

Photoinduced Molecular Transformations. Part 143.¹ (2 + 2) Photoaddition of 3-Hydroxy-1-benzopyran-2-one, 3-Benzyloxycarbonyloxy-1-benzopyran-2-one, and their 8-Methoxy Derivatives, with Alkenes and Formation of 1,2-Disubstituted 1,2-Dihydrofuro[2,3-*c*][1]benzopyran-4-ones by way of β -Scission of Cyclobutanoxyl Radicals Generated from the Resulting [2 + 2] Photoadducts

Kazuhiro Kobayashi, Masayoshi Suzuki and Hiroshi Suginome*

Organic Synthesis Division, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

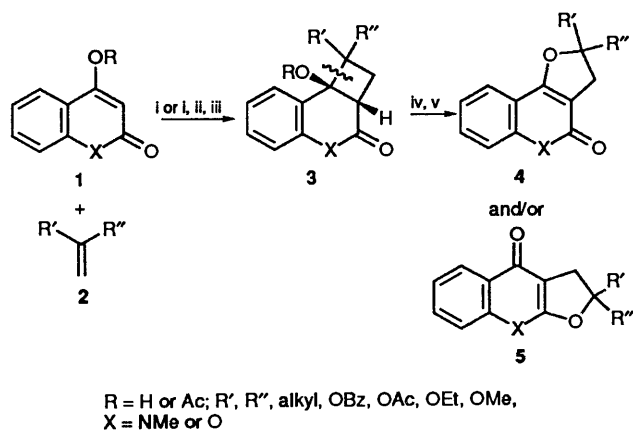
Direct photoaddition of 3-hydroxy-1-benzopyran-2-one with 2,3-dimethylbut-2-ene in *tert*-butyl alcohol gave tetrahydro-2a-hydroxycyclobuta[*c*][1]benzopyran-3-one (63%) arising from a (2 + 2) photoaddition while photoaddition of 3-(benzyloxycarbonyloxy)-1-benzopyran-2-one and its 8-methoxy derivative with cyclopentene gave 65:35 and 40:60 mixtures of *cis-cisoid-cis*- (65%) and *cis-transoid-cis* photoadducts (75%). Removal of the protecting groups of these adducts by hydrogenolysis gave the corresponding *cis-cisoid-cis* cyclobutanols (37 and 24%, respectively).

Similar (2 + 2) photoadditions of the protected 3-hydroxy-1-benzopyran-2-one and its 8-methoxy derivative with cyclohexene gave a mixture of *cis-cisoid-cis* and *cis-transoid-cis* adducts, respectively. Removal of the protecting groups from each adduct gave 85:15 and 70:30 mixtures of the *cis-cisoid-cis* (86%) and *cis-transoid-cis* cyclobutanols (70%).

Photolysis of the hypiodites generated *in situ* from these cyclobutanols induced regioselective β -scissions of the corresponding cyclobutanoxyl radicals to give furo[2,3-*c*][1]benzopyran-4-ones (20–34%) together with 4-(*trans*-2-iodocycloalkyl)-1-benzopyran-2-ones (7–25%). The pathways leading to the formation of the products arising from the β -scission are discussed.

The synthesis of heterocycles by inserting a heteroatom into alicyclic compounds is of importance in organic synthesis, and a variety of methods have been reported for this process. As part of our program to explore the potential of the β -cleavage of alkoxy radicals for organic synthesis,² we investigated a number of (2 + 2) photoadditions between enolised 1,3-dicarbonyl compounds, e.g., 4-hydroxycoumarin and alkenes, followed by a β -scission of the cyclobutanoxyl radicals derived from the resulting cyclobutanols.^{3–5} These radical fragmentations were found to take place regioselectively and result in a transformation of the cyclobutane rings into furan rings by incorporation of the alkoxy oxygen. Thus, 4-hydroxycoumarin **1** (R = H; X = O)³ and 4-hydroxyquinolin-2(1*H*)-one **1** (R = H; X = NMe)⁴ gave the cyclobutanols **3** upon (2 + 2) photoaddition and these were transformed into several furocoumarins **4** (X = O), furochromones **5** (X = O), furo[2,3-*c*]quinolin-4(5*H*)-ones **4** (X = NMe) and furo[2,3-*b*]quinolin-4(9*H*)-ones **5** (X = NMe) (see Scheme 1).

In a similar fashion, 3-acetoxyquinolin-2(1*H*)-one **6** reacted



R = H or Ac; R', R'', alkyl, OBz, OAc, OEt, OMe,
X = NMe or O

Scheme 1 Reagents and conditions: i, *hν*, MeOH; ii, MeI–NaH–DMF; iii, K₂CO₃–MeOH–H₂O; iv, HgO–I₂–benzene; v, *hν*

with acyclic or cyclic alkenes **7** to give the regioselective photoadducts **9**. In these reactions the alkoxy radicals generated from the intermediate cyclobutanols **8** induced regioselective β -scissions of the non-ring fusion bonds to give the furo[2,3-*c*]quinolin-4(5*H*)-ones **9** accompanied by the 8- or 7-membered keto lactams **10**, **11** and **12**, arising from β -scission of the ring-fusion bonds of cyclobutanoxyl radicals⁵ (see Scheme 2).

An extension of the reactions of the quinolinone adducts to the coumarin series has both mechanistic and synthetic interest and here we report the results of such an investigation. The investigation has indicated that there are some differences in the selectivity in the β -scission of alkoxy radicals generated from the photoadducts **8** of the quinolinone series.

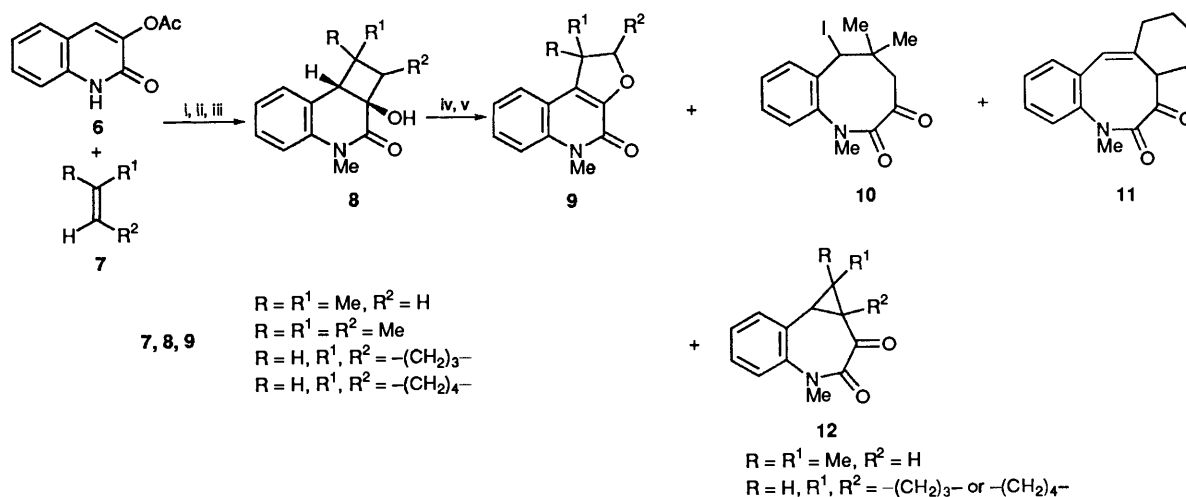
Results

(2 + 2) Photoadditions of 3-Hydroxy-**13** and 3-Benzyloxycarbonyloxy-1-benzopyran-2-ones **17** and their 8-Methoxy Derivative **18** with the Alkenes **15**, **19** and **20** (Scheme 3).—There are no reports of the photoaddition of 3-hydroxycoumarins and their 3-*O*-protected derivatives with alkenes.

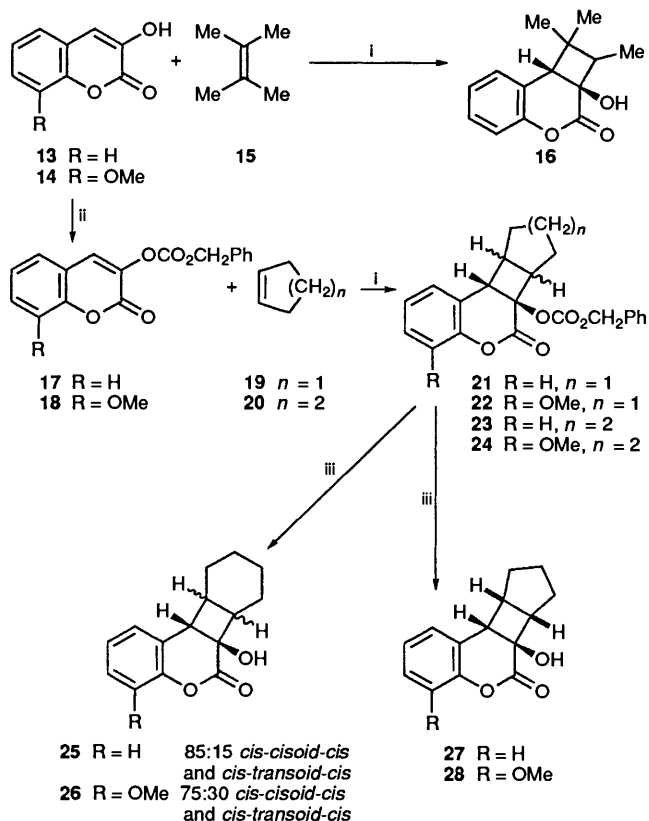
3-Hydroxycoumarin **13**,⁶ 3-benzyloxycarbonyloxy-1-benzopyran-2-one **17** and its 8-methoxy-derivative **18** were used as substrates for the photoaddition. Protection of the 3-hydroxy group of 3-hydroxycoumarin **13** and 3-hydroxy-8-methoxycoumarin **14**⁷ by the benzyldienecarbonyl group was carried out by a standard method.

2,3-Dimethylbut-2-ene **15**, cyclopentene **19** and cyclohexene **20** were used as alkenes for the photoadditions, which were carried out essentially as reported by us⁴ for preparing the photoadducts of 3-acetoxyquinolin-2(1*H*)-one **6** with alkenes.

Irradiation of 3-hydroxycoumarin **13** and 58 equiv. of 2,3-dimethylbut-2-ene **15** in *tert*-butyl alcohol for 19 h with a 500-W high-pressure mercury arc through a Pyrex filter gave a (2 + 2) photoadduct **16** as virtually the sole product (63%); no (2 + 2) photoadduct, however, was formed in the photoaddition of 3-



Scheme 2 Reagents and conditions: i, $h\nu$, MeOH; ii, NaH-MeI-DMF; iii, K_2CO_3 -MeOH- H_2O ; iv, $\text{HgO}-\text{I}_2$ -benzene; v, $h\nu$



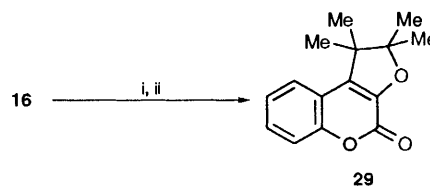
Scheme 3 Reagents and conditions: i, Bu^tOH, $h\nu$; ii, PhCH_2OCOC -pyridine; iii, Pd/C- H_2 -AcOEt

hydroxycoumarin **13** with cyclopentene **19** under similar conditions. A similar irradiation of the protected coumarin **17**, or its 8-methoxy derivative **18**, in *tert*-butyl alcohol containing an excess of cyclopentene **19** did give a 65:35 mixture of *cis-cisoid-cis* and *cis-transoid-cis* adducts **21** (65%) or a 40:60 mixture of *cis-cisoid-cis* and *cis-transoid-cis* photoadducts **22** (75%), respectively. The ratios of these stereoisomers were determined by analyses of their ^1H NMR spectra (for details of the analysis, see Experimental section). Removal of the protecting group from the stereoisomeric mixture, **21** or **22**, by hydrogenolysis with Pd-C as the catalyst gave (6a α , 6b α , 9a α , 9b α)-(±)-6a,6b,7,8,9a,9b-hexahydro-6a-hydroxy-9*H*-cyclopenta[3,4]cyclobuta[1,2-*c*][1]benzofuran-6-one **27** (37%) and its 8-methoxy derivative **28** (24%) (57 and 60% yields based on the protected *cis-cisoid-cis* adducts), respectively. None of

cis-transoid-cis isomers were isolated from the products of the hydrogenolysis. The stereochemistries of the *cis-cisoid-cis* adducts **27** and **28** were determined by comparing their ^1H NMR spectra with those of the corresponding [2 + 2] photoadducts of 3-hydroxyquinolin-2(1*H*)-one with cyclopentene reported previously by us⁵ (for details of the analysis, see Experimental section).

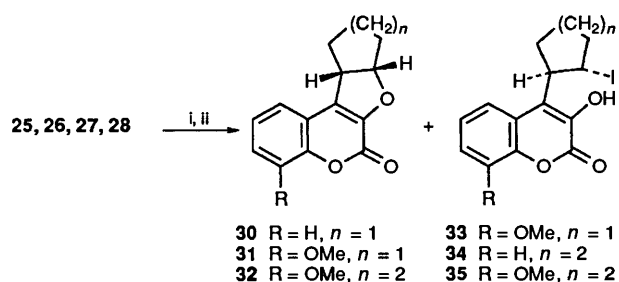
A similar photoaddition of the protected coumarin **17**, or its 8-methoxy derivative **18**, with cyclohexene **20** in *tert*-butyl alcohol gave mixtures of the stereoisomers of the [2 + 2] photoadducts, **23** and **24**, respectively. Removal of the protecting group of the adducts **23** and **24** gave an 85:15 mixture of *cis-cisoid-cis* and *cis-transoid-cis* adducts **25** (80%) as well as a 70:30 mixture of *cis-cisoid-cis* and *cis-transoid-cis* adduct **26** (70%), respectively (Scheme 3). Stereochemical assignments for the photoadducts **25** and **26** were made on the basis of an analysis of their ^1H NMR spectra.

Products arising from the Photoreactions of the Hypoidites of the Fused Cyclobutanols 16 and 25–28 (Scheme 3).—Transformation of the cyclobutanol **16** in benzene with red mercury(II) oxide and iodine (each 3 equiv.) into the corresponding hypoidite by a standard procedure, followed by irradiation with Pyrex-filtered light for 4 h under a nitrogen atmosphere, gave an amorphous product **29** (21%). The molecular formula of product **29** was determined to be $\text{C}_{15}\text{H}_{16}\text{O}_3$ by high-resolution mass spectrometry. The IR spectrum indicated that product **29** was a furanocoumarin. The ^1H NMR spectrum showed a singlet at δ 1.44 (12 H, 4 Me), a multiplet at δ 7.15–7.4 (3 H, 6-, 7-, 8-ArH) and a doublet at 7.60 (1 H, the furanocoumarin 9-H). These spectral results along with a consideration of the formation mechanism indicated that product **29** was 4*H*-1,2-dihydro-1,1,2,2-tetramethylfuro[2,3-*c*]-benzopyran-4-one



Scheme 4 Reagents and conditions: i, $\text{HgO}-\text{I}_2$ -benzene; ii, $h\nu$

Photolysis of the hypoidite of the cyclobutanol **27** in benzene for 1.5 h similarly gave the annelated coumarin **30** (34%), while photolysis of the hypoidite prepared from its 8-



Scheme 5 Reagents and conditions: i, HgO-I₂-benzene; ii, h ν

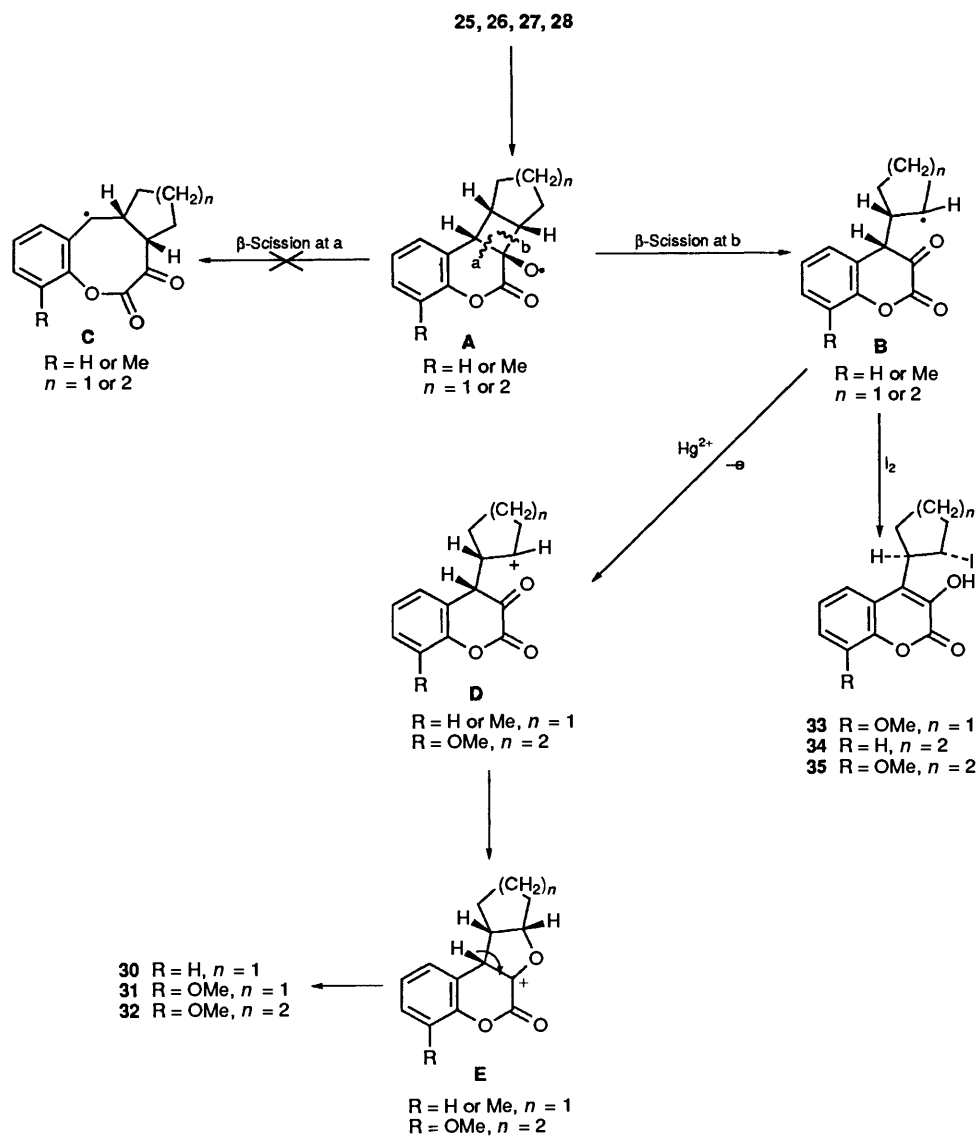
methoxy derivative **28** gave the annelated coumarin **31** (20%) along with the product **33** (7%). High-resolution mass spectrometry indicated that product **33** had the molecular formula C₁₅H₁₅IO₄ and its IR spectrum indicated the presence of a coumarin skeleton and a hydroxy group. The ¹H NMR spectrum of **33** showed signals at δ 3.18 (ddd) and 4.88 (ddd) assignable to an allylic proton as well as a proton attached to the cyclopentane carbon having an iodine. The coupling constant (10.26 Hz) indicated a *trans* disposition of the two protons. These spectral results, together with the mechanism of

formation indicated that product **33** was 4-(*trans*-2-iodocyclopentyl)-8-methoxy-1-benzopyran-2-one.

A similar photolysis of the hypoiodite generated *in situ* from a mixture of the stereoisomeric cyclobutanol derivatives **25** and red mercury(II) oxide and iodine in benzene gave a crystalline product **34** (25%) as the only isolable product. High-resolution mass spectrometry indicated its molecular formula to be C₁₅H₁₅IO₃, whilst its IR, ¹H NMR and mass spectral data indicated that the structure of product **34** was 4-(*trans*-2-iodocyclohexyl)-1-benzopyran-2-one, which was homologous to product **33**. No furocoumarin was obtained in this reaction.

Finally, photolysis of the hypoiodite generated from a mixture of stereoisomers of the cyclobutanol derivatives **26** under the conditions mentioned above gave a major crystalline product **32** (20%) along with a minor product **35** (4%).

The molecular formula of the major product **32** was C₁₆H₁₆O₄ and analyses of the IR, ¹H NMR and mass spectra indicated it to be a tetracyclic furocoumarin homologous to furocoumarin **31**. The molecular formula of the minor product **35** was C₁₆H₁₇IO₄ (high-resolution mass spectrometry). Analyses of the IR, ¹H NMR, and mass spectra indicated that the structure was 4-(*trans*-2-iodocyclohexyl)-8-methoxy-1-benzopyran-2-one, which was homologous to 3-hydroxy-4-alkylcoumarin **33**.



Scheme 6

Discussion

The foregoing results have indicated that the [2 + 2] photoadducts are formed in 63–70% yields due to the photoaddition of 3-hydroxy- or 3-benzyloxycarbonyloxy-1-benzopyran-2-one and its 8-methoxy derivative with cyclic and acyclic alkenes, analogous to 3-acetoxyquinolin-2(1*H*)-one.⁵

The above experiments indicated that the photoaddition of 3(benzyloxycarbonyloxy)-1-benzopyran-2-ones with cyclopentene or cyclohexene gave predominantly sterically disfavoured *cis-cisoid-cis* adducts over *cis-transoid-cis* adducts. The preferential formation of these sterically unfavourable adducts is parallel to the behaviour shown in the photoaddition of excited 4-hydroxycoumarin,³ 4-hydroxy-2-quinoline,⁴ and 3-acetoxyquinolin-2(1*H*)-one⁵ with olefins reported by us. This behaviour is in contrast to that of the excited cyclic enones in which sterically favoured *cis-transoid-cis* adducts have always been the predominant photoadducts⁸ and may imply the involvement of a mechanism which differs from that for the photoaddition of excited cyclic enones. As we pointed out in earlier papers,^{3–5} these additions may involve a singlet exciplex, although the mechanistic details have yet to be investigated.

The experiments described above suggest that the exclusive β -cleavage of all the alkoxy radicals generated from cyclobutenols **16** and **25–28** by the photolysis of their hypiodites took place at the non-ring fusion bonds to give furo[2,3-*c*][1]-benzopyran-4-ones as the major products together with 4-alkyl-1-benzopyran-2-ones. This exclusive cleavage of the cyclobutanoxyl radicals contrasts with the results for radicals generated from cyclobutanols derived from 3-acetoxyquinolin-1(1*H*)-one, a nitrogen analogue of 3-hydroxy-1-benzopyran-2-one, reported previously.⁵

The probable paths leading to products **30–35** in β -scissions of the alkoxy radicals generated from the cyclobutanols **25–28** are shown in Scheme 6. Thus, photolysis of the hypiodites generated *in situ* by the reaction of iodine dioxide and cyclobutanols generates alkoxy radicals **A**. A selective β -scission at bond **b** gives a carbon-centred radical **B**. In contrast to the cyclobutanoxyl radicals derived from the nitrogen analogues **18**, no 7- or 8-membered ring arising from a β -scission of the ring fusion bond **b** through a carbon-centred radical **C** was obtained. Abstractions of an iodine atom and an enolization gave rise to products **33–35**, while a one-electron oxidation of the carbon-centred radicals **B**, followed by an intramolecular combination of the resulting cations **D** with the carbonyl oxygen, gave rise to intermediates **E**. Removal of a proton from the carbocations **E** afforded the furocoumarins **30** and **31**. These paths are entirely analogous to those from the alkoxy radicals derived from the nitrogen analogues **8** to products (Scheme 2) discussed in our previous paper.⁵

All of the methods for synthesizing 4*H*-furo[2,3-*c*][1]benzopyran-4-ones recently reported involve a [3,3] sigmatropic rearrangement of the 3-*O*-propyl- or 3-*O*-allyl-3-hydroxycoumarins.⁹ Annelation of the furan ring described here—[2 + 2] photoaddition of 3-hydroxy-1-benzopyran-2-one with olefins followed by a β -scission of alkoxy radicals generated from the resulting cyclobutanols—should be of use in synthesizing this class of heterocycles.

Experimental

General Method.—Regarding the general procedures, see previous paper.⁵

3-(Benzyloxycarbonyloxy)-1-benzopyran-2-one 17.—To a solution of 3-hydroxycoumarin **13**⁶ (200 mg, 1.23 mmol) in pyridine (2.1 cm³) was added benzyloxycarbonyl chloride (252 mg, 1.48 mmol). The mixture was stirred for 16 h under nitrogen and then poured into water and extracted with diethyl ether.

The extract was washed with water, dried (MgSO₄) and evaporated. The products were subjected to PLC on silica gel to give **17** (204 mg, 56%): *R*_f 0.44 (CH₂Cl₂); m.p. 121–123 °C (from Et₂O); $\nu_{\max}/\text{cm}^{-1}$ 1771 and 1732; δ_{H} (90 MHz) 5.31 (2 H, s, CH₂Ph) and 7.2–7.7 (10 H, m); *m/z* 297 [(*M* + 1)⁺, 0.05], 252 [(*M* – CO₂)⁺, 0.9] and 91 (PhCH₂⁺, 100) [Found: *M*⁺, 297.0745. C₁₇H₁₃O₅ (*M* + 1) requires *M*, 297.0763].

3-(Benzyloxycarbonyloxy)-8-methoxy-1-benzopyran-2-one 18.—Treatment of 3-hydroxy-8-methoxycoumarin **14**⁷ (75 mg, 0.391 mmol) with benzyloxycarbonyl chloride (133 mg, 0.782 mmol) in pyridine (0.69 cm³) as described above, gave **18** (68 mg, 53%): *R*_f 0.22 (CH₂Cl₂); m.p. 127–128 °C (from Et₂O); $\nu_{\max}/\text{cm}^{-1}$ 1757 and 1735; δ_{H} (90 MHz) 3.93 (3 H, s, OMe), 5.28 (2 H, s, CH₂Ph) and 6.9–7.5 (9 H, m); *m/z* 327 [(*M* + 1)⁺, 0.01], 282 [(*M* – CO₂)⁺, 1.5], 254 (4.4) and 91 (100) (Found: C, 66.25; H, 4.3. C₁₈H₁₄O₆ requires C, 66.26; H, 4.32%).

cis-1,2,2a,8b-Tetrahydro-2a-hydroxy-1,1,2,2-tetramethylcyclobuta[*c*][1]benzopyran-3-one 16.—A solution of 3-hydroxycoumarin **13** (233 mg, 1.44 mmol) and 2,3-dimethylbut-2-ene **15** (7.08 g, 84.1 mmol) in *tert*-butyl alcohol (3 cm³) was irradiated with a 500-W high-pressure Hg arc through a Pyrex-filter under a nitrogen atmosphere for 19 h. After evaporation of the solvent, the residue was purified by PLC on silica gel to give the cyclobutanol **16** (222 mg, 63%): *R*_f 0.60 (from 1:3 AcOEt–toluene); m.p. 175–177 °C (from Et₂O–hexane); $\nu_{\max}/\text{cm}^{-1}$ 3432 and 1726; δ_{H} (90 MHz) 0.68 (3 H, s), 1.01 (3 H, s), 1.14 (3 H, s), 1.31 (3 H, s), 3.28 (1 H, s, 8b-H) and 6.9–7.3 (4 H, m); *m/z* 246 (*M*⁺, 0.38), 229 [(*M* – OH)⁺, 1.1], 162 [(*M* – C₆H₁₂)⁺, 14] and 84 (100) (Found: C, 73.1; H, 7.45. C₁₅H₁₈O₃ requires C, 73.14; H, 7.37%).

(±)-(6 α ,6 β α ,9 α ,9 β α)- and (±)-(6 α ,6 β ,9 α ,9 β α)-6a-(Benzyloxycarbonyloxy)-6a,6b,7,8,9a,9b-hexahydro-9*H*-cyclopenta[3,4]cyclobuta[1,2-*c*][1]benzofuran-6-one **21.**—A solution of coumarin **17** (200 mg, 0.676 mmol) and cyclopentene **19** (5.81 g, 85.2 mmol) in *tert*-butyl alcohol (5.5 cm³) was irradiated for 100 h, as described for the preparation of the photoproduct **16**. Purification by PLC on silica gel gave the adduct **21** (a 65:35 *syn:anti* mixture) (160 mg, 65%): *R*_f 0.46 (1:3 EtOAc–hexane); m.p. 110–111 °C (after trituration with Et₂O–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1746; δ_{H} (400 MHz) 1.2–2.0 (5.65 H, m), 2.35–2.5 (0.7 H, m), 3.13 (0.35 H, d, *J* 5.37, 9b-H of *anti*) 3.2–3.4 (1.65 H, m), 3.85 (0.65 H, dd, *J* 10.34, and 1.95, 9b-H of *syn*), 5.0–5.3 (2 H, m, CH₂Ph) and 6.59–7.4 (9 H, m); *m/z* 364 (*M*⁺, 10) and 91 (100) (Found: C, 72.7; H, 5.55. C₂₂H₂₀O₅ requires C, 72.51; H, 5.53%).

(±)-(6 α ,6 β α ,9 α ,9 β α)- and (6 α ,6 β ,9 α ,9 β α)-6a-(Benzyloxycarbonyloxy)-4-methoxy-6a,6b,7,8,9a,9b-hexahydro-9*H*-cyclopenta[3,4]cyclobuta[1,2-*c*][1]benzofuran-6-one **22.**—Photoaddition of the coumarin **18** (230 mg, 0.706 mmol) and cyclopentene (9.61 g, 141 mmol) in *tert*-butyl alcohol (6 cm³) for 48 h gave the adduct **22** (a 40:60 *syn:anti* mixture) (208 mg, 75%): *R*_f 0.22 (1:3, EtOAc–hexane); m.p. 157–159 °C (after trituration with Et₂O–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1743; δ_{H} (400 MHz), 1.15–1.95 (5.4 H, m), 2.3–2.5 (1.2 H, m), 3.12 (0.6 H, d, *J* 5.37, 9b-H of *anti*), 3.2–3.4 (1.4 H, m, 9a-H and 6b-H of *syn*, 9a-H of *anti*), 3.85 (0.4 H, dd, *J* 10.20 and 1.96, 9b-H of *syn*), 3.87 and 3.89 (each 3 H, 2s, OMe), 5.04 (0.6 H, d, *J* 12.21, CHHPh of *anti*), 5.10 (0.4 H, d, *J* 12.21, CHHPh of *syn*), 5.11 (0.6 H, d, *J* 12.21, CHHPh of *anti*), 5.14 (0.4 H, d, *J* 12.21, CHHPh of *syn*), 6.53 (0.4 H, d, *J* 7.32, 3-H of *syn*), 6.58 (0.6 H, dd, *J* 7.32, 1.47, 3-H of *anti*), 6.8–6.85 (1 H, m), 7.0–7.1 (1 H, m) and 7.25–7.4

(5 H, m); m/z 394 (M^+ , 2.0), 303 [($M - \text{PhCH}_2$) $^+$, 7.3] and 91 (100) (Found: C, 70.4; H, 5.7. $\text{C}_{23}\text{H}_{22}\text{O}_6$ requires C, 70.04; H, 5.62%).

(\pm)-(6 α ,6 β ,9 α ,9 β)-6a,6b,7,8,9a,9b-Hexahydro-6a-hydroxy-9H-cyclopenta[3,4]cyclobuta[1,2-c][1]benzofuran-6-one **27**.—A mixture of the adduct **21** (132 mg, 0.363 mmol) and 5% Pd/C (19 mg, 0.0089 mmol) in AcOEt (3 cm^3) was stirred under an atmosphere of hydrogen for 45 min at room temperature, and then filtered through a Celite pad and washed with AcOEt. The combined filtrate and washings were evaporated to give a residue which was subjected to PLC on silica gel (1:3, EtOAc-hexane) to give **27** (31 mg, 37%); R_f 0.22; m.p. 120–121 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3400 and 1727; δ_{H} (400 MHz) 1.05–1.85 (6 H, m), 3.05 (1 H, t, J 7.81, 6b-H), 3.2–3.6 and 3.28 (2 H, br s and dt, J 10.26 and 7.81, OH and 9a-H), 3.83 (1 H, dd, J 10.26 and 1.47, 9b-H), 6.95–7.05 (2 H, m), 7.14 (1 H, td, J 7.81, 1.46) and 7.24 (1 H, td, J 7.81 and 1.46); m/z 230 (M^+ , 2.2) and 162 [($M - \text{C}_5\text{H}_8$) $^+$, 100] (Found: C, 73.1; H, 6.2. $\text{C}_{14}\text{H}_{14}\text{O}_3$ requires C, 73.03; H, 6.19%).

(\pm)-(6 α ,6 β ,9 α ,9 β)-6a,6b,7,8,9a,9b-Hexahydro-6a-hydroxy-4-methoxycyclopenta[3,4]cyclobuta[1,2-c][1]benzofuran-6-one **28**.—Hydrogenolysis of the adduct **22** (520 mg, 1.32 mmol) in EtOAc (12 cm^3) in the presence of 5% Pd/C (70 mg, 0.033 mmol) was carried out as described above to give **28** (82 mg, 24%); R_f 0.17 (1:3 EtOAc-hexane); m.p. 146–147 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3430 and 1735; δ_{H} (400 MHz) 0.8–1.35 (7 H, m), 1.45–1.55 (1 H, m), 2.72 (1 H, t, J 7.82, 6b-H), 2.94 (1 H, q, J 9, 9a-H), 3.50 (1 H, dd, J 10.25 and 1.95, 9b-H), 3.55 (3 H, s, OMe), 6.25 (1 H, d, J 7.81, 3-H), 6.50 (1 H, d, J 8.30, 1-H) and 6.74 (1 H, dd, J 8.30 and 7.8, 2-H); m/z 260 (M^+ , 15), 232 [($M - \text{CO}$) $^+$, 39] and 192 [($M - \text{C}_5\text{H}_8$) $^+$, 100] (Found: C, 69.1; H, 6.3. $\text{C}_{15}\text{H}_{16}\text{O}_4$ requires C, 69.21; H, 6.20%).

(\pm)-(6 α ,6 β ,10 α ,10 β)- and (6 α ,6 β ,10 α ,10 β)-6a,6b,7,8,9,10,10a,10b-Octahydrobenzo[3,4]cyclobuta[1,2-c][1]benzofuran-6-one **25**.—Photolysis of the coumarin **17** (200 mg, 0.676 mmol) and the cyclohexene **20** (17.0 g, 0.207 mol) in *tert*-butyl alcohol (1.1 cm^3) for 74 h under the same conditions as described above gave the crude adduct **23** (159 mg) which was subjected to hydrogenolysis with hydrogen (1 atm) and Pd/C (5%; 10 mg, 0.0047 mmol) in AcOEt (11 cm^3) for 45 min to afford the cyclobutanol **25** (a 85:15 *syn:anti* mixture) (132 mg, 80%); R_f 0.22 (1:3 EtOAc-hexane); m.p. 90–91 °C (after trituration with Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3442, 3398 and 1729; δ_{H} (400 MHz) 1.0–2.0 (8 H, m) 2.7–2.9 (2.15 H, m), 3.26 (0.15 H, d, J 10.26, 10b-H of *anti*), 3.73 (0.85 H, d, J 9.28, 10b-H of *syn*), 7.05–7.15 (3 H, m) and 7.2–7.3 (1 H, m); m/z 244 (M^+ , 1.6), 216 [($M - \text{CO}$) $^+$, 1.6] and 162 [($M - \text{C}_6\text{H}_{12}$) $^+$, 100] (Found: C, 73.7; H, 6.7. $\text{C}_{15}\text{H}_{16}\text{O}_3$ requires C, 73.75; H, 6.60%).

(\pm)-(6 α ,6 β ,10 α ,10 β)- and (6 α ,6 β ,10 α ,10 β)-6a,6b,7,8,9,10,10a,10b-Octahydro-4-methoxybenzo[3,4]cyclobuta[1,2-c][1]benzofuran-6-one **26**.—Irradiation of a solution of the coumarin **18** (250 mg, 0.767 mmol) and the cyclohexene **20** (12.3 g, 150 mmol) in Bu t OH (1.2 cm^3) for 48 h gave the crude adduct **24**, the hydrogenolysis of which in EtOAc (28 cm^3) in the presence of 10% Pd/C (36 mg, 0.034 mmol) gave **26** (a 70:30 *syn:anti* mixture) (147 mg, 70%); R_f 0.26 (1:3, EtOAc-hexane); m.p. 152–153 °C (after trituration with hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3432 and 1727; δ_{H} (400 MHz) 1.0–2.0 (8.3 H, m), 2.7–2.9 (1.7 H, m), 3.25 (0.3 H, d, J 9.76, 10b-H of *anti*), 3.73 (0.7 H, d, J 10.74, 10b-H of *syn*), 3.89 and 3.90 (each 3 H, 2s, OMe), 6.67 (0.7 H, d, J 8.30, 3 H of *syn*), 6.71 (0.3 H, dd, J 7.81 and 1.47, 3-H of *anti*), 6.85 (1 H, dd, J 8.30, 1-H) and 7.0–7.1 (1 H, m, 2-H); m/z 274 (M^+ , 7.6), 246 [($M - \text{CO}$) $^+$, 36] and 192 [($M - \text{C}_6\text{H}_{10}$) $^+$, 100] (Found: M^+ , 274.1188. $\text{C}_{16}\text{H}_{18}\text{O}_4$ requires M , 274.1205).

1,2-Dihydro-1,1,2,2-tetramethylfuro[2,3-c][1]benzopyran-4-one **29**.—A solution of the cyclobutanol **16** (123 mg, 0.50 mmol) in benzene (40 cm^3) containing red mercury(II) oxide (325 mg, 1.50 mmol) and iodine (381 mg, 1.50 mmol) in a Pyrex vessel was irradiated with a 100-W high-pressure Hg arc for 4 h under nitrogen. The mixture was filtered through a Celite pad; the filtrate was then washed with aqueous Na_2SO_3 and dried (MgSO_4). Evaporation of the solvent gave a residue which was purified by PLC on silica gel to afford the furocoumarin **29** (26 mg, 21%); R_f 0.22 (1:6, CH_2Cl_2 -toluene); amorphous; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1735 and 1623; δ_{H} (90 MHz) 1.44 (12 H, s, 4-Me), 7.15–7.4 (3 H, m) and 7.60 (1 H, d, J 7.49, 9-H); m/z 244 (M^+ , 100) (Found: M^+ , 244.1103. $\text{C}_{15}\text{H}_{16}\text{O}_3$ requires M , 244.1099).

cis-(\pm)-8,9,10,10a-Tetrahydro-7aH-cyclopenta[4,5]furo[2,3-c][1]benzopyran-6-one **30**.—A similar photolysis of the cyclobutanol **27** (20 mg, 0.087 mmol) in benzene (18 cm^3) in the presence of red mercury(II) oxide (56 mg, 0.26 mmol) and iodine (66 mg, 0.31 mmol) for 1.5 h gave **35** (7.9 mg, 34%); R_f 0.28 (1:3, EtOAc-hexane); m.p. 115–116 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 1717 and 1634; δ_{H} (400 MHz) 1.6–2.05 (5 H, m), 2.28 (1 H, dd, J 14.16 and 6.35), 4.05 (1 H, ddd, J 8.30, 7.81 and 3.42, 10a-H), 5.50 (1 H, ddd, J 7.81, 6.35 and 1.47, 7a-H) and 7.1–7.4 (4 H, m); m/z 228 (M^+ , 100) (Found: M^+ , 228.0774. $\text{C}_{14}\text{H}_{12}\text{O}_3$ requires M , 228.0787).

cis-(\pm)-8,9,10,10a-Tetrahydro-4-methoxy-7aH-cyclopenta[4,5]furo[2,3-c][1]benzopyran-6-one **31** and 4-(*trans*-2-Iodocyclopentyl)-8-methoxy-1-benzopyran-2-one **33**.—Photolysis of the cyclobutanol **28** (37 mg, 0.14 mmol) in benzene (20 cm^3) in the presence of red mercury(II) oxide (90 mg, 0.42 mmol) and iodine (107 mg, 0.42 mmol) for 1.5 h gave the product **31** (7.2 mg, 20%) and product **33** (3.8 mg, 7%). **31**: R_f 0.22 (1:3) EtOAc-hexane); m.p. 194–198 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 1726 and 1636; δ_{H} (400 MHz) 1.5–2.05 (5 H, m), 2.25–2.3 (1 H, m), 4.02 (1 H, ddd, J 8.30, 7.81 and 3.42, 10a-H), 5.49 (1 H, ddd, J 7.81, 5.86 and 1.47, 7a-H), 6.95–7.0 (2 H, m, 2- and 4-H) and 7.22 (1 H, dd, J 8.30 and 7.81, 3-H); m/z 258 (M^+ , 100) (Found: M^+ , 258.0920. $\text{C}_{15}\text{H}_{14}\text{O}_4$ requires M , 258.0892). **33**: R_f 0.36 (1:3, EtOAc-hexane); m.p. 171–173 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3342 and 1694; δ_{H} (400 MHz), 1.7–1.8 (1 H, m), 2.05–2.2 (2 H, m), 2.5–2.6 (2 H, m), 2.95–3.1 (1 H, m), 3.18 (1 H, ddd, J 10.26, 6.83 and 6.34, 1'-H), 3.97 (3 H, s, OMe), 4.88 (1 H, ddd, J 10.26, 5.86 and 4.88, 2'-H), 6.98 (1 H, dd, J 8.30 and 0.97, 7-H), 7.13 (1 H, dd, J 8.30 and 0.97, 5-H) and 7.24 (1 H, t, J 8.30, 6-H); m/z 386 (M^+ , 23) and 259 [($M - \text{I}$) $^+$, 100] (Found: M^+ , 386.0034. $\text{C}_{15}\text{H}_{15}\text{IO}_4$ requires M , 386.0016).

4-(*trans*-2-Iodocyclohexyl)-1-benzopyran-2-one **34**.—Photolysis of the cyclobutanol **25** (40 mg, 0.16 mmol) in benzene (18 cm^3) in the presence of red mercury(II) oxide (110 mg, 0.49 mmol) and iodine (120 mg, 0.49 mmol) for 1 h gave the product **34** (15 mg, 25%); R_f 0.33 (1:3, EtOAc-hexane); m.p. 144–146 °C (from Et_2O -hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3360 and 1708; δ_{H} (400 MHz) 1.0–2.3 (7 H, m), 2.7–2.9 (2 H, m), 5.01 (1 H, m, 2'-H), 7.3–7.45 (3 H, m) and 7.52 (1 H, d, J 8.30, 5-H); m/z 370 (M^+ , 21) and 243 [($M - \text{I}$) $^+$, 100] (Found: M^+ , 370.0081. $\text{C}_{15}\text{H}_{15}\text{IO}_3$ requires M , 370.0066).

cis-6a,7a,8,9,10,11,11a,11b-Octahydro-4-methoxybenzo[4,5]furo[2,3-c][1]benzopyran-6-one **32** and 4-(*trans*-2-Iodocyclohexyl)-8-methoxy-1-benzopyran-2-one **35**.—Photolysis of the cyclobutanol **26** (83 mg, 0.30 mmol) in benzene (33 cm^3) in the presence of red mercury(II) oxide (197 mg, 0.90 mmol) and iodine (230 mg, 0.90 mmol) for 1.5 h gave **32** (18 mg, 20%) and **35** (4.8 mg, 4.0%). **32**: R_f 0.10 (1:3, EtOAc-hexane); m.p. 194–198 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1730 and 1608; δ_{H} (400 MHz), 1.2–1.35

(2 H, m), 1.55–1.85 (4 H, m), 2.1–2.2 (1 H, m), 2.35–2.45 (1 H, m), 3.32 (1 H, ddd, J 10.25, 7.32 and 6.84, 11a-H), 3.95 (3 H, s, OMe), 4.82 (1 H, ddd, J 7.35, 6.84 and 3.91, 7a-H), 6.95–7.0 (2 H, m), 7.20 (1 H, t, J 8.30 and 7.81, 2-H); m/z 272 (M^+ , 27) and 192 (100) (Found: C, 70.6; H, 6.0. $C_{16}H_{16}O_4$ requires C, 70.57; H, 5.92%). **35**: R_f 0.12 (1:3 EtOAc–hexane); m.p. 185–187 °C; ν_{max}/cm^{-1} 3346 and 1696; δ_H (400 MHz) 1.4–1.55 (1 H, m), 1.65–1.75 (1 H, m), 1.9–2.05 (4 H, m), 2.2–2.3 (1 H, m), 2.7–2.85 (2 H, m), 3.96 (3 H, s), 5.01 (1 H, m, 2'-H), 6.97 (1 H, dd, J 8.30 and 0.98, 7-H), 7.08 (1 H, d, J 7.81, 5-H) and 7.24 (1 H, dd, J 8.30 and 7.81, 6-H); m/z 400 (M^+ , 13) and 273 [($M - I$) $^+$, 100] (Found: M^+ , 400.0194. $C_{16}H_{17}IO_4$ requires M , 400.0171).

References

- Part 142 in this series: K. Kobayashi, H. Takeuchi, S. Seko, Y. Kanno, S. Kujime and H. Sugimoto, *Helv. Chim. Acta*, in press.
- Int. alia*, (a) H. Sugimoto and S. Yamada, *J. Org. Chem.*, 1984, **49**, 3753; (b) H. Sugimoto and S. Yamada, *J. Org. Chem.*, 1985, **50**, 2489; (c) H. Sugimoto and S. Yamada, *Tetrahedron*, 1987, **43**, 3371; (d) H. Sugimoto and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3055; (e) H. Sugimoto, C. F. Liu and M. Tokuda, *J. Chem. Soc., Perkin Trans. 1*, 1985, 327; (f) H. Sugimoto, M. Itoh and K. Kobayashi, *Chem. Lett.*, 1987, 1527; (g) H. Sugimoto, J. B. Wang and G. Satoh, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1553; (h) H. Sugimoto and S. Yamada, *Chem. Lett.*, 1988, 245; (i) H. Sugimoto and J. B. Wang, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 193; (j) K. Kobayashi, H. Shimizu, M. Itoh and H. Sugimoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2435; (k) H. Sugimoto, H. Senboku and S. Yamada, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2199; (l) H. Sugimoto and J. B. Wang, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2825; (m) H. Sugimoto, G. Satoh, J. B. Wang, S. Yamada and K. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1239; (n) H. Sugimoto, Y. Yamamoto and K. Orito, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1033; (o) H. Sugimoto and J. B. Wang, *Steroids*, 1990, **55**, 353; (p) H. Sugimoto, S. Yamada and J. B. Wang, *J. Org. Chem.*, 1990, **55**, 2170; (q) K. Kobayashi, M. Itoh, A. Sasaki and H. Sugimoto, *Tetrahedron*, 1991, **47**, 5437; (r) K. Kobayashi, A. Sasaki, Y. Kanno and H. Sugimoto, *Tetrahedron*, 1991, **47**, 7245; (s) K. Orito, K. Yorita and H. Sugimoto, *Tetrahedron Lett.*, 1991, **32**, 5999; (t) H. Sugimoto, Y. Nakayama and H. Senboku, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1837; (u) H. Sugimoto and Y. Nakayama, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1843; (v) K. Kobayashi, Y. Kanno, S. Seko and H. Sugimoto, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3111; (w) H. Sugimoto and T. Kondoh, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3119; (x) K. Kobayashi, A. Konishi, Y. Kanno and H. Sugimoto, *J. Chem. Soc., Perkin Trans. 1*, 1993, 111; (y) K. Kobayashi, A. Konishi, M. Itoh and H. Sugimoto, *J. Chem. Soc., Perkin Trans. 1*, 1993, 825.
- H. Sugimoto, C. F. Liu, S. Seko, K. Kobayashi and A. Furusaki, *J. Org. Chem.*, 1988, **53**, 5952.
- H. Sugimoto, K. Kobayashi, M. Itoh, S. Seko and A. Furusaki, *J. Org. Chem.*, 1990, **55**, 4933.
- K. Kobayashi, M. Suzuki and H. Sugimoto, *J. Org. Chem.*, 1992, **57**, 599.
- K. N. Trivedi and S. Sethna, *J. Org. Chem.*, 1960, **25**, 1817.
- D. Chakravarti and R. Das, *J. Indian Chem. Soc.*, 1971, **48**, 371.
- For reviews of enone photochemical cycloaddition, see: (a) S. W. Baldwin, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker, New York, 1981, vol. 5, p. 123; (b) A. C. Weedon, in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum, New York, 1980, p. 91; (c) D. I. Schuster, G. Lem and N. A. Kaprinidis, *Chem. Rev.*, 1993, **93**, 22.
- (a) Y. A. Shaikh and K. N. Trivedi, *J. Ind. Chem. Soc.*, 1973, **50**, 41; (b) K. C. Majumdar, R. N. De, A. T. Khan, S. K. Chattopadhyay, K. Dey and A. Patra, *J. Chem. Soc., Chem. Commun.*, 1988, 777; (c) K. C. Majumdar and R. N. De, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1901; (d) K. C. Majumdar, A. T. Khan and D. P. Das, *Synth. Commun.*, 1989, **19**, 917; (e) K. C. Majumdar, A. T. Khan, A. K. Gupta and K. Dey, *Synth. Commun.*, 1990, **20**, 1249.

Paper 3/02366D

Received 26th April 1993

Accepted 23rd June 1993