	81	1:0.8
(1b)	50	48	15	1:1.2
(1c)	30	24	49	1:2.2
(1d)	10	0	78	1:0.7
(1e)	6	0	69	1:1
(1f)	18	0	72	1:1
(1g)	>50	ca. 100	0	
(1h)	50	ca. 0	10	b
(1i)	>50	ca. 100	0	
(1j)	>50	b	b	

[a] Determined by n.m.r. spectroscopy. [b] See text.

Table 4. Product distribution from the irradiation of the 1-benzoyl-indoles (1a—j) with methyl acrylate

	Time (h)	Unchanged (1) (%)	Combined yield of adducts (%)	Ratio of adducts[a] (10):(11):(12)
(1a)	30	0	67	1[b]:5:1.3[b]
(1b)	83	0	51	1[b]:5
(1c)	50	12	23	1[b]:7
(1d)	12	0	53	1[b]:3:4
(1e)	8	0	56	1:12:5
(1f)	40	0	46[c]	1:3:0.5
(1g)	>50	ca. 100	0	
(1h)	16	0	64	1:10
(1i)	54	30	53	(11i) only
(1j)	20	0	d	

[a] Determined by n.m.r. spectroscopy. [b] Tentative assignment. [c] Small amounts of two Fries rearrangement products were isolated. [d] One adduct was isolated in low yield from a complex mixture (see text).

acids (13b) and (13c);* treatment of these with thionyl chloride followed by lithium dimethylcopper,[5] and then Baeyer–Villiger oxidation of the resulting methyl ketones (14b) and (14c) with mCPBA (m-chloroperbenzoic acid) gave (3b) and (3c). The structures of the minor products have not been established yet.

Irradiation of compounds (1d—f) with methyl acrylate gave a mixture of at least three isomeric photoadducts. Two isomers (11d) and (12d) from (1d), and three pairs of isomers (10e) and (10f),(11e) and (11f), and (12e) and (12f) from (1e) and (1f) could be isolated as pure compounds. The distinguishing feature of the n.m.r. spectra of these adducts was the C-2a proton signal; this appeared as a triplet (J 6 Hz) or a doublet of doublets (J 6 and 7—9 Hz) in those of the 1-substituted isomers (10e), (10f), and (11d—f), but as a doublet (J 5.5—6 Hz) in the spectra from the 2-substituted isomers (12d—f). The stereochemistry of the 1-substituted isomers was ascertained by analysis of the n.m.r. spectra and spin-decoupling experiments. As can be seen in Tables 1 and 2, in the 1-exo-isomers the C-1 proton signal appeared as a doublet of doublets with J 4—5 and 7—9 Hz, whereas the same proton in the 1-endo-isomers gave a triplet with J 8—10 Hz. This may reflect the conformational difference in the cyclobutane ring between the exo- and endo-isomers.[7] The observed coupling constants of compounds (11d—f), (10e), and (10f) (see Table 2) are in good agreement

* That no epimerisation took place in this step was demonstrated by the fact that treatment of (13b) with diazomethane in ether gave (11b), and that the n.m.r. spectrum of (14c) closely resembles that of (11c).

with the assigned stereochemistry. Furthermore, compound (11d) was transformed into (11f) by treatment with hydroxylamine followed by trifluoroacetic anhydride in pyridine.[5] The stereochemistry of the 2-substituted isomers was unclear.

Compound (1g) did not undergo cycloaddition with methyl acrylate and was recovered unchanged.

Irradiation of the acetate (1h) with methyl acrylate gave a mixture of two photoadducts (10h) and (11h) in a ratio of ca. 1:10, which were isolated as pure compounds by column chromatography. Their structure and stereochemistry were determined on the basis of the coupling pattern of the C-2a and C-1 protons (see Table 2).

Irradiation of the methylthio derivative (1i) with methyl acrylate gave essentially a single adduct, whose structure was established to be (11i) by desulphurisation with Raney Ni in methanol to give (11a).

Irradiation of the chloro derivative (1j) with methyl acrylate gave a complex mixture from which one adduct was isolated in low yield by repeated chromatography. It was tentatively assigned the structure (11j) on the basis of the coupling pattern of the C-2a and C-1 protons (see Table 2).

The results summarised in Tables 3 and 4 indicate that the addition of vinyl acetate to the 1-benzoylindoles (1), particularly those with the electron-withdrawing group at the 3-position, proceeded in high yield with high regioselectivity (formation of the 1-substituted isomers only) but low stereo-selectivity (formation of ca. 1:1 mixtures of the endo- and

exo-isomers); on the other hand, methyl acrylate added to compounds (1) in moderate yield with high regioselectivity [formation of the 1-substituted isomers as the major products except in the case of (1d)] and high stereoselectivity (formation of the 1-*exo*-isomers as the major products). Thus, these studies show the generality of the formation of 1-substituted cyclobut[*b*]indoles from the 1-benzoylindoles (1) with vinyl acetate and methyl acrylate.

The observed regiochemical selectivity is similar to that observed in the photocycloaddition of 2-quinolones,[8] 1-isoquinolones,[9] coumarins,[10] indenes,[11] and thianaphthene 1,1-dioxides[12] to unsymmetrical olefins, which gives one regioisomer predominantly or exclusively regardless of the nature of the olefin, and is in sharp contrast with the results of the photocycloaddition of cyclic α,β-unsaturated ketones to unsymmetrical olefins.[13] The problem of orientation in the former cases has usually been explained in terms of the stability of the 1,4-diradical intermediate with the resonance-stabilised benzylic free radical [*e.g.*, structure (15)]. However, further work,

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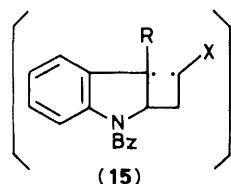
including a determination of the exact nature of the excited states, needs to be carried out in order to analyse the observed results in more detail.

Experimental

N.m.r. spectra were determined with an Hitachi R-22 spectrometer (90 MHz; SiMe$_4$ as internal standard). I.r. spectra were recorded with a JASCO IRA-1 spectrophotometer. Low- and high-resolution mass spectra were recorded with a JEOL JMS-D-300 instrument at 70 eV. Ether refers to diethyl ether.

General Procedure for the Preparation of the 1-*Benzoylindoles* (**1b—j**).—(*a*) 1-Benzoyl-3-chloroindole (**1j**) was prepared according to the reported procedure.[14]

(*b*) Essentially, the procedure of Illi[15] was employed. To an ice-cooled mixture of the indole (0.01 mol), tetrabutylammonium hydrogen sulphate (650 mg), and powdered sodium hydroxide (10 g, 0.26 mol) in methylene dichloride (1 l) was added dropwise benzoyl chloride (15 g) during 30 min. After being stirred at room temperature for 2 h, the mixture was filtered and the filtrate concentrated. The residual solid was recrystallised from ethanol to give the following products. 1-Benzoyl-2-methylindole (**1b**).[3b] 1-Benzoyl-3-methylindole (**1c**) (68%), m.p. 75—76 °C;[16] ν$_{max.}$ (KCl) 1 660 cm^{-1}; δ(CDCl$_3$) 2.20 (3 H, d, *J* 1.5 Hz, 3-Me), 6.97 (1 H, d, *J* 1.5 Hz, 2-H), 7.05—7.75 (8 H, m, arom) and 8.2—8.4 (1 H, m, 7-H). 1-Benzoyl-3-cyanoindole (**1f**) (81%), m.p. 108—109 °C (Found: C, 78.1; H, 3.9; N, 11.3. C$_{16}$H$_{10}$N$_2$O requires C, 78.03; H, 4.09; N, 11.38%); ν$_{max.}$ (KCl) 2 240 and 1 690 cm^{-1}; δ(CDCl$_3$) 7.2—7.9 (9 H, m, arom) and 8.15—8.4 (1 H, m, 7-H). 3-*Acetoxy*-1-*benzoylindole* (**1h**) (69%), m.p. 87 °C (Found: C, 72.9; H, 4.5; N, 5.1. C$_{17}$H$_{13}$NO$_3$ requires C, 73.11; H, 4.69; N, 5.02%); ν$_{max.}$ (KCl) 1 750 and 1 675 cm^{-1}; δ(CDCl$_3$) 2.30 (3 H, s, COMe), 7.1—7.85 (9 H, m, arom), and 8.3—8.45 (1 H, m, 7-H). 1-Benzoyl-3-methylthioindole (**1i**) (72%), m.p. 60—61.5 °C (Found: C, 72.1; H, 4.8; N, 5.1. C$_{16}$H$_{13}$NOS requires C, 71.88; H, 4.90; N, 5.24%); ν$_{max.}$ (KCl) 1 675 cm^{-1}; δ(CDCl$_3$) 2.33 (3 H, s, SMe), 7.1—7.75 (9 H, m, arom), and 8.15—8.4 (1 H, m, 7-H).

(*c*) To a solution of the indole (0.1 mol) in 1,2-dimethoxyethane (200 ml) was added a solution of potassium carbonate (40 g) in water (70 ml) and then benzoyl chloride (22 g) at room temperature. The mixture was stirred for 6 h, and the organic layer was separated, dried (MgSO$_4$), and concentrated. The residual solid was recrystallised from ethanol to give the following. 1-*Benzoyl*-3-*formylindole* (**1d**) (70%), m.p. 81—83.5 °C (Found: C, 76.7; H, 4.3; N, 5.6. C$_{16}$H$_{11}$NO$_2$ requires C, 77.09; H, 4.45; N, 5.62%); ν$_{max.}$ (KCl) 1 670 cm^{-1}; δ(CDCl$_3$) 7.2—7.9 (9 H, m, arom), 8.1—8.35 (1 H, m, 7-H), and 10.1 (1 H, s, CHO). 3-*Acetyl*-1-*benzoylindole* (**1e**) (65%), m.p. 130—131 °C (Found: C, 77.4; H, 4.9; N, 5.4. C$_{17}$H$_{13}$NO$_2$ requires C, 77.55; H, 4.98; N, 5.32%); ν$_{max.}$ (KCl) 1 695 and 1 660 cm^{-1}; δ(CDCl$_3$) 2.47 (3 H, s, COMe), 7.2—7.9 (8 H, m, arom), and 8.0—8.4 (1 H, m, 7-H).

(*d*) A solution of 2-cyanoindole (14.2 g, 0.1 mol) in anhydrous dimethylformamide (50 ml) was added dropwise to a suspension of 50% sodium hydride in oil (6.5 g) in dry dimethylformamide (1.2 l) under nitrogen at room temperature during 30 min, and the mixture was stirred for 0.5 h. Benzoyl chloride (20 g) was added dropwise and the mixture was stirred at 50—60 °C for 3 h. The mixture was diluted with 10% acetic acid (50 ml) and extracted with ether. The extract was washed with 10% sodium hydrogen carbonate and water, dried (MgSO$_4$), and concentrated. The residual solid was recrystallised from ethanol to give 1-*benzoyl*-2-*cyanoindole* (**1g**) (1.3 g, 8.3%), m.p. 169—170 °C (Found: C, 77.8; H, 4.4; N, 11.3. C$_{16}$H$_{10}$N$_2$O requires C, 78.03; H, 4.09; N, 11.38%); ν$_{max.}$ (KCl) 2 240 and 1 645 cm^{-1}; δ(CDCl$_3$) 6.9—7.8 (10 H, m, arom).

General Procedure for the Photoirradiation of 1-*Benzoylindoles* (**1b—f**) *and Vinyl Acetate.*—According to the procedure reported by Julian and Foster,[1] a degassed solution of the 1-benzoylindole (**1b—f**) (0.8 mmol), vinyl acetate (1 ml), and acetophenone (0.3 g) in benzene (20 ml) was irradiated with an Eikosha 350-W high-pressure mercury lamp in a Pyrex tube for the time shown in Table 3. The solvent and excess of vinyl acetate were removed under reduced pressure. The residue was chromatographed (silica gel, n-hexane–ethyl acetate) to give a crude mixture of the photoproducts. The yields and product ratios are shown in Table 3. The photoadducts from (**1b**) and (**1c**) could not be separated by conventional means. The adducts (**2d—f**) and (**3d—f**) were separated by careful chromatography (silica gel, n-hexane–ethyl acetate). The n.m.r spectral data are listed in Table 1. The following were obtained. endo-1-*Acetoxy*-3-*benzoyl*-7b-*formyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (**2d**) was an oil (Found: *m/z* 335.1155. C$_{20}$H$_{17}$NO$_4$ requires *M*, 335.1155); ν$_{max.}$ (CHCl$_3$) 1 740, 1 725, and 1 640 cm^{-1}. The exo-*isomer* (**3d**) had m.p. 138.5—139.5 °C (from ethyl acetate–n-hexane) (Found: C, 71.4; H, 5.0; N, 4.2. C$_{20}$H$_{17}$NO$_4$ requires C, 71.63; H, 5.11; N, 4.18%); ν$_{max.}$ (CHCl$_3$) 1 735, 1 710, and 1 655 cm^{-1}. endo-1-*Acetoxy*-7b-*acetyl*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (**2e**) had m.p. 166.5—167.5 °C (from ethyl acetate–n-hexane) (Found: C, 72.2; H, 5.4; N, 4.0. C$_{21}$H$_{19}$NO$_4$ requires C, 72.19; H, 5.48; N, 4.01%); ν$_{max.}$ (CHCl$_3$) 1 740, 1 710, and 1 650 cm^{-1}; The exo-*isomer* (**3e**) had m.p. 153—154 °C (from ethyl acetate–n-hexane) (Found: C, 72.1; H, 5.4; N, 3.9%); ν$_{max.}$ (CHCl$_3$) 1 740, 1 710, and 1 650 cm^{-1}. endo-1-*Acetoxy*-3-*benzoyl*-7b-*cyano*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (**2f**) had m.p. 158.5—159 °C (from ethyl acetate–n-hexane) (Found: C, 72.3; H, 4.7; N, 8.4. C$_{20}$H$_{16}$N$_2$O$_3$ requires C, 72.28; H, 4.85; N, 8.43%); ν$_{max.}$ (KCl) 2 235, 1 725, and 1 655 cm^{-1}. The exo-*isomer* (**3f**) had m.p. 120—121 °C (from ethyl acetate–n-hexane) (Found: C, 72.2; H, 4.65; N, 8.2%); ν$_{max.}$ (KCl) 2 230, 1 735, and 1 650 cm^{-1}.

endo- *and* exo-3-*Benzoyl*-1-*hydroxy*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indoles* (**4b**) *and* (**5b**).—A solution

of a crude mixture (218 mg) of the photoproducts [obtained from (1b) and vinyl acetate], sodium hydroxide (32 mg), and water (0.2 ml) in ethanol (5 ml) was heated at 50—60 °C for 2 h and concentrated under reduced pressure. The residue was diluted with water, and the precipitated solid was collected and dried. Chromatography (alumina, chloroform) gave the products (4b) (54 mg, 29%) and (5b) (38 mg, 21%). *Compound* (4b) had m.p. 222—223 °C (from ethanol) (Found: C, 77.0; H, 6.15; N, 4.95. $C_{18}H_{17}NO_2$ requires C, 77.39; H, 6.13; N, 5.01%); $\nu_{max.}$ (KCl) 3 360 and 1 610 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.36 (3 H, s, 2a-Me), 2.2—2.75 (2 H, m, 2-H), 3.71 (1 H, dd, J 2 and 7 Hz, 7b-H), 4.25—4.65 (1 H, m, 1-H), 5.00 (1 H, d, J 5 Hz, OH), 6.8—7.75 (9 H, m, arom). *Compound* (5b) had m.p. 189—193 °C (from ethanol) (Found: C, 77.1; H, 5.9; N, 5.0%); $\nu_{max.}$ (KCl) 3 450 and 1 620 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.57 (3 H, s, 2a-Me), 2.13 (1 H, ddd, J 2, 5.5, and 13 Hz, 2-H), 2.96 (1 H, dd, J 8 and 13 Hz, 2-H), 3.3 (2 H, br, 7b-H and OH), 4.0—4.2 (1 H, m, 1-H), 6.15—6.4 (1 H, m, 4-H), and 6.7—7.85 (8 H, m, arom).

endo- and exo-3-*Benzoyl*-1-*hydroxy*-7b-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indoles* (4c) *and* (5c).—Using a similar procedure to that described above, the products (4c) (28%) and (5c) (52%) were obtained. *Compound* (4c) had m.p. 176—177 °C (from ethanol-water) (Found: C, 77.2; H, 6.1; N, 5.1. $C_{18}H_{17}NO_2$ requires C, 77.39; H, 6.13; N, 5.01); $\nu_{max.}$ (KCl) 3 325 and 1 620 cm^{-1}; δ [$(CD_3)_2SO$] 1.31 (3 H, s, 7b-Me), 1.8—2.4 (2 H, m, 2-H), 2.7—4.2 (2 H, m, 1- and 2a-H), 5.16 (1 H, d, J 6 Hz, OH), and 7.0—8.0 (9 H, m, arom). *Compound* (5c) had m.p. 209—211 °C (from ethanol) (Found: C, 77.3; H, 6.0; N, 5.0%); $\nu_{max.}$ (KCl) 3 450 and 1 630 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.26 (3 H, s, 7b-Me), 1.9—2.5 (2 H, m, 2-H), 3.85—4.05 (1 H, m, 1-H), 4.18 (1 H, dd, J 5 and 7 Hz, 2a-H), 5.30 (1 H, d, J 6 Hz, OH), and 7.05—8.0 (9 H, m, arom).

General Procedure for the Acetylation of the Cyclobutanols (4a—c) *and* (5a—c).—A solution of the cyclobutanol (100 mg) in acetic anhydride (2 ml) and pyridine (2 ml) [in the cases of (5b) and (5c), a catalytic amount of 4-(N,N-dimethylamino)-pyridine was added] was allowed to stand at room temperature overnight. The mixture was diluted with water and extracted with chloroform. The extract was washed with 10% hydrochloric acid, 10% sodium carbonate, and water, dried (MgSO$_4$), and concentrated. The residual solid was recrystallised from n-hexane–ethyl acetate. The n.m.r. spectral data are listed in Table 1. The following were obtained. endo-1-*Acetoxy*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (2a) (89%), m.p. 123—124 °C (Found: C, 74.4; H, 5.6; N, 4.7. $C_{19}H_{17}NO_3$ requires C, 74.25; H, 5.58; N, 4.56%); $\nu_{max.}$ (KCl) 1730 and 1640 cm^{-1}. The exo-*isomer* (3a) (87%) had m.p. 93.5—95 °C (Found: C, 74.35; H, 5.5; N, 4.8%); $\nu_{max.}$ (KCl) 1 725 and 1 640 cm^{-1}. endo-1-*Acetoxy*-3-*benzoyl*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (2b) (62%), m.p. 136—137 °C (Found: C, 74.5; H, 5.9; N, 4.4. $C_{20}H_{19}NO_3$ requires C, 74.74; H, 5.96; N, 4.36%); $\nu_{max.}$ (KCl) 1740 and 1640 cm^{-1}. The exo-*isomer* (3b) (68%), m.p. 124—125 °C (Found: C, 74.7; H, 6.1; N, 4.3%); $\nu_{max.}$ (KCl) 1 730 and 1 645 cm^{-1}. endo-1-*Acetoxy*-3-*benzoyl*-7b-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (2c) (92%) had m.p. 105—106 °C (Found: C, 75.0; H, 6.0; N, 4.3. $C_{20}H_{19}NO_3$ requires C, 74.74; H, 5.96; N, 4.36%); $\nu_{max.}$ (CHCl$_3$) 1730 and 1640 cm^{-1}. The exo-*isomer* (3c) (90%) had m.p. 116—117 °C (Found: C, 74.6; H, 6.0; N, 4.4%); $\nu_{max.}$ (CHCl$_3$) 1 740 and 1 640 cm^{-1}.

General Procedure for the Oxidation of the Cyclobutanols (4a—c) *and* (5a—c).—To a stirred solution of Collins reagent prepared from chromium trioxide (6.2 g) and pyridine (50 ml) in methylene dichloride (130 ml) was added in portions the cyclobutanol (0.01 mmol). The mixture was stirred at room temperature for 1 h and filtered. The filtrate was washed with

10% hydrochloric acid, water, and 10% sodium hydroxide, dried (Na$_2$SO$_4$), and concentrated. The residue was purified on a short silica gel column, with benzene–ethyl acetate (9 : 1) as eluant. The ketone (6a)^{3a} was obtained as an oil from compounds (4a) and (5a) in 70 and 65% yields, respectively. 3-*Benzoyl*-2a-*methyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indol*-1(2H)-*one* (6b) was obtained as an oil from (4b) and (5b) in 22 and 19% yields, respectively (Found: m/z 277.1103. $C_{18}H_{15}NO_2$ requires M, 277.1103); $\nu_{max.}$ (CHCl$_3$) 1 790 and 1 640 cm^{-1}; δ(CDCl$_3$) 1.94 (3 H, s, 2a-Me), 3.44 (1 H, dd, J 4 and 19.5 Hz, 2-H), 3.78 (1 H, dd, J 2 and 19.5 Hz, 2-H), 4.44 (1 H, dd, J 2 and 4 Hz, 7b-H), 6.05—6.25 (1 H, m, 4-H), and 6.75—7.6 (8 H, m, arom). The ketone (6c)^2 was obtained as an oil from (4c) and (5c) in 39 and 36% yields, respectively.

General Procedure for Reduction with Sodium Borohydride of the Cyclobutanones (6b) *and* (6c).—To a solution of the cyclobutanone (6b) and (6c) (0.25 mmol) in methanol (2 ml) was added in portions sodium borohydride (0.25 mmol) and the mixture was stirred at room temperature for 15 min. The mixture was diluted with ice-water, neutralised with 10% hydrochloric acid, and extracted with chloroform. The extract was washed with brine, dried (MgSO$_4$), and concentrated to give the cyclobutanols (4b) (64 mg, 82%) and (4c) (52 mg, 73%), respectively.

exo-3-*Benzoyl*-1-*hydroxy*-7b-*hydroxymethyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (7).—To an ice-cooled solution of compound (3d) (100 mg, 0.3 mmol) in anhydrous methanol (25 ml) was added in portions sodium borohydride (17 mg, 0.45 mmol) and the mixture was stirred for 30 min. After 10% sodium hydroxide (0.1 ml) had been added, the mixture was stirred at room temperature for another 1 h. The mixture was concentrated under reduced pressure, diluted with water, and extracted with chloroform. The extract was dried (MgSO$_4$) and concentrated to give the indole (7) (72 mg, 82%), m.p. 210—211 °C (from ethanol) (Found: C, 73.0; H, 5.8; N, 4.7. $C_{18}H_{17}NO_3$ requires C, 73.20; H, 5.80; N, 4.74%); $\nu_{max.}$ (KCl) 3 400 and 1 625 cm^{-1}; $\delta[(CD_3)_2SO]$ 2.1—2.6 (2 H, m, 2-H), 3.65—3.85 (2 H, m, 1-H and CH$_2$O*H*), 3.95—4.15 (1 H, m, 2a-H), 4.3—4.5 (2 H, m, C*H*$_2$OH), 5.30 (1 H, d, J 5.5 Hz, 1-OH), 6.95—7.5 (8 H, m, arom), and 7.6—8.05 (1 H, m, 4-H).

endo-3-*Benzoyl*-1-*hydroxy*-7b-*hydroxymethyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (9).—Using a similar procedure to that described above, compound (9) (85 mg, 96%) was obtained from (2d) (100 mg) as an oil; $\nu_{max.}$ (CHCl$_3$) 3 400 and 1 640 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.96 (1 H, ddd, J 6, 7.5, and 12 Hz, 2-H), 2.15—2.8 (1 H, m, 2-H), 3.35—3.7 (2 H, m, C*H*$_2$OH), 4.04 (1 H, bt, J 6 Hz, 2a-H), 4.2—4.45 (1 H, m, 1-H), 4.83 (1 H, t, J 6 Hz, CH$_2$O*H*), 5.02 (1 H, d, J 6 Hz, 1-OH), 6.9—7.75 (8 H, m, arom), and 7.8—8.1 (1 H, m, 4-H).

(1RS,6RS,8RS)-6-*Benzoyl*-3,3-*dimethyl*-4a,5,5a,6-*tetrahydro*-1H,3H-[1,3]*dioxino*[4',5':3,2]*cyclobut*[1,2-b]*indole* (8).—A solution of compound (7) (30 mg, 0.10 mmol) and toluene-p-sulphonic acid (10 mg) in acetone (7 ml) was allowed to stand at room temperature for 1 h. The mixture was made alkaline with 10% sodium hydroxide, concentrated, diluted with water, and extracted with chloroform. The extract was dried (MgSO$_4$) and concentrated to give the dioxinocyclobutindole (8) (32 mg, 95%), m.p. 193—194 °C (from ethyl acetate–n-hexane) (Found: C, 74.9; H, 6.2; N, 4.1. $C_{21}H_{21}NO_3$ requires C, 75.20; H, 6.31; N, 4.18%); $\nu_{max.}$ (KCl) 1 640 cm^{-1}; δ(CDCl$_3$) 1.40 (3 H, s, Me), 1.56 (3 H, s, Me), 2.25—2.7 (2 H, m, 7-H), 3.70, 3.88 (1 H each, ABq, J 12.5 Hz, 2-H), 4.36 (1 H, dd, J 2 and 4 Hz, 6- or 8-H), 4.80 (1 H, t, J 6 Hz, 8- or 6-H), 7.0—7.75 (8 H, m, arom), and 7.95—8.2 (1 H, m, 6-H).

General Procedure for the Conversion of the 3-Formyl Derivatives (2d) and (3d) into the 3-Cyano Derivatives (2f) and (3f).—A solution of (2d) (50 mg, 0.15 mmol), hydroxylamine hydrochloride (12 mg, 0.17 mmol), and sodium acetate (22 mg, 0.27 mmol) in ethanol (6 ml) was refluxed for 3 h. The mixture was concentrated under reduced pressure, diluted with water, and extracted with chloroform. The extract was dried (MgSO$_4$) and concentrated. The residue was dissolved in dry dioxane (0.2 ml), pyridine (0.05 ml, 0.61 mmol) was added, and the mixture then cooled to 0 °C. To the cooled mixture was added trifluoroacetic anhydride (31.5 mg, 0.15 mmol). This mixture was allowed to stand at room temperature overnight. The mixture was diluted with 10% hydrochloric acid (2 ml) and extracted with chloroform. The extract was dried (MgSO$_4$), concentrated, and chromatographed (silica gel, ethyl acetate-n-hexane, 2 : 1) to give the product (2f) (27 mg, 53%), m.p. 158.5—159 °C.

In a similar manner, (3d) (50 mg) was converted into (3f) (31 mg, 67%).

General Procedure for the Photoirradiation of the 1-Benzoylindoles (1a—j) *and Methyl Acrylate.*—A solution of the 1-benzoylindole (0.8 mmol) and methyl acrylate (1 ml) in degassed benzene (20 ml) was irradiated with a 350-W high-pressure mercury lamp in a Pyrex tube for the time shown in Table 4. After the solvent and excess of methyl acrylate had been removed under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate-n-hexane) to give a crude mixture of the photoadducts. The adducts (10b), (10c), and (10i) were isolated in a pure form by repeated recrystallisation of the crude mixtures from ethyl acetate-n-hexane. The adducts (10a), (10d—f), (10h), (11e), (11f), (11h), (12a), and (12d—f) were separated using medium-pressure column chromatography (silica gel, ethyl acetate-n-hexane). The product ratios and yields are shown in Table 4 and the n.m.r. data are summarised in Table 2. The following were obtained. *Methyl* endo-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]-*indole*-1-*carboxylate* (10a), m.p. 123—124 °C (from ethyl acetate-n-hexane) (Found: C, 73.9; H, 5.4; N, 4.5. C$_{19}$H$_{17}$NO$_3$ requires C, 74.25; H, 5.58; N, 4.56%); $v_{max.}$ (KCl) 1 720 and 1 615 cm^{-1}. *Methyl* 3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]-*indole*-2-*carboxylate* (12a), m.p. 150 °C (from ethyl acetate-n-hexane) (Found: C, 74.4; H, 5.5; N, 4.6%); $v_{max.}$ (KCl) 1 740 and 1 645 cm^{-1}. *Methyl* exo-3-*benzoyl*-7b-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (11c), m.p. 142.5—143.5 °C (from ethyl acetate-n-hexane) (Found: C, 74.8; H, 6.0; N, 4.4. C$_{20}$H$_{19}$NO$_3$ requires C, 74.74; H, 5.96; N, 4.36%); $v_{max.}$ (KCl) 1 730 and 1 635 cm^{-1}. *Methyl* exo-*benzoyl*-7b-*formyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (11d), m.p. 127—128 °C (from ethyl acetate-n-hexane) (Found: C, 71.7; H, 5.0; N, 4.3. C$_{20}$H$_{17}$NO$_4$ requires C, 71.63; H, 5.11; N, 4.18%); $v_{max.}$ (CHCl$_3$) 1 740sh, 1 730, and 1 645 cm^{-1}. *Methyl* 3-*benzoyl*-7b-*formyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-2-*carboxylate* (12d) was an oil (Found: m/z 335.1160. C$_{20}$H$_{17}$NO$_4$ requires M, 335.1158); $v_{max.}$ (CHCl$_3$) 1 740, 1 725, 1 660, and 1 640 cm^{-1}. *Methyl* exo-7b-*acetyl*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (11e), m.p. 162.5—163.5 °C (from ethyl acetate-n-hexane) (Found: C, 72.1; H, 5.3; N, 4.1. C$_{21}$H$_{19}$NO$_4$ requires C, 72.19; H, 5.48; N, 4.01%); $v_{max.}$ (KCl) 1 730, 1 705, and 1 640 cm^{-1}. *Methyl* endo-7b-*acetyl*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*in-dole*-1-*carboxylate* (10e), m.p. 131—132 °C (from ethyl acetate-n-hexane) (Found: C, 72.2; H, 5.4; N, 4.0%); $v_{max.}$ (CHCl$_3$) 1 740, 1 730, and 1 640 cm^{-1}. *Methyl* 7b-*acetyl*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-2-*carboxylate* (12e), m.p. 129—130 °C (from ethyl acetate-n-hexane) (Found: C, 72.3; H, 5.35; N, 4.0%); $v_{max.}$ (KCl) 1 730, 1 710, and 1 655 cm^{-1}. *Methyl* exo-3-*benzoyl*-7b-*cyano*-1,2,2a,7b-*tetrahydro*-3H-*cyclo*-

but[b]*indole*-1-*carboxylate* (11f), m.p. 138—139 °C (from ethyl acetate-n-hexane) (Found: C, 72.4; H, 4.7; N, 8.3. C$_{20}$H$_{16}$N$_2$O$_3$ requires C, 72.28; H, 4.85; N, 8.43%); $v_{max.}$ (CHCl$_3$) 2 250, 1 740, and 1 660 cm^{-1}. *Methyl* endo-3-*benzoyl*-7b-*cyano*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (10f) was an oil (Found: m/z 332.1163. C$_{20}$H$_{16}$N$_2$O$_3$ requires M, 332.1161); $v_{max.}$ (CHCl$_3$) 2 220, 1 740, and 1 660 cm^{-1}. *Methyl* 3-*benzoyl*-7b-*cyano*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]-*indole*-2-*carboxylate* (12f) was an oil (Found: m/z 332.1158); $v_{max.}$ (CHCl$_3$) 2 225, 1 735, and 1 640 cm^{-1}. *Methyl* exo-7b-*acetoxy*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*-[b]*indole*-1-*carboxylate* (11h), m.p. 164.5—165.5 °C (from ethyl acetate-n-hexane) (Found: C, 69.3; H, 5.2; N, 3.8. C$_{21}$H$_{19}$NO$_5$ requires C, 69.03; H, 5.24; N, 3.83%); $v_{max.}$ (KCl) 1 750, 1 735, and 1 650 cm^{-1}. *Methyl* endo-7b-*acetoxy*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxyl-ate* (10h) was an oil (Found: m/z 365.1261. C$_{21}$H$_{19}$NO$_5$ requires M, 365.1261); $v_{max.}$ (CHCl$_3$) 1 740 and 1 655 cm^{-1}. *Methyl* exo-3-*benzoyl*-7b-*methylthio*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (11i), m.p. 197 °C (from ethyl acetate-n-hexane) (Found: C, 67.8; H, 5.4; N, 4.1. C$_{20}$H$_{19}$NO$_3$S requires C, 67.96; H, 5.42; N, 3.96%); $v_{max.}$ (CHCl$_3$) 1 730 and 1 645 cm^{-1}.

exo-1-*Acetyl*-3-*benzoyl*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (14b).—A mixture of the ester (11b) (1.0 g, 3.1 mmol), sodium hydroxide (150 mg), and water (0.1 ml) in ethanol (10 ml) was stirred at 50 °C for 1 h. After the solvent had been evaporated off, the residue was dissolved in water, and the solution acidified with 10% hydrochloric acid. The precipitated crystals were collected, washed with water, and dried to give exo-3-*benzoyl*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylic acid* (13b) (800 mg, 84%), m.p. 233 °C (from ethanol) (Found: C, 74.0; H, 5.5; N, 4.5. C$_{19}$H$_{17}$NO$_3$ requires C, 74.25; H, 5.58; N, 4.56%); $v_{max.}$ (KCl) 2 500—3 000, 1 720, and 1 605 cm^{-1}; δ[(CD$_3$)$_2$SO] 1.50 (3 H, s, 2a-Me), 2.3—3.9 (5 H, m), 6.2—6.5 (1 H, m, 4-H), and 6.7—7.6 (8 H, m, arom). A mixture of the acid (13b) (300 mg, 0.98 mmol) and thionyl chloride (1 ml) was refluxed for 30 min. The excess of thionyl chloride was evaporated off under reduced pressure, and the residue was dissolved in anhydrous ether (9 ml). To this solution was added, dropwise, at −78 °C an ethereal solution of lithium dimethylcopper [prepared from methyl-lithium (5.6 mmol) and copper iodide (540 mg, 2.8 mmol)]. The mixture was stirred at −78 °C for 0.5 h and diluted with methanol. Saturated ammonium chloride solution was added. The organic layer was separated, washed with brine, dried (MgSO$_4$), and concentrated to give the ketone (14b) (200 mg, 60%), m.p. 118—119.5 °C (from ethyl acetate-n-hexane) (Found: C, 78.45; H, 6.2; N, 4.6. C$_{20}$H$_{19}$NO$_2$ requires C, 78.66; H, 6.27; N, 4.59%); $v_{max.}$ (KCl) 1 700 and 1 630 cm^{-1}; δ(CDCl$_3$) 1.61 (3 H, s, 2a-Me), 2.17 (3 H, s, COMe), 2.53 (1 H, ddd, J 2, 8, and 12 Hz, 2-H), 2.8—3.9 (2 H, m, 2- and 1-H), 3.71 (1 H, dd, J 1.5 and 4.5 Hz, 7b-H), 6.15—6.4 (1 H, m, 4-H), and 6.7—7.6 (8 H, m, arom).

exo-1-*Acetyl*-3-*benzoyl*-7b-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (14c).—Using a similar procedure to that described above, the product (14c) [160 mg, 22% overall yield from (11c)] was obtained from the ester (10c) (800 mg), m.p. 178.5 °C (from ethyl acetate-n-hexane) (Found: C, 78.4; H, 6.3; N, 4.55. C$_{20}$H$_{19}$NO$_2$ requires C, 78.66; H, 6.27; N, 4.59%); $v_{max.}$ (KCl) 1 690 and 1 640 cm^{-1}; δ(CDCl$_3$) 1.29 (3 H, s, 7b-Me), 1.95—2.25 (1 H, m, 2-H), 2.20 (3 H, s, COMe), 2.80 (1 H, ddd, J 5, 8, and 13 Hz, 2-H), 3.42 (1 H, dd, J 5 and 9 Hz, 1-H), 4.22 (1 H, dd, J 4 and 8 Hz, 2a-H), 7.05—7.55 (8 H, m, arom), and 7.95—8.2 (1 H, m, 4-H).

Baeyer–Villiger Oxidation of Compounds (14b) *and* (14c).—A

mixture of the ketone (14b) (50 mg, 0.16 mmol) and *m*-chloroperoxybenzoic acid (53 mg, 0.25 mmol) in methylene dichloride (10 ml) was refluxed for 20 h. The reaction mixture was washed with 10% sodium carbonate and water, dried (MgSO$_4$), and concentrated. The residue was chromatographed (silica gel, n-hexane–ethyl acetate, 4 : 1) to give the acetate (3b) (12 mg, 23%) and unchanged (14b) (23 mg, 46%).

Similar treatment of (14c) (13 mg) gave the isomeric product (3c) (8 mg, 58%).

Conversion of the Aldehyde (11d) *into the Cyanide* (11f).—Using a similar procedure to that described for the conversion of (3d) into (3f), the cyanide (11f) (30 mg, 98%) was obtained from compound (11d) (30 mg).

Desulphurisation of the Methylthio Derivative (11i).—A mixture of (11i) (50 mg, 0.14 mmol) and a large excess of Raney Ni W-7 in anhydrous methanol (5 ml) was refluxed for 8 h. The Raney Ni was filtered off, the filtrate was evaporated off, and the residue was chromatographed (silica gel, n-hexane–ethyl acetate, 3 : 1) to give compound (11a) (32 mg, 74%), m.p. 109.5—110 °C.

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