Photolysis of 2,3-Epoxy-7,7-diphenylbicyclo[3.2.0]heptan-6-ones and 2-*exo*, 3-*exo*-Dihydroxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one

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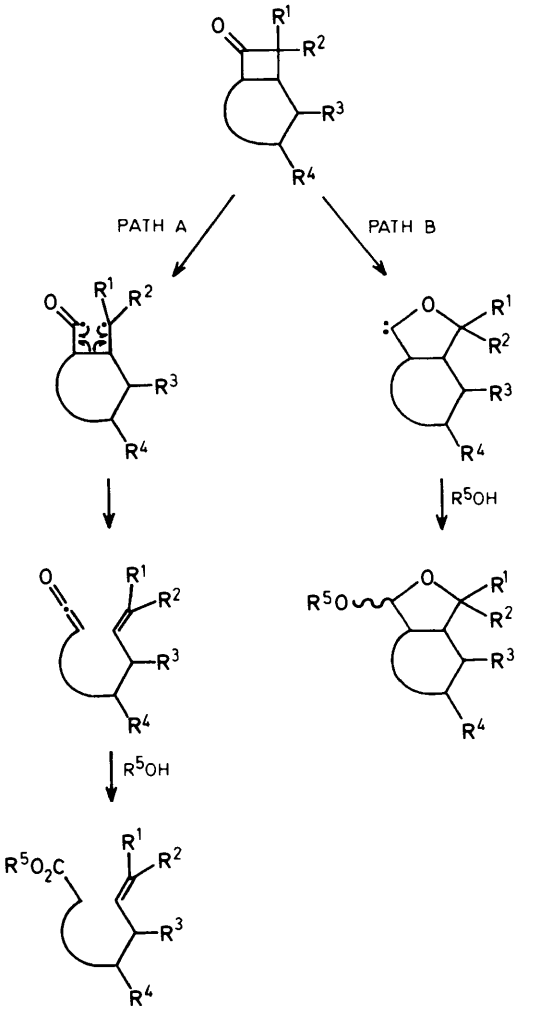
Photolysis of 2,3-*endo*-epoxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one (**2**) in methanol gave products (**4**), (**8**) derived from an oxacarbene intermediate and the products (**5**)—(**7**), (**9**) derived from an initially formed alkenylketene. Photolysis of the same epoxide in benzene containing methanol (0.2M) gave the oxo-ester (**10**) as a major product whilst photolysis of (**2**) in benzene alone gave the lactone (**11**). The isomeric epoxide (**3**) behaved in a similar fashion giving the oxo-ester (**10**) on photolysis in benzene–methanol and the lactone (**11**) on photolysis in benzene alone. The homologous epoxide (**13**) gave products (**14**), (**15**) resulting from photon-induced ring-expansion. The dihydroxy ketone (**16**) gave the hydroxy lactone (**17**) in 66% yield by intramolecular trapping of the intermediate ketene.

We have been interested in the photolysis of bicyclo-[3.2.0]heptanone derivatives for some time.[1,2] It occurred to us that a potential use in synthesis, particularly for the preparation of biologically important leukotrienes[3] and analogues, lay in the photochemically driven retro-[2 + 2]reaction of bicyclo-[*n*.2.0]alkan-(*n* + 3)-ones to give acyclic ω-alkenyl esters (Scheme 1, path A). The substituents R^1,R^2 adjacent to the carbonyl group must be designed to aid the requisite retro-[2 + 2]reaction pathway since products from this route are only formed to a minor extent in the unsubstituted system.[1] Thus the groups R^1,R^2 should act to stabilize the developing alkyl radical centre in order to promote the Norrish 1 cleavage in the desired sense and should, if possible, militate against ring expansion and the formation of unwanted cyclic acetals (Scheme 1, path B).

Initially we chose to study the photolysis of epoxides derived from 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one.[4] By coincidence, Lee-Ruff *et al.*, chose to study the photochemistry of the same systems as part of their investigations into the mechanism of the cyclobutanone → oxacarbene ring expansion reaction.[5] Where comparisons can be made, the results obtained by us and by the Canadian group are broadly similar, although we observed a greater number of side-products from our photolyses.

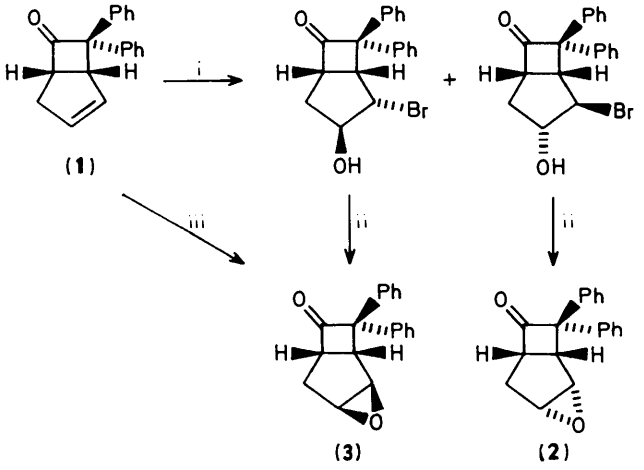
The epoxides (**2**), (**3**) required for the studies were obtained from 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (**1**)[6] in standard fashion (Scheme 2). Photolysis of the *endo*-epoxide (**2**) in methanol using a medium-pressure mercury lamp and quartz apparatus gave the bicyclic acetal (**4**) (30%) and the hydroxy esters (**5**), (**6**) (26%) as the major products. In addition small amounts of the lactone (**7**) (7%) and the hydroxy acetal (**8**) (2%) were obtained. In a second experiment the hydroxy ester (**9**) was obtained as a minor product. Obviously the alcohols (**5**), (**6**), (**8**), and (**9**) and the lactone (**7**) are obtained by methanolysis of the epoxide unit during the course of the photolysis.

Irradiation of the epoxide (**2**) in benzene containing methanol (0.2M) using the above apparatus gave the acetal (**4**) (24%) and the oxo ester (**10**) (26%) as the major products. The oxo ester (**10**) is formed from the intermediate epoxy ester by a [1,2]-hydride shift.[5] Careful chromatography of the reaction mixture and recrystallization led to the isolation of the lactone (**11**) (1%). A reaction using the same lamp and solvent system but employing Pyrex apparatus gave the acetal (**4**) (32%), the oxo ester (**10**) (29%), and the lactone (**11**) (2%). The lactone (**11**), which is presumably formed by intramolecular attack by the epoxide moiety on the ketene unit to give a reactive diradical or ylide (Scheme 3), was converted into the trisubstituted cyclobutane (**12**). The structure of the ester (**12**) was confirmed by *X*-ray crystallography.[4]

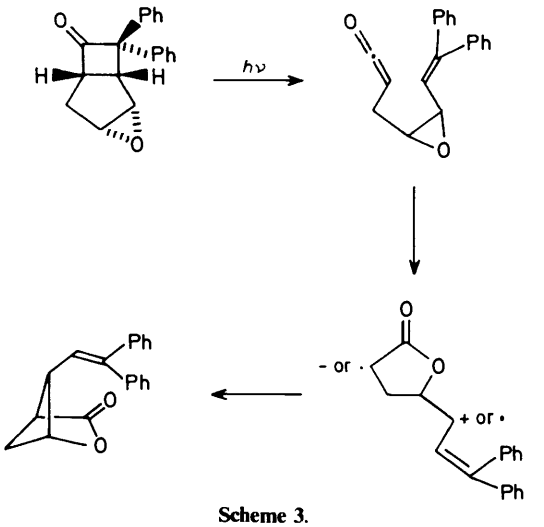


Scheme 1.

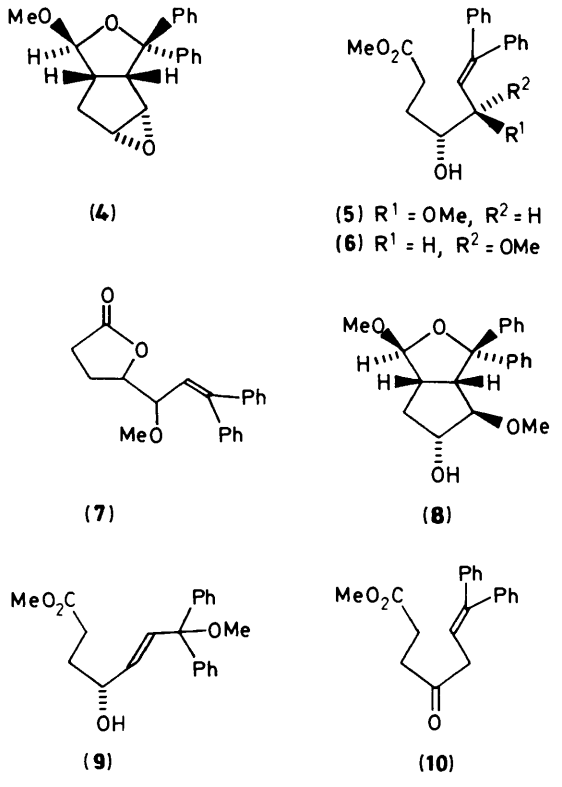
Photolysis of the *exo*-epoxide (**3**) in benzene containing



Scheme 2. *Reagents:* i, AcNHBr, Me_2CO, H_2O; ii, K_2CO_3, MeOH; iii, *m*-chloroperoxybenzoic acid, CH_2Cl_2



Scheme 3.

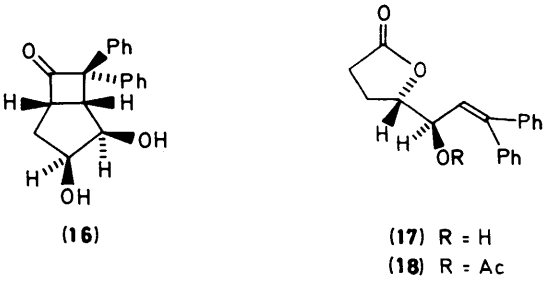


methanol (0.2M) using quartz apparatus gave the oxo ester (**10**) (47%), whilst photolysis of (**3**) in benzene alone gave the lactone (**11**) (48%). Similarly, photolysis of the *endo*-epoxide (**2**) in benzene solution through a quartz apparatus gave the lactone (**11**) (42%) as the only isolable product.

The bicyclic epoxide (**13**) was prepared. Photolysis of this epoxide in methanol or in benzene containing methanol gave the acetals (**14**) and (**15**) in the ratio 5:2 and in 53% yield. Photolysis of the epoxide (**13**) in benzene solution gave no identifiable products.

Finally we investigated whether an intermediate ketene (see Scheme 1) could be trapped effectively in an intramolecular fashion using a group other than an epoxide unit. Obviously it was necessary to design and use a substrate that would not lead to products derived from the other reactive intermediate namely the oxacarbene. Accordingly, the diol (**16**) was synthesized from the alkene (**1**) using osmium tetraoxide and *N*-methylmorpholine *N*-oxide. Photolysis of the diol (**16**) in dry benzene gave a good yield of the hydroxy lactone (**17**). For the purpose of structure elucidation the lactone (**17**) was converted into the corresponding acetate (**18**).

The studies showed that photochemically driven retro-[2 + 2]reactions of bicycloheptanone derivatives can be used to prepare δ-alkenyl esters and γ-lactones. The intramolecular trapping of an intermediate ketene by an adjacent nucleophile gave an indication as to how the retro-[2 + 2]reaction could be made to dominate the competing ring-expansion reaction, and we used this information to design the synthesis of two natural products.[7]



Experimental

Where necessary, solvents were dried and purified according to recommended methods.[8] Light petroleum refers to the fraction boiling in the range 40—60 °C. Ether is diethyl ether. Organic solutions were routinely dried over $MgSO_4$ and evaporation

refers to solvent removal on a rotary evaporator under reduced pressure. T.l.c. was performed on pre-coated plates (Merck silica gel 60F 254). Flash chromatography refers to the method of Still *et al.*[9] M.p.s were determined on a Kofler block and are uncorrected. B.p.s. were recorded as ranges during distillation. I.r. spectra were recorded on a Perkin-Elmer 297 grating spectrophotometer. ^{1}H N.m.r. and ^{13}C n.m.r. spectra were recorded on a Bruker WM 250 MHz spectrometer and a Perkin-Elmer 200 MHz spectrometer. Electron impact (e.i.) mass spectra and accurate mass determinations were obtained on Varian 311A and Finnigan 4500 machines.

2,3-endo-*Epoxy*-7,7-*diphenylbicyclo*[3.2.0]*heptan*-6-*one* (**2**) *and* 2,3-exo-*Epoxy*-7,7-*diphenylbicyclo*[3.2.0]*heptan*-6-*one* (**3**).—(a) To a stirred solution of 7,7-diphenylbicyclohept-2-en-6-one (**1**) (4 g, 15.4 mmol) in acetone (30 ml) and water (8 ml) at room temperature was added *N*-bromoacetamide (2.7 g, 19.3 mmol). The mixture was stirred at room temperature for 2 h. Water (15 ml) was added, followed by saturated aqueous sodium hydrogen sulphite and the acetone was removed under reduced pressure. The product was extracted into ethyl acetate (3 × 30 ml) and the combined extracts were dried and evaporated to give a white foam (5.6 g). Flash chromatography [ethyl acetate–toluene (1:8 v/v)] gave 2-*exo*-bromo-3-*endo*-hydroxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one (2.2 g, 39%) as a white solid, followed by 2-*endo*-bromo-3-*exo*-hydroxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one (0.78 g, 14%), also as a white solid. Recrystallisation of a sample of the former bromohydrin from light petroleum–ether gave white needles, m.p. 117—119 °C (Found: C, 64.05; H, 4.95. $C_{19}H_{17}BrO_2$ requires C, 63.85; H, 4.8%); $\nu_{max.}$(CHBr$_3$) 3 580 (OH) and 1 776 cm^{-1} (C=O); δ(CDCl$_3$) 7.52—7.12 (10 H, m, ArH), 4.40 (1 H, br s, 3-H), 4.14—4.02 (2 H, m, 1-H and 2-H), 3.87 (1 H, ddd, 5-H), 2.41 (1 H, m, 4-H *exo*), 2.16 (1 H, m, 4-H *endo*), and 1.64 (1 H, s, OH); *m/z* 356, 358 (M^+), 338, 340 ($M^+ - H_2O$), 277, 279 (M^+ − Br), and 258. Recrystallisation of a sample of the more polar bromohydrin from light petroleum gave white needles, m.p. 127—129 °C (Found: C, 64.0; H, 4.95. $C_{19}H_{17}BrO_2$ requires C, 63.85; H, 4.8%); $\nu_{max.}$(CHBr$_3$) 3 580 (OH) and 1 775 cm^{-1} (C=O); δ(CDCl$_3$), 7.6—7.16 (10 H, m, ArH), 4.37 (1 H, m, 3-H), 4.30 (1 H, m, 2-H), 4.08 (1 H, t, *J* 8 Hz, 1-H), 3.72 (1 H, *t*, *J* 8 Hz, 5-H), 2.58 (1 H, dd, 4-H *exo*), 2.29 (1 H, br s, OH), and 1.85 (1 H, m, 4-H *endo*); *m/z* 356, 358 (M^+), 338 ($M^+ - H_2O$), 277, 279 (M^+ − Br), 259, and 231.

To a stirred solution of 2-*exo*-bromo-3-*endo*-hydroxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one (500 mg, 1.4 mmol) in methanol at 0 °C was added dropwise a solution of potassium carbonate (500 mg, 3.6 mmol) in methanol (7 ml) during 5 min. The mixture was stirred at 0 °C for 15 min and at room temperature for 1.5 h. The solution was diluted with water (20 ml) and extracted with chloroform (3 × 20 ml). The combined organic extracts were dried and evaporated to give the *epoxide* (**2**) (342 mg, 89%), m.p. 158—160 °C (from ethanol); [Found: C, 82.55; H, 5.85. $C_{19}H_{16}O_2$ requires C, 82.6; H, 5.9%]; $\nu_{max.}$(CHBr$_3$) 1 771 cm^{-1} (C=O); δ(CDCl$_3$) 7.7—7.1 (10 H, m, ArH), 3.8—3.6 (4 H, m, 1-H, 2-H, 3-H, and 5-H), 2.59 (1 H, dd, 4-H-*exo*), and 1.97 (1 H, d, 4-H-*endo*).

To a stirred solution of 2-*endo*-bromo-3-*exo*-hydroxy-7,7-diphenylbicyclo[3.2.0]heptan-6-one (0.7 g, 1.9 mmol) in methanol (10 ml) at 0 °C was added dropwise a solution of potassium carbonate (1 g, 7.2 mmol) in methanol (10 ml) during 5 min. The mixture was stirred at room temperature for 1 h, diluted with water (20 ml), and extracted with dichloromethane (3 × 20 ml). The combined organic fractions were dried and evaporated to give a white solid. Flash chromatography [ethyl acetate–light petroleum (1:8, v/v)] gave the exo-*epoxy ketone* (**3**) (486 mg, 91%), m.p. 121—123 °C (from ethanol) (Found: C, 82.65; H, 5.9. $C_{19}H_{16}O_2$ requires C, 82.55; H, 5.9%); $\nu_{max.}$(CHBr$_3$) 1 765 cm^{-1} (C=O); δ(CDCl$_3$) 7.6—7.1 (10 H, m, ArH), 3.95 (1 H, d, *J* 7.5 Hz, 1-H), 3.62 (1 H, ddd, *J* 7.5, 7.5, and 2.0 Hz, 5-H), 3.39 (1 H, s, 3-H), 3.24 (1 H, s, 2-H), and 2.24 (2 H, m, 2 × 4-H); *m/z* 276 (M^+) and 258 (M^+ − CO).

(b) To a stirred solution of the bicyclic ketone (**1**) (4.3 g, 16.5 mmol) in dichloromethane (40 ml) was added, portionwise, *meta*-chloroperoxybenzoic acid (3.6 g, 16.6 mmol, 85% pure) at room temperature during 5 min; the mixture was stirred for 15 h, filtered, and the solvent evaporated to give a white solid. The residue was taken up in ether (60 ml), washed with aqueous sodium hydroxide (3%, 2 × 30 ml), water (2 × 30 ml), dried and evaporated to give a white crystalline product. Flash chromatography [ethyl acetate–light petroleum (9:1, 6:1 followed by 3:1)], gave the exo-*epoxide* (**3**) (3.6 g, 78%) as a white solid, and the endo-*epoxide* (**2**) (0.8 g, 17%) also as a white solid. Both epoxides were identical (t.l.c., n.m.r., and i.r.) with authentic material prepared from the isomeric bromohydrins.

2,3-exo-*Epoxy*-8,8-*diphenylbicyclo*[4.2.0]*octan*-7-*one* (**13**).—To a stirred solution of 8,8-diphenylbicyclo[4.2.0]oct-2-en-7-one[6] (4.9 g, 18.0 mmol) in dichloromethane (50 ml) was added, portionwise, *meta*-chloroperoxybenzoic acid (85% pure; 3.3 g, 18.9 mmol) at room temperature during 5 min. The mixture was stirred for 32 h, filtered, and the solvent evaporated to give a white solid. The residue was taken up in ether (60 ml), and the solution washed with aqueous sodium hydroxide (3%; 2 × 30 ml) and water (2 × 30 ml) dried and evaporated to give a white crystalline product (4.9 g). Recrystallisation from ethanol gave the *epoxide* (**13**) as white needles (3.7 g, 71%), m.p. 107—109 °C (Found: C, 82.45; H, 6.25. $C_{20}H_{18}O_2$ requires C, 82.7; H, 6.3%); $\nu_{max.}$(CHBr$_3$) 1 770 cm^{-1} (C=O); δ (CDCl$_3$) 7.5—7.1 (10 H, m, ArH), 3.85 (1 H, d, *J* 10 Hz, 1-H), 3.4 (1 H, m, 6-H), 2.95 (1 H, s, 3-H), 2.75 (1 H, d, 2-H), 2.1—1.7 (4 H, m, 2 × 4-H, and 2 × 5-H); *m/z* 290 (M^+) 262, and 246.

2-exo,3-exo-*Dihydroxy*-7,7-*diphenylbicyclo*[3.2.0]*heptan*-6-*one* (**16**).—To a mixture of *N*-methylmorpholine *N*-oxide monohydrate (0.52 g, 3.85 mmol), tetrahydrofuran (16 ml), t-butyl alcohol (10 ml), and osmium tetraoxide (20 mg, 2 mol%) in water (6 ml) was added 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (**1**) (1 g, 3.84 mmol) with stirring. After 10 h at room temperature the reaction mixture was diluted with dichloromethane (20 ml) and washed successively with 15% aqueous sodium hydrogen sulphite (3 × 30 ml), 10% hydrochloric acid (8 × 20 ml) and saturated aqueous sodium hydrogen carbonate. The aqueous washes were back-extracted with dichloromethane (3 × 20 ml) and the combined organic fractions were dried and evaporated to yield a white solid. Flash chromatography [ethyl acetate–light petroleum (1:3, v/v)] gave the title compound, which was recrystallised from ether to give the *dihydroxy ketone* (**16**) as white needles (0.91 g, 80.6%), m.p. 147—149 °C; $\nu_{max.}$(Nujol) 3 520, 3 350, and 1 765 cm^{-1}; δ(CDCl$_3$) 7.1—7.4 (10 H, m, ArH), 3.9 (1 H, m, 3-H), 3.65—3.85 (3 H, m, 5-, 2-, and 1-H), 2.4 (1 H, m, OH), 2.23 and 1.94 (2 H, m, 2 × 4-H), and 2.2 (1 H, m, OH) (Found: M^+, 294.1245. $C_{19}H_{18}O_3$ requires *M*, 294.1256).

Photolysis of 2,3-endo-*Epoxy*-7,7-*diphenylbicyclo*[3.2.0]-*heptan*-6-*one* (**2**).—(a) *In Methanol.* A stirred solution of the epoxy ketone (**2**) (1.63 g, 5.9 mmol) in dry methanol was deoxygenated using a stream of argon for 0.5 h. The stirred solution was irradiated under an atmosphere of argon using a medium-pressure mercury lamp and a quartz filter for 4 h. The solvent was removed under reduced pressure to give an oil. Chromatography using a Jobin Yvon Chromatospac Prep 100 [column capacity 1.5 kg; ethyl acetate–toluene (1:8, v/v)] gave, in order of elution, the *epoxy acetal* (**4**) (30%) as white needles, m.p. 154—156 °C (from ethanol); (Found: C, 77.95; H, 6.65.

$C_{20}H_{20}O_3$ requires C, 77.9; H, 6.55%); $\nu_{max.}$(CHBr$_3$) 992 cm^{-1}; δ(CDCl$_3$) 7.6—7.1 (10 H, m, ArH), 4.91 (1 H, d, *J* 3 Hz, 2-H), 3.61 (1 H, dd, *J* 8 Hz, 5-H), 3.42 (1 H, s, 7-H), 3.03 (1 H, s, 6-H), 3.32 (3 H, s, OMe), 2.65 (1 H, ddd, *J* 8, 3, and 2 Hz, 1-H), 2.26 (1 H, dm, 4-H-*endo*), and 1.98 (1 H, dd, 4-H-*exo*); *m/z* 308 (M^+) and 277 (M^+ − OMe); a 2:1 mixture of the *esters* (**5**), (**6**) (26%) (Found: C, 74.05; H, 7.15. $C_{21}H_{22}O_4$ requires C, 74.1; H, 7.1%); $\nu_{max.}$(CHBr$_3$) 3 580 (OH), 2 825 (OCH$_3$), and 1 729 cm^{-1} (ester); δ(CDCl$_3$) 7.45—7.05 (10 H, m, ArH), 6.08 (1 H, d, 6-H), 3.8—3.6 (2 H, m, 4-H and 5-H), 3.67 (3 H, s, CO_2CH_3), 3.27 (3 H, s, OCH$_3$), 2.6—2.3 (2 H, m, 2 × 2-H) and 2.0—1.5 (2 H, m, 2 × 3-H); the minor isomer had δ 7.45—7.05 (10 H, m, ArH), 5.94 (1 H, d, *J* 8 Hz, 6-H), 3.8—3.6 (2 H, m, 4-H and 5-H), 3.67 (3 H, s, CO_2CH_3), 3.27 (3 H, s, OCH$_3$), 2.6—2.3 (2 H, m, 2 × 2-H), and 2.0—1.5 (2 H, m, 2 × 3-H); *m/z* 338 (M^+); the *lactone* (**7**) as an oil (Found: C, 78.05; H, 6.6. $C_{20}H_{20}O_3$ requires C, 77.9; H, 6.55%); $\nu_{max.}$(CHBr$_3$) 2 830 (OCH$_3$) and 1 773 cm^{-1} (C=O); δ(CDCl$_3$) 7.5—7.1 (10 H, m, ArH), 5.97 (1 H, d, *J* 10 Hz, 6-H), 4.53 (1 H, q, 4-H), 3.99 (1 H, dd, *J* 10 and 3 Hz, 5-H), 3.27 (3 H, s, OCH$_3$), 2.55 (2 H, t, 2 × 2-H) and 2.25 (2 H, m, 2 × 3-H); *m/z* 308 (M^+); the *acetal* (**8**) (2%) as an oil (Found: C, 74.05; H, 7.0. $C_{21}H_{22}O_4$ requires C, 74.1; H, 7.1%); $\nu_{max.}$(CHBr$_3$) 3 565 cm^{-1} (OH); δ(CDCl$_3$) 7.66—7.1 (10 H, m, ArH), 5.01 (1 H, d, *J* 3 Hz, 2-H), 4.69 (1 H, d, *J* 2 Hz, 6-H), 4.16 (1 H, br s, 7-H), 3.88 (1 H, dd, *J* 8 and 2 Hz, 5-H), 3.4 (3 H, s, OCH$_3$), 3.34 (3 H, s, OCH$_3$), 2.83 (1 H, ddd, 1-H), 2.2—2.1 (2 H, m, 2 × 8-H), and 1.82 (1 H, s, OH); *m/z* 308 (M^+).

In a second experiment the *ester* (**9**) was obtained as an oil (Found: C, 74.25; H, 7.15. $C_{21}H_{22}O_4$ requires C, 74.1; H, 7.1%); $\nu_{max.}$(CHBr$_3$) 3 450 (OH), 2 825 (OCH$_3$), and 1 730 cm^{-1} (C=O); δ(CDCl$_3$) 7.5—7.1 (10 H, m, ArH), 6.4—6.1 (1 H, m, dd, *J* 15 and 1 Hz 5-H), 5.7—5.55 (1 H, dd, *J* 15 and 6 Hz, 6-H), 4.35—4.2 (1 H, q, 4-H), 3.7 (3 H, s, CO_2CH_3), 3.15 (3 H, s, OCH$_3$), 2.45 (2 H, t, 2 × 2-H), and 2.0—1.8 (2 H, m, 2 × 3-H); *m/z* 338 (M^+).

(*b*) *In* 0.2M *methanol–benzene.* The epoxy ketone (**2**) (1.0 g, 3.6 mmol) dissolved in a solution of dry methanol (0.2M) in benzene, was deoxygenated using a stream of argon for 0.5 h. Irradiation was carried out at room temperature under an atmosphere of argon using a medium-pressure mercury lamp through a quartz filter for 48 h. The solvents were removed under reduced pressure to give an oil. Chromatography [ethyl acetate–toluene (1:4, v/v)] gave starting material, the epoxy acetal (**4**) (24%), and the *oxo ester* (**10**) (36%) (Found: C, 77.9; H, 6.65. $C_{20}H_{20}O_3$ requires C, 77.9; H, 6.55%); $\nu_{max.}$(CHBr$_3$) 1 729 (ester) and 1 710 cm^{-1} (C=O); δ(CDCl$_3$) 7.4—7.1 (10 H, m, ArH), 6.30 (1 H, t, *J* 6 Hz, 6-H), 3.68 (3 H, s, CO_2CH_3), 3.28 (2 H, d, *J* 6 Hz, 2 × 5-H), and 2.75—2.5 (4 H, m, 2 × 3-H and 2 × 2-H); *m/z* 308 (M^+); and the bicyclic lactone (**11**) (1%) identical (t.l.c., i.r., ^{1}H n.m.r., and m.p.) with authentic material (*vide infra*).

Photolysis of the epoxy ketone (**2**) under the same conditions as described above, except using Pyrex apparatus, gave starting material, the epoxy acetal (**4**) (32%), the oxo ester (**10**) (29%), and the lactone (**11**) (2%).

Photolysis of 2,3-exo-*Epoxy*-7,7-*diphenylbicyclo*[3.2.0]-*heptan*-6-*one* (**3**) *in Methanol–Benzene.*—The epoxy ketone (**3**) (1.4 g, 5.1 mmol) dissolved in dry methanol (0.2M) and benzene (60 ml) was deoxygenated using a stream of argon. The solution was irradiated for 5 h at room temperature under an atmosphere of argon using a medium-pressure mercury lamp and a quartz filter. The solvent was removed to give an oil, chromatography of which over silica [ethyl acetate–light petroleum (1:6)] gave starting material and the oxo ester (**10**) (47%).

5-(2,2-*Diphenylvinyl*)-2-*oxabicyclo*[2.1.1]*hexan*-3-*one* (**11**).—(*a*) A stirred solution of the *endo*-epoxy ketone (**2**) (1.0 g, 3.6 mmol) in dry benzene (60 ml) was deoxygenated using a stream of argon. Irradiation was carried out at room temperature under an atmosphere of argon using a medium-pressure mercury lamp through a quartz filter for 11 h. The solvent was evaporated to give an orange oil (1.05 g), which crystallised with time. Chromatography [dichloromethane–light petroleum (2:1, v/v)] gave the *title compound* (**11**) (340 mg, 42%) as a white solid, m.p. 151—153 °C (from ethanol) (Found: C, 82.6; H, 5.8. $C_{19}H_{16}O_2$ requires C, 82.55; H, 5.85%); $\nu_{max.}$(CHBr$_3$) 1 790 cm^{-1} (C=O); δ(CDCl$_3$) 7.5—7.1 (10 H, m, ArH), 6.2 (1 H, d, *J* 9 Hz, CH=CPh$_2$), 4.73 (1 H, dt, *J* 7.5 and 1.0 Hz, 1-H), 3.38 (1 H, ddm, *J* 9 and 2.5 Hz, 5-H), 2.95 (1 H, dt, *J* 7.5 and 2.5 Hz, 4-H), 2.35 (1 H, dm *J* 9 and 2.5 Hz, 6-H-*exo*), and 2.21 (1 H, dm, *J* 9 Hz, 6-H-*endo*); δ_C(CDCl$_3$) 176.9 (s, C-3), 146.9 (s, CPh$_2$), 139.9 and 127.9 (ArC), 120.6 (d, *C*H=CPh$_2$), 81.7 (d, C-1), 59.6 (d, C-5), 49.9 (d, C-4), and 45.5 (t, C-6); *m/z* 276 (M^+) and 246.

(*b*) The *exo*-epoxy ketone (**3**) (600 mg, 2.2 mmol) was photolysed as described in (*a*) to give the title compound (288 mg, 48%) as white needles, m.p. 151—153 °C (from ethanol).

Methyl cis-3-*Hydroxy*-2-(2,2-*diphenylvinyl*)*cyclobutane*-1-*carboxylate* (**12**).—To a stirred solution of the lactone (**11**) (97 mg, 0.35 mmol) in methanol (15 ml) at room temperature was added toluene-*p*-sulphonic acid (67 mg, 0.35 mmol). After 22 h methanol was removed under reduced pressure to give a pale brown oil (103 mg). Chromatography (eluant dichloromethane) gave the lactone (**11**) (5 mg, 5%) and the *cyclobutane* (**12**) (90 mg, 88%) as a white solid, m.p. 112—113 °C (from ethyl acetate) (Found: C, 77.95; H, 6.5. $C_{20}H_{20}O_3$ requires C, 77.9; H, 6.55%); $\nu_{max.}$(CHBr$_3$) 3 440 (OH) and 1 725 cm^{-1} (C=O); δ(CDCl$_3$) 7.5—7.1 (10 H, m, ArH), 6.27 (1 H, d, *J* 11 Hz, C*H*=CPh$_2$), 4.3 (1 H, td, 3-H), 3.73 (3 H, s, CO_2CH_3), 3.6 (1 H, m, 2-H), 2.98 (1 H, q, 1-H), and 2.65—2.36 (2 H, m, 2 × 4-H); *m/z* 308 (M^+), 290, and 276.

Photolysis of 2,3-exo-*Epoxy*-8,8-*diphenylbicyclo*[4.2.0]*octan*-7-*one* (**13**).—A stirred solution of the epoxy ketone (**13**) (1.28 g, 4.4 mmol) in dry 0.2M-methanol-benzene was deoxygenated using a stream of argon. Irradiation was carried out at room temperature under an atmosphere of argon using a medium-pressure mercury lamp through a quartz filter for 31 h. The solvent was evaporated to give a brown oil. Chromatography [ethyl acetate–light petroleum (1:20, v/v) followed by (1:10, v/v)] gave the *acetal* (**14**) (537 mg, 38%) as white needles, m.p. 151—153 °C (from ethanol) (Found: C, 78.2; H, 6.85. $C_{21}H_{22}O_3$ requires C, 78.25; H, 6.9%; $\nu_{max.}$(CHBr$_3$) 992 cm^{-1}; δ(CDCl$_3$) 7.59—7.08 (10 H, m, ArH), 5.07 (1 H, d, *J* 4 Hz, 2-H), 3.51 (1 H, d, *J* 7 Hz, 5-H), 3.4 (3 H, s, OCH$_3$), 3.04 (1 H, br s, 7-H), 2.75 (1 H, d, 6-H), 2.34 (1 H, m, 1-H), and 2.34—1.43 (4 H, m, 2 × CH$_2$); *m/z* 322 (M^+) and 291; followed by the *acetal* (**15**), m.p. 125—126 °C (from ethanol) (Found: C, 78.25; H, 6.85. $C_{21}H_{22}O_3$ requires C, 78.25; H, 6.9%); $\nu_{max.}$(CHBr$_3$) 995 cm^{-1}; δ(CDCl$_3$) 7.64—7.11 (10 H, m, ArH), 4.98 (1 H, d, *J* 7 Hz, 2-H), 3.59 (3 H, s, OCH$_3$), 3.28 (1 H, d, *J* 8 Hz, 5-H), 3.09 (1 H, br s, 7-H), 2.79 (1 H, d, 6-H), 2.25 (1 H, m, 1-H), and 2.35—1.54 (4 H, m, 2 × 8-H and 2 × 9-H); *m/z* 322 (M^+) and 291.

Photolysis of 2-exo,3-exo-*Dihydroxy*-7,7-*diphenylbicyclo*-[3.2.0]*heptan*-6-*one* (**16**).—A stirred solution of the dihydroxy ketone (**16**) (0.5 g) in dry benzene (180 ml) was irradiated at room temperature under an atmosphere of argon using a glass, medium-pressure lamp for 24 h. The solvent was evaporated to yield a thick yellow oil which crystallised. Flash chromatography [ethyl acetate–light petroleum (1:8, v/v)] gave the γ-lactone (**17**) (0.33 g, 66%) as a white solid, m.p. 142—143 °C (Found: C, 77.8; H, 6.1. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.2%); $\nu_{max.}$(Nujol) 3 370 and 1 775 cm^{-1}; δ(CDCl$_3$) 7.1—7.4 (10 H, m, ArH), 6.0 (1 H, dm, *J* 8 Hz, 7-H), 4.4—4.6 (2 H, m, 6- and 5-H), 2.45—2.6 (2 H, m, 2 × 3-H), and 2.2—2.4 (3 H, m, 2 × 4-H, OH); M^+ 294.

To the γ-lactone (**17**) (100 mg, 0.34 mmol) in dry dichloromethane (10 ml) under an atmosphere of argon was added acetic anhydride (69 mg), pyridine (219 mg) and a catalytic amount of 4-dimethylaminopyridine. The mixture was stirred at room temperature overnight, extracted with water (2 × 30 ml) and aqueous sodium hydrogen carbonate (50 ml) and the aqueous washes were back-extracted with dichloromethane (2 × 30 ml). The combined organic fractions were dried and evaporated to give a pale yellow oil. Flash chromatography [ethyl acetate–light petroleum (1:5, v/v)] gave the acetate (**18**) (0.101 g, 88%) as an oil; $\nu_{max.}$(neat) 1 775 and 1 740 cm^{-1}; δ($CDCl_3$) 7.18—7.4 (10 H, m, ArH), 5.95 (1 H, d, *J* 10 Hz, 7-H), 5.5 (1 H, dd, *J* 10 and 4 Hz, 6-H), 4.60 (1 H, m, 5-H), 2.50 (2 H, m, 2 × 3-H), 2.1—2.3 (2 H, m, 2 × 4-H), and 2.05 (3 H, s, Me) (Found: M^+, 336.1408. $C_{21}H_{20}O_4$ requires *M*, 336.1362).

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