Photolysis of Substituted Cycloenones. Part 1. 5-Hydroxycyclopentenones

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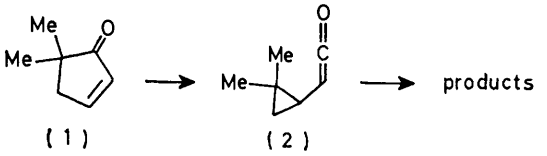
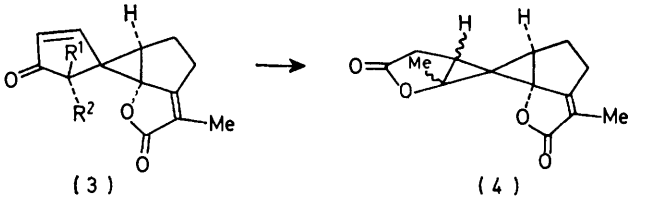
The preparation and photolysis of some 5-hydroxycyclopentenones is described. They undergo photochemical rearrangement to give 2-oxa[3.1.0]bicyclohexan-3-ones (γ-lactones derived from cyclopropanol acetic acid). The reactions appear to proceed *via* a singlet excited state and are not stereospecific. Lactones were not obtained in a few cases where the enone has a 4-phenyl substituent.

THE photochemistry of cyclopentenones has been the subject of many investigations,[1] and several photochemical rearrangements have been reported. In particular, Agosta *et al.*[2,3] have found that 5-substituted cyclopentenones [*e.g.* (1)] undergo photochemical α-



(1) (2)

cleavage to afford products derived from the cyclopropane ketene (2). We have reported[4] that the complex 5-hydroxycyclopentenones, 4-hydroxyphotosantonene and its 4α-isomer (3a and b) undergo photochemical reaction *via* a singlet excited state to give the cyclopropane lactones (4a and b) respectively. We suggested that this reaction proceeded *via* the appropriate hydroxycyclopropylketen.



(3) (4)

a; R^1 = Me, R^2 = OH
b; R^1 = OH, R^2 = Me

a; Me and H α
b; Me and H β

We now show that the rearrangement is a general one, but with some exceptions. Furthermore, the reaction, contrary to earlier indications,[4] is *not* stereospecific, though, in the one case tested, there is some stereoselectivity.

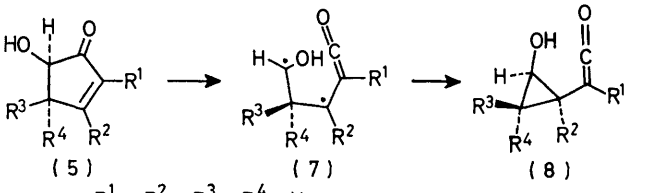
RESULTS AND DISCUSSION

Preparation of Starting Materials.—The starting materials were prepared by lead tetra-acetate oxidation of the corresponding cyclopentenone[5,6] followed by base-, or better, acid-catalysed hydrolysis[7] of the 5-acetate. Most of the parent cyclopentenones were prepared by published procedures noted in the Experimental section.

2,4,4-Trimethylcyclopentenone[8,9] was prepared in 76% yield using Conia's method[10] by heating isobutyl methacrylate with polyphosphoric acid. We also used Conia's method to prepare a mixture of 4-methyl-3-phenyl-[11] and 3-methyl-4-phenyl-cyclopentenones by heating isopropyl cinnamate with polyphosphoric acid. The former was separated from the mixture of cyclopentenones by fractional crystallisation of the semicarbazones, the semicarbazone being reconverted to the ketone by ceric nitrate oxidation.[12]

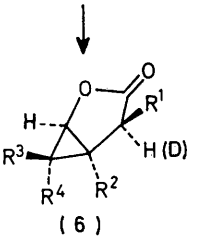
Some of the 5-acetoxy-compounds have already been described by Russell *et al.*,[6] but we describe the preparation of a number of new 5-acetoxy-derivatives. The 5-hydroxy-compounds are all new. We were unable to separate completely *cis*- and *trans*-3,4-dimethyl-5-hydroxycyclopentenones, but careful preparative t.l.c. afforded the *cis*-isomer (5e) in 76% purity, and the *trans*-isomer (5f) in 92% purity, the impurity in each case being the other isomer. Each of these isomeric mixtures was employed in the photochemical experiments.

Photolysis Experiments.—Photolysis of 5-hydroxycyclopentenone (5a) affords the lactone (6a) in 8% yield.



(5) (7) (8)

a; $R^1 = R^2 = R^3 = R^4$ = H
b; $R^1 = R^3 = R^4$ = H, R^2 = Me
c; R^1 = H, $R^2 = R^3 = R^4$ = Me
d; R^2 = H, $R^1 = R^3 = R^4$ = Me
e; $R^1 = R^4$ = H, $R^2 = R^3$ = Me
f; $R^1 = R^3$ = H, $R^2 = R^4$ = Me
g; $R^1 = R^4$ = H, R^2 = Ph, R^3 = Me
h; $R^1 = R^3$ = H, R^2 = Ph, R^4 = Me
i; $R^1 = R^3$ = H, $R^2 = R^4$ = Ph
j; $R^1 = R^4$ = H, R^2 = Me, R^3 = Ph
k; $R^1 = R^3$ = H, R^2 = Me, R^4 = Ph



(6)

The structure of the product follows from its i.r. ($\nu_{max.}$ 1 775 cm^{-1}) and its n.m.r. spectrum. In the latter, we can assign each proton signal. The 1-proton signal shows six lines at τ 5.64 ($J_{1.5}$ 6, $J_{1.6\alpha}$ 5, and $J_{1.6\beta}$ 1.5 Hz), the 4α- and 4β-protons as an AB quartet (τ 7.2 and 7.4, $J_{4\alpha,4\beta}$ 18 Hz) further split by coupling with the 5-proton ($J_{4\alpha,5}$ 6, $J_{4\beta,5} < 1$ Hz), the 5-proton as a multiplet at τ 8.3, and the 6α- and 6β-protons as multiplets centred at τ 9.00 and 9.48 respectively. When the 5-proton

signal is irradiated in decoupling experiments, the 4-protons collapse to an AB quartet, and the 6- and 1-protons form an ABX system.

Similar photolysis of 5-hydroxy-3-methylcyclopentenone (5b) affords the lactone (6b) in 6% yield, again recognised by its i.r. and n.m.r. spectra. In the latter, the 4-protons appear as a singlet. This is characteristic of those lactones where there is a methyl group at the 5-position. The 6- and 1-protons comprise an ABX system. Photolysis of 5-hydroxy-3,4,4-trimethylcyclopentenone (5c) similarly affords the lactone (6c).

These rearrangements are obviously related to those discovered by us previously [4] and to the known photochemical reaction of cyclopentenones.[2,3] Implicit in this is that the reaction should proceed *via* the hydroxyketen intermediate (8), with the possible intervention of a diradical (7). A diradical is not necessary as the rearrangement of the hydroxy-ketone to the hydroxyketen is symmetry-allowed. We have been unable to trap the keten but that is not surprising as the hydroxy group is held close to the keten, possibly by hydrogen bonding.

However, there are a number of experiments which point to this mechanism. When we photolysed (5a) in the presence of monodeuteriomethanol, deuterium is incorporated into the 4α-position and we were unable to detect any incorporation into the 4β-position, thus implying solvent attack from the unhindered α-face of the keten. Photolysis of 5-hydroxy-2,4,4-trimethylcyclopentenone (5d) afforded a product, which, as judged by its n.m.r. spectrum in hexadeuteriobenzene,* is mainly the 4β-methyl lactone (6d), again implying protonation from the less hindered side of the keten. As in the example above, photolysis in the presence of deuteriomethanol leads to incorporation of deuterium in the 4α-position.

The cases so far examined do not allow us to determine whether the relative stereochemistry of substituents at 4- and 5-positions in the cyclopentenones (5) is retained in the 6- and 1-positions in the lactones (6). Accordingly we photolysed the mixtures of *cis*- and *trans*-3,4-dimethyl-5-hydroxycyclopentenones (see above). The mixture rich (76%) in the *cis*-isomer (5e) afforded the lactones (6e and f) in the ratio of 45 : 55. Similarly the mixture rich (92%) in (5f) affords the lactones (6e and f) in the ratio 25 : 75. Based on these results we can estimate that the *cis*-hydroxycyclopentenone (5e) affords the lactones (6e) and (6f) in about equal proportions, while the *trans*-isomer affords the same lactones in the ratio of 23 : 77. Clearly there is preferential formation of the *trans*-lactone, *trans* in this case referring to the relative orientation of the 1- and 6-hydrogens. On the other hand, both *cis*- and *trans*-5-hydroxy-4-methyl-3-phenylcyclopentenones (5g) and (5h) undergo photolysis to afford the *cis*-lactone (6g) and we were unable to detect any of the isomeric lactone (6h).

This clearly shows that these reactions are not stereospecific as with the hydroxysantonenes.[4] Formation of either hydroxyketen [(8e) or (8f)] from either hydroxy-ketone [(5e) or (5f)] is symmetry-allowed, and both ring-closure modes could be concerted, or they may involve diradicals. The preferred ring-closure mode obviously depends on the different sizes of the 4-substituents (cyclopentenone numbering), and the interactions of the 4-substituents (R^3 and R^4) with the keten side chain and the other 3-substituent (R^2) in the transition state leading to (8). Where R^2 is large (*e.g.* Ph), then interaction between the phenyl and the *cis*-4-methyl is large, and the *cis*-cyclopropane (8g) is formed in preference to (8h).† Where R^2 is smaller (*e.g.* CH_3), then the interactions of the 4-substituents with the ketene side chain become the more important, leading to a preference for (8f) over (8e), and hence to (6f). In the hydroxyphotosantonenes, the two 4-substituents (cyclopentenone numbering) are of equal size, and ring-closure occurs in the mode which involves the minimum movement of bonds, thus affording the stereospecificity found.

We possess evidence which strongly suggests that this photolysis reaction proceeds *via* a singlet excited state. We find that the corresponding lactone is still formed when we photolyse the ketones (5c), (5d), and (5g) in the presence of the triplet quencher, ferrocene.[13] The reactions are of course slower, but we estimate that, in the cases of (5c) and (5d) and at the wavelength of the carbonyl $n \longrightarrow \pi^*$ maximum (310 nm), only a third of the light is transmitted by the solutions of ferrocene used. Furthermore there was no trace of lactone formed, when the ketones (5c) and (5d) were photolysed in the presence of the triplet-sensitiser propiophenone.

There is one aspect of the n.m.r. spectra of some of these lactones which deserves comment. In the unsubstituted lactone (6a) we assign the signal at higher field to the 6β (*endo*) hydrogen, and the signal at lower field to the 6α (*exo*) hydrogen. Indeed, in bicyclo[3.1.0]hexane, the 6-*exo* hydrogen signal lies at lower field than the 6-*endo* signal,[14] but we feel that an additional factor is the shielding of the *endo*-hydrogen by the lactone carbonyl group, though this may be offset by the proximity of the 2-oxygen. Furthermore, as the *cis*-coupling constant ($J_{1,6\alpha}$) should be greater than the *trans*-coupling constant ($J_{1,6\beta}$), this assignment is also confirmed by the half-widths of the two 6-proton multiplets. In the 5-methyl lactone (6b), the 6α (*exo*) and 6β (*endo*) hydrogen signals are much closer. A similar effect has been observed by Dauben and Wipke [15] in bicyclo[*n*.1.0]-systems. In the 6,6-dimethyl lactones, we assign the high-field signal to the *endo*-methyl.

No lactonic product was isolated from *trans*-3,4-diphenyl-5-hydroxycyclopentenone (5i) and from *cis*- and *trans*-5-hydroxy-3-methyl-4-phenylcyclopentenones (5j) and (5k). Apparently the presence of a 4-phenyl

* There is an overlap of signals in the n.m.r. spectrum measured in deuteriochloroform.

† While the formulae (5)—(8) imply one enantiomer, we are dealing in each case with a racemic mixture.

group causes the reaction to proceed by a different pathway. We were unable to isolate any low molecular-weight product.

EXPERIMENTAL

U.v. spectra were measured using Unicam SP 800 or Perkin-Elmer 402 instruments; i.r. spectra in Nujol or as liquid films using a Perkin-Elmer 157 instrument. N.m.r. spectra were measured in $CDCl_3$ (unless otherwise stated) using a Bruker WP60 or a Perkin-Elmer R-10 instrument. G.l.c. analysis was carried out using an Aerograph HiFy 600 instrument at 160 °C using a 5 ft × 4 mm 20% Carbowax column. T.l.c. analysis employed Merck silica gel HF 254 + 366, preparative t.l.c. Merck silica gel 60 PF 254 + 366, and Merck silica gel (0.05—0.2 mm) was used for column chromatography. Photolyses were carried out under nitrogen using a 250-W Hanovia medium-pressure lamp, through a quartz window.

Cyclopentenones.—*2,4,4-Trimethylcyclopentenone.* Isobutyl methacrylate (30 g) was added dropwise to stirred polyphosphoric acid (250 g) at 100 °C,[10] and the mixture stirred for 13.5 h. The mixture was cooled and poured onto ice, saturated with ammonium chloride, and then extracted with ether (3 × 60 ml). The ether extracts were washed with water, saturated sodium hydrogencarbonate solution, and water, and then dried. After removal of the solvent, the residue was distilled to give 2,4,4-trimethylcyclopentenone (20 g), b.p. 35—36 °C at 1 mmHg [lit., 66 °C at 20 mmHg]; $\lambda_{max.}$ 230 nm (log ε 4.07), [lit.,[8,9] $\lambda_{max.}$ 229 nm (log ε 4.03)]; $\nu_{max.}$ 1 708, 1 640, 1 325, and 990 cm^{-1} [lit.,[9] $\nu_{max.}$ 1 706 and 1 645 cm^{-1}]; τ(CCl_4) 2.98 (q, *J* 1 Hz, 3-H), 7.85 (s, 5-CH_2), 8.35 (d, *J* 1 Hz, 2-Me), and 8.81 (s, 2 × 4-Me) [lit.,[9] τ 3.07 (q), 7.87 (s), 8.33 (d), and 8.81 (s)].

4-Methyl-3-phenylcyclopentenone. Isopropyl cinnamate (100 g) was added dropwise to stirred polyphosphoric acid (500 g) at 100 °C and the heating continued for 1 h. The mixture was worked-up as above to afford a mixture of 3-methyl-4-phenylcyclopentenone and 4-methyl-3-phenylcyclopentenone, b.p. 145—148 °C at 5 mmHg. The mixture could not be separated by t.l.c.; $\nu_{max.}$ 1 705, 1 685 (C=O), 1 610, and 1 590 cm^{-1} (C=C). The n.m.r. spectrum showed peaks for 3-methyl-4-phenylcyclopentenone and 4-methyl-3-phenylcyclopentenone. The latter's spectrum is recorded below, the former shows peaks at τ 2.50 (Ph), 3.9 (m, 2-H), 6.10 (m, 4-H), 7.70 (5-CH_2, AB portion of ABX spectrum), and 8.8 (3-Me).

The ketonic mixture (2 g) in methanol (10 ml) was added to semicarbazide hydrochloride (2 g) and sodium acetate (2.5 g, crystals) in water (10 ml), and the mixture heated for 1 h at 100 °C. The semicarbazones crystallised on cooling, and were fractionally crystallised from ethanol. The first fraction afforded 4-methyl-3-phenylcyclopentenone semicarbazone (800 mg), m.p. 200—203 °C [lit.,[11] 203 °C]. Later fractions afford mixtures.

The semicarbazone (600 mg) in ethanol (20 ml) at −20 °C was added to ceric ammonium nitrate (4.11 g) in 0.5N nitric acid (25 ml) and ethanol (25 ml) at −20 °C.[12] The mixture was stirred at −25 °C for 5 min, ice–water (70 ml) was added, and the mixture immediately extracted with ether. The ether layer was washed and dried. Removal of the solvent afforded an oil, purified by preparative t.l.c. to give 4-methyl-3-phenylcyclopentenone; $\nu_{max.}$ 1 685, 1 595, and 1 565 cm^{-1}; τ 2.46 (m, 3-Ph), 3.59 (d, *J* 1.3 Hz), 6.44 (m, 4-H), 7.44 (AB portion of ABX system, 5-CH_2, $J_{5\alpha,5\beta}$ 19.0, $J_{4,5\beta}$ 6.3 and $J_{4,5\alpha}$ 1.9 Hz), and 8.76 (d, *J* 7.1 Hz, 4-Me).

5-Acetoxycyclopentenones.— *5-Acetoxycyclopentenone.* Cyclopentenone[16] (7 g), lead tetra-acetate (40 g), and dry benzene (200 ml) were refluxed for 7 h. The reaction mixture was cooled, the lead diacetate formed was collected and washed with ether. The filtrate and washings were diluted with ether (100 ml) and washed with dilute sodium hydrogencarbonate solution and water. The organic layer was dried over magnesium sulphate, and the solvent removed *in vacuo*. The residue was fractionally distilled to afford *5-acetoxycyclopentenone* (3 g), b.p. 78—80 °C at 0.7 mmHg (Found: C, 59.7; H, 5.7. $C_7H_8O_3$ requires C, 60.0; H, 5.75%); M^+ 140; $\nu_{max.}$ 1 745 (acetate), 1 720 (cyclopentenone), 1 585, 1 370, and 1 230 cm^{-1}; $\lambda_{max.}$ 223 nm (log ε 4.31); τ(CCl_4) 2.31 (m, 3-H), 3.84 (m, 2-H), 4.99 (dd, $J_{5,4\alpha}$ 7, $J_{5,4\beta}$ 3 Hz, 5-H), 6.88 (m, 4β-H), 7.55 (m, 4α-H, $J_{4\alpha,4\beta}$ 19 Hz), and 7.97 (OAc).

5-Acetoxy-2,4,4-trimethylcyclopentenone. 2,4,4-Trimethylcyclopentenone (20 g), lead tetra-acetate (80 g), and benzene (200 ml) were refluxed for 63 h. Working up as above, the product was *5-acetoxy-2,4,4-trimethylcyclopentenone* (9.1 g), b.p. 76—77 °C at 1.3 mmHg (Found: C, 65.65; H, 7.75. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.75%); M^+ 182; $\nu_{max.}$ 1 740, 1 715, 1 625, 1 230, and 1 035 cm^{-1}; $\lambda_{max.}$ 231 nm (log ε 3.95); τ(CCl_4) 2.88 (q, *J* 1 Hz, 3-H), 5.10 (s, 5-H), 7.89 (s, OAc), 8.28 (*J* 1 Hz, 2-Me), 8.73 (4β-Me), and 9.00 (4α-Me).

trans-*5-Acetoxy-3-methyl-4-phenylcyclopentenone.* The mixture of 3-methyl-4-phenyl- and 4-methyl-3-phenylcyclopentenones (6 g), lead tetra-acetate (20 g), and benzene (250 ml) were refluxed for 63 h. The product was a mixture of 5-acetoxy-compounds (6 g) from which trans-*5-acetoxy-3-methyl-4-phenylcyclopentenone* (0.5 g) could be separated by preparative t.l.c. and by crystallisation from ethanol (as rhombs), m.p. 63—65 °C (Found: C, 72.8; H, 6.2. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1%); $\nu_{max.}$ 1 740, 1 710, and 1 615 cm^{-1}; $\lambda_{max.}$ 229 (log ε 4.7); τ 2.67 (m, 4-Ph), 3.82 (m, 2-H), 4.85 (d, *J* 3.1 Hz, 5-H), 6.10 (m, 4-H), 7.92 (OAc), and 8.1 (3-Me).

trans-5-*Acetoxy-3,4-diphenylcyclopentenone.* 3,4-Diphenylcyclopentenone[17] (6 g), lead tetra-acetate (15 g), and benzene (150 ml) were refluxed for 66.5 h. The product was *trans*-5-acetoxy-3,4-diphenylcyclopentenone (5 g), rhombs, purified by preparative t.l.c. (from hexane–ethyl acetate), m.p. 76—78 °C; $\nu_{max.}$ 1 740, 1 710, 1 590, and 1 565 cm^{-1}; $\lambda_{max.}$ 290 nm (log ε 4.8); τ 2.60 (3-Ph), 2.82 (4-Ph), 3.23 (d, *J* 1.5 Hz, 2-H), 4.90 (d, *J* 2.3 Hz, 5-H), 5.46 (dd, *J* 2.3 and 1.5 Hz, 4-H), and 7.87 (OAc). The compound decomposed on further purification.

5-Hydroxycyclopentenones.—*5-Hydroxycyclopentenone* (5a). Concentrated hydrochloric acid (2 ml) in water (4 ml) were added to 5-acetoxycyclopentenone (500 mg) in methanol (10 ml) under nitrogen. The mixture was stirred at room temperature for 30 h. The acid was neutralised with sodium hydrogencarbonate, and methanol was removed under reduced pressure at room temperature. The product was purified by preparative t.l.c. to give *5-hydroxycyclopentenone* (55 mg) (M^+ at *m/e* 98.036 704; $C_5H_6O_2$ requires *m/e* 98.036 755); $\nu_{max.}$ 3 350, 1 710, and 1 575 cm^{-1}; $\lambda_{max.}$ 220 nm (log ε 3.53); τ 2.31 (dt, $J_{3,2}$ 6.0 and $J_{3,4}$ 2.9 Hz, 3-H), 3.78 (dt, $J_{2,3}$ 6.0 and $J_{2,4}$ 2.1 Hz, 2-H), 5.64 (m, 5-H and 5-OH) and 7.12 (m, 4-CH_2).

5-Hydroxy-3-methylcyclopentenone (5b). 5-Acetoxy-3-methylcyclopentenone[6] (1.3 g) similarly afforded *5-hydroxy-*

3-*methylcyclopentenone* (260 mg) (Found: M^+ at *m/e* 112.052 65. $C_6H_8O_2$ requires *m/e* 112.052 42); $\nu_{max.}$ 3 360, 1 700, and 1 615 cm^{-1}; $\lambda_{max.}$ 219 nm (log ε 3.87), τ 4.00 (m, 2-H), 5.70 (X portion of ABX system, $J_{AX} + J_{BX}$ 10 Hz, 5-H), 6.55 (OH, exchangeable with D_2O), 7.4 (AB portion of the ABX system, 4-CH_2), and 7.8 (s, 3-Me).

5-*Hydroxy*-3,4,4-*trimethylcyclopentenone* (5c). The corresponding 5-acetate [6] (8 g), 0.5N aqueous potassium hydroxide (47 ml), and methanol (47 ml) were set aside at room temperature under nitrogen for 15 min. The reaction was followed by t.l.c. The reaction mixture was brought to pH 6 with acetic acid, the methanol removed *in vacuo*, the residue extracted with ether, and the ether layer dried over magnesium sulphate. After removal of the solvent, the residue was distilled *in vacuo*, to give 5-*hydroxy*-3,4,4-*trimethylcyclopentenone* (3 g), b.p. 85 °C at 1.5 mmHg (Found: C, 68.1; H, 8.4. $C_8H_{12}O_2$ requires C, 68.5; H, 8.6%); M^+ 140; $\nu_{max.}$ 3 390, 1 700, and 1 610 cm^{-1}; $\lambda_{max.}$ 231 nm (log ε 4.14); τ (CCl_4) 4.18 (q, *J* 1 Hz, 2-H), 5.8 (OH, exchangeable with D_2O), 6.15 (5-H), 7.92 (d, *J* 1 Hz, 3-Me), 8.73 (4β-Me), and 8.92 (4α-Me).

5-*Hydroxy*-2,4,4-*trimethylcyclopentenone* (5d). The corresponding acetate (8 g), 0.5N potassium hydroxide (47 ml) and methanol (47 ml) afforded, after work-up, a mixture (t.l.c.) which was separated by column chromatography over silica to give 5-hydroxy-2,4,4-trimethylcyclopentenone (1.8 g), b.p. 68—70 °C at 3 mmHg (Found: C, 68.65; H, 8.5%); M^+ 140; $\nu_{max.}$ 3 400, 1 710, and 1 630 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 4.84); τ(CCl_4), 2.96 (q, *J* 1 Hz, 3-H), 5.5 (exchangeable OH), 6.13 (5-H), 8.29 (d, *J* 1 Hz, 2-Me), 8.76 (4β-Me), and 8.97 (4α-Me): and 2-*hydroxy*-3,5,5-*trimethylcyclopentenone* (1.2 g), b.p. 68—70 °C at 3 mmHg (Found: C, 68.6; H, 8.7%); M^+ 140; $\nu_{max.}$ 3 300, 1 700, and 1 655 cm^{-1}; $\lambda_{max.}$ 260 nm (log ε 3.2), τ 2.78 (OH exchangeable), 7.75 (s, 4-CH_2), 8.05 (3-Me), and 8.9 (2 × 5-Me).

cis- *and* trans-3,4-*Dimethyl*-5-*hydroxycyclopentenones* (5e) *and* (5f). The mixture of *cis*- and *trans*-5-acetoxy-3,4-dimethylcyclopentenones [6] (1 g), 0.5N potassium hydroxide (9 ml), and methanol (9 ml) were set aside at room temperature under nitrogen for 15 min. The product (225 mg) was a mixture of *cis*- and *trans*-5-hydroxyketones, b.p. 99 °C at 7.3 mmHg. The mixture could be separated (partially) by careful preparative t.l.c. to give cis-3,4,-*dimethyl*-5-*hydroxycyclopentenone* (5e) (100 mg) (75% pure) (Found: C, 66.4; H, 8.1. $C_7H_{10}O_2$ requires C, 66.65; H, 8.0%); $\nu_{max.}$ 3 360, 1 700, and 1 615 cm^{-1}; $\lambda_{max.}$ 229 nm (log ε 3.96); τ 4.05 (m, 2-H), 5.74 (d, *J* 5.6 Hz, 5-H), 6.97 (m, 4-H and exchangeable OH), 7.86 (3-Me), and 8.88 (d, *J* 7 Hz, 4-Me): the *trans*-isomer (5f) (125 mg), (92% pure) (Found: C, 67.1; H, 8.0%); $\nu_{max.}$ 3 350, 1 695, and 1 610 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 3.96); τ 4.05 (m, 2-H), 6.17 (d, *J* 3.3 Hz 5-H), 6.7 (OH, exchangeable), 7.2 (m, 4-H), 7.89 (d, *J* 1.3 Hz, 3-Me), and 8.67 (d, *J* 7.1 Hz, 4-Me).

cis- *and* trans-5-*Hydroxy*-3-*methyl*-4-*phenylcyclopentenones and* cis- *and* trans-5-*hydroxy*-4-*methyl*-3-*phenylcyclopentenones*. The unseparated mixture of acetoxy-ketones (6 g) described above, concentrated hydrochloric acid (10 ml), water (20 ml), and methanol (150 ml) was set aside for 46 h at room temperature. The reaction was followed by t.l.c. The residue was chromatographed over silica to give a mixture of 4-methyl-3-phenyl- and 3-methyl-4-phenyl-cyclopentenones (mostly the latter), which had not reacted in the acetylation reaction, and a mixture of 5-hydroxy-compounds (2.97 g). This mixture was subjected to preparative t.l.c. [hexane–ether–ethyl acetate–chloroform (5 : 2 : 2 : 1)] using multidevelopment techniques followed by fractional crystallisation to afford in order of decreasing polarity: (*a*) cis-5-*hydroxy*-3-*methyl*-4-*phenylcyclopentenone* (5j) (90 mg) as rhombs (from EtOAc), m.p. 143—145 °C (Found: C, 76.85; H, 6.4. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%); $\nu_{max.}$ 3 400, 1 705, and 1 615 cm^{-1}; $\lambda_{max.}$ 218 nm (log ε 4.09); τ 2.75 (m, 4-Ph), 3.80 (m, 2-H), 5.58 (dd, *J* 5 and 7 Hz, 5-H), 5.88 (d, *J* 7 Hz, 4-H), 7.78 (d, *J* 5 Hz, OH), and 8.00 (3-Me). On shaking with D_2O the doublet at τ 7.78 disappears, the signal at τ 5.58 becomes a doublet, and a DHO peak appears at τ 5.35. (*b*) trans-5-*Hydroxy*-4-*methyl*-3-*phenylcyclopentenone* (5h) (300 mg) as rhombs (from ethyl acetate), m.p. 115 °C (Found: C, 76.7; H, 6.4%), $\nu_{max.}$ 3 300, 1 690, 1 590, and 1 565 cm^{-1}; $\lambda_{max.}$ 218 and 283 nm (log ε 3.94 and 4.27); τ 2.54 (s, 3-Ph), 3.64 (d, *J* 1.5 Hz, 2-H), 5.50 (OH, exchangeable), 5.96 (d, *J* 2.3 Hz, 5-H), 6.70 (m, 4-H), and 8.67 (d, *J* 7.3 Hz, 4-Me). (*c*) cis-5-*Hydroxy*-4-*methyl*-3-*phenylcyclopentenone* (5g) (1.59 g) as needles (from ethyl acetate), m.p. 155—156 °C (Found: C, 76.8; H, 6.5%); $\nu_{max.}$ 3 300, 1 680, 1 595, and 1 560 cm^{-1}; $\lambda_{max.}$ 224 and 287 nm (log ε 3.60 and 3.96); τ 2.43 (m, 3-Ph), 3.47 (2-H), 5.52 (d, *J* 6.5 Hz, 5-H), 6.3 (m, 4-H), 6.75 (5-OH), and 8.76 (d, *J* 7.1 Hz, 4-Me). (*d*) trans-5-*Hydroxy*-3-*methyl*-4-*phenylcyclopentenone* (5k) (900 mg), as needles (from ethyl acetate), m.p. 126—128 °C (Found: C, 76.2; H, 6.7%), $\nu_{max.}$ 3 350, 1 690, 1 610, and 1 600 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 4.02); τ 2.75 (m, 4-Ph), 3.85 (m, 2-H), 5.85 (d, *J* 2.5 and 3 Hz, 5-H), 6.25 (m, 4-H), 7.19 (d, *J* 3 Hz, OH exchangeable), and 8.06 (3-Me).

trans-3,4-*Diphenyl*-5-*hydroxycyclopentenone* (5i). The 5-acetoxy-ketone (4 g), methanol (100 ml), concentrated hydrochloric acid (5 ml), and water (10 ml) under nitrogen were stirred at room temperature for 72 h. The product was purified by chromatography to give trans-3,4-*diphenyl*-5-*hydroxycyclopentenone* (2 g) as rhombs, m.p. 149 °C (from ethyl acetate) (Found: C, 81.7; H, 5.51. $C_{17}H_{14}O_2$ requires C, 81.61; H, 5.6%); $\nu_{max.}$ 3 275, 1 675, 1 580, and 1 560 cm^{-1}; $\lambda_{max.}$ 278 nm (log ε 4.3); τ 2.59 (m, 3-Ph), 2.79 (s, 4-Ph), 3.30 (d, *J* 1.5 Hz, 2-H), 5.60 (dd, *J* 1.5 and 2.3 Hz, 4-H), 5.80 (d, *J* 2.3 Hz, 5-H), and 6.75 (OH, exchangeable).

Photolysis Experiments.—2-*Oxabicyclo*[3.1.0]*hexan*-3-*one* (6a). 5-Hydroxycyclopentenone (100 mg) in benzene (520 ml) was photolysed for 2.15 h. The reaction was followed by t.l.c. The solvent was removed under reduced pressure and the residue separated by preparative t.l.c. The least polar fraction consisted of a mixture of hydrocarbons which was not examined further. A later fraction gave the *cyclopropane lactone* (6a) (8 mg) (Found: M^+ at *m/e* 98.036 894. $C_5H_6O_2$ requires *m/e* 98.036 775); $\nu_{max.}$ 1 775 cm^{-1}.

5-*Methyl*-2-*oxabicyclo*[3.1.0]*hexan*-3-*one* (6b). 5-Hydroxy-3-methylcyclopentenone (5b) (400 mg) in benzene (520 ml) was irradiated for 5 h. The product isolated after chromatography was the *cyclopropyl-lactone* (6b) (25 mg) (Found: M^+ at *m/e* 112.052 2. $C_6H_8O_2$ requires *m/e* 112.052 4); $\nu_{max.}$ 1 775 cm^{-1}; τ 5.84 (dd, $J_{1,6\alpha}$ 5.5, $J_{1,6\beta}$ 2.5 Hz, 1-H), 7.34 (4-CH_2), 8.70 (5-Me), 9.20 (dd, $J_{6\alpha,6\beta}$ 7.5, $J_{6\alpha,1}$ 5 Hz, 6α-H), and 9.30 (dd, $J_{6\alpha,6\beta}$ 7.5, $J_{6\beta,1}$ 2.5 Hz, 6β-H).

5,6,6-*Trimethyl*-2-*oxabicyclo*[3.1.0]*hexan*-3-*one* (6c). The hydroxy-enone (5c) (500 mg) in benzene (500 ml) was irradiated for 17 h. The product, purified by chromatography, was the lactone (6c) (100 mg), b.p. 65 °C at 3.5 mmHg (Found: C, 68.5; H, 8.75. $C_8H_{12}O_2$ requires C,

68.55; H, 8.6%); M^+ 140; $\nu_{max.}$ 1 775 cm^{-1}; $\tau(CCl_4)$ 6.46 (1-H), 7.55 (4-CH_2), 8.73 (5-Me), 8.92 (6α-Me), and 9.00 (6β-Me).

4,6,6-*Trimethyl*-2-*oxabicyclo*[3.1.0]*hexan*-3-*one* (6d). The hydroxy-ketone (5d) (500 mg) in benzene (500 ml) was irradiated for 19 h. The product was chromatographed to give the *lactone* (6d) (100 mg), b.p. 60 °C at 2.5 mmHg (Found: C, 68.8; H, 8.7. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%); M^+ 140; $\nu_{max.}$ 1 770 cm^{-1}; $\tau(CCl_4)$ 6.2 (d, *J* 6 Hz, 1-H), 7.15 (dq, *J* 7 and 7 Hz, 4-H), 8.75 (d, *J* 7 Hz, 4-Me), 8.75 (m, 5-H), 8.95 (6α-Me), and 9.0 (6β-Me).

5,6α-*Dimethyl*-2-*oxa*- *and* 5,6β-*dimethyl*-2-*oxa*-*bicyclo*[3.1.0]*hexan*-3-*one*. (*a*) *trans*-3,5-Dimethyl-5-hydroxycyclopentenone (5f) [92% pure] (100 mg) in benzene (500 ml) was photolysed for 7 h. The product, purified by preparative t.l.c., was a mixture of the two lactones (33 mg), b.p. 60 °C at 3.5 mmHg (Found: C, 66.8; H, 8.0. Calc. for $C_7H_{10}O_2$: C, 66.65; H, 8.0%); $\nu_{max.}$ 1 780 cm^{-1}.

The two lactones could not be separated by t.l.c., but it was possible to estimate the ratio of *trans*- (6f) and *cis*-isomers (6e) as 3 : 1 based on the n.m.r. spectrum. The n.m.r. assignments for (6e) were τ 6.00 (1-H, *J* 5 Hz), 7.43 (s, 4-CH_2), 8.71 (s, 5-Me), 9.00 (m, 6-H), 9.00 (d, *J* 4 Hz, 6-Me). The assignments for (6f) were τ 6.3 (d, 1-H, *J* 1 Hz), 7.36 (s, 4-CH_2), 8.71 (s, 5-Me), 9.00 (m, 6-H), and 9.00 (d, *J* 4 Hz, 6-Me).

(*b*) Photolysis of the *cis*-3,4-dimethyl-5-hydroxycyclopentenone (5e) (100 mg) [76% pure] in benzene (500 ml) for 7.5 h afforded a mixture of (6e) and (6f) (40 mg) in the ratio 45 : 55.

6β-*Methyl*-2-*oxa*-5-*phenylbicyclo*[3.1.0]*hexan*-3-*one* (6g). (*a*) *cis*-5-Hydroxy-4-methyl-3-phenylcyclopentenone (5g) (500 mg) in benzene (520 ml) was photolysed for 5 h. The product was purified by t.l.c. to give the *lactone* (100 mg) (Found: C, 76.6; H, 6.5. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%); $\nu_{max.}$ 1 775 cm^{-1}; τ 2.75 (m, 5-Ph), 5.48 (d, *J* 5.4 Hz, 1-H), 7.06 (AB quartet, *J* 18 Hz, 4-CH_2), 8.77 (d, *J* 5.9 Hz, 6-Me), and 8.75 (m, 6-H).

(*b*) Photolysis of the *trans*-isomer (5h) (100 mg) afforded the same lactone (8 mg).

Quenching and Sensitivity Experiments.—(*a*) 5-Hydroxy-3,4,4-trimethylcyclopentenone (5c) (300 mg), ferrocene (1 g), and benzene (520 ml) were irradiated for 65 h. The lactone (6d) (60 mg) was isolated after chromatography.

(*b*) 5-Hydroxy-2,4,4-trimethylcyclopentenone (5d) (300 mg), ferrocene (1 g), and benzene (520 ml) were irradiated for 65 h. The lactone (6d) (60 mg) was isolated after chromatography.

(*c*) *cis*-5-Hydroxy-4-methyl-3-phenylcyclopentenone (5g) (100 mg), ferrocene (400 mg), and benzene (520 ml) were irradiated for 23 h. The lactone (6 g) (15 mg) was isolated by chromatography.

(*d*) 5-Hydroxy-3,4,4-trimethylcyclopentenone (5c) (200 mg), propiophenone (4 g), and benzene (520 ml) were irradiated for 7 h. The starting material had disappeared (t.l.c.), no lactone was detected, and the main products appeared to be polymers.

(*e*) 5-Hydroxy-2,4,4-trimethylcyclopentenone (5d) (200 mg), propiophenone (4 g), and benzene (520 ml) were irradiated for 7 h. The starting material had disappeared (t.l.c.), no lactone was detected, and the main product appeared to be polymeric.

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